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Cite as: Appl. Phys. Lett. **114**, 093301 (2019); <https://doi.org/10.1063/1.5058195>

Submitted: 18 September 2018 . Accepted: 19 February 2019 . Published Online: 06 March 2019

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ABSTRACT

By diluting poly(dioctylfluorene) (PFO) with low molecular weight polystyrene (PS), electron trapping and trap-assisted recombination can be strongly suppressed. For polymer light-emitting diodes (PLEDs) consisting of a PFO:PS (1:3) blend, a doubling of the efficiency is expected owing to trap dilution. Experimentally, we observe a much larger efficiency increase of nearly an order of magnitude. The electroluminescence and photoluminescence spectra of the PFO:PS blend show a sharpening of the vibrational peaks with regard to pristine PFO with the emission maximum at 436 nm. This spectral feature is characteristic of the formation of the β -phase in PFO upon PS addition. From the analysis of the absorption spectra, the fraction of the β -phase induced by blending typically amounts to 13%. The strong PLED efficiency enhancement therefore arises from the combined effect of β -phase formation (~ 4 times) and trap dilution (~ 2 times).

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In the past few decades, polymer light-emitting diodes (PLEDs) have attracted much interest as next generation solid-state lighting and display elements owing to their compatibility with large scale (flexible) production.^{1–5} In order to realize full-color displays with high color purity, efficient and durable blue light emission is of essential importance.^{6–8} Among the currently available blue light-emitting semiconducting polymers, poly(9,9-dioctylfluorene) (PFO) is one of the most widely studied polymers, exhibiting good processability, high photoluminescence quantum efficiency, and good thermal and electrochemical stabilities.^{9–11} Nevertheless, as is the case in most disordered organic semiconductors, electron transport is dominated by charge trapping. The recombination of trapped electrons with free holes (positive charge carriers) is a loss process, as it is usually non-radiative.^{12,13} Recently, we demonstrated that the PLED efficiency is doubled by alleviating electron trapping via simultaneous dilution of both the transport and trap sites in the conducting polymer through the addition of a wide bandgap inert polymer.^{14,15} In the case of PFO, we showed that the same is achieved if the traps are emissive.¹⁶ Depending on synthesis conditions, PFO may or may not contain fluorenone defects, originating from the oxidation of monomers at the 9-position. These moieties exhibit a lower bandgap than the PFO backbone and give rise to a broad green emission band. Diluting fluorenone-containing PFO with low molecular weight (~ 1000 g/mol)

polystyrene (PS) suppresses the green emission, effectively restoring the deep-blue luminescence of the PFO backbone.¹⁶

In the present work, we show that by diluting (ketone-free) PFO with a substantial fraction (75%) of low molecular weight PS, the PLED efficiency is not merely doubled, as is observed for poly(p-phenylene vinylene)^{14,15} but rather increased by an order of magnitude. We propose that this large increase in efficiency is due to a *dual effect* associated with the blending of the semiconductor with polystyrene. We show that blending leads not only to the suppression of trap-assisted recombination but also to the formation of a significant fraction of the strongly luminescent PFO β -phase.¹⁷ PFO ($\bar{M}_w = 230.000$ g/mol, $\bar{D} = 3.02$) was synthesized via the Yamamoto method according to the known procedures.^{18,19} Polystyrene (PS) (atactic, $\bar{M}_w = 1.100$ g/mol, $\bar{D} = 1.15$) was synthesized via anionic polymerization of styrene and was used as an inert material. The charge transport in PFO:PS blend films was studied using dual (PLED) and single carrier devices. The OLEDs had an architecture comprising glass/ITO (100 nm)/poly(3,4 ethylenedioxythiophene):poly(styrene sulfonic acid) PEDOT:PSS (60 nm)/PFO(:PS)/Ba (5 nm)/Al (100). The electron- and hole-only devices (EO and HO) had a glass/Al (30 nm)/PFO(:PS)/Ba (5 nm)/Al (100 nm) and a glass/ITO (100 nm)/PEDOT:PSS (60 nm)/PFO(:PS)/MoO₃ (10 nm)/Al (100 nm) architecture, respectively.

