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Novel Electroluminescent Polymers with Fluoro Groups in Vinylene Units

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ABSTRACT: New electroluminescent polymers with fluoro groups in vinylene units, poly(*p*-phenylenedifluorovinylene) (PPDFV) and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS−PPDFV), have been synthesized by GILCH polymerization. These polymers have been used as the electroluminescent (EL) layers in double-layer light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al). PPDFV shows photoluminescence around $\lambda_{max} = 580$ nm (exciting wavelength, 410 nm) and yellow electroluminescence around $\lambda_{max} = 565$ nm. DMOS−PPDFV shows PL around $\lambda_{max} = 495$ nm and green EL around $\lambda_{max} = 540$ nm. The current−voltage−luminance ($I-V-L$) characteristics of the polymers show turn-on voltages of 3.0 V approximately. Two fluoro groups were introduced on every vinylene units of poly(*p*-phenylenevinylene) (PPV) and poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS−PPV) to give PPDFV and DMOS−PPDFV in an attempt to increase the electron affinity of the parent polymer. It was found that the efficiency of PLED of DMOS−PPDFV was about 7 times higher than that of DMOS−PPV.

Introduction

Caused by the prospective application as large-area light-emitting diodes (LEDs),[1−3] numerous reports about PLEDs have been published since the discovery of electroluminescence (EL) from a conjugated polymer, poly(*p*-phenylenevinylene) (PPV).[4] However, to be utilized in the single-layer devices with high work function metal as the cathode, PPV has the drawback that it is a poor electron acceptor due to its high LUMO energy. To overcome the imbalance of charge carrier injection or mobility, the most frequently used solutions have been either to use additional organic charge-transporting layers between the emissive layer and one or both of the electrodes[5−7] or to adjust the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone. It was shown by Bredas et al. that introduction of electron-withdrawing groups onto the arylene rings or the vinyl groups 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] Abundant derivatives of PPV have been reported with electron-withdrawing substituents such as halide,[9−13] cyano,[14] trifluoromethyl,[15] or methylsulfonyl−phenyl[16] on the arylene rings. Other examples with electron-withdrawing groups on the vinylene group of conjugated polymers have also been reported.[5,17−21] In the present paper, we report the synthesis and electroluminescence properties of new EL polymers, poly(*p*-phenylenedifluorovinylene) (PPDFV) and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS−PPDFV), which contain two fluoro groups in every vinylene units to reduce the barrier of electron injection.

Experimental Section

General. Used all reagents were purchased from Aldrich and used without further purification. Solvents were purified by normal procedure and handled under a moisture-free atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 (200 MHz) and Varian Gemini-500 (500 MHz) spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. An Oriel InstaSpec CCD detection systems of Busan Branch of Korea Basic Science Institute was used for photoluminescence spectroscopy.

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between the emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of PEDOT/PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin-casting ODCB (*o*-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in a vacuum, and aluminum electrodes were deposited on top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current−voltage ($I-V$) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measurements mentioned above were carried out under air and at room temperature.

To examine electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto platinum plate as a working electrode with an area of 1 cm^2. Film thickness was controlled in the range of about 3 μm by the amount of solution. After coating, the film adhering to the electrode was dried in a vacuum oven for 10 h. The electrochemical measurements were performed with 0.1 M tetrabutylammonium tetrafluoroborate (TBAF, freshly distilled, Aldrich) solution in acetonitrile. A platinum wire and a Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetric waves

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were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

Synthesis of α,α-Dibromo-*p*-xylene (1). A stirred mixture of 6 g (56.51 mmol) of *p*-xylene and 20.1 g (113.2 mmol) of *N*-bromosuccinimide (NBS) in CCl_4 (200 mL) at room temperature was irradiated with the light source (300 W) for 1 h. The reaction mixture was filtered in order to remove generated succinimide. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (60 × 150 mm column, SiO_2, 100% of hexane) to give 9.9 g (67%) of the desired final α,α′-dibromo-*p*-xylene (**1**), white solid; R_f 0.25 (SiO_2, hexane 100%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 4.48 (s, 4H), 7.37 (s, 4H)

