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Deep blue light-emitting diode based on high molecular weight poly(9,9-dioctylfluorene) with high efficiency and color stability

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Abstract

A highly efficient deep blue polymer light-emitting diode based on poly(9,9-dioctylfluorene) is demonstrated. The performance is found to increase significantly with the molecular weight. Two different molecular weights are compared, one is 71,000 and the other is 365,000. The electroluminescent efficiency and color stability are improved by slightly doping hole traps into the emission layer and bilayer structure. The maximum efficiency is 3.8 cd/A with the corresponding external quantum efficiency of 3.7% at deep blue with Commission Internationale de L'Eclairage (CIE) coordinate at (0.15, 0.09). Stable blue emission is maintained up to 6600 cd/m^2 without growth of green shoulder in emission spectrum.
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Conjugated polymer light-emitting diodes (PLED) have generated a great deal of interest due to their easy solution process, potentially high emission efficiency and many optoelectronic applications. Therefore, they are viewed as the material for light-weight large-area flat panel display of the new generation. One promising way for display application is using the white PLED combined with color filters. For this purpose highly efficient blue PLED is critical to achieve white PLED through energy transfer by using the blue emitters as the host and red/green emitter as the dopants [1,2]. Deep blue PLED is more essential than the sky blue one in making white light. However the deep blue material still remains a challenge due to their large band gap and difficulty in charge balance. Up to now, the highest reported efficiency for deep blue PLED is about 3 cd/A by the Covion company with unavailable chemical structure [3]. The most well-known and commonly used materials for deep blue PLED are polyfluorene (PF) and its derivatives due to their high photoluminescence quantum efficiency [4–7]. However, they

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still suffer from low electroluminescence (EL) efficiency due to the poor charge balance caused by the difficulty in electron injection and transport. In addition, the color is unstable due to the formation of excimer in its liquid crystalline phase and ketone defect in the presence of oxygen [8,9]. Among all the PF derivative poly(9,9-dioctylfluorene) (PFO) is archetypical and the easies to synthesize. It would greatly reduce the barriers to make high-performance blue PLED using simply PFO. The optical and morphological properties of PFO have been shown to depend sensitively on the molecular weight [10]. In general the higher molecular weight implies better stability and purity of the material. The low molecular weight polymers are also known to have poor color stability due to easier chain motions under device operation. Removal of the low molecular weight components is known to improve the performance [11]. So far the efficiency remains far lower than the Covion material even with molecular weight control. In this work we employ a high molecular weight PFO with MW up to 365,000 to demonstrate a deep blue PLED with efficiency as high as 3.8 cd/A with corresponding external quantum efficiency 3.7%, which is even better than the Covion blue PLED. Color stability is also improved relative to the low molecular weight counterpart. High molecular weight is found to enhance the electron current resulting in a better charge balance. Moreover, the efficiency is significantly enhanced by the doping of hole traps [12]. Instead of using a cross-linking polymer [13], a soluble hole-transport layer (HTL) is added by buffer liquid method [14] to increase the efficiency.

