8978 *Macromolecules* **2004,** *37,* 8978−8983

Ladder Bis-Silicon-Bridged Stilbenes as a New Building Unit for Fluorescent π-Conjugated Polymers

Caihong Xu,[†] Hiroshi Yamada,[†] Atsushi Wakamiya,[†] Shigehiro Yamaguchi,[*,†] and Kohei Tamao[‡]

Department of Chemistry, Graduate School of Science, Nagoya University, and PRESTO, Japan Science and Technology Agency (JST), Chikusa, Nagoya 464-8602, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

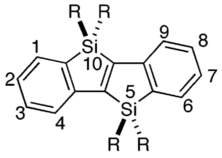
Received July 3, 2004; Revised Manuscript Received August 8, 2004

ABSTRACT: π-Conjugated polymers containing the bis-silicon-bridged stilbene (5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene) skeleton in the main chain have been synthesized. Our synthesis uses 3,8-dimethoxy derivatives (**2**) and 3,8-difluoro derivatives (**3**) of the bis-silicon-bridged stilbene as the key precursors. Thus, their regioselective ortho-metalation reactions with appropriate bases (*sec*-butyllithium for **2** and $\mathrm{Li^{t}Bu_2ZnTMP}$ for **3**) followed by quenching with electrophiles afford various 2,7-difunctionalized bis-silicon-bridged stilbenes. By using the 2,7-difunctionalized derivatives as starting materials, a series of π-conjugated polymers, including homopolymers of the bis-silicon-bridged stilbene skeleton and copolymers between the bis-silicon-bridged stilbene unit and other types of monomer units, such as bithiophene and diethynylbenzene, have been synthesized by cross-coupling methodologies. While all the homopolymers of the bis-silicon-bridged stilbene skeleton exhibit an intense blue to greenish-blue emission, the copolymers with the bithiophene and diethynylbenzene units show green and orange emissions, respectively, suggesting easy tuning of the emission colors over a wide range.

Introduction

The photophysical and electrical properties of π-conjugated polymeric materials highly depend on the nature of their building units. One valuable class of building units is the ladder-type π-conjugated framework,[1,2] wherein the enhanced π-conjugation by its annelated coplanar structure leads to a set of desirable properties such as intense photoluminescence[3] and high charge carrier mobility.[4] Much effort has been devoted to exploring new ladder-type building units in a broad spectrum of research fields including organic light-emitting diodes,[5−8] thin film transistors,[9,10] stimulated polymer lasers,[11] molecular-scale devices,[12] and sensory materials.[13] As a new promising entry, we focused our attention on a bis-silicon-bridged stilbene skeleton, i.e., 5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene **1** (Chart 1). In this skeleton, the silicon bridges would not only stiffen the *trans*-stilbene structure in a coplanar fashion but also contribute to the electronic structure through an orbital interaction. Thus, $\sigma^*-\pi^*$ conjugation between the σ^* oribital of two exocyclic σ-bonds on the silicon atoms and the π^* orbital of the stilbene framework decreases the LUMO energy level compared to that of the parent stilbene.[14] The first synthesis of compound **1** (R = Me) was achieved by Barton and co-workers on the basis of the thermal or photo rearrangement of 5,6-disiladibenzo[*c,g*]cyclooctynes.[15] They also synthesized some attractive polymeric systems bearing this skeleton as a pendant group.[16] We independently have recently reported the efficient synthesis of the bis-silicon-bridged stilbenes based on the newly developed intramolecular reductive double cyclization of bis(*o*-silylphenyl)acetylenes.[17] The next step of our research is the incorporation of this skeleton into a π-conjugated main chain and evaluation of its potential as a new building unit. Herein reported are the functionalization of the bis-silicon-bridged stilbenes, synthesis of a series of new π-conjugated polymers, and elucidation of their fundamental photophysical properties.

Chart 1. Structure of Bis-Silicon-Bridged Stilbene



1

Results and Discussion

Monomer Designs and Synthesis. To employ the bis-silicon-bridged stilbene as a building unit for π-conjugated polymers, it is essential to introduce certain functional groups, such as halogens and metal functionalities required for further polycondensation using the transition-metal-catalyzed coupling methodologies, onto the 2,7-positions of the skeleton. As key precursors for the regioselective functionalization, two types of molecules, the 3,8-dimethoxy derivative **2** and the 3,8-difluoro derivative **3**, were designed on the basis of the following ideas. First, the incorporation of the methoxy and fluorine ortho-directing substituents would facilitate the functionalization through the ortho-metalation reactions.[18] Second, these two types of molecules would serve as an electron-donating building unit and electron-accepting building unit, respectively. In fact, the preliminary molecular orbital calculations suggest the electron-donating nature (high-lying HOMO) of **2** and the electron-accepting nature (low-lying LUMO) of **3**, as shown in Figure 1.[19] We envisioned that the use of these building units with the contrasting electronic nature would lead to a series of new polymeric systems with varied electronic structures.

[†] Nagoya University.

[‡] Kyoto University.

[*] To whom correspondence should be addressed. E-mail: yamaguchi@chem.nagoya-u.ac.jp.

