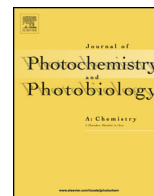




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Modulating the photoluminescence of europium-based emitting polymers: Influence of the matrix on the photophysical properties



Jose Garcia-Torres^{a,*}, Pau Bosch-Jimenez^b, Elena Torralba-Calleja^b, Manus Kennedy^c, Hind Ahmed^c, John Doran^c, David Gutierrez-Tauste^b, Llorenç Bautista^a, Monica Della Pirriera^b

^a Advanced Materials Lab, R+D Department, Leitat Technological Center, c/de la Innovació, 2, Terrassa 08225, Spain

^b Renewable Energies Lab, R+D Department, Leitat Technological Center, c/de la Innovació, 2, Terrassa 08225, Spain

^c Dublin Energy Lab, School of Physics, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

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ABSTRACT

A series of luminescent materials have been prepared by the ternary europium complex $\text{Eu}(\text{tta})_3(\text{phen})$ ($\text{tta} = 2\text{-thenoyltrifluoroacetate}$, $\text{phen} = 1,10\text{-phenanthroline}$) embedded into different polymer matrixes (polystyrene, poly(vinyl difluoride), poly(acrylonitrile) and poly(methyl methacrylate)) in order to investigate the effect of the polymer on the luminescent properties of the hybrid materials. Fourier transform infrared spectra (FTIR), UV/vis spectra, scanning electron microstructure (SEM) and luminescent properties of the europium complex and the hybrid materials are described in detail. In all cases, interaction between the polymer and the europium complex was observed from the above techniques. This interaction was strong enough to lead to a variation in the photoluminescent properties of the hybrid films: while poly(vinyl difluoride) doped polymers showed a reduce quantum yield ($\phi = 24\%$), a dramatic/significant enhanced in this parameter (ϕ up to 73%) was observed for the other materials in comparison with the ϕ value of the precursor complex (30.5%). This result may support the conclusion that while some polymers could interact with the complex, act as antennae and transfer energy to the central $\text{Eu}(\text{III})$ ion, other quench the luminescence of the complex. Based on this high ϕ , these films could be applied in top optical applications such as light-emitting diodes and/or active polymer optical fibers.

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1. Introduction

In recent years, the interest in lanthanide ions ($\text{Ln}(\text{III})$) and their complexes has increased because of their excellent luminescent properties such as narrow emission bands or long lifetimes [1,2], suitable for a wide range of applications: chemosensors, probes and labels in a variety of biological and chemical devices, tunable lasers, amplifiers for optical communications, luminescent probes for analyses, components of the emitting materials in multilayer organic light emitting diodes or efficient light conversion molecular devices [3–8], among others. Despite these interesting properties, lanthanide ions lack of practical applications because of two main drawbacks: (1) the low absorption coefficients because of the Laporte-forbidden $4f\text{--}4f$ transition which prevent direct excitation of the luminescent of the $\text{Ln}(\text{III})$ ions and (2) the efficient nonradiative deactivation of their excited states by high energy oscillators such as C–H, N–H or O–H bonds coming from solvent molecules [9]. In order to overcome these problems, a strategy has

been developed that involves the so-called *antenna effect* [10,11]. This effect is based on the sensitization of the lanthanide ions by suitable organic chromophores. These chromophoric ligands which chelate to lanthanide ions should be able to absorb and transfer energy efficiently to the central metal but also to encapsulate and protect the central ion from the solvent molecules [12,13]. In this sense, up to date research efforts have been mainly dedicated to the design of new ligands in order to increase the efficiency of ligand-to-metal transfer which in turn will impact on the performance of molecular devices. Among the most studied ligands, β -diketones has emerged as one of the important *antennas* because of the effectiveness of the energy transfer from this ligand type to the $\text{Ln}(\text{III})$ cation and so has been demonstrated by the high number of published papers in the engineering of new ligands to enhance photoluminescence properties of lanthanide complexes [14–19].

