Synthesis and Color Tuning of Poly(*p*-phenylenevinylene) Containing Terphenyl Units for Light Emitting Diodes

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New PPV based conjugated polymers, containing terphenyl units, were prepared as the electroluminescent (EL) layer in light-emitting diodes (LEDs). The prepared polymers, poly[2,5-bis(4-(2-etylhexyloxy)phenyl)-1,4-phenylenevinylene] (BEHP-PPV), poly[2-(2-ethylhexyloxy)-5-(4-(4-(2-etylhexyloxy)phenyl)phenyl)-1,4-phenylenevinylene] (EEPP-PPV) and poly[2-(2-ethylhexyloxy)-5-(9,9-bis(2-etylhexyl)fluorenyl)-1,4-phenylenevinylene] (EHF-PPV), were soluble in common organic solvents and used as the EL layer in double layer light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al). The polymers were prepared by the Gilch reaction. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersities (PDI) of these polymers were in the range of 9000-58000, 27000-231000, 2.9-3.9, respectively. These polymers have quite good thermal stability with decomposition starting above 320-350. The polymers show photoluminescence (PL) with maximum peaks at around 526-562 nm (exciting wavelength, 410 nm) and blue EL with maximum peaks at around λ_{max} = 526-552 nm. The current-voltage-luminance (*I-V-L*) characteristics of polymers show turn-on voltages of 5 V. Even though both of EEPP-PPV and BEHP-PPV have the same terphenyl group in the repeating unit, EEPP-PPV with directly substituted alkoxy group in the back bone has longer effective conjugation length than BEHP-PPV, and exhibits red shift in the PL spectra. Both of EEPP-PPV and EHF-PPV have ter-phenyl units and directly substituted alkoxy group in back bone. EHF-PPV with fluorenyl unit attached to the PPV backbone has shorter effective conjugation length than EEPP-PPV with biphenyl unit, and exhibits blue shift in the PL spectra.

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

Introduction

Because of the academic interest and potential applications as large-area light-emitting displays, much attention have been focused at electroluminescence (EL) devices based on organic thin layer.[1-4] Since the polymeric light-emitting diodes based on poly(p-phenylenevinylene) (PPV) were investigated by Burroughes *et al.*,[5] many studies of polymer light-emitting diodes (PLED)s have been reported.[6-9]

By carefully choosing the conjugated polymer backbone or altering the side-chain functionalities, one should be able to fabricate EL devices in a variety of colors. Many derivatives of PPV have been reported with various substituents such as alkoxyl,[10] silyl,[11] phenyl,[12,13] fluorenyl,[14,15] halide,[16-18] cyano,[19] or trifluoromethyl[20] on the arylene rings. It has been possible to generate conjugated polymers with electroluminescence and photoluminescence across the full spectrum; red,[21] yellow-orange,[22] yellow,[23] yellow-green,[24] green,[25] and blue.[26] Conjugated polymers in general have a tendency to aggregate or stack as a consequence of their extensive π-delocalization. The solubility of the materials results from the presence of long alkyl chains which afford some conformational mobility to the polymer chains. Poly(2,5-dialkoxy-1,4-phenylenevinylene)s with long solubilizing xxalkoxy chains can be dissolved in conventional

organic solvents such as chloroform, toluene, or tetrahydrofuran.[27] Their emission and absorption spectra are red-shifted relative to PPV itself, and the polymers' fluorescence and electroluminescence quantum yields are greater than parent PPV. This benefit may be a consequence of the long alkyl chains isolating the polymer chains from each other.

Fluorenyl-substituted derivatives show interesting unique chemical and physical properties because they contain a rigid planar biphenyl unit and are easily substituted at the C-9 position, which improves the polymer processability.[14,28,29] Incorporating the 9,9-bis(2-ethylhexyl)-fluorene unit,[28] where alkyl chains are out of plane to the fluorene residue, into the parent PPV backbone forms a new type of conjugated polymer.

PPVs are normally synthesized by two methods: precursor route and direct solution polymerization for organic soluble polymers. Several synthetic approaches for soluble polymers have been established including, dehydrohalogenation (Gilch route), Wittig-Horner reaction, Heck and Suzuki reaction, and so on. Among the methods investigated, the Gilch procedure is very simple and can normally result in polymers with high molecular weights, narrow polydispersity indices and high structural regularity. A few PPV derivatives such as MEH-PPV, OC_1C_{10}-PPV, and phenyl-substituted PPVs (Ph-PPVs) with such promising properties have been successfully prepared through the Gilch route.[30]

In this study, our research interest has been focused in the synthesis and characterization of soluble, high molecular weight poly(*p*-phenylenevinylene) derivatives with terphenyl units. The synthesized polymers are poly[2-(2-ethylhexyl-oxy)-5-(4-(4-(2-ethylhexyloxy)phenyl)phenyl)-1,4-phenyl-enevinylene] (EEPP-PPV), poly[2,5-bis(4-(2-etylhexyloxy)-phenyl)-1,4-phenylenevinylene] (BEHP-PPV) and poly[2-(2-ethylhexyloxy)-5-(9,9-bis(2-etylhexyl)-fluorene-2-yl)-1,4-phenylenevinylene] (EHF-PPV). In order to get pure monomers, morpholine groups were introduced as protect-ing group. After introduction of the bromide groups again in the last steps, all polymers were synthesized with the Gilch reaction. Energy levels measured from cyclic voltammetry reveal that the influences of the substitution patterns on the HOMOs and LUMOs of BEHP-PPV, EEPP-PPV and EHF-PPV are different. By the introduction of proper side chain, one can control the effective conjugation length and thus the color of the polymers.[31] EEPP-PPV and BEHP-PPV have same terphenyl units, but EEPP-PPV with directly sub-stituted alkoxy group in the PPV back bone has longer effective conjugation length than BEHP-PPV, and exhibits red shift in fluorescence spectra. EHF-PPV, with dialkylated fluorene unit substituted on the PPV backbone, contains one kind of terphenyl unit and directly substituted alkoxy group in the backbone. EHF-PPV showed shorter effective conju-gation length than EEPP-PPV.

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. ^{1}H 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. Flash column chromatography was performed with 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 fluores-cent 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 the polymers. Molecular weights and polydisper-sities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. For the EL experiment, poly(3,4-ethylenedioxy-thiophene) (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 and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting *o*-dichlorobenzene (ODCB) 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 mm². For the determination of device characteristics, current-voltage (*I-V*) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measure-ments 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 an area of 1 cm². 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 perform-ed on 0.1 M tetrabutylammonium tetrafluoroborate (TBAF, freshly distilled, Aldrich) solution in acetonitrile. A platinum wire and a Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetric waves were produced by using EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

Synthesis of 1-Bromo-4-[(2-ethylhexyl)oxy]benzene (3). To a stirred solution of 10 g (57.80 mmol) of 4-bromophenol (**1**), 4.00 g (60.69 mmol) of potassium hydroxide and 0.87 g (5.8 mmol) of sodium iodide in 150 mL of ethyl alcohol at room temperature under argon atmosphere was added 11.24 mL (60.69 mmol) of 2-ethylhexyl bromide (**2**). After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with ethyl acetate, and washed with 2 times of 30 mL of water and 30 mL of saturated sodium chloride solution. The organic phase was dried over MgSO₄, and concentrated under reduced pres-sure. The yellow oil was purified by column chromato-graphy to provide 10.5 g (93%) of the desired compound **3** as yellow oil: R_f 0.45 (SiO₂, hexane 100%); ^{1}H-NMR (200 MHz, CDCl₃) δ (ppm) 0.87-1.73 (m, 15H), 3.79 (d, 2H, *J* = 5.9 Hz), 6.77 (d, 2H, *J* = 8.8 Hz), 7.35 (d, 2H, *J* = 9.20 Hz); ^{13}C-NMR (50 MHz, CDCl₃) δ (ppm) 11.07, 14.05, 23.01, 23.83, 29.05, 30.49, 39.32, 70.80, 112.46, 116.33, 132.13, 158.51.

