A New Europium(III) PVC Membrane Potentiometric Sensor Based on 4-(2-Hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one

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A new europium ion-selective electrode based on 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (HMTDT) as membrane carrier was prepared. The electrode has a wide concentration range between 1.0×10^{-1} and 1.0×10^{-6} mol dm^{-3} with a near-Nernstian slope of 19.7 ± 0.4 mV per decade and a detection limit of 7.8×10^{-7} mol dm^{-3}. The potentiometric response is independent of the pH of the solution in the pH range 3.5–7.8. It has a relatively fast response time and can be used for at least 2 months without any considerable divergence in potentials. The proposed sensor had very good selectivities for a wide variety of metal ions. The practical utility of the electrodes has been demonstrated by their use as indicator electrodes in the potentiometric titration of Eu^{3+} ions with EDTA and for the determination of Eu^{3+} in different solutions.

Because of their special photogenic, magnetic, mechanical, and nuclear properties rare earth metals are very important in industry; they are used in production of glass and ceramic industry, metallurgy, electronics, and agriculture and natural sciences. Therefore, methods for sensitive accurate and rapid separation (cause of high similarity among lanthanides), purification and determination are of great of importance. Spectroscopic methods, such as flow injection chemiluminescence,[1] indirect bioluminescent,[2] luminescence spectrometry[3] have been employed. Simultaneous spectrofluorimetric determination using chemometric methods,[4] luminescence determination of microquantities after preconcentration on a polyurethane foam[5] and other methods have been used to sense Eu in conjunction with UV–vis and X-ray spectroscopy.[6–10] Also, electrochemical techniques, such as differential pulse polarography, potentiometry, ion-exchange voltammetry, square wave voltammetry, are used to determine different metals.[11–15] Another technique that is used is chemi-nucleic methods, e.g., neutron activation and γ-coincidence spectrometry.[16]

But all of these methods are expensive and need complicated equipment. Potentiometry using ion-selective electrodes is a fast, inexpensive, and simple method for determination of ions. There are many studies on determination of lanthanides by this method but there has been only one report so far on the determination of europium by an ion selective electrode with a narrow dynamic range (from 7.0×10^{-5} to 0.10 mol dm^{-3}) and high detection limit (5.0×10^{-5} mol dm^{-3}).[17] Therefore, we prepared another selective sensor for determining of Eu^{III}. In recent years, researchers have introduced several PVC-based sensors for lanthanide ions, such as La^{3+},[18–26] Ce^{3+},[27,28] Gd^{3+},[29–31] Yb^{3+},[32–34] Eu^{3+},[17] Tb^{3+},[35] Sm^{3+},[36–38] Dy^{3+},[39] Nd^{3+},[40] Ho^{3+},[41] and Pr^{3+}.[42]

We have recently reported a number of highly selective and sensitive PVC-membrane ion-selective electrodes for other ions.[43–52] The aim of this work is fabrication of a highly selective and sensitive europium(III) PVC membrane electrode based on 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (HMTDT) as an excellent ionophore for the selective and sensitive potentiometric determination of Eu^{III} ion over a wide concentration range (Fig. 1).

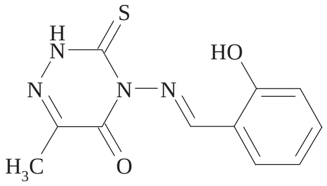

Fig. 1. Structure of HMTDT.

Experimental

Reagents. Reagent grade 2-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), benzyl acetate (BA), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Merck and Aldrich, used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification, except for vacuum drying over P_2O_5. Triply distilled, de-ionized water was used throughout.

