

Eco-friendly luminescent hybrid materials based on Eu^{3+} and Li^+ co-doped chitosan, Raquel Alves^a, Leandro P. Ravaro^b, Agnieszka Pawlicka^c, Maria Manuela Silva^{a*} Andrea S. S. de Camargo^{b*}

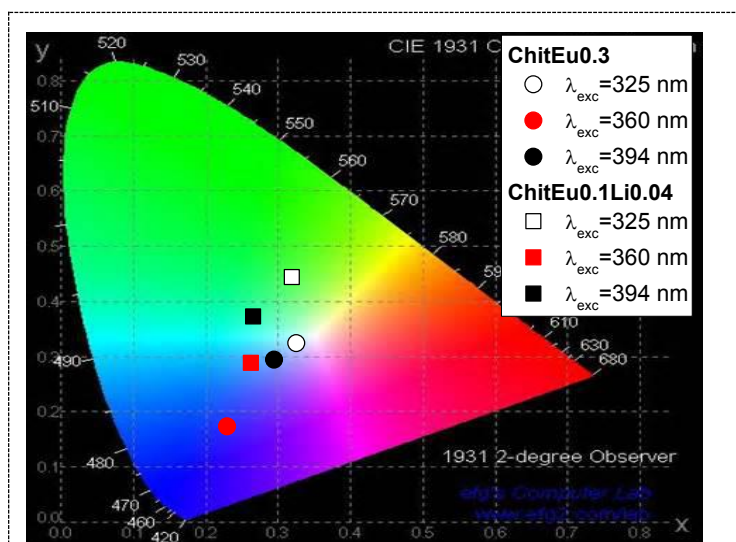
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Graphical Abstract (GA)



Chitosan doped with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ presents emissions from blue to red that can be tuned to yield white light. Addition of Li^+ can lead to electroluminescent devices.

Eco-friendly luminescent hybrid materials based on Eu^{3+} and Li^+ co-doped chitosan

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Abstract

Biopolymer-based materials have been of particular interest as alternatives do synthetic polymers due to their low toxicity, biodegradability and biocompatibility. Among them, chitosan is one of the most studied ones and has recently been investigated for the application as solid state polymer electrolytes. Furthermore, it can serve as a host for luminescent species such as rare earth ions, giving rise to materials with increased functionality, of particular interest for electrochemical devices. In this study, we investigate chitosan based luminescent materials doped with Eu^{3+} and Li^+ triflate salts from the structural, photophysical and conductivity points of view. Because the host presents a broad emission band in the blue to green, while Eu^{3+} emits in the red, fine tuning of emission colour and/or generation of white light is possible by optimizing composition and excitation scheme. Europium lifetimes ($^5\text{D}_0$) are in the range 270 – 350 μs and quantum yields are as high as 2%. Although Li^+ does not interfere with the luminescent properties, it grants ion-conducting properties to the material suggesting that a combination of both properties could be further explored in multifunctional device.

Keywords: Chitosan; polymer electrolyte; europium, lithium, electroluminescent devices

Introduction

The low toxicity biodegradability and biocompatibility of chitosan make it one of the most widely studied polymers from an application point of view. The applications areas include waste water treatment, food industry, agriculture, paper and pulp industry, cosmetics, medicine, tissue engineering, bioseparation and biocatalysis.¹⁻³ From the physicochemical standpoint, chitosan is a water soluble polymer that can be formed into films, hydrogels and scaffolds, under mild acidic conditions. Moreover, the polycationic character confers upon chitosan a high affinity for the association and delivery of therapeutic hydrophilic macromolecules such as proteins, hormones and DNA, thus effectively, protecting their bioactivity against enzymatic and hydrolytic degradation.^{3, 4} As chitosan is water soluble, it is possible to mix it with different inorganic salts and produce polymer electrolytes (PEs) for electrochemical devices assembling.⁵ PEs are composed of a host macromolecule and a guest salt, have been widely studied in the field of solid state electrochemistry, because of commercial interest in their application. Polymer electrolytes based on natural polymers have attracted a lot of attention due to their mechanical, optical and electrical properties.⁶ The mixed cation approach which basically involves the use of two guest salts instead of a single one, is attractive and usually results in an improvement of the conductivity of PEs.⁷

Besides the technological aspects, biopolymer based materials call attention for the possibility of developing environmentally friendly (multi)functional materials that can combine, for instance, high ionic conductivity and efficient luminescent properties.^{8, 9} In this regard, trivalent lanthanide ions are the most studied luminescent species due to their versatile narrow band emissions in a large spectral range (from visible to near-infrared). Application opportunities are found in, but not restricted to, lighting devices, displays, amplifiers and lasers. The long lifetime of the lanthanide ions excited states allows the use of time-resolved spectroscopy to suppress background fluorescence, reaching very low detection limits, which is relevant for biological applications such as biomarkers and cell imaging.¹⁰ Complexes and salts display high quantum efficiencies in the near-UV (Ce^{3+}), visible

(Tm³⁺- blue; Tb³⁺ and Er³⁺- green; Dy³⁺- yellow; Sm³⁺- orange; Eu³⁺- red) and NIR (Nd³⁺, Er³⁺, Tm³⁺ and Yb³⁺).

