Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 6735



Development of polymeric sensing films based on a tridentate bis(phosphinic amide)-phosphine oxide for detecting europium(III) in water[†]

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Received 3rd February 2012, Accepted 23rd March 2012 DOI: 10.1039/c2dt30257h

A novel europium(III) membrane luminescence sensor based on a tridentate bis(phosphinic amide)phosphine oxide, PhPO($C_6H_4POPhN(CH(CH_3)_2)_2$) (1), is described. The new luminescent complex, $[Eu(1)_2]Cl_3 2$, which is formed between europium(III) and ligand 1 and has a 1:2 stoichiometry, has been evaluated in solution. It has the excellent spectroscopic and chemical characteristics that make it appropriate for sensing film applications. All the parameters (polymer, plasticizer, ligand and ionic additive) that can affect the sensitivity and selectivity of the membrane sensor and instrumental conditions have been carefully optimized. The best sensing response ($\lambda_{exc} = 229.04 \text{ nm}$, $\lambda_{em} = 616.02 \text{ nm}$) was observed for 33.4:65.1:1.5 (%, w/w) PVC: DOS: 1. The sensing film shows a good response time (10 min) and a very good selectivity toward europium(III) with respect to other lanthanides(III) ions, such as La, Sm, Tb and Yb. The newly-developed sensing film has a linear range from 1.6×10^{-7} to 5.0×10^{-6} mol L⁻¹ for Eu ions with a very low detection limit (4.8×10^{-8} mol L⁻¹) and good sensitivity $(9.41 \times 10^{-7} \text{ a.u. mol}^{-1} \text{ L}^{-1})$ to europium. Complexes of $[\text{Eu}(1)_2]\text{Cl}_3(2)$ and $[\text{Eu}(1)]\text{Cl}_3(4)$ were isolated by mixing ligand 1 with Eu(Cl₃)·6H₂O in acetonitrile at room temperature in ligand : metal molar ratios of 1:2 and 1:1, respectively. The 1:1 derivative is the product of thermodynamic control when a molar ratio of ligand to europium salt of 1:1 is used. The new compounds have been characterized in both the solid form (IR, MS-TOF, elemental analysis, TGA and X-ray diffraction) and in solution (multinuclear magnetic resonance). In both europium complexes, the ligand acts as a tridentate chelate. Thermogravimetric (TG) studies demonstrated that neither complex 2 or 4 possess any water molecules directly bound to the lanthanide metal, which corroborates the X-ray structure. The investigation of the solution behaviour of the Y(III) complexes with pulsed gradient spin-echo (PGSE) NMR diffusion measurements showed that average structures with 1:1 and 1:2 stoichiometries are retained in acetonitrile solutions.

Introduction

Rare earth elements (REEs) are widely distributed in the Earth's crust at very low concentrations and have been the focus of

increasing interest in the last years due to their applications as important components in lasers, phosphors, coloured glasses, magnetic bubble memory films, the synthesis of single molecule magnets, fibre optics, refractive index lenses, high-intensity lighting, superconductors, ceramics and catalysts. In addition, they have also been used in refining and the metallurgic and nuclear industries, as well as agriculture, medicine and natural sciences.¹

Diverse REE toxicity tests have been carried out in animals. They have revealed that REEs provoke alterations in the reproductive and nervous system and that they can cause liver and spleen damage.² For these and other reasons, there has been increased interest in the determination of REEs in the last decade.³

Europium is a prominent and reactive member of the rare earth family whose determination is necessary due to its applications in many different fields.⁴

The most used analytical methods for europium(III) detection in water samples are: spectrophotometry, fluorescence, 5^{a} inductively coupled plasma optical emission spectrometry

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[†]Electronic supplementary information (ESI) available: 1D and 2D NMR spectra, absorption spectra, luminescence intensity graphs as a function of the organic solvent, ionic strength and pH in solution, luminescence intensity graphs as a function of the type of plasticizer, the concentration of the plasticizer, ligand 1, the ionic additive, pH, type of buffer and ionic strength in the sensing solid membranes and spectro-photometry calibration curves. CCDC 855721. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2dt30257h.

(ICP-OES),^{5b} inductively coupled plasma mass spectrometry (ICP-MS),^{5c} multiple square wave voltammetry (MSWV)^{5d} and chelation ion chromatography (CIC) with absorbance detection.^{5e} All of these methods require expensive instrumentation, long analytical times and sample pretreatments and, consequently, they are not suitable for the analysis of large numbers of samples.

Due to this limitation, several europium-selective electrode sensors have been recently developed; however, there are very few reports of these electrodes in the literature.^{6–8} They simplify the analytical process and enable the monitoring of specific species *in situ* and in real time. They are based on the immobilization of ligand species, which complex with the Eu(III) ions.

Zamani *et al.*^{6b} developed a potentiometric sensor based on anion selective electrode using 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (HMTDT) immobilized in PVC as a membrane carrier for the determination of europium(III) in water samples. They reported a detection limit of 7.8×10^{-7} mol L⁻¹ and good selectivity for a wide variety of metal ions, improving the characteristics of previously reported europium(III) in selective sensors.⁷

More recently, Ganjali *et al.*^{7c} evaluated 4*E*-4-(2-phenylviaze-nyl)-2-((*E*)-(2-aminoethylimino)methyl) phenol (PMP) as a neutral ion carrier in the construction of an europium(III) PVC-based membrane sensor. It exhibited a near-Nernstian response of 18.8 ± 0.2 mV per decade of europium activity in the range of 4.0×10^{-7} - 1.0×10^{-2} mol L⁻¹ with a detection limit of 1.5×10^{-7} mol L⁻¹ and selectivity coefficients in the range of 7.5×10^{-6} - 2.4×10^{-4} .

Optical sensors have generally demonstrated several advantages over electrochemical ones.⁹ In particular, the optical determination of the europium(III) ion has shown higher sensitivity and selectivity over an electrochemical determination.^{7d,10} An optical chemosensor capable of detection at very low concentration levels (6.2×10^{-8} M) has also been reported,^{7d} demonstrating the effectiveness of novel luminescence sensing probes for the determination of this ion.

Trivalent lanthanide ions are weak luminescent species in water due to their low molar absorptivities and poor quantum yields.¹¹ However, the lanthanides present a rich photophysical and coordination chemistry for the formation of luminescent complexes.¹² These complexes show a large Stokes shift, long luminescent lifetimes and emission spectra with very narrow bands. The disadvantage of their weak light absorption is solved by the grafting of an antenna¹³ onto the ligand complexing the lanthanide ion. The antenna absorbs energy from UV-visible radiation and transfers it to the lanthanide ion that emits electromagnetic radiation in the visible region. These particular characteristics make them attractive for multiple applications, such as chiral NMR shift reagents and magnetic resonance imaging contrast agents,14 luminescent labels for biomedical analysis,15 mild reagents and catalysts in organic synthesis¹⁶ and as molecular magnetic materials.¹⁷

Molecules derived from phosphinic moieties can be considered as potential sensitizing ligands and they commonly possess a conjugated π -electron system and multiple coordination modes, which allows them to be good activators of europium(III) ion luminescence and good candidates to form stable complexes. These complexes absorb energy at the characteristic wavelength of the ligand and emit radiation at the characteristic wavelengths of the europium(III) ion. These observed characteristic line-type bands at 594, 618, 660 and 704 nm correspond to the transitions of the europium(III) ion $({}^{5}D_{0} \rightarrow {}^{7}F_{1}, {}^{5}D_{0} \rightarrow {}^{7}F_{2}, {}^{5}D_{0} \rightarrow {}^{7}F_{3}, {}^{5}D_{0} \rightarrow {}^{7}F_{4}$, respectively).¹⁸ The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition was selected to determine the europium(III) concentration as the luminescence signal of the complex at this emission wavelength is proportional to the europium(III) concentration in solution.

