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Full Length Article

Spectroscopic studies of different poly3hexylthiophene chain environments in a polyfluorene matrix

P.L. Santos [a,*], L.A. Cury [b], F.B. Dias [a], A.P. Monkman [a]

[a] OEM Research Group, Department of Physics, University of Durham, Durham DH1 3LE, United Kingdom
[b] Departamento de Fisica, Instituto de Ciencias Exatas, Univesidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Minas Gerais, Brazil

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ABSTRACT

Optical properties of blends made of poly(9,9-dioctyl-fluorene-2,7-diyl) (PFO) and poly(3-hexylthiophene-2,5-diyl) (P3HT) were investigated and compared to those of poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2) by steady state optical spectroscopy. In addition to the individual emissions of PFO and P3HT chromophores, the blends composed by these two polymers show a new peak emission around 590 nm. The new peak is attributed to well dissolved, "isolated", P3HT chains dispersed into the PFO matrix. It was observed that the well dissolved P3HT chains are activated by Förster energy transfer, where PFO and P3HT molecules act as a donor and an acceptor, respectively. Further, emission from ordered aggregates of P3HT is clearly observed and the interplay between aggregate and isolate P3HT chains was studied. In contrast to the PFO:P3HT blends, the emission spectra from F8T2 co-polymer show clear interaction in the ground state between the dioctylfluorene and bithiophene monomer-units, giving rise to a wholly new chromophore conformation on the backbone.

1. Introduction

For many organic electronic devices it is well known that "morphology", however complex, plays a major role in the overall physical characteristics of the device. Moreover, in our search for ways to increase efficiency of devices, we look to more complex materials and combinations of materials. This though has a direct consequence on morphology, especially when blends or admixtures of molecules or polymers are used. Here we set out to explore the effects on morphology that mixing two well-known polymers has, using the photophysics of the resultant films as a way to probe how morphological changes, directly or indirectly impinge on the photophysics.

Mixing different semiconductor polymers provides a practical way to tuning their optical properties. This can be used as a simple way to produce thin active films for fabrication of polymer light emitting diodes (PLEDs) for example [1]. Such blending will cause morphology changes, which may be manipulation in order to affect processes such as self-absorption or energy transfer, which possibly may improve the luminance efficiency [2,3] or charge separation and transport in the context of a photovoltaic cell [4,5]. Blending materials can also induce new optically active or quenching states such as aggregate state or dimer phenomena, which can shift emission spectrum to longer wavelengths, change photoluminescence quantum yields or charge pair generation efficiency for example [6,7]. These properties could be very important for example when trying to achieve white emission, one of the most important developments in the field of polymer emitting devices, where complex mixtures are used in order to gain broad white emission and balanced electron and hole transport within a single "emission" layer [8–11].

Polyfluorenes have been extensively studied for display applications, owing to their pure blue and efficient electroluminescence coupled with a high charge carrier mobility and good processability [12]. Several studies have been reported, including mixing of polyfluorenes with different emissive materials and applying them in single or multiple layers [13,14]. We also know that many polyfluorenes form there own distinct phases in films, commonly known as the beta phase [15–17], thus it is a ideal component of a blend to study. Polythiophenes and their regioregular forms are another class of well-known semiconductor polymers known to show complex morphology and morphological controlled photophysics, where side chain structure and quality of solvent/environment also plays a significant role in their photophysical properties [18–20]. Thus this paring is an ideal test bed to study how blending effects the many possible different interactions between guest–guest, guest–host and host–host. In solution (as in films) the effects of concentration also effect optical properties, i.e. the emissive states of isolated chromophores can only be observed in very low concentrations, thus solution state spectroscopy can help

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[*] Corresponding author.
E-mail address: p.l.dos-santos@durham.ac.uk (P.L. Santos).

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to give us further understanding of the complex blend films. In this work, the optical properties of poly(3-hexylthiophene-2,5-diyl) (P3HT) in low concentrations and blends of P3HT and poly (9,9-dioctyl-fluorene-2,7-diyl) (PFO) in different ratios were studied. This pairing is ideal to study due to the small overlap between emission bands of the two components while retaining good overlap between PFO emission and P3HT absorption. We show that the absorption and emission characteristics of P3HT vary significantly depending on its concentration in solutions. Interestingly, we show that the emission of the isolated chromophores observed for the low concentrated solutions is also detected when P3HT is dispersed in a PFO matrix. The blends exhibited emission spectra covering the entire visible range, from 400 nm to 750 nm, which occurs via inefficient Förster energy transfer [21–23] from the PFO molecules to P3HT sites. We find that in the blend films, emission spectra from three different P3HT chain environments and PFO domains can be observed. Controlling energy transfer processes becomes a difficult task because it depends on the interfaces between these two materials and their relative amounts of the different chain environments. We also discuss the optical properties of blends in comparison to that of poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2), which is a copolymerization of dioctylfluorene and bithiophene units to highlight the role that complex intermixing and chain environments has on photophysical properties of blend films and how difficult it can be to control such blend films.

2. Material and methods

P3HT (regio-random, average molecular weight 54,000 – 75,000) toluene solutions in different concentrations were produced: 0.01 mg/mL, 0.06 mg/mL, 0.10 mg/mL, 0.20 mg/mL and 4.3 mg/mL. Toluene solutions of PFO (average molecular weight 250,000) and F8T2 (average molecular weight $> 20,000$) with concentrations of 5.5 mg/mL and 4.0 mg/mL were also produced, respectively. All solutions were then stirred for 24 h.

