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Synthesis and Device Performance of a Highly Efficient Fluorene-Based Blue Emission Polymer Containing Bulky 9,9-Dialkylfluorene Substituents

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ABSTRACT: We have prepared a series of highly efficient and pure blue-emitting polyfluorene (PF)-type polymers that contain 9,9-di(9,9-dihexylfluoren-2-yl)fluorene and 9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl)fluorene units. The photoluminescence (PL) results show that the size of the side groups strongly influences the color purity and color stability because of the superior ability of large groups to prevent interchain interactions between polymer chains. In contrast to *n*-octyl functional groups, the PF with 9,9-(dihexylfluoren-2-yl) and 3,4-di(2-methyl)butyloxyphenyl side groups exhibits good PL characteristics as a blue-light-emitting polymer (LEP), showing highly enhanced color integrity and color stability against oxidative conditions over PFs based on 9,9-dioctylfluorene. When $N^4,N^{4'}$-bis(4-methoxyphenyl)-$N^4,N^{4'}$-diphenylbiphenyl-4,4′-diamine (**13**) is incorporated into the polymer backbone, the polymer exhibits a highly efficient electroluminescence performance with a luminous efficiency of 4.12 cd/A and Commission Internationale d'Eclairage (CIE) coordinates of (0.15, 0.15) in a structure of indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene)−poly(styrenesulfonic acid) (PEDOT:PSS, 25 nm)/LEP (90−110 nm)/LiF (2 nm)/Al (1500 nm).

Introduction

Blue-light-emitting polymers (LEPs) have been intensively studied in recent years because of their potential applications in full-color displays and white polymer light-emitting diodes (PLEDs).[1] In addition, blue LEPs play an important role in enhancing the efficiencies of green-, red-, and white-light-emitting materials because these materials are generally prepared by introducing appropriate doping components into blue-emitting materials. This approach is based on the wide energy band gap of blue-emissive materials, which means they transfer their energy into red or green dopant materials by Förster and Dexter mechanisms, thereby enabling green, red, and white emission.[2,3] Furthermore, blue LEPs are important for the development of cost-effective white LEDs for next-generation applications such as general light and backlight source for liquid-crystal displays (LCDs).[4,5] Therefore, developing efficient, stable, and deep blue LEPs is essential to realizing such applications.

Polyfluorenes (PFs) have been widely investigated as blue LEPs because of their superior properties, such as high photoluminescence (PL) quantum efficiency as well as thermal and chemical stability. However, PLEDs based on conventional alkyl-substituted PFs (e.g., poly[9,9-dioctylfluorene]) exhibit poor electroluminescence (EL) efficiency and insufficient color stability because of their interchain interactions, aggregations of polymer chains, and oxidative degradation during device operation.[14−23] Several methods have been suggested to resolve such drawbacks of the PFs, which include introduction of bulky end-capping moieties,[6] blending of layered silicates,[7] adoption of star-shaped structures,[8] and substitution of bulky side groups on the PFs.[9−12] Among these methods, the incorporation of bulky side functional groups into PFs, in particular the attachment of bulky aromatic substituents at the 9-position of fluorene, has been reported to give high EL efficiency and good color stability.[2,9−12] However, the use of certain bulky moieties generated negative effects on the electrical performances of PLEDs,[9,11] even though the bulky side groups effectively suppressed the PL luminescence quenching and enhanced the color purity of blue LEPs by shielding the polymer backbones. In general, modifying PFs by attaching aromatic substituents that are too bulky can unnecessarily increase the interchain distance of the polymers, leading inevitably to the formation of electrically isolated regions and hence to low charge transport through thin films of the polymer.[9,11] PFs containing these types of bulky structures generally exhibit low maximum luminance and require a high operating voltage. Therefore, appropriate side groups, which minimize the interchain interactions and do not degrade the EL characteristics, have to be incorporated into the polymers.

In the present work, we prepared a novel fluorene-based blue LEP that contains 9,9-(dihexylfluoren-2-yl) and 3,4-di(2-methyl)-butyloxyphenyl side groups. We show that these side groups effectively shield the polymer backbone from the formation of aggregates and suppress interchain interactions, resulting in efficient blue EL performance. The PL and EL results show that the PF based on 9,9-di(9,9-dihexylfluoren-2-yl)fluorene and 9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl) fluorene units (DFF-FCF) shows a narrow emission band with high color stability against oxidative conditions, in addition to high EL efficiency, because of the superior ability of its side groups to prevent interchain interactions between polymer main chains while not degrading the EL characteristics.

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Experimental Section

Materials. All of reagents including 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (MDOF, **14**) and 2,2′-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (MDOFB, **15**) were obtained from Aldrich, TCI, and STREM chemicals and used without further purification.

Preparation of (9-(9,9-Dihexylfluoren-2-yl)-2,7-dibromofluoren-9-ol) (MFOHF, 4). 9,9-Dihexyl-2-bromofluorene (**1**) (8 g, 19.35 mmol) in 30 mL of THF was added dropwise to a 10 mL of THF containing magnesium turnings (0.47 g, 19.35 mmol) at a temperature of 60 °C, and this solution was refluxed. After 2 h, a solution of Grignard reagent of 9,9-dihexyl-2-bromofluorene (**2**) in THF was cooled to room temperature and added dropwise to a THF solution of 2,7-dibromo-9-fluorenone (**3**) (5.45 g, 16.13 mmol) at a temperature of 0 °C. After 4 h of reaction at room temperature, the reaction solution was poured into water and extracted with diethyl ether. The solvent was evaporated using rotary evaporator, and the product was separated by column chromatography. After being dried under vacuum, the product (**4**) was obtained as a white solid (7.1 g, yield 65%). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.72−7.41 (m, 8H, Ar H), 7.41−7.22 (m, 4H, Ar H), 6.98 (dd, 1H, Ar H), 2.56 (s, 1H, OH), 2.12−1.83 (m, 4H, CH$_2$), 1.21−0.93 (m, 12H, CH$_2$), 0.76 (t, 6H, CH$_3$), 0.60 (br, 4H, CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 152.63, 151.66, 151.39, 141.33, 140.99, 140.77, 137.95, 132.86, 128.72, 127.64, 127.17,124.35, 123.26, 122.96, 122.06, 120.17, 120.11, 120.02, 84.10, 77.71, 77.46, 77.21, 55.60, 40.70, 31.92, 30.11, 24.23, 23.01, 14.48. FD-MS (*m*/*z*): calcd for $C_{38}H_{40}Br_2O$, 670.14; found, 670.26. Elemental analysis: calcd for $C_{38}H_{40}Br_2O$: C, 67.86; H, 5.99; O, 2.38; found: C, 67.84; H, 5.97.

Preparation of (9,9-Di(9,9-dihexylfluoren-2-yl)-2,7-dibromofluorene) (MDFF, 6). To a solution of 9,9-dihexylfluorene (**5**) (7.03 g, 21.01 mmol) and methanesulfonic acid (1.22 g, 12.67 mmol) in dichloromethane (40 mL), 9-(9,9-dihexylfluorene-2-yl)-2,7-dibromofluoren-9-ol (**4**) (7.1 g, 10.56 mmol) in dichloromethane (40 mL) was added dropwise at 0 °C for 1 h. The reaction mixture was stirred at room temperature for 3 h. After that, the reaction mixture was washed with deionized water several times, and the dichloromethane was evaporated under reduced pressure. The residue was purified by column chromatography to afford a white solid (**6**) (6.1 g, yield 62%). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.66−7.59 (m, 4H, Ar H), 7.52 (d, 2H, Ar H), 7.50−7.45 (m, 4H, Ar H), 7.24−7.34 (m, 8H, Ar H), 6.99 (dd, 1H, Ar H), 1.97−1.79 (m, 8H, CH$_2$), 1.18−0.97 (m, 24H, CH$_2$), 0.78 (t, 12H, CH$_3$), 0.60 (br, 8H, CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 154.34, 151.49, 151.27, 143.59, 141.03, 140.82, 138.46, 131.26, 129.75, 127.53, 127.23, 126.72, 123.22, 122.27, 122.08, 122.06, 66.59, 55.58, 40.73, 32.04, 30.21, 24.39, 23.06, 14.50. FD-MS (*m*/*z*): calcd for $C_{63}H_{72}Br_2$, 986.40; found, 986.45. Elemental analysis: calcd for $C_{63}H_{72}Br_2$: C, 76.50; H, 7.34; Br, 16.16; found: C, 76.36; H, 7.35.

