

Photo- and Electroluminescent behavior of Eu^{3+} Ions in Blends with Poly(vinyl-carbazole)

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Foi sintetizado o complexo tris(tenoiltrifluoracetato)(2,2'-bipiridina)europio(III), $\text{Eu}(\text{tta})_3\text{bipy}$, e suas características luminescentes foram avaliadas. A emissão de blendas deste complexo com poli(9-vinil carbazol) (PVK-Eu), variando a composição do $\text{Eu}(\text{tta})_3\text{bipy}$ de 1% até 8% em massa ($\text{Eu}(\text{tta})_3\text{bipy}/\text{PVK}$, m/m), apresentou picos de fotoluminescência em 425 nm e 613 nm, com intensidades dependentes da composição da blenda. Dispositivos emissores de luz (LED's) de dupla camada, com configuração ITO/PEDOT-PSS/blends/Ca-Al apresentaram emissão de luz vermelha com voltagem mínima de 9 V e pico máximo em 617 nm; eficiência na luminescência foi de 0.04 cd A^{-1} . Medidas resolvidas no tempo indicaram que a microestrutura da matriz polimérica não afetou as propriedades eletro-ópticas das blendas.

The complex tris(thenoyltrifluoroacetate)(2,2'-bipyridine)europium(III), $\text{Eu}(\text{tta})_3\text{bipy}$, was synthesized and assessed for luminescence behavior. The emission of its blends with poly(9-vinyl carbazole) (PVK-Eu), varying in composition from 1 to 8% ($\text{Eu}(\text{tta})_3\text{bipy}/\text{PVK}$, m/m) showed PL at 425 nm and at 613 nm, with intensities which depended on the blend composition. Double-layer LED devices with configuration ITO/PEDOT-PSS/Blend/Ca-Al emitted red light with turn-on voltages of 9 V and emission maxima at 617 nm; its luminance efficiency was 0.04 cd A^{-1} . Time resolved measurements indicated that the microstructure of the matrix had practically no effect on the electro-optical properties of the blends.

Keywords: europium, PVK, electroluminescence

Introduction

The synthesis of appropriate electroluminescent polymers and of small organic molecules for the construction of RGB displays (designation for red, green and blue) is still a challenge,¹ because full color displays require pure hues and the luminescent compounds typically present spectra with wide emission, due to vibronic progression.²

In the red part of electromagnetic spectra filtering is usually necessary to sharpen the emission, because the human eye has a lower sensitivity in this region. Therefore, is important to minimize the loss in emission efficiency brought about by the broadening due to vibronic or transfer processes.³ In this context organic complexes of the trivalent europium ion (Eu^{3+}) are strong candidates to application in red light emission devices due to their high fluorescence at

613 nm, with essentially monochromatic emission, which minimizes the need for filtering. These systems also provide an enhanced theoretical yield. As is well known, spin statistics dictate that the singlet states which fluoresce provide a 25% maximum yield, whereas in these complexes with organic ligands, the quantum yield could reach 100%. However, this theoretical value is not actually attained due to phosphorescence quenching in intramolecular energy transfer processes.²⁻⁴ The electronic transitions of lanthanides result from different electronic distributions of 4f orbitals that are effectively shielded from external influence by the overlap of $5s^2$ and $5p^6$ orbitals.^{2,3,5}

The interaction of Eu^{3+} ions with organic molecules and derived complexes have been well studied. The behavior of the ion in relation to polymer chains has been addressed by some authors,⁶⁻¹⁰ particularly when solution and solid state properties are involved. Intramolecular energy transfer in lanthanide coordination compounds and their use in electroluminescent devices have been recently explored.¹¹⁻¹³

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In this contribution we present some results related to the photophysical behavior of molecular complexes of Eu^{3+} in solution and film form in the presence of poly(9-vinyl carbazole) (PVK). The electroluminescent properties of the blends are also discussed.

