Electronic Supplementary Information for Dalton Transactions

Supporting Information

For

Synthesis, radii dependent self-assembly crystal structures and luminescent properties of rare earth (III) complexes with a tripodal salicylic derivative

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Table S1 Representative bond lengths (Å) and angles (˚) for $[La_2L_2(DMF)_4]\cdot 4DMF\cdot 4EtOH\cdot 2H_2O$

La(1)-O(8)	2.472(2)	La(1)-O(4)	2.519(2)	La(1)-O(12)	2.523(3)	La(1)-O(5)#1	2.520(2)
La(1)-O(10)	2.535(3)	La(1)-O(13)	2.541(3)	La(1)-O(11)	2.593(3)	La(1)-O(7)#1	2.618(2)
La(1)-O(8)#1	2.700(2)						
O(8)-La(1)-O(4)	78.95(8)	O(12)-La(1)-O(13)	73.80(9)	O(5)#1-La(1)-O(7)#1	84.78(8)		
O(8)-La(1)-O(12)	148.06(8)	O(5)#1-La(1)-O(13)	71.46(8)	O(10)-La(1)-O(7)#1	143.08(8)		
O(4)-La(1)-O(12)	75.02(9)	O(10)-La(1)-O(13)	117.78(9)	O(13)-La(1)-O(7)#1	76.68(9)		
O(8)-La(1)-O(5)#1	69.39(7)	O(8)-La(1)-O(11)	85.03(8)	O(11)-La(1)-O(7)#1	152.23(8)		
O(4)-La(1)-O(5)#1	131.64(8)	O(4)-La(1)-O(11)	120.68(9)	O(8)-La(1)-O(8)#1	70.85(8)		
O(12)-La(1)- O(5)#1	142.54(8)	O(12)-La(1)-O(11)	92.53(10)	O(4)-La(1)-O(8)#1	65.66(7)		
O(8)-La(1)-O(10)	75.82(8)	O(5)#1-La(1)-O(11)	92.51(9)	O(12)-La(1)-O(8)#1	113.37(9)		
O(4)-La(1)-O(10)	69.93(8)	O(10)-La(1)-O(11)	50.77(9)	O(5)#1-La(1)-O(8)#1	69.81(8)		
O(12)-La(1)-O(10)	78.07(9)	O(13)-La(1)-O(11)	76.27(9)	O(10)-La(1)-O(8)#1	128.20(8)		
O(5)#1-La(1)-O(10)	131.30(8)	O(8)-La(1)-O(7)#1	119.27(7)	O(13)-La(1)-O(8)#1	113.83(8)		
O(8)-La(1)-O(13)	135.47(8)	O(4)-La(1)-O(7)#1	79.85(8)	O(11)-La(1)-O(8)#1	153.76(8)		
O(4)-La(1)-O(13)	145.03(8)	O(12)-La(1)-O(7)#1	73.94(9)	O(7)#1-La(1)-O(8)#1	48.56(7)		

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

Table S2 Representative bond lengths (Å) and angles (˚) for $[Eu_2L_2(DMF)_4]\cdot 2DMF$

Eu-O(7)	2.375(2)	Eu-O(4)	2.431(2)	Eu-O(11)	2.449(2)	Eu-O(8)#1	2.495(2)
Eu-O(10)	2.428(2)	Eu-O(13)	2.440(2)	Eu-O(12)	2.459(2)	Eu-O(7)#1	2.645(2)
Eu-O(5)#1	2.429(2)						
O(7)-Eu-O(10)	75.29(7)	O(5)#1-Eu-O(11)	87.96(8)	O(4)-Eu-O(8)#1	80.25(7)		
O(7)-Eu-O(5)#1	72.37(7)	O(4)-Eu-O(11)	124.11(7)	O(13)-Eu-O(8)#1	74.74(8)		
O(10)-Eu-O(5)#1	131.66(7)	O(13)-Eu-O(11)	93.26(8)	O(11)-Eu-O(8)#1	149.86(7)		
O(7)-Eu-O(4)	78.18(7)	O(7)-Eu-O(12)	139.05(8)	O(12)-Eu-O(8)#1	75.12(8)		
O(10)-Eu-O(4)	70.85(7)	O(10)-Eu-O(12)	115.41(8)	O(7)-Eu-O(7)#1	71.26(7)		
O(5)#1-Eu-O(4)	133.37(7)	O(5)#1-Eu-O(12)	72.34(7)	O(10)-Eu-O(7)#1	129.19(7)		
O(7)-Eu-O(13)	145.88(7)	O(4)-Eu-O(12)	142.54(7)	O(5)#1-Eu-O(7)#1	70.93(7)		
O(10)-Eu-O(13)	75.80(8)	O(13)-Eu-O(12)	71.07(8)	O(4)-Eu-O(7)#1	65.71(7)		
O(5)#1-Eu-O(13)	141.66(8)	O(11)-Eu-O(12)	74.84(8)	O(13)-Eu-O(7)#1	115.61(7)		
O(4)-Eu-O(13)	75.50(8)	O(7)-Eu-O(8)#1	121.53(7)	O(11)-Eu-O(7)#1	151.06(7)		
O(7)-Eu-O(11)	83.81(8)	O(10)-Eu-O(8)#1	142.87(8)	O(12)-Eu-O(7)#1	115.00(7)		
O(10)-Eu-O(11)	53.41(7)	O(5)#1-Eu-O(8)#1	85.25(8)	O(8)#1-Eu-O(7)#1	50.33(6)		

