

Supplementary Information

Synthesis and crystal structures of lanthanide 4-benzyloxy benzoates: Influence of electron-withdrawing and electron-donating groups on luminescent properties

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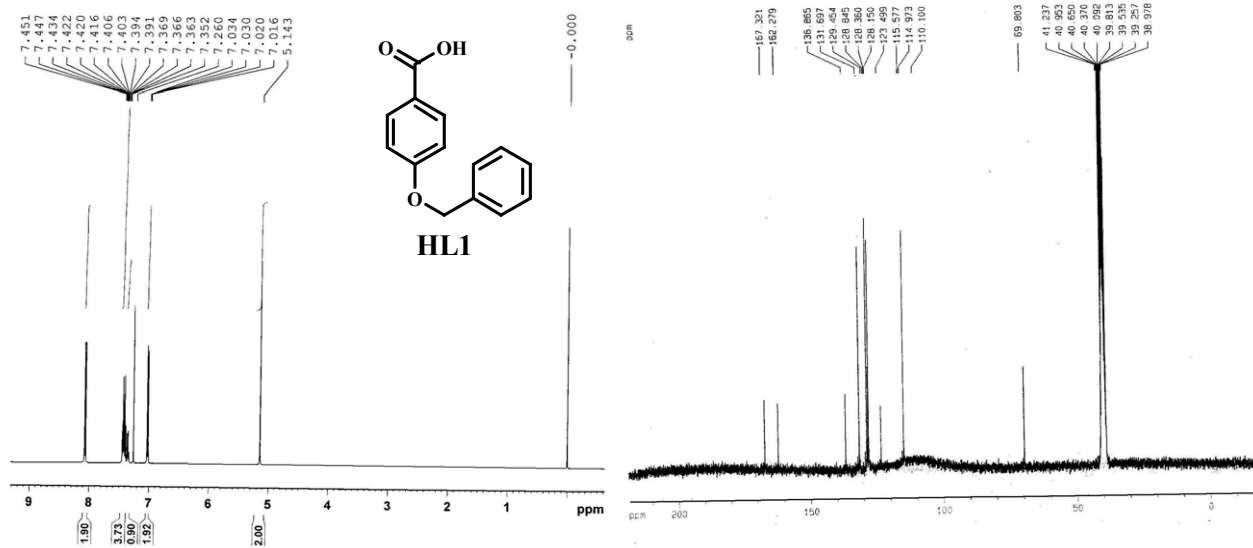


Fig. S1 ¹H NMR spectrum of HL1 in CDCl₃ and ¹³C NMR in DMSO-d₆ solutions.