Studies of the family of Eu³⁺-doped d-Ut(300)-based di-urethanesils hybrids prepared by the sol-gel process indicate that the materials are promising full colour emitters with quantum yield ranging from 0.7 to 8.1 % .¹¹ Another hybrids co-doped with Eu³⁺, Tb³⁺ and Tm³⁺ have evidenced the chromaticity of the emission, and it was shown that their optical features were strongly influenced by environmental conditions, such as temperature variations, suggesting the application of these materials in sensing.¹² Eu³⁺-doped DNA and agar membranes⁹ have also been recently investigated, as well as Eu³⁺-doped chitosan, which showed interesting spectroscopic properties.¹³ Recently Tsvirko et al¹⁴ have studied absorption, photoluminescence and time resolved decay properties of films of chitosan doped with Eu³⁺ β-diketonate complex. They have observed, that these new material has very good luminescence emission in VIS region and high quantum efficiency of about 47%. Roosen and Binnemans¹⁵ proposed a chitosan modified with ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) stationary phase for trivalent rare-earth ions separation using dilute nitric acid solution as eluent. Liu et al¹⁶ have studied bio-organic-inorganic hybrids containing silica, chitosan and Eu³⁺ or Tb³⁺ ions. They have observed that the Eu³⁺ ions have the same local coordination in the chitosan core of these core-shell (chitosan-silica) hybrids as in Eu³⁺ doped chitosan. Additionally they have also found a small amount of Eu³⁺ in silica shell.

Because the host polymer emits broadly in the blue to green spectral region and Eu³⁺ in the red¹⁶, the combination offers the possibility of tuning the emission colour and obtaining white light, through control of composition and proper excitation scheme. In this contribution, we extend the investigation to Eu³⁺ and Li⁺ containing natural-polymer-based membranes, which might offer the possibility of increased electrochemical functionality. These new samples can have both the emission properties due to the Eu³⁺ ions and can conduct Li⁺ ions, thus they can be applied in electrochemical devices such as displays. Consequently, the chitosan-based membranes are characterized not only by

their structure and morphology, but also by their ionic conductivity and photophysical properties. The CIE (*Comission Internationale d'Éclairage*) chromaticity coordinates are given for several samples along with the respective quantum yields and excited state lifetime values.

Experimental

Samples preparation

The electrolytes were prepared according to the following procedure: 0.20 g of chitosan (Sigma-Aldrich; medium molecular weight) was dispersed in 10 mL of 1 % acetic acid solution (Sigma-Aldrich) under magnetic stirring over night to complete dissolution. Then, 0.25 g of glycerol (Himedia; 99.5 %) and different quantities of europium (Sigma-Aldrich; 98 %) and lithium triflate (Sigma-Aldrich; 99.995 %) salts were added and the solutions were under stirring for a few minutes. Samples have been represented by the notation $\text{ChiEu}_n\text{Li}_m$, where n is the lanthanide salt mass and m is the lithium salt mass in the electrolytes (Table 1). The viscous solutions poured on Petri plates, cooled at room temperature, and then the electrolyte films obtained were subjected to a final drying procedure in which the temperature was raised from 25 °C to 60 °C over a period of two days to form transparent membranes (Figure 1). During this period the oven was periodically evacuated and purged with dry argon. The thickness was determined with a micrometer (Mitutoyo, Japan), which varied between 0.070 and 0.175 ± 0.001 mm. After drying process, samples were conditioned in a glovebox under argon atmosphere.

Table 1. Relevant details of the synthetic procedure of the $\text{ChiEu}_n\text{Li}_m$ samples.

Samples	$\text{Eu}(\text{CF}_3\text{SO}_3)_3$		LiCF_3SO_3		Thickness mm
	m / g ^[a]	wt / %	m / g ^[a]	wt / %	
Chitosan	-	-	-	-	0.145
ChiEu _{0.05}	0.05037	20.11	-	-	0.130
ChiEu _{0.05} Li _{0.09}	0.05090	14.51	0.09476	27.01	0.069
ChiEu _{0.05} Li _{0.2}	0.05605	10.88	0.23535	49.57	0.159
ChiEu _{0.1}	0.10270	33.88	-	-	0.109
ChiEu _{0.1} Li _{0.04}	0.10197	28.99	0.04412	12.54	0.141
ChiEu _{0.1} Li _{0.05}	0.10140	27.75	0.05237	14.33	0.107
ChiEu _{0.1} Li _{0.1}	0.10546	25.36	0.10711	25.76	0.077
ChiEu _{0.25}	0.25068	55.34	-	-	0.144
ChiEu _{0.25} Li _{0.05}	0.25120	50.30	0.04707	9.42	0.170
ChiEu _{0.3}	0.30040	59.85	-	-	0.172