To obtain sensing films for the detection of Eu(III) ions based on polymer inclusion membranes (PIMs),¹⁹ two components are necessary: (1) a luminescent Eu(III)-sensing probe, and (2) a solid support in which the ligand can be immobilized. PIMs offer numerous advantages, such as effective reagent immobilization, simple preparation, versatility and good mechanical properties.²⁰ The sensitivity and selectivity of PIMs depend on their chemical composition; for example, the nature of the immobilized ligand, the nature of the plasticizers and the ionic additives used.²¹ In terms of solid supports, polyvinyl chloride (PVC) is one of the most commonly used bases for developing these films.²²

Lanthanide ions are oxophilic and, therefore, are expected to interact strongly with polarized oxygen-bearing functional groups. All the lanthanide-based membrane sensors reported to date make use of systems with nitrogen, oxygen or sulphur pendants.^{20a,21a,c,23} It has been well established that the phosphinoyl (P=O) group interacts with lanthanide cations more strongly than other functionalities.²⁴ As a consequence, simple phosphine oxides,²⁵ phosphonates²⁶ and multifunctional ligands bearing PO moieties^{8,27} have been extensively investigated in f-block coordination.²⁸ Representative examples of mono-, bi-, tri- and tetra-dentate molecules related to the title compound are shown in Fig. 1.

Ligands bearing several soft donors in their structure are expected to have increased stability and selectivity toward lanthanides. This suggests that ligand 1 may represent an excellent candidate as a sensitizing agent for the recognition of europium(III) ions. The synthesis of ligand 1 (see the Experimental section) has been described previously²⁹ and 1 has been characterized by X-ray crystallography and NMR spectroscopy. Compound 1 is a *meso* compound containing two *ortho*-substituted phosphinic amide fragments bridged by a central phosphine oxide core, which provides an excellent pocket of three P==O groups suitable for coordination chemistry. In fact, ligand 1 has



Fig. 1 Representative examples of phosphorous-based ligands for f-block coordination.

already shown its coordination abilities to yttrium(III) nitrate and provided complexes with stoichiometries of 1:1 and 1:2.²⁹

In this work a new luminescence Eu(III)-sensing probe was synthesized and characterized by spectrophotometry, luminescence spectrometry, X-ray crystallography and multinuclear mono- and bi-dimensional NMR, together with PGSE diffusion NMR studies. In addition, ligand **1** was immobilized in a PVC liquid membrane in order to develop a highly selective and sensitive optical Eu(III)-sensing film. To our knowledge, this is the first time that a ligand-sensitized luminescence sensing film has been used for the detection of europium(III) ions.

Results and discussion

Synthesis and solution NMR

The mononuclear complex, $[Eu(1)_2Cl_3]$ (2), was obtained as an analytically pure compound from the reaction of two equivalents of 1 with europium(III) chloride, $Eu(Cl)_3 \cdot (H_2O)_6$, in acetonitrile (Scheme 1). The product is insoluble in diethyl ether and hexane and precipitates a few minutes after the addition of any of these solvents into a concentrated solution of the aforementioned mixture. The solid can therefore be easily isolated by filtration. Similar to the formation of the yttrium complex, $[Y(1)_2(NO_3)_3]$ (3),²⁹ the synthesis of 2 proved to be diastereospecific, where only the product of the *face*-to-*face* binding of the two tridentate ligands to the lanthanide was detected (see below).

When different $Eu(Cl)_3: 1$ stoichiometries were assayed, *e.g.*, 1:1, 1:3, 1:4, the ³¹P NMR spectra showed exclusive formation of complex **2** or the coexistence of **2** and the free ligand in agreement with a stable complex not prone to dissociate and/ or aggregate (see Diffusion NMR studies below). All attempts to obtain crystals of **2** suitable for X-ray analysis failed and the structure could only be assigned based on spectrometric methods.

Electrospray mass spectrometry (ESI-MS), as a soft molecular detection technique, is the method of choice for elemental and structural information as the degree of declustering and molecular fragmentation in the mass spectrometer interface region can be adjusted. No addition of inert salt was required to fix the ionic strength in order to prevent the formation of ionic aggregates, which can scatter the signal. The ESI-TOF spectrum shows the formation of the [1:2] complex (2) due to the observation of the [M–Cl] peak at 1671.4 together with its specific



Scheme 1 The synthesis of the complex $[Eu(1)_2Cl_3]$ (2). The structure shown is consistent with the fragments observed by ESI-MS.

isotopic distribution profile (Fig. S1[†]). The existence of this ion clearly demonstrates the incorporation of two ligand entities and two chlorine atoms directly bound to the metal. The elemental analysis of the freshly prepared samples supports the proposed composition. The results were found to be consistent with the europium metal bearing two ligand units and three chlorides.

The interaction of metal ions with the phosphoryl oxygen causes considerable changes in the PO stretching frequency, which is easily identified by its high intensity. The infrared spectrum of complex **2** (as a KBr disk) displays bands in the range of 1100–1203 cm⁻¹, which can be assigned to these P==O stretching vibrations (Fig. S2†).²⁹ The shift of these absorptions to lower frequencies (*ca.* 20–50 cm⁻¹), with respect to the corresponding bands in the free ligand, support the binding to the europium cation. However, this region of the IR spectrum is complicated and does not allow the unequivocal identification of the coordination mode to the metal.

The ³¹P NMR spectrum of complex 2 consists of three broad signals with the same integral: a broad singlet for P_A (δ_P +3.42 ppm, $W_{1/2}$ 21 Hz) that resolves into a broad pseudo triplet $({}^{3}J_{PP} \approx 7.0 \text{ Hz}, \text{ Fig. S3}^{\dagger})$ upon resolution enhancement processing, a broad doublet for P_B (δ_P –35.31 ppm, ³J_{PP} 8.6 Hz) and a broad singlet for P_C (δ_P -86.4 ppm, $W_{1/2}$ 22 Hz) (see Scheme 1). These chemical shifts are significantly scattered in contrast to the ones found for its diamagnetic yttrium analogue (3), *i.e.* $\delta_{\rm P}$ 42.0, 40.3 and 34.3 ppm, respectively. In fact, the isotropic shifts, δ_{iso}^{30} which measure the interaction between the unpaired spin on the central metal ion and the nuclear spins of the ligand atoms are -38.6, -75.6 and -120.7 ppm. The presence of only three signals in the spectrum indicates that the two ligands in 2 are in rapid exchange. This means that, in solution, the flexibility of the ligands produces an average structure with a plane of symmetry that may include the chlorides anions bound to the europium metal.

In general, the values of the contact shifts detected by paramagnetic NMR depend on the extent of spin delocalization within the ligand framework and the character of the bonds between the metal ion and the ligating atoms. In paramagnetic complexes, two mechanisms (contact and pseudocontact interactions) are generally considered responsible for the NMR isotropic shift. With lanthanide ions, such as Eu^{3+} , the mechanism responsible for the isotropic shifts is generally attributed to the pseudocontact interaction.^{31,32} Although this interaction may induce significant line broadening of the signals due to rapid relaxation, 1D and 2D NMR spectra of **2** were acquired.

The ¹H NMR spectrum of **2** exhibited averaged signals for the two ligand molecules incorporated in the complex. The whole set of signals recorded in CD₃CN at 25 °C span from $\delta_{\rm H}$ –0.88 to 9.88 ppm, which suggests that they are located in an almost diamagnetic region. The broadest signals correspond to the diastereotopic Me groups of one NiPr₂ group characterized by two signals, which are significantly downfield shifted ($\delta_{\rm H}$ 1.88 and 4.00 ppm). The second set of signals, attributed to the other isopropyl group, were not located and this is probably a consequence of rapid transverse relaxation. The same behaviour was observed in the ¹³C NMR spectrum (Fig. S4†), with the NiPr₂ fragment appearing at $\delta_{\rm C}$ 23.9 and 26.9 ppm for the methyl carbons and $\delta_{\rm C}$ 52.7 ppm for the methine group.

