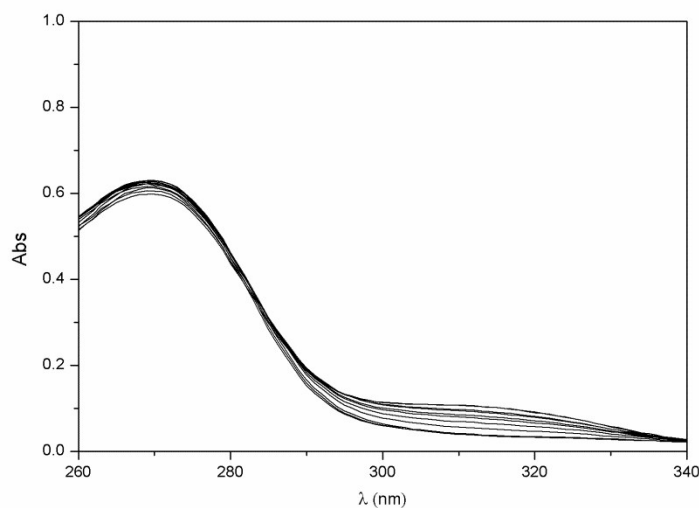
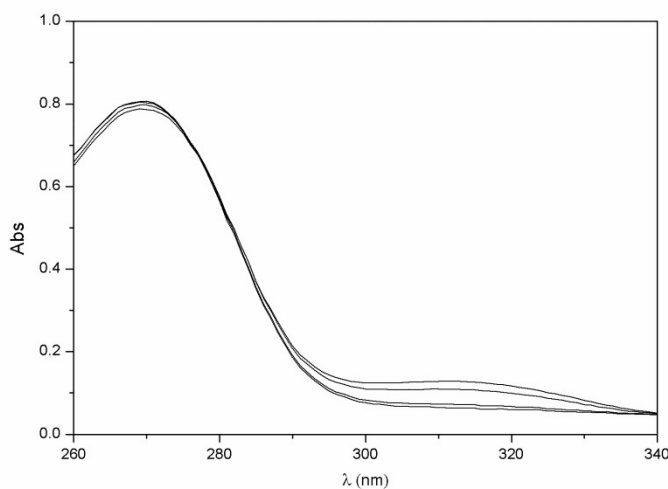


## Tuning of the sensing properties of luminescent $\text{Eu}^{3+}$ complexes towards the nitrate anion

### Electronic Supplementary Information

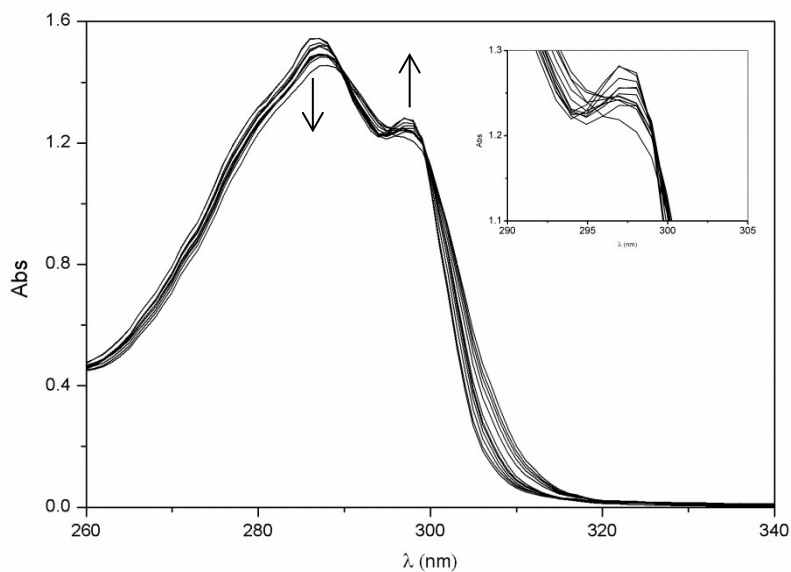


(a)

