

# Synthesis of oligomers having a pendant dithienosilole unit and their applications to EL device materials

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## Abstract

Oligomers bearing dithienosilole as a pendant were prepared by radical polymerization of the corresponding dithienosilole monomer using AIBN as an initiator. The resulting oligomers exhibited high solubility in common organic solvents and strong photofluorescences ( $\Phi = 0.72\text{--}0.76$ ) in THF which are a little higher than that of monomeric dithienosilole DTS(TMS)<sub>2</sub>. Applications of the oligomers to EL devices as hole transporting materials were examined and the maximum electroluminescence of 2140 cd/m<sup>2</sup> was obtained from a device composed of ITO/oligomer/Alq<sub>3</sub>/Mg–Ag.

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## 1. Introduction

Since Burroughes et al. [1] introduced poly(phenylene vinylene) (PPV) to organic light emitting diodes (OLEDs), various  $\pi$ -conjugated polymers have been developed and applied to electroluminescent (EL) device materials. An advantage of using polymeric materials in EL devices may arise from their readily processability for the preparation of uniform, large area, and flexible thin films by spin- or cast-coating. In addition, better morphological stability of the amorphous phase is often noted for polymeric materials as compared with monomeric compounds. However,  $\pi$ -conjugated polymer usually exhibited poor solubility in organic solvent unless long side chains are introduced to the polymers. This is due to low flexibility of their backbone. An alternative

approach to develop soluble polymeric EL device materials is obviously the construction of a flexible backbone bearing  $\pi$ -conjugated functional groups like poly(vinyl carbazole) that is known as a common hole-transporting material for EL devices [2].

We have synthesized dithienosilole (DTS, Chart 1) as a novel  $\pi$ -conjugated moiety, in which  $\beta,\beta'$ -positions of 2,2'-bithiophene are intramolecularly linked by a silylene bridge. The DTS derivatives have been studied as either electron or hole transporting materials in EL devices [3]. For example, when DTS substituted with electron deficient pyridyl groups (DTS(Pyridyl)<sub>2</sub>) was employed in an EL device with the structure of ITO/TPD/Alq<sub>3</sub>/DTS(Pyridyl)<sub>2</sub>/Mg–Ag, where TPD, Alq<sub>3</sub>, and DTS(Pyridyl)<sub>2</sub> are hole transporting, emissive, and electron transporting materials, respectively, the maximum luminance reached 16 000 cd/m<sup>2</sup>. It was also found that polymers containing DTS and organosilanylene units in the backbone as repeating components worked as efficient hole transporting materials [4].

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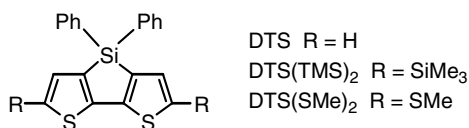


Chart 1.

In this paper, we report the synthesis of novel oligomers having a DTS unit as a pendent, which show high solubility in common organic solvents. The optical and electrochemical properties of the resulting oligomers and their applications to hole transporting materials in double-layer EL devices are described.

## 2. Results and discussion

### 2.1. Preparation of DTS-substituted oligoethylene derivatives

Scheme 1 shows the synthetic route to oligomers **1** and **2**. The monomers, vinyl-DTSs **4** and **5** were prepared in 24% and 80% yields, respectively, from the reactions between 3,3'-dilithio-5,5'-bis(trimethylsilyl)-2,2'-bithiophene with the corresponding dichlorosilanes, dichlorophenyl(*p*-vinylphenyl)silane and dichloromethylvinylsilane. Oligomerization of vinyl monomers **4** and **5** was carried out in chlorobenzene using AIBN as a radical initiator at 90 °C. The terminal point of the polymerization was determined by disappearance of the monomers via <sup>1</sup>H NMR analysis or thin layer chromatography (TLC). The resulting mixtures were reprecipitated from ethanol for oligomer **1** and methanol for oligomer **2** to afford the corresponding oligomers in 60% and 26% yields, respectively. The lower yield of oligomer **2** would result from the high solubility of lower molecular weight products even in methanol. Characterization of the resulting oligomers was carried out by the <sup>1</sup>H NMR and elemental analysis. Although <sup>1</sup>H NMR