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

Table S3 Representative bond lengths (Å) and angles (°) for $\{[GdL(DMF)(H_2O)_2]\cdot DMF\}_\infty$

Gd(1)-O(12)	2.378(5)	Gd(1)-O(13)	2.389(4)	Gd(1)-O(14)	2.399(4)	Gd(1)-O(8)#1	2.411(5)
Gd(1)-O(1)	2.452(5)	Gd(1)-O(5)	2.473(5)	Gd(1)-O(7)#1	2.474(4)	Gd(1)-O(2)	2.491(5)
Gd(1)-O(4)	2.514(5)						
O(12)-Gd(1)-O(13)	82.4(2)	O(14)-Gd(1)-O(5)	124.56(18)	O(8)#1-Gd(1)-O(2)	78.53(16)		
O(12)-Gd(1)-O(14)	83.99(19)	O(8)#1-Gd(1)-O(5)	147.87(18)	O(1)-Gd(1)-O(2)	52.28(15)		
O(13)-Gd(1)-O(14)	150.84(15)	O(1)-Gd(1)-O(5)	95.06(18)	O(5)-Gd(1)-O(2)	73.43(17)		
O(12)-Gd(1)-O(8)#1	126.45(18)	O(12)-Gd(1)-O(7)#1	73.70(18)	O(7)#1-Gd(1)-O(2)	126.74(17)		
O(13)-Gd(1)-O(8)#1	82.21(18)	O(13)-Gd(1)-O(7)#1	78.09(16)	O(12)-Gd(1)-O(4)	76.5(2)		
O(14)-Gd(1)-O(8)#1	85.40(18)	O(14)-Gd(1)-O(7)#1	73.38(16)	O(13)-Gd(1)-O(4)	126.72(17)		
O(12)-Gd(1)-O(1)	146.5(2)	O(8)#1-Gd(1)-O(7)#1	52.99(16)	O(14)-Gd(1)-O(4)	74.15(16)		
O(13)-Gd(1)-O(1)	125.98(16)	O(1)-Gd(1)-O(7)#1	124.90(17)	O(8)#1-Gd(1)-O(4)	147.88(18)		
O(14)-Gd(1)-O(1)	76.94(16)	O(5)-Gd(1)-O(7)#1	139.93(17)	O(1)-Gd(1)-O(4)	71.95(18)		
O(8)#1-Gd(1)-O(1)	79.56(17)	O(12)-Gd(1)-O(2)	143.27(18)	O(5)-Gd(1)-O(4)	51.79(17)		
O(12)-Gd(1)-O(5)	73.41(19)	O(13)-Gd(1)-O(2)	74.43(16)	O(7)#1-Gd(1)-O(4)	137.59(17)		
O(13)-Gd(1)-O(5)	75.47(18)	O(14)-Gd(1)-O(2)	128.54(16)	O(2)-Gd(1)-O(4)	94.94(17)		

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

Table S4 Representative bond lengths (Å) and angles (°) for $\{[TbL(DMF)(H_2O)_2]\cdot DMF\}_\infty$