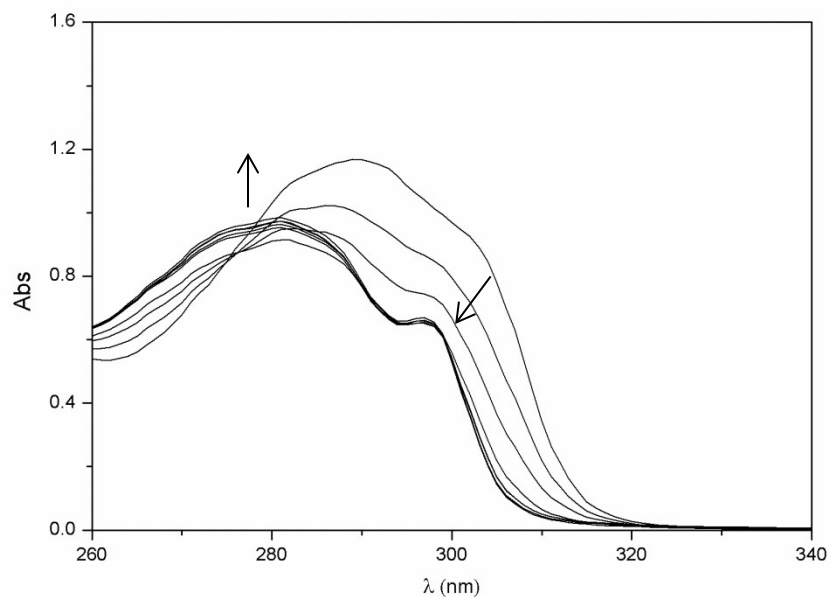


(b)

**Figure S1.** Electronic spectra of: (a) solution containing  $\text{Eu}(\text{OTf})_3:\text{L}2$  in 1:1 molar ratio ( $C_{\text{Eu}} = 0.019 \text{ mmol L}^{-1}$ ,  $V_0 = 2.0 \text{ mL}$ ), titrated with a  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution ( $2.4 \text{ mmol L}^{-1}$ , 16 additions of  $4 \mu\text{L}$ ); final  $C_{\text{Eu}}/C_{\text{L}}/C_{\text{nitrate}} = 1/1/4$ . (b) solution containing  $\text{Eu}(\text{OTf})_3:\text{L}2$  in 1:2 molar ratio ( $C_{\text{Eu}} = 0.0096 \text{ mmol L}^{-1}$ ,  $V_0 = 2.0 \text{ mL}$ ) titrated with a  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution ( $2.4 \text{ mmol L}^{-1}$ , 8 additions of  $4 \mu\text{L}$ ); final  $C_{\text{Eu}}/C_{\text{L}}/C_{\text{nitrate}} = 1/2/4$ .

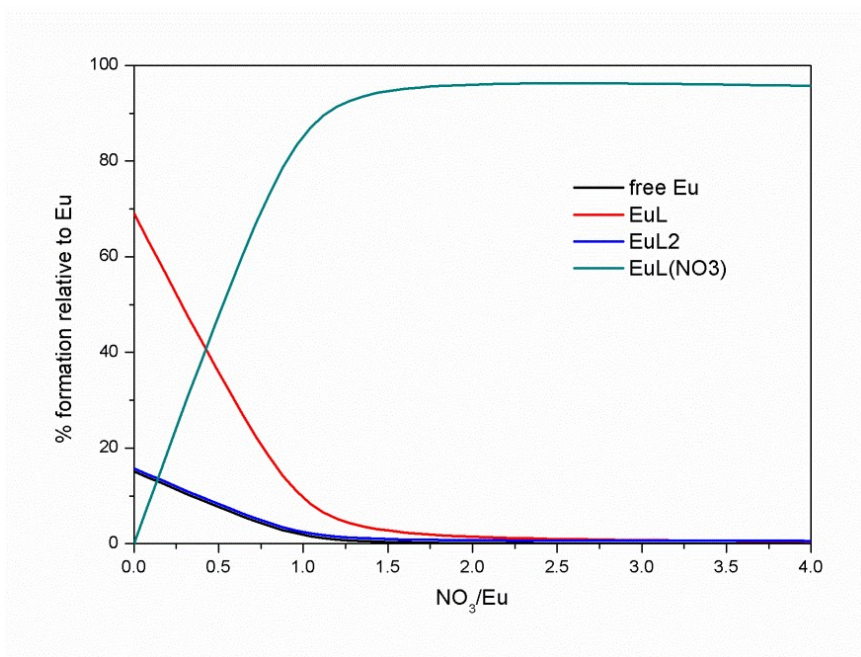


(a)

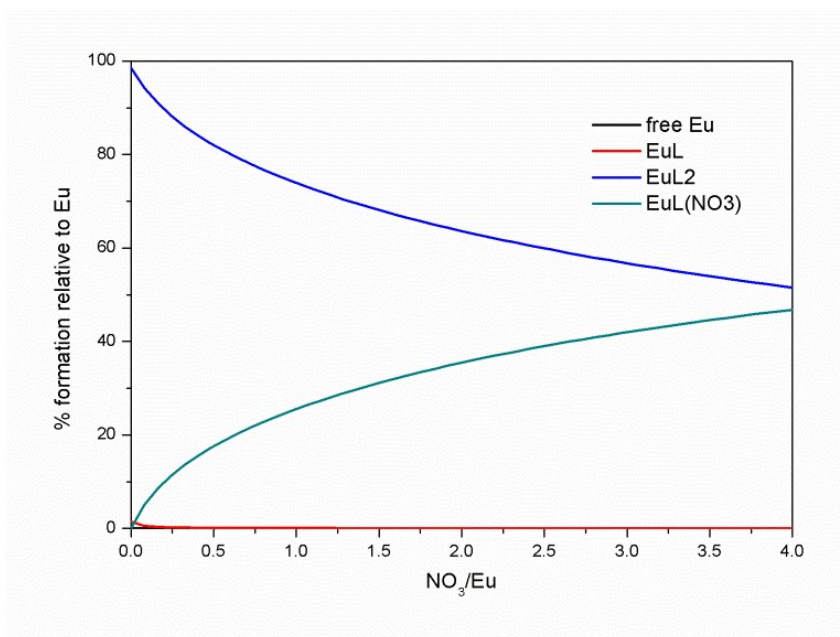


(b)

