### APPENDIX A. SUPPLEMENTARY DATA

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

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Fig. S17. <sup>31</sup>P NMR spectrum (202 MHz) for ligand 3 in MeOD at RT.

Fig. S18. <sup>13</sup>C NMR spectrum (125 MHz) for ligand 3 in MeOD at RT.

Fig. S19. <sup>1</sup>H COSY NMR spectrum (500 MHz) for ligand 3 in MeOD at RT.

**Fig. S20.** <sup>31</sup>P NMR spectra (202 MHz) for ligand **3** in MeOD at 20 °C in the presence of different stoichiometries of europium (EuCl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>) and terbium (TbCl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>).



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



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



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



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



**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<sup>-1</sup>. [Eu<sup>3+</sup>] =  $1.0 \ge 10^{-6}$  M.  $\lambda_{exc/em} = 229.06/616.02$  nm, excitation and emission slit widths of 5 nm, 700 V detector voltage,  $t_d = 120$   $\mu$ s and  $t_g = 5$  ms.



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



**Fig. S11.** Effect of pH on solid phase. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL<sup>-1</sup>. [Eu<sup>3+</sup>] = 1.0 x 10<sup>-6</sup> M.  $\lambda_{exc/em}$  = 229.06/616.02 nm, excitation and emission



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<sup>-1</sup>. [Eu<sup>3+</sup>] = 1.0 x 10<sup>-6</sup> M.  $\lambda_{exc/em} = 229.06/616.02$  nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t<sub>d</sub> = 120 µs and t<sub>g</sub> = 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<sup>-1</sup>.  $[Eu^{3+}] = 1.0 \times 10^{-6} \text{ M}$ , pH = 5.0.  $\lambda_{exc/em} = 229.06/616.02$  nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t<sub>d</sub> =

120  $\mu$ s and t<sub>g</sub> = 5 ms.



Fig. S14. Calibration graph of the europium(III) membrane sensors. Optimum membrane composition: Nafion:Ligand as 262.3:0.6 mg mL<sup>-1</sup>. [Blank] = 25 mM acetate buffer at pH 5.0;  $[Eu^{3+}] = 1.0 \times 10^{-7}$ -5.0 x 10<sup>-6</sup> 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,  $t_d = 120 \ \mu s$  and  $t_g = 5 \ ms$ .



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







Fig. S19. <sup>1</sup>H COSY NMR spectrum (500 MHz) for ligand 3 in MeOD at 20 °C.





Fig. S20. <sup>31</sup>P NMR spectra (202 MHz) for ligand 3 in MeOD at 20 °C in the presence of different stoichiometries of europium and terbium.