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Dynamic Fluoride Anion Coordinating Si-Containing π-Conjugating Polymers

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ABSTRACT: Three types of poly[dialkylsilylenephenyleneethynylenephenylene]s (dialkyl: **2** for *n*-dodecylmethyl; **5a** for di-*n*-hexyl; **5b** for di-*n*-hexyl-*co*-dimethyl) were newly prepared by the AB- and AA−BB-type coupling reactions. These polymers afforded moderate molecular weights (M_w) in the range 7.6×10^3−27×10^3. As the amount of tetra-*n*-butylammonium fluoride (TBAF) increases in a THF solution of **2**, two π−π* absorption bands at 298 and 317 nm due to the phenyleneethynylenephenylene moiety significantly decreased. Simultaneously, a new intense absorption band at 390 nm characteristic of intramolecular charge transfer (ICT) appeared in place of the original ICT absorption band at 342 nm. Also, the intensity of fluorescence band around 393 nm (excited at 342 nm) significantly decreased upon the addition of TBAF. The changes in UV−vis absorption and fluorescence spectra of the polymers were readily seen by naked eye. As for **2**, a novel three-step titration curve of UV absorbance (or apparent GPC retention time) as a function of fluoride concentration was found. It was thus assumed that **2** underwent anion charge-driven coil-to-globule conformational transitions in the presence of TBAF. In addition, the complex forming abilities of the polymers with fluoride ion were greatly dependent on the nature of alkyl groups attached to the silicon atom of the polymers.

Introduction

In recent years, silicon-containing π-electron molecules and silicon-containing polymers have attracted much attention because of their novel photophysical and electrical properties due to through-space interaction between π-electron systems linked by a silylene moiety.[1] Indeed, modulation in coordination number of 13 and 14 group main elements such as boron and silicon causes dramatic changes in photophysical properties of the π-electron systems.[2] Because silicon atom remarkably possesses specific affinity toward fluoride ion, certain tetracoordinate silanes with n-$Bu_4N^+F^-$ (TBAF) can readily afford the corresponding pentacoordinate silicates.[3] This reaction can often be observed by ordinary colorimetric and fluorometric methods.[2a,c,d]

From the viewpoint of semiconductor physics, silylene−π-electron alternating copolymers may be regarded as a new type of σ−π hetero-junction semiconducting conjugating polymer, in which electronic structure and photophysical properties could be modulated by doping fluoride ion as mentioned above. Although many workers reported synthesis and properties of various silylene−π-electron copolymers in terms of potential applications, such as semiconductors, photo- and electroluminescent materials, and ceramic precursors, little attention has been paid to their ion-sensing ability so far. Recently, we synthesized well-defined poly(silylenephenyleneethynylenephenylene)s by a Pd/Cu-catalyzed AB-type coupling reaction and found that the combination of silylene and phenyleneethynylenephenylene units in the polymer is effectively able to form intramolecular charge transfer (ICT) in both ground and excited states.[4] This led to the idea that the photophysical properties of the σ−π hetero-junction polymer may be modulated by changing coordination number of the silicon atom, if through-space interaction between the π electron systems bridged by silylene moiety occurred.

On the basis of the idea, we tested fluoride ion-sensing abilities for three types of poly[dialkylsilylenephenyleneethynylenephenylene]s (dialkyl: **2** for *n*-dodecylmethyl; **5a** for di-*n*-hexyl; **5b** for di-*n*-hexyl-*co*-dimethyl) among many σ−π conjugating polymer candidates by means of colorimetric and fluorometric methods. Here we demonstrate that the present polymers significantly cause changes in UV−vis absorption and fluorescence in response to fluoride ion. These photophysical changes were easily observed by naked eye. As for **2**, a novel three-step titration curve of UV absorbance (or retention time of GPC) as a function of fluoride concentration was found. Polymer **2** was assumed to undergo coil-to-globule conformational transitions induced by anion charge in the presence of TBAF. Additionally, the complex forming abilities of the polymers with fluoride ion greatly depended on the nature of alkyl groups attached to silicon atom of the polymers.