Isotropic shifts were calculated for all the protons of the ligand backbone, which showed the protons that are most affected by the metal (Table S1[†]). The protons showing the largest paramagnetic shift are shown in red in Fig. 2. The protons which showed the large δ_{iso} values are tabulated in Fig. 2 and reflect the preferred conformation of the complex in solution.

The proton spectrum consists of 22 signals, which points to an effective C_{2v} symmetry of the complex in solution. This feature is confirmed by the ¹³C spectrum, which shows 30 NMR peaks for the 42 carbon nuclei of the ligand backbone. There are some chemical equivalences located at the two phenyl rings linked to phosphorus A and C, one of each showing equivalent *meta* and *ortho* carbons. Some of these are evident as indicated by the 2-D exchange spectroscopy (Fig. S5[†]).

The assignment of the ¹³C NMR spectrum was accomplished in combination with DEPT-135 and 2D HMQC and HMBC experiments (Fig. S6–S8⁺). The analysis of the ¹H, ³¹P gHMQC spectrum optimized for the observation of the phosphorus– proton long-range couplings allowed the assignment of the proton signals of the different P-phenyl rings (Fig. 3).

From the 2D map one can establish several observations that support our hypothesis: (a) the phosphorus signal located at 3.42 ppm (P_A) gives 11 correlations, therefore defining the protons located at rings I, II and II' (see the inset structure in Fig. 3); (b) the phosphorous signals, P_B and P_C , correlate with 7



Fig. 2 Selected ¹H isotropic shifts (δ_{iso}) for complex 2 at 300 MHz in CD₃CN at 25 °C.



Fig. 3 1 H, 31 P gHMQC spectrum (300 MHz) of complex 2 in CD₃CN at 25 °C.

and 6 protons, respectively, which is consistent with non-bridging phosphinic amide units; (c) the four correlations common to P_A and P_B belong to the protons of phenyl ring II, whereas those shown by both P_A and P_C , correspond to ring II'; (d) by default, the remaining correlations are assigned to protons of ring III.

Some complementary proton information was obtained through the COSY spectrum (Fig. 4).† The correlations observed allowed the complete assignment of the protons of ring I, the unravelling of the whole spin system of ring II, the identification of the methine signals of the NiPr₂ moieties and the assignment of the lowest frequency signal ($\delta_{\rm H}$ –0.88 ppm) to H-18.

Pulsed gradient spin-echo (PGSE) NMR diffusion methods are currently widely used,33 particularly when associated with ion pairing or molecular volumes.³⁴ PGSE measurements offer a novel view of the interaction between the metal salt derived cations and anions in solution.35 However, very little diffusion data have been described when f-block metals are involved³⁶ and this is most probably due to the difficulties associated to obtaining reliable diffusion constants, D, through NMR methods when rapid transverse relaxation is present. Furthermore, the measured solvent dependencies of D offer a hint as to what extent a solvent promotes ion pairing and/or aggregation, which could induce significant changes in reactivity. It has been recognized that a variety of organic and inorganic salts dissolved in chloroform often lead to more than 95% ion pairing; whereas the use of coordinating solvents, such as methanol or acetonitrile, afford much less or no ion pairing at all. As demonstrated in previous studies, it is assumed that up to 100% ion pairing occurs if the cation and the anion reveal approximately identical D-values, which affords hydrodynamic radii, $r_{\rm H}$, (via the Stokes-Einstein equation) that are substantially greater than those estimated by either crystallography or quantum chemical calculations.



Fig. 4 COSY-45 spectrum (300 MHz) of complex 2 in CD₃CN at 25 °C.

The calculated $r_{\rm H}$ values assume spherical shapes; hence, they do not represent the real shape of the molecules. Nevertheless their use is well established for comparisons, since they offer a rapid and easy method to recognize ion pairing and/or aggregation. To learn more about how lanthanide salts interact and to specifically determine whether there might be a preferred salt structure in the europium species described above, we measured the ¹H PGSE spectrum as a function of concentration. Diffusion data for ligand **1** and its Y(NO₃)₃ 1 : 2 (**3**) complex have been previously described²⁹ and have been included here for comparison. We decided to use acetonitrile solutions for these measurements, as it has been previously shown that, for some dicationic ruthenium species, a surprising large amount of ion pairing can be found, which in fact has considerable implications on the catalysis outcome.³⁷

From the measured *D* values for **1**, **2** and **3**, we estimated (*via* the Stokes–Einstein equation) the hydrodynamic radii, $r_{\rm H}$, to be 5.8, 8.2 and 8.8 Å, respectively (Table 1). The results obtained for **2** are in reasonable agreement with the values derived from the crystallographic data of **3** (8.2 Å), given that the solvent molecules and non-bonded nitrates included in the solid-state lattice cannot be excluded from the r_{X-ray} calculation. The small fluctuation between **2** and **3** can be rationalized by taking into account the possible contributions of the chloride ions. They can be completely separated by the solvent or at least partially paired with the cationic entity. Consequently, the exchange between the free and bound chlorides cannot be excluded, which could represent a source of uncertainty.

Interestingly, a 2-fold and 6-fold dilution of complex 2 (down to 30 and 10 mM, respectively) did not produce any significant change in the *D* value (or $r_{\rm H}$), which strongly suggests that complex 2 is not prone to dissociation in acetonitrile over relatively short periods of time.

When ligand 1 and EuCl₃ in a ratio of 1:1 were allowed to react at room temperature over long reaction times an interesting behaviour was observed. After 8 h of reaction, a new species began to appear (*ca.* 6%) as evidenced by the ³¹P NMR spectrum (Fig. 5). After 36 h, two clear sets of signals were identified and assigned to the already known complex 2 (δ_P 3.42, -35.31

Table 1 *D* and $r_{\rm H}$ values for ligand 1 and the europium (2) and yttrium (3) complexes at ambient temperature in an acetonitrile solution

	Conc (mM)	[M]	$D^a \times 10^{10} \text{ m}^2 \text{ s}^{-1}$	$r_{\rm H}({\rm \AA})^b$	$r_{\text{X-ray}}$ (Å)
2	60	EuCl ₃	7.287	8.2	
2	30	EuCl ₃	7.237	8.2	
2	10	EuCl ₃	7.222	8.2	
4	10	EuCl ₃	8.633	6.9	6.7
1^e	Sat		10.138	5.8	5.9
3^e	60	$Y(NO_3)_3$	6.636	8.8	8.2
CH ₃ CN		/-	34.210^{d}	1.7	

^{*a*} The experimental error in the *D* values is $\pm 2\%$. ^{*b*} The viscosity, η , used in the Stokes–Einstein equation is 0.363×10^{-3} kg m⁻¹ s⁻¹. The value of η was taken from www.knovel.com. ^{*c*} The value was deduced from the X-ray structure by considering the volume of the crystallographic cell divided by *Z*. Note that this is only an estimate since both molecular structures contain several solvent molecules in the crystal lattice (see ref. 29). ^{*d*} The average value of the same signal in the three different samples is given based on **2**. ^{*e*} Data taken from ref. 29.



Fig. 5 ³¹P NMR spectrum (121 MHz) of complex **2** in acetonitrile at 25 °C after 48 h. General conditions: 80 scans accumulated.

and -86.4 ppm) and a new species 4 (δ_P 55.76, -17.46 and -43.13 ppm).

³¹P NMR monitoring of this process showed that the group of signals attributed to complex **4** increased with time, which also produced the progressive diminution of the relative concentration of complex **2** (Fig. 5). Similar behaviour has already been observed for the complexes formed when **1** and $Y(NO_3)_3$ react under different stoichiometries²⁹ and in dota³⁸ and dota-like³⁹ macrocyclic ligands, which show two consecutive steps: (1) the fast formation of a di- or, in some cases, a mono-protonated intermediate, which (2) converts to the final 1 : 1 complex in a slow rate-determining step. The thermodynamic equilibrium was reached after *ca*. 120 h with a ratio between **2** and **4** of 0.2 : 1.

