Supplementary Information

Insight into the roles of structures and energy levels of mono- and bis-β-diketones on sensitizing Nd(III) NIR-luminescence

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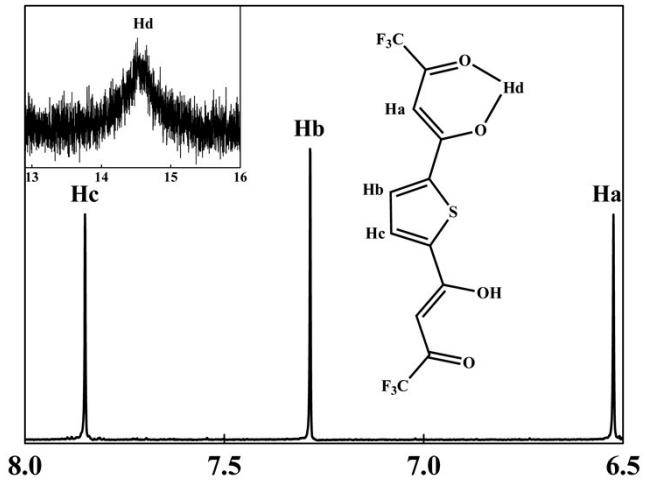


Figure S1 400 MHz ^{1}H NMR spectrum of BDT in $CDCl_3$

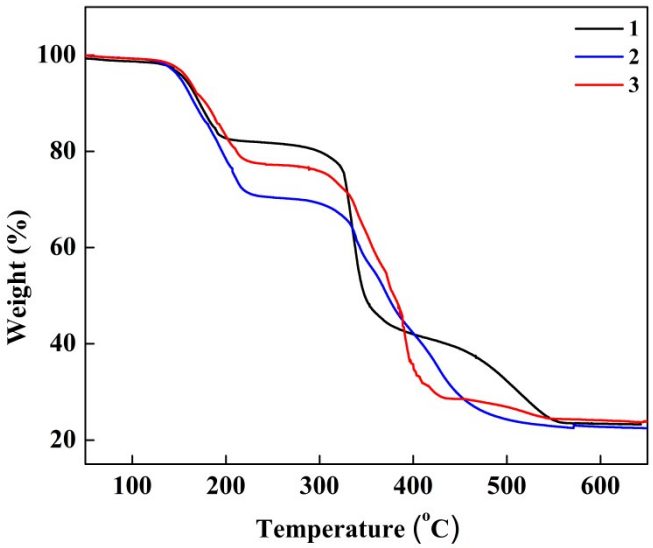


Figure S2 Thermogravimetric curves of **1**, **2** and **3**.

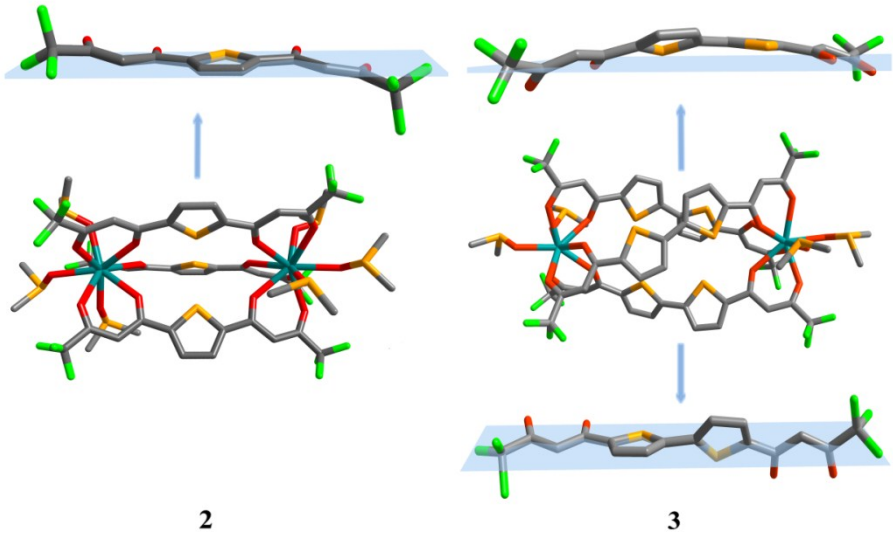


Figure S3 The bending patterns of the ligands in **2** and **3**.