Results and Discussion

Scheme 1 outlines the synthesis of three types of poly[dialkylsilylenephenylene-ethynylenephenylene]s (dialkyl: **2** for *n*-dodecylmethyl; **5a** for di-*n*-hexyl; **5b** for di-*n*-hexyl-*co*-dimethyl). Polymer **2** was obtained by the AB-type coupling reaction. Introduction of a long alkyl chain such as the *n*-dodecyl group to the silylene moiety afforded a good solubility for **2**. The molecular weight (M_w) was evaluated to be 7.6×10^3 ($M_w/M_n = 1.3$) by gel permeation chromatography (GPC). Also, polymers **5a** and **5b**, containing two *n*-hexyl groups on silicon,

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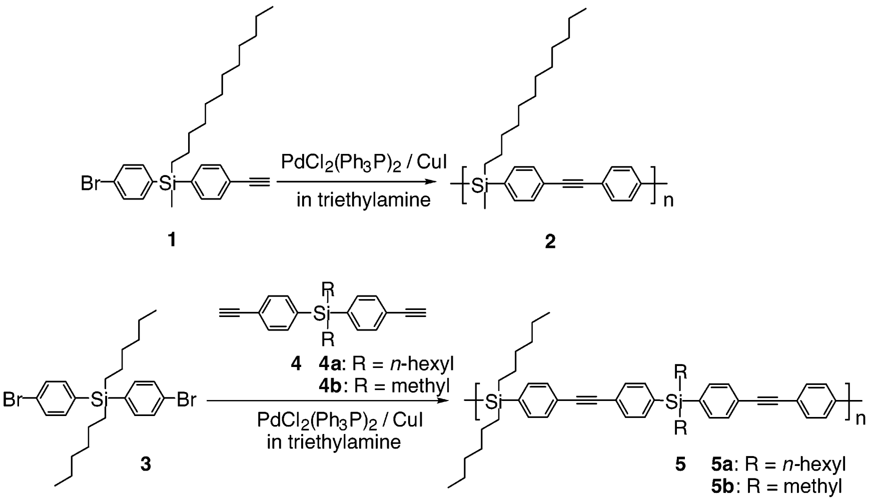
Scheme 1. Synthesis of Poly(silylenephenyleneethynylenephenylene)s (2 and 5) from the AB- and AA−BB-type Coupling Reactions



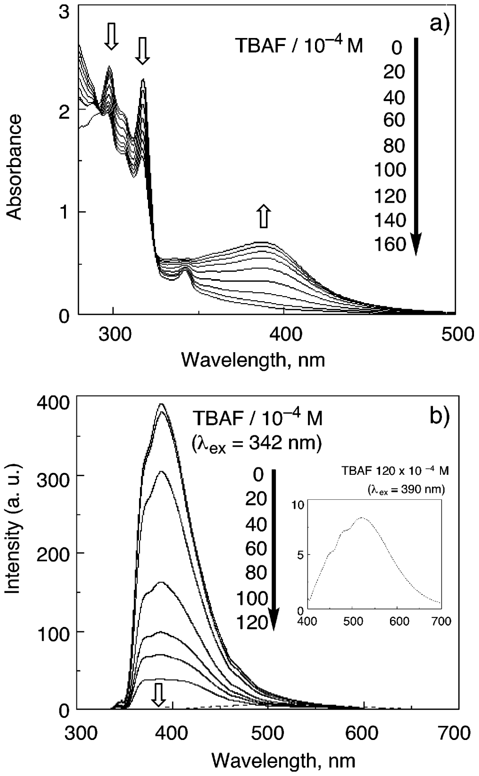


Figure 1. Variation in (a) UV−vis and (b) emission spectra of **2** upon addition of TBAF ($c = 1.0 \times 10^{-4}$ M, at 25 °C in THF).

were synthesized by the AA−BB-type coupling reaction to compare the affinities toward fluoride ion. Polymers **5a** and **5b** gave somewhat higher molecular weights (**5a**, $M_w = 27 \times 10^3$, $M_w/M_n = 2.4$; **5b**, $M_w = 8.7 \times 10^3$, $M_w/M_n = 2.1$) compared to **2**. This is because **5a** and **5b** have better solubility due to the two *n*-hexyl groups than **2**.