10.1021/ma0486546 CCC: $27.50

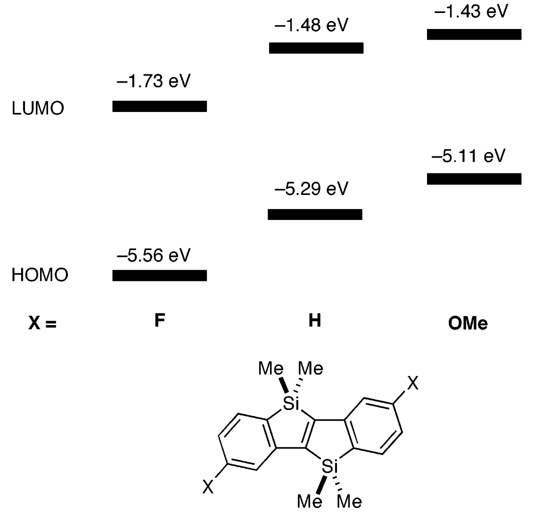
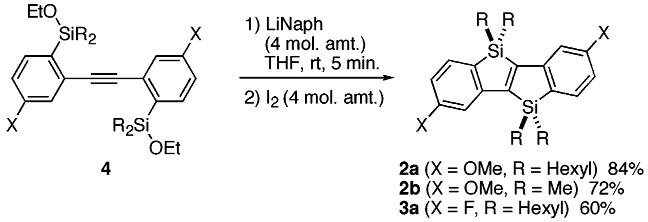
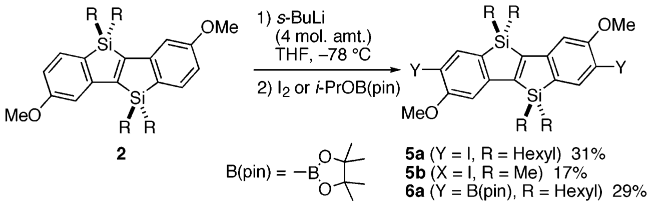


Figure 1. Kohn–Sham HOMO and LUMO energy levels of the bis-silicon-bridged stilbenes calculated at the B3LYP/6-31G(d) level of theory.

Scheme 1



Scheme 2

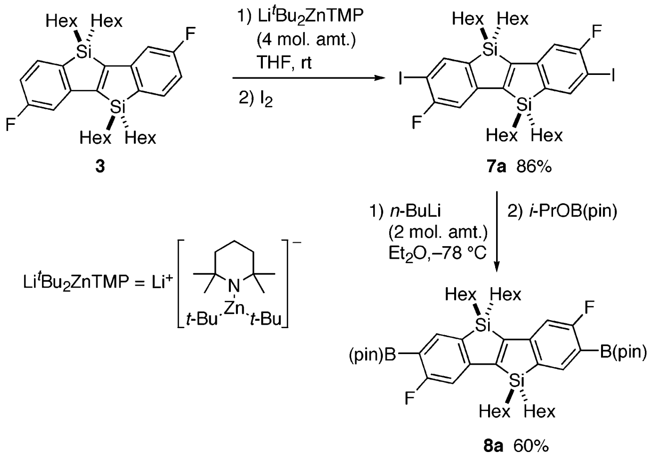


Both compounds **2** and **3** were prepared using our recently reported intramolecular reductive cyclization, as shown in Scheme 1. Thus, the reaction of bis(*o*-silylphenyl)acetylenes **4** with 4 mol amounts of lithium naphthalenide followed by quenching with iodine gave the desired cyclized product in 60–84% yields. These results well demonstrate the tolerance of functional groups such as alkoxy and fluorine in the present cyclization.

Functionalization. We examined the ortho-metalation reactions of compounds **2** and **3**. After the screening of several bases, we found that the ortho-metalation of the 3,8-dimethoxy derivatives **2** with *sec*-butyllithium cleanly proceeded to produce 2,7-dilithiated intermediates, which were further transformed into several functionalized derivatives, such as diiodides **5** and diboronic ester **6** in moderate yields, by treatment with appropriate electrophiles, i.e., iodine and ^{i}PrOB(pin) (pin = pinacolato), respectively, as shown in Scheme 2.

In the case of the 3,8-difluoro derivative **3**, while the use of *sec*-butyllithium or *tert*-butyllithium only afforded a complex mixture and no metalation occurred with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) or analogous magnesium bisamide Mg(TMP)$_2$, a zincate complex Li^{t}Bu$_2$ZnTMP[20] was found to be very effective for the ortho-metalation. Thus, the reaction of **3** with Li^{t}Bu$_2$ZnTMP, prepared from LiTMP and di-*tert*-butylzinc, underwent the ortho-metalation to give a dizincate intermediate, which was further transformed into the diiodide **7** by treatment with iodine in 86% yield. Notably, this functionalization was far more efficient compared with the case of **2**. However, an attempt to synthesize the diboronic ester **8** by direct treatment of the dizincate intermediate with ^{i}PrOB(pin) resulted in the decomposition of the target molecule during workup, the reason for which is unclear at this time. Therefore, we adopted an alternative way to form compound **8**. Thus, the halogen–lithium exchange of the diiodide **7** with *n*-butyllithium followed by the reaction with ^{i}PrOB(pin) successfully gave **8** in 60% yield.

