

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

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F. J. Sainz-Gonzalo,^a C. Popovici,^b M. Casimiro,^b A. Raya-Barón,^b F. López-Ortiz,^{*b} I. Fernández,^{*b} J. F. Fernández-Sánchez^{*a} and A. Fernández-Gutiérrez^a

A new europium(III) membrane luminescent sensor based on a new tridentate bis(phosphinic acid) phosphine oxide (**3**) system has been developed. The synthesis of this new ligand is described and its full characterization by NMR, IR and elemental analyses is provided. The luminescent complex formed between europium(III) chloride and ligand **3** was evaluated in solution, observing that its spectroscopic and chemical characteristics are excellent for measuring in polymer inclusion membranes. Included in a Nafion membrane, all the parameters (ligand and ionic additives) that can affect the sensitivity and selectivity of the sensing membrane as well as the instrumental conditions were carefully optimized. The best luminescence signal ($\lambda_{\text{exc}} = 229.06$ nm and $\lambda_{\text{em}} = 616.02$ nm) was exhibited by the sensing film having a Nafion : ligand composition of 262.3 : 0.6 mg mL⁻¹. The membrane sensor showed a short response time ($t_{95} = 5.0 \pm 0.2$ min) and an optimum working pH of 5.0 (25 mM acetate buffer solution). The membrane sensor manifested a good selectivity toward europium(III) ions with respect to other trivalent metals (iron, chromium and aluminium) and lanthanide(III) ions (lanthanum, samarium, terbium and ytterbium), although a small positive interference of terbium(III) ions was observed. It provided a linear range from 1.9×10^{-8} to 5.0×10^{-6} M with a very low detection limit (5.8×10^{-9} M) and sensitivity (8.57×10^{-7} a.u. per M). The applicability of this sensing film has been demonstrated by analyzing different kinds of spiked water samples obtaining recovery percentages of 95–97%.

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1 Introduction

It has been demonstrated that rare earth elements (REEs) provoke alterations and damage in animals.¹ Furthermore, REEs can accumulate in humans producing liver damage and lung embolisms when they are inhaled during long-term exposure in the working environment. Europium, one member of REEs, is found to have many applications as a component in fluorescent lamps, lasers, ceramics and catalysts for oil and atomic industries. Thus, the growing increase in europium dumping and its toxic properties and adverse effects have promoted the need for determining europium in the last few years.²

Nowadays, europium(III) determination in water samples is performed by usual analytical methods such as fluorescence,³ spectrophotometry,⁴ inductively coupled plasma mass spectrometry (ICP-MS),⁵ inductively coupled plasma optical

emission spectrometry (ICP-OES),⁶ chelation ion chromatography (CIC) with absorbance detection⁷ and multiple square wave voltammetry (MSWV).⁸ These methods are time consuming and/or too expensive for most analytical laboratories. In addition, they do not allow the remote and/or *in situ* determination of europium(III).

Chemical sensors have emerged as a powerful alternative to the traditional methods because they offer advantages of low cost, portability, selectivity, measurement in real time and simple operations. Zamani *et al.*⁹ have made a potentiometric sensor based on an ion selective electrode using 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one (HMTDT) as a membrane carrier for the determination of europium(III) in water. The detection limit was 7.8×10^{-7} M and good selectivity was obtained for many trivalent metal ions such as Tb(III), Yb(III), La(III), Sm(III), Ce(III), Fe(III) and Cr(III) among others, improving the analytical characteristics of a previously reported europium(III) ion selective electrode.¹⁰

However, optical sensors have demonstrated several advantages against electrochemical devices.^{11–14} Among others, optical sensors do not require reference electrodes, show relatively shorter response times, are inert against sample flow rate or stirring speed, are immune to exterior electromagnetic field interference and can be mass-produced as disposable sensors.

^aDepartment of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuentenueva s/n, 18071 Granada, Spain. E-mail: jffernan@ugr.es; Fax: +34 958243328; Tel: +34 958240451

^bDepartment of Chemistry and Physics, Laboratory of Organic Chemistry, University of Almería, Ctra. Sacramento s/n, 04120 Almería, Spain. E-mail: ifernan@ual.es; Fax: +34 950015481; Tel: +34 950015644

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In addition, they have also been demonstrated to be advantageous in terms of sensibility and selectivity *versus* europium(III) electrochemical ones,^{15–18} where only a few of these optical sensing layers have been described.^{19,20}

Ligand-sensitized luminescence of lanthanides²¹ is a detection technique with great importance for trace determination of lanthanide ions.^{22,23} This detection procedure can be implemented in the solid phase by immobilizing a ligand agent into a polymeric liquid membrane^{1,9,10,16,24–26} known as the polymer inclusion membrane (PIM).²⁷ Both the nature of the immobilized ligand and the nature of ionic additives used have an enormous influence on the selectivity and sensitivity of these PIMs.^{24,28,29}

The stability and selectivity of the immobilized ligand can be enormously increased if its structure accommodates properly the ions *via* suitable donors (N, O and/or S) with enough flexibility. For this purpose, the use of molecules derived from aromatic multidentate P(O)(OH) phosphinic moieties as potential sensitizing ligands, which possess conjugated π -electron systems, represents an emerging field.^{19,30} Several ligands based on phosphonic or phosphinic acid arms have been used for the complexation of lanthanides.^{31–37} Curiously, some research has been carried out toward functional resins containing several phenylphosphonic acid ligands that have been used in ion-exchange coordination of Eu(III) among other metals.³⁸

Trivalent cations display absorption and emission bands that correspond to Laporte-forbidden f–f transitions. Because the 4f orbitals are relatively insensitive to the ligand field, these optical bands are line-like and characteristic of each metal. As a consequence of the parity rule and/or change in spin multiplicity, these absorptions have very low molar absorptivities, making the direct excitation of the metals very inefficient. This problem is overcome by using a strongly absorbing chromophore to sensitize Ln(III) emission in a process known as the antenna effect.³⁹ Initial excitation occurs *via* the chromophore, which transfers energy to Ln(III), populating the metal-centered excited state, which then emits.⁴⁰ In this sense, the resulting luminescence emitted signal is proportional to the europium(III) concentration in solution.

In this paper, we have first synthesised a new tridentate ligand containing two diphenylphosphinic acid side-arms connected through the *ortho* position to a phenylphosphine oxide moiety, and second, developed a selective and highly sensitive membrane luminescent sensor based on this new species for the determination of europium(III) ions in water, including different kinds of spiked water samples.