Figure 1a shows the change in UV−vis absorption of **2** by adding TBAF as a fluoride ion source. As the amount of TBAF increases, $\pi-\pi^*$ absorption bands at 298 and 317 nm of phenyleneethynylenephenylene moiety decreases, while an intense absorption band characteristic of ICT newly appears at 390 nm in place of a weak original ICT absorption band at 342 nm. This significant red shift of ICT absorption band is explicable

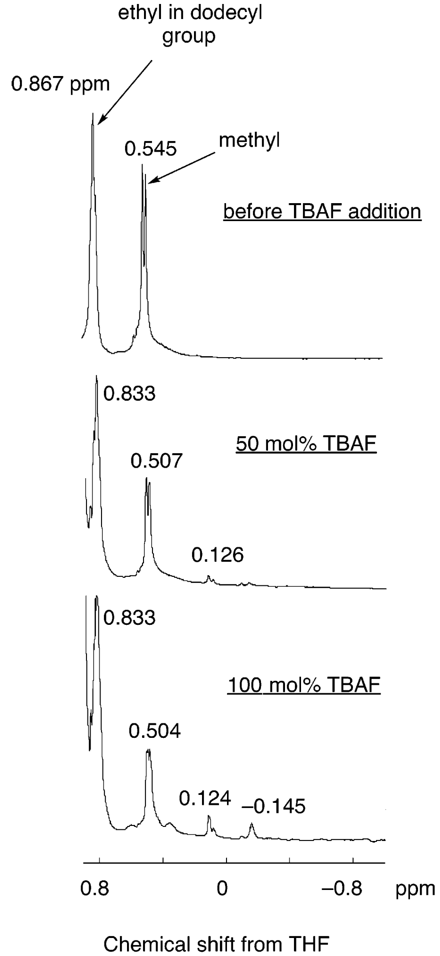
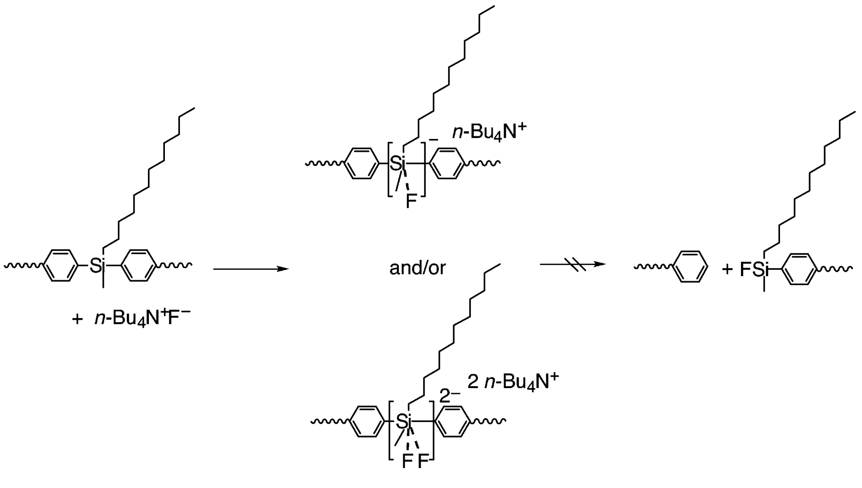


Figure 2. Variation of ^{1}H NMR spectra of **2** upon addition of TBAF ($c = 4.5 \times 10^{-2}$ M, at 25 °C in THF-d_8).

in terms of the idea that dynamic coordinative interaction between fluoride ion and silicon atom in the polymer chain leads to a more polar ground state of the polymer.