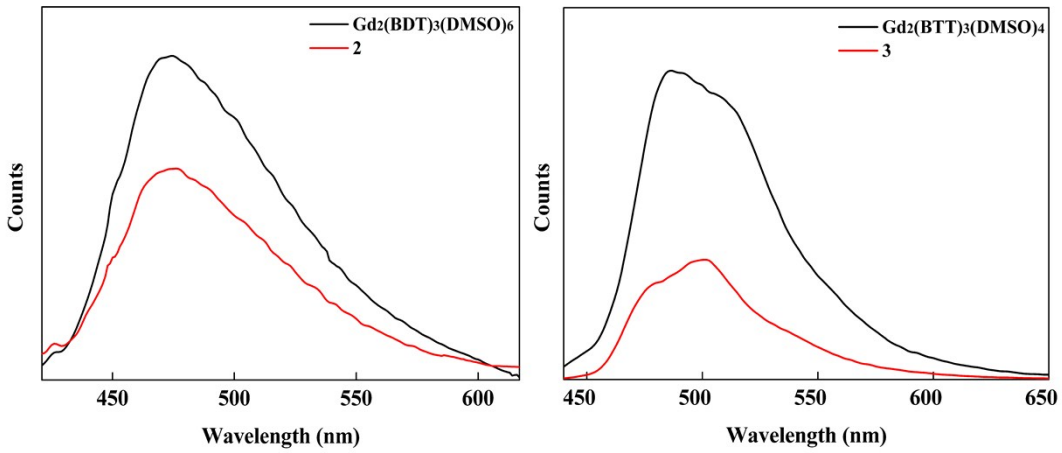


Figure S4 Fluorescence spectra of BDT and BTT in their Nd (red line) and Gd(III) complexes (black line).

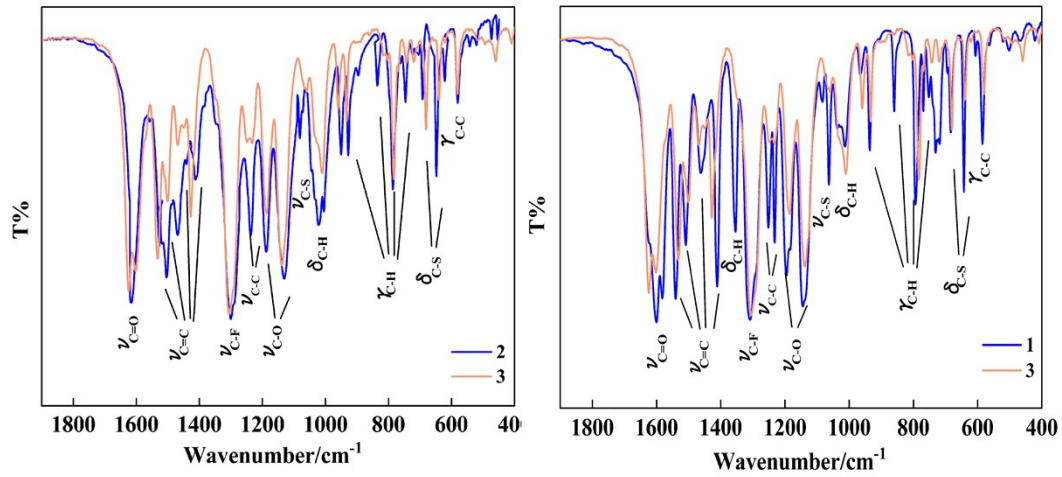


Figure S5 FT–IR spectra of **1**, **2** and **3**.