2 Experimental

2.1 Chemicals and reagents

Nafion perfluorinated resin solution, 20 wt% in a mixture of lower aliphatic alcohols–water containing 34% water, was purchased from Aldrich. Glycerol was obtained from Scharlau and potassium tetrakis(4-chlorophenyl)borate (KTPClPB) was purchased from Fluka. Absolute ethanol, methanol, anhydrous sodium acetate, potassium hydrogen phthalate, iron(III) nitrate,

chromium(III) nitrate and aluminium(III) nitrate were obtained from Panreac. Sodium chloride was purchased from Riedel-de Haën. Hydrate chloride salts of the lanthanides used were all of the highest purity available and were obtained from ABCR. All chemicals and reagents were of analytical grade and were used as received without further purification.

2.2 Instrumentation and apparatus

An Aminco Bowman Series 2 Luminescence Spectrometer (Sim Aminco, Madison, USA) interfaced with a computer was used to obtain the luminescence spectra and the relative luminescence intensity measurements in solution using 111-QS suprasil quartz cuvettes (light path = 10 × 10 mm), which were purchased from Hellma (Hellma, Jamaica, USA). A Cary Eclipse Varian Fluorescence Spectrophotometer (Varian Australia, Mulgrave, Australia) equipped with a front surface accessory was used to obtain the luminescence spectra and the relative luminescence intensities of the membrane sensors. A MicropH2000 Crison pHmeter (Crison Instruments, Alella, Spain) was used to adjust the pH of the employed solutions.

A WS-400B-6NPP/LITE Laurell spin coater (Laurell Technologies, North Wales, USA) was applied for the polymer inclusion membrane preparation by using a spin coating technique. A G560E Vortex-Genie 2 mixer (Scientific Industries, Bohemia, USA) was used to obtain the polymer solution. Solution sonication was achieved by an Ultrasons Selecta ultrasonic bath (JP Selecta, Abrera, Spain).

¹H (500 MHz), ¹³C (125 MHz), and ³¹P (202 MHz) NMR spectra were recorded in MeOD on a Bruker Avance 500 spectrometer using a direct TBO (¹H/³¹P/BB) probe head. Chemical shifts are referenced to internal tetramethylsilane for ¹H and ¹³C, and to external 85% H₃PO₄ for ³¹P. Standard Bruker software was used for acquisition and processing routines. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (*J*) are measured in Hertz (Hz). Data are reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *h* = heptet, *br* = broad, *m* = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were recorded on Agilent Technologies LC/MSD TOF and HP 1100 MSD equipment with electrospray ionization. Melting points are uncorrected and were registered in a Büchi B-540 apparatus. Carbon and hydrogen elemental analyses were carried out with an Elementar vario MICRO cube. Infrared spectra (4000–400 cm^{−1}) were recorded in Mattson-Genesis II FTIR equipment.

The thickness and the roughness of the polymeric membrane were measured by using an AFM. AFM images were obtained using an Innova Scanning Probe Microscope (Bruker AXS). Images were taken in contact mode using a silicon tip (model MPP-31123) attached to the end of a cantilever with a low spring constant (0.9 N m^{−1}, 20 kHz). Variations in the interactive forces between the tip and surface (the tip is in permanent contact with the sample) result in a topography-based deflection of the cantilever that is recorded by a photodiode. The image resolution was 1024 × 1024 lines, whereas the scanning area was 50 × 50 μ m. Images were analyzed and

transformed into three-dimensional plots with the Nanoscope image processing software. AFM was also used to estimate the surface roughness in contact mode.

2.3 Synthesis of bis(phosphinic acid) phosphine oxide 3

All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of nitrogen by using standard techniques for manipulating air-sensitive compounds. The solvents were dried prior to use in a Pure Solv 400-4-MD system, according to the procedure described by Pangborn and Grubbs.⁴¹ Commercial reagents, except organolithium bases, were distilled prior to use. TMEDA was distilled from KOH. Compounds **1** (ref. 42 and 43) and **2** (ref. 30) have been described previously. Compound **3** was synthesized as indicated in Scheme 1.

2 mL of concentrated H₂SO₄ was added dropwise to an aqueous solution constituted by THF (10 mL), H₂O (20 mL) and precursor **2** (1 g, 1.38 mmol) at room temperature. After 30 min at this temperature the pH was adjusted to 14 using 1 N NaOH. The reaction was then concentrated under vacuum in order to reduce the main part of the organic solvent and diisopropylamine. The resulting aqueous solution was washed two times with CH₂Cl₂ (10 mL) and its pH was adjusted to 2 using 2 N HCl. The mixture was then stored overnight at 4 °C, filtered, and the solid was sequentially washed with cold distilled water (2 × 10 mL) and after with CH₂Cl₂ (2 × 10 mL). Finally, the solid was dried in an oven at 80 °C for at least 12 h, to provide **3** as a white solid (0.38 g, 49%). Mp 181–183 °C. IR (KBr disk): ν_{\max} cm⁻¹ 3596 (st, OH), 1438, 1243 (st, P=O), 1210, 1127, 1086, 934. ¹H NMR (MeOD, 20 °C): 7.05 (ddd, 2H, ³J_{HH} 7.5 Hz, ³J_{PH} 15.3 Hz, ⁴J_{PH} 4.3 Hz, H-10), 7.27 (m, 6H, H-2, H-13), 7.38 (m, 4H, ³J_{HH} 7.0 Hz, H-3, H-14), 7.49 (t, 2H, ³J_{HH} 7.3 Hz, H-9), 7.61 (t, 1H, ³J_{HH} 7.5 Hz, H-4), 7.61 (dd, 4H, ³J_{HH} 7.5 Hz, ⁴J_{PH} 12.9 Hz, H-12), 7.76 (t, 2H, ³J_{HH} 7.5 Hz, ⁴J_{PH} 1.3 Hz, H-8), 8.28 (ddd, 2H, ³J_{HH} 7.9 Hz, ³J_{PH} 13.2 Hz, ⁴J_{PH} 3.7 Hz, H-7); ¹³C NMR (MeOD, 20 °C): 136.90 (dd, ³J_{PC} 127.7 Hz, ⁴J_{PC} 9.2 Hz, C-6), 135.15 (dd, ³J_{PC} 10.8 Hz, ⁴J_{PC} 9.3 Hz, C-7), 134.76 (dd, ³J_{PC} 14.1 Hz, ⁴J_{PC} 11.1 Hz, C-10), 133.03 (d, ³J_{PC} 140.1 Hz, C-11), 132.86 (dd, ³J_{PC} 104.3 Hz, ⁴J_{PC} 11.0 Hz, C-5), 132.19 (d, ³J_{PC} 22.0 Hz, ⁴J_{PC} 2.8 Hz, C-8), 132.01 (d, ³J_{PC} 2.9 Hz, C-4), 131.86 (d, ³J_{PC} 9.8 Hz, C-2), 131.66 (d, ³J_{PC} 3.0 Hz, C-14), 131.17 (d, ³J_{PC} 10.8 Hz, C-12), 130.87 (dd, ³J_{PC} 13.0 Hz, ⁴J_{PC} 2.7 Hz, C-9), 130.28 (d, ³J_{PC} 110.6 Hz, C-1), 128.47 (d, ³J_{PC} 12.5 Hz, C-3), 127.86 (d, ³J_{PC} 13.7 Hz, C-13); ³¹P NMR (MeOD, 20 °C): 43.04 (³J_{PP} 10.6 Hz), 28.60 (³J_{PP} 10.6 Hz). MS-ESI, m/z: 559 (M + 1, 100). Analysis: calcd (%) for C₃₀H₂₅O₅P₅·(+2H₂O): C, 60.61; H, 4.92. Found: C, 61.63; H, 4.64.

