

# Synthesis of diarylenenaphthylene- and diaryleneanthrylene-containing organosilicon polymers and their applications to organic EL devices

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## Abstract

Stille coupling reactions of bis(stannylphenyl- and stannylthienyl)silane with dibromonaphthalene and bis(bromothieryl)anthracene gave the corresponding polymers containing naphthylene or anthrylene units in the backbone. Applications of the polymers to electroluminescent (EL) devices were examined and it was found that the diphenyleneanthrylene-containing polymer can be used as a good hole-transporting material in a double-layered EL device.

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**Keywords:** Organosilicon polymer; Hole transport; Organic EL device

## 1. Introduction

There is growing interest in polymers and oligomers whose backbone is composed of an alternating arrangement of an organosilanyl unit and a  $\pi$ -conjugated system, because of their potential use as highly functionalized materials such as photoresists, organic semiconductors in their doped states, and heat-resistant materials [1]. Recently, it has been demonstrated that the substitution of silicon into a  $\pi$ -electron system enhances luminescence properties [2] and thus, several attempts have been made to prepare Si- $\pi$  alternating polymers, which constitute a new class of organic photo- [3] and electroluminescent materials [4].

On the other hand, we have reported that polymers having extended  $\pi$ -conjugated units, such as anthracene [5a], pyrene [5b], and oligothiophenes [4b,5c], are usable as

excellent hole-transporting materials in multi-layered EL devices. In those polymers, the electron-donating organosilanyl units would elevate the HOMO energy levels of the  $\pi$ -conjugated units to enhance hole affinity of the polymers. The organosilanyl units are expected also to improve solubility and processability of the polymers. Generally, however, the electroluminescence properties of these polymers are not sufficiently high to allow their use as single-layered EL device materials. Although some silanyl-oligothienylene alternating polymers have been previously reported to be applicable to single-layered EL devices [4c,4d], the device efficiencies are usually low [4d]. In hopes of obtaining these types of polymers with improved electroluminescence properties, we prepared organosilicon polymers containing diarylnaphthalene and diarylanthracene units, which are known as highly emissive chromophores. In contrast to our expectations, the resulting polymers did not show electroluminescence in single-layered devices, but were found to be usable as hole-transporting materials in double-layered EL devices [6].

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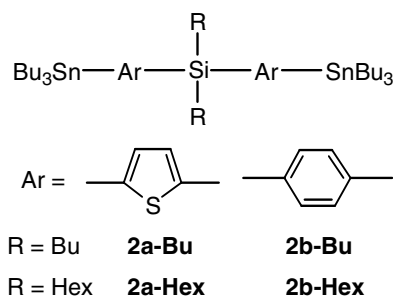


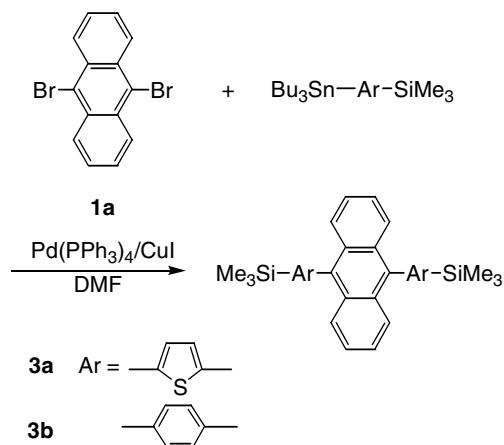
Chart 1.

## 2. Results and discussion

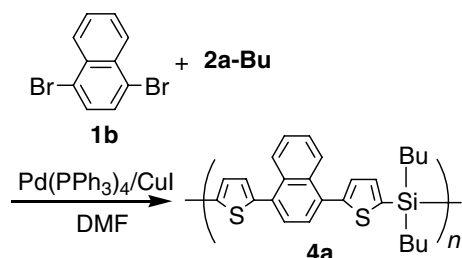
### 2.1. Polymer synthesis

First, we examined the Stille coupling of 9,10-dibromoanthracene (**1a**) with bis(tributylstannylthienyl)dibutylsilane (**2a-Bu**) and bis(tributylstannylphenyl)dibutylsilane (**2b-Bu**) (Chart 1). The  $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ -catalyzed reactions in DMF, followed by reprecipitation of the organic products from chloroform/methanol afforded the corresponding polymeric substances in approximately 80% yield. However, the molecular weights of the polymers determined by GPC were only approximately  $M_n = 2000$ , probably due to the low reactivities of the monomers arising from steric repulsion between the adjacent anthracene and thiophene or benzene rings. This is evident from model reactions shown in Scheme 1, which proceeded very slowly to give rather low yields of coupling products **3a** (78%) and **3b** (34%), even after reaction for 5 days. Use of acetonitrile as solvent increased the polymer molecular weights to  $M_n = \text{ca. } 4000$ . However, the  $^1\text{H}$  NMR spectra of the polymers revealed many unidentified small signals in the aromatic CH region, which would have arisen from side reactions such as, for example, homo coupling of **2a-Bu** and **2b-Bu**.

