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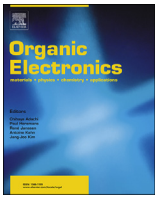

Highly efficient blue polyfluorenes using blending materials as hole transport layer

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ABSTRACT

Efficient blue polyfluorenes have been generated by incorporating the hole transport material *N*-([1,1′-biphenyl]-4-yl)-9,9-dimethyl-*N*-(4-(9-phenyl-9*H*-carbazol-3-yl)-phenyl)-9*H*-fluoren-2-amine (BCFN) into poly(9,9-dioctylfluorene) (PFO) as an emissive layer. BCFN has an appropriate highest occupied molecular orbital (HOMO) energy level and high hole transport/electron barrier properties, which can effectively reduce the hole injection barrier and improve the charge carrier injection and transport. These properties resulted in a significant improvement in the electroluminescent (EL) performance of PFO. To further improve the EL performance of PFO, the blend hole transport layer, PVK [Poly(N-vinylcarbazole)]:BCFN with weight ratio of 3:7, was inserted between the PEDOT:PSS and the emissive layer. The blend hole transport layer effectively reduced exciton quenching and markedly decreased the hole injected barrier. A maximum luminous efficiency (LE_{max}) of 4.31 cd A^{-1} was obtained with the CIE coordinates of (0.17, 0.13). The device maintained a LE_{max} of 4.27 cd A^{-1} at a luminance of 1000 cd m^{-2}. In addition, stable EL spectra were obtained and were nearly identical when the applied voltage was increased from 5 to 11 V. These results indicate that blending the appropriate hole transport material can be an efficient method to improve device performance based on the large band gap of blue-lighting materials.

1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted considerable attention from both scientific and industrial communities due to their potential application in display and lighting source fields, which can provide a low-cost, large-area device by solution process [1–7]. The generation of highly efficient, solution-processed full-color displays for commercialization requires the development of a high-performance emitter that can be processed using a low-cost solution processing technique [8,9]. Solution-processed blue-light fluorescent PLEDs have significantly lagged behind the green-light and red-light fluorescent PLEDs, and the development of highly efficient, blue light-emitting polymers for PLEDs remains a great challenge [10–14]. The primary problem of previous blue light-emitting polymers was the instability of the blue emissions that resulted from a large injection barrier and an unbalanced charge transportation [15–18]. Therefore, it is of vital importance to incorporate an appropriate hole injection/transport material to depress the hole injection barrier from the anode to the emissive layer, which can simultaneously attain a balanced charge carrier injection/transport in the emissive layer.

Among the reported blue light-emitting polymers, poly(9,9-dioctylfluorene) (PFO) is considered to be one of the most promising materials to apply in high-performance blue PLEDs due to its unique characteristics, such as low-cost, high color purity, and high photoluminescence efficiency [19–22]. However, several critical issues with this polymer have hindered the development of highly efficient and stable blue emission, including the generation of a low-energy fluorenone, relatively deep-lying highest occupied molecular orbital (HOMO) energy levels, and imbalanced charge transportation [23–25]. To address these issues, a range of charge

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transport units were incorporated into the backbone and side-chain of PFO to improve its performance [26–28].

In general, triphenylamine (TPA) and carbazole (Cz) derivatives have been used to decrease the hole injection barrier and improve the hole transport properties due to their appropriate HOMO energy levels and their excellent hole transport properties [29–32]. For example, highly efficient PFO derivatives that incorporated different TPA and Cz derivatives to facilitate hole injection and transportation have been developed [33,34]. Such PFO derivatives efficiently decreased the turn-on voltage and improved the device performance compared to the pristine PFO film. However, the color purity required further improvement because the electroluminescence (EL) spectra was broadened upon the incorporation of these moieties. Considering the complexity of the synthesis of such materials and intermediates, the development of a simple and efficient method to achieve high efficiency and color purity of a blue device was of utmost importance.

In this manuscript, we describe a method for blending the TPA-Cz derivative *N*-([1,1′-biphenyl]-4-yl)-9,9-dimethyl-*N*-(4-(9-phenyl-9*H*-carbazol-3-yl)-phenyl)-9*H*- fluoren-2-amine (BCFN), which has an appropriate HOMO energy level and high hole mobility, into the emissive layer of PFO to decrease the hole injection barrier and balance the charge transportation. The efficiency of the resulting devices was considerably improved, and a better color purity of blue emission was obtained. To further improve the blue device performance, a blend hole transport layer (PVK:BCFN = 3:7, wt/wt) was introduced between PEDOT:PSS and the emissive layer. The blend hole transport layer further improved the device performance with a maximum luminous efficiency ($LE_{\max}$) of 4.31 cd A^{-1} and a peak luminance ($L_{\max}$) of 14708 cd m^{-2}. Moreover, the device maintained a $LE_{\max}$ of 4.27 cd A^{-1} at a luminance of 1000 cd m^{-2}, which is the highest value thus far reported for PFO-based devices.

