Novel Poly(*p*-phenylenevinylene)s Derivatives with CF_3-Phenyl Substituent for Light-Emitting Diodes

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New PPV derivatives which contain electron-withdrawing trifluoromethyl (CF_3) group, poly[2-(2-ethylhexyloxy)-5-(4-trifluoro methylphenyl)-1,4-phenylenevinylene] ($EHCF_3P$-PPV), and poly[2-(2-ethylhexyloxy)-5-(3,5-bis(trifluoromethyl)-phenyl)-1,4-phenylenevinylene] ($EHBCF_3P$-PPV), have been synthesized by GILCH polymerization. As the result of the introduction of the electron-withdrawing CF_3 group to the phenyl substituent, the LUMO and HOMO energy levels of $EHCF_3P$-PPV (2.8, 5.1 eV) and $EHBCF_3P$-PPV (3.0, 5.3 eV) were lower than those of known poly[2-(2-ethylhexyloxy)-5-phenyl-1,4-phenylenevinylene] (EHP-PPV) (2.6, 4.9 eV). These polymers have been used as the electroluminescent (EL) layers in double layer light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al). $EHCF_3P$-PPV, and $EHBCF_3P$-PPV show maximum photoluminescence (PL) peaks at λ_{max} = 550, 539 nm, and maximum EL peak at λ_{max} = 545, 540 nm, respectively. The current-voltage-luminance (*I-V-L*) characteristics of the polymers show that turn-on voltages of $EHCF_3P$-PPV and $EHBCF_3P$-PPV are around 4.0 and 3.5 V, respectively.

Key Words : Electroluminescence, PPV, Polymer, PLED, Light-emitting diodes (LEDs)

Introduction

Since the discovery of electroluminescence (EL) from a conjugated polymer, poly(*p*-phenylenevinylene) (PPV),[1] numerous reports about polymeric light-emitting diodes (PLEDs) have been published, caused by the prospective application as large-area light-emitting diodes (LEDs).[2-4]

In conjugated polymers, EL is known to be generated by the injection of electrons from one electrode and holes from the other, recombination, and radiative decay of the excited state. To be used in the single layer devices with high work function metal as the cathode, PPV has the disadvantage that it is a poor electron acceptor due to its high LUMO energy. The high LUMO energy level usually causes the imbalance of charge injections and poor device efficiency. Balancing the rates of injection of electrons and holes from opposite electrodes into the light-emitting polymer is required to achieve the high electroluminescence efficiency. Using additional organic charge-transporting layers,[5-7] and adjusting the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone[8,9] were reported to overcome the imbalance of charge carrier injection or mobility. To improve the electron injection and the potential efficiency of the polymer LEDs, numerous derivatives of PPV with halide,[10-14] cyano,[15] trifluoromethyl,[16] and methylsulfonyl-phenyl[17] on the arylene rings, or on vinylene,[5,18-23] have been reported. The introductions of electron-withdrawing substituent on the arylene ring or on the vinylene portion of PPV lower both the HOMO and LUMO of the conjugated polymers, which result in the lower barrier of electron injection into the light-emitting layer.

In the present paper, we report the synthesis and properties of two new EL polymers, PPV derivatives, which contain electron-withdrawing CF_3-phenyl, or bis(CF_3)-phenyl group, poly[2-(2-ethylhexyloxy)-5-(4-trifluoromethylphenyl)-1,4-phenylenevinylene] ($EHCF_3P$-PPV) and poly[2-(2-ethylhexyloxy)-5-(3,5-bis(trifluoromethyl)-phenyl)-1,4-phenylenevinylene] ($EHBCF_3P$-PPV). The effects of the electron-withdrawing CF_3-phenyl group on the physical and electrochemical properties of $EHCF_3P$-PPV and $EHBCF_3P$-PPV, as well as the performance of these polymers as emissive layers in LEDs, were examined.

