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Novel Poly(*p*-phenylenevinylene)s with an Electron-Withdrawing Cyanophenyl Group†

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ABSTRACT: Novel poly(*p*-phenylenevinylene) derivatives with an electron-withdrawing cyanophenyl group on the polymer backbone, poly[2-(2′-ethylhexyloxy)-5-(4′-cyanophenyl)-1,4-phenylenevinylene] (PEHCNPV) and poly[2-dimethyloctylsilyl-5-(4′-cyanophenyl)-1,4-phenylenevinylene] (PSi8CNPV), were synthesized via the Gilch polymerization. These polymers were completely soluble in common organic solvents and showed good thermal stability up to 400 °C. Surprisingly, they showed very high glass transition temperatures (above 180 °C), indicating that electroluminescenece (EL) devices constructed from these polymers should have good thermal stability. The presence of the electron-withdrawing cyanophenyl group lowered the HOMO and LUMO energy levels of PEHCNPV and PSi8CNPV relative to those of common PPV derivatives. Light-emitting diodes (LEDs) with the configuration ITO/PEDOT/polymer/LiF/Al were fabricated using the novel polymers. The LED devices based on PEHCNPV and PSi8CNPV exhibited maximum electroluminescence at 546 and 513 nm, respectively. In particular, the LED device containing PSi8CNPV emitted pure green light with a CIE (Commission Internationale de L'Eclairage) chromaticity coordinate of (0.330, 0.599), which is very close to that of the standard green (0.30, 0.60) used for high definition television (HDTV), a maximum external quantum efficiency of 0.67%, and a maximum brightness of 2900 cd/m^2.

Introduction

Since the discovery of electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV),[1] PPV and its derivatives have been extensively studied due to their potential applications as emissive layers in light-emitting diodes (LED)s.[2,3] However, PPV has the shortcoming that it is a poor electron acceptor due to its high LUMO energy. As a consequence, construction of an efficient LED based on PPV requires the use of a metal with a low work function for electron injection (e.g., calcium), which is problematic due to the high susceptibility of such metals to atmospheric degradation.[4]

Many approaches have been taken to overcome the imbalance of charge carrier injection or mobility. The most common practices have been either to use a charge carrier transporting material to block the major charge carrier and to enhance the injection of the minor charge carrier[5−7] or to align the energy band of the polymer by introducing electron-withdrawing groups as pendant groups or as part of the polymer backbone.[5] Bredas et al. have shown that introduction of an electron-withdrawing group onto the arylene ring or the vinyl group of PPV lowers the HOMO and LUMO energies of the polymer, thereby permitting the use of a higher work function metal in the LED device.[8]

A number of PPV derivatives have been prepared using electron-withdrawing substituents such as halide,[9−11] cyano,[12] trifluoromethyl,[13] or methylsulfonylphenyl on the arylene ring.[14] However, the poor solubility of the fully conjugated polymers meant that these PPVs could be obtained only via a bromo-precursor route or bis-sulfonium salts precursor route through a thermal elimination procedure. In general, the EL external efficiencies of single-layer devices constructed using these PPV derivatives are much lower than that of PPV. The insolubility of PPV derivatives in all solvents led to the cessation of research into their electrochemical properties and the optimal configuration of LED devices based on PPVs. In view of their low EL external efficiencies, PPV derivatives were recommended as useful electron-conducting/hole-blocking (ECHB) materials rather than as emissive materials.

In the present study, we report the synthesis of two new PPV derivatives that contain an electron-withdrawing cyanophenyl group: poly[2-(2-ethylhexyloxy)-5-(4-cyanophenyl)-1,5-phenylenevinylene] (PEHCNPV) and poly[2-dimethyloctylsilyl-5-(4-cyanophenyl)-1,4-phenylenevinylene] (PSi8CNPV). In addition, we investigate the effects of the electron-withdrawing properties of the cyanophenyl group on the physical and electrochemical properties of PEHCNPV and PSi8CNPV, as well as the performance of these polymers as emissive layers in LEDs.

Experimental Section

Instrumentation. NMR spectra were recorded using a Bruker AVANCE 400 spectrometer with tetramethylsilane as the internal reference. Elemental analysis of the final monomers and polymers was performed using an automatic elemental analyzer (Fisons EA 1110). The number and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) analysis on a Waters GPC-150C instrument, using THF as eluent and polystyrene as standard. TGA and DSC were performed under nitrogen atmosphere at a heating rate of 10 °C/min with a DuPont 9900 analyzer. UV−visible and photoluminescence spectra were measured using a Jasco V-530 UV/vis spectrometer and a Spex Fluorolog-3 spectrofluorometer, respectively. The configuration of the EL device was ITO/PEDOT/polymer/LiF/Al. The PEDOT [poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)] employed as the hole-injection layer was spin coated onto

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† This paper is dedicated to Professor Jung-Il Jin for the occasion of his 60th birthday.