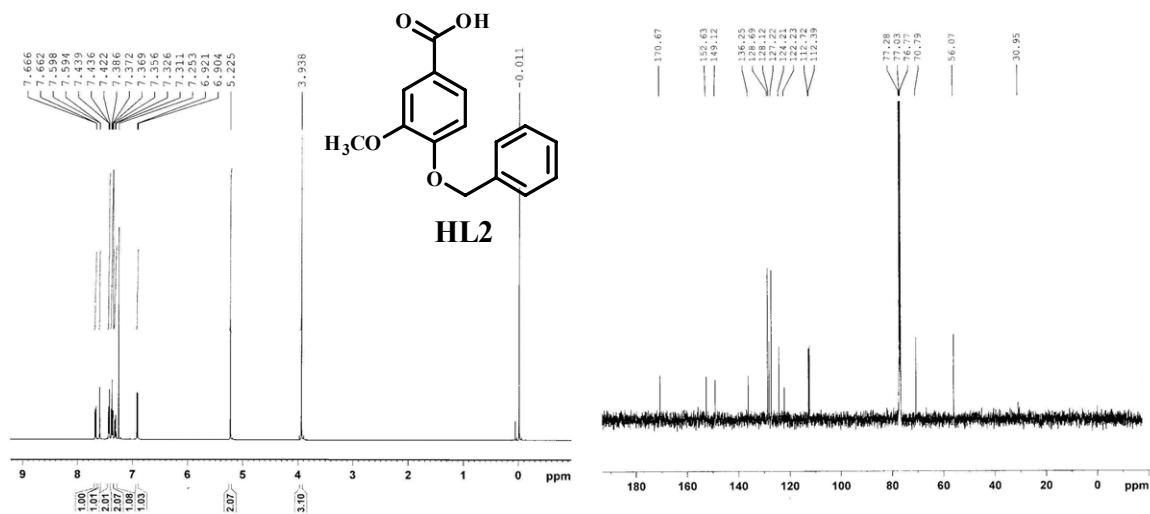


Fig. S2 ¹H and ¹³C NMR spectra of HL2 in CDCl₃ solution.

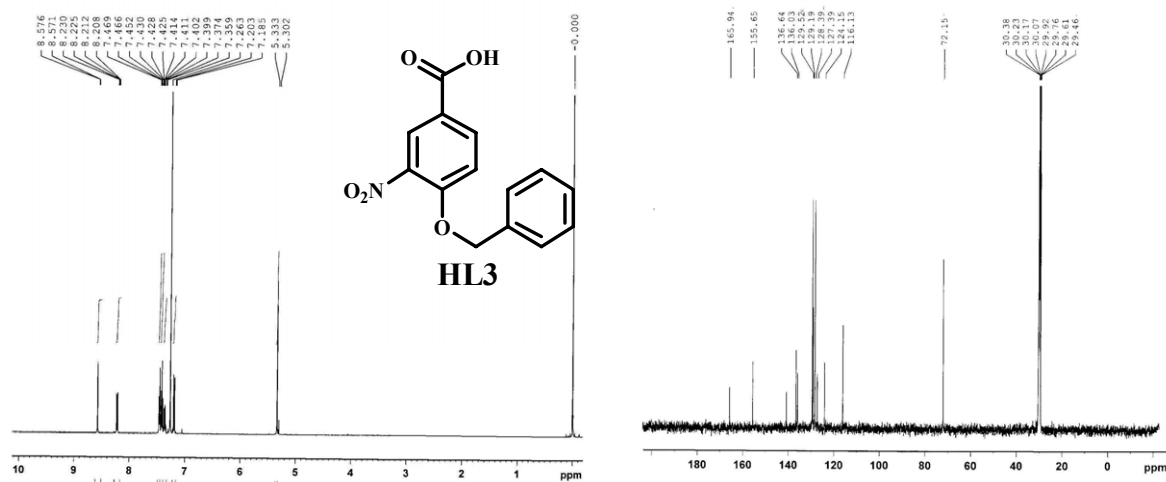


Fig. S3 ¹H NMR spectrum of HL3 in CDCl₃ solution and ¹³C NMR in acetone-d₆ solution.