To reduce steric repulsion, we next chose dibromonaphthalene (**1b**) and bis(bromothiényl)anthracene (**1c**) as the

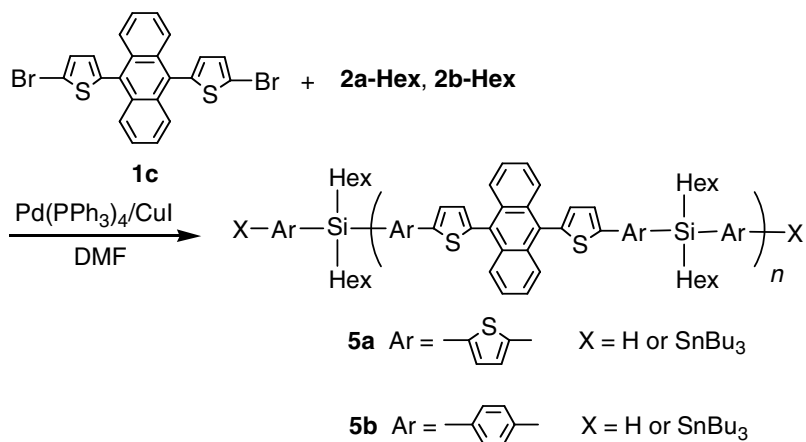


Scheme 1.



Scheme 2.

monomers (Schemes 2 and 3). The results of the polymerization are summarized in Table 1. The structure deduced from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of naphthylene-containing polymer **4a** was consistent with the silylene-dithienylenenaphthylene alternating structure. In contrast, an attempt to prepare a similar naphthylene-containing polymer from the reaction of **1b** with **2b-Bu** under the same conditions was unsuccessful. Although the reaction gave a polymeric substance with  $M_n = 4700$ , its NMR spectra showed only broad and multiple signals, together with tiny peaks that were ascribable to naphthylene units.



Scheme 3.

Table 1  
Polymer synthesis by Stille coupling reactions

Polymer	Yield <sup>a</sup>	M <sub>w</sub> <sup>a,b</sup>	M <sub>n</sub> <sup>a,b</sup>	M <sub>p</sub> (°C)	λ <sub>max</sub> (nm) <sup>c</sup>	
					Abs	Emission
<b>4a</b>	81	18,000	9200	81–89	233, 338	442
<b>5a</b>	78	5100	3700	>300	262, 330, 384, 403	494
<b>5b</b>	94	6700	5200	212–219	264, 299, 382, 403	488

<sup>a</sup> After purification from chloroform–methanol.

<sup>b</sup> Determined by GPC, relative to polystyrene standards.

<sup>c</sup> In THF.

As shown in Table 1, anthrylene-containing polymers **5a** and **5b** were obtained in good yields similar to **4a**, but their molecular weights determined by GPC were much lower than that of **4a**. The <sup>1</sup>H NMR spectrum of polymer **5a** showed larger integration values for alkyl CH and thiophene ring protons than expected, probably due to the end group effects (see Section 3). Since its <sup>13</sup>C NMR spectrum did not show any signals assignable to bromothieryl Br–C carbons (113–118 ppm), thieryl silyl and tributylstannylthienylsilyl groups were likely to be involved as the major end groups in the polymer chain, the former of which would be formed by hydrolysis of the tributylstannyl units (see Scheme 3). On the basis of the above considerations, the degree of polymerization was estimated to be  $n = 3.7$  from the <sup>1</sup>H NMR spectrum, in good agreement with that determined by GPC. It was also suggested that approximately 10% of the terminal thieryl groups were substituted with a tributylstannyl group (molecular weight = ca. 3000). Similarly, the <sup>1</sup>H NMR spectrum of polymer **5b** suggested the degree of polymerization to be  $n = 6.3$  and the incorporation ratio of tributylstannyl units on the terminal thiophene rings to be approximately 40% (molecular weight = ca. 4800). Polymers **4a**, **5a**, and **5b** were obtained as solids. They were soluble in common organic solvents including halocarbons, aromatic hydrocarbons, and ethers, but not in methanol. The optical properties of the present polymers are also summarized in Table 1.

