Development of polymeric sensing films based on a new tridentate bis(phosphinic amide)-phosphine oxide for determining Europium(III) in water

F. J. Sainz-Gonzalo,[a] M. Casimiro,[b] C. Popovici,[b] A. Rodríguez-Diéguez,[c] J. F. Fernández-Sánchez,*[a] I. Fernández,*[b] F. L. Ortiz,*[b] A. Fernández-Gutiérrez[a]

[a] *Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuentenueva s/n, 18071 Granada, Spain. Fax: +34 958243328; E-mail: jffernan@ugr.es*
[b] *Laboratory of Organic Chemistry, University of Almería, Ctra. Sacramento s/n, 04120 Almería, Spain. Fax: +34 950 015481; Tel: +34 950 015648; E-mail: ifernan@ual.es*
[c] *Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, Av. Fuentenueva s/n, 18071 Granada, Spain. Fax: +34-958248526.*

Contents:

Chemical and reagents

Hydrate chloride salts of the lanthanides used were all of the highest purity available and were obtained from ABCR. Bis(2-ethylhexyl) adipate (DOA), 2-nitrophenyloctyl ether (NPOE), potassium tetrakis(4-chlorophenyl) borate (KTpClPB), high molecular weight poly vinyl chloride (PVC) and succinic acid were purchased from Fluka. Bis(2-ethylhexyl) sebacate (DOS) and dioctyl phthalate (DOP) were obtained from Aldrich. Absolute ethanol, anhydrous sodium acetate and potassium hydrogen phthalate were purchased from Panreac. Tetrahydrofurane (THF) was obtained from Lab-Scan. Deuterated chloroform and acetonitrile were purchased from Cambridge Isotope Laboratories, Inc. Sodium chloride was purchased from Riedel-de Haën. Neutral dihydrate sodium citrate was obtained from Merck. D-tryptophan was purchased from Sigma. All chemicals and reagents were of analytical grade except for bis(2-ethylhexyl) sebacate (reagent grade) and were used as received without further purification.

Aqueous solutions were prepared using doubly distilled water obtained from a Milli-Q Plus 185 ultrapure water system (Millipore, Billerica, USA). Stock and working standard solutions of ligand 1 and lanthanide ions were stored in amber glass bottles at 4 ºC.

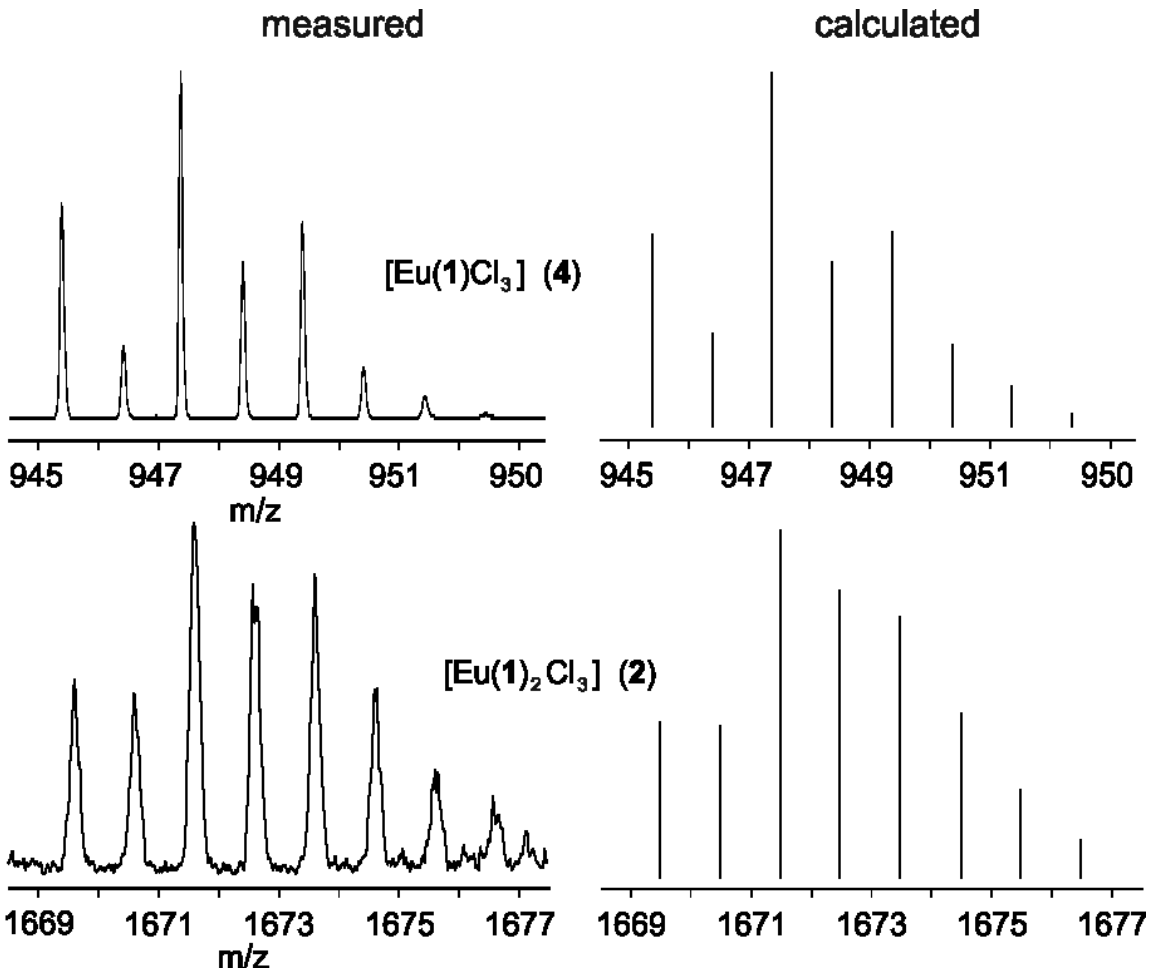

Figure S1. ESI-TOF mass spectra in the positive ion mode calculated and simulated of **2** and **4** in CD_3CN. Note that the optical range for TOF analyzers is below *ca*. 1500 and therefore a significant reduction in the signal/noise is observed.

