APPENDIX A. SUPPLEMENTARY DATA

A novel tridentate bis(phosphinic acid)-phosphine oxide based Europium(III)-selective Nafion membrane luminescent sensor

F.J. Sainz-Gonzalo[a], C. Popovici[b], M. Casimiro[b], A. Raya-Barón[b], J.F. Fernández-Sánchez[a,*], F. López-Ortiz[b], I. Fernández[b,*], A. Fernández-Gutiérrez[a]

[a] *Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuentenueva s/n, 18071 Granada, Spain*

[b] *Laboratory of Organic Chemistry, University of Almería, Ctra. Sacramento s/n, 04120 Almería, Spain*

Index

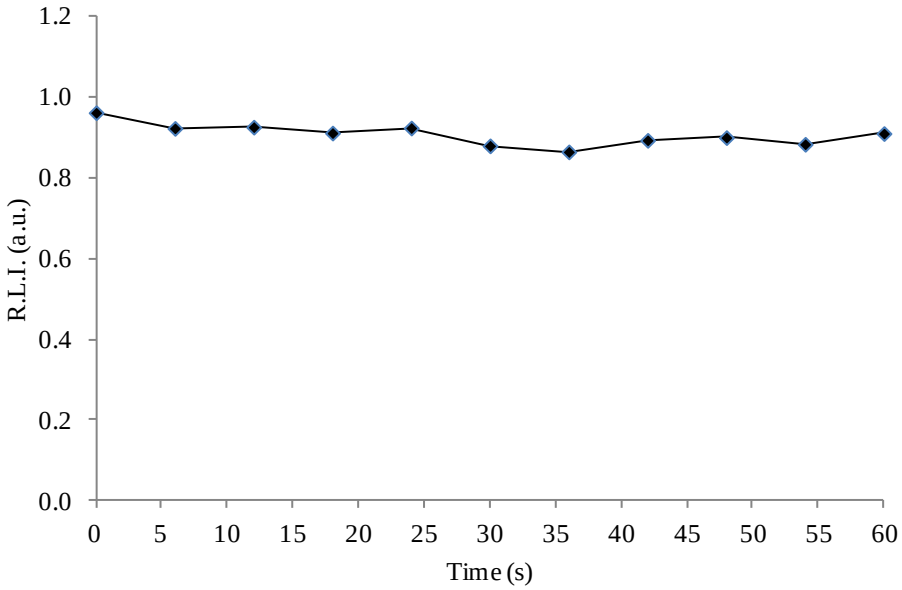

Fig. S1. Formation time of 1:2 europium(III)-ligand complex in solution. [Eu^{3+}] = 7.5 x 10^{-6} M [Ligand] = 1.5 x 10^{-5} M in water.

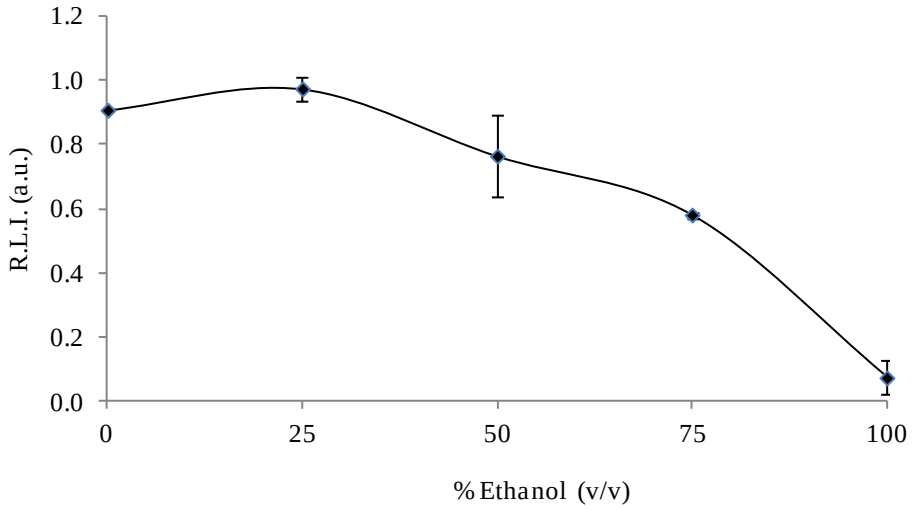

Fig. S2. Luminescence intensity of 1:2 europium(III)-ligand complex versus EtOH percentage. [Eu^{3+}] = 5.0 x 10^{-7} M and [Ligand] = 2.0 x 10^{-6} M.

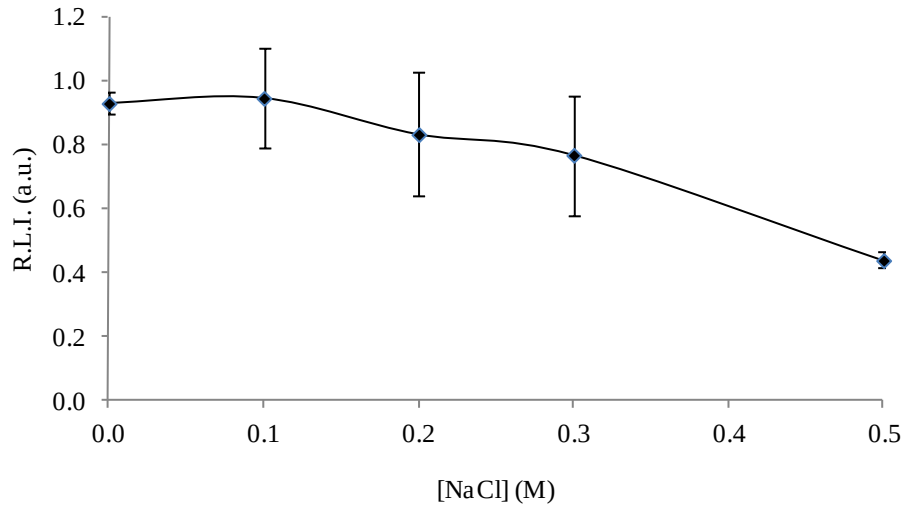

Fig. S3. The influence of NaCl concentration on the 1:2 europium(III)-ligand complex luminescence intensity in water. [Eu^{3+}] = 5.0 x 10^{-7} M and [Ligand] = 2.0 x 10^{-6} M.

