

Sterically Hindered and Highly Thermal Stable Spirobifluorenyl-Substituted Poly(*p*-phenylenevinylene) for Light-Emitting Diodes

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Received November 25, 2002

ABSTRACT: The sterically hindered and highly thermal stable spirobifluorenyl-substituted poly(*p*-phenylenevinylene) derivative was synthesized by Gilch polymerization. The defect-free polymer structure was characterized by various spectroscopies. The polymer was completely soluble in common organic solvents, and it had high thermal stability with high T_g of 205 °C. The polymer film showed maximum emission at 515 nm with a shoulder peak at around 560 nm and showed photoluminescence efficiency of $26 \pm 5\%$. The study of thermal annealing of PL spectrum showed inhibited excimer formation. A cyclic voltammetry study revealed that the HOMO and LUMO energy level of the polymer are 3.08 and 5.46 eV, respectively. The EL spectrum from the device using polymer as emitting material showed a maximum peak of 515 nm, corresponding to the green region ($x = 0.31$, $y = 0.61$) in CIE (Commission Internationale de l'Eclairage) chromaticity coordinates. The LED based on polymer was shown to have a maximum brightness of 1155 cd/m² at 12.6 V and a maximum power efficiency of 0.118 lm/W (143 cd/m², 7.8 V, 1.67 mA).

Since the first report of polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,¹ great progress has been made in the study of PLEDs due to their promising application in the field of patterned light source and flat panel display. Much work has been done to develop novel luminescent polymeric materials with good processability, environmental stability, and intense luminance as well as to optimize the device structures to improve the efficiencies.^{2–7}

PLEDs based on PPV and its derivatives offer several advantages associated with their intrinsic characteristics of thermal stability, solution processability, and simple device architectures. These characteristics offer the potential for cheaper manufacturing routes. Although noticeable improvements have been made in many areas in LED application, there still remains drawbacks such as impurity, short lifetime, and low device quantum efficiency.

A wide variety of PPV derivatives had been synthesized and applied in LED applications; very few are attractive for commercial exploitation because very few have high PL efficiencies in solid states.^{9–14} The major reason is that conjugated backbones tend to stack with each other due to the favorable interchain interactions, which lead to a self-quenching process of excitons.^{15,16} Introducing appropriate substituents such as 3,7-dimethyloctyl¹² and dimethyloctylsilyl¹⁷ to the PPV backbone to prevent its close packing should therefore increase its PL efficiency. However, the PPV derivatives containing the longer flexible alkyl or alkoxy substituents have low T_g or low morphological stability. Therefore, the introduction of both proper alkyl/alkoxy and bulky rigid aryl substituents makes excellent PPVs having a high quantum efficiency due to the inhibition

of interchain interaction and TBB defects, good solubility, high T_g , and morphological stability.

Fluorene derivatives show interesting and unique chemical and physical properties because they contain a rigid planar biphenyl unit.¹⁸ Spiro-annulated molecules utilize the spiro bridge to connect two conjugated moieties. The tetrahedral bonding atom at the center of a spiro-annulated molecule maintains a 90° angle between the connected conjugated moieties via a σ -bonded network. This structure feature would be expected to reduce the probability of the interchain interactions and prevent the close packing of the polymer chains, resulting in good solubility of polymer. In addition, the spiro-annulated segment would be expected to enhance the rigidity of the polymer, leading to significant increase in both T_g values and thermal stability.¹⁹ To enhance the thermal and morphological stability, we designed a new soluble PPV derivative containing a *tert*-butyl spirobifluorenyl group in the side chain of PPV ring. Additionally, the bulky *tert*-butyl spirobifluorenyl group minimizes an intermolecular interaction and a self-quenching process of excitons.

Recently, soluble PPVs were prepared following the Gilch procedure of polydehydrohalogenation for solution polymerization.²⁰ For PPVs prepared following the Gilch procedure, Becker et al.²¹ discovered the presence of a defect structure built into the polymer main chain: tolan-bis-benzyl moieties (TBB). The introduction of asymmetric substituents of an alkoxy group as a strong electron-donating group could reduce the amount of TBB defect structures, because the halomethyl moiety of the ortho position of the alkoxy group had the stronger acidity.²²

