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Poly(silyleneethynylenephenylene) and Poly(silylenephenyleneethynylenephenylene)s: Synthesis and Photophysical Properties Related to Charge Transfer

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ABSTRACT: Novel poly(dimethylsilyleneethynylenephenylene) [**5**] and poly(dimethyl (or diphenyl) silylenephenyleneethynylenephenylene)s [**6**'s] without diyne defects were synthesized by using the Pd/Cu-catalyzed AB-type coupling reaction. **6**'s showed small but clear π-to-σ charge-transfer absorption bands at longer wavelengths (>340 nm) than those of $\pi-\pi^*$ absorption bands (<320 nm), whereas the charge-transfer absorption band was not found in **5**. When **6**'s were excited at the $\pi-\pi^*$ absorption wavelengths, two type of emission were observed: One is the vibronically structured emission with a maximum around 325 nm due to the locally excited π^* state, and the other is the intramolecular charge-transfer emission having a broad and structureless band (emission λ_{max} ca. 370 nm) with a large Stokes shift. On the other hand, when excited at the charge-transfer absorption wavelengths, **6**'s exhibited only the intramolecular charge-transfer emission with a maximum above 390 nm. This suggests that the indigo blue light emission of **6**'s is due to the charge-transfer phenomenon and not to the locally excited π^* state. The charge-transfer character of **6**'s was clearly verified by the shift of emission in polar solvents.

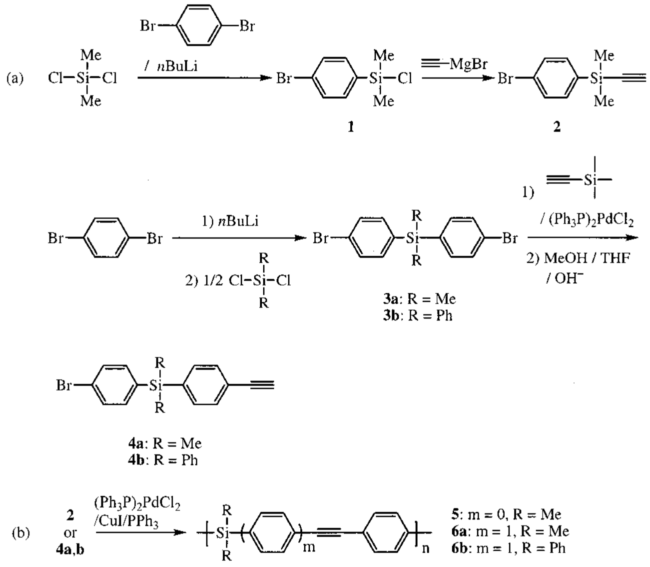
Introduction

The $\sigma-\pi$ conjugated polymers containing alternating arrangements of silylene and π electron moieties possess potential as semiconductors,[1] photo- and electroluminescent materials,[2] and ceramic precursors.[3] The unique electrical and optical propeties of these materials can be attributed to through-space interaction between π electrons bridged by silylene moiety and also the delocalization of electrons through the silylene linkages.

Some arylsilane compounds show intramolecular charge-transfer absorption[4] and, when photoexcited, exhibit intramolecular charge-transfer emission.[5] Thus, in the molecular design of new types of silylene−arylene $\sigma-\pi$ conjugated polymers, it is important to estimate the extent of intramolecular charge transfer in the ground and excited states which affects their optical properties. Although various $\sigma-\pi$ conjugated polymers have been synthesized so far, little attention has been paid to the charge-transfer phenomenon. Recently, we have synthesized highly regio- and stereoregular all-trans and all-cis poly(silylenephenylenevinylene)s.[6] These polymers are very soluble and thermally stable. Interestingly, their emission properties are affected by the geometric structure; e.g., the cis-type polymer showed charge-transfer emission, while the trans-type one exhibited $\pi-\pi^*$ state emission.[7] The ethynylene group is more π-electron-rich than the vinylene group. Thus, it is interesting to synthesize new types of $\sigma-\pi$ conjugated organosilicon polymers containing ethynylene moieties and study their absorption and emission properties with respect to the charge-transfer phenomenon.

