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Highly Photoluminescent and Blue-Green Electroluminescent Polymers: New Silyl- and Alkoxy-Substituted Poly(*p*-phenylenevinylene) Related Copolymers Containing Carbazole or Fluorene Groups

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ABSTRACT: A series of silyl- and alkoxy-substituted poly(*p*-phenylenevinylene) related copolymers containing carbazole and fluorene groups, poly[9,9-*n*-dihexyl-2,7-fluorenediylvinylene-*alt*-2,5-bis(trimethylsilyl)-*p*-phenylenevinylene] (PFBTS−PPV), poly[*N*-ethylhexyl-3,6-carbazolevinylene-*alt-2,5*-bis(trimethylsilyl)-*p*-phenylenevinylene] (PCBTS−PPV), poly[9,9-*n*-dihexyl-2,7-fluorenediyl-vinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (PFMEH−PPV), and poly[*N*-ethylhexyl-3,6-carbazolevinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (PCMEH−PPV), have been synthesized through the well-known Wittig polycondensation reaction. The synthesized polymers were completely soluble in common organic solvents and exhibited good thermal stability up to 400 °C. They showed UV−vis absorbance and photoluminescence (PL) in the ranges of 355−430 and 480−540 nm, respectively. The maximum emission peaks of dialkoxy-substituted PCMEH−PPV and PFMEH−PPV appeared at 520 and 540 nm, respectively, which were both blue-shifted about 55−75 nm compared to that of MEH−PPV. Especially, PCBTS−PPV and PFBTS−PPV showed much more blue-shifted emission maximum peaks at 480 and 495 nm corresponding to the blue and greenish-blue lights, respectively. Although PCBTS−PPV and PFBTS−PPV consist of conjugated segments without any kinked linkages, they showed far more blue-shifted emissions compared with other PPV related copolymers due to little electron-donating effect of the silyl substituent. Moreover, PFBTS−PPV and PCBTS−PPV showed extremely high PL efficiencies. Surprisingly, the PL_{eff} ($\Phi = 0.81$) of PFBTS−PPV is one of the highest values among the currently reported solid film PL_{eff} of PPV derivatives. The single-layer light-emitting diode was fabricated in the configuration of ITO (indium−tin oxide)/polymer/Al. Electroluminescence (EL) maxima of PCBTS−PPV and PFBTS−PPV were shown at 480 and 500 nm, respectively, each corresponding to the blue and greenish-blue emission. The measurement of current vs electric field strength showed the threshold biases of PCBTS−PPV and PFBTS−PPV to be about 1.8×10^8 and 1.2×10^8 V/m, and PCBTS−PPV and PFBTS−PPV showed 13 and 32 times higher relative EL quantum efficiencies compared to that of MEH−PPV.

Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted a great deal of attention in recent years because of their interesting electroluminescent properties and their potential for application as the active emitting layer in light-emitting diodes (LED).[1−6] Organic polymer LEDs have many advantages for the development of a large-area visible light-emitting display because of the good processability, low operating voltage, fast response time, and color tunability over the full visible range by the control of the HOMO−LUMO band gap of the emissive layer. Recently, Zhang et al. reported the improved quantum efficiency in green light-emitting diodes made by a silyl-substituted soluble PPV derivative, poly[2-(3-*epi*-cholestanol)-5-dimethylthexylsilyl-1,4-phenylenevinylene] (CS−PPV).[7] The effects of silicon substitution on the luminescence properties are gaining interest in the field of polymer LEDs.[8]

The blue EL—already difficult to achieve with inorganic semiconductors—has been sought in conjugated polymers having a high HOMO−LUMO energy band gap, such as partially eliminated poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), poly(alkylfluorene), and copolymers containing confined conjugated segments such as CNMBC (conjugated−nonconjugated multiblock copolymer) type polymers.[9−11] Among them, polyfluorene derivatives have extremely high luminescence efficiencies in solution (rivaling those of many laser dyes), which are largely maintained in the polymer films.[10] As a result, polyfluorenes have been intensively studied recently as the blue light-emitting materials. But they showed rather poor processability and mechanical properties and high operating voltage in light-emitting diode devices.

In this paper, we report on the syntheses and light-emitting properties of alkoxy- and silyl-substituted poly(*p*-phenylenevinylene) related copolymers containing carbazole or fluorene groups. We attempted to gain highly efficient blue light emission by incorporating the carbazole or fluorene unit and substituting side groups with slight electron-donating effect[12] into the polymer main chain. The carbazole unit is known as a hole-transporting and electroluminescent material,[13] and the fluorene unit as a highly efficient and thermally stable material as mentioned above.[14] The luminescent effects and electronic properties of silicon substitution have been reported elsewhere and in our previous works.[8,12] On the basis of these considerations, we succeeded in synthesizing new blue-green light-emitting alternating