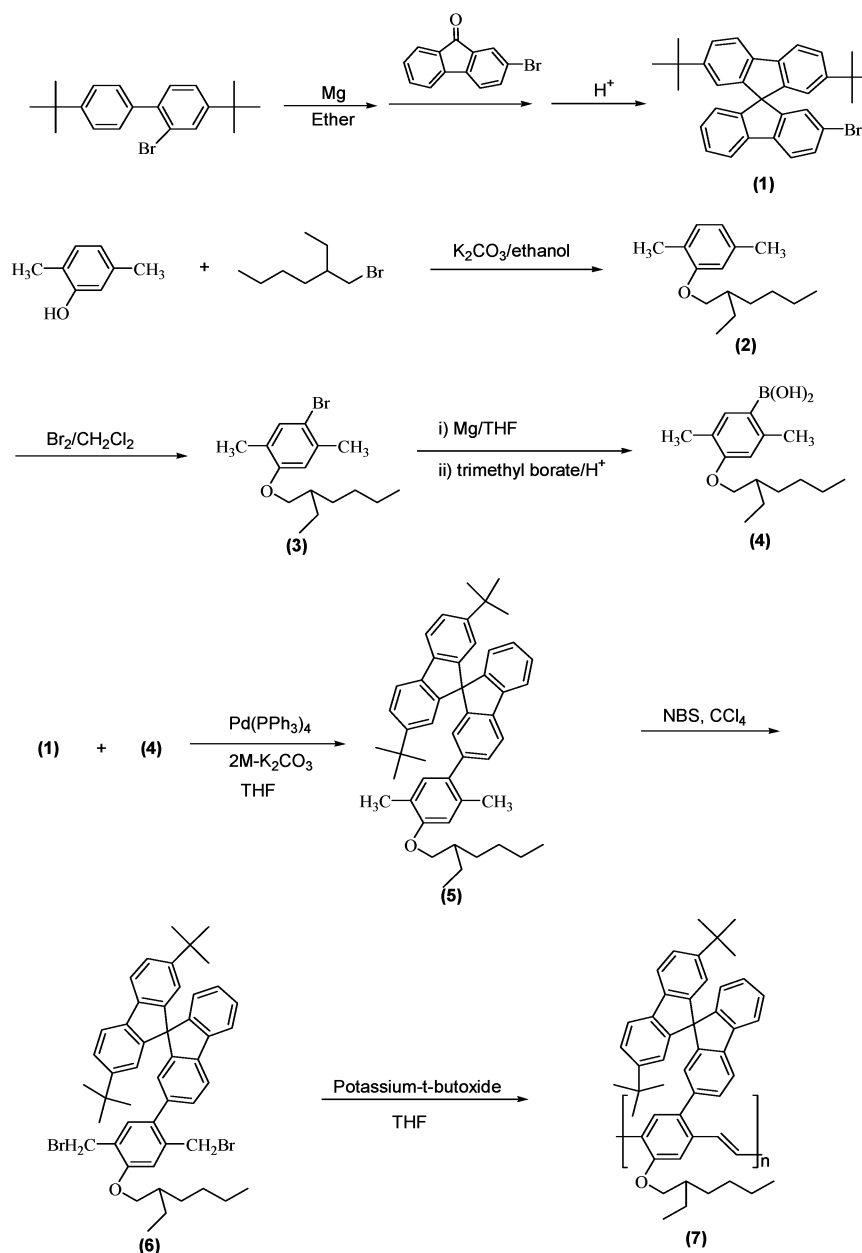
In this study, we report a new soluble PPV derivative containing a *tert*-butylspirobifluorenyl group in the 5-position of the PPV ring and an ethylhexyloxy group in the 2-position of PPV ring. The bulky *tert*-butylspirobifluorenyl group enhances the thermal stability with high T_g and solubility and minimizes an intermolecular

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Scheme 1. Synthetic Scheme of Monomer and Polymer



interaction and a self-quenching process of excitons. The introduction of a 2'-ethylhexyloxy group in the other side chain increases solubility and reduces TBB moieties. The asymmetric structure designed herein can also provide the polymer film with an amorphous property since asymmetry leads to the formation of configuration isomers of the repeat units along the polymer backbone and causes the decrease in crystallinity of the resulting polymer.²³

Results and Discussion

The method for preparing the monomer and the polymer is outlined in Scheme 1. The monomer was prepared via a manifold chemical reaction such as bromination, Grignard reaction, Suzuki coupling reaction, cyclization, etc. The polymer, poly(2-(2'-ethylhexyloxy)-5-(2''-(2''',7''''-di-*tert*-butyl)-9'',9''''-spirobifluorenyl)-1,4-phenylenevinylene) (EHSBF-PPV), was obtained through the typical Gilch method. 1H NMR and FT-IR spectra agree with the proposed structures of various

