Polymer matrix sensitizing effect on photoluminescence properties of Eu^{3+}-β-diketonate complex doped into poly-β-hydroxybutyrate (PHB) in film form

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In this work is reported the sensitization effect by polymer matrices on the photoluminescence properties of diaquatris(thenoyltrifluoroacetonate)europium(III), [$Eu(tta)_3(H_2O)_2$], doped into poly-β-hydroxybutyrate (PHB) with doping percentage at 1, 3, 5, 7 and 10% (mass) in film form. TGA results indicated that the Eu^{3+} complex precursor was immobilized in the polymer matrix by the interaction between the Eu^{3+} complex and the oxygen atoms of the PHB polymer when the rare earth complex was incorporated in the polymeric host. The thermal behaviour of these luminescent systems is similar to that of the undoped polymer, however, the T_{onset} temperature of decomposition decreases with increase of the complex doping concentration. The emission spectra of the Eu^{3+} complex doped PHB films recorded at 298 K exhibited the five characteristic bands arising from the $^5D_0 \rightarrow {}^7F_J$ intraconfigurational transitions ($J = 0$–4). The fact that the quantum efficiencies η of the doped film increased significantly revealed that the polymer matrix acts as an efficient co-sensitizer for Eu^{3+} luminescent centres and therefore enhances the quantum efficiency of the emitter $^5D_0$ level. The luminescence intensity decreases, however, with increasing precursor concentration in the doped polymer to greater than 5% where a saturation effect is observed at this specific doping percentage, indicating that changes in the polymeric matrix improve the absorption property of the film, consequently quenching the luminescent effect.

Introduction

Nowadays, the trivalent rare earth ions (RE^{3+}) are extensively employed in the development of luminescent materials for exhibiting monochromatic emission colours owing to their intrinsic optical properties. The essence of electronic spectroscopy of RE^{3+} ions is associated with their characteristic narrow emission bands arising from the intraconfigurational 4f–4f transitions and long lifetimes, which make these ions unique among the luminescent coordination compounds. Eu^{3+} ion is widely used in photoluminescent materials because of its narrow emission bands resulting in monochromatic red emission colour; the main excited state is the $^5D_0$ level separated from the ground terms ^7F_J (J = 0–6) by around 12000 cm^{-1}; long lifetimes of the emitter $^5D_0$ level (ms); and large Stokes shift, among other factors.[1,2]

Eu^{3+} complexes have been routinely applied in the development of efficient light conversion molecular devices (LCMDs), assuming high efficiency in the sequence of strong absorption of ligand, energy transfer from ligand to Eu^{3+} ion, and finally emission from the emitter $^5D_0$ level of the metal ion.[3] In the design of highly luminescent RE^{3+} complexes containing organic moieties, those with β-diketonate ligands are the most investigated among the RE^{3+} coordination compounds in recent years.[4,5] The great importance in research on the luminescence properties of RE^{3+} complexes is mainly attributed to their widespread applications such as medical diagnosis, electroluminescence, triboluminescence, optical markers and even laser materials.[6–9]

It has always been a challenging task for research communities to develop a simple and attractive method for creating highly luminescent materials for optical devices and applications that combines the intrinsic luminescent properties of lanthanide ions and the unique physical and chemical properties of polymers and plastics. Although there have been several works reported in the literature on photoluminescence properties of polymer systems doped with RE^{3+} complexes,[10–16] no literature has been reported on luminescence studies of systems containing PHB polymer doped with rare earth complexes. Poly-β-hydroxybutyrate (PHB) is a polymer which has similar physical properties to polypropylene (PP), suggesting its potential applications as wrappings, containers, plastic mouldings, *etc*. In addition, PHB is an environment friendly material owing to its biodegradable properties which make it an advantageous material as the host structure in luminescent devices. There is a considerable increase in research relating to biodegradable materials;[17,18] however, photoluminescent biodegradable materials and their potential applications are still not widely studied.