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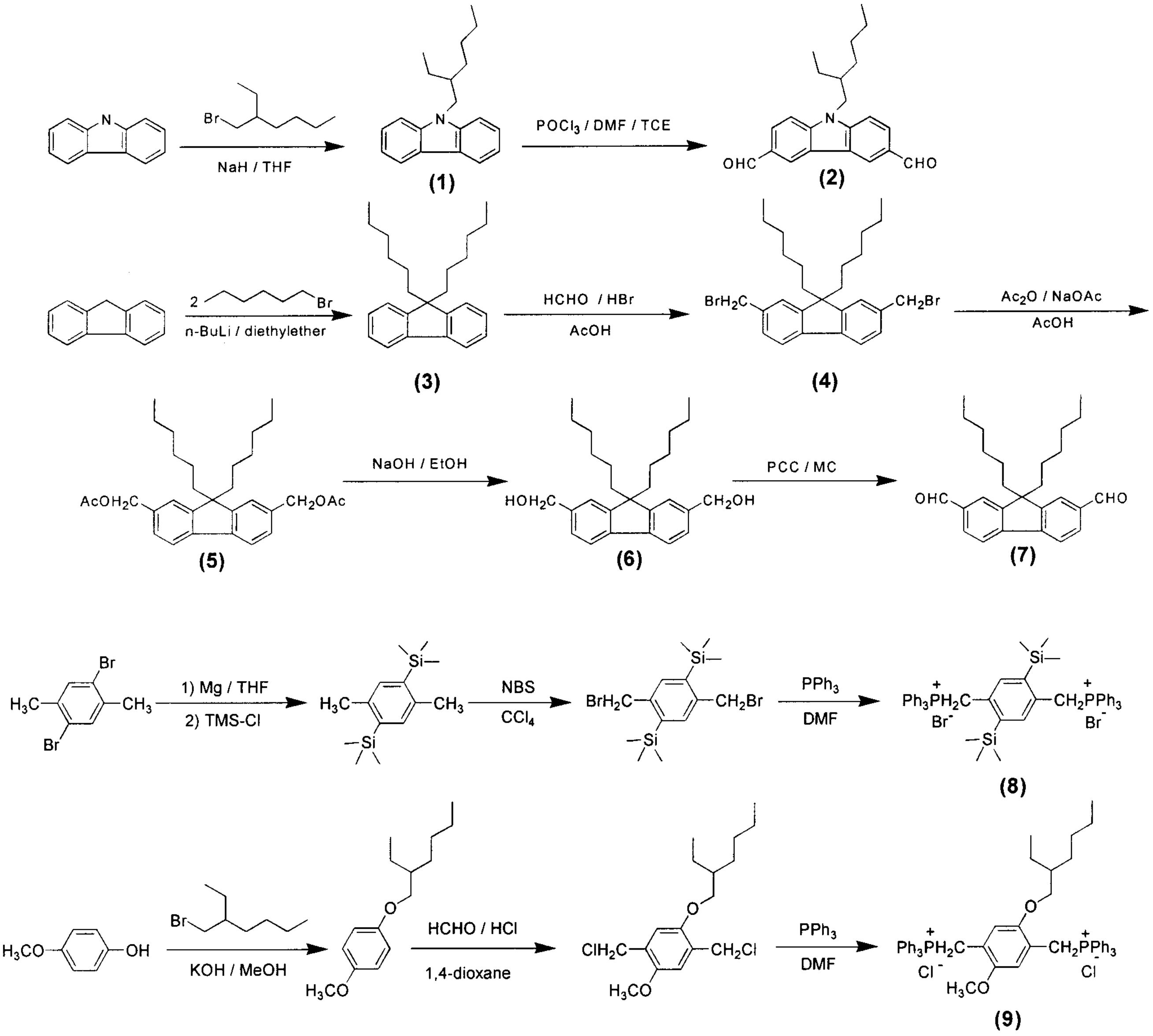
Scheme 1. Synthetic Routes to the Monomers of Dialdehyde and Diphosphonium Salts



copolymers having highly photo- and electroluminecent properties.[12,15] The synthetic route and details are given in Schemes 1 and 2 and in the Experimental Section.

Experimental Section

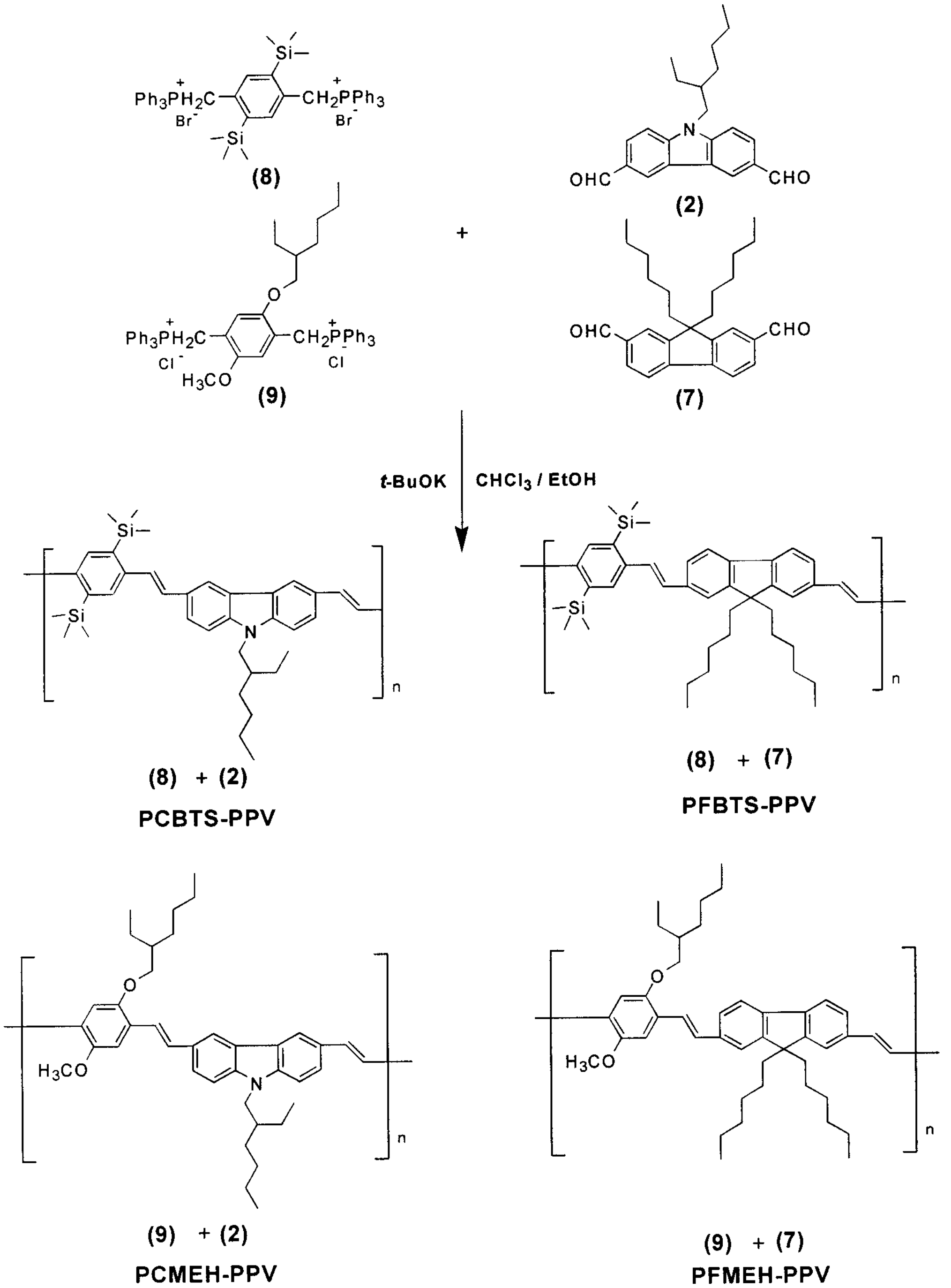
Materials. 2,5-Dibromo-*p*-xylene, trimethylsilyl chloride (TMS−Cl), *N*-bromosuccinimide (NBS), triphenylphosphine (PPh_3), 2-ethylhexyl bromide, 4-methoxyphenol, potassium *tert*-butoxide, carbazole, fluorene, *n*-hexyl bromide, *n*-butyllithium, phosphorus oxychloride ($POCl_3$), and pyridinium chloromate (PCC) from Aldrich Chemical Co. were used without any further purification. Tetrahydrofuran (THF) was dried and fractionally distilled from sodium. All other solvents and reagents were analytical-grade quality, purchased commercially, and used without any further purification.