Synthesis of Ionophore. 4-Amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (1.58 g, 10 mmol) was dissolved in 1-butanol (20 mL). Salicylaldehyde (1.5 g, excess) was added to the solution, and the mixture was refluxed for 4 h. After cooling, the precipitate that formed was filtered off and recrystallized from ethanol to afford 1.6 g of the desired product.[53] Yield: 69.8%; mp, 226 °C; ^{1}H NMR (d_6-DMSO): δ 13.69 (s, 2H, NH, OH), 8.8 (s, 1H, vinyl H), 8 (d, 1H, phenyl H), 7.7 (d, 1H, phenyl H), 7.3 (t, 1H, phenyl H), 2.1 (s, 3H, CH_3). IR, (KBr disc): 3250 (O–H st.),

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3150 (N–H st.), 3095 (vinyl H st.), 2980 (C–H st.), 1680 (carbonyl st.), 1620, 1595, 1560, 1521 (aromatic ring), 1275 (C–N st.), 1150, 750 cm^{-1}. Ms, *m*/*z*: 262 (M$^+$, 18), 261 (M − 1, 59), 259 (100), 238 (9), 157 (12), 143 (96), 118 (59), 102 (40), 101 (35), 91 (29), 69 (92), 45 (31), 43 (22), 41 (21), 28 (49), 18 (11).

Electrode Preparation. Membrane solutions were prepared by thoroughly dissolving HMTDT (4.0 mg), powdered PVC (30 mg), NPOE (64 mg), and TPB (2.0 mg) in fresh THF (5 mL). The resulting clear mixture was concentrated slowly until an oily mixture was obtained. A Pyrex tube (3–5 mm o.d. on top) was dipped into the mixture for about 5 s so that a transparent membrane of about 0.3 mm thickness was formed.[17] The tube was pulled out from the mixture and kept at room temperature for 12 h. The tube was then filled with a solution of $EuCl_3$ (1.0×10^{-3} mol dm^{-3}). The electrode was finally conditioned for 24 h by soaking in a Eu^{III} ion solution (1.0×10^{-2} mol dm^{-3}). A silver/silver chloride electrode was used as an internal reference electrode.

Potential Measurements. The EMF measurements with the polymeric membrane were carried out using the following cell assemblies:

$$\text{Ag/AgCl|internal solution, } 1.0 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{EuCl}_3\text{|} \\ \text{PVC membrane|test solution|Hg/Hg}_2\text{Cl}_2\text{, KCl (satd.)} \quad (1)$$

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. EMF observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye–Hückel procedure.[54]

Results and Discussion

Potential Response of the Electrode Based on HMTDT. The existence of four nitrogen donating atoms in the structure of HMTDT should increase both the stability and selectivity of its complexes with transition and heavy metal ions, especially lanthanide ions. To the best of our knowledge, there is no report on the stability of HMTDT complexes with different cations. Thus, the complexation of HMTDT with a number of common cations was conductometrically investigated in an acetonitrile solution at 25 ± 0.05 °C in order to detemine the stability and selectivity of the resulting complexes.[55,56] The molar conductance vs [HMTDT]/[M^{n+}] mole ratio plots showed the formation of 1:1 complexes between HMTDT and all cations investigated. The results showed the selective behavior of the ionophore toward Eu^{3+} and other metal ions are in the order of $Eu^{3+} \gg Tb^{3+} > Yb^{3+} > Ce^{3+} > Sm^{3+} > La^{3+} > Cr^{3+} \approx Fe^{3+} > Co^{2+} > Pb^{2+} > Cd^{2+} > Na^+$. Thus, HMTDT may be used as a suitable selective ionophore in the fabrication of an Eu^{3+} ion-selective membrane electrode.

In order to check the suitability of HMTDT as an ion carrier for different metal ions, it was used as a neutral carrier to prepare a number PVC membrane ion-selective electrodes under identical conditions for a large number of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. The potential responses of these electrodes, prepared under the same experimental conditions (except for 24 h conditioning in a 1.0×10^{-3} mol dm^{-3} of the corresponding cations), are given in Figs. 2a and 2b. From Figs. 2a and 2b, except for Eu^{3+} ion which has a sensitive response, the sensitivities of the other metal ions, based on the emf vs pM^{n+} plots are much lower than expected (59, 29, and 19 mV per decade for mono, di, and trivalent cations, respectively).

