

Analyte-triggered luminescence of Eu^{3+} ions encapsulated in Nafion membranes -preparation of hybrid materials from *in membrane* chemical reactions-



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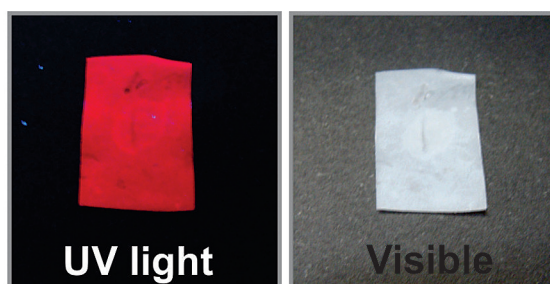
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HIGHLIGHTS

- Luminescence enhancement by complexation of Eu^{3+} ions to oxalate inside Nafion.
- Performance of chemical reactions inside Nafion/polymer membranes.
- An easy and novel method to prepare luminescent solid devices.
- Possibility to develop luminescent sensors by analyte-triggered optical response.

GRAPHICAL ABSTRACT



Nafion/ Eu^{3+} /oxalate

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ABSTRACT

The possibility to perform chemical reactions inside polymer materials opens a unique opportunity to control and prepare materials for diverse solid-state applications. Based on the affinity of Eu^{3+} ions for oxygen functionalities, in this work we report the luminescence enhancement of Eu^{3+} ions inserted in Nafion membranes ($\text{Naf}/\text{Eu}^{3+}$) by in-situ complexing to oxalate. The formation of a europium-oxalate type complex enhances Eu^{3+} luminescence emission, which could be exploited for the construction of devices for oxalate sensing and the fabrication of highly luminescent materials. Possible analytical applications of $\text{Naf}/\text{Eu}^{3+}$ membranes were evaluated by fluorescence spectroscopy through the linear response with concentration. The complex formation was followed by infrared spectroscopy and SEM-EDS analysis.

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1. Introduction

In view of the fact that the electric f-f dipole transitions are parity forbidden, lanthanides have low absorption coefficients for ultraviolet (UV)-visible light. Furthermore, lanthanide-based luminescence suffers from an efficient non-radiative deactivation

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of their excited states by species containing high-energy oscillators such as O–H bonds decreasing the luminescence intensities and excited-state lifetimes. Nevertheless, lanthanide ions play an important role in the development of luminescent materials for several applications [1,2]. In order to decrease the non-radiative decay processes, several approaches has been reported. One of them involves the preparation of solid inorganic complexes formed by solid-state reactions at high temperature that obviously represent a disadvantage. Other approaches include the encapsulation of Ln^{3+} ions into low-energy C–F oscillators [3], zeolites [4] or sol–gel silica [5]. In this respect, Nafion (an ion-exchange polymer) offers a unique opportunity to design luminescent materials since its specific sites accomplish for electrostatic attachment of lanthanide species [6] and provides chemical, mechanical, and high-temperature stability. Nafion can also be used as a solid reactor for chemical reactions [7]. The optical properties of rare earth ions trapped in host-polymer matrixes have received much attention in terms of fundamental and technological importance [8,9]. Previously, Okamoto and coworkers [10] have inserted lanthanide ions in Nafion membranes as fluorescent probes to demonstrate the existence of an ion cluster structure in the polymer. In an earlier work by the same authors [11,12], they studied lanthanide salts inserted in polymers in order to investigate the energy transfer process and the ion aggregate formation. They found that an asymmetric environment increases the transition probability for the fluorescence emission of the lanthanide ions.

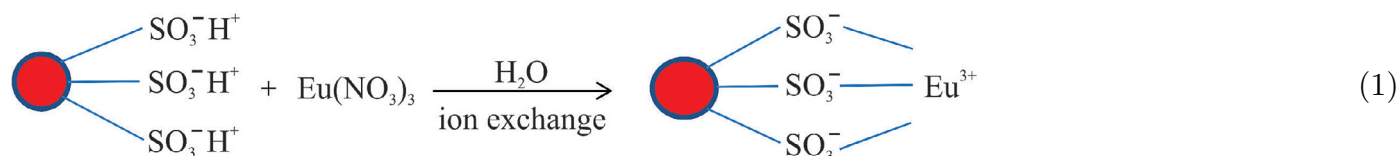
On the one hand, the luminescence properties of Eu^{3+} make it a good candidate for its use as luminescent probe of biological substances. The coordination properties of this ion have been exploited for sensing and quantification of avidin [13] and metallic cations

