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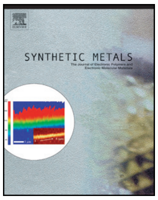

Tuning the emission color of a single-layer polymer light-emitting diode with a solution-processed external layer

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ABSTRACT

The emission color of a single-layer polymer light-emitting diode (PLED) was tuned using an external layer. We combine an electroluminescent polymer, known as poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT), embedded in a diode-like structure (ITO/PEDOT-PPS/F8BT/Ca/Al), and a film of poly(vinyl alcohol) (PVA) containing one of the xanthene dyes, either Erythrosin B (ERB) or Rose Bengal (RB), used as an external photoluminescent layer. The emission color is tuned from the CIE coordinates (0.34, 0.64) for the bare F8BT-diode to (0.39, 0.57) using a ~42 μm PVA:RB film and to (0.35, 0.61) using a ~55 μm PVA:ERB film. It was obtained based on trivial photophysical processes: xanthene dyes partially absorb the electroluminescence (EL) emissions coming from the F8BT-diode, decaying radiatively and emitting light by photoluminescence (PL). This method is versatile and may be extended to other combinations of EL and PL materials, tuning the color output and giving different CIE color coordinates. Because both the EL and PL layers are polymer-based systems, they can be used in the development of flexible displays and illumination sources. Furthermore, the PL layer is a self-supported film formed by water-soluble materials, with the advantage of being environmentally friendly, commercially available and low-cost. The PLED delivered a brightness of 123 cd/m^2 at 9 V.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted intense attention due to their potential applications in solid-state lighting and flat panel and flexible displays, which are ascribed to several advantageous characteristics, such as high efficiency, low power consumption, large-area potential, and mechanical flexibility [1,2]. They can also be designed to emit light in a broad range of colors [3]. Different colors of polymer light-emitting diodes (PLEDs) can be obtained by changing the chemical structures of the materials used as the active layer, and based on this, efforts have been made in synthetic processes [4–6]. Other strategies such as blending two conjugated polymers [7–9] or using multiple components in the emissive layer, such as dye [10,11], quantum dots [12,13] or nanorods [14] incorporated into a polymeric matrix, can be used to achieve the desired emission color. In some cases, the color of the emission can be influenced by the morphology of the emissive layer and energy transfer processes (trivial or FRET) [15]. Because mixtures of components can undergo a phase separation process, all of these blending methods are likely to have issues with the color stability, affecting device reproducibility and performance [7].

To obtain different colors in the same device, fabrications of color-tunable (CT) OLEDs have been explored [2,16]. One strategy adopted was to use stack structures, in which transparent intermediate electrodes are inserted between upper and lower OLEDs, and the color is tuned by independently operating the upper and lower OLEDs. In this case, color tunability was achieved, but the processability was rather complicate [17–20]. Other color-tuning concepts have explored voltage-dependent changes in emission color, and in this case, color shifts are the result of a variety of mechanisms, *e.g.*, voltage-dependent charge trapping, a

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spatial shift of the recombination zone, a modified exciton distribution, or exciton quenching at high current densities [16,21]. The control of this process is rather difficult, and the driving voltage also unavoidably results in an undesired change in device brightness, resulting in several drawbacks [16].

An additional aim is how to obtain white color in a certain device. Several attempts have been developed and in general multicomponent systems are required [9,11,12,16,19–23]. For example, the down-color conversion of blue light is also described in the literature as a tool to tune colors of diodes and it is a common technique for the production of inorganic white light emitting diode (LED) [24]. In 2002, Duggal et al. [25] demonstrated that white light emissions could be obtained by combining blue LEDs with color-conversion layers (CCLs). In that work, a color conversion layer (CCL) was spun onto the opposite side of a blue OLED to absorb some blue light and re-emit red light. In general, the efficiency of the down-converted white organic light-emitting diode (WOLED) was lower than that of the blue OLED because of the Stokes loss and limited color conversion rate during the down-conversion [25].

In a recent work, we demonstrated that white color emission may be generated in a diode composed of one component EL layer of poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9,9-di-(5′-pentanyl-fluorenyl-2,7-diyl))] (PFOFPen) and an external photoluminescent layer of MEH-PPV [26]. According to this scheme, the greenish color emitted by 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 electroluminescent spectrum. Both PL and EL emissions are transmitted through the foil, tuning the output color to white. A major phenomenological advantage of this assembly process is that there are no resonant energy transfer processes, which normally decrease the device emission efficiencies, and moreover, there are no phase separation and morphological complications because no blending materials are demanded. Using the same strategy, it is proposed here to tune the emission color of the diode by an external PL layer of commercial dyes dissolved in a commercial polymer, both of which are water-soluble materials. The active layer in the diode was composed by either the poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3] thiadiazol-4,8-diyl)] (F8BT) or by poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO). The external layer was formed by a water-soluble plastic film of poly(vinyl alcohol) (PVA) with dissolved xanthene dye, Erythrosin B (ERB), or Rose Bengal (RB), both dyes with a photoluminescence quantum yield (PLQY) about 0.01 in ethanol [27], (chemical structures are shown in Fig. 1).

