

Synthesis and Effect on *t*-Butyl PBD of the Blue Light Emitting Poly(phenyl-9,9-dioctyl-9',9'-dihexanenitrile)fluorene

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Received January 27, 2006; Revised April 20, 2006

Abstract: A novel, blue light-emitting polymer, poly(phenyl-9,9-dioctyl-9',9'-dihexanenitrile)fluorene (PPFC6N), containing an alkyl and cyano group in the side chain, was synthesized by Suzuki polymerization and characterized. The polymer structure was confirmed by ¹H-NMR. The number average molecular weight and the weight average molecular weight of the obtained polymer were 9,725 and 9,943 respectively. The resulting polymer was thermally stable with a glass transition temperature (*T_g*) of 93 °C, and was easily soluble in common organic solvents such as THF, toluene, chlorobenzene and chloroform. The HOMO and LUMO energy levels of the polymer were revealed as 5.8 and 2.88 eV by cyclic voltammetry study, respectively. The ITO/PEDOT:PSS (40 nm)/PPFC6N (80 nm)/LiF (1 nm)/Al (150 nm) device fabricated from the polymer emitted a PL spectrum at 450 nm and showed a real blue emission for pure PPFC6N in the EL spectrum. When *t*-butyl PBD was introduced as a hole blocking layer, the device performance was largely improved and the EL spectrum was slightly shifted toward deep blue. The device with PPFC6N containing *t*-butyl PBD layer showed the maximum luminance of 3,200 cd/m² at 9.5 V with a turn-on voltage of 7 V.

Keywords: PLED, hole blocking layer, polyfluorene derivative, *t*-butyl PBD.

Introduction

Since the first report on electroluminescence from a conjugated polymer, poly(*p*-phenylenevinylene) (PPV), many studies of polymeric light-emitting diodes (PLEDs) have been reported due to their potential application in full color flat panel displays. PLEDs present many advantages such as easy fabrication with low cost, low operating voltages, color tunability, flexibility, etc. For developing practical PLEDs with a high quantum efficiency, low voltage and long lifetime, the design of processable conjugated polymers with high purity and photoluminescence (PL) efficiency, good thermal and oxidation stability, and balance of charge carrier mobility are required.¹ And considerable efforts have been carried out in the field of PLEDs to obtain brightness and operating voltages suitable for commercial applications.^{2,3}

A blue electroluminescence emitter is essential for the development of a full color changing medium technology of the RGB filtered white emission.⁴⁻⁶ Since the polyfluorene

was applied in this field, electrochemical properties of fluorene containing polymers including poly(dioctylfluorene) (PFO) have attracted much attention. Polyfluorene derivatives have been extensively studied seemingly due to the ease of designing synthetic route and controlling the physical and optical properties.⁷ Boration or bromination at C-2 and -7 of fluorene makes the unit a polymer precursor and functionalization at C-9 offers the control of polymer solubility and interchain interactions in the film.⁸⁻¹⁵ Fluorene-based polymers are usually highly fluorescent, which is a required aspect for electroluminescence applications.¹⁶⁻¹⁸ In the electroluminescent devices, balancing the injection rates of electrons and holes in the emitting layer is required to achieve high electroluminescence efficiency. Since it was revealed that the electron injection is more difficult than hole injection for the conjugated polymers, it is necessary to increase electron affinity in the polymer chain for reducing the barrier to electron injection.¹⁹

Since the fluorene is active in the electro-reaction when it is biased in PLED, it leads an unwanted defect (e.g., keto defect) in the polymer back-bone, that is responsible of the broad

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green shoulder in the main blue spectrum. In this work, in order to reduce such a electro-activation of the fluorene, we have tried to synthesize a blue emissive polymer, poly(phenyl-9,9-dioctyl-9',9'-dihexanenitrile) fluorene (PPFC6N), by introducing the phenylene and -CN group in the polymer main chain and applied to the PLED. As a further investigation of the PLED, we introduced a hole blocking layer, *t*-butyl PBD, in the PLED. Since the *t*-butyl PBD emits a deep blue while it blocks hole, we expected an enhanced blue emission and thus reducing the broad green emission as well as increasing the over-all device performance.

Experimental

Materials. 9,9-Dioctylfluorene-2,7-bis(trimethylenborate), 1,4-dibromobenzene, 2,7-dibromo-9H fluorene, *n*-bromohexanenitrile and triethylbenzyl ammonium chloride and tetrakis(triphenylphosphine) palladium(0) [(PPh₃)₄Pd(0)] were purchased from Aldrich, and used without further purification.