Scheme 3

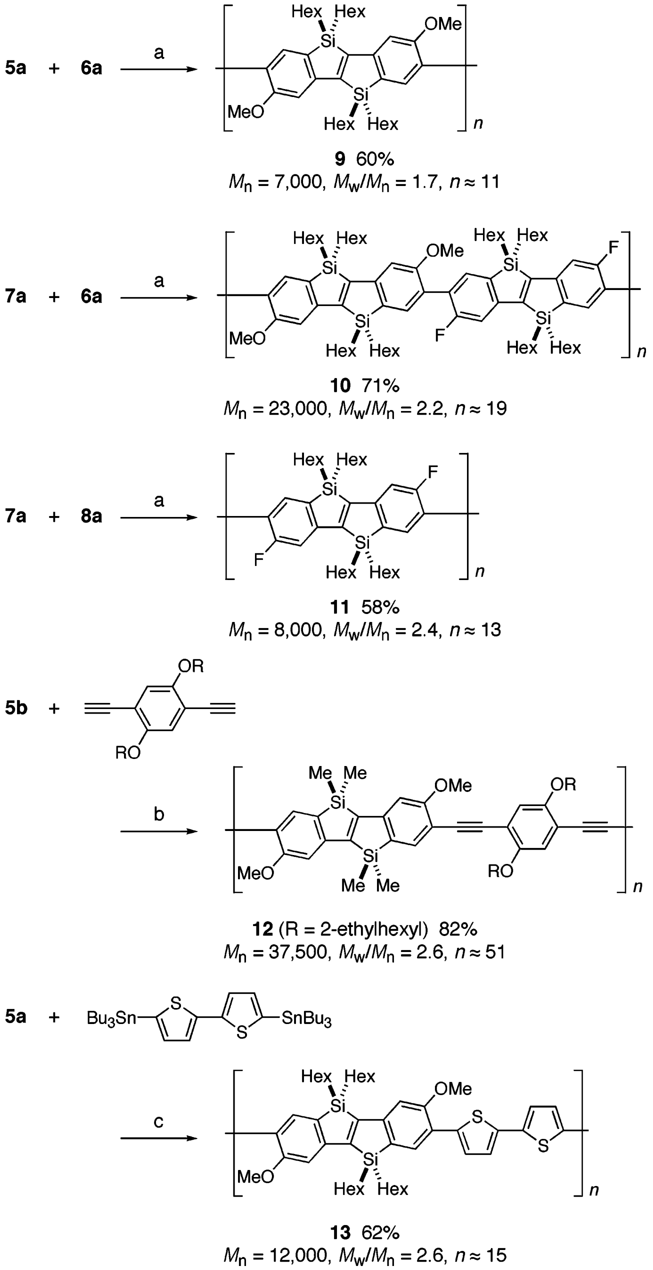


Polymer Synthesis. With the difunctionalized derivatives in hand, we next carried out the synthesis of a series of π-conjugated polymers based on the various cross-coupling methodologies shown in Scheme 4. Thus, the Suzuki–Miyaura coupling of the diiodide **5a** with the diboronic ester **6a** in the presence of a Pd(dba)$_2$/PPh$_3$ catalyst system and Cs$_2$CO$_3$ as a base in dioxane[21] produced the homopolymer **9** in 60% yield as a yellow powder. Similarly, the alternating copolymer **10** consisting of dimethoxy- and difluoro-substituted bis-silicon-bridged stilbene units was prepared in 71% yield by the coupling of the diiodide **7a** and the diboronic easter **6a**, and the homopolymer **11** was obatined as a yellow powder in 58% yield by the coupling of the difluoro derivatives **7a** and **8a**.

We also synthesized several alternating copolymers with other types of monomer units. Thus, the Sonogashira coupling of **5b** with 2,5-bis(2-ethylhexyloxy)-1,4-diethynylbenzene using a Pd(PPh$_3$)$_4$/CuI catalyst system afforded the corresponding copolymer **12** as a yellow powder in 82% yield. In addition, the Migita–Kosugi–Stille coupling of **5a** with 5,5′-bis(stannyl)bithiophene gave the copolymer **13** as a red powder in 62% yield.

All the produced polymers are air-stable and soluble to common organic solvents such as THF and chloroform due to the flexible alkyl chains on the silicon atoms or comonomer units. The number-averaged molecular weights (M_n) for the polymers, estimated by means of the GPC measurements with polystyrene standards, are in the range of 7000–37 500, and the degrees of polymerization (DP) vary from ca. 11 to 51. Although the molecular weights are not sufficiently high in some cases, these examples clearly demonstrate that the difunctionalized bis-silicon-bridged stilbene derivatives **5**–**8** serve as versatile key precursors for various types of π-conjugated polymers.

Scheme 4[a]



[a] Reagents and conditions: a, $Pd(dba)_2$ (0.02 mol amt), PPh_3 (0.1 mol amt), Cs_2CO_3, 1,4-dioxane or 1/1 toluene/H_2O, reflux; b, $Pd(PPh_3)_4$ (0.1 mol amt), CuI (0.2 mol amt), 3/1 toluene/*i*-Pr_2NH, 60 °C; c, $Pd_2(dba)_3$ (0.05 mol amt), P(2-furyl)$_3$ (0.2 mol amt), THF, reflux.

Table 1. Photophysical Properties of Bis-Silicon-Bridged Stilbene-Containing π-Conjugated Polymers 9−13

	UV−vis absorption[a]		fluorescence[a]	
polymer	λ_{max}/nm	log ϵ[b]	λ_{max}/nm[c]	Φ_F[d]
9	420	4.24	476	0.36
10	418	4.56	467	0.51
11	422	4.59	454	0.63
12	482	3.65	506	0.15
13	494	4.75	547	0.025

[a] In THF. [b] Per monomer unit. [c] Excited at the absorption maximum wavelengths. [d] Determined with perylene as a standard.

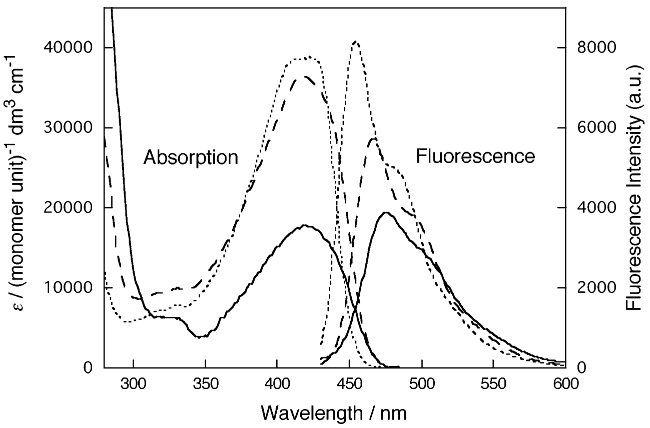


Figure 2. UV−vis absorption and fluorescence spectra of polymers **9**, **10**, and **11** in THF: solid line, polymer **9**; dashed line, polymer **10**; dotted line, polymer **11**.

Table 2. Fluorescence Lifetimes and Related Parameters for Polymers 9−11

polymer	τ_s/ns[a]	k_r/10^8 s^{-1} [b]	k_{nr}/10^8 s^{-1} [b]
9	1.61	2.2	4.0
10	1.27	4.0	3.9
11	1.05	6.0	3.5

[a] Fluorescence lifetimes measured in THF upon excitation of laser at 405 nm. [b] The radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) are calculated by the following equations: $k_r = \Phi_F/\tau_s$, $k_{nr} = (1 - \Phi_F)/\tau_s$.

