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Optical and morphological investigations of non-homogeneity in polyfluorene blends

J. Morgado[a,b], E. Moons[c], R.H. Friend[a], F. Cacialli[a,*]

[a]*Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 0HE, UK*
[b]*Instituto Superior Técnico, Av. Rovisco Pais, Lisboa, Portugal*
[c]*CDT Ltd., Madingley Road, Cambridge CB3 0HJ, UK*

Abstract

We report investigations of organic light-emitting diodes with an active layer consisting of poly(9,9-dioctylfluorene), PFO, blended with a green emitting derivative (F8BT). We used indium tin oxide (ITO) anodes with and without a hole transporting layer, consisting of doped poly(3,4-ethylene dioxythiophene). We also studied the incorporation of an oxadiazole based hole-blocking/electron transporting layer, HBL, namely 2-(4-biphenylyl)-5-butylphenyl-1,3,4-oxadiazole, PBD, between the emissive layer and the Ca/Al cathodes. The presence of this layer reduces the range of radiative recombination in a region closer to the HBL interface, and therefore, allows investigation of depth-dependent structural non-uniformities of the emissive layer. We find marginal alterations of the electroluminescence spectra depending on the weight concentration of the F8BT in the range 5–25%. Efficient energy transfer from the host (PFO) to the guest (F8BT) ensures that the emission spectra are dominated by the green component. However, we find that blue emission from the PFO host is much more intense for the structures incorporating the HBL than for those without it. We propose that phase separation phenomena of the blend induced by the spin-coating of the PBD-based layer, are responsible for the higher weight of the blue component. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyfluorene; Blends; Phase separation; AFM

1. Introduction

Polyfluorenes constitute a family of interesting organic semiconductors for application in light-emitting diodes, (LEDs). They display electroluminescence (EL) [1], and photoluminescence (PL) and a high ionisation potential. Recently, circularly polarised emission has been demonstrated by embedding oligofluorenes in a glass forming chiral nematic liquid crystal [2].

The possibility of preparing useful optoelectronic materials by mixing different semiconductors in solution is an important advantage of organic over inorganic semiconductors. This approach allows decoupling of the electronic transport and luminescence functionalities, and therefore, a greater freedom in the choice of optimum structures. The EL efficiency and the value of both turn-on and operating voltage can be improved effectively with this strategy [3], which also allows for harvesting of both fluorescence and phosphorescence, where one of the components displays efficient phosphorescent emission [4,5]. For polymeric blends, control over the active layer morphology is a very important issue, as in general the small value of the entropy of mixing leads to phase separation of polymeric components, even if chemical differences are minimum. These phenomena enrich and complicate the physics of devices, with addition of new properties which need to be understood for optimum design.

Here, we report the fabrication of LEDs which make use of poly(9,9-dioctylfluorene), PFO, blended with a green-emitting derivative, namely: poly(9,9-dioctylfluorene-alt-benzothiadiazole), F8BT. Efficient energy transfer from the host (PFO) to the guest (F8BT) ensures that the emission spectra are dominated by the green component. However, we find that blue emission from the PFO host is much more intense for structures incorporating a hole-blocking layer (HBL), between the cathode and the emissive blend film.

2. Experimental

We prepared three different blends with 25, 15 and 5% by weight of F8BT in PFO, which we refer to as F75, F85, and

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[*] Corresponding author. Tel.: +44-1223-333-318; fax: +44-1223-353-397.
E-mail address: fc10004@cam.ac.uk (F. Cacialli).

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F95, respectively. Thin films of both the pure components and the blends were spin-cast from xylene solutions onto spectrosil or indium tin oxide (ITO), coated glass substrates. The polyfluorenes peak molecular weight, determined against polystyrene standards, *M*p, was in the range from 1.5×10^5 to 2×10^5 for PFO and from 1×10^5 to 3×10^5 for F8BT. Polydispersity values are 1.5–2 for F8BT and 2–2.5 for PFO. For atomic force microscopy (AFM), we used polymers with peak molecular weights at the higher end of the scale, whereas lower molecular weight polymers were used for luminescence experiments.

Absorption and PL spectroscopy were carried out on thin-films deposited onto spectrosil substrates by means of a Hewlett-Packard B453 UV–VIS spectrophotometer (absorption) and of a CCD UV-enhanced spectrograph (PL). The PL efficiency was determined on films deposited on spectrosil substrates, using a nitrogen purged integrating sphere. Excitation was with the multi-line UV mode of an Ar-ion laser. Note that, the main lines are at ~351 and 363.8 nm, and that both PFO and F8BT have very similar absorption coefficients at these wavelengths.