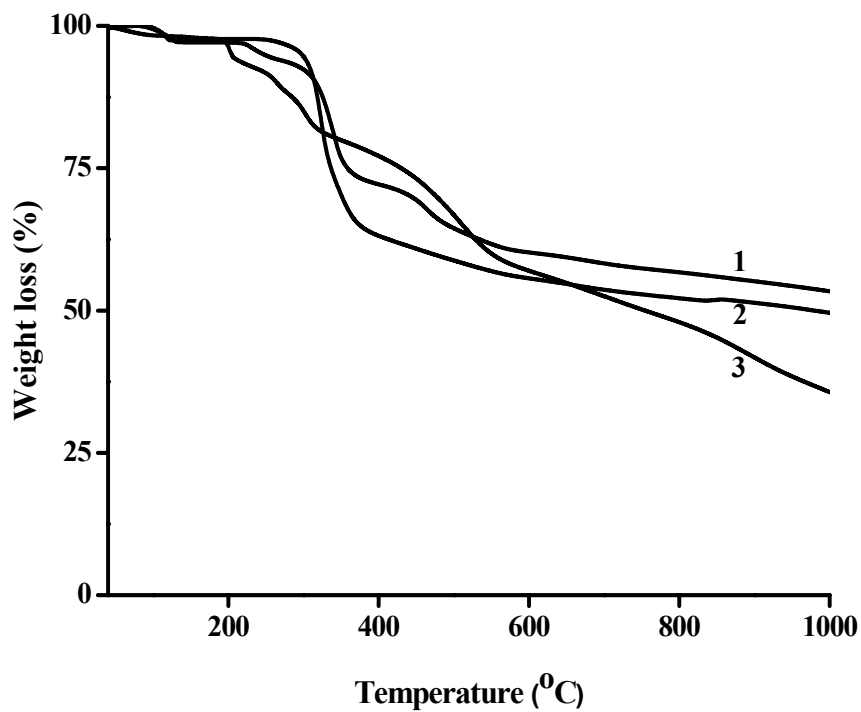


Fig. S4 Thermogravimetric plot for complexes 1-3.

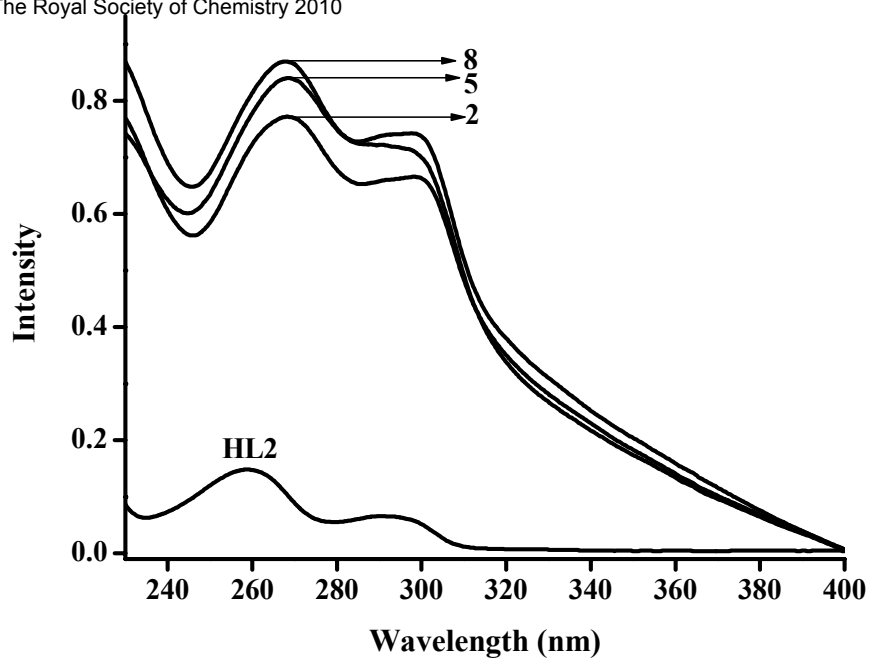


Fig. S5 UV-visible absorption spectra of 3-methoxy-4-benzyloxy benzoic acid and complexes **2**, **5** and **8** in CH_3CN solution (2×10^{-5} M).