Experimental Section

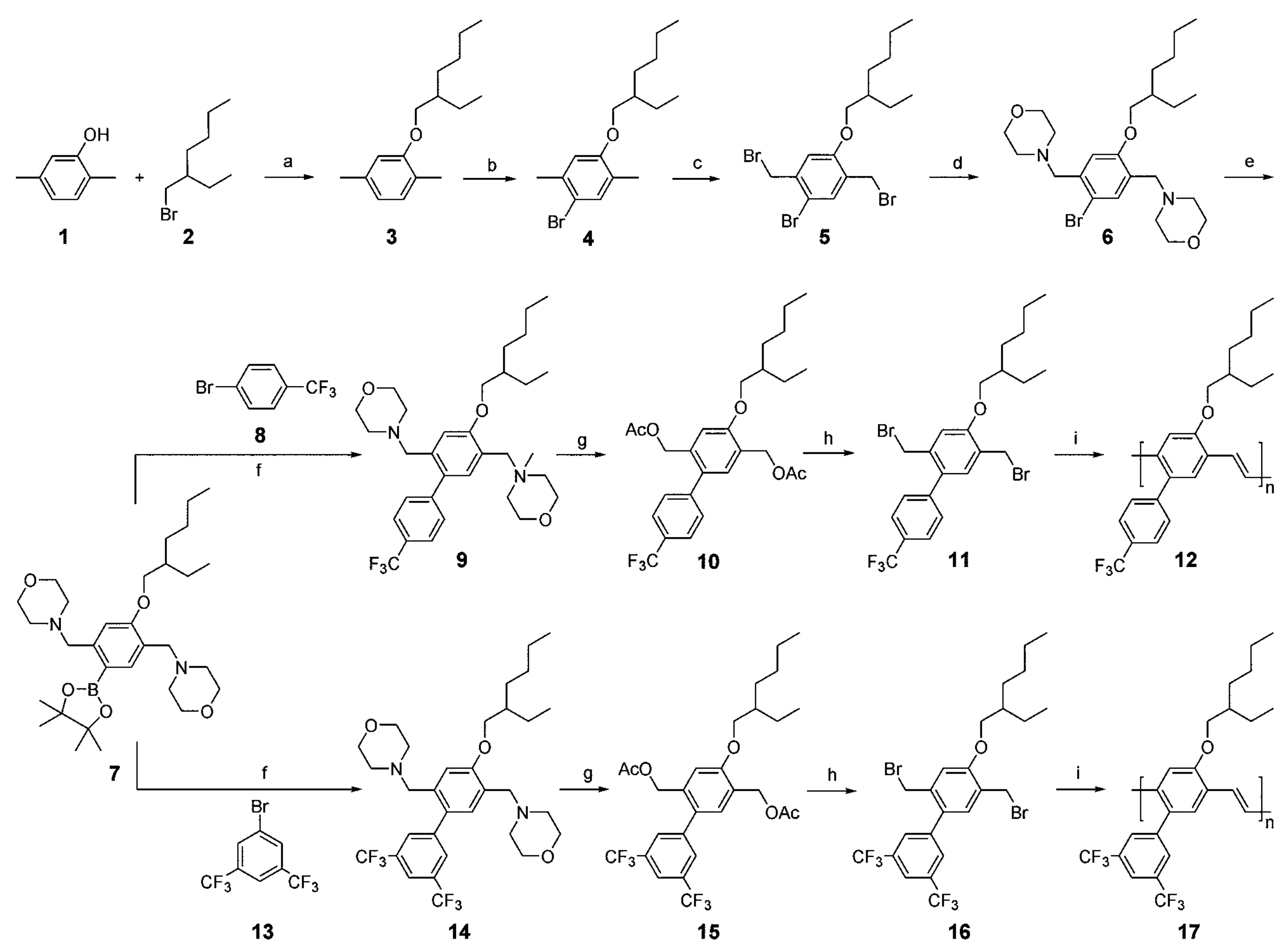
General. Used all reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 (200 MHz), Unityplus-300 (300 MHz) and Inova-500 (500 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminium plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/VIS spectrophotometer. The PL and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, Xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of polymers. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting ODCB (*o*-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and aluminum electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current-voltage (I-V) characteristics were measured using a Keithley 236 Source Measure Unit. All processing steps and measurements mentioned above were carried out under air and at room temperature. To examine electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto a platinum plate as a working electrode with the area of 1 cm^2. Film thickness was controlled in the range of about 3 μm by the amount of solution. After coating, the film adhering to the electrode was dried in a vacuum oven for 10 h. The electrochemical measurements were performed on 0.1 M tetrabutylammonium tetrafluoroborate (TBAF, freshly distilled, Aldrich) solution in acetonitrile. A platinum wire and a Ag/$AgNO_3$ electrode were used as a counter electrode and a reference electrode, respectively. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

Synthesis of 2-[(2-Ethylhexyl)oxy]-1,4-dimethylbenzene (3). To a stirred solution of 10 g (81.85 mmol) of 2-hydroxy-*p*-xylene (**1**), 5.95 g (90.05 mmol) of potassium hydroxide, and 1.25 g (8.2 mmol) of sodium iodide was added the solution of 16.7 mL (90.05 mmol) of 2-ethylhexyl bromide (**2**) in 200 mL of ethyl alcohol. After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with 300 mL of ethyl acetate, and washed with 2 × 30 mL of water and with 30 mL of saturated sodium chloride solution. The organic layer was dried with magnesium sulfate, filtered, and concentrated *in vacuo.* The resulting product was purified by silica gel chromatography to give 17.65 g (92%) of desired product **3**; R_f 0.5 (SiO_2, hexane 100%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.89-0.99 (m, 6H), 1.29-1.56 (m, 8H), 1.74 (m, 1H), 2.19 (s, 3H), 2.33 (s, 3H), 3.87 (d, 2H, J = 26 Hz), 6.67 (s, 1H), 6.69 (d, 2H, J = 31 Hz), 7.04 (d, 2H, J = 38 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 11.21, 14.04, 15.75, 21.38, 23.04, 24.10, 29.11, 30.72, 39.59, 70.02, 111.73, 120.38, 123.66, 130.17, 136.40, 157.27.

Synthesis of 1-Bromo-4-[(2-ethylhexyl)oxy]-2,5-dimethylbenzene (4). To a stirred solution of 17.65 g (75.3 mmol) of 2-[(2-ethylhexyl)oxy]-1,4-dimethylbenzene (**3**) in 200 mL of DMF at room temperature under argon was added 16.1 g (90.3 mmol) of NBS. The reaction mixture was stirred for 2 h at room temperature, and concentrated under reduced pressure. The reaction mixture was diluted with 300 mL of ethyl acetate, and washed with 5 × 30 mL of water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography to give 16.2 g (68.65%) of desired product **4**; R_f 0.6 (SiO_2, hexane 100%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.78-0.97 (m, 6H), 1.27-1.57 (m, 8H), 1.73 (m, 1H), 2.16 (s, 3H), 2.35 (s, 3H), 3.81 (d, 2H, J = 26 Hz), 6.68 (s, 1H), 7.26 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 11.19, 14.05, 15.47, 22.85, 23.04, 24.07, 29.10, 30.68, 39.52, 70.42, 113.28, 114.25, 126.33, 133.52, 135.52, 156.57.

