

Synthesis and Properties of Bis(methylthio)dithienosilole and Its Oxides

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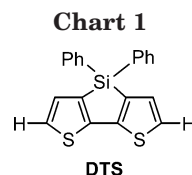
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A dithienosilole (DTS) possessing methylthio (SMe) groups at the α, α' -positions of the thiophene rings was prepared. The electronic states were tunable by oxidation of the sulfur atoms of DTS(SMe)₂ with the corresponding amount of *m*CPBA, giving DTS(SOMe)₂ or DTS(SO₂Me)₂, and the UV absorption and fluorescence maxima shifted to higher energy regions by oxidation. DTS(SMe)₂ and the oxides were also examined with cyclic voltammetry, which showed a reversible two-step oxidation for DTS(SMe)₂. A polymer having DTS and sulfide as repeating units was prepared, and its properties were examined. We found that DTS(SMe)₂ and poly(DTS sulfide) are potentially useful as hole-transporting materials in electroluminescence (EL) devices. The structure of DTS(SMe)₂ was identified by X-ray crystallography.

Introduction

Silole-based π -conjugated compounds have received considerable attention, due to the unique optical and electrochemical characteristics of silole, presumably derived from the $\sigma^*-\pi^*$ interaction between a silicon atom and the butadiene fragment.^{1,2} Research on the functionalities of silole-containing monomeric and polymeric materials has been carried out.²

Recently, dithienosilole (DTS; Chart 1), in which the 3,3'-positions of 2,2'-bithiophene are linked by a silylene unit to form a silole-fused tricyclic system, has been prepared, and its applications to EL devices as electron-transporting and emissive materials have been examined.³ Of those, DTS species having electron-withdrawing pyridyl groups at the α, α' -positions (dipyridylDTS) exhibited good electron-transporting properties in its



film and the EL device composed of ITO/TPD/Alq₃/dipyridylDTS/Mg–Ag emitted a high luminance of 16 000 cd/m².^{3c} In addition, the vacuum-deposited film of DTS substituted with a tricyanoethenyl group at the α -position showed vapor-chromic behaviors upon contact with organic solvent vapors.⁴ Thus, by employing specific substituents on the DTS moiety, the properties of DTSs should be tunable, giving unique functionalities of DTS.

It was previously reported that substitution of α -oligothiophenes with strongly electron donating arylthio groups at the α, α' -positions induced red shifts of the absorption maxima, relative to the signals of their parents, due to conjugative overlap of the sulfur lone pair orbitals with the oligothiophene chromophore increasing the HOMO energy levels of the oligothiophenes.^{5a} Also, introduction of alkylthio groups at the α, α' - or β, β' -positions of oligothiophenes improved electrochemical stability, showing two reversible oxidation peaks in the cyclic voltammograms due to the formation of cation radicals and dications.⁵

In this paper, we report the preparation of a new DTS substituted with methylthio groups at the α, α' -positions, DTS(SMe)₂ (**2**), and its electronic and electrochemical properties as well as an X-ray structure. We also show

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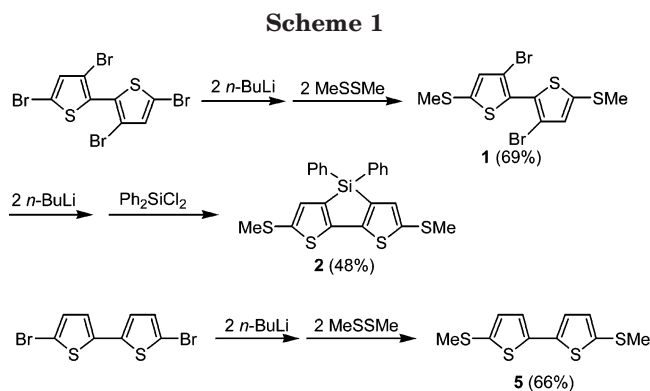
(1) (a) Tamao, K.; Yamaguchi, S.; Shozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867. (b) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715. (c) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 4552. (d) Kanno, K.-I.; Ichinohe, M.; Kabuto, C.; Kira, M. *Chem. Lett.* **1998**, 99. (e) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327. (f) Yamaguchi, S. *Synth. Met.* **1996**, *82*, 149. (g) Hong, S. Y.; Song, J. M. *Chem. Mater.* **1997**, *9*, 297.

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that tuning of electronic transitions (λ_{\max}) is possible by step-by-step oxidation of methylthio groups of **2**, affording DTS(SOMe)₂ (**3**) and DTS(SO₂Me)₂ (**4**). In addition, the preparation and properties of polymer **9** having DTS and sulfide as repeating components are described. Finally, EL device performance using **2** and polymer **9** as hole-transporting materials is introduced.