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precleaned ITO/glass substrate at a spin speed of 2500 rpm for 40 s. Thin polymer films with a thickness of approximately 80 nm were then spin coated onto the PEDOT layer from a 0.5 wt % polymer solution in chloroform. LiF and Al were deposited onto the polymer films using the vacuum evaporation method at a pressure of 10^{-6} Torr. Electroluminescence spectra were measured with a Minolta CS-1000. The current/voltage and luminescence/voltage characteristics were measured using a current/voltage source (Keithley 238) and a luminescence detector (Minolta LS-100). Cyclic voltammetry was performed on an AUTOLAB/PGSTAT12 with a three-electrode cell in a solution of Bu_4NBF_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s. The ionization potentials (IP) of polymers were obtained using atmospheric photoelectron spectroscopy (RIKEN Keiki AC-2). All measurements were performed at room temperature under ambient atmosphere.

Materials. All reagents were purchased from Aldrich and used without further purification. PEDOT was purchased from Bayer. THF was distilled over benzophenone and sodium. 1-(2′-Ethylhexyloxy)-2,5-dimethylbenzene (**1**), and 4-bromo-1-(2′-ethylhexyloxy)-2,5-dimethylbenzene (**2**) were synthesized according to procedures outlined in the literature.[14]

1-(2′-Ethylhexyloxy)-4-(4′,4′,5′,5′-tetramethyl(1′,3′,2′-dioxaborolan-2-yl))-2,5-dimethylbenzene (3). *n*-BuLi (1.6 M in hexane, 59.5 mL, 1.05 equiv) was added dropwise to a solution of compound **2** (28.2 g, 90 mmol) in 200 mL of THF at −78 °C. The mixture was then stirred for 2 h at the same temperature. After stirring, 2-isopropyl-4,4,5,5-tetramethyldioxaborolane (20 g, 1.2 equiv) was added to the solution at −78 °C. The solution was then stirred overnight at room temperature, after which the reaction was quenched by addition of water and extracted with methylene chloride. The extract was dried over anhydrous magnesium sulfate and the solvent evaporated. The colorless oil product (28 g, 85%) was obtained by column chromatography in hexane (pretreated with 2 wt % triethylamine). ^{1}H NMR ($CDCl_3$, ppm): δ 7.5 (s, 1H), 6.6 (s, 1H), 3.8 (d, 2H), 2.5 (s, 3H), 2.1 (s, 3H), 1.7 (m, 1H), 1.5−1.2 (m, 20H), 0.9−0.8 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 159.3, 144.5, 138.0, 122.7, 112.2; aliphatic (C) 82.8, 69.6, 39.3, 30.5, 28.9, 24.6, 23.9, 22.9, 22.0, 15.3, 13.9, 11.0.

1-(Dimethyloctylsilyl)-4-bromo-2,5-dimethylbenzene (4). *n*-BuLi (1.6 M in hexane, 65.6 mL, 1.05 equiv) was added dropwise to a solution of 2,5-dibromo-*p*-xylene (26.4 g, 0.1 mol) in 300 mL of THF at −78 °C. The mixture was then stirred for 2 h at the same temperature. After stirring, chlorodimethyloctylsilane (22.7 g, 0.12 mol) was added to the solution at −78 °C. The solution was then stirred for 6 h at room temperature, after which the reaction was quenched by addition of water and extracted with methylene chloride. The extract was dried over anhydrous magnesium sulfate and the solvent evaporated. The colorless oil product (30.8 g, 87%) was obtained by column chromatography in hexane. ^{1}H NMR ($CDCl_3$, ppm): δ 7.32 (s, 1H), 7.24 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 1.27−1.24 (m, 12H), 0.89−0.77 (m, 5H), 0.29 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 142.7, 136.9, 133.8, 133.2, 126.0; aliphatic (C) 33.5, 31.9, 29.2, 23.9, 22.6, 22.3, 22.1, 15.9, 14.0.

1-(Dimethyloctylsilyl)-4-(4′,4′,5′,5′-tetramethyl(1′,3′,2′-dioxaborolan-2-yl))-2,5-dimethylbenzene (5). This compound was synthesized following the procedure described above for **3**, starting from **4** (17.8 g, 50 mmol). Compound **5** was obtained as a colorless oil (17.1 g, 85%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.53 (s, 1H), 7.24 (s, 1H), 2.48 (s, 3H), 2.39 (s, 3H), 1.34−1.24 (m, 24H), 0.90−0.78 (m, 5H), 0.28 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 140.8, 140.6, 139.5, 136.7, 136.1, 82.3; aliphatic (C) 33.6, 31.9, 29.2, 24.8, 23.9, 22.6, 22.2, 21.7, 15.9, 14.0.

1-(2′-Ethylhexyloxy)-4-(4′′-cyanophenyl)-2,5-dimethylbenzene (6). A mixture of **3** (11.2 g, 31 mmol), 4-bromobenzonitrile (5.52 g, 30 mmol), and Na_2CO_3 (4.26 g, 40 mmol) in 40 mL of water was dissolved in 80 mL of toluene/20 mL of ethanol. One gram (1 mmol) of tetrakis(triphenylphospino)-palladium(0), $Pd(PPh_3)_4$, was added to this solution, after which the reaction mixture was maintained at 100 °C for 1 day. The reaction was quenched by a 1 N HCl solution and then extracted with ethyl acetate. The extract was washed with water, aqueous $NaHCO_3$ solution, and water. After washing, the extract was dried over anhydrous magnesium sulfate and the solvent was evaporated. The pure solid product (9.1 g, 87%) was obtained by column-chromatography in hexane-diethyl ether (30/1). ^{1}H NMR ($CDCl_3$, ppm): δ 7.6 (d, 2H), 7.4 (d, 2H), 6.9 (s, 1H), 6.7 (s, 1H), 3.9 (d, 2H), 2.2 (d, 6H), 1.7 (m, 1H), 1.5−1.2 (m, 8H), 0.9−0.8 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 157.1, 146.7, 133.2, 131.6, 131.3, 129.9, 124.4, 118.9, 112.7, 109.8; aliphatic (C) 70.0, 39.4, 30.5, 28.9, 23.9, 22.9, 20.2, 15.5, 11.0.