Synthesis of 2-[4-[(2-Ethylhexyl)oxy]phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4). To a stirred solution of 5 g (25.8 mmol) of 1-bromo-4-[(2-ethylhexyl)oxy]ben-zene (**3**) in 30 mL of dry THF at −78 °C under argon atmosphere was added 17.74 mL (28.38 mmol) of the *n*-BuLi (1.6 M *n*-hexane solution). After stirring at −78 °C for 2 h, the reaction mixture was treated with 6.32 mL (30.96 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxa-borolane at −78 °C. The solution was allowed to warm to room temperature and stirred for additional 3 h. The reaction

mixture was quenched with water, and extracted with 250 mL of diethyl ether. After removing the solvent under reduced pressure, the yellow residue was purified by column chromatography to provide 8.1 g (95%) of the desired final borolane product **4** as yellow oil: R_f 0.2 (SiO_2, CH_2Cl_2/hexane = 1/9); ¹H-NMR (200M Hz, $CDCl_3$) δ (ppm) 0.87-0.95 (s, 6H) 1.19-1.54 (m, 8H), 1.32 (s, 12H), 1.57-1.74 (m, 1H), 3.85 (d, 2H, J = 5.9 Hz), 6.88 (d, 2H, J = 8.8 Hz), 7.73 (d, 2H, J = 8.8 Hz); ¹³C-NMR (75 MHz, $CDCl_3$) δ (ppm) 11.07, 14.04, 23.02, 23.85, 24.79, 24.83, 29.05, 30.51, 39.33, 70.28, 83.47, 113.89, 136.44, 162.02.

Synthesis of 4-[2,5-Dibromo-4-(4-morpholinylmethyl)-benzyl]morpholine (7). To a stirred solution of 10 g (37.89 mmol) of *p*-xylene compound **5**, 360 mg (1.5 mmol) of BPO and 14.83 g (83.4 mmol) of NBS in 100 mL of CCl_4 at room temperature under argon atmosphere 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 16 g of brown oil containing a mixture of brominated products **6**. A mixture of the crude residue, 13.2 mL (151.54 mmol) of morpholine, and 26.4 mL (151.54 mmol) of diisopropylethylamine in 50 mL of THF was stirred at room temperature for 18 h. Solvent was removed by evaporation under reduced pressure, and the reaction mixture was extracted with ethyl acetate. The obtained crude product was recrystallized with MeOH to provide 15.1 g (46%) of the desired final morpholinyl product **7** as white solid: R_f 0.4 (SiO_2, EtOAc/hexane = 1/2); ¹H-NMR (200 MHz, $CDCl_3$) δ (ppm) 2.50 (t, 8H, J = 4.56 Hz), 3.52 (s, 4H), 3.71 (t, 8H, J = 4.58 Hz), 7.64 (s, 2H); ¹³C-NMR (75 MHz, $CDCl_3$) δ(ppm) 53.52, 61.47, 66.95, 123.34, 134.32.

Synthesis of 1,4-Bis[4-[(2-ethylhexyl)oxy]phenyl]-2,5-bis(4-morpholinylmethyl)benzene (8). To a stirred solution of 8.1 g (24.5 mmol) of borolane compound **4** in 20 mL of DME, 10 mL of ethyl alcohol and 20 mL of aqueous Na_2CO_3 (2 M) at room temperature under Ar atmosphere was added 3.73 g (8.6 mmol) of morpholinyl compound **7**. After the solution was purged with argon for 20 min, 0.99 g (0.86 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 2.0 g (34.7%) of product **8** as white solid: R_f 0.40 (SiO_2, EtOAc/hexane = 1/4); ¹H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.89-0.99 (m, 12H), 1.22-1.79 (m, 18H), 2.41 (br, 8H), 3.42 (s, 4H), 3.66 (br, 8H), 3.89 (d, 4H, J = 5.5 Hz), 6.95 (d, 4H, J = 8.8 Hz), 7.25 (s, 2H), 7.40 (d, 4H, J = 8.8 Hz); ¹³C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.15, 14.11, 23.07, 23.90, 29.11, 30.57, 39.45, 53.26, 60.19, 67.10, 70.51, 113.90, 130.69, 131.36, 132.23, 133.23, 140.93, 158.54.

Synthesis of 1,4-Bis[(acetyloxy)methyl]-2,5-bis[4-[(2-ethylhexyl)oxy]phenyl]benzene (9). A stirred solution of 1.6 g (2.38 mmol) of compound **8** and 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 1.15 g (76.6%) of product **9**: R_f 0.40 (SiO_2, EtOAc/hexane = 1/5); ¹H-NMR (200 MHz, $CDCl_3$) δ (ppm) 0.91-0.99 (m, 12H), 1.21-1.79 (m, 18H) 2.04 (s, 6H), 3.89 (d, 4H, J = 5.5 Hz), 5.10 (s, 4H), 6.96 (d, 4H, J = 8.1 Hz), 7.29 (d, 4H, J = 8.1 Hz), 7.40 (s, 2H); ¹³C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.15, 14.11, 21.00, 23.07, 23.90, 29.11, 30.57, 39.45, 64.19, 70.51, 114.35, 130.19, 131.75, 133.20, 133.76, 140.95, 158.95, 170.71.

Synthesis of 1,4-Bis(bromomethyl)-2,5-bis[4-[(2-ethylhexyl)oxy]phenyl]benzene (10). To a stirred solution of 1.1 g (1.74 mmol) of acetylated compound **9** in methylene chloride at room temperature 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 1.0 g (85.4%) of product **10**: R_f 0.20 (SiO_2, EtOAc/hexane = 1/50); ¹H-NMR (200 MHz, $CDCl_3$) δ(ppm) 0.86-1.00 (m, 12H), 1.28-1.81 (m, 18H), 3.92 (d, 4H, J = 5.5 Hz), 4.48 (s, 4H), 7.01 (d, 4H, J = 8.4 Hz), 7.40 (s, 2H), 7.42 (d, 4H, J = 8.8 Hz); ¹³C-NMR (125 MHz, $CDCl_3$) δ (ppm) 11.57, 14.51, 23.45, 24.27, 29.48, 30.92, 32.21, 39.76, 70.86, 114.66, 130.28, 131.57, 133.32, 135.77, 141.34, 159.24.

Synthesis of Poly[2,5-bis(4-(2-etylhexyloxy)phenyl)-1,4-phenylenevinylene] (BEHP-PPV) (11). To a stirred solution of 0.50 g (0.743 mmol) of the monomer **10** in 50 mL of dry THF at room temperature was added 4.5 mL (4.5 mmol) of potassium *tert*-butoxide (1.0 M THF solution) at a rate of 4.5 mL/h using a syringe pump. 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 h at room temperature, and poured into 500 mL of methanol while 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 to generate 200 mg sample of polymer **11** as yellow fiber.