Experimental

Equipment

The complexes and the polymer were characterized by FTIR spectrometry and the data compared with the literature. Samples for FTIR measurements were prepared as KBr disks, the spectra were taken in a Biorad Excalibur Series spectrophotometer, FTS 3500 GX, in the spectral range of 400-4000 cm^{-1} , with resolution of 2 cm^{-1} and 32 scans. Absorption spectra were obtained using a Shimadzu UV 2401 PC, in THF solution and in film form. Fluorescence spectra were obtained using a spectrophotometer Shimadzu RF 5301 PC, in THF solution and in film form. Thermogravimetric analyses (TGA) were made on a Netzsch TG209 cell system with a TGA 2950 thermogravimetric analyzer at a heating rate of 20 $^{\circ}\text{C min}^{-1}$ and under a nitrogen flow rate of 15 mL min^{-1} . Differential scanning calorimetry (DSC) was performed using the Netzsch equipment series 204 F1 with a heating rate of 10 $^{\circ}\text{C min}^{-1}$, under dry nitrogen flux of 15 mL min^{-1} in the range 25-300 $^{\circ}\text{C}$.

Film and device fabrication

Film

Optical properties in solid state were studied in cast films from THF solutions onto quartz plates, in appropriate thickness to obey Beer's law.

OLED

A hole injection layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) (Bayer Corporation) was first spin-coated on top of the ITO (OFC Corporation, 20 ohms sq^{-1}), then dried at 100 $^{\circ}\text{C}$ for 1 h under vacuum. Solutions of polymer (20 mg mL^{-1} in chloroform) were filtered through 0.2 1/4 m Millex-FGS Filters (Millipore Co.) and were then spin coated onto PEDOT:PSS layer under nitrogen and speed 2000 rpm. Calcium layer (thickness *ca.* 400 nm) was evaporated onto the polymer at about 10^{-7} Torr, followed by a protective coating of aluminum. The devices were characterized using a system described elsewhere.¹⁴ The final configuration of the LED was ITO/PEDOT:PSS/blend/Ca/Al.

Time-resolved luminescence measurements

Luminescence spectra and luminescence decays were recorded with a Thermo Laser Science. VSL-337ND-S (Oriol 79070) pulsed nitrogen laser ($\lambda_{\text{em}} = 337.1 \text{ nm}$; < 4 ns Full-Width at Half-Maximum, FWHM) for the photoexcitation of the sample; a 1/4 m Oriol Cornerstone 260 emission monochromator for the spectral resolution of the luminescence emission, coupled to an Oriol 74063 diffraction grating (0.15 nm max. resolution at 546.1 nm, 1200 lines mm^{-1} , blaze at 350 nm), an Oriol mod. 59470 (Schott GG385) color glass filter to block the excitation light at the micrometer-driven entrance slit, and an Oriol 77348 fast (2.2 ns rise-time) side-on photomultiplier tube set to -600 V or -700 V at the micrometer-driven exit slit, for acquisition of the organic emission or europium emission, respectively. The entrance and exit slitwidth were set to 50 μm and 5 μm , respectively, to reach a 0.4 nm spectral resolution. A Tektronix TDS3032B (300 MHz, 2 channels, 2.5 GSamples s^{-1}) Digital Oscilloscope terminated to 255 Ω or 10 k Ω , was used to detect the organic emission or europium emission, respectively, with 500 points for each decay curve. With these settings, the measured RC time constants of the instrumentation, for acquisition of the organic emission or europium emission, were 15.94 ns and 642.0 ns, respectively.

Reagents

All reagents were purchased from Aldrich, Acros, Synth or VETEC. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Tetrahydrofuran (THF): First, the THF was dried with CaH_2 and distilled. It was further dried and fractionally distilled from sodium under a nitrogen atmosphere.⁶ Ethanol (Synth, 99,5% PA ACS) was distilled over calcium hydride under a nitrogen atmosphere.