2.4 Solution preparation

Aqueous solutions were prepared using doubly distilled water obtained from a Milli-Q Plus 185 ultrapure water system (Millipore, Billerica, USA). Stock ligand solution was prepared in absolute ethanol and europium(III) solutions were prepared with doubly distilled water. Stock and working standard solutions of ligand and lanthanide ions were stored in amber glass bottles at 4 °C.

2.5 Luminescence measurements

The luminescence measurements in solution were performed at $\lambda_{\text{exc/em}} = 232.00/616.02$ nm, which correspond to the maxima excitation and emission wavelengths of the 1 : 2 Eu(III) : 3 complex. A delay of 120 μ s on measuring was used to avoid the fluorescence background and the problems originated from the lamp such as reflection, intensity fluctuations, *etc.* Table 1 lists the optimized instrumental variables for the measurements carried out in both solution and solid phase.

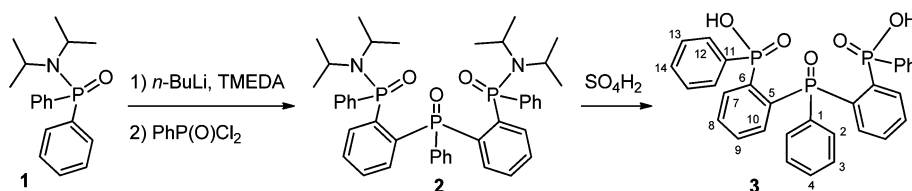
The luminescence measurements of the membranes were performed at $\lambda_{\text{exc/em}} = 229.06/616.02$ nm, which correspond to the maxima excitation and emission wavelengths of the 1 : 2 Eu(III) : 3 complex in the solid phase (see Table 1 for the optimum instrumental variables). The membrane response was considered as the difference between the luminescence intensity of the membrane in the presence of Eu(III) and the luminescence intensity of the membrane in the absence of lanthanide ions. The blank solution contained the same chemical composition as the standard solution but without the lanthanide(III) ions.

In both cases, all the experiments were carried out in triplicate for error issues, and the response time was determined to be t_{95} , which is the required time to obtain 95% of the signal.

The luminescence lifetime was recorded by using a time-resolved method; the sample (or luminescent material) is excited with light pulses, and the intensity signal that changes as a function of time (usually as an exponential decay curve) is measured and analyzed. The time when the intensity decays to e^{-1} (~38.8%) of the initial value is the lifetime.⁴⁴

2.6 Membrane preparation

The optimum membrane solution was prepared by mixing thoroughly in a closed vial 786.8 mg (262.3 mg mL⁻¹) of Nafion perfluorinated resin solution and 1.8 mg (0.6 mg mL⁻¹) of ligand (sensitizing agent) in 2.25 mL of MeOH. The obtained mixture was stirred continuously with a mixer until its complete dissolution. A volume of 300 μ L of the resulting solution was



Scheme 1 Synthesis of ligand **3**.

Table 1 Optimized instrumental conditions for measuring in solution and in the solid phase^a

Variable	Optimum value (solution)	Optimum value (solid phase)
$\lambda_{\text{exc/em}}$ (nm)	232.00/616.02	229.06/616.02
Slit width _{exc/em} (nm)	8/8	10/10
Detector voltage (V)	700	500
Total decay time (ms)	—	20
Delay time t_d (μ s)	120	120
Gate time t_g (μ s)	150	5000
Number of flashes	—	1

^a —: not reported.

deposited on the acetate sheet and spin-coated at 700 rpm at room temperature until the complete solvent mixture evaporation, obtaining ultrathin and homogeneous sensing films on acetate sheets. The polymeric membranes were stored in a closed receptacle at room temperature in the absence of light until its use. Three membrane replicates were made for each experimental point.

2.7 Water sample preparation

One drinking (tap) and two irrigation (irrigation ditch and well) water samples were used for demonstrating the applicability of the sensing film. After analyzing the three samples, it was observed that Eu(III) ions were not detected, so they were spiked at the 10^{-6} M concentration level. The samples were prepared by adding to the water sample up to 25 mM acetate buffer solution at pH 5.00.

3 Results and discussion

3.1 Study of the europium(III)-ligand complex in solution

3.1.1 Spectroscopic characterization. Ligand **3** has been synthesized for the first time by acidic hydrolysis of precursor **2** as mentioned in the Experimental section. To our delight, the synthesis of compound **2** in a multi-gram scale increased the yield significantly from 55% up to 65%. The isolation procedure of ligand **3** excludes the possibility of obtaining precursor **2** together with any other species derived from partial hydrolysis since all of them are insoluble in the aqueous phase whereas **3** is partially soluble. Consecutive dichloromethane cleanups of compound **3** help for its purification. This partial solubility of compound **3** is the main reason why its isolated yield is not higher than 49%. This interesting compound contains two *ortho*-substituted phosphinic acid fragments bridged by a central phosphine oxide core which form a pocket of three P=O groups suitable for binding to oxophilic metals. In the ^{31}P NMR spectrum one can clearly observe a triplet at δ 43.04 ($^3J_{\text{PP}}$ 10.6 Hz) assigned to the phosphine oxide moiety and a doublet at δ 28.60 ($^3J_{\text{PP}}$ 10.6 Hz) which corresponds to the two magnetically equivalent phosphinic acid units. To help the full assignment of ligand **3**, ^1H and ^{13}C NMR spectra were also acquired showing a pattern of signals assigned to the