Synthesis of 4-Bromo-4-[(2-ethylhexyl)oxy]-1,1-biphenyl (13). To a stirred solution of 10 g (40.14 mmol) of 4-bromo-4-hydroxybiphenyl (**12**), 3.18 g (48.17 mmol) of potassium hydroxide and 0.6 g (4.08 mmol) of sodium iodide in 150 mL of ethyl alcohol at room temperature under argon atmosphere was added 11.16 mL (60.22 mmol) of 2-ethylhexyl bromide (**2**). After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with ethyl acetate, and washed with 2 times of 30 mL of water and 30 mL of saturated sodium chloride solution. The obtained crude
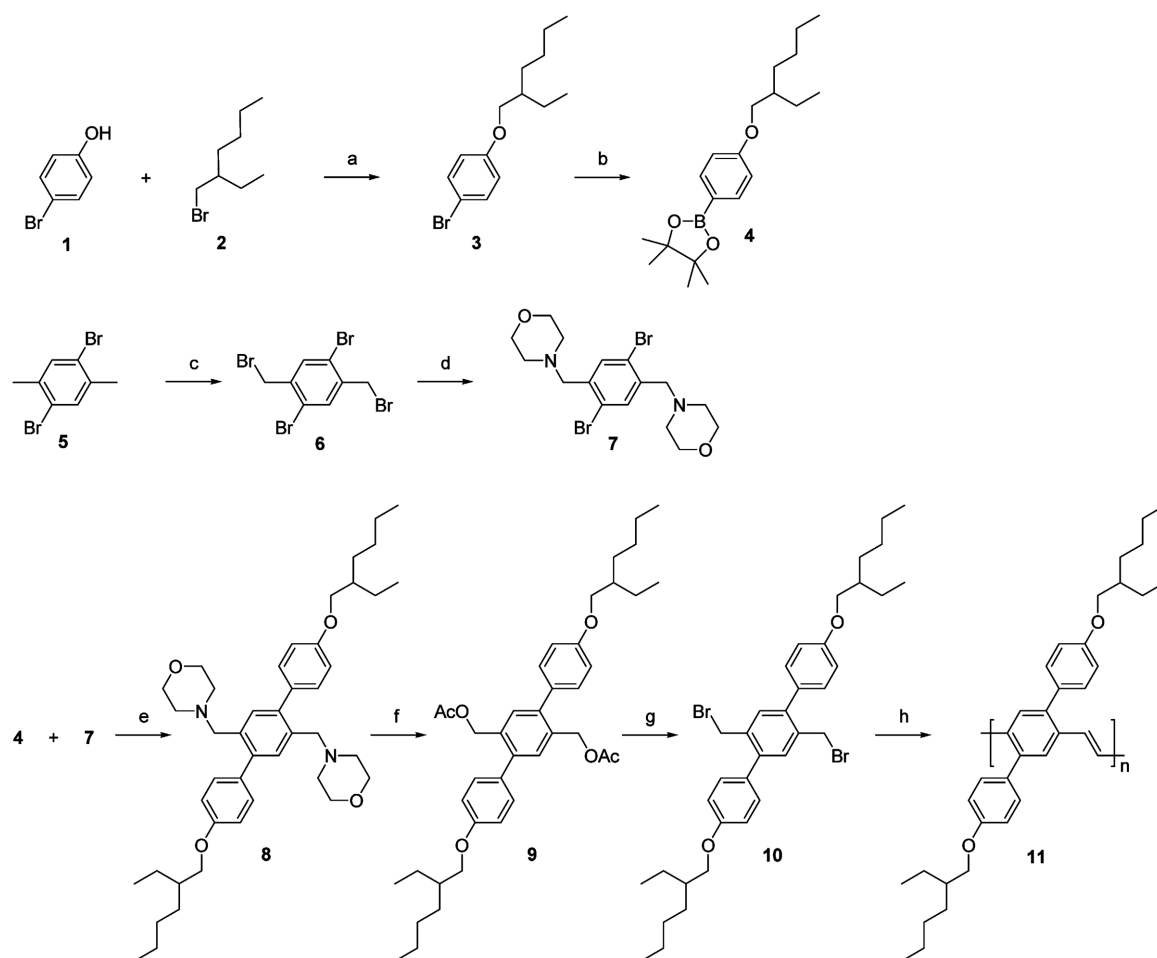
Scheme 1. Synthetic Routes for BEHP-PPV: (a) KOH, EtOH, reflux; (b) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C; (c) NBS (2eq), *hν*, CCl₄; (d) Morpholine, EtN(*i*-Pr)₂, THF (e) Pd(PPh₃)₄, Na₂CO₃, DME, H₂O; (f) Ac₂O, reflux; (g) HBr, CH₂Cl₂; (h) *tert*-BuOK, THF

product was recrystallized with MeOH to provide 9.71 g (67%) of the desired product **3**: R_f 0.4 (SiO₂, hexane 100%); ^{1}H-NMR (200 MHz, CDCl₃) δ (ppm) 0.81-1.64 (m, 15H), 3.87 (d, 2H, J = 5.5 Hz), 6.96 (d, 2H, J = 8.8 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.47 (d, 2H, J = 8.8 Hz), 7.52 (d, 2H, J = 8.0 Hz); ^{13}C-NMR (50 MHz, CDCl₃) δ (ppm) 11.32, 14.29, 23.27, 24.10, 29.31, 30.75, 39.61, 70.86, 112.26, 115.15, 128.13, 128.50, 130.93, 131.98, 142.39, 157.51.

Synthesis of 2-[4-[(2-Ethylhexyl)oxy][1,1-biphenyl]-4-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). To a stirred solution of 5 g (13.8 mmol) of 4-bromo-4-[(2-etylhexyl)oxy]-1,1-biphenyl (**13**) in dry THF (50 mL) at −78 °C under argon atmosphere was added 10.4 mL (16 mmol) of *n*-BuLi (1.6 M *n*-hexane solution). After stirring for 2 h at −78 °C, the reaction mixture was treated with 3.38 mL of (16.6 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolan −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 250 mL of ether. After removing the solvent under reduced pressure, the yellow residue was purified by column chromatography to provide 4.6 g (82%) of the desired final

borolane product **4** as yellow oil: R_f 0.3 (SiO₂, hexane 100%); ^{1}H-NMR (200 MHz, CDCl₃) δ (ppm) 0.90-0.97 (s, 6H) 1.22-1.53 (m, 8H), 1.32 (s, 12H), 1.74 (m, 1H), 3.88 (d, 2H, J = 5.5 Hz), 6.97 (d, 2H, J = 8.8 Hz), 7.55 (d, 2H, J = 8.8 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.86 (d, 2H, J = 8.1 Hz); ^{13}C-NMR (75 MHz, CDCl₃) δ (ppm) 11.13, 14.09, 23.07, 23.90, 24.88, 29.10, 30.56, 39.42, 70.61, 83.75, 114.84, 125.96, 128.18, 133.21, 135.26, 143.60, 159.28.

Synthesis of 2-[(2-Ethylhexyl)oxy]-1,4-dimethylbenzene (16). To a stirred solution of 10 g (81.85 mmol) of 2-hydroxy-*p*-xylene (**15**), 5.95 g (90.05 mmol) of potassium hydroxide and 1.25 g (8.2 mmol) of sodium iodide in 200 mL of ethyl alcohol at room temperature under argon atmosphere was added 16.7 mL (90.05 mmol) of 2-ethylhexyl bromide (**2**). After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with ethyl acetate, and washed with 2 times of 30 mL of water and 30 mL 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 **16**: R_f 0.5 (SiO₂,

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-di-methylbenzene (17). To a stirred solution of 17.65 g (75.3 mmol) of 2-[(2-ethylhexyl)oxy]-1,4-dimethylbenzene (**6**) in 200 mL of DMF at room temperature under argon atmosphere was added 16.1 g (90.3 mmol) of NBS. The reaction mixture was stirred at room temperature for 2 h, 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 **7**: 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-morpholinylmethyl)benzyl]morpholine (19). To a stirred solution of 16.2 g (51.7 mmol) of compound **17**, 250 mg (1 mmol) of BPO and 22 g (124.1 mmol) NBS in CCl$_4$ (100 mL) at room temperature under argon atmosphere 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 18.84 g of brown crude product **18**. A mixture of the crude product **18**, 8.37 mL (96 mmol) of morpholine and 13.94 mL (80 mmol) diisopropylethylamine in 50 mL of THF 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 7.2 g (28.8%) of the desired final morpholinyl product **19** as white solid: 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 1-[(2-Etylhexyl)oxy]-4-(4-[[4-(2-etylhexyl)-oxy]phenyl]phenyl)-2,5-bis(4-morpholinylmethyl)benzene (20). To a stirred solution of 2.0 g (4.96 mmol) of borolane compound **14** in 20 mL of DME, 10 mL of ethyl alcohol and 20 mL of aqueous Na$_2$CO$_3$ (2 M) was added 2.4 g (4.96 mmol) of morpholinyl compound **19**. After the solution was purged with nitrogen for 20 min, 0.6 g (0.496 mmol) of tetrakis(triphenylphosphine)palladium(0) (Pd[P(Ph)$_3$]$_4$) was added. The reaction mixture was refluxed with vigorous

