Novel Electroluminescent PPV Copolymers Containing Si-phenyl and Difluorovinylene Units

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New electroluminescent copolymers with fluoro groups in vinylene units, poly(2-(3'-dimethyloctylsilylphenyl)-*p*-phenylenevinylene-*co-p*-phenylenedifluorovinylene)s (SiPhPPVPDFVs), have been synthesized by the Gilch polymerization. The fluoro groups were introduced onto the vinylene units to increase electron affinity of the copolymers. The HOMO energy levels of the copolymers were between 5.30–5.35 eV. The EL spectra of devices with the configuration of ITO/PEDOT:PSS/polymer/Al showed maximum peaks between 526–560 nm. By adjusting the feed ratios of PPDFV in SiPhPPVPDFVs, the CIE coordinates moved from yellow to green. The luminescence efficiencies of the copolymers at room temperature ranged from 0.35–2.03 cd/A. SiPhPPVPDFV3 showed the maximum brightness of 4451 cd/m² and the highest luminescence efficiency of 2.03 cd/A. Introduction of up to 30% of PPDFV in the copolymers with *m*-SiPhPPV enhanced the device performance to result in high current density, brightness and efficiency due to increased electron injection ability caused by the presence of fluoro groups in the vinylene units.

KEY WORDS: Conjugated Polymers / PPVs / LEDs / Luminescence /

Since the discovery of electroluminescence (EL) from conjugated polymers, polymer light-emitting diodes (PLEDs) have been broadly investigated for their interesting physical properties and potential for EL applications.^{1–3} Because of the prospective application as large-area light emitting diodes (LEDs), most of the research in the field of polymer-based electroluminescent devices has been focused on main-chain conducting polymers such as: poly(plenylenevinylene) (PPV),⁴ poly(*p*-phenylene) (PPP),⁵ poly(thiophene),⁶ poly(fluorene) (PF),⁷ and their copolymers and soluble derivatives.^{8–12}

PPV and its derivatives, which have attracted much attention and a large number of studies, have been reported. The synthesis of these polymers by Gilch polymerization increased the possibility of employing this promising class of polymers for LEDs. Caused by the presence of vinylene units, PPV derivatives exhibit emissions of longer wavelength as compared to PF or PPP without vinylene units. There are several examples of PPVs which show high efficiencies, long lifetimes, and emissions of red to green colors in LEDs.^{13,14} The poly(2-(3'-dimethyloctylsilylphenyl)-*p*-phenylenevinylene (SiPhPPV) and copolymers were introduced as highly soluble and efficient materials. The bulky dimethyldodecylsilylphenyl group was introduced into the *meta* position of the phenyl substitute to inhibit the intermolecular interaction between the resulting polymer chains. The *meta* substituent linkage also improves the amorphous state and processability, resulting in copolymers with improved optical and electroluminescent properties over those of the homopolymer.¹⁵

It has been known that recombination of electrons and holes injected from cathodes and anodes produce emissions in the

luminescent polymer layer of the LEDs. Balanced charge injection from both electrodes and comparable mobility of both charge carrier types are important for high device efficiencies.^{16,17} The application of additional organic charge-transporting layers between the emissive layer and electrodes or adjustment of the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone have been previously attempted for improvement of charge carrier injection properties and mobility. It was reported that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be lowered by the introduction of electron-withdrawing groups onto the arylene rings and the vinylene groups of the polymer.¹⁸ The electron-withdrawing substitutes such as halide,^{19,20} cyano,²¹ trifluoromethyl,²² and methylsulfonyl-phenyl²³ groups have been introduced onto the arylene rings of PPV derivatives. Several conjugated polymers with cyano or fluoro groups on vinylene units have also been reported.^{24,25}

In our previous work, we reported on the synthesis and electroluminescence properties of new EL polymers, poly(*p*-phenylenedifluorovinylene) (PPDFV), containing two fluoro groups on every vinylene unit to reduce the barrier of electron injection.^{26,27} Herein we report the synthesis of the copolymers with SiPhPPV and PPDFV by the Gilch reaction. Synthesized poly(2-(3'-dimethyloctylsilylphenyl)-*p*-phenylenevinylene-*co-p*-phenylenedifluorovinylene)s (SiPhPPVPDFVs) were then incorporated with PPDFV to investigate the effects of the electron withdrawing fluorine atom on the optical and device properties of the copolymers.