The hole-injection layers of poly(3,4 ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (Heraeus Clevis 4083) were spin-coated from a 1.3 wt. % dispersion in water and dried at 140 °C for 10 min. The thin films of PFO and its blends with PS were spin-coated from chlorobenzene to obtain films with a ~ 100 nm thickness. Top contacts of Ba (5 nm)/Al (100 nm) (OLED and EO) and MoO₃ (10 nm)/Al (HO) were thermally evaporated at 10^{-7} Torr. Electrical characterization was carried out in an inert (N₂) atmosphere with a Keithley 2400 source meter. The light output was recorded with a calibrated Si photodiode, and electroluminescence (EL) spectra were recorded with a USB4000 UV-Vis-ES spectrometer. UV-Vis absorption spectra were recorded with a dual-beam Shimadzu UV-2600 spectrophotometer. Photoluminescence (PL) spectra were recorded using a TIDAS Mono RS232 spectrometer.

We commence with studying how diluting PFO with PS affects the electron and hole transport in single carrier devices. In Fig. 1, the current density measured as a function of voltage is plotted for devices comprising a PFO:PS blend (ratio, 1:3 w/w) as an active layer. The figure compares the results with those obtained for reference devices based on unblended PFO. As expected, for unblended PFO, the electron current is three to four orders of magnitude lower than the hole current due to charge trapping.¹³ As we have shown before, by introducing PS in the system, the electron current increases drastically owing to the elimination of trapping and becomes as high as the hole current.¹⁶ Interestingly, the (non-trap-limited) hole current remains unaffected by blending with PS, where we would have expected a decrease due to the spatial separation of transport sites, making charge carrier hopping more difficult. This may indicate that the presence of PS in the blend causes a morphological change in the semiconductor, upon which the hole mobility is enhanced.

As a next step, we study the effect of blending on the efficiency of the dual carrier device, i.e., the actual PLEDs. In earlier work, we demonstrated that a doubling in efficiency is obtained upon full elimination of electron trapping.^{14,15} This effect is in agreement with theoretical predictions obtained by modeling of the PLED, taking all loss processes quantitatively into account.¹² Figure 2(a) shows that the present PFO:PS blend behaves qualitatively similar: whereas the total

current density, which is dominated by trap-free hole transport, remains unaffected by the blending, the light output of the device increases considerably as evidenced by the increase in photocurrent density. In other words, the luminous efficiency (LE) of the device, expressed in Cd/A, increases upon blending with PS. However, in contrast to our earlier observations, Fig. 2(b) shows that for PFO, blending with PS causes the LE not to increase by a mere factor two but by a full order of magnitude: 1 Cd/A versus 0.1 Cd/A for unblended PFO,²⁰ i.e., exceeding the theoretical prediction by a factor of five.

In terms of absolute numbers, the efficiencies we measure are in good agreement with earlier studies on PFO-based OLEDs with a similar device architecture,^{20–22} whereby we note that variations in material properties (such as PFO molecular weight²²), processing intricacies,²¹ and brightness dependence²² typically give some spreading in the reported numbers. Other studies have specifically focused on maximizing OLED efficiency, with recent progress in emitters exhibiting thermally activated delayed fluorescence (TADF) showing good prospects.²³ However, since in the present study we are primarily interested in understanding how structure-function relations affect the photophysical behavior, efficiency maximization is out of the scope of this work. Instead, we are interested in the information obtained from the *relative* comparison of the efficiencies of devices based on PS-blended and unblended PFO.