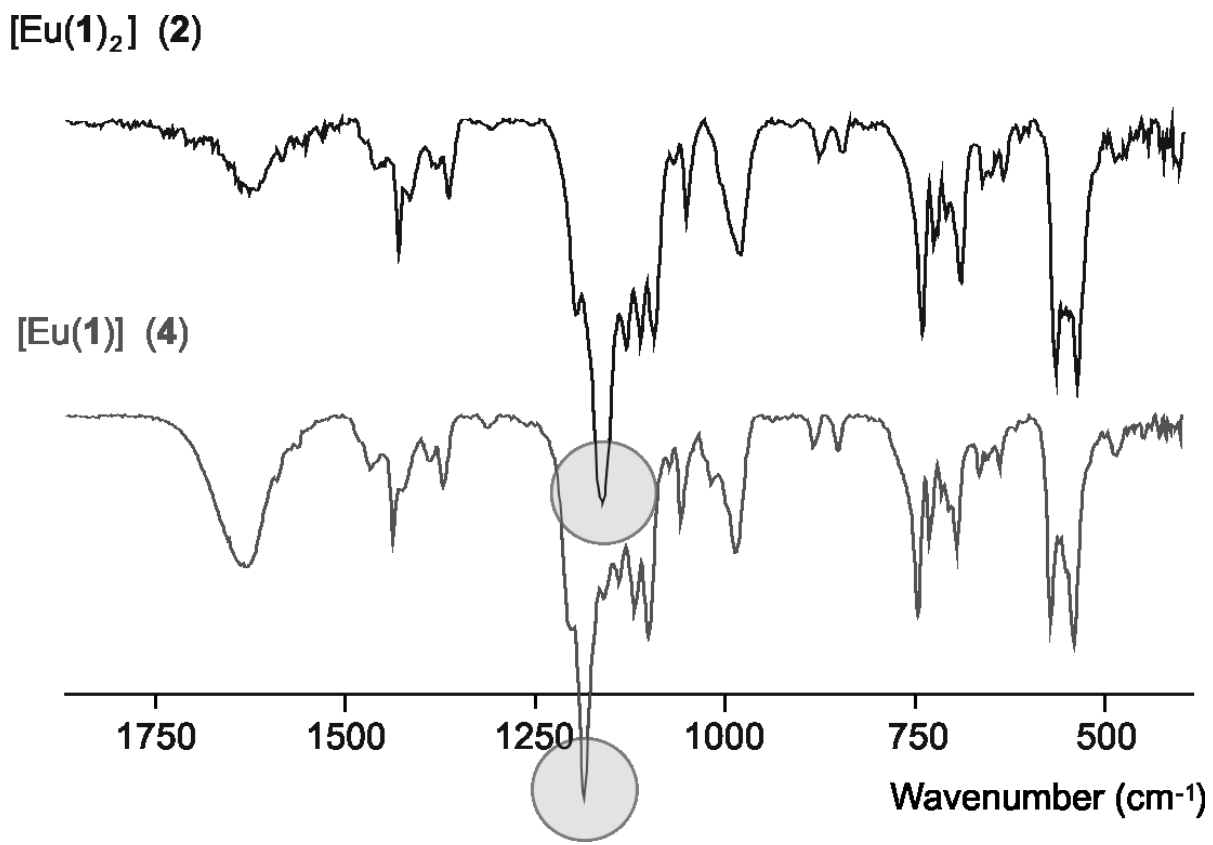

Figure S2. IR (KBr disk) spectra of **2** and **4**.

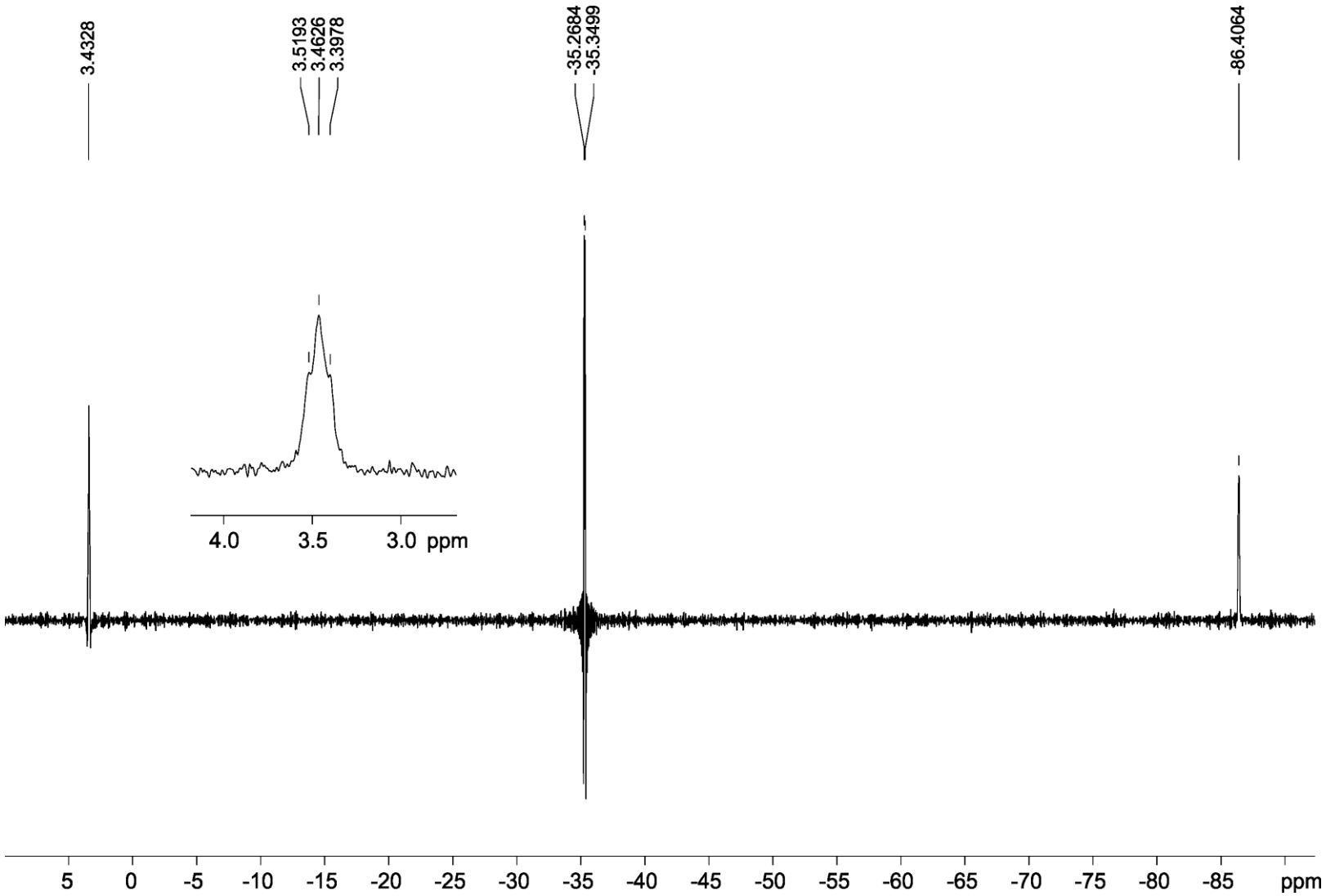

Figure S3. ^{31}P NMR (202.4 MHz) spectrum of **6** in CD_3CN at RT.