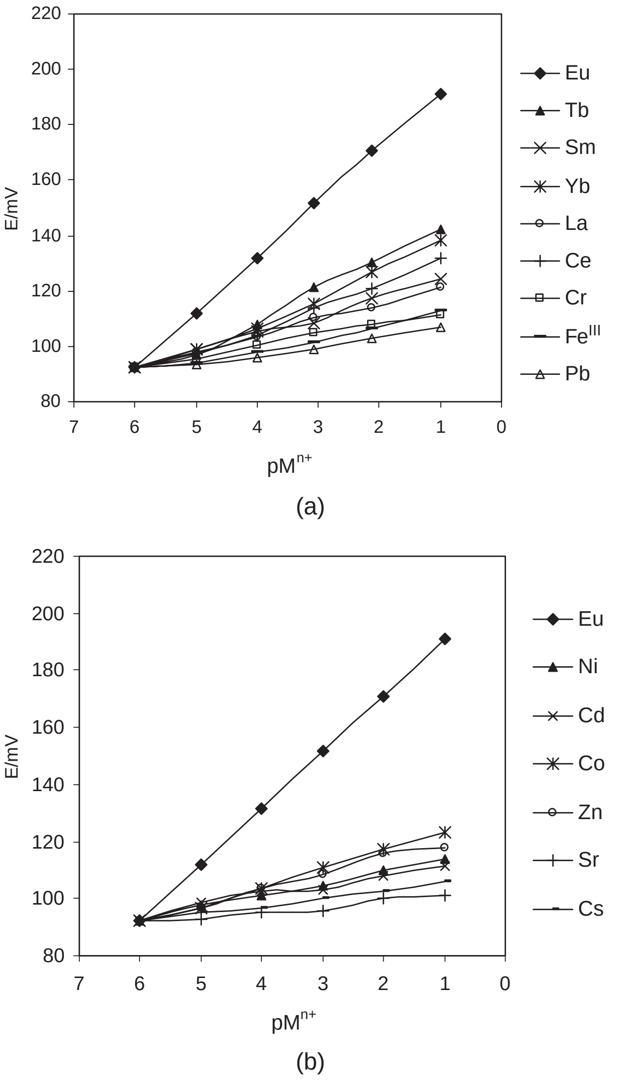

Fig. 2. Potential responses of various ion-selective electrodes based on HMTDT.

The Effect of Membrane Composition on the Potential Response of the Eu^{III} Sensor. It is well-known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of the HMTDT employed but also significantly on the membrane composition and additives used.[57,58] Thus, the influences of the membrane composition, nature and amount of plasticizer, and amount of NaTPB, which is a lipophilic additive on the potential response of the Eu^{3+} sensor were investigated and the results are summarized in Table 1. Membranes with NPOE, are the only ones that had a stable potential response. This is due to the polarity of NPOE that facilitates the extraction of europium ions with high charge density from aqueous solution to the organic membrane phase. It is noteworthy that the nature of plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its complex.[57,58] The influence of the quantity of HMTDT in the membranes with an NPOE/PVC ratio of about 2 was investigated, and the results are shown

Table 1. Composition of the Membranes

Membrane No.	Composition/wt %				Slope /mV (decade)$^{-1}$	Concentration range /mol dm^{-3}
	PVC	Plasticizer	NaTPB	HMTDT		
1	30	NPOE, 67	0	3	8.6 ± 0.3	1.0×10^{-4}–1.0×10^{-1}
2	30	NPOE, 66	0	4	13.4 ± 0.5	1.0×10^{-4}–1.0×10^{-1}
3	30	NPOE, 65	0	5	11.1 ± 0.2	1.0×10^{-4}–1.0×10^{-1}
4	30	NPOE, 64	2	4	19.7 ± 0.4	1.0×10^{-6}–1.0×10^{-1}
5	30	NPOE, 63	3	4	16.8 ± 0.3	1.0×10^{-6}–1.0×10^{-1}
6	30	BA, 64	2	4	15.6 ± 0.5	1.0×10^{-6}–1.0×10^{-1}
7	30	DBP, 64	2	4	14.9 ± 0.6	1.0×10^{-6}–1.0×10^{-1}