Synthesis of 4-{2-Bromo-5-[(2-ethylhexyl)oxy]-4-(4-morpholinyl methyl)benzyl}morpholine (6). To a stirred solution of 16.2 g (51.7 mmol) of *p*-xylene compound **4**, 250 mg (1 mmol) of BPO, and 22 g (124.1 mmol) of NBS in 100 mL of CCl_4 at room temperature was emitted the light source for 1 h. The reaction mixture was filtered in order to remove succinimide. The reaction mixture was concentrated *in vacuo* to give a brown oil (18.84 g) containing a mixture of brominated products **5**. A mixture of the crude residue, 8.37 mL (96 mmol) of morpholine, and 13.94 mL (80 mmol) of diisopropylethylamine in THF (50 mL) was reacted at room temperature for 18 h. Solvent was removed by evaporation under reduced pressure, and the reaction mixture was extracted with ethyl acetate. The organic layer was purified by column chromatography to provide the desired final morpholinyl product **6** as white solid (7.2 g, 28.8%); R_f 0.4 (SiO_2, EtOAc : hexane = 1 : 2). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.87-0.96 (m, 6H), 1.25-1.52 (m, 8H) 1.71 (m, 1H), 2.45-2.54 (m, 8H), 3.47 (s, 2H), 3.55 (s, 2H), 3.68-3.74 (m, 8H), 3.84 (d, 2H, J = 5.5 Hz), 7.00 (s, 1H), 7.48 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm) 11.24, 14.08, 23.05, 24.05, 29.15, 30.70, 39.52, 53.56, 55.88, 62.12, 67.03, 70.59, 113.56, 114.53, 133.96, 156.80.

Synthesis of 4-{2-[(2-Ethylhexyl)oxy]-4-(4-morpholinylmethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl}morpholine (7). To a stirred solution of 7.15 g (14.79 mmol) of 4-{2-bromo-5-[(2-ethylhexyl)oxy]-4-(4-morpholinyl methyl)benzyl}morpholine (**6**) in dry THF (50 mL) under argon atmosphere at −78 °C was added 10.1 mL (16.27 mmol) of *n*-BuLi (1.6 M *n*-hexane solution). After the addition of *n*-BuLi, the mixture was stirred at −78 °C for 2 h. To the reaction mixture 3.6 mL (17.75 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop-wise at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 3 h. The reaction mixture was quenched by water, and extracted with ether. The solvent was removed by evaporation under reduced pressure. The yellow oil was purified by column chromatography to provide the desired final borolane product **7** as yellow oil (5.96 g, 76%); R_f 0.3 (SiO_2, EtOAc : hexane = 1 : 4). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.87-



Scheme 1. (a) KOH, EtOH, reflux; (b) NBS, DMF; (c) NBS (2eq), CCl_4; (d) Morpholine, EtN(*i*-Pr)$_2$, THF; (e) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *n*-BuLi, THF, −78 °C; (f) Pd(PPh$_3$)$_4$, Na_2CO_3, DME, H_2O; (g) Ac_2O, reflux; (h) HBr, CH_2Cl_2; (i) *tert*-BuOK, THF.

1.98 (s, 15H), 1.33 (s, 12H), 2.47 (m, 8H), 3.50 (s, 2H), 3.66 (m, 10H), 3.86 (d, 2H, J = 5.1 Hz), 6.85 (s, 1H), 7.61 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.62, 14.48, 23.42, 24.38, 24.97, 25.32, 29.48, 31.02, 39.88, 53.73, 53.78, 56.72, 62.56, 63.8, 67.23, 67.32, 70.34, 83.46, 112.92, 121.02, 130.70, 138.88, 159.65.

Synthesis of 4-{[4-[(2-Ethylhexyloxy)-6-(4-morpholinylmethyl)-4-trifluoromethyl][1,1-biphenyl]-3-yl]methyl}-morpholine (9). To a stirred solution of 4.0 g (6.03 mmol) of borolane compound **7** in 30 mL of DME (1,2-dimethoxyethane), 15 mL of ethyl alcohol, and 30 mL of aqueous Na_2CO_3 (2 M) was added 1.25 mL (9.05 mmol) of 1-bromo-4-(trifluoromethyl)benzene (**8**). After the solution was purged with nitrogen for 20 min, 0.69 g (0.6 mmol) of tetrakis(triphenylphosphine) palladium (0) (Pd[P(Ph)$_3$]$_4$) was added. The reaction mixture was refluxed with vigorous stirring under nitrogen for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography to give 3.2 g (96.7%) of product **9** as white solid; R_f 0.40 (SiO_2, EtOAc : Hex = 1 : 2). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 0.84-0.99 (m, 6H), 1.26-1.63 (m, 8H) 1.70-1.79 (m, 1H), 2.36 (t, 4H, J = 4.40 Hz), 2.51 (t, 4H, J = 4.76 Hz), 3.35 (s, 2H), 3.57 (s, 2H), 3.62-3.72 (tt, 8H, J = 4.40 Hz, J = 4.76 Hz), 3.92 (d, 2H, J = 5.50 Hz), 7.04 (s, 1H), 7.21 (s, 1H), 7.49 (d, 2H, J = 8.06 Hz), 7.63 (d, 2H, J = 8.43 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.68, 14.51, 23.45, 24.46, 29.54, 31.10, 39.94, 53.59, 53.85, 56.55, 60.72, 67.37, 70.71, 112.96, 124.96, 124.99, 129.00 (q, CF_3, J = 32.8 Hz), 130.20, 132.50, 133.24, 135.80, 145.21, 157.32.

