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Palladium-Catalyzed Direct Synthesis, Photophysical Properties, and Tunable Electroluminescence of Novel Silicon-Based Alternating Copolymers

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ABSTRACT: A new class of silicon-based alternating copolymers with a uniform π-conjugated segment regulated by organosilicon units was synthesized using the Heck reaction between distyrylsilane monomers and appropriate arylene dibromides. The incorporation of organosilicon units with the aromatic or aliphatic groups on the silicon atoms into π-conjugated systems improved their processability and interrupted the π-conjugation length. They could be spin-cast onto various substrates to give highly transparent homogeneous thin films. Their glass transition temperatures were in the range 94−127 °C. They show strong absorption bands around 356−416 nm, which corresponds to the $\pi-\pi^*$ transition of the conjugated segments. The maximum photoluminescence appeared around 440−526 nm in the blue or green emission region. Their optical properties depend on the arylene dibromides in the Heck reaction. The single-layered light-emitting diode of an Al/**SiPhPPV** or **SiHMPPV**/ITO glass exhibits a threshold voltage of 10−12 V from the $I-V$ curve. The electroluminescence (EL) of the **SiPhPPV** or **SiHMPPV** gives an emissive peak at 450 nm. Furthermore, the multilayered light-emitting diodes of an Al/LiAl/**SiPhPVK**/PANI/ITO glass and an Al/LiAl/**SiPhFPV** or **SiHMFPV**/ITO glass shows a threshold voltage of 6−12 V. The EL device based on **SiPhPVK** exhibits the blue emissive color at 467 nm, when an operating voltage of 7 V was applied. When an operating voltage of 11 V was applied, however, the EL device emits a white color. The EL spectra of the **SiPhFPV** and **SiHMFPV** polymers, obtained at an applied voltage of 12 V, show two strong peaks in the blue emissive region as well as in the green region.

Introduction

Since the first demonstration of the polymer light-emitting diodes from poly(p-phenylenevinylene) (PPV) thin film sandwiched between hole- and electron-injection electrodes by the Cambridge group,[1] electroluminescent (EL) devices based on π-conjugated polymeric thin layers have attracted much attention because of their applications such as large area flat-panel displays and light-emitting diodes.[2−10] Light emission is thought to arise from the exciton resulting from the electron−hole combination within the polymer. To easily mobilize and recombine a hole as well as an electron within the polymer, a number of different π-conjugated polymers have been synthesized and extended efforts have been made to obtain high performance devices from polymeric materials.[2−19] EL polymeric materials offer a number of advantages, such as low operating voltages, three primary R/G/B colors with the control of $\pi-\pi^*$ energy gap through changes in the molecular structure, fast response time, high quality of display, and ease of processability, compared to inorganic EL materials.[8]

However, the polymeric EL materials confront two important problems of low EL efficiency and short lifetime. The EL efficiency of devices can be affected by the homogeneity of film quality, the injection efficiency of carriers from electrodes to organic materials, and the material's EL efficiency. The two former can be solved by thin film fabricating processes, but the latter can be only achieved by developing materials with high EL efficiency. Recently, many research groups have tried to improve the quantum efficiency and to synthesize short-wavelength light-emitting polymers for blue light.[11−19] The quantum efficiency (photons emitted/charge injected) of a device is dependent on balancing the charges injected. The greatest efficiencies can be achieved when the rate of electron injection is balanced with the rate of hole injection.

Very recently, the main material efforts have been focused on developing blue light-emitting diodes capable of operating at ambient temperature, low voltages, and easy processability with low price.[16,20,21] The luminescence usually arises at energies just below the onset of the absorption, and can therefore be tuned by varying the HOMO−LUMO gap of the polymer. The HOMO−LUMO gap is related to the conjugation length in the polymer, which is a measure of the extent of the delocalization of the π-electrons. To achieve the control of the conjugation length, and hence of the optical properties of a polymer, it is desirable to isolate small conjugated oligomers of well-defined structure in the polymer. These chromophores can be incorporated in the side chains of the polymer[22,23] or in the backbone. We

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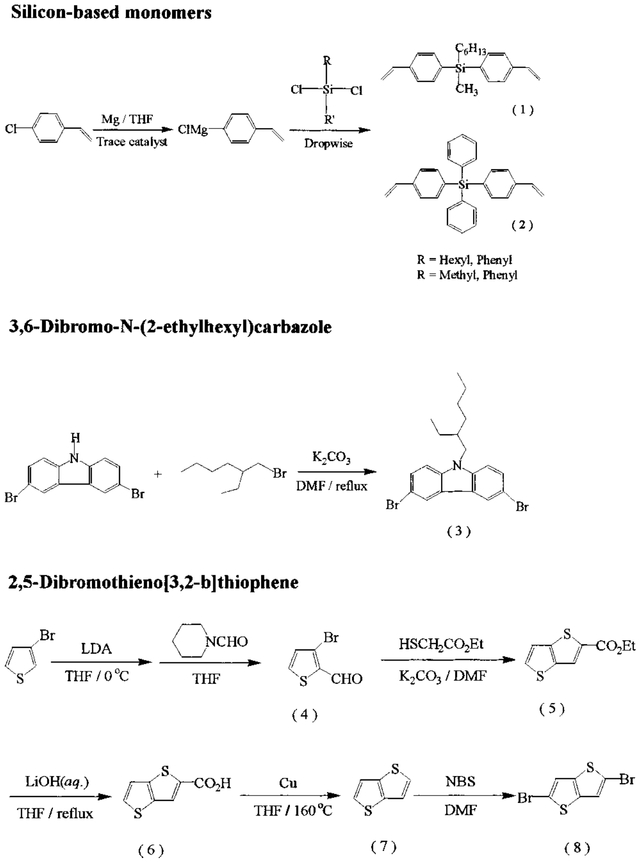
Scheme 1. Synthetic Routes to Silicon-Based Monomers, 3,6-Dibromo-*N*-(2-ethylhexyl)carbazole and 2,5-Dibromothieno[3,2-*b*]thiophene



reported the development of a new type of processable silicon-based copolymers in the polymer main chain by the well-known Wittig reactions for blue light-emitting diodes.[8,18−19] The introduction of organosilicon units with aromatic or flexible aliphatic groups into π-conjugated systems improved their processability and limited the π-conjugation length, resulting in blue light-emitting diodes.[8,18,19,24] Surprisingly, the silicon-based copolymers with a relatively short π-conjugation length exhibited blue light-emitting diodes operated at the low voltages, due to the lowering of the LUMO level in luminescent polymers and the d-orbital participation of silicon atoms.[25]

However, the Wittig olefination methodolgy requires a further cis-to-trans isomerization reaction, accomplished by heating the crude polymers having a mixture of cis and trans double bonds with a trace of iodine in toluene. Its heat treatment produces the desired silicon-based alternating copolymers with quantitatively trans double bonds, which are critical to maximize the luminescence efficiency and to adjust the emissive colors. Also, to overcome the problem of low quantum efficiency due to the formation of the triplet state arising from the unreacted or remained aldehyde functional groups in the silicon-based copolymers obtained from the Wittig reaction,[8,18−19] the Wittig synthetic route could require an additional end-capped reaction between unreacted aldehydes and monofunctionalized Wittig reagents to achieve this tolerable percentage of unreacted aldehyde groups. Therefore, to skip these two further reactions, the Heck reaction was used for the synthesis of the silicon-based alternating copolymers (see Scheme 2). In this paper, we describe the direct synthesis, photophysical properties, and tunable electroluminescence of the silicon-based copolymers by the Pd-catalyzed Heck reaction of distyrylsilane monomers with various aromatic or heteroaromatic dibromides.

Experimental Section

Materials. 4-Chlorostyrene, dichlorodiphenylsilane, 1,4-dibromobenzene, 2,5-dibromothiphene, palladium(II) acetate, 2-ethylhexyl bromide, 3,6-dibromocarbazole, and phosphorus trichloride were purchased from Aldrich and used without further purification. *N*-Hexylmethyldichlorosilane was purchased from Huls, Inc. Tris(*o*-tolyl)phosphine was synthesized according to the literature. All of the solvents and other chemicals were used after purification, according to conventional methods when required.

Monomer Synthesis. The synthesis of monomers was carried out as follows (see Scheme 1).