**Figure S2.** Electronic spectra of: (a) solution containing 1:1  $\text{Eu}(\text{OTf})_3\text{:L3}$  molar ratio ( $C_{\text{Eu}} = 0.0795 \text{ mmol L}^{-1}$ ,  $V_0 = 2.0 \text{ mL}$ ), titrated with a  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution ( $12.0 \text{ mmol L}^{-1}$ , 7 additions of  $3 \mu\text{L}$  + 8 additions of  $3.5 \mu\text{L}$ ); final  $C_{\text{Eu}}/C_{\text{L}}/C_{\text{nitrate}} = 1/1/4$ . (b) solution containing  $\text{Eu}(\text{OTf})_3\text{:L3}$  in 1:2 molar ratio ( $C_{\text{Eu}} = 0.0394 \text{ mmol L}^{-1}$ ,  $V_0 = 2.0 \text{ mL}$ ) titrated with a  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution ( $2.4 \text{ mmol L}^{-1}$ , 8 additions of  $3.5 \mu\text{L}$ ); final  $C_{\text{Eu}}/C_{\text{L}}/C_{\text{nitrate}} = 1/2/4$ .



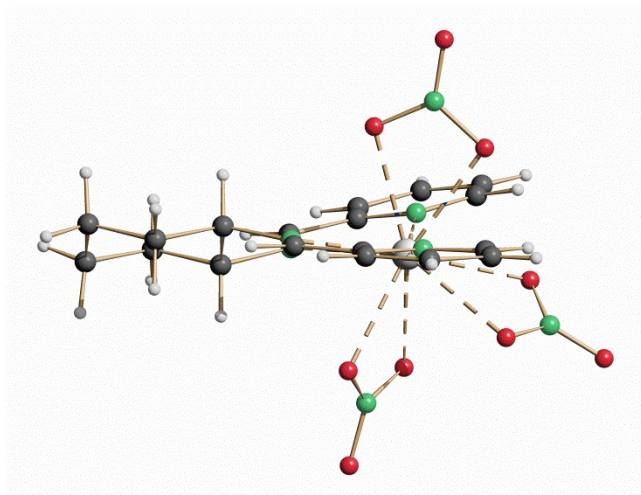
(a)



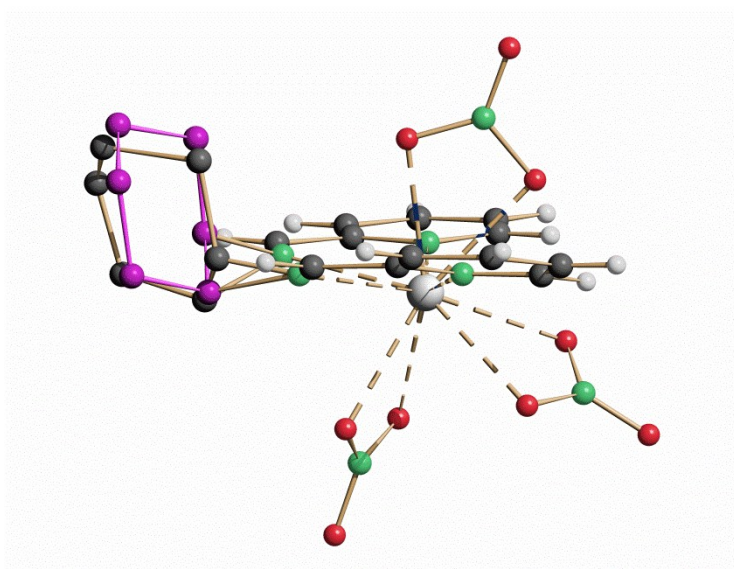
(b)

**Figure S3.** Speciation during the titration of (a)  $\text{EuL}_3(\text{OTf})_3$  and (b)  $\text{Eu}(\text{L}_3)_2(\text{OTf})_3$  with  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$

