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White emission in polymer light-emitting diodes: Color composition by single-layer electroluminescence and external photoluminescence component

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ABSTRACT

White emitting devices were obtained through a single component system by combining two materials with different emission properties: a greenish electroluminescent polymer, known as poly[(9,9-diocytfluorenyl-2,7-diyl)-alt-co-(9,9-di-(5'-pentanyl)fluorenyl-2,7-diyl)] (PFOFPen), embedded in a diode-like structure (ITO/PEDOT-PPS/PFOFPen/Ca/Al) and a photoluminescent red-emitting material, poly[2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-phenylenevinylene] (MDMO-PPV). A thin film of the red emitter component (MDMO-PPV) was deposited on a quartz plate and mounted on the opposite face of the glass/ITO substrate. The white color composition (0.35, 0.31) was obtained based on trivial photophysics processes: MDMO-PPV partially absorbs the higher energy electroluminescence (EL) emission coming from the PFOFPen-diode, decaying radiatively and emitting red light via photoluminescence (PL), matching with the transmitted greenish light. White emission is thus accomplished by choosing the proper materials with overlapped absorption spectra, adjusting the absorbance ratio by changing the MDMO-PPV layer film thickness, and the lower energy PL intensity until reaching the CIE white coordinates.

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1. Introduction

White organic light-emitting diodes (WOLEDs) have become one of the most challenging and coveted applications on recent lighting technology [1]. So far, fabrication of WOLEDs uses three main strategies: (i) development of an active layer that is composed of a mixture of different polymers forming blends or polymer-dyes with different color emissions [2]; (ii) manufacturing of a device with a single molecular structure that exhibits simultaneously blue, green and red emissions [2]; or (iii) in a multilayer device structure, which employs light-emitting layers with different color emissions [3]. Although all of them have been successfully reported in the literature, each of those methods involves particular difficulties. For example, the latter (i) requires mixtures of components, which, in general, are immiscible, with very precise but unpredictable amounts of materials. Particularly in the case of polymer blends, since polymers are immiscible or miscible in very small amounts, they undergo a phase separation process, being their morphology very complex and composition dependent, affecting the devices reproducibility and performance [4]. Nevertheless, the device performance of polymer blends has been improved due to the formation of bulk heterojunctions [5]. The second strategy requires production of a single molecule that emits a white spectrum, where precise control of molecular engineering is required that, in some cases, involves the development of new synthetic routes with high reaction yields and strategies for obtaining high purified materials [2,6]. The third WOLED demands a more challenging fabrication, since previously deposited layers are easily dissolved as the subsequent ones are deposited. Therefore, for large-scale industrial application a simplified and low-cost process is always more desirable for manufacturing and assembling white organic light-emitting diodes [1,7].

Aiming at the development of such streamlined processes we report a new strategy to transform a single greenish emitter layer device into a white emitter by partially using the electroluminescence of the device as an excitation source of a strong photoluminescent material. This was achieved by spin-coating a thin layer of a red emitter polymer on the transparent face of a greenish emitting device, as illustrated in Fig. 1a. According to this scheme, the greenish emission of the light-emitting device is partially absorbed by the thin red foil, generating excited state molecules. When this red material decays radiatively, its output light emission will complement the greenish electroluminescence spectrum, both PL and EL emissions are transmitted through the foil, tuning the color of the device output. By adjusting the thickness of the thin layer of colored
photoluminescent film, the greenish emission combined to the red emission gives a bright white emitting device. The advantage of this approach is that by knowing the molar absorptivity coefficient of the red color photoluminescent material and its PL quantum yield, one may calculate the required thickness of the thin layer foil in order to achieve the desired white color. A major phenomenological advantage of this assembling process is that there are no resonant energy transfer processes, which normally decrease device emission efficiencies and, moreover, there are no phase-separation and morphological complications, since no blending materials are demanded. The effectiveness of this strategy was demonstrated using the poly[9,9-diocystylfluorenyl-2,7-diyl]-alt-co-[9,9-di-[5'-pentanyl]-fluorenyl-2,7-diyl] (PFOFPen), a blue–green emitter and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as a red emitter. Chemical structures are shown in Fig. 1b and c, respectively.

2. Materials

Materials were purchased from American Dye Source (PFOFPen-ADS150BE) and Sigma-Aldrich (MDMO-PPV). The blue emitting ITO/PEDOT-PPS/PFOFPen/Ca/Al devices were fabricated by spin-coating 80 nm of PEDOT-PSS (purchased from ClevisTM) onto cleaned ITO substrates (25 Ω/cm² from Delta Technologies) and dried for 5 min at 383 K. Subsequently, 90 nm of a PFOFPen active layer was spin-coated using a THF solution (5.0 mg mL⁻¹) in a controlled atmosphere environment and then annealed for 15 min at 340 K. Finally 30 nm of calcium and 100 nm of aluminum electrode were thermally evaporated, using shadow masks, under a pressure of 10⁻⁶ mbar within an MBraun-Evaporator glovebox. The MDMO-PPV red colored foil (thickness was 100 nm) was spin-coated using a THF solution (3.0 mg mL⁻¹) onto a cleaned quartz substrate, also within a controlled atmosphere environment.