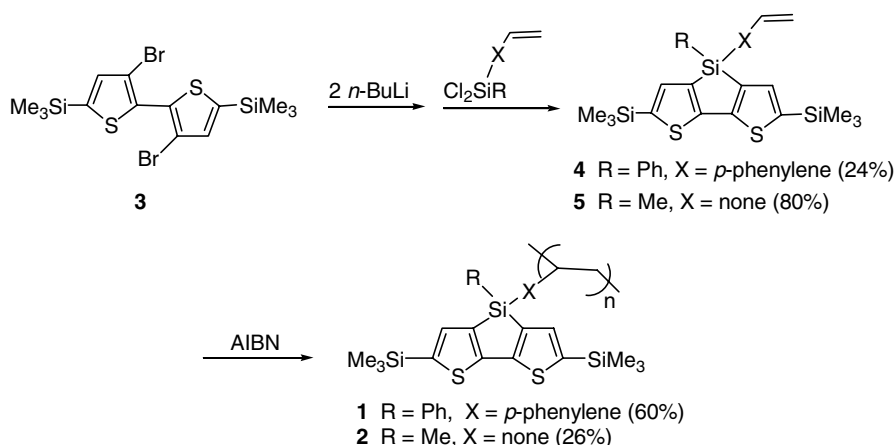
spectra of the oligomers displayed generally broad peaks for aromatic and aliphatic groups probably due to the effects of end-groups and diastereomeric environment of the backbone, <sup>1</sup>H NMR integration ratios and the data of combustion elemental analysis well agree with the proposed structures shown in Scheme 1.

### 2.2. Optical and electrochemical properties of oligo(vinyl-dithienosilole)s

Some properties of the oligomers are summarized in Table 1. Molecular weights (Mw) of the oligomers determined by GPC were 4500 (Mw/Mn = 1.12) for oligomer **1** and 3700 (Mw/Mn = 1.07) for oligomer **2**, respectively. Both oligomers showed good solubility in common organic solvents such as THF, chloroform, ether, and benzene. The UV absorption (356 nm) and emission λ<sub>max</sub> (425 nm) of oligomer **1** in THF are coincident with those of monomeric DTS(TMS)<sub>2</sub> (Chart 1). The λ<sub>max</sub> of absorption and emission for oligomer **2** shifted to higher energy regions only slightly by 3 and 5 nm from those of oligomer **1** and DTS(TMS)<sub>2</sub>, respectively, indicating that substituents on silole silicon did not exert considerable influence on the electronic states of the DTS-containing oligomers (see Fig. 1).

Both oligomers showed strong fluorescence in THF when irradiated with a UV lamp. Fluorescence quantum yields of the oligomers in solution phase were calculated using a 9,10-diphenylanthracene solution as a standard to be 0.76 for oligomer **1** and 0.72 for oligomer **2**, respectively, which are a little higher than that of DTS(TMS)<sub>2</sub> (Φ = 0.69) under the same conditions (see Table 1).

Electrochemical properties of oligomers were also studied by cyclic voltammetry (CV). For both of the oligomers, the first CV cycle revealed a sharp, irreversible oxidation peak in an anodic region, but the peak disappeared in the second cycle, showing that the oligomer



Scheme 1.

Table 1  
Properties of oligomers **1** and **2**

Oligomer	Molecular weight <sup>a</sup>		Fluorescence quantum yield ( $\Phi$ ) <sup>b</sup>	Peak potential <sup>c</sup> /V vs. Ag/Ag <sup>+</sup>
	Mw	Mw/Mn		
<b>1</b>	4500	1.12	0.76	0.96
<b>2</b>	3700	1.07	0.72	0.90

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

<sup>b</sup> Measured in THF using 9,10-diphenylanthracene as a standard.

<sup>c</sup> First oxidative potential.