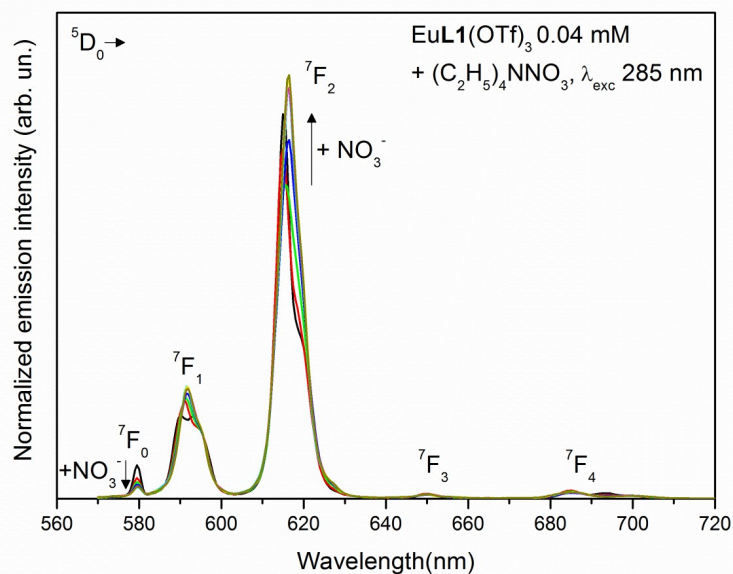
(a)



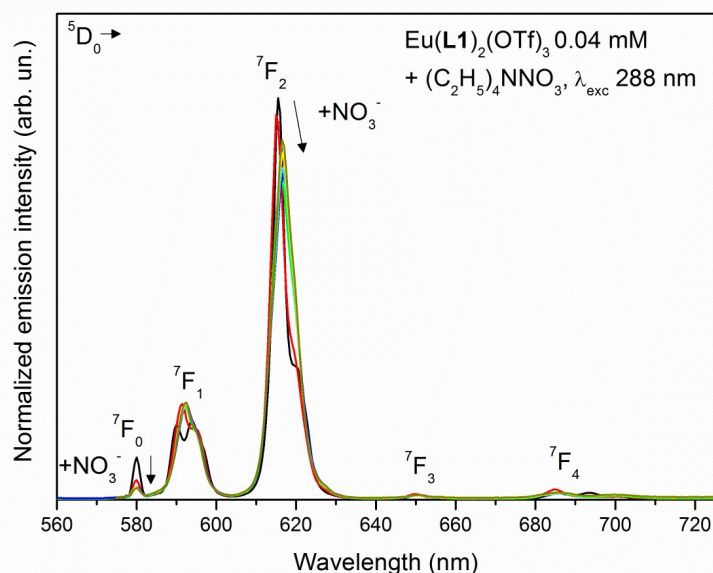
(b)



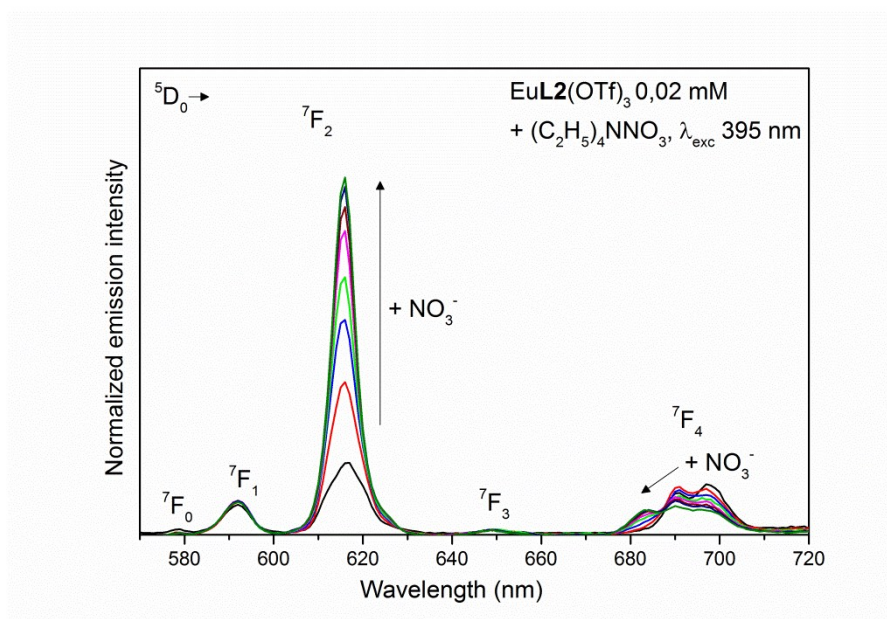
**Figure S4.** Molecular crystal structure of (a)  $\text{EuL1}(\text{NO}_3)_3$  and (b)  $\text{EuL3}(\text{NO}_3)_3$ . View parallel to the  $\text{N}_4$  square plane.