compounds (1–6) and polymer showing no evidence of defects. In the 1H NMR spectrum, the aromatic and vinyl protons appeared in the range 7.8–6.6 ppm, and oxymethylene and alkyl protons appeared at around 3.6–3.7 and 1.8–0.6 ppm, respectively (Figure 1). It is reported²⁰ that PPVs contained head-to-head (H–H) (or tail-to-tail, T–T) couplings as the result of a side reaction. They assigned the CH_2-CH_2 groups resulting from H–H couplings to peak around 2.7–2.9 ppm. As shown in the 1H NMR spectrum of EHSBF-PPV, it is clear that this side reaction could not be detected with 1H NMR measurements. The result indicates that the TBB defects are highly suppressed because the steric hindrance of the bulky spirobifluorenyl group and the bromomethyl moiety of the ortho position of the 2'-ethylhexyloxy group have stronger acidity than that of the meta position of the 2'-ethylhexyloxy group.

The polymer was completely soluble in common organic solvents such as chloroform, THF, xylene, toluene, chlorobenzene, etc. The good solubility of

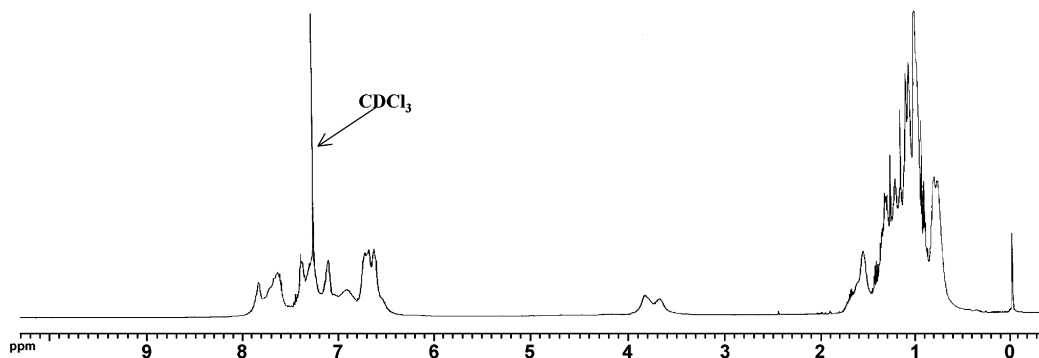


Figure 1. ^1H NMR spectrum of EHSBF-PPV.

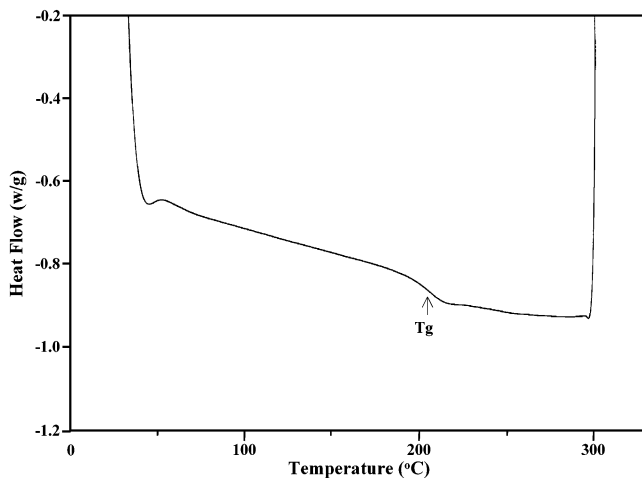


Figure 2. DSC curve of EHSBF-PPV.

EHSBF-PPV may result from the bulky and asymmetric nature of substituents. The molecular weight measurement was carried out by gel permeation chromatography (GPC) with polystyrene as the standard for calibration. GPC analysis reveals that the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymer are 366 200 and 2 267 000, respectively, with a polydispersity index of 6.19. The polymer showed high molecular weight. It may be due to high solubility of polymer containing a bulky spirobifluorenyl group and a flexible 2'-ethylhexyloxy group.

Thermogravimetric analysis (TGA) was carried out for the bulk state polymer with a rate of $10\text{ }^\circ\text{C}/\text{min}$ in a nitrogen gas. TGA of the EHSBF-PPV showed 5% weight loss at $380\text{ }^\circ\text{C}$ and 10% weight loss at $405\text{ }^\circ\text{C}$. The glass transition temperature (T_g) of EHSBF-PPV by means of differential scanning calorimetry (DSC) with a rate of $10\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere showed at $205\text{ }^\circ\text{C}$ (Figure 2). It has been known that materials with a high glass transition temperature as the active emissive can provide device longevity.²² Usually, highly soluble PPV derivatives have low T_g because they have flexible long alkyl or alkoxy groups. However, EHSBF-PPV with a bulky and rigid spirobifluorenyl group had high T_g as well as good solubility.