## 2.2. Applications to EL device systems

Polymers **4a**, **5a**, and **5b** were examined as EL device materials. Fig. 1 shows the current density-bias voltage (I–V) and luminance-bias voltage characteristics of the double-layered EL devices with the structure ITO/polymer spin-coated film/Alq<sub>3</sub>/Mg–Ag (Alq<sub>3</sub> = tris(8-quinolinolato)aluminum (III)). The device fabricated with polymer **5a** did not produce any detectable light, probably due to poor film quality arising from the high crystallinity of the polymer. In fact, the spin-coated films of polymer **5a** were always cloudy. The devices fabricated with polymers **4a** and **5b** emitted green light arising from Alq<sub>3</sub> emission. As can be seen in Fig. 1, the device fabricated with polymer **5b** showed better EL performance with the maximum current density and luminance of 460 mA/cm<sup>2</sup> and 1300 cd/

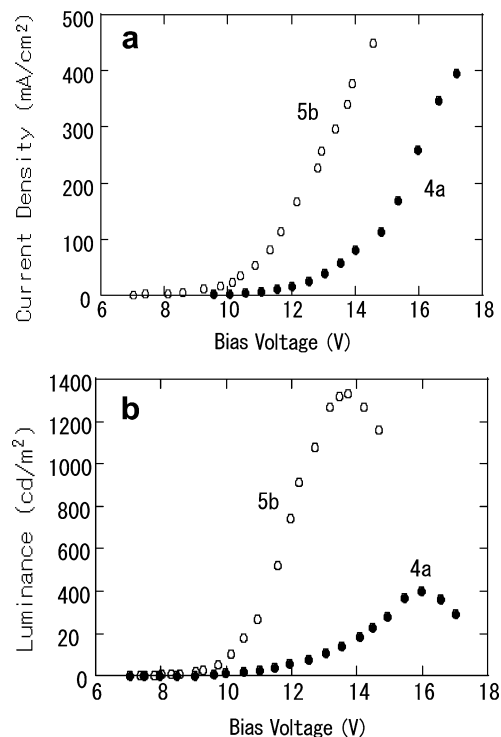


Fig. 1. I–V (a) and L–V (b) plots for the devices of ITO/**4a** or **5b**/Alq<sub>3</sub>/Mg–Ag.

m<sup>2</sup>, respectively, than the device fabricated with **4a**. In both cases, the current density increased along the applied voltage, while the luminance profile involved maximum points. This seems to indicate that the devices were not completely damaged by applying high voltage, but the interface structure, probably that of polymer/Alq<sub>3</sub>, changed depressing the carrier blocking. The I–V characteristics of the device fabricated with polymer **5b** exhibited a turn-on voltage of approximately 9 V, which is slightly inferior to that of a similar device having a hole-transporting film of diethynylanthrylene-containing polymer **6a** shown in Chart 2, but comparable to those of the devices fabricated with polymer **6b** and PVK, a typical hole-transporting material [5a]. We also fabricated single-layered devices with **4a** and **5b** (ITO/polymer spin-coated film/Mg–Ag), but observed no emission from them.

In conclusion, we prepared naphthylene- and anthrylene-containing organosilicon polymers. In contrast to our

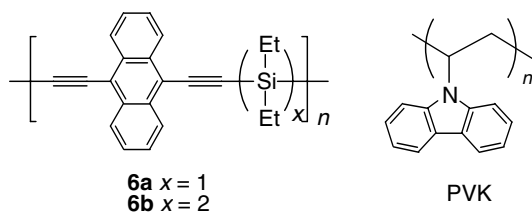


Chart 2.

expectations, none of these polymers showed electroluminescence properties in single-layered devices, but polymers **4a** and **5b** were found to be usable as hole-transporting materials in multi-layered EL device systems.

### 3. Experimental

#### 3.1. General procedure

All reactions were carried out in dry nitrogen. DMF was dried over  $\text{CaH}_2$  and distilled immediately before use. Di(bromothieryl)- [7] and di(bromophenyl)silanes [3e] were obtained as reported in the literature.

#### 3.2. Preparation of stannyl compounds

For the preparation of stannyl compounds, the corresponding bromides were lithiated with *n*-butyllithium in ether and the lithiated thienyl- and phenylsilanes were treated with tributyltin chloride. After filtration of the lithium salts and evaporation of the solvent, the residue was heated at 250 °C for 4 h under reduced pressure (ca. 1 mmHg) to remove volatile substances. The resulting viscous oil was used for the following coupling reactions without further purification.

