Research Letter

Polymer Light-Emitting Diodes Efficiency Dependence on Bipolar Charge Traps Concentration

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The efficiency of light-emitting diodes (LEDs) based on poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-1,4-benzo-{2,1′-3′}-thiadiazole], F8BT, is optimized upon simultaneous doping with a hole and an electron trapping molecule, namely, N,N′-Bis(3-methylphenyl)-N,N′-diphenylbenzidine and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, respectively. It is shown that, for devices with poly(3,4-ethylene dioxythiophene) doped with polystyrene sulfonic acid as hole-injection layer material and magnesium cathodes, the efficiency is nearly doubled (from ca. 2.5 to 3.7 cd/A) upon doping with ca. 0.34% by weight of both compounds.

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1. Introduction

Polymer light-emitting diodes (LEDs) have suffered significant developments since the first report of electroluminescence observation in conjugated polymers in 1990 [1]. This technology is now available in the first commercial products incorporating polymer displays. A very successful combination of materials development and device engineering has been at the origin of this tremendous evolution. Doping of the active polymer layer has been one the approaches used to improve devices efficiency (in particular upon use of phosphorescent dopants [2]) and tune the emission colour, upon use of energy accepting dopants [3, 4]. Studies on LEDs based on this kind of composites have shown that the emission from the dopants is generally amplified, with respect to the emission obtained upon photoexcitation, due to charge trapping and direct recombination at the dopants [3, 4]. Sainova et al. [5] have shown that doping a blue emitting polyfluorene copolymer with various hole transporting materials (in 3% by weight) leads to an improvement of colour stability. Furthermore, they showed that the use of a dopant with lower ionization potential, acting as hole trapping, leads to a significant efficiency improvement. A similar strategy is widely used in the optimization of LEDs based on sublimed, low-molecular-weight organic materials [6, 7]. In this paper we explore the use of bipolar doping, that is, using a hole and an electron trapping dopant, to improve the efficiency of poly[(9,9-dioctyfluorenyl-2,7-diyl)-alt-1,4-benzo-{2,1′-3′}-thiadiazole] (F8BT) based LEDs. By varying the dopant concentration we find a concentration range leading to improved electroluminescence (EL) efficiency. An increase from ca. 2.5 to 3.7 cd/A was obtained upon doping with ca. 0.34% by weight of both compounds.

2. Experimental

Solutions of F8BT (from American Dye Source, ADS133YE) in chloroform were doped with N,N′-Bis(3-methylphenyl)-N,N′-diphenylbenzidine, or TPD, and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, or PBD (both from Aldrich). For the preparation of each solution, the same weight of the two dopants was used. Table 1 shows the compositions of the different solutions (and films) used in this study. Assuming a specific gravity of 1 g/cm³ for the films of neat F8BT and the composites, the concentration number by volume unit of each dopant is also shown in Table 1.

Indium-tin-oxide-(ITO)-coated glass substrates were cleaned with acetone and 2-propanol and treated with oxygen plasma. PEDOT: PSS (or PEDOT, for short, Baytron P from Bayer) was spin coated on top and annealed on a hot
plate at 150°C for 2 minutes, in air. Its final thickness is 45–50 nm, as measured with a Dektak profilometer. Thin films (thicknesses of ca. 85–90 nm) of neat F8BT or dye doped F8BT were then spun coated on top of PEDOT from chloroform solutions. Magnesium cathodes were thermally doped with the electron acceptor PEDOT from 45–50 nm, as measured with a Dektak profilometer. Thin films from [9, 10], respectively. Ionization potentials (Ip) and emission potentials are demonstrated in Figure 1.

The rationale behind the choice of these two dopants is described in [8]. The devices were characterised as described in [8].

### 3. Results and Discussion

The workfunction of PEDOT:PSS and Mg was taken from [9, 10], respectively. Ionization potentials (Ip) and electron affinities (EA) of TPD and PBD were taken from [11] and [12], respectively. Based on cyclic voltammetry measurements on drop-cast films of F8BT, we previously determined Ip = 5.9 eV and EA = 2.42 eV [13]. We note that this EA value for F8BT is much lower than the value of 3.2 eV estimated [14] from Ip, considering the optical gap (2.4 eV) and assuming an exciton binding energy of 0.3 eV. In spite of this difference, we consider that the value obtained from CV is closer to the relevant energy for electron transfer, due to the closer similarity of processes.