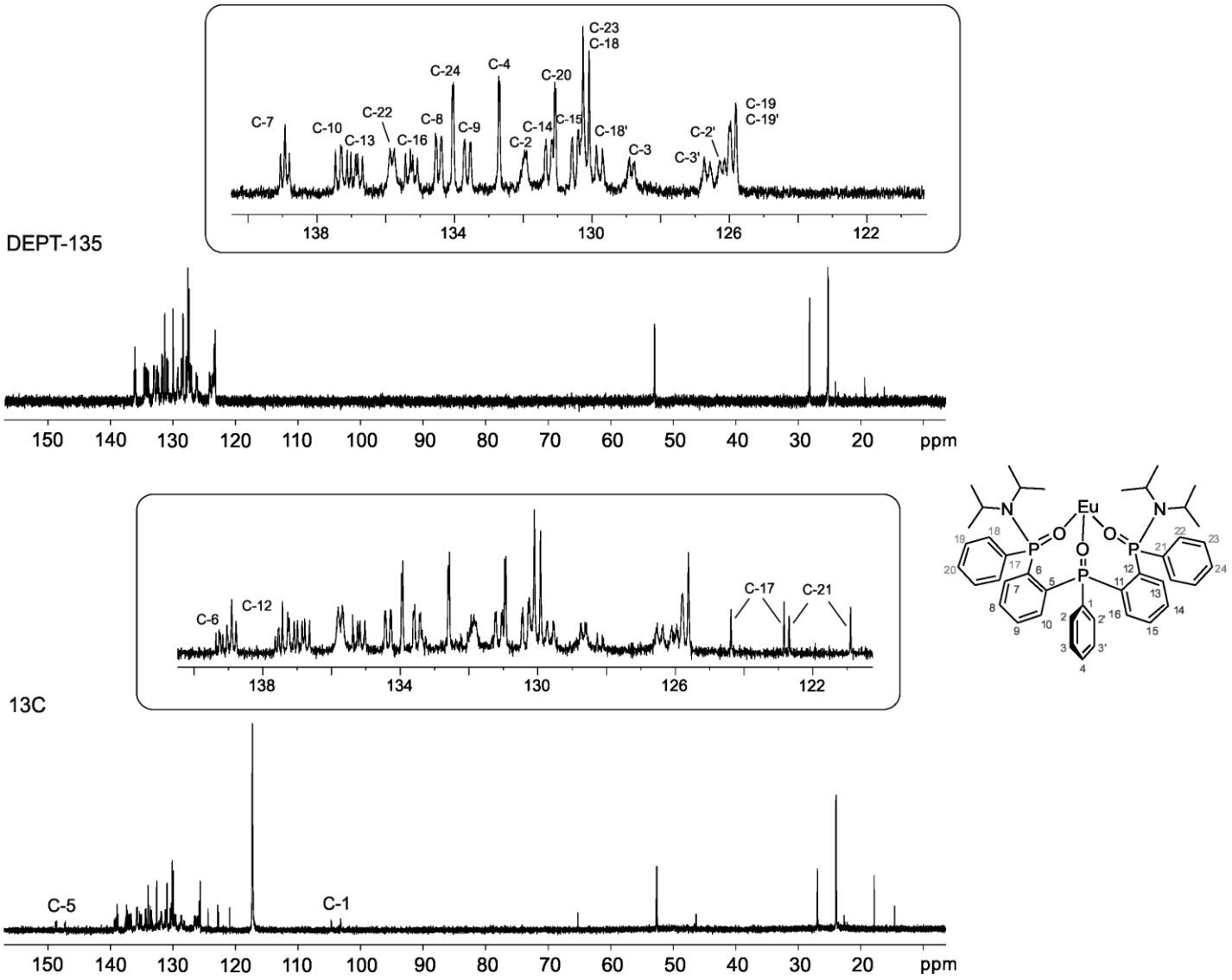

Figure S4. ^{13}C and DEPT-135 NMR (75.5 MHz) spectrum of **2** in CD_3CN at RT.

Table S1. ^{1}H isotropic shifts (δ_{iso}) for complex **2** at 300 MHz in CD_3CN at 25 ºC.

			[Eu(**1**)$_2$Cl$_3$] (**2**)	[Y(**1**)$_2$(NO$_3$)$_3$] (**3**)	δ_{iso}
Ring I		H-2	4.42	8.58	4.16
		H-2’	4.58	6.56	2.01
		H-3	6.28	7.90	1.62
		H-3’	6.79	7.48	0.69
		H-4	7.16	7.85	0.69
Ring II		H-7	9.88	8.38	-1.50
		H-8	8.66	7.98	-0.68
		H-9	7.93	7.65	-0.28
		H-10	6.14	7.00	0.86
Ring III		H-18	-0.88	8.07	8.95
		H-18’	5.96	7.13	1.17
		H-19	4.85	6.90	2.05
		H-19’	5.96	7.13	1.17
		H-20	5.96	7.13	1.17
Ring II’		H-13	6.23	6.48	0.25
		H-14	5.89	6.88	0.99
		H-15	5.45	6.98	1.53
		H-16	3.93	7.02	3.09
Ring III’		H-22	8.77	8.20	-0.57
		H-22’	8.77	8.20	-0.57
		H-23	8.22	7.79	-0.43
		H-23’	8.22	7.79	-0.43
		H-24	8.50	7.79	-0.71

Table S2. ^{1}H isotropic shifts (δ_{iso}) for complex **4** at 300 MHz in CD_3CN at 25 ºC.

			$[Eu(\mathbf{1})_2Cl_3]$ (**4**)	$[Y(\mathbf{1})_2(NO_3)_3]$ (**5**)	δ_{iso}
Ring I		H-2	4.84	7.53	2.69
		H-2’			
		H-3	6.70	7.10	0.4
		H-3’			
		H-4			
Ring II		H-7	12.34	8.56	3.78
		H-8	9.24	8.04	1.2
		H-9	8.09	7.37	0.72
		H-10	6.78	6.47	0.31
Ring III		H-18	5.67	7.80	2.13
		H-18’			
		H-19	5.17	7.23	2.06
		H-19’			
		H-20		7.80	
Ring II’		H-13	6.03	6.34	0.31
		H-14	7.06	6.34	0.72
		H-15	7.41	6.70	0.71
		H-16	7.94	7.07	0.87
Ring III’		H-22	8.95	8.32	0.63
		H-22’			
		H-23	8.02	7.80	0.22
		H-23’			
		H-24	3.43		

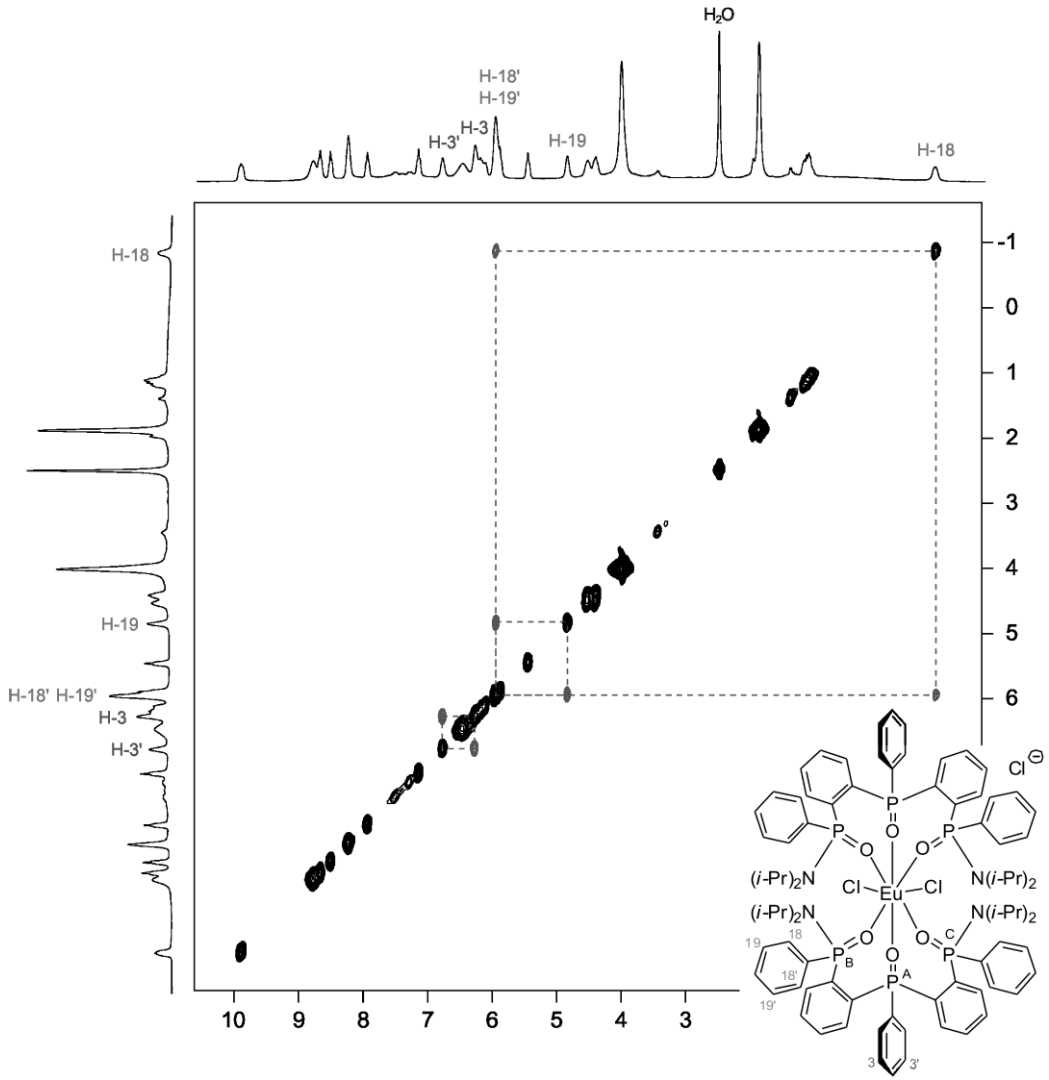

Figure S5. ^{1}H EXSY NMR spectrum (t_m = 500 ms) of **2** in CD_3CN at RT.

