Preparation of Poly(silylene-*p*-phenylene)s Containing a Pendant Fluorophor and Their Applications to PL Imaging

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Received June 14, 2004; Revised Manuscript Received October 26, 2004

ABSTRACT: Poly(silylene-*p*-phenylene)s bearing an anthrylethynyl, pyrenylethynyl, or terthienyl group as the pendant were obtained in moderate yield, by substitution reactions of poly[ethoxy(methyl)silylene-*p*-phenylene] with the corresponding organolithium reagents in THF. The polymers exhibited photoluminescent (PL) properties in solutions as well as in the films. They were photoactive and irradiation of the films in air with a low-pressure mercury lamp led to a decrease of PL efficiencies, being applicable to PL imaging of the films. The present polymers can be used also as hole-transporting materials in double-layer electroluminescent (EL) devices and the devices with the structure of ITO/polymer film/Alq3/Mg−Ag emitted a green EL arising from Alq3 emission.

Introduction

Organic photoluminescent (PL) materials are of importance in the area of organic optical devices. In particular, those applicable to PL imaging have attracted a recent interest. Several approaches to pattern PL images have been made, most commonly by using acid-sensitive fluorescent dyes.[1] In this process, polymer films containing an acid sensitive fluorescent dye and a photoacid generator are irradiated through a photo mask then the resulting films are heated to induce the reaction of the fluorophor with proton in the irradiated area, leading to changes of the PL color and/or efficiencies. Recently, a new methodology was reported, in which compounds having both a fluorescent site and a quenching nitroxide unit were irradiated in the presence of a radical initiator.[2] The photogenerated radical coupled with the nitroxide to increase the fluorescence efficiencies. In these processes, the fluorophores and reagents were used in polymer matrixes in order to avoid the staking of fluorophores that would decrease the PL efficiencies. In general, however, it may be difficult to avoid phase separation as well as aggregation of the fluorophores in the matrixes during preparation, operation, or storage of the films, which cause a significant decrease of the PL efficiencies. Although applications of stilbene-type fluorophores, whose photolysis leads to nonemissive [2 + 2] dimers, to PL imaging have been also reported, these must be used in forms of well-aligned LB films.[3]

Recently, we demonstrated that nucleophilic substitution of poly(ethoxysilylenephenylene)s provides a convenient approach to variously substituted poly(silylenephenylene)s.[4] In these reactions, highly electrophilic properties of the EtO−Si bond originate the smooth substitution on the polymers.[5] In the hope of obtaining single component and simply accessible PL imaging materials, we prepared poly(silylene-*p*-phenylene)s bearing an anthrylethynyl, pyrenylethynyl, or terthienyl group as the pendant by substitution reactions of poly[ethoxy(methyl)silylene-*p*-phenylene] with the corresponding organolithium reagents. In these polymers, silyl-substitution was anticipated to increase the fluorescence intensities of the fluorophors,[6] and to accelerate the photo oxidation of the fluorophors making it possible to use the polymer films for sensitive PL imaging.[7] In addition, sterically large silylenephenylene units would hinder the $\pi-\pi$ stacking of the fluorophores leading to high quantum yields of the polymers. Applications of the polymers to hole-transporting materials in electroluminescence (EL) devices also were studied. The π-conjugated fluorophors with electron-donating silyl-substitution were expected to possess high-lying highest occupied orbital, giving rise to high hole-affinity of the present polymers.

Results and Discussion

Polymer Synthesis. Poly(silylene-*p*-phenylene)s bearing a pendant fluorophor (**1**−**3**) were synthesized as shown in Scheme 1. The reactions of poly[ethoxy(methyl)silylene-*p*-phenylene] ($M_w = 13500$, $M_n = 8500$), prepared by Grignard coupling of bromophenyl(diethoxy)methylsilane[4] with the corresponding organolithium reagents, afforded the expected polymers, as summarized in Table 1. As shown in Table 1, incorporation of the fluorophores into the polymers (x/y) could be controlled by changing the polymer/reagent ratio, but attempts to obtain fully substituted polymers were unsuccessful, even when 2-fold excess of the reagents were employed.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC), relative to polystyrene standards. The values were in good