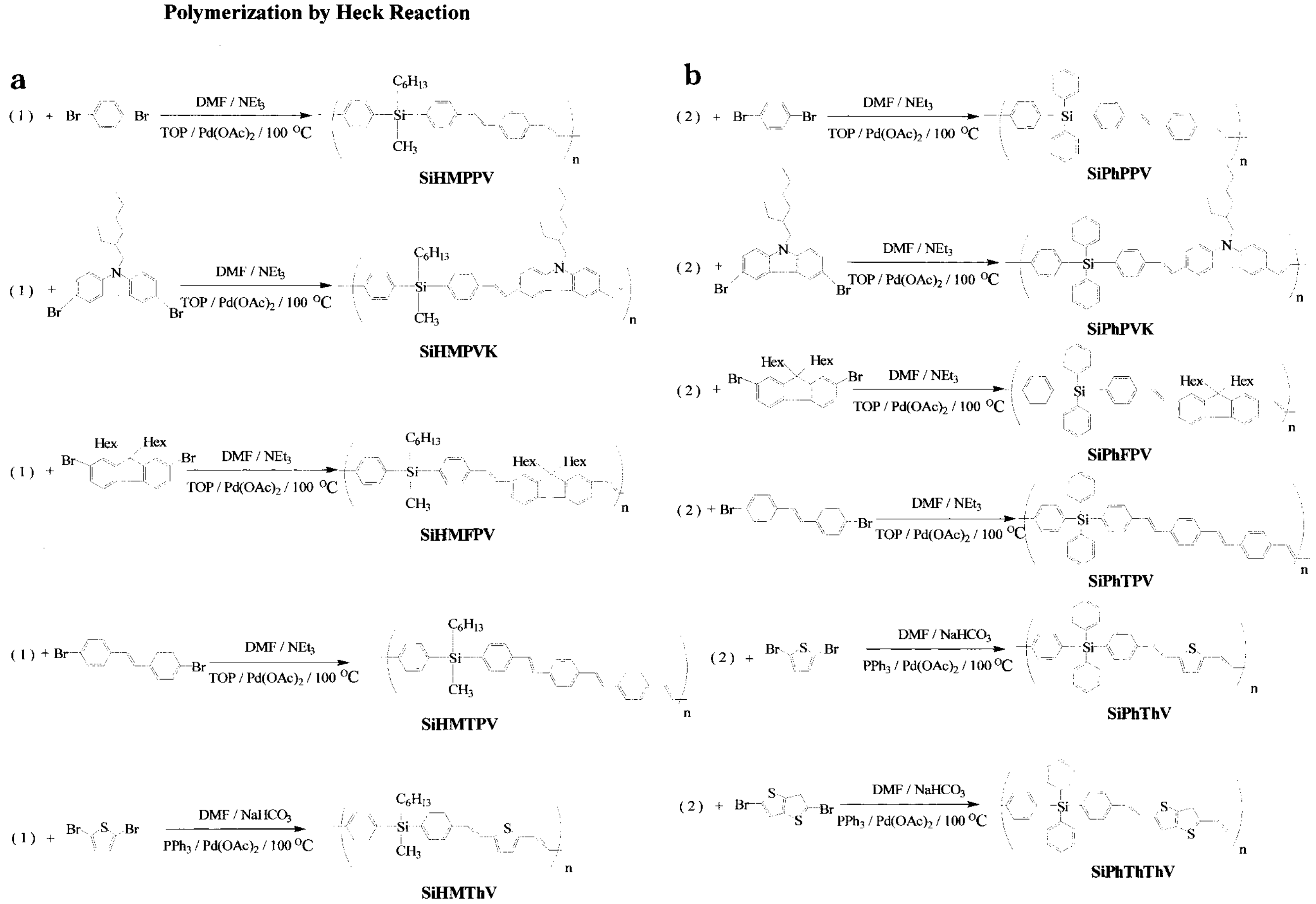
Distyrylhexylmethylsilane (DSHMS) (1). A mixture of *p*-chlorostyrene (10 g, 0.072 mol) and magnesium turnings (3.5 g, 0.144 mol) in dry THF (70 mL) was stirred at room temperature for 6 h under a nitrogen atmosphere. If the reaction becomes too violent, an ice bath is used to cool it down. A solution of dichlorohexylmethylsilane (5.77 g, 0.029 mol) in dry THF (20 mL) was added dropwise during stirring, and then stirring is continued at room temperature for 5 h. An aqueous solution of 0.1 M HCl was added until precipitation occurred. The reaction mixture was filtered off the precipitation and extracted with diethyl ether. The ether layer was washed with water, dried over anhydrous magnesium sulfate, and filtered and the solvent removed by evaporation. Purification of the crude product by column chromatography (silica gel, with hexane/ethyl acetate (4/1) as an eluent) gave the product as a yellow liquid (5.04 g). The product yield was 52%. ^{1}H NMR ($CDCl_3$, ppm): 0.3 (s, Si−CH_3, 6H); 0.8−1.3 (m, Si-aliphatic, 13H); 5.2 (d, CH=CH_2, 2H); 5.7 (d, CH=CH_2, 2H); 6.7 (q, CH=CH_2, 2H); 7.4−7.5 (d; aryl CH, 8H). ^{13}C NMR ($CDCl_3$, ppm): −1.52, 14.21, 16.64, 22.65, 23.09, 31.58, 33.15, 114.34, 125.51, 133.39, 136.65, 137.94, 138.47. Anal. Calcd for $C_{28}H_{40}Si$: C, 83.10; H, 9.96; Si, 6.94. Found: C, 83.16; H, 9.93; Si, 6.91.

Distyryldiphenylsilane (DSDPS) (2) was synthesized by a synthetic method to that used for distyrylhexylmethylsilane (DSHMS) (**1**). Purification of the crude product by column chromatography (silicagel, with hexane/ethyl acetate (5/1) as an eluent) gave the product as a colorless liquid (5.04 g). The product yield was 45%. ^{1}H NMR ($CDCl_3$, ppm): 5.2 (d, CH=CH_2, 2H); 5.7 (d, CH=CH_2, 2H); 6.7 (q, CH=CH_2, 2H); 7.3−7.6 (m, aryl CH, 18H). ^{13}C NMR ($CDCl_3$, ppm): 114.67, 125.46, 127.70, 129.90, 134.34, 134.71, 134.81, 135.01, 136.44, 138.89. Anal. Calcd for $C_{28}H_{24}Si$: C, 86.55; H, 6.22; Si, 7.23. Found: C, 86.54; H, 6.28; Si, 7.18.

3,6-Dibromo-*N*-(2-ethylhexyl)carbazole (3).[26] To a stirred mixture of 3,6-dibromocarbazole (2 g, 6.15 mmol) and potassium carbonate (1.7 g, 12.3 mmol) in dry DMF (30 mL) was added 2-ethylhexyl bromide (1.78 g, 9.22 mmol) at room temperature. It was heated to reflux for 60 h. It was poured into ice water (150 mL) and then extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. It was purified by silica gel column chromatography (hexane/ethyl acetate = 3/1) to give a yellow oil. The product yield was 82% (3.3 g). IR (KBr pellet, cm^{-1}): 1337 (ν_{C-N}); 748, 723 (ν_{C-H} carbazole ring out of plane). ^{1}H NMR ($CDCl_3$, ppm): 0.82−0.89 (m, 6H. 2-CH_3); 1.21−1.31 (m, 8H. 4-CH_2); 2.02 (m, 1H. −CH−); 4.07 (d, 2H. −NCH_2−); 7.2−8.1 (m, 6H. aromatic protons of carbazole).

2,5-Dibromothieno[3,2-*b*]thiophene (8).[27] Thieno[3,2-*b*]thiophene (**7**) was synthesized from 3-bromothiophene as indicated in a cited reference (see Scheme 1).[27] A solution of 21.34 g (0.12 mol) of NBS in 150 mL of DMF was added to a stirred and ice-cooled solution of 8.35 g (59.58 mmol) of thieno[3,2-*b*]thiophene (**7**) in 70 mL of DMF. After the mixture was stirred for 3 h under ice cooling, crushed ice was added and the resulting mixture was extracted with CH_2Cl_2. The extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to aluminum oxide column chro-

Scheme 2. (a) Synthesis of Silicon-Based Copolymers with Flexible Aliphatic Group into the Organosilicon Unit. (b) Synthesis of Silicon-Based Copolymers with Rigid Aromatic Group into the Silicon Unit



matography. Mp: 135 °C; IR (KBr pellet, cm^{-1}): 3095 ($\nu_{C-H(aromatic)}$), 1616 and 1480 ($\nu_{C=C}$), 1014 (ν_{C-Br}). ^{1}H NMR (CDCl$_3$, ppm): 7.62 (s, 2H). Anal. Calcd for $C_6H_2S_2Br_2$: C, 24.18; H, 0.68; S, 21.52; Br, 53.62. Found: C, 24.32; H, 0.70; S, 21.03; Br, 53.95.

Polymerization. The synthesis of silicon-based copolymers were carried out using well-know Heck reaction between distyrylsilane monomers and aromatic or heteroaromatic dibromides, as shown in Scheme 2.

Copoly[hexylmethylsilane/phenylene/bis(phenylenevinylene)] (SiHMPPV). 1,4-Dibromobenzene (0.209 g, 0.89 mmol) was dissolved in 5 mL of dry DMF at 50 °C under a nitrogen atmosphere. Pd(OAc)$_2$ (9.98 mg, 0.0445 mmol) and tris(*o*-tolyl)phosphine (TOP: 0.081 g, 0.267 mmol) were added, dissolved, and stirred for 1 h. Distyrylhexylmethylsilane (0.3 g, 0.897 mmol) and (C$_2$H$_5$)$_3$N (1.07 g, 10.6 mmol) were added, dissolved, and heated overnight to 100 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and poured into a large amount of methanol. The resulting precipitate was stirred for 1 h in methanol. The crude polymeric product was filtered off and dissolved in hot chloroform (100 mL). The solution was filtered through a glass filter to remove residual catalyst particles and precipitated in methanol. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days, yielding 52% of a yellow polymeric product.