Synthesis of α,α′-Difluoro-*p*-xylene (2). To a stirred solution of 10 g (37.88 mmol) of α,α-dibromo-*p*-xylene (**1**) in 20 mL of tetrahydrofuran (THF) at room temperature, 98.5 mL (98.5 mmol) of 1.0 M TBAF (tetrabutylammonium fluoride) in THF was added. After stirring for 24 h at 50 °C, the reaction mixture was concentrated in vacuo to remove the solvent. After adding hexane, the mixture was stirred for 1 h and filtered. The filtrate was concentrated in vacuo and purified by column chromatography to give 2.3 g (42.9%) of the desired α,α-difluoro-*p*-xylene (**2**), yellow oil; R_f 0.28 (SiO_2, hexane 100%). ^1H NMR (200 MHz, acetone-d_6) δ (ppm): 5.43 (d, 4H, $J = 49.4$ Hz), 7.47 (s, 4H). ^{13}C NMR (50 MHz, acetone-d_6) δ (ppm): 84.90 (d, $J = 163.5$ Hz), 128.80 (d, $J = 6.5$ Hz), 138.13 (d, $J = 20$ Hz).

Synthesis of 1,4-Bis(bromofluoromethyl)benzene (3). A stirred mixture of 716 mg (5.04 mmol) of α,α′-difluoro-*p*-xylene (**2**) and 1.79 g (10.07 mmol) of NBS in CCl_4 (20 mL) at room temperature was irradiated with the light source (300 W) for 1 h. The reaction mixture was filtered in order to remove generated succinimide. The filtrate was concentrated in vacuo and purified by flash column chromatography (15 × 150 mm column, SiO_2, 100% of hexane) to give 688 mg (45.5%) of the desired final 1,4-bis(bromofluoromethyl)benzene (**3**), white solid; R_f 0.20 (SiO_2, hexane 100%). ^1H NMR (200 MHz, acetone-d_6) δ (ppm): 7.86 (d, 2H, $J = 48$ Hz), 7.72 (s, 4H). ^{13}C NMR (50 MHz, acetone-d_6) δ (ppm): 92.74 (d, $J = 249.5$ Hz), 126.63 (d, $J = 6.5$ Hz), 141.94 (d, $J = 20$ Hz). Anal. Calcd for $C_8H_6Br_2F_2$: C, 32.04; H, 2.02; F, 12.67. Found: C, 31.88; H, 2.23; F, 12.30.

Synthesis of Poly(*p*-phenylenedifluorovinylene) (PPDFV) (4). To a stirred solution of 781 mg (2.6 mmol) of 1,4-bis(bromofluoromethyl)benzene (**3**) in 20 mL of THF at 40 °C under argon was added, drop by drop, 62.4 mL (15.6 mmol) of a 0.25 M solution of potassium *tert*-butoxide in THF using the dropping funnel over a period of 1 h. During this addition, the reaction mixture had color change from colorless via greenish to yellow, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 10 h at room temperature. The reaction mixture was slowly poured into 200 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature to generate 660 mg of the crude polymer as yellow power. The resulting polymer was redissolved in 200 mL of DMF at 60 °C, cooled to 40 °C, and reprecipitated by dropwise addition of 500 mL methanol. The precipitated polymer was filtered and dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol to generate 200 mg (55.7%) of poly(*p*-phenylenedifluorovinylene) (PPDFV) (**4**) as light yellow polymer fibers. ^1H NMR (300 MHz, DMF-d_6) δ (ppm): 7.19 (brs). ^{13}C NMR (75 MHz, DMF-d_6) δ (ppm): 68.3, 127.1, 129.5. Anal. Calcd for $C_8H_4F_2$: C, 69.57; H, 2.92; F, 27.51. Found: C, 68.82; H, 2.80; F, 26.04.

Synthesis of Dimethyloctylsilyl-*p*-xylene (5). To a stirred solution of 22.34 g (121 mmol) of 2-bromo-*p*-xylene in 50 mL of THF was slowly added 75.6 mL (121 mmol) of 1.60 M solution of *n*-C_4H_9Li in hexane at −78 °C. After 2 h at −78 °C, 25 g (121 mmol) of chlorodimethyloctylsilane was slowly added to the reaction mixture at −78 °C over 2 h. After 3 h at room temperature, the reaction mixture was quenched with dilute aqueous hydrochloric acid solution. The oragnic layer was separated and washed with water 150 mL (3 × 50 mL). The combined aqueous phase was extracted with diethyl ether 150 mL (3 × 50 mL). The combined organic layer was dried with $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography (60 × 150 mm column, SiO_2, 100% of hexane) to give 22.4 g (81 mmol, 67%) of dimethyloctylsilyl-*p*-xylene (**5**); R_f 0.36 (SiO_2, hexane 100%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.28 (s, 1H), 7.09 (s, 2H), 2.43 (s, 3H), 1.41−1.14 (m, 12H), 0.97−0.75 (m, 5H), 0.33 (s, 6H).