The AB-type polycondensation does not require stoichiometrical consideration unlike the AA−BB-type one. In this study, we synthesized novel poly(silyleneethynylenephenylene) [**5**] and poly(silylenephenyleneethynylenephenylene)s [**6a**, **6b**] without diyne defects by using the Pd/Cu-catalyzed AB-type coupling reaction (Scheme 1). Polymers **6a** and **6b** exhibited unusual absorption and emission based on intramolecular charge-transfer ground and excited states. This result agrees with the idea that the indigo blue light emission of these polymers is due to the charge-transfer phenomenon but not to locally excited π^* state. Furthermore, quantum yields of the charge-transfer emissions were fairly high.

Scheme 1. (a) Synthesis and (b) Polymerization of (4-Bromophenyl)dimethylethynylsilane (2), [4-{(4-Bromophenyl)dimethylsilyl}]phenylacetylene (4a), and [4-{(4-Bromophenyl)dimethylsilyl}]phenylacetylene (4b)



Experimental Section

Synthesis of Monomers [Scheme 1a]. (4-Bromophenyl)-chlorodimethylsilane (**1**): A 300 mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a

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magnetic stirring bar and flushed with dry nitrogen. After *p*-dibromobenzene (12.7 g, 53.5 mmol) and diethyl ether (200 mL) were placed in the flask at 0 °C, a hexane solution of *n*-butyllithium (34 mL, 1.59 M, 53.5 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. Then, this reaction mixture was added slowly into a 1 L round-bottomed flask in which diethyl ether (300 mL) and dichlorodimethylsilane (6.9 g, 53.5 mmol) had been placed beforehand. After completion of addition, stirring was continued at 0 °C and then gradually warmed to room temperature overnight. The salts were removed by filtration of the reaction mixture through a sintered glass (G3) filled with Celite. Diethyl ether was evaporated at room temperature. The crude product was purified by distillation to give the desired product (yield 9.4 g, 70%) as colorless liquid; bp 80 °C/1.0 mmHg (250 °C/760 mmHg). ^{1}H NMR (CDCl$_3$, δ): 7.48−7.60 (m, 4H, aromatic) and 0.68 ppm (s, 6H, (SiCH_3)$_2$).

(4-Bromophenyl)dimethylethynylsilane (**2**): A 300 mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. After compound **1** (9.4 g, 37.4 mmol) and diethyl ether (100 mL) were placed in the flask at 0 °C, a THF solution of ethynylmagnesium bromide (75 mL, 0.5 M, 37.4 mmol) was added dropwise and then gradually warmed to room temperature for 2 h. After treatment with cold aqueous ammonium chloride, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane) to give the desired product (yield 5.8 g, 65%) as a colorless liquid. ^{1}H NMR (CDCl$_3$, δ): 7.47−7.53 (m, 4H, aromatic), 2.53 (s, 1H, CH), and 0.42 ppm (s, 6H, (SiCH_3)$_2$). ^{13}C NMR (CDCl$_3$, δ): 135.2, 131.0 (d), 124.5, 95.3, 95.1, 87.5, −1.2 (d) ppm. Anal. Calcd for BrC$_{10}$H$_{11}$Si: Br, 33.42; C, 50.23; H, 4.60. Found: Br, 33.55; C, 50.28; H, 4.71.

Bis(4-bromophenyl)dimethylsilane (**3a**): A 1 L round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Diethyl ether (500 mL) and *p*-dibromobenzene (38.0 g, 160 mmol) were placed in the flask. The solution was cooled at 0 °C, to which a hexane solution of *n*-butyllithium (102 mL, 1.56 M, 160 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. A solution of dichlorodimethylsilane (9.6 mL, 80 mmol) in diethyl ether (20 mL) was added dropwise, and stirring was continued for 4 h. After removal of insoluble salts by filtration, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was recrystallized from hexane to give the desired product (yield 19.0 g, 64%) as a colorless solid. ^{1}H NMR (CDCl$_3$, δ): 7.51−7.32 (t, 8H, aromatic) and 0.56 ppm (s, 6H, (SiCH_3)$_2$).

Bis(4-bromophenyl)diphenylsilane (**3b**): This compound was prepared similarly to **3a** using dichlorodiphenylsilane; yield 66%, white solid. ^{1}H NMR (CDCl$_3$, δ): 7.61−7.35 ppm (m, 18H, aromatic).