stirring under argon atmosphere for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was washed with brine and dried over MgSO$_4$. The crude product was purified by column chromatography to give 2.6 g (78.0%) of product **20** as white solid: R_f 0.20 (SiO$_2$, EtOAc/hexane = 1/4); ^{1}H-NMR (200 MHz, CDCl$_3$) δ (ppm) 0.88-0.99 (m, 12H), 1.25-1.61 (m, 16H) 1.74 (m, 2H), 2.40 (br, 4H), 2.53 (br, 4H), 3.45 (s, 2H), 3.59 (s, 2H), 3.65-3.70 (m, 8H), 3.89 (d, 2H, J = 5.9 Hz), 3.92 (d, 2H, J = 6.2 Hz), 6.99 (d, 2H, J = 8.8 Hz), 7.09 (s, 1H), 7.25 (s, 1H), 7.39 (d, 2H, J = 8.1 Hz), 7.57 (d, 4H, J = 8.4 Hz); ^{13}C-NMR (125 MHz, CDCl$_3$) δ (ppm) 11.43, 11.61, 14.41, 14.44, 23.36, 23.39, 24.16, 24.39, 29.38, 29.48, 30.82, 31.05, 39.68, 39.91, 53.63, 53.79, 56.67, 60.59, 67.32, 67.39, 70.62, 70.82, 112.74, 115.11, 126.37, 127.31, 127.52, 128.24, 130.40, 132.88, 133.31, 134.37, 139.36, 139.76, 157.05, 159.28.

Synthesis of 1,4-Bis[(acetyloxy)methyl]-2-[(2-etylhex-yl)oxy]-5-(4-[4-[(2-etylhexyl)oxy]phenyl]phenyl)benzene (21). A stirred solution of 2.6 g (3.87 mmol) of compound **20** in 100 mL acetic anhydride was refluxed for 80 h. After the solvent was removed by evaporation under reduced pressure, the residue was diluted with ethyl acetate and water. The organic phase was washed with brine and dried over MgSO$_4$. The crude product was purified by column chromatography to give 1.5 g (61.4%) of product **21**: R_f 0.30 (SiO$_2$, CH$_2$Cl$_2$/hexane = 1/1)]; ^{1}H-NMR (200 MHz, CDCl$_3$) δ (ppm) 0.89-0.99 (m, 12H), 1.21-1.67 (m, 16H) 1.74 (m, 2H), 2.09 (s, 6H), 3.90 (d, 2H, J = 5.5 Hz), 3.95 (d, 2H, J = 5.1 Hz), 5.07 (s, 2H) 5.19 (s, 2H), 7.00 (d, 2H, J = 9.2 Hz), 7.02 (s, 1H), 7.31 (s, 1H), 7.36 (d, 2H, J = 8.1 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.59 (d, 2H, J = 7.7 Hz); ^{13}C-NMR (125 MHz, CDCl$_3$) δ (ppm) 11.41, 11.50, 14.37, 14.39, 21.29, 21.34, 23.33, 23.35, 24.15, 24.26, 29.37, 29.41, 30.82, 30.90, 39.67, 39.75, 61.94, 64.82, 70.60, 70.81, 112.50, 115.12, 124.79, 126.77, 128.29, 130.00, 131.70, 133.14, 134.39, 134.59, 138.43, 139.99, 156.77, 159.35, 171.07, 171.20

Synthesis of 1,4-Bis(bromomethyl)-2-[(2-etylhexyl)-oxy]-5-(4-[[4-(2-etylhexyl)oxy]phenyl]phenyl)benzene (22). To a stirred solution of 1.5 g (2.37 mmol) of acetylated compound **21** in methylene chloride at room temperature under argon atmosphere 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 1.1 g (68.8%) of product **22**: R_f 0.40 (SiO$_2$, EtOAc/hexane = 1/20); ^{1}H-NMR (200 MHz, CDCl$_3$) δ (ppm) 0.93-1.02 (m, 12H), 1.26-1.66 (m, 16H) 1.71-1.85 (m, 2H), 3.90 (d, 2H, J = 5.9 Hz), 4.00 (d, 2H, J = 5.1 Hz), 4.48 (s, 2H) 4.55 (s, 2H), 7.00 (d, 2H, J = 8.4 Hz), 7.03 (s, 1H), 7.27 (s, 1H), 7.47 (d, 2H, J = 8.1 Hz), 7.58 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.1 Hz); ^{13}C-NMR (125 MHz, CDCl$_3$) δ (ppm) 11.42, 11.58, 14.40, 14.41, 23.36, 24.16, 24.34, 28.54, 29.38, 29.41, 29.99, 30.83, 30.94, 32.68, 39.68, 39.81, 70.72,
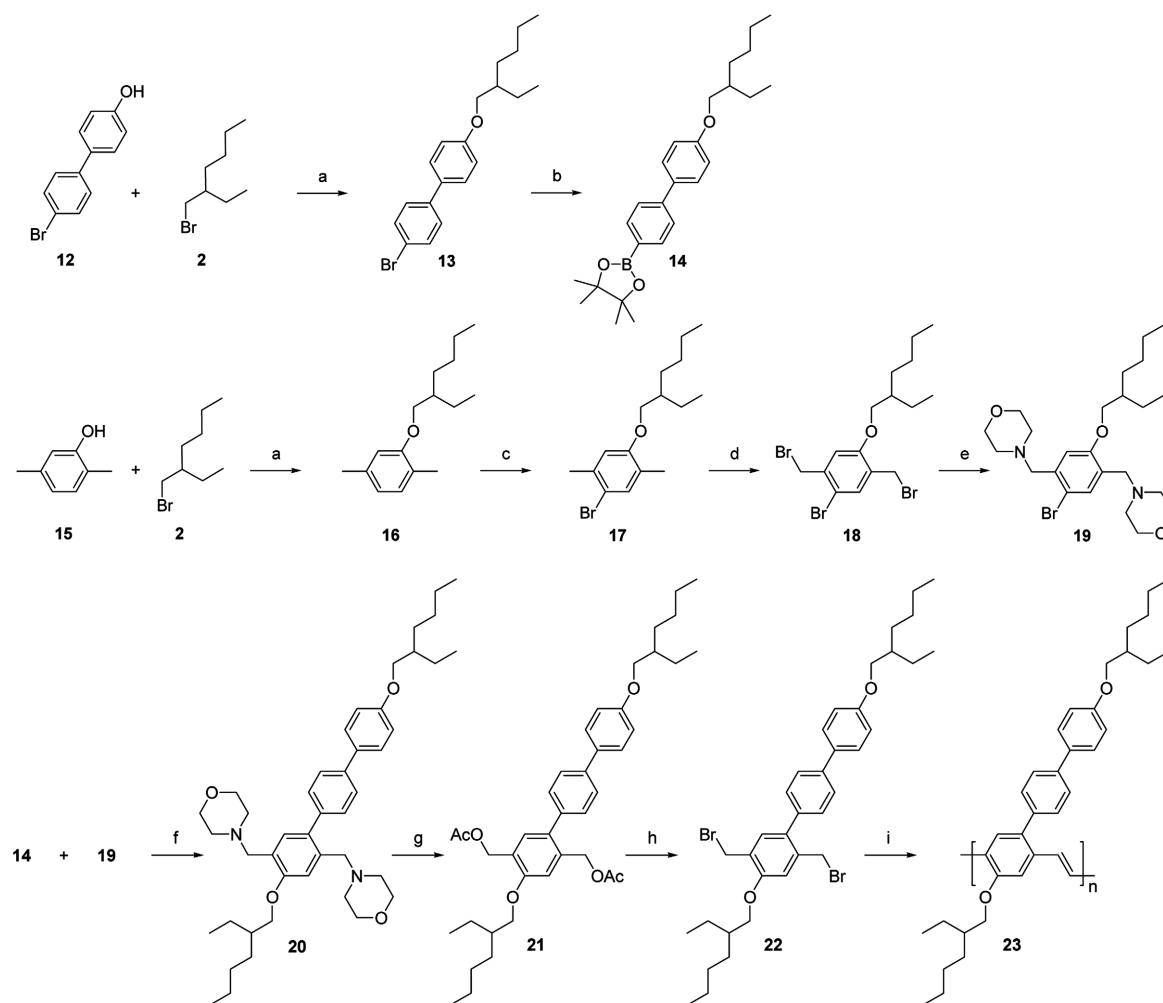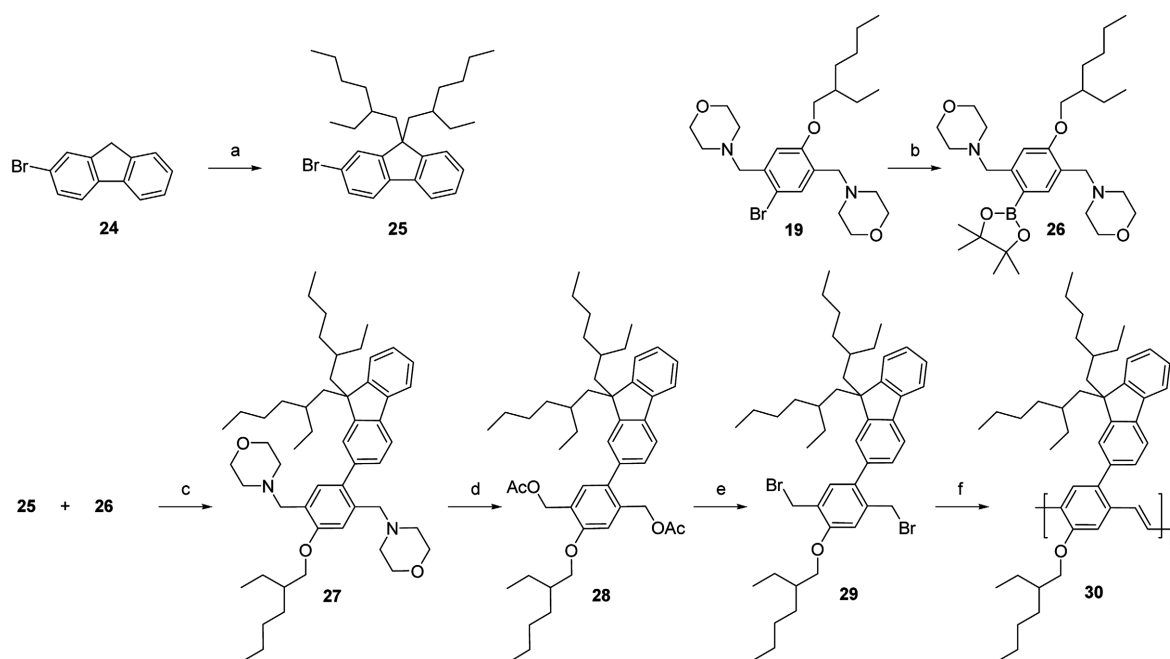
Scheme 2. Synthetic Routes for EEPP-PPV: (a) KOH, EtOH, reflux; (b) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C; (c) NBS, DMF; (d) NBS (2eq), *h*ν, CCl₄; (e) Morpholine, EtN(*i*-Pr)₂, THF; (f) Pd(PPh₃)₄, Na₂CO₃, DME, H₂O; (g) Ac₂O, reflux; (h) HBr, CH₂Cl₂; (i) *tert*-BuOK, THF