Synthesis of {5-[(Acetyloxy)methyl]-4-[(2-ethylhexyl)-oxy]-4-(trifluoromethyl)[1,1-biphenyl]-2-yl}methyl acetate (10). 3.1 g (5.65 mmol) of coupling compound **9** was dissolved in 100 mL acetic anhydride and heated at reflux for 80 h. After the solvent was removed by evaporation under reduced pressure, the mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography to give 1.45 g (52.0%) of product **10**; R_f 0.30 (SiO_2, EtOAc : hexane = 1 : 10). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 0.89-0.98 (m, 6H), 1.33-1.61 (m, 8H) 1.70-1.78 (m, 1H), 2.06 (s, 3H), 2.09 (s, 3H), 3.94 (d, 2H, J = 5.50 Hz), 4.98 (s, 2H), 5.18 (s, 2H), 7.02 (s, 1H), 7.24 (s, 1H), 7.44 (d, 2H, J = 8.06 Hz), 7.66 (d, 2H, J = 8.06 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ

(ppm) 11.07, 13.91, 20.75, 20.77, 22.92, 23.91, 29.03, 30.55, 39.40, 61.32, 64.06, 70.45, 112.41, 124.82, 125.06, 125.11, 129.06, 129.64, 131.05, 132.82, 134.33, 143.69, 156.92, 170.40, 170.64.

Synthesis of 2,5-Bis(bromomethyl)-4-[(2-ethylhexyl)-oxy]-4-(trifluoromethyl)-1,1-biphenyl (11). To a stirred solution of 1.00 g (2.02 mmol) of acetylated compound **10** in methylene chloride was added 15 mL of a 30 % HBr/acetic acid. The solution was stirred overnight at ambient temperature. The mixture was diluted with methylene chloride and water. The organic layer was washed successively with aqueous $NaHCO_3$, and dried over $MgSO_4$. The crude product was purified by column chromatography to give 0.98 g (90.5%) of product **11**; R_f 0.40 (SiO_2, hexane 100%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 0.84-1.03 (m, 6H), 1.29-1.65 (m, 8H) 1.81-1.86 (m, 1H), 4.02 (d, 2H, J = 5.13 Hz), 4.39 (s, 2H), 4.56 (s, 2H), 7.04 (s, 1H), 7.23 (s, 1H), 7.57 (d, 2H, J = 8.06 Hz), 7.72 (d, 2H, J = 8.06 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm) 11.22, 14.05, 22.64, 23.06, 24.07, 27.74, 29.16, 30.68, 31.53, 31.60, 39.58, 70.66, 113.50, 125.30, 125.36, 127.14, 129.56, 129.91, 132.44, 132.75, 136.86, 143.25, 157.07.

Synthesis of EHCF$_3$P-PPV (12). To a stirred solution of 300 mg (0.559 mmol) of monomer **11** in dry THF (50 mL) was added 3.4 mL (3.4 mmol) of potassium *tert*-butoxide (1.0 M THF solution) by a syringe pump over 1 h. During the addition, the reaction mixture had color change from colorless via yellow to orange, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred additionally for 12 h at room temperature. The reaction mixture was poured into 500 mL of methanol with stirring. The precipitated polymer was filtered off, and the resulting polymer was dissolved again in THF. The dissolving polymer was slowly poured into 500 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature. A 150 mg sample of polymer **12** was obtained as orange fiber. ^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm) 0.7-1.0 (brs, 6H), 1.2-1.9 (m, 9H), 4.1 (brs, 2H), 7.0-7.9 (m, 8H).

Synthesis of 4-{[4-[(2-Ethylhexyl)oxy]-6-(4-morpholinyl-methyl)-3,5-bis(trifluoromethyl)[1,1-biphenyl]-3-yl]-methyl}-morpholine (14). To a solution of 5.0 g (7.54 mmol) of borolane compound **7** in 30 mL of DME (1,2-dimethoxy-ethane), 15 mL of ethyl alcohol, and 30 mL of aqueous Na_2CO_3 (2 M) was added 1.93 mL (11.3 mmol) of 1-bromo-3,5-bis(trifluoromethyl)benzene (**13**). After the solution was purged with argon for 20 min, 0.87 g (0.75 mmol) of tetrakis(triphenyl phosphine)palladium (0) ($Pd[P(Ph)_3]_4$) was added. The reaction mixture was refluxed with vigorous stirring under nitrogen for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography to give 3.5 g (75.2%) of product **14** as white solid; R_f 0.40 (SiO_2, EtOAc : hexane = 1 : 4). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.87-0.99 (m, 6H), 1.22-1.63 (m, 8H) 1.70-1.79 (m, 1H), 2.39 (br, 4H), 2.52 (br, 4H), 3.25 (s, 2H), 3.59-3.66 (m, 8H), 3.71 (s, 2H), 3.91 (d, 2H, J = 5.13 Hz), 6.86 (s, 1H), 7.30 (s, 1H), 7.82 (s, 1H), 8.09 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.64, 14.49, 23.44, 24.43, 29.51, 31.06, 39.91, 53.38, 53.88, 56.40, 61.61, 67.20, 70.85, 114.43, 120.47, 120.50, 128.75, 130.19, 130.20, 131.17 (q, CF_3, J = 32.8 Hz), 132.06, 132.26, 132.78, 143.51, 157.46.