Photophysical Properties. UV−vis absorption and fluorescence data for the produced polymers **9**−**13** in THF solutions are summarized in Table 1. In this section, the results are discussed with respect to the following two points, i.e., the substituent effect in a series of bis-silicon-bridged stilbene polymers **9**−**11** and the varied emission colors in a series of polymers **9**, **12**, and **13**.

All the polymers **9**−**11**, consisting only of the bis-silicon-bridged stilbene skeleton, show intense blue to greenish-blue fluorescence. To observe the substituent effect of the methoxy and fluorine substituents in these polymers, the UV−vis absorption and fluorescence spectra of **9**−**11** are shown in Figure 2. There are a couple of notable points: (1) All the polymers have essentially the same absorption maxima around 420 nm. In the fluorescence spectra, however, the emission maximum wavelength shifts to a shorter wavelength by about 20 nm as the content of the 3,8-difluoro-substituted stilbene units increases. As a consequence, the polymer **11** has the smallest Stokes shift among these three polymers. (2) The quantum yields (Φ_F) of the polymers tend to increase as the ratio of the fluoro-substituted stilbene units increases from **9** to **10** to **11**. The fluorescence lifetime (τ_s) measurements indicate that this is mainly due to the faster radiative decay process with an increase in the fluoro-substituted stilbene content, as shown by the data listed in Table 2. Thus, their radiative rate constants (k_r) increase from **9** to **11** by a factor of 2.7, while the nonradiative rate constants (k_{nr}) remain nearly constant. These facts suggest that as the content of the 3,8-difluorostilbene units increases, the structural relaxation in the excited state is reduced due to the lower steric requirements of the fluorine substituent.

Figure 3 shows the fluorescence spectra of polymers **9**, **12**, and **13**. The fluorescence properties of these copolymers are highly dependent on the nature of the combined comonomer units. Thus, copolymer **12** containing 1,4-diethynylbenzene units has its emission band with the maximum wavelength at 506 nm, while copolymer **13** with bithiophene comonomer units has its

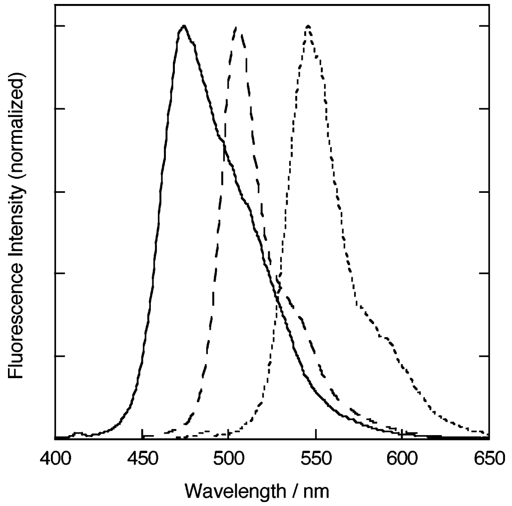


Figure 3. Fluorescence spectra of polymers **9**, **12**, and **13** in THF: solid line, polymer **9**; dashed line, polymer **12**; dotted line, polymer **13**.

emission maximum at 547 nm. These values are longer than that of homopolymer **9** by 30 and 71 nm, respectively, suggesting possible emission color tuning over a wide range by choosing the appropriate comonomer units. Actually, the emission color of **12** is green and that of **13** is orange, while homopolymer **9** shows a greenish-blue emission. For these two copolymers, another notable feature is the remarkably narrow band shapes of the emission. The bandwidths (fwhm) are only 34 nm for **12** and 26 nm for **13**. These features may be beneficial in terms of the emission color purity and thus enhance the potential utilities of the present polymers.

Conclusion

In summary, we have prepared a series of π-conjugated homopolymers and copolymers containing the bis-silicon-bridged stilbene skeleton and have determined their photophysical properties from the viewpoints of the substituent effects as well as the possible emission color tuning. This work demonstrates the versatile utility of the bis-silicon-bridged stilbene as a new building unit for the fluorescent π-conjugated systems. In particular, the crucial step of the present synthesis is the regioselective functionalization of the bis-silicon-bridged stilbene skeleton based on the ortho-metalation reaction. We have shown that not only the methoxy group but also fluorine can be used as the ortho-directing group for the present purpose. The resulting electron-donating 3,8-dimethoxy-substituted and electron-accepting 3,8-difluoro-substituted bis-silicon-bridged stilbene derivatives would serve as a pair of key precursors with contrasting electronic nature for the future development of new materials for organic (opto)electronics.

Experimental Section

Melting points (mp) were measured on a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were measured with a Varian Mercury 300 spectrometer, a JEOL EX-270 spectrometer, or a JEOL A-400 spectrometer in $CDCl_3$. UV−vis absorption spectra and fluorescence spectra measurements were performed at room temperature with a Shimadzu UV-3100PC spectrometer and a Perkin-Elmer LS50B spectrometer, respectively, in a degassed spectral grade THF. Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70−230 mesh, Merck). Recycle preparative gel permeation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with chloroform or toluene as an eluent. The molecular weights of polymers were estimated by the GPC analysis with polystyrene as a standard. 1,2-Bis(2-bromo-5-methoxyphenyl)acetylene and 1,2-bis(2-bromo-5-fluorophenyl)acetylene were prepared by the similar procedures as reported previously[17] and fully characterized by means of NMR spectroscopy and elemental analysis. All experiments were carried out under an argon or a nitrogen atmosphere.