1-Dimethyloctylsilyl-4-(4′-cyanophenyl)-2,5-dimethylbenzene (7). This compound was synthesized following the procedure described above for **6**, starting from **5** (8.0 g, 20 mmol). Compound **7** was obtained as a white solid (6.8 g, 90%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.70 (d, 1H), 7.44 (d, 1H), 7.33 (s, 1H), 6.98 (s, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 1.32−1.23 (m, 12H), 0.90−0.83 (m, 5H), 0.33 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 146.7, 141.2, 140.4, 138.0, 137.1, 131.9, 130.9, 130.6, 129.9, 118.9, 110.5; aliphatic (C) 33.6, 31.9, 29.2, 24.0, 22.6, 22.4, 19.8, 15.9, 14.1.

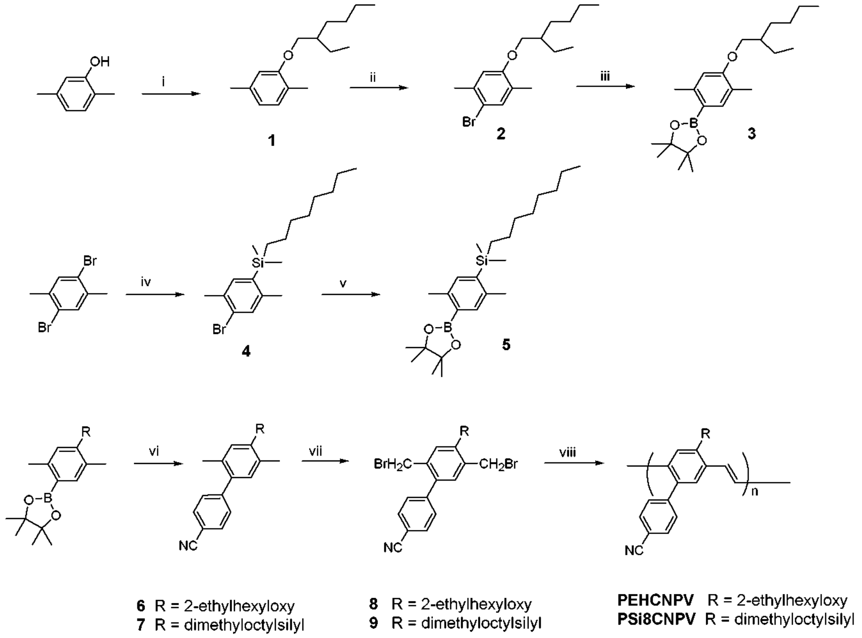
1,4-Bisbromomethyl-2-(2′-ethylhexyloxy)-5-(4′′-cyanophenyl)benzene (8). Compound **6** (8.2 g, 24 mmol) was reacted with *N*-bromosuccinimide (NBS) (9.6 g, 53 mmol) in 50 mL of carbontetrachloride. A small amount of benzoylperoxide was added as an initiator. The reaction mixture was refluxed for 6 h under a nitrogen atmosphere. After cooling, the solution was filtered and washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated and precipitated from hexane. The product was obtained as a white solid (4.7 g, 40%). Anal. Calcd for $C_{23}H_{27}Br_2NO$: C, 56.00; H, 5,52; N, 2.84. Found: C, 55.89; H, 5.46; N, 2.93. ^{1}H NMR ($CDCl_3$, ppm): δ 7.7 (d, 2H), 7.5 (d, 2H), 7.1 (s, 1H), 6.9 (s, 1H), 4.5 (s, 2H), 4.3 (s, 2H), 3.9 (d, 2H), 1.8 (m, 1H), 1.5−1.2 (m, 8H), 0.9−0.8 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 157.2, 144.3, 143.3, 136.7, 132.2, 132.1, 129.9, 127.2, 118.8, 113.5, 111.3; aliphatic (C) 70.5, 39.4, 30.6, 29.0, 27.7, 23.9, 23.0, 20.2, 14.0, 11.2.

1,4-Bisbromomethyl-2-dimethyloctylsilyl-5-(4′-cyanophenyl)benzene (9). This compound was synthesized by following the procedure described above for **8**, starting from **7** (5.6 g, 15 mmol). Compound **9** was obtained as a white solid (3.4 g, 43%). Anal. Calcd for $C_{25}H_{33}Br_2NSi$: C, 56.08; H, 6.21; N, 2.62. Found: C, 55.92; H, 6.12; N, 2.67. ^{1}H NMR ($CDCl_3$, ppm): δ 7.75 (d, 2H), 7.58 (d, 3H), 7.28 (s, 1H), 4.58 (s, 2H), 4.35 (s, 2H), 1.32−1.23 (m, 12H), 0.90−0.83 (m, 5H), 0.40 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 144.2, 143.9, 141.1, 139.8, 138.1, 134.0, 132.3, 132.2, 129.6, 111.7; aliphatic (C) 33.5, 33.2, 31.9, 31.0, 29.2, 23.9, 22.6, 16.4, 14.1.