4-[(4-Bromophenyl)dimethylsilyl]phenylacetylene (**4a**): A 500 mL round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Triethylamine (300 mL), (Ph$_3$P)$_2$PdCl$_2$ (100 mg, 0.10 mmol), CuI (200 mg, 1.07 mmol), PPh$_3$ (200 mg, 0.71 mmol), and **3a** (19.0 g, 51.3 mmol) were placed in the flask, and the mixture was stirred for 4 h at 80 °C. After the completion of reaction had been confirmed by TLC, the resulting solution was filtered, and then the solution was evaporated. Methanol (ca. 200 mL), THF (ca. 200 mL), and NaOH (ca. 2 g) were added to the crude product and stirred for 1 h. After the volatiles had been evaporated, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (eluent, hexane) to give the desired product (yield 7.3 g, 45%) as white solid; mp 49−50 °C. ^{1}H NMR (CDCl$_3$, δ): 7.58−7.30 (m, 8H, aromatic), 3.12 (s, 1H, CH), and 0.51 ppm (s, 6H, (SiCH_3)$_2$). ^{13}C NMR (CDCl$_3$, δ): 138.7, 136.5, 135.7, 133.9, 131.3, 131.0, 124.2, 122.9, 83.6, 77.9, −2.6 ppm (d). Anal. Calcd for BrC$_{16}$H$_{15}$Si: Br, 25.35; C, 60.98; H, 4.76. Found: Br, 25.52; C, 60.72; H, 4.74.

4-[(4-Bromophenyl)diphenylsilyl]phenylacetylene (**4b**): This compound was prepared similarly to **4a** using compound **3b**. **3b** was sparely soluble in triethylamine unlike **3a**, so that piperidine was used instead of triethylamine. The crude product was purified by flash column chromatography (eluent, hexane:benzene = 10:1) to give the desired product (yield 24%) as white solid; mp 158−159 °C. ^{1}H NMR (CDCl$_3$, δ): 7.60−7.35 (m, 18H, aromatic) and 3.13 ppm (s, 1H, CH). ^{13}C NMR (CDCl$_3$, δ): 137.8, 136.2, 136.1, 134.9, 133.0, 132.7, 131.4, 131.2, 130.0, 128.0, 124.9, 123.5, 83.5, 78.3 ppm. Anal. Calcd for BrC$_{26}$H$_{19}$Si: Br, 18.19; C, 71.09; H, 4.32. Found: Br, 18.71; C, 71.01; H, 4.23.

Polymerization [Scheme 1b]. The following polymerization procedures are exemplary: Triethylamine (20 mL), THF (20 mL), (Ph$_3$P)$_2$PdCl$_2$ (21.0 mg, 3.0 μmol), CuI (5.7 mg, 3.0 μmol), PPh$_3$ (15.7 mg, 6.0 μmol), and **2** (0.48 g, 2.0 mmol) were placed in the flask, and the mixture was stirred at 50 °C for 2 days. The resulting solution was filtered. Then the solution was concentrated and poured into a large amount of methanol under stirring to precipitate the formed polymer. The polymer was purified by reprecipitation from dichloromethane into methanol (1:10).

Measurements. NMR spectra were measured in CDCl$_3$ solution at 25 °C on a JEOL EX-400 spectrometer. The weight- and number-average molecular weights (M_w and M_n, respectively) of polymers were determined by gel permeation chromatography (GPC); eluent CHCl$_3$, Shodex K-805, K-804, and K-803 polystyrene gel columns (Showa Denco, Co., Japan), polystyrene calibration. The measurements of thermogravimetric analysis (TGA) were conducted with a Perkin-Elmer TGA-7 analyzer in N$_2$ at a heating rate of 10 °C/min. IR, UV, and emission spectra were measured on Shimadzu FTIR-8100 (KBr pellet), Shimadzu UV-2200, and JASCO FP-750 spectrophotometers, respectively. Emission quantum yields were determined relative to quinine sulfate in 1 N H$_2$SO$_4$ assuming a quantum yield of 0.546 at an excitation wavelength of 365 nm.

Results and Discussion

In this study, we employed Pd/Cu-catalyzed coupling reaction under the Heck condition. The polymerization of the present monomers (**2**, **4a**, and **4b**) with (Ph$_3$P)$_2$-PdCl$_2$ and CuI in THF and triethylamine (volume ratio 1:1) quantitatively provided light-yellow polymers [Scheme 1b; poly(silyleneethynylenephenylene) (**5**) and poly(silylenephenyleneethynylenephenylene)s (**6a** and **6b**)]. The molecular weights (M_w) of **5**, **6a**, and **6b** were 33 × 10^3 (M_w/M_n 3.5), 30 × 10^3 (M_w/M_n 4.5), and 50 × 10^3 (M_w/M_n 2.9), respectively. All the present polymers were soluble in common organic solvents such as toluene, THF, cyclohexane, and CHCl$_3$.

