

## Graphical Abstract

Oxidative homo-coupling of 2,6-bis(tributylstannyl)dithienosiloles afforded poly(dithienosilole-2,6-diyl)s as novel polythiophene derivatives with intrachain silicon bridges, which exhibited red-shifted UV absorption maxima, as compared with those of silole-free polythiophenes. Alternate copolymers also were prepared by cross-coupling reactions of 2,6-dibromodithienosiloles with distannylthiophene or bithophene. Applications of the resulting polymers to electroluminescence devices and a field effect transistor were also studied.

# Synthesis of Silicon-Bridged Polythiophene Derivatives and Their Applications to EL Device Materials

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**ABSTRACT:** Palladium-catalyzed oxidative homo-coupling of 2,6-bis(tributylstannyl)dithienosiloles with CuCl<sub>2</sub> afforded poly(dithienosilole-2,6-diyl)s as novel polythiophene derivatives with intrachain silicon bridges, which exhibited red-shifted UV absorption maxima by about 100 nm from those of the corresponding silole-free polythiophenes. Alternate copolymers also were prepared by palladium-catalyzed cross-coupling reactions of 2,6-dibromodithienosiloles with distannylthiophene or bithophene. These polymer films were applied to single and double-layered organic electroluminescence devices. It was found that some of the resulting polymers exhibited electroluminescence properties and emitted red light in EL devices with the structure of ITO/polymer/Mg-Ag. Introducing an electron-transporting Alq<sub>3</sub>

layer between the polymer film and the Mg-Ag cathode led to remarkable improvement of the device performance. An application of the copolymer to a field effect transistor was also studied.

**Key Words:** Polythiophene; Silole; Electroluminescence; Stille reaction

## INTRODUCTION

Polythiophenes are of importance as functionality materials such as carrier transporting materials and emissive materials. Many efforts to control the polythiophene properties by introducing functional side groups have been made. Recent example includes the synthesis of polythiophenes bearing bi(thienylvinylene)<sup>1</sup> and quarteraniline<sup>2</sup> side groups, which were shown to be usable as photovoltaic materials and to undergo site-specific doping, respectively. Introduction of nitrogen bridges between the adjacent bithiophene units, forming bithiophene-condensed pyrrole rings (dithionopyrrole), has been also studied, and it was demonstrated that the bridge led to reduced polymer band gaps and enhanced emission quantum yields.<sup>3</sup>

Some years ago, we have demonstrated that similar intramolecular bridging of bithiophene unit at the  $\beta,\beta'$ -position by a silicon linkage enhances the conjugation of the resulting dithienosilole unit (DTS).<sup>4-6</sup> This is not only due to coplanarity of the two thiophene rings fixed by the bridge, but also to the electronic effect of the silicon  $\sigma^*$ -orbital that interacts with the  $\pi^*$ -orbital of the bithiophene unit to lower the LUMO energy level.<sup>4</sup> The low-lying LUMO makes it possible to use the DTS-based compounds as efficient electron transporting materials for multi-layered electroluminescence (EL) device systems. In fact, the device with the structure of ITO/TPD/Alq3/**DTSPy2**/Mg-Ag (for **DTSPy2**, see Chart 1), where TPD (N,N'-diphenyl-N,N'-di(*m*-tolyl)biphenyl-4,4'-diamine) and Alq3 (tris(8-quinolinolato)aluminum (III) complex) layers were a hole-transport and an emitter, respectively, emitted a strong green light with the maximum luminance of 16 000 cd/m<sup>2</sup>.<sup>6</sup>

We have been interested also in introducing the DTS skeleton into the backbone<sup>7,8</sup> or side chain<sup>9</sup> of polymeric systems. Very recently, we found that electro polymerization of **DTSSi2**

gave polymers in good yield (Scheme 1).<sup>10</sup> In this polymerization, however, decomposition of the silole unit always competed the polymerization to an extent, giving partially decomposed poly(dithienosilole-2,6-diyl)s (**pDTS1**). Interestingly, the polymers exhibited a red shifted absorption maximum in their UV spectra, as compared with those of simple silole-free poly(alkylthiophene)s, in spite of the existence of the decomposed units. We also prepared  $\pi$ -conjugated homo- and cooligomers containing DTS unit(s), and demonstrated that their UV absorption and emission maxima changed depending on the conjugated chain length and the structures.<sup>11</sup> Preparation and optical properties of copolymers composed of DTS and fluorenylene units have been reported by Jen et al.<sup>12</sup>

In this paper, we report oxidative Stille homo-coupling of 2,6-distannyldithienosilole (**1**), which proceeded smoothly to afford poly(dithienosilole-2,6-diyl)s. The spectral analysis of the polymers obtained under optimized conditions indicated that no significant decomposition had occurred in this polymerization. Copolymerization of dibromodithienosilole (**2**) with distannylthiophene or bithiophene derivatives,  $\text{Ar}(\text{SnBu}_3)_2$  ( $\text{Ar}$  = thienylene or bithienylene), gave the corresponding copolymers,  $(\text{DTS-Ar})_n$ . Potential utilities of the resulting homo- and copolymers as EL device materials as well as field effect transistor (FET) materials also are described.

## RESULTS AND DISCUSSION

### Synthesis of Poly(dithienosilole-2,6-diyl)s

Scheme 2 represents the synthetic route to the homopolymers, including the preparation of 2,6-bis(tributylstannyl)dithienosiloles (**1a** and **1b**) from the respective bromides (**2a** and **2b**) and their Pd-catalyzed oxidative polymerization with  $\text{CuCl}_2$ . The reactions at 0°C for 24 h, followed by reprecipitation of the organic products from chloroform/hexane, gave polymers **3a** and **3b**, as dark orange-red and purple solids, respectively. Yields, molecular weights, and UV absorption  $\lambda_{\text{max}}$  in THF for polymers **3a** and **3b**, obtained under various reaction conditions are listed in

Table 1. Carrying out the reactions at room temperature led to the formation of the polymers with blue-shifted absorption maxima, although the molecular weights were comparable to those obtained by the reactions at 0°C. This is indicative of that some decomposition of silole ring system would be involved in the reactions at room temperature, similar to the electro polymerization, reported previously.<sup>10</sup> Using Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst gave only low molecular weight polymers. Attempted oxidation by FeCl<sub>3</sub> and an organic reagent (ethyl 2,3-dibromo-3-phenylpronionate) afforded no polymeric substances.