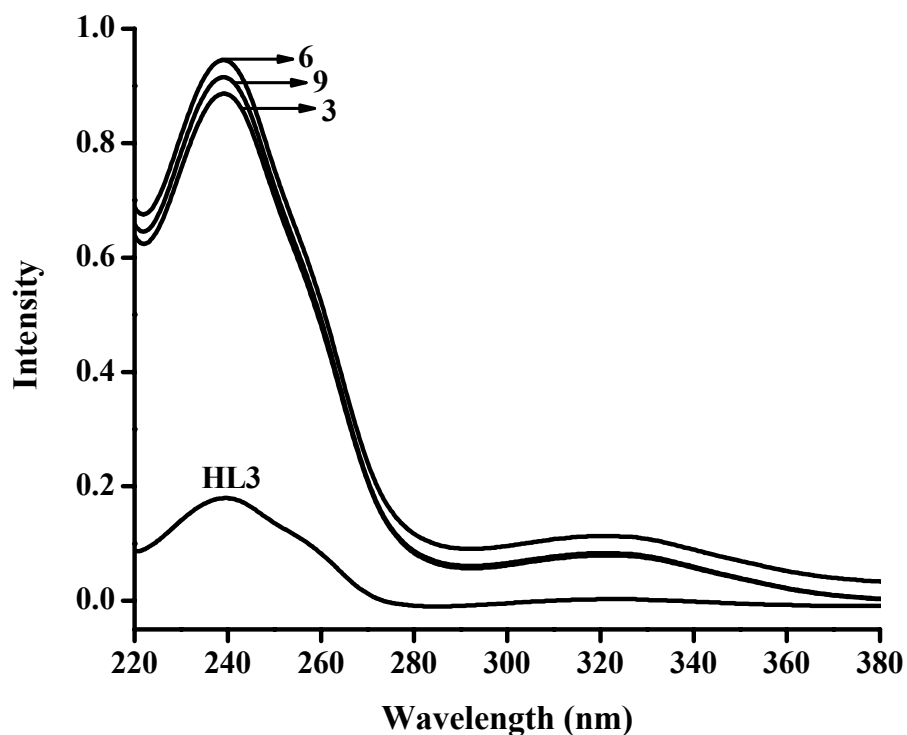


Fig. S6 UV-visible absorption spectra of 4-(benzyloxy)-3-nitro benzoic acid and complexes **3**, **6** and **9** in CH_3CN solution (2×10^{-5} M).

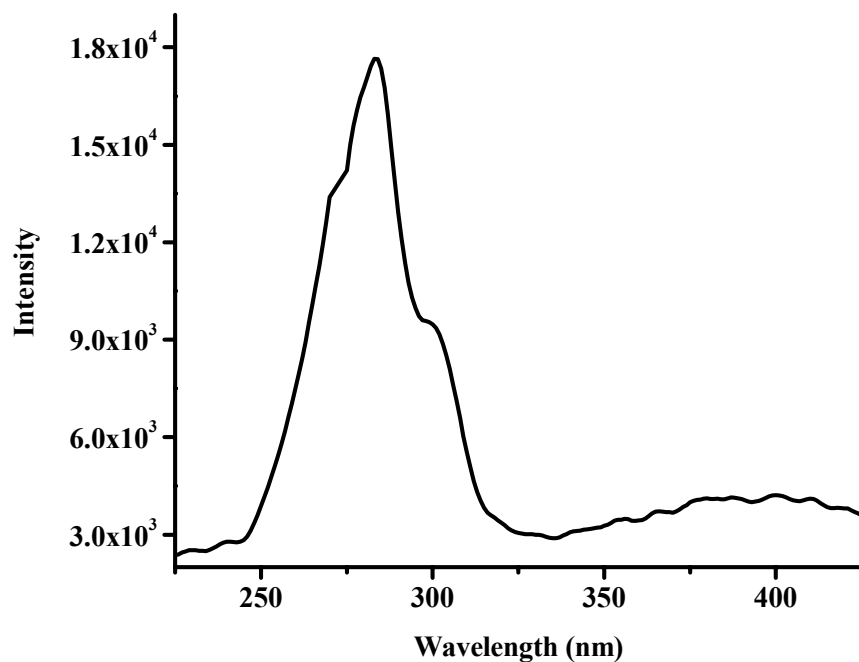


Fig. S7 Room-temperature excitation spectrum for complex 3.