^[a] the balance error was of $\pm 0.00001\text{g}$

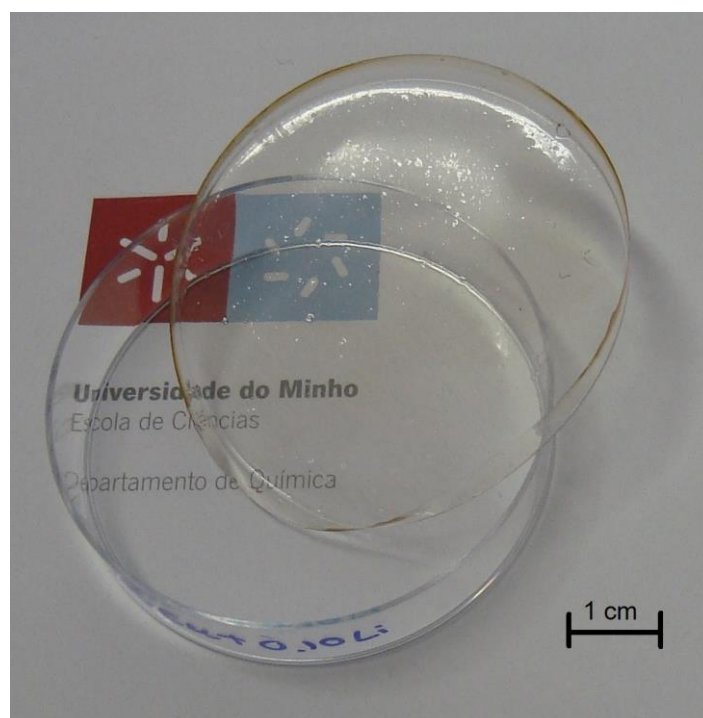


Figure 1. Photograph of a representative $\text{ChiEu}_n\text{Li}_m$ film. Petri plate diameter was 5.2 cm.

Characterization techniques

The X-Ray diffraction measurements were performed at room temperature in a PANalytical X'Pert Pro diffractometer equipped with an X'Celerator detector. The film samples were exposed to monochromated $\text{CuK}\alpha$ radiation with $\lambda = 1.541 \text{ \AA}$ over a scattering angle (2θ) range from 3 to 60 °.

In these measurements, samples were placed on a Si wafer, in order to minimise any diffuse scattering from the substrate.

The surface morphology of the films prepared at different ratios was evaluated using scanning electron microscopy (SEM) micrographs, obtained in a LEO 440 instrument. All film samples were pre-coated with a conductive layer of sputtered gold. The micrographs were taken at 10 kV at different magnifications.

Total ionic conductivities of samples were determined using a constant volume support equipped with gold blocking electrodes and located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 65 kHz and 500 mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range from 20 to 90 °C. Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating-cooling-heating cycles. The excellent reproducibility of the results obtained using this procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

Room temperature emission and excitation spectra of the polymer films, as well as excited state lifetime decays were measured in a Horiba Jobin Yvon spectrofluorimeter model Fluorolog FL3-221 using continuous wave or pulsed (flash) xenon lamps. Quantum yield measurements of Eu-doped and Eu/Li-co-doped samples were measured in an integrating sphere from Horiba Jobin Yvon model Quanta Phi F3029, properly connected to the spectrofluorimeter.

Results and Discussion

Structural and Morphological Characterization

Figure 2 depicts the XRD patterns of film samples of $\text{ChiEu}_n\text{Li}_m$, i.e., non-doped chitosan and its mixture with either $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ or both $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ and LiCF_3SO_3 . The diffractograms of all

samples, similarly to other ionic conducting membranes based on natural macromolecules, display a broad Gaussian in shape peak centered at *ca.* 21 ° that can be assigned to chitosan crystal form type II.^{6, 17-21} For samples of ChiEu_{0.1} and ChiEu_{0.1}Li_{0.05} the same single broad peak is observed at 21 °, similarly to DNA-Eu³⁺ samples²². However, as observed in other studies the doping of polymer matrix with inorganic salt can induces long range disorder in the diffraction patterns²³. This observation strongly suggests that an increase of the amorphous content was promoted by the presence of salts. As a consequence of the increase of the amorphous content some regions of matrix become more crystalline. Although is seams contradictory it might be explained as the increased disorder created by the salt among the neighboring chitosan chains forces chain segments, which are not located within the amorphous domain to gather in well-defined regions and organize in a more regular manner. Similar behavior was also previously observed for polymer electrolytes based on europium salt and polyethylene oxide (PEO).²⁴ The polymer electrolytes ChiEu_{0.1}Li_{0.04} and ChiEu_{0.1}Li_{0.1} exhibit Bragg peaks at 21 °, similar to ChiEu_{0.1}Li_{0.0}, ChiEu_{0.1}Li_{0.05} and non-doped chitosan matrix, and very sharp lonely peak at 10 °. Chitosan powder has two peaks at 2 Θ = 10.9 and 20.1 °.^{25, 26} The peak at about 10-11 ° of the ChiEu_{0.1}Li_{0.04} and ChiEu_{0.1}Li_{0.1} is much sharper than the peak of chitosan powder and ressamble more the one found in free LiCF₃SO₃ or a polymer-salt crystalline complex. Nunes et al²⁷ also detected a peak at about 10-11 ° for the system d-U(2000)_nLiCF₃SO₃, although this system have a series of other peaks in salt rich domains. The position of these peaks coincides exactly with the location of the diffraction peaks of the crystalline complex with stoichiometry 3:1 that is formed between PEO and LiCF₃SO₃.²⁸ The peak at 10 ° in present study can be attributed to the sample or some impurity. No peak at approximately 29 °, which was ascribed to the diffraction of Eu-rich domains in the case of the system U(2000)_nEu(CF₃SO₃)₃ was detected.²⁹ Differently to the U(2000)_nEu(CF₃SO₃)₃ compounds in present study the samples of ChiEu_{0.1}Li_{0.04} and ChiEu_{0.1}Li_{0.1} did not reveal any peaks at approximately 29°. The obtained results prove that the addition of the guest europium triflate salt to chitosan matrix inhibits the formation of crystalline phases of free Eu(CF₃SO₃)₃ or chitosan / salt complexes.

