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BEHP-PPV and P3HT blends for light emitting devices

M. Valadares [a,*], I. Silvestre [a], H.D.R. Calado [b], B.R.A. Neves [a], P.S.S. Guimarães [a], L.A. Cury [a]

[a] Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, Minas Gerais, Brazil
[b] Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, Minas Gerais, Brazil

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ABSTRACT

Photoluminescence (PL) and electroluminescence (EL) emissions from blended films composed by Poly[2-(2′,5′-bis(2′-ethyl-hexyloxy)phenyl)-1,4-phenylenevinylene] (BEHP-PPV) and poly(3-hexylthiophene) (P3HT) conjugated polymers are investigated. A PL broad emission spectrum within the visible range was obtained for the BEHP-PPV/P3HT blends. The electroluminescence (EL) spectra of light emission devices fabricated with the blended films with 50% and 25% relative concentration of P3HT present a similar broad emission but shifted to higher wavelengths with increasing applied bias. This tuning capacity was interpreted as due to a change in the effective gap of the blended system caused by the redistribution of injected carriers in the BEHP-PPV/P3HT interfaces of the blend under bias.

1. Introduction

Conjugated polymers are electroluminescent materials which present large quantum efficiency at room temperature. This fact, associated with their attractive functional properties of traditional semiconductors, their solubility in common organic solvents, and easy processability and low costs in comparison with the traditional semiconductors, places the conjugated polymers as a class of electronic plastic materials with wide potential applications in optoelectronics [1–3] and photovoltaic devices [4–6]. The possibility to use conjugated polymers as base materials for organic light emitting devices (OLEDs) was reported for the first time in the decade of 1990 [7,8]. The fabrication and study of polymer blends [9–15] has been a natural extension of polymer science because different aspects of the constituent polymer materials can be combined to create new compounds with wider potential applications. In this picture, conjugated polymer blended materials have been employed in order to obtain OLEDs with white emission [16–19] and tunable emission [20–22]. Devices containing only one blended film as active layer have the additional advantage of the simplicity in the fabrication process, which reduces the costs in production.

We study blended films of Poly[2-(2′,5′-bis(2′-ethyl-hexyloxy) phenyl)-1,4-phenylenevinylene] (BEHP-PPV) and poly(3-hexylthiophene) (P3HT). The BEHP-PPV presents an increased stability compared to other PPV derivatives [23,24], which is an important factor for technological applications. The P3HT, as well, has been extensively used for electric and photovoltaic applications [25–30]. From our knowledge there are no works treating blends of BEHP-PPV/P3HT in the literature, despite the potential applications of both materials. The technological interest of this system, besides being a blend of green and red emitter polymers, is the combination of the electrical stability and resistance to oxidation of the BEHP-PPV and the good electronic properties presented by P3HT.

We observe a broad emission region in the visible range for the blended films. The OLEDs fabricated also presented a broad band electroluminescence region, with the peak intensity shifting to higher wavelengths with increasing bias. The EL emission characteristics agree with the interpretation that injected carriers induce an effective HOMO–LUMO bending at each internal BEHP-PPV/P3HT interfaces of the blended material, decreasing the emission gap and reducing the BEHP-PPV contribution to the emission spectrum.

2. Experimental details

The polymerization procedure of the regioregular P3HT used in this work is described in [14]; the BEHP-PPV was acquired from Aldrich. Solutions of pure P3HT and BEHP-PPV conjugated polymers were prepared by dissolving them into chloroform ($CHCl_3$) solvent and subsequently stirred for 7 days. Both solutions had concentrations of 15 mg/ml. Three blend solutions of BEHP-PPV/P3HT, with 25%, 50% and 75% relative concentration of P3HT, were prepared by mixing the appropriate volumes of the corresponding polymers. Spin-coated films from each final solution were done at 500 rpm inside a glove-box under a pure nitrogen atmosphere.

* Corresponding author. Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Avenida Antonio Carlos, 6627, 31270-901, Belo Horizonte, MG, Brazil. Tel.: +55 31 34096610; fax: +55 31 34095600.
E-mail address: marcelov@fisica.ufmg.br (M. Valadares).

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Photoluminescence (PL) spectra of the blended and pure films were measured at room temperature. All samples were put together inside an immersion cryostat under vacuum in order to avoid any photo-oxidation effect. The cryostat was mounted on top of a XY-driver, which enables us to change samples by small displacements without losing the optical alignment. A Q-switched Nd:YAG laser emitting at 355 nm was used as the excitation source. The PL emission was collected in a backscattering configuration and focused into an Ocean Optics USB2000 Miniature Fiber Optic Spectrometer.

The OLED structures for the 50% and 25% relative concentrations of P3HT in the blend and for the pure BEHP-PPV and P3HT materials were fabricated with the respective active layers sandwiched by fluoride thin oxide (FTO) and aluminum layers, respectively the anode and cathode contacts. In all structures a PEDOT:PSS layer was deposited by spin-coating at 1000 rpm between the FTO contact layer and the active layer. A thin LiF (lithium fluoride) layer (~2 nm) was evaporated over the polymer layer before evaporating the aluminum contact. The electroluminescence emission was detected by the same Ocean Optics USB2000 Miniature Fiber Optic Spectrometer as in the PL measurements.

3. Results and discussions

The PL spectra for the pure BEHP-PPV and P3HT materials and the blends with 25%, 50% and 75% relative P3HT concentrations are shown in Fig. 1. All changes observed in the shape of the spectra of the blends seem to be straightforwardly related to the evolution of the contribution of the emission of the P3HT constituent to the PL spectrum as its relative concentration in the blend is increased [31].