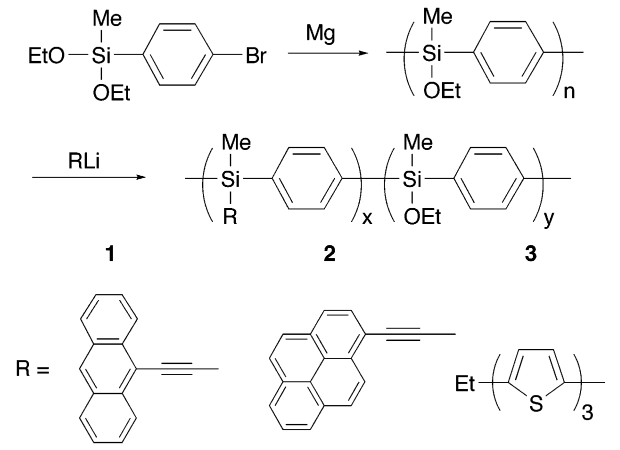
10.1021/ma040108p CCC: $30.25

Table 1. Synthesis and Properties of Polymers

polym	reagent/equiv	*x/y*[a]		yield /%	mp/°C	M_w[b] (M_n/M_n)	Φ	
		^{1}H NMR	EA				in film	in THF
1a	0.5	14/86	15/85	77	128−135	16000 (1.6)	0.05−0.07	0.48
1b	0.6	28/72	28/72	91	142−153	17000 (2.6)	0.02−0.03	
1c	0.8	32/68	35/65	86	170−179	30000 (3.6)	0.02−0.03	
1d	1.0	49/51	49/51	93	>300	18000 (1.9)	0.02−0.03	0.23
1e	2.0	73/27	73/27	61	>300	38000 (4.6)	<0.01	0.12
2a	0.45	16/84	15/85	45	138−147	18000 (1.8)	0.44−0.61	
2b	0.55	23/77	22/78	37	146−152	26000 (2.7)	0.62−0.73	0.34
2c	0.83	30/70	30/70	53	149−158	37000 (2.8)	0.34−0.41	
2d	2.0	78/22	78/22	76	218−227	13000 (1.6)	0.07−0.08	0.13
3a	0.20	12/88	12/88	86	85−93	14000 (1.6)	0.02−0.03	
3b	0.26	17/83	23/77	90	105−112	20000 (1.6)	0.03−0.04	0.11
3c	0.35	28/72	28/72	91	112−115	21000 (1.7)	0.01−0.02	
3d	0.65	50/50	50/50	87	119−123	20000 (1.6)	0.01−0.02	
3e	1.0	73/27	73/27	78	133−137	19000 (1.7)	0.01−0.02	0.08

[a] The *x*/y ratio was determined by the ^{1}H NMR spectrum or elemental analysis. [b] Determined by GPC, relative to polystyrene standards.

Scheme 1



agreement with those calculated from the molecular weights of the starting polymer, but the poly dispersities (M_w/M_n) were rather large, indicating that some side reactions including the cleavage of the polymer backbone and cross-linking reactions had occurred to an extent. Polymers **1**−**3** were soluble in common organic solvents, such as aromatic solvents, ethers, and chlorocarbons, but barely soluble in alcohols and saturated hydrocarbons. They could be spin-coated to thin solid films from the solutions. The polymer with the higher *x/y* ratio melted at the higher temperature. Introduction of more rigid and large π-conjugated substituents in place of the ethoxy groups and/or inerchain interaction by π-stacking as indicated by the emission spectra of the polymers (see bellow) seemed to be responsible for the increase. For large increase of melting temperatures going from **1c** to **1d** is probably due to the cross-linking reactions during the measurements. In fact, DSC analysis of polymer **1d** in a nitrogen atmosphere revealed a broad exothermic peak around 250 °C and the polymer became hardly soluble after heating at 280 °C.