Poly[*n*-hexylmethylsilylene/bis(phenylenevinylene)/3,6-*N*-2-ethylhexylcarbazolediyl)] (**SiHMPVK**), poly[diphenylsilylene/bis(phenylene-vinylene)/3,6-*N*-2-ethylhexylcarbazolediyl)] (**SiPhPVK**), copoly[*n*-hexylmethylsilylene/bis(phenylenevinylene)/9,9′-dihexylfluorenediyl] (**SiHMFPV**), copoly[diphenylsilylene/bis(phenylenevinylene)/9,9′-dihexylfluorenediyl] (**SiPhFPV**), copoly[hexylmethylsilane/phenylene/bis(terphenylenevinylene)] (**SiHMTPV**), copoly[diphenylsilane/phenylene/bis(phenylenevinylene)] (**SiPhPPV**), and copoly[diphenylsilane/phenylene/bis(terphenylenevinylene)] (**SiPhTPV**) were synthesized by a similar synthetic method. Also, 9,9′-dihexylfluorenediyl/bis(phenylenevinylene)/diphenylsilylane as a model compound, corresponding to copoly[diphenylsilylene/bis(phenylenevinylene)/9,9′-dihexylfluorenediyl] (**SiPhFPV**), was synthesized by a similar synthetic method.[28,29]

Copoly[hexylmethylsilylene/bis(phenylenevinylene)/thiophenylidene] (SiHMThV). 2,5-Dibromothiopene (0.215 g, 0.897 mmol) was dissolved in 6 mL of dry HMPA (hexamethylphosphoramide) at 50 °C under a nitrogen atmosphere. Pd(OAc)$_2$ (9.87 mg, 0.044 mmol) triphenylphosphine (0.07 g, 0.266 mmol) were added, dissolved, and stirred for 1 h. Distyrylhexylmethylsilane (0.3 g, 0.897 mmol) and NaHCO$_3$ (0.376 g, 4.485 mmol) were added, dissolved, and heated overnight to 100 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and poured into a large amount of methanol. The resulting precipitate was stirred for 1 h in methanol. The crude polymeric product was filtered off and dissolved in hot chloroform (100 mL). The solution was filtered through a glass filter to remove residual catalyst particles, and precipitated in methanol. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days, yielding 50% of a red polymeric product. Copoly[diphenylsilylene/bis(phenylenevinylene)/thiophenylidene (**SiPhThV**) and copoly[diphenylsilylene/bis(phenylenevinylene)/thieno-2,5-*b*)thiophenylidene] (**SiPhThThV**) were synthesized by a similar synthetic method.

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded with the use of Bruker AM 300 spectrometers, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Chloroform (CDCl$_3$) was mainly used as solvent for recording NMR spectra. Infrared spectra were measured as neat oil or KBr pellets on a Perkin-Elmer spectrometer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standards calibration

Table 1. Polymerization Results and Thermal Properties of Silicon-Based Copolymers

polymers	yield (%)	M_w [a] × 10^{-3}	M_w/M_n	T_{ID} [b] (°C)	T_g (°C)	UV(λ_{max}) (nm)	PL(λ_{max}) (nm)
SiHMPPV	52	8.5	1.8	180	94	356, 365	470
SiHMPVK	51	2.3	1.5	175	106	322, 356	440
SiHMFPV	70	9.8	1.9	185	96	378	470
SiHMTPV	66	2.7	1.6	200	112	386	470
SiHMThV	50	10.3	1.8	150	94	400	520
SiPhPPV	48	6.3	1.5	250	127	355, 365	470
SiPhPVK	43	3.7	1.2	253	102	325, 356	440
SiPhFPV	77	12.7	2.2	250	109	380	476
SiPhTPV	45	4.5	1.6	253	110	374, 388	463
SiPhThV	55	13.3	3.4	225	112	407	526
SiPhThThV	50	18.6	4.8	200	116	416	512

[a] M_n and M_w of the polymers were determined by gel permeation chromatography using polystyrene standards. [b] Temperature at which initial loss of mass was observed.

(Waters high-pressure GPC assembly model M590 pump, μ-styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, a refractive index detector, solvent = THF). UV−visible absorption spectra were obtained in chloroform or as a thin film on a Shimadzu 3101 PC spectrophotometer. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer at room temperature utilizing a lock-in amplifier system with chopping frequency of 150 Hz, and the polymer films were excited with 350 nm of ultraviolet light from the xenon lamp. A DuPont 990 Thermal analyzer attached with 951 TGA and 910S DSC module was used to record thermal gravimetric analysis and differential scanning calorimetry (DSC), respectively. For the measurement of EL, the polymer light emitting diode was constructed as follows. The glass substrate coated with transparent ITO electrode was thoroughly cleaned by successive ultrasonic treatments in acetone, isopropyl alcohol, and ethyl alcohol, dried with nitrogen gas, and heated for drying. The polyaniline film onto ITO glass was achieved by spin casting the polyaniline solution containing 1 wt % in water, followed by drying at 100 °C for 50 min. The polymer film was prepared by spin casting the **SiPhPVK** solution containing 2 wt % in cyclohexanone, **SiHMFPV**, or **SiPhFPV** solution containing 1 wt % in 1,2-dichloroethane. Uniform and pinhole free films with a thickness of around 100 nm were easily obtained from polymer solutions. Lithium−aluminum alloy was deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below 4×10^{-6} Torr, yielding active areas of 0.04 cm^2. Aluminum was deposited onto the surface of the alloy by vacuum evaporation at pressure below 4×10^{-6} Torr. For the measurement of device characteristics, current−voltage ($I-V$) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). All processes and measurements mentioned above were carried out in air at room temperature.

Time-Resolved PL Spectroscopy. The picosecond time-resolved fluorescence experiments were carried out using time correlated single photon counting (TCSPC) method as described in detail previously.[28] The picosecond excitation pulses at 600 nm were obtained from a cavity-dumped picosecond dye laser (Coherent 702) synchronously pumped by a mode-locked Ar ion laser (Coherent Innova 200). The cavity dumped beam from the dye laser has 2 ps pulse width and an average power of ca. 40 mW at 3.8 MHz dumping rate when rhodamine 6G for gain dye was used. The excitation pulses at 410 nm were obtained from a femtosecond Ti:sapphire laser with an average power of 600 mW at 820 nm. The pump pulses at the desired wavelength were generated by frequency doubling with a α-BBO crystal. The emission was collected at a 45° angle with respect to the excitation laser beam by 5 and 25 cm focal length lenses, focused onto a 32 cm monochromator (Jobin-Yvon HR320), and detected with a microchannel plate photomultiplier tube (Hamamatsu R2809U). The signal was amplified by a wideband amplifier (Phillip Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time-to-amplitude converter (Tennelec), a counter (Ortec), and a multichannel analyzer (Tennelec/Nucleus) and were finally stored in a computer.

Results and Discussion

The Grignard reaction between *p*-styrylmagnesium chloride and dialkyl- or diaryldichlorosilane yields the synthetic products of alkyl/aryl-substituted dichlorosilanes with high conversion (see Scheme 1). The chemical structures of the final monomers were identified by FT-IR, ^{1}H NMR (see Figure 1a), ^{13}C NMR (see Figure 1b), and elemental analysis. Figure 1 showed the typical ^{1}H NMR and ^{13}C NMR spectra of the distyrylsilane monomers such as distyrylhexylmethylsilane **(DSHMS)** and distyryldiphenylsilane **(DSDPS)**. In particular, the vinyl groups of the distyrylsilane monomers appeared around 5.2−6.8 ppm in ^{1}H NMR and the methyl groups of **DSHMS** appeared around −1.52 ppm in ^{13}C NMR. These results indicate that the distyrylsilane monomers were successfully synthesized.

The other monomers of 3,6-dibromo-*N*-(2-ethylhexyl)-carbazole (**3**)[26] and 2,5-dibromo thieno[3,2-*b*]thiophene (**8**)[27] were prepared as shown in Scheme 1. Also, their chemical structures were identified by FT-IR, ^{1}H NMR, and ^{13}C NMR (see Supporting Information).