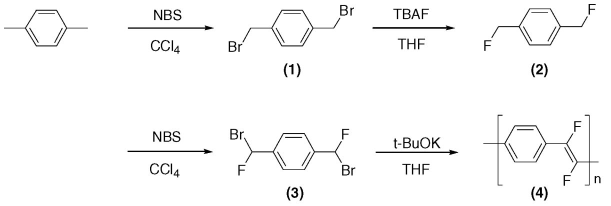
Synthesis of 2-Dimethyloctylsilyl-1,4-bis(bromomethyl)benzene (6). A stirred mixture of 20 g (72.3 mmol) of dimethyloctylsilyl-*p*-xylene (**5**) and 25.93 g (145 mmol) of NBS in CCl_4 (50 mL) at room temperature was irradiated with the light source (300 W) for 1 h. The reaction mixture was filtered in order to remove generated succinimide. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (60 × 150 mm column, SiO_2, 100% of hexane) to give 23.5 g (54.2 mmol, 75%) of 2-dimethyloctylsilyl-1,4-bis(bromomethyl)benzene (**6**), colorless oil: R_f 0.32 (SiO_2, hexane 100%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 1H), 7.43 (s, 2H), 4.61 (s, 2H), 4.48 (s, 2H), 1.43−1.19 (m, 12H), 0.99−0.88 (m, 5H), 0.42 (s, 6H).

Synthesis of 2-Dimethyloctylsilyl-1,4-bis(fluoromethyl)benzene (7). To a stirred solution of 10 g (23.0 mmol) of 2-dimethyloctylsilyl-1,4-bis(bromomethyl)benzene (**6**) in 20 mL of THF at room temperature, 69.0 mL (69.0 mmol) of 1.0 M solution of TBAF (tetrabutylammonium fluoride) in THF was added. After stirring for 24 h at 50 °C, the reaction mixture was concentrated in vacuo to remove solvent. After adding hexane to the residue, the mixture was stirred for 1 h and filtered. The filtrate was concentrated in vacuo and purified by column chromatography (60 × 150 mm column, SiO_2, 100% of hexane) to give 2.0 g (19.2 mmol, 28%) of 2-dimethyloctylsilyl-1,4-bis(fluoromethyl)benzene (**7**), colorless oil; R_f 0.33 (SiO_2, hexane 100%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.51 (s, 1H), 7.44 (s, 2H), 5.57 (d, 2H, $J = 48$ Hz), 5.50 (d, 2H, $J = 48$ Hz), 1.43−1.19 (m, 12H), 0.99−0.81 (m, 5H), 0.32 (s, 6H).

Synthesis of 2-Dimethyloctylsilyl-1,4-bis(bromofluoromethyl)benzene (8). A stirred mixture of 700 mg (2.24 mmol) of 2-dimethyloctylsilyl-1,4-bis(fluoromethyl)benzene (**7**) and 800 mg (4.47 mmol) of NBS in CCl_4 (50 mL) at room temperature was irradiated with the light source (300 W) for 1 h. The reaction mixture was filtered in order to remove generated succinimide. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (20 × 150 mm column, SiO_2, 100% of hexane) to give 500 mg (1.06 mmol, 48%) of 2-dimethyloctylsilyl-1,4-bis(bromofluoromethyl)benzene (**8**), colorless oil; R_f 0.32 (SiO_2, hexane 100%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.87−7.27 (m, 5H), 1.43−1.17 (m, 12H), 0.85 (m, 5H), 0.38 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 145.97 (d, $J = 17.7$ Hz), 139.47 (d, $J = 19.55$ Hz), 136.37, 130.84 (d, $J = 6.3$ Hz), 127.39 (d, $J = 5.5$ Hz), 126.72, 126.60, 93.90, 88.87, 33.37, 31.86, 29.17, 23.77, 22.64, 16.35, 14.10. Anal. Calcd for $C_{18}H_{28}Br_2F_2Si$: C, 45.97; H, 6.00; F, 8.08. Found: C, 45.66; H, 5.92; F, 7.81.