Figure 3 shows the UV-vis and PL spectra of dilute EHSBF-PPV solution (in chloroform) and EHSBF-PPV thin film. As shown in the absorption spectrum, the absorption maxima (λ_{max}) of the EHSBF-PPV solution and EHSBF-PPV film showed a strong absorption band at 440 nm (solution) and 433 nm (film) with band edge at 521 nm . The optical energy band gap

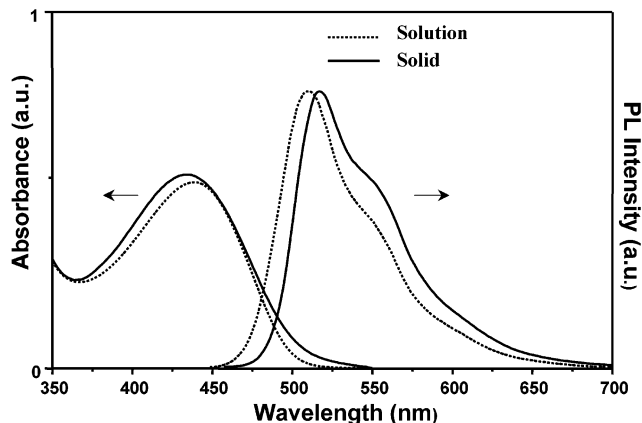


Figure 3. UV-vis and PL spectra of dilute EHSBF-PPV solution (in CHCl_3) and EHSBF-PPV film.

of the polymer was 2.38 eV calculated from the threshold of the optical absorption. Upon UV excitation at 440 nm , the PL of EHSBF-PPV solution (in chloroform) showed maximum emission at 510 nm with a shoulder peak at around 550 nm . The maximum emission for the PL of EHSBF-PPV film showed at 515 nm with a shoulder peak at around 560 nm . When the PL of EHSBF-PPV film was compared with that of MEH-PPV film, the PL spectrum of EHSBF-PPV was blue-shifted about 60 nm .²⁵ The result indicates that EHSBF-PPV has steric hindrance due to the bulky spirobifluorenyl group, leading to blue-shifted absorption of the PL spectrum. PL_{eff} was $26 \pm 5\%$ when the film PL efficiency of the obtained polymer using optically dense configuration and diphenylanthracene (dispersed in PMMA film with a concentration less than 10^{-3} M , assuming PL_{eff} of 0.83) as a standard was measured.²⁶⁻²⁸

Figure 4 showed PL spectra of EHSBF-PPV before and after thermal annealing at $210\text{ }^\circ\text{C}$ under N_2 for several hours. It is well-known that excimers provide nonradiative relaxation pathways which lead to reduced emission efficiency relative to exciton luminescence. The excimer is formed by an interaction of an excited chromophore with an unexcited neighbor(s), forming a more delocalized, and therefore lower energy, excited-state complex. In general, the excimer formation of the polymer is measured by the appearance of a long wavelength emission band upon annealing. Thus, the PL spectra of EHSBF-PPV were measured before and after thermal annealing at $210\text{ }^\circ\text{C}$ in N_2 for several hours. But a long wavelength emission band by the excimer formation was not observed, and PL_{eff} was not decreased after thermal annealing as well. The results supposed that the presence of bulky spirobifluorenyl group could strongly inhibit excimer formation.

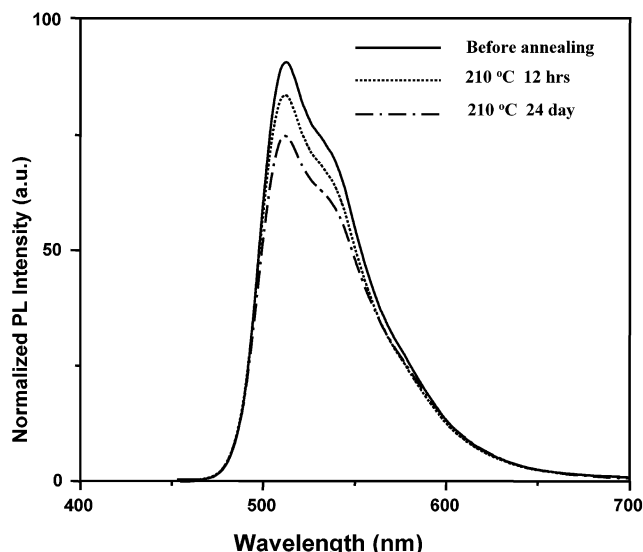


Figure 4. Film emission studies of EHSBF-PPV film annealed at 210 °C.