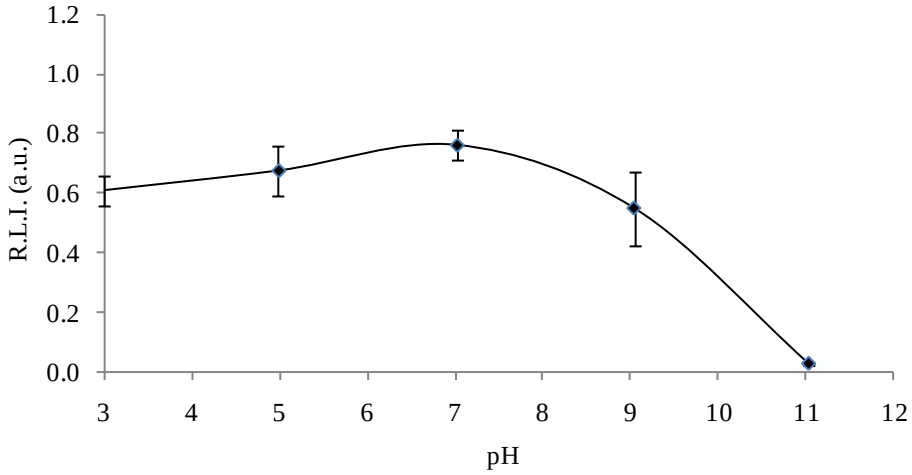

Fig. S4. Effect of pH on the complex luminescence intensity in water. [Eu^{3+}] = 5.0 x 10^{-7} M and [Ligand] = 2.0 x 10^{-6} M.

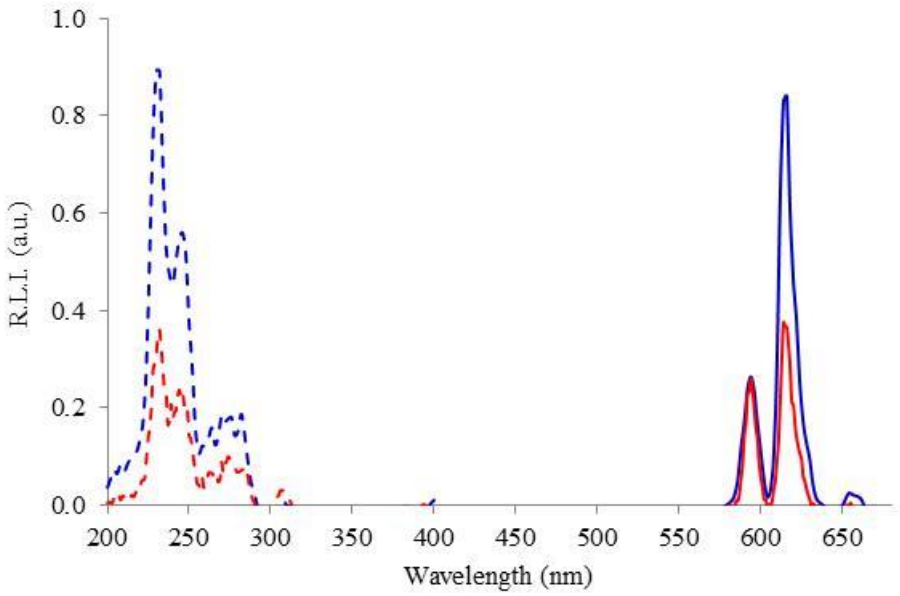

Fig. S5. Excitation (dashed lines) and emission spectra (solid lines) of 1:1 (red) 1:2 (blue) europium(III)-3 complex in water.

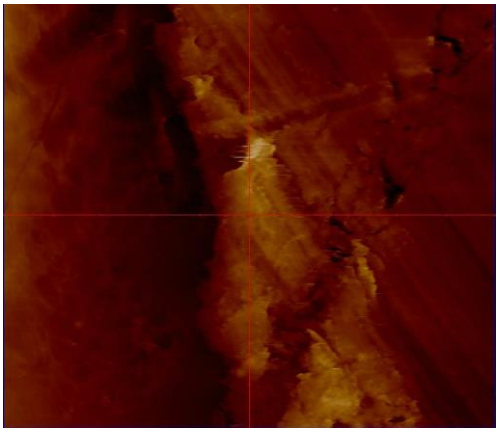

Fig. S6. 2D Image of AFM in which is possible to distinguish the scanning direction (red line) and the concentrical lines which appear in the coated section (resolution 1024 lines, size 50 x 50 μm).

