Synthesis and Electroluminescent Properties of Poly(*p*-phenylenevinylene)s with 3′,3′-Diheptyl-3,4-propylenedioxythiophene Pendant Group for Light-Emitting Diode Applications

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ABSTRACT: Using the Gilch polymerization method, we synthesized a new series of green electroluminescent polymer, poly[1,4-{2-(3,3′-diheptyl-3,4-propylenedioxythiophen-2-yl)}phenylenevinylene], poly(PDOT−PV), which is a series of fully conjugated poly(*p*-phenylenevinylene) derivatives with a propylenedioxythiophene (PDOT) moiety as a side-chain. We also synthesized copolymers, poly(PDOT−PV-*co*-*m*-SiPhPV), of poly(PDOT−PV) with poly[2-(3-dimethyldodecylsilyphenyl)-1,4-phenylenevinylene], poly(*m*-SiPhPV), segments. The resulting polymers were highly soluble in common organic solvents and could be easily spin-coated onto an indium−tin oxide coated glass substrate to obtain high quality optical thin films. The weight-average molecular weight (M_w) and polydispersity of poly(PDOT−PV) were 22.0 × 10^4 and 5.3, respectively, and those of poly(PDOT−PV-*co*-*m*-SiPhPV) were in the ranges (23.2−36.7) × 10^4 and 5.0−5.8, respectively. The stability of the resulting polymers is adequate for the fabrication of devices, and they provide longevity to devices because they have high glass transition temperatures (T_g). We fabricated polymer light-emitting diodes (PLEDs) in ITO/PEDOT/light-emitting polymer/cathode configurations using either double-layer LiF/Al or triple-layer Alq_3/LiF/Al cathode structures. For PLEDs containing poly(PDOT−PV) and poly(PDOT−PV-*co*-*m*-SiPhPV), the performance was highest using triple-layer cathodes. The turn-on voltages of PDOT-based light-emitting polymers were in the range of 6.0−9.0 V, and the maximum brightness and luminance efficiency were 5127 cd/m^2 at 18 V and 3.75 cd/A at 9 V.

Introduction

Since the discovery, by Burroughes et al., that poly(*p*-phenylenevinylene) (PPV) can be used as emitting materials in light-emitting diodes (LEDs), derivatives of PPV have been the most promising classes of conjugated polymers for use in LEDs due to their ability to form high molecular weight polymers with high luminance efficiencies.[1−6] Moreover, a variety of PPV derivatives have been used successfully in other devices, for example, in organic thin film transistors, active semiconductors, nonlinear optical devices, and photovoltaic cells as well as in electroluminescent devices. Therefore, PPV derivatives have become an important new area in polymer science.[7−9] In particular, PPV derivatives have been extensively studies for use as an emissive layer in polymer LEDs (PLEDs) because they have many attractive properties such as self-emission, low operating voltages, color stability, fast switching time, simple and low cost fabrication, and the potential to be used in full color flat panel and flexible displays.[10−12] Therefore, many studies have focused on the further improvement of the properties and synthesis of PPV derivatives.[13−15] The efficiency of a semiconductor device is determined by the amount of charge carrier injection, the probability of charge capture, and the balance between the injection rates of electrons and holes from opposite contacts into the device.[16−18] Therefore, to improve the luminance efficiency of PLEDs, many research groups have used a combination of electron transport materials, or they have attached electron transport moieties on the side chain of the polymer backbone or on the polymer main chain.[19−20] Recently, we used Gilch polymerization to synthesize a new chemically modified PPV-based homopolymer and copolymers containing a 1,3,4-oxadiazole derivative. These new polymers may improve PLED performance due to better electron injection and efficient energy transfer from the modified 1,3,4-oxadiazole side group to the PPV main chain.[21] Generally, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have

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many interesting properties, including stability in oxidized state, a low-band gap, a high electrochromic contrast, and a rapid switching time.[22,23] Moreover, the insertion of PEDOT doped with poly(styrenesulfonate) (PSS) for hole injection and as a transport layer in multilayer devices dramatically improves the lifetime and the luminance efficiency.[24,25] The poor solubility of 3,4-ethylenedioxythiophene (EDOT) and PEDOT, however, is a significant limitation to their practical use.[26,27] Another disadvantage of PEDOT:PSS is its acidic nature with pH values of 1.3−2.0, which causes etching of ITO, leading to damage of the emitting layer and device instability. Therefore, soluble PEDOT derivatives with transparency in the conducting state are sought for the fabrication of devices with improved properties. To solve these problems, we previously synthesized a new type of EDOT derivative, 3′3′-diheptyl-3,4-propylenedioxythiophene (PDOT). The resulting regiosymmetric polymer, poly(PDOT), had high solubility in common organic solvents and fairly good conductivity with low optical absorption in the visible region.[28] More recently, we reported the synthesis of a new series of statistical copolymers with poly(9,9-dialkylfluorenyl-2,7-vinylene), poly(FV), and highly luminescent poly[2-(3-dimethyldodecylsilylphenyl)-1,4-phenylenevinylene], poly(*m*-SiPhPV), using the Gilch polymerization method.[29−31] The introduction of the bulky dimethyldodecylsilylphenyl substitutents on the phenyl side group in the PPV backbone reduces the intermolecular interactions between the resulting polymer chains, which improves device performance.[32−35] In the present study, we used Gilch polymerization to generate a novel PPV-based homopolymer with a PDOT moiety as a side chain, poly[1,4-{2-(3′,3′-diheptyl-3,4-propylenedioxythiophen-2-yl)}-phenylenevinylene], poly(PDOT−PV), and statistical copolymers, poly(PDOT−PV-*co*-*m*-SiPhPV), with poly(*m*-SiPhPV) segments. These new polymers have good solubility and high molecular weights. We describe their thermal, optical, and electrochemical properties as well as their electroluminescent properties when used in PLEDs.