The amorphous nature of the chitosan based electrolyte system provides a clear advantage relative to other semi crystalline systems, since the absence of crystallinity results in improvements in optical, mechanical and electrochemical behaviour, especially because ionic movement occurs preferentially in the amorphous phase.³⁰⁻³²

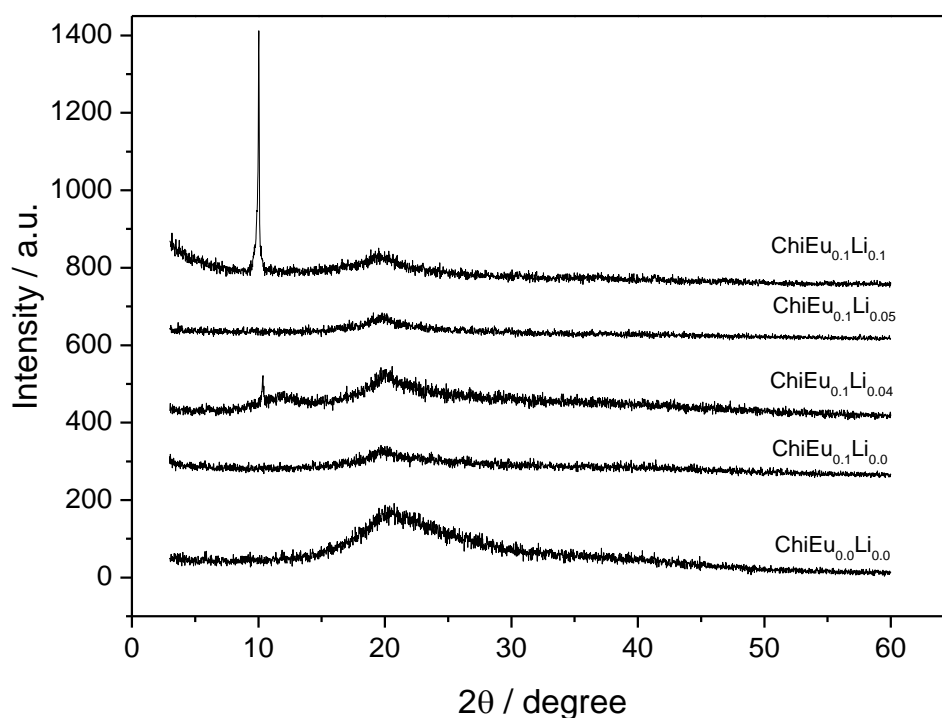


Figure 2. XRD patterns of $\text{ChiEu}_n\text{Li}_m$ samples.

Scanning electron micrographs illustrating the morphology of chitosan and $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ and LiCF_3SO_3 are shown in Figure 3. The good homogeneity without any phase separation and very good surface uniformity at the micrometre scale of samples containing 0.1 g of Eu^{3+} -triflate (without Li^+) can be observed in the SEM micrographs in Figure 3a. Similar results were obtained for agar-based films.³³ Other SEM images reproduced in Figure 3 (b, c and d) show that the samples containing mixture of both salts exhibit an irregular texture, and are very similar to the samples solid polymer electrolyte based on (PEG) with high LiClO_4 concentration²³. The micrograph of $\text{ChiEu}_{0.1}\text{Li}_{0.04}$ (Figure 3b) shows a porous morphology evolving from large to lower pore. The pores have different sizes and it is not a surface effect. It can occur because the degree of porosity is due to the low

evaporation temperature of the solvent during the sample preparation. At the same time, the polymer chains show a reduced mobility, which hinders them to occupy the free space left by the evaporated solvent.³⁴ The images recorded for samples $\text{ChiEu}_{0.1}\text{Li}_{0.05}$ and $\text{ChiEu}_{0.1}\text{Li}_{0.1}$ reveal clearer lines that can be either undissolved or recrystallized salt, which confirms XRD data.