Instrumentations. The synthesized compounds were identified by ^1H NMR spectra that were collected on a Bruker AM 200 and AVANCE 400 spectrometers. The melting points were determined using an Electrothermal model 1307 digital analyzer. The elemental analyses were performed by the Seoul Branch Analytical Laboratory of the Korea Basic Science Institute. The FT-IR spectra were obtained by EQUINOX 55 and UV−vis spectra were measured on Shimadzu UV-3100S spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under nitrogen at a heating rate of 10 °C/min with DuPont 9900 analyzer. The PL spectra of the polymers were obtained using Perkin-Elmer LS-50 luminescence spectrometer. The film thicknesses of the polymers were founded by using a Tencor Alpha-Step 500 profiler. The EL spectra were measured by using a dual grating-monochromator (Spex 270M) with a photomultiplier tube (Hamamatsu R955) as a detector. The EL spectra were recorded at 2 nm resolution by a computer through the photon counter (SR400) averaging the signal from the PMT while applying direct current from the current/voltage source (Keithley 238). For the measurement of device properties, current−voltage ($I-V$) and light intensity−voltage ($L-V$) characteristics were measured by using the current/voltage source and an optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias, and the emitted light was collected with a silicon photodetector (Newport 818SL) placed in front of the device and recorded by a computer. All the measurements mentioned above were performed in air and at room temperature.

Carbazole Dialdehyde Monomer. It was synthesized by an adapted literature procedure.[16]

9-(2-Ethylhexyl)carbazole (1). To a two-necked flask containing carbazole (20.0 g, 120 mmol), 2-ethylhexyl bromide (30.3 mL, 160 mmol), and 250 mL of anhydrous THF was

Scheme 2. Synthetic Routes to PCBTS−PPV, PFBTS−PPV, PCMEH−PPV, and PFMEH−PPV



added 6.5 g of sodium hydride (60% dispersion in mineral oil) (160 mmol). This mixture was refluxed with stirring for 48 h. After reaction was completely promoted, the reaction mixture was extracted with methylene chloride, and the unreacted 2-ethylhexyl bromide and carbazole were removed by vacuum distillation (40 °C/3 mmHg) and column chromatography, respectively. A pure colorless liquid was obtained (15.1 g, 45.0%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.11 (d, 2H, Ar H), 7.43 (m, 4H, Ar H), 7.26 (m, 2H, Ar H), 4.17 (d, 2H, −N*CH*$_2$CH(Et)−), 2.08 (m, 1H, −NCH$_2$*CH*(Et)−), 1.35 (m, 8H, −*CH*$_2$−), 0.87 (m, 6H, −*CH*$_3$). Anal. Calcd for $C_{20}H_{25}N_1$: C, 85.96; H, 9.04; N, 5.01. Found: C, 86.01; H, 9.01; N, 4.99.

9-(2-Ethylhexyl)carbazole-3,6-dicarbaldehyde (2). A 500 mL three-necked flask containing 16.7 mL (220 mmol) of anhydrous DMF was cooled in an ice bath. To this solution, 16.8 mL (180 mmol) of phosphorus oxychloride was added dropwise for 30 min. Compound **1** (5.0 g, 18 mmol) in 30 mL of 1,1,2-trichloroethane was added to the above solution and heated to ca. 90 °C for 2 days. This solution was cooled to room temperature, poured into ice water, and neutralized to pH 6−8 by dropwise addition of saturated aqueous sodium hydroxide solution. The mixture was extracted with ethyl acetate. The extract was dried with anhydrous magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on a silica gel column using *n*-hexane/ethyl acetate (10/1, by volume) as an eluent. A pure white solid was obtained (2.9 g, 48.0%); mp 112 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 10.12 (s, 2H, -*CHO*), 8.65 (s, 2H, Ar H), 8.05 (d, 2H, Ar H), 7.51 (d, 2H, Ar H), 4.24 (d, 2H, −N*CH*$_2$-CH(Et)−), 2.05 (m, 1H, −NCH$_2$*CH*(Et)−), 1.32 (m, 8H, −*CH*$_2$−), 0.87 (m, 6H, -*CH*$_3$). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.53; N, 4.18. Found: C, 79.02; H, 7.89; N, 4.37.

Fluorene Dialdehyde Monomer. 9,9-Di-*n*-hexylfluorene (3). Compound **3** was synthesized by the reaction of fluorene and *n*-hexyl bromide using *n*-butyllithium in THF according to the literature procedure.[17]

2,7-Bis(bromomethyl)-9,9-di-*n*-hexylfuorene (4). A two-necked flask containing 4 g (10 mmol) of compound **3** and 3 g (100 mmol) of paraformaldehyde was placed in an ice bath. To this flask, 80 mL of 30% HBr solution in acetic acid was added carefully, and the mixture was stirred for 24 h at 60−70 °C. The resulting mixture was extracted with methylene chloride, and the organic portion was concentrated. Finally, the viscous liguid was obtained by column chromatography with the yield of 81% (4.2 g). ^{1}H NMR ($CDCl_3$, ppm): δ 7.61 (d, 2H, Ar H), 7.34 (d, 4H, Ar H), 4.58 (s, 4H, $-CH_2$Br), 1.92 (m, 4H; α-CH_2 of hexyl group at 9-position of fluorene), 1.06 (12H; $\beta\sim\delta$-CH_2), 0.76−0.75 (10H; ϵ-CH_2 and CH_3). Anal. Calcd for $C_{27}H_{36}Br_2$: C, 62.32; H, 6.97. Found: C, 62.36; H, 6.92.