In this work, the synthesis, characterization and luminescent properties of PHB polymer films doped with an

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Eu^{3+}-β-diketonate complex precursor, diaquatris(thenoyltrifluoroacetonate)europium(III), [Eu(tta)$_3$(H$_2$O)$_2$], at 1, 3, 5, 7, and 10% (mass) are reported. The goal of this work is to develop a simple and feasible method for luminescent material production, hence to obtain information about the photoluminescence behaviour of the optical material prepared in polymer film form. The sensitization effect of the polymer matrices on the Eu^{3+} luminescent centre is discussed in detail based on excitation and emission spectra, luminescence decay curves, experimental intensity parameters and emission quantum efficiencies.

Experimental

2-Thenoyltrifluoroacetone (1.33 g; 6 mmol) was dissolved in 30 mL of ethanol. NaOH (1 N; 6 mL) and a solution of $EuCl_3 \cdot 6H_2O$ (0.73g; 2 mmol) in 10 mL of water were successively added to the solution. Water (200 mL) was added and the mixture was heated to 60 °C for a few minutes. The complex precipitated during cooling to room temperature.[1] The precipitate was filtered off then washed with water and dried in vacuum. Yield: 1.53 g (90%).

Poly-β-hydroxybutyrate was supplied in powder form by Usina da Pedra PHB do Brazil S.A. (Serrana-SP, Brazil) and had an weight average molecular weight (M_w) of 380 000 g mol^{-1}, with PHB accounting for 99.9% of the dry material. The PHB polymer was doped with this Eu^{3+} complex in the proportions of 1, 3, 5, 7 and 10% (w/w). The PHB powder was dissolved in chloroform followed by addition of the required amount of the Eu^{3+} complex in chloroform solution. The mixed solution was heated at 40 °C for 30 min then the polymer film was obtained after the evaporation of excess solvent at 60 °C.[11]

Carbon and hydrogen contents were determined by usual microanalytical procedures using an elemental analyzer model CHN 2400 (Perkin-Elmer).

Thermogravimetric analyses (TGA) were achieved with a TG/SDTA 822 thermobalance (Mettler-Toledo), using sapphire crucibles containing around 10 mg of the sample, under dynamic nitrogen atmosphere (50 mL min^{-1}), at a heating rate of 10 °C min^{-1}.

The infrared absorption spectra of the samples were measured by using a Bomem model MB102 FTIR spectrophotometer in the range 4000–400 cm^{-1}.

The excitation and emission spectra of the powdered and film samples were recorded in a SPEX Fluorolog-2 spectrofluorometer, model FL212 system, 450 W xenon lamp as excitation source and double grating 0.22 m SPEX 1680 monochromators. All spectra were recorded using a detector mode correction. The luminescence decay curves of the emitter levels were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorometer. The luminescence instruments were fully controlled by a DM3000F spectroscopic computer program and the spectral intensities were automatically corrected for the photomultiplier response.

Results and discussion

The C and H contents determined by elemental analytical methods for the Eu^{3+} complex agreed with the formula [Eu(tta)$_3$(H$_2$O)$_2$]; calculated for $Eu_1O_8C_{24}H_{16}F_9S_3$ was: C, 33.85%; H, 1.89% and found: C, 33.75%; H, 1.96%. The Eu^{3+} content was estimated by complexometric titration with EDTA in methanol solution.[19]

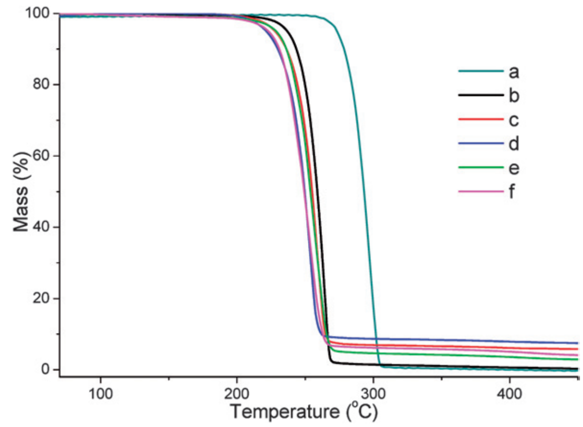

Fig. 1 Thermogravimetric curves of undoped PHB (a) and PHB : x% Eu(tta)$_3$ doped films where x = 1 (b), 3 (c), 5 (d), 7 (e) and 10 (f). All these curves were recorded in an inert atmosphere of N_2.