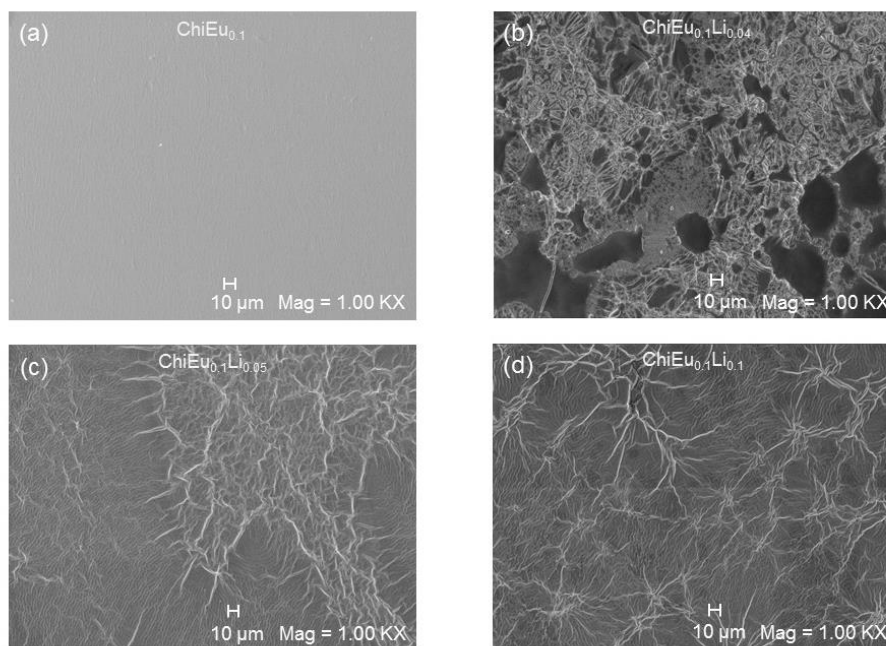


Figure 3. SEM micrographs of the $\text{ChiEu}_{0.1}$ (a) and $\text{ChiEu}_{0.1}\text{Li}_m$ for $m = 0.04$ (b), 0.05 (c) and 0.1 (d) samples.

Ionic conductivity of electrolytes

The ionic conductivities of various electrolyte compositions over the temperature range from 20 to 90 °C, and as a function of salt content are illustrated in Figure 4. These obtained results show a continuous variation in conductivity that is almost linear with respect to $1/T$ over a range of salt compositions. This plot demonstrates that all the doped samples exhibit a typical behavior for polymer electrolytes where hopping mechanism of ionic charge species is predominant. This behavior is similar to that exhibited by the same matrices doped with different salts³⁵⁻³⁷ and contrasts with that of semi-crystalline materials based on commercial polyethylene oxide (PEO) host

matrices.³⁸ The ionic conductivity (σ_i) values were calculated for each heating cycle using the relation of $\sigma_i = d/R_b A$, where R_b is the bulk resistance, d is the thickness and A is the area of the sample. As shown in Figure 4 (fittings) the ionic conductivity temperature dependence follows the Arrhenius equation of $\sigma_i = \sigma_0 \exp(-E_a/RT)$, where σ_0 , is the pre-exponential factor, E_a is the apparent activation energy for ion transport, R is the gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) and T is the temperature.

Table 2 and Figure 4 show the ionic conductivities (σ_i), and activation energy values (E_a), obtained from equation 1 and 2, respectively.

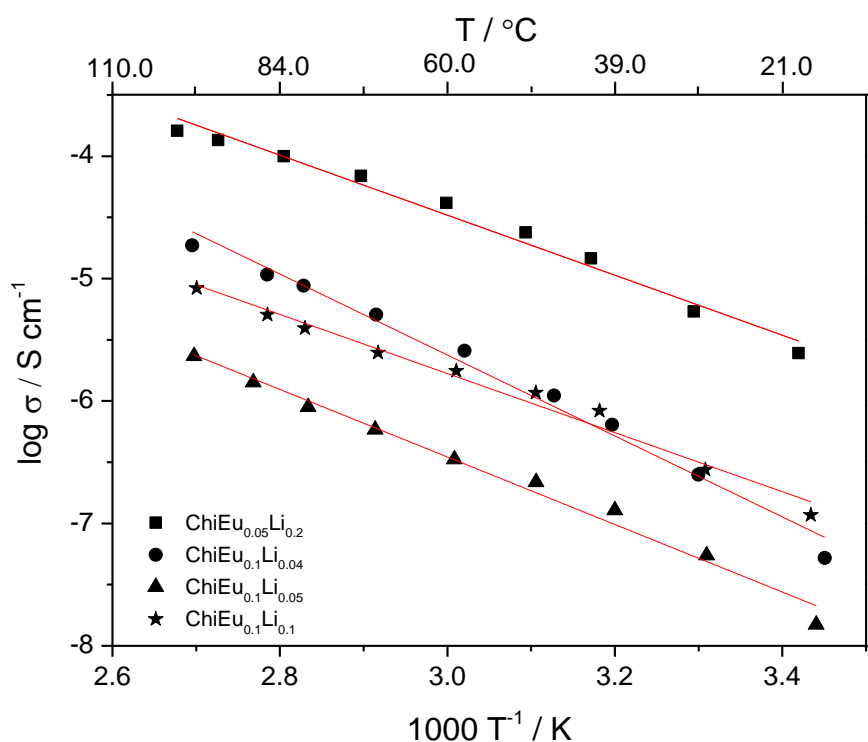


Figure 4. Conductivity plot of the ChiEu_nLi_m samples.

Table 2. Ionic conductivity and activation energy of the ChiEu_nLi_m samples.