PL Properties of Polymers 1—3. UV spectra of polymers **1**−**3** revealed absorption bands due to the fluorophores in addition to that of silylene-phenylene backbone around at 240 nm. The absorption band of the silylene−phenylene unit did not move depending on the fluorophor, indicating that no evident interaction took place between them. The polymers exhibited strong photofluorescence and emitted a blue green or green light when irradiated with a low-pressure mercury lamp in solutions as well as in films. Figure 1 represents fluorescence spectra of THF solutions (2.0×10^{-5} silylene−phenylene unit mol/L) and spin-coated films of some of the polymers, **1**−**3**. Fluorescence maxima of the corresponding monomeric compounds are shown in Chart 1, for comparison. As can be seen in Figure 1a, the fluorescence spectra of polymers **1** in THF revealed intense bands at 400−480 nm, ascribed to the emission from isolated ethynylanthracene fluorophores with a broad shoulder over 500 nm whose intensity was relatively enhanced by increasing *x/y* ratios. This broad shoulder may be ascribed to the eximer emission arising from stacking of the fluorophores and its relative intensity was further enhanced by measuring the spectra in the solid state (Figure 1b). In contrast to this, the spectra of polymers **2** showed a broad maximum at about 500 nm as the major peak even in the solutions (Figure 1c), indicating the favored eximer formation of ethynylpyrene fluorophores. The maxima of the films were slightly red-shifted as the *x/y* ratios increased. To know more about the origin of the fluorescence bands, we measured the PL lifetimes. Thus, monitoring PL decay of polymer **2b** in THF at 400 nm gave $\tau_1 = 3.7$ ns, while the PL at 500 nm underwent decay with $\tau_1 = 21.3$ ns. The fluorescence spectra of polymers **3** revealed a strong band and a shoulder, presumably due to the isolated and stacked fluorophores, respectively, in solutions (Figure 1e), the latter of which was relatively enhanced in the solid state (Figure 1f), similar to polymers **1**.

In Table 1, relative fluorescence quantum efficiencies of spin-coated films of polymers **1**−**3** are also summarized. The values were determined by using 9,10-diphenylanthracene dispersed in a polystyrene film as a standard.[8] Since the fluorescence intensities of the polymer films, even that of the standard film, were unstable and were not well reproducible, we could not determine the exact values. In Table 1, therefore, only the value ranges obtained from at least 5 times measurements are listed. The efficiencies tended to decrease as increasing *x/y* ratios. High quantum efficiencies were obtained for polymers **2** with the best value of 0.62−0.73 for **2b** (*x/y* = 22/78). Enhanced fluorescence of pyrene by the formation of its excimer is well-known.[9] Although the origin of a decrease of the quantum efficiencies on going from **2b** to **2d** is unclear, it may be explained by self-quenching in the solid states with high concentrations of the fluorophor. Films of polymers **1** and **3**, in contrast, exhibited much lower quantum efficiencies.