The polymer structures were verified by the spectrometric analysis. As expected, polymers **3a** and **3b** prepared at 0°C exhibited red-shifted absorption maxima from that of **pDTS1**, prepared electrochemically (Scheme 1,  $\lambda_{\text{max}} = 487 \text{ nm}$ )<sup>10</sup> and regio regular poly(3-hexylthiophene) (head to tail content > 95%,  $\lambda_{\text{max}} = 458 \text{ nm}$ ). This clearly indicates the strong effects of the silicon bridge, which efficiently enhance the conjugation. However, the  $\lambda_{\text{max}}$  of **3a** was at slightly higher energy than that of **3b**. Since it is known that the substituents on the silicon atom do not considerably affect the silole electronic states,<sup>13</sup> this high energy shift may be understood by that some decomposition had been involved in the polymerization, presumably due to the oxidative cleavage of Si-thiophene bonds. Although we have not had any data to identify the structure of the decomposed parts in the polymers clearly, the fact that no absorption bands due to Si-O or O-H vibration were observed in IR spectra of the polymers seems to indicate that the decomposition would form bithiophene units. The incorporation ratios of the bithiophene units were estimated to be 10% at most for each of the polymers on the basis of the integration ratios of their <sup>1</sup>H NMR signals. However, no signals other than those expected for DTS units appeared in the <sup>13</sup>C NMR spectra, suggesting that the contents of the decomposed units in these polymers were small, if present. The molecular weight of polymer **3a** was determined to be slightly smaller than that of **3b**. For **3a**, the high-molecular weight fraction was insoluble in chloroform and was probably removed by filtration. Combustion elemental analysis of the polymers suggested the carbon contents lesser than the theoretical values. This, however,

may be due to the heat-resistant properties of the polymers. In fact, thermo gravimetric (TG) analysis of polymer **3a** in air revealed only 73% weight loss based on the initial weight at 800°C, which was too high to be ascribed only to the formation of SiO<sub>2</sub>. The residue obtained from the TG analysis was black solid, indicating the formation of carbon-containing inorganic substances. Contamination of tributystannyl units, presumably at the polymer ends, may also affect the combustion analysis. However, the Energy Dispersive X-ray Spectroscopy (EDS) analysis of a cast film of polymer **3a** indicated that the contamination was very low (Sn/S atomic ratio = ca. 1/50). The polymers were soluble in chlorocarbons, ethers, and aromatic solvents, but polymer **3a** always showed inferior solubility than **3b**. Both of the polymers were insoluble in alcohols and saturated hydrocarbons.

Polymers **3a** and **3b** showed red-shifted absorption maxima in their solid films from those in solutions, probably due to the interaction of  $\pi$ -conjugated systems in the condensed phase. Electrochemical properties of the polymers were examined by cyclic voltammograms (CVs) on their spin-coated films. The polymer films underwent irreversible oxidation at 0.39 V vs Ag/Ag<sup>+</sup>. No cathodic counterparts were observed at all, similar to simple monomeric DTS derivatives.<sup>5</sup>

### Synthesis of Copolymers

Next, we carried out copolymerization of **2a,b** with distannylthiophene or bithiophene under the Pd-catalyzed distannylhalogenative conditions (Stille-coupling) in refluxing THF (Scheme 3), and the results are summarized in Table 2.<sup>14</sup> In these reactions, using CuI as a cocatalyst is essential to obtain high molecular weight polymers. In fact, a similar reaction of **2a** and distannylthiophene in the absence of CuI resulted in the formation of a polymer only with a low molecular weight (Mw = 2500). We also examined copolymerization of **1a** with dibromothiophene and bithiophene under the same conditions. However, these reactions gave polymers with relatively low molecular weights (Mw = 4000-6200). Polymers **4b** and **5b** were soluble in chlorocarbons, ethers, and aromatic solvents, while **4a** and **5a** were slightly soluble in

these organic solvents. In order to improve the solubility, we introduced butyl groups on the thiophene and bithiophene units (polymers **6a** and **7a** in Chart 2). Polymers **6a** and **7a** showed good solubility in chloroform and THF, as expected. The structures of the present copolymers were verified mainly by the NMR spectra. Some unidentified broad and multiple signals with low intensities appeared in the aromatic CH region of the  $^1\text{H}$  NMR spectra, but all the major signals were assignable to those of the expected alternate structures.

Chloroform solutions of the present homo- and copolymers are purple to pink as the transparent colors and exhibit orange to red photoluminescence. The optical and electrochemical properties of these copolymers are summarized in Table 3. As can be seen in Table 3, the optical properties of the present polymers are considerably affected by the polymer structures. Thus, the UV absorption and emission maxima moved to shorter wavelength in the order of **3b** > **4b** > **5b**, as introducing silicon-free thiophene units into the polymer chain, indicating the electronic effects of the silole unit, which enhanced the conjugation (Figure 1). In contrast to this, the UV  $\lambda_{\text{max}}$  of polymer **3a** is at higher energy than that of **4a**. This again indicates the formation of decomposed units in the polymer chain of **3a** to an extent. The UV absorption edge ( $\lambda_{\text{edge}}$ ) of **3a** appeared at lower energy than that of **4a**, presumably reflecting the enhanced conjugation by the silicon-bridge. The emission maxima of the polymers shifted in the same order as that of the absorptions.

### **Applications of the DTS-Containing Polymers to EL Device and FET Materials**

Spin-coated films of polymers **3b**, **4b**, **6a**, and **7a** afforded red color EL in the single layered devices of ITO/polymer/Mg-Ag, although the luminance of the devices was low, which was at most  $6 \text{ cd/m}^2$  at the bias voltage of 11V for the device with polymer **4b** (Figure 2). Introducing a vapor-deposited electron-transporting tris(8-quinolinolato) aluminum (III) (Alq3) layer on the polymer film improved the device performance with polymers **6a** and **7a** (ITO/polymer/Alq3/Mg-Ag). The double layered device with **7a** gave the maximum luminance

of about 500 cd/m<sup>2</sup> at 13V (Figure 3). The light color from this double layered device was green-yellow, as the results of overlapping of the emission from both the Alq3 and polymer layers as can be seen in Figure 4. In contrast to this, a red light derived only from the polymer emission was observed for the device with **6a** (Figure 4). The double layered devices with other polymers, including **3b** and **4b**, were also fabricated. However, these devices emitted only weak lights with the luminances lesser than 10 cd/m<sup>2</sup>. We also examined the polymer films as the bottom-contact type field effect transistor (FET) materials. Of those, only polymer **3b** was found to be FET active, although the mobility was rather low ( $\mu_{\text{FET}} = 1.0 \times 10^{-7} \text{ cm}^2/\text{Vs}$ ). Presumably, two aryl substituents which cover the  $\pi$ -conjugated main chain prevent the carrier hopping between the polymer chains.

## CONCLUSION

Based on the results described above, we demonstrated that introduction of intra chain silicon bridges into polythiophene backbone forming DTS units efficiently enhances the  $\pi$ -conjugation. Copolymers composed of alternating DTS and thiophene or bithiophene units showed clear changes of the UV spectra, depending on the contents of the DTS units in the backbone. Some of the resulting polymers were found to be applicable to carrier transporting materials and emissive materials in EL device systems. The information would be useful in molecular designing of novel polythiophene-based functional materials.