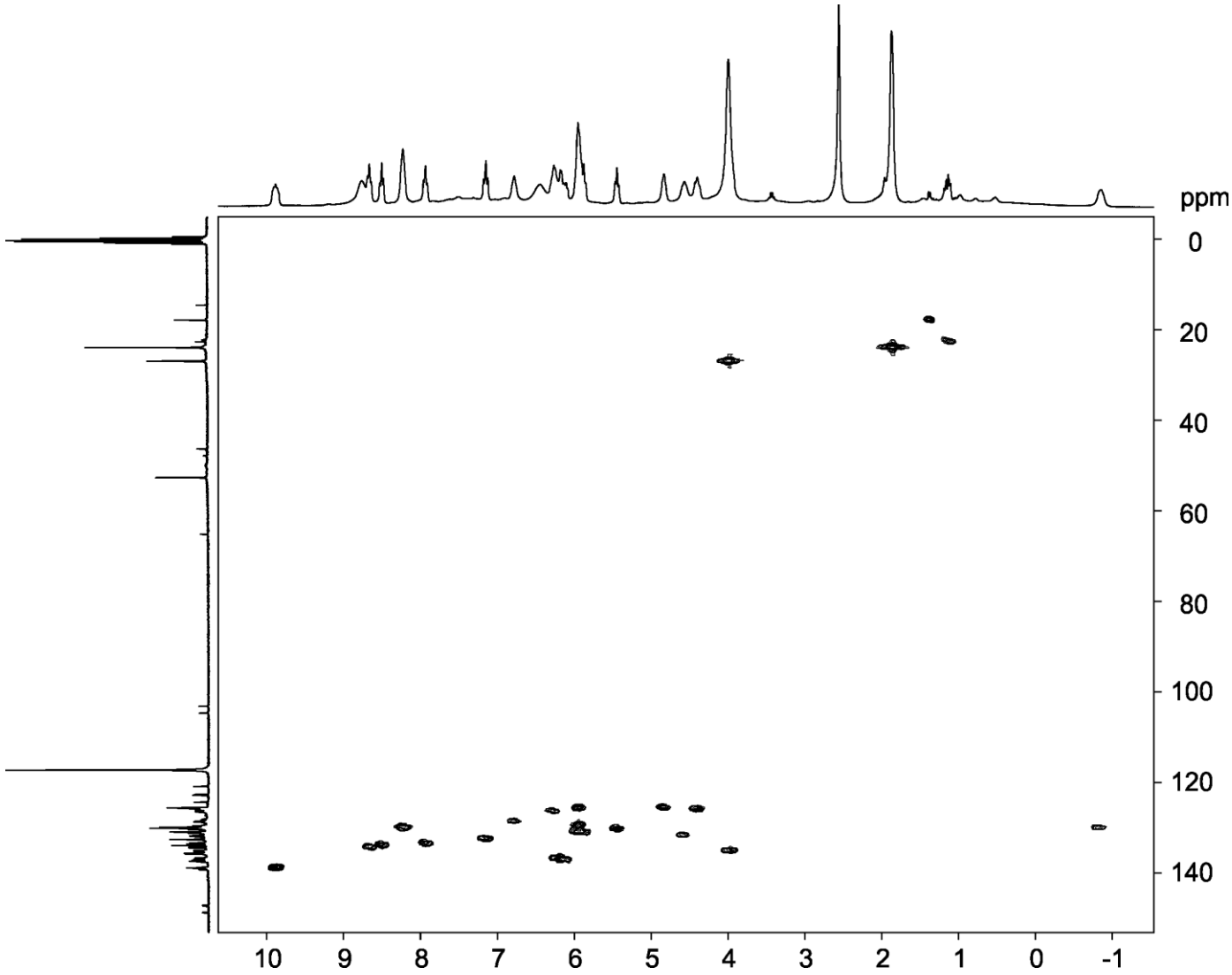

Figure S6. ^{1}H, ^{13}C gHMQC NMR spectrum of **2** in CD_3CN at RT.

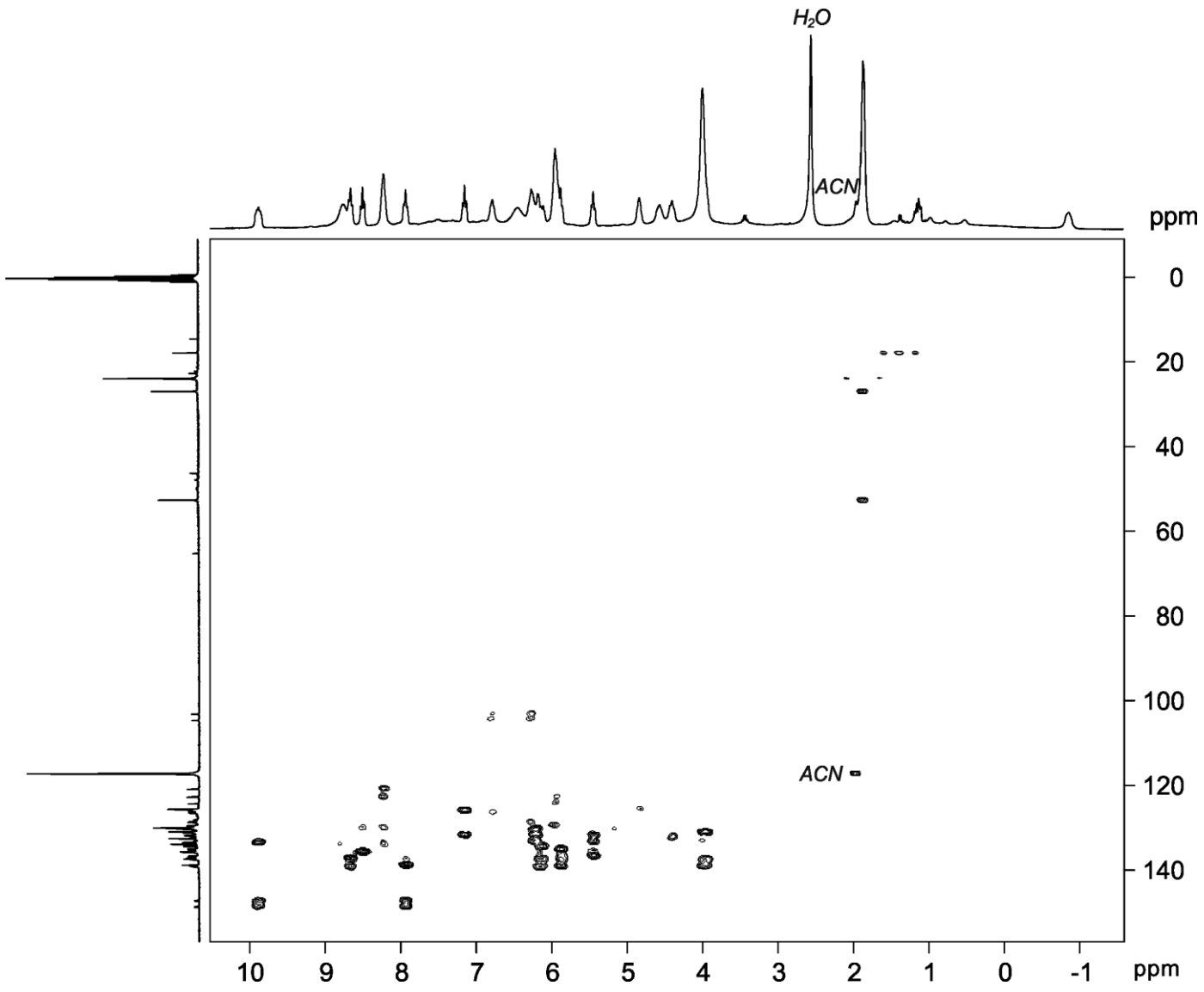

Figure S7. ^{1}H, ^{13}C gHMBC NMR spectrum of **2** in CD_3CN at RT.