1,2-Bis[2-(ethoxydihexylsilyl)-5-methoxyphenyl]acetylene (4a). To a solution of 1,2-bis(2-bromo-5-methoxyphenyl)-acetylene (10.5 g, 26.5 mmol) in Et_2O (350 mL) was added a hexane solution of *n*-BuLi (1.6 M, 36.6 mL, 58.6 mmol) dropwise at −35 °C. After stirring for 4 h at −30 to −25 °C, dihexyldichlorosilane (17.1 mL, 61.1 mmol) was added dropwise at −78 °C. The reaction mixture was stirred for 10 h at the same temperature and then was allowed to warm to room temperature. Ethanol (20 mL) and triethylamine (10 mL) were added, and the mixture was further stirred for 4.5 h. After filtration and concentration of the filtrate, the resulting mixture was passed through a silica gel column (hexane/EtOAc, 10/1, $R_f = 0.60$) and the obtained crude product was further purified by a preparative GPC with toluene as an eluent to give 16.6 g of **4a** (22.9 mmol) in 86% yield as a yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.78−0.82 (m, 12H), 1.00−1.06 (m, 8H), 1.19−1.32 (m, 38H), 3.77 (q, $J = 7.0$ Hz, 4H), 3.82 (s, 6H), 6.89 (dd, $J = 2.7, 8.1$ Hz, 2H), 7.12 (d, $J = 2.7$ Hz, 2H), 7.55 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.17, 14.31, 18.70, 22.66, 23.36, 31.60, 33.34, 55.05, 58.78, 92.57, 113.84, 117.08, 129.38, 130.43, 136.44, 160.03. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ 6.24. HRMS (EI): Calcd for $C_{44}H_{74}O_4Si_2$: 722.5126. Found: 722.5112.

1,2-Bis[2-(ethoxydimethylsilyl)-5-methoxyphenyl]acetylene (4b). To a solution of 1,2-bis(2-bromo-5-methoxyphenyl)-acetylene (5.50 g, 13.9 mmol) in Et_2O (280 mL) was added a hexane solution of *n*-BuLi (1.6 M, 18.6 mL, 29.8 mmol) dropwise at −35 °C. After stirring for 4 h at −30 to −25 °C, (*N,N*-diethylamino)dimethylchlorosilane (5.0 g, 30.2 mmol) was added dropwise at −25 °C. The reaction mixture was stirred for 12.5 h and was allowed to room temperature. Then, 3.7 mL of ethanol (63.4 mmol) and ammonium chloride (0.40 g, 7.5 mmol) were added to the mixture, followed by stirring for 23 h at room temperature. The mixture was filtered and concentrated and then purified by column chromatography on florisil (100−200 mesh, hexane/EtOAc, 5/1, $R_f = 0.56$) to give 5.85 g (13.2 mmol) of **4b** in 95% yield as a white solid: mp 69−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.48 (s, 12H), 1.22 (t, $J = 6.9$ Hz, 6H), 3.75 (q, $J = 6.9$ Hz, 4H), 3.82 (s, 6H), 6.90 (dd, $J = 2.4, 8.4$ Hz, 2H), 7.12 (d, $J = 2.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 0.72, 18.67, 55.15, 58.75, 92.73, 113.66, 117.38, 129.26, 131.60, 135.88, 160.21. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ 6.46. Anal. Calcd for $C_{24}H_{34}O_4Si_2$: C, 65.11; H, 7.74. Found: C, 65.37; H 7.79.

1,2-Bis[2-(ethoxydihexylsilyl)-5-fluorophenyl]acetylene (4c). This compound was prepared in 93% yield as a yellow brown oil essentially in the same manner as described for **4a** using 1,2-bis(2-bromo-5-fluorophenyl)acetylene as a starting material: ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.81 (t, $J = 6.9$ Hz, 12H), 0.99−1.05 (m, 8H), 1.21−1.36 (m, 32H), 3.78 (q, $J = 6.9$ Hz, 2H), 7.06 (dt, $J = 2.6, 8.3$ Hz, 2H), 7.25 (dd, $J = 2.6, 9.4$ Hz, 2H), 7.64 (dd, $J = 6.6, 8.3$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.55, 14.02, 18.50, 22.54, 23.17, 31.46, 33.14, 58.84, 92.52 (d, $^4J_{CF} = 3.7$ Hz), 115.14 (d, $^2J_{CF} = 19.5$ Hz), 118.78 (d, $^2J_{CF} = 22.0$ Hz), 129.62 (d, $^3J_{CF} = 8.5$ Hz), 135.47 (d, $^4J_{CF} = 3.7$ Hz), 137.24 (d, $^3J_{CF} = 7.3$ Hz), 162.32 (d, $^1J_{CF} = 248.9$ Hz). Anal. Calcd for $C_{42}H_{68}F_2O_2Si_2$: C, 72.15; H, 9.80. Found: C, 72.36; H, 9.93.

5,5,10,10-Tetrahexyl-3,8-dimethoxy-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (2a). A mixture of granular lithium (309 mg, 44.6 mmol) and naphthalene (5.72 g, 44.6 mmol) in THF (55 mL) was stirred at room temperature for 4 h. To the resulting solution of lithium naphthalenide was added a solution of **4a** (8.03 g, 11.1 mmol) in THF (50 mL) at room temperature. After stirred for 5 min, the reaction mixture was quenched with a THF solution of iodine (11.3 g, 44.5 mmol). A saturated $Na_2S_2O_3$ aqueous solution was then added, and the mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography with hexane ($R_f = 0.15$) as an eluent to give 5.89 g (9.30 mmol) of **2a** in 84% yield as a pale yellow viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, $J = 6.6$ Hz, 12H), 0.86−1.02 (m, 8H), 1.12−1.32 (m, 32H), 3.84 (s, 6H), 6.72 (dd, $J = 2.1$, 7.8 Hz, 2H), 6.84 (d, $J = 2.1$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.71, 14.14, 22.65, 24.15, 31.48, 33.10, 55.13, 110.16, 112.35, 129.85, 133.31, 152.28, 161.30, 165.04. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ 2.46. Anal. Calcd for $C_{40}H_{74}O_2Si_2$: C, 75.88; H, 10.19. Found: C, 75.61; H, 10.53.