Poly[2-(2′-ethylhexyloxy)-5-(4′′-cyanophenyl)-1,4-phenylenevinylene] (PEHCNPV). The monomer **8** (0.98 g, 2 mmol) was dissolved in 60 mL of anhydrous tetrahydrofuran, and the solution was cooled to 0 °C. At this temperature, 12 mL (12 mmol) of potassium *tert*-butoxide (1 M in THF) in 60 mL of anhydrous tetrahydrofuran was slowly added dropwise to the solution under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was then slowly added to an excess of methanol. The precipitated polymer was dissolved in chloroform and reprecipitated from methanol several times. After filtration, the polymer was dried under high vacuum to yield 0.28 g (47%) of yellow-orange PEHCNPV. M_n: 103 000, M_w: 765 000, PDI: 7.42. Anal. Calcd for $(C_{23}H_{25}NO)_n$: C, 83.34; H, 7.60; N, 4.23. Found: C, 82.96; H, 7.52; N, 4.31. ^{1}H NMR ($CDCl_3$, ppm): 7.6−6.6 (br, 8H), 4.0 (br, 2H), 1.6 (br, 1H), 1.4 (br, 8H), 0.9 (br, 6H). ^{13}C NMR ($CDCl_3$, ppm): aromatic (C) 156.9, 145.3, 135.5, 131.9, 130.5, 128.5, 118.5, 110.8, 109.0; aliphatic (C) 39.5, 30.7, 29.7, 29.0, 24.1, 23.0, 18.6, 14.0, 11.2.

Poly[2-dimethyloctylsilyl-5-(4′-cyanophenyl)-1,4-phenylenevinylene] (PSi8CNPV). Monomer **9** (1.07 g, 2 mmol) was dissolved in 60 mL of anhydrous tetrahydrofuran, and the solution was cooled to 0 °C. At this temperature, 12 mL (12 mmol) of potassium *tert*-butoxide (1 M in THF) in 60 mL of anhydrous tetrahydrofuran was slowly added dropwise

Scheme 1. Synthetic Pathways to the Monomers and Polymers[a]



[a] (i) 2-Ethylhexyl bromide, KOH, MeOH, reflux; (ii) NBS, glacial acetic acid, 0 °C to room temperature; (iii) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C; (iv) *n*-BuLi, dimethyloctylchlorosilane, THF, −78 °C to room temperature; (v) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C; (vi) 4-bromobenzonitrile, Pd(PPh$_3$)$_4$, toluene/EtOH/Na$_2$CO$_3$ (*aq*), reflux; (vii) NBS, BPO, CCl$_4$, reflux; (viii) potassium *tert*-butoxide, THF, 0 °C to room temperature.

to the solution under nitrogen atmosphere. The reaction and workup procedure were carried out as described for PEHCNPV. Greenish-yellow PSi8CNPV (0.4 g, 53%) was obtained. M_n: 198 000, M_w: 927 000, PDI: 4.68. Anal. Calcd for $(C_{25}H_{31}NSi)_n$: C, 80.37; H, 8.36; N, 3.75. Found: C, 79.94; H, 8.23; N, 3.80. ^{1}H NMR (CDCl$_3$, ppm): 6.8−7.9 (br, 8H), 1.2 (br, 12H), 0.9 (br, 5H), 0.4 (br, 6H). ^{13}C NMR (CDCl$_3$, ppm): aromatic (C) 145.0, 142.8, 140.0, 133.1, 132.1, 130.3, 127.9, 126.5, 123.4, 118.5, 111.5; aliphatic (C) 33.6, 31.9, 29.2, 24.0, 22.6, 16.6, 14.0.

Table 1. Physical Properties of the Polymers

polymer	yield (%)	M_n	M_w	PDI	T_g (°C)	T_d[a] (°C)
PEHCNPV	47	103 000	765 000	7.42	192	401
PSi8CNPV	53	198 000	927 000	4.68	180	417

[a] Temperature resulting in 5% weight loss based on initial weight.

Results and Discussion

Synthesis and Characterization. A number of approaches have been taken to introduce an electron-withdrawing group into the side chains of PPV to enhance the electron affinity. These include the palladium-catalyzed coupling reaction of phenylboronic acid[15] or arylstannane[14] with haloarenes and the nickel-catalyzed Grignard coupling reaction between a bromo-substituted oxadiazole and a bromo-substituted arylene to form the corresponding monomer.[16] In the present study, we introduced the cyanophenyl group into the polymer side chain by the Suzuki coupling reaction of 4-bromobenzonitrile with boronic ester to obtain compounds **6** and **7** in 87% and 90% yield, respectively. The final monomers, compounds **8** and **9**, were easily polymerized by the Gilch polymerization with potassium *tert*-butoxide in THF. The monomer and polymer syntheses are shown in Scheme 1. The resulting polymers were brittle dark-yellow fibers. Previous studies of PPV derivatives found that fully conjugated PPVs containing electron-withdrawing groups such as halogen (Cl, Br),[9−11] trifluoromethyl,[13] 4-methylsulfonylphenyl, or phenyl on the arylene ring[15] were so insoluble in all solvents that they needed to be synthesized either by the halogen precursor route or using bis-sulfonium salts. In contrast, the fully conjugated polymers containing a cyanophenyl group described here can be synthesized through the standard Gilch polymerization and are completely soluble in common organic solvents such as chloroform, THF, dichloromethane, and nitrobenzene. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were 103 000−198 000 and 765 000−927 000 with a polydispersity of 4.68−7.42, as determined by GPC using THF as eluent and polystyrene as standard. The chemical structures of the polymers were confirmed by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectrum of PEHCNPV in CDCl$_3$ showed vinylene peaks at 7.0−7.1 ppm, but did not contain the benzylic proton peaks at 4.5 and 4.3 ppm of the monomer (compound **8**). All other peaks showed good correspondence with the chemical structure of PEHCNPV. The results of the characterization of the polymers are listed in Table 1.

