Spectroscopic studies of different poly3hexylthiophene chain environments in a polyfluorene matrix

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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 donor and acceptor, respectively. Further, emission from ordered aggregates of P3HT are 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 shows clear interaction in the ground state between the dioctylfluorene and bithiophene monomer-units, giving rise to a wholly new chromophore conformation on the backbone.

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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

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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 ad-mixtures 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, 9, 10, 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, 16, 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, 19, 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 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 betweem emission bands of the two components whilst 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, 22, 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 hours.

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: $\mathrm{P3HT}_{(0.05)}$:$\mathrm{PFO}_{(0.95)}$, $\mathrm{P3HT}_{(0.50)}$:$\mathrm{PFO}_{(0.50)}$ and $\mathrm{P3HT}_{(0.30)}$:$\mathrm{PFO}_{(0.70)}$, 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 seconds.

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

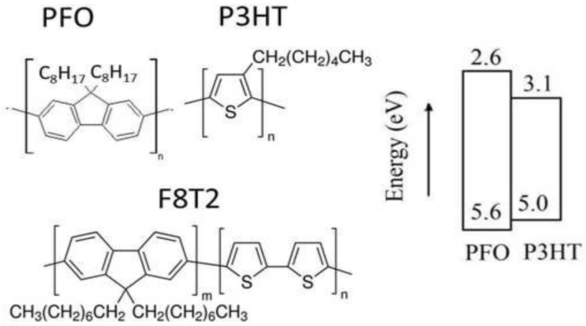

Figure 1: (Color online) Chemical structures of compounds used in this study PFO, P3HT and F8T2; and HOMO-LUMO levels for PFO and P3HT.

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 figure 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 figure 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 vibronic bands centered at 466 nm and at 498 nm. The P3HT film shows an electronic emission at 660 nm and shoulder band at 690 nm. It can be noticed that there is a spectral overlap between the absorption of P3HT film and the emission of PFO film, the majority emission of the PFO is located at the growing up side of the absorption spectrum of the P3HT film. This condition satisfies the requirement for Förster energy transfer, in which PFO acts as the donor and P3HT the acceptor. The blend emission spectrum presents individually the emission of the PFO and P3HT as well as an additional peak around 590 nm, resulting in a full range white emission from blue to red wavelengths, 400 nm

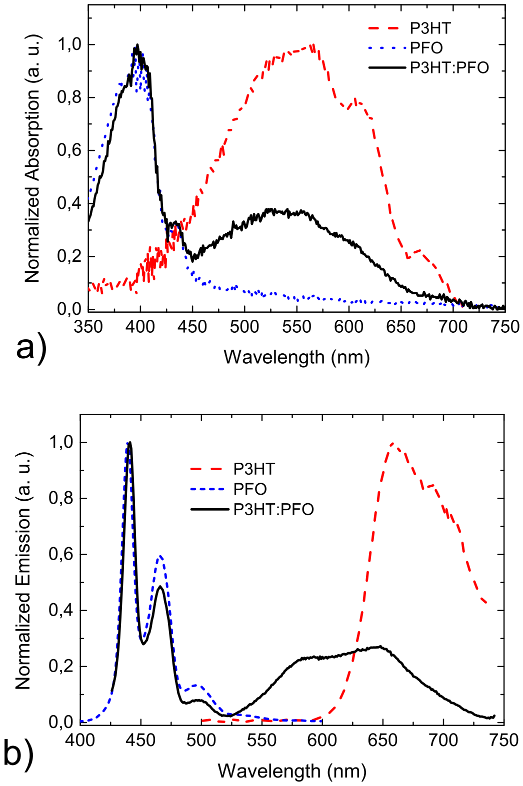

Figure 2: (Color online) a) Normalized absorption spectra of thin film of P3HT (dashed line), PFO (dot line) and blend P3HT:PFO (full line). b) Normalized emission spectra of the same films.

- 750 nm. The peak around 590 nm indicates that a new emission channel is activated when P3HT and PFO polymers are dispersed together. Further, it can be seen that the P3HT emission has lost much of its shoulder beyond 675 nm.