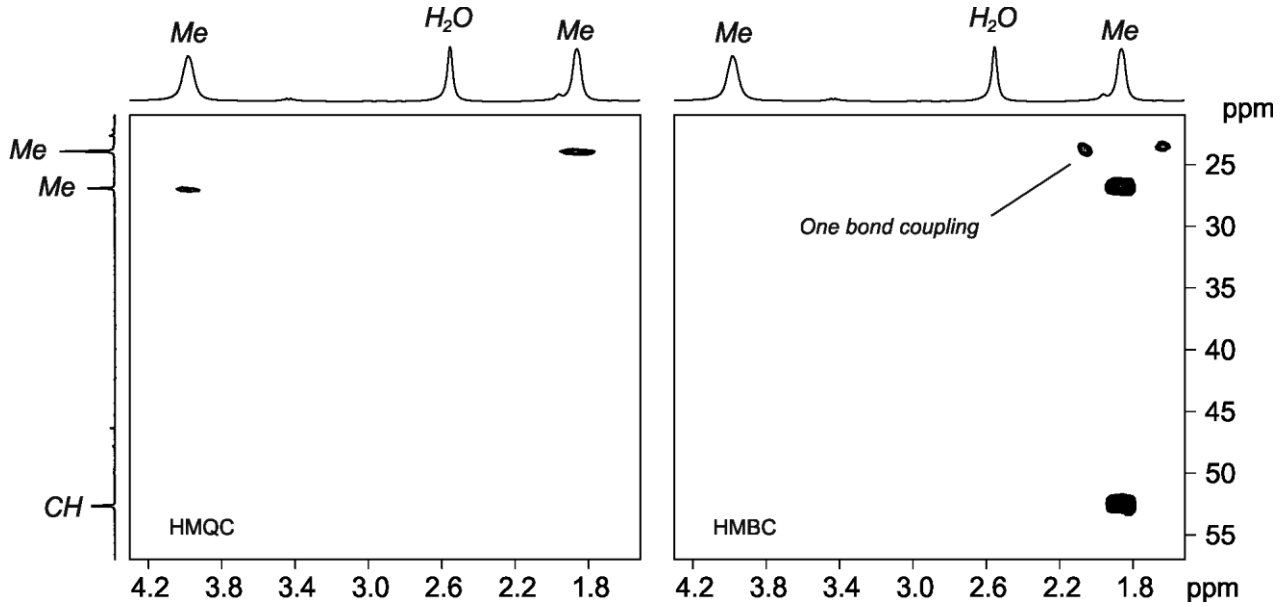

Figure S8. ^{1}H, ^{13}C gHMQC and gHMBC NMR expansions of the N*i*Pr$_2$ region for complex **2** in CD_3CN at RT.

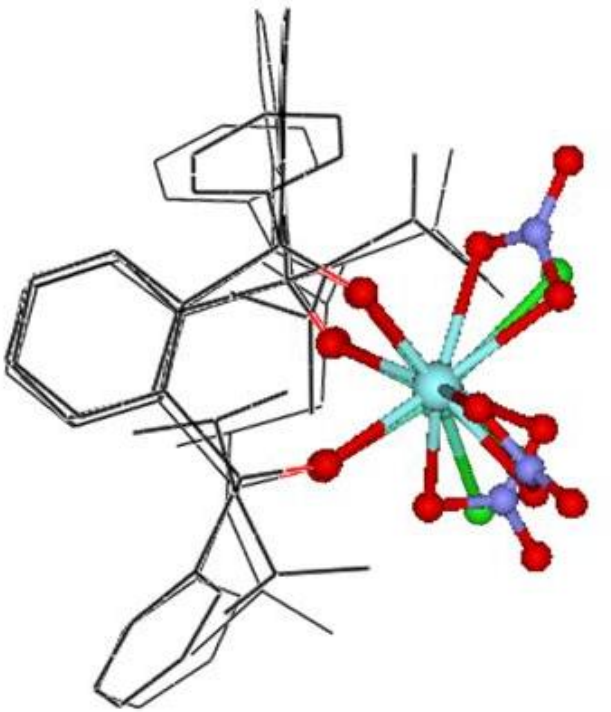

Figure S9. X-ray structures overlay for [Eu(**1**)Cl_3] (**4**) and [Y(**1**)$(NO_3)_3$] (**5**). For complex **5** only one conformation out of the two existing in the asymmetric unit is shown.