The silicon-based alternating copolymers in the polymer main chain were synthesized by the Heck reaction of the distyrylsilane monomers with various aromatic or heteroaromatic dibromides, as shown in Scheme 2. Previously, it was reported that this type of processable silicon-based alternating copolymers was developed by the well-known Wittig reaction for blue light-emitting diodes.[8,18−19] The organosilicon units with aromatic or flexible aliphatic group was introduced into π-conjugated systems to interrupt the π-conjugation length.[8,18,19,24] The blue light-emitting diodes fabricated from the silicon-based alternating copolymers operated at the low voltages of less than 9 V, presumably due to the lowering of the LUMO level of polymers and the d-orbital participation of silicon atoms.[25] Instead of the Wittig method, the Heck synthetic route for the preparation of the silicon-based copolymers was used for the main following reasons. (1) The Heck route could overcome the problem of low quantum efficiency arising from the formation of the triplet state from the unreacted or remained aldehyde functional groups in the same silicon-based copolymers obtained from the Wittig reaction.[8,18−19] (2) To obtain quantitatively a trans-double bond from a cis-double bond, the Wittig reaction requires a further postreaction isomerization step, achieved by heating the crude polymers with a trace of iodine in toluene.[29] On the other hand, the Heck reaction directly produces the desired polymers with trans configuration, which is important to increase the luminescence efficiency and the emissive wavelength.

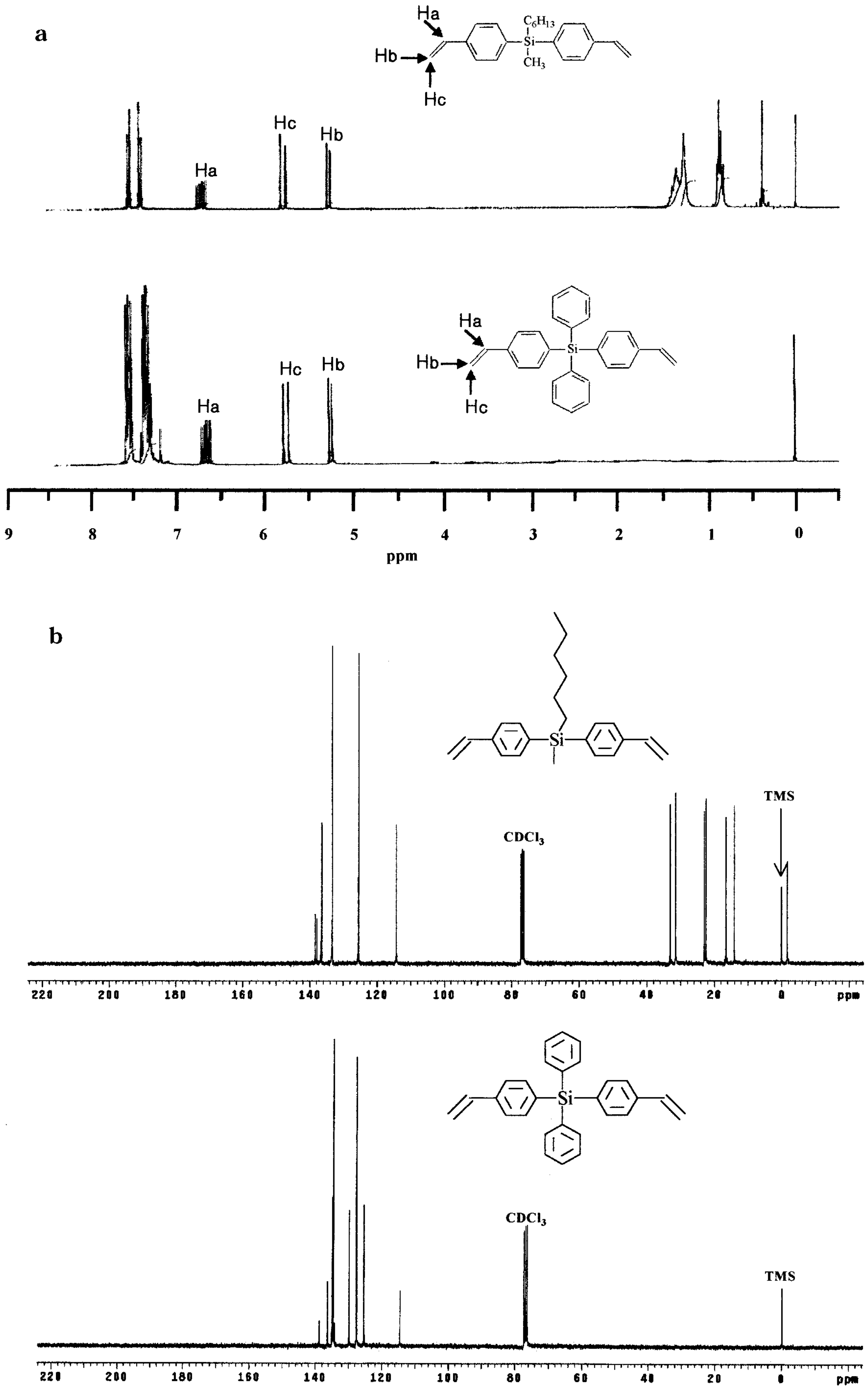


Figure 1. (a) ^{1}H NMR spectra of di-*p*-styrylhexylmethylsilane and di-*p*-styryldiphenylsilane. (b) ^{13}C NMR spectra of di-*p*-styrylhexylmethylsilane and di-*p*-styryldiphenylsilane.

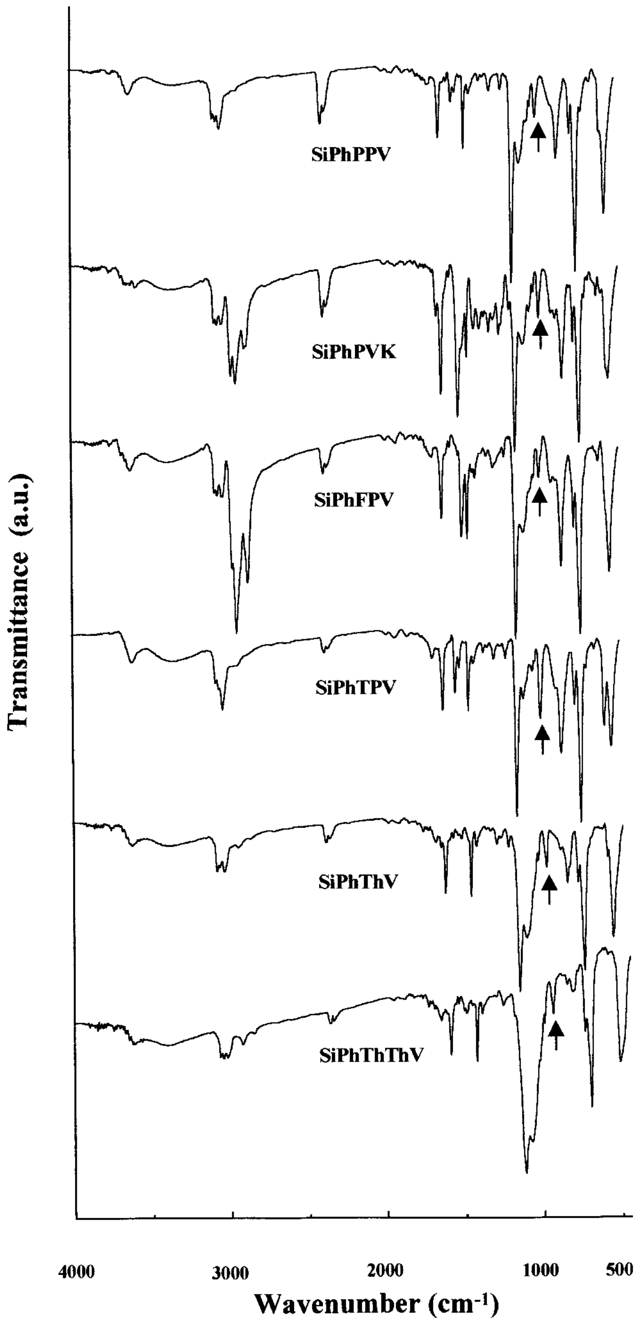


Figure 2. IR spectra of silicon-based copolymers.

The polymerization results of silicon-based copolymers are summarized in Table 1. The weight-average molecular weights (M_w) of the resulting polymers, as determined by gel permeation chromatography using polystyrene standards, were in the range 2.3 × 10^3 to 1.9 × 10^4 with a polydispersity index of 1.2−4.8. The resulting polymers were highly soluble in common organic solvents such as THF, chloroform, DMF, methylenechloride, etc. The incorporation of organosilicon units into the polymer rigid backbone would afford processable electroluminescent materials. It indicates that the introduction of organosilicon units in the rigid polymer backbone enhances the solubility of rigid polymers by reducing the crystallinity through side chain interactions and the longer Si−C bonds (than C−C bonds) in the main chain. They can be spin-cast onto various substrates to give highly transparent homogeneous thin films.