Crystals of 4 could be grown by concentrating this mixture at -30 °C for several hours. The solid-state structural characterization of the new species was achieved by single crystal X-ray diffraction, IR, combustion analysis and MS-TOF and all of them provided satisfactory results. The ESI-TOF spectra evidenced the 1:1 (metal:ligand) structure for complex 4 due to the observation of the [M-Cl] peak at 947.1 together with its specific isotopic distribution profile. The Eu-based cluster is identified by the isotope pattern arising from ¹⁵¹Eu/¹⁵³Eu as indicated by the simulated distribution (Fig. S1⁺). The IR spectrum of complex 4 (as a KBr disk) displays bands in the range of 1100-1203 cm⁻¹, which are again assigned to the P=O stretching vibrations (Fig. S2[†]). Interestingly, the strongest band in this region shifted 15 cm^{-1} to a higher frequency with respect to the corresponding bands in the bicapped complex 2, which supports a weaker binding to the europium cation.

The ¹H NMR spectrum of **4** showed 20 resonances that are significantly broader than those of **2**, which is indirect evidence of a faster paramagnetic relaxation. As for complex **2**, the *N*-isopropyl groups afforded two sets of signals: $\delta_{\rm H}$ 2.02 and 2.65 ppm for the methyls and $\delta_{\rm H}$ 3.25 ppm for the four methines. The analysis of the COSY spectrum allowed the assignment of most of the proton resonances (Fig. 6).

The monocapped complex (4) showed a similar behaviour in terms of its isotropic shifts as the bicapped analogue (2), although several resonances couldn't be assigned due to issues



Fig. 6 COSY-45 spectrum (300 MHz) of complex 4 in CD₃CN at 25 °C.



Fig. 7 Selected ¹H isotropic shifts (δ_{iso}) for complex 4 at 300 MHz in CD₃CN at 25 °C.

with overlap (Table S2†). As in complex **2**, signals H-2, H-7, H-18 and H-19 showed the largest shifts compared to the yttrium complex **5** (chosen as a diamagnetic reference) and demonstrate how these rings are twisted in solution towards the europium metal. It is interesting to note how the protons showing the higher isotropic shifts ($\delta_{iso} > 2$ ppm) are all involved in the metallacycle constructed through P_A and P_B (shown in bold in Fig. 7). This ring is the most puckered of the two existing systems, as will be shown in the solid-state discussion.

Unfortunately, ¹³C NMR and 2D heteronuclear correlations could not be measured. This is probably due to the very short relaxation times, which prevented the observation of any signal.

The X-ray structure was refined in the triclinic $P\overline{1}$ space group and showed a 1 : 1 stoichiometry and the relative stereochemistry of the chiral phosphorus atoms was found to be (R^*, S^*) (Fig. 8). Complex 4 crystallizes with two acetonitrile molecules in the crystal lattice and, interestingly, no water and/or acetonitrile molecules were found coordinated to the europium atom, which constructs a six-coordinate environment. Crystallographic data and structural refinement details for 4 are summarized in Table 2.

The Eu(III) ion is coordinated to three oxygen atoms from the tridentate ligand 1 and three chloride anions, in which the coordinated polyhedron of the europium atom exhibits a distorted



a)

Fig. 8 (a) ORTEP view of 4. Thermal ellipsoids are drawn at the 50% probability level. Crystallization acetonitrile molecules and hydrogen atoms have been omitted for clarity. (b) A view of the metal environment and coordination mode of ligand 1.

octahedral geometry in a facial configuration (Fig. 8b). The structural parameters can be compared with those of (Y(1)) $(NO_3)_3$ (5).²⁹ The phosphorus atom geometries are tetrahedral, with min/max bond angle variations of 105.2(2)-120.90(18) for P1, 105.21(18)-118.15(18) for P2 and 105.4(2)-115.42(19) for P3. The Eu–O(P) distances in 4 (2.326(3), 2.275(3) and 2.338(3) Å) are comparable to those observed in 5 (2.378(3), 2.250(3))and 2.233(3) Å) and are thus not affected by the trans effect caused by the chlorine atoms coordinated to the europium ion (Eu-Cl distances: 2.6262(11), 2.6493(11) and 2.6558(11) Å). As in 5, the tripodal ligand is coordinated by the three phosphinoyl moieties with Eu–O–P bond angles of 136.38(17)°, 163.40(18)° and 157.65(19)° for P1, P2 and P3, respectively. As expected, metal coordination is accompanied by an appreciable increase of the P=O bond length (1.499(3), 1.492(3) and 1.507(3) Å for P1, P2 and P3, respectively) compared with the mean value of 1.482 Å reported for non-coordinated phosphinic amide analogues.⁴⁰ It should be noted that the EuO₃Cl₃ coordination sphere observed in **4** is infrequently found in Eu³⁺ complexes,⁴¹ where higher coordination numbers are usually preferred.

The *facial* configuration of the ligand implies the existence of two seven-membered metallacycles formed by the binding of the P=O groups to the Eu(III) ion. Inspection of the crystal structure data revealed that both metallacycles acquire an almost perpendicular disposition imposed by the tetrahedral configuration of P1 and the existing metal bite of the trident with a dihedral angle of 88.66°. In addition, as was already observed in its yttrium analogue **5**, it is worth noting that complex **4** has a parallel

 Table 2
 Crystallographic data and structural refinement details for 4

Compound	4
Chemical formula	C46H57Cl3EuN4O3P3
$M(\text{gmol}^{-1})$	1065.18
$T(\mathbf{K})$	103
λ (Å)	0.71073
Cryst. syst.	Triclinic
Space group	$P\overline{1}$
a(Å)	10.8547(8)
$b(\mathbf{A})$	10.9159(8)
$c(\dot{A})$	23.1074(16)
α (°)	83.8250(10)
$\beta(\circ)$	86.7060(10)
γ (°)	63.3850(10)
$V(Å^3)$	2433.5(3)
Z	2
$\rho (g \text{ cm}^{-3})$	1.454
$\mu (\text{mm}^{-1})$	1.595
Unique reflections	12 499
R(int)	0.0250
GOF on F^2	1.048
$R_1 \left[I > 2\sigma(I) \right]$	0.039
$wR_2 [I > 2\sigma(l)]$	0.093

disposition with regards to the phenyl ring bound to P3 and the *ortho* substituted ring connected to P1 and P2 (with a distance between the centroids of 3.371 Å). The mean least-squares planes defined by these aromatic rings have a dihedral angle of intersect at 4.52° . This significant alignment is also obvious in **5** (Fig. S9†) and agrees with a puckered metallacycle established through P1 and P2 with a P1–C2E–C1E–P2 angle of $25.7(6)^{\circ}$ compared to the second metallacycle, which has a bond angle of $0.6(6)^{\circ}$. Complex **4** shows an arrangement of the tridentate ligand around the metal similar to **5**, with bond angles in the range of $73.66-81.04^{\circ}$ for **4** and $76.08-80.81^{\circ}$ for **5**, and indicates that the presence of chlorides or nitrate anions in the structure does not modify significantly the geometry of the complex.

Returning to the diffusion discussion, the hydrodynamic radius estimated for 4 (6.9 Å, Table 1), fits reasonably well with the radius calculated from the solid-state structure (r_{X-ray} 6.7 Å) and provides strong evidence that the solid-state structure is retained in solution even in the presence of coordinating acetonitrile and/or water molecules.

The next section is divided into two parts. The solution luminescent study is discussed first followed by the implementation of **2** in solid phase membranes.