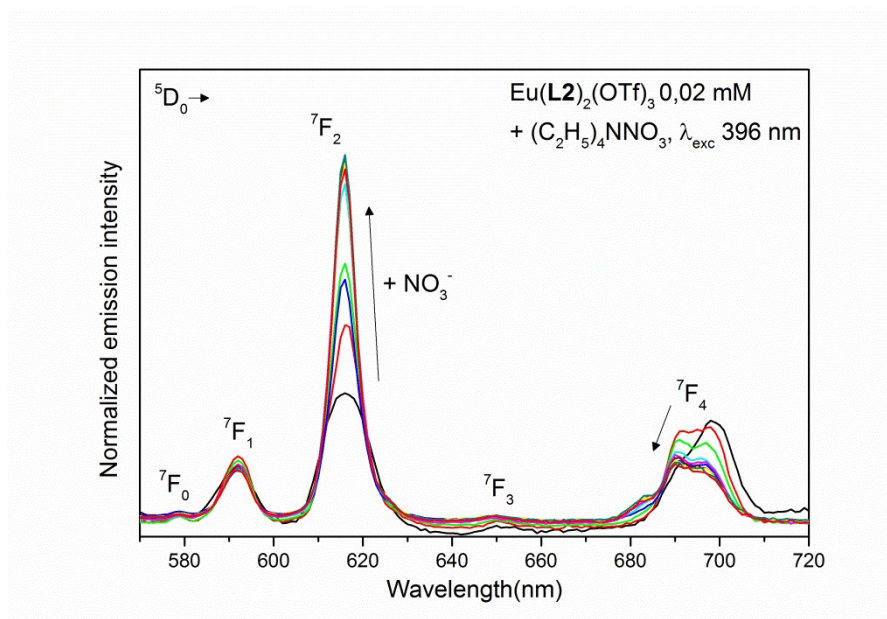
**Figure S5.** Evolution of the luminescence emission spectrum of 0.04 mM AN solution of  $\text{EuL1(OTf)}_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band. As the  $\lambda_{\text{exc}} = 285$  nm,  $\text{L} \rightarrow \text{Eu}^{3+}$  energy transfer (ET) has been exploited (*antenna effect*).



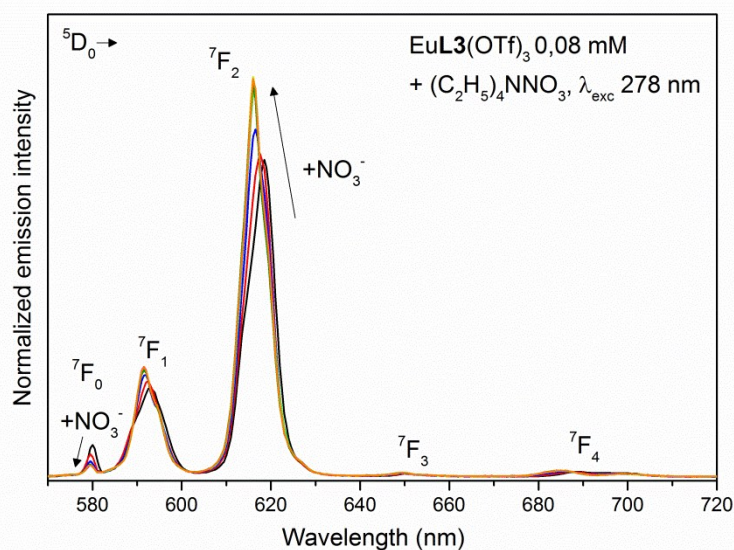
**Figure S6.** Evolution of the luminescence emission spectrum of 0.04 mM AN solution of  $\text{Eu(L1)}_2(\text{OTf})_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band. As the  $\lambda_{\text{exc}} = 288$  nm,  $\text{L} \rightarrow \text{Eu}^{3+}$  energy transfer (ET) has been exploited (*antenna effect*).



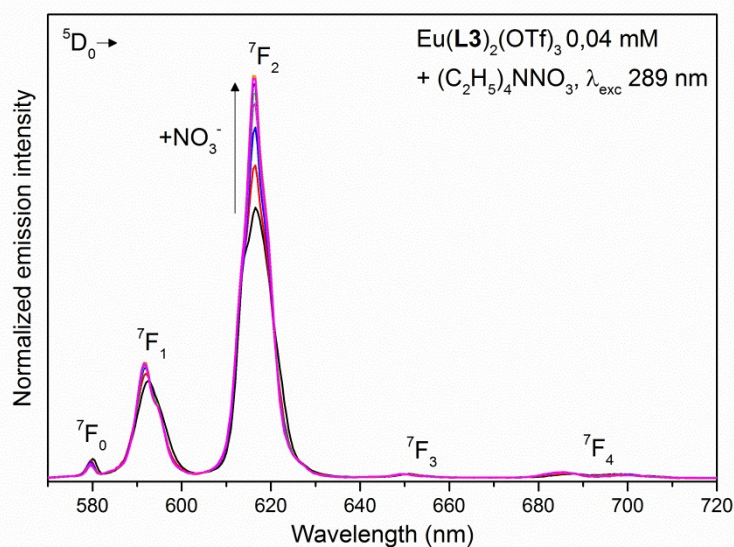
**Figure S7.** Evolution of the luminescence emission spectrum of 0.02 mM AN solution of  $\text{EuL2(OTf)}_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band.