## EXPERIMENTAL

### General Procedure

All reactions were carried out in dry nitrogen. THF was dried over calcium hydride and distilled under reduced pressure, which was stored over activated molecular sieves until use. Compound **2a** and 3,3'-dibromo-5,5'-bis(trimethylsilyl)bithiophene were prepared as reported in the literature.<sup>4,5</sup>



### Preparation of Bis(butylphenyl)dichlorosilane

In a 300 mL flask fitted with a dropping funnel was placed 3.5 mL (30 mmol) of tetrachlorosilane and 10 mL of THF. To this was added slowly from the dropping funnel 4-butylphenylmagnesium bromide in 60 mL of THF. The resulting mixture was heated to reflux for 5 h. The solvent was evaporated and the residue was distilled under reduced pressure to give the title compound (6.25 g, 56% yield).

Bp: 170°C (3.0 mmHg). MS (70 eV, m/z): 364 ( $M^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.92 (t, 6H,  $J = 7.09$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.31-1.42 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.54-1.66 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.63 (t, 4H,  $J = 7.59$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.26 (d, 4H,  $J = 8.22$  Hz, *m*-phenylene protons), 7.65 (d, 4H,  $J = 8.22$  Hz, *o*-phenylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 13.91, 22.35, 33.30, 35.75, 128.45, 128.96, 134.13, 146.97.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $\text{C}_{20}\text{H}_{26}\text{SiCl}_2$ : C, 65.74%; H, 7.17%. Found: C, 65.40%; H, 7.12%.

### Preparation of Bis(butylphenyl)bis(trimethylsilyl)dithienosilole

To a solution of 3.10 g (6.00 mmol) of 3,3'-dibromo-5,5'-bis(trimethylsilyl)bithiophene in 80 mL of ether was added 8.60 mL (12.0 mmol) of a 1.54 M butyllithium in hexane at -80°C and the mixture was stirred at room temperature for 1h. The mixture was again cooled to -80°C and 2.42 g (6.00 mmol) of bis(butylphenyl)dichlorosilane was added to the mixture. After stirring the mixture at room temperature for 1h, 40 mL of THF was added and the mixture was heated to reflux for 10 h. The mixture was then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extract was combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column to give 3.51 g of the crude title compound contaminated with 2-3% of an unidentified compound, which was used for the following reaction without further purification.

MS (70 eV, m/z): 602 ( $M^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.32 (s, 18H, TMS protons), 0.91 (t, 6H,  $J = 7.29$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.27-1.38 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.53-1.61 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.59 (t, 4H,  $J = 7.74$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.18 (d, 4H,  $J = 7.92$  Hz, *m*-phenylene protons), 7.28 (s, 2H, DTS protons), 7.55 (d, 4H,  $J = 7.92$  Hz, *o*-phenylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.15, 13.91, 22.39, 33.43, 35.76, 128.30, 128.99, 135.51, 136.60, 141.94, 142.32, 145.12, 155.42.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $\text{C}_{34}\text{H}_{46}\text{S}_2\text{Si}_3$ : C, 67.71%; H, 7.69% Found: C, 66.67%; H, 7.69%.

### Preparation of **2b**

To a solution of 3.50 g (5.80 mmol) of **1a** in 80 mL of ether was added 0.58 mL (11.6 mmol) of bromine at  $0^\circ\text{C}$ . After stirring the resulting mixture for 5 h, the solvent was evaporated and the residue was washed with ethanol to give analytically pure **2b** (2.90 g, 80 % yield).

Mp:  $151\text{-}152^\circ\text{C}$ . MS (70 eV, m/z): 616 ( $M^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.91 (t, 6H,  $J = 7.26$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.30-1.38 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.55-1.63 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.60 (t, 4H,  $J = 7.59$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.14 (s, 2H, DTS protons), 7.18 (d, 4H,  $J = 7.59$  Hz, *m*-phenylene protons), 7.49 (d, 4H,  $J = 7.59$  Hz, *o*-phenylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 13.90, 22.34, 33.39, 35.76, 112.20, 127.03, 128.55, 132.22, 135.33, 139.89, 145.82, 149.81.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $\text{C}_{28}\text{H}_{28}\text{Br}_2\text{S}_2\text{Si}$ : C, 54.55%; H, 4.58%. Found: C, 54.46%; H, 4.53%.

### Preparation of **1a** and **1b**

Monomers **1a** and **1b** were prepared by dilithiation of **2a** and **2b** with *n*-butyllithium in ether at  $-80^\circ\text{C}$ , followed by treatment of the resulting dilithio derivatives with 2 equiv of tributyltin chloride. The distannyl compounds, thus obtained, were used for the following polymerization without purification, after removal of volatile substances under reduced pressure ( $< 1$  mmHg) at room temperature.

### Preparation of Polymers 3a and 3b

In a 20 mL Shrenk tube was placed 0.191 g (0.200 mmol) of **1a**, 8 mg (0.02 mmol) of Pd(OAc)<sub>2</sub>, 52 mg (0.4 mmol) of CuCl<sub>2</sub>, and 2 mL of THF and the mixture was stirred at 0°C for 24 h. To this was added 5 mL of chloroform and the resulting precipitates were filtered. The solvent was evaporated and the residue was reprecipitated from chloroform/hexane to give polymer **3a** as a purple solid (30.5 mg, 41% yield).

Mp: > 300°C. GPC (THF): Mw = 8100, Mw/Mn = 1.65. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 2.35 (s, 6H, Me), 7.19-7.25 (m, 6H, DTS and tolyl *m*-protons), 7.54 (br s, 4H, tolyl *o*- protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.57, 129.10, 134.66, 135.33, other signals could not be observed due to the low solubility. E<sub>LEM</sub>. A<sub>NAL</sub>. Calcd. for (C<sub>22</sub>H<sub>16</sub>S<sub>2</sub>Si)<sub>n</sub>: C, 70.92%; H, 4.33%. Found: C, 61.30%; H, 4.37%.

Polymer **3b** was prepared in a similar method to above as a purple solid.

Mp: > 300°C. GPC (THF): Mw = 13200, Mw/Mn = 1.56. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.89-0.93 (br m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.24-1.34 (br m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.54 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.59 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.18-7.25 (m, 6H, DTS and *m*-phenylene protons), 7.55 (br s, *o*-phenylene protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 13.93, 22.36, 33.43, 35.76, 126.16, 127.87, 128.50, 134.56, 135.42, 138.94, 141.74, 145.55. E<sub>LEM</sub>. A<sub>NAL</sub>. Calcd. for (C<sub>28</sub>H<sub>28</sub>S<sub>2</sub>Si)<sub>n</sub>: C, 73.63%; H, 6.18%. Found: C, 62.33%; H, 5.67%.

### Preparation of Polymers 4a,b, 5a,b, 6a and 7a

A mixture of 0.106 g (0.2 mmol) of **2a** and equimolar amount of 2,5-bis(tributylstannyl)thiophene, prepared by the reaction of dilithiothiophene and tributyltin chloride, 12 mg (0.010 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 mg (0.01 mmol) of CuI, and 2 mL of THF was heated to reflux for 24 h. To the resulting mixture was added 5 mL of chloroform and the mixture was filtered to remove any insoluble substances. After evaporation of the solvent, the

residue was reprecipitated from chloroform/hexane to give of polymer **4a** as a blue purple solid (0.0545 g, 60 % yield).