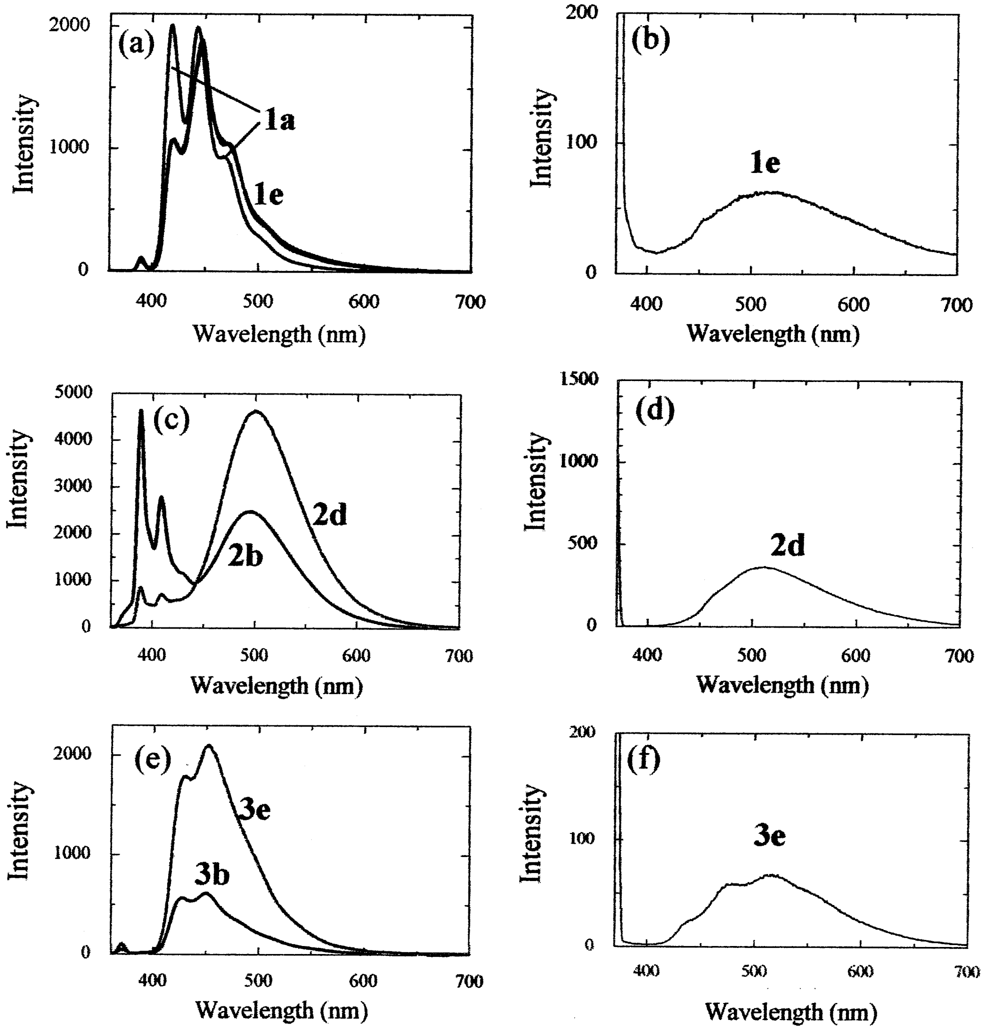
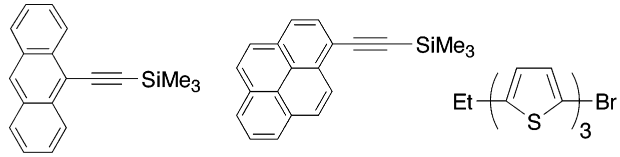


Figure 1. Fluorescence spectra of polymers **1**−**3** in THF of 2.0 × 10^{-5} silylene-phenylene unit mol/L (left) and in films (right).

Chart 1



λ_{em} 416, 440, 466 nm

386, 407, 428 nm

415, 449 nm

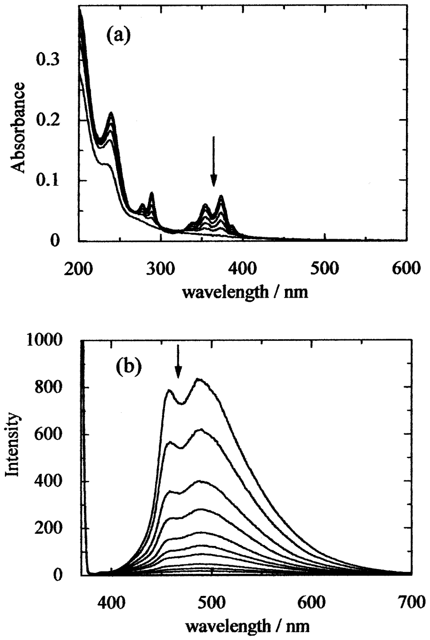


Figure 2. Changes upon irradiation of a film of polymer **2b** in (a) UV and (b) fluorescence spectra.

Patterning of PL Images. Spin-coated films of polymers **1**−**3** on quartz plates were irradiated with a low-pressure mercury lamp in air and the reaction progress was monitored by UV and fluorescence spectra, as illustrated for polymer **2b** (*x*/*y* = 22/78) in Figure 2. After 15 min of irradiation, the UV and fluorescence bands almost disappeared and the IR spectra of the resulting films showed the absorption bands ascribed to siloxane and carbonyl units at 1100 and 1745 cm^{-1}, respectively, indicating that some oxidation reactions had occurred. When an irradiated film of **2b** was dissolved in deuteriochloroform and was analyzed with respect to the ^1H NMR spectrum, all aromatic protons disappeared and new multiple olefin signals appeared at 5.1−5.8 ppm, together with those at 0.8−0.9, 1.4−2.1, and 3.3−4.2 ppm. These results clearly indicated that not only the phenylene group but also the ethynylpyrene fluorophor were decomposed by photooxidation. Although we have not yet obtained enough data to discuss detailed mechanism for the photodegradation of the polymers, similar photodegradation has been reported for silylene−diethynyleneanthracene and