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EXPERIMENTAL

Reagents and Materials

Potassium *tert*-butoxide, tetrahydrofuran (THF) and methanol (MeOH) were purchased from Aldrich or TCI and used without further purification. All starting reagents and solvents were used in the reactions under nitrogen. 1,4-bis(bromomethyl)-2-(3'-dimethyldodecylsilylphenyl)benzene and 1,4-bis(bromofluoromethyl)benzene were prepared according to the literature reports.^{15,27}

Synthesis of Poly(2-(3'-dimethyloctylsilylphenyl)-*p*-phenylene-vinylene-co-*p*-phenylenedifluorovinylene)s (SiPhPPVPDFVs)

SiPhPPVPDFVs with various feed ratios of SiPhPPV¹⁵ and PDFV²⁷ contents were synthesized. To a stirred solution of 1,4-bis(bromomethyl)-2-(3'-dimethyldodecylsilylphenyl)benzene (**1**) and 1,4-bis(bromofluoromethyl)benzene (**2**) (total amount of 1.5 mmol) in 20 mL of THF at 20 °C under argon was added 36 mL (9.0 mmol) of a 0.25 M solution of potassium *tert*-butoxide in THF by a syringe pump over 1 h. Over the 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 the crude polymer as yellow powder. The resulting polymer was redissolved in 100 mL of THF at 60 °C, cooled to 40 °C, and reprecipitated by drop-wise 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 100 mL of THF/1.0 L of methanol to generate SiPhPPVPDFVs (SiPhPPVPDFV1 (copolymer with 10 mol % PDFV in the feed), SiPhPPVPDFV3 (copolymer with 30 mol % PDFV in the feed) and SiPhPPVPDFV5 (copolymer with 50 mol % PDFV in the feed)). The polymer fibers had colors ranging from sky blue to light yellow. The yields of the polymers were from 34 to 46%.

Characterization Methods

¹H and ¹³C NMR spectra were recorded with a Varian Gemini-200 (200 MHz), a Unityplus-300 (300 MHz), and an Inova-500 (500 MHz) spectrometer with chemical shifts recorded in ppm units with TMS as the internal standard. Flash chromatography was performed using Merck silica gel 60 (particle size 230–400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The photoluminescence (PL) and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, a xenon

lamp was used as the excitation source with the incident beam taking the maximum absorption peak of the polymers. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. For EL experimentation, poly(3,4-ethylenedioxythiophene) (PEDOT), doped with poly(styrenesulfonate) (PSS) as the hole-injection-transport layer, was introduced between the emissive layer and indium tin oxide (ITO) glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting an *o*-dichlorobenzene (ODCB) solution of the polymer. The prepared emissive polymer thin film had a uniform surface with a thickness of 110 nm. The emissive film was dried *in vacuo* and aluminum electrodes deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{−7} Torr, yielding active areas of 4 mm². For the determination of device characteristics, current-voltage (*I*–*V*) characteristics were measured using a Keithley 236 source measure unit. All processing steps and 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 a platinum plate as a working electrode. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

