

## Luminescent polymer electrolytes based on chitosan and containing europium triflate

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**Abstract:** Solid polymer electrolytes based on chitosan and europium triflate were prepared by solvent casting and characterized by X-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM), and photoluminescence spectroscopy. The X-ray diffraction exhibited that the samples were essentially amorphous with organized regions over the whole range of the salt content studied. The AFM analysis demonstrated that the smoother sample had roughness of 4.39 nm. Surface visualization through SEM revealed good homogeneity without any phase separation for more conductive samples and the less conductive showed some imperfections on the surface. The emission and excitation spectra displayed the characteristic bands of  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  in addition to broad bands corresponding to the polymer host. The excited state  $^5\text{D}_0$  lifetime values ranged from 0.29–0.37 ms for the studied samples.

**Keywords:** solid polymer electrolytes; natural polymers; photoluminescence spectroscopy; rare earths

In past years the most studied solid polymer electrolytes (SPEs) were based on poly(ethylene oxide) PEO and lithium salts, but due to the low ionic conductivity ( $10^{-7}$ – $10^{-8}$  S/cm) at room temperature they are limited in terms of applications<sup>[1]</sup>. More recent studies aim to develop solid polymer electrolyte systems based on natural polymers such as polysaccharides and proteins, which are interesting due to their natural abundance, low cost, and environmentally friendly nature<sup>[2]</sup>. Furthermore, polysaccharides and their derivatives can be processed as films/membranes with good adhesion to glass and metal surfaces as well as an excellent transparency<sup>[2]</sup>. There are several natural polymers used in SPEs of which gelatin<sup>[3]</sup>, cellulose<sup>[4]</sup>, starch<sup>[5]</sup>, pectin<sup>[6]</sup>, and chitosan<sup>[7]</sup> are some examples.

Chitosan can be prepared by deacetylation of chitin, one of the most abundant natural polysaccharides<sup>[8]</sup>. It is a polymer of  $\beta$ -1,4-linked 2-amino-2-deoxy-D-glucopyranose, and it has good mechanical strength and is chemically and thermally stable up to 200 °C<sup>[9,10]</sup>. The amine group ( $\text{NH}_2$ ) in chitosan structure can act as electron donor and interacts with inorganic salts. The interaction between nitrogen donor and lithium cation was proven by X-ray photoelectron spectroscopy<sup>[11]</sup>. On the other hand, X-ray diffraction of chitosan films shows amorphous structure, and thermal analysis reveals quite high glass transition temperature ( $T_g \approx 200$  °C)<sup>[11]</sup>.

Chitosan is used as the host polymer in electrolytes

because it is able to dissolve ionic salts. It is a widely studied polymer due to specific properties such as biocompatibility, bioactivity, low toxicity, environmentally friendly characteristics, and also due to its promising potential in biomedical, pharmaceutical, and industrial applications<sup>[12]</sup>. A chitosan film shows low electrical conductivity, and a way to improve ionic conductivity values is by adding a plasticizer like glycerol<sup>[13]</sup>. The addition of a plasticizer reduces the glass transition temperature and increases segmental motion, which results in an increase in conductivity<sup>[14]</sup>.

Trivalent lanthanides ions exhibit fascinating optical properties and are currently the most important luminescent ions in optical devices. The long lifetime of the lanthanides excited states allows the use of time-resolved spectroscopy to suppress background fluorescence, reaching very low detection limits<sup>[15]</sup>. This is especially relevant in biological applications such as in biomarkers, medical diagnosis and cell imaging<sup>[16,17]</sup>, however, the lanthanide ions also find spread use in lighting devices, displays, optical fibers and amplifiers for telecommunications and lasers. Complexes and salts based on  $\text{Ln}^{3+}$  ions display efficient emissions in the near-UV ( $\text{Ce}^{3+}$ ), visible ( $\text{Tm}^{3+}$ -blue;  $\text{Tb}^{3+}$  and  $\text{Er}^{3+}$ -green;  $\text{Dy}^{3+}$ -yellow;  $\text{Sm}^{3+}$ -orange;  $\text{Eu}^{3+}$ -red) and NIR ( $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Yb}^{3+}$ )<sup>[18–21]</sup>. Because practical applications of these compounds in the liquid state is somewhat limited, the dispersion in different host matrices is an excellent alterna-