Solution luminescence

Luminescence properties. The formation of a luminescent complex between the Eu(III) ion and ligand **1** was clearly observed. Fig. 9a shows the excitation and emission spectra of the formed complex together with the almost nonexistent excitation and emission bands for ligand **1** (grey spectrum in Fig. 9a). The maximum excitation wavelength observed was 286 nm. The observed emission wavelengths were 594, 618, 660 and 704 nm, which correspond to the characteristic europium(III) transitions.¹⁸ The emission wavelength corresponding to the hypersensitive transition produced the highest relative



Fig. 9 Luminescence characterization of 2 in solution; (a) luminescence spectra of 1, 2 and the Eu(III) salt and (b) the luminescence decay in protonated (black line) and deuterated (grey line) solvents.

luminescence intensity at 618 nm. An important characteristic of the luminescent complex is the capability of light absorption, which is described by the molar extinction coefficient (ε). A plot of the absorbance *vs.* the concentration of complex **2** showed a linear behaviour in the range of the concentrations studied, characterized by a molar extinction coefficient of 1081 mol⁻¹ L cm⁻¹ at 286 nm.

The stoichiometry of the complex formed between europium(III) and ligand **1** was studied *via* the method of Joe and Jones, ⁴² which shows a clear 1:2 stoichiometry complex, as indicated by NMR spectroscopy. It is important to mention that this study was performed immediately after mixing ligand **1** and EuCl₃·6H₂O, so that a kinetic situation was always reached (Fig. S10†). Together with the metal:ligand ratio, another critical parameter for the appropriate characterization of any luminescent complex is the formation constant (β_{mlh}). Complex formation with organic ligands competes with hydrolysis and the stability of Ln(III) complexes is typically evaluated in terms of the equilibrium constant established according to eqn (1) and (2):⁴³

$$m\mathbf{M} + l\mathbf{L} + h\mathbf{H} \leftrightarrow \mathbf{M}_m\mathbf{L}_l\mathbf{H}_h$$
 (1)

$$\beta_{mlh} = [\mathbf{M}_m \mathbf{L}_l \mathbf{H}_h] / [\mathbf{M}]^m [\mathbf{L}]^l [\mathbf{H}]^h \tag{2}$$

The formation constant for complex **2** was calculated following the reported methods,⁴² which established a $\log\beta_{120}$ value of 10.44 (25° C, pH 7.0, 75% EtOH (v/v) and 30 mmol L⁻¹ NaCl) and is comparable to the other formation constant reported for europium complexes in solution.^{7d} However, complex **2** shows a pEu of 6.1, which is lower than other europium analogues.⁴⁴

The luminescence quantum yield of complex 2 was determined by the relative comparison procedure using D-tryptophan as a standard.⁴⁵ The estimated relative luminescence quantum yield of complex 2 was $\Phi = 8\%$. The emission quantum yields of related phosphorous-based tridentate structures are in the range of 60-65% when bearing LVF (low vibrational frequency) structures.⁴⁶ For europium complexes bearing no LVF ligands, quantum yields of 2–12% are usually obtained.^{36b,47} The Φ results from a combination of energy transfers from the ligand chromophore and some non-radiative deactivation pathways (possibly back energy transfer from the metal to the chromophore) combined with some solvent oscillators from the inner coordination sphere. Fig. 9b shows the variation of the relative luminescence intensity versus time and this has been used to determine the luminescence lifetime (τ) in both protonated and deuterated solvents. In each case, the decay profile was analyzed as a single exponential component, indicative of a single emissive species with $\tau_{\rm H}$ 1815 and $\tau_{\rm D}$ 2385 µs. The measured lifetimes can be utilised to deduce the inner-sphere coordination environment in terms of the degree of lanthanide hydration, q^{48} This lifetime measurement indicates that the Eu(III) complex, 2, does not contain inner-sphere water molecules (q = 0.1, uncertainty ± 0.2), indicating that the coordination of two tridentate ligands and chlorides is enough to saturate the europium inner sphere.

In order to corroborate the lack of water molecules bound to the metal, TGA studies were carried out on the two europium complexes (Fig. S11†). The thermal decomposition of both complexes occurs in a multi-step process. The decomposition of complexes 2 and 4 proceeds with an endothermic peak in the temperature range of 40–110 °C, corresponding to the lattice solvent molecules. In the temperature range where the loss of coordinated water is expected to occur (*ca.* 115–200 °C), both complexes are stable. Above *ca.* 190 °C for 2 and *ca.* 230 °C for 4, removal of the chloride atoms from the chelates and decomposition of the tridentate ligand species become evident.

Effect of the media. It is known that the media can affect the luminescence intensities of luminophores.^{45b} In order to obtain a deeper understanding, the effect of the addition of organic solvents, such as ethanol, the changes in the ionic strength and the changes in pH the were evaluated. The absence of EtOH induced the precipitation of the ligand (1) in an aqueous solution where the tested percentages were 25, 50, 75 and 100% (v/v) (Fig. S12†). These results indicate increments in the luminescence intensity with higher loadings of ethanol. However, since a minimum amount of water is needed in order to detect Eu(m) ions in water samples, the selected ethanol percentage was 75% (v/v).

The effect of ionic strength (*I*) was studied by adding different concentrations of NaCl (0, 65, 125, 185 and 245 mmol L^{-1}) (Fig. S13†). Overall, the ionic strength did not significantly affect the luminescent activity and a random NaCl concentration of 30 mmol L^{-1} was selected.

The influence of pH on the luminescence intensity was studied over a range of 3.0-11.0 (Fig. S14[†]). The relative luminescence intensity remained approximately constant from pH 5.0 to 9.0, beyond which a drastic drop was observed. This drift at higher pH values could be caused by the formation of Eu(OH)₃,

which is not soluble under these conditions. However, it is noteworthy that a significant increase of the relative luminescence intensity was observed at pH values below 5.0. Furthermore, the excitation and emission wavelengths at pH 5.0 were 286 nm and 618 nm, respectively, whereas at pH 3.0 they were 274 nm and 614 nm, respectively. This hypsochromic shift could be ascribed to the formation of the corresponding diphosphoric acid, PhPO(C₆H₄POPhOH)₂ (**6**), which arises from the hydrolysis of the P–N bond, and is currently under study.⁴⁹ For this reason the working pH range was considered to be 5.0–9.0.

Luminescence of the sensing film

Luminescence characterization. It was observed that the europium (III) ion showed a very strong luminescence intensity for the PVC membrane based on ligand 1 among different lanthanides tested. This is most probably due to the selective interaction of the ligand and the europium(III) ion and the fast exchange kinetics of the resulting complex. The excitation and emission spectra of the optimized membrane after exposure to europium(III) are shown in Fig. 10. As can be seen, the two observed emission peaks correspond to the characteristic line-type bands of the europium(III) ion with regards to the buffer emission signal. Only, the most intense line-type bands were observed and the emission maximum (616 nm) was almost unchanged compared to the one observed in solution (618 nm).

In addition, a wide excitation band was observed with regards to the buffer excitation signal. This band could be assigned to a combination of $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ transitions centred on the diphenylphosphinic amide and diphenylphosphine oxide units of **1**. The excitation maximum was shifted by 57 nm (229.06 nm) with respect to that of the excitation maximum in solution (286.00 nm). This modification is probably due to the different environments of complex **2** in an aqueous solution and the liquid membrane, so other components of the membrane may affect the observed luminescence (see below). Regarding the temporal stability of the acquired signal, preliminary studies demonstrated that 10 min were necessary to obtain the maximum luminescence signal, as is usual with metal-based sensors.



Fig. 10 Luminescent spectral characterization of the optimized membrane sensor in the absence (grey line) and presence of europium(III) (black line).

