



# A luminescent europium ionic liquid to improve the performance of chitosan polymer electrolytes



R. Leones<sup>a,b</sup>, P.M. Reis<sup>b,c</sup>, R.C. Sabadini<sup>d</sup>, L.P. Ravaro<sup>e</sup>, I.D.A. Silva<sup>e</sup>, A.S.S. de Camargo<sup>e</sup>, J.P. Donoso<sup>e</sup>, C.J. Magon<sup>e</sup>, J.M.S.S. Esperança<sup>b,c</sup>, A. Pawlicka<sup>d</sup>, M.M. Silva<sup>a,\*</sup>

<sup>a</sup> Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

<sup>b</sup> Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal

<sup>c</sup> LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>d</sup> Instituto de Química de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, SP, Brazil

<sup>e</sup> Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

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## ABSTRACT

Ionically conductive and luminescent chitosan solid polymer electrolytes (SPEs) were prepared through the solvent casting method and characterized with respect to their thermal behavior, morphology, structure, ionic conductivity, optical, and photophysical properties. The characterization was performed by analysis of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), complex impedance and photoluminescence spectroscopies. The chitosan-SPEs were doped with different quantities of 1-ethyl-3-methylimidazolium europium(III) tetrathiocyanate ( $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$ ). The chitosan<sub>n</sub> $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$  membranes exhibited a semi-crystalline morphology and good thermal stability ( $T_{\text{onset}} \approx 134^\circ\text{C}$ ). The sample with the highest ionic conductivity was the chitosan<sub>4</sub> $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$  with  $1.34 \times 10^{-5}$  and  $1.97 \times 10^{-4} \text{ S cm}^{-1}$  at 30 and  $80^\circ\text{C}$ , respectively. The photoluminescence analysis showed intense red emission corresponding to the  $^5\text{D}_0 \rightarrow ^7\text{D}_2$  transition, as it is typical for  $\text{Eu}^{3+}$  luminescent materials. The chitosan<sub>0.5</sub> $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$  sample emitted red luminescence with a lifetime of 0.397 ms. The chitosan<sub>1</sub> $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$  exhibited the best equilibrium between the membrane's optical and photophysical features. These results encourage future investigations of these materials for application in electroluminescent devices.

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## 1. Introduction

Organometallic complexes of trivalent lanthanides (Ln(III)) display intense luminescence in the visible and near-infrared regions and may find application in light-emitting devices, displays, sensors, medical visualization devices, and biological analysis. They present narrow emission bands, long decay times, and a large Stokes shift [1,2].

Generally, Ln(III) ions show absorption and emission bands that correspond to the Laporte forbidden f–f transitions, resulting in a very inefficient  $\text{Ln}^{3+}$  direct excitation. Such drawback can be overcome by using a strongly absorbing chromophore (organic ligand), i.e., the “antenna effect”. Thus, the organic ligands absorb energy and transfer it to the emitting rare earth ion. Consequently,

the very low absorption of the ion is overcome and sharply defined emission spectra with high color purity are obtained [3]. Therefore, the choice of a proper antenna is critical for the efficiency of the lanthanide complex. Arenz et al. [4] showed that ionic liquids lead to a dramatic increase of the lifetimes of the excited states and quantum yields of emission.

Ionic liquids (ILs) are composed entirely by ions typically of a large organic cation and an organic or an inorganic anion [5]. The possibility to design ILs for specific applications by tuning their properties and interactions through the combination of thousands of cations or anions is one of their most advantageous features [6]. Furthermore, ILs have attracted a lot of attention due to the almost null volatility [7], non-flammability [8], and high thermal stability [9] of many of these compounds. Generally, ILs also show good electrochemical properties, such as high ionic conductivity and wide electrochemical stability windows [10]. Thus, lanthanide-based ILs combine both the luminescence of lanthanide complexes and the conductivity of ILs. For this purpose, europium-based IL

\* Corresponding author.

E-mail address: [nini@quimica.uminho.pt](mailto:nini@quimica.uminho.pt) (M.M. Silva).

was synthesized. Upon excitation, europium (III) complexes emit characteristic red luminescence corresponding to the  $^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$  [11]. In order to avoid the luminescence intensity saturation, to increase the thermal and mechanical stabilities, and to overcome the limited application of these compounds in the liquid state, lanthanide complexes should be dispersed into a host matrix [12,13].

The primary goal of this work was to develop a new family of materials exhibiting simultaneously high ionic conductivity and high luminescence. To achieve such goal we produced solid polymer electrolytes (SPEs) based on the biopolymer chitosan and 1-ethyl-3-methylimidazolium europium(III) tetrathiocyanate ( $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$ ) IL through the solvent casting method. The use of a biopolymer was motivated by natural polymers' biocompatibility, biodegradability, low cost, and abundance [14]. Chitosan is a polysaccharide obtained by deacetylation of chitin, which can be found in crustacean shells, fungi, molluscan organs, and insects. Chitosan is a linear copolymer of  $\beta$ -(1-4) linked glucosamine and N-acetylglucosamine [15–18], and it is already widely used in the pharmaceutical, food packaging and biomedical industries. Chitosan physical and chemical properties differ depending on its molecular weight, degree of acetylation, and the intramolecular distribution residues [15–20]. Furthermore, its polar functional groups, namely ether, hydroxyl, and primary amine make it a very well-suited SPE matrix host due to chitosan's ability to dissolve ionic salts [21–23].