Results and Discussion

Synthesis and Oxidations of DTS(SMe)₂ (2). 3,3'-Dibromo-5,5'-bis(methylthio)-2,2'-bithiophene (**1**) was obtained in 69% yield from the reaction of 2 equiv of dimethyl disulfide and 3,3'-dibromo-5,5'-dilithio-2,2'-bithiophene, prepared from lithiation of 3,3',5,5'-tetrabromo-2,2'-bithiophene. The reaction of dichlorodiphenylsilane and 3,3'-dilithio-5,5'-bis(methylthio)-2,2'-bithiophene obtained from **1** afforded 2,6-bis(methylthio)-4,4'-diphenyldithienosilole (DTS(SMe)₂, **2**) in 48% yield. From a similar reaction, bis(methylthio)-2,2'-bithiophene (BT(SMe)₂, **5**) was obtained in 66% yield from 5,5'-dibromo-2,2'-bithiophene, as shown in Scheme 1.

Oxidation of bis(methylthio) compounds **2** and **5** was carried out as shown in Scheme 2. Compound **2** was oxidized with 2 and 4 equiv of *m*CPBA in CH₂Cl₂ at room temperature to afford the corresponding oxides **3** (82%) and **4** (66%), respectively. Similar to this, oxides **6** (87%) and **7** (61%) were prepared from **5**. Oxidation of **2** and **5** with excess *m*CPBA (8 equiv) under the same oxidation conditions as above again gave oxides **4** and **7**. No formation of any thiophene oxides was detected.⁶

Optical and Electrochemical Properties of DTS(SO_xMe) (x = 0–2). Table 1 summarizes the optical and electrochemical properties of compounds **2–7** and polymer **9**. Introduction of methylthio groups on the α,α' -

Table 1. Results of UV and CV Measurements for Compounds 2–7 and Polymer 9

compd	UV ^a		emission ^a / nm	CV/V (vs Ag/Ag ⁺) ^c
	λ_{\max} / nm	ϵ/M^{-1} cm ⁻¹		
2	381	18 000	478	0.45 (<i>E</i> ^{1/2}), 0.64 (<i>E</i> ^{2/2})
3	365	16 200	436	1.12
4	354	14 100	430	1.92
5	344	26 800	427	0.52 (<i>E</i> ^{1/2}), 0.70 (<i>E</i> ^{2/2})
6	333	15 100	408	1.66
7	318	16 200	400	1.70
9	385	10 800 ^b	486	1.04 ^d

^a In THF. ^b Based on the monomer unit. ^c In an acetonitrile solution containing 100 mM of LiClO₄ as the supporting electrolyte and 2 mM of the substrate at a scan rate of 100 mV/s. ^d In an acetonitrile solution containing 100 mM of LiClO₄ as the supporting electrolyte and a spin-coated polymer on an ITO working electrode at a scan rate of 100 mV/s.

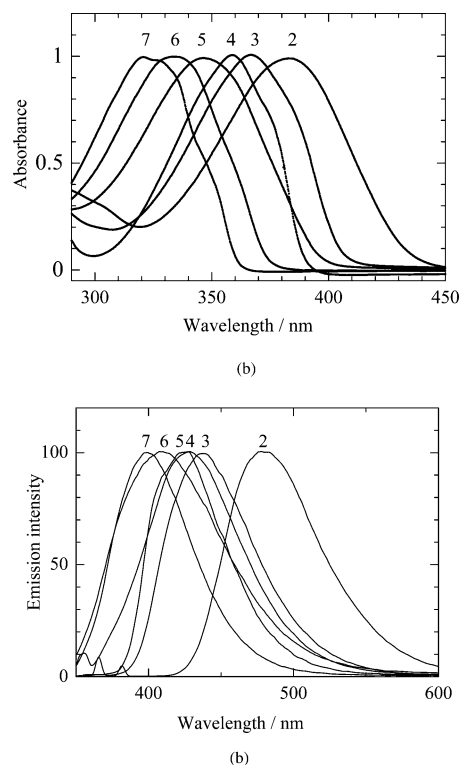


Figure 1. UV and emission spectra of compounds **2–7** in THF.

positions of DTS led to a red shift of the absorption maximum by 25 nm relative to unsubstituted DTS ($\lambda_{\max} = 356$ nm; see Chart 1),^{3a} indicating that a substitution effect of SMe groups lowers the HOMO–LUMO band gap of the molecule. As DTS(SMe)₂ (**2**) was oxidized leading to **3** and **4**, the UV λ_{\max} values shifted to higher energy regions by 16 and 27 nm, respectively. The UV λ_{\max} values of the bithiophene systems **5–7** also shifted in a fashion similar to that for the DTS system, and the blue shifts of emission maxima were observed by step-by-step oxidation of methylthio groups. The UV and emission spectra of compounds **2–7** in THF are presented in Figure 1. When the data of DTSs are compared with those of bithiophene derivatives, it is obvious that the silicon bridge considerably affects the electronic states to reduce the band gaps.