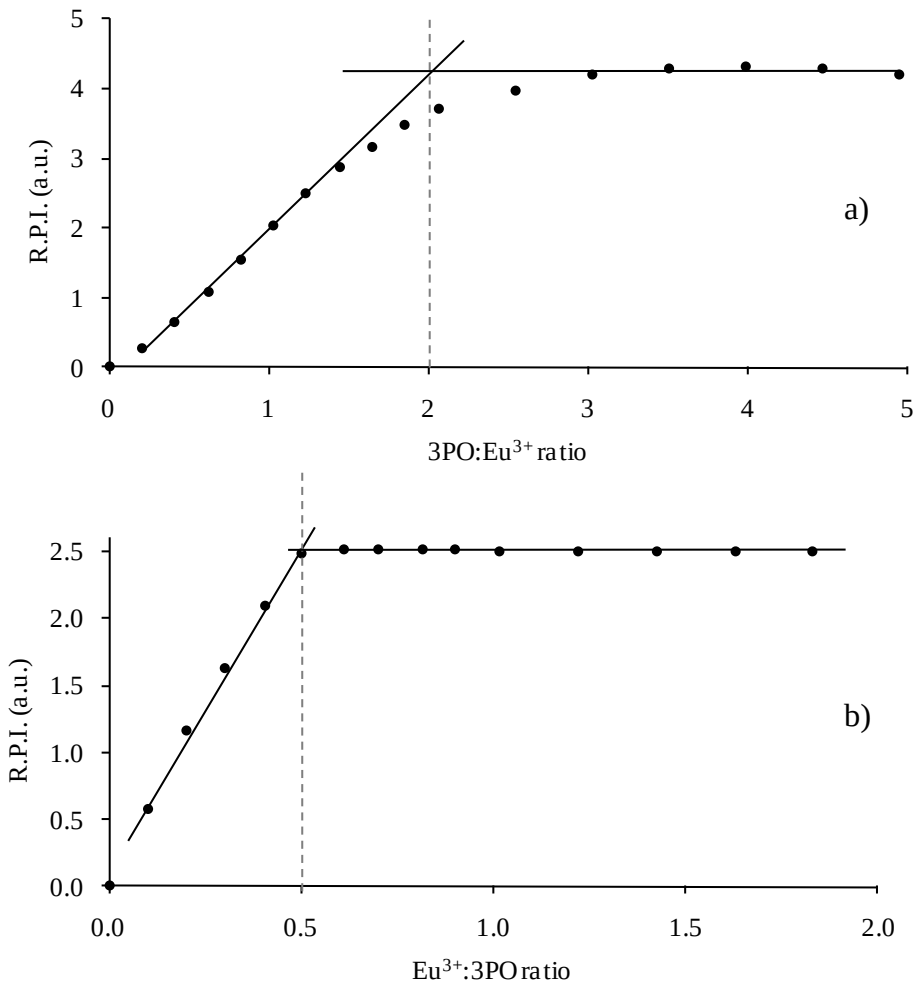

Figure S10. Response of the complex luminescence intensity versus a) Ligand:Eu^{3+} ratio ([Eu^{3+}]= 8.0 x 10^{-6} M, 75% EtOH, v/v, [NaCl]= 31 mM and pH=7.0); and b) Eu^{3+}:Ligand ratio ([Ligand]= 8.3 x 10^{-6} M, 75% EtOH, v/v; [NaCl]= 31 mM and pH=7.0).

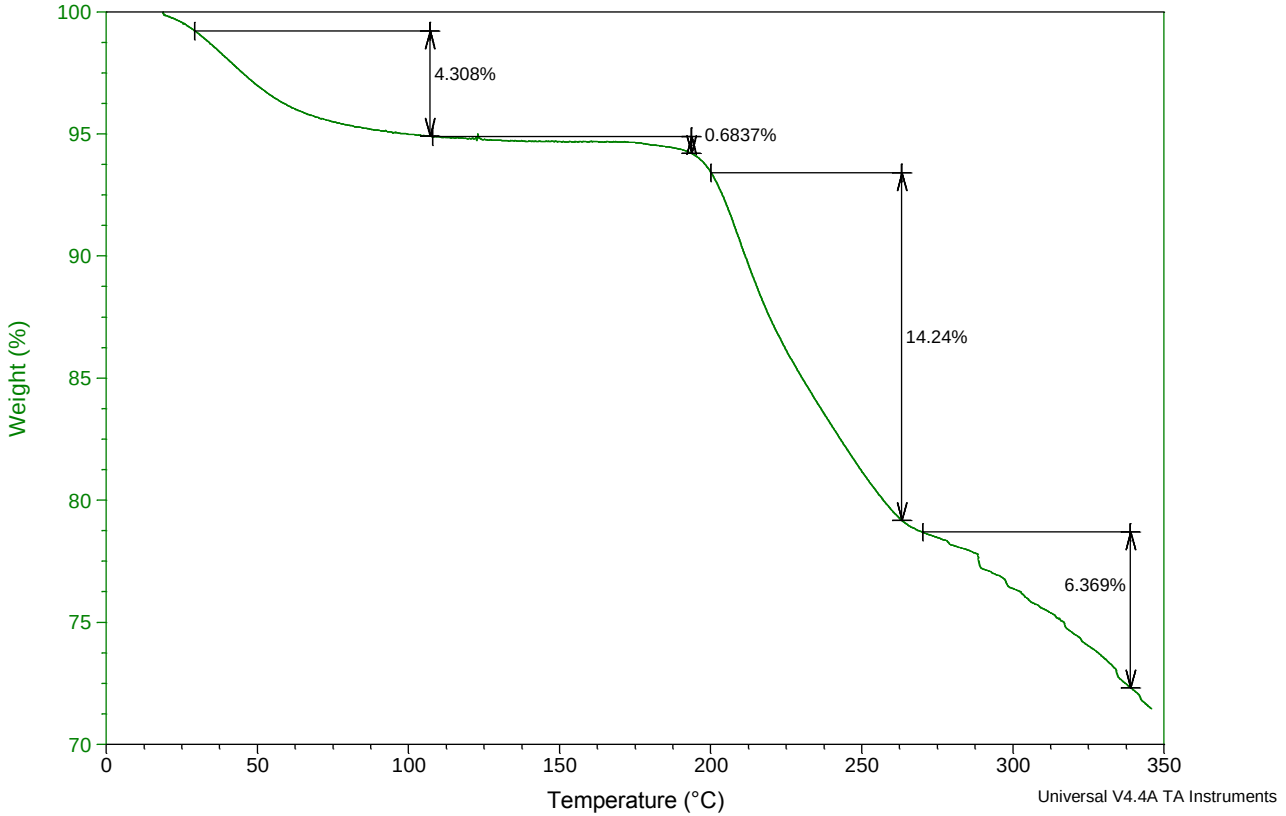

Figure S11. TGA spectrum for complex **2** at the heating rate of 10ºC/min under nitrogen atmosphere.

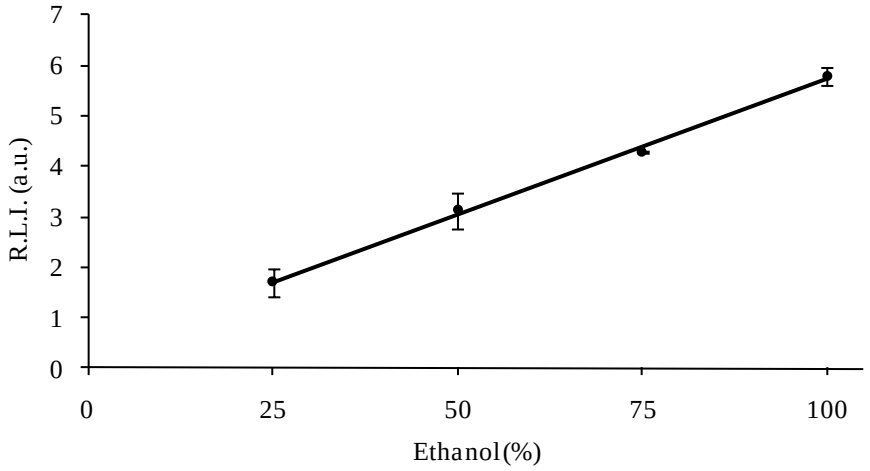

Figure S12. Luminescence intensity versus EtOH percentage in solution. $[Eu^{3+}]=[Ligand]= 9.6 \times 10^{-5}$ M.

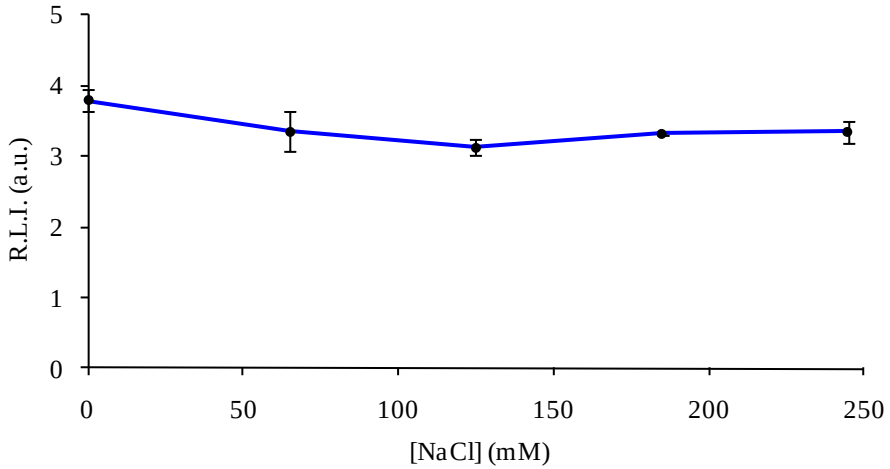

Figure S13. Influence of NaCl concentration on the luminescence intensity in solution. $[Eu^{3+}]=[Ligand]= 9.6 \times 10^{-5}$ M (75% EtOH, v/v).