To investigate whether the order of magnitude increase in efficiency is accompanied by spectral changes induced by blending, we plot the *normalized* electroluminescence (EL) and the *absolute* photoluminescence (PL) spectra, respectively, recorded on PLEDs and films of unblended (dash black) and PS-blended PFO (solid red) in Fig. 3. Clearly, introducing PS into PFO leads to a drastic change in the spectral features. Unblended PFO exhibits a vibronic progression with peaks situated at $\lambda = 423, 448$, and 476 nm associated with the 0–0, 0–1, and 0–2 transitions, respectively.²⁴ In both the EL and PL spectra of the PFO:PS blend, the peaks appear significantly red-shifted at $\lambda = 436, 465$, and 495 nm. These two spectral fingerprints evidence the presence of different morphological states in the PFO upon blending with PS. The spectra for the unblended PFO are representative for the amorphous (glassy) phase,^{24,25} whereas the ones for the PFO:PS blend are consistent with the presence of a significant fraction of the so-called β -phase.²⁶

In the amorphous phase, the PFO chains are disordered, featuring a broad distribution of inter-monomer torsion angles.^{27–29} In contrast, in β -phase domains, chains locally adopt a fully extended conformation in which the inter-monomer torsion angle²⁸ is 160° but the staggered orientation of the monomer units.^{24,27,30–32} Interestingly, our experiments demonstrate that the polystyrene induces this conformational change in the PFO. As seen in Figs. 3(a) and 3(b), the enhanced conformational order in the β -phase is expressed by well-resolved vibronic features and a red-shifted emission owing to the increase in the conjugation length.³³ The enhanced electronic delocalization in β -phase PFO reduces the bandgap by ~ 0.2 eV, as determined from the shift in the 0–1 transition. Owing to the excellent spectral overlap, energy transfer from the amorphous phase to the β -phase is highly efficient, typically occurring on a picosecond time scale.³⁰ For this reason, already $<2\%$ of the β -phase content in the amorphous matrix is known to fully dominate the emission spectrum of PFO.¹⁷

Since the above fact implies that the quantification of the amount of the β -phase in the sample based on the emission spectrum is

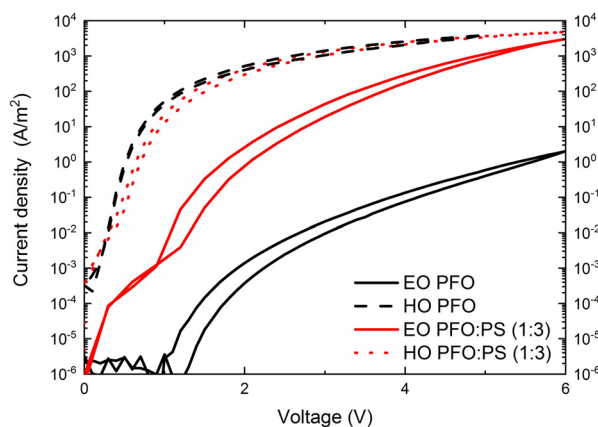


FIG. 1. Hole and electron current density versus voltage for unblended PFO (dash black) and PFO:PS blend (1:3 w/w, solid red). The thickness for the hole-only (HO) and electron-only (EO) devices amounts to 100 nm.

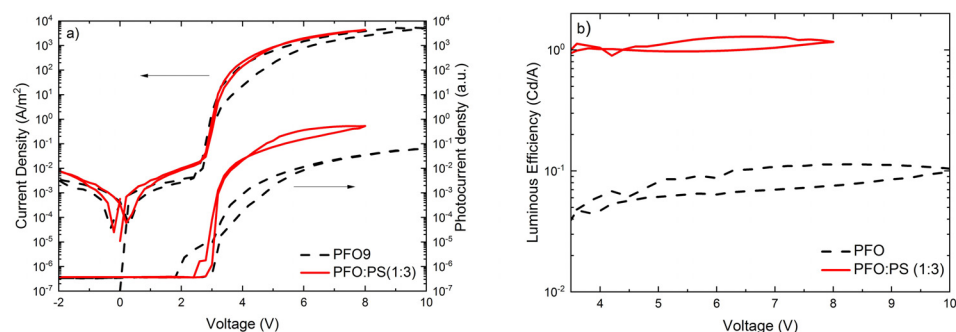


FIG. 2. (a) Current density- and photocurrent density-voltage characteristics of PLEDs: unblended PFO (dash black) and blend with PS (1:3 w/w, solid red). (b) luminous efficiency of the devices in part (a).