Experimental Section

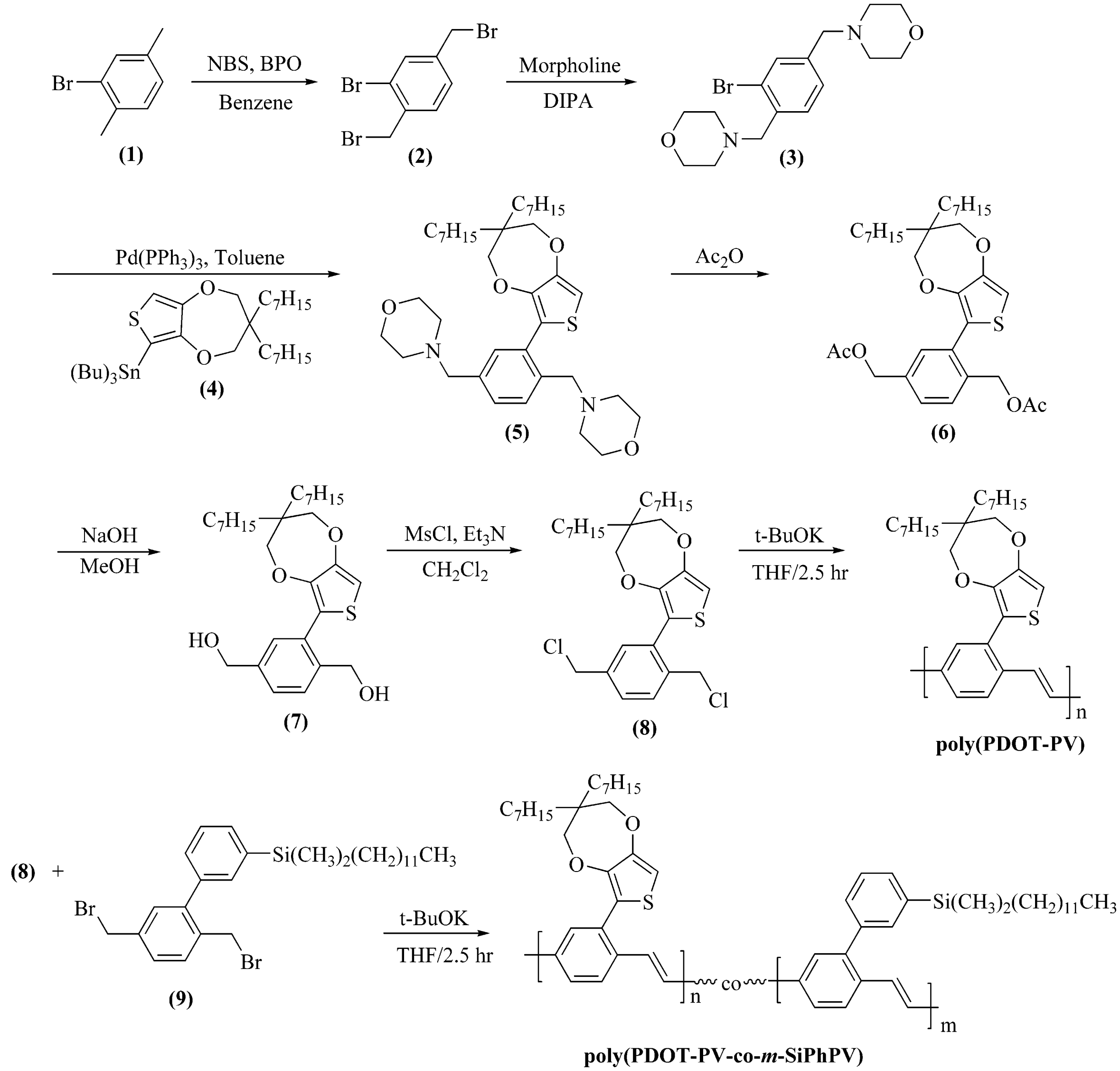
Materials and Characterization. All reagents were purchased from Sigma-Aldrich and were used without further purification. Solvents were purified by standard procedures and were handled under a moisture free atmosphere. Column chromatography was performed using silica gel (Merck, 250−430 mesh). 2-Tributylstannyl-3′,3′-diheptyl-3,4-propylenedioxythiophene was prepared as previously described.[28] The electro-optical properties of poly(*m*-SiPhPV) were measured in our previous report.[31] ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm units with chloroform as an internal standard. UV−visible spectra were recorded with a Shimadzu UV-3100 spectrophotometer with a baseline correction and normalization carried out using Microsoft Excel software. The emission spectra for dilute solutions were determined using a Hitachi F-4500 fluorescence spectrophotometer. Solid-state emission measurements were carried out by supporting each film on a quartz substrate that was mounted to receive front-face excitation at an angle of less than 45°. Each polymer film was excited with several portions of visible light from a xenon lamp. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851, DSC 822 analyzer under an N_2 atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 50−100 mV/s in 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. Each polymer film was coated on a Pt disk electrode (0.2 cm^2) by dipping the electrode into the polymer solution (10 mg/mL). A platinum wire was used as the counter electrode, and an $Ag/AgNO_3$ electrode was used as the reference electrode. All of the electrochemical experiments were performed in a glovebox under an Ar atmosphere at room temperature. To measure electroluminescence properties, the PLED was constructed as follows. Each glass substrate was coated with a transparent ITO electrode (80 nm thick, 20 Ω/sq sheet resistance), washed thoroughly in acetone, isopropyl alcohol, and distilled water, dried under nitrogen gas, heat dried, and finally treated with UV-ozone. The polymer films were prepared through spin-casting of polymer solution in concentration of 0.1 wt % in toluene. Uniform and pinhole free films with a thicknesses of approximately 100 nm were coated on a 30 nm layer of PEDOT:PSS layer (Baytron P Al4083) on the ITO substrate used as the hole injection and transport layer. The film thickness was measured with an α-Step IQ surface profiler (KLA Tencor, San Jose, CA). Tris(8-hydroxyquinoline)aluminum (Alq_3), LiF, and aluminum metal were deposited on top of each polymer film through a mask by vacuum evaporation at a pressure below 10^{-6} Torr, yielding an active area of 4 mm^2. To characterize the device, the current density−voltage-luminescence ($J-V-L$) changes were measured using a current/voltage source meter (Keithley 238) and an optical power meter (CS-1000, LS-100). All processes and measurements mentioned above were carried out in the open air at room temperature.