The Pd/Cu-catalyzed polymerizaton of diethynylarenes and dihaloarenes occasionally forms minor amounts of 1,3-diyne moiety as defect in the polymer backbone.[8] As a result, the polymers gradually become insoluble when stored in the solid state. The structure of the present polymers was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectra. These spectral data supported the selective formation of polymers with the expected structures. The IR spectra of the present polymers exhibited absorptions around 2200 cm^{-1}, which indicates the presence of the ethynylene group. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of **5** and **6a**. The ^{1}H NMR spectra of **5** and **6a** clearly show a singlet peak due to methyl protons and multiple peaks due to phenylene protons. In the ^{13}C NMR spectrum of **5**, signal *b* at 92 ppm is due to the ethynyl carbon adjacent to the silicon atom, and signal *c* at 107 ppm is assigned

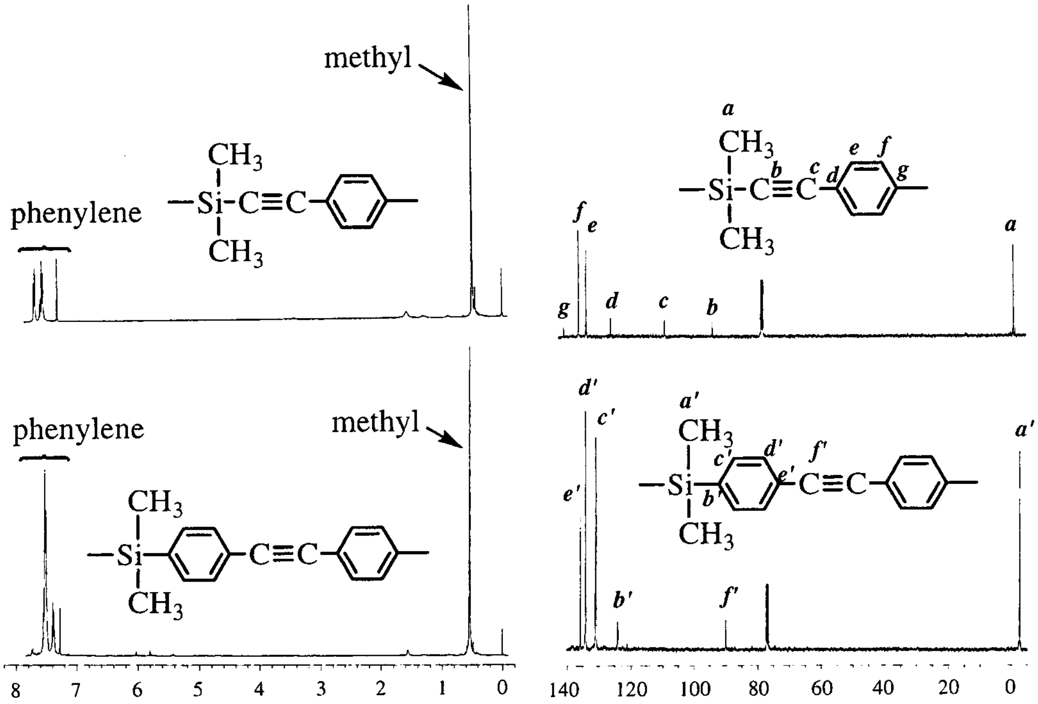

Figure 1. ^{1}H and ^{13}C NMR spectra of **5** and **6a** (in $CDCl_3$, 25 °C).

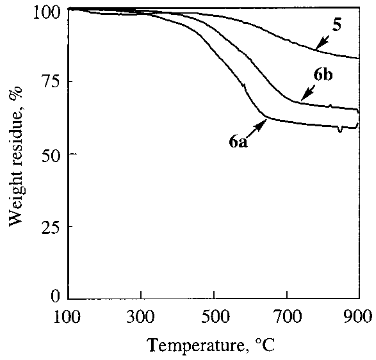

Figure 2. TGA curves of **5**, **6a**, and **6b** (heating rate 10 °C/min, in N_2).

to the ethynyl carbon bonded to the phenylene group. **6a** exhibits signal f' due to the ethynyl carbons at 90 ppm. No diyne carbon signal, which should appear around 75 and 80 ppm,[8] was found. Similarly, **6b** showed a signal due to the ethynylene carbons at 91 ppm but no diyne carbon signal. Thus, the present polymers have no diyne defect in the backbone. Accordingly, when kept under ambient conditions for a month, the present polymers remained completely soluble.