UV spectra of DTSs were measured in several solvents such as chloroform, ether, DMF, and ethanol to

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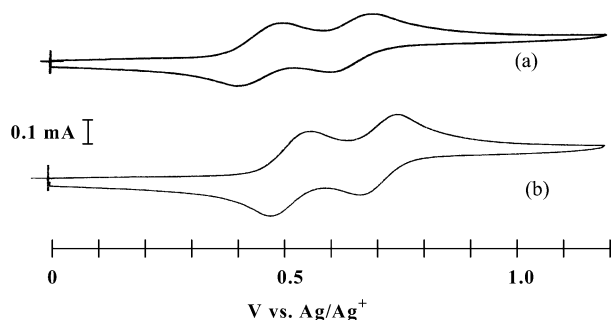


Figure 2. CV diagrams of compounds **2** (a) and **5** (b) obtained in acetonitrile.

study the solvent dependence. Among the solvents, ethanol showed interesting shifts of λ_{\max} . Thus, the λ_{\max} values of DTSs **2–4** in ethanol were blue-shifted relative to those obtained in THF. However, those shifts of **3** and **4** were found to be derived from the cleavage of the silylene bridge of DTS in ethanol to give the corresponding bithiophene derivatives, which were identified by the ^1H NMR spectra. On the other hand, DTS **2** showed a shift of λ_{\max} to a higher energy region by 16 nm in polar ethanol without structure damage, while the other solvents gave very close absorption maxima at 380 nm for chloroform, 381 nm for ether, and 382 nm for DMF. DTS **2** is stable enough toward ethanol to allow its purification through recrystallization from chloroform/ethanol (see the Experimental Section). No reaction occurred by treating **2** in boiling chloroform/ethanol in air. The weakness of the silylene unit of **3** and **4** in ethanol, therefore, may be induced by the electron deficiency of bithiophene moieties. Oxidation of SME groups, presumably, reduces the electron donation of the groups.

The cyclic voltammograms (CVs) of methylthio derivatives **2** and **5** gave two sets of reversible peaks. In contrast, oxides **3**, **4**, **6**, and **7** afforded only one irreversible oxidative peak in the anodic range. For bis(methylthio)DTS **2**, clear $E^{1/2}$ and $E^{2/2}$ values were found at 0.45 and 0.64 V vs Ag/Ag^+ in acetonitrile, respectively, while these values for bis(methylthio)bithiophene **5** were at 0.52 and 0.70 V, respectively, as shown in Figure 2, indicating that the HOMO energy level of **2** is higher than that of **5**. Although the CV oxidation potentials do not directly correlate with the HOMO energy levels, the structural similarities would permit us to estimate the relative order of HOMO energy levels of compounds by comparing their CV potentials. The loss of the lone pair electrons of the sulfur atom by oxidation gave rise to only one irreversible oxidation peak at 1.12 V for **3** and 1.66 V for **6**, respectively. Complete oxidation of sulfur atoms to bis(methylsulfonyl) species **4** and **7** shifted the oxidation CV peaks even more positively, giving irreversible peaks at 1.92 and 1.70 V, respectively. It is also meaningful to compare the CVs between DTS (Chart 1) and DTS(SMe)₂. The CV diagram of DTS gave the first oxidation peak at 0.87 V with an irreversible pattern. Thus, the introduction of electron-donating SMe groups to DTS largely stabilized the DTS system electrochemically and elevated the HOMO energy level. Decomposition of silylene bridges of DTS oxides **3** and **4** by the supporting electrolyte LiClO_4 was not observed by NMR investigations, unless an electric charge was supplied.

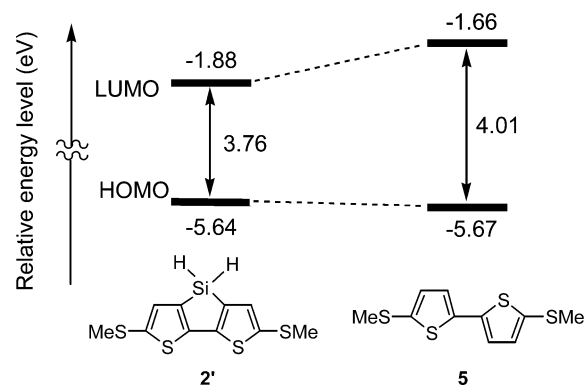


Figure 3. Relative HOMO and LUMO energy levels of **2'** and **5**.

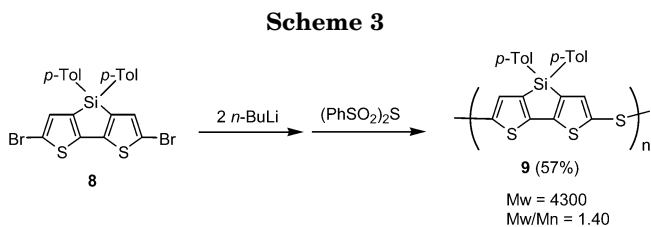


Figure 3 shows the energy diagrams of model compounds **2'** and **5**, derived from molecular orbital (MO) calculations at the level of B3LYP/6-31G^{**}.⁷ The calculations demonstrate that the existence of the silylene unit significantly lowers the LUMO energy by 0.22 eV from that of **5**. This is probably due to the $\sigma^*-\pi^*$ interaction between the silicon atom and the bithiophene fragment, as observed for simple dithienosiloles.^{3b} In addition, the HOMO energy level of **2'** lies slightly higher, by 0.03 eV, than that of **5**. The smaller HOMO–LUMO energy gap and the higher lying HOMO predicted by these computational calculations are in accordance with the experimental results described above.