disubstituted ring in addition to those due to the P-phenyls. In the ^1H NMR spectrum, there are two resonances which appear more evident assigned to H7 and H10, both showing up as double doublet of doublets. In the ^{13}C NMR counterpart, the C_{ipso} carbons of the two different P-phenyl rings C1 and C11 are readily identified by doublets at δ 130.28 and 133.03 ppm with $^1J_{\text{PC}}$ coupling constants of 110.6 and 140.1 Hz, respectively. On the other hand, the C_{ipso} carbons C5 and C6, located on the two isochronous *ortho*-functionalized rings, appeared as doublet of doublets at δ 132.86 ($^3J_{\text{PC}}$ 104.3 Hz, $^4J_{\text{PC}}$ 11.0 Hz) for C5 and at δ 136.90 ($^3J_{\text{PC}}$ 127.7 Hz, $^4J_{\text{PC}}$ 9.2 Hz) for C6, with the latter shifted down-field by the influence of the PO(OH) entity directly attached to it. The carbon and hydrogen elemental analysis supports the empirical formulae of **3**, whereas the IR spectrum evidenced the P=O and hydroxyl groups with stretching bands at 1243 and 3596 cm^{-1} , respectively.

The immediate formation of lanthanide complexes was unravelled by ^{31}P NMR monitoring of 1 : 1 and 1 : 2 methanol solutions of the corresponding lanthanide ($\text{EuCl}_3 \cdot (\text{H}_2\text{O})_6$ and $\text{TbCl}_3 \cdot (\text{H}_2\text{O})_6$) with ligand **3** (Fig. S20†). It is worth mentioning that in the case of europium as the lanthanide of choice the signals are extremely broad, with $W_{1/2} \approx 400$ Hz and ^{31}P coordination chemical shifts in the range of 150 ppm. In the case of terbium the paramagnetism induces extremely fast T_2 relaxation and therefore no signals were detected. The full solution and solid state characterization of these complexes is underway in our laboratories.

Interaction of metal ions with the phosphine oxide and phosphinic acid moieties causes considerable changes in the PO stretching frequency, which is usually identified by high intensity signals. The infrared spectrum of methanolic solutions consisting of equimolecular amounts of ligand **3** and $\text{LnCl}_3 \cdot (\text{H}_2\text{O})_6$ ($\text{Ln} = \text{Eu}$ or Tb) displays bands in the range 1120–1220 cm^{-1} that can be assigned to these P=O stretching vibrations. The shift of these absorptions to lower frequencies (*ca.* 25–55 cm^{-1}) with respect to the corresponding bands in the free ligand (1130–1243 cm^{-1}) supports the binding to the lanthanide metal. However, this region of the IR spectrum is complicated and does not allow the unequivocal identification of the coordination mode to the metal.

The formation of the luminescent complex between europium(III) ions and ligand **3** is depicted in Fig. 1a, which shows the uncorrected excitation and emission spectra of the formed complex. The individual excitation and emission spectra of europium(III) ions and ligand in solution are not shown because they did not present any luminescence signal. The observed excitation wavelengths were 232, 246 and 276 nm. The emission wavelengths were 594, 616 and 654 nm, which correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transitions of the europium(III) ion, respectively.⁴⁰ The emission wavelength corresponding to the hypersensitive transition without inversion centre ($^5\text{D}_0 \rightarrow ^7\text{F}_2$, 616 nm) produced the highest relative luminescence intensity. Therefore, the optimum excitation and emission wavelengths of the europium(III)-ligand complex were 232.00 nm and 616.02 nm, respectively. An important parameter in luminescent complexes is the luminescence lifetime (τ). The decrease of the relative luminescence intensity *versus* time

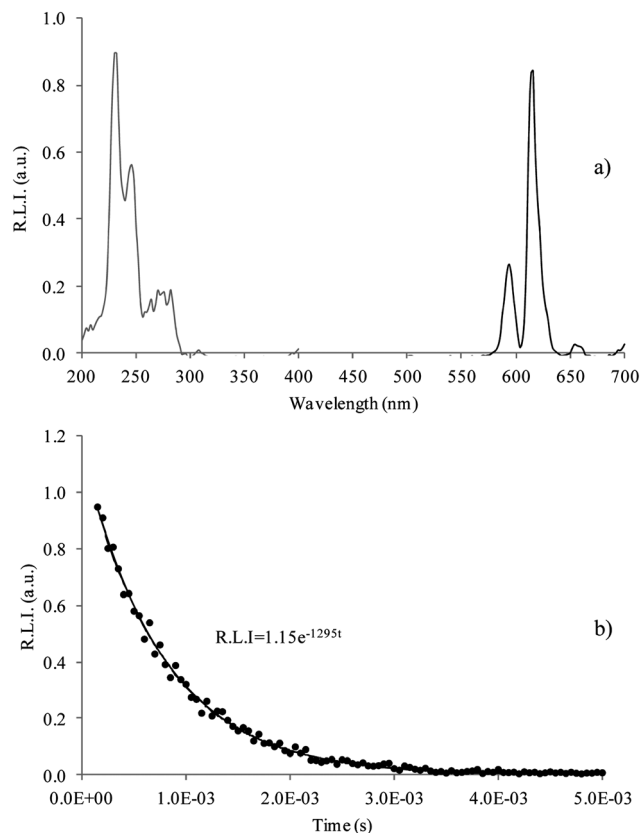


Fig. 1 Spectral characterization of the 1 : 2 europium(III)-3 complex in water. (a) Excitation (grey line) and emission spectra (black line) and (b) luminescence decay curve. $[Eu^{3+}] = 7.5 \times 10^{-6}$ M, $[ligand] = 1.5 \times 10^{-5}$ M.

is shown in Fig. 1b. The experimental data were fitted with an exponential decay model obtaining the following equation: $R.L.I. = 1.15 \times e^{-1295t}$, so the estimated luminescence lifetime was established in 770 μ s.

Fig. S1 in the ESI† shows the luminescence intensity *versus* time once the ligand and the europium salt are mixed. As can be deduced, the response signal is constant over an hour and no signs of decomposition seem to occur during the whole measurement. In the same sense, it is important to point out that time zero in this case is the minimum time required to mix the components and start the measurement that can be estimated to be *ca.* a minute.

3.1.2 Effect of non-aqueous solvent. The luminescence properties are principally related to the molecular structure of the luminophore but the media, and in particular the solvent in which the luminophore is dissolved, have a dramatic effect on the luminescence properties.⁴⁴

The interactions between the luminophore and the solvent are principally electrostatic interactions and the luminescence intensity and maxima excitation wavelengths are affected by the difference between fundamental and excited states' stabilization electrostatic energies.