3,8-Dimethoxyl-5,5,10,10-tetramethyl-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (2b). This compound was prepared essentially in the same manner as described for **2a** in 72% yield as colorless crystals: mp 215−217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.43 (s, 12H), 3.84 (s, 6H), 6.74 (dd, $J = 2.4$, 7.8 Hz, 2H), 6.85 (d, $J = 2.4$ Hz, 2H), 7.47 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ −3.14, 55.25, 110.21, 112.28, 131.19, 132.98, 151.30, 161.46, 164.79. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ −1.78. Anal. Calcd for $C_{20}H_{24}O_2Si_2$: C, 68.13; H, 6.86. Found: C, 67.97; H, 6.86.

3,8-Difluoro-5,5,10,10-tetrahexyl-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (3a). This compound was prepared essentially in the same manner as described for **2a** in 60% yield as colorless crystals: mp 67−68 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.79 (t, $J = 6.6$ Hz, 12H), 0.86−1.06 (m, 8H), 1.16−1.29 (m, 32H), 6.89 (ddd, $J = 2.3$, 7.9, 9.6 Hz, 2H), 6.95 (dd, $J = 2.3$, 9.9 Hz, 2H), 7.65 (dd, $J = 6.6$, 7.9 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.2, 14.0, 22.5, 23.9, 31.3, 32.9, 112.4 (d, $^2J_{CF} = 20.7$ Hz), 112.7 (d, $^2J_{CF} = 18.4$ Hz), 133.1 (d, $^3J_{CF} = 8.6$ Hz), 134.1 (d, $^4J_{CF} = 3.6$ Hz), 152.6 (d, $^3J_{CF} = 7.3$ Hz), 164.8 (d, $^1J_{CF} = 247$ Hz), 165.1 (d, $^4J_{CF} = 1.6$ Hz). Anal. Calcd for $C_{38}H_{58}F_2Si_2$: C, 74.94; H, 9.60. Found: C, 74.68; H, 9.65.

5,5,10,10-Tetrahexyl-2,7-diiodo-3,8-dimethoxy-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (5a). To a solution of **2a** (2.02 g, 3.19 mmol) in THF (65 mL) was added a cyclohexane/hexane solution of *s*-BuLi (0.97 M, 13.8 mL, 13.39 mmol) dropwise at −78 °C. After stirring for 8 h at −78 to −50 °C, a THF (10 mL) solution of iodine (3.40 g, 13.40 mmol) was added at −78 °C, and the mixture was allowed to warm to room temperature over 12 h with stirring. A saturated $Na_2S_2O_3$ aqueous solution was added, and the mixture was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was passed through a silica gel column with hexane ($R_f = 0.13$) as an eluent, followed by further purification by a preparative GPC (toluene) to give 0.88 g (1.00 mmol) of **5a** in 31% yield as a pale yellow solid: mp 76−78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0. 80 (t, $J = 6.6$ Hz, 12H), 0.82−1.0 (m, 8H), 1.12−1.37 (m, 32H), 3.91 (s, 6H), 6.75 (s, 2H), 7.84 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.54, 14.12, 22.62, 24.13, 31.45, 33.05, 56.10, 84.12, 108.81, 132.50, 142.59, 152.32, 159.41, 164.67. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ 3.63. Anal. Calcd for $C_{40}H_{62}I_2O_2Si_2$: C, 54.29; H, 7.06. Found: C, 54.43; H, 7.11.

5,5,10,10-Tetramethyl-2,7-diiodo-3,8-dimethoxy-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (5b). This compound was prepared essentially in the same manner as described for **5a** in 17% yield as a pale yellow solid: mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.44 (s, 12H), 3.92 (s, 6H), 6.72 (s, 2H), 7.89 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ −3.24, 56.18, 84.39, 108.30, 133.70, 142.39, 151.31, 159.59, 164.34. ^{13}Si NMR (53.5 MHz, $CDCl_3$): δ −0.78. HRMS (EI): Calcd for $C_{20}H_{22}I_2O_2Si_2$: 603.9248. Found: 603.9267.

5,5,10,10-Tetrahexyl-3,8-dimethoxy-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxabororan-2-yl)-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (6a). To a solution of **2a** (1.99 g, 3.14 mmol) in THF (60 mL) was added a cyclohexane/hexane solution of *s*-BuLi (0.97 M, 13.6 mL, 13.19 mmol) dropwise at −78 °C. After stirring for 8 h at −78 to −50 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.64 g, 14.2 mmol) was added at −78 °C, and the mixture was allowed to warm to room temperature over 12 h with stirring. The mixture was poured into water and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was passed through a short silica gel column with a 1/1 hexane/chloroform mixed solvent as an eluent, followed by the further purification by a preparative GPC (toluene) to give 0.81 g (0.91 mmol) of **6a** in 29% yield as a pale yellow solid: mp 160−162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, $J = 6.6$ Hz, 12H), 0.90−1.00 (m, 8H), 1.10−1.42 (m, 32H), 3.87 (s, 6H), 6.81 (s, 2H), 7.80 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.78, 14.17, 22.63, 24.20, 24.92, 31.50, 33.13, 55.67, 83.19, 108.43, 128.62, 140.47, 155.48, 166.55, 166.63. ^{29}Si NMR (53.5 MHz, $CDCl_3$): δ 2.78. HRMS (FAB): Calcd for $C_{52}H_{86}B_2O_6Si_2$: 884.6149. Found: 884.6167.