Preparation of 9-(9,9-Dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)-butyloxyphenyl)-2,7-dibromofluorene (MFCF, 8). To a dichloromethane solution (80 mL) of 1,2-di(2-methyl)butyloxybenzene (**7**) (7.44 g, 29.74 mol) and methanesulfonic acid (1.72 g, 17.84 mmol), 9-(9,9-dihexylfluorene-2-yl)-2,7-dibromofluoren-9-ol (**4**) (10.0 g, 14.87 mmol) in dichloromethane (80 mL) was added dropwise at 0 °C for 1 h, and the reaction mixture was left further for 3 h at room temperature. The reaction mixture was washed with deionized water several times and dried using a rotary evaporator. The residue was purified using column chromatography to afford a white solid (**8**) (10.4 g, yield 81%). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.64−7.59 (m, 1H, Ar H), 7.59−7.55 (d, 2H, Ar H), 7.52−7.43 (m, 5H, Ar H), 7.35 (s,1H, Ar H), 7.24−7.36 (m, 4H, Ar H), 6.88 (dd, Ar H), 6.76−6.69 (m, 2H, Ar H), 6.64 (dd, 1H, Ar H), 3.84−3.70 (m, 2H, CH$_2$), 3.69−3.55 (m, 2H, CH$_2$), 1.97−1.83 (m, 5H, CH, CH$_2$), 1.82−1.73 (m, 1H, CH), 1.62−1.45 (m, 2H, CH$_2$), 1.32−1.17 (m, 2H, CH$_2$), 1.16−0.99 (m, 15H, CH$_2$), 0.98−0.91 (m, 6H, CH$_2$), 0.88 (t, 3H, CH$_3$), 0.78 (t, 6H, CH$_3$), 0.61 (br, 4H, CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 154.04, 151.53, 151.36, 149.46, 149.29, 143.76, 140.99, 140.71, 138.39, 137.34, 131.22, 129.78, 127.50, 126.12, 123.82, 123.22, 122.18, 122.01, 120.94, 120.08, 119.81, 112.20, 113.55, 74.57, 74.20, 65.98, 55.52, 40.72, 35.29, 30.27, 26.62, 26.56, 24.40, 23.12, 17.03, 16.89, 14.49, 11.85, 11.81. FD-MS (*m*/*z*): calcd for $C_{54}H_{64}Br_2O_2$, 902.33; found, 902.30. Elemental analysis: calcd for $C_{54}H_{64}Br_2O_2$: C, 71.67; H, 7.13; O, 3.54; found: C, 71.55; H, 7.14.

Preparation of 9-(9,9-Dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)-butyloxyphenyl)fluorene-2,7-bisboronic Glycol Ester (MFCFB, 9). MFCF (**8**) (7.0 g, 7.74 mmol) was dissolved in 60 mL of THF and cooled to −78 °C. After that, 1.6 M of *n*-butyllithium solution in hexane (10.15 mL, 16.25 mmol) was slowly added, and the reaction mixture was further reacted at room temperature. After 1 h, triethyl borate (5.53 mL, 32.49 mmol) was added at −78 °C, and the reaction mixture was left to stir for 12 h at room temperature. The reaction mixture was poured into the 3 N hydrochloric acid and left for 4 h with vigorous agitation. The organic layer was extracted with ethyl acetate and washed with deionized water several times. After evaporation of ethyl acetate by using a rotary evaporator, the reaction mixture was washed with toluene twice. To a round flask containing reaction mixture, toluene (50 mL) and ethylene glycol (1.2 g, 19.34 mmol) were added, and a Dean Stark apparatus was installed. The solution was refluxed for 12 h to remove water. The product MFCFB (**9**) was obtained after recrystallization using toluene and hexane (yield 43%). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.90 (s, 2H, Ar H), 7.85−7.78 (m, 2H, Ar H), 7.59 (d, 1H, Ar H), 7.45 (s, 1H, Ar H), 7.40 (d, 1H, Ar H), 7.32−7.22 (m, 3H, Ar H), 6.88 (dd, 1H, Ar H), 6.76 (s, 1H, Ar H), 6.72−6.64 (m, 2H, Ar H), 4.37−4.26 (m, 8H, CH$_2$), 3.81−3.66 (m, 2H, CH$_2$), 3.66−3.52 (m, 2H, CH$_2$), 1.97−1.83 (m, 5H, CH, CH$_2$), 1.82−1.73 (m, 1H, CH), 1.62−1.42 (m, 2H, CH$_2$), 1.31−1.13 (m, 2H, CH$_2$), 1.13−1.06 (m, 4H, CH$_2$), 1.06−0.96 (m, 11H, CH$_2$), 0.95−0.89 (m, 6H, CH$_2$), 0.88−0.82 (t, 3H, CH$_3$), 0.86 (t, 6H, CH$_3$), 0.78 (t, 6H, CH$_3$), 0.60 (br, 4H, CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 152.14, 151.40, 151.08, 149.19, 148.72, 145.06, 143.30, 141.34, 140.01, 138.68, 134.44, 133.05, 127.10, 127.02, 126.25, 124.20, 123.14, 121.06, 120.50, 119.90, 119.49, 115.10, 113.52, 74.34, 74.23, 66.38, 65.68, 55.41, 40.66, 35.26, 35.18, 31.94, 30.18, 26.59, 26.52, 24.27, 23.10, 16.99, 16.88, 14.46, 11.78, 11.74. FD-MS (*m*/*z*): calcd for $C_{58}H_{72}B_2O_6$, 886.55; found, 886.63. Elemental analysis: calcd for $C_{58}H_{72}B_2O_6$: C, 78.55; H, 8.18; O, 10.82; found: C, 78.32; H, 8.20.

Preparation of *N*^{4},*N*$^{4'}$-Bis(4-bromophenyl)-*N*^{4},*N*$^{4'}$-bis(4-methoxyphenyl)biphenyl-4,4′-diamine (MTPD, 13). Tris(dibenzylideneacetone)dipalladium (0.89 g, 0.96 mmol) and diphenylphosphinoferrocene (0.83 g, 1.47 mmol) were added to 300 mL of anhydrous toluene. The solution was stirred at 90 °C for 30 min, and then 4,4′-dibromobiphenyl (**10**) (10 g, 32.05 mmol), 4-methoxyaniline (**11**) (8.05 g, 64.10 mmol), and sodium *tert*-butoxide (6.67 g, 67.31 mmol) were added to the solution. After 4 h, 1,4-dibromobenzene (**12**) (19.28 g, 80.13 mmol) was added, and reaction mixture was refluxed for 8 h. The reaction mixture was cooled to room temperature and washed with deionized water. The reaction mixture was dried using a rotary evaporator and purified by using column chromatography to afford a yellowish solid (15.50 g, yield 68%). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.40 (d, 4H, Ar H), 7.29 (d, 4H, Ar H), 7.12−7.02 (m, 8H, Ar H), 6.92 (d, 4H, Ar H), 6.85 (d, 4H, Ar H), 3.80 (s, 6H, OCH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 156.95, 146.94, 140.50, 134.93, 132.44, 127.83, 127.72, 124.46, 123.65, 115.35, 114.38, 55.92. FD-MS (*m*/*z*): calcd for $C_{38}H_{30}Br_2N_2O_2$, 704.07; found, 704.18. Elemental analysis: calcd for $C_{38}H_{30}Br_2N_2O_2$: C, 64.60; H, 4.28; Br, 22.62; N, 3.97; O, 4.53; found: C, 65.05; H, 4.35; N, 3.92.

Preparation of Poly[2,7-(9,9-dioctylfluorene)] (DOF, P1) Using MDOF (14) and MDOFB (15) in a Molar of 5:5. To a mixture of 2,2′-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane)

(**15**) (0.81 g, 1.40 mmol), 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (**14**) (0.80 g, 1.40 mmol), and K_3PO_4 (1.53 g, 7.21 mmol), the mixed solvent of dioxane (12 mL), toluene (4 mL), and deionized water (2.7 mL) was added. The reaction mixture was degassed with N_2 for 30 min, and then solutions of $P(o\text{-Toly})_3$ (0.013 g, 0.04 mmol) in toluene (0.5 mL) and $Pd(OAc)_2$ (0.002 g, 0.01 mmol) in toluene (0.5 mL) were added sequentially. The polymerization was carried out at 90 °C with vigorous stirring. After 8 h, a solution of 2,2′-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis-(1,3,2-dioxaborinane) (**15**) (0.03 g, 0.06 mmol) in toluene (0.5 mL) was added, and the reaction mixture was refluxed for 4 h; then an excess of 4-bromobenzene (0.1 g) was added to end-cap the polymer. After another 4 h, the reaction mixture was poured into the mixture of toluene (30 mL) and NaCN water solution (2 wt %, 30 mL) and vigorously stirred for 4 h. The organic phase was washed with deionized water several times and poured into methanol. The precipitate was filtered and dissolved in THF (20 mL). The polymer solution was slowly dropped into methanol, and the polymer was collected by filtration. After the precipitation procedure was repeated three times, the slightly greenish polymer was obtained. GPC: M_n 84 500, M_w 162 500, PDI 1.92. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.82−7.80 (d, 2H, Ar H), 7.66 (br, 4H, Ar H), 2.12 (br, 4H, CH_2), 1.30−1.02 (m, 20H, CH_2), 0.98−0.70 (m, 10H, CH_2, CH_3). Elemental analysis: calcd for $C_{29}H_{40}$: C, 89.63; H, 10.37; found: C, 88.6; H, 10.51.