Thermal Properties. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min. Figure 1 shows that the polymers lose less than 5% of their weight on heating to 400 °C, demonstrating their good thermal stability. Surprisingly, PEHCNPV and PSi8CNPV showed very high glass transition temperatures (T_g) of 192 and 180 °C, respectively, which are much higher than those of MEH−PPV[17] and cyclohexyl or phenyl silyl-substituted PPVs.[18] The T_g's were also obtained from the second heating cycle. A melting point or any other first-order transition attributed to liquid crystal behavior was not observed in the heating or cooling cycles in the range of 30−250 °C. The higher T_g of PEHCNPV in comparison to PSi8CNPV may be due to the more closely packed

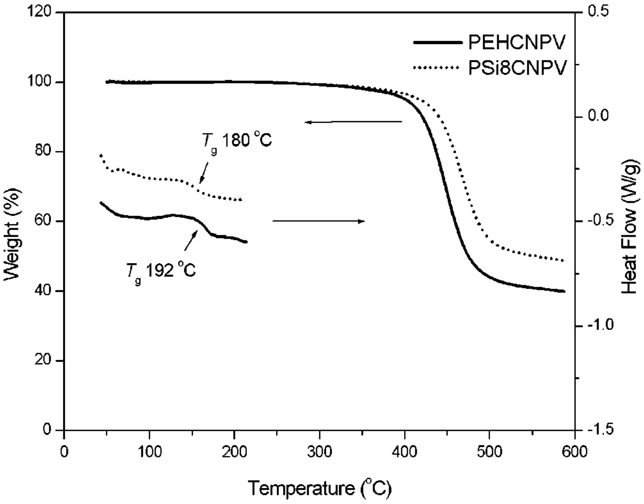


Figure 1. TGA traces and DSC thermograms of PEHCNPV and PSi8CNPV.

structure of the polymer chains in PEHCNPV. The DSC results indicate that the polymers possess high values of T_g due to the intermolecular and intramolecular interactions between the polar cyanophenyl electron-withdrawing groups, which should serve to significantly enhance the lifetime of EL devices based on these polymers.[19,20]

Optical and Photoluminescence Properties. The UV−vis absorption spectra and photoluminescence (PL) spectra of PEHCNPV and PSi8CNPV in dilute solutions of chloroform and as thin films are shown in Figure 2, and the related data are listed in Table 2. The UV−vis absorption maxima of PEHCNPV and PSi8CNPV appear at 446 and 427 nm for the chloroform solutions and at 452 and 434 nm for the thin films, respectively. The band gaps of PEHCNPV and PSi8CNPV estimated from the absorption edges are 2.34 and 2.47 eV, respectively. The band gap of PSi8CNPV is very similar to the band gaps previously reported for disilyl-substituted PPVs.[21] The PL spectra of the polymers, both in solution and as thin films, all consist of a typical vibronically structured band comprising a maximum, a shoulder, and a tail. The PL spectrum of the PEHCNPV thin film exhibits a maximum at 538 nm and a shoulder at 561 nm, which are blue-shifted about 12−17 nm relative to the corresponding features measured from polymers containing 4-methylsulfonylphenyl as an electron-withdrawing group (550 nm, 575 nm (sh)) or a phenyl group (555 nm, 590 nm (sh)) on the arylene ring.[14] The blue-shift in the spectroscopic features of PEHCNPV indicates that the inclusion of the cyano group at the 4-position of the phenyl group, which allows conjugation through the cyano and phenyl, creates an electron-withdrawing group that is more effective than the methylsulfonyl group. The PL spectra of PSi8CNPV in solution and thin film show emission maxima at 497 and 513 nm and shoulders at 527 and 547 nm, respectively, which are almost the same as the wavelengths reported for disilyl-substituted PPVs.[21] The PL quantum yields of PEHCNPV and PSi8CNPV were 0.43 and 0.62, respectively.