In order to evaluate the effect of the electrostatic interactions between the complex and the solvent on the luminescence properties of the complex, ethanol was selected as a model solvent because it is miscible with water and has a relatively

high dielectric constant which allows for the solubilization of both ligand and europium(III).

Several percentages of ethanol (0, 25, 50, 75 and 100% (v/v)) were added to the sample. The results are shown in the ESI (Fig. S2†) and indicate that the luminescence signal is equal at 0 and 25% of ethanol. At higher percentages, *i.e.* 50% and 75%, the relative luminescence intensity decreased gradually until its disappearance when the sample contains exclusively ethanol. Thus, the use of organic media such as ethanol does not improve the luminescence signal and therefore no organic media were used for the rest of the experiments.

3.1.3 Effect of ionic strength. The influence of ionic strength on the luminescence intensity was evaluated in order to determine its applicability in real samples. The ionic strength was controlled by using sodium chloride (NaCl) at different concentrations from 0.1 to 0.5 M. ESI (Fig. S3†) shows the variation of the relative luminescence intensity *versus* NaCl concentration making evident that the ionic strength does not significantly affect the luminescence signal for concentrations lower than 0.3 M and causes an erosion of the luminescence signal when higher concentrations of NaCl are employed. To enhance the detection limits, the current study was therefore performed without NaCl.

3.1.4 Effect of pH. The pH dependence of the complex luminescence intensity was evaluated for a sample containing 5.0×10^{-7} M Eu(III) in water. The pH was adjusted between 3.0 and 11.0 by using HCl and/or NaOH. The results are depicted in the ESI (Fig. S4†). It can be seen that the relative luminescence intensity was independent of the solution pH in a range of 3.0 to 9.0. This wide working pH could be useful to measure environmental and industrial water samples without the need for pH adjustment. For higher pHs, the luminescence signal decreases drastically which is attributed to the formation of insoluble $Eu(OH)_3$ ($K_{ps} = 9.38 \times 10^{-27}$) that precipitates at pH higher than 7.5 when the concentration of Eu(III) is 5.0×10^{-7} M. For this reason, although the adequate working pH covered a wide range, a neutral pH of 7.0 was selected as the optimum.

3.1.5 Stoichiometry of the europium(III)-ligand complex. The stoichiometry of the complex formed between the europium(III) ion and ligand was studied by using the mole-ratio method (Yoe and Jones method)⁴⁵ (Fig. 2) in the mixture based on ethanol and water at a ratio of 75 : 25, respectively.

Fig. 2a shows the relative luminescence intensity *versus* Eu(III) : ligand ratio maintaining a constant europium(III) ion concentration. Two inflection points at 1 : 1 and 1 : 2 Eu(III) : ligand ratios can be observed. These can be interpreted as the formation of two different stoichiometries. The decrease of the luminescence signal observed for higher concentrations of ligand was attributed to an auto-quenching phenomenon. These results were also corroborated by carrying out the same experiment but keeping constant the ligand concentration (Fig. 2b). As the obtained results agreed in both cases, it is concluded that the ligand promotes the formation of two europium(III) complexes with Eu(III) : ligand stoichiometries of 1 : 1 (low luminescence complex) and 1 : 2 (high luminescence complex). ESI (see Fig. S5†) shows the luminescence emission spectra of 1 : 1 and 1 : 2 complexes. It is possible to conclude

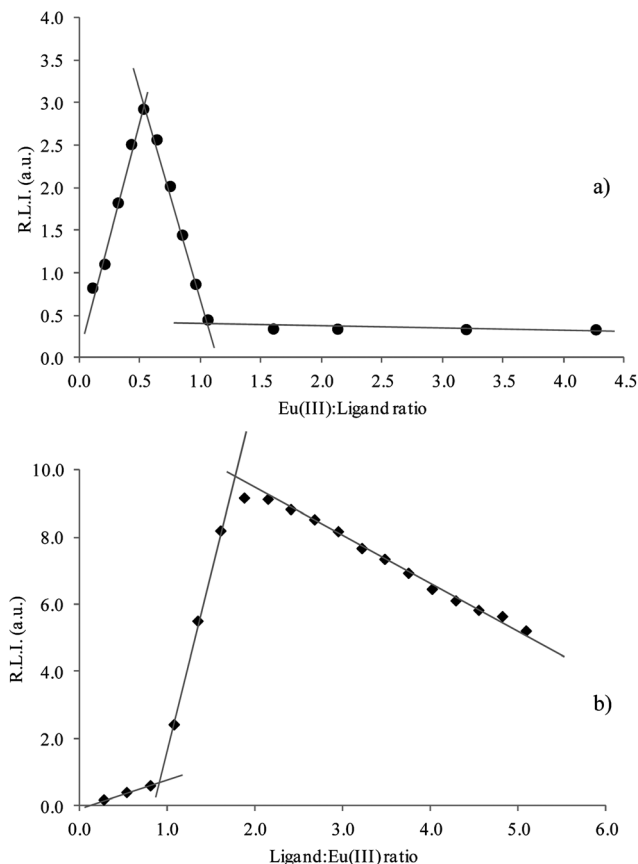


Fig. 2 Determination of the stoichiometry of the complex in a mixture of water–ethanol (75 : 25). (a) Keeping the Eu(III) concentration constant ($[Eu^{3+}] = 7.5 \times 10^{-6}$ M; pH = 7.0) and (b) keeping the concentration of the ligand constant ($[ligand] = 3.8 \times 10^{-6}$ M; pH = 7.0).

that the 1 : 1 complex emits at the same wavelength as the 1 : 2 complex (594, 616 and 654 nm, which correspond to the $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transitions of the europium(III) ion, respectively) but with less intensity.

Attending to the Eu(III) and ligand concentrations used for the characterization study in solution, the existing complex is the one with the 1 : 2 Eu(III)–3 stoichiometry.

3.2 Characterization of sensing films

In order to obtain the sensing film, ligand **3** should be solubilised in a polymeric liquid membrane. Several solvents and polymers were tested and it was realised that ligand **3** was not soluble in nonpolar solvents such as THF and, in addition, it was not possible to solubilise it on classical polymeric supports such as PVC with or without plasticizers on it. Thus, more polar solvent (methanol) and more hydrophilic polymeric supports such as Nafion were used.