The general synthetic routes toward the polymers are outlined in Scheme 1. The key intermediate in this synthesis was the introduction of bent-type dodecyldimethylsilylphenyl substitute and difluoro vinylene unit. For the synthesis of monomer unit **1**, 1,3-dibromobenzene was coupled with chlorododecyldimethylsilane using *n*-BuLi in THF to generate 1-bromo-3-(dimethyldodecylsilyl)benzene. This compound was coupled a second time with *p*-xylene-2-magnesium bromide in THF to provide 1,4-Dimethyl-2-(3'-dimethyldodecylsilylphenyl)benzene, which was brominated using NBS and light source (300 W) to generate 1,4-bis(bromomethyl)-2-(3'-dimethyldodecylsilylphenyl)benzene.¹⁵ For the synthesis of the second monomer unit **2**, *p*-xylene was brominated using *N*-bromosuccinimide (NBS) and a light source (300 W) to provide 1,4-bis(bromomethyl)benzene. The resulting dibromide was fluorinated with tetrabutylammonium fluoride (TBAF) to generate 1,4-bis(fluoromethyl)benzene, which was brominated again using NBS and a light source to generate 1,4-bis(bromofluoromethyl)benzene.²⁷ The various feed ratios of monomers **1** and **2** were used for the preparation of SiPhPPVPDFVs by the Gilch reaction, with an excess amount of potassium *tert*-butoxide in THF at 20 °C for 24 h under Ar atmospheres. The copolymers were soluble in various organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and ODCB.

Scheme 1. Synthetic routes for polymers.

Table I. Characterization of the SiPhPPVPDFVs

Polymer	Yield (%)	M_w^a ($\times 10^3$)	PDI ^a	T_d^b (°C)
SiPhPPVPDFV1	40	43	2.68	430
SiPhPPVPDFV3	34	39	2.56	410
SiPhPPVPDFV5	46	30	2.19	385

^aMolecular weight (M_w) and Polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. ^bOnset decomposition temperature (5% weight loss) measured by TGA under N_2 .

Table I summarizes the polymerization results and molecular weights of the copolymers. These copolymers have weight-average molecular weights (M_w) of 30,000–43,000 with polydispersity indices (M_w/M_n) of 2.19–2.68. The thermal properties of the copolymers were determined by TGA measurements. All these copolymers showed good thermal stability, with onset decomposition temperature (T_d , 5% weight loss) of 385–430 °C under nitrogen.

Optical Absorption and Photoluminescence Properties

The optical and photoluminescence properties of the copolymers were both investigated in thin solid films. Transparent and uniform copolymer films were prepared on quartz plates by spin-casting from their respective ODCB solution at room temperature. The absorption and emission data for the copolymers are summarized in Table II. As shown in Figure 1, the maximum absorption spectra of the *m*-SiPhPPV-*co*-PPDFV (90:10 wt %) (SiPhPPVPDFV1), *m*-SiPhPPV-*co*-PPDFV (70:30 wt %) (SiPhPPVPDFV3), and *m*-SiPhPPV-*co*-PPDFV (50:50 wt %) (SiPhPPVPDFV5) in thin films have relatively sharp peaks at 427, 414, and 407 nm, respectively. The blue shift of the maximum absorption in SiPhPPVPDFV5 is likely due to the introduction of the PPDFV moiety and steric effects of the polymer main chain, originating from the increase in electron density along the π -conjugated polymer backbone through incorporation of the PPDFV segment and extension of the effective conjugation length of the copolymers. The

Figure 1. UV-vis absorption spectra of SiPhPPVPDFVs in thin film.

Figure 2. Photoluminescence spectra of SiPhPPVPDFVs in thin film.

absorption onset wavelengths of SiPhPPVPDFVs were 517–521 nm, which corresponded to band gaps of 2.38–2.40 eV. Figure 2 shows the PL spectra of the SiPhPPVPDFVs in the thin film with maxima at 556 nm. The $S_1 \rightarrow S_0$ 0-1 transitions exhibited emission maxima at 556 nm with vibronic features of $S_1 \rightarrow S_0$ 0-0 and 0-2 transition at 525 nm and 595 nm. Although the PPDFV content was increased up to 50% in the copolymer system, the emission peaks of these polymers were similar, having the same maximum and full width at half maximum (fwhm). The absolute PL quantum efficiency (Φ_{PL}) of the SiPhPPVPDFVs in the thin film were measured in an integrating sphere at room temperature in air to be 18.3–28.2%.