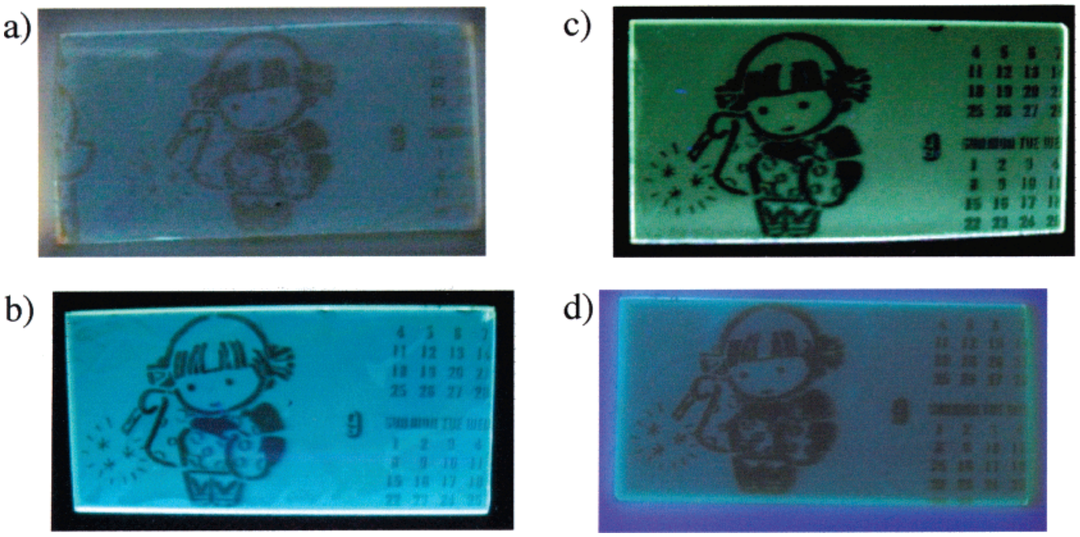


Figure 3. PL images prepared by irradiation of spin-coated films of (a) **1b**, (b) **2b**, (c) **2d**, and (d) **3a** in air.

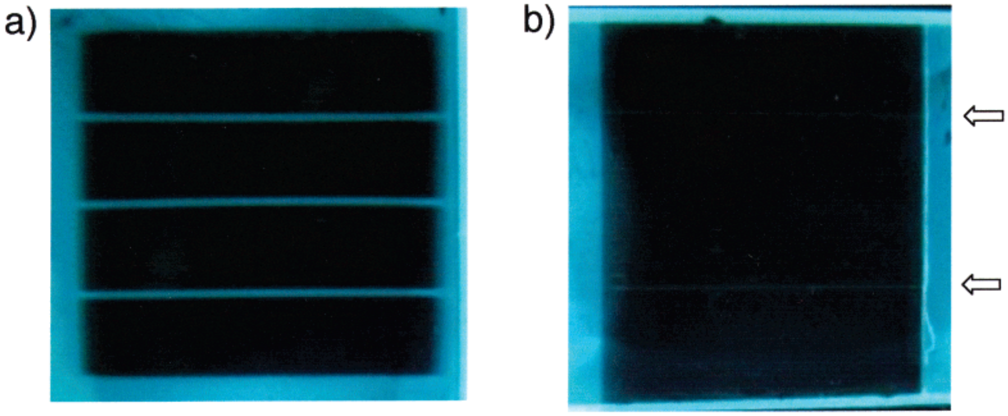


Figure 4. Patterned PL lines prepared by using polymer **2b** with the thickness of (a) 250 μm and (b) 20 μm.

silylene-diethynylenepyrene polymers, previously.[10] Presumably, silyl radicals arising from photoinduced homolytic scission of Si–C bonds added to oxygen, leading to silyl peroxides that oxidized fluorophors. A similar mechanism has been proposed previously for the photooxidation of poly[4-(trimethylsilylmethyl)styrene] in air.[7a]

The irradiated films of polymers **1**–**3** were no longer emissive and irradiation through a photo mask led to clear patterning of PL images. Examples that were produced by using polymers **1b**, **2b**, **2d**, and **3a**, respectively, are presented in Figure 3. Fine patterning was also possible and emissive line with the width of 20 μm could be produced as shown in Figure 4.