Poly(9-vinyl carbazole) (PVK) (Aldrich, $M_w = 1.100.000 \text{ kg mol}^{-1}$), 2,2'-bipyridine (Acros, 99+%), tris(thenoyltrifluoroacetate)europium(III) trihydrate, $\text{Eu}(\text{tta})_3 \cdot 3(\text{OH}_2)$ (Acros, 95%), potassium bromide (KBr spectroscopic grade Acros, 99%), calcium hydride (CaH_2 Acros, 93%) calcium chloride (CaCl_2 , Vetec PA, 96%), were used as received.

Syntheses of tris(thenoyltrifluoroacetate)(2,2'-bipyridine) europium(III) complex ($\text{Eu}(\text{tta})_3\text{bipy}$)

Tris(thenoyltrifluoroacetate)europium(III) trihydrate, $\text{Eu}(\text{tta})_3 \cdot 3(\text{OH}_2)$, (0.4 g, 0.46 mmol) and 2,2'-bipyridine (0.1 g, 0.64 mmol), were refluxed for 4 hours in 20 mL absolute ethanol. The light yellow powder formed was

filtered and recrystallized in 30 mL of a mixture of EtOH/THF (1/1). The yield was 215 mg (43%) of Eu(tta)₃bipy. mp (°C): 221-223. FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1627, 1605, 1537, 1411, 1320, 1189, 1140, 792, 642. UV-Vis $\lambda_{\max}/\text{cm}^{-1}$: 268, 288, 344. NMR ¹H at 298 K (200 MHz, CDCl₃) δ_{H} (ppm): 13.86, 9.86, 8.55, 7.00, 6.53, 6.23; TGA (maximum rate of weight loss at, °C): 321.^{10,16,17}

Poly(9-vinyl-carbazole) and tris(thenoyltrifluoroacetate) (2,2'-bipyridine) europium(III) (PVK-Eu) blends

The blends were prepared from the Eu(tta)₃bipy complex and PVK by mixing the appropriate solutions in THF in the following ratios: 1, 2, 4 and 8% (Eu(tta)₃bipy/PVK, m/m) which were designated as B₀ (0% Eu³⁺, pure PVK), B₁ (1% Eu³⁺), B₂ (2% Eu³⁺), B₄ (4% Eu³⁺) and B₈ (8% Eu³⁺).

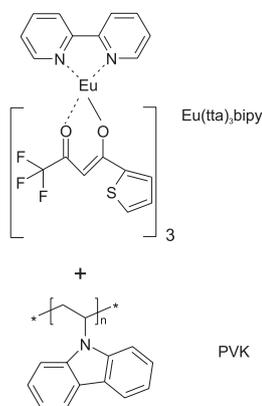


Figure 1. Materials used in the blends.

Results and Discussion

The materials involved in blend preparation are illustrated in Figure 1. To obtain red emission, an efficient energy transfer from the PVK to the europium salt is needed. From Figure 2 it can be seen that this condition is fulfilled, due to the good overlap between PVK emission and Eu(tta)₃bipy complex absorption.

The FT-IR spectral region comprised between 1750-500 cm⁻¹ of the blends is displayed in Figure 3. A progressive increase in the absorptions of the europium complex bands between 1630 and 1550 cm⁻¹ (ν C=O diketone, ν C=C aryl rings and ν C=N bipyridine ring), in 1411 cm⁻¹ (ν C-O diketone), in 1320 cm⁻¹ (ν C-N bipyridine ring), 1189 cm⁻¹ (ν C-F tta ligand), and 792 cm⁻¹ (ν C-S tta ligand) is observed, as expected, with increasing amounts of the complex in the blends. A sharp endotherm was present in the DSC thermogram of the europium complex at 221-223.°C (lit. 224 °C). These results along with the ¹H NMR and TGA profile, atested that the desired complex structure was obtained, with the necessary purity.