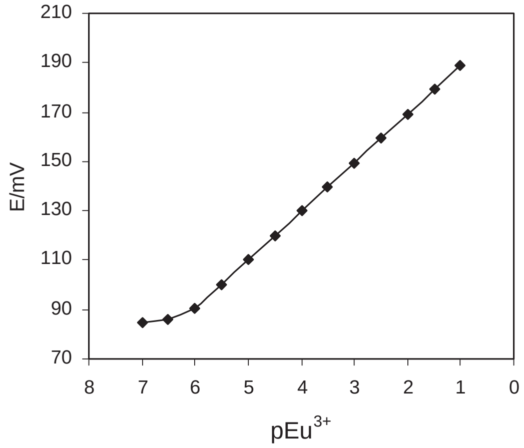

Fig. 3. Calibration curve of the europium electrode (membrane no. 4) based on HMTDT.

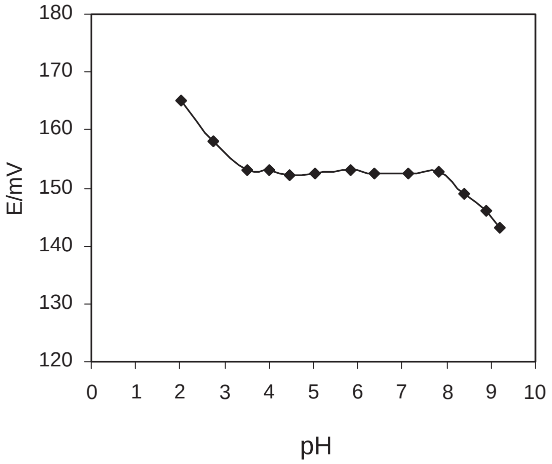

Fig. 4. The effect of the pH of the test solutions (1.0×10^{-3} mol dm^{-3}) on the potential response of the europium sensor (membrane no. 4).

in Table 1. As seen, the best electrode response is occurred with about 4% of HMTDT. However, addition of 2% NaTPB increased the sensitivity of the electrode response considerably such that the membrane electrode demonstrates a Nernstian behavior. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes not only diminishes the ohmic resistance,[59] but also enhances their response behavior and selectivity.[60,61] Table 1 shows that the best response characteristics was obtained with a membrane composition of 30% PVC, 64% NPOE, 4% HMTDT, and 2% NaTPB (no. 4).

Slope and Detection Limit. Critical response characteristics of the sensor were assessed according to IUPAC recommendations.[62] The emf response of the PVC membrane at varying concentrations of europium ions (Fig. 3) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-1} mol dm^{-3}. The slope of the calibration curve was 19.7 ± 0.4 mV per decade of Eu^{3+} ions activity. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration curve, was 7.8×10^{-7} mol dm^{-3}. The standard deviation of ten replicate measurements is ±0.5 mV. The membrane electrode prepared could be used for at least 2 months without any measurable divergences in the responses.

The Influence of pH on the Response of the Membrane Sensor. The pH dependence of the membrane electrode was tested over a pH range of 2.0–9.0 at a 1.0×10^{-3} mol dm^{-3} of europium ion concentration, and the results are illustrated in Fig. 4. The potential remains fairly constant in the pH range of 3.5–7.8 (the pH of the solutions was adjusted by either HNO_3 or NaOH solutions). Beyond this range, a gradual change in the potential was detected. The observed potential drift at the higher pH values could be due to the formation of hydroxy complexes of Eu^{III} in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responds to hydrogen ions.

Stability and Life-Time. For investigation of stability and lifetime of the Eu^{III} sensor, four electrodes were tested over a period of 8 weeks. During this period, the electrodes were in daily use over extended period of time, i.e., one hour per day. A slight gradual decrease in the slopes from 19.7 to 18.4 mV per decade was observed.