3.2.1 Thickness and roughness of the sensing film. The thickness and roughness of the sensing film have been studied by AFM in tapping mode (resolution of 1024 lines and size of $50 \times 50 \mu\text{m}$). For this, the polymeric sensing layer was removed in one section of the sample by simple dissolution with acetone and the thickness was determined by measuring the difference in the Z axis (Fig. 3).

Fig. 3a shows a 3D image from which it is possible to distinguish between the coated (right) and uncoated (left) sections. The coated section shows concentric lines which could correspond to the spin-coating directions of the polymeric films. These lines are real and cannot be considered as artefacts because the scanning was done from the left to the right (see ESI, Fig. S6†) and they do not appear in the uncoated sections.

Fig. 3b shows the height profile which shows that the thickness of the sensing films is established to be $1.2 \mu\text{m}$.

In order to demonstrate the homogeneity of the thickness and the roughness of the sensing film, a determined area of the coated and uncoated sections was analysed by measuring the average height and roughness (R_a) (see ESI, Fig. S7†). It shows that the coated section has an average height of $3.38 \mu\text{m}$ while the uncoated section shows an average height of $2.19 \mu\text{m}$. In addition, the R_a values of the coated and uncoated sections are practically the same: 230 and 217 nm, respectively, confirming, the homogeneity of the thickness of the films.

3.2.2 Spectral characterization. When the sensing film based on **3** immobilized into Nafion is exposed to Eu(III) ions, it shows a very strong luminescence emission to its most intense emission peak (hypersensitive transition) among different lanthanides tested. This is most probably due to the selective interactions of the ligand and europium(III) ions, and the fast formation of the resulting europium(III)–ligand complex.

Fig. 4 shows the excitation and emission spectra of the optimized membrane sensor in the presence of europium(III) ions. It shows, on the one hand, four emission peaks (593, 616, 655 and 700 nm) which correspond to the $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transitions of the europium(III) ion, respectively. The highest luminescence peak corresponds to 616.02 nm ($^5D_0 \rightarrow ^7F_2$ transition), which was practically the same emission wavelength as the highest luminescence peak in solution (618.00 nm). Thus it is possible to conclude that the immobilization of the ligand into the liquid membrane does not affect the chemical structure of the ligand. On the other hand, a wide excitation band with two maximum peaks (229 and 273 nm) was observed. These peaks arise from the excitation of the phenyl groups of the ligand in π -conjugation with phosphinoyl groups. The absolute excitation maximum (229.06 nm) was not modified with respect to that of the solution (232.00 nm).

Furthermore, the t_{95} response time was calculated to be 5.0 ± 0.2 min when the sensing film was exposed to 10^{-6} M Eu(III) ions under optimal conditions (see ESI Fig. S8†). This reaction time could be explained by a slow diffusion rate of europium(III) ions into the membrane, which was produced by their relatively high ionic volume. Therefore, it should be reduced by replacing Nafion with another water insoluble, hydrophilic polymer which allows faster diffusion of Eu(III) into the polymeric liquid membrane. To the best of our knowledge, there are not many hydrophilic water insoluble polymers which can be chemically compatible with ligand **3**. Therefore, novel hydrophilic water-insoluble polymers with fast diffusion of Eu(III) should be synthesized.

3.2.3 Ligand concentration. The dependence of ligand concentration on the luminescence intensity of the sensing film was also studied. Five entries from 0.0 to 1.5 mg mL^{-1} were tested (see ESI, Fig. S9†). The graph shows that the sensing response to

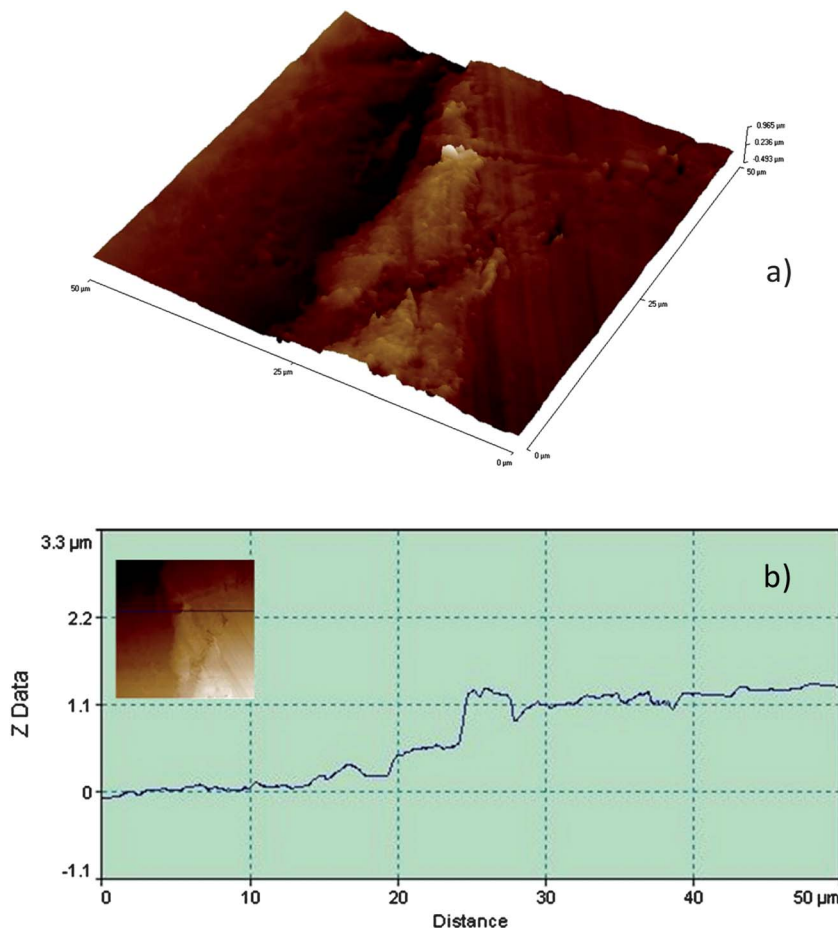


Fig. 3 Determination of the thickness and roughness of the sensing film by AFM. (a) 3D image and (b) height profile. Coated (right) and uncoated (left) sections.