Synthesis of {5-[(Acetyloxy)methyl]-4-[(2-ethylhexyl)-oxy]-3,5-bis(trifluoromethyl)[1,1-biphenyl]-2-yl}methyl acetate (15). A stirred solution of compound **14** (3.5 g, 5.67 mmol) in 100 mL of acetic anhydride was refluxed for 80 h. After the solvent was removed by evaporation under reduced pressure, the mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography to give 1.32 g (41.39%) of product **15**; R_f 0.30 (SiO_2, EtOAc : hexane = 1 : 10). ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.91-0.98 (m, 6H), 1.35-1.58 (m, 8H) 1.71-1.79 (m, 1H), 2.06 (s, 3H), 2.09 (s, 3H), 3.95 (d, 2H, J = 5.49 Hz), 4.88 (s, 2H), 5.18 (s, 2H), 7.03 (s, 1H), 7.25 (s, 1H), 7.82 (s, 2H), 7.87 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.55, 14.44, 21.11, 21.33, 23.40, 24.30, 29.45, 30.93, 39.74, 61.59, 64.63, 70.91, 113.71, 121.26, 121.29, 125.60, 129.78, 129.80, 131.25, 131.72 (q, CF_3, J = 33.6 Hz), 131.93, 134.57, 142.25, 157.56, 170.51, 170.94.

Synthesis of 2,5-Bis(bromomethyl)-4-[(2-ethylhexyl)-oxy]-3,5-bis(trifluoromethyl)-1,1-biphenyl (16). To a stirred solution of 1.00 g (1.78 mmol) of acetylated compound **15** in methylene chloride was added 15 mL of a 30% HBr/acetic acid. The solution was stirred overnight at ambient temperature. The mixture was diluted with methylene chloride and water. The organic layer was washed successively with aqueous $NaHCO_3$, and dried over $MgSO_4$. The crude product was purified by column chromatography to give 0.75 g (69.7%) of product **16**; R_f 0.30 (SiO_2, EtOAc : hexane = 1 : 50). ^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm) 0.84-1.01 (m, 6H), 1.26-1.68 (m, 8H) 1.74-1.85 (m, 1H), 4.00 (d, 2H, J = 5.13 Hz), 4.31 (s, 2H), 4.54 (s, 2H), 7.02 (s, 1H), 7.21 (s, 1H), 7.91 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.62, 14.47, 23.42, 24.40, 27.90, 29.47, 30.98, 31.39, 39.83, 71.00, 113.88, 121.54, 121.57, 127.68, 129.58, 129.60, 131.23, 131.97 (q, CF_3, J = 33.5 Hz), 132.58, 137.23, 141.76, 157.67.

Synthesis of EHBCF$_3$P-PPV (17). To a stirred solution of 300 mg (0.496 mmol) of the monomer **16** in dry THF (50 mL) was added 3 mL (3 mmol) of potassium *tert*-butoxide (1.0 M THF solution) by a syringe pump over 1 h. During this addition, the reaction mixture had color change from colorless via yellow to orange, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred additionally for 12 hr at room temperature, and poured into 500 mL of methanol with stirring. The precipitated polymer was filtered off, and the resulting polymer was dissolved again in THF. The solution was slowly poured into 500 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature. A 140 mg sample of polymer **17** was obtained as orange fiber. ^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) 0.7-1.0 (brs, 6H), 1.2-1.9 (m, 9H), 4.1 (brs, 2H), 7.0-8.2 (m, 7H).

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. In the first step, 2-hydroxy-*p*-xylene (**1**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol. 2-[(2-Ethylhexyl)oxy]-1,4-dimethylbenzene (**3**) was brominated at the *para*-position with NBS in DMF. The compound **4** was brominated again at the benzyl positions with NBS and light source (300W) in CCl$_4$. The resulting bromide compound **5** was reacted with morpholine in diisopropylethylamine to generate morpholine compound **6**,[24] which was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and n-butyl lithium in THF to generate borolane compound **7**. In order to synthesize EHCF$_3$P-PPV (**12**), the commercially available 1-bromo-4-(trifluoromethyl)benzene (**8**) was coupled with previously prepared compound **7** using tetrakis(triphenyl phosphine)palladium catalyst and sodium carbonate in DME and water by Suzuki coupling.[25] This coupled compound **9** was acetylated with acetic anhydride, and brominated with HBr in methylene chloride to generate the monomer **11**. The polymer, EHCF$_3$P-PPV (**12**), was prepared by the Gilch reaction,[26] with the monomer **11**, and an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h under argon atmosphere. In order to synthesize EHBCF$_3$P-PPV (**17**), the commercially available 1-bromo-3,5-bis(trifluoromethyl)-benzene (**13**) was chosen as the starting material and coupled with previously prepared compound **7** using tetrakis(triphenylphosphine) palladium catalyst and sodium carbonate in DME and water by Suzuki coupling. The coupled compound **14** was acetylated with acetic anhydride, and brominated with HBr in methylene chloride to generate monomer **16**. The polymer of this monomer was prepared by Gilch polymerization. The monomer and potassium *tert*-butoxide in THF was used to obtain EHBCF$_3$P-PPV (**17**).