Fig. 1 shows thermogravimetric curves of samples in film form of PHB polymer and PHB doped with the Eu^{3+} complex at a ratio of 1, 3, 5, 7 and 10% (w/w) recorded under an inert atmosphere of N_2. It is shown in Fig. 1a that the undoped PHB polymer film decomposes in a one step event under thermal degradation and its decomposition starts at 281 °C. Similarly, the samples of PHB polymer doped with the Eu^{3+} complex also presented curves of decomposition under an inert atmosphere with only one decomposition event (Fig. 1b–f). As indicated in Fig. 1, the doped PHB films exhibit decreasing onset temperatures of decomposition (T_{onset}) of 245, 243, 240, 237 and 236 °C with increasing doping percentages of 1, 3, 5, 7 and 10%, respectively. The maximum displacement of T_{onset} was 45 °C for the PHB : 10% Eu(tta)$_3$ system in comparison to that of the undoped polymer film.

As can be seen, the TG curves (Fig. 1) recorded in the temperature interval from 25 to 200 °C exhibited no mass loss event. This reveals that the water molecules coordinated to the Eu^{3+} ion of the dihydrate complex precursor are absent after the doping reaction process. When the [Eu(tta)$_3$(H$_2$O)$_2$] complex is embedded into the PHB polymer matrix, the coordination of the two water molecules is replaced by the interaction between the Eu^{3+} complex and the oxygen atoms of the PHB polymer, in agreement with the results of other polymer systems previously analyzed.[20]

The displacement of the C=O stretching band from 1665 cm^{-1} for the free tta ligand to 1608 cm^{-1} in the IR spectra of the compounds provides good evidence that the metal ion is coordinated through the oxygen atoms. Besides, this band presents increasing intensity with increased doping concentration from 1 to 10%. The broad absorption band assigned to the H_2O vibrational modes in the [Eu(tta)$_3$(H$_2$O)$_2$] complex precursor spectrum identified in the 3500–3200 cm^{-1} region (ν_s and ν_{as} OH) are absent for the PHB : x% Eu(tta)$_3$ systems confirming that the polymer films are anhydrous. Fig. 2 illustrates in a schematic way how the europium complex is coordinated to the polymer backbone.

Fig. 3 shows the excitation spectra of the polymer doped with the Eu(tta)$_3$ complex at different doping concentrations (1, 3, 5, 7

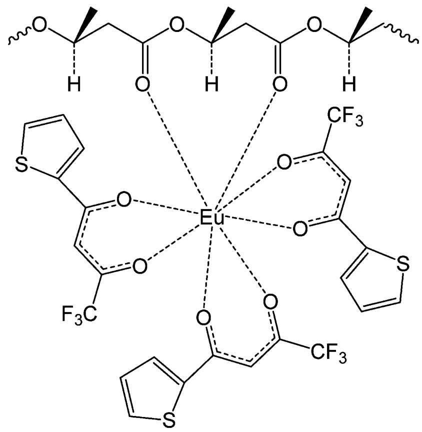

Fig. 2 A schematic illustration of the structure of $Eu(tta)_3$ complex doped in polymer.

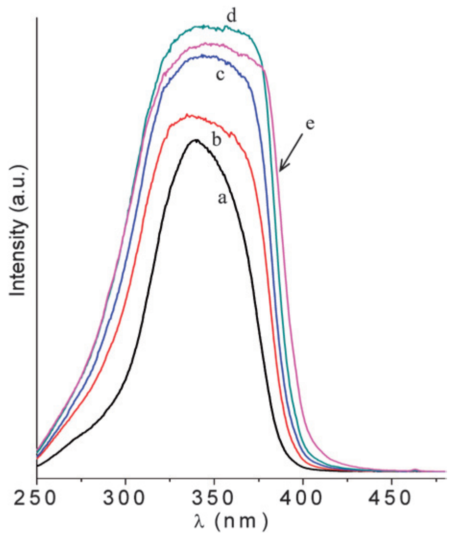

Fig. 3 Excitation spectra of PHB : x% $Eu(tta)_3$ polymer film systems recorded at 298 K, under emission monitored at 613 nm: a) $x = 1$; b) $x = 3$; c) $x = 5$; d) $x = 7$ and e) $x = 10$.