However, in recent years the research in this field has moved to the incorporation of these luminescent materials through chemical anchoring into different kinds of matrixes (organic, inorganic or organic/inorganic) because it has been observed that the matrix (1) confers chemical and thermal stability as well as mechanical resistance to the complex [20,21] and (2) improves the photoluminescence properties of the lanthanide complexes

* Corresponding author. Tel.: +34 93 788 23 00; fax: +34 93 789 19 06.

E-mail address: garcia.torres.jm@gmail.com (J. Garcia-Torres).

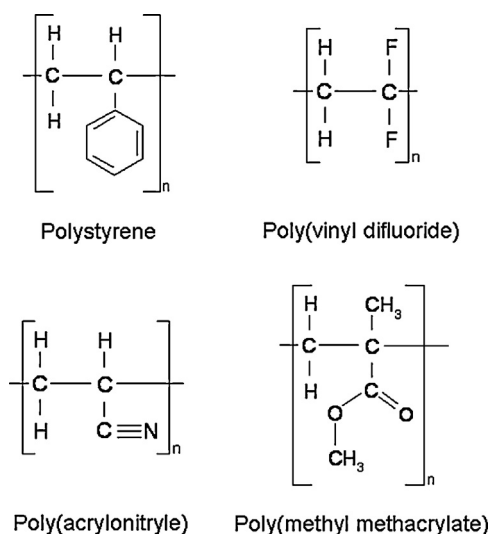


Fig. 1. Chemical structure of polystyrene (PS), poly(vinyl difluoride) (PVDF), poly(acrylonitrile) (PAN) and poly(methyl methacrylate) (PMMA) polymers.

[22,23]. However, less effort has been dedicated to the study of composite materials where the lanthanide complex is physically encapsulated into the host. In this sense, the objective of the present paper is to prepare different lanthanide complex/polymer hybrid materials in order to enhance the luminescent properties and discuss the effect of the interaction between the host matrix and the lanthanide complex molecules in terms of infrared and UV/vis spectroscopies on both the microstructure and the photophysical properties of these hybrids. Among the different lanthanide complexes developed, in this study the authors have shown their interest in the (1,10-phenantroline)tris(2-thenoyltrifluoroacetato)europium(III) complex ($\text{Eu}(\text{tta})_3(\text{phen})$) because of its excellent photoluminescent properties [24–28]. On the other hand, polymers are ideal candidates to be used as a matrix because they possess attractive features such as mechanical strength, flexibility, ease of processing and low cost. In this study, the polymers that will be used as a host are polystyrene (PS), poly(vinyl difluoride) (PVDF), poly(acrylonitrile) (PAN) and poly(methyl methacrylate) (PMMA) which chemical structure is shown in Fig. 1. As illustrated in this figure, it can be clearly seen that these polymers have a simple structure and are quite similar just differing on the pendant groups. It is expected that the different substituents (phenyl, fluor, cyano and ester) will differently interact with the Eu(III) ions and hence will modify the luminescent properties of the resulting hybrid materials.

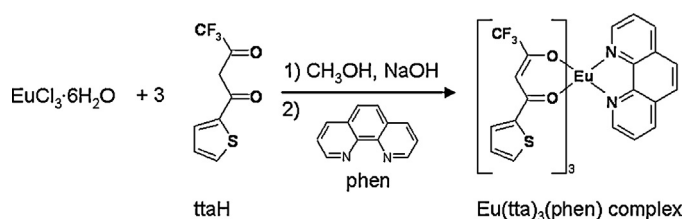
2. Experimental

2.1. Materials

Europium chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%, Sigma–Aldrich), 2-thenoyltrifluoroacetone (ttaH, Fluka) and 1,10-phenantroline (phen, >99%, Sigma–Aldrich), polystyrene (PS) (Sigma–Aldrich, $M_w = 350,000$), poly(vinyl difluoride) (PVDF) (Sigma–Aldrich, $M_w = 275,000$), poly(acrylonitrile) (PAN) (Sigma–Aldrich, $M_w = 150,000$) and poly(methyl methacrylate) (PMMA) (Sigma–Aldrich, $M_w = 350,000$) were used as received. All the solvents and chemicals used were of analytical reagent grade.