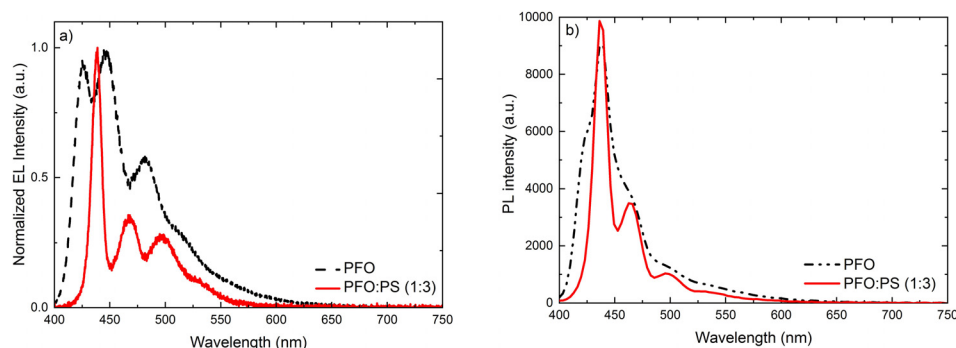


FIG. 3. (a) Electroluminescence (EL) spectra of PLEDs based on unblended PFO (dash black) and PFO:PS (1:3 w/w, solid red) as emissive layers. The EL spectra have been normalized relative to the band corresponding to the 0–1 transition (448 nm, unblended PFO) and 0–0 transition (PFO:PS blend) at 436 nm. (b) Photoluminescence (PL) spectra (in absolute counts) of PFO and PFO:PS (1:3) films ($d = 100$ nm) cast from chlorobenzene.

difficult, we record the UV-Vis absorption spectra of the films of PS-blended and unblended PFO (Fig. 4). The unblended sample exhibits a featureless absorption band with $\lambda_{\text{max}} = 383$ nm, characteristic of fully amorphous PFO.²⁴ In contrast, the spectrum of the PFO:PS blend appears as a linear superposition of the same band and a redshifted, more structured signal, giving rise to a shoulder at ~ 435 nm. The latter feature results from absorption by a fraction of β -phase PFO embedded in the amorphous matrix.²⁶ The fact that the unblended sample exclusively contains amorphous PFO allows us to estimate the β -phase content in the blend by subtracting the contribution of the amorphous component.^{21,34,35} This procedure involves normalizing

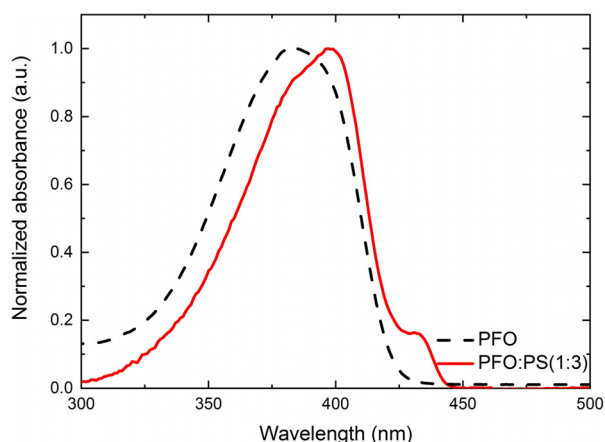


FIG. 4. Peak-normalized absorption spectra of unblended PFO (dash black) and PFO:PS (1:3 w/w, solid red) films cast from chlorobenzene.

the spectrum of the unblended PFO to that of the PFO:PS blend at $\lambda = 354$ nm, i.e., a wavelength where the β -phase does not absorb.²¹ Subtraction yields the percentage of the β -phase in the blend film, tacitly assuming the effective extinction coefficient in both phases to be similar. For the 1:3 PFO:PS blend, we calculate the amount of the β -phase to be $\sim 13\%$.