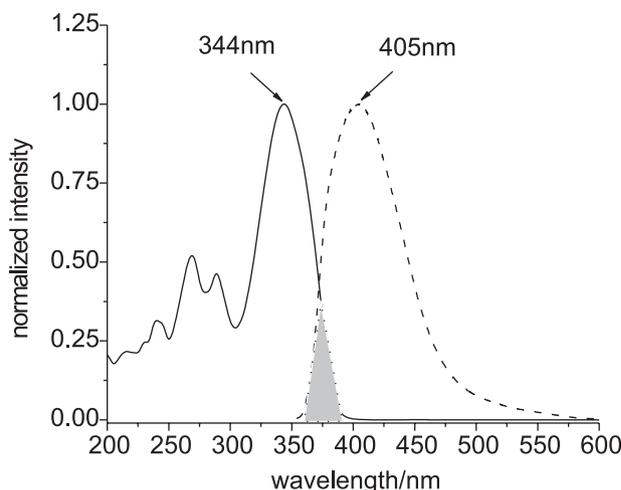


Figure 2. Absorption spectra of Eu(tta)₃bipy complex (—) and solid state emission of PVK (----). The gray area represents the spectral overlap.

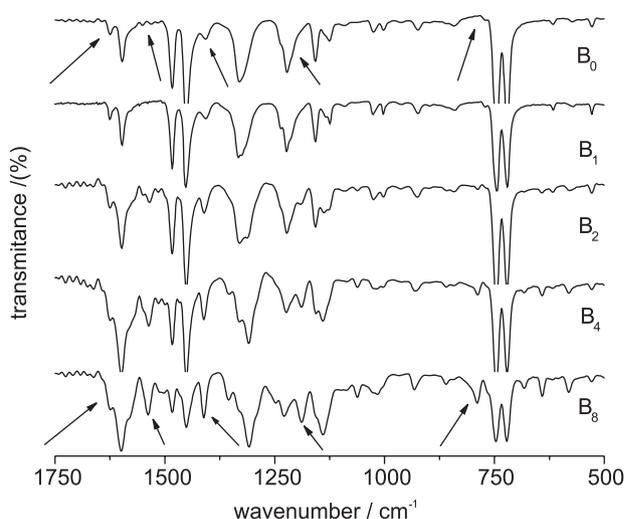


Figure 3. FTIR spectra of PVK and PVK-Eu blends: B₀ stands for pure PVK, B₁, B₂, B₄ and B₈ for blends containing 1%, 2%, 4% and 8% of Eu(tta)₃bipy respectively. The bands assigned with arrows are commented in the text.

Photophysical characterization of PVK-Eu blends

Spectroscopy in solution

The photophysical study was performed in the UV-Vis region using THF solutions (0.1 mg blend mL⁻¹ THF). The absorption spectra of PVK, of Eu(tta)₃bipy and of the blends in THF solution are shown in Figure 4. Apart from the intrinsic differences among the absorption profiles it can be assumed that no changes in the electronic ground state or aggregate formation have occurred. On the other hand, the fluorescence emission spectra collected with excitation at 344 nm revealed progressive changes as shown in Figure 5.

For pure PVK the emission is centered at 375 nm, and for pure Eu(tta)₃bipy at 613 nm, and the results of Figure 5 show that in solution, all the blends present incomplete

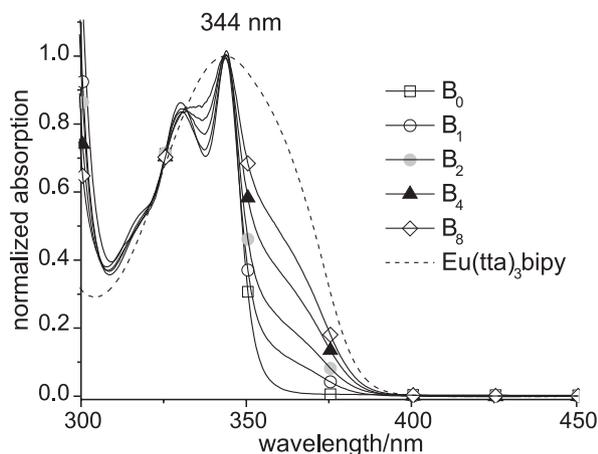


Figure 4. Absorption spectra of PVK and PVK-Eu blends: B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively. PVK and PVK-Eu blends in THF solutions ($0.1 \text{ mg blend mL}^{-1}$ THF) and $\text{Eu}(\text{tta})_3\text{bipy}$ ($10^{-4} \text{ mol L}^{-1}$ solutions in THF).