In order to investigate the peak around 590 nm, emission spectra of blends with different composition ratios of PFO and P3HT were measured. Figure 3 shows the relation between the peak around 590 nm and the peak related to the pure P3HT film emission, around 650 nm. The spectral region was limited between 500 nm and 750 nm, the range where the second emission peak of the P3HT:PFO blend is located, for better comparison. It is seen that as the concentration of P3HT in the PFO matrix decreases, the emission around 590 nm starts to dominate the emission at 650 nm, progressively. Eventually, for low concentration of P3HT, the 650 nm emission peak nearly vanishes, whilst the emission around 590 nm remains dominant.

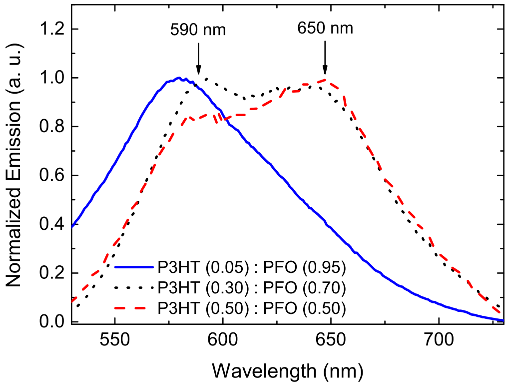

Figure 3: (Color online) Normalized emission spectra of the second emission peak of the P3HT:PFO blend films with different composition ratios. Blend film are composed of P3HT$_{(0.05)}$:PFO$_{(0.95)}$(full line), P3HT$_{(0.30)}$:PFO$_{(0.70)}$(dot line) and P3HT$_{(0.5)}$:PFO$_{(0.5)}$(dashed line).

Figure 4 shows the green-red emission for the blend film (1:1 ratio) excited at different wavelengths. The peak around 590 nm appears only when the blend is excited at 395 nm and 430 nm, in other words, when the PFO molecules are excited. When the blend is excited at 560 nm, which is the wavelength around the maximum absorption of P3HT film, the 590 nm emission is not observed. This suggests that the emission peak at 590 nm is directly resultant from the PFO excited molecules. The excitation spectra of the blend films monitored at 580 nm (Fig.5) shows a strong peak around 370 nm, signature for the absorption of the PFO chromophores. Hence, confirming that the 590 nm blend emission originates from the excitation of the PFO molecules, but the emission arises from a P3HT molecule as it is clearly not seen in the pure

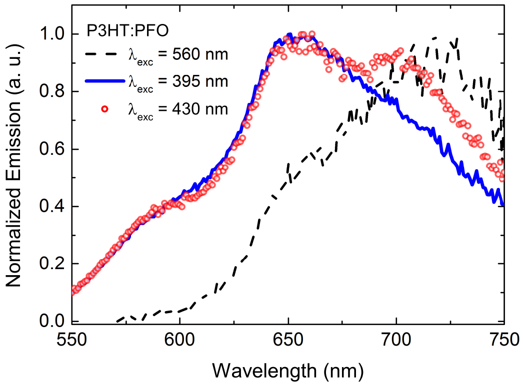

Figure 4: (Color online) Normalized emission spectra of the second emission peak of P3HT:PFO blend film (1:1 ratio) excited at 560 nm (dashed line), at 395 nm (full line) and at 430 nm (dot line).

PFO spectra, suggesting that an intermolecular Förster energy transfer from the PFO to the P3HT chromophores must occur.

Figure 6(a) shows the absorption spectrum of the most diluted P3HT solution (0.01 mg/mL). It can be noticed that the absorption spectra for this solution is blue shifted in comparison to the P3HT film absorption (Fig.2(a)). Figure 6(b) shows emission spectra for P3HT solutions of different concentrations. Upon increasing the concentration, the emission peak shifts to lower energies, showing a large difference of the emission between the lowest and highest concentrations. The red-shift observed for this concentration is most likely a result of aggregation of P3HT blocks. The aggregation of P3HT has been demonstrated for a variation of solvents before. [20] In our work, we can notice the aggregation phenomena as a result of the solution concentration. For cast films made from those high concentration solutions we will assume such pre-formed P3HT aggregates exist.