Optimization of the sensing films. The effect of the plasticizer nature on the luminescent intensity of the membrane sensor was investigated. In its simplest form, it is a high-boiling organic solvent which, when added to a rigid substance, imparts flexibility. Different plasticizers (dioctyl adipate, DOA; dioctyl sebacate, DOS; dioctyl phthalate, DOP and 2-nitrophenyl octyl ether, NPOE) were evaluated and their effect analyzed (Fig. S15[†]). It was observed that the ester plasticizers, DOA and DOS, produced higher luminescence intensities compared to DOP and almost no signal was obtained with NPOE. Sebacate DOS (C10) derivatives usually possess better features, such as volatility and low temperature flexibility, than adipate DOA (C6) and, therefore, DOS was selected as the optimum plasticizer for the development of our sensing films. Five different percentages of DOS were tested; i.e., 0, 20, 40, 65, and 90% (Fig. S16⁺). It was observed that a percentage of 90% of plasticizer produced films with relatively poor mechanical properties and the resulting films were very difficult to handle. 65% provided the best reproducibility of results and this percentage was chosen for the further development of the final sensing membrane. The influence of ligand 1 and the percentage of the ionic additive on the membrane luminescence signal were investigated collectively by varying the concentrations of both ligand 1 and potassium tetrakis(4-chlorophenyl) borate (KTpClPB) (both up to 3.5% (w/w)). KTpClPB is an alkaline lipophilic salt, which is usually incorporated into membranes for electroneutrality reasons. The different compositions tested in this study and their luminescence intensities are shown in Table 3.

A total of 12 membranes were evaluated according to their chemical composition (Fig. S17†). No significant differences between them were observed and it was therefore deduced that the concentration of ligand 1 does not influence the membrane luminescence and that the addition of an ionic additive is not necessary since it does not produce a considerable enhancement of the luminescence. The addition of KTpCIPB to the membrane composition was consequently discarded, which reduces the cost of the membrane sensor fabrication process. In agreement with the X-ray studies, it was assumed that the contact ion pair, EuCl₃, diffuses into the membrane, which agrees with the electroneutrality principle which governs the PIMs.

The pH dependence of the sensing films over a range of 1.0-11.0 at 1.0×10^{-6} mol L⁻¹ of Eu(III) was evaluated (Fig. S18[†]). Its dependence followed a distorted Gaussian profile over the range of pH values assayed. A maximum luminescence intensity was obtained at pH 5.0, which perfectly matches the apparent pH measured in solution. Fast exchange kinetics are assumed to be produced inside the membrane at this pH. At pH > 5.0, a significant drift was observed, which could be ascribed to the formation of $Eu(OH)_3$ as mentioned before. At pH < 5.0, a gradual decrease on the luminescence intensity was observed, which was attributed to the gradual decomposition of complex 2. A pH value of 5.0 was considered to be the optimum value for analyzing europium(III) ions in water samples, so the requirement of a buffer solution was mandatory in order to obtain satisfactory results. Different buffer solutions, such as citrate, acetate, hydrogen phthalate and succinate, whose working pH range covered the optimum pH of 5.0, were analyzed. The buffer solutions were adjusted to pH 5.0 with concentrated HCl/NaOH.

 Table 3
 Percentages of ligand 1 and the ionic additive used in the composition of the membranes

	-		Membrane composition (%, w/w)					
Membrane No.	PVC ^a	Ligand	KTpClPB ^b	DOS ^c				
1	31.4	3.5	0.0	65.1				
2	30.2	3.5	1.2	65.1				
3	29.7	3.5	1.8	65.1				
4	27.9	3.5	3.5	65.1				
5	31.6	2.5	0.8	65.1				
6	31.2	2.5	1.3	65.1				
7	29.9	2.5	2.5	65.1				
8	32.7	1.5	0.8	65.1				
9	32.4	1.5	1.0	65.1				
10	31.9	1.5	1.5	65.1				
11	32.4	2.5	0.0	65.1				
12	33.4	1.5	0.0	65.1				

^a Polyvinylchloride.
 ^b Potassium tetrakis(4-chlorophenyl) borate.
 ^c Bis(2-ethylhexyl) sebacate.



Fig. 11 Luminescence signals of the optimized sensing membrane with different buffer solutions. $[Eu^{3+}] = 1.0 \times 10^{-6}$ M; pH 5.0; buffer concentration = 0.1 M.

The luminescence intensities for these different buffer solutions are depicted in Fig. 11.

A luminescence signal was not observed in the membranes when sodium citrate was used as a buffer. It is well known that citrate acts as a strong coordinating agent for lanthanides,⁵⁰ thereby forming stable complexes with europium(III) ions in solution and inhibiting their diffusion into the membrane.⁵¹ Acetate and succinate slightly reduced the luminescence intensity, whereas the hydrogen phthalate buffer solution provided the maximum enhancement. A reasonable explanation for this behaviour is that the acetate and succinate anions partially complex europium, while the hydrogen phthalate does not bind europium at all, which allowed all of these ions to diffuse inside the membrane and consequently provided the most intense signal. Therefore, the hydrogen phthalate solution at pH 5.0 was chosen to be the buffer solution of choice to prepare the europium(III) water samples for subsequent analysis.

The influence of the buffer concentration (ionic strength) on the sensing film was also tested at 0, 25, 50, 75 and 100 mmol L^{-1} (Fig. S19†). The luminescence signal was not affected by



Fig. 12 Luminescence responses of the optimized sensing membrane as a function of the lanthanide(III) ion.

the ionic strength of these solutions but they did result in larger errors in the measurements, so a minimum hydrogen phthalate buffer concentration of 25 mmol L^{-1} was selected as the optimum.

The selectivity of the sensing film. The selective behavior is clearly one of the most important parameters of a sensing film. Four lanthanide(III) ions (lanthanum, samarium, terbium and ytterbium) were selected as interfering ions in order to check the selectivity of the sensing membrane. Fig. 12 shows the results of this study. Lanthanum, samarium and ytterbium(III) ions had lower signals than the terbium(III) ion, which provided a negligible luminescence signal with regards to the europium(III) ion signal. Therefore, it can be concluded that significant lanthanide interferences were not observed and the luminescent signals were additive for the lanthanide(III) ions.

The luminescence intensities of the sensing membranes at various concentrations of europium(III) in solution are depicted in the ESI (Fig. S20†). The results indicated a linear working concentration range from 1.6×10^{-7} to 5.0×10^{-6} mol L⁻¹, a detection limit (DL) of 4.8×10^{-8} mol L⁻¹ and a quantification limit (QL) of 1.6×10^{-7} mol L⁻¹. The sensitivity of the proposed sensing films is the highest reported to date. To the best of our knowledge, the lowest detection limit published in the literature^{7d} is one order of magnitude higher than the one reported here.

Experimental

Instrumentation and apparatus

Aminco Bowman Series 2 Luminescence Spectrometer (Sim Aminco, Madison, USA) interfaced with a computer was used to perform the luminescence spectroscopy and the relative luminescence intensity measurements in solution were performed 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, Mulgrave, Australia) equipped with a front surface accessory was used to measure the luminescence spectra and relative luminescence intensities of the sensing films.

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

Thermogravimetric measurements were carried out on a TGA Q50 (TA Instruments). The experiments were performed in the temperature range of 20 to 350 °C at heating rates of 10 °C min⁻¹ on each sample. The average sample amount was 7 mg and the nitrogen flow rate was 50 mL min⁻¹.