Sample	Conductivity / S cm ⁻¹		E _a / kJ mol ⁻¹
	30 °C	80 °C	
ChiEu _{0.3}	1.58x10 ⁻⁸	3.33x10 ⁻⁶	92.17
ChiEu _{0.25}	1.56x10 ⁻⁶	7.57x10 ⁻⁵	64.92
ChiEu _{0.25} Li _{0.05}	3.14x10 ⁻⁸	4.47x10 ⁻⁶	84.11
ChiEu _{0.05}	1.74x10 ⁻⁷	3.45x10 ⁻⁶	57.18
ChiEu _{0.05} Li _{0.09}	6.66x10 ⁻⁸	1.04x10 ⁻⁶	46.56
ChiEu _{0.05} Li _{0.2}	5.38x10 ⁻⁶	8.77x10 ⁻⁵	46.93
ChiEu _{0.1}	1.57x10 ⁻⁷	1.73x10 ⁻⁵	74.38
ChiEu _{0.1} Li _{0.04}	1.79x10 ⁻⁷	8.48x10 ⁻⁶	63.30
ChiEu _{0.1} Li _{0.05}	4.42x10 ⁻⁸	9.07x10 ⁻⁷	52.81
ChiEu _{0.1} Li _{0.1}	2.32x10 ⁻⁷	3.89x10 ⁻⁶	46.20

Over the whole range of temperatures studied, the sample with the highest ionic conductivity is the ChiEu_{0.05}Li_{0.2} with values of 5.38 x 10⁻⁶ and 8.77 x 10⁻⁵ S cm⁻¹, at 30 and 80 °C, respectively. These values are higher than those obtained for analogous polymer electrolytes incorporating europium salt³¹ and very similar to those doped with lithium salts.³⁹ Besides temperature, ionic conductivity also depends strongly on the guest salt, both in type and concentration. Usually, increasing guest salt concentration results in an ionic conductivity increase, which is not at all observed in present study. A high amount of Eu(CF₃SO₃)₃ can play opposite effects. Although the number of charge carriers increased with the increase of salt amount, a high concentration of salt lead to the decrease of free volume, as well as available coordination sites. Additionally, the influence of ion pairing should also be taken into account. The fitted E_a values of all the SPEs are depicted in Table 2, where one can observe that most of E_a values decrease with the increase of ionic conductivity. This behaviour was normally expected, since the lower the energy barrier, the easier the ionic movement. This is probably due to the given reason above.

Photophysical properties

Figure 5 present the photoluminescence emission spectra of the representative sample ChiEu_{0.3} measured with excitation at different wavelengths. Besides the typical bands of Eu³⁺ corresponding to transitions from the excited state ⁵D₀ to lower lying ⁷F_J states, there is superimposed broad band whose energy in the blue-green spectral region is highly dependent on the chosen excitation wavelength. Similar broadbands have been observed for other bio-polymer hybrid electrolytes and their nature is attribute to the electron-hole recombination in the polymer host.^{9,40} At 360 and 394 nm there is concomitant excitation of the Eu³⁺ ion and the host. At 325 nm (30769 cm⁻¹) Eu³⁺ displays the small peak around 390 nm, also seen for excitations at 360 nm, which is a self-absorption related to radiative energy transfer. This peak was already observed in Eu³⁺-based di-ureasil samples⁴¹. The fact that intense emission from the ion is observed is due to host-ion energy transfer. This assumption is confirmed by examining the excitation spectrum in Figure 6, which was recorded by monitoring the europium emission at 616 nm. In this spectrum, not only the broad polymer band appears, confirming the host → ion energy transfer, but one can also see why excitation at 394 nm is preferable in Eu³⁺-doped systems to achieve higher emission intensities as seen in Figure 5. The fact that the ⁵D₀ → ⁷F₀ transition band displays only one, well defined, peak gives strong evidence that the Eu³⁺ ion occupies a sole site of symmetry in the SPE samples. Moreover, the high intensity of the hypersensitive transition ⁵D₀ → ⁷F₂ with respect to the purely magnetic dipole transition ⁵D₀ → ⁷F₁ indicates that such site is of low symmetry, with no inversion center.

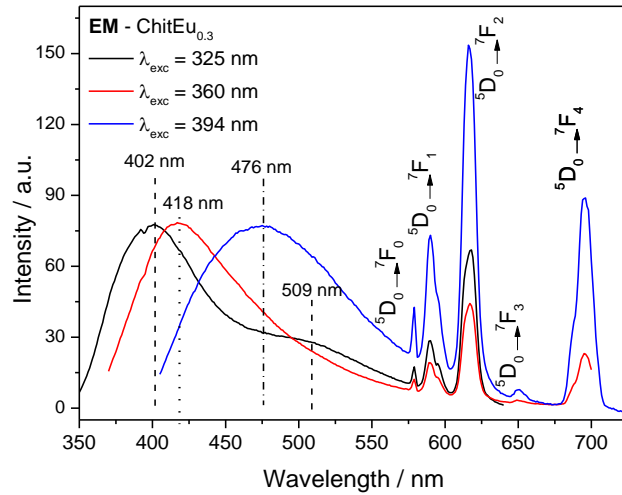


Figure 5. Emission spectra of the sample ChiEu_{0.3} with excitation at different wavelengths. The characteristic transitions of Eu³⁺ are indicated nearby the respective bands.