Synthesis of Poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS−PPDFV) (9). To a stirred solution of 400 mg (0.85 mmol) of 1,4-bis(bromofluoromethyl)benzene (**8**) in 20 mL of THF at 40 °C under argon was added, drop by drop, 20.4 mL (5.10 mmol) of a 0.25 M solution of potassium *tert*-butoxide in THF using the dropping funnel over a period of 1 h. During this addition, the reaction mixture had color change from colorless via greenish to yellow, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 10 h at room temperature. The reaction mixture was slowly poured into 200 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature to generate 660 mg of the crude polymer as green power. The resulting polymer was redissolved in 100 mL of THF (60 °C), cooled to 40 °C, and reprecipitated by dropwise addition of 500 mL of methanol. The precipitated polymer was dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol to generate 97 mg

Scheme 1. Synthetic Routes for Monomer and Polymer of PPDFV



Scheme 2. Synthetic Routes for Monomer and Polymer of DMOS−PPDFV

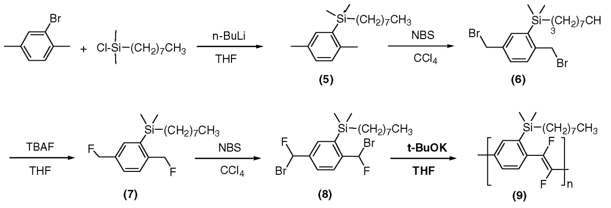


Table 1. Polymerization Results of PPDFV and DMOS−PPDFV

polymers	yield (%)	M_n[a]	M_w[a]	PDI[a]
PPDFV	55.7	161 000	287 000	1.77
DMOS−PPDFV	19.3	28 000	78 000	2.79

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

(37%) of poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS−PPDFV) (**9**) as a light green polymer power. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.41−7.17 (brs, 3H, aromatic proton), 1.45−0.96 (brs, 14H, (CH$_2$)$_7$), 0.74 (brs, 3H, CH$_3$), 0.35 (brs, 6H, Si(CH$_3$)$_2$). Anal. Calcd for $C_{18}H_{26}F_2Si$: C, 70.08; H, 8.50; F, 12.32. Found: C, 69.09; H, 8.32; F, 11.58.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1 and Scheme 2. For the preparation of PPDFV, *p*-xylene was brominated using NBS and light source (300 W) to generate α,α′-dibromo-*p*-xylene (**1**). The resulting dibromide was fluorinated with tetrabutylammonium fluoride (TBAF)[22] and then brominated[23] again using NBS and light source to generate 1,4-bis(bromofluoromethyl)benzene (**3**), the monomer for PPDFV. The DMOS−PPDFV was also synthesized in five steps. 2-Bromo-*p*-xylene, as the starting material, was coupled with chlorodimethyloctylsilane using *n*-butyllithium in THF to generate dimethyloctylsilyl-*p*-xylene, which was brominated, fluorinated, and then brominated to generate 1,4-bis(bromofluoromethyl)-2-dimethyloctylsilylbenzene (**8**), the monomer for DMOS−PPDFV. The structure and purity of the monomers were confirmed by ^{1}H NMR and ^{13}C NMR. The polymers of these monomers were prepared by the Gilch reaction,[24] with an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h under an Ar atmosphere. Known poly(2-dimethyloctylsilyl-*p*-phenylenevinylene (DMOS−PPV)[25] was also synthesized, using a similar method, to be compared with DMOS−PPDFV.The resulting PPDFV, brittle dark-yellow polymer was soluble in organic solvents such as dimethylformamide (DMF) and *o*-dichlorobenzene (ODCB). The emissive polymer film was obtained by spin-casting an ODCB solution of PPDFV. The DMOS−PPDFV was soluble in various organic solvents such as chloroform, chlorobenzene, THF, dichloromethane, and ODCB. The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) of the PPDFV were 161 000, and 287 000 with polydispersity of 1.77 as determined by GPC using DMF as the eluent and polystyrene as the standard. $\bar{M}_n$ and $\bar{M}_w$ of the DMOS−PPDFV were 28 000 and 78 000 with polydispersity of 2.79 as determined by GPC using THF as the eluent. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C /min. PPDFV and DMOS−PPDFV lose less than 5% of their weights on heating to 550 and 350 °C, respectively. The TGA thermograms of the polymers are shown in Figure 1. The polymers 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.