Tb(1)-O(12)	2.359(3)	Tb(1)-O(13)	2.369(3)	Tb(1)-O(14)	2.388(3)	Tb(1)-O(8)#1	2.399(3)
Tb(1)-O(1)	2.436(3)	Tb(1)-O(5)	2.466(3)	Tb(1)-O(7)#1	2.471 (3)	Tb(1)-O(2)	2.479(3)
Tb(1)-O(4)	2.504(3)						
O(12)-Tb(1)-O(13)	82.23(13)	O(14)-Tb(1)-O(5)	124.32(11)	O(8)#1-Tb(1)-O(2)	78.03(11)		
O(12)-Tb(1)-O(14)	83.46(13)	O(8)#1-Tb(1)-O(5)	147.53(11)	O(1)-Tb(1)-O(2)	52.46(10)		
O(13)-Tb(1)-O(14)	150.48(10)	O(1)-Tb(1)-O(5)	95.18(13)	O(5)-Tb(1)-O(2)	73.63(12)		
O(12)-Tb(1)-O(8)#1	126.74(11)	O(12)-Tb(1)-O(7)#1	73.79(12)	O(7)#1-Tb(1)-O(2)	126.55(11)		
O(13)-Tb(1)-O(8)#1	82.15(13)	O(13)-Tb(1)-O(7)#1	77.86(10)	O(12)-Tb(1)-O(4)	76.18(13)		
O(14)-Tb(1)-O(8)#1	86.00(12)	O(14)-Tb(1)-O(7)#1	73.40(10)	O(13)-Tb(1)-O(4)	127.05(11)		
O(12)-Tb(1)-O(1)	146.13(12)	O(8)#1-Tb(1)-O(7)#1	53.20(10)	O(14)-Tb(1)-O(4)	73.54(11)		
O(13)-Tb(1)-O(1)	126.59(10)	O(1)-Tb(1)-O(7)#1	124.78(11)	O(8)#1-Tb(1)-O(4)	147.78(12)		
O(14)-Tb(1)-O(1)	76.98(11)	O(5)-Tb(1)-O(7)#1	139.94(11)	O(1)-Tb(1)-O(4)	71.91(12)		
O(8)#1-Tb(1)-O(1)	79.49(12)	O(12)-Tb(1)-O(2)	143.55(12)	O(5)-Tb(1)-O(4)	52.20(10)		
O(12)-Tb(1)-O(5)	73.42(13)	O(13)-Tb(1)-O(2)	74.82(10)	O(7)#1-Tb(1)-O(4)	137.21(11)		
O(13)-Tb(1)-O(5)	75.49(11)	O(14)-Tb(1)-O(2)	128.77(10)	O(2)-Tb(1)-O(4)	95.44(11)		

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

Table S5 Representative bond lengths (Å) and angles (°) for $\{[YL(DMF)(H_2O)_2]\cdot DMF\}_\infty$

Y(1)-O(12)	2.337(4)	Y(1)-O(13)	2.331(4)	Y(1)-O(14)	2.358(4)	Y(1)-O(8)#1	2.369(4)
Y(1)-O(1)	2.411(4)	Y(1)-O(5)	2.438(4)	Y(1)-O(2)	2.457(4)	Y(1)-O(7)#1	2.463(4)
Y(1)-O(4)	2.482(4)						
O(13)-Y(1)-O(12)	82.02(16)	O(14)-Y(1)-O(5)	124.75(15)	O(8)#1-Y(1)-O(7)#1	53.88(13)		
O(13)-Y(1)-O(14)	149.86(13)	O(8)#1-Y(1)-O(5)	146.73(15)	O(1)-Y(1)-O(7)#1	124.45(15)		
O(12)-Y(1)-O(14)	83.51(16)	O(1)-Y(1)-O(5)	95.48(16)	O(5)-Y(1)-O(7)#1	139.98(15)		
O(13)-Y(1)-O(8)#1	81.87(15)	O(13)-Y(1)-O(2)	74.93(14)	O(2)-Y(1)-O(7)#1	126.47(15)		
O(12)-Y(1)-O(8)#1	127.44(15)	O(12)-Y(1)-O(2)	143.33(15)	O(13)-Y(1)-O(4)	127.80(15)		
O(14)-Y(1)-O(8)#1	86.23(15)	O(14)-Y(1)-O(2)	129.07(14)	O(12)-Y(1)-O(4)	76.16(16)		
O(13)-Y(1)-O(1)	127.25(14)	O(8)#1-Y(1)-O(2)	77.31(14)	O(14)-Y(1)-O(4)	73.25(15)		
O(12)-Y(1)-O(1)	145.97(16)	O(1)-Y(1)-O(2)	53.10(13)	O(8)#1-Y(1)-O(4)	147.27(15)		
O(14)-Y(1)-O(1)	76.66(14)	O(5)-Y(1)-O(2)	73.39(15)	O(1)-Y(1)-O(4)	71.80(15)		
O(8)#1-Y(1)-O(1)	78.91(15)	O(13)-Y(1)-O(7)#1	77.50(13)	O(5)-Y(1)-O(4)	52.90(14)		
O(13)-Y(1)-O(5)	75.64(15)	O(12)-Y(1)-O(7)#1	73.85(15)	O(2)-Y(1)-O(4)	95.88(15)		
O(12)-Y(1)-O(5)	73.50(16)	O(14)-Y(1)-O(7)#1	73.12(14)	O(7)#1-Y(1)-O(4)	136.81(15)		