Synthesis of 2-Bromo-1,4-bis(bromomethyl)benzene (2). Into a 500 mL three-neck flask were added 2-bromo-1,4-dimethylbenzene **(1)** (10.0 g, 54.0 mmol), *N*-bromosuccinimide (NBS) (21.1 g, 0.12 mol), catalytic amounts of benzoyl peroxide (BPO), and 150 mL of benzene. The mixture was refluxed, and the reaction was verified by thin layer chromatography (TLC). The mixture was then cooled to room temperature, and the succinimide was removed by filtration. The mother liquor was poured into excess water and extracted twice with 40 mL of dichloromethane. The combined organic layer was washed twice with 30 mL of water, dried over anhydrous $MgSO_4$, and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by column chromatography on silica gel using hexane as an eluent to give **2** (12.1 g, 65%), mp 91.6 °C. ^{1}H NMR: δ (ppm) 4.40, 4.57 (s, 4H, CH_2Br on aromatic ring), 7.30−7.33 (d, 1H, aromatic proton), 7.41−7.43 (d, 1H, aromatic proton), 7.61 (s, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 31.3, 32.7, 124.4, 128.5, 131.4, 133.6, 137.0, 139.9. Anal. Calcd for $C_8H_7Br_3$: C, 28.03; H, 2.06. Found: C, 27.98; H, 2.03.

Synthesis of 4-[2-Bromo-4-(morpholinomethyl)benzyl]morpholine (3). A mixture of 12.0 g (35.0 mmol) of brominated compound **2**, morpholine (6.74 mL, 77.0 mmol), and diisopropylamine (10.8 mL, 77.0 mmol) in THF (60 mL) was reacted at room temperature for 20 h. Solvent was removed by evaporation under reduced pressure, and the reaction mixture was extracted twice with ethyl acetate (30 mL). The organic layer was purified by column chromatography on silica gel (hexane:ethyl acetate = 1:1) to give **3** (10.1 g, 81%), mp 90.7 °C. ^{1}H NMR: δ (ppm) 2.41−2.52 (d, 8H, $\mathrm{NC\underline{H_2}CH_2O}$), 3.43, 3.57 (s, 4H, CH_2N on aromatic ring), 3.69−3.72 (d, 8H, $\mathrm{NCH_2C\underline{H_2}O}$), 7.23−7.24 (d, 1H, aromatic proton), 7.38−7.41 (d, 1H, aromatic proton), 7.53 (s, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 53.2, 61.6, 62.0, 66.5, 66.6, 124.2, 127.5, 130.2, 132.7, 135.5, 138.4. Anal. Calcd for $C_{16}H_{23}BrN_2O_2$: C, 54.09; H, 6.53; N, 7.89; O, 9.01. Found: C, 53.58; H, 6.03; N, 7.50; O, 8.53.

Synthesis of 4-[2-(3′,3′-Diheptyl-3,4-propylenedioxythiophen-6-yl)-4-(morpholinomethyl)benzyl]morpholine (5). A solution of 4-[2-bromo-4-(morpholinomethyl)benzyl]morpholine **(3)** (5.60 g, 8.73 mmol) and 2-tributylstannyl-3′,3′-diheptyl-3,4-propylenedioxythiophene **(4)** (3.10 g, 8.73 mmol) in dry toluene (50 mL) was purged by the passage of nitrogen through the solution, and a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (5 mg) was added all at once. The reaction mixture was refluxed for 12 h and extracted twice with diethyl ether (30 mL). The organic layers were dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation under reduced pressure. The dark reaction

Scheme 1. Synthetic Routes for Monomer and Polymers



mixture was purified by column chromatography on silica gel (hexane:diethyl ether = 1:9) to give **5** (5.20 g, 96%). ^{1}H NMR: δ (ppm) 0.85−0.89 (t, 6H, 2CH$_3$), 1.17−1.42 (m, 24H, 12CH$_2$), 2.36−2.45 (d, 8H, $NC\underline{H_2}CH_2O$), 3.43−3.72 (m, 8H, CH$_2$N on aromatic ring, 2CH$_2$O), 3.82−3.89 (d, 8H, $NCH_2C\underline{H_2}O$), 6.45 (s, 1H, thiophene proton), 7.23 (s, 1H, aromatic proton), 7.25−7.26 (d, 1H, aromatic proton), 7.49−7.50 (d, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 14.0, 22.5, 22.7, 29.1, 30.3, 31.7, 31.9, 43.7, 53.4, 53.5, 60.0, 62.9, 66.9, 67.0, 103.0, 120.0, 128.6, 129.2, 132.1, 132.3, 136.0, 136.3, 145.3, 149.0. Anal. Calcd for $C_{37}H_{58}N_2O_4S$: C, 70.88; H, 9.32; N, 4.47. Found: C, 69.35; H, 9.44; N, 4.15.

Synthesis of 6-[2,5-Bis(acetoxymethyl)phenyl]-3′,3′-diheptyl-3,4-propylene dioxythiophene (6). The coupling compound **5** (5.20 g, 8.28 mmol) was dissolved in acetic anhydride (100 mL) and heated at reflux for 4 days. After the solvent was removed by evaporation under reduced pressure, the mixture was diluted with ethyl acetate (20 mL) and water (20 mL). The organic phase was separated and washed with brine and dried over anhydrous MgSO$_4$. The crude product was purified by column chromatography on silica gel (hexane:ethyl acetate = 2:1) to give **6** (2.30 g, 49%). ^{1}H NMR: δ (ppm) 0.84−0.89 (t, 6H, 2CH$_3$), 1.23−1.62 (m, 24H, 12CH$_2$), 2.10 (s, 6H, 2CH$_3$COO), 3.87, 3.89 (s, 4H, 2CH$_2$O), 5.10, 5.14 (s, 4H, CH$_2$OAc on aromatic ring), 6.45 (s, 1H, thiophene proton), 7.32 (s, 1H, aromatic ring), 7.36−7.37 (d, 1H, aromatic proton), 7.45−7.47 (d, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 14.1, 20.7, 22.7, 25.2, 29.3, 30.2, 31.8, 34.1, 65.5, 68.4, 77.3, 77.6, 94.8, 114.3, 127.3, 127.8, 128.7, 133.1, 136.3, 140.6, 147.7, 152.4, 170.2. Anal. Calcd for $C_{33}H_{48}O_6S$: C, 69.20; H, 8.45; O, 16.76; S, 5.60. Found: C, 70.42; H, 9.69; O, 17.23; S, 4.21.