#### 3.3. Model reactions

A mixture containing 90 mg (0.20 mmol) of **1a**, 34 mg (0.10 mmol) of 2-tributylstannyl-5-trimethylsilylthiophene, 6 mg (5 mol%) of  $\text{Pd}(\text{PPh}_3)_4$ , and 1 mg (5 mol%) of  $\text{CuI}$  in 2 mL of DMF was heated at 80 °C for 5 days. The resulting mixture was poured into 100 mL of 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 the solvent was evaporated, the residue was subjected to chromatography on a silica gel column with hexane as eluent to give 38 mg (78% yield) of **3a** as a yellow solid: mp 259 °C;  $^1\text{H NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 0.32 (s, 18H), 7.12 (d, 2H, thiophene,  $J = 3.3$  Hz), 7.22 (d, 2H, thiophene,  $J = 3.3$  Hz), 7.63 (dd, 4H, anthracene,  $J = 3.3, 7.0$  Hz), 8.58 (dd, 4H, anthracene,  $J = 3.3, 7.0$  Hz); UV ( $\lambda_{\text{max}}$  in THF) 261 nm ( $\epsilon = 101,000$ ), 362 (6200), 380 (13,800), 401 (14,600). Anal. Calc. for  $\text{C}_{28}\text{H}_{34}\text{S}_2\text{Si}_2$ : C, 69.08; H, 6.21. Found: C, 68.90; H, 6.16%.

The reaction of **1a** with 1-tributylstannyl-4-trimethylsilylbenzene was carried out in a similar fashion to that above. Data for **3b**: 34% yield; sublimation point 292 °C;  $^1\text{H NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 0.39 (s, 18H), 7.32 (dd, 4H, anthracene,  $J = 3.1, 6.8$  Hz), 7.46 (d, 4H, phenylene,  $J = 7.7$  Hz), 7.70 (dd, 4H, anthracene,  $J = 3.1, 6.8$  Hz), 7.74 (d, 4H, phenylene,  $J = 7.7$  Hz); UV ( $\lambda_{\text{max}}$  in THF) 262 nm ( $\epsilon = 98,500$ ), 358 (5,500), 376 (11,800), 396 (11,500). Anal. Calc. for  $\text{C}_{32}\text{H}_{34}\text{Si}_2$ : C, 80.95; H, 7.22. Found: C, 79.95; H, 7.27%. Combustion elemental analysis of this compound always afforded carbon content less than the calculated value. This disagreement may arise from its being hardly combustible. Combustion with an oxidizing agent under oxygen-rich conditions improved the results slightly, but still gave unsatisfactory results. The pale gray color of the ash obtained by the analysis seemed to indicate that trace carbon was present in the ash.

#### 3.4. Synthesis of di(bromothieryl)anthracene

A mixture of 3.70 g (11.0 mmol) of 9,10-dithienylanthracene [8], 3.85 g (21.6 mmol) of NBS, 150 mL of chloroform, and 150 mL of acetic acid was refluxed for 10 h. The resulting mixture was washed with water several times and was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column with hexane/benzene = 4/1 as eluent to give 2.70 g (50% yield) of **1c** as a light yellow solid: mp 290–291 °C; MS  $m/z$  498 ( $\text{M}^+$ );  $^1\text{H NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 6.96 (d, 2H,  $J = 3.6$  Hz), 7.27 (d, 2H,  $J = 3.6$  Hz), 7.44 (q, 4H,  $J = 3.1, 6.8$  Hz), 7.92 (q, 4H,  $J = 3.1, 6.8$  Hz);  $^{13}\text{C NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 113.1, 126.1, 126.4, 129.5, 130.0, 130.1, 131.3, 140.5. Anal. Calc. for  $\text{C}_{22}\text{H}_{12}\text{Br}_2\text{S}_2$ : C, 52.82; H, 2.42. Found: C, 52.82; H, 2.49%.