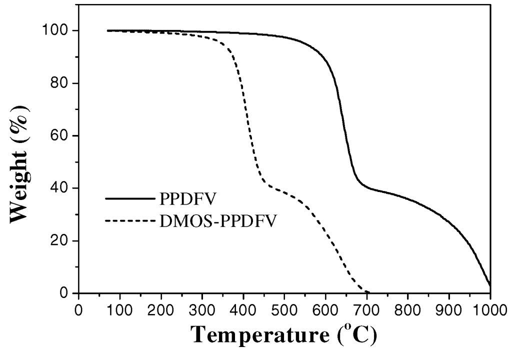


Figure 1. TGA of PPDFV and DMOS−PPDFV.

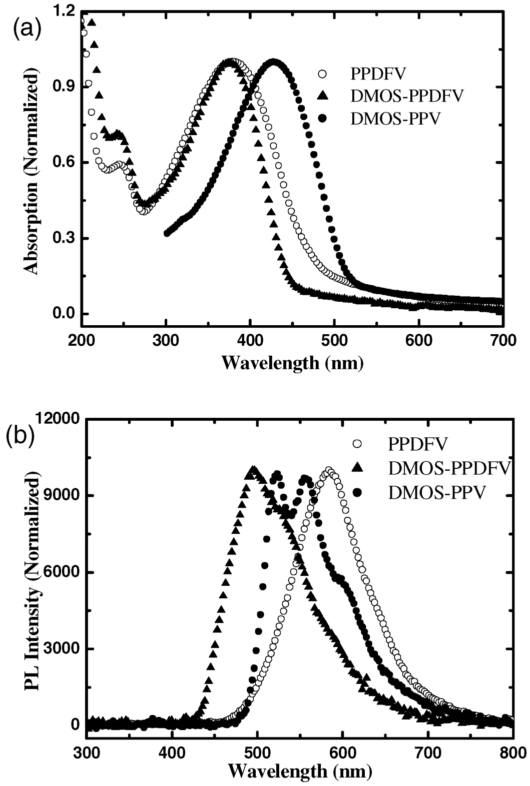


Figure 2. (a) UV−vis absorption and (b) PL spectra of PPDFV, DMOS−PPV, and DMOS−PPDFV.

Optical and Photoluminescence Properties. The UV−vis absorption spectra and photoluminescence spectra of PPDFV and DMOS−PPDFV as thin films are shown in Figure 2. The thin films were prepared by spin-coating on quartz plates from the polymer solutions

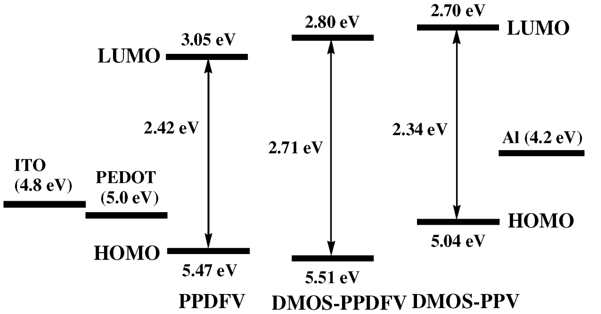


Figure 3. Energy band diagram of PPDFV, DMOS−PPV, and DMOS−PPDFV.

with *o*-dichlorobenzene (ODCB). The PPDFV exhibit absorption spectra with a maximum peak of 390 nm, which are blue-shifted about 30 nm relative to PPV,[3] attributed to the $\pi-\pi^*$ transition of the conjugated backbones. DMOS−PPDFV has a strong absorption band at around 385 nm, which is attributed to the $\pi-\pi^*$ transition of the conjugated segments. The absorption onset wavelengths of PPDFV and DMOS−PPDFV were 512 and 457 nm, which correspond to band gaps of 2.42 and 2.71 eV. The PL spectra of the polymers all consist of a typical vibronically structured band comprising a maximum, a shoulder, and a tail.