3. Results and discussions

Fig. 2a presents the electrical and optical output characteristics of the ITO/PEDOT-PPS/PFOFPen/Ca/Al device. The diode-like current–voltage characteristics (open circles in Fig. 2a) exhibit a good rectification ratio, with low turn-on voltage, (approx. 2.5 V), which is confirmed by the luminance–voltage curve, (solid squares of Fig. 2a). It is worth mentioning that although non-optimized polymer light-emitting diode (PLED) structures were used, considerable brightness of 250 cd/m² at 9 V was obtained. The electroluminescence spectrum of the PFOFPen-device at 4.5 V is shown in Fig. 2b (continuous blue line in the high energy spectral region of 400–620 nm). This broader spectrum is composed of two components: an emission with a well-defined vibrational structure, where the most intense 0–0 band peaked at 424 nm attributed to the fluorene chains in a disordered arrangement [9] and a lower energy band, with vibrational progressions occurring at 450, 486 and 521 nm, attributed to the fluorene aggregates [8,9]. The overlap of these two emissions confers a greenish color with CIE electroluminescence coordinates of (0.22, 0.30) (point 1 in Fig. 3b).

The dashed black line in Fig. 2b shows the absorption spectrum of MDMO-PPV films, whose maximum is located at 500 nm. It is worth mentioning that all the absorption range is overlapped by the PFOFPen electroluminescence emission and, therefore, PFOFPen may optically excite the MDMO-PPV film. The red open circles in Fig. 2b presents the photoluminescence emission from MDMO-PPV, excited at 500 nm, whose maximum is located at 590 nm, with CIE photoluminescence coordinates of (0.58, 0.42) (point 2 in Fig. 3b). Moreover, the MDMO-PPV film thickness was chosen to provide 50% of transmission, thus obtaining an optimized white color composition.

The white emission system was assembled by placing the colored foil with a thin layer of the red-emitting MDMO-PPV conjugated

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**Fig. 1.** (a) Scheme for the process used in the device composed of an electroluminescent PFOFPen component (b) and a photoluminescent material MDMO-PPV component (c), giving white light output.

**Fig. 2.** (a) Current–voltage–luminance characteristics of ITO/PEDOT-PPS/PFOFPen/Ca/Al (solid squares curve), revealing low turn on voltage and relatively high brightness, and voltage–luminance properties of the PFOFPen diode combined with the MDMO-PPV PL film (solid circles curve) and (b) electroluminescence spectrum from ITO/PEDOT-PPS/PFOFPen/Ca/Al diode (continuous blue), absorption curve of MDMO-PPV (dashed black) and photoluminescence spectrum of MDMO-PPV excited at 500 nm (open red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
choosing correct materials. Also be applied to tune the output light to other wavelengths, by method is not just restricted to white light production, but can pure white light (0.33, 0.33). It is worth mentioning that this emitting diode and the colored MDMO-PPV (2) and the emission of the combined EL light-emitting diode (1), photoluminescence spectrum of MDMO-PPV colored foil may be attributed to the simultaneous decrease of the PFOFPen output luminance diminished by a factor of 2.5, approximately. This between both emitted colors in order to obtain the CIE coordinates for and phase separation related complications. Moreover, combinations of different EL and PL materials may produce easy to tune devices with different CIE color coordinates. Besides, our method can be applied to any kind of supporting substrate, including flexible ones, allowing its application to the development of flexible display and illumination sources.

**Fig. 3.** (a) Emission spectrum from a combined device formed by a ITO/PEDOT-PPS/ PFOFPen/Ca/Al diode and a quartz substrate covered with spin-coated colored film of MDMO-PPV; (b) CIE coordinates of electroluminescence spectrum of PFOFPen polymer spun on a quartz substrate in front of the glass-ITO substrate. Thus, part of the greenish EL of the ITO/PEDOT-PPS/ PFOFPen/Ca/Al device was absorbed by the colored foil producing excitons that decay radiatively, generating red-color PL. The luminescence characteristics of the WOLED (ITO/PEDOT-PPS/PFOFPen/Ca/ Al+MDMO-PPV film), is shown as red circles in Fig. 2a. The overall output luminance diminished by a factor of 2.5, approximately. This may be attributed to the simultaneous decrease of the PFOPen emission which has been absorbed by the MDMO-PPV in solid state only, partially, transformed in emitted photons.

**Fig. 3a** shows the emission over the entire spectral range produced by an overlap of the PFOFPen electroluminescence and the MDMO-PPV photoluminescence. The thickness of the colored film (≈ 100 nm) was adjusted to deliver an adequate balance between both emitted colors in order to obtain the CIE coordinates (0.35, 0.31) (point 3 in Fig. 3b), close to the ideal coordinates for pure white light (0.33, 0.33). It is worth mentioning that this method is not just restricted to white light production, but can also be applied to tune the output light to other wavelengths, by choosing correct materials.

4. Conclusions

The method described here successfully demonstrates that careful combination of EL and PL is an easier strategy compared with other methodologies which use multiple components to build white emitting devices. The major requirement for correct color tuning is to define the thickness of the colored foil, satisfying the compromise between its absorption of the higher energy emission to produce EL and its PL emission with a higher intensity to supply the lower energy light component required for the CIE coordinates. Because this methodology is a one-component system, the processing can be run using several types of methodologies, such as roll-to-roll, ink-jet printing and spray deposition. There are also no further morphology and phase separation related complications. Moreover, combinations of different EL and PL materials may produce easy to tune devices with different CIE color coordinates. Besides, our method can be applied to any kind of supporting substrate, including flexible ones, allowing its application to the development of flexible display and illumination sources.

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