[7-(Acetyloxymethyl)-9,9-di-*n*-hexylfluoren-2-yl]methyl Acetate (5). A mixture of 4.0 g (7.7 mmol) of compound **4**, anhydrous sodium acetate (3.2 g, 38.6 mmol), acetic anhydride (2.17 mL, 23.1 mmol), and acetic acid (40 mL) was stirred at 90 °C for 3 h. The reaction mixture was cooled and extracted with methylene chloride. After evaporation of the solvent under reduced pressure, the yellow liquid was obtained (3.1 g, 83.7%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.65 (d, 2H, Ar H), 7.34 (d, 4H, Ar H), 5.15 (s, 4H, $-CH_2O-$), 2.12 (s, 6H, $-OCOCH_3$), 1.93 (m, 4H; α-CH_2 of hexyl group at 9-position of fluorene), 1.02 (12H; $\beta\sim\delta$-CH_2), 0.77−0.70 (10H; ϵ-CH_2 and CH_3). Anal. Calcd for $C_{31}H_{42}O_4$: C, 77.79; H, 8.84. Found: C, 77.71; H, 8.87.

[9,9-Dihexyl-7-(hydroxymethyl)fluoren-2-yl]methan-1-ol (6). A mixture of compound **5** (5.2 g, 10.7 mmol) and sodium hydroxide (2.17 g, 54.3 mmol) in 80 mL of ethanol was stirred at 40 °C for 2 h. After cooling, the mixture was poured into 100 mL of distilled water. Concentrated hydrochloric acid was added dropwise to the above solution until pH of the suspension changed to 7. This solution was extracted with methylene chloride and evaporation of the organic layer under reduced pressure afforded viscous liquid (3.1 g, 78.9%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.64 (d, 2H, Ar H), 7.28 (d, 4H, Ar H), 4.74 (s, 4H, $-CH_2$OH), 1.93 (m, 4H; α-CH_2 of hexyl group at 9-position of fluorene), 1.03 (12H; $\beta\sim\delta$-CH_2), 0.77−0.70 (10H; ϵ-CH_2 and CH_3). Anal. Calcd for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71; Found: C, 82.19; H, 9.69.

9,9-Di-*n*-hexylfluorene-2,7-dicarbaldehyde (7). A solution of diol compound **6** (3.0 g, 8.2 mmol) in 100 mL of methylene chloride was stirred and cooled with an ice bath while pyridium chlorochromate (5.3 g, 24.6 mmol) was added in a portionwise manner over a period of 20 min. The mixture was then stirred for 8 h at room temperature until the oxidation was complete (monitored by TLC). After a dark brown suspension had formed, it was diluted with 150 mL of diethyl ether and stirred for further 30 min. The mixture was then filtered through silica gel to remove inorganic and insoluble particles. The solution was washed with 100 mL of 1 N HCl and then with water and dried over $MgSO_4$. The ether solution was filtered and concentrated, and the remaining yellow viscous liquid was purified by column chromatography (eluent: *n*-hexane/ethyl acetate = 10:1). The pure yellow liquid was obtained with the yield of 2.1 g (70.0%). ^{1}H NMR ($CDCl_3$, ppm): δ 10.07 (s, 2H, $-CHO$), 7.89 (s, 6H, Ar H), 2.04 (m, 4H; α-CH_2 of hexyl group at the 9-position of fluorene), 0.98 (12H; $\beta\sim\delta$-CH_2), 0.74−0.50 (10H; ϵ-CH_2 and CH_3). Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85. Found: C, 82.33; H, 8.81.

Bisphosphonium Salt Monomer of PCBTS−PPV and PFBTS−PPV. 2,5-Bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium Bromide) (8). It was synthesized as in our previous work.[18]

Bisphosponium Salt Monomer of PCMEH−PPV and PFMEH−PPV. 1-(2-Ethylhexyloxy)-4-methoxy-2,5-xylenebis(triphenylphosphonium Chloride) (9). It was synthesized by an adapted literature procedure.[12,19]

Polymerization of PCBTS−PPV and PFBTS−PPV. Poly[*N*-ethylhexyl-3,6-carbazolevinylene-*alt*-2,5-bis(trimethylsilyl)-*p*-phenyl- enevinylene] (PCBTS−PPV). A solution of 1.0 g (1.1 mmol) of 2,5-bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) **(8)** and 0.36 g (1.1 mmol) of 9-(2-ethylhexyl)carbazole-3,6-dicarbaldehyde **(2)** in 10 mL of chloroform was prepared. Potassium *tert*-butoxide (0.62 g, 5.5 mmol) was dissolved in 10 mL of ethanol, and this base solution was carefully dropped into the solution of monomers. After 48 h, the polymer product was precipitated from methanol. The crude polymer was filtered and then purified by a Soxhlet extraction in methanol for 3 days. The polymer yield was 0.42 g (42.0%). $T_g = 121$ °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.9 (br m, 2H, Ar H), 7.5 (br m, 4H, carbazole Ar H, br m, 2H, vinylic H), 7.2 (br m, 2H, carbazole Ar H), 6.8 (br d, 2H, vinylic H), 4.2 (br s, 2H, $-NCH_2-$), 2.0 (br s, 1H), 1.4−0.2 (br m, 32H). FT-IR (KBr pellet, cm^{-1}): 961 (trans HC=CH). Anal. Calcd for $C_{36}H_{47}Si_2N_1$: C, 78.63; H, 8.61; N, 2.55. Found: C, 78.09; H, 8.51, N, 2.49.