Organosilicon polymers containing unsaturated functional groups such as ethynylene and vinylene groups tend to retain weight up to high temperature. For instance, poly(silyleneethynylene)s[3a] cross-link at relatively low temperature to be converted to silicon carbides in high char yields. The thermal stability of the present polymers was examined by thermogravimetric analysis (Figure 2). The weight residues of **5**, **6a**, and **6b** at 900 °C in N_2 were 83, 61, and 64%, respectively. Thus, these polymers kept weight up to high temperature owing to cross-linking of ethynylene groups. Especially, the high char yield of **5** indicates that this polymer possesses potential usefulness as a precursor for ceramic fiber.

Figure 3a shows UV spectra of the present polymers. The comparison with the UV spectrum of diphenylacetylene [λ_{max} (ϵ_{max}) 287 nm (22 200 M^{-1} cm^{-1}) and 295 nm (27 300 M^{-1} cm^{-1}), in methanol[9]] suggests that the absorption bands of **6a** at 298 and 318 nm correspond to π–π* transition involving only the phenyleneethynylenephenylene moiety. Similarly, the absorption maxima of **6b** due to π–π* transition appeared at 300 and 320 nm. **5** exhibited an absorption maximum at 272 nm due to π–π* transition. The π–π* absorption bands of **6a** and **6b** shifted to longer wavelengths by ca. 20 nm or more as compared to that of **5**. Thus, the insertion of a phenylene moiety into **5** is effective to extend π character conjugation in the main chain. The absorption of **6b** is slightly red-shifted compared to that of **6a**, despite the main-chain phenylene and side-chain phenyl groups through silicon. Diarylsilanes (e.g., 4,4′-substituted dimethyldiphenylsilane[4a] and dimethyldithienylsilane[4c]) show a small π-to-σ charge-transfer absorption band at a longer wavelength than that of the absorption band due to the π–π* transition. As seen in Figure 3a, **6a** and **6b** possess a small but clear absorption at longer

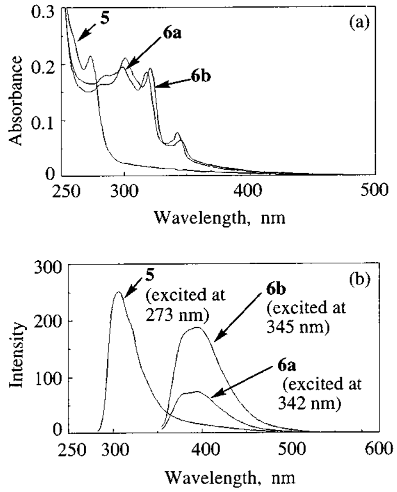

Figure 3. (a) UV and (b) emission spectra of **5**, **6a**, and **6b** (in $CHCl_3$, 7.9 × 10^{-6} mol/L).

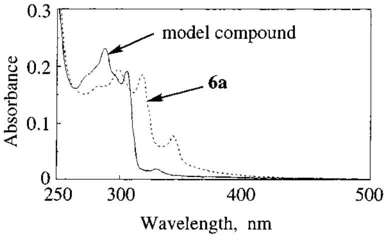

Figure 4. UV spectra of a model compound, 1-[*p*-(trimethylsilyl)phenyl]-2-phenylacetylene, and **6a** (in $CHCl_3$, 7.9×10^{-6} mol/L).

wavelengths (342 and 345 nm, respectively), whereas no absorption band was found around the same UV region in **5**. This suggests that intramolecular charge transfer occurs between phenyleneethynylenephenylene π unit and the silylene σ unit at the ground state, but it hardly takes place between the ethynylenephenylene π unit and the silylene σ unit. When **5**, **6a**, and **6b** were excited at 272, 342, and 345 nm, repectively, these polymers exhibited emission maxima at 307, 394, and 395 nm, respectively (Figure 3b). In accordance with these emission spectra, **6a** and **6b** emitted visible indigo blue light in dilute solution, whereas **5** emitted no visible lights. The quantum yields of these emission of **5**, **6a**, and **6b** were 0.24, 0.26, and 0.82, respectively.