For LEDs preparation, we used commercial ITO substrates (Asahi), and treated them with a 10 min oxygen plasma exposure. This treatment is useful in order to optimise a variety of surface properties such as work function, roughness and hardness, sheet-resistance, and surface energy [6,7]. The PEDOT:PSS (Bayer) was coated from a water dispersion so as to give a ~30–40 nm thick layer after drying (~90°C; 1 h) and is expected to bring about an increase of ~0.5 eV of the anode work function [8]. Active layers were spin-coated from xylene solutions on either the bare ITO or on ITO/PEDOT substrates so as to give film thickness of 80–210 nm, whereas the HBL layer was spin-cast from an acetone solution of 2-(4-biphenylyl)-5-butylphenyl-1,3,4-oxadiazole, PBD (75 wt.%) in poly-(methylmethacrylate), PMMA, so as to give a thickness in the range 25–140 nm. Cathodes (Al or Ca/Al) thermal evaporation completed the preparation of the diodes which were then tested in a 10^{-2} mbar vacuum. Other details are as reported earlier [3]. AFM images were taken by means of a Dimension 3100 (Digital Instruments, Santa Barbara) microscope operated in tapping mode, in air and at room temperature. The TESP tips were used for the observations reported in here with a resonance frequency of 350–400 kHz.

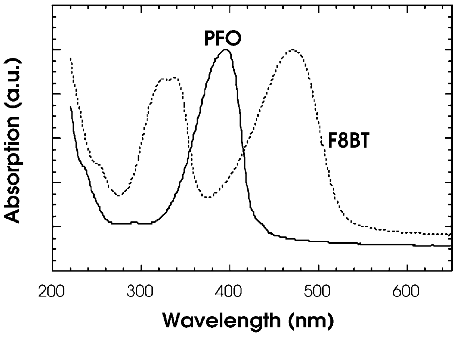

Fig. 1. The optical absorption spectra of thin films of PFO and F8BT on spectrosil.

3. Results

Fig. 1 displays the absorption of PFO and F8BT films on spectrosil discs, and in Fig. 2(A) we report the PL (full lines) and EL (dashed lines) emission of both the pure compounds (PFO and F8BT), and the blends (F95, F85, and F75). The EL spectra are from LEDs with a PEDOT:PSS coated ITO anode and a Ca/Al cathode. In Fig. 2(B), we report the EL spectra of the 2-layer LEDs, i.e. incorporating the oxadiazole-based HBL, in addition to the active layer. Note, here the presence of a blue component, which is not detected in the EL spectra of the single-layer devices (Fig. 2).

In order to clarify the mechanism responsible for the blue components, we also measured the PL spectra of these devices. For this, we used again an UV excitation beam impinging on the cathode-free areas of the LEDs. Fig. 3(A)

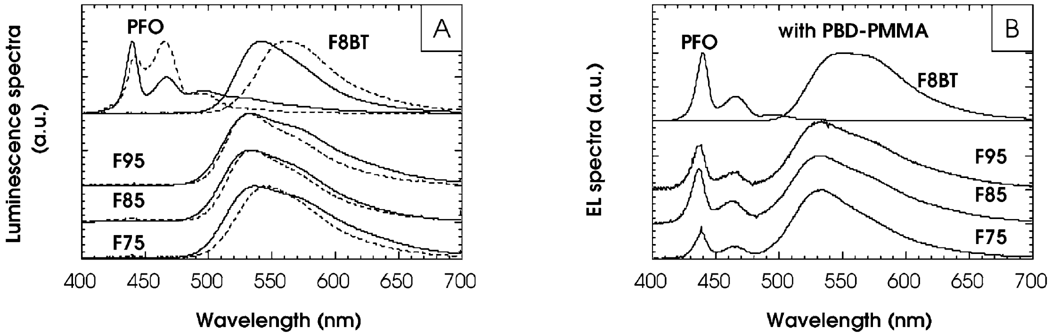

Fig. 2. (A) Electroluminescence (EL) (full line), and photoluminescence (PL) (dashed line), spectra for thin films of PFO, F8BT and related blends. The EL spectra are from LEDs with a PEDOT hole transporting layer and a Ca/Al cathode (~4 mm^2 area), but no hole-blocking layer. PFO emission is nearly completely quenched in both PL and EL for all the blends, indicating efficient energy transfer; (B) EL spectra of LEDs with a PMMA-PBD HBL. Note, the emission from PFO, not present in (A).