Poly[9,9-*n*-dihexyl-2,7-fluorenediylvinylene-*alt*-2,5-bis(trimethylsilyl)-*p*-phenylenevinylene] (PFBTS−PPV). A solution of 1.0 g (1.1 mmol) of 2,5-bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) **(8)** and 0.42 g (1.1 mmol) of 9,9-di-*n*-hexylfluorene-2,7-dicarbaldehyde **(7)** in 10 mL of chloroform was prepared. Potassium *tert*-butoxide (0.62 g, 5.5 mmol) was dissolved in 10 mL of ethanol, and this base solution was carefully dropped into the solution of monomers. The following synthetic procedures were performed in analogy to the procedures given for PCBTS−PPV. The polymer yield was 0.43 g (43.0%); $T_g = 117$ °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.8 (br m, 2H, Ar H), 7.5 (br m, 4H, Ar H, br m, 2H, vinylic H), 7.2 (br m, 2H, Ar H), 6.7 (br m, 2H, vinylic H), 2.2−0.1 (br m, 44H). FT-IR (KBr pellet, cm^{-1}): 962 (trans HC=CH). Anal. Calcd for $C_{41}H_{57}Si_2$: C, 81.25; H, 9.48. Found: C, 81.19; H, 9.51.

Polymerization of PCMEH−PPV and PFMEH−PPV. Poly[*N*-ethylhexyl-3,6-carbazolevinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (PCMEH−PPV). A solution of 1.0 g (1.2 mmol) of 1-(2-ethylhexyloxy)-4-methoxy-2,5-xylenebis(triphenylphosphonium chloride) **(9)** and 0.39 g (1.2 mmol) of 9-(2-ethylhexyl)carbazole-3,6-dicarbaldehyde **(2)** in 10 mL of chloroform was prepared. Potassium *tert*-butoxide (0.62 g, 5.5 mmol) was dissolved in 10 mL of ethanol, and this base solution was carefully dropped into the solution of monomers. The following synthetic procedures were performed in analogy to the procedures given for PCBTS−PPV. The polymer yield was 0.39 g (39.0%); $T_g = 68$ °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.7 (br m, 2H, Ar H), 7.4 (br m, 4H, carbazole Ar H, br m, 2H, vinylic H), 7.2 (br m, 2H, carbazole Ar H), 6.8 (br m, 2H, vinylic H), 4.1 (br s, 2H, $-NCH_2-$), 3.8 (br s, 2H, $-OCH_2-$), 3.5 (br s, 3H, $-OCH_3$), 2.0 (br s, 2H), 1.3 (br s, 16H), 0.8 (br s, 12H). FT-IR (KBr pellet, cm^{-1}): 961 (trans HC=CH). Anal. Calcd for $C_{39}H_{52}N_1O_2$: C, 82.64; H, 9.25; N, 2.47. Found: C, 82.59; H, 9.51, N, 2.49.

Poly[9,9-*n*-dihexyl-2,7-fluorenediyl-vinylene-*alt*-2-methoxy-5-(2-ethylhexyl oxy)-*p*-phenylenevinylene] (PFMEH−PPV). A solution of 1.0 g (1.2 mmol) of 1-(2-ethylhexyloxy)-4-methoxy-2,5-xylenebis(triphenylphosphonium chloride) **(9)** and 0.47 g (1.2 mmol) of 9,9-di-*n*-hexylfluorene-2,7-dicarbaldehyde **(7)** in 10 mL of chloroform was prepared. Potassium *tert*-butoxide (0.62 g, 5.5 mmol) was dissolved in 10 mL of ethanol, and this base solution was carefully dropped into the solution of monomers. The following synthetic procedures were performed in analogy to the procedures given for PCBTS−PPV. The polymer yield was 0.31 g (31.0%); $T_g = 72$ °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.9−7.1 (br m, 6H, Ar H, br m, 2H, vinylic H), 6.7 (br m, 2H, vinylic H), 4.1 (br s, 2H, $-OCH_2-$), 3.8 (br s, 3H, $-OCH_3$), 2.2−0.6 (br m, 41H). FT-IR (KBr pellet, cm^{-1}): 963 (trans HC=CH). Anal. Calcd for $C_{44}H_{58}O_2$: C, 85.38; H, 9.45. Found: C, 85.29; H, 9.51. All the synthetic routes and polymer structures are shown in Schemes 1 and 2.

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH−PPV). The well-known MEH−PPV was synthesized by the method of dehydrohalogenation route (the Gilch procedure).[20,21] The final polymer was soluble in common organic solvents.

Results and Discussion

All the synthesized polymers were highly soluble in common organic solvents such as tetrahydrofuran, chloroform, methylene chloride, 1,2-dichloroethane, cy-

Table 1. Polymerization Results of PC(PF)BTS−PPV and PC(PF)MEH−PPV

polymers	yield (%)	M_n[a]	M_w[a]	PDI[a]
PCBTS−PPV	42	8400	14 900	1.76
PFBTS−PPV	43	8800	16 900	1.90
PCMEH−PPV	39	6800	14 100	2.05
PFMEH−PPV	31	6600	12 900	1.95

[a] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

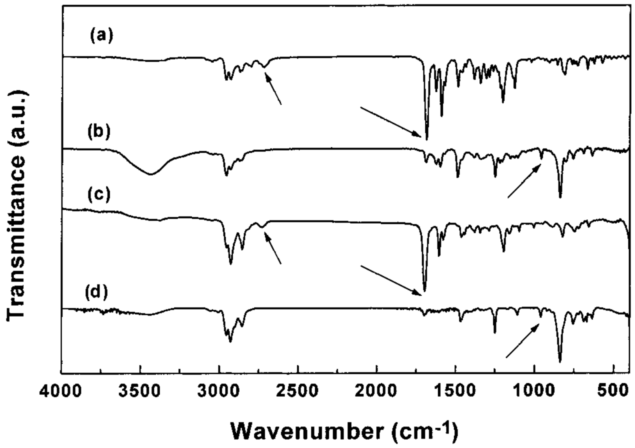


Figure 1. FT-IR spectra of (a) 9-(2-ethylhexyl)carbazole-3,6-dicarbaldehyde, (b) PCBTS−PPV, (c) 9,9-di-*n*-hexylfluorene-2,7-dicarbaldehyde, and (d) PFBTS−PPV in KBr pellets.