As mentioned above, **6a** and **6b** exhibited very clear intramolecular charge-transfer absorption bands. To confirm this finding, we synthesized a model compound, 1-[*p*-(trimethylsilyl)phenyl]-2-phenylacetylene, whose structure is close to that of the repeating unit of **6a**, according to the literature method.[10] Figure 4 compares UV spectra of **6a** and the model compound. The model compound shows a small but obvious charge-transfer absorption band at a longer wavelength (λ_{max} 329 nm) besides the $\pi-\pi^*$ absorption band (λ_{max} 287 and 305 nm). This means that the $\sigma-\pi$ combination between the silylene and phenyleneethynylenephenylene units is effective to give rise to the intramolecular charge transfer in the ground state. The charge-transfer absorption of **6a** is much stronger than that of the model compound, which is explicable in terms of the idea that the π-to-σ charge transfer is amplified in polymers by a high-density through-space interaction between π electrons of phenylene groups bridged by silylene moiety.

Some of silyl-substituted aromtic compounds form intramolecular charge transfer in the excited state. Consequently, both a shorter wavelength emission with vibronically structured band ascribed to the locally excited π^* state and a longer wavelength emission with structureless broad band due to the charge-transfer excited state are observed simultaneously.[2a,5] Very interestingly, the emission spectra of **6a** and **6b** appreciably changed with excitation wavelengths. As shown in Figure 5, when **6a** is excited at a $\pi-\pi^*$ absorption wavelength (298 or 318 nm), two types of emission are observed: one is the vibronically structured emission with a maximum at 325 nm and shoulders at 338 and 349 nm due to the locally excited π^* state, and the other is the intramolecular charge-transfer emission having a broad and structureless band (emission λ_{max} values are 369 and 377 nm when excited at 298 and 318 nm, respectively) with a large Stokes shift. On the other hand, when excited at the charge-transfer absorption wavelength (342 nm), this polymer exhibits only the intramolecular charge-transfer emission with a maximum at 394 nm. This means that the intramolecular charge-transfer absorption causes the charge-transfer emission selectively. Similarly, **6b** exhibited two types of emissions, i.e., $\pi-\pi^*$ emission (emission λ_{max} 328 nm; shoulders appear at 341 and 351 nm) and charge-transfer emission (emission λ_{max} 369 nm) when excited at 300 or 320 nm. Further, **6b** showed only intramolecular charge-transfer emission (emission λ_{max} 395 nm) when excited at 345 nm. It suggests that the indigo blue light emission of **6a** and **6b** is due to the charge-transfer phenomenon but not to locally excited π^* state. It is noteworthy that, when the excitation wavelength is shifted up to the charge-transfer region in these polymers, the two kinds of excited species reduce into one, i.e., only the charge-transfer species. On the other hand, **5** showed no shift of emission wavelength at all upon the modulation of excitation wavelength.

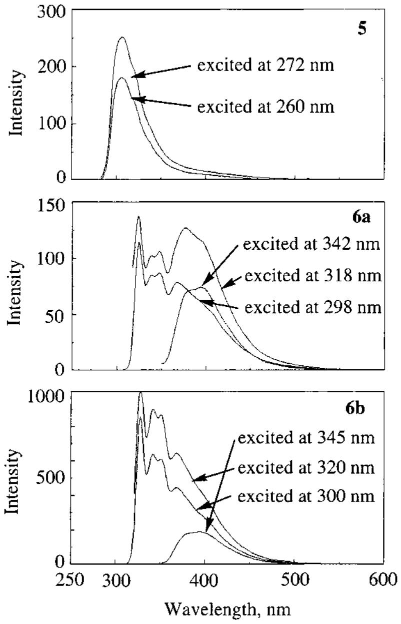

Figure 5. Variation of emission spectra of **5**, **6a**, and **6b** on excitation wavelength (in $CHCl_3$, 7.9×10^{-6} mol/L).