^{1}H NMR study on TBAF dependency of **2** may give a more definitive proof for the existence of the new ICT complexes, as shown in Figure 2. As the amount of TBAF increases, the proton signal at 0.545 ppm due to the methyl group gradually decreases compared to that

Scheme 2. Proposed Hypercoordinate Structures Induced by a Dynamic Interaction between the Silicon Atom and Fluoride Ion



for the ethyl protons at 0.867 ppm, while new peaks around +0.12 and −0.14 ppm appear, and all alkyl and aromatic peaks slightly shift to upfiled by about 0.04 ppm. The new upfield peaks may be attributed to hyper- (e.g., penta- and hexa-) coordinate structures on the silylene moiety, because hypercoordinate silicates are more electron-rich and shielded than the corresponding tetracoordinate silanes, indicating the higher electron-density within the same polymer chain after the addition of TBAF. However, no methyl protons due to silyl fluoride, which may come from decomposition of Si−aryl bond, were found.

Since the ICT absorption band shifted to longer wavelength by ca. 40 nm after the addition of TBAF, dramatic change in color from almost colorless to orange was recognized by naked eye. The schematic chemical reaction between **2** and TBAF is shown in Scheme 2.

Figure 1b displays variation in fluorescence spectra of **2** with TBAF concentration. When **2** is excited at the original ICT absorption wavelength of 342 nm, the intensity of fluorescence at 393 nm decreased with increasing the TBAF concentration. Furthermore, when **2** is excited at the new ICT absorption wavelength of 390 nm after the addition of 120-fold excess TBAF, a weak and broad fluorescence band (see, the inset of Figure 1b) newly appears at 521 nm with a large Stokes shift. The new ICT excited state is thought to be induced by dynamic coordinative interaction between fluoride and silicon atom of the polymer chain. In accordance with the fluorescence spectra, **2** emitted indigo-blue light when excited at 342 nm before the addition of TBAF, while emitting weak yellowish green light when excited at 390 nm after the addition of 120-fold excess TBAF.

Figure 3 illustrates the unique three-step relationship between UV absorbance of **2** and fluoride concentration: The first step indicates a moderate slope at less than 25-fold excess TBAF, the second step shows a steep change in the range from 25 to 100-fold concentration, and the third step turns to a gentle slope at more than 100-fold excess TBAF. Because polyelectrolyte is known to undergo coil-to-globule change with an increase in the degree of ionization,[5] **2** with fluoride ion may undergo such a conformational transition accompanied by a change of hydrodynamic volume in solution.

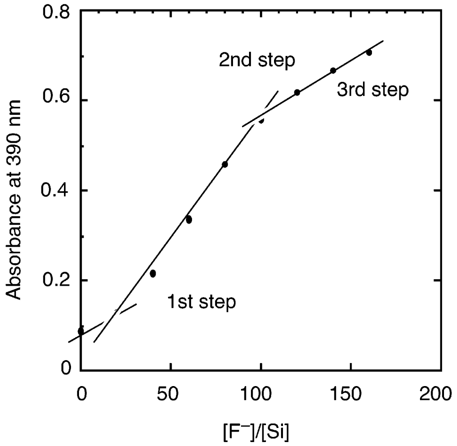


Figure 3. Plot for fluoride complexation with **2** ($c = 1.0 \times 10^{-4}$ M, at 25 °C in THF).

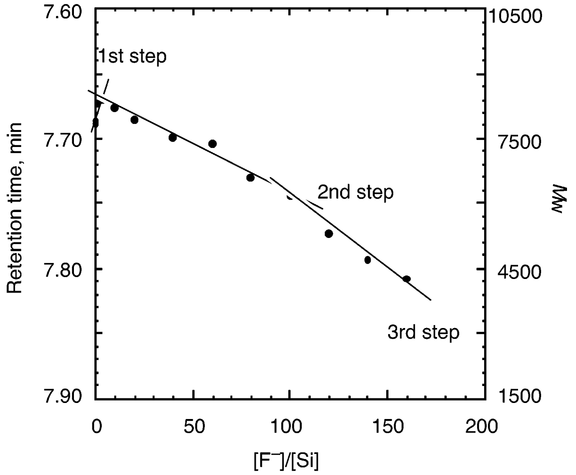


Figure 4. Plot of retention time vs TBAF concentration in **2** solution ($c = 1.73 \times 10^{-3}$ M, at 40 °C in THF). The corresponding molecular weight was roughly estimated from a calibration with polystyrene standards.

