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Suppressing the energy transfer in polymer blends films upon addition of a co-solvent



J. Pereira^a, J. Farinhas^a, J. Morgado^{a,b,*}

^a Instituto de Telecomunicações, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

^b Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

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ABSTRACT

Energy transfer in conjugated polymer blends is an important process in optoelectronics, with its efficiency very sensitive to the details of phase separation in films. Modification of the relative composition of the blend has been the usual strategy to tune the energy transfer efficiency. In this letter we report on a new approach to switch-off that process: the use of a co-solvent. In particular, we find that the addition of 1,8-diiodooctane to xylene solutions of poly(9,9-dioctylfluorene): poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (PFO:F8BT), blends, 99:1 by weight, suppresses the energy transfer in films. This leads to a change from green light-emitting diodes into whitish emitting diodes. This energy transfer suppression is attributed to a stronger phase segregation, with the concomitant formation of larger domains of the two polymers, thereby increasing the distance between energy donor (PFO) and acceptor (F8BT) sites.

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1. Introduction

Polymer blends have been used to extend the absorption range of organic photovoltaic cells [1] and to tune the emission color of polymer light-emitting diodes (PLEDs) [2]. The use of conjugated polymer blends in PLEDs has also been used to improve the emission efficiency by combining polymers with complementary charge transport properties. Blends of poly(9,9-dioctylfluorene) (PFO) and poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) are among the best studied polymer blends in this context, [3] as these two polymers combine complementary hole and electron mobilities with an efficient energy transfer, due to a large overlap of PFO emission and F8BT absorption spectra, leading to green emitting devices [4]. High electroluminescence, EL, efficiencies were reported for blends consisting of 95:5, PFO to F8BT, weight ratio [5]. There was a report showing that the exposure of such blend to a non-solvent (acetone) was able to reduce the efficiency of the energy transfer and induce the appearance of a residual PFO emission. This was a surface directed process, amplified by the device structure, as recombination was essentially occurring close to the surface of the active layer film, which had been in contact with acetone [6].

In the context of the organic photovoltaic cells based on blends

* Corresponding author at: Instituto de Telecomunicações, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal.

E-mail address: jorge.morgado@lx.it.pt (J. Morgado).

of conjugated polymers and fullerenes, the importance of the domains size formed upon spontaneous phase separation was early recognized. In such bulk heterojunction solar cells, too large domains of either component lead to exciton loss associated to inefficient charge generation via exciton dissociation. Therefore the preparation details of such films and the use of post-film formation processes (temperature and solvent annealing) were shown to have a profound impact on the device efficiency [7]. In particular, the use of additives has been explored, [8] such as alcohols and, probably the most commonly used additive currently, 1,8-diiodooctane (DIO) and is still routinely used [9]. DIO, though not always leading to efficiency increase, appears to reduce the size of the domains, leading to finer morphologies, with a material-dependent change of the polymer phase crystallinity [10]. These effects are related to DIO's high boiling point and dissimilar interactions with the blends components.

In this letter we report on recent findings about the role of DIO addition to xylene solutions of PFO:F8BT blends. At variance with the general DIO-promoted finer phase separation in blends of conjugated polymers and fullerenes, DIO promotes the suppression of the very efficient energy transfer from PFO to F8BT, that we find in films prepared by spin coating from regular xylene solutions, and which we attribute to the formation of larger domains of the polymers. We find also that this coarsen phase separation is not specific of this particular polymer pair. We believe this effect has broad implications for polymer-based optoelectronic devices in general and in particular for PLEDs.

