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Study of energy transfer in polymer blends of TFB: P3HT

Estudo da transferência de energia em blendas poliméricas de TFB: P3HT

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Abstract

In order to study the optical properties of TFB polymer and its blend with P3HT polymer, absorption and photoluminescence (PL) measurements were performed for both polymers, and for a blend, TFB: P3HT (95:05), deposited on glass slides using the spin coating technique. Different solvents were used to prepare the samples in order to compare the effects that they might have on the emission and energy transfer between the polymers. Decay time measurements were performed, to find out if this parameter changes in the TFB prepared with different solvents, and also in the presence of P3HT. The photoluminescence measurements of the polymers show no change in the emission of these polymers as we change the solvents used in the preparation of the solutions. However, for the blend there is a change in energy transfer between the polymers depending on the solvent, which shifts the emission color of the sample for the blue or red. On the photoluminescence spectra of the blend an emission in 575 nm, which did not appear in the TFB and P3HT samples is observed. From the decay time measurements, we observed that the 575 nm emission has a long decay time, compatible with the emission by isolated molecules.

Keywords: Energy transfer. Absorption. Photoluminescence. Photoluminescence time decay.

Resumo

Com o objetivo de estudar as propriedades ópticas do polímero TFB, e de sua blenda com o polímero P3HT, foram realizadas medidas de absorção e fotoluminescência (PL) para ambos polímeros, e de uma blenda TFB:P3HT (95:05), depositados sob lâminas de vidro, pela técnica de deposição por centrifugação. Foram utilizados diferentes solventes na preparação das amostras, a fim de comparar os possíveis efeitos dos mesmos na emissão e transferência de energia entre os dois polímeros. Medidas de tempo de decaimento foram realizadas para verificar se esse parâmetro se altera para o TFB preparado a partir de diferentes solventes, e quando na presença de P3HT. Os resultados das medidas de fotoluminescência dos polímeros isolados mostram que não há mudança na forma da emissão desses polímeros conforme se alteram os solventes utilizados no preparo das soluções. Entretanto, no caso da blenda, ocorre mudança na transferência de energia entre os polímeros, dependendo do solvente, deslocando a cor de emissão da amostra para o azul ou vermelho. No espectro de fotoluminescência da blenda é observada uma emissão em 575 nm, a qual não aparece na fotoluminescência das amostras do TFB e P3HT isolados. A partir das medidas de tempo de decaimento, vimos que, nas amostras de TFB, não há alteração considerável com a mudança do solvente. Já para a blenda, nota-se que a presença do P3HT faz com que o tempo de decaimento do TFB diminua, especialmente quando o solvente utilizado foi o clorofórmio.

Palavras-chave: Transferência de energia. Absorção. Fotoluminescência. Tempo de decaimento de fotoluminescência.

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Introduction

Semiconductor polymers, or conjugate polymers, are organic materials that have a structure that alternates between single and double bonds along the polymer chain. These materials present properties of interest for the manufacture of electronic and optoelectronic devices, such as Organic Light Emitting Diode (OLEDs), which are widely used in displays, sensors, flat panel monitors and for general lighting purposes (DING et al., 2002; GREENHAM et al., 1993; YANG; HU; KARASZ, 1998). The advantage of polymers over inorganic materials is their malleability, simplicity of manufacturing techniques and low cost of production (KIM et al., 2001; MCGEHEE et al., 1998). In addition, the possibility of easily modifying the structure and consequently the properties of these materials has increasingly attracted research focus. Significant advances in the efficiency of these electronic and optoeletronic devices are still expected.

There is currently great interest in the manufacture of WOLEDs (White Organic Light-Emitting Diode) (KAMTEKAR; MONKMAN; BRYCE, 2010; KIM; SEO; MOON, 2014; LEE; LEE, 2014) since they could offer efficiency over conventional light bulbs.

One way to obtain white light is using polymer blends, that is, the combination of two or more polymers, where the energy transfer phenomenon is explored (FRANCHELLO, 2014; MONDAL et al., 2014). Particulary in the Förster energy transfer, the donor material, with higher energy, decay from the excited state to the ground state, transfering its energy to an acceptor material, with lower energy, that becomes excited. The condition for that to happen is that the emission spectrum of the donor and the absorption spectrum of the acceptor overlaps. For WOLEDs, donor polymers of higher energy emission (blue / violet) are mixed with acceptor polymers of less energetic emission (green / yellow and orange / red) (HUANG et al., 2014; RENZI, 2015), and the change of materials ratio, allows to tune the blend emission color.