Preparation of Poly[2,7-((9,9-di(9,9-dihexylfluoren-2-yl)-fluorene))-*alt*-(2,7-(9,9-dioctylfluorene))] (DFF-DOF, P2) Using MDFF (6) and MDOFB (15) in a Molar Ratio of 5:5. The DFF-DOF (**P2**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MDFF (**6**) (0.80 g, 0.50 equiv) and MDOF (**14**) (0.47 g, 0.50 equiv) were used as monomers, and a slightly yellowish-white polymer was obtained. GPC: M_n 95 600, M_w 282 200, PDI 2.95. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.93−7.83 (d, 2H, Ar H), 7.79−7.13 (m, 24H, Ar H), 2.08−1.73 (m, 12H, CH_2), 1.22−0.82 (m, 44H, CH_2), 0.82−0.52 (m, 30H, CH_2, CH_3). Elemental analysis: calcd for $C_{92}H_{112}$: C, 90.7; H, 9.27; found: C, 90.2; H, 9.25.

Preparation of Poly[2,7-(9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di-(2-methyl)butyloxyphenyl)fluorene)] (FCF, P3) Using MFCF (8) and MFCFB (9) in a Molar Ratio of 5:5. The FCF (**P3**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MFCF (**8**) (0.60 g, 0.50 equiv) and MFCFB (**9**) (0.59 g, 0.50 equiv) were used as monomers, and a slightly yellowish-white polymer was obtained. GPC: M_n 301 100, M_w 2 139 900, PDI 7.11. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.75−7.02 (m, 12H, Ar H), 6.90−6.63 (m, 4H, Ar H), 3.82−3.51 (m, 4H, OCH_2), 1.92−1.61 (m, 6H, CH_2), 1.59−1.07 (m, 4H, CH_2), 1.07−0.52 (m, 34H, CH_2, CH_3). Elemental analysis: calcd for $C_{54}H_{64}O_2$: C, 87.1; H, 8.56; O, 4.29; found: C, 86.1; H, 8.56.

Preparation of Poly[2,7-((9,9-di(9,9-dihexylfluoren-2-yl)-fluorene))-*alt*-(2,7-(9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl)fluorene)] (DFF-FCF, P4) Using MDFF (6) and MFCFB (9) in a Molar Ratio of 5:5. The DFF-FCF (**P4**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MDFF (**6**) (0.60 g, 0.50 equiv) and MFCFB (**9**) (0.56 g, 0.50 equiv) were used as monomers, and a slightly yellowish-white polymer was obtained. GPC: M_n 171 700, M_w 546 500, PDI 3.18. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.77−7.04 (m, 30H, Ar H), 6.88−6.81 (br, 3H, Ar H), 6.74−6.62 (m, 3H, Ar H), 3.82−3.52 (m, 4H, OCH_2), 1.94−1.63 (m, 14H, CH_2), 1.58−1.07 (m, 4H, CH_2), 1.07−0.48 (m, 78H, CH_2, CH_3). Elemental analysis: calcd for $C_{117}H_{136}O_2$: C, 89.3; H, 8.71; O, 2.03; found: C, 88.83; H, 8.71.

Preparation of DOF-TPD (P5) Using MDOF (14), MDOFB (15), and MTPD (13) in a Molar Ratio of 4:5:1. The DOF-TPD (**P5**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MDOF (**14**) (0.55 g, 0.40 equiv), MDOFB (**15**) (0.69 g, 0.50 equiv), and MTPD (**13**) (0.17 g, 0.10 equiv) were used as monomers, and a greenish polymer was obtained. GPC: M_n 62 900, M_w 138 900, PDI 2.21. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.85−7.51 (m, 6.4H, Ar H), 7.50−7.43 (m, 0.4H, Ar H), 7.20−7.10 (m, 1.3H, Ar H), 6.93−6.85 (d, 0.4H, Ar H), 3.82 (s, 0.7H, OCH_3), 2.12 (br, 4H, CH_2), 1.25−1.00 (m, 20H, CH_2), 0.98−0.74 (m, 10H, CH2, CH3). Elemental analysis: calcd for $C_{299}H_{390}N_2O_2$: C, 88.8; H, 9.72; N, 0.69; O, 0.79; found: C, 88.5; H, 9.73; N, 0.69.

Preparation of DFF-DOF-TPD (P7) Using MDFF (6), MDOFB (15), and MTPD (13) in a Molar Ratio of 4:5:1. The DFF-DOF-TPD (**P7**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MDFF (**6**) (0.80 g, 0.40 equiv), MDOFB (**15**) (0.58 g, 0.40 equiv), and MTPD (**13**) (0.14 g, 0.10 equiv) were used as monomers, and a greenish polymer was obtained. GPC: M_n 48 400, M_w 111 300, PDI 2.30. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.98−7.88 (d, 2H, Ar H), 7.82−7.04 (m, 23.2H, Ar H), 6.93−6.84 (br, 1.6H, Ar H), 3.88−3.76 (s, 1.2H, OCH_3), 2.12−1.72 (m, 10.4H, CH_2), 1.20−0.50 (m, 65.2H, CH_2, CH_3). Elemental analysis: calcd for $C_{435}H_{518}N_2O_2$: C, 90.0; H, 8.99; N, 0.48; O, 0.55; found: C, 89.6; H, 8.99; N, 0.59.

Preparation of FCF-TPD (P6) Using MFCF (8), MFCFB (9), and MTPD (13) in a Molar Ratio of 4:5:1. The FCF-TPD (**P6**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MFCF (**8**) (0.55 g, 0.40 equiv), MFCFB (**9**) (0.67 g, 0.40 equiv), and MTPD (**13**) (0.11 g, 0.10 equiv) were used as monomers, and a greenish polymer was obtained. GPC: M_n 101 000, M_w 282 600, PDI 2.80. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.80−6.98 (m, 13.8H, Ar H), 6.93−6.60 (m, 4.9H, Ar H), 3.82−3.51 (m, 4.7H, OCH_2), 1.98−1.07 (m, 10H, CH_2), 1.07−0.52 (m, 34H, CH_2, CH_3). Elemental analysis: calcd for $C_{524}H_{606}N_2O_{20}$: C, 86.8; H, 8.42; N, 0.39; O, 4.41; found: C, 83.9; H, 8.00; N, 0.39.

Preparation of DFF-FCF-TPD (P8) Using MDFF (6), MFCFB (9), and MTPD (13) in a Molar Ratio of 4:5:1. The DFF-FCF-TPD (**P8**) was prepared following the same procedure as used in the preparation of DOF (**P1**). The MDFF (**6**) (0.55 g, 0.40 equiv), MFCFB (**9**) (0.62 g, 0.50 equiv), and MTPD (**13**) (0.10 g, 0.10 equiv) were used as monomers, and a greenish polymer was obtained. GPC: M_n 267 700, M_w 1 340 500, PDI 5.01. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.80−6.96 (m, 31.2H, Ar H), 6.90−6.62 (m, 5.6H, Ar H), 3.84−3.52 (m, 5.2H, OCH_3, OCH_2), 1.92−1.63 (m, 12.4H, CH_2), 1.58−1.08 (m, 4H, CH_2), 1.08−0.52 (m, 69.2H, CH_2, CH_3). Elemental analysis: calcd for $C_{560}H_{638}N_2O_2$: C, 88.6; H, 8.47; N, 0.37; O, 2.53; found: C, 88.9; H, 8.54, N, 0.39.