The chemical structure of the resulting copolymers was identified by FT-IR, ^{1}H NMR, ^{13}C NMR, and UV−visible spectroscopies, etc. Figure 2 shows the typical FT-IR spectra of the silicon-based copolymers. Vinyl C═C bonds in the monomer showed vanishingly a weak absorption peak at 1600 cm^{-1}. On the other hand, the out-of plane bending mode of the trans-vinylene groups in the polymer showed a newly weak and sharp absorption peak at 960 cm^{-1}. It indicates the formation of the silicon-based alternating polymers with trans double bonds. Figure 3 shows the ^{1}H NMR spectra of the **SiHMPVK**, **SiPhPVK**, and **SiPhFPV**. As the polymerization proceeded, the terminal vinyl peak of the monomers present at 5.2 and 5.7 ppm disappeared, and a newly vinylic proton peak in the polymer overlapped with 7.0−7.5 ppm aromatic protons. Also, the broad peaks around 0.2−2.0 ppm were assigned to the alkyl protons adjacent to the silicon atom and nitrogen atom in a carbazole unit. The broad peak around 4.1 ppm was assigned to the α-methylene protons adjacent to a nitrogen atom in a carbazole unit. These results indicate that relatively high molecular weight polymers were obtained with the disappearance of terminal vinylic proton peaks in the distyrylsilane monomers.

The thermal behavior of the silicon-based copolymers was evaluated by means of DSC and TGA under a nitrogen atmosphere. Also, the thermal properties of the polymers are presented in Table 1 and shown in Figure 4. All the copolymers did not show any definite melting points, implying that the silicon-based copolymers could be amorphous. Also, this fearure was identified by the broad pattern of the X-ray diffraction. The copolymers have T_g values in the range of 94−127 °C. The T_g of **SiPhPPV** is higher than that of **SiHMPPV**. Similarly, the T_g of **SiPhFPV** is a little higher than that of **SiHMFPV**. These results indicate that bulky phenyl group in the SiPh series produces a little more rigid structure than the flexible alkyl group due to steric hindrance between the four surrounding phenyl groups on a silicon atom. All of the polymers showed good thermal stability up to 300 °C, since a small amount (or less than 5%) of weight loss began to occur at 300 °C in a nitrogen atmosphere.

Figure 5−7 show the UV−visible absorption and photoluminescence (PL) spectra of the resulting copolymers in chloroform. As shown in the absorption spectra, two maximum absorption wavelengths (λ_{max}) of **SiHMPPV** and **SiPhPPV** exhibit at 355 and 365 nm, which are attributed to the π−π* transitions of the π-conjugated segment (see Figure 5), respectively. Furthermore, we also introduced a carbazole unit into silicon-based copolymers to prepare copolymers containing both silyl groups and carbazole units, since carbazole-containing polymers have good electro-and photoactive properties due to their high hole-transporing mobility.[16,22−23] The absorption spectra of **SiHMPVK** and **SiPhPVK** show two peaks of a strong absorption band of the π−π* transition of the carbazole segments around 322 nm and a strong absorption band of the π−π* transition of the π-conjugated segment around 356 nm, while **SiHMPVK** synthesized by Wittig reaction showed strong absorption band around 311 nm by carbazole segments and 352 nm by π-conjugated segment (see Figure 6). Also the absorption spectra of **SiHMFPV** and **SiPhFPV** show a strong absorption band of the π−π* transition of the π-conjugated segment around 380 nm (see Figure 6).

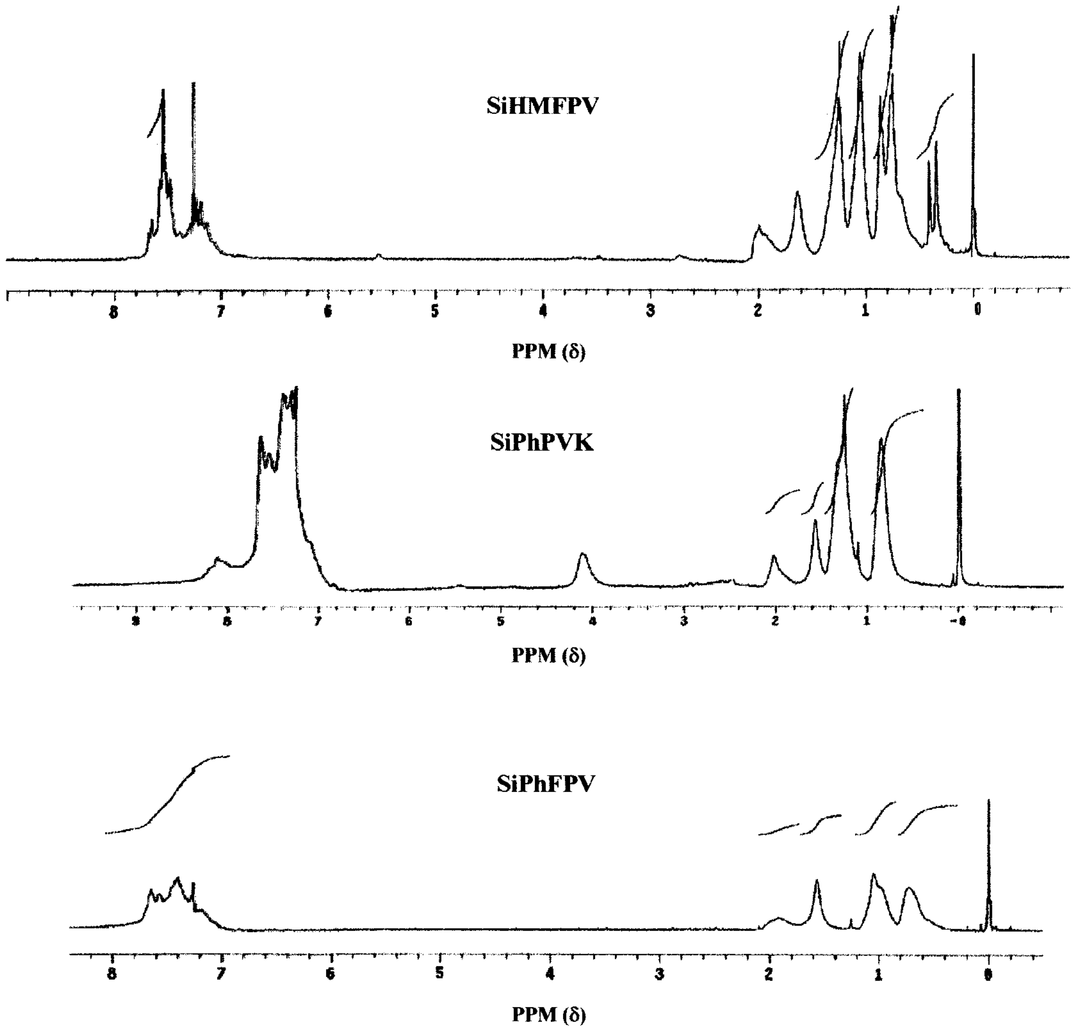


Figure 3. ^{1}H NMR spectra of **SiHMFPV**, **SiPhPVK**, and **SiPhFPV**.

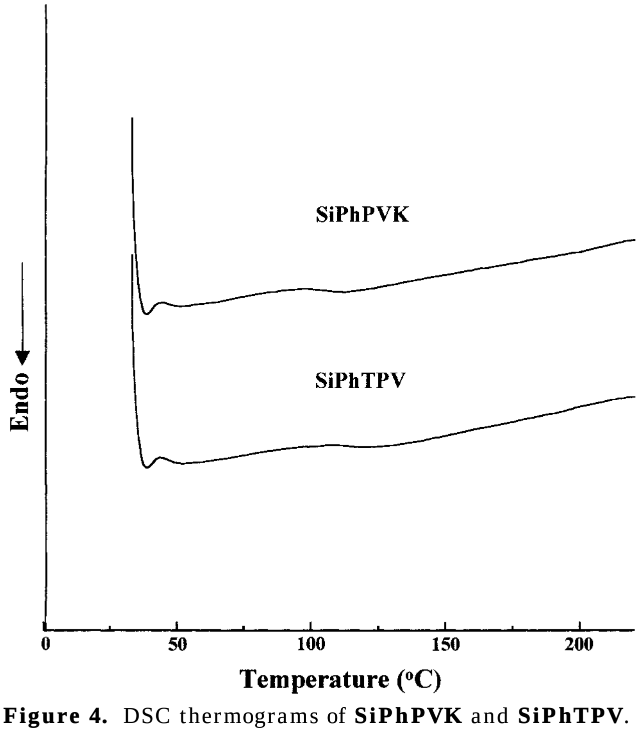


Figure 4. DSC thermograms of **SiPhPVK** and **SiPhTPV**.

The maximum absorption wavelength (λ_{max}) of **SiHMThV**, **SiPhThV**, and **SiPhThThV** appears at the longer wavelength of 400, 407, and 416 nm, due to the strong delocalization of the π-conjugated thiophene units, respectively (see Figure 7).