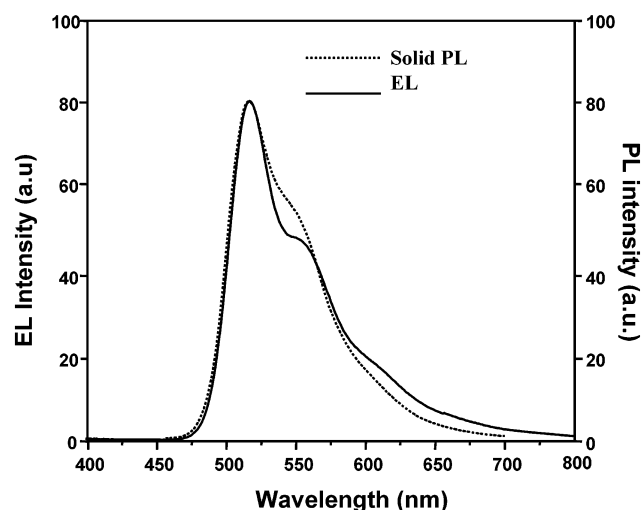


Figure 5. Solid PL and EL spectra of EHSBF-PPV.

To study the ionization energy and the optical energy gap, the electrochemical analysis was carried out using cyclic voltammetry (CV). The CVs of polymer-coated ITO and Al plate were measured in a three-electrode compartment cell with a Pt wire counter electrode and an Ag/AgNO₃ (0.1 M) reference at a scan rate of 50 mV/s. The electrolyte was 0.1 M Bu₄NClO₄ solution in anhydrous acetonitrile, and the cell was purged with nitrogen. The reduction and oxidation peak potentials for EHSBF-PPV are measured to be $E_{\text{red}} = -1.72$ V and $E_{\text{ox}} = 0.66$ V, respectively. The optical energy band gap for the EHSBF-PPV was 2.38 eV. From the electrochemical data, the HOMO and LUMO energy level of the polymer are 3.08 and 5.46 eV, respectively.³² The electrochemical band gap of the EHSBF-PPV containing a bulky spirobifluorenyl group had much bigger HOMO and LUMO values than those of MEH-PPV.²⁵

Figure 5 showed the solid PL and EL spectra of EHSBF-PPV. The EL spectrum from the ITO/PEDOT/EHSBF-PPV/LiF/Al device using PEDOT as a hole injection layer²⁹ and LiF as an electron injection layer³⁰ shows the EL maximum at 515 nm and the shoulder at around 560 nm which is similar to that of PL. It can be explained that both EL and PL originate from the same radiative decay process of the singlet exciton.³¹ The color

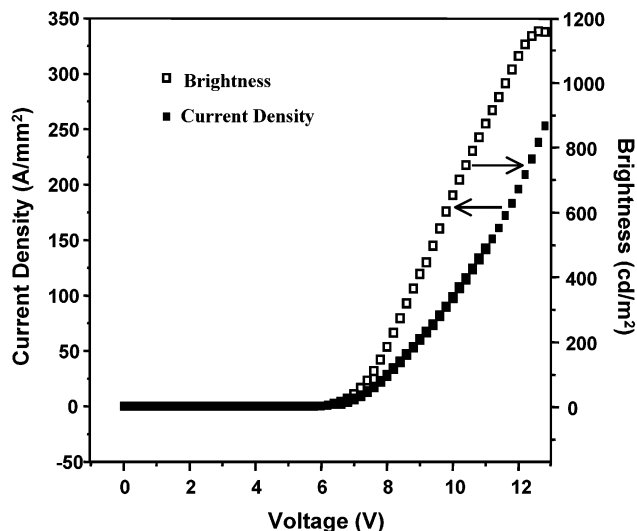


Figure 6. Current-voltage-luminance characteristics of PLED of EHSBF-PPV.

was green ($x = 0.31$, $y = 0.61$) at 200 cd/m² in CIE (Commission Internationale de l'Éclairage) chromaticity coordinates.

The current-voltage-brightness ($I-V-L$) characteristic of the device is shown in Figure 6. The turn-on voltage of the device was observed at about 6.0 V (0.0404 mA), and the maximum power efficiency was measured to be 0.118 lm/W (143 cd/m², 7.8 V, 1.67 mA). The maximum brightness of the device showed 1155 cd/m² at 12.6 V. To achieve a higher EL performance, optimization of the device structure will be necessary.