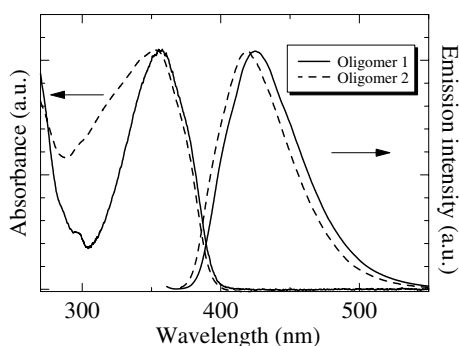
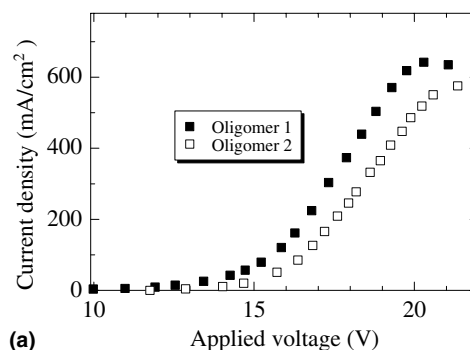


Fig. 1. UV and emission spectra of oligomers **1** and **2** in THF.

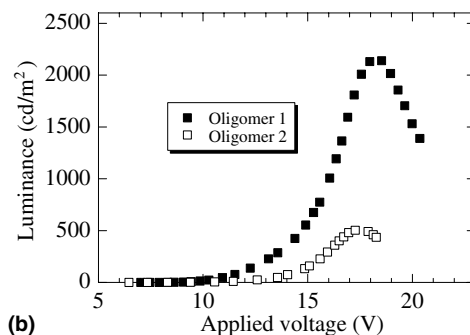
films decomposed after the first scan. The first oxidation potential of oligomer **1** is positively shifted from that of oligomer **2** but only slightly, again indicating similar electronic states of the oligomers.

### 2.3. Application of oligo(vinyldithienosilole)s to EL devices

The performance of double layer EL devices was demonstrated employing spin-coated films of oligomers **1** and **2** as the hole transporting materials. The plots of current density–voltage ( $I$ – $V$ ) and luminance–voltage ( $L$ – $V$ ) of the devices with the structure of ITO/oligomer/Alq<sub>3</sub>/Mg–Ag are summarized in Fig. 2. The maximum current densities of the devices having oligomers **1** and **2** are 640 mA/cm<sup>2</sup> at 20.5 V and 580 mA/cm<sup>2</sup> at 21.5 V, respectively. The device with oligomer **2** showed a little lower EL efficiency than that with oligomer **1**, in respect to the current density. In contrast, the luminance of the device having oligomer **1** reached 2140 cd/m<sup>2</sup> at 18.5 V, which is much stronger than that of the device having oligomer **2** (500 cd/m<sup>2</sup> at 17 V). The lower maximum luminance for the device with oligomer **2** substituted by methyl group on silole silicon would be due to the low thermal stability of the oligomer film toward the Joule heat caused by an applied voltage rather than the carrier mobility of the oligomer film. The maximum luminances of the EL devices with oligomer **1** or **2** as a hole transporting layer were larger than that of the device with monomeric DTS substituted with methylthio



(a)



(b)

Fig. 2.  $I$ – $V$  (a) and  $L$ – $V$  (b) plots of oligomers **1** and **2** in the device of ITO/oligomer/Alq<sub>3</sub>/Mg–Ag.

(MeS) groups at the  $\alpha, \alpha'$ -positions (DTS(SMe)<sub>2</sub> in Chart 1) (maximum luminance = 480 cd/m<sup>2</sup>) [5]. The external EL efficiencies of the EL devices were 0.10% for oligomer **1** at 18 V, and 0.04% for oligomer **2** at 17 V, respectively. The EL  $\lambda_{\text{max}}$  of the devices with oligomer **1** or **2** were coincident with that of the Alq<sub>3</sub> emission (Fig. 3). The single layer EL devices having the present oligomers gave no detectable luminance at all.

In conclusion, we prepared highly soluble novel oligomers having DTS as a pendent. The resulting oligomers exhibited strong photofluorescences ( $\Phi = 0.72$ – $0.76$ ) in THF. A strong luminance (2140 cd/m<sup>2</sup>) was observed from the EL device with oligomer **1** as a hole transporting material.