Synthesis of 6-[2,5-Bis(hydroxymethyl)phenyl]-3′,3′-diheptyl-3,4-propylene dioxythiophene (7). A solution of 6-[2,5-bis-(acetoxymethyl)phenyl]-3′,3′-diheptyl-3,4-propylenedioxythiophene **(6)** (2.30 g, 4.02 mmol) in methanol (23 mL) and 1 N NaOH (10 mL) was refluxed for 2 h. The reaction mixture was cooled to room temperature, acidified with 2 N HCl, and extracted twice with ethyl acetate (20 mL). The organic layer was purified by column chromatography on silica gel (hexane:ethyl acetate = 2:1) to give **7** (1.96 g, 99%). ^{1}H NMR: δ (ppm) 0.84−0.89 (t, 6H, 2CH$_3$), 1.23−1.62 (m, 24H, 12CH$_2$), 3.87, 3.89 (s, 4H, 2CH$_2$O), 4.57, 4.70 (s, 4H, CH$_2$OH on aromatic ring), 6.45 (s, 1H, thiophene proton), 7.32 (s, 1H, aromatic ring), 7.36−7.37 (d, 1H, aromatic proton), 7.45−7.47 (d, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 14.1, 22.7, 25.2, 29.3, 30.2, 31.8, 34.1, 65.4, 68.3, 77.3, 77.6, 94.8, 114.3, 127.3, 127.8, 128.7, 133.1, 136.3, 140.6, 147.7, 152.4. Anal. Calcd for $C_{29}H_{44}O_4S$: C, 71.27; H, 9.07; O, 13.09; S, 6.56. Found: C, 70.98; H, 8.51; O, 14.23; S, 5.01.

Synthesis of 6-[2,5-Bis(chloromethyl)phenyl]-3′,3′-diheptyl-3,4-propylene dioxythiophene (8). To a dichloromethane (20 mL) solution of 6-[2,5-bis(hydroxymethyl)phenyl]-3′,3′-diheptyl-3,4-propylenedioxythiophene **(7)** (1.90 g, 3.89 mmol), triethylamine (1.57 g, 15.5 mmol), and methanesulfonyl chloride (1.34 g, 11.7 mmol) were added. The mixture was stirred for 4 days at room temperature. Water was added to this solution, and the product was extracted three times with ethyl acetate (20 mL). The organic layers

Table 1. Polymerization Results and Thermal Properties of Poly(PDOT−PV), Poly(PDOT−PV-*co*-*m*-SiPhPV), and Poly(*m*-SiPhPV)

polymer	feed ratio	M_w[a] (10^4)	PDI[a]	yield (%)	DSC (T_g)	TGA[b]
poly(PDOT−PV)	100:0	22.0	5.3	59	156	362
poly(PDOT−PV-co-*m*-SiPhPV) (73:27)[c]	66:33	31.2	5.0	75	154	377
poly(PDOT−PV-co-*m*-SiPhPV) (53:47)[c]	50:50	23.2	5.2	60	149	377
poly(PDOT−PV-co-*m*-SiPhPV) (34:66)[c]	33:66	36.7	5.8	75	142	376
poly(*m*-SiPhPV)	0:100	25.6	5.4	62	154	408

[a] M_w and PDI of the polymers were determined by GPC using polystyrene standards. [b] TGA was measured at temperature of 5% weight loss for the polymers. [c] Calculated from ^{1}H NMR.

were dried over anhydrous $MgSO_4$, filtered, and purified by column chromatography on silica gel (hexane:ethyl acetate = 10:1) to give **8** (1.80 g, 88%). ^{1}H NMR: δ (ppm) 0.85−0.88 (t, 6H, $2CH_3$), 1.25−1.42 (m, 24H, $12CH_2$), 3.86, 3.90 (s, 4H, $2CH_2O$), 4.58, 4.66 (s, 4H, CH_2Cl on aromatic ring), 6.51 (s, 1H, thiophene proton), 7.32 (s, 1H, aromatic ring), 7.39−7.42 (d, 1H, aromatic proton), 7.56−7.59 (d, 1H, aromatic proton). ^{13}C NMR: δ (ppm) 14.1, 22.6, 22.8, 29.2, 30.4, 31.8, 32.0, 43.9, 44.0, 45.5, 104.0, 118.1, 128.6, 130.3, 131.7, 132.3, 137.1, 137.4, 145.9, 149.2. Anal. Calcd for $C_{29}H_{42}Cl_2O_2S$: C, 66.27; H, 8.05; Cl, 13.49; O, 6.09; S, 6.10. Found: C, 67.02; H, 7.59; Cl, 12.12; O, 4.92; S, 5.02.

Synthesis of Poly[1,4-{2-(3,3′-diheptyl-3,4-propylenedioxythiophen-2-yl)}phenylenevinylene], Poly(PDOT−PV), Using the Gilch Reaction. To a stirred solution of 6-[2,5-bis(chloromethyl)phenyl]-3′,3′-diheptyl-3,4-propylenedioxythiophene **(8)** (0.2 g, 0.38 mmol) in dry THF (20 mL) at 0 °C under N_2 atmosphere was gradually added 2.5 mL of 1.0 M potassium *tert*-butoxide in THF using a syringe pump over a 30 min period. During this addition, the reaction mixture changed from colorless to greenish, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. The polymer was sequentially end capped with a small amount of 4-*tert*-butylbenzyl bromide for 1 h. The polymerization solution was poured into methanol (400 mL), and the crude polymer was Soxhlet-extracted with methanol to remove the impurities and oligomers. After the standard polymer purification procedures were carried out, the solution of the polymer in chloroform was dialyzed against chloroform for 5 days with stirring to remove the medium molecular weight fraction. The resulting purified polymer was reprecipitated in methanol, filtered, and vacuum-dried to give a bright greenish yellow polymer fiber, poly(PDOT−PV) (0.1 g, 59%). ^{1}H NMR: δ (ppm) 0.79−0.81 (br, 6H, $2CH_3$), 0.18−1.54 (br, 24H, $12CH_2$), 3.73−3.87 (br, 4H, $2CH_2O$), 6.53 (br, 1H, thiophene proton), 7.14−7.60 (br, 5H, aromatic proton and vinylic protons). Anal. Calcd for $C_{29}H_{40}O_2S$: C, 76.94; H, 8.91; O, 7.07; S, 7.08. Found: C, 76.24; H, 9.02; O, 7.06; S, 7.05.