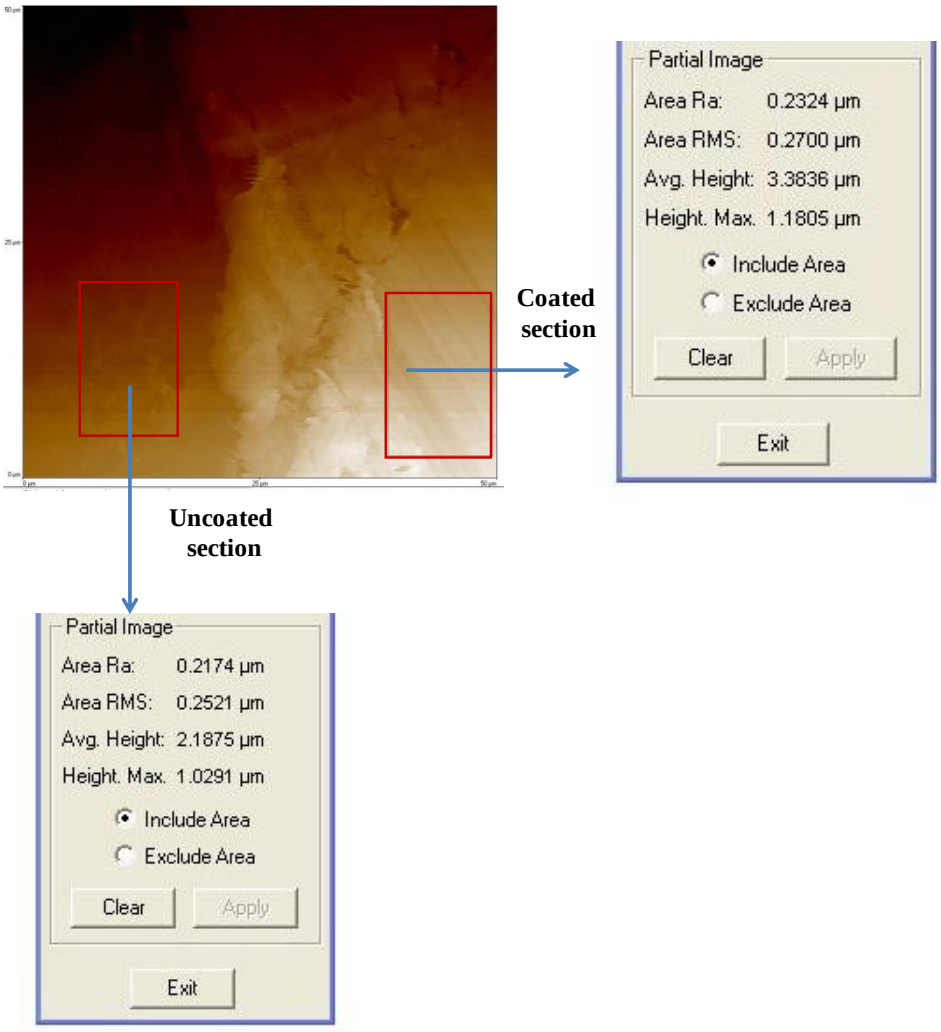

Fig. S7. Analysis of roughness and average height of coated and uncoated sections

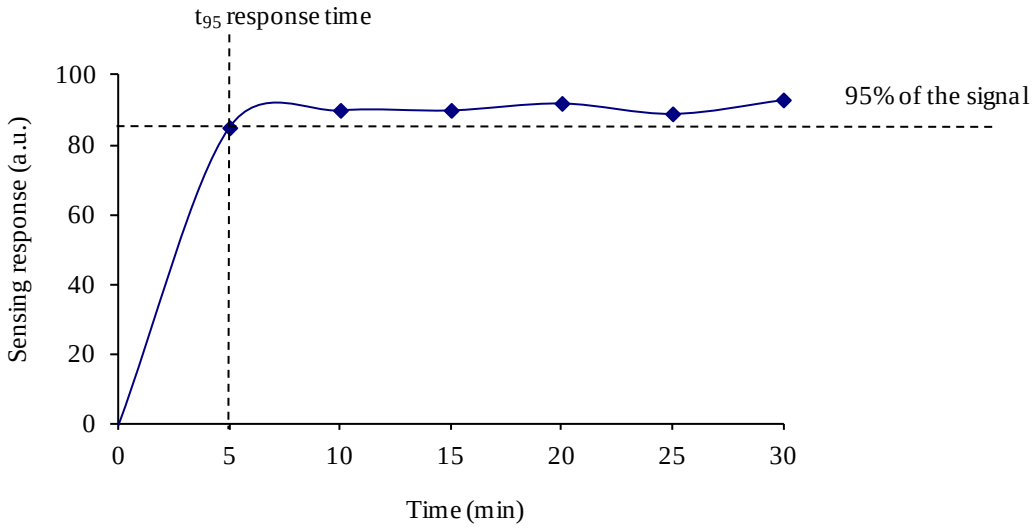

Fig. S8. Determination of the response time.