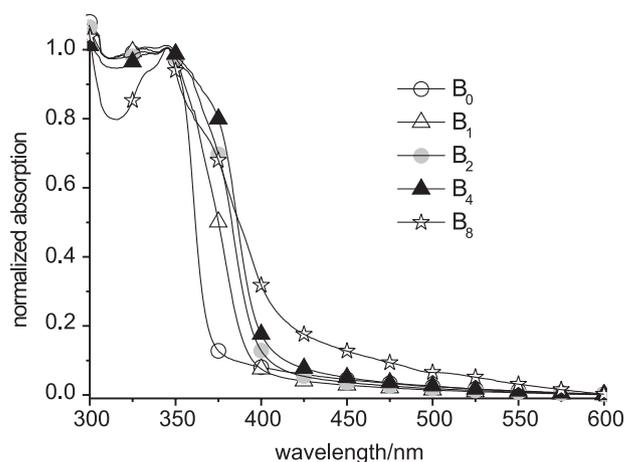


Figure 6. Absorption spectra of PVK and PVK-Eu blends in the solid state (film form): B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively.

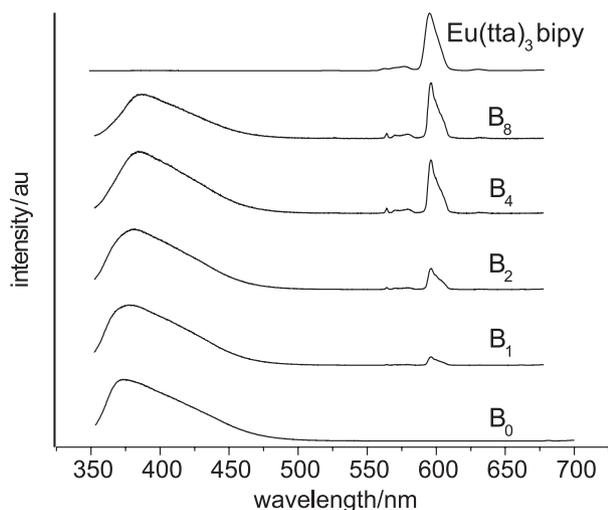


Figure 5. Emission spectra of PVK and PVK-Eu blends in THF solutions ($0.1 \text{ mg blend mL}^{-1}$ THF) and $\text{Eu}(\text{tta})_3\text{bipy}$ ($10^{-4} \text{ mol L}^{-1}$) with λ_{exc} in 344 nm: B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively.

energy transfer, since both emission peaks were present in the spectra relative to every component ratio.

Spectroscopy in the solid state

The absorption profiles of cast films did not show any difference from those taken in solution, with the absorption peaking at 344 nm, Figure 6. The emission spectra, on the other hand, had some new features, Figure 7. The polymeric matrix emission showed a redshift to 405 nm, attributed to excimer formation¹⁸ and was not seen in concentrations of Eu^{3+} higher than 2%. As compared to the solution behavior described above, a more efficient energy transfer has taken place in the solid state.¹⁹

There is no conclusive explanation for the complete transfer in the solid state but not in solution. It has been suggested that the solvent could act as an alternative non-radiative channel for triplet state decay, involving a spin-orbit coupling with solvent molecules lowering the efficiency of the transfer process.²⁰

Electroluminescence characterization of the PVK-Eu blends

The turn on voltage, the electroluminescent peak and the device efficiency for each blend composition are presented in Table 1 and the corresponding EL spectra are depicted in Figure 8. Two findings are relevant here: the small redshift seen for the most concentrated blends, and the complete absence of PVK