The PL spectrum of the PPDFV thin film exhibits a maximum at 580 nm, which is red-shifted about 40 nm relative to that of PPV.[3] PPDFV shows interesting spectral properties as was reported to other fluorine-substituted PPV derivatives. The PPVs with fluorine substitution on the phenylene units have UV absorption maximum peaks that are blue-shifted relative to that of PPV but have PL emissions that are substantially red-shifted relative to that of PPV.[9,11,13] These results are not well understood, but red-shifted PL emission of fluorine substituted PPVs clearly reflect the electronic effects of fluorine substitution. A reasonable suggestion is that the excitons generated in fluorine-substituted PPVs may be trapped in shallow trap states associated with charge separation between polymer backbone and highly electronegative fluorine atoms. Therefore, this donor−acceptor pair recombination process exhibits a longer wavelength emission in fluorine-substituted PPVs.[3] On the other hand, the PL spectrum of the DMOS−PPDFV thin film exhibits a maximum at 495 nm, which is blue-shifted about 30 nm relative to that of DMOS−PPV. The blue shift in the spectroscopic features of DMOS−PPDFV as compared to that of DMOS−PPV indicates the decrease of the effective conjugation length by the inclusion of the fluoro group at the vinyl position. The effective conjugation length of DMOS−PPDFV was decreased by the possible steric effect between the fluoro group and the bulky trialkylsilyl group.

Electrochemical Properties of the Polymers. The energy band diagrams, as shown in Figure 3, of polymers were determined from the band gaps, which were estimated from the absorption edges, and the HOMO energy levels, which were estimated from cyclic voltammetry.[26] The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode (~0.05 cm^2) coated with a thin polymer film was used as the working electrode. A Pt wire and a Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. All measurements were calibrated against an internal standard, ferrocene (F_c), which has the IP value (−4.8 eV) of the F_c/F_c^+ redox system.[27] All of the polymers exhibit irreversible processes in an oxidation scan. The band gap and HOMO level are 2.42 and 5.47 eV for PPDFV, 2.7l and 5.51 eV for DMOS−PPDFV, and 2.34 and 5.04 eV for DMOS−PPV. The HOMO and LUMO energy levels of DMOS−PPDFV are lower than those of DMOS−PPV, which can be attributed to the introduction of the electron-withdrawing fluoro groups. The higher work function of the LUMO of DMOS−PPDFV as compared to that of DMOS−PPV indicates that the electron injection process is easier in DMOS−PPDFV than in DMOS−PPV.

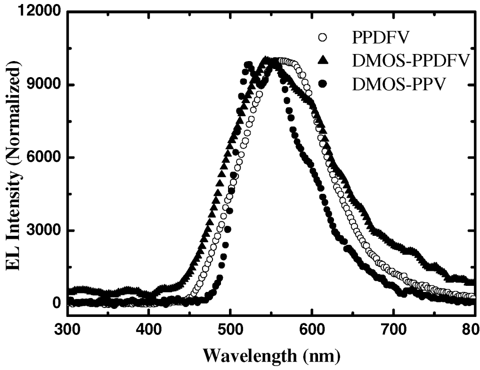


Figure 4. Electroluminescence (EL) spectra of PPDFV, DMOS−PPV, and DMOS−PPDFV with a configuration of ITO/PEDOT:PSS/polymer/Al.

Electroluminescent Properties and Current−Voltage−Luminance. The normalized electroluminescence (EL) spectra and the current−voltage characteristics of the ITO/PEDOT/polymers/Al device are shown in Figure 4. The PEDOT:PSS was spin-coated from aqueous solution with isopropyl alcohol (10 wt %) on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin-casting an ODCB (*o*-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in a vacuum, and the aluminum electrode were deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below about 10^{-6} mbar, yielding an active area of 4 mm^2. The current−voltage ($I-V$) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measurements mentioned above were carried out under air and at room temperature.

The EL spectra of PPDFV and DMOS−PPDFV exhibit maximum peaks at 565 and 540 nm, which correspond to yellow and green light, respectively.