In this letter, three types of device are fabricated, including the doped host–guest emission layer (EML) in single layer structure (type I), HTL/EML bilayer device (type II), and HTL/host–guest EML bilayer device (type III). Fig. 1A shows the schematic energy profile for type I devices and Fig. 1B for type II. Low molecular weight PFO (MW = 71,000) and high molecular weight HMW-PFO (MW = 365,000) purchased from American Dye Source (ADS) are chosen as light-emitting polymers without any further purification. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(N-(4-sec-butylphenyl))diphenylamine)] (TFB, MW = 197,000, purchased from ADS) are chosen as dopant for type I devices and HTL for the bilayer devices (type II and type III). Single layer PLEDs based on PFO and HMW-PFO without any TFB are made as standard devices. All PLED devices
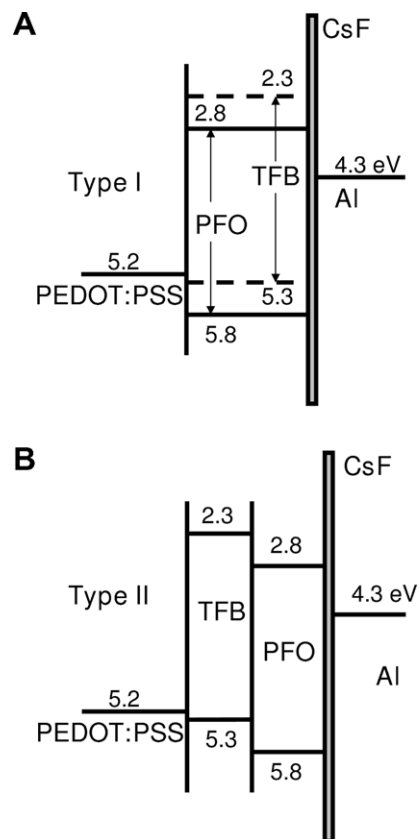

Fig. 1. Schematic electronic energy profile for the (A) type I (PFO: 1 wt% TFB) device structure (B) type II (TFB/ PFO) device structure. The numbers are in eV.

are fabricated on glass substrates with poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) layer on a patterned ITO layer. For type I devices 1 wt% of TFB is blended into PFO and HMW-PFO individually as the dopant. The film is formed by spin-coating and baking at 120 °C in vacuum (10^{-3} torr) for 40 min to remove the solvent. For type II and type III devices TFB dissolved in toluene is spin-coated to make a 30 nm thin film then baked at 180 °C in vacuum for 40 min. PFO and HMW-PFO are also dissolved in toluene and spin-coated to make bilayer devices (type II and III) by a liquid buffer layer to prevent the dissolution problem [14]. For the bilayer structure, PFO layer is baked in vacuum at 120 °C for 1 h to remove the residual 1,2-propylene glycol liquid buffer and organic solvent. Except for the PEDOT:PSS layer all the fabrication processes are carried out in the glove box to reduce oxygen adsorption of PFO. CsF (2 nm)/Al (100 nm) are deposited as cathode by thermal evaporation [15].

Finally all devices are packaged in the glove box. The film thickness is measured by Kosaka ET4000 Surface Profiler. The EL efficiency is measured by photo research PR650 spectrophotometer integrated with Keithley 2400 multimeter. The PL efficiency is measured by an integrating sphere system. Ionization potential (IP) is measured by cyclic voltammetry and electron affinity (EA) is calculated by IP plus band gap determined by the ultraviolet absorption spectrum. Below we present the low molecular weight results first and the high molecular weight results latter.

Fig. 2 shows the results of PFO-based devices. The maximum efficiency of type I (PFO: 1 wt% TFB) device are 2.3 cd/A with the corresponding EQE of 1.99%, which is three times higher than that of the standard PFO device (EQE = 0.63%) without TFB doping. This indicates that TFB plays the role of hole trap in the host–guest EML and the effective hole mobility is reduced. The efficiency is enhanced due to the better carrier balance. The maximum effi-

ciency of type II device (TFB/PFO) is 1.64 cd/A with the corresponding EQE of 1.29%, which is also two times higher compared to the standard one. As seen in Fig. 1B, at the interface between TFB and PFO there is a hole barrier from the TFB side and electron barrier from the PFO side. The recombination zone is hence expected to concentrate in the PFO region near the interface, unlike the case of single layer PFO where the recombination zone is expected to be near the cathode due to the low electron mobility. The cathode quenching effect in the bilayer structure is therefore less severe than the single layer case, thus explaining the improved efficiency in type II even without any doping. The type III device (TFB/PFO: 1 wt% TFB) combines the functions of type I and type II devices. The maximum efficiency of type III is 1.5 cd/A with the corresponding EQE of 1.18%. The efficiency of type III does not get better than type I or type II device. Compared with device I, the HTL in device III may cause too much hole injection and destroy the balance already established by TFB doping. Compared with device II, the holes in device III may be less confined at the interface due to the easy injection from HTL into the TFB dopants to cause more cathode quenching.