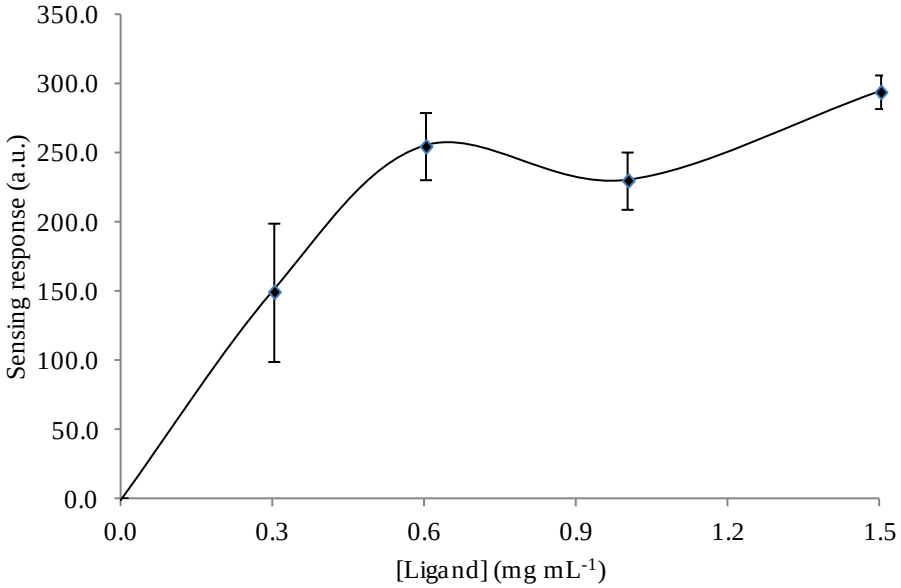

Fig. S9. Effect of ligand concentration on the sensing response. Membrane composition: Nafion:Ligand:KTpClPB as 262.3:0-1.5:0.6 mg mL^{-1}. $[Eu^{3+}]$ = 1.0 x 10^{-6} M. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 5 nm, 700 V detector voltage, t_d = 120 μs and t_g = 5 ms.

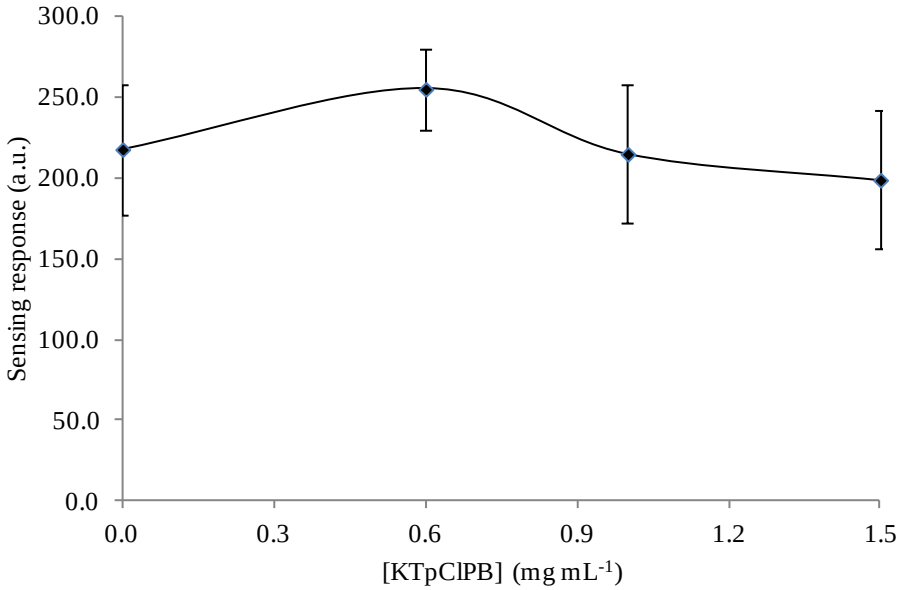

Fig. S10. Variation of the sensing response versus ionic additive concentration. Membrane composition: Nafion:Ligand:KTpClPB as 262.3:0.6:0-1.5 mg mL^{-1}. $[Eu^{3+}]$ = 1.0 x 10^{-6} M. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 5 nm, 700 V detector voltage, t_d = 120 μs and t_g = 5 ms.

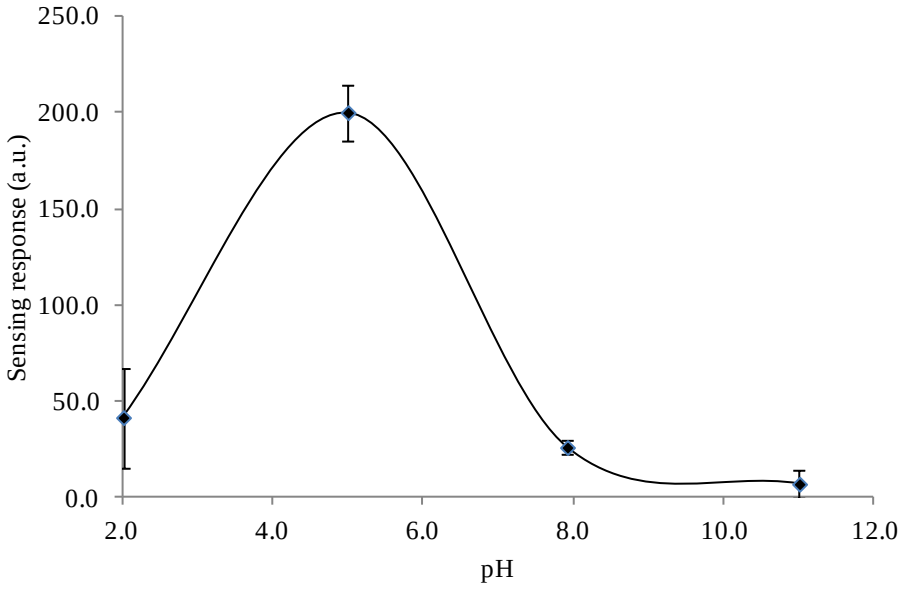

Fig. S11. Effect of pH on solid phase. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL^{-1}. $[Eu^{3+}]$ = 1.0 x 10^{-6} M. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 5 nm, 700 V detector voltage, t_d = 120 μs and t_g = 5 ms.