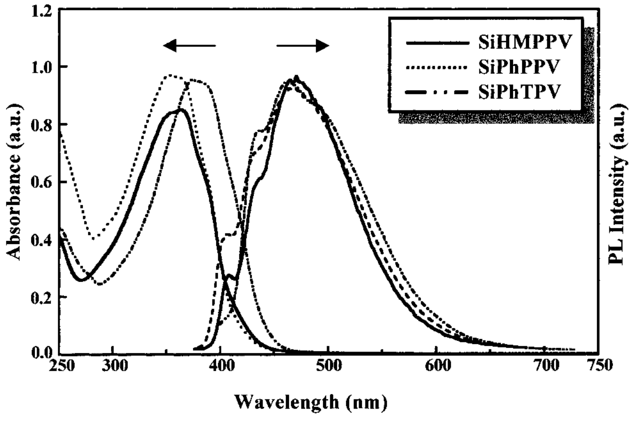


Figure 5. UV-visible spectra of **SiHMPPV**, **SiPhPPV**, and **SiPhTPV** as well as PL spectra of **SiHMPPV**, **SiPhPPV**, and **SiPhTPV** in $CHCl_3$.

Their photoluminescence (PL) spectra similarly shifts to those observed in the absorption spectra for the solution sample. With an excitation wavelength of 365 nm, the **SiHMPPV** and **SiPhPPV** spectra show a peak at 470 nm, indicating a blue emission. **SiHMFPV** and **SiPhFPV** exhibit a PL peak at 470 nm for **SiHMFPV** and 476 nm **for SiPhFPV**. It indicates a blue emission.

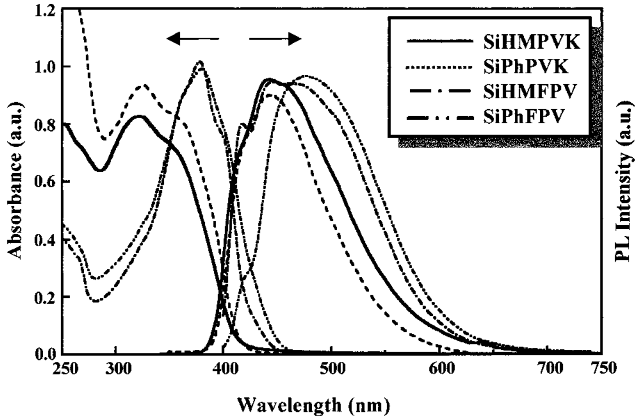


Figure 6. UV-visible spectra of **SiHMPVK**, **SiPhPVK**, **SiHMFPV**, and **SiPhFPV** as well as PL spectra of **SiHMPVK**, **SiPhPVK**, **SiHMFPV**, and **SiPhFPV** in $CHCl_3$.

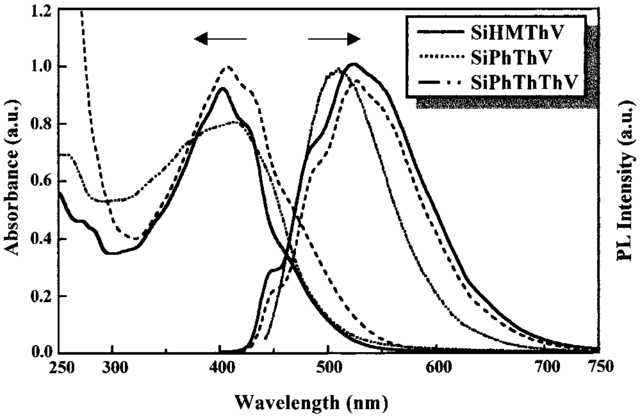


Figure 7. UV-visible spectra of **SiHMThV**, **SiPhThV**, and **SiPhThThV** as well as PL spectra of **SiHMThV**, **SiPhThV**, and **SiPhThThV** in $CHCl_3$.

With an excitation wavelength of 410 nm, the PL spectra of **SiHMThV**, **SiPhThV**, and **SiPhThThV** exhibit a peak at 520, 526, and 512 nm in the green region, respectively. These results indicate that the regular π-conjugated system is effectively interrupted by the organosilicon units to reduce π-conjugated length. With an excitation wavelength of 356 nm, the PL spectra of both **SiHMPVK** and **SiPhPVK** give a peak in the blue emission region at 440 nm (see Figure 6).

The single-layered light-emitting diode of an Al/**SiPhPPV** or **SiHMPPV**/ITO glass was fabricated. The threshold voltage is in the range 10−12 V from the *I*−*V* curve. The electroluminescence (EL) spectrum of the **SiPhPPV** or **SiHMPPV** showed a peak at 450 nm, when the operating voltage of 12 V was applied. It was previously reported that blue light-emitting diodes of the silicon-based copolymers are operated at the low voltages due to the lowering of the LUMO level and the d-orbital participation of silicon atoms.[25]

Furthermore, the multilayered light-emitting diodes of an Al/LiAl/**SiPhPVK**/PANI/ITO glass[30] and an Al/LiAl/**SiPhFPV** or **SiHMFPV**/ITO glass were fabricated. The polymer film was prepared by spin casting the **SiPhPVK** solution containing 2 wt % in cyclohexanone, and **SiHMFPV** as well as **SiPhFPV** solution containing 1 wt % in 1,2-dichloroethane. Uniform and pinhole-free films with a thickness of around 100 nm were easily obtained from the polymer solutions.

Figure 8 and Figure 9 show the current−voltage (*I*−*V*) characteristics of the multilayered light-emitting diodes of an Al/LiAl/**SiPhPVK**/PANI/ITO glass, an Al/LiAl/**SiPhFPV**/ITO glass and an Al/LiAl/**SiHMFPV**/ITO glass. The forward bias current is obtained when the ITO electrode is positively biased and the Al electrode negatively. The current increases with increasing the forward bias voltage and the reverse bias current remains small, which is a typical rectifying characteristics. As can be seen from the *I*−*V* curve, the threshold voltage of **SiPhPVK** is in the range 6−12 V. Figure 11 shows the EL spectra of the multilayered light-emitting diodes of both an Al/LiAl/SiPhPVK/PANI/ITO glass and an Al/LiAl/SiPhFPV/ ITO glass. The EL spectrum of the SiPhPVK gives a peak at 467 nm, when an operating voltage of 7 V was applied. When an operating voltage of 11 V was applied, however, the EL spectrum of the SiPhPVK gives a peak at 467 nm and an additional strong EL emissive band in the red region. Therefore, two EL peaks may combine to produce a white EL color, when an operating voltage of higher than 11 V is applied (see Figure 10a). Also, we found that the intensity of two EL peaks increases with the applied voltage (see Figure 10b).

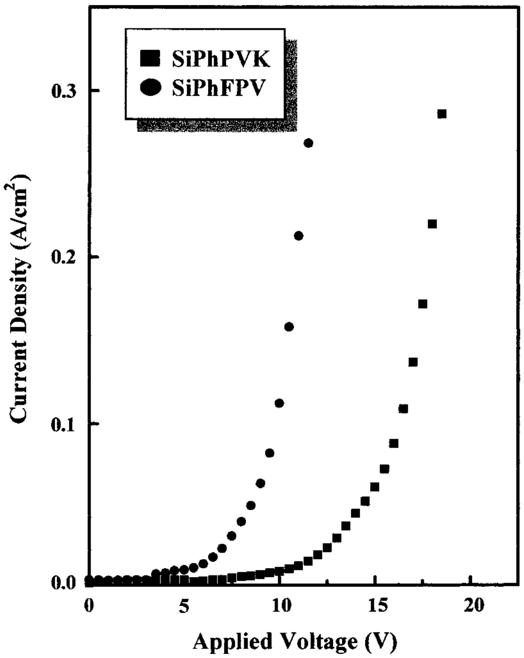


Figure 8. Current−voltage (*I*−*V*) characteristics of the multilayer light-emitting diode of Al/LiAl/**SiPhFPV**/ITO and Al/LiAl/**SiPhPVK**/PANI/ITO glasses.

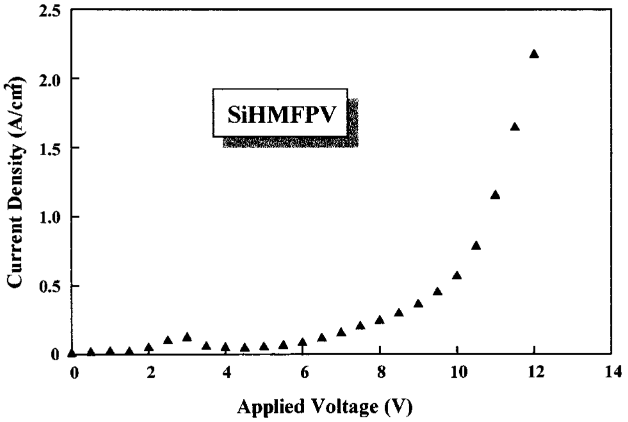


Figure 9. Current-voltage (*I*−*V*) characteristics of the multilayer light-emitting diode of Al/LiAl/**SiHMFPV**/ITO glass.