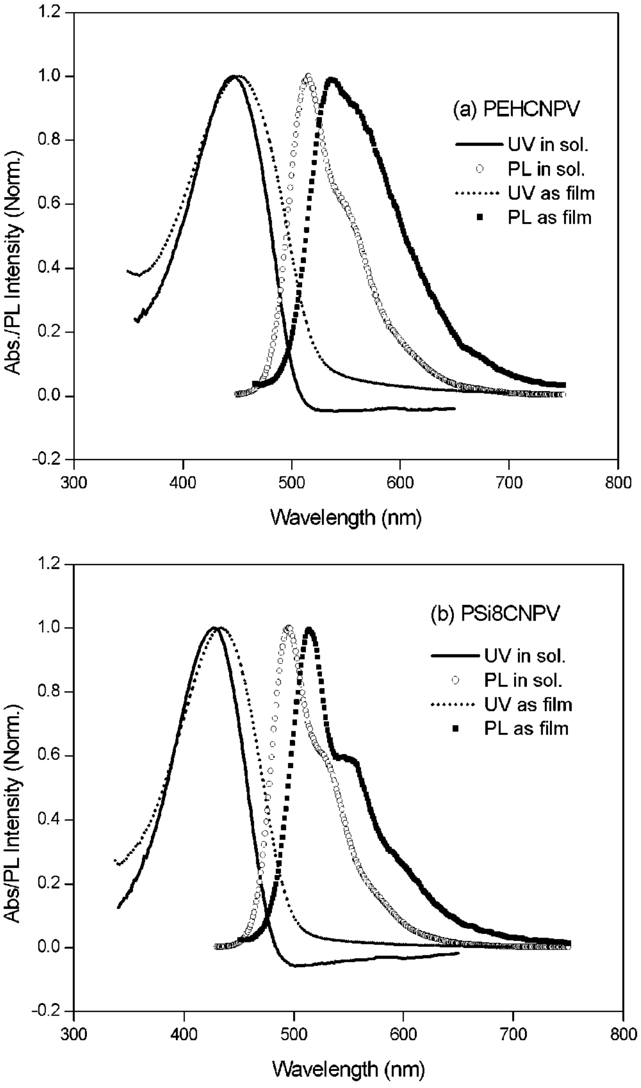


Figure 2. UV−visible absorption and photoluminescence spectra of (a) PEHCNPV and (b) PSi8CNPV.

Table 2. Optical Properties of the Polymers

	λ_{max} (UV, nm)		λ_{max} (PL, nm)[a]			
polymer	solution	film	solution	film	E_g (eV, (UV/nm))[b]	Φ_{PL}[c]
PEHCNPV	446	452	516 (547)	538 (561)	2.37 (522)	0.43
PSi8CNPV	427	434	496 (527)	513 (547)	2.47 (501)	0.62

[a] Values in parentheses represent shoulder peaks. [b] Determined from the absorption edge (value in parentheses) of the UV−vis spectrum. [c] PL quantum yields of the polymers in chloroform were determined by comparison to quinine sulfate in 0.10 M H_2SO_4 as standard.

Electrochemical Properties of the Polymers. Cyclic voltammetry (CV) was employed to investigate the redox behavior of the polymers and to estimate their HOMO and LUMO energy levels. The electrochemical processes probed by cyclic voltammetry are similar to those involved in the charge injection and transport processes in LED devices.[21] The polymer films were coated onto a Pt electrode and scanned positively and negatively at a scan rate 50 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. All measurements were calibrated using ferrocene (Fc) as the standard.[22] Figure 3 shows the CV curves of the p- and n-doping processes of the polymers. During the cathodic scan, the polymers exhibit reversible n-doping processes. The onset of reduction for PEHCNPV and PSi8CNPV occurred at voltages of −1.67 and −1.64 V (vs SCE), respectively, which correspond to a LUMO energy level of about −2.7 eV. As shown in Figure 4, these LUMO energy levels are much lower than those of PPV[23] and silyl-substituted PPVs.[18] The electrochemical stability of the

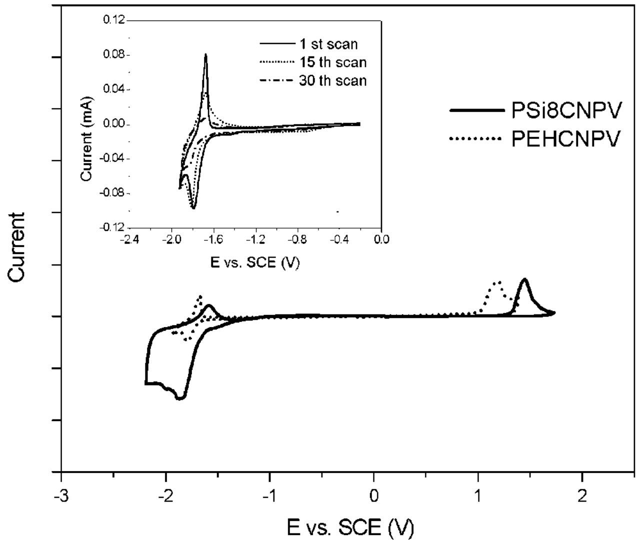


Figure 3. Cyclic voltammograms of PEHCNPV and PSi8CNPV. Inset: n-doping multiscans of PEHCNPV.