The low concentration P3HT solutions show the peak emission around 590 nm. Similar peak emission occurring in P3HT:PFO blends can thus be attributed to the emission of the same isolated P3HT chains, but in the blend

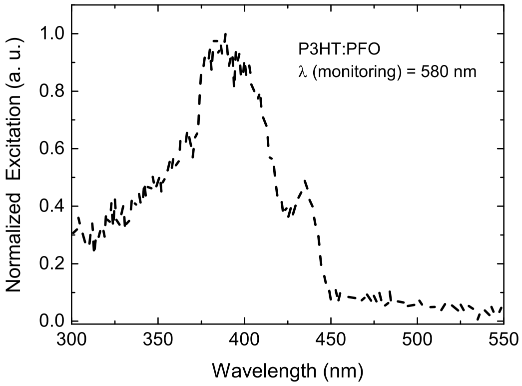

Figure 5: (Color online) Normalized PLE spectrum monitored at 580 nm for P3HT:PFO blend film (1:1 ratio). It shows similar spectrum of PFO absorption (Fig 1.b).

case, the P3HT chains are isolated due the dispersion of them into the PFO matrix. For the most concentrated solution, all emission is observed beyond 650 nm. This fact, considering films made from concentrated solutions, enable us to identify the shoulder at 675 nm as arising presumably from P3HT aggregated states with higher conformational order. Therefore, P3HT molecules show three different emission states in the blend, the aggregate emission, peak around 650 nm, highly ordered aggregate emission at 675 nm and the well dissolved chains emission, peak around 590 nm.

Figure 4 and 5 suggest that the well dissolved P3HT chains are activated by Förster energy transfer, from the PFO host to the P3HT guest. When the blend is excited at 560 nm the well dissolved P3HT chromophores do not absorb light, because as shown in Fig.6(a) they have a vanishing absorption in this wavelength, making the excitation of PFO chromophores necessary for its emission. To support this analysis, we have also investigate the absorption spectra of all the blends. Figure 7 shows that the absorption around 560 nm decreases considerably in the blend films by decreasing the amount of P3HT molecules. This is an expected result because the amount of P3HT reaches just 5% with respect to the amount of PFO and the PFO absorption became

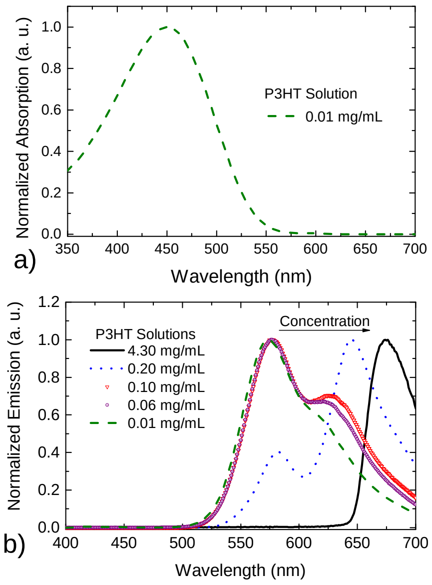

Figure 6: (Color online) a) Normalized absorption spectrum for the most diluted P3HT solution (b) normalized emission spectra for P3HT solutions in different concentrations. Highest concentration (full line), shows a red-shift compared to the lowest concentration (dash line).

dominant, but this result also indicates that the P3HT that remain in the films are displayed in isolated chains and do not absorb around 560 nm any more. However, the energy transfer process in the blends appears to be not efficient, since it is not observed a strong reduction from the PFO emission intensity as it would be expected in a full donor-acceptor exciton energy transfer. There must be domains of PFO where chains are outside the Förster interaction radius and so the energy transfer channels compete with the pure emission of the chromophores. The Förster radius was estimated to be (1.4 +/- 0.1) nm (see appendix), which implies that excitons in PFO domains bigger than R_0 may emit in PFO chromophores, instead of transfer energy to P3HT chromophores. For efficient energy transfer in the polymer blends the exciton migration time in the donor polymer domain must be faster than the radiative and non radiative