Based on the relative position of the frontier levels (assuming vacuum level alignment) we conclude that TPD acts a hole trap with respect to F8BT, while PBD is an electron trap. As evidenced in Figure 1, the electron trapping energy (difference between EA(F8BT) and EA(PBD)) is ca. 0.2 eV, smaller than the hole trapping energy of 0.5 eV (difference between Ip(F8BT) and Ip(TPD)). Supporting evidence comes from studies of LEDs showing that doping F8BT with 2% by weight of TPD causes a much more significant decrease of the current than does a similar doping with PBD (also 2% by weight) with respect to LEDs based on neat F8BT. Furthermore, both PBD and TPD are blue emitters. No energy transfer occurs from F8BT to any of the two dopants. In solid state, the photoluminescence (PL) emission of TPD (with smaller energy gap than PBD) peaks at ca. 420 nm, while the emission of F8BT peaks at about 550 nm. No spectral overlap occurs between F8BT emission and TPD absorption. Any exciton formed at the dopant sites would be, instead, transferred to F8BT. In fact, the electroluminescence spectra of the doped devices are the same as that of the devices based on neat F8BT, without any evidence of dopants interference.

For the preparation of the composites, we used the same amount, by weight, of each dopant. Due to the lower molecular weight of PBD, this is always present in higher concentration number per unit volume, as observed in Table 1. However, the effect of this higher concentration with respect to TPD is attenuated by its lower charge trapping energy, as discussed above.

Figure 2 shows typical results obtained for the LEDs prepared with neat F8BT and with the composites A to F described in Table 1.

Figure 2(a) shows that doping of F8BT leads to a decrease of the current flowing through the devices. Such current decreases upon increase of dopant concentration. Both disorder and charge trapping contribute to this effect, and both explain the observed trend. In view of the relative position of the frontier levels, we consider that charge trapping is likely the most effective factor, supporting the relative energetic position of the frontier levels shown in Figure 1. The luminance-voltage behaviour is also strongly dependent on dopant concentration: the maximum luminance increases from device A (110 cd/m²) to nea F8BT (16200 cd/m²), being this maximum luminance attained at increasing voltages upon increase of dopant concentration. A significantly different luminance-voltage behaviour is observed for the device prepared with the composite having the highest dopants concentration (device A). For the other devices, they all have similar behaviour, with similar values for the light-onset voltage (3 to 3.5 V).

The electroluminescence (EL) efficiencies shown in Figure 2(c) are maximized at intermediate doping levels (compositions C, D, and E). A decrease of dopant concentration leads to efficiencies closer to that of neat F8BT, while higher concentrations (above composition E) lead to an efficiency decrease.

The above results are explained in terms of electron trapping at PBD sites and hole trapping at TPD sites. The presence of these bipolar traps improves the charge balance within the emissive layer leading to an efficiency increase. At intermediate dye concentration levels (ca. 10²⁰ to 10²¹ cm⁻³) we find maximum efficiencies. We attribute the decrease of EL efficiency at the too high concentrations to trapped charge-induced luminescence quenching. At the lowest concentrations we observe a decrease of the trapping effect, approaching the behaviour of the devices based on neat F8BT.

### 4. Conclusions

Doping with adequate bipolar charge trapping dyes can lead to an increase of polymer LEDs efficiency, providing their concentration is optimised. For the studied system, composition D is the one giving, on average, the highest efficiency, with an increase of ca. 60% with respect to neat F8BT. Furthermore, the use of bipolar dopant concentrations in the range of compositions D to E lead to maximum EL efficiency while allowing for maximum luminances (ca. 10⁴ cd/m²) not much different from those of neat F8BT-based LEDs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of each dopant in % by weight</th>
<th>PBD conc. (10¹⁹ cm⁻³)</th>
<th>TPD conc. (10¹⁸ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>3.43</td>
<td>2.35</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1.72</td>
<td>1.18</td>
</tr>
<tr>
<td>C</td>
<td>0.67</td>
<td>1.14</td>
<td>0.781</td>
</tr>
<tr>
<td>D</td>
<td>0.34</td>
<td>0.578</td>
<td>0.396</td>
</tr>
<tr>
<td>E</td>
<td>0.096</td>
<td>0.163</td>
<td>0.112</td>
</tr>
<tr>
<td>F</td>
<td>0.019</td>
<td>0.0319</td>
<td>0.0219</td>
</tr>
</tbody>
</table>

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Figure 1: Frontier levels energy of the LEDs components.

Figure 2: (a) Current-voltage, (b) Luminance-voltage, and (c) electroluminescence (EL) efficiency for the devices prepared with neat F8BT and the composites identified in Table 1. The device identification (A to F) is that of the corresponding composite used as active layer.
Acknowledgment

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References