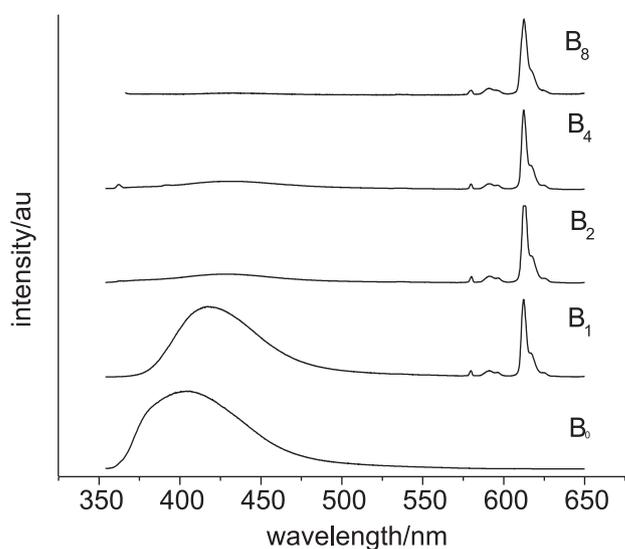


Figure 7. Photoluminescence spectra of PVK and PVK-Eu blends in the solid state (film form): B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively.

emission, noting however that in the film photoluminescence a subtle curvature could be seen at the PVK emission. These observations can be attributed to the different excitation mechanisms. In EL the ion can be directly excited, whereas in PL the emission depends of energy transfer from the ligand. In any case, the transfer from PVK is complete in EL emission; the most relevant feature of these devices.^{3,21,22} The redshifted emission of the pure PVK (B_0 in Figure 8) was attributed to the luminescence of aggregate species as ground state and/or excimers as noted before in the literature.²³ The occurrence of related forms deriving from the interaction of the complex with the matrix could not be detected, and needs more detailed work to be clarified. Devices built with the complex alone were unstable and it was not possible to get any information about their behavior with the LED configuration used.

Table 1. EL $\lambda_{\text{max}}^{\text{EL}}$, turn on voltage and luminance for PVK-Eu blends

Blend	$\lambda_{\text{max}}^{\text{EL}} / \text{nm}$	Turn-on Voltage / V	Luminance Efficiency / (cd A^{-1})
B_1	607	7	3×10^{-2}
B_2	607	9	6×10^{-3}
B_4	614	9	1.3×10^{-2}
B_8	617	9	4×10^{-2}

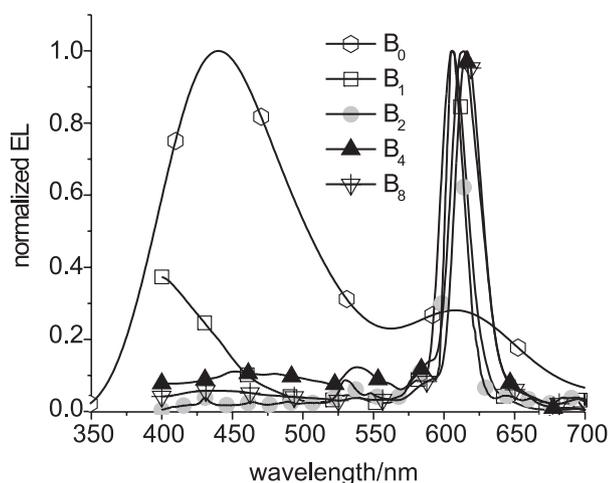


Figure 8. EL spectra of the PVK and PVK-Eu blends: B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively. The diode configuration: ITO/PEDOT:PSS/blend/Ca/Al.

The relationships between current vs. EL intensity and vs. voltage are shown in Figure 9. The turn on voltages are in the 7–9 V range (Table 1), and the highest emission intensity was observed for the B_8 sample (8% m/m Eu^{3+}) as found for the film photoluminescence, peaking at 617 nm, with a brightness of

66 cd m^{-2} at 17 V at a current density of 250 mA cm^{-2} . It is noteworthy that the blend containing 1% Eu^{3+} (B_1) presented a more intense EL emission than the blends with 2 and 4% (B_2 and B_4). A plausible explanation for this effect is that in B_1 , the luminescence comes from both PVK and from the complex, whereas in the other blends, only the ion is the emitting species. Beyond that point, the intensity increases with the amount of the complex in the blends.