The voltage−current density characteristics of the devices fabricated from PPDFV and DMOS−PPDFV are shown in Figure 5. For PPDFV and DMOS−PPDFV, the turn-on voltages are approximately 3−4 V, and the current densities increase in an exponential manner with increasing forward bias, which is typical of diode characteristic. The maximum brightness of DMOS−PPDFV is 750 cd/m^2 at 7.5 V. However, PPDFV reaches a brightness of 95 cd/m^2 at 7.0 V. As shown in Figure 3, the higher work function of the LUMO of DMOS−PPDFV as compared to that of LUMO of DMOS−PPV indicates the electron injection process is easier in DMOS−PPDFV than in DMOS−PPV. From this result, higher quantum efficiency of DMOS−PPDFV as com-

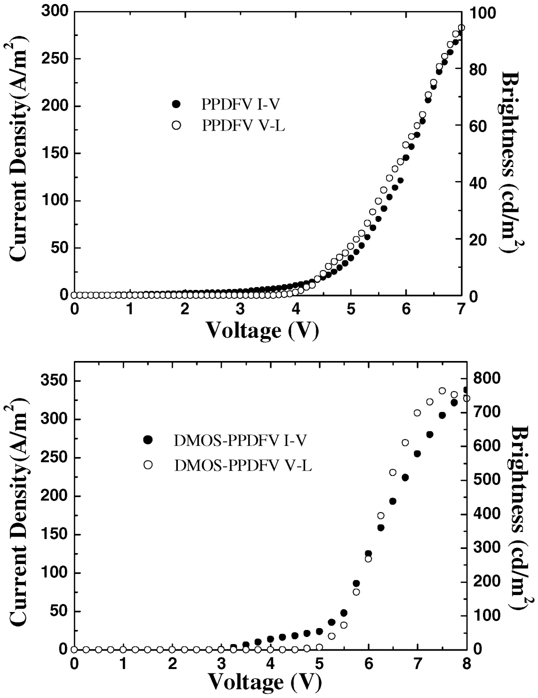


Figure 5. Current–voltage–luminescence (*I*–*V*–*L*) characteristics of PLEDs of PPDFV, DMOS–PPV, and DMOS–PPDFV with a configuration of ITO/PEDOT:PSS/polymer/Al.

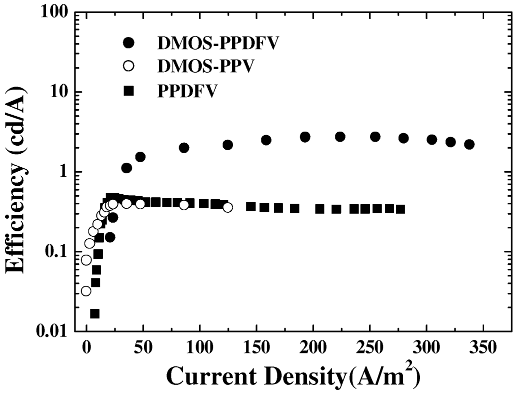


Figure 6. Efficiencies of PLEDs of PPDFV, DMOS–PPDFV, and DMOS–PPV with a configuration of ITO/PEDOT:PSS/polymer/Al.

pared to that of DMOS–PPV can be expected due to its improved electron injection ability from the cathode.

Figure 6 shows the EL efficiency of DMOS–PPDFV is higher than that of DMOS–PPV. The luminescence efficiency of the polymer LEDs with PPDFV and DMOS–PPDFV at room temperature were about 0.47 cd/A at 4.6 V and 2.7 cd/A at 6.5 V, respectively.

Conclusion

We have synthesized, by the Gilch reactions, new PPV derivatives, poly(*p*-phenylenedifluorovinylene) (PPDFV) and poly(2-dimethyloctylsilyl-1,4-phenylene–difluorovinylene) (DMOS–PPDFV), with fluoro groups in vinylene units. These polymers have quite good thermal stability. The polymer LEDs of PPDFV and DMOS–PPDFV emit bright yellow and green light with maximum peak around 565 and 540 nm, respectively. Both polymers have low turn-on voltages of 3–4 V in the Al/polymer/PEDOT/ITO device. The highest efficiency of PPDFV was observed to be 0.47 cd/A at 4.6 V, and that of DMOS–PPDFV was observed to be 2.7 cd/A at 6.5 V, which was higher than that of DMOS–PPV (0.39 cd/A at 7.0 V) due to the improved electron injection ability from the cathode caused by the fluoro functionality.

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