clohexanone, and so on. They could be spin-cast onto various substrates giving highly transparent and homogeneous thin films. The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers, determined by gel permeation chromatography using polystyrene standards, were in the range of 6600−8800 and 12 900−16 900 with polydispersity index of 1.76−2.05. The polymerization results of PCBTS−PPV, PFBTS−PPV, PCMEH−PPV, and PFMEH−PPV polymers are summarized in Table 1. Figure 1 shows the typical FT-IR spectra of PCBTS−PPV, PFBTS−PPV, and their corresponding dialdehyde monomers. The comparison of the FT-IR spectrum of (a) carbazole dialdehyde monomer to that of (b) PCBTS−PPV shows a drastic decrease of the band intensities at 1681 and 2727 cm^{-1}, which correspond to the strong aldehyde carbonyl and aldehydic hydrogen absorption peaks of the dialdehyde monomer, respectively. On the other hand, a weak and sharp absorption peak at 961 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene in PCBTS−PPV has appeared.[18] This proves the formation of a vinylene double bond, and consequently the polymerization reactions have been successful. Parts a and b of Figure 2 show the ^1H NMR spectra of PCBTS−PPV and PFBTS−PPV, respectively. As the polymerization proceeded, the aldehyde peak of the dialdehyde monomer at 10.12 ppm almost disappeared, and new vinylic proton peaks appeared at 6.8 ppm (broad doublet) and 7.5 ppm along with aromatic protons of a carbazole unit in the ^1H NMR spectrum of PCBTS−PPV (a). Also, the broad peaks around 0.2−2.0 ppm were assigned as the methyl protons adjacent to the silicon atom and protons of ethylhexyl part. Above all, the broad peak around 4.2 ppm due to the α-methylene protons adjacent to the nitrogen atom in the carbazole unit was easily assigned. Thermal properties of the synthesized polymers were evaluated by the means of TGA under nitrogen atmosphere. Figure 3 shows that all of the polymers exhibited good thermal stability. The weight losses of the polymer were less than 5% on heating to about 400 °C. The DSC measurements showed glass transitions at around 121 and 117 °C for trimethylsilyl-substituted PCBTS−PPV and PFBTS−PPV, respectively. But, due to the flexibility of ethylhexyloxy substituent in PCMEH−PPV and PFMEH−PPV compared to the trimethylsilyl substituent, PCMEH−PPV and PFMEH−PPV exhibited relatively low glass transitions at around 68 and 72 °C, respectively. All of the four copolymers did not show either an endo or exo curve in DSC thermograms due to side chain scission or thermal cross-linking until the temperature of initial decomposition.

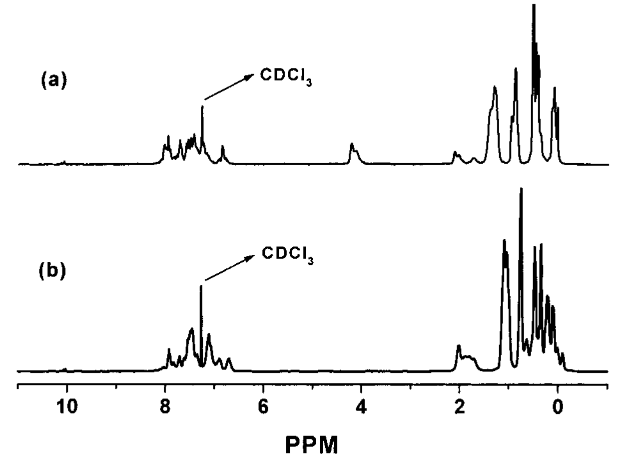


Figure 2. ^1H NMR spectra of (a) PCBTS−PPV and (b) PFBTS−PPV in $CDCl_3$.

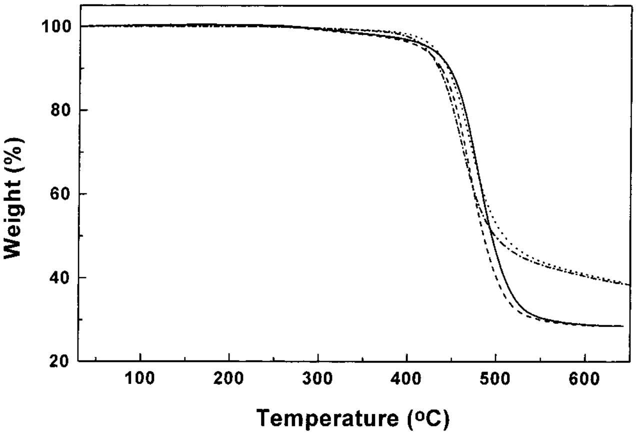


Figure 3. TGA thermograms of PCBTS−PPV (—), PFBTS−PPV (− −), PCMEH−PPV (- - -), and PFMEH−PPV (− - −).

Optical and Photoluminescence Properties. Figure 4 shows the UV−vis absorption spectra of the thin films of PC(PF)BTMS−PPV and PC(PF)MEH−PPV coated onto the quartz plate. As shown in the absorption spectra, the well-known MEH−PPV[20] showed a maximum absorption wavelength (λ_{max}) at 510 nm. PFMEH−PPV and PCMEH−PPV showed absorption maxima at 430 and 410 nm, respectively. The absorption peaks at 310 and 250 nm of PCMEH−PPV are due to the carbazole unit in the copolymer main chain. These blue-shifted UV−vis maximum wavelengths compared to that of MEH−PPV are due to the carbazole (or fluorene) unit in the alternating copolymer system of PCMEH−PPV (or PFMEH−PPV). In the case of silyl-substituted alternating copolymers, PCBTS−PPV and PFBTS−PPV, far more blue-shifted UV−vis absorption maxima

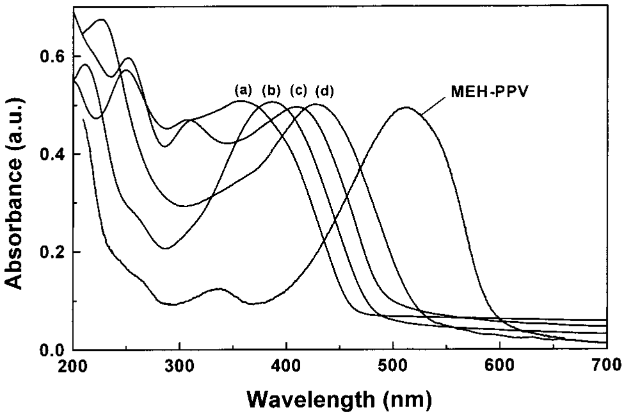


Figure 4. UV−vis spectra of (a) PCBTS−PPV, (b) PFBTS−PPV, (c) PCMEH−PPV, and (d) PFMEH−PPV thin films coated on a quartz plate.