removing of water from around the Eu^{3+} ion will prompt an increase in the luminescence observed when bound to oxygen species and forming a europium oxalate compound. It is known [25] that SO_3^- clusters in Nafion membranes (Scheme 1) are partially hydrophilic, then we expect that a subsequent insertion of the oxalate anion into a Naf/ Eu^{3+} modified membrane, will provide a displacement of water which would produce a more hydrophobic environment with a consequent increase in the luminescence observed after formation of a compound with oxalate.

2. Experimental

Chemicals. Nafion membrane (thickness 0.07 in), 5% Nafion solution in a mixture of aliphatic alcohols, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 99.9% trace metal basis grade (Sigma), $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ 99.999% and the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate (HMImPF_6) were all purchased from Sigma-Aldrich and used without further purification. $\text{Na}_2\text{C}_2\text{O}_4$ 99.99% was from Baker. All solutions were prepared with Milli-Q water (Millipore 18.2 M Ω) before each experiment.

Sample preparation. Before loading, the membrane was washed with hot nitric acid during 30 min. After, it was thoroughly washed with deionized water and boiled further with water for several times. The membranes cleaned in this way were immersed in freshly prepared 0.01 M Eu^{3+} aqueous solution by 24 h to ensure a complete loading of the Eu^{3+} by cationic exchange according to equation (1). After this time, the membrane was removed, rinsed with water and dried at room conditions before spectroscopic measurements.



[14]. As has been established in the past few years, these low absorption coefficients may be surmounted by employing strong absorbing co-reactant ligands that emit intense visible bands under UV excitation [15,16]. It is well known that Ln^{3+} ligand coordination occurs through ionic-bonding interactions [17], which leads to a strong preference for negatively charged donor groups as O, N, and S [2]. On the other hand, oxalate is involved in a number of diseases related to renal failure, hyperoxaluria, and intestinal illness when it has been found in biological fluids such as blood or urine. An oxalate low-content diet is frequently involved in the treatment of the maladies mentioned above, then the detection and quantification of oxalate in foodstuffs as well as in biological fluids is significant. The current available methods for oxalate detection such as liquid and gas chromatography [18,19] and capillary electrophoresis often require sample pretreatment, expensive equipment, and large amount of reagents [20,21]. Also, other methods have been reported based on the formation of a dinuclear metal complex [22] or based on a direct binding of the Ln^{3+} ions to the analyte that can be used for fluorescent detection of oxalate and other substances [23,24].

Herein, we would like to report the luminescence enhancement of Eu^{3+} and the possibility to use this approach to design solid-polymer oxalate sensors based on the idea that an efficient

Aqueous oxalate solutions at different concentrations were prepared with deionized water with concentrations ranging from 1×10^{-6} to 0.1 M oxalate in which the Naf/ Eu^{3+} membranes were immersed for 15 min. Then, the membranes were removed, washed with water and dried at ambient conditions. These samples were used for spectroscopic measurements.

Electrode preparation. For electrochemical studies, a glassy carbon (GC) electrode was used as substrate to deposit a Nafion membrane from solution. First, the electrode was polished using diamond paste of 3, 0.25 and 0.1 μm diameter successively, followed by rinsing with acetone and later cleaned abundantly with deionized water (Milli-Q water, 18M Ω) for several times in an ultrasonic bath. To prepare a coated-GC/Nafion electrode, one aliquot of a 5% Nafion solution was deposited onto the electrode surface, and the solvent was allowed to evaporate at room temperature. Once dried, the GC/Nafion electrode was immersed in a 0.01 M Eu^{3+} solution during 24 h until a complete loading of the membrane.

Electrochemical measurements. All the electrochemical measurements were carried out with an Epsilon (Bioanalytical Systems) potentiostat-galvanostat. The software Basi-Epsilon EC (ver. 2.13.77) was used for data acquisition. A conventional three electrode glass cell was employed. A GC/Naf/ Eu^{3+} electrode were used as working electrode; the counter electrode was a Pt wire and

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