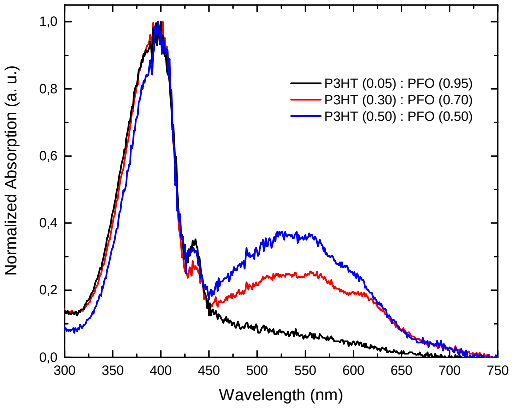

Figure 7: (Color online) Normalized absorption spectra of blend films. The blends are composed of $\mathrm{P3HT}_{(0.05)}$:$\mathrm{PFO}_{(0.95)}$(black), $\mathrm{P3HT}_{(0.30)}$:$\mathrm{PFO}_{(0.70)}$(red) and $\mathrm{P3HT}_{(0.5)}$:$\mathrm{PFO}_{(0.5)}$(blue).

decays. In this case, part of the exciton population of a donor chains have time to find an energy transfer site before decay, and this will be directly controlled by the conformation of the chromophores disposed in steady state.

Figure 8 shows the emission of the 1:1 blend as a function of temperature. All of the emission peaks become well resolved and red shift on cooling down the sample, as expected for polymers.[27] Upon decreasing the temperature from 290 K to 80 K the area of the P3HT emission band remains relatively unchanged, whereas an increase in the emission intensity of PFO is observed. We would expect the same behavior for the P3HT emission, but its shape invariance is interpreted in part by the fact that the main P3HT emission comes from the aggregated region where the molecular organization reached already its maximum conformation. Consequently, decreasing the temperature would not lead a substantial improvement in its intensity. Note also the peak emission around 590 nm, which comes from exciton energy transfer (EET) of the PFO donor sites as discussed previously in the text, remains practically unchanged. Most likely, the higher intensity of the non-aggregated P3HT chains in low temperature is

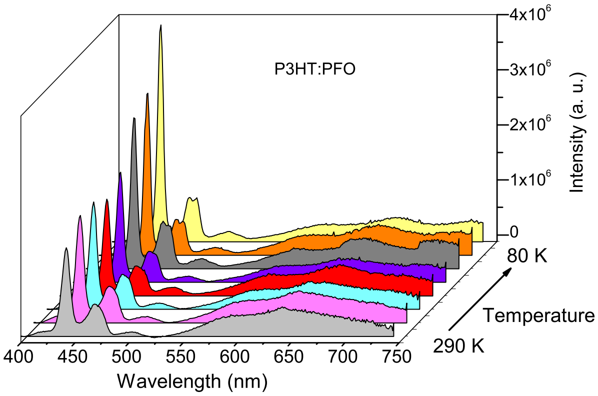

Figure 8: (Color online) Emission obtained at different temperatures for the P3HT:PFO blend (1:1 ratio). First peak, which is related to PFO emission, decreases with increasing temperature. Second peak, which is related to P3HT emission, remains practically with the same intensity.

compensate by the slows down of the exciton migration by cooling, making no variation in its intensity.

Figure 9 shows the absorption and emission spectra of the regular copolymer, F8T2. The spectra are in good agreement with previous report spectra. [28, 29]This copolymer is formed by dioctylfluorene and bithiophene monomers. The absorption spectrum is similar to that of P3HT "isolated"chains. However, the emission spectrum presents a new shape characteristic. The emission is well structured, onset at 500 nm. The spectrum clearly suffers from self-absorption given the narrowness of the 0-0 band in comparison to the vibronic replicas so it is not possible to judge how stiff the F8T2 chains are in film. This indicates that when dioctylfluorene and bithiophene monomers are copolymerized in the same molecules, they are sufficiently conjugated to form a new chromophore and the individual characteristics are lost.

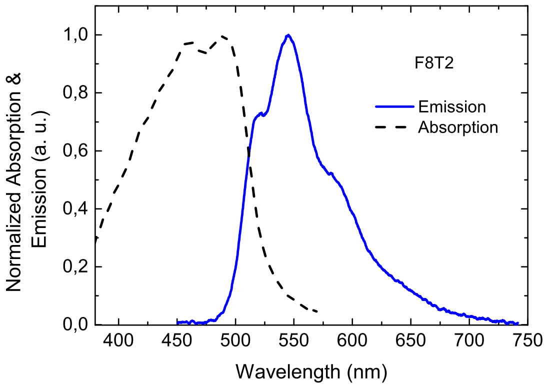

Figure 9: (Color online) Normalized emission (full line) and absorption (dashed line) spectra for the single thin film of F8T2.