3,8-Difluoro-5,5,10,10-tetrahexyl-2,7-diiodo-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (7a). To a THF (17.5 mL) solution of 2,2,6,6-tetramethylpiperidine (609 μL, 3.61 mmol) was added a hexane solution of *n*-BuLi (1.56 M, 2.1 mL, 3.28 mmol) at −78 °C. The mixture was stirred at 0 °C for 30 min. A THF (7.5 mL) solution of di-*tert*-butylzinc, prepared from $ZnCl_2$(tmeda) (995 mg, 3.94 mmol) and *t*-BuLi (1.45 M, 5.4 mL, 7.88 mmol), was added to the mixture at −78 °C, followed by stirring at 0 °C for 30 min. After warming to room temperature, a THF (7.5 mL) solution of **3a** (500 mg, 0.82 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. A THF (8.5 mL) solution of iodine (2.32 g, 9.14 mmol) was then added at −78 °C. The resulting mixture was gradually warmed to room temperature with stirring for 17 h. A saturated $Na_2S_2O_3$ aqueous solution was added, and the mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography with hexane as an eluent ($R_f = 0.75$) to give 607 mg (0.71 mmol) of **7a** in 86% yield as pale yellow crystals: mp 92−94 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.80 (t, $J = 6.6$ Hz, 12H), 0.89−1.05 (m, 8H), 1.16−1.23 (m, 32H), 6.94 (d, $J = 8.9$ Hz, 2H), 7.82 (d, $J = 6.9$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.0, 14.0, 22.5, 23.8, 31.3, 32.8, 79.4 (d, $^2J_{CF} = 25.6$ Hz), 112.8 (d, $^2J_{CF} = 23.2$ Hz), 137.1 (d, $^4J_{CF} = 3.7$ Hz), 142.5, 152.4 (d, $^3J_{CF} = 7.3$ Hz), 163.2 (d, $^1J_{CF} = 245$ Hz), 164.7 (d, $^4J_{CF} = 2.5$ Hz). HRMS (FAB): Calcd for $C_{38}H_{56}F_2I_2Si_2$: 860.1978. Found: 860.1990.

3,8-Difluoro-5,5,10,10-tetrahexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxabororan-2-yl)-5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene (8a). To a solution of **7a** (516 mg, 0.60 mmol) in Et_2O (30 mL) was added a hexane solution of *n*-BuLi (1.39 M, 870 μL, 1.21 mmol) dropwise at −78 °C. After stirred for 10 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (980 μL, 4.80 mmol) was added at the same temperature. After stirred for 2 h at −78 °C, the mixture was gradually warmed to room temperature over 17 h. The insoluble salts were removed by filtration, and the filtrate was concentrated under reduced pressure. The mixture was purified by a recycle preparative GPC using chloroform as an eluent to give 327 mg (0.38 mmol) of **8a** in 60% yield as a white powder: mp 168−170 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.78 (t, 6.9 Hz, 12H), 0.86−0.98 (m, 8H), 1.13−1.27 (m, 32H), 1.38 (s, 24H), 7.17 (d, $J = 7.6$ Hz, 2H), 7.84 (d, $J = 6.6$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.3, 14.0, 22.5, 23.9, 24.8, 31.3, 32.9, 83.7, 112.4 (d, $^2J_{CF} = 23.2$ Hz), 133.5 (d, $^4J_{CF} = 3.7$ Hz), 140.4 (d, $^3J_{CF} = 8.6$ Hz), 155.9 (d, $^3J_{CF} = 8.5$ Hz), 166.8, 169.7 (d, $^1J_{CF} = 253$ Hz), 179.4. HRMS (FAB): Calcd for $C_{50}H_{80}B_2F_2O_4Si_2$: 860.5749. Found: 860.5765.

Polymer 9. A mixture of **5a** (52 mg, 59 μmol), **6a** (52 mg, 59 μmol), $Pd(dba)_2$ (0.7 mg, 1.2 μmol), PPh_3 (1.5 mg, 5.7 μmol), and Cs_2CO_3 (80 mg, 250 μmol) in 1.5 mL of dioxane was stirred at 90 °C for 48 h. After addition of water, the reaction mixture was extracted with $CHCl_3$. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. After concentrated under reduced pressure, the mixture was dissolved into a small amount of $CHCl_3$ and poured into a vigorously stirred MeOH to form yellow precipitates. The reprecipitation procedure was repeated twice using MeOH and EtOH as a poor solvent to give 44 mg of homopolymer **9** in 60% yield as a yellow powder: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80−1.60 (m, 52H), 3.87 (s, 6H), 6.98 (s, 2H), 7.50 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.76, 14.21, 22.70, 24.44, 31.57, 33.39, 55.48, 108.94, 125.12, 129.16, 136.04, 151.58, 158.50, 164.90. M_n = 7000, M_w = 11 800, M_w/M_n = 1.7.

Polymer 10. This polymer was prepared essentially in the same manner as described for **9** by the reaction of **6a** and **7a** in 71% yield as a yellow powder: ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.84 (br, 24H), 1.02 (br, 16H), 1.23 (br, 48H), 1.44 (br, 16H), 7.00 (br, 2H), 7.06 (br, 2H), 7.49 (br, 2H), 7.57 (br, 2H). M_w = 57 000, M_n = 23 000, M_w/M_n = 2.2.

Polymer 11. A mixture of **7a** (43.0 mg, 50 μmol), **8a** (43.0 mg, 50 μmol), $Pd_2(dba)_3$ (0.92 mg, 1.0 μmol), PPh_3 (1.29 mg, 4.9 μmol), and Cs_2CO_3 (652 mg, 2.00 mmol) in a 1/1 toluene/H_2O mixed solvent (2 mL) was stirred at 105 °C for 48 h. The reaction mixture was extracted with $CHCl_3$, and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was dissolved with a small amount of $CHCl_3$ and poured into a vigorously stirred MeOH to form yellow precipitates. The reprecipitation procedure was repeated twice using hexane as a poor solvent to give 35 mg of polymer **11** in 58% yield as a yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (br, 12H), 1.04 (br, 8H), 1.22 (br, 32H), 7.10 (br, 2H), 7.59 (br, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 12.3, 14.0, 22.6, 24.0, 31.4, 32.9, 83.7, 112.8 (d, $^3J_{CF}$ = 13.4 Hz), 121.3 (d, $^3J_{CF}$ = 11.0 Hz), 134.5, 135.4, 152.1, 161.7 (d, $^1J_{CF}$ = 11.0 Hz), 165.2. M_w = 19 000, M_n = 8000, M_w/M_n = 2.4.