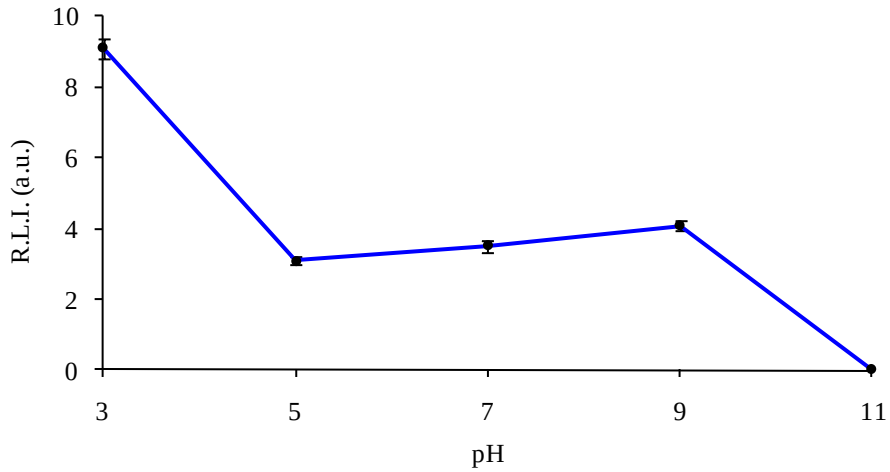

Figure S14. The pH effect on the complex luminescence intensity in solution. [Eu^{3+}]= [Ligand]= 9.6 x 10^{-5} M (75% EtOH, v/v; [NaCl]= 31 mM).

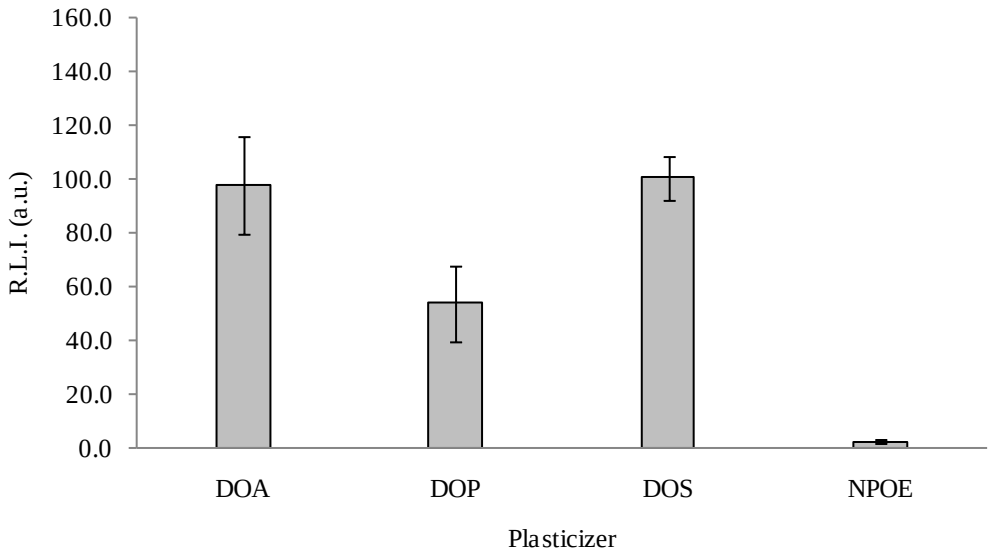

Figure S15. The plasticizer effect on the luminescence signals of the membrane sensors. *DOA* bis(2-ethylhexyl) adipate, *DOP* dioctyl phthalate, *DOS* bis(2-ethylhexyl) sebacate and *NPOE* 2-nitrophenyloctyl ether. Membrane composition: PVC:Plasticizer:Ligand:KTpClPB as 32.8:64.7:1.5:1.0 (%, w/w). $[Eu^{3+}]=1.0 \times 10^{-6}$ M in distilled water.

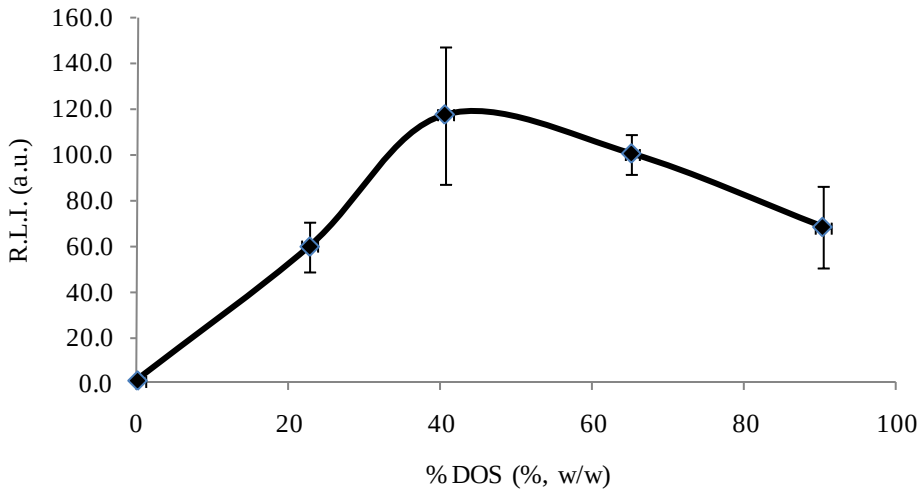

Figure S16. Luminescence intensities of the membrane sensors versus DOS plasticizer percentage. *DOS* bis(2-ethylhexyl) sebacate. Membrane composition: PVC:DOS:Ligand:KTpClPB as 7.5-97.5:0-90.0:1.5:1.0 (%, w/w). $[Eu^{3+}]=1.0 \times 10^{-6}$ M in distilled water.

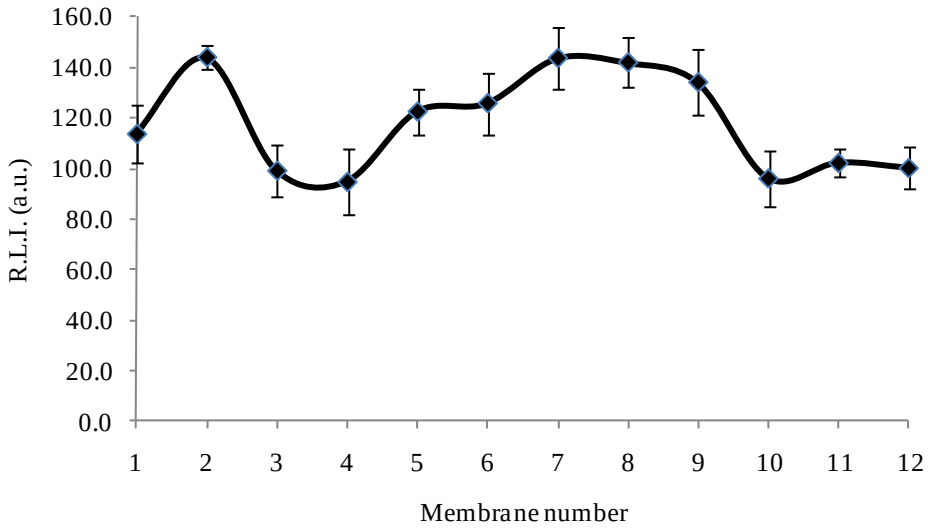

Figure S17. The joint effect of the ligand and ionic additive percentages on the luminescence responses of the membrane sensors. Membrane composition: PVC:DOS:Ligand:KTpClPB as 27.9-33.4:65.1:1.5-3.5:0-3.5 (%, w/w). $[Eu^{3+}]=1.0 \times 10^{-6}$ M in distilled water. Table 2 shows the composition of each membrane.