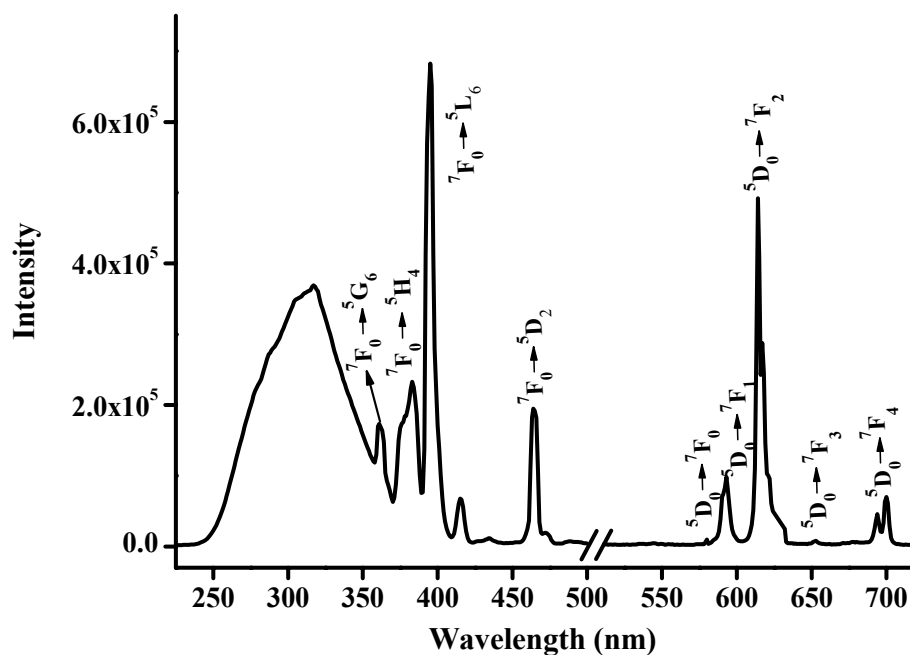


Fig. S8 Room-temperature excitation and emission spectra for complex 4 ($\lambda_{\text{ex}} = 314$ nm) with emission monitored at approximately 612 nm.

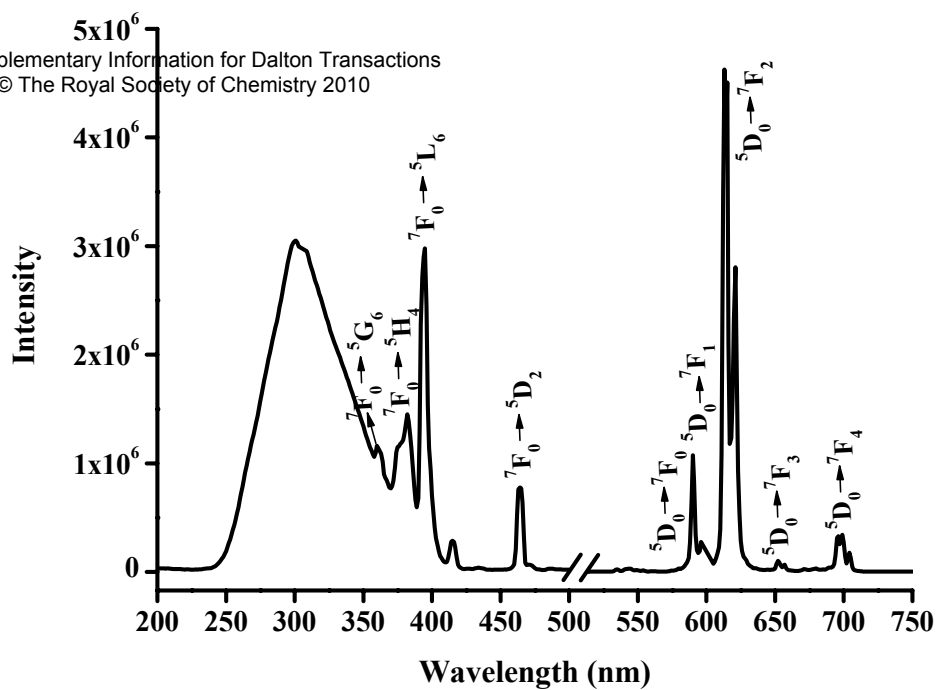


Fig. S9 Room-temperature excitation and emission spectra for complex **5** ($\lambda_{\text{ex}} = 300\text{ nm}$) with emission monitored at approximately 612 nm.