To know how the binding of fluorophores as the polymer pendant affects the PL properties of the films, we examined patterning of a PL image by employing 9-(trimethylsilylethynyl)pyrene blended in poly[ethoxy(methyl)silylene-*p*-phenylene] in a ratio of 22/78. Thus, the blend was spin-coated on a quartz plate and the film was irradiated through a photomask. Figure 5 shows the resulting PL image that appears rather heterogeneous with nonemissive spots in the nonirradiated area, in contrast to those of polymers **1**–**3** shown in Figures 3 and 4.

Utilization of Polymers 1—3 as Hole-Transports in EL Devices. We next examined polymers **1**–**3** having the highest *x*/*y* ratio among the respective polymers, as hole-transporting materials in EL devices.

Figure 5. PL image prepared by irradiation of a film of poly[ethoxy(methyl)silylene-*p*-phenylene] containing (trimethylsilylethynyl)pyrene in air.

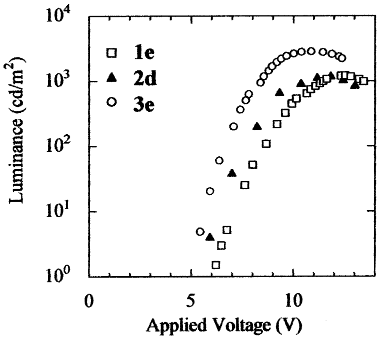


Figure 6. Luminance–voltage (*L*–*V*) plots of EL devices with the structure of ITO/polymer film/Alq3/Mg–Ag.

Figure 6 represents luminance–voltage (*L*–*V*) plots of EL devices with the structure of ITO/polymer film/Alq3/Mg–Ag where Alq3 (tris(8-quinolinolato)aluminum(III)) was used as the electron-transporting-emitter, and ITO (indium−tin−oxide) and Mg−Ag are the anode and cathode, respectively. The devices emitted a green light arising from Alq3 emission, when bias voltage exceeded 5−6 V. No emission from the polymers was observed at all. The device with polymer **3e** (*x*/*y* = 73/27) showed the best results among the devices examined, and the maximal luminance reached 3000 cd/m^2 at 11 V. At this voltage, the current density of the device reached 500 mA/cm^2. The present device performance is a little inferior, but comparable to a similar device having a film of poly(vinylcarbazole) that is known as a common hole-transport, in place of the silicon polymer film.[11] Devices without the Alq3 layer (ITO/polymer film/Mg−Ag) emitted no detectable luminance up to 30 V of the bias voltage.

In conclusion, we found that nucleophilic substitution reactions of poly(ethoxysilylenephenylene) readily proceeded to give fluorophor-substituted polymers. Their applications to PL imaging as well as hole-transporting materials in EL device systems were demonstrated. Poly(silylenephenylene) seems to be useful as the backbone of functionality polymeric materials. Studies to introduce other functional substituents on the polymer system are underway.

Experimental Section

General Methods. All reactions were carried out under an inert atmosphere. THF used as the reaction solvent was dried over sodium−potassium alloy and distilled just before use. Poly[ethoxy(methyl)silylene-*p*-phenylene][4] and ethynylanthracene[12] were prepared as reported in the literature. Ethynylpyrene was prepared in a fashion similar to that for ethynylanthracene.[13] NMR spectra were recorded on a JEOL model JNM-LA 400 spectrometer. IR spectra were measured on a Shimadzu FT-IR model 8700 spectrometer. UV and fluorescence spectra were measured on Hitachi U-3210 and Shimadzu RF5000 spectrophotometers, respectively. Molecular weights of the polymers were determined by gel-permeation chromatography relative to polystyrene standards, using Shodex 806 and 804 columns that were connected in series, eluting with THF.