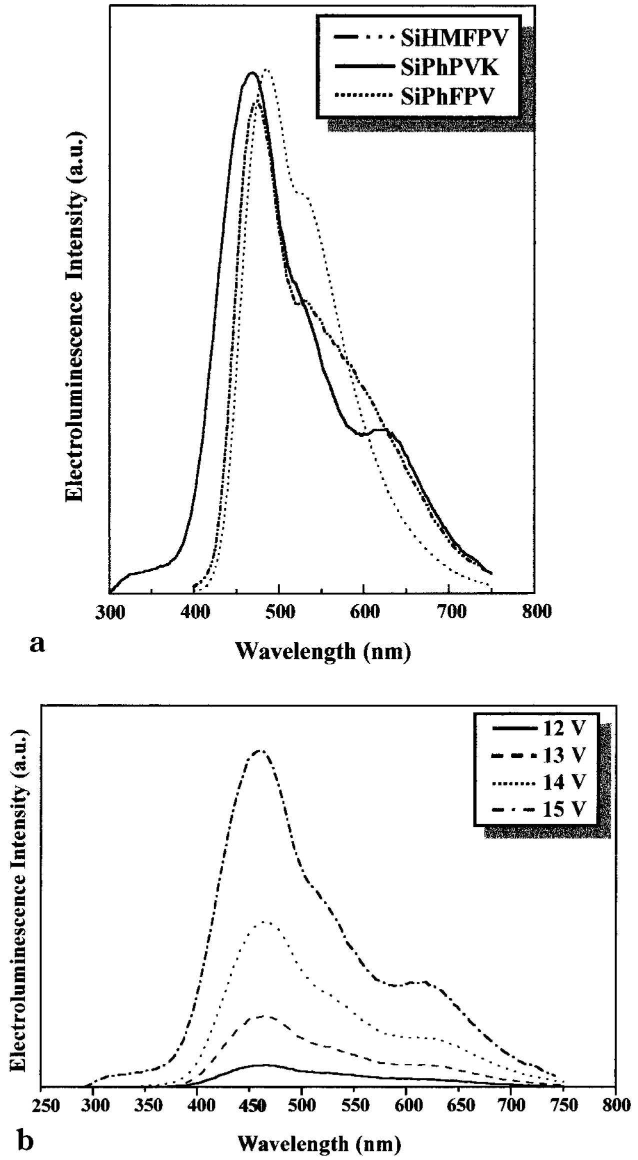


Figure 10. (a) Electroluminescence spectra of the multilayer light-emitting diode of Al/LiAl/**SiHMFPV**/ITO, Al/LiAl/**SiPhPVK**/PANI/ITO, and Al/LiAl/**SiPhFPV**/ITO glasses at a fixed operating voltage at 12 V. (b) Electroluminescence spectra of the multilayer light-emitting diode of Al/LiAl/**SiPhPVK**/PANI/ITO glass at various operating voltages.

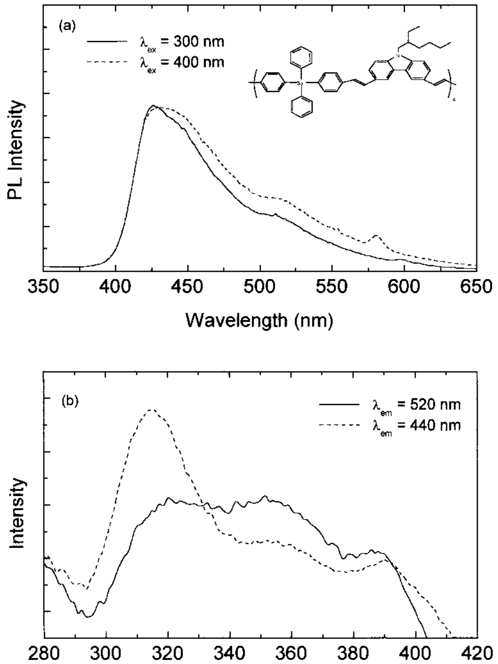


Figure 11. (a) PL spectra of **SiPhPVK** with two photoexcitation wavelengths at 300 and 400 nm. (b) PL excitation spectra for **SiPhPVK** at two probes of 440 and 520 nm.

As shown in Figure 10a, the shorter wavelength EL peak can be attributed to the π-conjugated segment in the main chain.[8,18−19,24] The longer wavelength EL peak at 620 nm from **SiPhPVK** prepared by the Heck reaction in the present study was red-shifted much more than that of **SiPhPVK** (the EL peak at 570 nm; see ref 8) prepared by the Wittig reaction.[8] It may be due to the formation of isomers with different structures from the Heck reaction.[31]

Figure 11a shows the PL spectra of **SiPhPVK** with photoexcitation at two different wavelengths corresponding to the absorption maximum positions. These two excitation wavelengths at 300 and 400 nm were chosen for selective photoexcitation of carbazole and SiPh segments in **SiPhPVK**, respectively. The PL spectra of **SiPhPVK** exhibit the emission maximum band around 440 nm, in addition to the emission band at 520 nm. Upon photoexcitation of carbazole unit at 300 nm, the intensity ratio between these two bands is different from that obtained with photoexcitation of SiPh segment at 400 nm.[24] From this result, we can suggest that the origin of these two emission bands is different. Thus, we measured the excitation spectra in the wavelength range from 280 to 420 nm at emission wavelengths of 440 and 520 nm (see Figure 11b). The two electronic transitions at around 310 and 360 nm are mainly responsible for the PL emission bands at shorter and longer wavelengths, respectively. It is interesting to note that the peak position at 310 nm, observed from the excitation spectrum monitored at the emission wavelength of 440 nm, is found to be almost the same as the shorter absorption band. In addition, two excitation spectra in the wavelength range from 280 to 420 nm at emission wavelengths at 440 and 520 nm were observed obviously different (see Figure 11b). However, the PL spectra of **SiPhPPV** exhibit the same emission maximum band around 460 nm, which is attributed to the $\pi-\pi^*$ transition of the π-conjugated segment, with photoexcitation at three different wavelengths (see Figure 12a). Also, the excitation spectra of **SiPhPPV** (Figure 12b) monitored at two different wavelengths of 460 and 520 nm, unlike **SiPhPVK**, show the same spectral feature. Considering the above results, it is not unreasonable to suppose that the shorter wavelength emission band results from the carbazole segments. Meanwhile, it is not straightforward to assign the origin of the emission band at low energy side to the conjugated SiPh segments in **SiPhPVK**, because no such emission band is found in either PL or EL spectra from a **SiPhPPV** thin film. Therefore, it may be considered that the longer wavelength emission band in **SiPhPVK** could result from the formation of either the exciplex between excited-state carbazole and PPV segment or the excimer between a ground state and an excited state of carbazole segments.[32,33]

In fact, it is well-known that a carbazole unit with small substituent group in the polymer could easily form an excimer between ground and excited states of carbazole units. In our system, however, the longer wave-

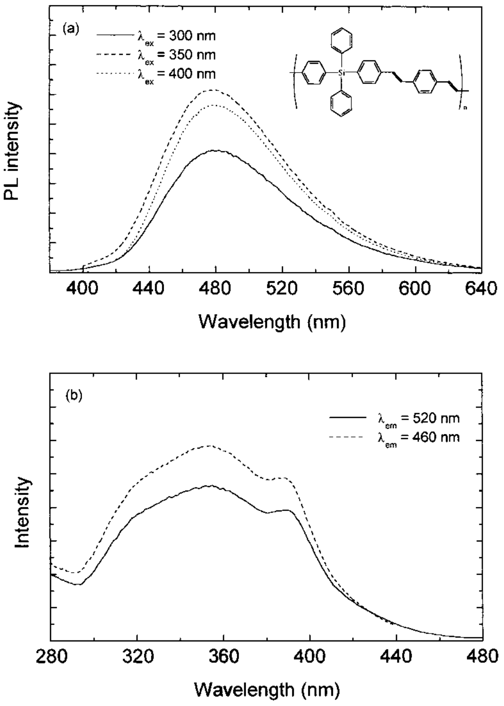


Figure 12. PL spectra for **SiPhPPV** with three photoexcitation wavelengths at 300, 350, and 400 nm. (b) PL excitation spectra for **SiPhPVK** at two probes of 460 and 520 nm.

length emission is mainly due to the optical transition of SiPh main chain because the carbazole unit in our system has a branched and bulky alkyl chain which should hinder the excimer formation between carbazole units. And the absence of the PL band at around 530 nm, with two selective ptotoexcitation wavelengths of carbazole and SiPh segments in a **SiPhPVK** solution with a wide concentration range, as depicted in Figure 13, parts a and b, led us to confirm that any type of intermolecular interaction is not appropriate. The other probable explanation can be drawn from the stabilized excited-state arising from the intramolecular interaction. Since the carbazole unit in **SiPhPVK** has a high hole affinity, the SiPh unit may possess the electron affinity with respect to the carbazole unit. Thus, we can suggest that the long wavelength emission in **SiPhPVK** originates from another stabilized excited state, e.g., the CT state.[34]

To gain further insight into the nature of the long wavelength emission, we measured the PL decay profiles of **SiPhPVK** with photoexcitations at 300 and 400 nm. Figure 14 shows the PL decay profiles of **SiPhPVK** monitored at 430, 480, and 550 nm which shows a strong dependence on the monitoring wavelengths. The long wavelength PL lifetime of **SiPhPVK**, which is believed to be due to the charge transfer process, is approximately 1.5 ns.[35] Owing to the distribution in conjugation lengths in the polymers, a rapid energy migration is likely to occur along the chain or between the chains upon photoexcitation. As a result, the PL lifetime becomes slightly longer as the probe wavelength increases. However, the PL lifetime at 550 nm seems to be too long to be explained in terms of the energy migration process. The characteristic feature of the charge transfer formation along with a long tail emission is the relatively long emission lifetime. Thus, we can suggest that the charge-transfer process between carbazole and SiPh units in the same chain induces the long wavelength emission of **SiPhPVK**.[36] It is generally accepted that upon photoexcitation with high energy the PL decay in polymers becomes fast as compared to the photoexcitation with lower energy because of defect sites. However, upon photoexcitation with high energy (300 nm) in Figure 14a, the PL decay time of **SiPhPVK** is longer than that obtained by photoexcitation at lower energy (400 nm) in Figure 14b. Therefore, we can suggest that the charge-transfer process is facile upon photoexcitation of a carbazole unit in SiPhPVK as compared with the photoexcitation of SiPh unit.