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

Table S6 Photophysical characterization of the europium and terbium complexes

		λ_{max}[a]/nm	RFI/a.u.	τ/ms	Φ[b] (%)
L	Eu	579	57		
		591	100		
		614	259	0.374	1.32
	Tb	491	2194		
		545	7413	1.07	43.47
		584	484		
		620	184		

[a] Excitation and emission passes = 2.5 nm. [b] Luminescence lifetimes and quantum yield values are reported here with an error of ± 10%.

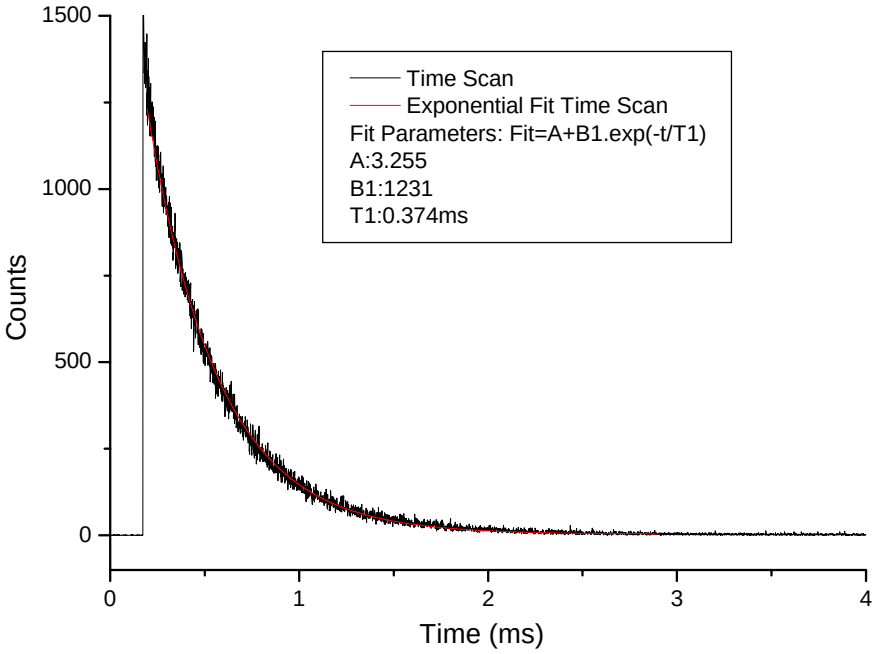

Fig. S1 The room-temperature solid-state phosphorescence lifetime of Eu^{3+} complex.