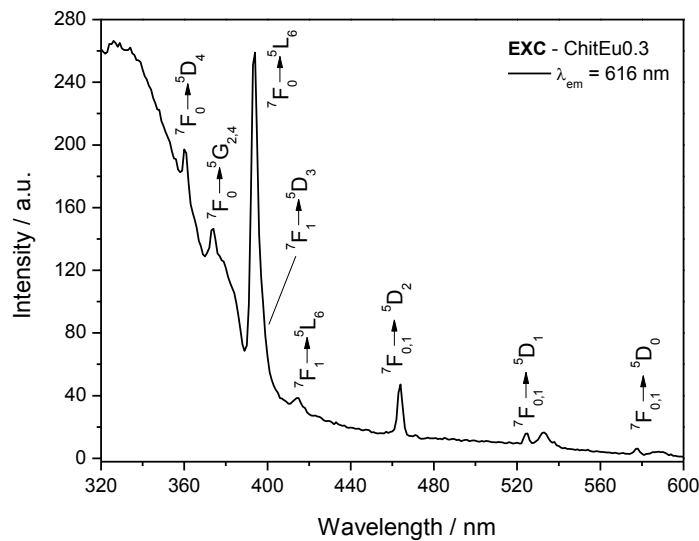


Figure 6. Excitation spectrum of the sample ChiEu_{0.3} measured by monitoring the emission at 616 nm. The characteristic transitions of Eu³⁺ are indicated by the respective bands.

The fact that the intense polymer emission accompanies that of Eu³⁺, even when excitation is done at 394 nm, suggests the combination of these bands to generate tunable visible (or white light).

In Figure 7, a comparison of emission intensities and lineshapes is made for samples co-doped with

Li⁺. It comes out as no surprise that no changes of relative intensities and lineshapes of Eu³⁺ bands, as a function of lithium concentration is observed. Still, a new functionality (PEs) is added and could potentially be combined with Eu³⁺-emission in a multifunctional material.

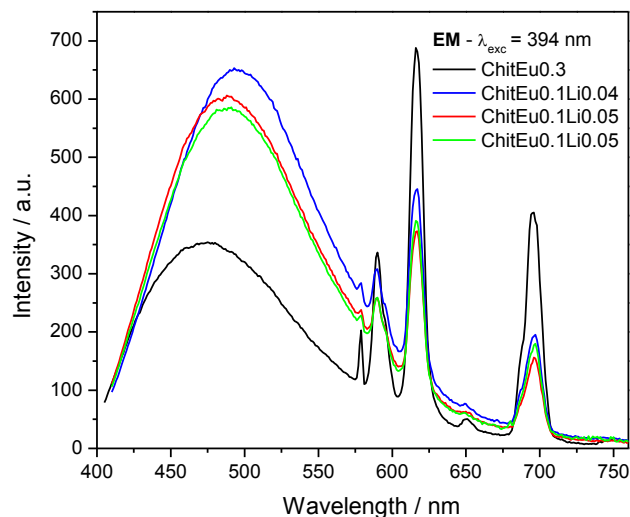


Figure 7. Comparison of emission spectra of samples doped with different amounts of Eu(CF₃SO₃)₃ and Li(CF₃SO₃)₃. All the spectra were measured with excitation at 394 nm.

In Figure 8, representative luminescence decay curves measured for the excited state ⁵D₀ by monitoring the emission at 616 nm (⁵D₀ → ⁷F₂) in different ChitEu_nLi_m samples are presented. Except for the sample with higher Li⁺ content, the curves could all be fitted with single exponential functions yielding the average lifetime values presented in Table 3. For comparison, the lifetime values were also calculated as the area below the curves and also by assuming the value when intensities drop by a factor 1/e, yielding very similar results. The lifetime values for the samples containing lithium are slightly higher than for the sample, which does not contain. The values are in the range of those determined for Eu³⁺-doped agar (194 μs), DNA (528 μs),⁹ and for poly(ε-caprolactone)/siloxane biohybrids (225 and 262 μs).⁴⁰ In the latter case, the higher value also corresponds to a sample where the Li⁺ concentration is higher indicating that it can be positively interfering (decreasing) the number of hydroxyl ions in the first coordination sphere of the RE ion.

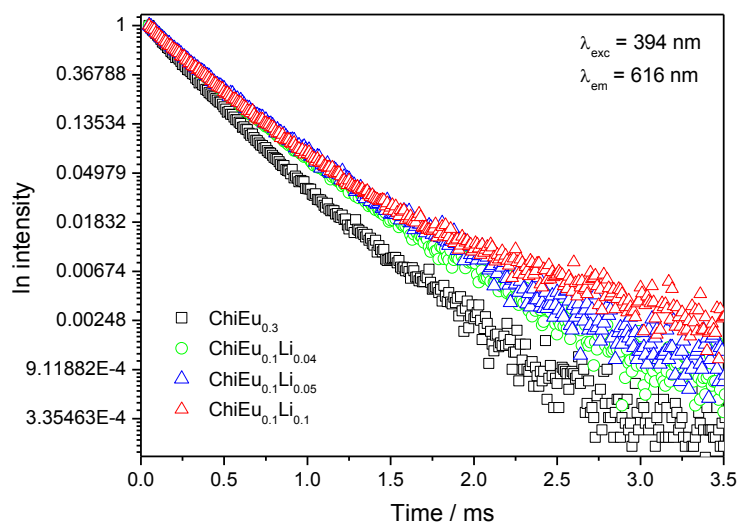


Figure 8. Fluorescence decay curves of ChiEu_{0.3} and ChiEu_{0.1}Li_n ($n = 0.04, 0.05, 0.1$ wt%) samples determined by single exponential fittings; $\lambda_{\text{exc}} = 394$ nm, $\lambda_{\text{em}} = 616$ nm.