The excitation spectrum of **5** is essentially the same as its absorption spectrum (see Figures 3a and 6); i.e., when the emission wavelength was fixed at 307 nm, the excitation spectrum exhibited a maximum at 275 nm. The shape of excitation spectrum hardly changed even though the emission wavelength was shifted in the range of 270−400 nm. This means that the excitation of **5** is based on the simple π and π^* states. In contrast, the shape of excitation spectra of **6a** and **6b** appreciably changed when the emission wavelength was shifted (Figure 6); e.g., when the emission was fixed at 394 nm, the excitation spectrum of **6a** showed two excitation maxima around 320 and 340 nm. The excitation band around 340 nm, however, disappeared when the emission was fixed at 325, 338, or 349 nm. **6b** showed the same tendency. This means that the excitation band around 320 nm is related to the $\pi-\pi^*$ excited state, while the band around 340 nm is related to the charge-transfer excited state. This interpretation agrees well with the results that the proportion of the excited states in **6a** and **6b** depends on the excitation wavelength and that the short wavelength emission does not occur from the charge-transfer excited state.

In general, the intramolecular charge-transfer emission band red-shifts with increasing solvent polarity.[5c,f]

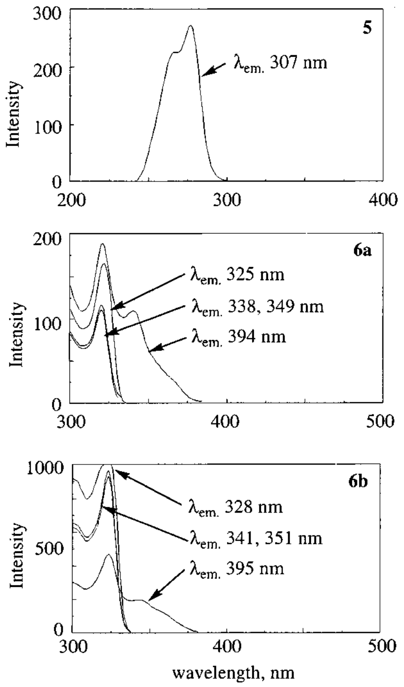

Figure 6. Excitation spectra of **5**, **6a**, and **6b** (in CHCl$_3$, 7.9×10^{-6} mol/L).

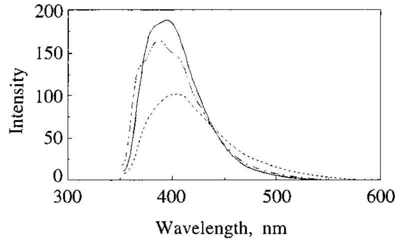

Figure 7. Emission spectra of **6b** in various solvents [benzonitrile (- - -), CHCl$_3$ (—), cyclohexane (— - —), 7.9×10^{-6} mol/L].

To gain definitive evidence for the existence of intramolecular charge transfer in poly(silylenephenylene-ethynylenephenylene)s, we examined solvent effects on the emission property. The dielectric constant (D) values of cyclohexane, CHCl$_3$, and benzonitrile are 2.05 (at 25 °C),[11] 4.9 (at 20 °C),[11] and 25.2 (at 25 °C),[12] respectively. As estimated from these D values, the solvent polarity is in the order benzonitrile $\gg$ CHCl$_3$ $>$ cyclohexane. As shown in Figure 7, the emission intensity of **6b** was smaller in benzonitrile than in cyclohexane and CHCl$_3$. This is explained in terms of the increase of nonradiative transition in more polar solvents. Further, the emission spectrum in benzonitrile was more structureless and broader than in cyclohexane or CHCl$_3$, and the emission band shifted toward longer wavelengths in polar solvents; e.g., emission $\lambda_{\max}$ 387 nm in cyclohexane, emission $\lambda_{\max}$ 395 nm in CHCl$_3$, and emission $\lambda_{\max}$ 405 nm in benzonitrile. Thus, this solvent shift of emission of **6b** indicates that the emitting state is polar. The same tendency was observed in **6a** as well.

In conclusion, we successfully synthesized novel poly(silyleneethynylenephenylene) and poly(silylenephenyleneethynylenephenylene)s without diyne defects by using the Pd/Cu-catalyzed AB-type coupling reaction. We found that the $\sigma-\pi$ combination between the silylene and phenyleneethynylenephenylene units in poly(silylenephenyleneethynylene-phenylene)s is effective to form intramolecular charge transfer in both ground and excited states and that the indigo blue light emission of these polymers originates from the charge transfer. The charge-transfer character of these polymers was clearly verified by the shift of emission in polar solvents. The present study on charge-transfer phenomenon will be helpful to design new $\sigma-\pi$ conjugated organosilicon polymers for light-emitting diode materials.

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