#### 3.5. Polymer synthesis

A mixture containing 0.143 g (0.500 mmol) of **1b**, 0.442 g (0.500 mmol) of **2a-Bu**, 29 mg (5 mol%) of  $\text{Pd}(\text{PPh}_3)_4$ , and 5 mg (5 mol%) of  $\text{CuI}$  in 10 mL of DMF was heated at 60 °C for 50 h. The resulting mixture was poured into 100 mL of water and extracted with chloroform. The organic layer was separated and washed several times with 10% hydrochloric acid. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue was subjected to reprecipitation from chloroform–methanol and then from chloroform–hexane to give 0.168 g (78% yield) of **4a** as a pale gray solid:  $^1\text{H NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 0.93–1.57 (m, 18H), 7.40 (d, 2H, thienylene,  $J = 2.9$  Hz), 7.48 (d, 2H, thienylene,  $J = 2.9$  Hz), 7.52 (br dd, 2H, naphthylene H on C5 and C8,  $J = 3.2, 6.2$  Hz), 7.63 (br s, 2H, naphthylene H on C2 and C3), 8.34 (dd, 2H, naphthylene H on C6 and C7,  $J = 3.2, 6.2$  Hz);  $^{13}\text{C NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ) 13.79, 14.60, 25.91, 26.59, 126.2, 126.5, 127.5, 129.0, 132.0, 132.7, 136.2, 136.4, 147.9; UV ( $\lambda_{\text{max}}$  in THF) 233 nm ( $\epsilon = 45,100$ ), 338 (21,900). Anal.

Calc. for  $(C_{26}H_{28}S_2Si)_n$ : C, 72.17; H, 6.52. Found: C, 69.52; H, 6.37%.

Polymers **5a** and **5b** were prepared in a similar fashion to that above. They were purified by reprecipitation from chloroform–methanol. Data for **5a**: dark green solid;  $^1H$  NMR ( $\delta$  in  $CDCl_3$ ) 0.88–1.50 (m, 39.2H), 7.08–7.56 (m, 1.6H, thienylene), 7.27–7.37 (m, 8.0H, thienylene), 7.43 (br s, 4H, anthrylene), 8.00 (br dd, 4H, anthrylene,  $J = 6.6, 3.0$  Hz);  $^{13}C$  NMR ( $\delta$  in  $CDCl_3$ ) 14.11, 14.70, 22.61, 23.67, 31.41, 33.19, 124.1, 125.2, 125.3, 125.9, 126.4, 126.7, 129.8, 130.5, 131.4, 135.0, 137.0, 138.1, 138.8, 143.2, some signals due to terminal groups may also be included; UV ( $\lambda_{max}$  in THF) 261 nm ( $\epsilon = 94,500$ ), 330 (38,900), 384 (23,300), 403 (26,200). Anal. Calc. for  $(C_{42}H_{42}S_4Si)_{3.7}(C_{20}H_{32}S_2Si)_{0.9}(C_{44}H_{84}S_2SiSn_2)_{0.1}$ : C, 70.62; H, 6.42. Found: C, 62.61; H, 6.16%. Data for **5b**: yellowish green solid;  $^1H$  NMR ( $\delta$  in  $CDCl_3$ ) 0.86–1.38 (m, 41.2H, Hex), 7.18–7.76 (m, 13.6H), 7.53–7.66 (m, 4H, anthrylene), 7.97–8.06 (m, 4H, anthrylene);  $^{13}C$  NMR ( $\delta$  in  $CDCl_3$ ) 12.62, 14.11, 22.61, 23.74, 31.45, 33.45, 123.3, 125.0, 125.8, 126.4, 126.7, 127.7, 130.7, 131.4, 134.8, 135.3, 135.6, 136.1, 138.5, 145.8, some signals due to terminal groups may also be included; UV ( $\lambda_{max}$  in THF) 262 nm ( $\epsilon = 97,000$ ), 299 (34,400), 382 (19,600), 403 (21,800). Anal. Calc. for  $(C_{46}H_{46}S_2Si)_{6.3}(C_{24}H_{36}Si)_{0.6}(C_{48}H_{88}SiSn_2)_{0.4}$ : C, 78.67; H, 7.08. Found: C, 74.36; H, 6.68%. The lower carbon contents determined by combustion elemental analysis of the present polymers than the theoretical values may be due to their being hardly combustible, similar to the case of compound **3b**.

### 3.6. Preparation of EL devices

A thin film (ca. 70 nm) of polymer **4a**, **5a**, or **5b** was prepared by spin coating from chloroform solution on an anode, an indium–tin–oxide (ITO)-coated glass plate (Nippon Sheet Glass Co.). An electron-transporting-emitting layer was then prepared by vacuum deposition of Alq3 at  $1 \times 10^{-5}$  torr to a thickness of 60–70 nm on the polymer film. Finally, a layer of magnesium–silver alloy with an atomic ratio of 10:1 was deposited on the Alq3 layer surface as the top electrode at  $1 \times 10^{-5}$  torr.

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