In this work a study of the absorption and emission properties of Poly (9,9-dioctylfluorenyl-2,7-diyl) -co-(4,4 ‘- (N- (4-sec-butylphenyl) diphenylamine) films) (TFB), acting as donor, and Poly (3-hexylthiophene-2,5-diyl) (P3HT), as acceptor, deposited from different solvents (dichlorobenzene, chloroform and toluene) ,was performed.

Films of TFB:P3HT blends with low acceptor ratio (5 %) were prepared and studied in these solvents, being their effects on the emission of the separated polymers analyzed, as well as the energy transfer betweeen the donor and acceptor in the blends.

Emission decay time measurements of the TFB polymer and the TFB:P3HT (5 %) blend were performed in order to understand the emissions observed and the energy transfer in the blends.

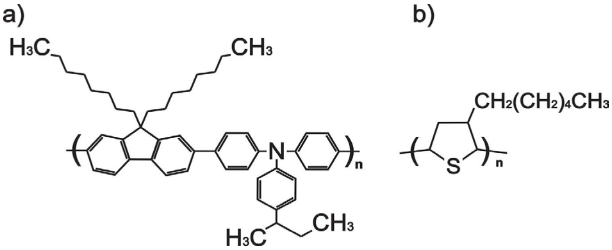
The paper was organized as follows: the next section presents the materials and experimental techniques, followed by the results and the relevant analysis and finally, the conclusions.

Experimental

Sample Preparation

In this work Poly ([9,9-dioctylfluorenyl-2,7-diyl) -co- (4,4 ‘- (N- (4-sec-butylphenyl) diphenylamine)] (TFB) was used as the donor material, and the Poly (3-hexylthiophene-2,5-diyl) (P3HT) as acceptor; both are shown in Fig. 1. Both were obtained from the Sigma Aldrich company.

Figure 1. Polymers a) TFB e b) P3HT.



Source: The author.

Samples were prepared with the TFB and P3HT polymers separately, as well as samples with the TFB:P3HT (95:05) blends, diluted in dichlorobenzene (DCB), chloroform ($ClCH_3$) and toluene (TL) in the form of films, deposited with concentrations of 8 mg / mL. Different solvents were used in the preparation of the samples in order to compare their possible effects on the emission and energy transfer between the two polymers. The films were deposited on quartz slides previously washed in ultrasound for 30 minutes, 15 minutes in acetone and 15 minutes in isopropyl alcohol. For deposition, the Spin Coating technique was used, performed for 1 minute at 800 rpm. The evaporation of the solvent, drying of the samples, was done at room temperature under vacuum.

EXPERIMENTAL TECHNIQUES

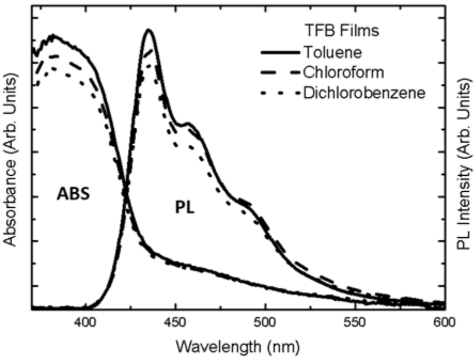
The samples were characterized according to the data obtained from absorption, photoluminescence and time resolved fluorescence measurements. The absorption spectra were obtained with a UV-Vis spectrometer (Shimadzu UV-2600). The photoluminescence spectra (PL) were obtained using laser excitation at 375 nm, and the 514 nm line, of an Ar^+ laser. The photoluminescence emission was detected by an Ocean Optics USB2000+ Spectrometer. Photoluminescence decay time measurements were performed using a FluoTime 200, from PicoQuant, which uses the time-correlated single photon counting (TCSPC) technique and is equipped with a MCP detector, with a 375 nm diode pulsed laser (10 MHz).

Results and Discussion

Photoluminescence and absorption measurements

Fig. 2 shows the normalized absorption and photoluminescence (PL) spectra of the TFB polymer for the films deposited from the solutions in the three solvents. PL spectra were obtained from 375 nm excitation.