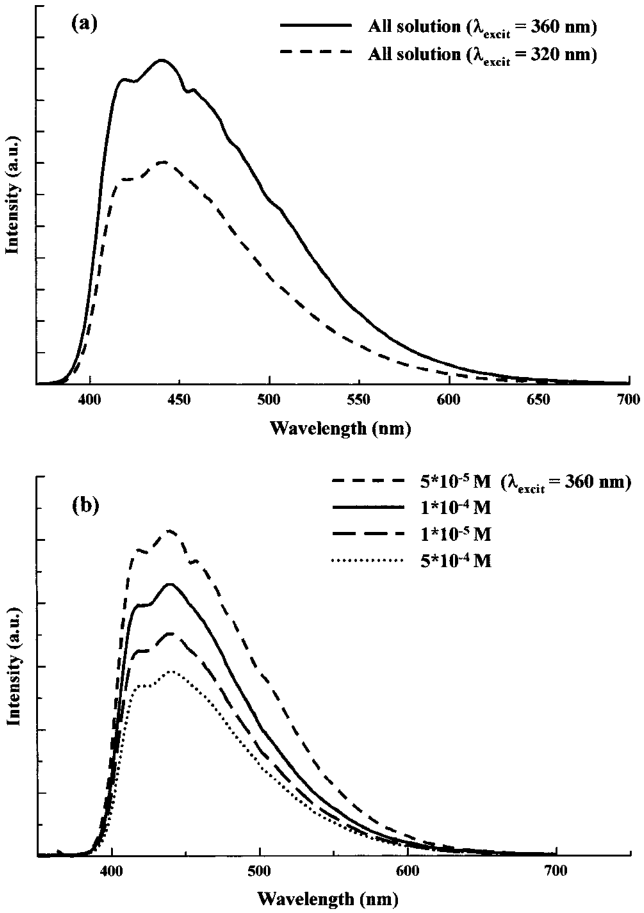


Figure 13. (a) PL spectra of **SiPhPPV** with two photoexcitation wavelengths at 320 and 360 nm. (b) PL spectra of **SiPhPPV** in details with a photoexcitation wavelength of 360 nm at various concentrations in THF solutions.

Similarly, the EL spectra of the **SiPhFPV** and **SiHMFPV** polymers show peaks at 485 and 475 nm and an additional strong EL band in the green region, when an operating voltage of 12 V was applied. Their PL decay profiles at all probes with photoexcitation of 300 nm exhibited approximately the single-exponential decay. From the PL decay profiles, the PL decay at longer wavelength is much slower than that at shorter wavelength, indicating excimer formation between the ground state and the excited states of a fluorine unit (see Figure 15).[28]

Summary

Silicon-based alternating copolymers as electroluminescent materials were synthesized by means of the Heck reaction. The resulting polymers were highly soluble in common organic solvents. They can be spin-cast onto various substrates to give highly transparent homogeneous thin films. Their glass transition

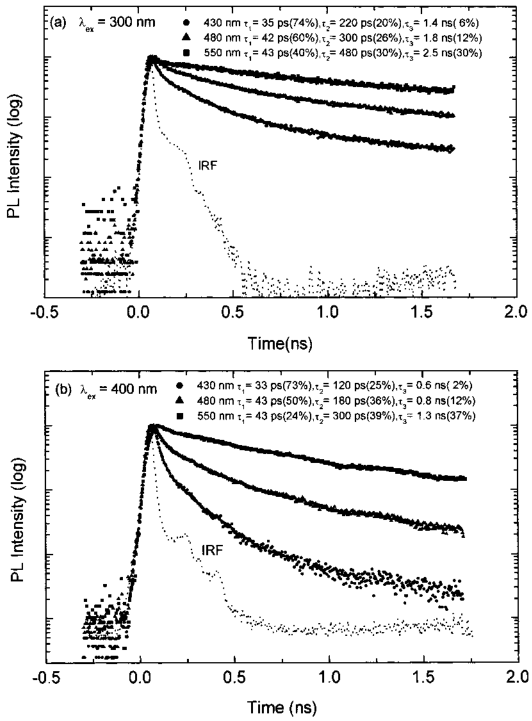


Figure 14. Transient PL decay profiles for **SiPhPVK** monitored at 430, 480, and 550 nm with two photoexcitation wavelengths of (a) 300 and (b) 400 nm.

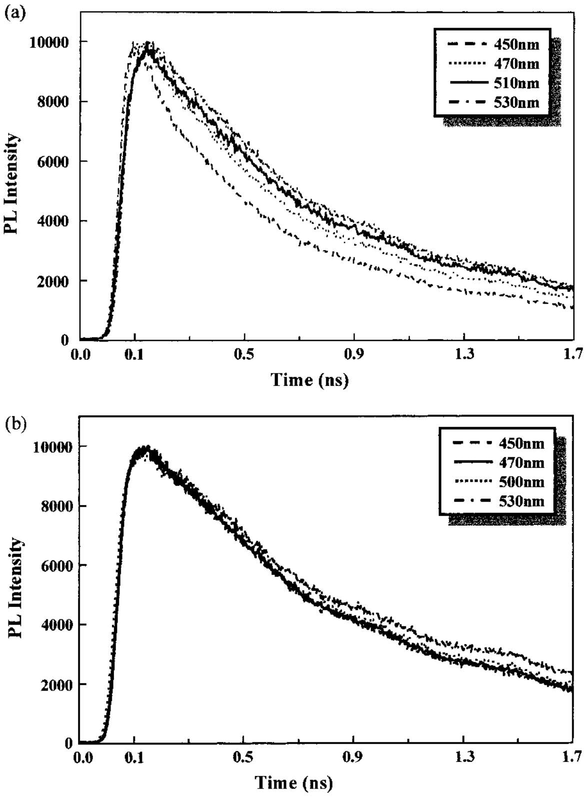


Figure 15. Transient PL decay profiles for (a) **SiPhFPV** and (b) the corresponding model compound at various probes with an photoexcitation wavelength of 300 nm.

temperatures were in the range of 94−127 °C. The polymers were thermally stable up to 300 °C under nitrogen. The UV−visible absorption spectra of the present polymers show strong bands at around 356−416 nm, which correspond to the $\pi-\pi^*$ transition of the conjugated segments, depending on the π-conjugation length and arylene dibromides. The maximum PL wavelength appeared around 440−526 nm in the blue or green emission region, depending on the arylene dibromides. The single layer light-emitting diode of an Al/**SiPhPPV** or **SiHMPPV**/ITO glass shows the threshold voltage range of 10−12 V from the *I*−*V* curve. The electroluminescence (EL) spectrum of the **SiPhPPV** or **SiHMPPV** exhibits a peak at 450 nm. Furthermore, the multilayer light-emitting diodes of an Al/LiAl/**SiPhPVK**/PANI/ITO glass and an Al/LiAl/**SiPhFPV** (or **SiHMFPV**)/ITO glass show the threshold voltage range 6−12 V. The EL spectrum of the **SiPhPVK** depicts a peak at 467 nm, when an operating voltage of 7 V was applied. When an operating voltage of 11 V was applied, however, the EL spectrum of the **SiPhPVK** gives a peak at 467 nm and an additional strong EL emissive band in the red region, leading to a white EL color. The former peak can be attributed to the π-conjugated segment in the main chain. The latter peak could result from the formation of an excimer between the ground and the excited states of a carbazole unit. The EL spectra of the **SiPhFPV** and **SiHMFPV** polymers, operated at the applied voltage of 12 V, show a peak at 485 and 475 nm and an additional strong band in the green region, respectively. And, the intensity of two EL peaks increases with the applied voltage.

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Supporting Information Available: Figures showing FT-IR, ^{1}H NMR, and ^{13}C NMR data for the monomers of 3,6-dibromo-*N*-(2-ethylhexyl)carbazole (**3**) and 2,5-dibromo thieno[3,2-*b*]thiophene (**8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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