The structure and purity of the monomers were confirmed by ^{1}H-NMR, and ^{13}C-NMR. EHCF$_3$P-PPV and EHBCF$_3$P-PPV, brittle orange polymer was soluble in various organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and ODCB. The known phenyl-substituted PPV, poly[2-(2-ethylhexyloxy)-5-phenyl-1,4-phenylenevinylene] (EHP-PPV),[17] was also synthesized using analogous method to be compared with EHCF$_3$P-PPV (**12**), and EHBCF$_3$P-PPV (**17**). But EHP-PPV showed very poor solubility with any solvent, in our hands, for obtaining the polymer film. The emissive polymer film was obtained by spin-casting an ODCB solution of EHCF$_3$P-PPV and EHBCF$_3$P-PPV. The results of polymerization of EHCF$_3$P-PPV and EHBCF$_3$P-PPV are summarized in Table 1. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersities (PDI) of EHCF$_3$P-PPV and EHBCF$_3$P-PPV were in the range of 8000-12000, 42000-72000, 5.3-6.0, respectively, as determined by GPC using THF as an eluent and polystyrene as the standard. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min, and glass transition temperature (T$_g$) was not measured in the range of 50-300 °C. EHCF$_3$P-PPV and EHBCF$_3$P-PPV lose less than 5% of their weights on heating to 270 °C and 300 °C, respectively. The high thermal stability of the resulting polymers prevents the deformation of the polymer morphology and degradation of the polymer light-emitting device by applied electric field of the LED.

Table 1. Polymerization Results of MEH-PPV-*co*-Si-PPDFV

Polymers	M_n[a]	M_w[a]	PDI[a]	T$_d$
EHCF$_3$P-PPV	8,000	42,000	5.3	270 °C
EHDCF$_3$P-PPV	12,000	72,000	6.0	300 °C

[a] M$_n$, M$_w$, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

Optical and Photoluminescence Properties. The UV-vis absorption spectra and PL spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV as thin films are shown in Figure 1 and

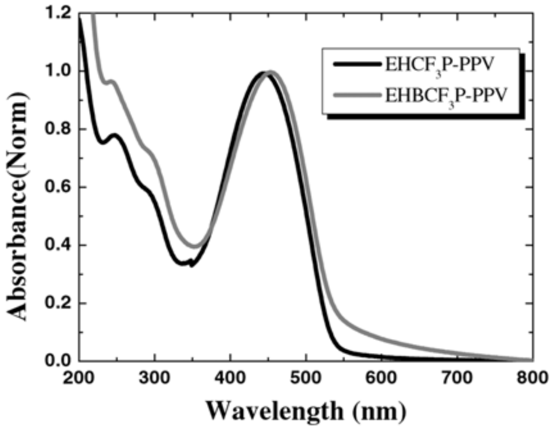


Figure 1. UV-vis absorption spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV.

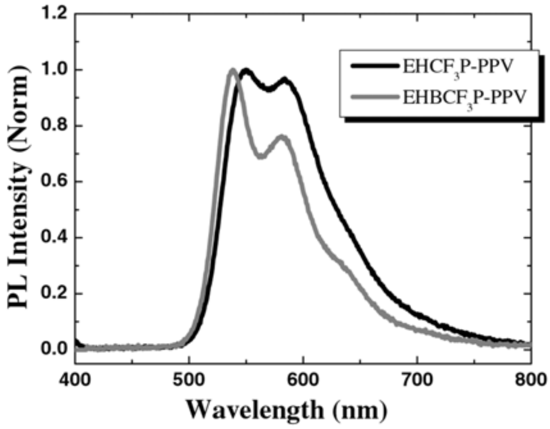


Figure 2. Photoluminescence spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV.

Figure 2. The thin films were prepared by spin-coating on quartz plates from the polymer solutions with ODCB. The EHCF$_3$P-PPV and EHBCF$_3$P-PPV exhibit absorption spectra with a maximum peak of around 446 nm attributed to π-π^* transition of the conjugated backbones. The absorption onset wavelengths of EHCF$_3$P-PPV and EHBCF$_3$P-PPV were 539 nm and 536 nm, which were a little bit shorter than 541 nm of EHP-PPV.[17] The PL spectra of the polymers all consist of a typical vibronically structured band comprising a maximum, a shoulder, and a tail. The PL spectrum of the EHCF$_3$P-PPV and EHBCF$_3$P-PPV thin film exhibits a maximum at 550 nm and 537 nm (exciting wavelength, 410 nm), which were blue-shifted as compared to 555 nm of EHP-PPV.[17] The shoulder and tail of PL spectrum of the EHCF$_3$P-PPV and EHBCF$_3$P-PPV thin film are at around 580 nm and 640 nm.

Electrochemical Properties of the Polymers. The energy band diagrams of polymers, as shown in Figure 3, were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry.[27] All measurements were calibrated against an internal standard, ferrocene (F$_c$), which has the IP value (−4.8 eV) of the F$_c$/F$_c^+$ redox system.[28] All of the polymers exhibit irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.50, 0.70, and 0.90 V for EHP-PPV,[17] EHCF$_3$P-PPV and EHBCF$_3$P-PPV, respectively, which correspond to HOMO energy level of 4.88, 5.10, and 5.31 eV. The LUMO energy levels of polymers can be calculated with the HOMO and optical band gap. The LUMO energy levels of EHP-PPV, EHCF$_3$P-PPV and EHBCF$_3$P-PPV were thus determined to be 2.60, 2.80 and 3.00 eV, respectively. The higher work function of the LUMO of EHCF$_3$P-PPV and EHBCF$_3$P-PPV as compared to that of EHP-PPV indicate that the electron injection process is easier in case of EHCF$_3$P-PPV and EHBCF$_3$P-PPV as compared to the case of EHP-PPV.

Electroluminescent Properties and Current-Voltage-Luminance. The normalized electroluminescence (EL) spectra are shown in Figure 4. The EL spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV show maximum peaks at 545, and 540 nm, which were blue-shifted as compared to 560 nm of EHP-PPV.[17] These features are similar to those observed in the PL spectra of the corresponding polymer films.