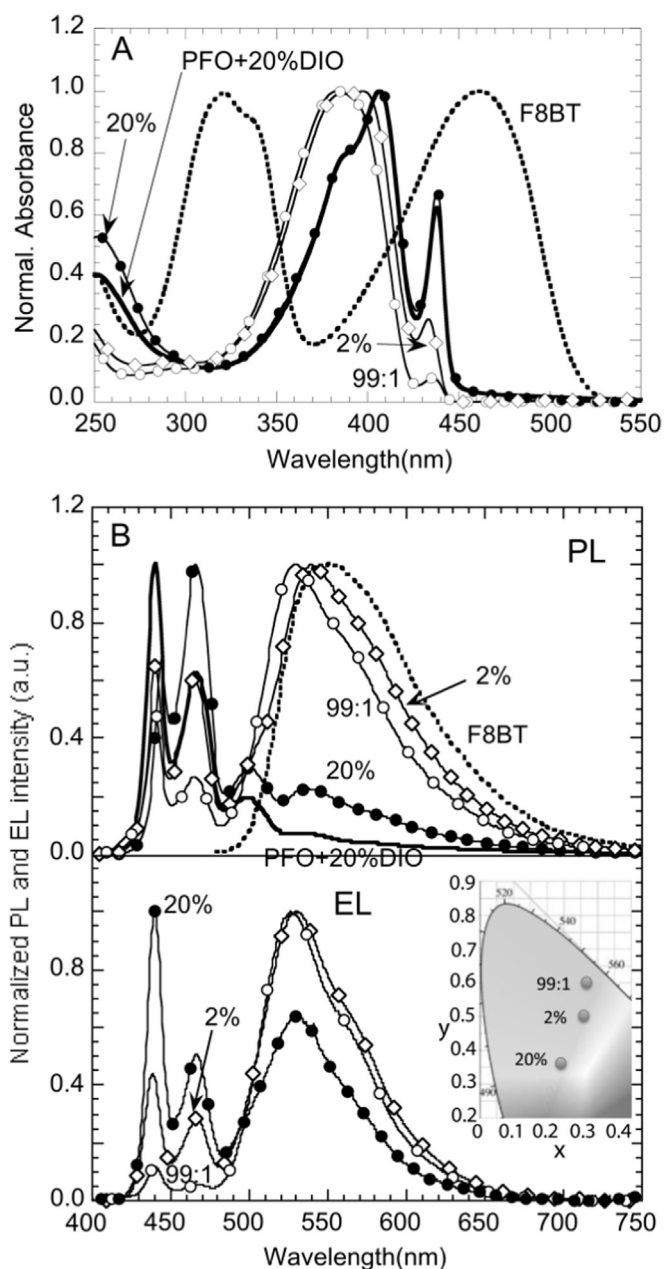


Fig. 1. Normalized absorbance (A) and photoluminescence (PL) and electroluminescence (EL) spectra (B) of the PFO:F8BT, 99:1, blend without and with 2% and 20% DIO added to the solution. PL spectra of neat films of F8BT and PFO (prepared from a xylene solution with 20% DIO content) are also shown. PL spectra of the blends were obtained upon excitation at 385 nm, while the PL of PFO film prepared from a solution with DIO was obtained upon excitation at 407 nm (absorption maximum). The inset shows the CIE coordinates in the chromaticity diagram of the EL spectra.

2. Materials and methods

PFO and F8BT were obtained from ADS and used as received. Solutions were prepared inside the globe box. A starting solution of PFO:F8BT, 99:1, by weight, were prepared in xylene at 0.8%, by weight. Two additional solutions were prepared by adding DIO in 2% and 20% by weight.

PLEDs with ITO/PEDOT:PSS/blend/LiF/Al structure were prepared and tested as described in Ref. [11]. PEDOT:PSS (40 nm thick) was deposited by spin coating on glass/ITO (Visiointek) substrates from an aqueous dispersion (Clevios P VP.AI 4083, from Heraeus) and annealed in air at 120 °C for 10 min. These glass/ITO/

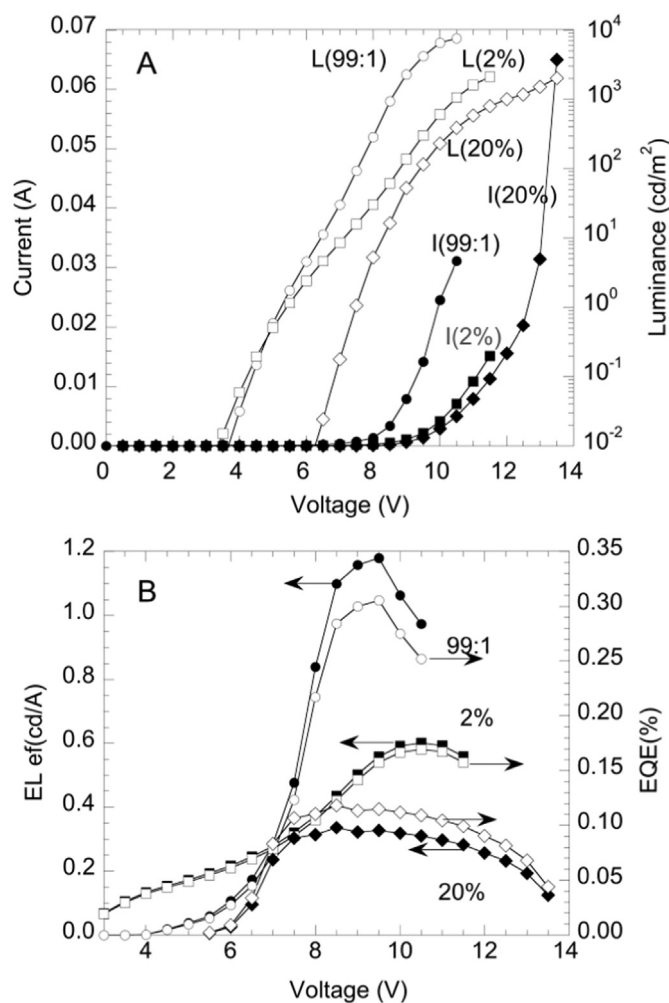


Fig. 2. A. Current (I) and luminance (L) of the devices prepared with the PFO:F8BT blends as a function of the applied voltage, and B. corresponding luminous and external quantum efficiency (EQE).

PEDOT:PSS substrates were then transferred inside a glove box to finalize device fabrication. Films of PFO:F8BT were deposited by spin coating at 1800 rpm to give films with thicknesses in the range 80–90 nm. PLEDs were finalized by depositing 1.5 nm of LiF followed by a top layer of ca. 80 nm aluminum, defining pixel areas of 4 mm². Electroluminescence (EL) spectra were recorded with a ScanSci CCD spectrograph. Absorption and photoluminescence (PL) spectra of films deposited on spectrosil substrates were obtained using a Cecil 7200 UV/VIS spectrophotometer and a SPEX fluorolog 2121 fluorimeter, respectively. AFM images were obtained with a Nano Observer from Concept Scientific Instruments (Les Ulis, France) using non-contact mode with cantilevers having resonant frequencies between 200 kHz and 400 kHz and silicon tips of under 10 nm radii. Gwydion (version 2.26) software was used for data processing.

3. Results and discussion

Fig. 1 shows the absorption, PL and EL spectra for the various blends. F8BT contribution to the blends absorption spectrum is negligible, which is consistent with the very low F8BT content. The PL spectrum of the 99:1 blend has contributions from both materials. Despite the very low content of F8BT, which is not noticeable in the absorption this dominates the emission spectrum. Additionally, we find that the emission maximum of FBT in the

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