and 10%) recorded at 298 K in the spectral range of 250 to 480 nm, by monitoring the emission at 613 nm. As shown in Fig. 3a–e, the spectral region from 250 to 420 nm is dominated by an intense broad band which is assigned to the polymer absorption and subsequent efficient intramolecular energy transfer to the Eu^{3+} ion. Furthermore, the typical intra-configurational transitions are absent in these excitation spectra, owing to efficient energy transfer from the organic moiety to the metal ion. These facts suggest the polymer matrices serve as efficient co-sensitizers for the Eu^{3+} ions.

The emission spectra of the undoped PHB polymer and PHB : 5% $Eu(tta)_3$ films recorded at 298 K in the range from 360 to 730 nm under excitation at 338 nm are shown in Fig. 4a and b, respectively. The absence of the broad polymer emission band in the doped film indicates highly efficient energy transfer *via* the polymer matrix to the Eu^{3+} ion and therefore confirms the polymer matrix acts as co-sensitizer in the photoluminescence process. The inset in Fig. 4 shows a a picture of the PHB : 5%

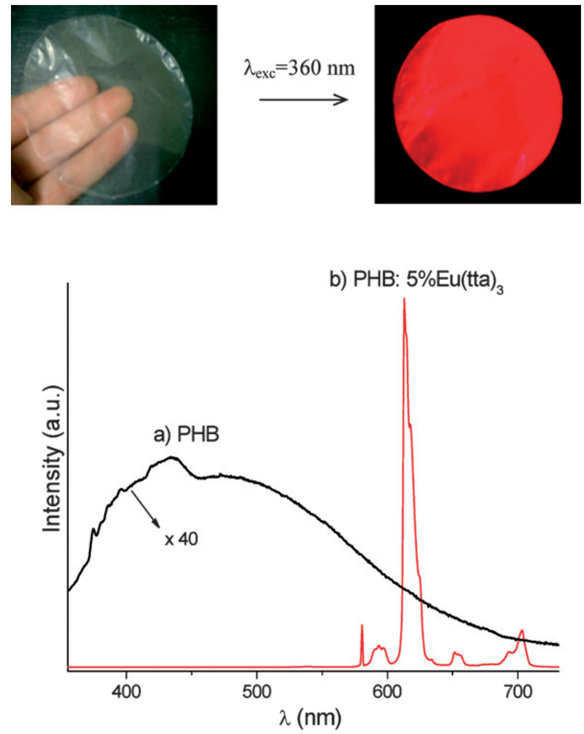

Fig. 4 Emission spectra recorded at 298 K, under excitation monitored at 338 nm: a) undoped PHB film (amplified 40 times) and b) PHB : 5% $Eu(tta)_3$ film. The inset shows the red emission colour of the film when irradiated with an ultraviolet lamp at 365 nm.

$Eu(tta)_3$ polymer film. The polymer material is a homogeneous transparent thin plastic film and displays strong monochromatic red emission under the irradiation of an ultraviolet lamp with wavelength at around 365 nm.

In Fig. 5 are exhibited emission spectra of PHB : x% $Eu(tta)_3$ systems where a) $x = 1$; b) $x = 3$; c) $x = 5$; d) $x = 7$ and e) $x = 10$, recorded at 298 K under excitation at 338 nm. These spectral data present five emission bands assigned to the characteristic $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions of the Eu^{3+} ion. The transition of highest intensity is dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition around 612 nm, indicating that the rare earth ion is not found in a site with inversion centre symmetry. In addition, the presence of only one sharp peak in the region of the $^5D_0 \rightarrow {}^7F_0$ transition at 580 nm suggests the occurrence of a single chemical environment around the Eu(III) ion of symmetry type C_s, C_n or C_{nv}.