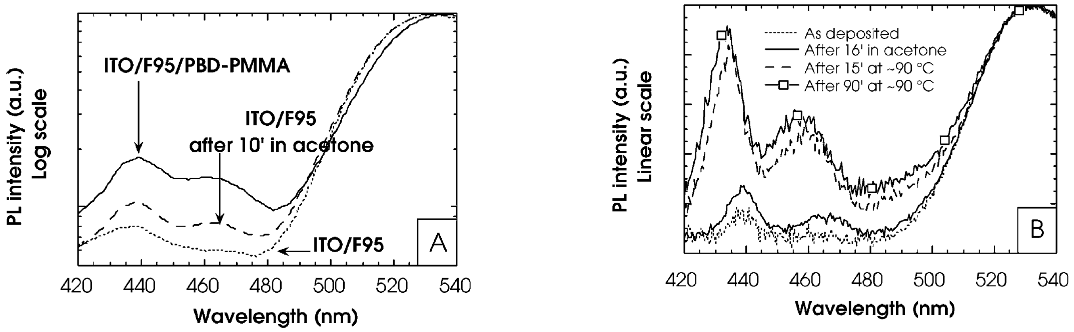

Fig. 3. (A) PL spectra of an ITO/F95 sample before and after a 10 min immersion into acetone, and of an ITO/F95/PBD-PMMA sample. All spectra are normalised to F8BT PL peak. Note the growth of PFO emission with respect to F8BT; (B) comparison of PL spectra for as-deposited and "16 min acetone" samples with samples heated at ∼908 for 15 min (broken line) and ∼90 min (open squares and full line).

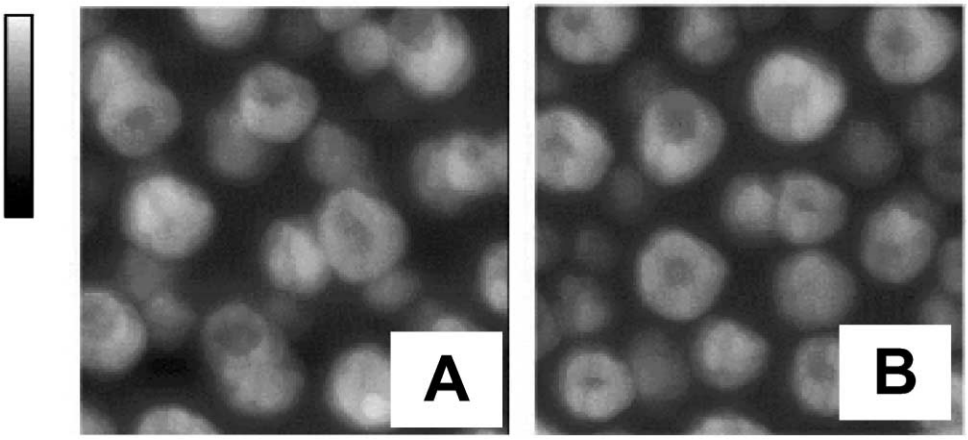

Fig. 4. The 2 μm × 2 μm AFM tapping mode topographic images of an F75 blend film spun from a xylene solution onto an ITO-coated substrate: (A) before the treatment; (B) after the treatment. The vertical scale is are 0–90 nm.

reports spectra of an ITO/F95 sample before and after 10 min immersion into an acetone bath, and of an ITO/F95/PBD-PMMA sample. Fig. 3(B) displays instead further PL investigations of F95 spun on spectrosil, aimed at clarifying the effect of heat treatments on the PL emission. All the spectra have been normalised to the peak of the F8BT emission. Note, the growth of the PFO emission with respect to that from F8BT.

Interestingly, AFM investigations do not reveal major morphological differences before and after the acetone treatments. However, different surface morphologies are indeed observed depending on the relative concentration of the two polymeric components and their molecular weights (in the range $M\text{p} = 1 \times 10^5$ to 3×10^5). As expected, the occurrence of surface features, which are suggestive of phase separation [9], is more evident for the highest molecular weights and at the highest F8BT content, but little or no difference of the surface morphology is detected upon acetone treatment. Fig. 4 shows, for example, AFM images of an F75 film deposited onto an ITO coated substrate before and after a 15 min immersion in acetone.