Synthesis of Poly[1,4-{2-(3,3′-diheptyl-3,4-propylenedioxythiophen-2-yl)}phenylenevinylene]-*co*-(2-(3-dimethyldodecylsilyphenyl)-1,4-phenylenevinylene)], Poly(PDOT−PV-*co*-*m*-SiPhPV), (50:50 mol %). To a stirred solution of 6-[2,5-bis(chloromethyl)phenyl]-3′,3′-diheptyl-3,4-propylenedioxythiophene **(8)** (0.12 g, 0.19 mmol) and 1,4-bis(bromomethyl)-2-(3-dimethyldodecylsilylphenyl)benzene **(9)** (1.0 g, 0.19 mmol) in dry THF (20 mL) at 0 °C under N_2 atmosphere was gradually added 1.0 M potassium *tert*-butoxide in THF (2.5 mL) using a syringe pump over a 30 min period. The reaction and purification methods for polymerization were similar to those used for poly(PDOT−PV). The copolymer, poly(PDOT−PV-co-*m*-SiPhPV), with various feed ratios of comonomers was synthesized using a method similar to that for poly(PDOT−PV-co-*m*-SiPhPV) (50:50 mol %). The composition ratios of the polymers were calculated from the integration ratios of the 0.70−0.98 and 3.70−4.05 ppm peaks in the ^{1}H NMR spectra. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.27 (br, 6H, $Si(CH_3)_2$), 0.70−0.98 (m, 11H, $SiCH_2$ and $-3CH_3$), 0.90−1.48 (m, 44H, $(CH_2)_{10}$ and $2(CH_2)_6$), 3.70−4.05 (br, 4H, $2CH_2O$), 6.45−6.60 (br, 1H, thiophene proton), 7.00−7.80 (br, 14H, aromatic protons and vinylic protons). Anal. Calcd for $(C_{57}H_{80}O_2SSi)_n$: C, 79.66; H, 9.37; S, 3.95. Found: C, 79.67; H, 9.26; S, 3.83.

Results and Discussion

Synthesis and Characterization. The general synthetic routes leading to the monomer 6-[2,5-bis(chloromethyl)phenyl]-3′,3′-diheptyl-3,4-propylenedioxythiophene (**8**), the corresponding polymer, poly(PDOT−PV), and its copolymers, poly(PDOT−PV-*co*-*m*-SiPhPV), are outlined in Scheme 1. Commercially available 2-bromo-1,4-dimethylbenzene **(1)** was brominated with NBS and a catalytic amount of BPO in benzene. The resulting bromide **2** was reacted with morpholine in diisopropylamine to generate morpholine compound **3**, which was coupled with previously prepared PDOT derivative **4** using tetrakis(triphenylphosphine)palladium(0) in toluene by the Suzuki coupling reaction. The coupled compound **5** was acetylated with an excess of acetic anhydride and converted to the hydroxy compound **7** by refluxing in methanol with aqueous 1 N NaOH. The newly designed monomer **8** was prepared in good yield from the reaction of **7** with methanesulfonyl chloride in the presence of triethylamine. The homopolymerization of monomer **8** was performed by the Gilch polymerization with an excess of potassium *tert*-butoxide in THF in an ice bath under an N_2 atmosphere. In addition, we copolymerized with the monomer **8** and 1,4-bis(bromomethyl)-2-(3-dimethyldodecylsilylphenyl)benzene **(9)** at various feed ratios to improve the performance of PLEDs. During the polymerization, the reaction mixture became progressively more viscous and homogeneous without any detected precipitates, and it produced intense fluorescent light under UV illumination. A small amount of 4-*tert*-butylbenzyl bromide was added to the reaction mixture to end-cap the polymer chain and then the collected polymers were further purified by Soxhlet extraction through methanol and chloroform to remove the unreacted monomer, oligomers, and inorganic impurities. The structure and thermal properties of the polymers were identified by ^{1}H NMR spectroscopy, elemental analysis, TGA, and DSC thermograms.

The chloromethyl proton peaks of the monomer **8** in the ^{1}H NMR spectrum at 4.58 and 4.66 ppm disappeared during the polymerization, and a clear proton peak corresponding to the thiophene moiety appeared at 6.53 ppm along with new vinylic proton peaks at 7.0 ppm and an aromatic proton peaks. The other peaks were consistent with the proposed chemical structures of the polymer. The resulting polymers were highly soluble at room temperature in common organic solvents such as chloroform, THF, and toluene, producing bright green solutions, and were easily spin-coated onto a glass substrate. These properties can be attributed to the 3,3-diheptyl-3,4-propylenedioxythiophene and dimethyldodecylsilyl pendant groups in resulting polymers. Therefore, excellent solubility is one of the most attractive features of the resulting polymers, and this should greatly improve the ability to fabricate devices.

The polymerization results, molecular weights, and thermal properties of poly(PDOT−PV) and its copolymers, poly(PDOT−PV-*co*-*m*-SiPhPV) are summarized in Table 1. The GPC analysis revealed that the weight-average molecular weight (M_w) and polydispersity of poly(PDOT−PV) and poly(PDOT−

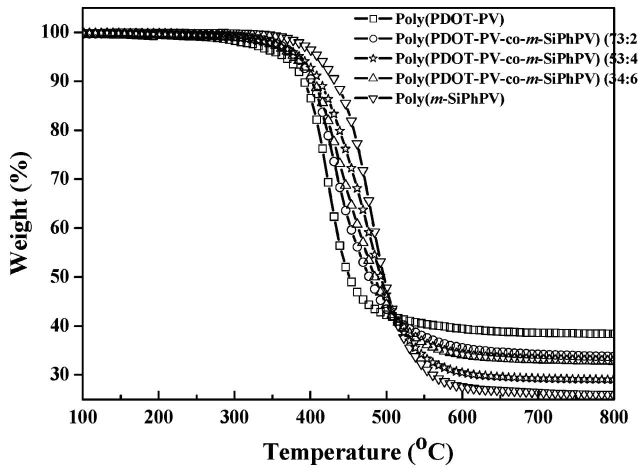


Figure 1. TGA thermogram of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV).

PV-*co*-*m*-SiPhPV) were found to be in the range of (22.0–36.7) $\times 10^4$ and 5.0–5.8, respectively. The actual molar ratios of poly(PDOT–PV) and poly(*m*-SiPhPV) in the copolymers were calculated by integration of ^{1}H NMR peak areas for the methylene protons next to silicon and the three terminal methyl protons with methylene protons next to oxygen in the thiophene substitutents.