Characterizations. NMR spectra were recorded on a Bruker Advance DRX 500 spectrometer. Mass spectra were obtained using a Jeol JMS-T100 AccuTOF GC mass spectrometer. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were measured using a Waters GPC system equipped with PLgel Olexis columns (300 × 7.5 mm, 10 μm), a Waters 2414 refractive index detector, and a Waters 1515 pump. Two polystyrene standards (EasyCal, PS2) were used for calibration, and THF is used as an eluent. Differential scanning calorimetry (DSC) was performed on a Metter DSC 822 at a heating rate of 10 °C/min, and the glass transition temperature (T_g) was obtained from the second heating scan. Elemental analysis was carried out using a FlashEA 1112 CHNS analyzer (Thermo Electron Corp.). Absorption spectra in chloroform solutions were recorded on a Jasco V-530 UV−vis spectrophotometer, and photoluminescent spectra were obtained on a Shimadzu RF-5300PC spectrofluorometer with a excitation at 375 nm.

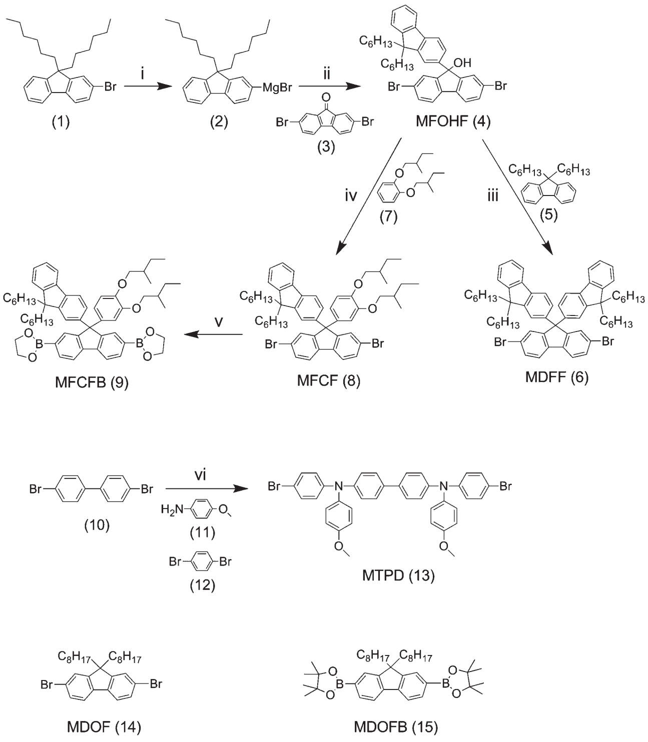
Device Fabrication and Measurement. The patterned ITO glass substrates were cleaned by ultrasonication in acetone, methanol, and deionized water, after which being dried by N_2 blowing and dry-cleaned using UV ozone for 10 min. The PEDOT:PSS (AI4083, H.C. Stack) was spin-coated on the cleaned ITO glass at a rate of 4000 rpm, and then the substrates were baked at 200 °C for 20 min in a N_2 glovebox. The LEP solutions (0.8−1.2 wt %) were prepared by dissolving LEPs in toluene with heating and spin-coated at a rate in the range 800−2000 rpm. The thickness of LEP layer was measured using Alpha-Step IQ profilometer (KLA-Tencor). The spin-coated substrates were baked at 120 °C for 30 min in a N_2 glovebox and transferred to the vacuum evaporation chamber for cathode deposition. The LiF (2 nm) and Al (150 nm) were sequentially deposited on the LEP layer under a pressure of $5.0 \times 10^{-7}-1.0 \times 10^{-6}$ Torr. The fabricated devices have 6.0 mm^2 of active area. The measurements of current−voltage−luminance ($I-V-L$) characteristics were carried out on a McScience Polaronix IVL tester equipped with Minolta LS-100 luminenscence detector, and EL spectra were measured with a Photo Research PR650 spectrophotometer.

Results and Discussion

Synthesis. Scheme 1 illustrates the chemical structures and synthetic routes of four different monomers we prepared in this study: (9,9-di(9,9-dihexylfluoren-2-yl)-2,7-dibromofluorene) (MDFF, **6**), (9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di-(2-methyl)butyloxyphenyl)-2,7-dibromofluorene) (MFCF, **8**), (9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl)fluorene-2,7-bisboronic glycol ester) (MFCFB, **9**), and (N^4,$N^{4'}$-bis(4-bromophenyl)-N^4,$N^{4'}$-bis(4-methoxyphenyl)biphenyl-4,4′-diamine) (MTPD, **13**). First, (9-(9,9-dihexylfluoren-2-yl)-2,7-dibromofluoren-9-ol) (MFOHF, **4**) was prepared by reacting the Grignard reagent of 9,9-dihexyl-2-bromofluorene (**1**) with 2,7-dibromo-9-fluorenone (**3**). Then, MDFF (**6**) and MFCF (**8**) were synthesized by the addition of MFOHF (**4**) under acidic conditions to 9,9-dihexylfluorene (**5**) and 1,2-di(2-methyl)butyloxybenzene (**7**), respectively. MFCFB (**9**) was prepared by successive reaction of MFOHF (**4**) with triethyl borate and ethylene glycol. Their chemical structures were identified by ^1H NMR, ^{13}C NMR, FD-MS, and elemental analysis (see the Supporting Information).

The Suzuki polymerization was carried out in a mixture of toluene and 1,4-dioxane with the use of $Pd(OAc)_2$ and $P(o\text{-}Toly)_3$ catalysts and then terminated by adding an excess of 4-bromobenzene.[13] Four different polymers were prepared using the monomers combinations MDOF/MDOFB (DOF, **P1**), MDFF/MDOFB (DFF-DOF, **P2**), MFCF/MFCFB (FCF, **P3**), and MDFF/MFCFB (DFF-FCF, **P4**) (Scheme 2). These polymers have different substituents: DOF (**P1**), DFF-DOF (**P2**), FCF (**P3**), and DFF-FCF (**P4**) have substituents of *n*-octyl; (9,9-dihexylfluoren-2-yl)/(*n*-octyl) in a 1:1 molar ratio; (9,9-dihexylfluoren-2-yl)/(3,4-di(2-methyl)butyloxyphenyl) in a 1:1 molar ratio; and (9,9-dihexylfluoren-2-yl)/(3,4-di(2-methyl)butyloxyphenyl) in a 3:1 molar ratio at the 9-position of fluorene, respectively. Poly[2,7-((9,9-di(9,9-dihexylfluoren-2-yl)-fluorene))-*alt*-(2,7-(9,9-dioctylfluorene))] (DFF-DOF, **P2**) has a bulkier side group structure than that of DOF (**P1**) because of the 9,9-dihexylfluoren-2-yl side groups, and poly[2,7-(9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl)fluorene)] (FCF, **P3**) has a more bulky structure in comparison with DFF-DOF (**P2**) because of the 3,4-di(2-methyl)butyloxyphenyl side groups. For a PF with very bulky side groups, we prepared poly[2,7-(9,9-di(9,9-dihexylfluoren-2-yl)fluorene)-*alt*-(2,7-(9-(9,9-dihexylfluoren-2-yl)-9-(3,4-di(2-methyl)butyloxyphenyl)fluorene))] (DFF-FCF, **P4**) (Scheme 2). In addition, polymers with MTPD (**13**) (DOF-TPD (**P5**), FCF-TPD (**P6**), DFF-DOF-TPD (**P7**), and DFF-FCF-TPD (**P8**)) were also prepared to further improve EL performance by enhancing the hole transporting properties of the polymers.

Scheme 1. Molecular Structures and Synthetic Routes of the Monomers[a]



[a] Conditions: (i) Mg, THF, 60 °C; (ii) THF, 0 °C; (iii), (iv) methanesulfonic acid, dichloromethane, 0 °C; (v) 1.6 M BuLi, triethyl borate, THF, HCl, −78 °C; ethylene glycol, toluene, reflux; (vi) $Pd_2(dba)_3$, dppf, sodium *tert*-butoxide, toluene, 90 °C.

The feed ratios of the monomers and the resulting molecular weights of the polymers are summarized in Table 1. The polymers FCF (**P3**), DFF-FCF (**P4**), FCF-TPD (**P6**), and DFF-FCF-TPD (**P8**) based on MDFF (**6**) and MFCF (**8**) exhibited relatively high number-average molecular weights (M_n) ranging from 101 to 301 kDa. However, these polymers could be readily dissolved in common solvents such as toluene, xylene, and chlorobenzene because of the large number of alkyl chains within the side groups. Thus, these polymers formed uniform thin films on a substrate via the spin-coating method. In contrast, DOF showed rather poor solubility in common solvents, leading to precipitation during the polymerization.