To further support this idea, we tested an apparent retention time of **2** in the absence and presence of TBAF by the GPC method. Figure 4 shows the unique change in the apparent retention time in GPC of **2** as a function of TBAF concentration. As expected, **2** seems to behave like a polyelectrolyte in the presence of fluoride ion. The apparent retention time shifted to a shorter retention time in the initial lower TBAF concentration but shifted to a longer time at more than 20-fold excess TBAF.

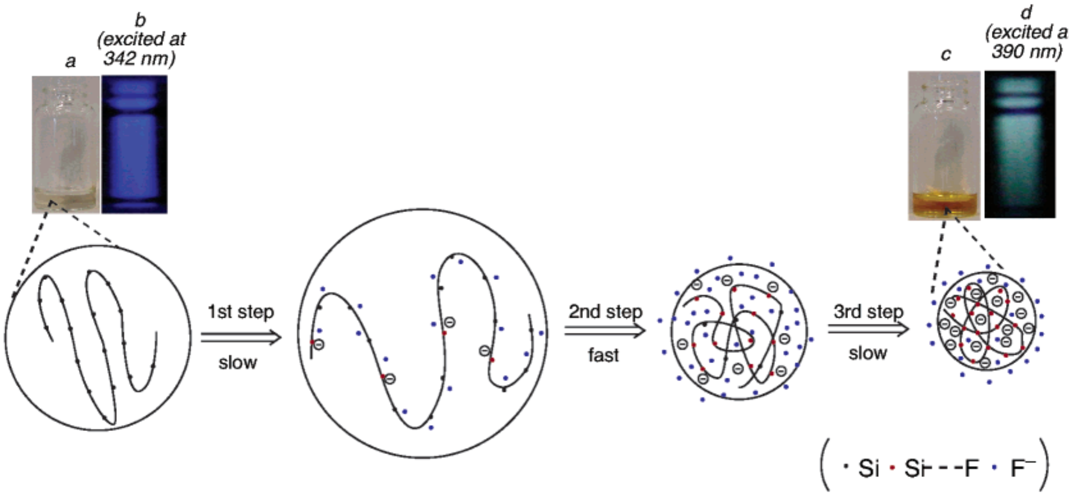


Figure 5. Proposed schematic models of **2** in the three steps: first step: global shape expansion, second step: expanded coil-to-shrunk coil change, and third step: shrunk coil-to-globule change (the circle signifies hydrodynamic volume in each step). The pictures show the actual changes in color (a → c) and fluorescence (b → d) (a and b, **2**; c and d, **2** + TBAF in THF).

These results led to the idea that the three-step relationship results from certain critical conformational changes: first step, global shape expansion due to charge repulsion within the polymer chain; second step, subsequent rapid expanded coil-to-shrunk coil change; and third step, slow shrunk coil-to-globule change. The proposed anion charge-driven conformational transition is schematically shown in Figure 5.

In synthetic aromatic silicon chemistry, rate-enhanced electrophilic desilylation was reported.[6] Actually, some arylsilane compounds are easily decomposed by a specific fluoride ion source. The UV−vis spectra of **2**, however, clearly exhibited the isosbestic points at 293 and 325 nm, as shown in Figure 1a. Noteworthily, the UV−vis and fluorescence spectra of **2** after addition of TBAF were completely recovered to the original spectra by washing with water. Becasue the TBAF/THF system is not so effective for desilylation of arylsilanes,[7] **2** may afford an air-stable polymer complex with fluoride ion without any significant decomposition. This may be uniqueness of the $\sigma-\pi$ conjugating polymer, when compared to silicon-containing π-electron molecular systems.