The TGA results for poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) are shown in Figure 1. The TGA thermograms show that the polymers have high thermal stability, exhibiting 5% weight loss in an N_2 atmosphere at temperature between 362 and 376 °C. However this is lower than the thermal stability of poly(*m*-SiPhPV), which has bulky dimethyldodecylsilyl substituents on the phenyl side-group. This can be explained by the introduction of diheptyl side chains via ether linkage into the thiophene pendant group. The glass transition temperatures (T_g) of poly(PDOT–PV) and poly(PDOT–PV-*co*-*m*-SiPhPV) were found to be between 142 and 156 °C. These polymers had higher thermal stabilities than dialkyloxy-substituted PPVs or poly(9,9-dialkylfluorene)s.[36,37] The stability of the polymers is adequate for the fabrication of devices and the T_g values indicate that the polymer should not deform or degrade in an applied electric fields.

Optical, Electrochemical, and Electroluminescent Properties of the Polymers. We next measured the absorption and emission spectra of the polymer films spin-cast on quartz substrates from toluene solutions. The absorption spectra of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) in the film state are shown in Figure 2. The centers of the absorption maxima were at approximately 440 nm. There was little deviation in the peak maxima as the number of dimethyldodecylsilylphenyl units in poly(PDOT–PV-*co*-*m*-SiPhPV) was increased, but they were slightly red-shifted compared to that for poly(PDOT–PV). These results suggest that the presence of dimethyldodecylsilylphenyl units in the poly(PDOT–PV-*co*-*m*-SiPhPV) backbone improves the flexibility of the copolymer chains compared to the homopolymer because their highly branched side chains can provide a larger spatial probability and, therefore, conformational relaxation of the whole copolymer chains. Hence, the maxima of the UV–visible absorption spectra for the copolymers show marginal bathochromic shifts compared to the maxima for the homopolymers.

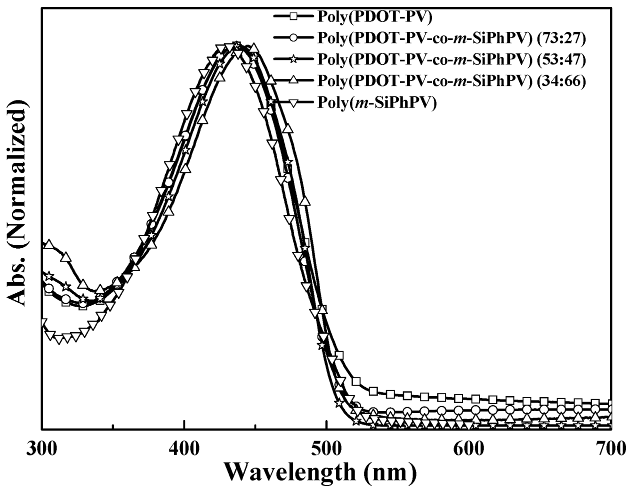


Figure 2. UV–visible absorption of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) in the solid state.

To investigate the charge carrier injection properties of the resulting polymers and evaluate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, we carried out redox measurements using cyclic voltammetry. The HOMO binding energies for the standard ferrocene/ferrocenium (4.8 eV) were 5.60–5.70 eV for the polymers. The band gaps of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV), obtained from the onsets of the absorption spectra, were 2.38–2.43 eV. The LUMO energy levels were calculated from the values of the band gaps and HOMO energies. The energy band diagrams of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV), are displayed in Figure 3, showing that the major carriers are the holes rather than the electrons due to the lower band offsets between the ITO and HOMO energy levels. As the poly(PDOT–PV) content increased, the HOMO energy levels of poly(PDOT–PV-*co*-*m*-SiPhPV) decreased relative to that of poly(*m*-SiPhPV), and the band offsets were 0.59–0.79 eV for hole injections at the interface of the PEDOT/HOMO state. This implies that the poly(PDOT–PV) segment facilitates the hole injection from the ITO electrodes. However, the LUMO energy levels of poly(PDOT–PV-*co*-*m*-SiPhPV) were slightly increased relative to that of poly(PDOT–PV), which the electrons are easily injected from the Al electrode. These results coincide well with the PLED performance of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV).

The photoluminescence (PL) emission spectra of poly(PDOT–PV), poly(PDOT–PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) in the thin film state are shown in Figure 4a. Notably, the PL spectra of poly(PDOT–PV) show significantly more pronounced vibronic structures than that for the previously reported phenyl-substituted PPV derivative.[38] On the other hand, there was a similar red shift in the PL emission maxima for films compared to solutions of the polymers.

The PL emission spectrum of poly(PDOT–PV) in Figure 4a shows two peaks centered at 511 and 542 nm as well as a weak shoulder centered at about 578 nm. This vibronic structure is also observed in the PL spectrum for poly(PDOT–PV) in solution. The energy values between these vibronic structures were, on average, approximately 160 meV, which is very similar to the value for the C–C double bond stretching mode. The PL emission peaks were slightly red-shifted, as was the case in the absorption spectra. As the poly(*m*-SiPhPV) content in poly(PDOT–PV-*co*-*m*-SiPhPV) was increased, the intensity of the shoulder peaks in the PL emission consistently increased. This may be due to the presence of an additional band that can superimposed on the mutual PL band, which can be observed as a more pronounced second vibronic band. Such an additional

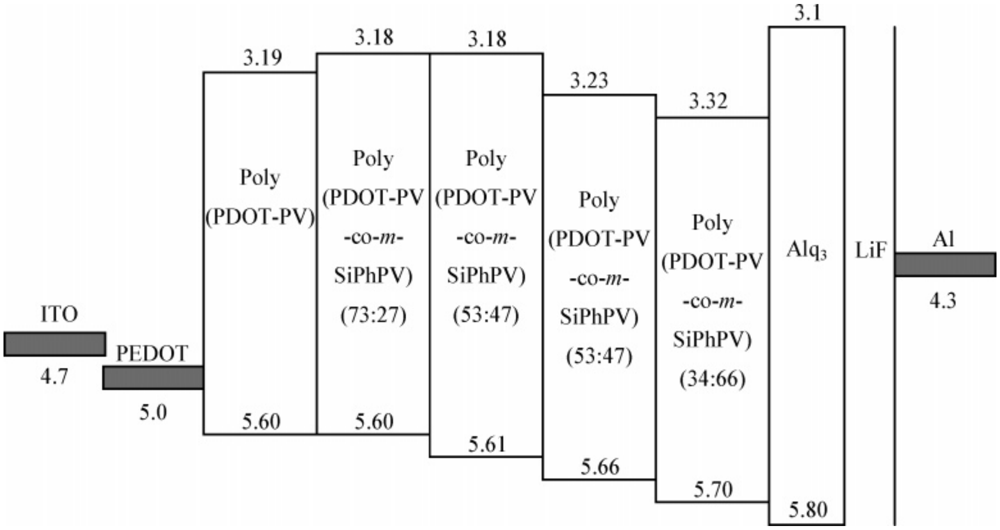


Figure 3. Hypothesized energy band diagram of ITO/PEDOT/light emitting polymer/Alq_3/LiF/Al device.