Thermal Properties. The thermal transition temperatures of the polymers were determined using differential scanning calorimetry (DSC) under an N_2 atmosphere at a scan rate of 10 °C/min (Table 2). DOF (**P1**) showed a T_m of 167 °C, consistent with previous results.[13] In the case of DFF-DOF (**P2**), no T_m was observed, presumably due to the bulky side groups of MDFF (**6**), indicating a desirable amorphous characteristic for LEPs. DFF-DOF (**P2**) exhibited relatively low thermal stability (glass transition temperature, T_g = 91 °C). On the other hand, DFF-FCF (**P4**) and FCF (**P3**), which have more rigid and bulkier side groups, exhibited higher T_gs of 120 and 125 °C, respectively. Moreover, when MTPD (**13**) is incorporated into these polymers, the thermal stabilities were further improved. Although DOF-TPD exhibited rather low thermal stability (T_g = 90 °C), DFF-FCF-TPD (**P8**) and FCF-TPD (**P6**) showed much higher T_gs of 133 and 170 °C, respectively.

Photoluminescence Properties. Figure 1 shows the normalized UV−vis absorption and PL spectra of DOF (**P1**), DFF-DOF (**P2**), FCF (**P3**), and DFF-FCF (**P4**) in dilute solution. The polymers exhibit similar PL spectra, having distinct vibronic bands at 419 and 445 nm and a shoulder around 470 nm upon excitation at 375 nm. This is attributed to the

Scheme 2. Chemical Structure of the Polymers

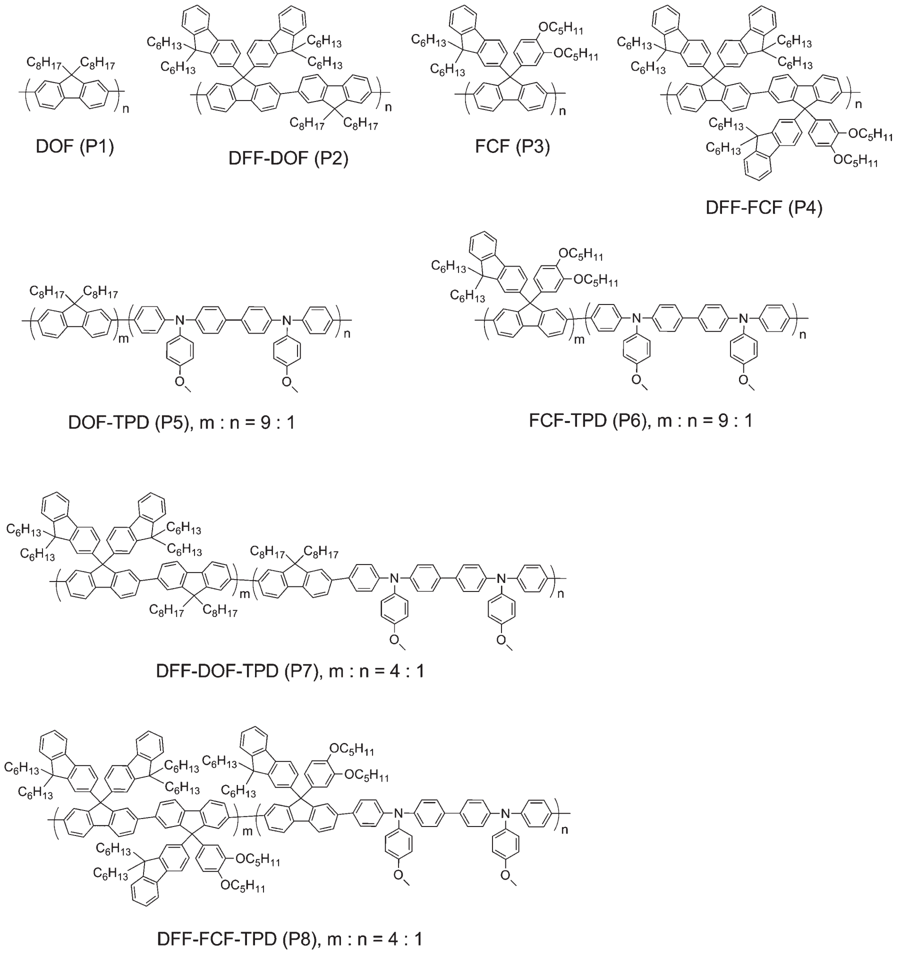


Table 1. Feed Ratios of the Monomers and the Molecular Weights of the Polymers

polymers	feed composition (mol %)	M_w (Da)	M_n (Da)	PDI	transition temperature (°C)
DOF	MDOF (50)/MDOFB (50)	163K	85K	1.9	167 (T_m)
DOF-TPD	MDOF (40)/TPD (10)/MDOFB (50)	139K	63K	2.2	90 (T_g)
DFF-DOF	MDFF (50)/ MDOFB (50)	282K	96K	3.0	91 (T_g)
DFF-DOF-TPD	MDFF (40)/TPD (10)/MDOFB (50)	111K	48K	2.3	102 (T_g)
FCF	MFCF (50)/MFCFB (50)	2140K	301K	7.1	125 (T_g)
FCF-TPD	MFCF (40)/TPD (10)/MFCFB (50)	283K	101K	2.8	170 (T_g)
DFF-FCF	MDFF (50)/MFCFB (50)	547K	172K	3.2	120 (T_g)
DFF-FCF-TPD	MDFF (40)/TPD (10)/MFCFB (50)	1341K	268K	5.0	133 (T_g)

Table 2. EL Performance and Characteristics of Light-Emitting Diodes

polymers	color coordinate [x, y]	EL λ_{max} [nm]	turn-on voltage [V]	max brightness [cd/m^2]	max efficiency [cd/A]	efficiency at 1000 cd/m^2 [cd/A]
DOF	0.16, 0.11	428	5.2	950	0.29	
DOF-TPD	0.17, 0.19	468	3.3	1280	0.58	0.54
DFF-DOF	0.16, 0.11	444	5.4	350	0.26	
DFF-DOF-TPD	0.16, 0.17	468	3.3	1530	1.33	1.21
FCF	0.16, 0.10	416	4.6	450	0.63	
FCF-TPD	0.15, 0.13	452	4.0	3230	2.33	2.27
DFF-FCF	0.16, 0.09	444	5.6	530	0.59	
DFF-FCF-TPD	0.15, 0.15	456	3.2	4010	4.12	3.90

fact that the distance between polymer main chains in dilute solution is sufficient to make interchain interactions negligible. In addition, the PL spectra of the polymers based on MDFF (**6**) and MFCF (**8**) in dilute solution are similar to that of DOF (**P1**), indicating that under these conditions the bulky side groups within the polymers do not alter the torsion angle along the polymer main chains.[11] However, absorption bands around 311 nm, which is a characteristic peak of fluorenyl side groups, are different for the polymers. DFF-FCF (**P4**), DFF-DOF (**P2**), and FCF (**P3**) show strong absorption peaks at 311 nm, while DOF (**P1**) has no absorption peak in this region.

To examine the thermal stability and color stability of the polymers, we measured the PL spectra of films of the polymers (Figure 2). The thin films were prepared on a quartz plate by spin-coating the polymer solutions in toluene, followed by drying at room temperature or annealing at 170 °C for 3 h in air or annealing at 170 °C for 3 h under a N_2 atmosphere. As shown in Figure 2a, λ_{max} (426 nm) of the DOF (**P1**) film is significantly red-shifted to a longer wavelength (434 nm) after thermal annealing under N_2. Furthermore, the shapes of the peaks at 426 and 438 nm become well-defined, indicating an extended conformation of the DOF (**P1**) backbone or increased interchain interactions. These findings thus indicate that the ordering of the intramolecular or intermolecular structure is considerably enhanced after thermal annealing under N_2. When the DOF (**P1**) films were annealed in air, however, a new broad peak centered at 525 nm appeared, indicating color instability of the PFs.[15−17] Such color instability is a major problem hindering the use of PFs as blue LEPs because the growth of green emission makes it difficult to obtain efficient and pure blue emission.[7,10,12] Although the origin of this green emission band under oxidative conditions is a topic of debate, it is suggested that the PL spectral changes result from a change in the chemical structure of PFs caused by oxidative degradation and from increased interchain interactions due to the formation of an aggregated or cross-linked structure.[14−21] In contrast, DFF-DOF (**P2**), FCF (**P3**), and DFF-FCF (**P4**) exhibit enhanced color stability (Figure 2b−d) in comparison with DOF (**P1**). The intensities of the green emission for the DFF-DOF (**P2**) and FCF (**P3**) films are also significantly increased when they are annealed in air, although they are much weaker than that of DOF (**P1**). However, DFF−FCF (**P4**) (Figure 2d) shows highly improved color stability against oxidative conditions, and almost no peak shift is observed after thermal annealing.