For a dye to be successfully used as an external PL layer in combination with an electroluminescent device, some features should be considered: (i) the electronic absorption of the dye must overlap with the electroluminescent light output of the PLED; (ii) the dye should exhibit a high molar absorptivity coefficient, (iii) the dye emission should be red-shifted compared with the PLED emission, broadening the emission color range, (iv) the dye should have a good photobleaching stability, and (v) the dye should have good solubility in the polymer matrix used as a dye support. All of these characteristics are present in the xanthene dyes.

These dyes are relatively photostable in PVA [28–30]. We also have shown the effect of the external layer thickness in the color tuning and luminescence yield. For large-scale production, a simplified and low-cost process is always more desirable for the manufacture and assembly of OLEDs, and xanthene dyes have the advantage of, besides being low-cost compounds, also being water soluble, with characteristics of being environmentally friendly materials. The diode structure may be represented by PVA: xanthene dye/ITO/PSS:PEDOT/conjugated polymer/Ca/Al.

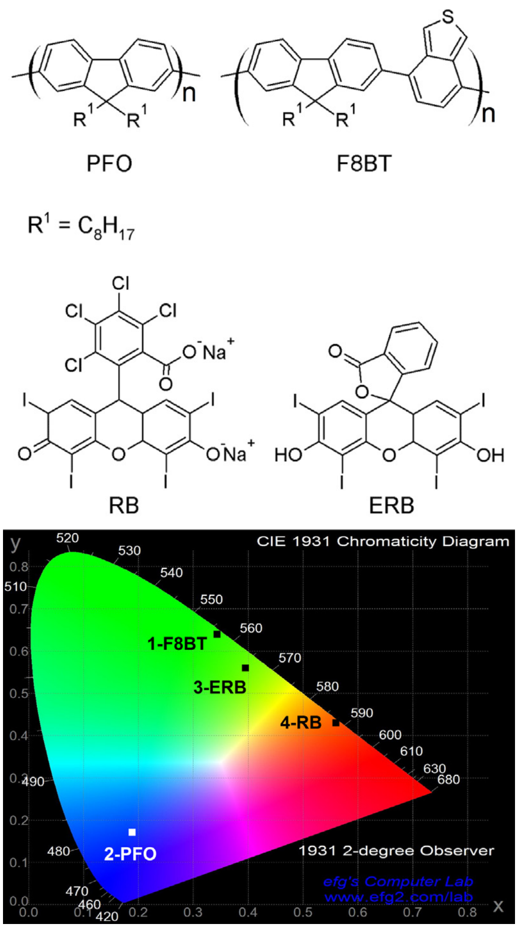

Fig. 1. Chemical structure of the polymers PFO and F8BT, employed as the active layer of the PLEDs, the RB:PVA and EB:PVA (0.01% mol/mol), used as the external PL layers, and the CIE coordinates of PFO-diode and F8BT-diodes and of the PL of the PVA:ERB and PVA:RB films.

2. Experimental methods

2.1. Materials

Poly[9,9-dioctylfluorenyl-2,7-diyl]-end capped with dimethylphenyl—PFO ($\overline{M}_n = 40.000–150.000\,\mathrm{g\,mol^{-1}}$) was purchased from American Dye Source (ADS129BE). F8BT ($\overline{M}_n = 22.000–24.000\,\mathrm{g\,mol^{-1}}$), polyvinylcarbazole—PVK ($\overline{M}_w = 1.100.000\,\mathrm{g\,mol^{-1}}$), PVA (hydrolysis degree > 99%, $\overline{M}_w = 124.000–186.000\,\mathrm{g\,mol^{-1}}$), RB, ERB, toluene (99,8%) and chlorobenzene (99,8%) were purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was purchased from H.C. Starck (Clevios P VP AI 4083). RB and ERB were purified by recrystallization before use [31]. All other chemicals were used as received. ITO-glass substrates (Corning Eagle XG/1737, 7–10 Ω/sq) were cut, cleaned and patterned before use.

2.2. PLED assembly

Light-emitting diodes with the configuration ITO/PEDOT:PPS/PVK/PFO/Ca/Al or ITO/PEDOT:PPS/PVK/F8BT/Ca/Al were fabricated. A 70 nm layer of PEDOT:PSS was deposited by spin-coating onto ITO and dried at 110 °C in a vacuum oven overnight. Subsequently, the active layer was spin-coated (2000 rpm/30 s) from chlorobenzene solutions of PVK (5 mg/mL) and PFO (10 mg/mL) or from a toluene solution of F8BT (5 mg/mL). The solutions were filtered through a PTFE membrane (Millipore, 0.45 μm) immediately