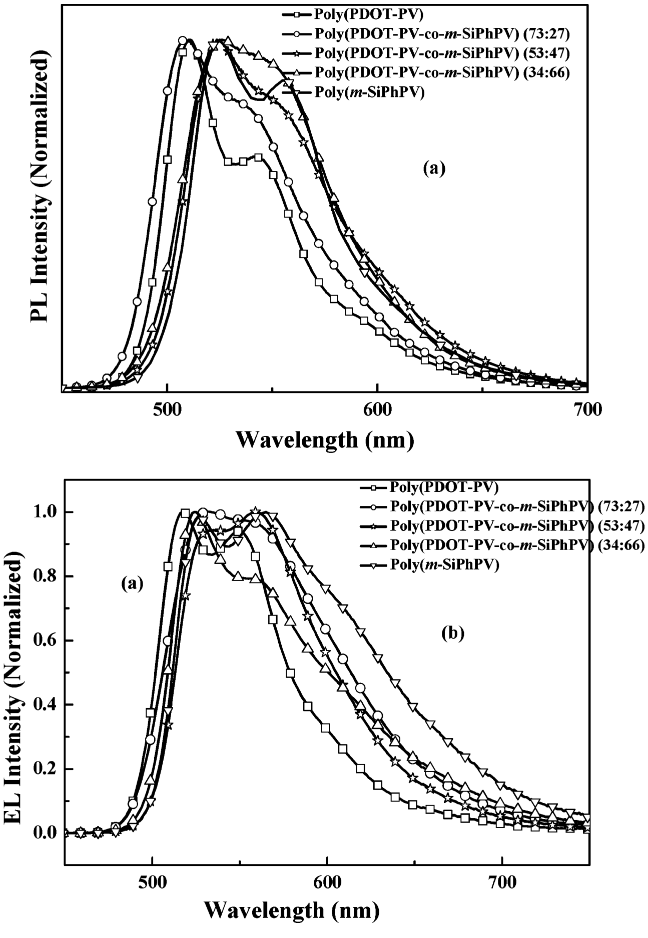


Figure 4. PL spectra (a) and EL spectra (b) of the ITO/PEDOT/light emitting polymer/Alq_3/LiF/Al device.

band feature might be due to the extended intermolecular interaction of the conjugated branches as previously reported for many thiophene derivatives pendant system.[39]

The EL spectra in Figure 4b also show vibronic structures, but the fine structures are somewhat less resolved, and the second vibronic bands are more extended than in the PL spectra. This extended trend in the EL spectra may be due to the effective charge carrier transport energy within a randomly disordered polymeric solid and subsequent charge carrier recombination from the most probable sites with those energies.[40]

The fluorescence quantum yield (Φ_{PL}) of the poly(PDOT−PV), poly(PDOT−PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) were determined to be 69−73% in a $CHCl_3$ solution relative to the 9,10-diphenylanthracene as a standard (Φ_{PL}: 91%).

We fabricated double-layered PLEDs with two different cathode structures based on poly(PDOT−PV), poly(PDOT−PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) and compared them with ITO/PEDOT:PSS/light-emitting polymer/cathodes. The cathodes were either bilayer of LiF (0.5 nm)/Al (200 nm) (cathode 1) or triple layer of Alq_3/LiF/Al (cathode 2) with a 15 nm Alq_3 layer between the emitting and electron injection layers as an electron transport layer for improved device performance.

Figure 4b shows the EL spectra of poly(PDOT−PV), poly(PDOT−PV-*co*-*m*-SiPhPV), and poly(*m*-SiPhPV) for cathode 2 devices. The EL spectra of the PLEDs were almost identical to their PL spectra as shown in Figure 4a. This confirms that the EL emission of cathode 2 devices originates in the light-emitting polymers and that the Alq_3 layer serves as an electron transport layer. The maximum emission peak of poly(PDOT−PV) was at 517 nm, with a shoulder peak at 549 nm. Also, poly(*m*-SiPhPV) exhibited bimodal peaks at 525 and 562 nm, which correspond to a bluish green color. The emission maximum of poly(PDOT−PV-*co*-*m*-SiPhPV) were located between the maxima for the homopolymers.

We next evaluated the device performance of bilayer and triple layer cathode structures and the results are tabulated in Table 2. The current density−voltage (*J*−*V*) characteristics of the ITO/PEDOT/light-emitting polymer/Alq_3/LiF/Al devices are shown in Figure 5a. The turn-on voltages of the bilayer and triple layer cathode structures are between 5.5 and 9.0 V, and devices containing poly(PDOT−PV-*co*-*m*-SiPhPV) (34:66 wt %) have the highest turn-on voltage. This is due to the higher energy barrier or band offset between the ITO and the HOMO state for polymers based on poly(PDOT−PV-*co*-*m*-SiPhPV) (34:66 wt %) than for those based on poly(PDOT−PV), which causes a drastic decreases in hole injection. The current density increased exponentially with the forward bias voltage, which is a typical diode characteristic. The luminescence−voltage (*L*−*V*) characteristics are shown in Figure 5b. The maximum luminescence of poly(PDOT−PV) and poly(PDOT−PV-*co*-*m*-SiPhPV) devices with a LiF/Al cathode were 674 and 2879 cd/m^2, respectively, which is much lower than that of poly(*m*-SiPhPV) devices. However, by inserting an Alq_3 layer as an electron transport layer between the light-emitting polymer and

Table 2. PLED Performance of Poly(PDOT−PV), Poly(PDOT−PV-*co*-*m*-SiPhPV), and Poly(*m*-SiPhPV)

polymer	cathode	turn-on (V)	L_{max}[a] (cd/m^2, V)	LE_{max}[b] (cd/A, V)
poly(PDOT−PV)	Alq_3/LiF/Al	6.0	1693 (17)	0.68 (9)
	LiF/Al	6.0	674 (18)	0.44 (9)
poly(PDOT−PV-co-*m*-SiPhPV) (73:27)	Alq_3/LiF/Al	6.0	3897 (18)	2.70 (11)
	LiF/Al	6.0	958 (21)	1.14 (11)
poly(PDOT−PV-co-*m*-SiPhPV) (53:47)	Alq_3/LiF/Al	6.0	5127 (18)	3.75 (9)
	LiF/Al	6.0	2879 (21)	2.81 (10)
poly(PDOT−PV-co-*m*-SiPhPV) (34:66)	Alq_3/LiF/Al	8.0	1889 (26)	3.13 (16)
	LiF/Al	9.0	1028 (29)	2.46 (16)
poly(*m*-SiPhPV)	Alq_3/LiF/Al	6.0	2544 (19)	2.35 (16)
	LiF/Al	5.5	6370 (20)	3.27 (13)

[a] Maximum luminescence. [b] Maximum luminance efficiency.