Figure 2. Normalized absorption and photoluminescence spectra of the TFB polymer films deposited from three different solvents.



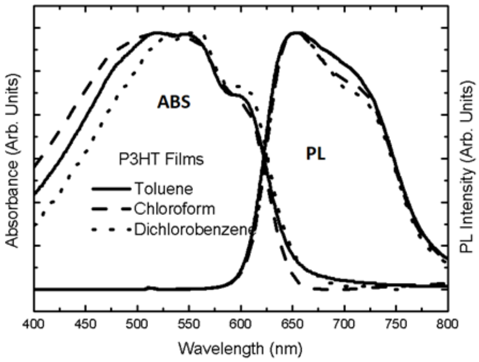
Source: The author.

The TFB and PFO (amorphous phase) absorption spectra are similar and have the maximum at 390 nm (RENZI, 2015). The emission peak at 435 nm is attributed to the purely electronic transition (0-0) of the TFB, and the peaks at 460 and 490 nm are attributed to the vibrational transitions (0-1) and (0-2), respectively (HOU; KOEBERG; BRADLEY, 2003). The photoluminescence measurements presented in Fig. 2 show that there was no change in the position of the peaks of the emission spectra of the polymers regardless of the solvent used, although a change in intensity occurred. It is observed that the intensity is lower for the dichlorobenzene sample and higher for the Toluene sample.

Although the TFB presents the structure of PFO (9,9 dioctylfluorenyl – 2,7 diyl) in its monomer, the formation of different phases in this polymer does not occur as it happens in the case of PFO (MONKMAN et al., 2008). In the PFO, when the beta phase occurs, in addition to the vitreous phase, an absorption peak appears at 438 nm and in the photoluminescence spectra, the peaks of the beta phase are displaced to lower energies (RENZI et al., 2016).

Fig. 3 presents the normalized absorption and photoluminescence spectra, with excitation at 514 nm, of the P3HT for films deposited from each solvent. In order to obtain equivalent intensities in all spectra, different excitation powers were used for each film. The films in toluene and chloroform presented higher emission, with excitation powers of 0.08 and 0.09 mW, respectively. In the case of dichlorobenzene, the intensity of luminescence of the films was almost 2x less intense, requiring a power of 0.17 mW to reach the same intensities of the other films.

Figure 3. Normalized absorption and photoluminescence spectra of the P3HT polymer films deposited from three different solvents.

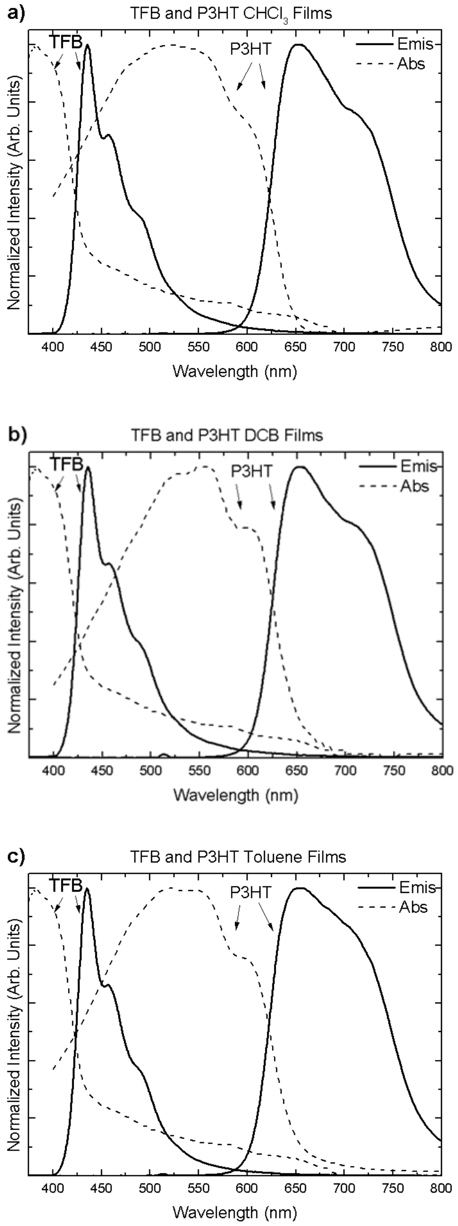


Source: The author.