Mp: > 300°C. GPC (THF): Mw = 8100, Mw/Mn = 1.74. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 2.35 (s, 6H, Me), 7.03 (br s, 2H, thienyl ring protons), 7.20-7.25 (m, 6H, DTS and tolyl *m*-protons), 7.56 (br d, 4H, J = 7.80 Hz, tolyl *o*-protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.64, 129.14, 135.47, other signals could not be observed due to the low solubility. E<sub>LEM.</sub> A<sub>NAL.</sub> Calcd. for (C<sub>26</sub>H<sub>18</sub>S<sub>3</sub>Si)<sub>n</sub>: C, 68.68%; H, 3.99%. Found: C, 65.01%; H, 4.08%.

Other copolymers were prepared in a similar method to above. Polymer **4b** was obtained as a purple solid.

Mp: > 300°C. GPC (THF): Mw = 9600, Mw/Mn = 1.41. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.88 (br t, 6H, J = 7.02 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.58 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.61 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.05 (br s, 2H, thienylene ring protons), 7.21-7.25 (m, 6H, DTS and *m*-phenylene protons), 7.58 (br s, 4H, *o*-phenylene protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 13.93, 22.37, 33.44, 35.78 (Bu), 123.99, 126.24, 128.50, 135.45, 145.57, other signals could not be observed. E<sub>LEM.</sub> A<sub>NAL.</sub> Calcd. for (C<sub>32</sub>H<sub>30</sub>S<sub>3</sub>Si)<sub>n</sub>: C, 71.32%; H, 5.61%. Found: C, 66.71%; H, 5.07%.

Polymer **5a** was obtained as a red purple solid.

Mp: > 300°C. GPC (THF) Mw = 9700, Mw/Mn = 1.6. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 2.35 (s, 6H, Me), 7.05 (br s, 4H, thienylene ring protons), 7.20-7.69 (m, 10H, DTS and tolyl ring protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.63, 129.16, 135.49, other signals could not be observed due to the low solubility. E<sub>LEM.</sub> A<sub>NAL.</sub> Calcd. for (C<sub>30</sub>H<sub>20</sub>S<sub>4</sub>Si)<sub>n</sub>: C, 67.12%; H, 3.76%. Found: C, 61.13%; H, 4.26%.

Polymer **5b** was obtained as a red purple solid.

Mp: > 300°C. GPC (THF): Mw = 12800, Mw/Mn = 1.68. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.87-0.94 (br m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33-1.36 (br m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.58-1.64 (br m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.61 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.09 (br s, 4H, thienylene ring protons),

7.22-7.25 (m, 6H, DTS and *m*-phenylene protons), 7.60 (br s, 4H, *o*-phenylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 13.93, 22.36, 33.44, 35.77, 124.21, 128.49, 130.77, 130.90, 134.47, 134.58, 135.45, 135.79, 145.62, other signals could not be observed.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $(\text{C}_{36}\text{H}_{32}\text{S}_4\text{Si})_n$ : C, 69.63%; H, 5.19%. Found: C, 62.78%; H, 5.08%.

Polymer **6a** was obtained as a red brown solid.

Mp: 128-130°C. GPC (THF):  $M_w = 5300$ ,  $M_w/M_n = 1.26$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.91 (br t, 6H,  $J = 7.44$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.31-1.37 (br m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.56-1.67 (br m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.35 (s, 6H, Me), 2.73 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.18-7.90 (m, 10H, DTS and tolyl ring protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 13.86, 21.64 (Me), 23.03, 28.00, 32.75, 127.66, 127.86, 128.32, 129.09, 130.77, 134.03, 134.71, 135.44, 139.97, 140.59.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $(\text{C}_{34}\text{H}_{34}\text{S}_3\text{Si})_n$ : C, 72.03%; H, 6.04%. Found: C, 64.97%; H, 5.74%.

Polymer **7a** was obtained as a red brown solid.

Mp: > 300°C. GPC (THF):  $M_w = 8000$ ,  $M_w/M_n = 1.27$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.88 (br t, 6H,  $J = 6.92$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.33 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.53 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.35 (s, 6H, Me), 2.53 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.04 (s, 2H, thienylene ring protons), 7.18-7.25 (m, 6H, DTS and tolyl *m*-protons), 7.54 (br d, 4H,  $J = 7.08$  Hz, tolyl *o*-protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 13.90, 21.55, 22.48, 28.74, 32.79, 125.05, 126.18, 127.44, 129.12, 135.36, 135.54, 136.98, 138.84, 138.97, 140.66, 141.60, 143.35.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for  $(\text{C}_{38}\text{H}_{36}\text{S}_4\text{Si})_n$ : C, 70.32%; H, 5.59%. Found: C, 65.07%; H, 5.36%.

### Fabrication of EL Devices

A thin film (30-40 nm) of the polymer was prepared by spin-coating from a solution of polymer in chloroform on an anode, indium-tin-oxide (ITO) coated on a glass substrate. An electron-transporting layer was then prepared by vacuum deposition of Alq<sub>3</sub> at  $1 \times 10^{-5}$  torr with a thickness of 50 nm on the polymer film, if required. Finally a layer of magnesium-silver alloy

with an atomic ratio of 10:1 (200 nm) and silver (100 nm) were deposited on the Alq layer surface, in this order, as the top electrode.

### **Fabrication of FET Devices**

A polymer film was prepared by spin-coating of a solution (3.6 g/L in chloroform) at 3000 rpm on doped Si wafers with a 230 nm thermally grown SiO<sub>2</sub> as the bottom contact type. The drain-source channel length and width were 10 μm and 20 mm, respectively. FET characteristics of the device were analyzed under vacuum at room temperature. The mobility was determined in the saturation regime of  $i_d$  as reported in the literature.<sup>15</sup>

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**Table 1.** Synthesis of Polymers **3a** and **3b**.

polym	cat	temp	yield/% <sup>a)</sup>	Mw <sup>a,b)</sup>	Mw/Mn <sup>a,b)</sup>	UV $\lambda_{\max}$ /nm <sup>c)</sup>
<b>3a</b>	Pd(OAc) <sub>2</sub>	0°C	41	8400	1.7	545
		rt	33	10 000	1.8	440
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	0°C	87	3500	1.1	539
		rt	88	2700	1.1	536
<b>3b</b>	Pd(OAc) <sub>2</sub>	0°C	33	13 200	1.6	561

<sup>a)</sup> After reprecipitation. <sup>b)</sup> Determined by GPC. <sup>c)</sup> In THF.