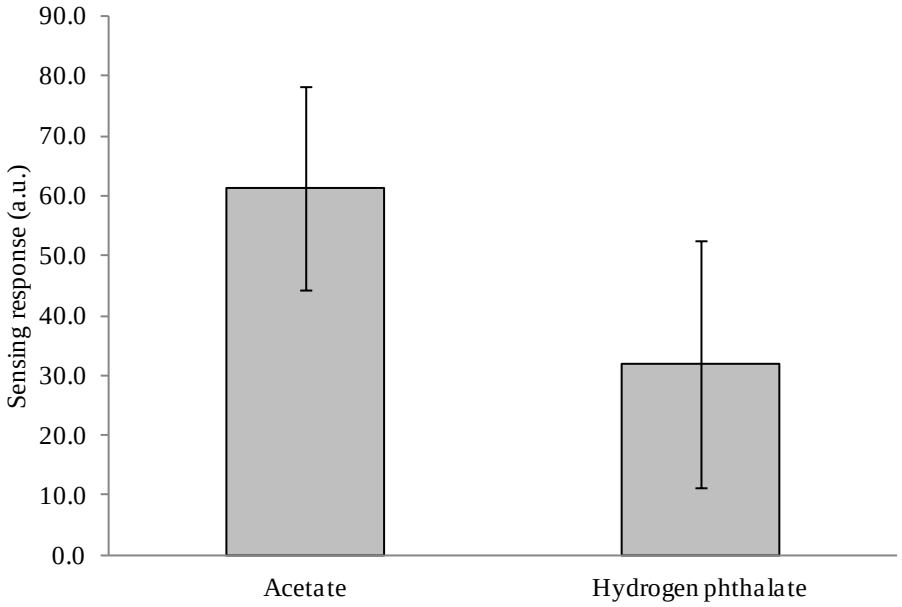

Fig. S12. Sensing response of the film in different 75 mM buffer solutions at pH = 5.0. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL^{-1}. $[Eu^{3+}]$ = 1.0 x 10^{-6} M. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t_d = 120 μs and t_g = 5 ms.

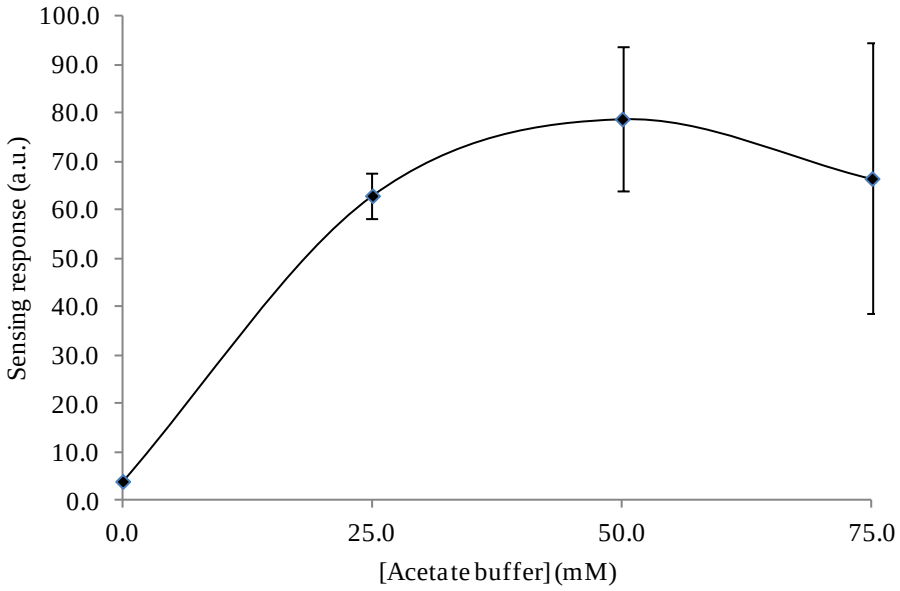

Fig. S13. Effect of the ionic strength on the sensing response. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL^{-1}. $[Eu^{3+}]$ = 1.0 x 10^{-6} M, pH = 5.0. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t_d = 120 μs and t_g = 5 ms.

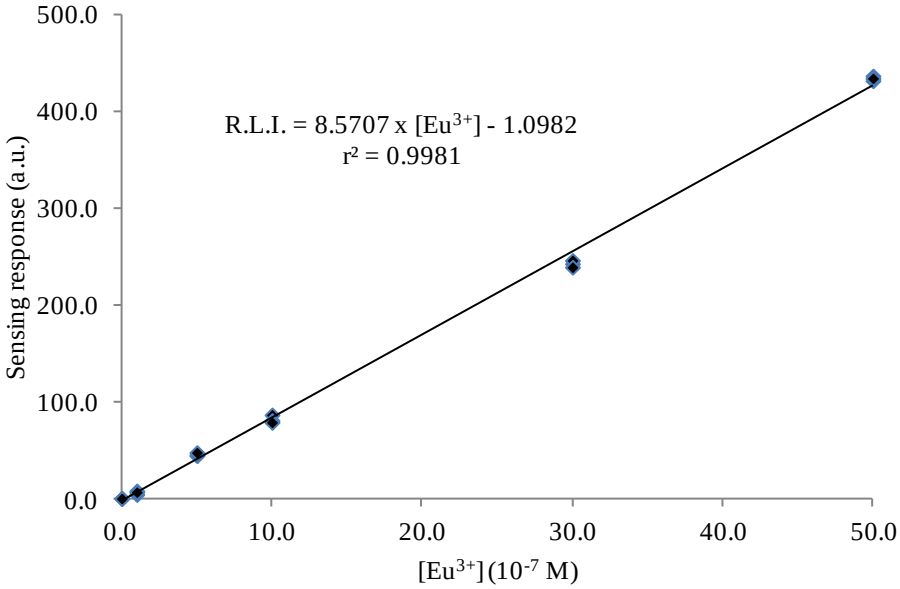

Fig. S14. Calibration graph of the europium(III) membrane sensors. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL^{-1}. [Blank] = 25 mM acetate buffer at pH 5.0; $[Eu^{3+}]$ = 1.0 x 10^{-7}-5.0 x 10^{-6} M in 25 mM acetate buffer solution at pH 5.0. $\lambda_{exc/em}$ = 229.06/616.02 nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t_d = 120 μs and t_g = 5 ms.