Preparation and Properties of Polymer 9. Polymerization between 2,6-dithio-4,4'-di-*p*-tolylDTS, prepared from 2,6-dibromo-4,4'-di-*p*-tolylDTS,^{3b} and bis(phenylsulfonyl)sulfide was carried out as shown in Scheme 3, to give polymer **9** in 57% yield with $M_w = 4300$ (PD = 1.40). In this case, we employed the *p*-tolyl group as the silole silicon substituent, which we anticipated would increase the solubility of the polymer and would help the polymer characterization by NMR spectroscopy. Oxidation of polymer **9** with 2.5 equiv of *m*CPBA afforded a poorly soluble powder, which could be assigned to the corresponding sulfoxide polymer, showing absorption peaks at 1332 and 1143 cm^{-1} ($-\text{SO}_2-$) in the IR spectrum.

UV and emission λ_{\max} values of polymer **9** in a solution and a film are summarized in Figure 4. The

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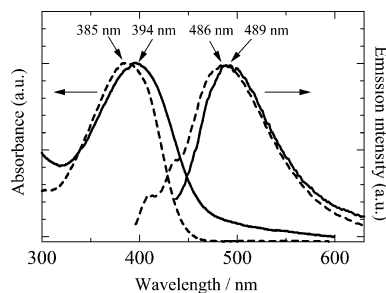
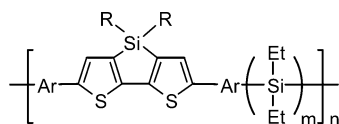


Figure 4. UV and emission spectra of polymer **9** in THF (dashed line) and in the solid state (solid line).

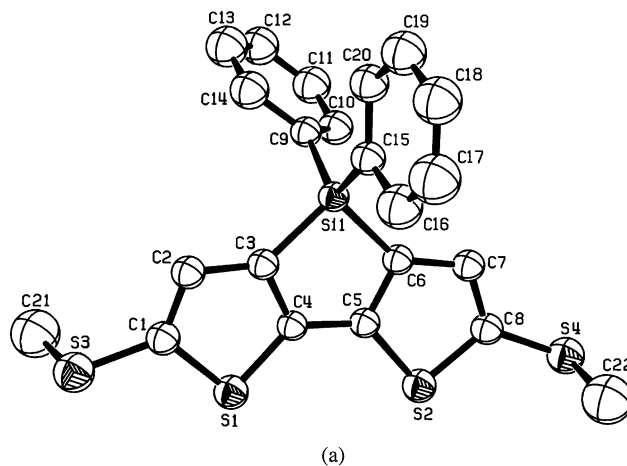
Chart 2



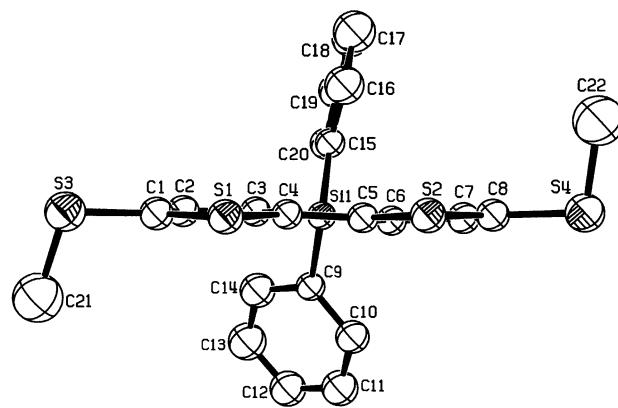
λ_{\max} values of UV absorption and emission of polymer **9** in THF were red shifted by 4 and 8 nm, respectively, relative to those of **2**, despite the fact that polymer **9** is not a fully conjugated system. A similar red shift of the UV λ_{\max} value was also reported for oligo(thienyl sulfide) species^{8a} and poly[bis((3,4-ethylenedioxy)-2-thenyl sulfide)]^{8b} relative to the corresponding monomeric model compounds, dithienyl sulfide and bis(arylthio)arene, and this was explained by intra- and/or interchain electronic coupling of π -conjugated units in the polymers. The electronic state of a spin-coated film of polymer **9** showed the λ_{\max} values in both UV and emission spectra were red-shifted from those of the solution by 9 and 3 nm, respectively.

The CV diagram of polymer **9** revealed an irreversible oxidation peak in the anodic region, different from the case of DTS(SMe)₂. The spin-coated film of polymer **9** on ITO was electrochemically unstable, showing the complete disappearance of the first oxidation peak in the second cycle (0–2.0 V vs Ag/Ag⁺). Although the first oxidation potential (1.04 V) of polymer **9** shifted to a more positive region than that of DTS(SMe)₂, it seems hard to compare the values, due to the different measurement conditions (see the Experimental Section).