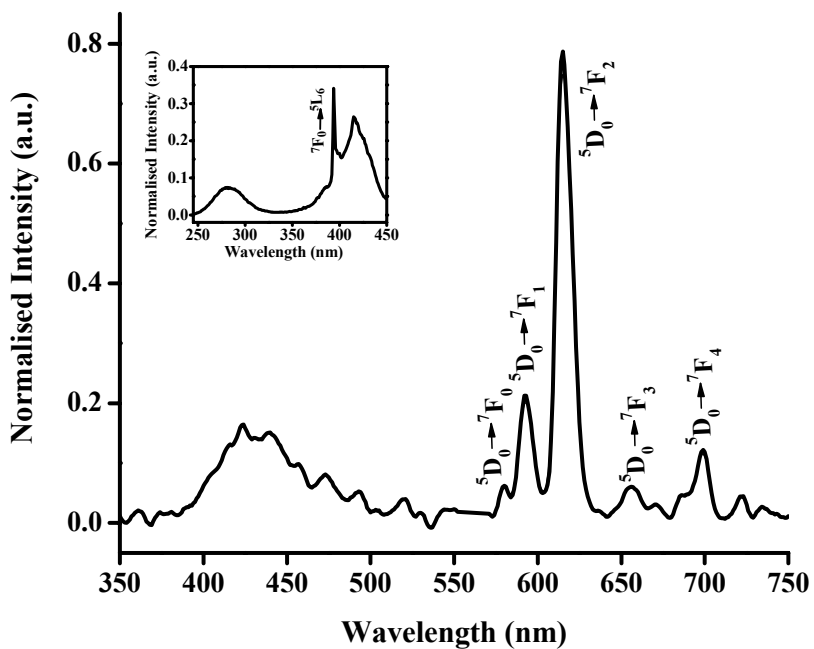


Fig. S10 Room-temperature emission spectrum for complex **6** ($\lambda_{\text{ex}} = 280\text{ nm}$). (Inset shows the excitation spectrum of the complex **6** with emission monitored at approximately 612 nm).