Preparation of Polymers 1a—e. In a 100 mL two necked flask were placed 0.50 g (2.50 mmol) of 9-ethynylanthracene and 20.0 mL of THF and the flask was cooled to −78 °C. To this was added dropwise 2.72 mL (2.50 mmol) of a 0.92 M methyllithium−diethyl ether solution. After this was stirred at room temperature for 3 h, a solution of 0.21 g of poly[ethoxy(methyl)silylene-*p*-phenylene] (M_w = 13500, M_n = 8500) in 6.0 mL of THF was added slowly to the mixture at −78 °C, and the resulting mixture was stirred at room temperature for 12 h. After hydrolization with water, the organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from chloroform-ethanol to give 0.21 g of polymer **1e** (*x*/*y* = 73/27): IR $\nu_{C\equiv C}$ 2138 cm^{-1}. Anal. Calcd for $((C_{23}H_{16}Si)_{0.73}(C_9H_{12}OSi)_{0.27})_n$: C, 82.95; H, 5.40. Found: C, 82.89; H, 5.22. NMR spectra of **1e** revealed signals ascribed to both the units of anthrylethynyl- and ethoxy-substituted units, the later of which appeared at almost the same positions as those of the starting polymer. Data for the anthrylethynyl-substituted unit: ^{1}H NMR (δ in CDCl$_3$) 0.90 (s, 3H, MeSi), 7.45−7.63 (m, 4H, anthracene), 7.83 (br s, 2H, anthracene), 7.90 (s, 4H, phenylene), 8.36 (br s, 1H, anthracene), 8.53 (br s, 2H, anthracene); ^{13}C NMR (δ in CDCl$_3$) −1.83 (SiMe), 101.74, 105.37 (C≡C), 116.41, 125.61, 126.60, 126.94, 128.60, 130.89, 133.14, 133.94 (anthracene), 134.18, 137.05 (phenylene); ^{29}Si NMR (δ in CDCl$_3$) −25.16.

Polymers **1a**−**1d** were obtained in a fashion similar to that given above. Their *x*/*y* ratios were determined by integration of the ^{1}H NMR spectra that are consistent with the values based on the combustion elemental analysis within the error range.

Preparation of Polymers 2a—d. Polymers **2a**−**d** were obtained in the same manner as for polymer **1e**, using 1-ethynylpyrene instead of 9-ethynylanthracene. In these reactions, 1,4-dipyranylbutadiyne that could not be separated from the polymers by reprecipitation was formed as a byproduct in approximately 5−10% yield. The polymers, therefore, were subjected to preparative GPC for purification. Data for **2c** (for NMR, data only for the substituted unit are given): IR $\nu_{C\equiv C}$ 2150 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.88 (s, 3H, MeSi), 7.66−8.14 (m, 8H, pyrene), 7.82 (s, 4H, phenylene), 8.55 (br s, 1H, pyrene); ^{13}C NMR (δ in CDCl$_3$) −1.95 (SiMe), 95.82, 107.57 (C≡C), 116.94, 124.00, 124.20, 124.30, 125.38, 125.73(2C), 126.21, 127.12, 128.42, 128.59, 130.11, 130.85, 131.03, 131.59, 132.45 (pyrene), 133.78−133.92 (m), 136.95 (phenylene); ^{29}Si NMR (δ in CDCl$_3$) −25.38. Anal. Calcd for $((C_{25}H_{16}Si)_{0.30}(C_9H_{12}OSi)_{0.70})_n$: C, 75.87; H, 6.09. Found: C, 75.60; H, 6.25.