When a film of polymer **9** prepared by spin casting was treated with FeCl₃ vapor as a dopant, a conductivity of 2.3×10^{-3} S/cm was achieved. This result is comparable with those of polymers composed of diaryl-substituted DTS and silicon units as repeating components (Chart 2)^{3c}. In this series, the maximum conductivity (7.0×10^{-3} S/cm) was obtained from the polymer with R = Ph, Ar = thienylene, and $m = 2$ upon doping with FeCl₃, and the values for other polymers were in the range of 5.5×10^{-4} – 3.3×10^{-5} S/cm. In comparison with the relative conjugation lengths derived from UV absorption of the polymers (λ_{\max} 420–440 nm) in Chart 2 and polymer **9** (λ_{\max} 385 nm), the relatively high conductivity of polymer **9** seems to be induced mainly by the enhanced intermolecular hopping of charge carriers rather than the movement of them along the polymer chains.



(a)



(b)

Figure 5. ORTEP drawing (50% probability ellipsoids) of **2**: (a) top view; (b) side view. Hydrogen atoms are omitted for clarity.

Crystal Structure of Compound 2. The crystal structure of **2** was determined by an X-ray single-crystal diffraction study. An ORTEP drawing of **2** is presented in Figure 5. Table 2 shows the crystal data, experimental conditions, and summary of structural refinement details for **2**, and selected bond distances and angles are given in Table 3. The dithienosilole moiety is almost coplanar, as indicated by the sums of bond angles at silole sp² carbons, which are 359.4° for C(3), 360.5° for C(4), 360.2° for C(5), and 359.8° for C(6). The two methyl groups of the methylthio moieties are placed in a trans conformation with dihedral angles of 102.8° for C(2)–C(1)–S(3)–C(21) and 76.6° for C(7)–C(8)–S(4)–C(22), respectively.

Fabrication of EL Devices with Compound 2 and Polymer 9. The high-lying HOMO energy level of **2** estimated from the electrochemical experiment (CV) and the theoretical calculations for its model compound (**2'** in Figure 3) inspired us to employ **2** as a hole-transporting material in an EL device. Polymer **9**, having DTS and sulfur as alternating components, was utilized as a hole-transporting material as well. The compositions of prepared EL devices were ITO (indium tin oxide)/**2** (40 nm)/Alq₃ (50 nm)/Mg–Ag and ITO/polymer **9** (30 nm)/Alq₃ (60 nm)/Mg–Ag, respectively, where Alq₃ (tris(8-quinolinolato)aluminum(III)) was used as an emitting electron transport layer in both devices. The plots of current density–voltage and luminance–voltage of the devices with **2** and polymer

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Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement Details for 2

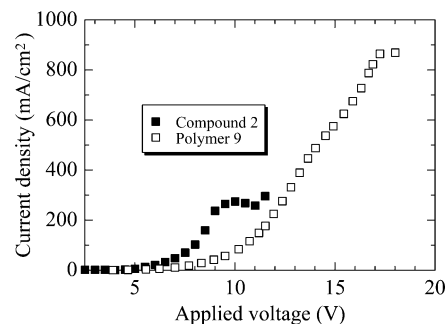
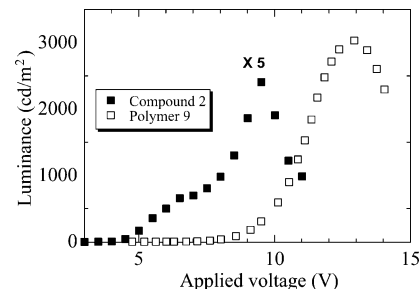
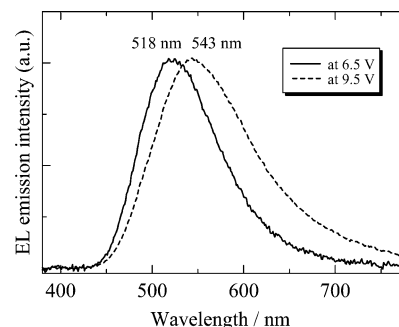
mol formula	C ₂₂ H ₁₈ S ₄ Si
mol wt	438.71
space group	P $\bar{1}$ (No. 2)
cell dimens	
<i>a</i> , Å	7.9176(5)
<i>b</i> , Å	12.0194(7)
<i>c</i> , Å	12.0845(7)
α , deg	79.475(3)
β , deg	85.387(2)
λ , deg	74.614(2)
<i>V</i> , Å ³	1089.5(1)
<i>Z</i>	2
<i>D</i> _{calcd} , g/cm ³	1.337
<i>F</i> ₀₀₀	456.00
cryst size, mm ³	0.50 × 0.30 × 0.10
cryst color	yellow
μ , cm ⁻¹	4.96
diffractometer	Rigaku RAXIS-RAPID
temp, °C	23.0
wavelength, Å	0.710 69 (Mo K α)
monochromator	graphite
no. of obsd rflns (<i>I</i> > 3 σ (<i>I</i>))	4014
<i>R</i>	0.041
<i>R</i> _w ^a	0.024

^a The weighting scheme is $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

Table 3. Selected Distances (Å) and Angles (deg) for 2 with Their Esd's in Parentheses