70.84, 113.64, 115.15, 126.85, 127.07, 128.29, 129.80, 132.95, 133.07, 134.21, 137.11, 137.99, 140.16, 156.82, 159.40.

Synthesis of Poly[2-(2-ethylhexyloxy)-5-(4-(4-(2-etyl-hexyloxy)phenyl)phenyl)-1,4-phenylenevinylene] (EEPP-PPV) (23). To a stirred solution of 0.55 g (0.818 mmol) of the monomer **12** in 50 mL of dry THF was added 4.9 mL (4.9 mmol) of the potassium *tert*-butoxide (1.0 M THF solution) using 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 and poured into 500 mL of methanol while 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 to give 300 mg of polymer **23** as orange fiber.

Synthesis of 2-Bromo-9,9-bis(2-ethylhexyl)-9*H*-fluor-

ene (25). A solution of 5 g (20.4 mmol) of 2-bromo-9H-fluorene (**24**) and catalytic amounts of triethylbenzyl-ammonium chloride in 40 mL of DMSO was stirred at 60 °C under nitrogen. After stirring for 1 h at 60 °C, the reaction mixture was treated with 9.46 g (48.96 mmol) of 2-ethylhexyl bromide (**2**), After additional 1 h at 60 °C, the reaction mixture was treated with 20 mL of 50% aqueous NaOH at room temperature and stirred for 5 h. An excess amount of ethyl acetate was added to the reaction mixture to generate the precipitation of NaOH. After filtering off NaOH formed, the organic layer was washed with 100 mL of aqueous 1.0 M HCl solution, and 150 mL of H₂O. The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by flash column chromato-graphy to give 9.1 g (95.0%) of dialkyl compound **25**: R_f 0.6 (SiO₂, hexane 100%); ¹H-NMR (200 MHz, CDCl₃): δ(ppm) 0.55-1.55 (m, 30H), 1.94 (d, 4H *J* = 4.8 Hz), 7.31-7.68 (m, 7H); ¹³C-NMR (125 MHz, CDCl₃) δ (ppm) 10.57, 10.72, 14.35, 14.42, 23.01, 23.09, 27.24, 27.40, 28.36, 28.46, 33.93, 33.97, 34.92, 44.69, 44.82, 55.44, 119.88, 120.63, 121.11, 124.28, 127.08, 127.12, 127.51, 129.97, 140.36,

Scheme 3. Synthetic Routes for EHF-PPV: (a) KOH, EtOH, reflux; (b) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C; (c) Pd(PPh₃)₄, Na₂CO₃, DME, H₂O; (d) Ac₂O, reflux; (e) HBr, CH₂Cl₂; (f) *tert*-BuOK, THF

140.46, 150.17, 152.95.

Synthesis of 4-[2-[(2-Ethylhexyl)oxy]-4-(4-morpholinyl-methyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzyl]morpholine (26). 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 **19** in 50 mL of dry THF at −78 °C under argon atmosphere 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 dropwise 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 obtained yellow residue was purified by column chromatography to provide 5.96 g (76%) of the desired borolane product **26** as yellow oil: R_f 0.3 (SiO₂, EtOAc/hexane = 1/4); ¹H-NMR (200 MHz, CDCl₃) δ(ppm) 0.87-1.98 (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); ¹³C-NMR (125 MHz, CDCl₃) 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-[5-[9,9-Bis(2-ethylhexyl)-9H-fluoren-2-yl]-2-[(2-ethylhexyl)oxy]-4-(4-morpholinylmethyl)benzyl]-morpholine (27). To a stirred solution of 2.7 g (4.07 mmol) of borolane compound **26** in 20 mL of DME, 10 mL of ethyl alcohol and 20 mL of aqueous Na₂CO₃ (2 M) at room temperature was added 2.5 g (5.32 mmol) of fluorene compound **25**. After the solution was purged with argon for 20 min, 0.46 g (0.4 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 MgSO₄. The crude product was purified by column chromatography to give 2.56 g (79.3%) of product **27** as white solid: R_f 0.30 (SiO₂, EtOAc/hexane = 1/4)]; ¹H-NMR (200 MHz, CDCl₃) δ(ppm) 0.47-1.76 (m, 45H), 1.97 (d, 4H, *J* = 4.76 Hz), 2.37 (br, 4H), 2.52 (br, 4H), 3.43 (s, 2H), 3.57 (s, 2H), 3.68 (br, 8H), 3.93 (d, 2H, *J* = 5.13 Hz), 7.14-7.38 (m, 6H), 7.66-7.71 (m, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ (ppm) 10.50, 10.95, 11.71, 14.39, 14.44, 14.53, 23.04, 23.17, 23.48, 24.49, 26.96, 27.45, 28.46, 28.81, 29.57, 31.13, 33.90, 34.03, 34.35, 34.93, 39.99, 45.04, 45.28, 53.80, 55.19, 56.80, 60.49, 67.46, 70.68, 112.21, 119.14, 119.73, 120.57, 124.22, 125.49, 126.58, 126.96, 128.75, 132.65, 135.11, 135.55, 139.55, 140.09, 141.28, 150.58, 150.65, 156.96.