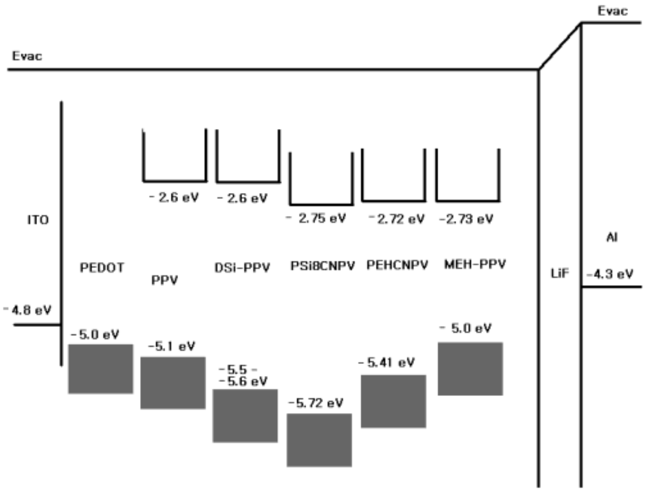


Figure 4. Energy band diagram of PPV, DSi−PPV (disilyl-substituted PPVs), PEHCNPV, and PSi8CNPV.

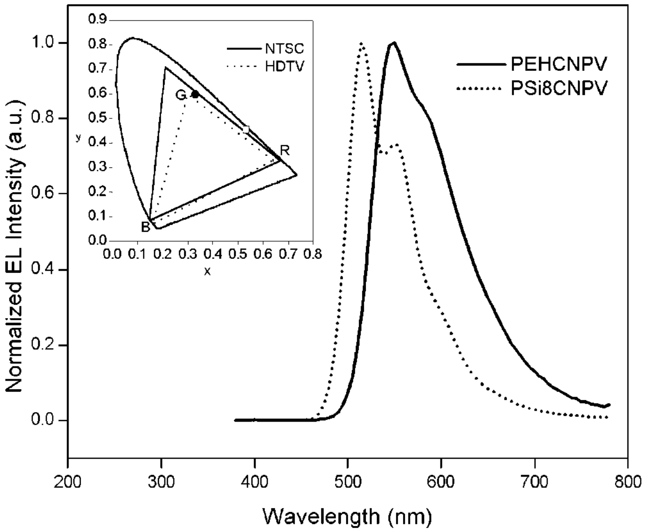


Figure 5. Electroluminescence spectra of PEHCNPV and PSi8CNPV in devices of configuration ITO/PEDOT/polymer/LiF/Al. Inset: CIE coordinates of the emissions from the PEHCNPV (□) and PSi8CNPV (●) devices.

polymers was investigated by performing n-doping multiscans on films of the polymers. The inset in Figure 3 shows the n-doping multiscan cyclic voltammograms of PEHCNPV. After 15 cyclic scans, the peak values are almost unchanged, and after 30 scans a slight change is observed in the cyclic voltammogram. In the anodic scan, the onset of oxidation of PEHCNPV and PSi8CNPV occurs at voltages of 1.02 and 1.33 V (vs SCE), respectively, corresponding to HOMO energy levels of −5.41 and −5.72 eV. The HOMO and LUMO energy levels of PSi8CNPV are lower than those of disilyl-substituted PPVs (about −2.6 and about −5.5 to −5.6 eV, respectively), which can be attributed to the introduction of the electron-withdrawing cyanophenyl group. The more negative energy of the LUMO of PSi8CNPV indicates that the electron injection process is easier in PSi8CNPV than in disilyl-substituted PPVs. However, the more negative energy of the HOMO of PSi8CNPV indicates that it is difficult to inject holes into the polymer. Overall, the energy levels of PSi8CNPV indicate that this polymer is not only an EL material suitable for use in polymer LEDs but also a good candidate electron-conducting/hole-blocking material. All of the data, including electrochemical band gaps, are listed in Table 3.

Electroluminescent Properties and Current−Voltage-Luminance (*I*−*V*−*L*) Characteristics. Devices with the configuration ITO/PEDOT/polymer/LiF/Al were fabricated to investigate the electroluminescent properties and the current−voltage-luminance characteristics of PEHCNPV and PSi8CNPV. Polymer films of thickness approximately 80 nm were spin-cast onto a PEDOT layer of thickness approximately 30 nm, which had been precast on the ITO substrate. The electroluminescence from the polymer in the device was greenish-yellow for PEHCNPV and green for PSi8CNPV. As shown in Figure 5, the EL spectra of PEHCNPV and PSi8CNPV show maximum peaks at 546 and 513 nm, and shoulder peaks at 571 and 549 nm, respectively. These features are similar to those observed in the PL spectra of the corresponding polymer films. The quality of emission spectra is typically defined by their CIE (Commission Internationale de L'Eclairage) chromaticity coordinates (x, y).[24] The CIE coordinates for the EL spectra of PEHCNPV and PSi8CNPV are (0.455, 0.532) and (0.330, 0.599), respectively. In particular, PSi8CNPV emits a pure green light with a CIE coordinate that is closer to the standard green (0.30, 0.60) used in high definition television (HDTV) than the CIE values of previously reported green light-emitting polymers.[25,26]

Table 3. Electrochemical Properties and Energy Levels of the Polymers

	p-doping (V)[a]			n-doping (V)[a]						
polymer	E_{onset}	E_{pa}	E_{pc}	E_{onset}	E_{pc}	E_{pa}	E_g (eV, Echem)	HOMO[b] (eV)	LUMO[b] (eV)	IP[c] (eV)
PEHCNPV	1.02	1.19		−1.67	−1.79	−1.67	2.69	−5.41	−2.72	−5.43
PSi8CNPV	1.33	1.45		−1.64	−1.85	−1.58	2.97	−5.72	−2.75	−5.79

[a] E_{onset}, E_{pa}, and E_{pc} stand for onset potential, anodic peak potential, and cathodic peak potential, respectively. [b] Calculated using the empirical equation: $E = -(E_{\text{onset}} + 4.39)$.[21] [c] Measured by RIKEN KeiKi AC-2.