Synthesis of 2,7-dibromo-9,9-dihexanenitrilefluorene. To a stirred solution of 2,7-dibromo-9H-fluorene (2 g, 6.2 mmol) in 30 mL of DMSO under nitrogen was added catalytic amounts of triethylbenzyl ammonium chloride. After stirring an hour at reflux, 3.0 g of *n*-bromohexanenitrile (17.0 mmol) was added to the reaction mixture. After stirring an additional hour at reflux, 10 mL of 50% NaOH was added to the mixture and stirred for 5 hrs at room temperature. The reaction mixture was diluted with 200 mL of ethyl acetate, and extracted with 10 mL of 1 M HCl and water. The organic layer was dried with MgSO₄ and concentrated under reduced pressure. The white crystal was purified by using column chromatography to give 2,7-dibromo-9,9-dihexanenitrilefluorene. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 7.49-7.43 (m, 6H, fluorene), 2.18-2.14 (m, 4H), 1.97-1.93 (m, 4H), 1.45-1.40 (m, 4H), 1.26-1.20 (m, 4H), 0.60-0.57 (m, 4H).

Synthesis of Poly(phenyl-9,9-dioctyl-9',9'-dihexanenitrile)fluorene. Carefully purified and dried 2,7-dibromo-9,9-dihexanenitrilefluorene (0.322 g, 0.574 mmol), 1,4-dibromobenzene (0.153 g, 0.574 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylenborate) (0.642 g, 1.15 mmol) and (PPh₃)₄Pd(0) (0.013 g, 1%mol), aliquat 336(0.01 mL) were dissolved in a mixture of toluene (10 mL, purified with sodium) and 2 M water (5 mL) solution of Na₂CO₃ (1.06 g, 10.0 mmol). The solution was refluxed by vigorous stirring for 3 days. The under nitrogen atmosphere, mixture was dissolved in chloroform and washed with EDTA and water. The mixture was precipitated from methanol and purified using Soxhlet extractor. The resulting product was dissolved in chloroform and poured in methanol that gave the crystallized polymer, PPFC6N. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 7.83-7.26 (m, 16H, fluorene, benzene ring), 2.17-2.10 (m, 4H), 1.15-0.80 (m, 50H).

Instruments. ¹H NMR spectra were recorded on a JNM

ECP-400 at 400 MHz. using CDCl₃ as the solvent at room temperature. Cyclic voltammetry (CV) experiment was performed using a Perkin Elmer TM Potentiostat/Galvanostat Model 263A. The three-electrode cells were used in all experiments. Platinum wire was used for counter electrodes. Working electrode was made of indium-tin-oxide (ITO) and Ag/AgCl (a saturated 3.5M KCl-AgCl solution, Princeton, NJ 08540.) was used as a reference electrode. The polymer was coated onto the ITO working electrode by spin coating the ITO into the viscous polymer solution in CHCl₃. Electrolyte solutions of 0.1 M Bu₄NClO₄ in DMF were used in our experiments. Cyclic voltammograms were obtained at a scan rate of 50 mV/sec. UV-vis spectrum was recorded on a UV-1601 PC, UV-visible spectrophotometer (SHIMADZU). Photoluminescence spectra were measured on a RF-5301 PC spectrofluorophotometer (SHIMADZU). Approximate relative fluorescence quantum efficiencies of the thin films were determined by using a thin film. The current-voltage (I-V), the luminance, and the external quantum efficiency were measured by using a calibrated silicon photodiode with a pico-ampere meter (Keithley 195 A) and a source meter (Keithley 2400).

Fabrication of the PLEDs. Poly(stylenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was spin coated onto the transparent anode, ITO, followed by the spin coating of the emitting polymer, PPFC6N. *t*-butyl PBD layer was prepared between the emitting layer and the cathode metal as hole blocking layer by vacuum evaporation. LiF/Al double layer was used as a cathode by vacuum evaporation. The evaporation rates of 0.1, 0.01, and 0.5 nm/sec, at a vacuum pressure of about 1.0 × 10⁻⁶ Torr, were maintained during the deposition of the *t*-butyl PBD, LiF, Al, respectively. The device structures used in this study are showed in Figure 2 and described below.

Device 1: ITO/PEDOT:PSS (40 nm)/PPFC6N (80 nm)/LiF (1 nm)/Al (150 nm).