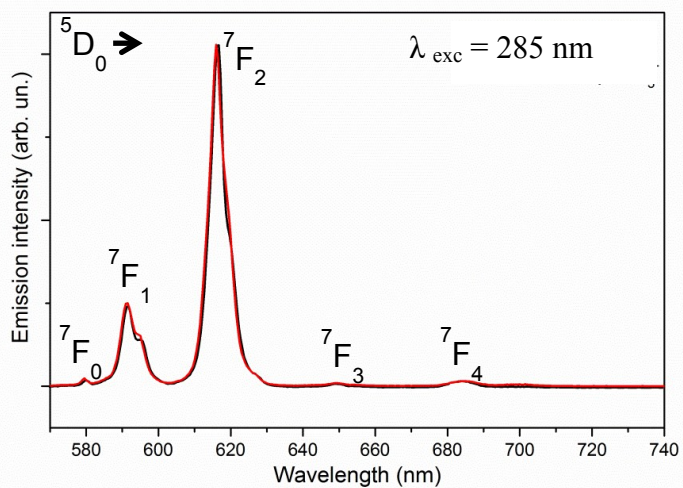
**Figure S8.** Evolution of the luminescence emission spectrum of 0.02 mM AN solution of  $\text{Eu(L2)}_2(\text{OTf})_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band.



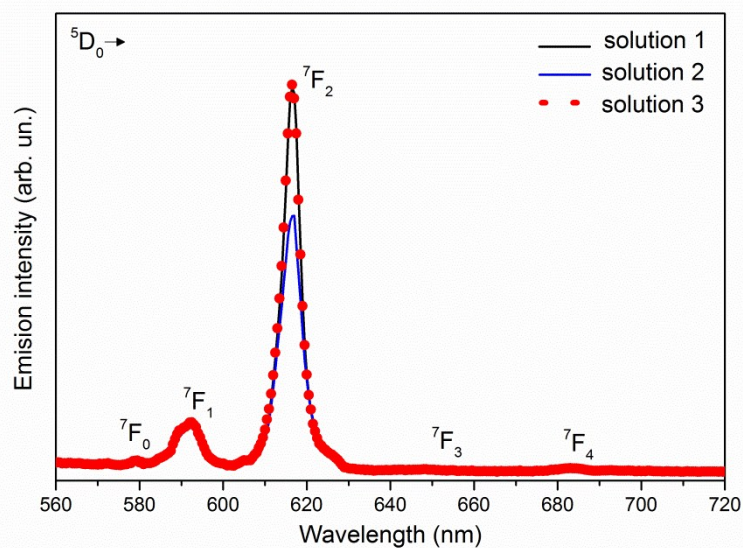
**Figure S9.** Evolution of the luminescence emission spectrum of 0.08 mM AN solution of  $\text{EuL3(OTf)}_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band. As the  $\lambda_{\text{exc}} = 278$  nm,  $\text{L} \rightarrow \text{Eu}^{3+}$  energy transfer (ET) has been exploited (*antenna effect*).



**Figure S10.** Evolution of the luminescence emission spectrum of 0.04 mM AN solution of  $\text{Eu(L3)}_2(\text{OTf})_3$  upon addition of the nitrate anion. All the spectra are normalized to the area of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission band. As the  $\lambda_{\text{exc}} = 289$  nm,  $\text{L} \rightarrow \text{Eu}^{3+}$  energy transfer (ET) has been exploited (*antenna effect*).

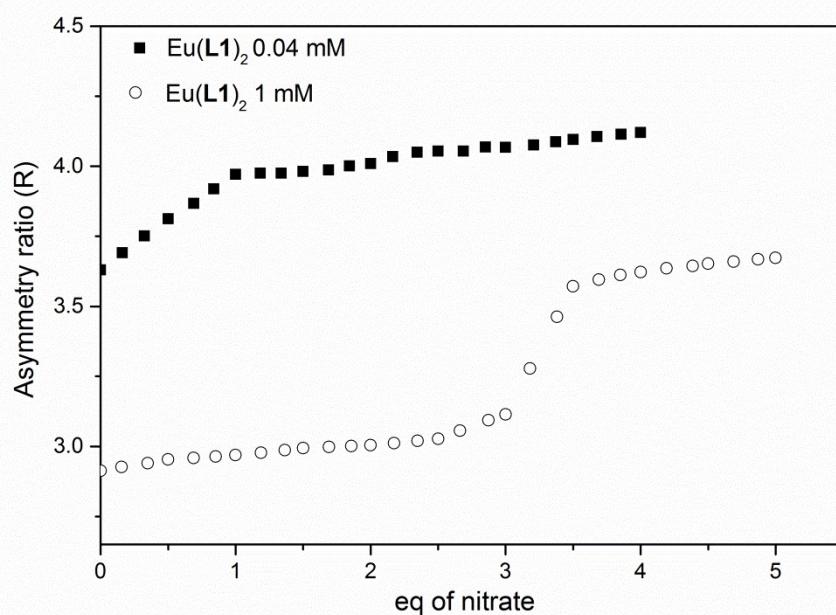


**Figure S11.** Luminescence emission spectra of 1 mM AN solution of  $\text{EuL1}(\text{NO}_3)_3$  (black line) and  $\text{EuL1} + 3.5$  eq of nitrate (red line).