It has been acknowledged that the presence of the β -phase in the light-emitting PFO layer has several notable advantages,¹⁷ such as reduced formation of (non-emissive) triplet excitons,³⁶ increased resilience against photobleaching,³⁷ and as we shall see below, a high luminescence quantum yield.³⁴ In the present work, the enhanced luminescence quantum yield is directly expressed by the fact that the films of pure PFO and PFO:PS (1:3) exhibit a similar PL intensity [Fig 3(b)], despite the fact that the latter only contains 25% of the active material. This result is consistent with the order of magnitude increase in OLED efficiency upon blending: multiplication of the expected increase in efficiency owing to trap suppression^{14,15} (factor 2) by a factor ~ 4 lower exciton density due to dilution with 75% of insulator reproduces the observed $10\times$ increase in efficiency fairly well. The addition of polystyrene thus has a dual effect in increasing the performance of PFO-based OLEDs: (i) elimination of electron trapping and (ii) increasing the luminescence quantum yield via inducing β -phase formation.

An interesting notion is that the apparent complete energy transfer from amorphous PFO to β -phase domains in principle makes light emission inhomogeneous at the nanoscale. However, on macroscopic length scales, our PLEDs light in a fully homogeneous manner. The presence of a significant amount of β -phase PFO in the blended sample furthermore might explain the unaffected hole current (Fig. 1) since it has been shown that the hole mobility is significantly higher

for β -phase PFO than for the amorphous phase.^{17,38} We reason that this mobility-enhancing effect of the β -phase may compensate for the suppression of the current density due to spatial separation of transport sites.

A remaining question is why β -phase PFO is encountered in the PFO:PS blend and not in the unblended sample. The development of the β -phase has been associated with PFO residing in a poorly accommodating environment. For instance, processing PFO from a poor solvent, such as diiodooctane,²¹ cyclohexane,²⁵ or methylcyclohexane,³⁹ gives rise to β -phase formation, whereas in good solvents such as chloroform and tetrahydrofuran (THF),²⁵ the process is not observed. Hence, the absence of β -phase PFO in our unblended sample suggests that chlorobenzene is a good solvent.

Following the same reasoning, the actual formation of the β -phase in the PFO:PS blend indicates that the polymers have limited compatibility and a thermodynamic driving force for phase separation exists, despite the fact that macro-phase separation is not observed (see [supplementary material](#)).²⁷ This may be a consequence of the phase diagram having a relatively small miscibility gap due to the low molecular weight of the polystyrene.⁴⁰ As a result, following the transition into the region of the two-phase coexistence, the composition of the blend remains near the critical point, which slows down mass transport over macroscopic distances. Hence, the rate of demixing is suppressed beyond that of film formation and vitrification. However, short-range processes, such as stretching of PFO chain segments into the β -phase configuration, may occur well. For more details and context, we refer to our prior work on evaporation-driven quenches of binary polymer solutions.^{41,42}

In summary, we have demonstrated how conformational changes in a luminescent conjugated polymer (polydiocylfluorene, PFO), brought about by blending with a flexible insulating polymer (polystyrene), drastically influences the optoelectronic behavior of the former. Blending induces the formation of PFO β -phase domains, consisting of fully extended chain segments with monomers oriented in a coplanar fashion. These ordered domains exhibit increased conjugation, a smaller optical bandgap, higher luminescence quantum yield, and enhanced charge carrier conduction compared to the amorphous (disordered) bulk. We demonstrate that polymer light-emitting diodes based on PFO blended with 75% polystyrene exhibit a ten-fold increase in luminous efficiency compared to devices based on unblended amorphous PFO. We semi-quantitatively show that this substantial increase has two contributions: i) alleviation of electron trapping owing to a change in the statistics between free and trapped charges as a consequence of the spatial separation of both transport and trap sites and ii) formation of a substantial amount ($\sim 13\%$) of β -phase PFO embedded in the amorphous matrix. The presence of the β -phase possibly counteracts a decrease in hole conduction due to the spatial separation of transport sites caused by dilution.

See [supplementary material](#) for AFM experiments on PFO and PFO:PS films in order to demonstrate that macro-phase separation between PFO and low molecular weight PS is absent.

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