**Table 2.** Synthesis of Copolymers.

polym	yield/% <sup>a)</sup>	Mw <sup>a,b)</sup>	Mw/Mn <sup>a,b)</sup>
<b>4a</b>	60	8100	1.6
<b>4b</b>	67	9600	1.4
<b>5a</b>	44	9700	1.6
<b>5b</b>	60	12 800	1.7
<b>6a</b>	45	5300	1.3
<b>7a</b>	44	8000	1.3

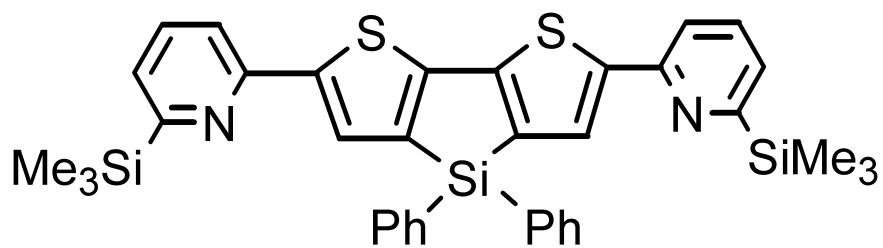
<sup>a)</sup> After reprecipitation. <sup>b)</sup> Determined by GPC.



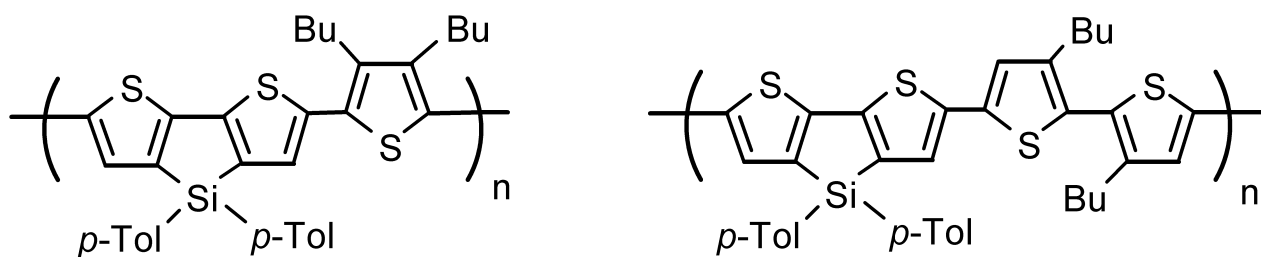
**Table 3.** Optical and Electrochemical Properties of DTS-Containing Polymers.

polym	UV $\lambda_{\max}$ /nm		$\lambda_{\text{edge}}$ /eV		emission <sup>a)</sup>	CV <sup>b)</sup>
	in THF	film	in THF	film	$\lambda_{\max}$ /nm in THF	Epa/V
<b>3a</b>	545	546	1.90	1.79	633	0.39
<b>3b</b>	561	580	1.80	1.78	641	0.42
<b>4a</b>	555	571	1.95	1.89	628	0.37
<b>4b</b>	546	565	1.88	1.84	630	0.40
<b>5a</b>	529	554	1.99	1.93	612	0.40
<b>5b</b>	532	558	1.92	1.86	611	0.42
<b>6a</b>	483	493	2.10	2.02	612	0.45
<b>7a</b>	482	490	2.12	2.04	592	0.44

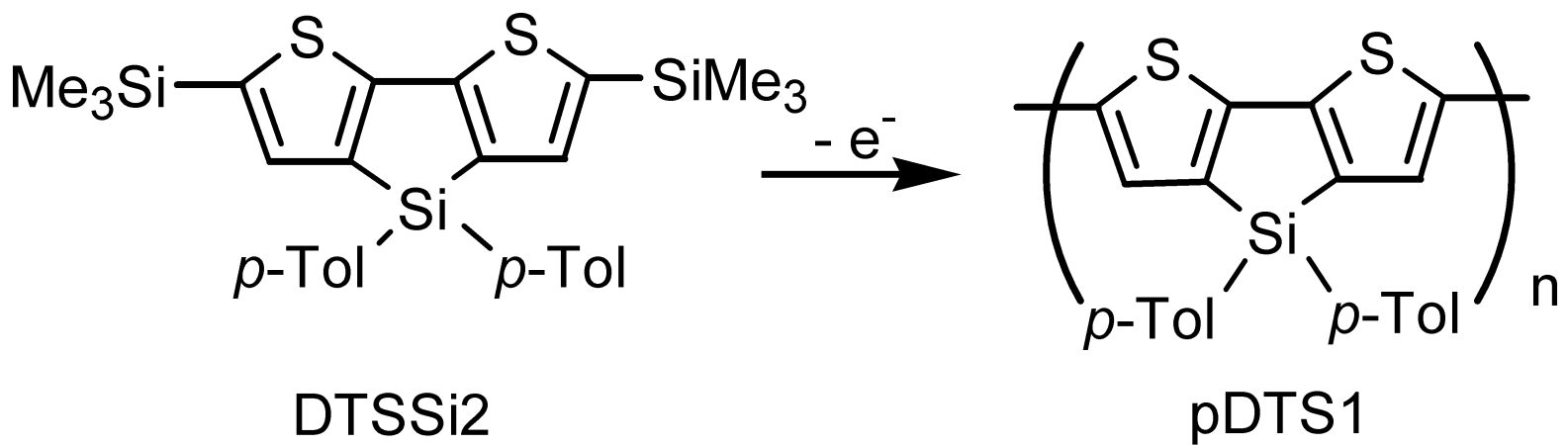
<sup>a)</sup> Excited at UV  $\lambda_{\max}$ . <sup>b)</sup> Oxidative peak potential for a polymer film on a Pt plate. The values are given versus Ag/Ag<sup>+</sup>.