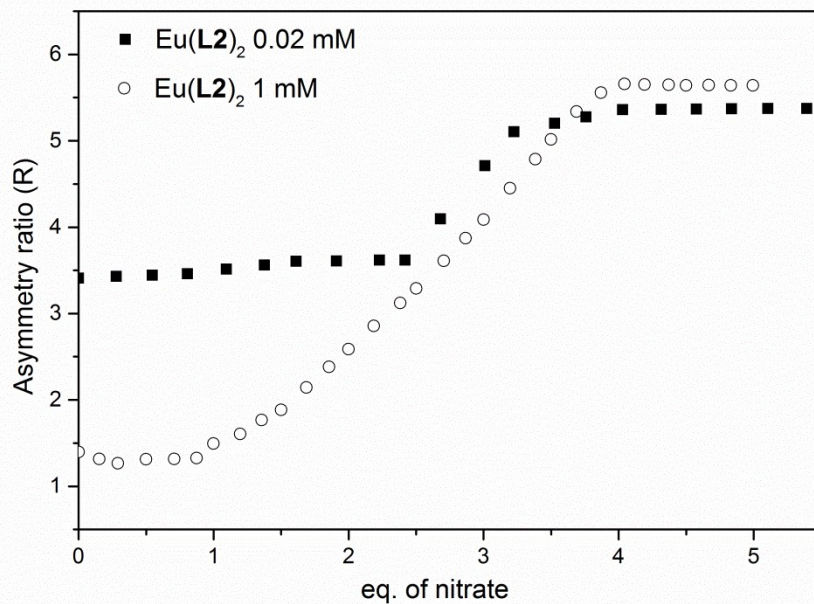


**Figure S12.** Luminescence emission spectra of 1 mM AN solution of  $\text{EuL2} + 4.5$  eq of nitrate (solution 1, black line),  $\text{EuL2}(\text{NO}_3)_3$  (solution 2, blue line) and  $\text{EuL2}(\text{NO}_3)_3 + 1$  eq of nitrate (solution 3, red dotted line).





**Figure S13.** Asymmetry ratio (R) vs nitrate concentration plot for Eu(L1)<sub>2</sub> at two different concentration (i.e. 0.04 and 1 mM).



**Figure S14.** Asymmetry ratio (R) vs nitrate concentration plot for Eu(L2)<sub>2</sub> at two different concentration (i.e. 0.02 and 1 mM).

Compound	EuL3(NO <sub>3</sub> ) <sub>3</sub> ·0.40C <sub>3</sub> H <sub>6</sub> O
Formula	C <sub>18</sub> H <sub>20</sub> EuN <sub>7</sub> O <sub>9</sub> ·0.40C <sub>3</sub> H <sub>6</sub> O
Fw	653.60
T, K	293(2)
λ, Å	0.71073
Crystal symmetry	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	9.7469(6)
<i>b</i> , Å	13.7146(8)
<i>c</i> , Å	20.006(1)
α	78.020(1)
β	76.941(1)
γ	86.008(1)
Cell volume, Å <sup>3</sup>	2547.7(3)
<i>Z</i>	4
D <sub>c</sub> , Mg m <sup>-3</sup>	1.704
μ(Mo-K <sub>α</sub> ), mm <sup>-1</sup>	2.524
F(000)	1299
Crystal size/ mm	0.15 x 0.25 x 0.30
θ limits, °	1.52 – 27.00
Reflections collected	27988
Unique obs. reflections [F <sub>o</sub> > 4σ(F <sub>o</sub> )]	8336 [R(int) = 0.0282]
Goodness-of-fit-on F <sup>2</sup>	1.022
R <sub>1</sub> (F) <sup>a</sup> , wR <sub>2</sub> (F <sup>2</sup> ) [I > 2σ(I)]	0.0346, 0.0836
Largest diff. peak and hole, e. Å <sup>-3</sup>	0.0830 and -0.578

<sup>a</sup> R<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub>|| / Σ|F<sub>o</sub>|.

<sup>b</sup> wR<sub>2</sub> = [Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> / Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup> where w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (aP)<sup>2</sup> + bP] where P = (F<sub>o</sub><sup>2</sup> + F<sub>c</sub><sup>2</sup>)/3.