The current-voltage-luminescence (I-V-L) density characteristics of the devices fabricated from EHCF$_3$P-PPV and EHBCF$_3$P-PPV are shown in Figure 5. In the forward bias, the turn-on voltage of EHCF$_3$P-PPV and EHBCF$_3$P-PPV are around 4.0 and 3.3 V, respectively, and the current densities increase in an exponential manner with increasing forward bias, which is typical of diode characteristic. In case of known EHP-PPV, the turn-on voltage was 18 V after consideration of the reproducible "current anormaly".[17]

The maximum brightness of EHCF$_3$P-PPV and EHBCF$_3$P-PPV are about 8 cd/m^2 at 10 V, and 6.3 cd/m^2 at 4.3 V, respectively, as shown in Figure 5. The low maximum brightness of the polymers could be attributed to the single

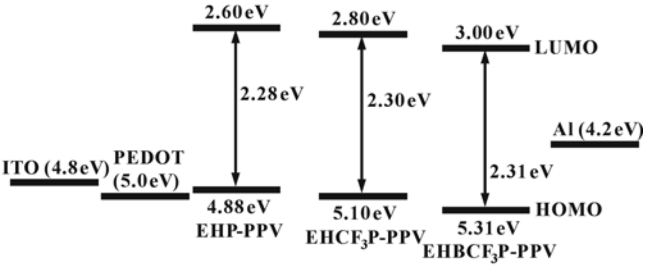


Figure 3. Energy band diagram of EHCF$_3$P-PPV and EHBCF$_3$P-PPV.

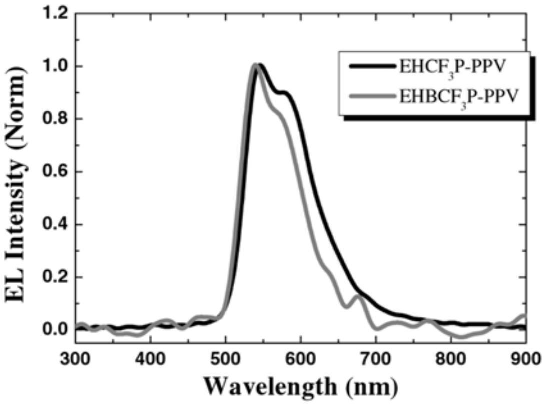


Figure 4. Electroluminescence spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV.

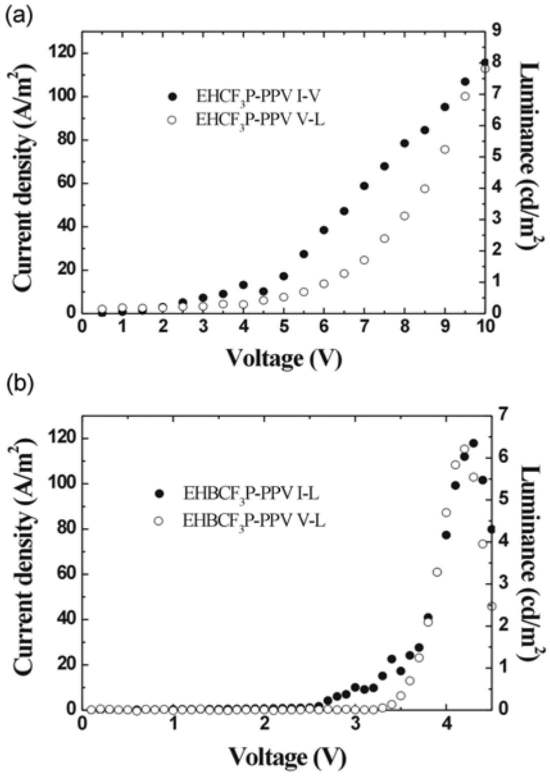


Figure 5. Current-voltage-luminescence (I-V-L) characteristics of PLEDs of EHCF$_3$P-PPV and EHBCF$_3$P-PPV with a configuration of ITO/PEDOT:PSS /polymer/Al.

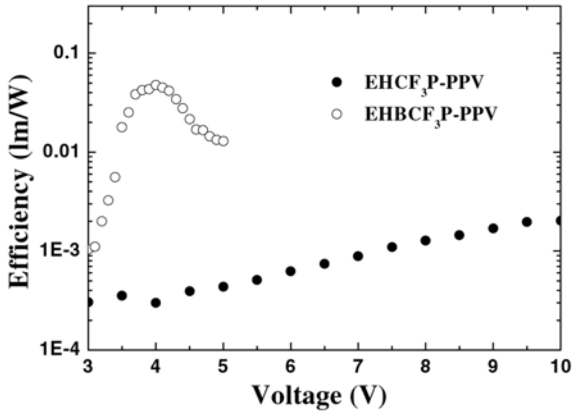


Figure 6. Efficiencies of PLEDs of EHCF$_3$P-PPV and EHBCF$_3$P-PPV with a configuration of ITO/PEDOT:PSS/polymer/Al.

layer device and poor morphology of the polymer films. The maximum EL efficiency of EHBCF$_3$P-PPV (0.05 cd/A), with two CF$_3$-groups, was higher than that of EHCF$_3$P-PPV (0.002 cd/A), with one CF$_3$-group, as shown in Figure 6, which was possibly caused by the lower LUMO level of EHBCF$_3$P-PPV.