Dynamic Response Time of the Eu^{III} Sensor. Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the concentration of the Eu^{3+} solution in the range 1.0×10^{-6} to 1.0×10^{-1} mol dm^{-3}, and the results are shown in Fig. 5. As can be seen, over the entire concentration range, the electrode reaches its equilibrium response in a very short time (<15 s).

Selectivity Coefficient Determination. One of the most important characteristics of a cation-selective membrane electrode is its relative response towards one ion over other ions present in the solution, which is usually expressed in terms of potentiometric selectivity coefficients.[63,64] In this work, the matched potential method was used for the evaluation of the selectivity of the sensor.[65] The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, i.e., $K_{\mathrm{MPM}} = a_A/a_B$.

The resulting selectivity coefficients values are given in Table 2. From the data given in Table 2, it is immediately obvious that the proposed Eu$^{\mathrm{III}}$ sensor is highly selective with respect to most of cations. In the case of other lanthanide ions (i.e. Tb^{3+}, Yb^{3+}, La^{3+}, Sm^{3+}, and Ce^{3+}), the selectivity coefficients are equal or smaller than 6.2×10^{-3}, which indicates that Eu$^{\mathrm{III}}$ ions can be identified in the presence of other lanthanides. As can be seen from Table 2, the selectivity coefficients for other metal ions tested are equal or smaller than 8.7×10^{-3}, indicating they would not significantly disturb the functioning of the proposed Eu$^{\mathrm{III}}$ membrane sensor. The surprisingly high selectivity of the membrane electrode for Eu^{3+} ions over other cations used, most probably arises from the strong tendency of the carrier molecules for Eu^{3+} ions.

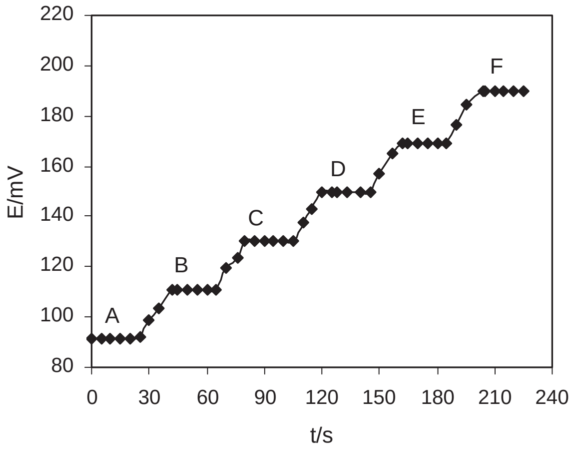

Fig. 5. Dynamic response time of the europium electrode (membrane no. 4) for step changes in the concentration of Eu^{3+}: A) 1.0×10^{-6} mol dm^{-3}, B) 1.0×10^{-5} mol dm^{-3}, C) 1.0×10^{-4} mol dm^{-3}, D) 1.0×10^{-3} mol dm^{-3}, E) 1.0×10^{-2} mol dm^{-3}, F) 1.0×10^{-1} mol dm^{-3}.

Table 2 compares the selectivity coefficients, detection limit, linear range, and response time of the proposed Eu^{3+} sensor with just one of the europium membrane electrode previously reported.[17] It is obvious that the proposed electrode is superior to the previously reported europium sensor.

Analytical Application. The proposed Eu^{3+} ion-selective membrane electrodes was successfully used as an indicator electrode in titration of Eu^{3+} (1.0×10^{-4} mol dm^{-3}) with a standard EDTA solution (1.0×10^{-2} mol dm^{-3} with pH = 10.0), and the resulting titration curve is shown in Fig. 6. As can be seen, the amount of Eu^{3+} ions in solution was accurately determined with the electrode.