¹H (300.13 MHz), ¹³C (75.47 MHz) and ³¹P (121.47 MHz) NMR spectra were recorded in CDCl₃ and CD₃CN, unless otherwise stated, on a Bruker Avance DPX300 equipped with a ONP ¹H/¹³C/¹⁹F/³¹P probe. Chemical shifts are reported in ppm with respect to tetramethylsilane for ¹H and ¹³C using the solvent signal as a reference and 85% H₃PO₄ was used as a reference for ³¹P. Standard Bruker software was used for the acquisition and processing. Elemental analyses were carried out with an Elementar Vario Micro cube system. Infrared spectra were recorded on a Mattson-Genesis II FTIR system. High resolution mass spectra were recorded on an Agilent Technologies LC/MSD TOF and HP 1100 MSD equipment with electrospray ionization (ESI). Melting points were recorded on a Büchi B-540 capillary melting point apparatus and were uncorrected. Diffusion measurements were performed using the Stimulated Echo Pulse Sequence⁵² on a Bruker Avance 500 without spinning. The shape of the gradient pulse was rectangular and its strength varied automatically over the course of the experiments. The calibration of the gradients was carried out via a diffusion measurement of HDO in D₂O, which afforded a slope of 2.022×10^{-4} . To check the reproducibility, three different measurements with different diffusion parameters (δ and/or Δ) were always carried out. The gradient strength was increased steps of 8% from 10% to 98%.

Crystal structure determination: single crystals of 4, suitable for XRD, were obtained by crystallization from a concentrated acetonitrile solution of 4 at -30 °C. The single crystals were covered with perfluoropolyalkyl ether oil and then mounted on top of a glass fibre. Subsequently, they were placed in a cold nitrogen stream in a low-temperature device to achieve solidification of the oil. Data collection for the X-ray structure determinations was performed with a Bruker Smart 1000 CCD diffractometer with a MoK α ($\lambda = 0.71073$ Å) radiation source and a low temperature device. All calculations were performed with SHELXTL (v6.12) and SHELXL-9753,54 and the data were corrected for absorption using SADABS.⁵⁵ The structures were solved by direct methods⁵⁶ and refined with full-matrix least-squares calculations on $F^{2,57}$ All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. The crystallographic data for the structure reported in this paper has been deposited in the Cambridge Crystallographic Data Centre (CCDC 855721⁺).

The optimum membrane solution was prepared by thoroughly mixing in a closed vial 33.4% (w/w) of powdered PVC, 65.1% (w/w) of bis(2-ethylhexyl) sebacate and 1.5% (w/w) of ligand 1 (the sensitizing agent) to obtain a total mass of 200 mg in 3.0 mL of THF. The obtained mixture was stirred continuously with the aforementioned mixer until its complete dissolution. A volume of 300 μ L of the resulting solution was deposited on the glassy material and spin-coated at 700 rpm at room temperature until complete solvent evaporation. The transparent, ultrathin and homogeneous film obtained was referred to as a polymeric inclusion membrane (PIM). Once the polymeric membrane was prepared, it was stored in a closed contained at room temperature in the absence of light until its use.

The membranes were immersed in 20 mL of the blank solution over 10 min, dried with a nitrogen flow and measured. Subsequently, they were immersed in 20 mL of the standard solution of Eu(III) during 10 min, dried and measured. When not in use, the membranes were kept in a closed container at room temperature. Finally, the membranes already measured were eliminated.

Luminescence characterization

Published on 23 March 2012 on http://pubs.rsc.org | doi:10.1039/C2DT30257H

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The luminescent measurements of complex $[Eu(1)_2]Cl_3$ (2) in solution were achieved at $\lambda_{exc/em} = 286/618$ nm, which correspond to the maxima excitation and emission wavelengths of the formed complex 2. A delay of the measurement time was selected to avoid a fluorescence background. Table 4 lists the optimized instrumental variables for the measurements carried out in both solution and in the membrane.

The complex 2 luminescence intensity in solution was considered to be the difference between the luminescence intensity before and after the addition of the europium(III) solution. The variation of the relative luminescence intensity of complex 2 *versus* time is depicted in the ESI (Fig. S21†). It shows that the formation of complex 2 was instantaneous and the gradual decrease in intensity was due to its photochemical degradation. Thus, all the measurements were developed just after their preparation. The molar extinction coefficient was calculated by an external calibration of complex 2 in solution mixing the europium(III) salt, EuCl₃·6H₂O, and ligand 1 in solution in adequate proportions. The reaction medium consisted of a mixture of ethanol and water (1:1). The relative luminescence quantum yield (Φ) of complex 2 was determined by the relative

Table 4The optimized instrumental variables used for themeasurements in solution and in the membrane

Variable	Optimum value (solution)	Optimum value (membrane)
$\lambda_{\rm exc/em}$ (nm)	286.00/618.00	229.06/616.02
Slit width exc/em (nm)	8/8	5/5
Detector voltage (V)	800	650
Total decay time (ms)		20
Delay time (us)	120	120
Gate time (ms)	0.150	5
Number of flashes	—	1

comparison procedure, using D-tryptophan in water as the standard.⁴⁵ Both the solution of D-tryptophan in water and the solution of complex 2 in the ethanol–water mixture (1:1) were measured under the same instrumental conditions at 286 nm.

The luminescence measurements of the membranes were carried out at $\lambda_{\text{exc/em}} = 229/616$ nm, which correspond to the maxima of excitation and emission wavelengths of complex **2** formed in the solid phase (Table 4). The membrane was placed on the front surface accessory located in the sample compartment of the luminescence spectrophotometer. The membrane response was considered as the difference between the luminescence intensities of the membrane immersed in the standard and blank solutions.⁵⁸ In both cases, all the experiments were carried out in triplicate to calculate the error. The hydration number, q, was obtained using eqn (3), where τ_{H} and τ_{D} , respectively, refer to the measured luminescence decay lifetime (in milliseconds) in protonated or deuterated solvents, using A = 1.2 and B = 0.25 (estimated error ± 0.2 water molecules).⁴⁸

$$q = A (1/\tau_{\rm H} - 1/\tau_{\rm D} - B)$$
(3)

Synthesis of complex 2

To a suspension of **1** (30 mg, 0.042 mmol) in 0.75 mL MeCN, $Eu(Cl)_3 \cdot 6H_2O$ (7.6 mg, 0.021 mmol) was added. After 15 min of stirring the reaction was complete. The slow evaporation of the corresponding solution provided 29 mg (83% yield) of the desired complex with more than 97% purity.