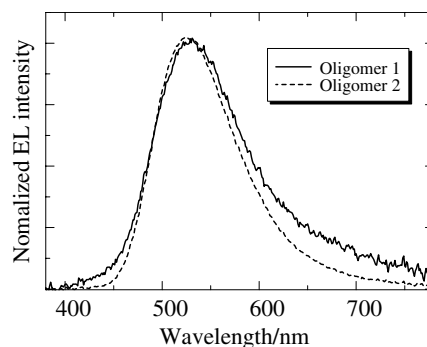


Fig. 3. EL spectra of the devices having oligomer **1** at 18 V or **2** at 17 V as a hole transporting layer.

### 3. Experimental

#### 3.1. General

All reactions were carried out under a dry nitrogen atmosphere. THF and ether were distilled from sodium–potassium alloy before use. Acetonitrile was dried over P<sub>2</sub>O<sub>5</sub>. NMR spectra were recorded on JEOL Model JNM-EX 270 and JEOL Model JNM-LA 400 spectrometers. Mass spectra were measured on a Hitachi M80B spectrometer. UV–Vis spectra were measured with a Hitachi U-3210 spectrophotometer, and emission spectra were recorded on a Shimadzu RF5000 spectrophotometer. IR spectra were measured with a Shimadzu FTIR Model 8700 spectrometer.

#### 3.2. Preparation of dichlorophenyl(*p*-vinylphenyl)silane

To a mixture of 1.05 g (43.20 mmol) of magnesium in 15 mL of THF was added 5.78 g (41.70 mmol) of 4-chlorostyrene slowly at room temperature. After refluxed for 3 h the resulting solution containing the Grignard reagent was transferred to a solution of 8.82 g (41.70 mmol) of PhSiCl<sub>3</sub> in 30 mL of ether at 0 °C. After the mixture was stirred overnight at room temperature, 100 mL of dry *n*-hexane was added to the mixture, then the mixture was filtered to remove MgCl<sub>2</sub>. After organic solvents were removed with rotary evaporation, the residue was distilled to give 47.60 g (41%) of dichlorosilane as colorless liquid. MS *m/z* 278 (M<sup>+</sup>); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 5.36 (d, 1H, *J* = 10.8 Hz, vinyl proton), 5.85 (d, 1H, *J* = 17.5 Hz, vinyl proton), 6.74 (dd, 1H, *J* = 10.8 and 17.5 Hz, vinyl proton), 7.44–7.53 (m, 5H, *m*- and *p*-Ph, and phenylene protons), 7.70–7.75 (m, 4H, *o*-Ph and phenylene protons); <sup>13</sup>C NMR (δ in CDCl<sub>3</sub>) 116.18, 126.03, 128.33, 131.11, 131.75, 131.98, 134.05, 134.39, 136.16, 140.77 [6].

#### 3.3. Preparation of **4**

To a solution of 3,3'-dilithio-5,5'-bis(trimethylsilyl)-2,2'-bithiophene prepared from the reaction of 1.00 g (2.13 mmol) of **3** and 2.70 mL (2.27 mmol) of a 1.58 M *n*-butyllithium/hexane solution in 15 mL of ether at –80 °C was added 0.59 g (2.13 mmol) of dichlorophenyl(*p*-vinylphenyl)silane at the same temperature. After the reaction temperature was raised to room temperature, 10 mL of THF was added. The reaction mixture was heated to reflux for 3 h, then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic extracts were combined and dried with MgSO<sub>4</sub>. The solvent was removed with rotary evaporation, and the residue was chromatographed on a silica gel column with *n*-hexane as an eluent to afford 0.26 g (24%) of **4** as pale yellow powder: m.p. 72–75 °C; MS *m/z* 516 (M<sup>+</sup>); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>)