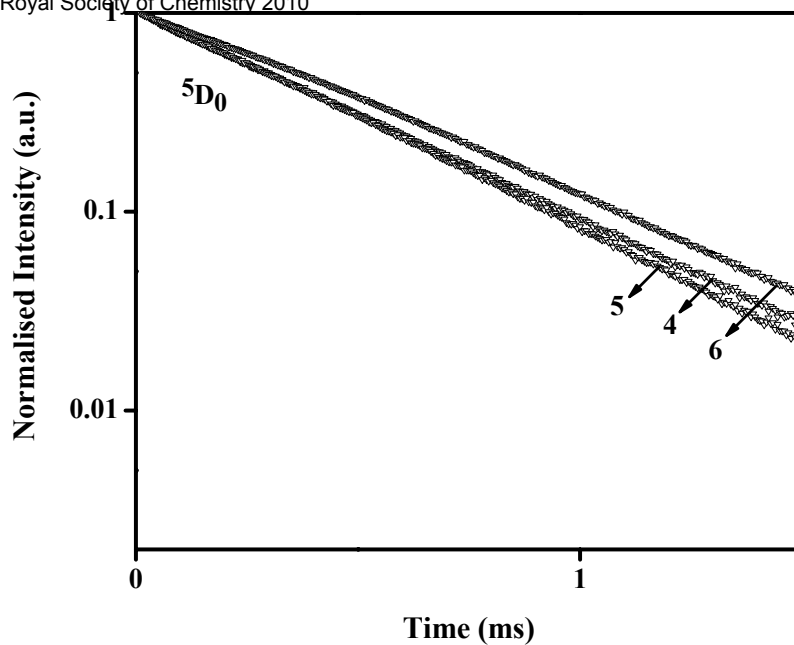


Fig. S11 Luminescence decay profile of complexes **4**, **5** and **6** excited at 314, 300 and 280 nm, respectively and monitored at approximately 612 nm.

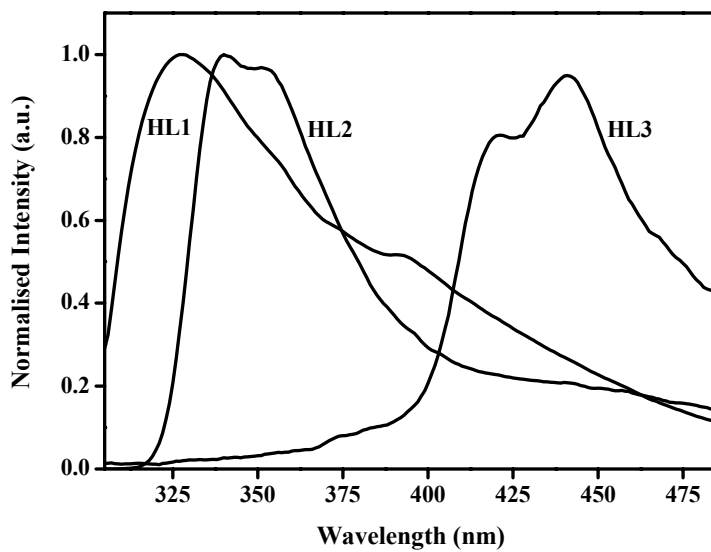


Fig. S12 Room-temperature emission spectra of ligands HL1-HL3.

Table S1 Infrared vibrational frequencies for the carboxylate functionalities of ligands HL1-HL3 and complexes **1-9**.

	$\nu_{\text{as}}(\text{C}=\text{O}) \text{ cm}^{-1}$	$\nu_{\text{s}}(\text{C}=\text{O}) \text{ cm}^{-1}$	$\Delta\nu_{(\text{C}=\text{O})} \text{ cm}^{-1}$
HL1	1686	1454	
HL2	1678	1454	
HL3	1689	1454	
1	1586, 1610	1380, 1439	230,147
2	1597, 1627	1395, 1423	232,174
3	1588, 1614	1350, 1424	264,164
4	1586, 1608	1380, 1432	228,154
5	1599, 1627	1396, 1423	231,176
6	1584, 1626	1338,1423	288,161
7	1586, 1610	1380, 1435	230,151
8	1599, 1628	1396, 1423	232,176
9	1589, 1615	1350, 1424	265,165

Table S2 Values for the absorption maxima and molar absorption coefficients for ligands HL1-HL3 and compounds **1-9** in acetonitrile solution ($c = 2 \times 10^{-5}$ M).

Compound	λ_{\max} π - π^* / ILCT (nm)	ϵ (mol^{-1} liter cm^{-1})
HL1	253	8.69×10^3
HL2	260, 295	7.39×10^3
HL3	238, 318	9.20×10^3
1	254	4.58×10^4
2	267, 299	3.86×10^4
3	239, 321	4.46×10^4
4	255	4.78×10^4
5	268, 299	4.21×10^4
6	239, 321	4.75×10^4
7	256	4.84×10^4
8	267, 299	4.35×10^4
9	239, 321	4.60×10^4