The good color stability of the polymers based on MFCF (**8**) and MDFF (**6**) likely results from the unique structure of the side groups. DFF-FCF (**P4**), which has the bulkiest side groups, shows the highest color stability; DFF-DOF (**P2**) and FCF (**P3**) also show enhanced color stability over DOF (**P1**). Thus, it is clear that the molecular structure of DFF-FCF (**P4**) is the most effective in eliminating green emission by shielding the polymer backbone, in which the green emission band is generated from the interchain interactions

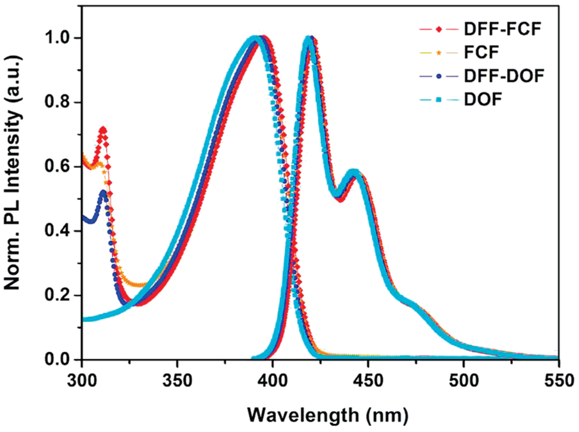


Figure 1. UV−vis absorption and photoluminescence spectra of prepared polymers in chloroform solution at 375 nm excitation.

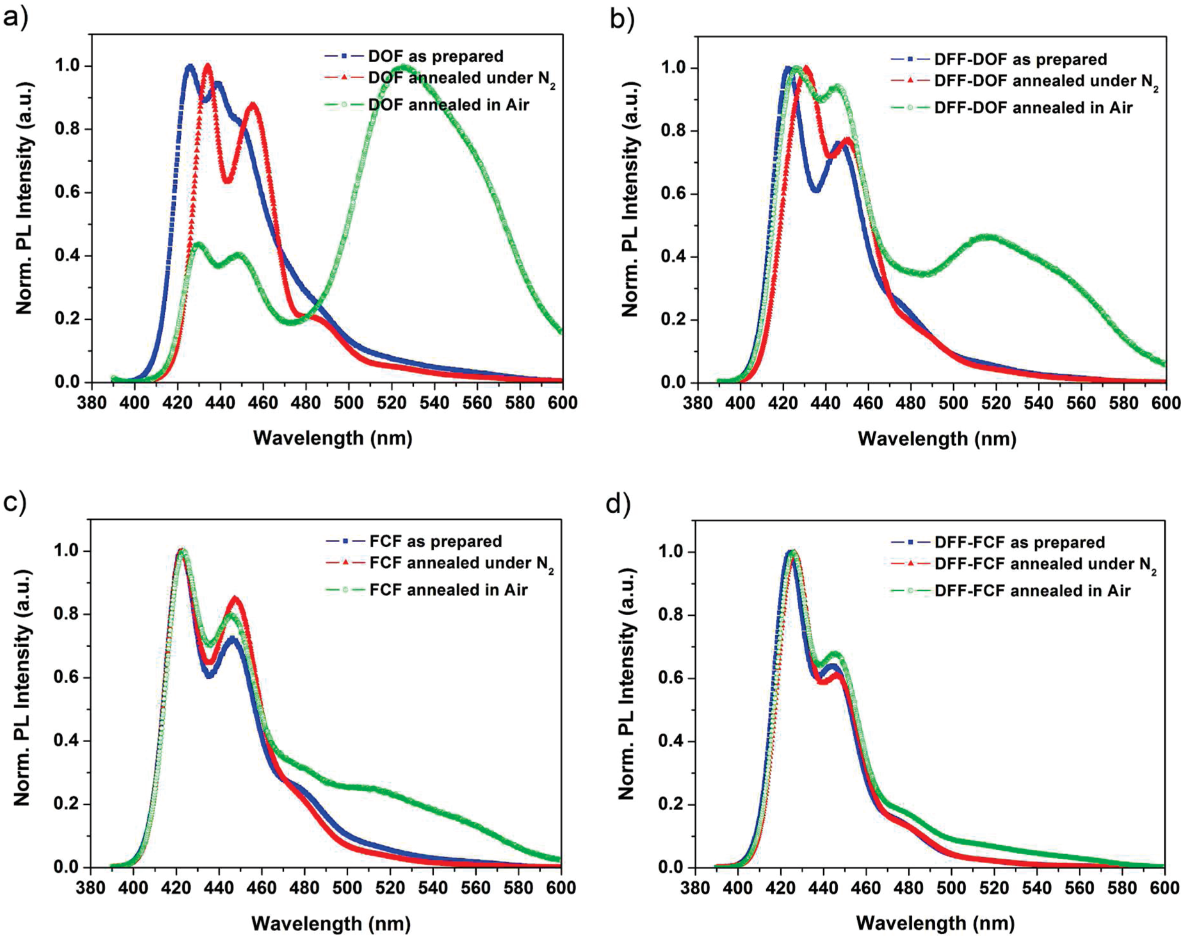


Figure 2. Photoluminescence spectra of spin-coated films after drying at room temperature (4 days) in air (squares), after annealing at 170 °C (3 h) in air (open circles), and after annealing at 170 °C (3 h) in a N_2 glovebox (triangles). (a) DOF, (b) DFF-DOF, (c) FCF, and (d) DFF-FCF.