Device 2: ITO/PEDOT:PSS (40 nm)/PPFC6N (80 nm)/*t*-butyl PBD (20 nm)/LiF(1 nm)/Al (150 nm).

Results and Discussion

The synthesis of the monomer and polymer, PPFC6N, is outlined in Figure 1. The resulting polymer was obtained with moderate average molecular weight, *M_n* for 9,725, *M_w* for 9,943 and PDI for 1.022 as typically obtained by the Suzuki type of polymerization reaction. The copolymer shows good solubility in common organic solvents, such as chloroform, THF, xylene and toluene. Figure 3 shows the UV absorption and PL emission spectrum for PPFC6N as solid film. The band gap energy of the polymer was estimated from the absorption spectrum and was found to be 425 nm (2.92 eV). The maximum absorption peak was exhibited at 375 nm. The PL spectrum of the polymer showed the

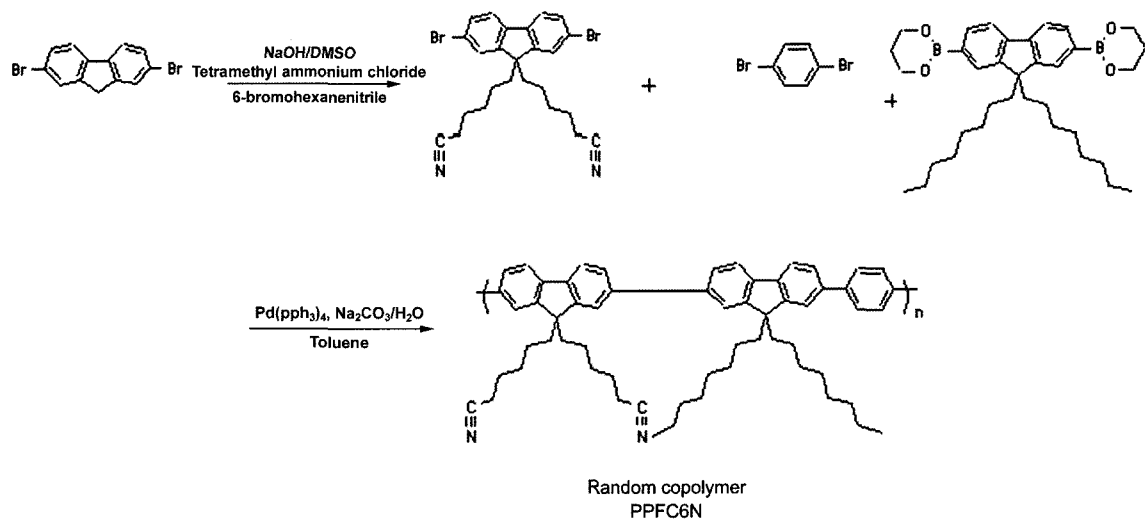


Figure 1. Molecular structure of PPFC6N.

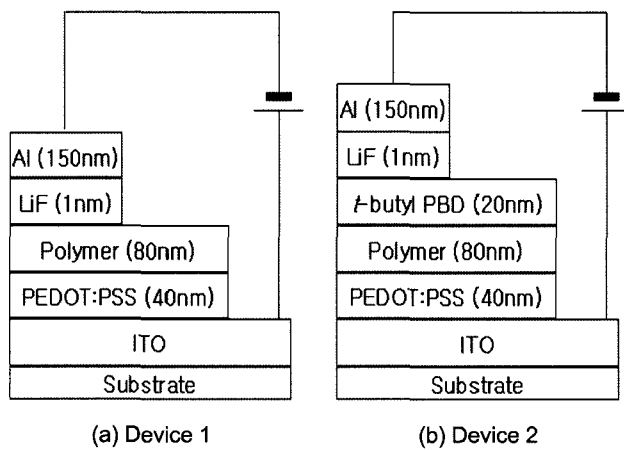


Figure 2. Schematic diagram of the device structure.