OLED structures for the 50% and 25% relative concentration of P3HT in the blend and for the pure BEHP-PPV and P3HT materials were fabricated in order to verify the optical properties observed in the respective films. Fig. 2 shows the EL curves for the blend with 50% relative P3HT concentration and the pure devices at a bias approximately 1 V above the threshold. The emission efficiency of the blended film is significantly higher than those of both pure devices. This higher emission efficiency of the blended system is observed for both blends at all biases. In addition, we also find that OLEDs fabricated with the blend can be operated at biases up to 7 V above threshold, similar to the values for the BEHP-PPV OLED, while OLEDs fabricated with P3HT typically withstand a maximum of 2 V above threshold. These properties make the BEHP-PPV/P3HT blend a very attractive material for fabrication of efficient OLEDs.

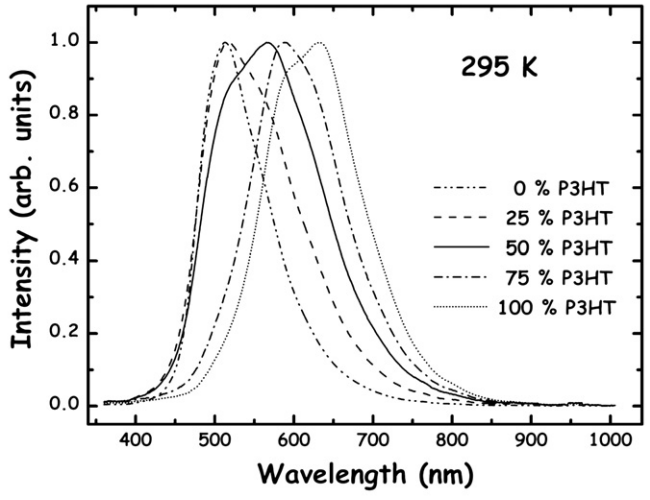

Fig. 1. Photoluminescence spectra at room temperature for the blends with 0%, 25%, 50%, 75% and 100% P3HT relative concentration. The excitation laser power was 0.300 mW.

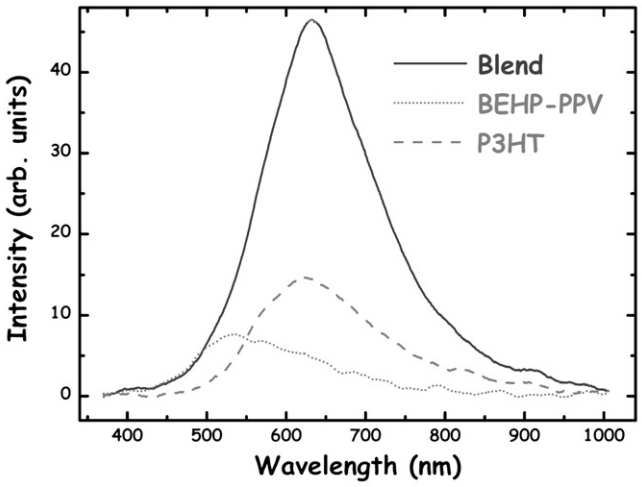

Fig. 2. EL curves for the blend with 50% relative P3HT concentration and the pure devices at a bias approximately 1 V above the threshold. The emission efficiency of the blended film is significantly higher than those of both pure devices. A similar result was observed for the blend with 25% relative P3HT concentration.

Broad band EL spectra were observed for the OLEDs but at wavelength positions higher than the corresponding PL spectrum (Fig. 3a and c). Similar behavior was observed by Yu et al. [32]. The small but clear shift of the EL spectra to higher wavelengths with increasing applied bias is shown in Fig. 3b and d. This wavelength displacement can be also observed in the CIE-1931 chromaticity diagram shown in Fig. 4, where we note that the eye apparent color goes to the edge, representing a more pure red color for both devices. In the blend with 50% relative P3HT concentration, the contribution of the BEHP-PPV to the final shape of the EL spectrum decreases considerably compared to the PL spectrum. This can be seen in Fig. 3a. Note in particular that the EL spectrum does not present the shoulder due to the BEHP-PPV emission around 500 nm, which is clearly seen in the PL spectrum. The higher contribution of the P3HT component to the EL spectrum qualitatively agrees with the higher emission efficiency of the P3HT as seen in the PL studies for blended films [31]. Although the EL shows an expressive decrease in the effective gap of the blended active layer (Fig. 3a) the main features on the EL spectrum, corresponding to the P3HT pure electronic (00 peak) and the first vibronic (01 peak) transitions, present the same separation as in the PL characteristics (see Fig. 3a). The relative positions and emission intensities of the electronic transitions in the P3HT are then not so affected by the applied voltage. The decrease of the contribution of the BEHP-PPV to the EL spectrum, however, is a strong indicative that carrier migration is occurring in this blended system.

The higher quantity of the BEHP-PPV polymer causes an orange emission for the device using a 25% relative P3HT concentration as active layer. However, its behavior is, qualitatively, the same presented by the 50% blend. All displacements observed were in the same order of magnitude for both devices (see Fig. 3).

The band lineup of a BEHP-PPV/P3HT interface shown in Fig. 5a presents the HOMO–LUMO energy positions for both materials and the work functions for the aluminum/lithium fluoride and for the fluoride thin oxide (FTO). The HOMO–LUMO energy positions for the P3HT and for the BEHP-PPV were taken from [33] and [34], respectively. In the LED structure the Al/LiF and the FTO/PEDOT:PSS layers are in contact directly with both BEHP-PPV and P3HT immiscible domains [31] distributed in both surfaces of the blended film. Fig. 5b and c shows the two possible configurations for the