Conclusion

A new high molecular weight PPV derivative, EHSBF-PPV, containing a bulky spirobifluorenyl substituent in the side chain was synthesized by the Gilch route. The introduction of the flexible group (2'-ethylhexyloxy) and bulky rigid group (2'',7''-di-*tert*-butylspirobifluorenyl) into the phenylene ring of PPV backbone reduced interchain interactions and enhanced solubility and thermal stability with high T_g as well as good film quality. The EL spectrum from the device using polymer as emitting material showed a maximum peak of 515 nm, corresponding to the green region ($x = 0.31$, $y = 0.61$) in CIE (Commission Internationale de l'Éclairage) chromaticity coordinates. The LED based on EHSBF-PPV was shown to have low turn-on voltage, brightness, and good efficiencies. The thermal and optoelectronic properties of the polymer imply that it is a promising material for the PLED application.

Experimental Section

2-Bromo-9,9'-(2',7'-di-*tert*-butyl)spirobifluorene (1). 2-Bromo-4,4'-di-*tert*-butylbiphenyl was synthesized according to ref 21. 2-Bromo-9,9'-(2',7'-di-*tert*-butyl)spirobifluorene (1) was synthesized by the following procedure: 15 g (43.6 mmol) of 2-bromo-4,4'-(di-*tert*-butyl)biphenylene diluted in anhydrous diethyl ether was slowly added to 1.24 g (516 mmol) of clean magnesium powders after initiation by 5 mol % of dibromoethane, and then this solution was refluxed for 8 h under a nitrogen atmosphere. When the Grignard reagent was formed, 10.5 g (365 mmol) of 2-bromofluorenone was slowly added to this solution with solid dropping funnel, and the mixture was refluxed for 3 h. The reaction mixture was cooled with an ice bath, and 150 mL of glacial acetic acid was slowly added. Diethyl ether was removed by distillation, and the mixture

was refluxed. One drop of HCl (35 wt %) was added, and the reaction mixture was refluxed for 1 h. The reaction mixture was cooled by room temperature, and the precipitate was filtered and washed with methanol several times, and the solid was dried in a vacuum oven. The product yield was 13 g (59%); mp 227 °C. FT-IR (KBr pellet, cm^{-1}): 3057, 2959, 2902, 2867, 1474, 1462, 1441, 1401, 1361, 1252, 1230, 1252, 1058, 964, 810, 765. ^1H NMR (CDCl_3): δ 6.6–8.8 (m, 13H, aromatic C–H), 1.2 (s, 18H, $-\text{CH}_3$).

2-(2'-Ethylhexyloxy)-*p*-xylene (2). In a 1 L four-neck round-bottom flask fitted with a dropping funnel, a low-temperature condenser, a gas outlet, and a magnetic stirrer bar, 70 g (573 mmol) of 2,5-dimethylphenol, 115 g (600 mmol) of 1-bromo-2-ethylhexane, 39.5 g of KOH (85% content purity, 600 mmol), and 6 g (40 mmol) of sodium iodide were dissolved in 620 mL of dry ethanol and heated to reflux for 64 h with magnetic stirring. The mixture was cooled to room temperature, and then the reaction solution was decanted from the solid formed and evaporated using a rotary evaporator. The residual solid was taken up in with 800 mL of toluene. The organic phases were combined, washed with 50 mL of 10% aqueous NaOH solution, and dried over MgSO_4 . The solvent was distilled off under reduced pressure with a rotary evaporator. The residue was distilled under reduced pressure (0.5 mmHg, 108–110 °C). 124.7 g (532 mmol, 93%) of 2-(2-ethylhexyloxy)-*p*-xylene (2) was obtained as a colorless oil; bp 108–110 °C/0.5 mmHg. FT-IR (KBr pellet, cm^{-1}): 3047, 3023, 2958, 2901, 2872, 2864, 1615, 1586, 1509, 1461, 1414, 1379, 1309, 1265, 1158, 1130, 1039, 997, 843, 802. ^1H NMR (CDCl_3): δ 6.98 (d, 1H, aromatic C–H), 6.63 (d, 2H, aromatic C–H), 3.82 (d, 2H, $-\text{OCH}_2$), 2.29 (s, 3H, aromatic CH_3), 2.17 (s, 3H, aromatic CH_3), 0.90–1.71 (m, 15H, aliphatic C–H).