Previous studies of lanthanide salt-based electrolytes suggested that an appropriate SPE composition should comprise a homogeneous and amorphous material with improved optical transparency [24]. Therefore, in the present work, the samples were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM), complex impedance spectroscopy, photoluminescence spectroscopy, and electron paramagnetic resonance (EPR). EPR is a sensitive technique which provides valuable information about the oxidation state of the paramagnetic ion and the local symmetry of the ion environment [25]. The EPR of divalent europium has been investigated in a variety of materials such as crystals [26–28], ceramics [29], glasses [30–32], zeolites [33], and polymer electrolytes based on natural polymers [34,35].

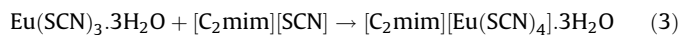
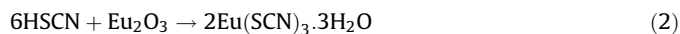
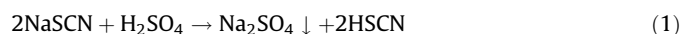
## 2. Experimental

### 2.1. Synthesis of $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4] \cdot 3(\text{H}_2\text{O})$

$\text{NaSCN}$  (6.48 g, 80 mmol) (Fluka, >98%) was dissolved in Milli-Q water (25 mL).  $\text{H}_2\text{SO}_4$  (2.2 mL, 40 mmol) (Merck, 96%) was added to this solution. The reaction produced a mixture of HSCN and  $\text{Na}_2\text{SO}_4$ . 50 mL of ethanol (Carlo Erba Reagents, 99.9%) were added to enable  $\text{Na}_2\text{SO}_4$  precipitation. The precipitate was removed by filtration and  $\text{Eu}_2\text{O}_3$  (4.68 g, 13.3 mmol) (Alfa Aesar, 99.9%) was added to the obtained filtrate. The heterogeneous mixture was left under stirring overnight. The reaction mixture containing  $\text{Eu}(\text{SCN})_3 \cdot 3\text{H}_2\text{O}$  was evaporated in rotavapor and dried in a vacuum line ( $10^{-3}$  bar) [2].

A mixture of 2.030 g (4.876 mmol) of  $\text{Eu}(\text{SCN})_3 \cdot 3\text{H}_2\text{O}$  and 0.825 g (4.876 mmol) of  $[\text{C}_2\text{mim}][\text{SCN}]$  (Iolitec, >98%) was reacted under stirring for 2 hours at  $120^\circ\text{C}$ , according to a similar procedure [36]. The mixture containing the desired IL,  $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4] \cdot 3\text{H}_2\text{O}$ , became yellow and was dried under vacuum.

The synthesis of the IL is described by Eqs. (1)–(3).



Elemental analysis was performed on the obtained orange solid. The results confirmed the production of the europium-based IL  $[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4] \cdot 3\text{H}_2\text{O}$ .

Calculated: % C: 21.86; % N: 15.29; % H: 3.12; % S: 23.34.

Measured: % C: 21.20; % N: 15.65; % H: 2.88; % S: 22.90.

Common characterization techniques such as NMR could not be used due to the paramagnetic properties of this IL.

### 2.2. SPEs preparation

0.2 g of chitosan (medium molecular weight and 75–85% deacetylated, Sigma-Aldrich 448877) were dissolved in 10 mL of 1% acetic acid (Sigma-Aldrich, >99.8%) solution and stirred overnight at room temperature until a homogeneous and viscous solution was formed. Then, 0.05–0.4 g of the IL and 0.2 g of glycerol (Himedia, 99.5%) as plasticizer were added to this solution. The resulting solution was casted onto Petri dishes and dried for 5 h at  $25^\circ\text{C}$ , then 12 h at  $40^\circ\text{C}$ , followed by 5 h at  $60^\circ\text{C}$  and then cooled down to  $25^\circ\text{C}$  for 2 h. The resulting flexible transparent membranes' thicknesses ranged from 0.120 to  $0.164 \pm 0.001$  mm (Fig. 1). The notation  $\text{chitosan}_n[\text{C}_2\text{mim}][\text{Eu}(\text{NCS})_4]$ , where  $n$  corresponds to the quotient between the mass of the polymer and the mass of the IL, was adopted.

### 2.3. SPEs characterization

TGA and DSC were performed in order to study the thermal behavior of the synthesized SPEs. For the DSC experiments, 40  $\mu\text{L}$  aluminum cans with perforated lids were sealed with each sample inside a glove box filled with dry argon. The analyses were carried out using a Mettler DSC 821e under a flowing argon atmosphere in the temperature range  $-60$  to  $200^\circ\text{C}$  and at a heating rate of  $5^\circ\text{C}\text{min}^{-1}$ . TGA analyses were performed with a Shimadzu TGA-50 equipment. The measurements were conducted between 30 and  $900^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C}\text{min}^{-1}$ , and under a nitrogen atmosphere with a  $60\text{ mL}\text{min}^{-1}$  flow rate. Before each analysis and aiming to eliminate the traces of any absorbed moisture, all samples were subject to a first run from 30 to  $105^\circ\text{C}$ , at a heating



Fig. 1. Photography of the  $\text{chitosan}_1[\text{C}_2\text{mim}][\text{Eu}(\text{SCN})_4]$  membrane.

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