Now we turn to the case of high molecular weight PFO with MW equal to 356,000. The basic physical picture and the relative efficiencies of the device types are the same as the low molecular weight PFO. However the absolute values of the performance parameters are greatly enhanced by the increasing molecular weight. The results of HMW-PFO devices are shown in Fig. 3. The maximum efficiency of type I device (HMW-PFO: 1 wt% TFB) is 2.8 cd/A for thickness of 100 nm with the corresponding EQE of 2.04%. When the thickness is reduced to 60 nm, the maximum efficiency is enhanced to the remarkable value of 3.8 cd/A with the corresponding EQE of 3.7% and power efficiency of 2.6 l m/W. The emission color is deep blue with Commission Internationale de L'Eclairage (CIE) coordinate = (0.15, 0.09). It is well-known that the main limiting factor for the blue polymer LED is the electron transport. Because of the small electron affinity electrons in PFO are highly susceptible to the impurities, with either chemical or structural nature, which commonly causes electron trap states inside the energy gap. High molecular weight polymers usually implies low impurity level after the synthesis. In addition, in the high molecular weight polymer there are much less chain ends which
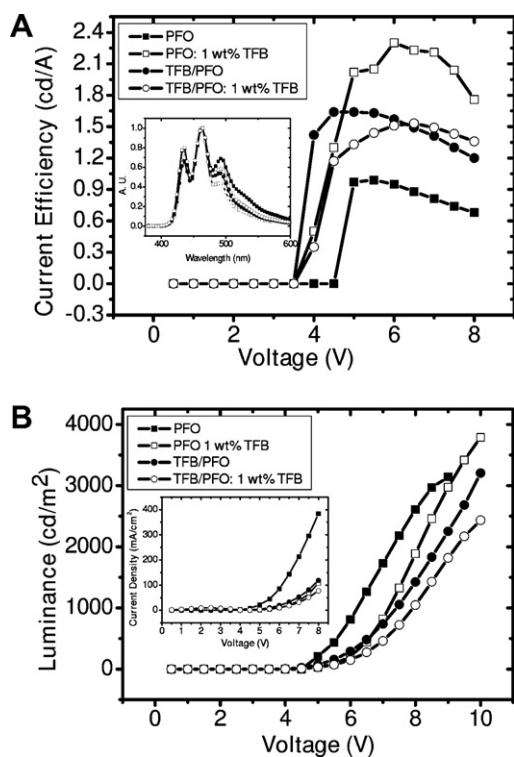

Fig. 2. The performances of PFO devices: standard PFO device (solid square), type I (PFO: 1 wt% TFB) device (open square), type II (TFB/PFO) device (solid circle) and type III (TFB/PFO: 1 wt% TFB) device (open circle). (A) The current efficiency. Insets are the EL spectra. (B) The luminance. Inset is the current density.
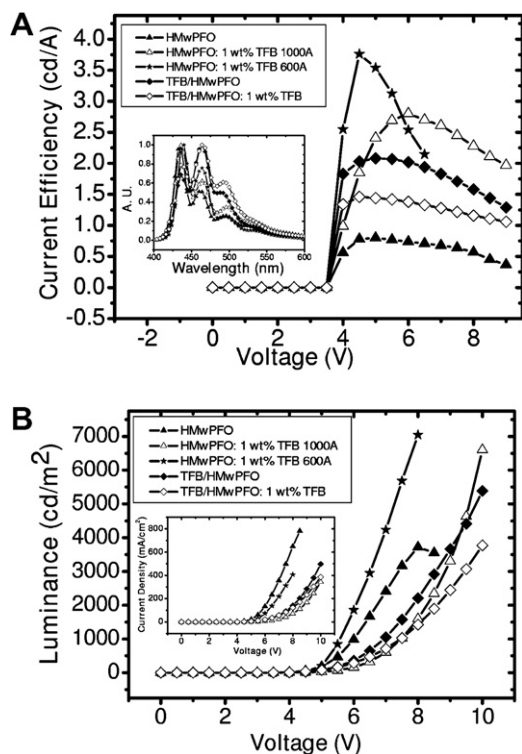
Fig. 3. The performances of HMW-PFO devices: standard HMW-PFO device (solid triangle), type I (HMW-PFO: 1 wt% TFB) device of thickness 100 nm (open triangle), type I (HMW-PFO: 1 wt% TFB) device of thickness 60 nm (solid star), type II (TFB/PFO) device (solid rhombus) and type III (TFB/PFO: 1 wt% TFB) device (open rhombus). (A) The current efficiency. Insets are the EL spectra. (B) The luminance. Inset is the current density.

