White emission from organic light emitting diodes based on energy down-conversion mechanisms

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Abstract

Balanced white electroluminescence (EL) emission from binary organic blends was achieved via intermolecular down-conversion processes: the exciplex and the Foerster transfer mechanisms. This was obtained by combining a low electronic affinity (EA) molecule, a diamine derivative (TPD), with two high electronic affinity substituted oligothiophenes having high and low ionization potential (IP), respectively. Both the energy down-conversion mechanisms were exploited in two single active-layer organic light emitting devices, showing stable white emission, independent of the applied voltage.

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1. Introduction

The achievement of white emission from organic light emitting diodes (OLEDs), which exhibit good electroluminescence (EL) performances (low turn-on voltage, high efficiency and high luminance), extreme flexibility and cheap fabrication technology, could have a tremendous impact on light industry and backlight applications. To date, the most used approach to fabricate white OLEDs consists of a combination of materials with different HOMO-LUMO gap, E_g , in multilayer structures realized by consecutive evaporations [1–6]. Clearly, using a unique blend made by the low- and the high-energy emitters, in a single-step spin coating fabrication, would be definitely more convenient in terms of cost and throughput.

In this work, we show that charge and energy intermolecular transfer between organic molecules can be used to achieve white emission from single active-layer OLEDs by means of either exciplex formation or Foerster transfer. The two mechanisms can be observed by blending a diamine derivative (TPD) with two high electronic affinity (EA) substituted oligothiophene-*S,S*-dioxides, i.e. a monomer having high ionization potential (IP), and a pentamer with low IP,

respectively. Both transfer mechanisms are exploited to obtain white EL with stable color coordinates, independent of the applied voltage.

2. Experimental

Our OLEDs were prepared by spin coating a hole-transporting layer of poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulphonate) (PSS) onto preliminarily O₂-plasma treated indium-tin-oxide (ITO) coated glass substrates. Then, we spin-cast the active media, i.e. a blend of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and 2,5-bis(trimethylsilyl)-thiophene-1,1-dioxide (STO) (device #1) and a blend of TPD and the pentamer, 3,3',4'',3'''-tetracyclehexyl-3'',4''-dimethyl-2,2':5'',2''':5'',2''':5''',2''':5''':quinguethiophene-1'',1''-dioxide (T5oCx) (device #2). The molecular structures of the employed compounds and their energy levels are shown in Fig. 1. A calcium electrode followed by an aluminum cap was finally deposited by thermal evaporation (10^{−6} mbar base pressure). The device characterization was performed at room temperature in air atmosphere. The photoluminescence (PL) characterization was carried-out on films deposited onto quartz glass substrates under He–Cd laser ($\lambda = 325$ nm) excitation.

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Fig. 1. Energy levels and molecular structures of the employed compounds: TPD (left), STO (center) and T5oCx (right); R = *n* – hexyl, R₁ = cyclo-hexyl.

3. Results and discussion

The PL spectra of TPD, STO, T5oCx and of the TPD/STO and TPD/T5oCx blends are shown in Fig. 2a and b, respectively. In both cases, we observe the blue emission of TPD [7] and a broad red shifted band, due to the emission from the charge transfer exciplex state between TPD and STO (#1) and to the non-radiative (Foerster) transfer from TPD (donor) to T5oCx (acceptor) (#2), respectively. In the

Fig. 2. (a) PL spectra of TPD (dotted line), STO (dashed line) and T5oCx (solid line). (b) PL spectra of the TPD/STO (open circles) and TPD/T5oCx blend (full squares). The relative molar concentrations were STO/TPD = 0.2 and T5oCx/TPD = 4.5×10^{-4} .

Fig. 3. EL spectra of the TPD/STO (open circles) and TPD/T5oCx blend (full squares).

TPD/T5oCx blend the Foerster transfer mechanism is favored by the strong spectral superposition existing between the emission spectra of TPD and the absorption of T5oCx [8–10], whereas the exciplex formation, in the TPD/STO blend, is induced by the different EA and IP of the two emitting materials. Both charge and energy transfer mechanisms can be schematized as:

where D^* , X , D and A stand for the excited donor (TPD), the intermediate-excited system, the ground state of the donor and that of the acceptor, respectively; $h\nu$ is the energy of the emitted photons; X the charge transfer exciplex complex (D^+A^-), and the unexcited donor–excited acceptor couple ($D + A^*$) for the blends #1 and #2, respectively.

The EL spectra from our binary blends are shown in Fig. 3. Unlike the PL spectrum, the EL spectrum of device #1 shows three distinct peaks localized at about 525, 580 and 650 nm, respectively, which can be attributed to exciplex states related to different molecular configurations, whose population is more favored under electrical pumping [11].

The EL color was characterized, according to the standard of the Commission Internationale de l'Eclairage (CIE), as a point in the two-dimensional space of coordinates (X , Y) (Fig. 4). The most balanced white EL emission was found to have CIE coordinates (0.39, 0.40) and (0.31, 0.34) for devices #1 and #2, obtained by relative molar concentrations, STO/TPD = 0.2 and T5oCx/TPD = 10^{-3} , respectively.

The exciplex-based OLED shows a turn-on voltage, V_{ON} , and a maximum luminance, L , of 5.5 V and about 270 mW/(m² sr) (at 15 V), whereas the Foerster transfer-based device exhibits V_{ON} = 3.1 V and L = 1020 mW/(m² sr) (at 5.4 V). Moreover, for both devices almost no dependence on the applied voltage was observed for the emitted color, whose CIE coordinates exhibit variations of less than 5% by increasing bias.

Fig. 4. CIE diagram with the color coordinates of the EL emission from the TPD/STO (open circle) and TPD/T5oCx blend (full square).

4. Conclusion

In summary, we reported on two approaches to obtain white emission from binary blends employed as emitting medium in single active-layer OLEDs. They are based on two different intermolecular transfer mechanisms, namely the charge transfer exciplex formation between two blue-emitting materials (TPD and STO) with different EA and IP, and the Foerster transfer from a high-energy com-

pound (TPD) towards a red-emitting pentamer (T5oCx). We successfully exploited both these mechanisms by fabricating OLEDs showing balanced white emission almost not depending on the applied voltage.

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