2. Results and discussion

2.1. Energy level alignment of materials

The molecular structures of PFO, PVK, and BCFN, and the energy level alignment of the device are shown in Fig. 1. PFO has a deep HOMO energy level of −5.83 eV and a deep lowest unoccupied molecular orbital (LUMO) energy level of −2.83 eV, indicating that a hole injection barrier of 0.73 eV existed between PEDOT:PSS and PFO. Thus, an appropriate hole transport layer (HTL) was desirable [35]. The BCFN has an appropriate HOMO energy level of about −5.3 eV. Therefore, the incorporation of BCFN can effectively reduce the hole injection barrier between PEDOT:PSS (−5.1 eV) and PFO (−5.83 eV) and potentially provide an effective cascade hole injection from the anode [36]. In addition, because both PVK and BCFN have relatively high LUMO energy levels of about −2.2 eV, the resulting HTL can also act as an electron blocking layer that can confine the injected electrons in the emissive layer. It is also worth noting that BCFN has relatively high glass transition temperature (T_g) of about 125 °C (Fig. S1, see the supporting information, SI), demonstrating its excellent stability upon thermal treatment.

2.2. Photophysical properties of blend film

To investigate the influence of BCFN on the photophysical properties of PFO, normalized UV–vis absorption and PL emission spectra of the blend films in quartz were generated, as shown in Fig. 2. The absorption of BCFN film without thermal annealing peaked at 353 nm. The distinct absorption peak at about 380 nm for blend films was attributed to the π-π^* transition of the conjugated PFO backbone. The maximum UV–vis absorption peak exhibited a slight blue shift from 382 to 374 nm with a spectral display that broadened with the increasing blend ratio of BCFN without thermal annealing, which was attributed to the addition of BCFN with a higher energy absorption band. The absorption spectra with thermal annealing were similar with that without thermal annealing except for a new shoulder absorption at about 430 nm (Fig. 2(c)). It is well known that PFO has many kinds of aggregated structures, such as α-phase, β-phase, and semi-crystal phase [37–39]. The different aggregated structures also provide different optophysical properties. Based on previous reports, the new shoulder absorption of the blend films at about 430 nm may be due to the formation of a semi-crystal structure of PFO [40,41].

The maximum emission of BCFN was observed at 413 nm. As shown in Fig. 2(b) and (d), the emission of BCFN had no significant contribution to that of the blend film, indicating that the emission of the blend film was mainly from the PFO. From Fig. 2(b) it is noted that the intensity of the shoulder peak located at about 422 nm

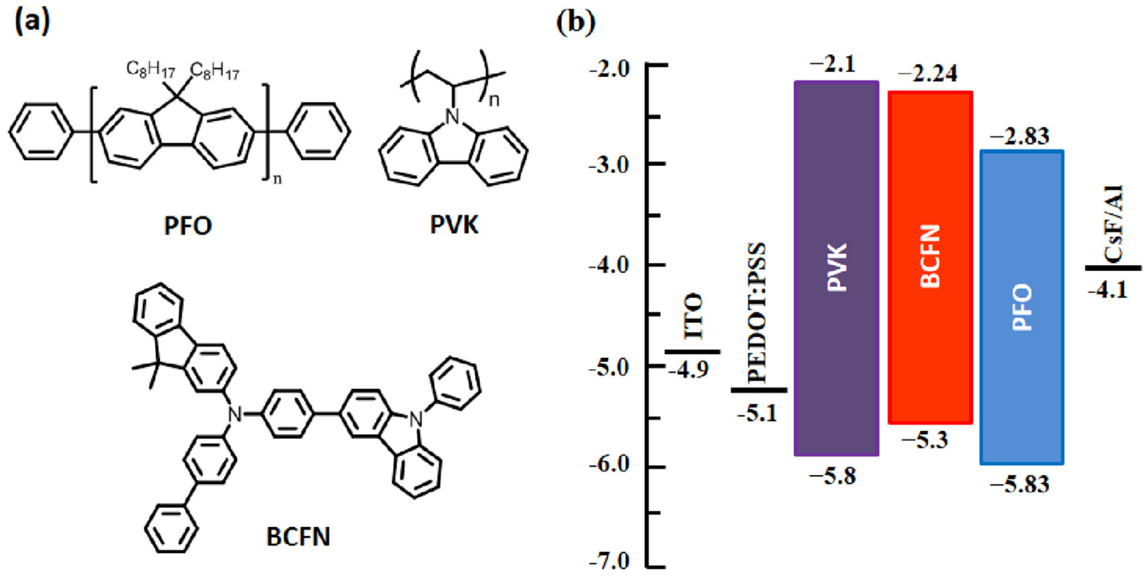

Fig. 1. Molecular structures of materials (a) and the energy level alignment of devices (b).