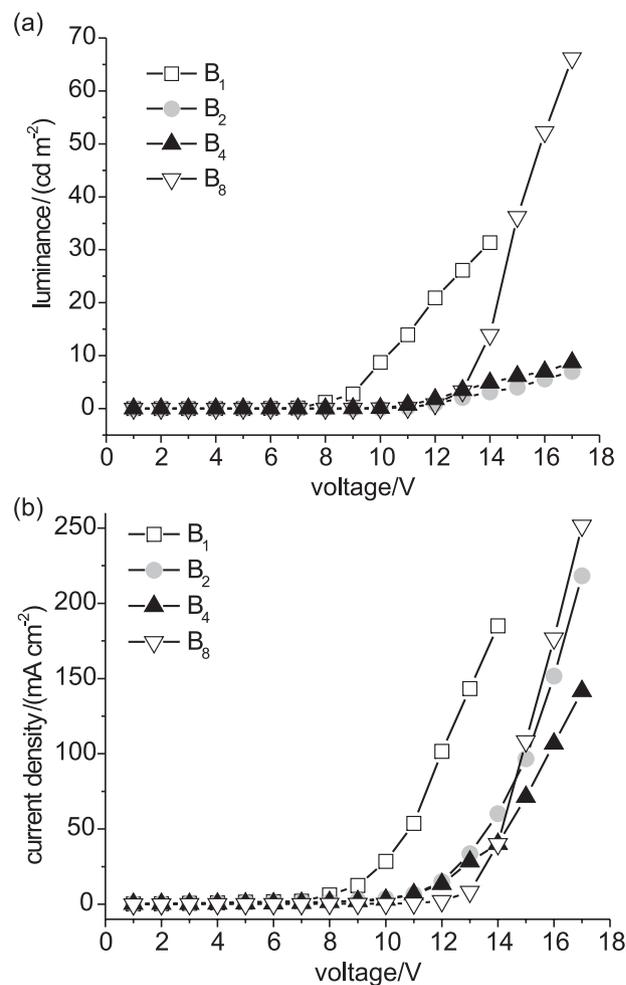


Figure 9. (a) Luminance versus voltage; (b) Current density versus voltage: B_0 stands for pure PVK, B_1 , B_2 , B_4 and B_8 for blends containing 1%, 2%, 4% and 8% of $\text{Eu}(\text{tta})_3\text{bipy}$ respectively.

Excited state lifetime measurements and time-resolved photoluminescence spectra of the blends PVK-Eu

The determination of the excited state lifetimes (τ) of the PVK-Eu blends was performed to investigate if the polymeric matrix interfered with the optical properties of the ion. In Figure 10 the fluorescence emission spectra of the blends in the region 570–640 nm are shown, together with the corresponding decay curves, and that of the pure Eu^{3+} complex as well.