Presumably, the methyl group on silicon atom is responsible for the acceptance of fluoride ion, and long alkyl groups are responsible for protection of the silicon atom from the fluoride ion attack. Now we assume that the fluoride ion attack toward silicon of the polymer chain might be influenced by the alkyl group size. This is because **5b**, containing the dimethylsilylene moiety, showed the same tendency as **2**, whereas no changes in both the UV−vis and fluorescence spectra were observed for **5a** with no methyl groups even after addition of more than a 160-fold excess of TBAF.

In addition, when other halide ion sources such as Cl^-, Br^-, and I^- n-Bu_4N^+ salts were added to **2** instead of TBAF, no changes in both UV−vis and fluorescence spectra were observed. This indicates that the polymer **2** possesses a high selectivity toward fluoride ion rather than the competing anions.

Conclusion

The photophysical properties of **2**, which are related to intramolecular charge transfer, significantly changed upon addition of fluoride ion. Indeed, dramatic changes in UV−vis absorption and fluorescence occurred upon addition of TBAF. A unique three-step linear relationship between UV absorbance (or retention time in GPC) of **2** and fluoride concentration was obtained. This relationship indicated anion charge-driven conformational transition (coil-to-globule change) of **2** in the presence of TBAF. The fluoride complex forming abilities of the present polymers were greatly dependent on the nature of the alkyl group attached to the silicon atom. The present work may be the first demonstration of fluoride ion sensing ability based on $\sigma-\pi$ conjugated organosilicon polymers, and our results should provide a new design concept for new silicon-containing conjugating polymers directed toward highly selective and highly sensitive anion recognition materials.

Experimental Section

Synthesis of Monomers. 4-[(4-Bromophenyl)dodecylmethylsilyl]phenylacetylene (1). Compound **1** was synthesized by modifying the literature method,[4] and dichlorododecylmethylsilane was used as a starting material. The data were as follows. Yield: 50%, colorless liquid. IR (KBr): 3303, 2955, 2923, 2853, 1253, 1100, 823 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.58−7.20 (m, 8H, aromatic), 3.10 (s, 1H, ethynyl), 1.58−0.88 (m, 25H, dodecyl), 0.51 (s, 3H, methyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 138.2, 136.0, 134.2, 131.3, 131.0, 124.1, 122.8, 83.6, 77.8, 33.5, 31.9, 29.5, 29.3, 29.1, 23.6, 22.7, 14.1, 13.8 ppm. Anal. Calcd for $BrC_{27}H_{37}Si$: C, 69.06; H, 7.94. Found: C, 69.16; H, 7.98.

Bis[4-bromophenyl]dihexylsilane (3). The compound **3** was synthesized by modifying the literature method,[4] and dichlorodi-n-hexylsilane was used as a starting material. The data were as follows. Yield: 64%, colorless liquid. ^{1}H NMR (CDCl$_3$, δ): 7.54−7.26 (m, 8H, aromatic), 1.45−0.75 (m, 26H, hexyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 136.3, 135.0, 131.0, 124.1, 33.3, 31.4, 23.5, 22.6, 14.1, 12.3 ppm.

Bis[4-ethynylphenyl]dihexylsilane (4a). A 100 mL round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. Triethylamine (500 mL), $(Ph_3P)_2PdCl_2$ (40 mg, 40 μmol), CuI (100 mg, 0.53 mmol), PPh$_3$ (100 mg, 0.35 mmol), trimethylsilylacetylene (1.85 g, 18.8 mmol), and **3** (4.0 g, 7.84 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. 100 mL), THF (ca. 100 mL), and NaOH (ca. 0.5 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. After diethyl ether was evaporated, the crude product was purified by flash column chromatography (eluent, hexane) to give the desired product (yield 0.6 g, 22%) as colorless liquid. ^{1}H NMR (CDCl$_3$, δ): 7.44 (s, 8H, aromatic), 3.10 (s, 1H, ethynyl), and 1.48−0.76 (m, 26H, hexyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 137.5, 134.6, 131.2, 122.8, 83.7, 77.8, 33.3, 31.4, 23.5, 22.6, 14.1, 12.2 ppm.