Electrochemical Properties

The energy band diagrams of the SiPhPPVPDFVs were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry. The CV was performed with a solution of tetrabutylammonium tetrafluoroborate

Table II. Characteristics of the UV-vis Absorption, Photoluminescence, and Electroluminescence Spectra

The Feed ratio of Copolymers	Abs λ_{max} (nm)	PL λ_{max}^a (nm)	fwhm ^b of PL	Φ_{PL}^c (%)	EL λ_{max}^a (nm)	fwhm ^b of EL
SiPhPPVPDFV1	427	561	112	24.9	560	102
SiPhPPVPDFV3	414	558	111	18.3	552	105
SiPhPPVPDFV5	407	556	114	28.2	547	100

^aThe data in the parentheses are the wavelengths of shoulders and subpeaks. ^bFull width at half-maximum of PL and EL spectra. ^cMaximum photoluminescence quantum efficiency.

Table III. Electrochemical Potentials and Energy Levels of SiPhPPVPDFVs

PPDFV Copolymers	E_{onset}^a (V)	HOMO ^b (eV)	LUMO ^c (eV)	E_g^d (eV)
SiPhPPVPDFV1	0.50	−5.30	−2.92	2.38
SiPhPPVPDFV3	0.55	−5.35	−2.96	2.39
SiPhPPVPDFV5	0.55	−5.35	−2.95	2.40

^aOnset oxidation potential measured by cyclic voltammetry. ^bCalculated from the oxidation potentials. ^cCalculated from the HOMO energy levels and E_g . ^dEnergy band gap was estimated from the onset wavelength of the optical absorption.

(Bu₄NBF₄) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode. Pt wire and an Ag/AgNO₃ electrode were used as the counter and reference electrode, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by the FC/FC⁺ redox system) was 4.8 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table III. HOMO levels were calculated according to the empirical formula ($E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.8)$ (eV). During the anodic scan, the oxidation onset potentials of SiPhPPVPDFVs were in the range of 0.50–0.55, and exhibited an irreversible p-doping process. HOMO energy levels of the present EL copolymers ranged from −5.30–−5.35 eV. When the PPDFV contents in the copolymers were increased, the HOMO energy levels decreased due to the electron withdrawing effect of the fluoro group. With higher contents of PPDFV in the copolymers, there will be more fluoro groups on the vinylene units, increasing the presence of the electron withdrawing fluoro groups on the vinylene units, thus reducing electron density of the back bone and causing an increase of the band gap. The LUMO energy level, −2.92–−2.96 eV, was calculated from the values of the band gap and HOMO energy level.

Electroluminescence Properties

The EL data for the copolymers are summarized in Table IV. The EL spectra of ITO/PEDOT/polymer/Al devices are shown in Figure 3. As compared to the PL spectra in thin films, the EL spectra of the copolymers showed an increase in the subpeak. In the case of SiPhPPVPDFV1, the emission maximum appeared at 560 nm with SiPhPPVPDFV3 exhibiting maximum peaks at 552 nm and SiPhPPVPDFV5 at 526 nm and 547 nm. As the PPDFV content increased up to 50% in the

Table IV. Device Performance Characteristics of SiPhPPVPDFVs

The Feed ratio of Copolymers	Turn-on voltage ^a (V)	Voltage ^b (V)	Current density ^b (mA/cm ²)	Luminance ^b (cd/m ²)	LE _{max} ^c (cd/A)	CIE (x, y) ^d
SiPhPPVPDFV1	6.5	15	1085	86	1.78	(0.43, 0.55)
SiPhPPVPDFV3	9	18	4451	220	2.03	(0.39, 0.55)
SiPhPPVPDFV5	6	14	4518	1413	0.35	(0.38, 0.57)

^aVoltages required to achieve a brightness of 1 cd/m². ^bMeasured under the condition of maximum brightness. ^cMaximum luminescence efficiency. ^dCalculated from the EL spectrum.