The luminescence decay curves of doped films were obtained by monitoring the emission at the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (613 nm) and excitation at the $^7F_0 \rightarrow {}^5L_6$ transition (394 nm). These data were adjusted with a first-order exponential decay function and the lifetime values (τ) of the emitter $^5D_0$ level of the doped systems were determined and are listed in Table 1. All τ values of doped polymer systems are higher than that of the hydrated Eu^{3+}complex indicating that radiative processes are operative in all the doped polymer films due to the absence of multiphonon relaxation by coupling with the OH oscillators from the $[Eu(tta)_3(H_2O)_2]$ complex.

The emission quantum efficiency (η) of the emitter $^5D_0$ level of the europium ion is determined on the basis of the emission spectra and lifetimes. The emission intensity, I, taken as the

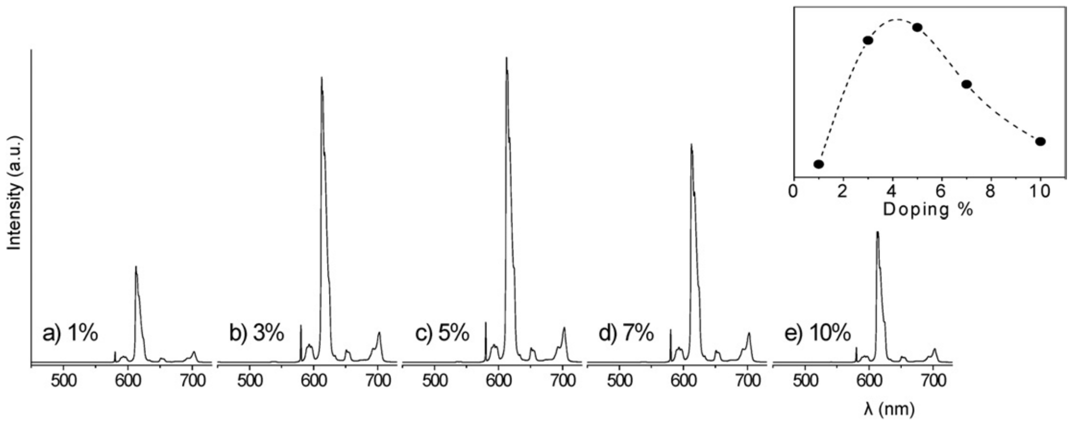

Fig. 5 Emission spectra of PHB : x%Eu(tta)$_3$ polymer film systems recorded at 298 K, under excitation at 338 nm: a) $x = 1$; b) $x = 3$; c) $x = 5$; d) $x = 7$ and e) $x = 10$. The inset demonstrates concentration quenching observed by monitoring the intensity of the $^5D_0 \rightarrow {}^7F_2$ intraconfigurational transition at 613 nm of Eu^{3+} ions doped into polymer films at different concentrations.

Table 1 Experimental intensity parameters (Ω_λ), emission quantum efficiencies (η), lifetimes (ms), radiative (A_{rad}), nonradiative (A_{nrad}) and total (A_{total}) emission coefficient rates for samples of PHB films with different doping percentages (at 1, 3, 5, 7 and 10%) and [Eu(tta)$_3$(H$_2$O)$_2$] complex,[1,11] based on emission spectra recorded at 298 K

%	$\Omega_2/10^{-20}$ cm^2	$\Omega_4/10^{-20}$ cm^2	A_{rad}/s^{-1}	A_{nrad}/s^{-1}	A_{total}/s^{-1}	τ/ms	η (%)
1	33.5	7.5	1161	1229	2390	0.418	49
3	37.5	8.3	1291	1305	2596	0.385	50
5	39.7	8.5	1359	1278	2637	0.379	52
7	39.6	8.7	1356	1451	2807	0.356	48
10	40.7	8.8	1391	1578	2969	0.337	47
[Eu(tta)$_3$(H$_2$O)$_2$]	33.0	4.6	923	2923	3846	0.260	29

integrated intensity S of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) emission curve, is given by:

$$I_{i-j} = \hbar\omega_{i-j}A_{i-j}N_i \approx S_{i-j} \quad (1)$$

where i and j are the initial ($^5D_0$) and final levels ($^7F_{0-4}$), respectively, $\hbar\omega_{i-j}$ is the transition energy, A_{i-j} is the Einstein coefficient of spontaneous emission, and N_i is the population of the emitter $^5D_0$ level.[21] The $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transitions must be neglected as they are not experimentally detected.[11] Since the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is insensitive to the chemical environments around the Eu^{3+} ion, it is considered as a reference for the whole spectrum. Consequently, the experimental coefficients of spontaneous emission, A_{0J}, were determined by the following equation:

$$A_{0J} = A_{01}\left(\frac{I_{0J}}{I_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0J}}\right) \quad (2)$$

where ν_{01} and ν_{0J} are the baricentres of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_J$ transitions, respectively.[22,23] Lifetime (τ), radiative (A_{rad}) and nonradiative (A_{nrad}) transition rates are related through the equation:

$$A_{tot} = \frac{1}{\tau} = A_{rad} + A_{nrad} \quad (3)$$

where A_{rad} can be obtained by summing over the radiative rates A_{0J} for each $^5D_0 \rightarrow {}^7F_J$ transition $A_{rad} = \sum_J A_{0J}$. Assuming that only nonradiative and radiative processes are essentially involved in the depopulation of the $^5D_0$ state, η can be expressed as:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \quad (4)$$

On the other hand, the experimental intensity parameters (Ω_2 and Ω_4) were determined from the emission spectra of Eu^{3+} ion in Fig. 5 based on the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions and the $^5D_0 \rightarrow {}^7F_1$ as the reference, and are estimated according to the following equation:[1]

$$A = \frac{4e^2\omega^3}{3\hbar c^3}\frac{1}{2J+1}\chi\sum_\lambda \Omega_\lambda\left\langle {}^5D\|U^{(\lambda)}\|{}^7F_J\right\rangle^2 \quad (5)$$

where $A_{0\lambda}$ is the coefficient of spontaneous emission, ω is the angular frequency of the transition, e is the electronic charge, $\hbar$ is Planck's constant over 2π, c is the velocity of light, χ is the Lorentz local field correction that is given by $n(n^2 + 2)^2/9$ with the refraction index $n = 1.5$, and $\langle {}^5D_0\|U^{(\lambda)}\|{}^7F_J\rangle^2$ values are the square reduced matrix elements whose values are 0.0032 and 0.0023 for $J = 2$ and 4, respectively.[20] The Ω_6 intensity parameter was not included in this study since the $^5D_0 \rightarrow {}^7F_6$ transition is not observed.

The radiative contributions (A_{rad}) for the depopulation of the emitter $^5D_0$ level were determined in order to verify the photoluminescence properties of the doped films and consequently their emission quantum efficiencies. All the η values of the doped polymer films are higher than that of the Eu^{3+} complex (η = 29%),[11] indicating that the polymeric matrix presents a luminescence sensitizer effect in the energy transfer process from the organic moiety to the Eu^{3+} ion.[24]

By monitoring the relative intensity of the $^5D_0 \rightarrow {}^7F_2$ intra-configurational transition of Eu^{3+} peak at 613 nm, as shown in Fig. 5 inset, it is observed that the 5% doped polymer present emission bands of higher intensities than films with other doping concentrations. Among these doped polymer films, the one with 5% doping concentration also presented the highest value of quantum efficiency (η = 52%; Table 1). In contrast, PHB : 10% $Eu(tta)_3$ presents the smallest value of η = 47% among the doped systems owing to the highest value of nonradiative contribution (A_{nrad} = 1578 s^{-1}), in spite of its highest value of radiative contribution (A_{rad} = 1391 s^{-1}). These results suggest that the nonradiative processes are responsible for the concentration quenching that occurred in polymer films with higher than 5% doping concentration of Eu^{3+} complex.