Conclusion

The research was focused at the syntheses of two new PPV derivatives, poly[2-(2-ethylhexyloxy)-5-(4-trifluoro methylphenyl)-1,4-phenylenevinylene] (EHCF$_3$P-PPV), and poly[2-(2-ethylhexyloxy)-5-(3,5-bis(trifluoromethyl)-phenyl)-1,4-phenylenevinylene] (EHBCF$_3$P-PPV), which contain electron-withdrawing trifluoromethyl group, by Gilch polymerization. M_n, M_w, and PDI values of these polymers were in the range of 8000-12000, 42000-72000, 5.0-5.6, respectively. T$_d$ values of EHCF$_3$P-PPV and EHBCF$_3$P-PPV were measured to be 270 °C, and 300 °C. The UV-visible absorption spectra of EHCF$_3$P-PPV and EHBCF$_3$P-PPV showed the maximum peaks at 446, 451 nm. The current-voltage-luminance (*I-V-L*) characteristics of the polymers show that turn-on voltages of EHCF$_3$P-PPV and EHBCF$_3$P-PPV are around 4.0 and 3.5 V, respectively, in the Al/polymer/PEDOT/ITO device. EHCF$_3$P-PPV, and EHBCF$_3$P-PPV show maximum photoluminescence (PL) peaks at $\lambda_{\max}$ = 550, 539 nm, and maximum EL peak at $\lambda_{\max}$ = 545, 540 nm, respectively. The maximum brightness of EHCF$_3$P-PPV and EHBCF$_3$P-PPV are about 8 cd/m^2 at 10 V, and 6.3 cd/m^2 at 4.3 V, respectively. As the result of the introduction of the electron-withdrawing CF$_3$ group to the phenyl substituent, the LUMO and HOMO energy levels of EHCF$_3$P-PPV (2.80, 5.10 eV) and EHBCF$_3$P-PPV (3.00, 5.31 eV) were lower than those of known EHP-PPV (2.60, 4.88 eV). The maximum EL efficiency of EHBCF$_3$P-PPV (0.05 cd/A), with two CF$_3$-groups, was higher than that of EHCF$_3$P-PPV (0.002 cd/A), with one CF$_3$-group, which was possibly caused by the lower LUMO level of EHBCF$_3$P-PPV.

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References and Notes

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
2. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
3. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A.; Bredas, J. L.; Lõgdlund, M.; Salameck, W. R. *Nature (London)* **1999**, *357*, 121.
4. Shim, H. K.; Jin, J. I. *Adv. Polym. Sci.* **2002**, *158*, 194.
5. Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature (London)* **1993**, *365*, 628.
6. Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenman, N. C.; Burn, P. L.; Holmes, A. B. *Appl. Phys. Lett.* **1992**, *61*, 2793.
7. Burn, P. L.; Grice, A. W.; Jajbakhsh, A.; Bradley, D. D. C.; Thomas, A. C. *Adv. Mater.* **1997**, *9*, 1171.
8. Bredas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *54*, 401.
9. Ko, S. W.; Jung, B.-J.; Ahn, T.; Shim, H.-K. *Macromolecules* **2002**, *35*, 6217.
10. Sarnecki, G. J.; Friend, R. H.; Moratti, S. C. *Synth. Met.* **1995**, *69*, 545.
11. Gurge, R. M.; Sarker, A.; Laht, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1996**, *29*, 4287.
12. Gurge, R. M.; Sarker, A.; Laht, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1997**, *30*, 8286.
13. Jin, J. I.; Kim, J. C.; Shim, H. K. *Macromolecules* **1992**, *25*, 5519.
14. Benjamin, I.; Faraggi, E. Z.; Avny, Y.; Davidov, D.; Neumann, R. *Chem. Mater.* **1996**, *8*, 352.
15. Lahti, P. M.; Sarker, A.; Garay, R. O.; Lenz, R. W.; Karasz, F. E. *Polymer* **1994**, *35*, 1312.
16. Grimsdale, A. C.; Cacialli, F.; Gruner, J.; Lix, C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1996**, *76*, 165.
17. Boardman, F. H.; Grice, A. W.; Ruther, M. G.; Sheldon, T. J.; Bradley, D. D. C.; Burn, P. L. *Macromolecules* **1999**, *32*, 111.
18. Bröms, P.; Fahlman, M.; Xing, K. Z.; Salaneck, W. R.; Dannetun, P.; Cornil, J.; dos Santos, D. A.; Brédas, J. L.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1994**, *67*, 93.
19. Lögdlund, M.; Brédas, J. L. *J. Chem. Phys.* **1994**, *101*, 4357.
20. Bröms, P.; Birgersson, J.; Johansson, N.; Lögdlund, M.; Salaneck, W. R. *Synth. Met.* **1995**, *74*, 179.
21. Jin, Y.; Ju, J.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Son, S. M.; Jin, S. H.; Lee, K.; Suh, H. *Macromolecules* **2003**, *36*, 6970.
22. Lux, A.; Holmes, A. B.; Cervini, J. E.; Davies, J. E.; Moratti, S. C.; Grüner, J.; Cacialli, F.; Friend, R. H. *Synth. Met.* **1997**, *84*, 293.
23. Jin, Y.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2004**, *37*, 6711.
24. Burke, W. J.; Bishop, J. L.; Warburton, J. A. *J. Org. Chem.* **1962**, *27*, 4003.
25. Sato, M.; Maruyama, G.; Tanemura, A. *J. Organomet. Chem.* **2002**, *655*, 23.
26. Becker, H.; Spreitzer, H.; Inbrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925.
27. Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.
28. Leeuw, D. M.; Simenon, M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.