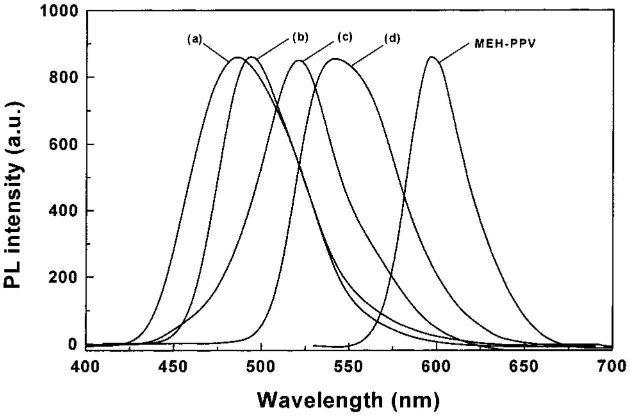


Figure 5. Photoluminescence (PL) spectra of (a) PCBTS−PPV, (b) PFBTS−PPV, (c) PCMEH−PPV, and (d) PFMEH−PPV thin films coated on a quartz plate.

were observed, originating from the lack of electron-donating ability and sterical hindrance of the trimethylsilyl substituent.[12] PCBTS−PPV and PFBTS−PPV showed the UV−vis absorption maxima at 355 and 385 nm, respectively. PCBTS−PPV additionally showed two absorption peaks at 310 and 250 nm resulting from the carbazole unit just as in PCMEH−PPV.

The PL spectra (Figure 5) showed a drastic change of emission color by the kind of substituents and whether the alternating system contains carbazole or fluorene. These PL spectra were recorded with the excitation wavelength corresponding to the maximum absorption wavelength of the polymer. In the PL spectra, the effects of alkoxy and silyl substituents in the copolymer systems were well coincident with the UV−vis absorption patterns of the polymers. The PL spectrum of MEH−PPV showed the emission maximum at 595 nm.[18] The emissions of PCMEH−PPV and PFMEH−PPV were blue-shifted about 75 and 55 nm, respectively, due to the carbazole and fluorene units in the alternating copolymer systems. PCMEH−PPV and PFMEH−PPV showed PL emission maxima at 520 and 540 nm, corresponding to the yellowish-green and yellow color, respectively. Because of the little electron-donating effect of the silyl substituent in PCBTS−PPV and PFBTS−PPV compared to the alkoxy substituent in PCMEH−PPV and PFMEH−PPV, PCBTS−PPV and PFBTS−PPV showed the blue PL emissions at 480 (blue) and 495 nm (greenish-blue), respectively. Thus, a blue light-emitting polymer, PCBTS−PPV, could be obtained by introducing a non-electron-donating substituent in the copolymer system containing a carbazole unit without any conjugation blocking segment like oxygen or alkyl spacers. Moreover, a silyl-substituted phenylene and fluorene containing copolymer, PFBTS−PPV, showed extremely high PL efficiency in the thin film state. We measured film PL efficiencies of four alternating copolymers using optically dense configuration and diphenylanthracene (dispersed in PMMA film with a concentration less than 10^{-3} M, assuming PL_{eff} of 0.83) as a standard.[22−26] PCBTS− and PFBTS−PPV exhibited very high solid film PL efficiencies (>50%), as shown in Table 2. And very interestingly, the PL_{eff} ($\Phi = 0.81$) of PFBTS−PPV is one of the highest values among the currently reported solid film PL_{eff} of PPV derivatives.[8,27] The highly enhanced PL_{eff} of PFBTS−PPV may be due to the substitution of the non-electron-donating trimethylsilyl group and the incorporation of the highly fluorescent fluorene unit in the conjugated main chain. Besides, introducing the bulky trimethylsilyl and *n*-hexyl substituents and copolymer system to our polymer backbone to prevent its close packing should therefore increase its PL efficiency. All the optical absorptions, PL emissions, and film PL efficiencies of the synthesized alternating copolymers are summarized in Table 2.

Table 2. UV−vis Spectra, Photoluminescence (PL) Spectra, and Quantum Yield of PC(PF)BTS−PPV and PC(PF)MEH−PPV

polymers	UV−vis λ_{max} (nm)[a]	PL λ_{max}(nm)[a]	Φ_{pl}[a]
PCBTS−PPV	355 (310, 250)[b]	480	0.64
PFBTS−PPV	385	495	0.81
PCMEH−PPV	410 (310, 250)[b]	520	0.59
PFMEH−PPV	430	540	0.26

[a] These values listed were measured in the thin film state onto the quartz plate. [b] These values listed in parentheses represent absorptions of the carbazole unit.

Electroluminescence Property and Current−Voltage−Luminescence (*I*−*V*−*L*) Characteristics. The LED structure consisted of an aluminum contact on the surface of the polymer which was spin-cast on the ITO glass from the solution of PCBTS−PPV and PFBTS−PPV polymer in 1,2-dichloroethane, respectively. The spin-casting technique yielded uniform films with thicknesses of about 100 nm. Aluminum was deposited onto the surface of the spin-cast films by vacuum evaporation method at pressures of about 10^{-6} Torr, yielding a circular active layer with a diameter of 5 mm. Figure 6a,b shows the current−electric field strength ($I-V/m$) and the luminescence−electric field strength ($L-V/m$) characteristics of the single-layer light-emitting diode of ITO/PCBTS−PPV or PFBTS−PPV/Al. The current increased with increasing forward bias voltage, which indicated typical rectifying characteristics. The threshold voltages of PCBTS−PPV and PFBTS−PPV polymers were about 1.8×10^8 and 1.2×10^8 V/m, respectively. PFBTS−PPV showed higher EL power at low threshold voltage than PCBTS−PPV due to the better π-electron delocalization of the fluorene group compared to the carbazole group (Figure 6b). We investigated the relative EL quantum efficiencies of PCBTS−PPV, PFBTS−PPV, and MEH−PPV in the same LED device condition (shown in Table 3).[18] The PCBTS−PPV exhibited 13 times higher EL quantum efficiency compared with MEH−PPV, while the PFBTS−PPV polymer, which is highly photoluminescent, showed about 32 times greater value than MEH−PPV.