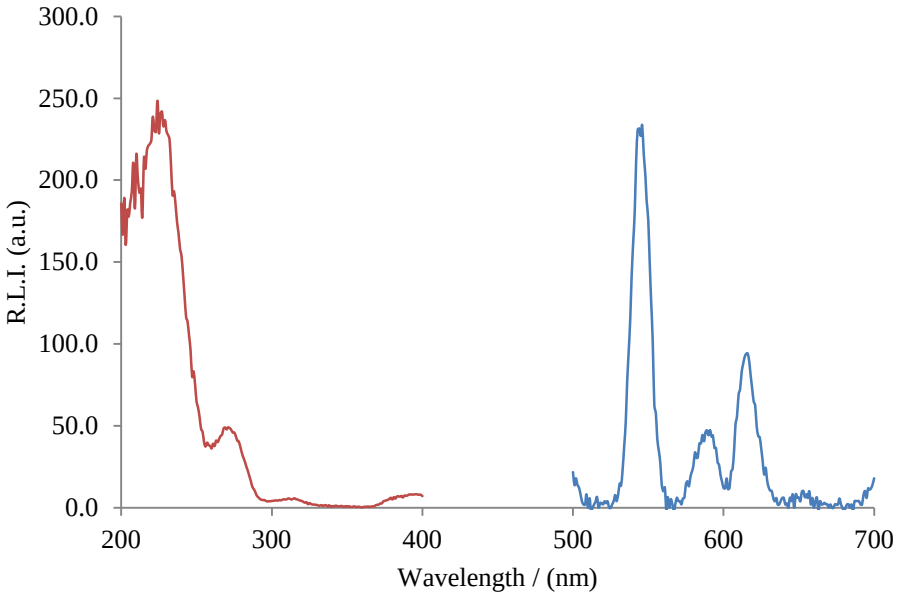

Fig. S15. Excitation and emission spectrum of the sensing film in presence of Tb(III) ion.

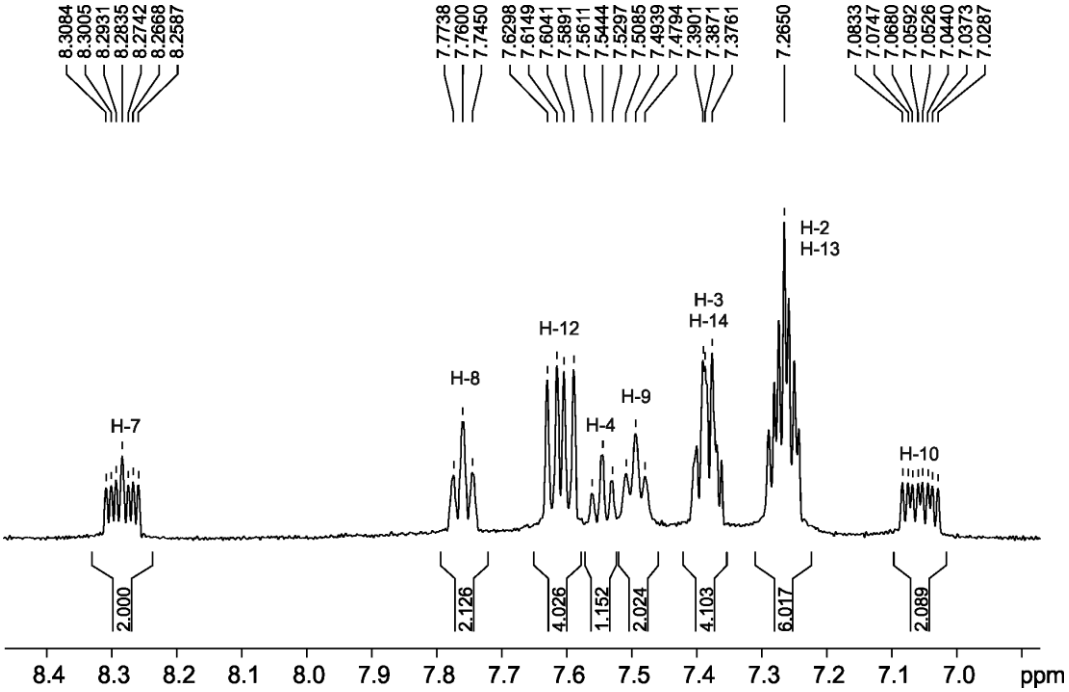

Fig. S16. ^{1}H NMR spectrum (500 MHz) for ligand **3** in MeOD at 20 ºC.