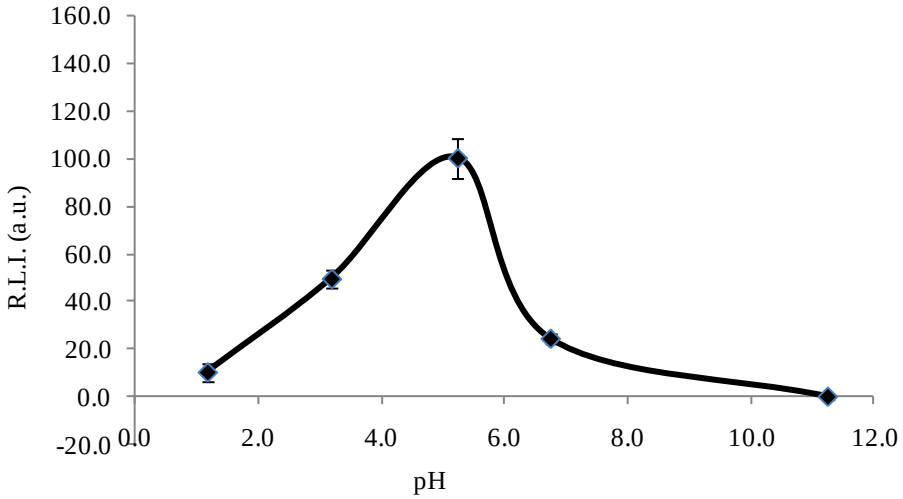

Figure S18. The pH effect on the luminescence signals of the europium sensors. Optimum membrane composition: PVC:DOS:Ligand:KTpClPB as 33.4:65.1:1.5:0 (%, w/w). $[Eu^{3+}]=1.0 \times 10^{-6}$ M in distilled water.

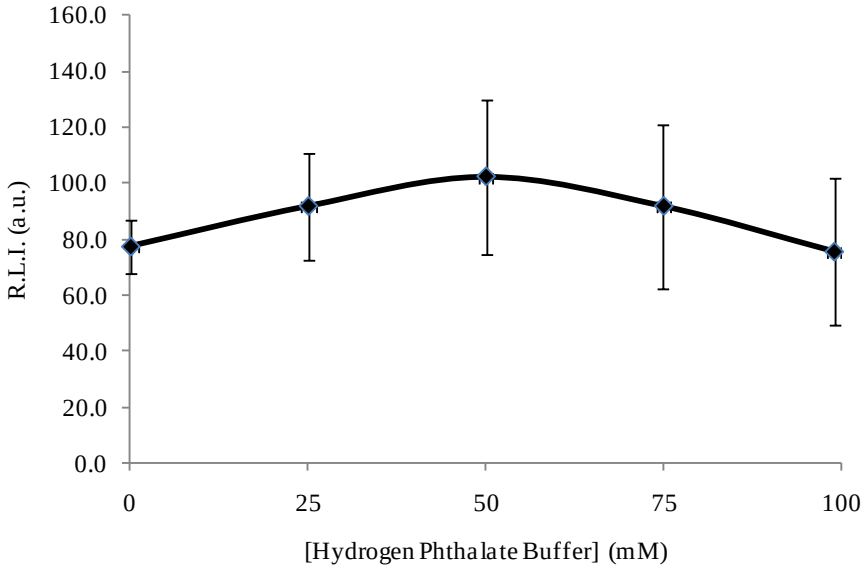

Figure S19. Effect of the ionic strength on the luminescence signals of the membrane sensors. Optimum membrane composition: PVC:DOS:Ligand:KTpClPB as 33.4:65.1:1.5:0 (%, w/w). $[Eu^{3+}]=1.0 \times 10^{-6}$ M in distilled water at pH 5.0 and in different hydrogen phthalate buffer concentration solutions at pH 5.0.

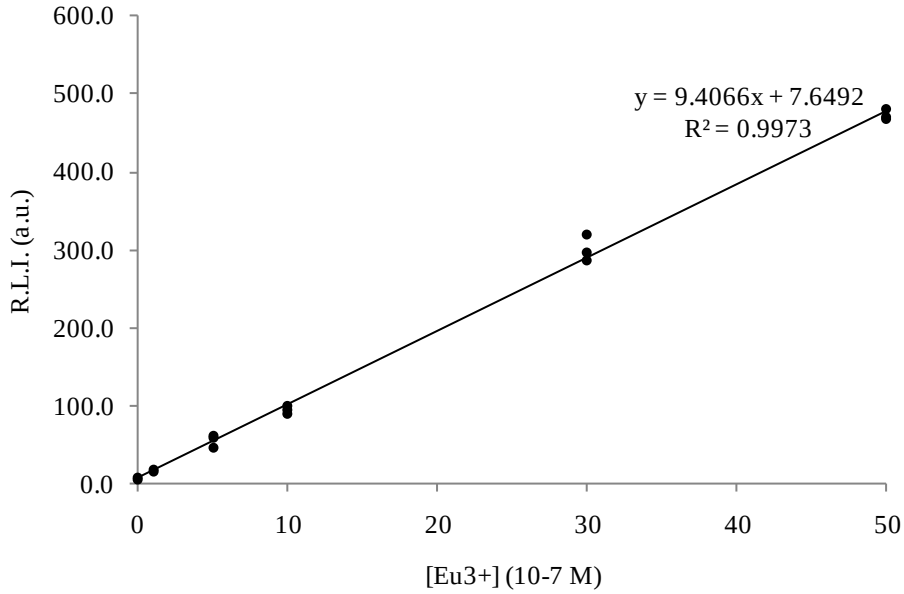

Figure S20. Calibration graph of europium(III) membrane sensors. Optimum membrane composition: PVC:DOS:Ligand:KTpClPB as 33.4:65.1:1.5:0 (%, w/w). [Blank]= 25 mM hydrogen phthalate buffer at pH 5.0 and $[Eu^{3+}]$=1.0 x 10^{-7}-5.0 x 10^{-6} M in 25 mM hydrogen phthalate buffer solution at pH 5.0.

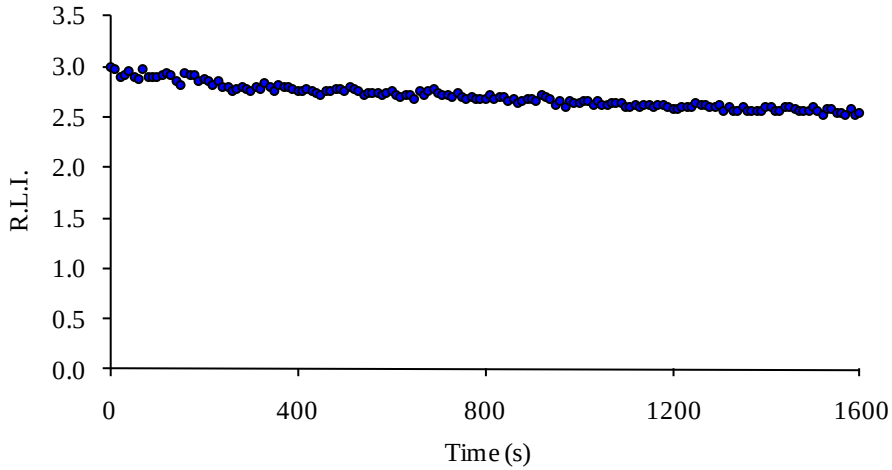

Figure S21. Variation of the luminescence emission in solution versus time.