2-Bromo-5-(2'-ethylhexyloxy)-*p*-xylene (3). 117 g (500 mmol) of compound 2, 350 mL of carbon tetrachloride, and 1.4 g (8.7 mmol) of iron(III) chloride were placed in a 1 L round-bottomed flask. In an ice bath, 80 g (507 mmol) of bromide was slowly added through the condenser. The mixture was stirred for 8 h. After the reaction mixture was washed with 5–10% sodium hydroxide and dried with magnesium sulfate, the solvent was distilled off by an evaporator. The crude product was purified by distillation (128–130 °C/0.5 mmHg). 131 g (420 mmol, 84%) of 2-bromo-5-(2'-ethylhexyloxy)-*p*-xylene (3) was obtained as a colorless oil; bp 128–130 °C/0.5 mmHg. FT-IR (KBr pellet, cm^{-1}): 3047, 2958, 2901, 2872, 2860, 1742, 1606, 1569, 1497, 1461, 1385, 1366, 1303, 1251, 1164, 1140, 960, 874, 838. ^1H NMR (CDCl_3): δ 7.23 (s, 1H, aromatic C–H), 6.66 (s, 1H, aromatic C–H), 3.80 (d, 2H, $-\text{OCH}_2$), 2.33 (s, 3H, aromatic CH_3), 2.14 (s, 3H, aromatic CH_3), 0.90–1.71 (m, 15H, aliphatic C–H).

4-(2-Ethylhexyloxy)-2,5-dimethylbenzene Boronic Acid (4). 35 g (112 mmol) of compound 3 was added to the mixture of magnesium powders (3.26 g, 134 mmol) and dry THF (200 mL). After the reaction mixture was refluxed for 2 h and cooled to -70 °C, 23 g (224 mmol) of trimethyl borate was added. The reaction mixture was stirred for 12 h at room temperature and worked up with 500 mL of 4 M HCl aqueous solution. The obtained crude solid product was washed with water several times and then washed with *n*-hexane several times. 13 g (47 mmol, 42%) of 4-(2'-ethylhexyloxy)-2,5-dimethylbenzene boronic acid (4) was obtained as a colorless solid; mp 76.9 °C. FT-IR (KBr pellet, cm^{-1}): 3860–3620, 3047, 2958, 2923, 2872, 2860, 2360, 2342, 1732, 1615, 1586, 1497, 1505, 1459, 1283, 1265, 1157, 1130, 1038, 1022, 997, 843, 802. ^1H NMR (CD_3OD): δ 6.95 (s, 1H, aromatic C–H), 6.61 (d, 1H, aromatic C–H), 3.80 (d, 2H, $-\text{OCH}_2$), 2.33 (s, 3H, aromatic- CH_3), 2.14 (s, 3H, aromatic CH_3), 0.90–1.71 (m, 15H, aliphatic C–H).

1,4-Dimethyl-2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)benzene (5). All catalysts and reaction were handled in a nitrogen atmosphere. To a mixture of compound 4 (6 g, 21.6 mmol), compound 1 (10.2 g, 20 mmol), 50 mL of 2 M K_2CO_3 solution, and 70 mL of THF, $\text{Pd}(\text{PPh}_3)_4$ (0.14 g, 0.6 mol %) was added as catalyst. After the reaction mixture was refluxed under a nitrogen atmosphere for 8 h, the reaction was terminated with water (50 mL). The crude product was extracted with diethyl ether and dried with

magnesium sulfate. After the solvent was distilled off under reduced pressure with a rotary evaporator, a viscous oil was obtained. The 1,4-dimethyl-2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)benzene (5) was purified by column chromatography (silica gel, with *n*-hexane as an eluent). The yield was 10.6 g (16 mmol, 80%); mp 85.2 °C. FT-IR (KBr pellet, cm^{-1}): 3063, 2958, 2924, 2866, 1611, 1579, 1510, 1476, 1461, 1413, 1362, 1318, 1252, 1238, 1218, 1160, 1124, 1040, 1003, 882, 820, 771, 738, 616, 570. ^1H NMR (CDCl_3): δ 6.56–7.86 (m, 15H, aromatic C–H), 3.79 (d, 2H, $-\text{OCH}_2$), 0.87–1.93 (m, 39H, aliphatic C–H). ^{13}C NMR (CDCl_3) (ppm): aromatic (C) 156.8, 150.6, 150.2, 148.5, 147.9, 142.3, 139.3, 133.2, 130.0, 126.8, 125.6, 124.3, 123.5, 121.9, 121.8, 120.4, 118.9, 113.7, aliphatic (C) 71.4, 66.3, 39.6, 34.7, 31.4, 30.6, 29.0, 24.0, 22.9, 21.2, 13.9, 11.1, 9.3.