4. Conclusions

P3HT: PFO blends were studied by steady-state photoluminescence and absorption in air at room temperature. The blend absorption spectrum indicates little or no ground state interaction between the two polymers, whereas the emission spectra show emission from the pure PFO and P3HT as well as a new peak around 590 nm. It was found that this new peak originates from P3HT molecules well dissolved into a PFO matrix and readily excited via intermolecular Förster energy transfer, from PFO to P3HT molecules. However, non-effective intensity reduction of the PFO donor occurs in the emission of the blend film, indicating that this energy transfer process is not efficient. The Förster radius, R_0, was estimated to be (1.4 +/- 0.1) nm, it implies that PFO domains are larger than this and so some chains are outside the R_0 energy transfer radius and so emission of the PFO chromophores, competes with energy transfer.

Aggregation formation in P3HT solutions was identified through analyzes of the emission spectra in different concentrations. The behavior of the P3HT absorption spectra for a much diluted solution was also analyzed, and showed a blue shift in comparison of the P3HT thin film made of a higher concentration solution. The study of the P3HT optical proprieties in different concentrations were essential to identify well diluted P3HT chains, and then prove that a P3HT:PFO blend has three different P3HT chain environments. Also, photoluminescence as a function of temperature measured in the blend film, reveals that P3HT emission that comes from the aggregated region is not affected by temperature; and the exciton migration to P3HT isolated chains slows down by cooling and PFO monomolecular decay processes out compete Förster transfer.

As a way to investigate the result of the copolymerization of dioctylfluorene and bithiophene units, we studied the steady-state photoluminescence and absorption of F8T2. The results show that F8T2 forms a new chomophore, due the individual characteristics of dioctylfluorene and bithiophene are not observed in the F8T2 thin film.

This study enables us to understand the underlying mechanisms of inter/intramolecular interaction between blends of two rather different luminescent polymers. Three P3HT chain environments and PFO domains were observed in the same emission spectra, due to the proper combination of the polyfluorene and the thiophene which may be difficult to control.

5. Appendix

The Förster radius R_0, defined as the donor/acceptor separation distance for which direct donor decay is equally likely to transfer energy to the acceptor, was estimated from the expression,[30]

$$R_0 = 0.211\{k^2\eta_d n^{-4}[\int_0^\infty f_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda]^{1/6}\} \qquad (1)$$

where k^2 is an orientation factor equal to 2/3 for randomly oriented dipoles, $\eta_d = 0.21$ is the donor PLQY,[31] $n = 1.9$ is the refractive index of the medium,[32] considering that P3HT molecules are dispersed into PFO matrix, $f_D(\lambda)$ is the PL spectrum of the donor normalized by area, and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor.

The evaluation of the spectral overlap integral is generally performed with the donor emission and acceptor absorption in solution, but this can vary from the spectra in films. In this work we used the emission spectrum of the PFO solution and the absorption spectrum of P3HT solution to calculate the Förster radius. The Förster radius was estimated to be $R_0 = (1.4 \pm 0.1)$ nm. The error occurs mainly by virtue of the molar weight of the acceptor, which vary from 54000 to 75000 g/mol.

The energy transfer rate from PFO to P3HT molecules may change according to the three different P3HT chain environments. The different P3HT chains show different absorption spectra, leading a change of the overlap between the donor emission and the acceptor absorption, and consequently, leading a change in the Förster radius. The overlap is bigger to the "isolated" P3HT chains, hence the energy transfer rate must be higher in this chain environment. The rate of energy transfer from a donor to an acceptor $\kappa_T(r)$ is given by, [30]

$$\kappa_T(r) = \frac{1}{\Gamma_D}(\frac{R_0}{r})^6 \tag{2}$$

where Γ_D is the decay time of the donor in the absence of acceptor, R_0 is the Förster distance, and r is the donor to acceptor distance.

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