0.33 (s, 18H, –SiMe<sub>3</sub>), 5.27 (d, 1H, *J* = 10.8 Hz, vinyl proton), 5.77 (d, 1H, *J* = 17.6 Hz, vinyl proton), 6.70 (dd, 1H, *J* = 10.8 and 17.6 Hz, vinyl proton), 7.28 (s, 2H, thiophene protons), 7.35–7.44 (m, 5H, *m*- and *p*-Ph, and phenylene protons), 7.60 (d, 2H, *J* = 8.0 Hz, phenylene protons), 7.65 (dd, 2H, *J* = 1.5 and 7.3 Hz, *o*-Ph); <sup>13</sup>C NMR (δ in CDCl<sub>3</sub>) 0.12, 114.87, 125.87, 128.12, 130.20, 131.66, 132.15, 135.45, 135.72, 136.44, 136.63, 139.29, 141.68, 142.24, 155.56; <sup>29</sup>Si NMR (in CDCl<sub>3</sub>) –6.70, –27.20. Anal. Calc. for C<sub>28</sub>H<sub>32</sub>S<sub>2</sub>Si<sub>3</sub>: C, 65.06; H, 6.24. Found: C, 65.10; H, 6.11%.

#### 3.4. Preparation of **5**

Compound **5** was prepared as described for **4** by using dichloromethylvinylsilane as a reactant: m.p. 61–63 °C; MS *m/z* 378 (M<sup>+</sup>); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 0.32 (s, 18H, –SiMe<sub>3</sub>), 0.50 (s, 3H –SiMe), 5.95 (s, 1H, *J* = 4.4 and 19.3 Hz, vinyl proton), 6.11 (1H, *J* = 4.4 and 14.4 Hz, vinyl proton), 6.20 (1H, *J* = 14.4 and 19.3 Hz, vinyl proton), 7.16 (s, 2H, thiophene protons); <sup>13</sup>C NMR (δ in CDCl<sub>3</sub>) –5.65, 0.10, 133.68, 135.27, 136.35, 141.64, 143.05, 154.97; <sup>29</sup>Si NMR (δ in CDCl<sub>3</sub>) –6.87, 19.80. Anal. Calc. for C<sub>17</sub>H<sub>26</sub>S<sub>2</sub>Si<sub>3</sub>: C, 53.91; H, 6.92. Found: C, 53.92; H, 6.82%.

#### 3.5. Preparation of oligomer **1**

To a solution of 0.100 g (0.193 mmol) of **4** in 0.10 mL of chlorobenzene was added 8.70 mg (0.053 mmol) of AIBN. After stirred at 90 °C for 20 h, the resulting mixture was reprecipitated twice from ethanol to give 60 mg (60%) of **1** as gray powder; m.p. 190–194 °C; <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 0.18 (s, 18H, –SiMe<sub>3</sub>), 0.43–1.80 (br, 3H, aliphatic protons), 6.28–7.73 (br, 11H, thiophene, phenyl, and phenylene protons). Anal. Calc. for (C<sub>28</sub>H<sub>32</sub>S<sub>2</sub>Si<sub>3</sub>)<sub>*n*</sub>: C, 65.06; H, 6.24. Found: C, 64.62; H, 6.46%.

#### 3.6. Preparation of oligomer **2**

Oligomer **2** was synthesized by the same method as described for oligomer **1** (26% yield): gray powder; m.p. 212–217 °C; <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) –0.60–0.43 (br, 21H, –SiMe and –SiMe<sub>3</sub>), 0.59–1.65 (br, 3H, aliphatic protons), 6.55–7.35 (br, 2H, thiophene protons). Anal. Calc. for (C<sub>17</sub>H<sub>25</sub>S<sub>2</sub>Si<sub>3</sub>)<sub>*n*</sub>: C, 53.91; H, 6.92. Found: C, 53.94; H, 6.98%.

#### 3.7. CV measurements

The CV measurements were carried out in acetonitrile using Ag/Ag<sup>+</sup> as a reference electrode, an oligomer-coated ITO glass as a working electrode, and a Pt wire as the counter electrode, respectively. The current–voltage curve was recorded at room temperature on a Hokuto Denko HAB-151 potentiostat/galvanostat.

### 3.8. Fabrication of EL devices

An oligomer solution (3.6 g/L in benzene) was spin-coated on an ITO electrode at the rate of 3000 rpm to give the film thickness of 30 nm, and then Alq<sub>3</sub> (an emissive layer) and Mg–Ag (a cathode) were deposited at  $1 \times 10^{-5}$  Torr on the spin-coated oligomer layer step by step with the thicknesses of 60 and 170 nm respectively.

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