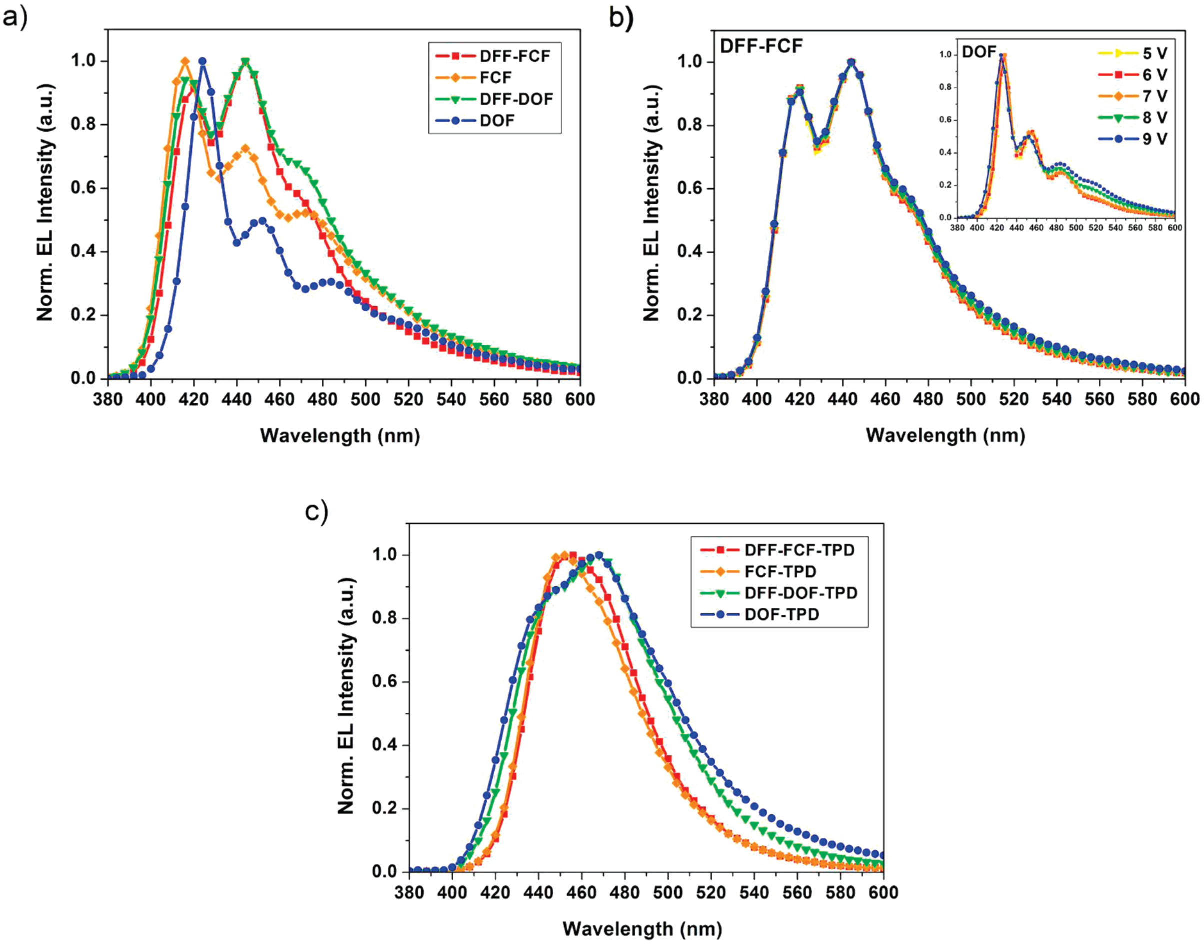


Figure 3. Electroluminescence spectra of light-emitting diodes; the device structure is ITO/PEDOT:PSS (25 nm)/polymers (90−110 nm)/LiF (2 nm)/Al (150 nm). (a) EL spectra of DFF-FCF, FCF, DFF-DOF, and DOF. (b) EL spectra of DFF-FCF and DOF for operating voltage from 5 to 9 V. (c) EL spectra of DFF-FCF-TPD, FCF-TPD, DFF-DOF-TPD, and DOF-TPD at 7 V.

and cross-linking between the polymer backbones. In addition, although DFF-FCF (**P4**) may also have defective alkyl-substituted fluorene as a side group, the effect of this defect on the green emission seems to be insignificant in DFF-FCF (**P4**). Oxidative degradation of the fluorene unit is currently considered as one of the major reasons for color instability. When the monoalkylated fluorene exists as an impurity on the polymer backbone, the fluorenone can be formed from this defective site under oxidative conditions, and just a small number of such defect sites causes an increase in green emission intensity.[15−18] However, it has been reported recently that blending a small amount (less than 4 wt %) of the fluorenone unit into poly[2,7-(9,9-dioctylfluorene)] barely affects the intensity of green emission, whereas the presence of fluorenone units covalently bound and conjugated to the polymer backbone significantly increases the intensity of green emission even at the low concentration of 0.6 mol %.[15,18] This is because the interchain energy transfer from the polymer backbone to the nonconjugated fluorenone (blended fluorenone) is less efficient than that from polymer backbone to the conjugated fluorenone. Therefore, the intensity of green emission is not noticeably increased when a small amount of fluorenone exists in an unconjugated form in the polymer film. Accordingly, DFF-FCF (**P4**) shows high color stability and almost no spectral changes after thermal annealing in air, even in the presence of a small amount of fluorenone, because the defective fluorene unit only exists in an unconjugated form.

Electroluminescence Properties. To investigate the EL characteristics of the polymers, we fabricated PLEDs with the simple structure of ITO/PEDOT:PSS (25 nm)/LEP (90−110 nm)/LiF (2 nm)/Al (1500 nm) in an N_2 atmosphere. The EL spectra of the polymers are shown in Figure 3, and their corresponding CIE coordinates are summarized in Table 2.

As shown in Figure 3a, DFF-FCF (**P4**), FCF (**P3**), DFF-DOF (**P2**), and DOF (**P1**) all exhibit deep blue EL emission with CIE coordinates ranging from (0.16, 0.09) to (0.16, 0.11). As expected from the PL results, however, DFF-FCF (**P4**) shows the deepest blue color with CIE coordinates of (0.16, 0.09) due to a weak emission band in the longer wavelength region around 470 nm. In addition, DFF-FCF (**P4**) generates highly stable blue EL emission over a wide range of operational voltages, which is attributed to its unique structure (Figure 3b). The CIE coordinates of (0.16, 0.09) at 5.2 V are slightly changed to (0.16, 0.11) at 9 V, indicating high color stability. Although DOF (**P1**) also exhibits deep blue EL emission with three emission peaks at 424, 452, and 484 nm and a weak shoulder at around 520 nm, the intensity of the shoulder peak around 520 nm noticeably increases with operating voltage. This indicates the degradation of color purity at high operating voltage (see inset of Figure 3b). The CIE coordinates of DOF (**P1**) are degraded from (0.16, 0.11) at 6.2 V to (0.18, 0.16) at 9 V. In addition to high color stability, DFF-FCF (**P4**) exhibits a higher luminous efficiency of 0.59 cd/A, compared to 0.29 cd/A for DOF (**P1**) and 0.26 cd/A for DFF-DOF (**P2**). From

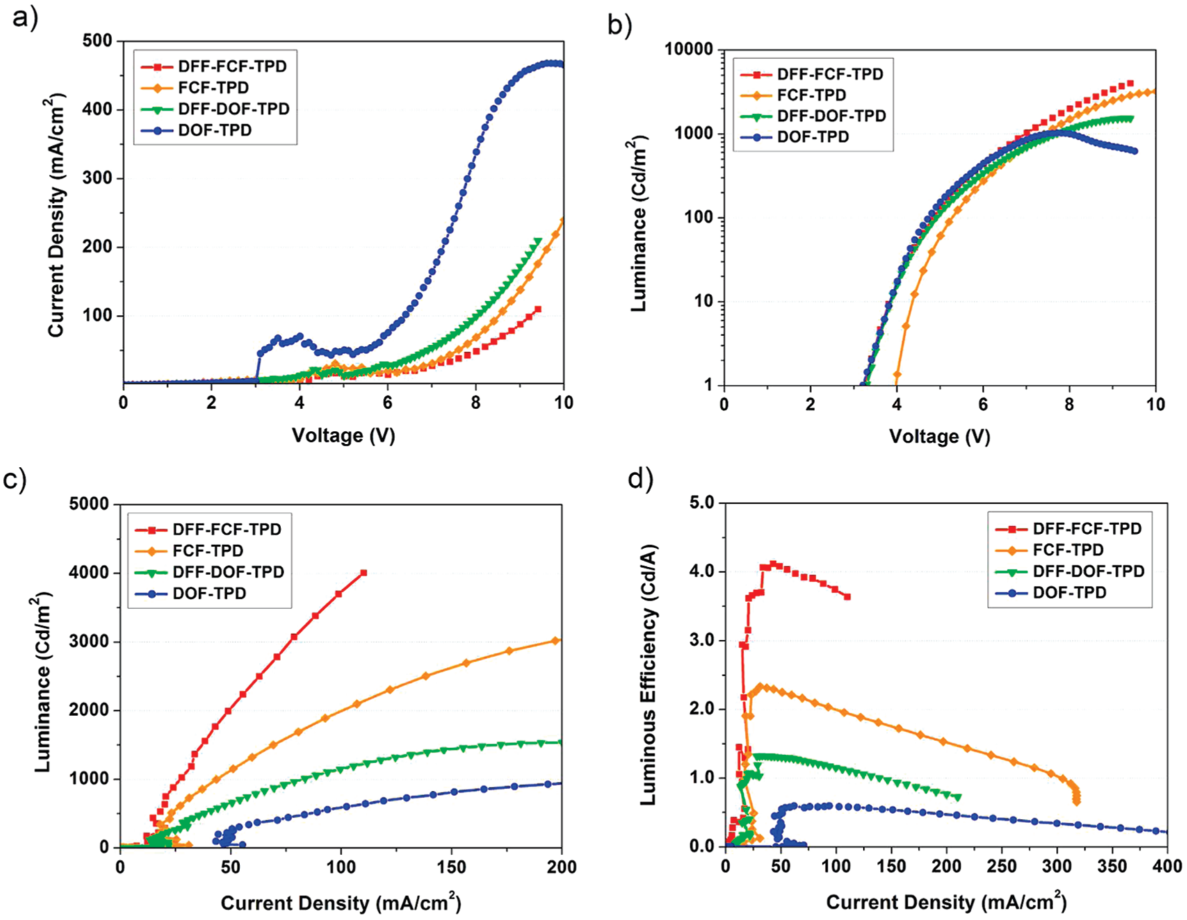


Figure 4. Characteristics of light-emitting diodes with a structure of ITO/PEDOT:PSS (25 nm)/DOF-TPD (990 nm), DFF-DOF-TPD (920 nm), FCF-TPD (970 nm), DFF-FCF-TPD (1020 nm)/LiF (2 nm)/Al (150 nm). (a) Current−voltage (*I*−*V*), (b) luminance−voltage (*L*−*V*), (c) luminance−current (*L*−*I*), (d) luminous efficiency−luminance (*E*−*L*).

these results, it is found that the structure of DFF-FCF (**P4**) is effective in suppressing the interchain interactions, while enhancing EL performance.