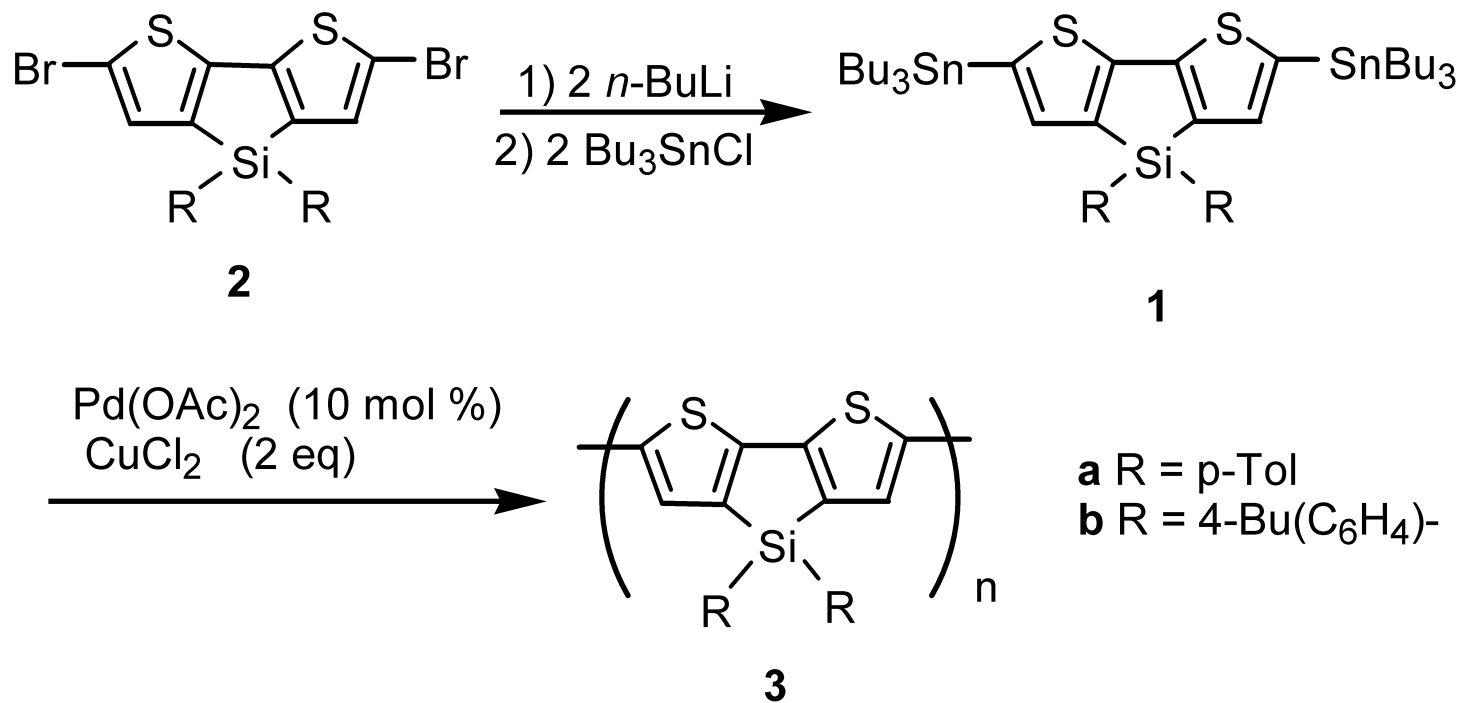
**Chart 1.** Structure of DTSPy2



**Chart2.** Structures of polymers 6a and 7a



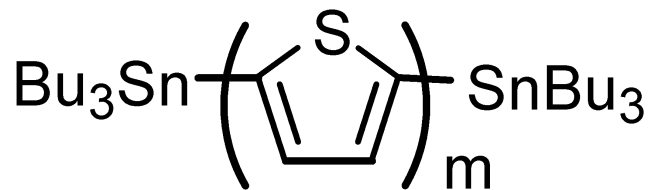
**Scheme 1.** Electro polymerization of **DTSSi2**.



**Scheme 2.** Pd-catalyzed oxidative coupling of bis(tributylstannyl)dithienosiloles.

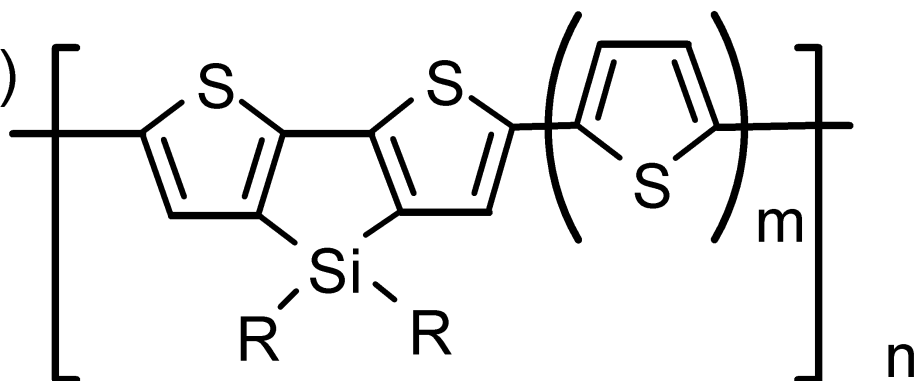
**2a and 2b**

+



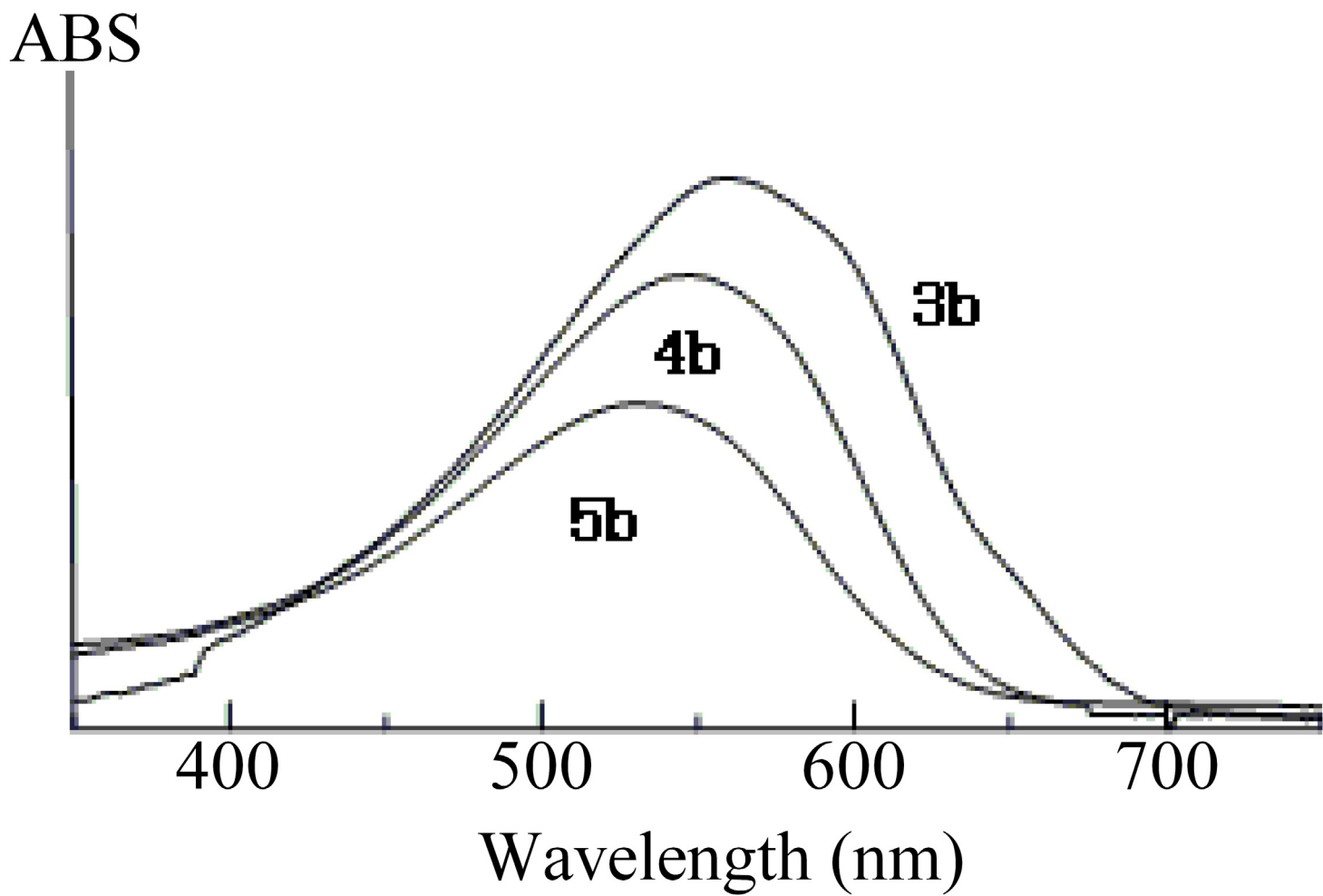
$m = 1, 2$

$\text{Pd}(\text{PPh}_3)_4$  (5 mol %)  
 $\text{CuI}$  (5 mol %)