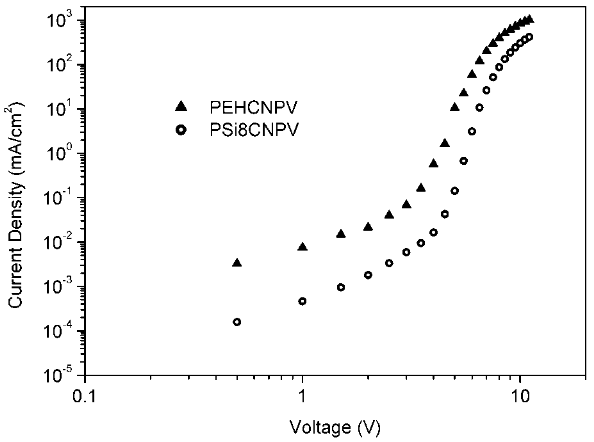


Figure 6. Logarithmic voltage−current density characteristics of PEHCNPV (▲) and PSi8CNPV (○).

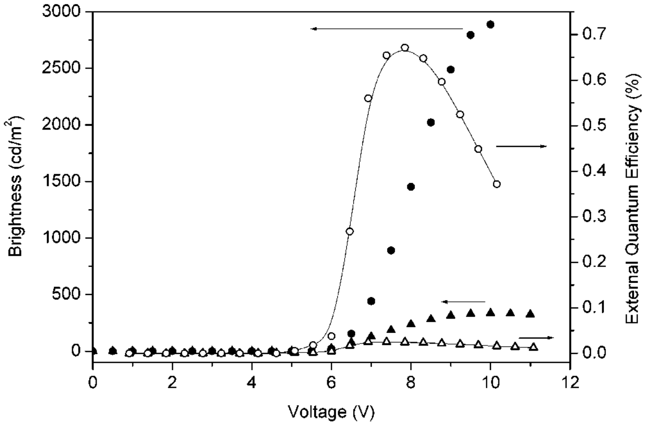


Figure 7. Voltage-brightness and external quantum efficiency plots of PEHCNPV (▲, brightness; -△-, quantum efficiency) and PSi8CNPV (●, brightness; -○-, quantum efficiency).

The voltage−current density characteristics of the devices fabricated from PEHCNPV and PSi8CNPV are shown in Figure 6. In the forward bias, the turn-on voltages (V_T) of PEHCNPV and PSi8CNPV are 3.0 and 4.0 V, respectively. The current density of PSi8CNPV is an order of magnitude lower than that of PEHCNPV. The higher turn-on voltage and lower current density of PSi8CNPV in comparison to PEHCNPV can be accounted for by the difference in the energy barrier between PEDOT and the respective polymers. As shown in Figure 4, the HOMO energy level of PSi8CNPV is at −5.72 eV, which is substantially lower than that of PEHCNPV (−5.41 eV). Figure 7 shows the voltage-brightness and external quantum efficiency plots for PEHCNPV and PSi8CNPV. The maximum brightness of PSi8CNPV is 2900 cd/m^2 at 10 V and 300 mA/cm^2 and the highest external quantum efficiency is 0.67% at 7.5 V, 51 mA/cm^2, and 890 cd/m^2. However, PEHCNPV reaches a brightness of 330 cd/m^2 at 10.5 V and 920 mA/cm^2 and has a relatively low external quantum efficiency of 0.025%. At present, there is no clear explanation for the disparity between the external quantum efficiencies of PEHCNPV and PSi8CNPV; however, we conjecture that the lower external quantum efficiency of PEHCNPV may be due to its more closely packed chain structure in comparison to PSi8CNPV.[27,28] The performance of devices employing PEHCNPV or PSi8CNPV as an emissive layer might be improved by introducing a graded hole transporting layer such as PVK,[29] PMMA mixed with TPD,[30] or fluorene-based poly(iminoarylene)s.[31] On the other hand, the low HOMO and LUMO energy levels of PSi8CNPV suggest the potential of this polymer for application as an electron-conducting/hole-blocking (ECHB) layer.[32] Further research into multilayer devices for enhanced green light emission is currently underway.

Conclusions

Two PPV derivatives containing a cyanophenyl group as an electron-withdrawing group, poly[2-(2′-ethylhexyloxy)-5-(4′-cyanophenyl)-1,4-phenylenevinylene] (PEHCNPV) and poly[2-dimethyloctylsilyl-5-(4′-cyanophenyl)-1,4-phenylenevinylene] (PSi8CNPV), were synthesized via the standard Gilch polymerization. The synthesized polymers were completely soluble in common organic solvents and had good thermal stabilities. In particular, they showed very high glass transition temperatures. The HOMO and LUMO energy levels of PEHCNPV and PSi8CNPV were lower than those of other PPVs. PSi8CNPV emitted pure green light with a peak at 513 nm and a CIE coordinate of (0.330, 0.599), which is very close to the standard green of HDTV. In future work, we will focus on the production of green light-emitting PPV-based polymers with improved external quantum efficiency.

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