Procedures for calculating radiative (A_{RAD}) and nonradiative (A_{NR}) decay rates, radiative lifetimes (τ_{RAD}), intrinsic quantum yields (Φ_{Ln}), energy transfer efficiencies (Φ_{sen}), and overall quantum yields (Φ_{overall}) for Eu^{3+} and Tb^{3+} complexes **1-6.**

The overall quantum yield (Φ_{overall}) for a Ln^{3+} coordination compound is the product of the intrinsic quantum yield Φ_{Ln} (measured upon f-f excitation), which reflects the extent of nonradiative deactivation processes that take place within the luminescent edifice, and the sensitization efficiency of the ligand (Φ_{sen}), which reflects the efficacy with which the latter transfers its excitation energy onto the metal ion.¹

$$\Phi_{\text{overall}} = \Phi_{\text{sen}} \Phi_{\text{Ln}} \quad (1)$$

Here, Φ_{sen} represents the efficiency of energy transfer from the ligand to the Ln^{3+} ion and Φ_{Ln} represents the intrinsic quantum yield of the Ln^{3+} ion, which can be calculated as shown in Equation (2).

$$\phi_{Ln} = \left(\frac{A_{RAD}}{A_{RAD} + A_{NR}} \right) = \frac{\tau_{obs}}{\tau_{RAD}} \quad (2)$$

For the Eu^{3+} complexes, the radiative lifetime (τ_{RAD}) can be calculated using Equation (3),² assuming that the energy of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition (MD) and its oscillator strength are constant

$$A_{RAD} = \frac{1}{\tau_{RAD}} = A_{MD,0} n^3 \left(\frac{I_{TOT}}{I_{MD}} \right) \quad (3)$$

where, $A_{MD,0}$ (14.65 s^{-1}) is the spontaneous emission probability of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition in vacuo,² I_{TOT}/I_{MD} is the ratio of the total area of the corrected Eu^{3+} emission spectrum to the area of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ band and n is the refractive index of the medium. An average index of refraction equal to 1.5 was employed.³ The intrinsic quantum yield of Tb^{3+} (Φ_{Tb}) can be estimated by means of Equation (4) using the assumption that the decay process at 77 K in deuterated solvents is purely radiative.⁴

$$\phi_{Tb} = \frac{\tau_{obs(298K)}}{\tau_{RAD(77K)}} \quad (4)$$

The radiative lifetime (τ_{RAD}), intrinsic quantum yields (Φ_{Ln}), and sensitization efficiencies (Φ_{sen}) of the ligands for Ln^{3+} complexes **1-6** were calculated and are presented in Table 3. The quantum yields were measured for complexes **1-6** by employing the technique for powdered samples described by Bril *et al.*⁵

References

- (a) M. Xiao and P. R. Selvin, *J. Am. Chem. Soc.*, 2001, **123**, 7067; (b) S.Comby, D. Imbert, C. Anne-Sophie, J.-C.G. Bünzli, L. J. Charbonniere and R. F. Ziessel, *Inorg. Chem.*, 2004, **43**, 7369.

2 (a) S. Viswanathan and A. de Bettenacourt-Dias, *Inorg. Chem.*, 2006, **45**, 10138; (b) Y. H. Kim, N. S. Baek and H. K. Kim, *Chem. Phys. Chem.*, 2006, **7**, 213.

3 (a) G. F. de Sa, O. L. Malta, C. de Mello Donega, A. M. Simas, R. L. Longo, P. A. Santa-Cruz and E. F. da Silva Jr, *Coord. Chem. Rev.*, 2000, **196**, 165; (b) D. B. Ambili Raj, S. Biju and M. L. P. Reddy, *Inorg. Chem.*, 2008, **47**, 8091.

4 (a) N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201; I. Nasso, S. Bedel, C. Galaup and C. Picard, *Eur. J. Inorg. Chem.*, 2008, **12**, 2064.

5 A. Bril., A. W De Jager- Veenis, *J. Electrochem. Soc.*, 1976, **123**, 396.