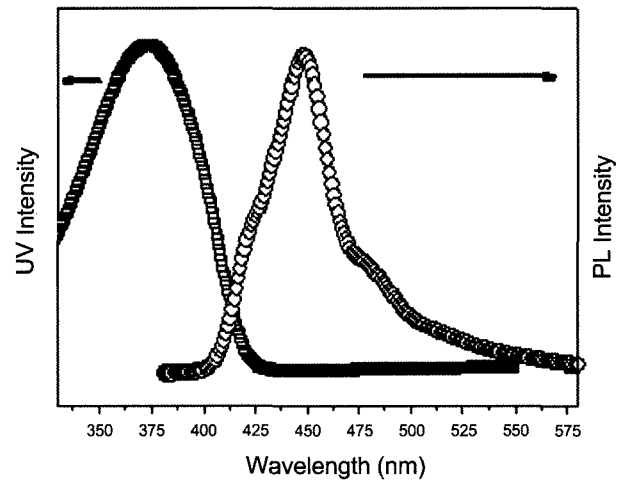


Figure 3. UV-vis absorption and photoluminescence (PL) spectra of PPFC6N.

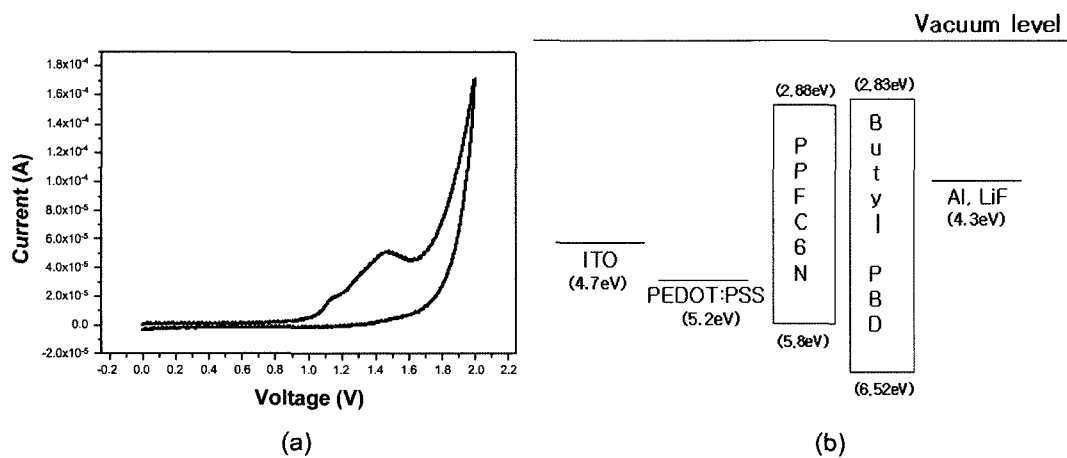


Figure 4. (a) Cyclic voltammogram of PPC6N films coated on ITO and (b) Band diagram of the device.

maximum emission peak of the real blue range 450 nm. Stoke's shift was measured as 0.55 eV from the PL_{max} and UV_{max} peak.

The electrochemical behavior of the polymer was investigated by cyclic voltammetry (CV) and outlined in Figure 4. The onset potential for oxidation was observed to be 1.0 V. On the other hand, E_g was estimated from UV_{onset} and calculated from $EA = IP - E_g$. According to the equation, $IP = ([E_{onset}]^{ox} + 4.8)$ eV, where $[E_{onset}]^{ox}$ was the onset potential for the oxidation of polymer, the HOMO and LUMO of the polymer was estimated to be 5.8 and 2.88 eV.

Figure 5 shows the EL spectra of devices 1 and 2 that were measured with a Shimadzu RF-53001PC. As Figure 5 shows, the maximum EL spectra appear at near 445 nm for the device 1 with small shoulder at 425 and at 425 nm for device 2. When *t*-butyl PBD layer was introduced in device as hole blocking layer, the EL was shifted to the blue showing it's main peak at 425 nm with small shoulder at 445 nm.

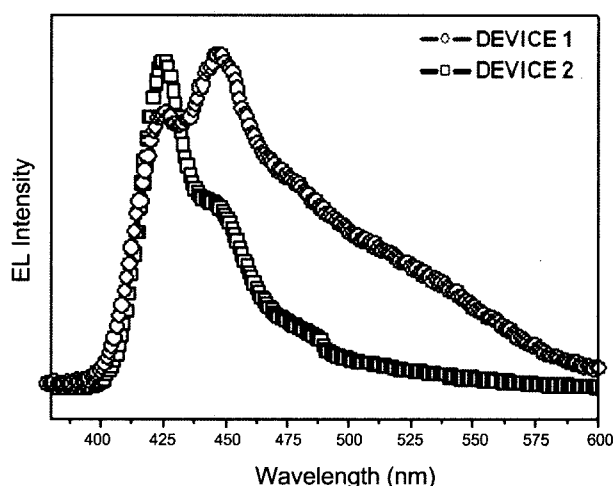


Figure 5. Electroluminescence (EL) spectra of device 1 and 2.