Figure 3. Electroluminescence spectra of devices with the configuration of ITO/PEDOT/copolymer/Al.

copolymer system, the maximum peaks were blue shifted and subpeaks increased. The emission colors of SiPhPPVPDFVs with the Commission international de l'Eclairage (CIE) coordinates from $x = 0.43$, $y = 0.55$ to $x = 0.38$, $y = 0.57$ were yellow-green. By adjusting the feed ratios of PPDFV in SiPhPPVPDFVs, the CIE coordinates moved from yellow to green.

Current Density-Voltage-Luminescence (J-V-L) Characteristics

The current density-voltage and luminescence-voltage characteristics of ITO/PEDOT/polymer/Al devices are shown in Figure 4. The copolymers with higher PPDFV contents can have higher current density due to increasing electron injection ability by the low electron density, caused by the presence of fluoro groups in vinylene units. However, SiPhPPVPDFV5

Figure 4. Current density-Voltage (J-V) (a) and Voltage-Luminescence (V-L) (b) characteristics of OLEDs of SiPhPPVPDFVs with the configuration of ITO/PEDOT/copolymer/Al.

Figure 5. Efficiencies of OLEDs of SiPhPPVPDFVs with the configuration of ITO/PEDOT/copolymer/Al.

showed the highest current density as this polymer had good solubility and low electron density with a high % of fluoro-substituted vinylene unit. The turn-on voltages of ITO/PEDOT/polymer/Al devices were about 6–9 V. The luminescence intensities of polymers were exponentially increased with an increase in voltage. The maximum luminescence ($L_{\max}$) of SiPhPPVPDFV5 was 4518 cd/m² at 14 V.

As shown in Figure 5, the luminescence efficiencies of the copolymers at room temperature ranged from 0.35–2.03 cd/A with the SiPhPPVPDFV3 showing the highest luminescence efficiency of 2.03 cd/A. PPDFV was previously reported by us as a polymer with high efficiency caused by its high electron injection ability,^{26,27} which originated from the presence of fluoro groups on vinylene units, but low solubility was still problematic. For the same reason, SiPhPPVPDFV3, which had the merit of improved electron injection ability through an increased PPDFV portion, showed high efficiencies. We conclude that the introduction of up to 30% of PPDFV in copolymers with *m*-SiPhPPV can enhance the best device performance to result in PL and EL spectra and high current density, brightness, and efficiency.

CONCLUSION

Copolymers with difluoro groups in vinylene unit, SiPhPPVPDFVs, were synthesized by the Gilch reaction. The SiPhPPVPDFVs exhibited absorption spectra with maximum peaks at 407–427 nm that would blue-shift with increasing amounts of PPDFV. This is originated from the decrease of the electron density along the π -conjugated polymer backbone through incorporation of the PPDFV segment and decrease of the effective conjugation length of the copolymers. In the PL spectra of SiPhPPVPDFVs as a thin film, the $S_1 \rightarrow S_0$ 0-1 transitions exhibited emission maxima at 556 nm. As the PPDFV content was increased up to 50% in the copolymer system, solubility improved as did thin film morphology for the solution process. The HOMO energy levels of the copolymers ranged from 5.30–5.35 eV, and the LUMO from 2.92–2.96 eV. The polymer LEDs of SiPhPPVPDFV with the configuration of ITO/PEDOT/polymer/Al emitted light with maximum peaks from 526–560 nm. The emission colors of SiPhPPVPDFVs were yellow-green depending on the obtained CIE coordinates.

The luminescence efficiencies of the copolymers at room temperature were about 0.35–2.03 cd/A. SiPhPPVPDFV3 showed the maximum brightness of 4451 cd/m² and the highest luminescence efficiency of 2.03 cd/A. In conclusion, the introduction of up to 30% of PPDFV in copolymers with *m*-SiPhPPV enhanced the device performance to result in high current density, brightness and efficiency due to the increased electron injection ability caused by the presence of fluoro groups in the vinylene units.

Acknowledgment. This work was supported by a grant-in-aid for the National Core Research Center Program from MOST and KOSEF (No. R15-2006-022-01001-0), and the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program.

Received: April 7, 2008

Accepted: July 6, 2008

Published: August 22, 2008

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