The peak at 654 nm is attributed to the purely electronic transition (0-0), and the shoulder at 713 nm, due to the first vibronic (0-1) state (NORIEGA et al., 2013). It can be seen in Fig. 3 that there is not a big difference between the spectra of the films deposited from solutions of toluene and dichlorobenzene; however, there is an increase in shoulder intensity at 713 nm, referring to the sample in chloroform. This increase in intensity leads one to believe that there is an increase in coupling of the purely electronic mode with vibrational modes.

In Fig. 4, the absorption and photoluminescence spectra of the TFB and P3HT polymers are presented in the same graph, in order to show the overlapping of the spectra.

Figure 4. Absorption and photoluminescence spectra of the TFB e P3HT polymers in: a) chloroform; b) dichlorobenzene, and c) toluene.



Source: The author.

It is observed in Fig. 4 that there is an overlap of the absorption spectrum of P3HT and emission spectrum of TFB, which indicates that there is the possibility of energy transfer between the polymers for all the solvents used in the solutions that were used in the manufacture of the films.

The absorption spectrum of P3HT in chloroform is wider in comparisson with the spectra in dichlorobenzene and toluene, which leads to a greater overlap of the photoluminescence spectrum of the TFB with the of absorption of P3HT for this solvent. Thus, it is expected that in this case, a greater energy transfer occurs between the polymers.

Fig. 5 shows the results of the photoluminescence measurements of the TFB: P3HT (5 % P3HT) blends deposited with the different solvents. The excitation of the films was performed using a laser at 375 nm, so that only the direct excitation of the TFB, and not the P3HT, occurred. This fact allows to verify if the transfer of energy between the two polymers occurs, which is the condition for the P3HT to emit energy.

Figure 5. Photoluminescence spectra of the TFB:P3HT 5 % films deposited with the three different solvents.

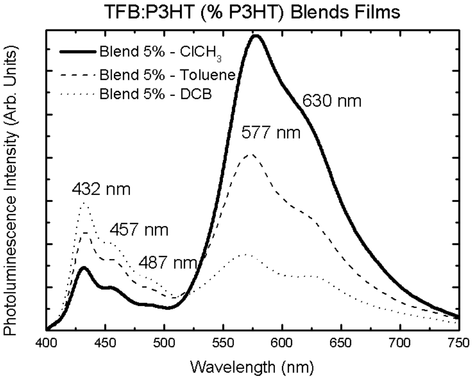


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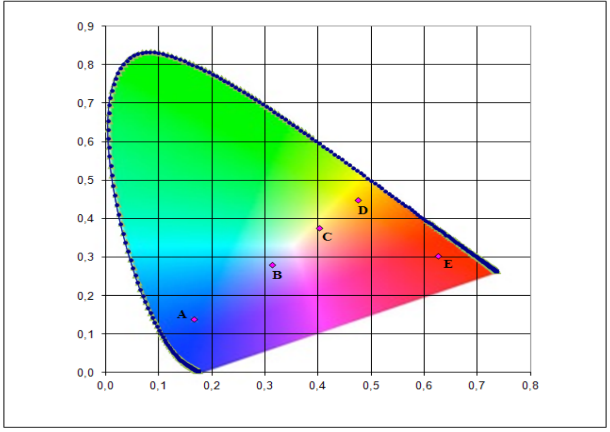
Fig. 5 shows that, for each solvent, the photoluminescence intensity is different for TFB (432, 457 and 487 nm) and for P3HT (630 nm). As expected, this emission of the two polymers demonstrates the occurence of energy transfer from TFB to P3HT. Comparing the spectra for the three solvents, it is noted that a greater transfer occurs with the chloroform, and there is less transfer to the dichlorobenzene.

Another important point in Fig. 5 is the emission around 575 nm, which is not associated with the emissions of any of the polymers separately. This intermediate emission in the blends can be associated to the emissions of the energetically isolated, small conjugated P3HT chains (RENZI et al., 2017), dispersed in the TFB matrix. Such emission, however, can only be observed due to the energy transfer between the polymers, since the direct absorption of light by these chains is very small.