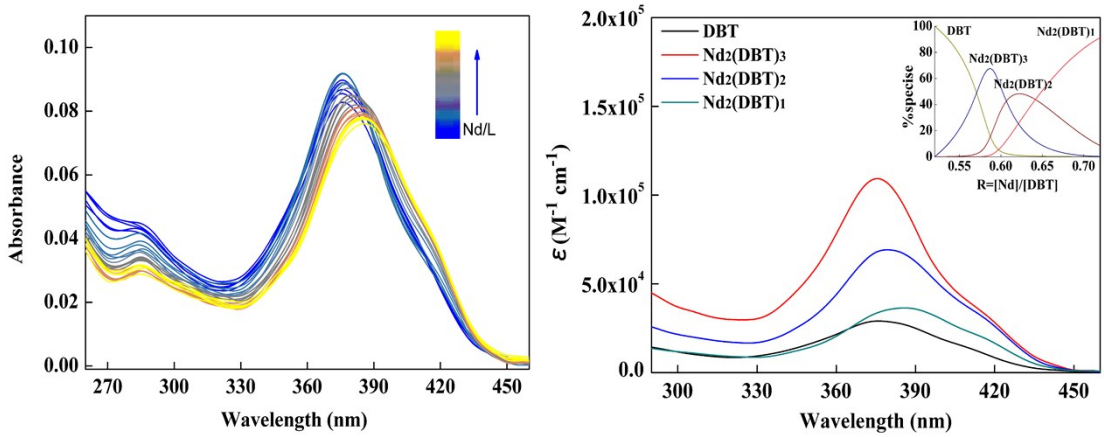


Figure S6 UV/Vis absorption spectra of a 3×10^{-6} M solution of $[BDT]^{2-}$ in DMSO upon addition of increasing amounts of $NdCl_3$, from 0 to 2.5 equiv. (left); Calculated UV/Vis absorption spectra of the species (right). Inset: Species distribution diagram drawn with the conditional constants reported in Table 1 for $Nd_2(BDT)_3$.

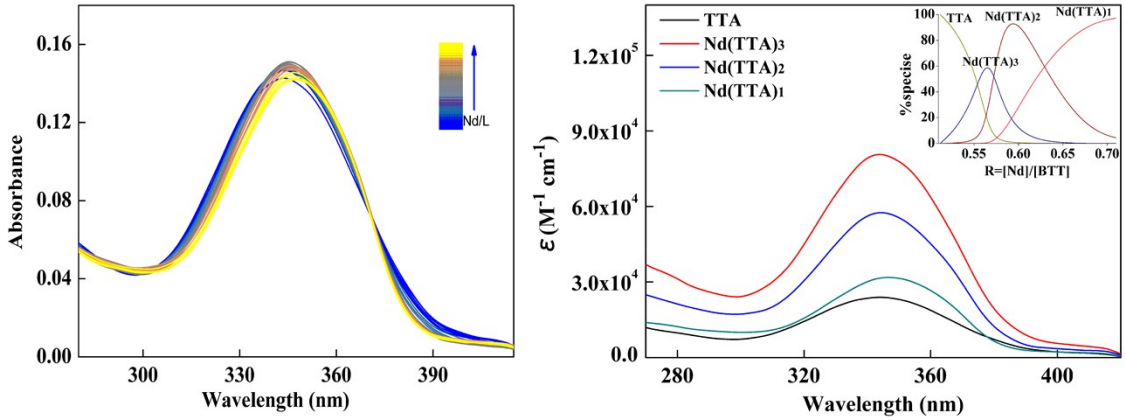


Figure S7 UV/Vis absorption spectra of a 6×10^{-6} M solution of $[TTA]^{-}$ in DMSO upon addition of increasing amounts of $NdCl_3$, from 0 to 1.25 equiv. (left); Calculated UV/Vis absorption spectra of the species (right). Inset: Species distribution diagram drawn with the conditional constants reported in Table 1 for $Nd(TTA)_3$.