**Table S1**

Selected bond lengths (Å) and angles (°) for the two complexes of EuL3(NO<sub>3</sub>)<sub>3</sub> in the asymmetric unit of the crystal

<i>Bond lengths for isomer 1</i>		<i>Bond lengths for isomer 2</i>	
Eu(1)-N <sub>im</sub> (1)	2.548(4)	Eu(2)-N <sub>im</sub> (8)	2.544(4)
Eu(1)-N <sub>im</sub> (2)	2.566(3)	Eu(2)-N <sub>im</sub> (9)	2.570(4)
Eu(1)-N <sub>py</sub> (3)	2.581(4)	Eu(2)-N <sub>py</sub> (10)	2.598(5)
Eu(1)-N <sub>py</sub> (4)	2.588(4)	Eu(2)-N <sub>py</sub> (11)	2.593(4)
Eu(1)-O(1)	2.521(3)	Eu(2)-O(10)	2.475 (4)
Eu(1)-O(2)	2.509(3)	Eu(2)-O(11)	2.460(4)
Eu(1)-O(4)	2.503(4)	Eu(2)-O(13)	2.520(4)
Eu(1)-O(5)	2.603(4)	Eu(2)-O(14)	2.523(4)
Eu(1)-O(7)	2.496(4)	Eu(2)-O(16)	2.529(4)
Eu(1)-O(9)	2.470(3)	Eu(2)-O(17)	2.504(4)
<i>Bond angles for isomer 1</i>		<i>Bond angles for isomer 2</i>	
N(1)-Eu(1)-N(2)	63.2(1)	N(8)-Eu(2)-N(9)	63.6(1)
N(1)-Eu(1)-N(3)	126.4(1)	N(8)-Eu(2)-N(10)	124.8(1)
N(1)-Eu(1)-N(4)	64.1(1)	N(8)-Eu(2)-N(11)	63.5(1)
N(2)-Eu(1)-N(3)	63.4(1)	N(9)-Eu(2)-N(10)	63.2(1)
N(2)-Eu(1)-N(4)	121.4(1)	N(9)-Eu(2)-N(11)	125.5(1)
N(3)-Eu(1)-N(4)	151.3(1)	N(10)-Eu(2)-N(11)	152.3(1)

**Table S2**

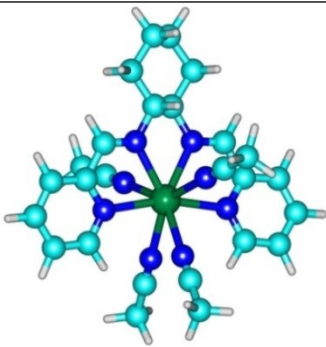
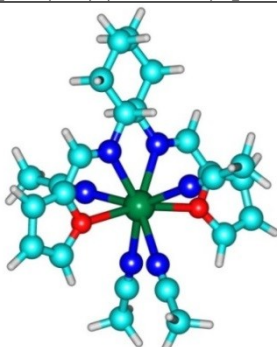
## Estimated intrinsic quantum yields

On the basis of: i) the observed emission lifetimes reported in our previous work (F. Piccinelli, M. Bettinelli, A. Melchior, C. Grazioli, and M. Tolazzi, *Dalt. Trans.*, 2015, **44**, 182–192) for the triflate complexes [EuL1 = 0.45 ms, EuL2 = 0.52 ms, Eu(L1)<sub>2</sub> = 0.72 ms and Eu(L2)<sub>2</sub> = 0.65 ms]; ii)  $\phi = \tau_{\text{obs}} / \tau_{\text{rad}}$  and the equation reported by Werts et al. for  $\tau_{\text{rad}}$  [M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven *Phys. Chem. Chem. Phys.*, 2002, **4**, 1542–1548], the estimated intrinsic quantum yields are: 6% (EuL1), 4.7% (EuL2), 18% [Eu(L1)<sub>2</sub>] and 13% [Eu(L2)<sub>2</sub>].

## DFT calculations

DFT calculations on the complexes [Eu(L1-2)(CH<sub>3</sub>CN)<sub>4</sub>]<sup>3+</sup> have been carried out in ref. 38. Additional Natural Bond Orbital analysis has been carried out here to obtain the Natural charges on each atom. The NBO charges give an estimate of the charge transfer from the ligand donor atoms to the metal cation.

**Table S3.** Natural Charges calculated on the Eu center and on the coordinating atoms of L1 and L2 for structures of the complexes optimized in ref. 38.

[Eu(L1)(CH <sub>3</sub> CN) <sub>4</sub> ] <sup>3+</sup>		[Eu(L2)(CH <sub>3</sub> CN) <sub>4</sub> ] <sup>3+</sup>	
			
atom	Natural charge/e <sup>-</sup>	atom	Natural charge/e <sup>-</sup>
Eu	1.35061	Eu	1.43286
N <sub>pyridine</sub>	-0.51638	N <sub>furane</sub>	-0.47897
N <sub>pyridine</sub>	-0.51638	N <sub>furane</sub>	-0.47897
N <sub>amine</sub>	-0.48836	N <sub>amine</sub>	-0.54369
N <sub>amine</sub>	-0.48836	N <sub>amine</sub>	-0.54369