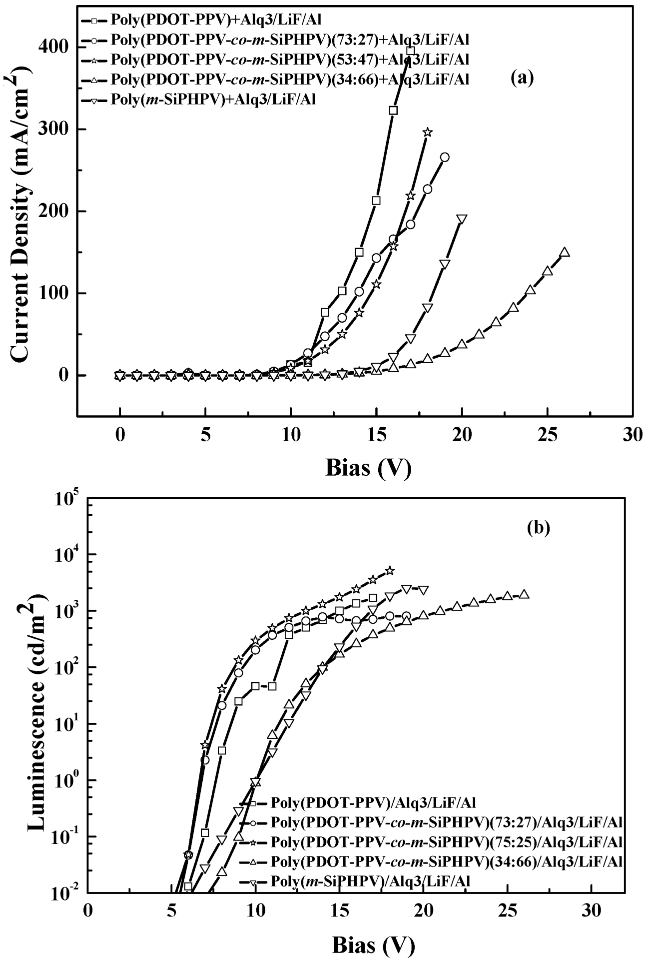


Figure 5. (a) Current density−voltage (*J*−*V*) and (b) luminescence−voltage (*L*−*V*) characteristic of the ITO/PEDOT/light-emitting polymer/Alq_3/LiF/Al devices.

the LiF layer, the maximum luminescence increased to 1693 and 5127 cd/m^2 for poly(PDOT−PV) and poly(PDOT−PV-*co*-*m*-SiPhPV) devices, which is higher than that of poly(*m*-SiPhPV).

The luminance efficiencies of the ITO/PEDOT/light-emitting polymer/cathode devices with triple layer (Alq_3/LiF/Al) cathodes are shown in Figure 6. The maximum luminance efficiency was found to be 3.75 cd/A with a triple layer (Alq_3/LiF/Al) cathode. The higher luminance efficiency of the triple layer cathode devices is attributed to their enhanced electron injection and transport, which results in efficient quenching of excitons into the light-emitting polymer. The results show that polymers synthesized in this study are promising light-emitting materials because of their high brightness and luminance efficiencies even at low operating voltages when used in Al cathode structures.

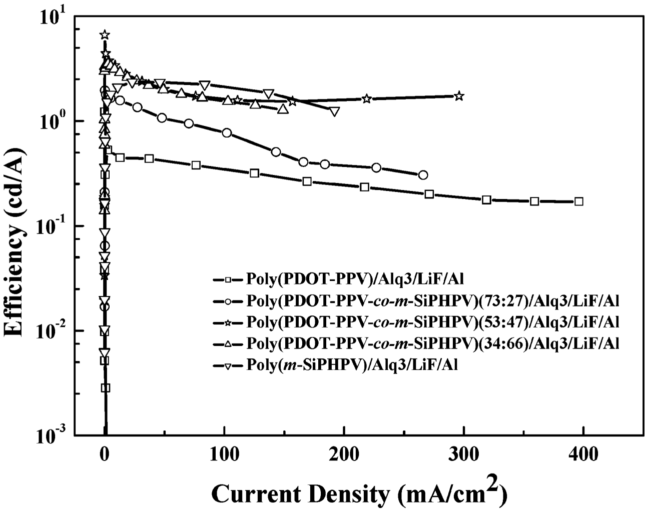


Figure 6. Luminous efficiency-current density curves of the ITO/PEDOT/light-emitting polymer/Alq_3/LiF/Al devices.

Conclusions

We synthesized and characterized a new series of soluble electroluminescent polymers based on poly(PDOT−PV), which has a propylenedioxythiophene (PDOT) moiety as a side chain, and its copolymers, poly(PDOT−PV-*co*-*m*-SiPhPV), containing various feed ratios of poly(*m*-SiPhPV) segments. The resulting polymers are highly soluble in common organic solvents, allowing them to be easily spin-coated onto glass substrates with high quality optical thin films. The stability of the polymers is adequate for the fabrication of devices, and the polymers provide longevity to the devices because they have high glass transition temperatures. We fabricated PLEDs in ITO/PEDOT/light-emitting polymer/cathode configurations using either bilayer of LiF/Al or triple layer of Alq_3/LiF/Al cathode structure. We found that the performance of PLEDs was higher with Alq_3/LiF/Al layer cathodes than with LiF/Al layer cathodes. The turn-on voltages were in the range of 6.0−9.0 V, and the maximum brightness and luminance efficiency were 5127 cd/m^2 at 18 V and 3.75 cd/A at 9 V, respectively, for poly(PDOT−PV-*co*-*m*-SiPhPV) (53:47 wt %) devices

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