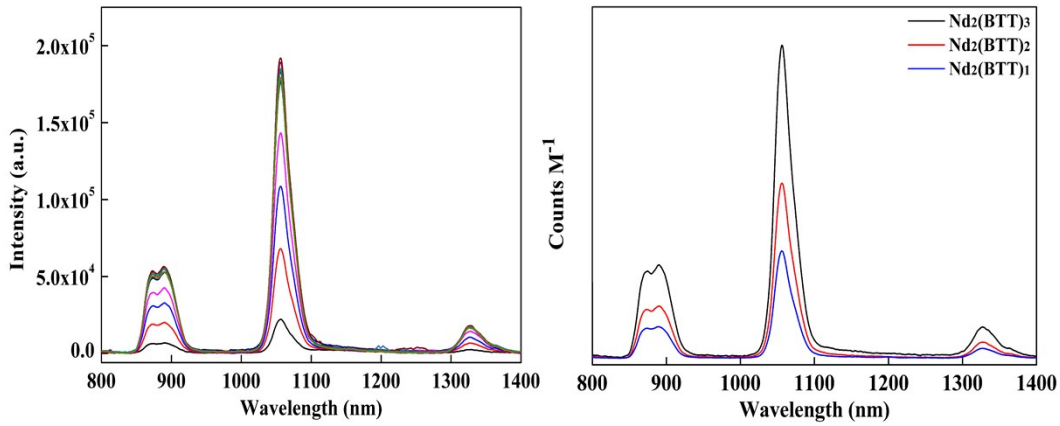


Figure S8 Emission spectra of a 3×10^{-6} M solution of $[BTT]^{2-}$ in DMSO upon addition of increasing amounts of $NdCl_3$, from 0 to 2.5 equiv. (left); Calculated emission spectra of the species (right).

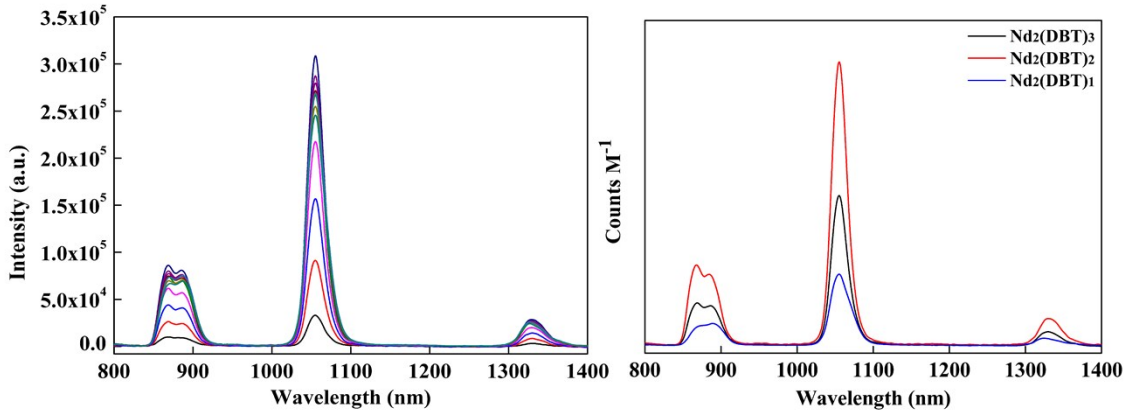


Figure S9 Emission spectra of a 3×10^{-6} M solution of $[BDT]^{2-}$ in DMSO upon addition of increasing amounts of $NdCl_3$, from 0 to 2.5 equiv. (left); Calculated emission spectra of the species (right).

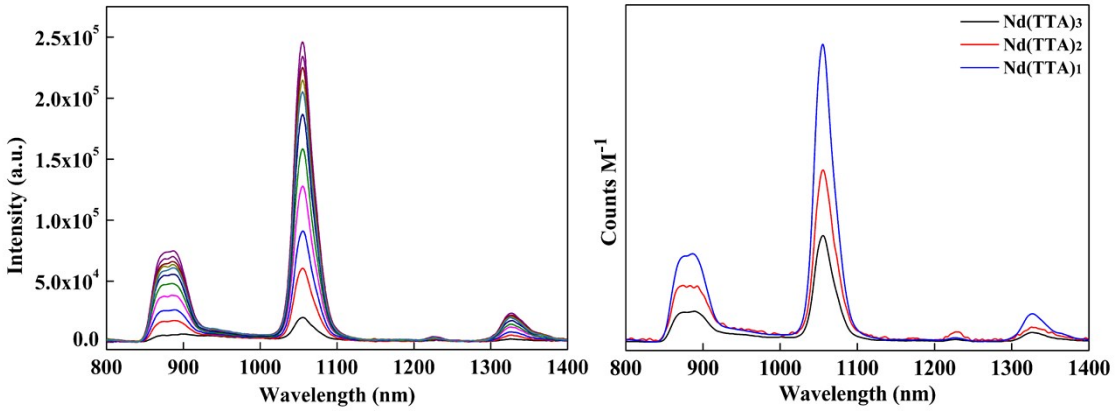


Figure S10 Emission spectra of a 6×10^{-6} M solution of $[TTA]^{-}$ in DMSO upon addition of increasing amounts of $NdCl_3$, from 0 to 1.25 equiv. (left); Calculated emission spectra of the species (right).

Table S1 Distances of metal centres to C–H bonds.