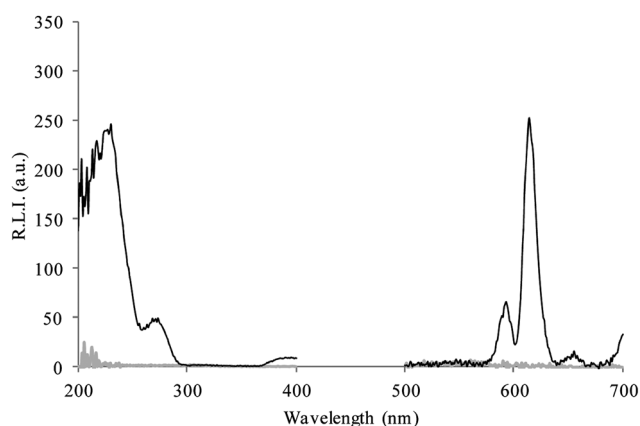


Fig. 4 Spectral characterization of the optimized sensing film in the absence of Eu(III) ions (grey line) and in the presence of europium(III) (black line). Optimum membrane composition: Nafion : ligand 262.3 : 0.6 mg mL⁻¹; [acetate buffer] = 25 mM at pH 5.0; [Eu³⁺] = 1.0 × 10⁻⁶ M. $\lambda_{\text{exc/em}}$ = 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.

Eu(III) ions increases gradually when the ligand concentration is lower than 0.6 mg mL⁻¹, and the response does not increase at all when higher concentrations of ligand are employed, therefore tuning the optimum ligand concentration to 0.6 mg mL⁻¹.

3.2.4 Ionic additive concentration. The influence of ionic additive concentration on the luminescence signal of the sensing membrane was investigated by varying the potassium tetrakis(4-chlorophenyl) borate (KTPClPB) concentration from 0.0 to 1.5 mg mL⁻¹. KTPClPB is an alkaline lipophilic salt, which was incorporated into the membrane for reasons of electroneutrality. ESI (Fig. S10†) shows that the sensing response to Eu(III) ions is not affected by the use of KTPClPB in the membrane composition so its use was discarded, reducing in this way the costs of the sensing film. The explanation for this phenomenon needs to assume the entrance of the europium bearing the three chlorides as a whole, *i.e.* EuCl₃, fulfilling in this way the electroneutrality principle which governs PIMs.

3.2.5 pH effect. The pH dependence of the sensing film was tested over the pH range from pH 2.0 to 11.0 at a 1.0 × 10⁻⁶ M Eu(III) concentration. The sensing response varied in a distorted Gaussian way (see ESI, Fig. S11†) over the studied range. This behavior makes necessary a prior pH adjustment before its direct use in environmental and industrial water samples.

The different impact that pH exerts in solution and in the membrane is probably due to the different medium in which the complex is formed. In solution, the ligand and Eu(III) are solubilized in the same medium, which consequently favors complex formation. In the membrane, the formation of the complex needs

to occur in the membrane where Eu(III) has to diffuse into it. Therefore, pH necessarily affects the diffusion of Eu(III) into the membrane, and does not affect at all the formation of the complex in solution where no pH has been yet imposed.

The maximum luminescence intensity was obtained at pH 5.0, for which fast diffusion of Eu(III) into the membrane should be achieved. For higher pH values, a relatively important drift was observed, which could be due to the formation of insoluble Eu(OH)₃ inhibiting the diffusion of any Eu(III) into the membrane. For lower pH values, a gradual decrease in the luminescence intensity was observed which could be due to competition issues between protons and Eu(III) to get inside the membrane. The pH value of 5.0 was considered the optimum for analyzing europium(III) ions in water samples.

3.2.6 Kind and concentration of the buffer solution. As discussed before, the use of a buffer solution is critical in order to maintain water samples at the optimum pH. For this purpose, different buffer solutions such as acetate and hydrogen phthalate, whose working pH range covered the optimum pH of 5.0, were studied. ESI (Fig. S12†) shows the sensing response for each buffer solution. Rather similar luminescence signals were obtained with both buffer solutions, the acetate-based one provided a higher sensing response. This behaviour could be explained since acetate is a well-known ligand for Eu(III) together with its relatively small size which should confer better diffusion into the membrane cavities when compared to hydrogen phthalate.

The influence of buffer solution concentration on the membrane sensors was also tested. ESI (Fig. S13†) depicts the sensing response with different concentrations of the acetate buffer at pH 5.0 (0, 25, 50, and 75 mM). The increase of the buffer concentration increases the sensing response up to 25 mM, keeping constant the signal for higher concentrations. When the concentration of buffer is higher than 25 mM, no significant differences are observed, so the acetate buffer concentration was tuned to 25 mM for further analysis.

3.3 Figures of merit

3.3.1 Analytical parameters. The luminescence intensity of the sensing films at different concentrations of europium(III) (see ESI, Fig. S14†) indicated a linear concentration range from 1.9×10^{-8} to 5.0×10^{-6} M. A linear fit ($R.L.I. = 8.5707 \times [Eu^{3+}] - 1.0982$; $r^2 = 0.9981$) was performed successfully with the

experimental data, in which graphical or mathematical interpolation could be carried out within the linear range to determine the europium(III) concentration. Other characteristic parameters may be summarized as follows: the slope of the calibration graph was 8.57×10^{-7} a.u. per M, the detection limit, calculated as the concentration of Eu(III) which produced an analytical signal three times the standard deviation of the blank signal (IUPAC criterion), was 5.8×10^{-9} M, the quantification limit was 1.9×10^{-8} M and the blank relative standard deviation for three replicate measurements was 13.9%.

Table 2 compares the figures of merit of the proposed sensing film with others previously published in the literature. It is worth mentioning that the detection limit of the proposed sensor is the best reached ever for any europium(III)-sensitive optical sensing film published in the literature. In addition, it has a wide linear dynamic range. In contrast, it shows a response time higher than other sensing films and evidences irreversibility, this specific feature being one of its main drawbacks. Further investigations have to be developed in order to improve this aspect.

It is important to point out that there are other luminescence methods in solution for the determination of Eu(III). Interestingly, Jenkins and Murray¹⁸ didactically introduced a quite simple and highly sensitive method (LOD of less than 0.1 nM) for determining Eu(III) in pond and tap water. However, as it was commented by the authors, these kinds of methods in solution are time consuming and require transporting the sample to the laboratory. In addition, they do not allow remote control or determination in hazardous environments, which represent the strongest advantages of the optical sensor presented herein, as we have demonstrated previously with a similar ligand.²⁰

3.3.2 Study of interferences and long-term stability. The selective behavior is clearly one of the most important parameters of a membrane sensor. Three metal(III) ions (iron, chromium and aluminum) and four lanthanide(III) ions (lanthanum, samarium, terbium and ytterbium) were selected as interfering ions in order to check the selectivity of the membrane sensor. Fig. 5 shows the results of this study. It presents that iron(III), chromium(III), aluminum(III), lanthanum(III), samarium(III) and ytterbium(III) ions provoked negligible signals whereas terbium(III) ions provided a detectable luminescence signal with regard to the europium(III) ion signal.