The experimental intensity parameters (Ω_2 and Ω_4) for the doped polymer films and $[Eu(tta)_3(H_2O)_2]$ complex are listed in Table 1. Large values of Ω_2 are observed and can be validated as a consequence of two concurrent factors. The first one is the symmetry around the Eu^{3+} ion, allowing the appearance of all odd-rank components in the noncentrosymmetric ligand field. The other factor is related to the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion,[3] suggesting that a dynamic coupling mechanism is operative and the chemical environment around the metal ion is highly polarizable.

As can be seen in Fig. 6, the emission spectrum of PHB : 5% $Eu(tta)_3$ polymer film under excitation at 338 nm assigned to the maximum absorption of the polymer system shows higher emission intensity than the emission spectrum recorded at 394 nm assigned to the $^7F_0 \rightarrow {}^5L_6$ transition of the Eu^{3+} ion. These spectral data indicate that beyond immobilizing the Eu^{3+} ions among matrices, the polymer also acts as sensitizer of the system which greatly enhances the luminescence of the Eu^{3+} ion. This result corroborates with the increased values of quantum efficiencies for the doped systems compared with hydrated Eu^{3+}complex (Table 1).

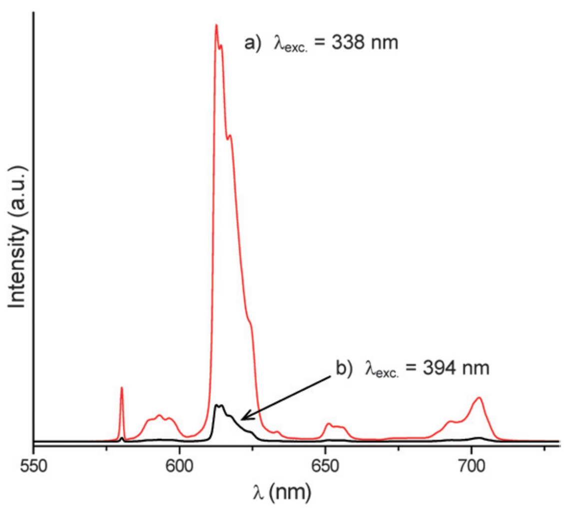

Fig. 6 Emission spectra of PHB : 5% $Eu(tta)_3$ polymer film recorded at 298 K: a) under excitation at the maximum absorption wavelength of the broad band from the PHB polymer (λ_{ex} = 338 nm) and b) excitation monitored at the $^7F_0 \rightarrow {}^5L_6$ transition of the Eu^{3+} ion (λ_{ex} = 394 nm).

Conclusion

The thermal behaviour of PHB polymer films doped with $[Eu(tta)_3(H_2O)_2]$ complex and undoped PHB film is similar; however, the onset temperature of decomposition decreases with increasing complex concentration. IR data indicate that the Eu^{3+} complex is anchored in the PHB polymeric network by the coordination of the carbonyl oxygen atoms of the host polymer matrix towards the Eu^{3+} ions.

The excitation spectra of PHB doped with the Eu^{3+} complex demonstrated strong absorption of the organic moiety in the ultraviolet range (250–500 nm) followed by highly efficient intramolecular energy transfer to the Eu^{3+} ion. The emission spectra exhibited the characteristic narrow bands arising from the intraconfigurational $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0–4) of the rare earth ion. The absence of the broad emission band of the polymer in the doped system indicated that the energy transfer *via* the polymer matrix to the Eu^{3+} ion is highly efficient, suggesting that the polymer matrix acts as a photoluminescent sensitizer.

Large values of the Ω_2 experimental intensity parameter indicate the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transitions and the Eu^{3+} ions are in a highly polarizable chemical environment. In addition, the higher values of quantum efficiency of the emitter $^5D_0$ level for the doped polymer films with respect to that of the hydrated complex confirmed the effect of luminescent sensitization induced by the polymer matrices. The highest value (η = 52%) was obtained for the PHB : 5% $Eu(tta)_3$ system; however, concentration quenching occurred when the precursor doping percentage exceeded 5%. In conclusion, the PHB : x% $Eu(tta)_3$ system presents characteristics and acts as an efficient light conversion molecular device (LCMD).

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