Si(1)–C(3)	1.868(3)	Si(1)–C(6)	1.869(4)	Si(1)–C(9)	1.864(4)
Si(1)–C(15)	1.860(4)	S(1)–C(1)	1.742(4)	S(1)–C(4)	1.725(3)
S(2)–C(5)	1.724(3)	S(2)–C(8)	1.744(4)	S(3)–C(1)	1.750(4)
S(3)–C(21)	1.780(5)	S(4)–C(8)	1.751(4)	S(4)–C(22)	1.780(5)
C(1)–C(2)	1.367(5)	C(2)–C(3)	1.423(5)	C(3)–C(4)	1.384(5)
C(4)–C(5)	1.452(5)	C(5)–C(6)	1.387(5)	C(6)–C(7)	1.417(5)
C(7)–C(8)	1.375(5)				
C(1)–S(1)–C(4)	90.7(2)	C(5)–S(2)–C(8)	90.9(2)		
C(1)–S(3)–C(21)	101.1(2)	C(8)–S(4)–C(22)	101.3(2)		
C(3)–Si(1)–C(6)	91.6(2)	C(3)–Si(1)–C(9)	109.8(2)		
C(6)–Si(1)–C(9)	114.3(2)	C(3)–Si(1)–C(15)	115.5(2)		
C(6)–Si(1)–C(15)	110.4(2)	C(9)–Si(1)–C(15)	113.5(2)		
S(1)–C(1)–S(3)	120.1(2)	S(1)–C(1)–C(2)	111.8(3)		
S(3)–C(1)–C(2)	128.1(3)	C(1)–C(2)–C(3)	113.2(3)		
Si(1)–C(3)–C(2)	140.3(3)	Si(1)–C(3)–C(4)	107.7(2)		
C(2)–C(3)–C(4)	111.4(3)	S(1)–C(4)–C(3)	112.7(3)		
S(1)–C(4)–C(5)	130.1(3)	C(3)–C(4)–C(5)	116.7(3)		
S(2)–C(5)–C(4)	131.1(3)	S(2)–C(5)–C(6)	112.8(3)		
C(4)–C(5)–C(6)	116.0(3)	Si(1)–C(6)–C(5)	108.0(2)		
Si(1)–C(6)–C(7)	140.5(3)	C(5)–C(6)–C(7)	111.3(3)		
C(6)–C(7)–C(8)	113.6(3)	S(2)–C(8)–S(4)	120.1(2)		
S(2)–C(8)–C(7)	111.3(3)	S(4)–C(8)–C(7)	128.6(3)		

9 are shown in Figures 6 and 7. The EL devices with **2** and polymer **9** emitted light with the maximum luminances of 480 cd/m² at 9.5 V and 3030 cd/m² at 13 V, respectively. The maximum current densities were 270 mA/cm² at 10 V for **2** and 870 mA/cm² at 18 V for polymer **9**, respectively. Turn-on voltages of the luminance and current density of the device having **2** are lower than those of polymer **9** by ca. 3 V. On the other hand, the maxima of the EL luminance and current density of polymer **9** are significantly higher than those of **2**; that is, polymer **9** emitted around 6 times stronger luminance than **2**. The enhanced EL properties of polymer **9** would result from the spin-coated, stable amorphous film of the polymer, which may allow us to apply high voltage. Interestingly, the device with **2** exhibited the conversion of the EL λ_{\max} value with an increase of applied voltage from 518 nm at 6.5 V to 543 nm at 9.5 V (Figure 8). The EL λ_{\max} value of 543 nm at 9.5 V was identical with that of Alq₃ emission. Since

**Figure 6.** Plots of the applied voltage vs current density derived from the EL devices ITO/**2** and polymer **9**/Alq₃/Mg–Ag.**Figure 7.** Plots of the applied voltage vs luminance derived from the EL devices ITO/**2** and polymer **9**/Alq₃/Mg–Ag.**Figure 8.** EL spectra derived from the EL device ITO/**2**/Alq₃/Mg–Ag.

the vapor-deposited film of **2** exhibited its PL λ_{\max} value at 480 nm, it may be suggested that the EL λ_{\max} value (518 nm) at lower voltages is derived from the formation of the exciplex at the interface of the **2** and Alq₃ layers. The appearance of EL spectra from the formation of exciplexes has been reported in the literature.⁹ The device using polymer **9** emitted a green EL derived from the Alq₃ layer.