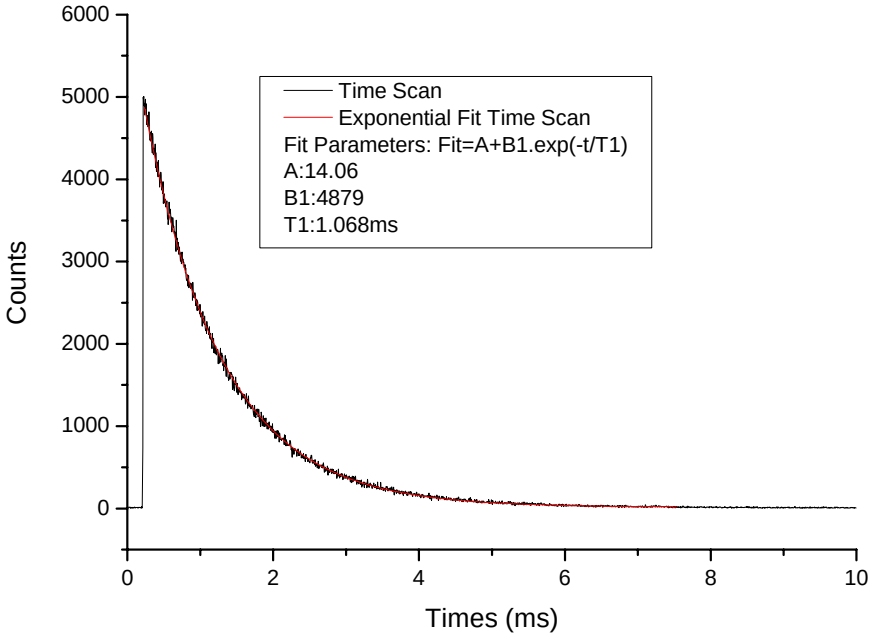

Fig. S2 The room-temperature solid-state phosphorescence lifetime of Tb^{3+} complex.

UV-Vis Spectrum of Ligand.

The Uv-Vis absorption spectrum of the free ligand **LH_3** (Figure S3) was measured in DMF solution (c = 1.0×10^{-4} M). The maximum absorption band at 292 nm is attributed to singlet-singlet π-π* salicylic acid group absorption of the ligand. The molar absorption coefficient (ε) is calculated as 8.6×10^3 L · mol^{-1}· cm^{-1}, revealing that the ligand has a strong ability of absorbing light and thus favor efficient antenna effect, making them potential candidates as sensitizing compound for lanthanide luminescence. A weak band at 262 nm is also evident, which is the absorption of DMF.

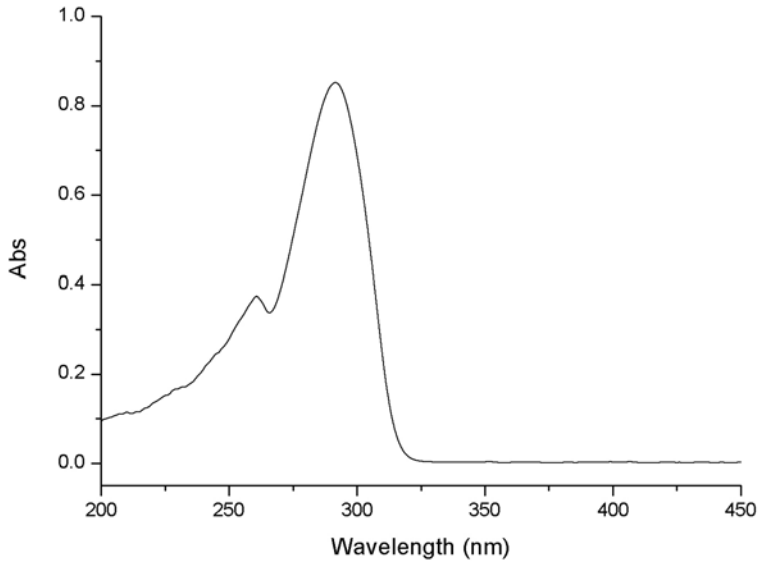

Fig. S3 Absorption spectra of LH_3 in DMF (1.0×10^{-4} M).

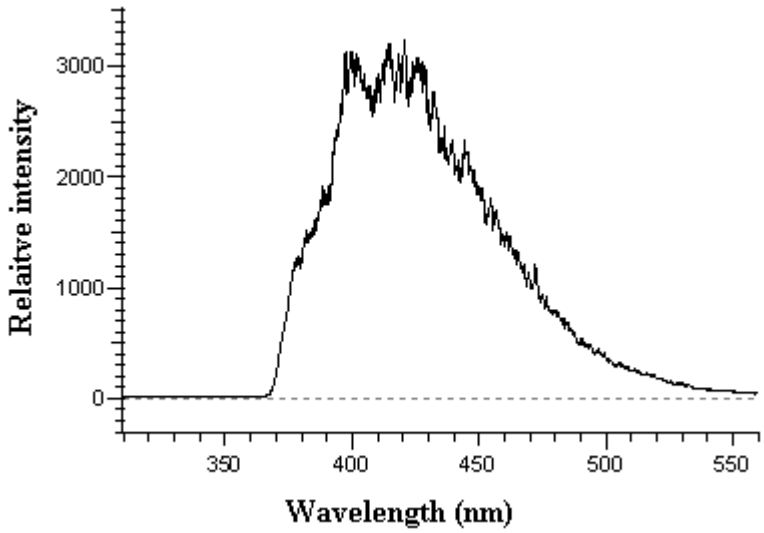

Fig. S4 Phosphorescence spectrum of Gd^{3+} complex excited at 300 nm at 77K.