Synthesis of 4-[(Acetyloxy)methyl]-2-[9,9-bis(2-ethyl-hexyl)-9H-fluoren-2-yl]-5-[(2-ethylhexyl)oxy]benzyl acetate (28). A stirred solution of 2.46 g (3.10 mmol) of compound **27** in 50 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 MgSO₄. The crude product was purified by column chromatography to give 1.2 g (52.3%) of product **28**: R_f 0.35 (SiO₂, EtOAc/Hex = 1/10); ¹H-NMR (200 MHz, CDCl₃) δ(ppm) 0.46-1.78 (m, 45H), 1.98 (d, 4H, *J* = 5.13 Hz), 2.08 (s, 6H), 3.95 (d, 2H, *J* = 5.13 Hz), 5.04 (s, 2H), 5.18 (s, 2H), 7.02 (s, 1H), 7.25-7.39 (m, 6H), 7.70 (d, 2H, *J* = 7.33 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ (ppm) 10.05, 10.27, 11.21, 13.93, 13.96, 14.06, 20.92, 21.10, 22.65,

22.73, 23.04, 24.00, 26.62, 26.93, 28.08, 28.35, 29.13, 30.63, 31.57, 33.60, 33.90, 34.55, 34.60, 39.49, 44.68, 44.83, 54.92, 61.76, 64.36, 70.35, 112.17, 119.24, 119.63, 124.04, 124.38, 125.07, 126.51, 126.78, 128.13, 131.31, 134.46, 135.11, 138.03, 140.41, 140.90, 150.46, 150.64, 156.40, 170.59, 170.81.

Synthesis of 2-[2,5-Bis(bromomethyl)-4-[(2-ethylhexyl)oxy]phenyl]-9,9-bis(2-ethylhexyl)-9*H*-fluorene (29). To a stirred solution of 700 mg (0.95 mmol) of acetylated compound **28** in methylene chloride at room temperature under argon atmosphere 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 680 mg (91.7%) of product **29**: R_f 0.25 (SiO_2, Hex 100%); ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 0.53-1.67 (m, 44H), 1.85 (m, 1H), 2.04 (d, 4H, $J = 4.88$ Hz), 4.03 (d, 2H, $J = 5.37$ Hz), 4.58 (s, 2H), 5.30 (s, 2H), 7.06 (s, 1H), 7.25-7.49 (m, 6H), 7.76 (t, 2H, $J = 7.81$ Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 10.07, 10.38, 11.24, 13.93, 13.99, 14.05, 22.63, 22.80, 23.02, 24.06, 26.55, 26.65, 27.05, 28.07, 28.39, 29.11, 30.66, 32.20, 33.55, 33.93, 34.63, 39.55, 44.78, 54.97, 70.51, 113.29, 119.40, 119.64, 124.02, 124.78, 126.55, 126.70, 126.77, 127.85, 132.62, 134.87, 136.85, 137.62, 140.60, 140.83, 150.56, 150.78, 156.44.

Synthesis of Poly[2-(2-ethylhexyloxy)-5-(9,9-bis(2-etylhexyl)-fluorene-2-yl)-1,4-phenylenevinylene] (EHF-PPV) (30). To a stirred solution of 500 mg (0.64 mmol) of the monomer **29** in 50 mL of dry THF at room temperature was added 3.8 mL (3.8 mmol) of potassium *tert*-butoxide (1.0 M THF solution) at a rate of 3.8 mL/h using a syringe pump. 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, and poured into 500 mL of methanol while 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 to generate 250 mg sample of polymer **30** was obtained as yellow fiber

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1, 2 and 3. For the preparation of BEHP-PPV (**11**), as shown in Scheme 1, the commercially available 4-bromophenol (**1**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol to provide 1-bromo-4-[(2-ethylhexyl)oxy]benzene (**3**). In second step, the compound **3** was coupled with the commercially available 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane using

n-butyl lithium in THF to generate the borolane compound **4**. Another starting material, the commercially available 1,4-dibromo-2,5-dimethylbenzene (**5**) was brominated with NBS and light source (300W) in CCl_4 to afford bromide compound **6**, which was converted to morpholine compound **7** by treatment with morpholine in diisopropyletylamine.[32] The resulting compound **7** was coupled with previously prepared compound **4** using tetrakis(triphenylphosphine) palladium catalyst and sodium carbonate in DME and water by Suzuki coupling.[33] This coupled compound **8** was acetylated with acetic anhydride, and brominated with HBr in methylene chloride to generate monomer **10**.[34] The polymer, BEHP-PPV (**11**), was prepared by the Gilch reaction, with the monomer **10**, and an excess amount of potassium *tert*-butoxide in THF at room temperature for 24 h under argon atmosphere. For the preparation of EEPP-PPV (**23**), as shown in scheme 2, the commercially available 4-bromo-4'-hydroxybiphenyl (**12**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol to provide compound **13**. The compound **13** was coupled with the commercially available 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane using *n*-butyl lithium in tetrahydrofuran (THF) to generate borolane compound **14**. Another starting material, the commercially available 2-hydroxy-p-xylene (**15**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol to afford 2-[(2-ethylhexyl)oxy]-1,4-dimethylbenzene (**16**), which was brominated at the para position from the alkoxy group by treatment with NBS in DMF. The resulting compound **17** was brominated again at the benzyl positions with NBS and light source (300W) in CCl_4 to afford bromide compound **18**, which was converted to morpholine compound **19** in diisopropylethylamine. The resulting compound **19** was coupled with previously prepared compound **14** using tetrakis(triphenylphosphine)-palladium catalyst and sodium carbonate in DME and water by Suzuki coupling. This coupled compound **20** was acetylated with acetic anhydride, and brominated with HBr in methylene chloride to generate monomer **22**. The polymer, EEPP-PPV (**23**), was prepared by the Gilch reaction, with the monomer **22**, and an excess amount of potassium *tert*-butoxide in THF at room temperature for 24 h under argon atmosphere. For the preparation of EHF-PPV (**30**), as shown in scheme 3, the commercially available 2-bromo-9H-fluorene (**24**) was chosen as the starting material and coupled with 2-ethylhexyl bromide (**2**) using sodium hydroxide and tetra-*n*-butyl ammonium bromide as phase transfer catalyst in DMSO. The previously prepared morpholine compound **19** was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and *n*-butyl lithium in THF to generate borolane compound **26**, which was coupled with previously synthesized fluorene compound **25** using tetrakis(triphenylphosphine)palladium catalyst and sodium carbonate in DME and water by Suzuki coupling. The coupled compound **27** was acetylated with acetic anhydride, and brominated with HBr in methylene chloride to generate monomer **29**. The polymer, EHF-PPV (**30**), was

Table 1. Polymerization results and thermal properties of BEHP-PPV, EEPP-PPV and EHF-PPV

Polymer	Yield (%)	$M_n{}^a$ ($\times 10^3$)	$M_w{}^a$ ($\times 10^3$)	PDI^a (M_w/M_n)	$T_g{}^b$ (°C)	$T_d{}^c$ (°C)
BEHP-PPV	53	12,000	41,000	3.2	–	350
EEPP-PPV	72	9,000	27,000	2.9	–	350
EHF-PPV	63	58,000	231,000	3.9	–	320

^{a}M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. ^{b}T_g was determined by DSC, but was not measured in the range of 50-300 °C and ^{c}T_d was measured at a temperature of 5% weight loss for the polymers by TGA.

prepared by the Gilch reaction, with the monomer **29**, and an excess amount of potassium *tert*-butoxide in THF at room temperature for 24 h under argon atmosphere.

The resulting BEHP-PPV, EEPP-PPV and EHF-PPV were soluble in organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and ODCB. The emissive polymer films were obtained by spin-casting an ODCB solution of the polymers. The results of polymerization of terphenyl-PPV derivatives are summarized in Table 1. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersities (PDI) of the resulting polymers were determined by gel permission chromatography. M_n, M_w, and PDI of these polymers were in the range of 9000-58000, 27000-231000, 2.9-3.9, respectively, as determined by GPC using THF as the eluant and polystyrene as the standard. The thermal properties of polymers were identified by TGA, and DSC thermograms. In the TGA thermograms, temperature of 5% weight loss for BEHP-PPV, EEPP-PPV and EHF-PPV was measured. The DSC data of polymers was obtained at heating increase rate of 10 °C/min under flowing nitrogen. The TGA data of the polymers exhibits high decomposition temperature (T_d) with decomposition starting above 320-350 °C, and glass transition temperature (T_g) was not measured in the range of 50-300 °C. 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.