Conclusions

We prepared a dithienosilole containing SME groups at the α, α' -positions. The introduction of methylthio groups to DTS clearly elevates the HOMO energy level relative to unsubstituted DTS as well as stabilizes electrochemically generated oxidation states. We also found that the absorption and emission maxima could be controllable, as the methylthio groups were oxidized step by step, leading to bis(sulfinyl)DTS (**3**) and bis(sulfonyl)DTS (**4**). The oxides obtained afforded blue

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shifts of the UV and emission λ_{max} values and irreversible oxidation profiles in CVs, different from the case for **2**. The EL devices employing **2** and polymer **9** as a hole transport material exhibited maximum luminances of 480 cd/m² at 9.5 V and 3030 cd/m² at 13 V, respectively. The EL λ_{max} value of the device using **2** shifted from 518 to 543 nm, depending on the applied voltage. It should be noted that this shift is reversible and may be potentially usable for voltage-controlled color changes, although the shift of λ_{max} in the present system was rather small.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere. THF and ether were distilled from sodium–potassium alloy before use. Dichloromethane and acetonitrile were distilled from CaH₂ and P₂O₅, respectively. 3,3',5,5'-Tetrabromo-2,2'-bithiophene was prepared as reported in the literature.¹⁰ 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.

Preparation of 1. To a solution of 6.50 g (13.4 mmol) of 3,3',5,5'-tetrabromo-2,2'-bithiophene in 100 mL of ether was added 17.0 mL (26.8 mmol) of a 1.57 M *n*-butyllithium/hexane solution at –80 °C. After the mixture was stirred for 0.5 h at –80 °C, 2.80 g (30.0 mmol) of dimethyl disulfide was added to the mixture. After it was stirred for 1 h at room temperature, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous MgSO₄, and the organic solvent was removed with rotary evaporation. The resulting mixture was chromatographed on a silica gel column with *n*-hexane as an eluent to give crude solids that were recrystallized from chloroform/*n*-hexane to afford 3.85 g (69%) of yellow solids: mp 53–55 °C; MS *m/z* 414 (M⁺); ¹H NMR (δ in CDCl₃) 2.53 (s, 6H), 6.96 (s, 2H); ¹³C NMR (δ in CDCl₃) 20.9, 111.6, 129.6, 132.2, 140.3. Anal. Calcd for C₁₀H₈Br₂S₄: C, 28.86; H, 1.94. Found: C, 28.88; H, 1.85.

Preparation of 2. To a solution of 3,3'-dilithio-5,5'-bis-(methylthio)-2,2'-bithiophene, prepared from the reaction of 0.42 g (1.0 mmol) of **1** and 1.27 mL (2.0 mmol) of a 1.57 M *n*-butyllithium/hexane solution in 15 mL of ether at –80 °C, was added 0.25 g (1.0 mmol) of dichlorodiphenylsilane at this temperature. After it was refluxed overnight, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous MgSO₄, and the organic solvent was removed with rotary evaporation. The resulting mixture was chromatographed on a silica gel column with *n*-hexane as an eluent to afford crude solids that were recrystallized from chloroform/ethanol to give 0.21 g (48%) of pale yellow crystals: mp 173–174 °C; MS *m/z* 438 (M⁺); ¹H NMR (δ in CDCl₃) 2.49 (s, 6H), 7.20 (s, 2H), 7.34–7.45 (m, 6H, *m*- and *p*-H of phenyl), 7.60 (dd, 4H, *J* = 7.9, 1.3 Hz, *o*-H of phenyl); ¹³C NMR (δ in CDCl₃) 22.77, 128.24, 130.49, 131.15, 134.43, 135.34, 138.41, 139.69, 152.27; ²⁹Si NMR (δ in CDCl₃) –19.85. Anal. Calcd for C₂₂H₁₈S₄Si: C, 60.23; H, 4.14. Found: C, 60.15; H, 4.14.

Preparation of 5. Compound **5** was prepared as described for **2** by using 5,5'-dibromo-2,2'-bithiophene in 66% yield: greenish yellow solids; mp 82–83 °C; MS *m/z* 258 (M⁺); ¹H NMR (δ in CDCl₃) 2.49 (s, 6H), 6.95 (s, 4H); ¹³C NMR (δ in

CDCl₃) 22.06, 123.74, 131.69, 136.55, 139.06. Anal. Calcd for C₁₀H₁₀S₄: C, 46.47; H, 3.90. Found: C, 46.47; H, 3.91.

Preparation of 3. To a solution of 0.0800 g (0.182 mmol) of **2** in 1 mL of dichloromethane was added 0.096 g (0.455 mmol) of *m*CPBA (80 wt %). The mixture was stirred overnight at room temperature and was poured into 50 mL of 10% aqueous NaHCO₃ and then extracted with chloroform. The extract was washed with water (50 mL \times 2) and dried over anhydrous MgSO₄. Evaporation of the solvent gave crude solids that were recrystallized from chloroform/*n*-hexane to give 0.070 g (82%) of colorless solids: mp 219–220 °C; MS *m/z* 470 (M⁺); ¹H NMR (δ in CDCl₃) 2.98 (s, 6H), 7.38 (t, 4H, *J* = 7.2 Hz, *m*-H of phenyl), 7.47 (t, 2H, *J* = 7.2 Hz, *p*-H of phenyl), 7.55–7.62 (m, 6H, *o*-H of phenyl and thiophene); ¹³C NMR (δ in CDCl₃) 44.32, 128.52, 129.18, 131.11, 132.15, 132.47, 135.32, 141.73, 153.51; ²⁹Si NMR (δ in CDCl₃) –19.47. Anal. Calcd for C₂₂H₁₈O₂S₄Si: C, 56.13; H, 3.85. Found: C, 56.11; H, 3.78.