Bis[4-ethynylphenyl]dimethylsilane (4b). The compound **4b** was prepared using bis[4-bromophenyl]dimethylsilane, similar to **4a**. The data were as follows. Yield: 25%, white solid. ^{1}H NMR (CDCl$_3$, δ): 7.46 (s, 8H, aromatic), 3.09 (s, 1H, ethynyl), and 0.55 (s, 6H, methyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 138.9, 134.0, 131.3, 122.9, 83.6, 77.8, 29.7 ppm.

Synthesis of Polymers. Poly[(*n*-dodecylmethyl)silylenephenyleneethynylenephenylene] (2). Triethylamine (10 mL), (Ph$_3$P)$_2$PdCl$_2$ (21.0 mg, 30 μmol), CuI (5.7 mg, 30 μmol), and **1** (469.6 mg, 1.0 mmol) were placed in the flask, and the mixture was stirred under reflux for 2 days. After the resulting solution was filtered, the solution was concentrated and poured into a large amount of acetone under stirring to precipitate the polymer formed. The data were as follows. Yield: 89%, brown gummy solid. IR (KBr): 2955, 2923, 2851, 1252, 1105, 823 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.62−7.29 (br, 8H, aromatic), 1.48−0.79 (br, 25H, dodecyl), 0.53 (br, 3H, methyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 136.0, 134.3, 130.7, 124.1, 90.3, 33.6, 31.9, 29.6, 29.3, 23.7, 22.7, 14.1, 13.9 ppm. Anal. Calcd for C$_{27}$H$_{37}$Si: C, 83.44; H, 9.34. Found: C, 76.13; H, 8.53. The significant difference between the calculated and found values may be ascribed to the fact that organosilicon polymers containing unsaturated functional groups such as ethynylene and vinylene groups tend to cross-link at a relatively low temperature and be thermally converted to silicon carbides in high char yield.[4,8]

Poly[dialkylsilylenephenyleneethynylenephenylene]s (Dialkyl: 5a for Di-*n*-hexyl; 5b for Di-*n*-hexyl-*co*-dimethyl). Triethylamine (10 mL), (Ph$_3$P)$_2$PdCl$_2$ (21.0 mg, 30 μmol), CuI (5.7 mg, 30 μmol), **3** (255 mg, 0.5 mmol), and **4** (**4a**, 130 mg, 0.5 mmol; **4b**, 200 mg, 0.5 mmol) were placed in the flask, and the mixture was stirred in reflux for 2 days. After the resulting solution was filtered, the solution was concentrated and poured into a large amount of methanol under stirring to precipitate the formed polymer. The data were as follows. **5a**. Yield: 95%, brown solid. ^{1}H NMR (CDCl$_3$, δ): 7.77−7.13 (br, 8H, aromatic), 1.81−0.56 (br, 26H, hexyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 137.0, 134.7, 130.8, 123.9, 90.2, 33.3, 31.4, 23.6, 22.6, 14.1, 12.3 ppm. **5b**. Yield: 90%, light brown solid. ^{1}H NMR (CDCl$_3$, δ): 7.79−7.03 (br, 8H, aromatic), 1.92−0.10 (br, 32H, alkyl) ppm. ^{13}C NMR (CDCl$_3$, δ): 137.0, 136.4, 134.7, 134.0, 131.6, 130.8, 129.0, 128.4, 90.1, 33.2, 23.4, 22.4, 14.2, 12.3 ppm.

Measurements. ^{1}H (400 MHz) NMR spectra were measured in THF-d_8 solution at 25 °C on a JEOL EX-400 spectrometer. Chemical shift was referred to the solvent (3.57 and 1.72 ppm for THF). The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers were evaluated using gel permeation chromatography (Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column, and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. The retention time of the polymer was measured on the same chromatography instrument. UV−vis, emission, and IR spectra were measured on JASCO UV-550, JASCO FP-6500, and HORIBA FT-730 spectrometers, respectively.

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