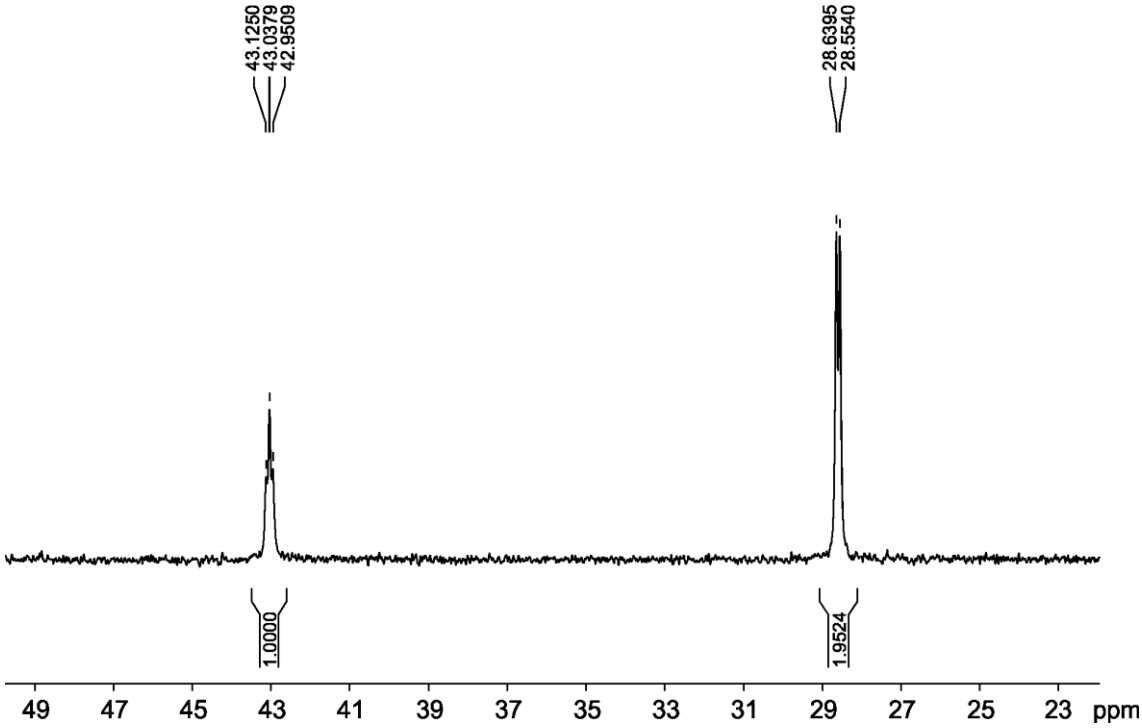

Fig. S17. ^{31}P NMR spectrum (202 MHz) for ligand **3** in MeOD at 20 ºC.

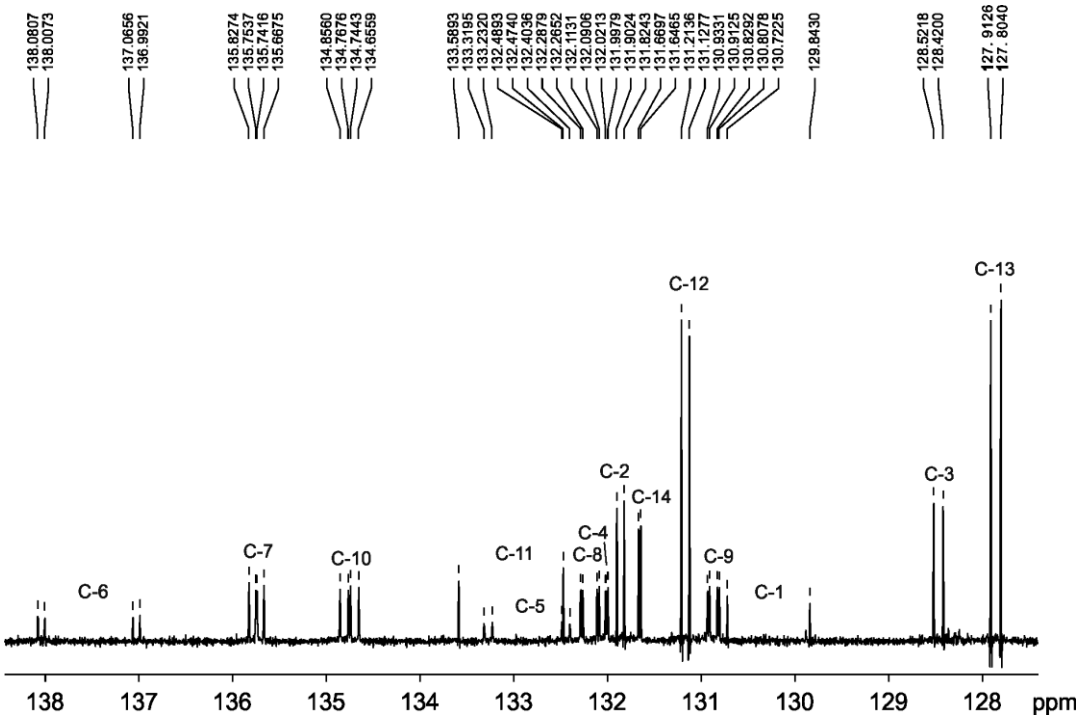

Fig. S18. ^{13}C NMR spectrum (125 MHz) for ligand **3** in MeOD at 20 ºC.