themselves are considered as some kind of traps [10]. Moreover, the chain entanglement and thermal as well mechanical stability are improved by the larger molecular weight and may result in less structural defects like aggregation formation. It is quite

intriguing that the reduction of the thickness has such a dramatic effect on the efficiency. Apparently the high electric field helps the electron injection and mobility, especially for the high molecular PFO with less traps, therefore in the thin samples the charge balance and enhance the efficiency are improved despite of the concurrent negative effect of more cathode quenching. The maximum efficiency of type II (TFB/HMW-PFO) device is 2.1 cd/A with corresponding EQE of 1.8% which are slightly higher than the low molecular weight counterpart. The maximum efficiency of type III (TFB/HMW-PFO: 1 wt% TFB) is 1.4 cd/A with corresponding EQE of 1.1% roughly the same as the low molecular weight counterpart. The luminance at a given voltage for HMW-PFO is however always much higher than low molecular weight PFO, supporting the assumption of higher electron current.

In addition to efficiency, another equally critical issue for blue PLED is the color stability at higher voltage. As discussed above polyfluorene is known to have the tendency to show pronounced green emission at the shoulder of the spectrum due to either aggregate or ketone defects. As a result it is commonly observed that the emission spectrum suddenly changes from blue to green beyond some critical voltage. The maximal luminance below which there is no spectral shift can be taken as a measure for the color stability. As shown in Table 1, in general HMW-PFO shows a much higher maximal luminance compared with PFO. In particular, type I device with 100 nm thickness sustains stable deep blue emission up to almost 7000 cd/m². Such brightness is more than enough for most of the display and lighting applications. Note also that the color stability of the three types are all enhanced relative to the standard single layer sample. We suspect

Table 1
Performance of PLEDs in this work

Label	Max. current efficiency (cd/A)	Max. EQE (%)	Max. power efficiency (l m/W)	Max. luminance (cd/m²)
PFO	1.0 (at 5.5 V)	0.63	0.6 (5 V)	2967 (at 8.5 V)
PFO: 1 wt% TFB	2.3 (6 V)	1.99	1.3 (5 V)	3788 (10 V)
TFB/PFO	1.6 (5 V)	1.29	1.1 (4.5 V)	3205 (10 V)
TFB/PFO: 1 wt% TFB	1.5 (6.5 V)	1.18	0.8 (5 V)	2435 (10 V)
HMW-PFO	0.8 (5 V)	0.62	0.5 (5 V)	3554 (8.5 V)
HMW-PFO: 1 wt% TFB (100 nm)	2.8 (6 V)	2.04	1.5 (5 V)	6604 (10 V)
HMW-PFO: 1 wt% TFB (60 nm)	3.8 (4.5 V)	3.7	2.6 (4.5 V)	4235 (7 V)
TFB/HMW-PFO	2.1 (5 V)	1.8	1.4 (4 V)	5388 (10 V)
TFB/HMW-PFO: 1 wt% TFB	1.4 (5 V)	1.1	1.0 (4 V)	3773 (10 V)

The Max. luminance is defined as the highest luminance before the growth of green peak in emission spectrum.

that with either TFB blending or bilayer structure the recombination zone of the device is moved away from the cathode where a higher concentration of oxygen or other defects are present and the polymers are less stable under electroluminescence.