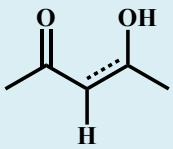
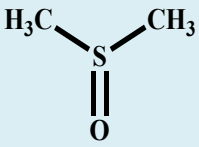
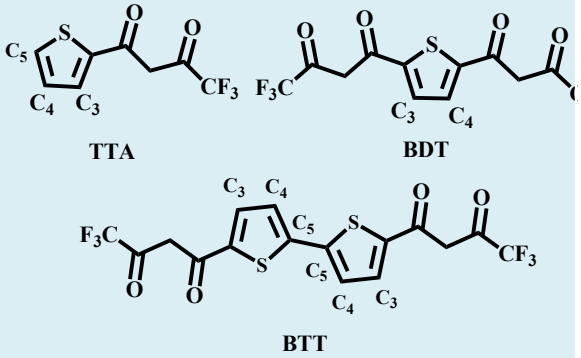
Complexes	 Methyne	 Solvents	 Thiophene rings		
	$Nd\cdots C_{methyne}$	$Nd\cdots C_{DMSO}$	$Nd\cdots C_3$	$Nd\cdots C_4$	$Nd\cdots C_5$
1	3.8032	4.1854	5.9504	6.9177	6.6266
	3.8798	4.3456	6.1007	7.0315	6.7011
	3.8853	4.6102	6.1395	7.0346	6.744
		5.0333			
Average	3.8516	4.5436	6.0635	6.9946	6.6905
2	3.9443	4.9360	6.0270	7.0299	
	3.9672	4.8609	6.0609	7.0567	
	3.9443	4.8395	6.0944	7.0816	
		4.8069			
		4.7058			
		4.5446			
Average	3.9646	4.7822	6.0607	7.0560	
3	3.7926	4.3003	5.7048	6.6877	
	3.8485	4.3412	5.8653	6.7991	
	3.8488	4.9135	6.0046	7.0816	
		4.9196			
Average	3.8299	4.6186	5.8582	6.8561	

Table S2 Crystal data and structure refinements for **1, 2** and **3**.

	1	**2**	**3**
Formula	$C_{28}H_{24}F_9NdO_8S_5$	$C_{50}H_{54}F_{18}Nd_2O_{19}S_{10}$	$C_{60}H_{54}F_{18}Nd_2O_{18}S_{12}$
Mr	964.01	1910.01	2078.35
Color	colorless	yellow	yellow
Cryst. syst.	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$
a (Å)	12.2314(2)	19.7938(5)	41.621(4)
b (Å)	17.1983(4)	28.2072(5)	11.9064(10)
c (Å)	17.3127(3)	15.0963(4)	16.7402(15)
a (deg)	90	90	90
β (deg)	91.1317(16)	118.891(4)	98.961(2)
γ (deg)	90	90	90
V (Å^3)	3641.15(12)	7379.7(3)	8194.5(13)
Z	4	4	4
ρ (g cm^3)	1.759	1.719	1.685
μ (mm^{-1})	1.804	1.782	1.661
F (000)	1908.0	3792.0	4128.0
R_1,[I>2σ(I)]	0.0519	0.0321	0.0682
wR_2,[I>2σ(I)]	0.1025	0.0720	0.1516
R_1,(all data)	0.0635	0.0466	0.1428
wR_2,(all data)	0.1091	0.0813	0.1916
GOF on F^2	1.036	1.064	0.992

Table S3 Binding constants and species distribution obtained by fitting the changes in emission spectra.

	Species	$\log\beta_{M/L}$	% Species for M/L	Concentration of species (10^{-6} M)
1	$\log\beta_{13}$	28.213	61.3	1.411
	$\log\beta_{12}$	22.168	23.1	0.531
	$\log\beta_{11}$	12.544	0.2	0.004
	$[TTA]^-$	–	15.4	0.354
2	$\log\beta_{23}$	28.200	68.1	0.754
	$\log\beta_{22}$	21.532	15.8	0.175
	$\log\beta_{21}$	14.160	1.1	0.012
	$[BDT]^{2-}$	–	14.1	0.156
3	$\log\beta_{23}$	28.164	65.3	0.725
	$\log\beta_{22}$	21.741	17.4	0.193
	$\log\beta_{21}$	14.189	0.8	0.009
	$[BTT]^{2-}$	–	16.5	0.183