Preparation of 5-Ethyl-5″-bromo-2,2′:5′,2″-terthiophene. In dark, NBS (20.20 g, 0.112 mol) was slowly added to a well-stirred solution of 5-ethyl-2,2′:5′,2″-terthiophene (29.5 g, 0.112 mol) in 500 mL of chloroform at 0 °C, and the mixture was stirred for 5 h. To this was added 300 mL of water and the organic layer was separated and the aqueous layer was extracted by chloroform. The organic layer and the extracts were combined, and dried over anhydrous Na$_2$SO$_4$. After the solvent was evaporated, the residue was recrystallized from hot ethanol twice to give 31.9 g (80% yield) of 5-ethyl-5″-bromo-2,2′:5′,2″-terthiophene as bright yellow solid: mp 146−147 °C; MS *m*/*z* 354 (M$^+$ for ^{79}Br); ^{1}H NMR (δ in CDCl$_3$) 1.32 (t, 3H, *J* = 7.6 Hz), 2.83 (2H, q, *J* = 7.6 Hz), 6.69 (d, 1H, *J* = 3.2 Hz), 6.87−6.98 (m, 5H); ^{13}C NMR (δ in CDCl$_3$): 15.83, 23.53, 110.79, 123.52, 123.64, 124.20, 124.53, 130.65, 134.12, 134.38, 137.31, 138.76, 147.38 (one carbon may overlap). Anal. Cacld for $C_{14}H_{11}BrS_3$: C, 47.32; H, 3.12. Found: C, 47.22; H, 3.11.

Preparation of Polymers 3a—e. In a 50 mL two necked flask were placed 0.22 g (0.61 mmol) of 5-ethyl-5″-bromo-2,2′:5′,2″-terthiophene and 10.0 mL of THF, and the flask was cooled to −78 °C. To this was added dropwise 0.39 mL (0.61 mmol) of a 1.58 M *n*-butyllithium−hexane solution and the resulting mixture was stirred at room temperature for 3 h. A solution of 0.10 g of poly[ethoxy(methyl)silylene-*p*-phenylene] (M_w = 13500, M_n = 8500) in 3.0 mL of THF was then added slowly to the mixture at −78 °C, and the mixture was stirred at room temperature for 12 h. After hydrolization with water, the organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from chloroform-ethanol to give 0.16 g of polymer **3e** (78% yield). Data for **3e** (for NMR, data only for the substituted unit are given):^{1}H NMR (δ in CDCl$_3$) 0.83 (s, 3H, MeSi), 1.30 (t, 3H, *J* = 7.58 Hz, Et), 2.82 (q, 2H, *J* = 7.58 Hz, Et), 6.64 (br s, 1H, thiophene), 6.93 (br s, 2H, thiophene), 7.01 (br s, 1H, thiophene), 7.13 (br s, 1H, thiophene), 7.18 (br s, 1H, thiophene), 7.57 (s, 4H, phenylene, overlapping with a signal of the unsubstituted unit); ^{13}C NMR (δ in CDCl$_3$) −2.57 (MeSi), 15.82 (CH_3−CH$_2$) 23.49 (CH_2−CH$_3$), 123.41, 123.54, 124.12, 124.78, 133.94, 135.17, 143.85, 147.06 (thiophene), 134.27, 137.05 (phenylene); ^{29}Si NMR (δ in CDCl$_3$) −15.69. Anal. Calcd for $((C_{21}H_{18}S_3Si)_{0.73}(C_9H_{12}OSi)_{0.27})_n$: C, 64.16; H, 4.97. Found: C, 64.37; H, 5.05.

Fabrication of EL Devices. A film of the polymer with an approximate thickness of 50 nm was prepared by spin-coating (2000 rpm) from a solution of polymer in chloroform (5 g/L) on an anode, indium−tin-oxide (ITO) coated on a glass substrate (Nippon Sheet Glass Co.). An electron-transporting-emitting layer with a thickness of 50 nm was then prepared by vacuum deposition of tris(8-quinolinolato)aluminum(III) (Alq3) at 1 × 10^{-5} Torr on the polymer film. Finally a layer of magnesium−silver alloy (Mg−Ag) with an atomic ratio of 10:1 was deposited on the Alq layer surface as the top electrode at 1 × 10^{-5} Torr.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 16350102) from the Ministry of Education, Science, Sports, and Culture of Japan, to which our thanks are due.We thank Sankyo Kasei Co., Ltd., and Tokuyama Co., Ltd., for financial support. We also thank Prof. Y. Harima for the measurements of PL lifetimes.

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MA040108P