In order to verify the emission color of each sample, the xy CIE (defined by the International Commission of the Eclairage – 1931) diagram was used. The emission intensity data obtained in the photoluminescence measurements were used to obtain the xy coordinates of the CIE color diagram for the polymers, and for the blend films in each solvent used in the deposition, as shown in Fig. 6.

Figure 6. CIE of the photoluminescence of the polymers (A) TFB, (E) P3HT, and of the TFB:P3HT 5 % blend in (B) dichlorobenzene, (C) toluene (D) chloroform.



Source: The author.

It was observed that the emission color for the samples constituted by the individual polymers does not change, independently of the solvent used. In the case of the blends, the dependence of the emission with the solvent used in the preparation of the films is evident, and the emission color of the sample is shifted to blue or red, depending on the smaller or larger energy transfer respectively. Another important observation related to the Fig. 6 is that among the blend samples, the solvent that provided emissions nearest to white (0.33:0.33) was the dichlorobenzene (0.31:0.29).

Photoluminescence Decay Time measurements

The photoluminescence decay time measurements were performed on the film of TFB in DCB, with detection in the wavelength referring to the purely electronic emission (0-0) of this polymer (432 nm).

The obtained decays present better adjustment when using two exponential decays; their times and contributions are presented in Table I.

Table I – Lifetimes referent to the decays of the TFB samples.

Solvent	Detection (nm)	τ_i (ns)	Error (ns)	Contribution (%)
DCB	432	1,50	0,28	44,7
		0,22	0,03	55,3

Source: The author.

Two exponential components related to the decay of the TFB are observed. The component with the shortest decay time has a greater contribution than the longer component. This time distribution may help to understand the distribution of the chains throughout the film. To each component a different form of distribution of the excited carriers is assigned. The longer decay times are related to the emission of more isolated chains. The shortest decays are related to the chains that are more susceptible to inter-chain interactions, which is related to the phenomenon of intermolecular energy transfer (NOME et al., 2011).

Photoluminescence decay time measurements were performed on the blends, with detection on the wavelengths related to the emissions of the individual polymers and also on the intermediate emission. Through the decay adjustments, the lifetimes and contributions of each component of the decay were obtained. Table II shows the lifetimes obtained from the TFB:P3HT (5 %) blends.

Table II – Lifetimes referent to the decays of the TFB:P3HT (95:05) blend samples.

Solvent	Detection (nm)	t_i (ns)	Error (ns)	Contribution (%)
DCB	432	2,01	0,53	40,1
		0,21	0,03	59,9
	575	4,90	0,14	55,3
		0,73	0,03	44,7
	640	4,70	0,13	54,9
		0,82	0,03	45,1

Source: The author.

Comparing the emissions in the 432 nm region of the TFB with the ones in the blend, it is possible to see, within the error, an increase in the longer time, which could be explained by an increase in the degree of energetic disorder of the system (RÖRICH, et al., 2017)

Another interesting feature noted in these results is the lifetime of the emission at 575 nm, which is quite long (greater than 4 ns). The long decay time is compatible with the previous atribution of this emission to the small isolated chains of P3HT, corroborating that idea.

Conclusions

The TFB and P3HT polymers show no change in their absorption and emission spectra depending on the solvent, except for P3HT in ClCH3, which exhibits slight enlargement and increased absorption near 450 nm. However, in the blends of these materials, the solvent change causes higher (ClCH3) or lower (DCB) energy transfer between the TFB and P3HT, allowing the change in the emission color of the blends depending on the solvent used. In the blends with low concentration of the acceptor, an emission appears around 575 nm, which was not observed in the TFB, **nor in the P3HT films. This intermediate emission has already been studied in other blends with thiophene (RENZI, et al., 2017; SILVA et al., 2016), and has been associated with small chains of P3HT, isolated, dispersed in a medium of the material matrix donor. In this way, besides dispersing the chains of P3HT, the TFB also transfers energy to these structures. In relation to the decay of this intermediate emission, the lifetimes were long (~ 5 ns), which agrees with the emission by isolated chains.**

The emission color coordinates (CIE) of the samples demonstrate the possibility of using the TFB: P3HT (5 %) blends in DCB solvent for the production of white light emitting devices (WOLEDs). Furthermore, the use of low concentrations of P3HT in the blend may allow the production of devices that have the possibility tuning the emission color of the electroluminescence through the saturation of the energy levels of the acceptor material simply by the application of different voltages on the device.

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