Optical and Photoluminescence Properties. The UV-vis absorption spectra and photoluminescence spectra of BEHP-PPV, EEPP-PPV and EHF-PPV containing ter-phenyl units as thin films are shown in Figure 1 and Figure 2. The thin films were prepared by spin-coating on quartz plates from the polymer solutions in ODCB. The absorption spectrum of BEHP-PPV, EEPP-PPV and EHF-PPV exhibited maximum peaks at 436 nm, 462 nm, and 470 nm, which were contributed from π-π^* transition of the conjugated main chains, respectively. The maximum absorption peak of BEHP-PPV was more blue-shifted than EEPP-PPV and EHF-PPV. BEHP-PPV and EEPP-PPV exhibit additional strong absorption peak at 280-285 nm due to π-π^* transition of terphenyl units. EHF-PPV also exhibit additional two absorption peaks at 280 and 315 nm due to π-π^* transition of fluorene units. The absorption onset wavelengths of BEHP-PPV, EEPP-PPV and EHF-PPV were 510, 563, and 546 nm,
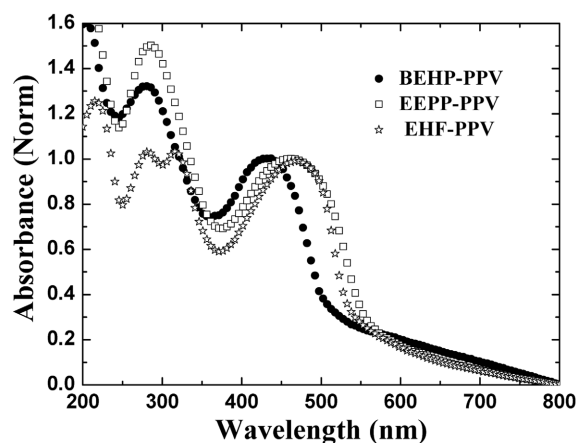
Figure 1. UV-vis absorption spectra of BEHP-PPV, EEPP-PPV and EHF-PPV in the solid state.
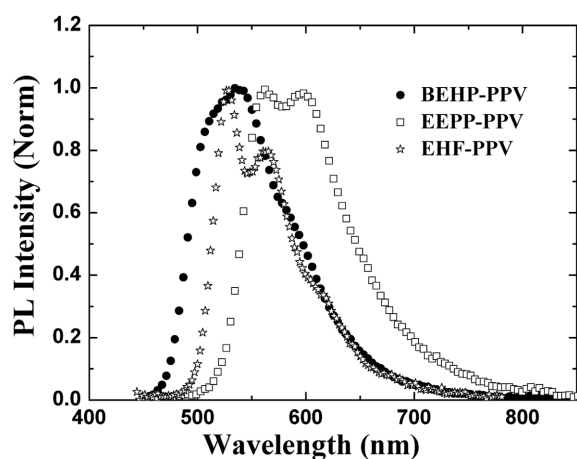
Figure 2. PL spectra of BEHP-PPV, EEPP-PPV and EHF-PPV in the solid state.

which correspond to band gaps of 2.43, 2.20 and 2.32 eV, respectively. Figure 2 shows emission spectra of the BEHP-PPV, EEPP-PPV and EHF-PPV thin films. The PL spectra of the polymers consist of a vibronically structured band comprising a maximum and shoulder. The PL spectrum of the BEHP-PPV thin film exhibits a maximum at 537 nm and a shoulder at 584 nm, and the PL spectrum of the EEPP-PPV thin film exhibits a maximum at 562 nm and a shoulder at 596 nm. BEHP-PPV was blue-shifted about 25 nm relative to the corresponding features measured from EEPP-PPV. The PL spectrum of the EHF-PPV thin film exhibits a maximum at 526 nm and two shoulders at 563 and 612 nm as the effect of fluorene units (exciting wavelength, 410 nm). The result demonstrates that the alkoxy group of EEPP-PPV, directly attached to the phenylene ring of PPV backbone, is generating red shift as compared to BEHP-PPV and EHF-PPV. The known BEH2P-PPV, BEH3P-PPV, and BEH3P-PPV[13] contain ortho substituent on the phenyl group attached to the phenylene ring of PPV. BEHP-PPV and EEPP-PPV which don't contain the ortho substituent on the phenyl group, show red-shifted maximum peaks of PL as compared to the case of BEH2P-PPV, BEH3P-PPV and
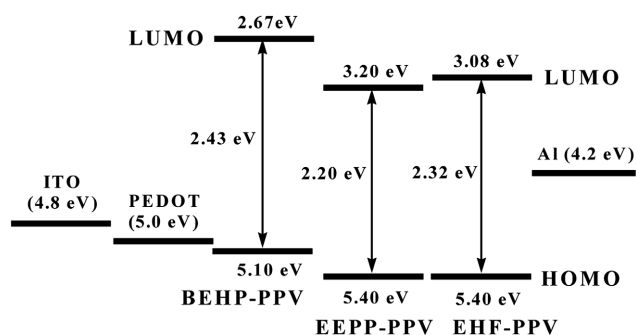
Figure 3. Energy band diagram of Polymers.

BEH3P-PPV. The λ_{max} values of BEH2P-PPV, BEH3P-PPV and BEH3P-PPV were at 502, 496, and 494 nm. In contrast to this, the λ_{max} values of BEHP-PPV and EEPP-PPV were at 537, and 562 nm. In case of BEH2P-PPV, BEH3P-PPV and BEH3P-PPV, the distortion of the phenyl ring by the ortho substituent was not increasing the effective conjugation lengths. As compared to this, in case of BEHP-PPV and EEPP-PPV, the biphenyl group of EEHP-PPV and two phenyl groups of BEPP-PPV were increasing the effective conjugation lengths.

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 (CV).[35] The CV was performed in a solution of tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm^2) coated with a thin polymer film was used as the working electrode. A Pt wire and a Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. All measurements were calibrated against an internal standard, ferrocene (F$_c$), which has the ionization potential value of the F$_c$/F$_c^+$ redox system.[36] Electrochemical properties of the polymers were measured to show that all of the polymers exhibit irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.7, 1.0, and 1.0 V for BEHP-PPV, EEPP-PPV and EHF-PPV, which correspond to HOMO energy level of 5.1, 5.4 and 5.4 eV, respectively. The LUMO energy levels of the polymers can be calculated with the HOMO and optical band gap. The LUMO energy levels of BEHP-PPV, EEPP-PPV and EHF-PPV were thus determined to be 2.67, 3.20, and 3.08 eV respectively.

Electroluminescent Properties and Current-Voltage-Luminance. The normalized electroluminescence spectra and the current-voltage-luminescence characteristics of the ITO/PEDOT/polymers/Al device are shown in Figure 4 and Figure 5. To decrease the operating voltage and smooth the surface roughness of the indium tin oxide (ITO) electrode, the hole injection-transport layer, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS), was spin-coated from aqueous solution with isopropyl

alcohol (10 wt %) on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin-casting a 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 the aluminum electrode were deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below about 10^{-6} mbar, yielding an active area of 4 mm^2. The forward bias current was obtained when the ITO electrode was positively biased and the aluminum electrode was negative.