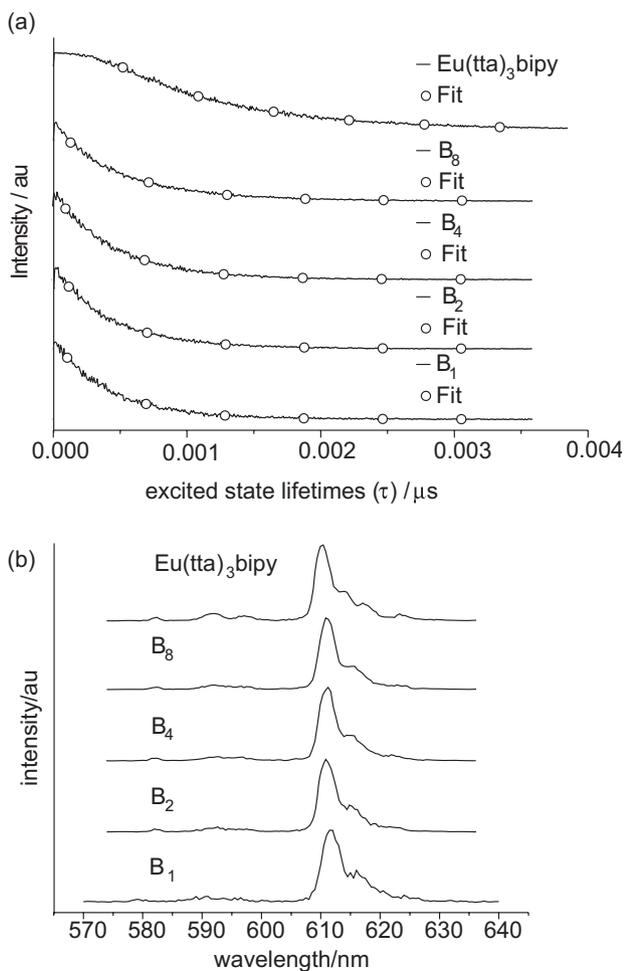


Figure 10. Decay curves (line) and exponential fit (circles) (a); Emission spectra for the samples (b): B₁, B₂, B₄ and B₈ for blends containing 1%, 2%, 4% and 8% of Eu(tta)₃bipy respectively.

The time-resolved emission spectra of the Eu(tta)₃bipy complex showed the highest intensity in the range 608–630 nm, which corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition. A $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition with higher intensity than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole could be due to the absence of a center of symmetry in the complex,²⁴ and also to the enhancement of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive transition by means of covalency of the ion and ligands. This was observed in the case of hydrated β -diketonate Eu(tta)₃(OH)₂ complex,^{25,26} where the Judd-Ofelt Ω_2 intensity parameter indicated that the Eu³⁺ ion are embedded in highly polarizable chemical environment. Higher values for Ω_2 intensity parameter have been reported when the water molecules in such complex are replaced by another ligands, and this has been ascribed to the enhancement of local asymmetry around the vicinity of europium.²⁷

However, for the Eu(tta)₃.nL complexes dispersed in poly(methylmethacrylate) (PMMA), the Ω_2 values are nearly the same when the synergetic L ligands are

substituted by others. The authors, therefore, assume that the chemical microenvironment is mainly controlled by the three tta⁻ ligands when Eu³⁺ ions are chelated with synergetic ligands in PMMA host. In our case, the relative intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions are kept nearly the same with the dispersion of the Eu(tta)₃bipy complex into PVK matrix, indicating that the Eu³⁺ ions are experiencing similar microenvironments in PVK.

The lifetimes extracted from the decay curves are shown in Table 2. It was observed that τ increases with the Eu³⁺ content in the blend, which can be attributed to an energy migration process among the Eu³⁺ complexes.

Table 2. Excited state lifetimes (τ , in μs), the associated error, the goodness-of-fit value (reduced chi-square, χ_r^2) of the regression and the emission peaks for the studied transition

Compound	τ / μs	Error in τ / μs	χ_r^2	$^5\text{D}_0 \rightarrow ^7\text{F}_2$ / nm
B ₁	421	+/- 3.46	0.993	611.5
B ₂	428	+/- 2.94	0.995	611.5
B ₄	454	+/- 2.75	0.997	611.9
B ₈	507	+/- 3.34	0.996	611.7
Eu(tta) ₃ bipy	909	+/- 7.68	0.996	610.8

Conclusions

The complex tris(thenoyltrifluoroacetate)(2,2'-bipyridine)europium(III), Eu(tta)₃bipy was prepared, showing PL at 613 nm. The emission of its blends with poly(9-vinyl carbazole), (PVK-Eu) varying in composition from 1 to 8% (Eu(tta)₃bipy/PVK, m/m) showed PL at 613 nm and at 425 nm, with intensities which depended on the blend composition. The two most concentrated blends showed no blue emission, because of complete energy transfer from PVK to Eu³⁺. The EL emission originated only by from the Eu³⁺ dopant at all blend compositions. Time resolved measurements indicate that the microstructure of the matrix had practically no effect on the electro-optical properties of the blends.

Acknowledgments

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