Polymer 12. A mixture of **5b** (50 mg, 84 μmol), 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (32 mg, 84 μmol), $Pd(PPh_3)_4$ (9.7 mg, 8.4 μmol), and CuI (3.3 mg, 17.2 μmol) in a 3/1 toluene/*i*-Pr_2NH mixed solvent (3.5 mL) was stirred at 60 °C for 48 h. After addition of water, the reaction mixture was extracted with $CHCl_3$. The organic layer was washed with 5% NH_4OH aqueous solution and brine, dried over $MgSO_4$, and filtered. After being concentrated under reduced pressure, the mixture was dissolved with a small amount of $CHCl_3$ and poured into a vigorously stirred MeOH to form yellow precipitates. The reprecipitation procedure was repeated twice using hexane as a poor solvent to give 50 mg of polymer **12** in 82% yield as a yellow powder: ^{1}H NMR (300 MHz, THF-d_8): δ 0.47 (s, 12H), 0.89−0.99 (br, 12H), 1.34 (br, 16H), 1.80 (br, 2H), 3.98 (br, 10H), 6.82 (s, 2H), 7.04 (s, 2H), 7.67 (s, 2H). ^{13}C NMR (67.8 MHz, THF-d_8): δ −2.66, 2.05, 12.40, 15.18, 24.69, 30.78, 32.20, 41.51, 56.58, 72.82, 109.55, 112.70, 115.81, 117.68, 132.00, 138.27, 152.60, 155.13, 163.72. M_n = 37 500, M_w = 97 600, M_w/M_n = 2.6.

Polymer 13. A mixture of **5a** (57 mg, 65 μmol), 5,5′-tributylstannyl-2,2′-bithiophene (48 mg, 65 μmol), $Pd_2(dba)_3\cdot CHCl_3$ (3.5 mg, 3.4 μmol), and tri(2-furyl)phosphine (3 mg, 13 μmol) in 2 mL of THF was stirred at 75 °C for 48 h. After addition of water, the reaction mixture was extracted with $CHCl_3$. The organic layer was washed with 5% NH_4OH aqueous solution and brine, dried over $MgSO_4$, and filtered. After being concentrated under reduced pressure, the mixture was dissolved into a small amount of $CHCl_3$ and poured into a vigorously stirred MeOH to form precipitates. The reprecipitation procedure was repeated twice using hexane as a poor solvent to give 32 mg of polymer **13** in 62% yield as a red powder: ^{1}H NMR (270 MHz, THF-d_8): δ 0.78−0.81 (br, 12H), 1.05−1.45 (m, 40H), 4.02 (s, 6H), 7.01 (s, 2H), 7.21 (d, J = 3.6 Hz, 2H), 7.51 (d, J = 3.6 Hz, 2H), 7.91 (s, 2H). ^{13}C NMR (67.8 MHz, THF-d_8): δ 14.08, 15.10, 24.15, 25.35, 33.08, 34.66, 56.30, 110.39, 122.37, 124.07, 126.75, 131.39, 132.87, 138.43, 140.11, 152.81, 158.90, 166.45. M_n = 12 000, M_w = 31 700, M_w/M_n = 2.6.

Acknowledgment. This work was supported by Grants-in-Aid (No. 12CE2005 for Elements Science and No. 15205014) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and PRESTO, Japan Science and Technology Agency (JST).

References and Notes

(1) For recent reviews: (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377. (b) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853−1864. (c) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267−1300.

(2) (a) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 9624−963. (b) Haryono, A.; Miyatake, K.; Natori, J.; Tsuchida, E. *Macromolecules* **1999**, *32*, 3146−3149. (c) Oyaizu, K.; Mikami, T.; Mitsuhashi, F.; Tsuchida, E. *Macromolecules* **2002**, *35*, 67−78. (d) Former, C.; Becker, S.; Grimsdale, A. C.; Müllen, K. *Macromolecules* **2002**, *35*, 1576−1582.

(3) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Göbel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995**, *240*, 373−378.

(4) Hertel, D.; Scherf, U.; Bässler, H. *Adv. Mater.* **1998**, *10*, 1119−1122.

(5) (a) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016−2020. (b) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Gaal, M.; List, E. J. W. *Macromolecules* **2003**, *36*, 8240−8245. (c) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987−6995.

(6) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922−6928.

(7) Patil, S. A.; Scherf, U.; Kadashchuk, A. *Adv. Funct. Mater.* **2003**, *13*, 609−614.

(8) Qiu, S.; Lu, P.; Liu, X.; Shen, F.; Liu, L.; Ma, Y.; Shen, J. *Macromolecules* **2003**, *36*, 9823−9829.

(9) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359−369.

(10) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159−1162.

(11) (a) Zenz, C.; Graupner, W.; Tasch, S.; Leising, G.; Müllen, K.; Scherf, U. *Appl. Phys. Lett.* **1997**, *71*, 2566−2568. (b) Kallinger, C.; Hilmer, M.; Haugeneder, A.; Perner, M.; Spirkl, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Müllen, K.; Gombert, A.; Wittwer, V. *Adv. Mater.* **1998**, *10*, 920−923.

(12) Ciszek, J. W.; Tour, J. M. *Tetrahedron Lett.* **2004**, *45*, 2801−2803.

(13) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087−12088.

(14) (a) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327−2334. (b) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974−11975.

(15) Serby, M.; Ijadi-Maghsoodi, S.; Barton, T. J. *XXXIIIrd Symposium on Organosilicon Chemistry*, Saginaw, MI, 2000; PA-35.

(16) Ma, Z.; Ijadi-Maghsoodi, S.; Barton, T. J. *Polym. Prepr.* **1997**, *38*, 249−250.

(17) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662−13663.

(18) Clayden, J. *Tetrahedron Organic Chemistry Series,* 1st ed.; Pergamon: Oxford, 2002; Vol. 23, Chapter 2.

(19) Gaussian 98: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, Jr., R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al− Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(20) Kondo, Y.; Shilai, M.; Uchiyama, M.; Sakamoto, T. *J. Am. Chem. Soc.* **1999**, *121*, 3539−3540.

(21) Zhu, Z.; Swager, T. M. *Org. Lett.* **2001**, *3*, 3471−3473.

MA0486546