In addition, solutions of P3HT (4.3 mg/mL) and PFO (5.5 mg/mL) were mixed to obtain three different blends with the ratios: $\text{P3HT}_{(0.05)}$:$\text{PFO}_{(0.95)}$, $\text{P3HT}_{(0.50)}$:$\text{PFO}_{(0.50)}$ and $\text{P3HT}_{(0.30)}$:$\text{PFO}_{(0.70)}$, where the subscript indicates the volume of each solution used from which films were then cast. The blend thin films and pure F8T2 thin film were fabricated by spin-coating on quartz substrates at 1000 rpm during 60 s.

The chemical structures of all materials studied in this work and the corresponding HOMO–LUMO levels of PFO and P3HT are displayed in Fig. 1 [24,25], which clearly illustrate that PFO would act as an energy donor and P3HT as an energy acceptor.

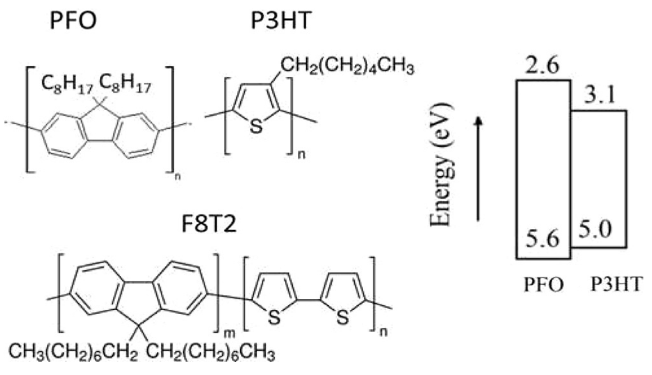

Fig. 1. Chemical structures of compounds used in this study PFO, P3HT and F8T2; and HOMO–LUMO levels for PFO and P3HT.

Absorption spectra were measured using a Shimadzu model UV3600 spectrophotometer in air atmosphere at room temperature. Steady-state photoluminescence (PL) and photoluminescence excitation (PLE) measurements were performed in a Jobin Yvon Horiba Fluorolog spectrometer equipped with a xenon lamp as the excitation source. Spectra were collected at room and low temperatures using a cryostat filled with liquid nitrogen.

3. Results and discussion

Thin films of pure PFO and P3HT, as well as a 1:1 blend, were characterized by absorption and emission. The measurements were performed in atmosphere at room temperature. The absorption spectra are shown in Fig. 2(a). PFO molecules absorb light between 350 and 450 nm, whereas the P3HT molecules absorb between 450 and 700 nm. The small absorption peak of the PFO film at 433 nm is attributed to beta phase [26]. The blend absorption spectrum is composed of an admixture of the absorption of the individual PFO and P3HT chromophores. This implies little or no ground state interaction between the two polymers.

The emission spectra of the same samples are shown in Fig. 2 (b). All films were excited at 375 nm, which corresponds to a wavelength around the maximum absorption for PFO and relatively small absorption for the P3HT. The emission of the PFO film shows a maximum intensity at 440 nm accompanied by two

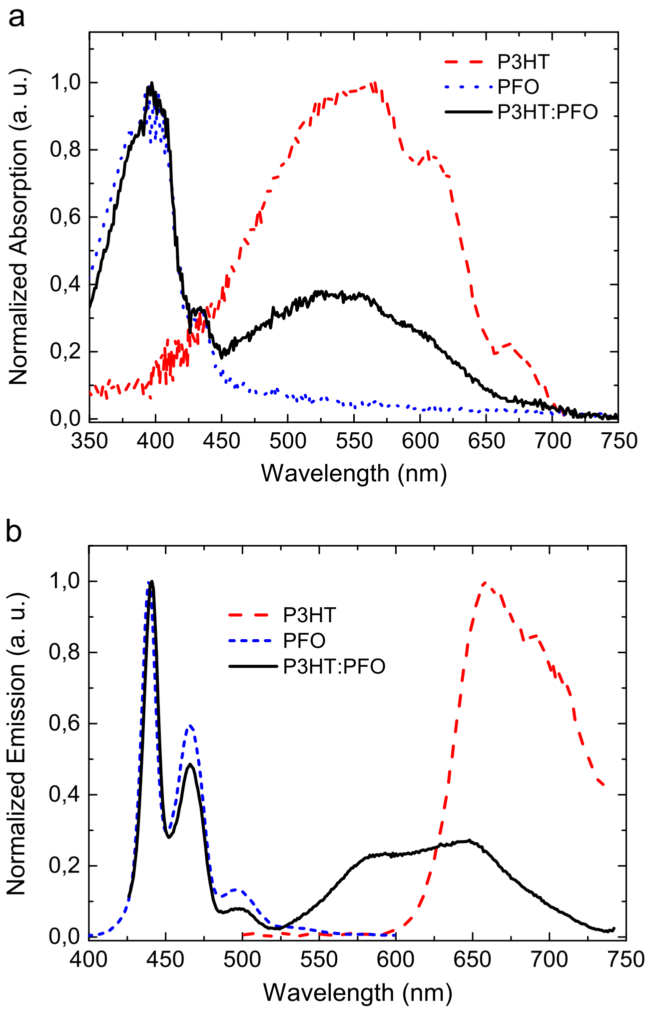

Fig. 2. (a) Normalized absorption spectra of thin film of P3HT (dashed line), PFO (dot line) and blend P3HT:PFO (full line). (b) Normalized emission spectra of the same films.