Preparation of Oxides 4, 6, and 7. Oxides **4**, **6**, and **7** were synthesized in a fashion similar to **3** by using **2** and **5** and the corresponding amounts of *m*CPBA.

Data for **4**: 66% yield; colorless solids; mp >300 °C; MS *m/z* 502 (M⁺); ¹H NMR (δ in CDCl₃) 3.23 (s, 6H, –SMe), 7.39–7.53 (m, 6H, *m*- and *p*-H of phenyl), 7.57 (dd, 4H, *J* = 8.0, 1.4 Hz, *o*-H of phenyl); ¹³C NMR (δ in CDCl₃) 46.20, 128.38, 128.69, 131.43, 135.31, 135.86, 143.35, 144.20, 154.82; ²⁹Si NMR (δ in CDCl₃) –19.24. Anal. Calcd for C₂₂H₁₈O₄S₄Si: C, 52.56; H, 3.31. Found: C, 52.53; H, 3.59.

Data for **6**: 87% yield; colorless powders; mp 157–159 °C; MS *m/z* 290 (M⁺); ¹H NMR (δ in CDCl₃) 2.95 (s, 6H, –SMe), 7.20 (d, 2H, *J* = 3.9 Hz, thiophene), 7.39 (d, 2H, *J* = 3.9 Hz, thiophene); ¹³C NMR (δ in CDCl₃) 44.58, 124.97, 129.88, 141.04, 147.69. Anal. Calcd for C₁₀H₁₀O₂S₄: C, 41.35; H, 3.47. Found: C, 41.44; H, 3.47.

Data for **7**: 61% yield; colorless powders; mp 226–228 °C; MS *m/z* 322 (M⁺); ¹H NMR (δ in CDCl₃) 3.22 (s, 6H, –SMe), 7.27 (d, 2H, *J* = 3.9 Hz, thiophene), 7.66 (d, 2H, *J* = 3.9 Hz, thiophene); ¹³C NMR (δ in CDCl₃) 46.05, 125.87, 134.15, 142.03, 141.81. Anal. Calcd for C₁₀H₁₀O₄S₄: C, 37.25; H, 3.13. Found: C, 37.29; H, 3.03.

Preparation of Polymer 9. To a solution of 2,6-dilithio-4,4'-ditolyl-dithienosilole, prepared from 0.30 g (0.56 mmol) of 2,6-dibromo-4,4'-dithienosilole and 0.71 mL (1.12 mmol) of 1.58 M *n*-butyllithium/hexane in 10 mL of THF at –80 °C, was added 0.18 g (0.56 mmol) of 0.18 g (0.56 mmol) of bis-(phenylsulfonyl) sulfide at the same temperature. The mixture was stirred for 5 h at room temperature and was poured into 100 mL of ethanol. The precipitate was filtered and was dissolved in a minimum amount of chloroform. The solution was poured again into 100 mL of ethanol, and the precipitate was collected to give 0.13 g (57%) of polymer **9** as greenish yellow powders: *M*_w = 4290 (*M*_w/*M*_n = 1.39); ¹H NMR (δ in CDCl₃) 2.23 (s, 6H, CH₃), 7.14 (br, 4H, phenylene), 7.25 (s, 2H, thiophene), 7.46 (br, 4H, phenylene); ¹³C NMR (δ in CDCl₃) 21.61, 127.02, 128.71, 129.100, 134.65, 135.39, 136.45, 141.71, 153.26; ²⁹Si NMR (δ in CDCl₃) –19.45. Anal. Calcd for C₂₂H₁₆S₃Si: C, 65.30; H, 3.99. Found: C, 63.79; H, 4.03.

X-ray Crystallographic Analysis of 2. The structure of **2** was solved by SIR92 direct methods¹¹ and expanded using DIRDIF94 Fourier techniques.¹² Hydrogen atoms were refined using the riding model. Neutral atom scattering factors were taken from Cromer and Waber.¹³ Anomalous dispersion effects

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were included in F_c .¹⁴ The values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁵ The values for the mass attenuation coefficients are those of Creagh and Hubbel.¹⁶ All calculations were performed using the CrystalStructure^{17,18} crystallographic software package.

CV Measurements. CV measurements for **2–7** and polymer **9** were carried out using a three-electrode system in an acetonitrile solution containing 100 mM of LiClO_4 as the supporting electrolyte and Ag/Ag^+ as the reference electrode with a sweep rate of 100 mV/s. For **2–7**, 2 mM of the substrate was dissolved in acetonitrile and Pt wires were used as the

working and counter electrodes. For polymer **9**, a thin solid film of the polymer was prepared by spin coating of the polymer solution in chloroform on an ITO working electrode and a Pt wire was used as the counter electrode. The current–voltage curve was recorded at room temperature on a Hokuto Denko HAB-151 potentiostat/galvanostat.

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Supporting Information Available: A CIF file giving crystal data for **2** and UV spectra of compounds **2–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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