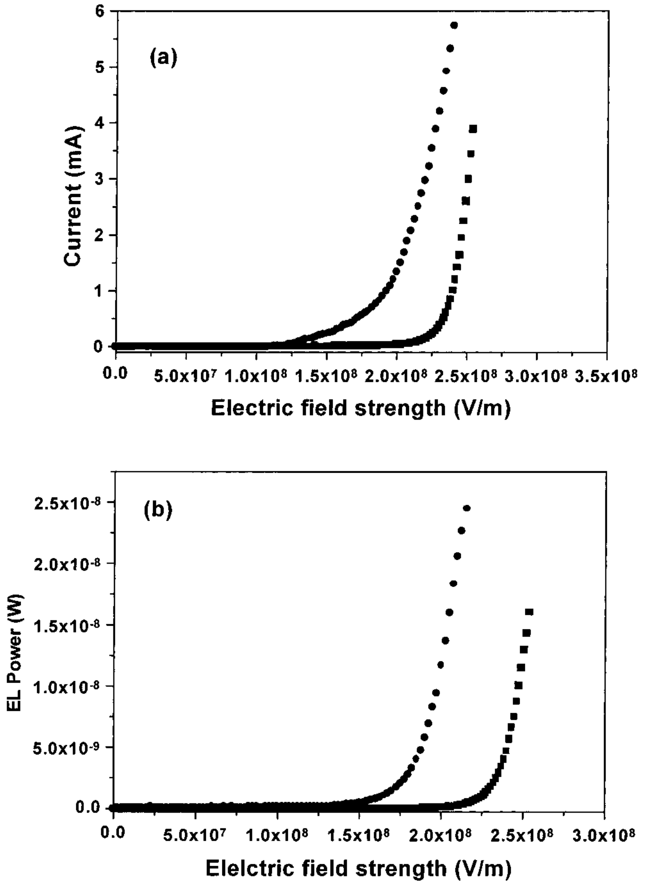


Figure 6. (a) Current−electric field strength (*I*−*V*/*m*) and (b) EL power−electric field strength (*L*−*V*/*m*) characteristics of the single-layer light-emitting diode of ITO/PCBTS−PPV/Al (■) and ITO/PFBTS−PPV/Al (●).

Table 3. Comparison of Relative EL Quantum Efficiency, Turn-On Voltage, and Emissive Wavelength of PCBTS−PPV, PFBTS−PPV and MEH−PPV

light-emitting polymer	rel EL quantum efficiency	turn-on voltage [electric field strength (V/m)]	emissive λ (nm)	emissive color
MEH−PPV	1	5×10^7	595	orange
PCBTS−PPV	13	1.8×10^8	480	blue
PFBTS−PPV	32	1.2×10^8	500	greenish-blue

The EL spectra of MEH−PPV, PFBTS−PPV, and PCBTS−PPV polymer films are shown in Figure 7. The MEH−PPV film showed EL emission maximum at 595 nm as reported elsewhere.[18] The EL spectra of PCBTS−PPV and PFBTS−PPV exhibited EL emissive bands at 480 and 500 nm, respectively. These wavelengths correspond to blue and greenish-blue light. These far blue-shifted EL emission maxima of PCBTS−PPV and PFBTS−PPV relative to MEH−PPV originate from the non-electron-donating effect of the trimethylsilyl substituent and the alternating systems containing carbazole or fluorene which are absent in MEH−PPV. The PFBTS−PPV and PCBTS−PPV which show good processability and high quantum efficiencies may make them good candidates for application in polymer LEDs.

Conclusions

We synthesized new silyl- and alkoxy-substituted poly(*p*-phenylenevinylene) related copolymers containing carbazole and fluorene groups, PC(PF)BTS−PPV and PC(PF)MEH−PPV. In the UV−vis and photoluminescence spectra, the synthesized polymers showed gradual approach to the blue light by using the silyl substituent and by the incorporation of the carbazole or fluorene unit into the copolymer main chain. Especially, PCBTS−PPV and PFBTS−PPV showed high PL efficiencies at about 480 and 495 nm, respectively. The LED devices of PCBTS−PPV and PFBTS−PPV gave maximum EL emissive band at 480 and 500 nm, which correspond to blue and greenish-blue color, respectively. Consequently, we synthesized highly efficient blue and greenish-blue photo- and electroluminescent polymers by a systematical approach using the non-electron-donating silyl-substituent and copolymer systems containing carbazole or fluorene units, even though it is very difficult to get a blue emission from PPV derivatives without any blocking segments and kink structures.

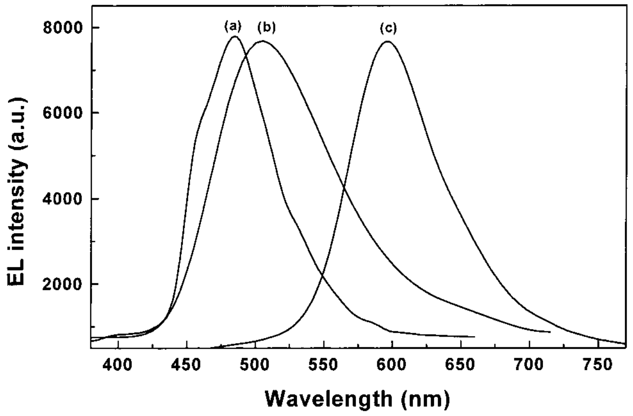


Figure 7. Electroluminescence (EL) spectra of the single-layer light-emitting diodes of (a) PCBTS−PPV, (b) PFBTS−PPV, and (c) MEH−PPV with a configuration of ITO/polymer/Al.

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