Figure 3c shows that MDFF (**6**) and MFCF (**8**) are effective in reducing the interchain interactions even after the MTPD (**13**) unit is incorporated into the polymer backbone. The EL spectra become broad and featureless when the MTPD (**13**) unit is introduced because the unit is randomly distributed on the polymer backbone during polymerization. However, DFF-FCF-TPD (**P8**) and FCF-TPD (**P6**) exhibit a narrow full width at half-maximum (fwhm) with the peaks at 456 and 452 nm showing deep blue emission with CIE coordinates of (0.15, 0.15) and (0.15, 0.13), respectively. On the other hand, DOF-TPD (**P5**) and DFF-DOF-TPD (**P7**) show rather broad spectra with a maximum emission band centered at 468 nm; their corresponding CIE coordinates are (0.17, 0.19) and (0.16, 0.17), respectively. As mentioned above, a hole transporting moiety such as MTPD (**13**) has been widely used to obtain high efficiency by reducing the hole injection barrier from the anode and enhancing the hole transport properties of the polymers.[2] Therefore, we could obtain greatly improved EL characteristics from the polymers containing the MTPD unit (**13**) (Figure 4). Interestingly, DFF-FCF-TPD (**P8**) exhibits greatly improved EL characteristics, showing a maximum luminous efficiency of 4.12 cd/A (at 1770 cd/m^2) with deep blue emission (CIE coordinates: (0.15, 0.15)) in a structure of ITO/PEDOT:PSS (25 nm)/LEP (90−110 nm)/LiF (2 nm)/Al (1500 nm). The luminance reaches its maximum of 4010 cd/m^2 at 9.4 V (110 mA/cm^2), with 3.90 cd/A as the corresponding luminous efficiency. The efficiency is much higher than that of well-known spirobifluorene-based LEPs. It has been reported that a spirobifluorene-based blue LEP exhibited a luminous efficiency of 3.0 cd/A with CIE coordinates of (0.15, 0.16).[2] The superior luminous efficiency of the DFF-FCF-TPD (**P8**) device is due to the unique structures of MDFF (**6**) and MFCF (**8**). In this structure, the interchain interactions are suppressed by the bulky side groups, thus reducing the probability of nonradiative decay. In addition, this structure enables the hole and electron transports to be more balanced and the holes and electrons to form excitons more efficiently. This can be further confirmed by the fact that DFF-FCF-TPD (**P8**) shows higher luminance (Figure 4c) and luminous efficiency (Figure 4d) compared with other polymers at the same current density. Although DFF-FCF-TPD (**P8**) shows the lowest charge transport because of the bulky structure of the side groups (Figure 4a), DFF-FCF-TPD (**P8**) exhibits promising EL characteristics. On the other hand, DOF-TPD (**P5**) exhibits the highest current density because the less bulky side groups enable the polymer main chains to be closely packed and to have higher interchain charge transports. However, only a small proportion of holes and electrons seem to undergo radiative-decay processes in DOF-TPD (**P5**). The maximum luminance efficiency is only 0.58 cd/A. DFF-DOF-TPD (**P7**) and FCF-TPD (**P6**) have current densities between those of DOF-TPD (**P5**) and DFF-FCF-TPD (**P8**), showing a clear relationship between the bulkiness of the side groups and current density; these polymers exhibit maximum luminance efficiencies of 1.33 cd/A (at 440 cd/m^2) and 2.33 cd/A (at 730 cd/m^2), respectively. Although these two polymers showed enhanced luminous efficiency compared to DOF-TPD (**P5**), we conclude that their side-group structures are not as effective in providing high efficiency as that of DFF-FCF-TPD (**P8**).

On the basis of our results, we conclude that the novel structures of MDFF (**6**) and MFCF (**8**) play a significant role in improving color purity and EL efficiency by increasing the probability of radiative decay and balancing the transport of holes and electrons. DFF-FCF-TPD (**P8**) has the most desirable structure among the polymers prepared in our study, showing a high luminous efficiency of 4.12 cd/A with CIE coordinates of (0.15, 0.15).

Conclusion

We prepared a novel blue-light-emitting PF containing 9,9-dihexylfluoren-2-yl and 3,4-bis(2-methylbutoxy)phenyl side groups. This DFF-FCF (**P4**) shows deep blue emission with high color stability against oxidative degradation. The nonconjugated bulky side groups of DFF-FCF (**P4**) play an important role in suppressing interchain interactions and the green emission from fluorenone that arises from defect impurities. Furthermore, DFF-FCF (**P4**) shows excellent EL performance. The side groups on MDFF (**6**) and MFCF (**8**) seem to provide a more balanced charge transport and increased radiative decay rate. Although DFF-FCF (**P4**) shows a rather low luminous efficiency of 0.59 cd/A with CIE coordinates of (0.16, 0.09), when MTPD (**13**) is incorporated into DFF-FCF (DFF-FCF-TPD, **P8**), the luminous efficiency is greatly improved to 4.12 cd/A with CIE coordinates of (0.15, 0.15). It is expected that the efficiency could be further improved by adjusting the compositions of MDFF (**6**), MFCF (**8**), and MTPD (**13**) and by optimizing the device structure. Therefore, we conclude that MDFF (**6**) and MFCF (**8**) are promising materials for efficient red and green LEPs as well as for blue LEPs. In addition, these materials can be successfully applied as a host for white LEPs.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of monomers and ^{1}H NMR of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kim, Y. H.; Kwon, S. K.; Yoo, D. S.; Rubner, M. F.; Wrighton, M. S. *Chem. Mater.* **1997**, *9*, 2699. (b) An, B. K.; Kim, Y. H.; Shin, D. C.; Park, S. Y.; Yu, H. S.; Kwon, S. K. *Macromolecules* **2001**, *34*, 3993. (c) Kim, Y. H.; Shin, D. C.; Kwon, S. K. *Polymer* **2005**, *46*, 4648. (d) Lee, K. S.; Kim, Y. H.; Lee, Y. K.; Jang, J.; Kwon, S. K. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 2316. (e) Kim, Y. H.; Park, J. W.; Shin, D. C.; You, H.; Kwon, S. K. *J. Polym. Sci., Polym. Chem.* **2007**, *45*, 5900.

(2) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature (London)* **2003**, *421*, 829.

(3) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737.

(4) Liu, J.; Cheng, Y.; Xie, Z.; Geng, Y.; Wang, L.; Jing, X.; Wang, F. *Adv. Mater.* **2008**, *20*, 1357.

(5) Luo, J.; Li, X.; Hou, Q.; Peng, J.; Yang, W.; Cao, Y. *Adv. Mater.* **2007**, *19*, 1113.

(6) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565.

(7) Park, J. H.; Lim, Y. T.; Park, O. O.; Kim, J. K.; Yu, Y. W.; Kim, Y. C. *Adv. Funct. Mater.* **2004**, *14*, 377.

(8) Sun, M.; Fu, Y.; Li, J.; Bo, Z. *Macromol. Rapid Commun.* **2005**, *26*, 1064.

(9) Pogantsch, A.; Wenzl, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Mullen, K. *Adv. Mater.* **2002**, *14*, 1061.

(10) Yu, W. L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.

(11) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.

(12) Chou, C. H.; Shu, C. F. *Macromolecules* **2002**, *35*, 9673.

(13) Kevin, T.; Heinrich, B.; Philipp, S.; Hubert, S.; Aurelie, F.; Amir, P.; Arne, B. German patent application DE 2001-10114477.

(14) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.

(15) Sims, M.; Bradley, D. D. C.; Ariu, M.; Koeberg, M.; Asimakis, A.; Grell, M.; Lidzey, D. G. *Adv. Funct. Mater.* **2004**, *14*, 765.

(16) Zhao, W.; Cao, T.; White, J. M. *Adv. Funct. Mater.* **2004**, *14*, 783.

(17) Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* **2003**, *36*, 4236.

(18) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.

(19) Montilla, F.; Mallavia, R. *Adv. Funct. Mater.* **2007**, *17*, 71.

(20) Becker, K.; Lupton, J. M.; Feldmann, J.; Nehls, B. S.; Galbrecht, F.; Gao, D.; Scherf, U. *Adv. Funct. Mater.* **2006**, *16*, 364.

(21) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Kla1rner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.

(22) Lee, T. W.; Park, O. O. *Adv. Mater.* **2000**, *12*, 801.

(23) Lee, T. W.; Park, O. O.; Kim, Y. C. *Org. Electron.* **2007**, *8*, 317.