1,4-Bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)benzene (6). 0.1 mg of BPO and 2.4 g (13.6 mmol) of *N*-bromosuccinimide were added to a solution of 4.5 g (6.8 mmol) of compound 5 in 50 mL of dry carbon tetrachloride. After the mixture was refluxed for 8 h, the floating solid succinimide byproduct was filtered away. The crude product was purified in *n*-hexane twice times to give 1.5 g (1.8 mmol, 27%) of 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)benzene (6) as white crystals; mp 144 °C. FT-IR (KBr pellet, cm^{-1}): 3061, 3030, 2958, 2927, 2867, 1608, 1506, 1475, 1460, 1411, 1361, 1319, 1250, 1212, 1162, 1038, 834, 820, 771, 754, 738, 570. ^1H NMR (CDCl_3): δ 6.70–7.91 (m, 15H, aromatic C–H), 4.54 (s, 2H, $-\text{CH}_2\text{Br}$), 4.14 (s, 2H, $-\text{CH}_2\text{Br}$), 3.88 (d, 2H, $-\text{OCH}_2$), 0.89–1.75 (m, 33H, aliphatic C–H). ^{13}C NMR (CDCl_3) (ppm): aromatic (C) 156.4, 150.7, 150.0, 149.7, 148.7, 141.3, 140.9, 139.2, 138.7, 136.8, 134.4, 132.2, 128.5, 127.8, 127.6, 127.5, 126.5, 125.0, 124.8, 120.5, 119.9, 119.8, 119.1, 113.2, aliphatic (C) 77.2, 77.0, 76.7, 70.4, 66.2, 39.4, 34.8, 31.6, 31.4, 30.6, 29.1, 28.2, 24.0, 23.0, 14.0, 11.2. Anal. Calcd for $\text{C}_{49}\text{H}_{54}\text{Br}_2\text{O}$: C, 71.88%; H, 6.65%. Found: C, 71.82%; H, 6.54%.

Poly(2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)-1,4-phenylenevinylene), EHSBF-PPV (7). *t*-BuOK (1.0 M) in THF (3 mL) was added to a solution containing 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(2''-(2''',7'''-di-*tert*-butyl)-9'',9'''-spirobifluorenyl)benzene (6) (0.82 g, 1 mmol) in THF (20 mL). After the solution was stirred for 10 h at room temperature and refluxed for 2 h, the mixture was cooled to room temperature. The polymer was obtained from precipitation in methanol (200 mL). The yield of the polymer after complete workup was 0.55 g (83%). FT-IR (KBr pellet, cm^{-1}): 3061, 2958, 2927, 2868, 1596, 1502, 1476, 1461, 1412, 1362, 1326, 1252, 1214, 1170, 1127, 1039, 970, 819, 770, 737: δ 6.6–7.8 (m, 17H, aromatic and vinyl C–H), 3.6–3.7 (broad, 2H, $-\text{OCH}_2$), 0.6–1.8 (m, 33H, aliphatic C–H). Anal. Calcd for $\text{C}_{49}\text{H}_{54}\text{O}$: C, 89.31%; H, 8.26%. Found: C, 89.28%; H, 8.29%.

Characterization. Melting points were determined using an Electrothermal Mode 1307 digital analyzer. ^1H NMR and ^{13}C NMR spectral data were expressed in ppm relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrometer, and the UV–vis absorption spectra were obtained in chloroform on a Shimadzu UV-3100 spectrophotometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high-pressure GPC assembly model M590 pump, μ -styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analyses were performed by a Leco Co. CHNS-932. TGA measurements were performed on a Perkin-Elmer series 7 analysis system under N_2 at a heating rate of 10 °C/min. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. For the measurements of device characteristics, current–voltage (I – V) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). The thickness of films was determined with

a Sloan Dektak. Cyclic voltammetry (CV) was performed on an EG&G Parc model 273A potentiostat/galvanostat system with a three-electrode cell in a solution of Bu₄NBF₄ (0.1 M) in acetonitrile at a scan rate of 100 mV/s. The polymer films were coated on a square Pt electrode (0.50 cm²) by dipping the electrode into the corresponding solutions and then drying in air. A Pt wire was used as the counter electrode, and a Ag/AgNO₃ (0.1 M) electrode was used as the reference electrode. Prior to each series of measurements the cell was deoxygenated with argon.

Fabrication of the LED: Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indium-tin oxide-coated glass substrate which had been washed with water, acetone, and isopropyl alcohol sequentially. A thin polymer film (900 Å) was spin-coated (3000 rpm, 50 s) from a filtered (0.2 μm filter) 1.0 wt % EHSBF-PPV solution in chlorobenzene on a PEDOT layer. LiF was vacuum-deposited as an electron injection layer (20 Å). An aluminum electrode (700 Å) was deposited on top of the device at a high vacuum (below 1 × 10⁻⁵ Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2000-005-E00005) and KOSEF (R03-2000-000-00016-0).

References and Notes

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MA021703Z