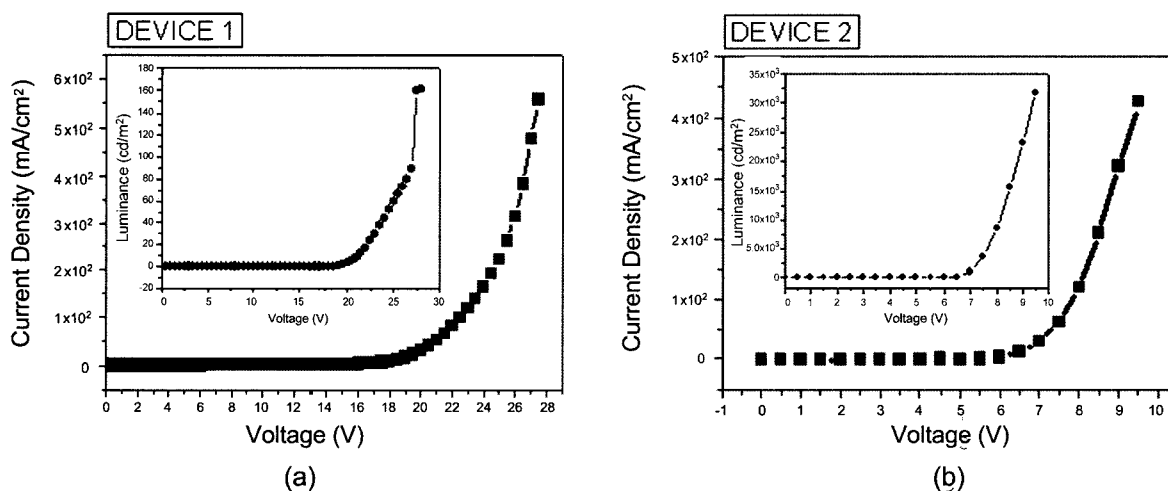


Figure 6. Current density - voltage and luminance - voltage relations (insert) of device 1 and 2.

The blue shift in device 2 indicates that *t*-butyl PBD layer with 20 nm thickness emitted deep blue excitation energy and probably this energy transfers to 425 nm that was the small shoulder of PPFC6N as shown in Figure 5. Figure 6 compares the current-voltage (I-V) relations and the luminance-voltage relations (insert) of the device 1 and 2. Figure 6(a) and (b) is clearly shown that the device with PPFC6N turn on near 15 V with maximum luminance of 170 cd/m^2 at 28 V while the device with PPFC6N containing *t*-butyl PBD layer turn on near 7 V with maximum luminance of 3,200 cd/m^2 at 9.5 V. Even though the device 2 showed higher luminance, EL was slightly blue-shift to 425 nm.

Conclusions

A novel real blue-emitting random copolymer, PPFC6N, was synthesized by palladium-catalyzed Suzuki coupling and the resulting polymer was completely soluble in common organic solvents. The PL spectrum shows that PPFC6N emits blue centered near 450 nm. By applying this polymer in PLED, the main peak of EL spectrum remained at 450 nm while the broad green shoulder appeared due to the keto effect. However, the oscillator strength of this green band is not that strong compared to that of the main peak at 450 nm. This may indicate that the introducing the phenylene and -CN group in the polymer main-chain could reduce the keto effect. The green shoulder was further reduced by introducing a deep blue emitting material, *t*-butyl PBD layer, as hole blocking layer due to the enhancement of the blue emission. However, we have noticed that the emission peak shifted from 450 to 425 nm. This indicates that *t*-butyl PBD and polymer both emitted deep-blue and blue in a PLED, respectively. In PLEDs performances, the device with only PPFC6N has a maximum luminance of 170 cd/m^2 at 28 V while the device with *t*-butyl PBD layer has a maximum luminance of 3,200 cd/m^2 at 9.5 V. Thus the green emission

was embedded to the strong blue spectrum when the *t*-butyl PBD was introduced in the device. In conclusion, introducing the suitable side group in the fluorene-based polymer reduced the unwanted green emission. In addition, introducing the deep-blue emitting material as a hole blocking layer further reduced green should be due to the relatively strong blue emission.

Acknowledgements. This Research was supported by Kyungsoong University Research Grants in 2005.

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