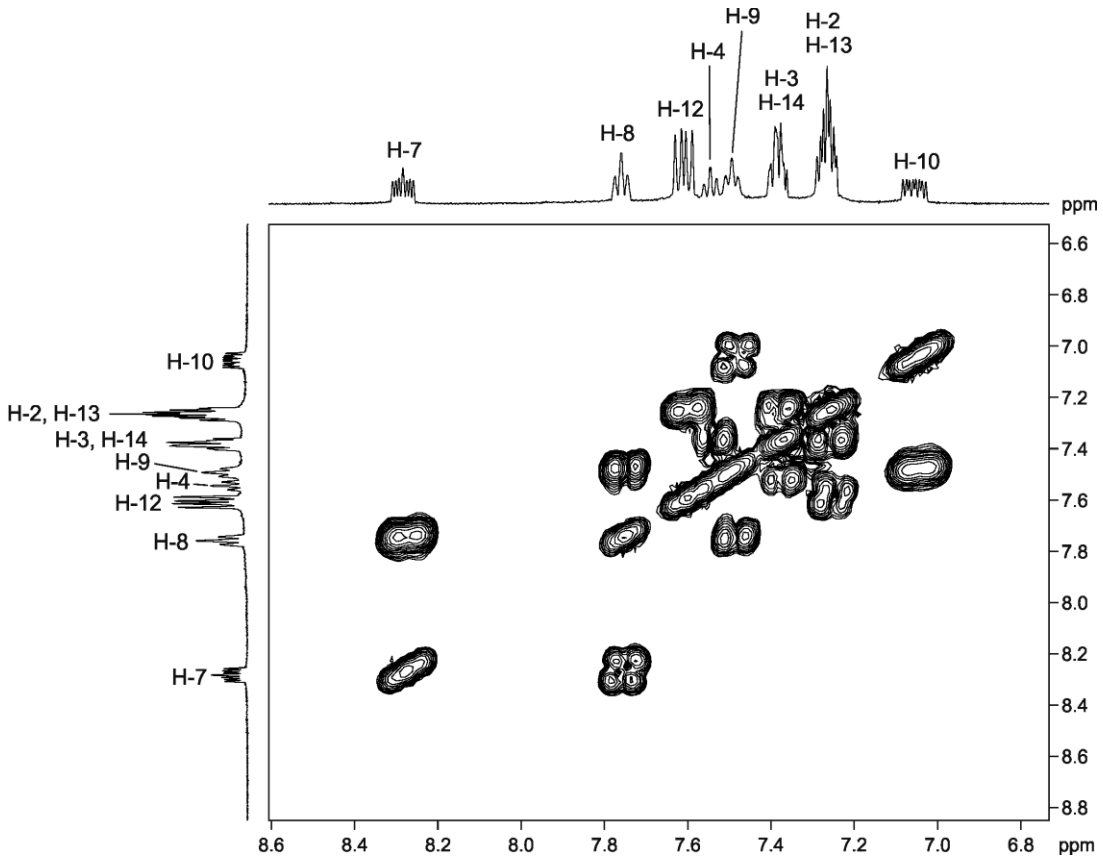

Fig. S19. ^{1}H COSY NMR spectrum (500 MHz) for ligand **3** in MeOD at 20 ºC.

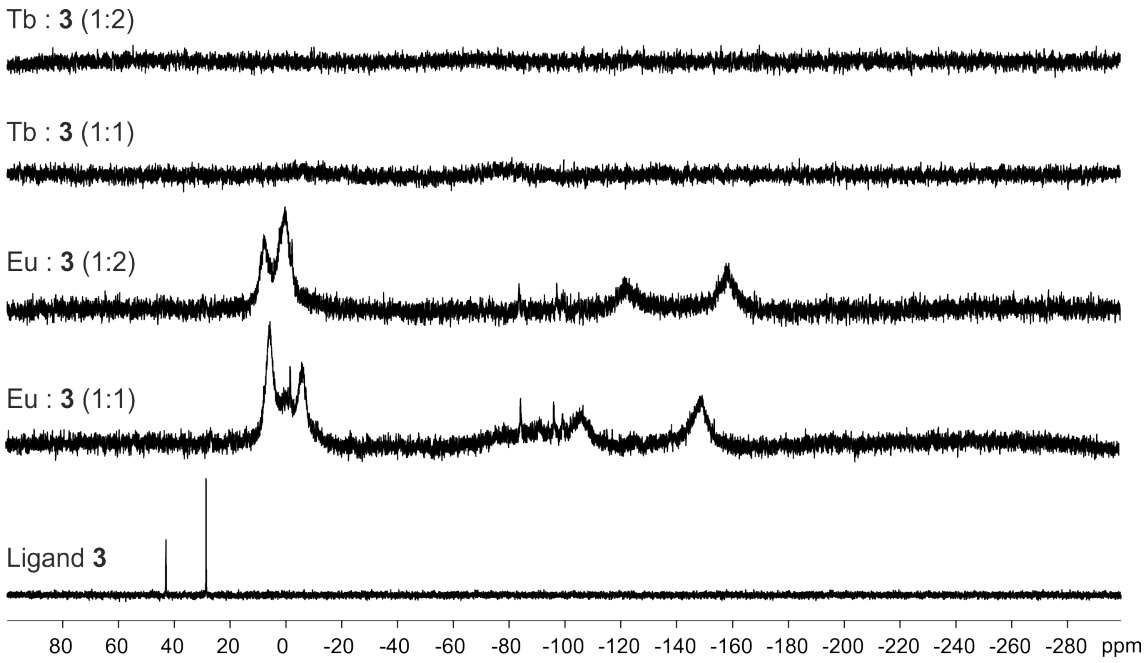

Fig. S20. ^{31}P NMR spectra (202 MHz) for ligand **3** in MeOD at 20 ºC in the presence of different stoichiometries of europium and terbium.