The mechanisms for the efficiency improvement are clarified by further experiments. Fig. 4A gives the direct evidence that TFB plays the role of hole trap by measuring the hole currents of hole-only devices with and without blending TFB. The hole current is reduced about one order of magnitude with a light TFB doping of 1 wt%. In addition, electron-only devices for PFO and HMW-PFO are compared. The results are shown in Fig. 4B. The effective work function of CsF/Al is 2.6 eV [16]. It there forms a Ohmic contact with PFO whose electron affinity is 2.8 eV, and the current is bulk-limited instead of injection limited. In the inset we calculate the electron mobility by using space-charge-limited current (SCLC) voltage–current relation $J_{SCLC} = \frac{9}{8}\varepsilon\mu_e\frac{(V-V_{bi})^2}{L^3}$. J is the current density, ε is the permittivity of the polymer, μ_e is the electron mobility, V is driving voltage, V_{bi} is the built-in voltage, and L is

the polymer thickness. Both the current and the electron mobility of HMW-PFO is higher than that of PFO. This might be due to the greater chain length of HMW-PFO for longer intrachain transport and the reduced impurities which act as electron traps as discussed above. Finally we compare the photoluminescence (PL) quantum efficiency. The PL efficiency is 40% for PFO and 50% for HMW-PFO. More surprisingly the PL efficiency is enhanced to 75% by slightly doping TFB into HMW-PFO, which might be attributed to the decrease of the aggregation formation in polyfluorene [17].

In conclusion, the PLED performance for PFO with high molecular weight up to 360 K is superior to the ordinary low molecular weight PFO. The high molecular weight implies a higher electron mobility and better color stability at high luminance. By blending a hole-transport polymer TFB into PFO as the hole trap to enhance the charge balance, the efficiency reaches as high as 3.8 cd/A (3.7%) in the deep blue for high molecular weight PFO. Maximal stable blue emission is also doubled by the molecular weight control. The originally unpromising PFO now reaches a even better performance than the Covion blue polymers with closed chemical structures.
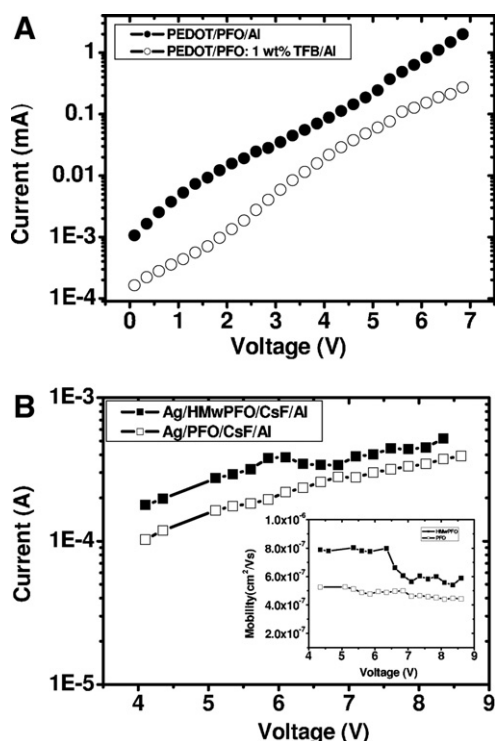
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Fig. 4. (A) Hole-only currents of PFO (solid circle) and PFO: 1 wt% TFB (open circle) devices. (B) Electron-only currents of HMW-PFO (solid square) and PFO (open square) devices. Inset is calculated electron mobility.

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