(2): Mp 236–238 °C. IR (KBr disk): v_{max}/cm^{-1} 3054 (w), 2973 (m), 1630 (m), 1437 (m), 1167 (s, st P=O), 1057 (w), 987 (m), 746 (s), 696 (s), 570 (s), 543 (s). ¹H NMR: -0.88 (H-18), 1.88 (CH(CH₃)₂), 3.93 (H-16), 4.00 (CH(CH₃)₂), 4.42 (H-2), 4.58 (H-2'), 4.85 (H-19), 5.45 (H-15), 5.89 (H-14), 5.96 (H-20,19',18'), 6.14 (d, ${}^{3}J_{\rm HH}$ 7.1 Hz, H-10), 6.23 (d, ${}^{3}J_{\rm HH}$ 8.2 Hz, H-13), 6.28 (H-3), 6.42 (CH(CH₃)₂), 6.79 (H-3'), 7.16 (t, ${}^{3}J_{\text{HH}}$ 7.3 Hz, H-4), 7.93 (t, ${}^{3}J_{\text{HH}}$ 7.3 Hz, H-9), 8.22 (H-23), 8.50 (t, ${}^{3}J_{\rm HH}$ 7.2 Hz, H-24), 8.66 (t, ${}^{3}J_{\rm HH}$ 7.3 Hz, H-8), 8.77 (H-22), 9.88 (d, ${}^{3}J_{\rm HH}$ 6.6 Hz, H-7). 13 C NMR: 23.92 (d, ${}^{3}J_{\rm PC}$ 4.6 Hz, CH(CH₃)₂), 26.96 (s, CH(CH₃)₂), 52.66 (d, ²J_{PC} 6.2 Hz, CH(CH₃)₂), 103.92 (d, ¹J_{PC} 115.3 Hz, C-1), 121.80 (d, ¹J_{PC} 135.2 Hz, C-21), 123.61 (d, ¹J_{PC} 116.54 Hz, C-17), 125.69 (d, ${}^{3}J_{PC}$ 14.1 Hz, C-19), 126.00 (d, ${}^{2}J_{PC}$ 11.6 Hz, C-2'), 126.45 (d, ³J_{PC} 12.4 Hz, C-3'), 128.66 (d, ³J_{PC} 11.2 Hz, C-3), 129.62 (d, $^{2}J_{PC}$ 14.1 Hz, C-18'), 130.02 (d, $^{3}J_{PC}$ 13.7 Hz, C-23), 130.10 (C-18), 130.35 (dd, $^{3}J_{PC}$ 12.8 Hz, $^{4}J_{PC}$ 1.6 Hz, C-15), 130.93 (d, ${}^{4}J_{PC}$ 2.5 Hz, C-20), 131.12 (d, ${}^{3}J_{PC}$ 14.5 Hz, ${}^{4}J_{PC}$ 2.5 Hz, C-14), 131.81 (C-2), 132.58 (d, ${}^{4}J_{PC}$ 2.5 Hz, C-4), 133.52 (d, ${}^{3}J_{PC}$ 13.1 Hz, ${}^{4}J_{PC}$ 2.3 Hz, C-9), 133.95 (d, ${}^{4}J_{PC}$ 2.5 Hz, C-24), 134.37 (d, ${}^{3}J_{PC}$ 11.8 Hz, ${}^{4}J_{PC}$ 2.3 Hz, C-8), 135.18 (d, ${}^{2}J_{PC}$ 15.9 Hz, ³J_{PC} 10.5 Hz, C-16), 135.75 (d, ²J_{PC} 10.3 Hz, C-22), 136.80 (d, ${}^{2}J_{PC}$ 15.5 Hz, ${}^{3}J_{PC}$ 10.4 Hz, C-13), 137.25 (d, ${}^{2}J_{PC}$ 14.3 Hz, ³J_{PC} 11.7 Hz, C-10), 137.53 (dd, ²J_{PC} 7.8 Hz, C-12), 139.26 (dd, ${}^{2}J_{PC}$ 7.0 Hz, C-6), 138.92 (t, ${}^{2}J_{PC}$ 9.7 Hz, C-7), 103.92 (d, ${}^{1}J_{PC}$ 106.5 Hz, ${}^{2}J_{PC}$ 12.3 Hz, C-5). ${}^{31}P$ NMR: -35.3 (d, ${}^{3}J_{PP}$ 8.9 Hz, P–B), -86.1 (P–C), 3.4 (t, ${}^{3}J_{PP}$ 6.7 Hz, P–A). MS-ESI, m/z: 1671.4813 (M-Cl) (17.1%). Analysis: Calcd (%) for C₈₄H₁₀₂Cl₃EuN₄O₆P₆·(+5H₂O): C, 56.11; H, 6.28; N, 3.12. Found: C, 55.54; H, 6.26; N, 3.00.

Synthesis of complex 4

To a suspension of 1 (30 mg, 0.042 mmol) in 0.75 mL MeCN, EuCl₃· $6H_2O$ (15.2 mg, 0.042 mmol) was added. After 18 h of stirring, a white solid precipitate was obtained and was filtered and washed with diethyl ether providing 24 mg (75% yield) of complex 4 as an air stable solid of more than 97% purity. Crystals suitable for X-ray diffraction analysis were obtained from an acetonitrile solution of 4 following storage at -30 °C for three days.

(4): Mp 269–271 °C (dec.). IR (KBr disk): v_{max}/cm^{-1} 3054 (w), 2974 (w), 1631 (m), 1437 (m), 1186 (s, st P=O), 1058 (w), 987 (m), 746 (s), 696 (s), 572 (s), 542 (s). ¹H NMR: 2.02 (CH(CH₃)₂), 2.64 (CH(CH₃)₂), 3.25 (CH(CH₃)₂), 3.43 (H-24), 4.84 (H-2), 5.17 (H-19), 5.67 (H-18), 5.83 (H-25), 6.03 (H-13), 6.70 (H-3), 6.78 (H-10), 7.06 (H-14), 7.41 (H-15), 7.94 (H-16), 8.02 (H-23), 8.09 (t, ³J_{HH} 7.5 Hz, H-9), 8.95 (H-22), 9.24 (H-8), 12.34 (H-7). Signals H-4 and H-20 not located. ³¹P-NMR: -43.7 (P–B), -18.6 (P–C), 54.6 (P–A). MS-ESI, *m/z*: 947.1691 (M–Cl) (68%). Analysis: Calcd (%) for C₄₂H₅₁Cl₃EuN₂O₃P₃: C, 51.31; H, 5.23; N, 2.85. Found: C, 51.67; H, 5.48; N, 2.50.

Conclusions

A new tridentate bis(phosphinic amide)-phosphine oxide, PhPO- $(C_6H_4POPhN(CH(CH_3)_2)_2)_2$ (1) was characterized to evaluate its potential for the development of an Eu(III)-sensing films. The complexes $[Eu(1)_2]Cl_3$ (2) and $[Eu(1)]Cl_3$ (4) were isolated by mixing ligand 1 with Eu(Cl₃)·6H₂O in acetonitrile at room temperature in a ligand to metal molar ratio of 1:2 and 1:1, respectively. The 1:1 derivative is the product of thermodynamic control when a molar ratio of the ligand to the europium salt of 1:1 was used and large reaction times were employed. The new compounds were characterised in both the solid (IR, MS-TOF, elemental analysis, TGA and X-ray diffraction) and in solution (multinuclear magnetic resonance). In both europium complexes, the ligand acts as a tridentate chelate. TGA studies illustrate that neither 4 or 5 possess any coordinated water molecules directly bound to the lanthanide metal, confirming their luminescent lifetimes and X-ray structures. The investigation of the solution behaviour of the Eu(III) complexes through multidimensional NMR and PGSE diffusion measurements showed that the average structures are in agreement with the 1:1 and 1:2 stoichiometries and are retained in acetonitrile solutions.

The spectroscopic (a large Stokes shift, long luminescence lifetime and an emission spectrum with very narrow bands) and chemical (operation over a wide range of pH values and no influence of the ionic strength of the buffer) characteristics of luminescent complex **2** in solution were excellent indicators to encourage the immobilization of **1** in a solid support. The results presented here demonstrate that PVC : DOS : **1** luminescence sensing films may be developed for the determination of europium(III) ions in aqueous media. The nature and percentage of the plasticizer, as well as ligand **1** and the ionic additive concentrations were investigated to optimize the chemical composition of the sensing film. The optimum membrane composition was 33.4:65.1:1.5 (%, w/w) PVC : DOS : **1**. The response of the sensing film was strongly influenced by the working pH, so a previous pH adjustment was necessary for the analysis of

europium(III) water samples. A hydrogen phthalate buffer solution, whose concentration was 25 mmol L^{-1} , was used to obtain the maximum luminescence signal, while maintaining the optimum pH of 5.0. The sensing phase was highly selective for the detection of europium(III) ions. It showed a short response time (10 min) and a linear range from 1.6×10^{-7} to 5.0×10^{-6} mol L^{-1} with a detection limit of 4.8×10^{-8} mol L^{-1} .

An extension of the present chemistry to other rare-earth elements is currently being done and future work will focus on tuning the ligand properties in order to increase the luminescence efficiency and to develop improved devices for detecting several gases for pollution control and environmental monitoring.

Acknowledgements

This work was supported by the Consejería de Innovación, Ciencia y Empresa of la Junta de Andalucia (projects P07-FQM-2625 and 2738), the Ministerio de Ciencia e Innovación (MICINN) and Fondos FEDER (projects CTQ2008-117BQU and 1394BQU). We thank Dr R. Romero for helpful discussions and technical assistance with the ESI-TOF analysis.

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