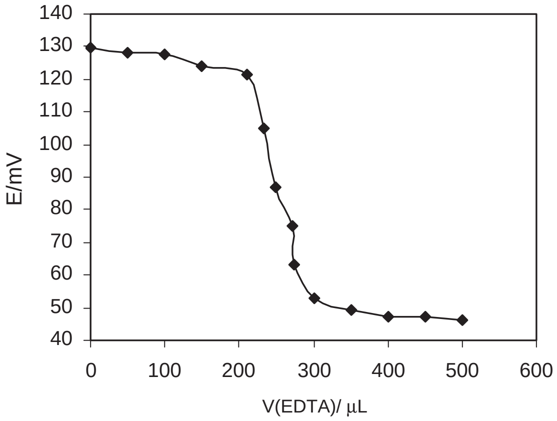

Fig. 6. Potentiometric titration curve of 25.0 mL 1.0×10^{-4} mol dm^{-3} solution of Eu^{3+} with 1.0×10^{-2} mol dm^{-3} of EDTA.

Table 2. Selectivity Coefficients for Various Interfering Ions for the Eu$^{\mathrm{III}}$ Ion-Selective Electrodes and a Comparison with the Previously Reported One

Interfering ion (B)	This work Selectivity coefficient ($K_{\mathrm{Eu,\,B}}$)	Log $K_{\mathrm{Eu,\,B}}$ (MPM)	Log $K_{\mathrm{Eu,\,B}}$ Ref. 25 (MPM)
Tb^{3+}	6.2×10^{-3}	−2.21	−1.55
Sm^{3+}	2.5×10^{-3}	−2.60	−1.54
Yb^{3+}	5.0×10^{-3}	−2.30	−1.58
La^{3+}	6.8×10^{-4}	−3.17	−1.52
Ce^{3+}	1.0×10^{-3}	−3.00	−1.55
Cr^{3+}	8.7×10^{-3}	−2.06	—
Fe^{3+}	7.5×10^{-3}	−2.12	—
Pb^{2+}	5.0×10^{-4}	−3.30	−2.36
Ni^{2+}	2.2×10^{-4}	−3.66	−2.40
Co^{2+}	7.7×10^{-4}	−3.11	−1.54
Cd^{2+}	1.0×10^{-4}	−4.00	−2.52
Zn^{2+}	1.5×10^{-3}	−2.82	−2.00
Sr^{2+}	3.8×10^{-4}	−3.42	—
Ca^{2+}	4.1×10^{-4}	−3.42	—
Mg^{2+}	3.0×10^{-5}	−3.39	—
Na^{+}	3.6×10^{-4}	−4.52	—
Cs^{+}	8.0×10^{-4}	−3.44	—
Detection limit	7.8×10^{-7} mol dm^{-3}		5.0×10^{-5} mol dm^{-3}
Linear range	1.0×10^{-6}–1.0×10^{-1} mol dm^{-3}		7.0×10^{-5}–1.0×10^{-1} mol dm^{-3}
Response time	<15 s		<20 s

Table 3. Determination of Eu^{III} Spiked in Tap and River Water Samples

Sample	Eu^{III} added /mg mL^{-1}	Found /mg mL^{-1}	Recovery /%
Tap water	0.25	(0.27$^{a)}$ ± 0.01)	108
	0.5	(0.52 ± 0.03)	104
River water	0.25	(0.26 ± 0.02)	104
	0.5	(0.51 ± 0.02)	102

a) Results are based on three measurements.

The proposed sensor was also successfully was to the determine the amount of Eu^{3+} ions in tap water and river water samples, and the results of triplicate measurements are summarized in Table 3. The amount of the europium ions, which were added to the water samples (0.25–0.5 mg mL^{-1}), could be determined by the sensor with relatively good accuracy.

Conclusion

Based on the above results, the potentiometric PVC-based membrane sensor based on HMTDT that we designed is an excellent Eu^{3+} selective sensor and can be used to determine the Eu^{III} content in the presence of considerable concentrations of common interfering ions. Applicable pH range, lower detection limit, and potentiometric selectivity coefficients of the proposed sensor make it superior to both the previously reported Eu^{3+} ion selective sensor and also to other methods used for the determinations of this ion.

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