By taking advantage of the concomitant emissions of polymer host and ion, and of the relative intensity variation depending on Eu^{3+} concentration and excitation wavelength, the colour tuning can be nicely achieved as indicated in Figure 9. In (a) the CIE chromaticity diagram presents the resultant colours for various ChiEu_mLi_n samples, where the ChiEu_{0.3} is almost placed at cross of $x = 0.3$ and $y = 0.3$ colour coordinates of CIE 1931 diagram (Fig. 9b). This sample has a blue colour and is closest one to the white point of this diagram. In Fig. 9(b) the resulting colours as a function of excitation wavelength are shown for this sample in comparison to that of ChiEu_{0.1}Li_{0.04}. The X- and Y-chromaticity coordinates are presented in Table 3 for all the samples, together with the quantum yield values φ , measured in an integrating sphere. The maximum φ value around 2.7 % is to be expected for Eu^{3+} inserted in an environment where hydroxyl groups can act as efficient luminescence quenchers. Still, the values are comparable to other polymer doped hosts⁴² and one way to increase efficiency would be to employ highly coordinated Eu^{3+} complexes for which quantum yields can be as high as 85 %.⁴³

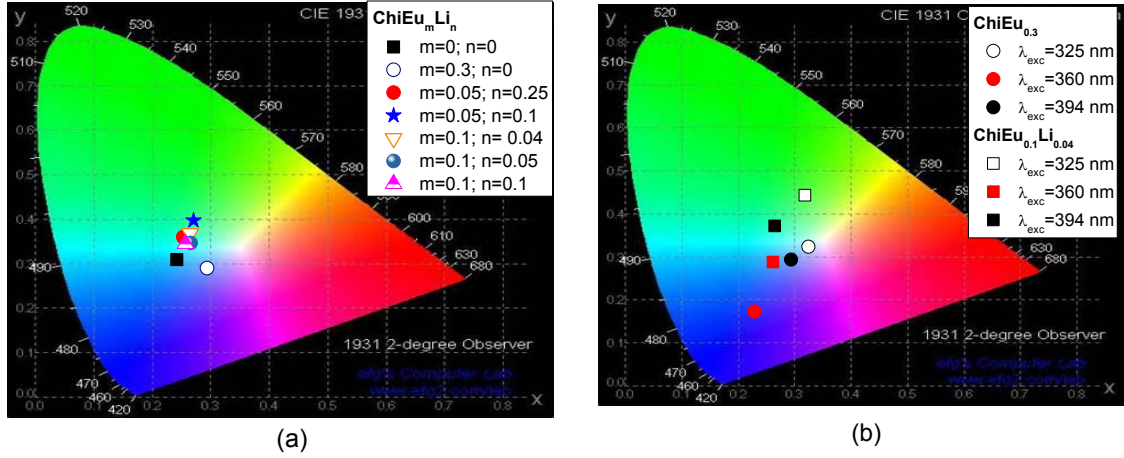


Figure 9. CIE chromaticity diagrams showing the (x,y) colour coordinates of emissions of ChiEu_mLi_n samples. (a) Dependence on Eu³⁺ and Li⁺ relative concentrations, $\lambda_{\text{exc}} = 394 \text{ nm}$; (b) Dependence on excitation wavelength for ChiEu_{0.3} sample.

Table 3. Experimental spectroscopic parameters of ChiEuLi_y samples (excited state ⁵D₀ lifetime τ , absolute quantum yields ϕ , CIE chromaticity coordinates (x and y)).

Sample	τ [⁵ D ₀] μs	ϕ $\pm 0.05 \%$	CIE x-coordinate	CIE y-coordinate
Chitosan	-	2.19	0.242	0.317
ChiEu _{0.3}	274	1.80 (394 nm)	0.294	0.298
		2.10 (360 nm)	0.229	0.176
		0.57 (325 nm)	0.325	0.328
ChiEu _{0.05} Li _{0.1}	341	2.24 (394 nm)	0.271	0.406
ChiEu _{0.05} Li _{0.25}	340	2.66 (394 nm)	0.253	0.368
ChiEu _{0.1} Li _{0.04}	344	2.40 (394 nm)	0.265	0.377
		0.32 (360 nm)	0.262	0.292
		0.71 (325 nm)	0.319	0.449
ChiEu _{0.1} Li _{0.05}	355	2.22 (394 nm)	0.260	0.354
ChiEu _{0.1} Li _{0.1}	351	2.30 (394 nm)	0.257	0.353

Conclusions

In this work we developed a novel luminescent and ion conducting biohybrid electrolyte doped with LiCF₃SO₃ and Eu(CF₃SO₃)₃ by means of the solvent casting method. The Gaussian-shaped broad X-

ray diffraction band confirms the predominantly amorphous nature of morphology of the SPEs studied here. Photophysical investigations indicate that by combining the emissions of the host matrix and the dopant Eu^{3+} ion it is possible to tune the final emission colour and also generate white light. Except for a small increase in europium $^5\text{D}_0$ lifetime values, the presence of Li^+ does not seem to interfere much with the emissive properties, but it does offer the perspective of further exploring these materials for multifunctional applications. The main benefit of this particular host-ions combination lies in the eco-friendly properties of the host (biodegradable, non-toxic) and biocompatible.

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