ESI (see Fig. S15†) shows the excitation and emission spectra of the optimized membrane sensor in the presence of

Table 2 Comparison of the figures of merit of the proposed sensing film with others previously published for detecting Eu(III)

Sensor number	Detection limit (M)	Quantification limit (M)	Sensitivity ^{a,b} (mV per decade or a.u. per M)	Working concentration range (M)	Working pH range	Lifetime (days)	Response time (s)	Reference
1 ^a	7.8×10^{-7}	1.0×10^{-6}	19.7 ± 0.4	1.0×10^{-6} to 1.0×10^{-1}	3.5–7.8	>60	<15	9
2 ^a	6.0×10^{-5}	8.0×10^{-5}	19.8 ± 0.1	8.0×10^{-5} to 1.0×10^{-1}	3.0–7.0	>60	<20	10
3 ^b	4.8×10^{-8}	1.6×10^{-7}	9.41×10^{-7}	1.6×10^{-7} to 5.0×10^{-6}	5.0	n.c.	600	19
4 ^b	1.0×10^{-8}	3.3×10^{-8}	n.c.	1.0×10^{-8} to 1.0×10^{-3}	5.0	n.c.	92	20
Proposed film	5.8×10^{-9}	1.9×10^{-8}	8.57×10^{-7}	1.9×10^{-8} to 5.0×10^{-6}	5.0	>180	300	This work

^a Electrochemical sensor. ^b Optical sensor. n.c.: not calculated.

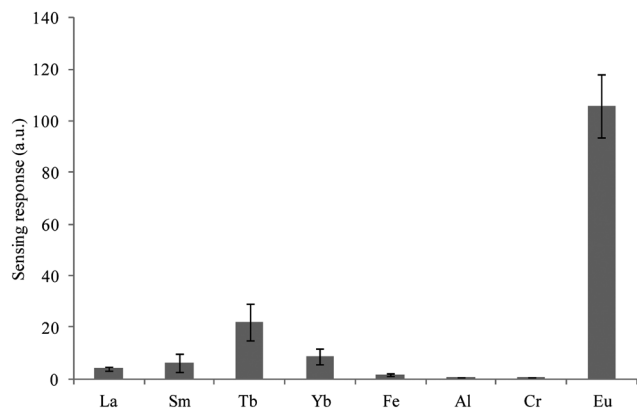


Fig. 5 Interference study. Optimum membrane composition: Nafion : ligand 262.3 : 0.6 mg mL⁻¹; [metal(III) ions] = 1.0×10^{-6} M in 25 mM acetate buffer solution at pH 5.0. $\lambda_{\text{exc/em}}$ = 229.06/616.02 nm, excitation and emission slit widths of 10 nm, 500 V detector voltage, t_d = 120 μ s and t_g = 5 ms.

terbium(III) ions. It shows three emission peaks (540, 856 and 612 nm), which correspond to the $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions of the Tb(III) ion, respectively. The highest luminescence peak corresponds to 540 nm ($^5D_0 \rightarrow ^7F_2$ transition), but the interference is due to the $^5D_4 \rightarrow ^7F_3$ (612 nm) transition because the measurements for determining Eu(III) are carried out at 618 nm. Therefore, other f-f emitted ions should be also borne in mind as potential interferents.

In comparison with other previously published sensing films,^{9,10,19,20} it is possible to conclude that the selectivity of the proposed sensing film is similar to other optical sensing films. It is worth mentioning that the electrochemical sensors seem to be more selective because they are not affected by the presence of Tb(III). In order to evaluate the long-term stability, the sensing films were prepared and stored in the absence of light and room temperature for 6 months. After that, they were used to determine Eu(III) ions in solution and the response signal was reduced only by 8.5%. Thus, it is possible to conclude that the sensing films can be stored in the absence of light for long-term periods.

3.4 Application of the sensing film

To test the predictive ability of our sensing film, one sample of tap drinking water from the city of Granada (Andalusia, Spain) and two water samples from an irrigation ditch and a well were spiked at the 10^{-6} M Eu(III) concentration level. The waters underwent no prior treatment.

Table 3 Analytical application results for drinking and irrigation water samples

Sample	[Eu(III)] added (M)	[Eu(III)] found (M)	Recovery percentage (%)	R.S.D. ^a (%)
Tap	10^{-6}	9.5×10^{-5}	94.5	8.8
Irrigation ditch	10^{-6}	9.8×10^{-5}	97.3	9.4
Well	10^{-6}	9.6×10^{-5}	95.9	8.9

^a For three replicates.

The samples were prepared by adding Eu(III) (10^{-6} M final concentration) and 25 mM acetate buffer solution at pH 5. The sensing films were exposed to the sample and luminescence was measured under optimal conditions (see Table 1).

The results are set out in Table 3. In all the cases the detection and quantification rates of the optical sensor were highly satisfactory, showing recovery percentages between 94.5 and 97.3% with relative standard deviations lower than 10%.

In comparison with other previously published sensing films,^{9,10,19,20} it is possible to conclude that the applicability of the proposed sensing film is similar.

4 Conclusions

The results presented herein demonstrate that a Nafion membrane luminescent sensor for determining europium(III) ions has been developed. For this, a new mixed ligand containing two diphenylphosphinic acid side-arms connected through the *ortho* position to a phenylphosphine oxide moiety was synthesized and fully evaluated as a sensitizing agent, and the phenomenon of ligand-sensitized luminescence of lanthanides was observed. The nature and concentration of the ligand and ionic additive concentrations were investigated; the optimum membrane sensor had a Nafion : ligand composition of 262.3 : 0.6 mg mL⁻¹. The response of the sensing film was strongly influenced by working pH, so acetate buffer solution (25 mM) at pH = 5.0 was used. The membrane sensor was rather selective for the determination of europium(III) ions, although a small positive interference of terbium(III) ions was observed. It showed a short response time ($t_{95} = 5.0 \pm 0.2$ min) and a linear range from 1.9×10^{-8} to 5.0×10^{-6} M with a detection limit of 5.8×10^{-9} M, which is the best detection limit reached for any europium(III)-sensitive optical sensing film published in the literature. The applicability of the proposed sensing film has been demonstrated by analyzing three different water samples, for which good recovery percentages with appropriate RSD were obtained.

Therefore, the developed sensing film constitutes a simple and very promising alternative to expensive and tedious analytical methods, which offers the possibility for practical sensing and the determination of europium(III) ion concentration in water. Further investigations on the reversibility of the developed membranes are underway in our laboratories.

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