4. Discussion

Comparison of F8BT absorption and PFO emission (Fig. 2(A), top) identifies a significant spectral overlap, suggesting efficient energy transfer of excitations from PFO to F8BT, via a Förster mechanism. Indeed emission from the blends is dominated by F8BT in both PL and EL.

Förster transfer is relatively long range, and accounts for exciton diffusion lengths of 5 nm or so in many conjugated polymers. In this particular case, we estimate the Förster transfer radius to be of ∼5 nm. Absence of PFO emission in the untreated blends with the lower Mp polymers ($\sim 10^5$) is, therefore, evidence that complete phase separation of the two components, if it occurs, is on this or a smaller scale.

Unexpectedly, the EL spectra of the LEDs incorporating PBD-PMMA display significant emission in the blue, which can be unequivocally assigned to PFO. Note that, PBD-PMMA acts essentially as a hole-blocking layer, forcing the recombination to happen close to the emissive-polymer/PBD-PMMA interface. Therefore, the observation of the blue component could be evidence that phase-separation between PFO and F8BT occurs in the interfacial layer, owing to the chemical difference of the materials and their presumably different surface energies. If this is the case, the presence of the HBL does not modify the properties of the blend surfaces but only acts as a tool for confining the emission to a region much smaller than that probed in PL, and therefore "amplifies" the detection a feature which is otherwise undetected.

Alternatively, the phase separation may be due to the spin-coating of the HBL layer, and indeed Fig. 3(A) and (B) show that a PL measurement also detects an increase of the blue component in both the LEDs structures and thin films after a variety of treatments ranging from spinning of a few drops of acetone (the solvent for the PBD-PMMA), to immersion into an acetone bath, to heating. The weight of the blue component with respect to the green one (F8BT) is here much smaller than in Fig. 2, but this is due to the relatively long region probed by the exciting beam. Heating at even moderate temperatures (<90°C), not only results in a much more prominent blue emission, but also in a slight blue-shift of the features, which allows us to exclude the presence of heating effects in the spectra of Fig. 2.

We conclude that the blue components in Fig. 2 are the result of the PBD layer deposition. These effects involve mainly the interfacial layer, as the effect is much more prominent in EL than in PL, owing to the strong confinement of the recombination in the EL experiment. Phase segregation induced by the device heating during operation can be excluded on the basis of the absence of spectral shifts. It is interesting that phase segregation is induced by a species (acetone) in which either blend components are essentially insoluble. We also notice that phase separation in a thin spin-coated film is usually an incomplete process, which has not reached thermodynamic equilibrium, and hence may leave a residual amount of one of the components in the regions which are rich in the other component [10]. We consider that, this is the reason for the minimum amount of blue emission in the blends before treatment. More precisely, we propose that even in the PFO-rich regions, effective energy transfer takes place from PFO to residues of F8BT, entangled within the PFO matrix. We notice that an F8BT "contamination" of less than 1% by weight is expected to be sufficient for complete quenching of the donor luminescence [3].

Essential lack of alteration of the morphological (i.e. topography) features upon acetone treament may look unexpected, when analysed in conjunction with the clear change in the spectral properties, but is in fact compatible with further segregation of the two phases. Owing to the small number of molecules involved in this process, the morphogical rearrangement is not easy to detect by AFM, but enough to avoid quenching of the PFO PL. The process has some resemblance with aggregation and/or precipitation of a polymer from a solution, by addition of a non-solvent. The difference here is that the "solvent" (though a poor one) is a solid polymer (PFO), and acetone plays the role of the "non-solvent". It is also possible that the presence of PBD:PMMA also plays a role in the further separation of F8BT from PFO, enhancing the effect of acetone. Although identification of the detailed mechanisms and interactions leading to phase separation is beyond our scope here, we consider that swelling of the polymer surfaces and/or preferential interaction of one of the two polymers with acetone enhance reptation of the macromolecular chains and drive the system towards further de-mixing. Furthermore, our results prove that luminescence measurements are sensitive probes of phase separation, segmental and chain dynamics, and of the interaction between a non-solvent and conjugated polymer blends.

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