Figure 4 shows the EL spectra of ITO/PEDOT/polymers/ Al devices. The EL spectra of BEHP-PPV, EEPP-PPV, and EHF-PPV show maximum peaks at 527, 553 and 526 nm, which correspond to yellow, orange and yellow light, respectively. These features are similar to those observed in the PL spectra of the corresponding polymer films. Both of EEPP-PPV and BEHP-PPV have same terphenyl units, but EEPP-PPV, with alkoxy group directly attached to the PPV backbone, has longer effective conjugation length than BEHP-PPV, and exhibits red shift in the EL spectrum. Both of EHF-PPV and EEPP-PPV have terphenyl units and directly substituted alkoxy group in back bone. In case of EHF-PPV, the 9,9-bis(2-ethylhexyl)fluorenyl unit, where alkyl chains are out of plane from the fluorene residue, was incorporated into the parent PPV backbone. EHF-PPV, with dialkylated fluorene unit substituted on the PPV backbone, contains one kind of terphenyl unit and directly substituted alkoxy group in the backbone. This dialkylated fluorenyl unit of EHF-PPV, as compared to the bi-phenyl unit of EEPP-PPV, shortened the effective conjugated length of EHF-PPV as compared to EEPP-PPV.

The current density-voltage and luminescence-voltage characteristics of ITO/PEDOT/polymers/Al devices are shown in Figure 5. The turn-on voltages of ITO/PEDOT/ polymer/Al devices are all about 5 V. The luminescence intensities of BEHP-PPV, EEPP-PPV, and EHF-PPV are exponentially increased with an increase of voltage.

The EL efficiency of BEHP-PPV, EEPP-PPV and EHF-PPV are 0.025, 0.007, and 0.081 cd/A, respectively as being
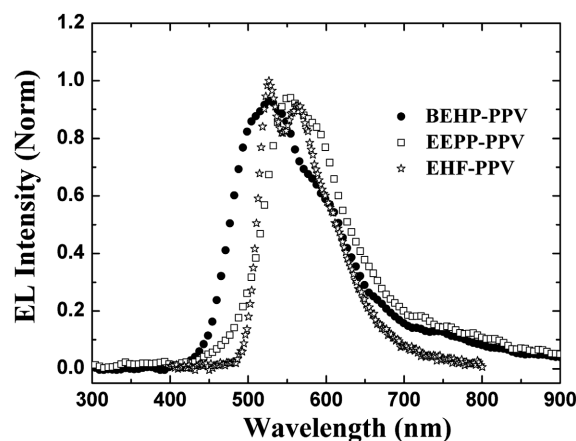

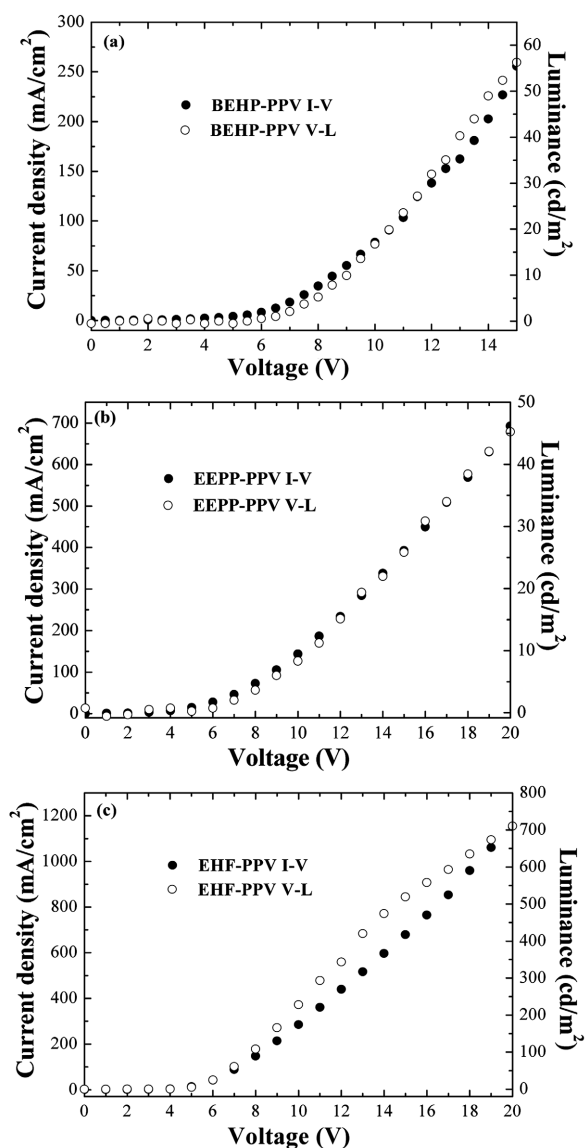**Figure 4**. EL spectra of BEHP-PPV, EEPP-PPV and EHF-PPV with a configuration of ITO/PEDOT:PSS/ polymer/Al.

Figure 6. Efficiency of PLEDs of BEHP-PPV, EEPP-PPV and EHF-PPV with a configuration of ITO/PEDOT:PSS/polymer/Al.

Conclusion

We have synthesized, new conjugated polymers, BEHP-PPV, EEPP-PPV and EHF-PPV containing terphenyl units by the Gilch polymerization. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersities (PDI) of these polymers were in the range of 9000-58000, 27000-231000, 2.9-3.9, respectively. These polymers have quite good thermal stability with decomposition starting above 320-350 °C.

BEHP-PPV, EEPP-PPV and EHF-PPV exhibited maximum absorption peaks at 436 nm, 462 nm, and 470 nm, maximum PL peaks at 537, 562, and 525 nm, maximum EL peaks at 527, 552, and 526 nm, and EL efficiencies of 0.025, 0.007 and 0.081 cd/A, respectively. The turn-on voltages of the polymers are about 5.0 V. EEPP-PPV and BEHP-PPV have ter-phenyl units, but EEPP-PPV with directly substituted alkoxy group in back bone has longer effective conjugation length as compared to BEHP-PPV, and exhibits red shift in the EL and PL spectra. In case of EHF-PPV, the 9,9-bis(2-ethylhexyl)fluorenyl unit, where alkyl chains are out of plane from the fluorene residue, was incorporated into the parent PPV backbone. This dialkylated fluorenyl unit of EHF-PPV, as compared to the bi-phenyl unit of EEPP-PPV, shortened the effective conjugated length of EHF-PPV. Even though all the efficiencies are not high, the efficiency of EHF-PPV is

Figure 5. Current-voltage-luminescence (I-V-L) characteristics of PLEDs of BEHP-PPV, EEPP-PPV and EHF-PPV with a configuration of ITO/PEDOT:PSS/polymer/Al.

shown in Figure 6. Even though all the efficiencies are not high, the efficiency of EHF-PPV is higher than the other two. Possibly this was caused by the higher molecular weight of EHF-PPV.
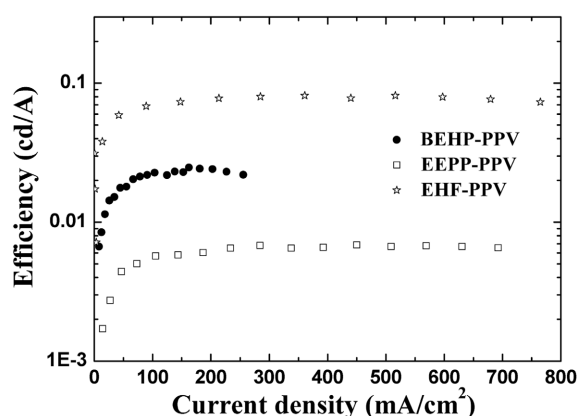
Table 2. Optical Properties and Device Performance Characteristics of BEHP-PPV, EEPP-PPV and EHF-PPV

Polymer	Abs (nm)[a]	PL λ_{max} (nm)[a]	EL λ_{max} (nm)	E_g (eV)[b]	HOMO (eV)[c]	LUMO (eV)	Turn-on (V)	LE_{max} (cd/A)[d]
BEHP-PPV	436	537	527	2.43	−5.10	−2.67	5	0.025
	280							(9.5 V)
EEPP-PPV	462	562	552	2.20	−5.40	−3.20	5	0.007
	285							(9 V)
EHF-PPV	470	526	526	2.32	−5.40	−3.08	5	0.081
	280, 315							(10 V)

[a]Determined from thin films on the quartz plate. [b]Calculated from the absorption spectra edges. [c]Determined from the onset of oxidative curve. [d]Maximum luminescence efficiency.

higher than the other two. Possibly this was caused by the higher molecular weight of EHF-PPV.

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