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tive to increase thermal, mechanical, and emissive stability in device applications<sup>[22]</sup>. In a study of a series of interesting  $\text{Eu}^{3+}$ -complex based hybrid organic/inorganic materials, prepared by the sol-gel technique, the authors obtained amorphous transparent monoliths, that were thermally stable up to 250 °C, intensely luminescent, and exhibited ionic conductivity of about  $10^{-5} \Omega^{-1}\text{cm}$  at 30 °C<sup>[23]</sup>. In another study, the family of  $\text{Eu}^{3+}$ -doped d-Ut(300)-based di-urethanesils were prepared by the sol-gel process, and it was verified that the formation of free salt occurs at higher salt content. These materials are promising fullcolor emitters with emission quantum yield ranging from 0.7% to 8.1%<sup>[24]</sup>. For hybrids co-doped with  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Tm}^{3+}$  the chromaticity of the emission was demonstrated, and it was shown that the optical features are strongly influenced by environmental conditions such as temperature variations, which suggest the application of these materials in sensing<sup>[25]</sup>.

In this work, we report the preparation and characterization of SPEs based on chitosan as host polymer, glycerol as plasticizer, and europium triflate salt. The samples were characterized by X-ray diffraction, SEM, AFM, and photoluminescence spectroscopy. The luminescent behaviour of europium ions in suitable polymer hosts has suggested that future developments may lead to the multicomponent solid-state displays, but with the added attraction of processing, which polymer host can provide. Additionally, the promising results of both ionic conductivity and optical properties feed back into investigations how the molecules can be engineered to create a new class of designer biomaterials.

## 1 Experimental

### 1.1 Preparation of solid polymer electrolytes

The polymer electrolytes were synthesized according to a procedure previously described in literature<sup>[26,27]</sup>. Samples were prepared by dispersion of 0.20 g of medium Mw chitosan (Sigma-Aldrich, Portugal) in 10 mL of 1% acetic acid solution (Sigma-Aldrich, Portugal), under magnetic stirring overnight for complete dissolution. Then, different quantities (0, 20.11 wt.%, 33.88 wt.%, 42.99 wt.%, 50.04 wt.% and 55.34 wt.%) of europium(III) trifluoro-methanesulfonate (Sigma-Aldrich, Portugal; 98%) salt and 0.25 g of glycerol as plasticizer (Himedia, India; 99.5%) were added to the mixture, which continued to stir for a few minutes. The notation chitosan- $_n\text{Eu}(\text{CF}_3\text{SO}_3)_3$  represents the samples, where  $n$  corresponds to the percentage of the europium triflate salt. The resulting solutions were then poured on Petri plates, dried at room temperature until films were formed, and then dried in an oven between 25–60 °C, for two days, to yield transparent films such as the representative one shown in Fig. 1. During this drying period, the oven was

periodically evacuated and purged with dry argon. The thickness was determined with a micrometer (Mitutoyo, Japan) and varied between 0.070 and  $0.144 \pm 0.001$  nm. After drying process, samples were conditioned in a glovebox under argon atmosphere.

### 1.2 Characterization techniques

The structure of the films was examined by X-ray diffraction measurements using a Rigaku UTMA4 instrument with  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15418$  nm) (Japan), in the angular range ( $2\theta$ ) from 5° to 60° and at room temperature.

The AFM images were obtained with a Nanosurf easyScan 2 AFM System (Nanosurf AG, Switzerland). In all AFM analyses, the non-contact mode was employed by using silicon AFM probes, a force constant of 48 N/m, and a resonance frequency of 190 kHz.

The SEM micrographs were obtained with an LEO model 440 microscope (England).

The photoluminescence spectra of the  $\text{Eu}^{3+}$ -doped samples were collected in a HORIBA Jobin Yvon spectrofluorimeter model Fluorolog FL3-221 (USA), equipped with CW xenon flash lamp and a visible detector (HORIBA PPD-850). The lifetime measurements were performed in the same equipment using a pulsed lamp.

## 2 Results and discussion

Fig. 2 shows the characteristic room temperature X-ray diffraction profile obtained for pure chitosan and samples plasticized with glycerol, containing different quantities of  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ . For pure chitosan one can observe a broad band centered at  $2\theta \approx 20.6^\circ$ , but the XRD patterns change with the addition of the europium salt. The Gaussian-shaped broad non-resolved band, centred at about  $2\theta = 20.6^\circ$  in the diffractograms depicted in Fig. 2, confirms the predominantly amorphous structure of the polymer electrolytes studied here. This result may be interpreted as an indication that the polymer chains are



Fig. 1 Photograph of a representative electrolyte film

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