2.2. Synthesis of $\text{Eu}(\text{tta})_3(\text{phen})$ complex

The $\text{Eu}(\text{tta})_3(\text{phen})$ was synthesized by the reaction of europium chloride with thenoyltrifluoroacetone (ttaH) in the presence of a



Scheme 1. Synthesis of (1,10-phenantroline)tris(2-thenoyltrifluoroacetato)europium (III) ($\text{Eu}(\text{tta})_3(\text{phen})$) complex. ttaH = 2-thenoyltrifluoroacetone, phen = 1,10-phenantroline.

base in methanol, followed by the addition of 1,10-phenantroline (phen) (Scheme 1) [29]. Typically, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (550 mg, 1.5 mmol) and thenoyltrifluoroacetone (850 mg, 3.8 mmol) were dissolved in separate flasks containing 20 ml and 25 ml of methanol, respectively. The ttaH solution was then added dropwise to the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ solution under stirring conditions during 30 min. The pH of this solution was adjusted to 8 by adding drop by drop a NaOH saturated methanol solution. The resulting solution was stirred again during 30 min. After that, the phenantroline ligand (220 mg, 1.2 mmol) was added to the europium solution. The resulting solution was left in the fume cupboard until precipitation. $\text{Eu}(\text{tta})_3(\text{phen})$ is a white solid with a poor solubility in methanol and therefore precipitates from the solution. The solid obtained was filtered off by a Büchner funnel, washed with methanol and dried under vacuum conditions. The synthesis yield was 80%. Elemental analysis (%): Anal. Calcd. for $\text{C}_{36}\text{H}_{20}\text{N}_2\text{O}_6\text{S}_3\text{F}_9\text{Eu}_1$ (995.71): C, 43.43; H, 2.02; N, 2.81; S, 9.66. Found: C, 43.22; H, 2.04; N, 2.92; S, 9.55. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 10.24 (s, 2H), 10.16 (s, 2H), 9.51 (s, 2H), 8.49 (s, 2H), 6.96 (s, 3H), 6.51 (s, 3H), 6.20 (s, 3H), 3.15 (s, 3H). The ^1H NMR spectra are available in the Supplementary Data (Fig. S1).

2.3. Synthesis of $\text{Eu}(\text{tta})_3(\text{phen})$ /polymer hybrid films

Hybrid films were prepared by physical entrapment of the $\text{Eu}(\text{tta})_3(\text{phen})$ complex into the polymer matrix. The good solubility of Eu(III) complex in organic solvents is favorable for its deposition by drop casting from solution. 1 g of the polymer was dissolved in 75 ml of the corresponding solvent under stirring. Table 1 summarizes the solvents and the conditions at which the different polymers employed were dissolved. After that, 10 mg of the europium complex were added to the polymer solution and stirred until the complex was completely dissolved and the solution was homogeneous. The homogeneity was checked by placing the solution under the UV lamp. A homogeneous red emission distribution throughout the whole solution was observed. A given volume of the resulting solution was spread on a microscopic glass slide and the solvent was allowed to evaporate. The deposition was performed over a restricted area ($3 \text{ cm} \times 2 \text{ cm}$) by using a mask in order to control the film thickness. Moreover, the substrate was weighted before and after film deposition in order to calculate the thickness. An analytical balance with a sensitivity of $\pm 0.01 \text{ mg}$ (5 decimal number balance) was used to weight the samples. The final thickness of all the films was around $2 \mu\text{m}$ and the total amount of the Eu(III) complex in the hybrid material was 1 wt.%. For the fabrication of the hybrid films, the glass substrates were cleaned with acetone and sonicated during 10 min. Then glasses were washed with isopropanol and sonicated again during 10 min. The cleaned substrates were washed with ethanol and then dried with compressed air.

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