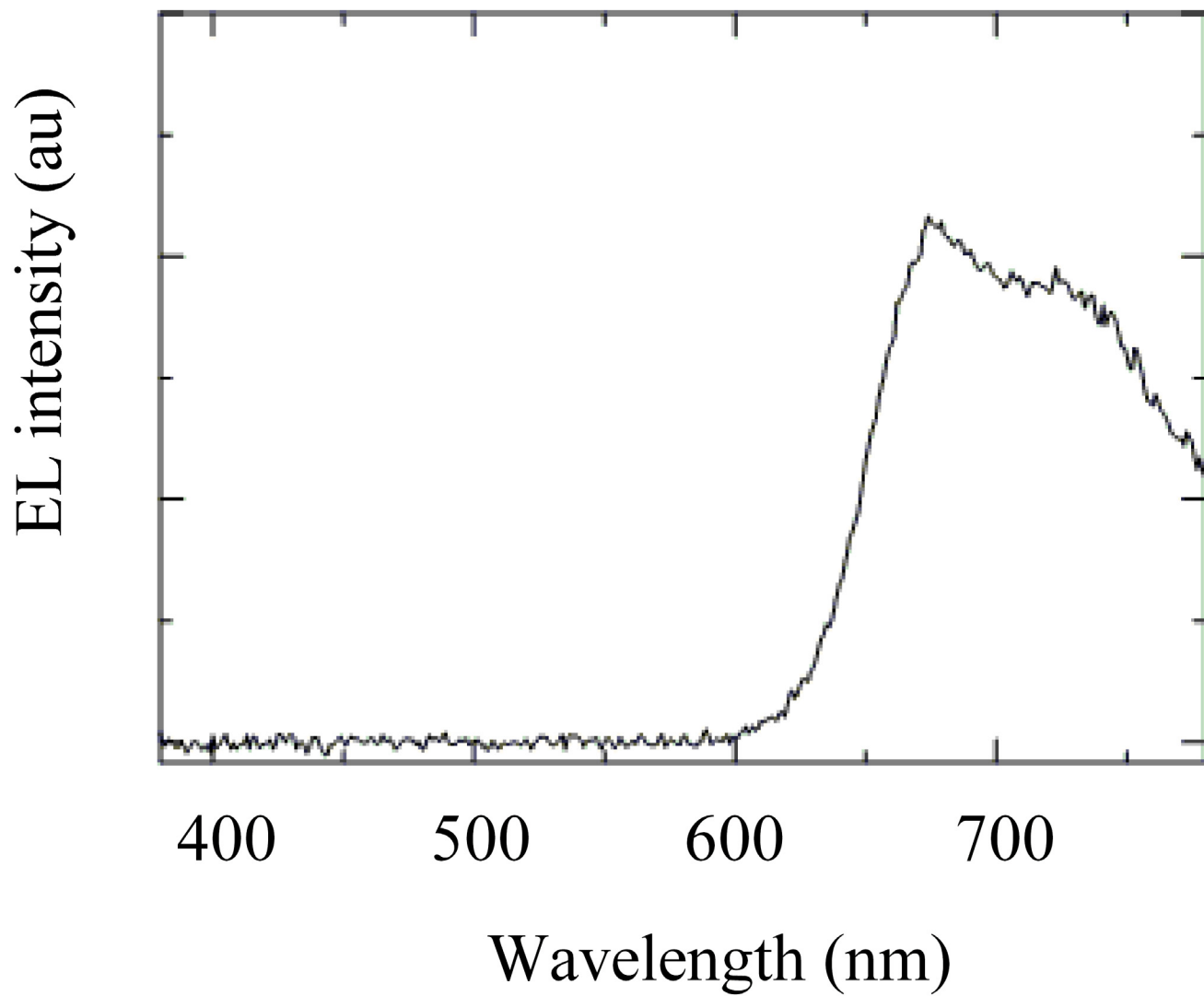


$4 m = 1$   
 $5 m = 2$

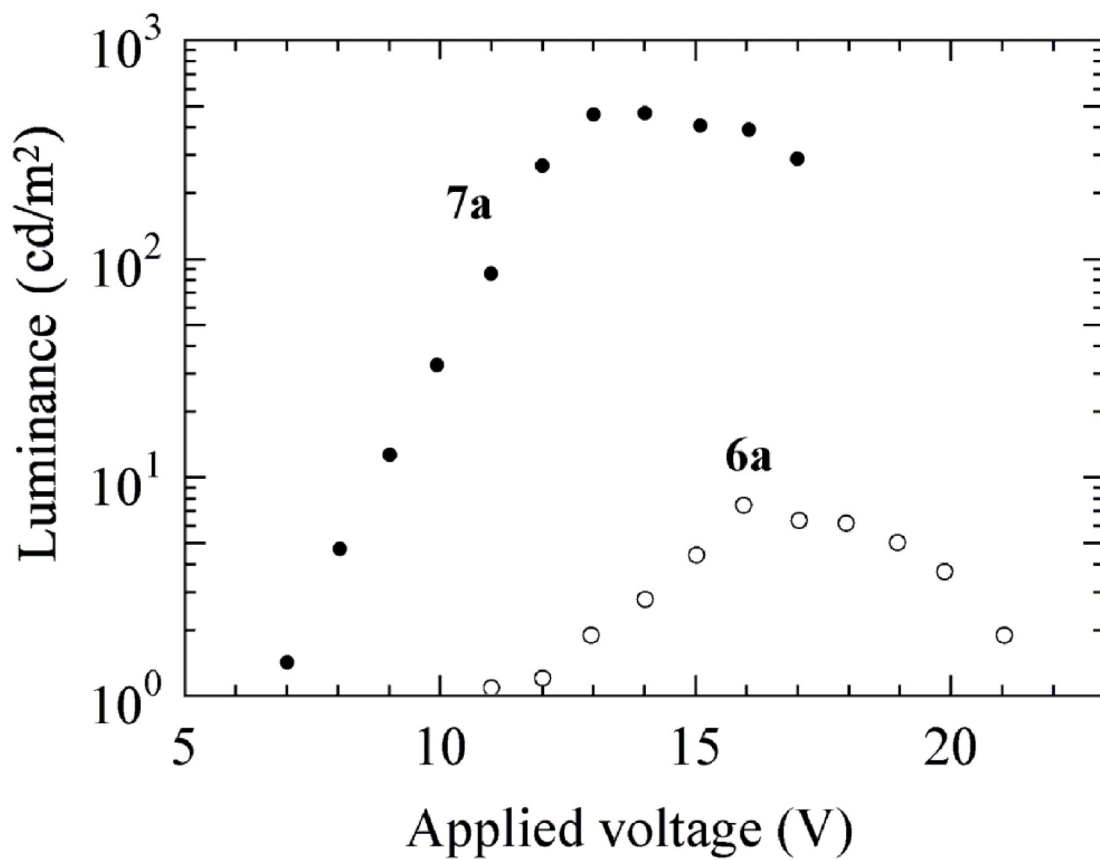
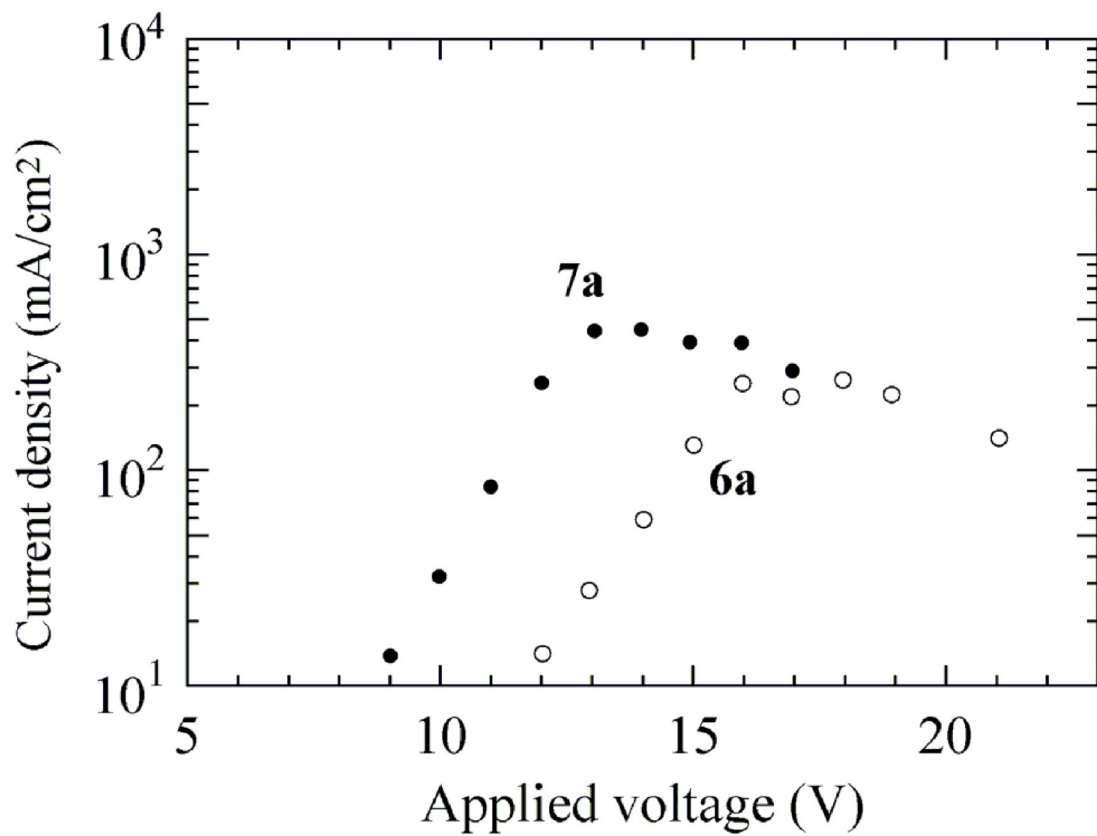
**Scheme 3.** Preparation of copolymers.



**Figure 1.** UV spectra of polymers **3b**, **4b**, and **5b** in THF.

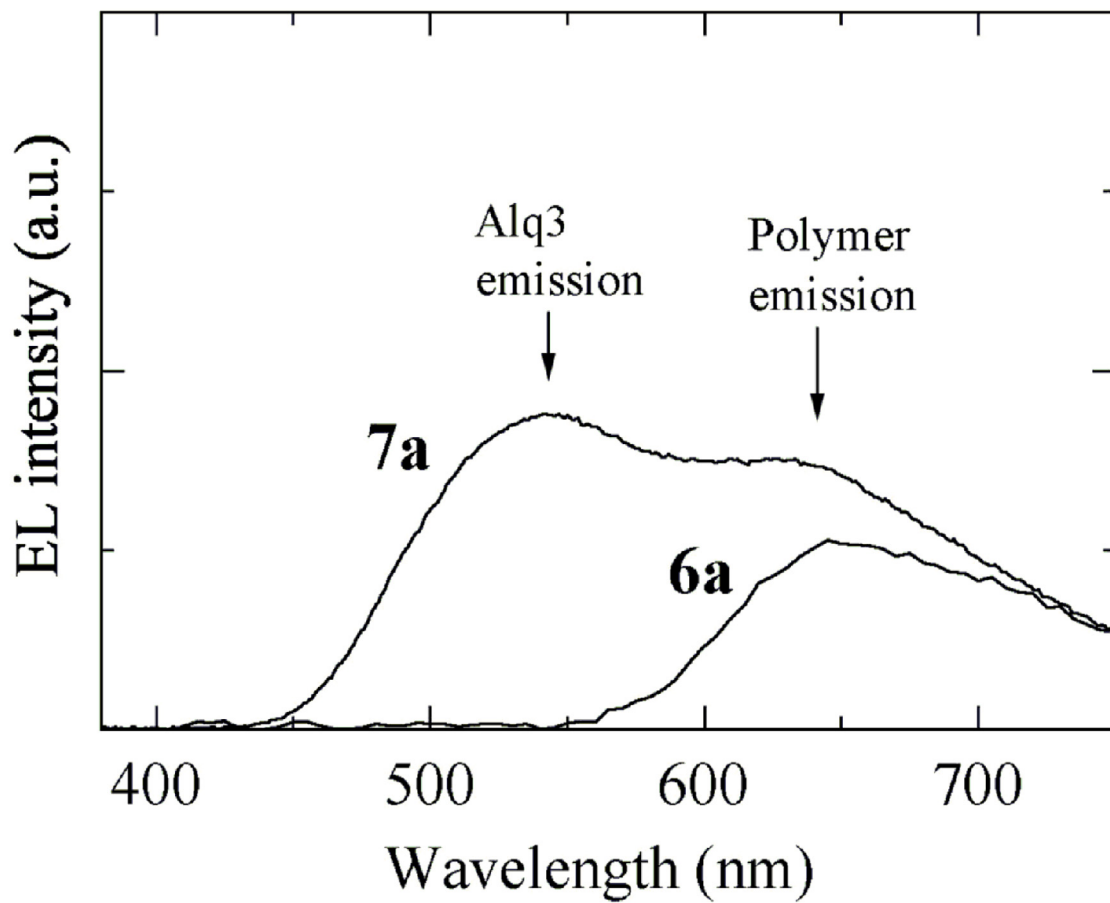


**Figure 2.** EL spectrum of the single layered devices with polymer **4b**.



**Figure 3.** Voltage-current (top) and voltage-luminance plots (bottom) for the double layered devices with **6a** and **7a**.





**Figure 4.** EL spectra of the double layered device with polymers **6a** at 13 V and **7a** at 16V.