

Synthesis and Properties of Novel Dithienothiasiline Derivatives

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Dithienothiasiline (DTTS), in which two thiophene rings are linked by sulfur and silicon atoms at the α,α' - and β,β' -positions of the thiophenes, respectively, was prepared. From the results of optical and electrochemical experiments, it was found that the band gap and HOMO energy level became larger and lower, respectively, as the bridging sulfur atom of DTTS was oxidized step-by-step by *m*CPBA (*m*-chloroperoxybenzoic acid). DTTSs substituted with trimethylsilyl, methylthio, and thienyl groups at α,α' -positions and a polymer containing DTTS and a sulfur atom as repeating components were prepared, and their electronic and electrochemical properties were investigated. When DTTSs and poly(DTTS sulfide) were introduced as hole-transporting materials in EL devices with the structure of ITO/DTTS or polymer/Alq₃/Mg–Ag, the maximum luminance of 4280 cd/m² derived from an Alq₃ emission was achieved. A film of poly(DTTS sulfide) became conducting upon doping with FeCl₃ with a conductivity of 1.6×10^{-3} S/cm.

Introduction

Recently, bithiophene derivatives intramolecularly linked by a heteroatom have attracted much interest. In particular, those having a silicon moiety (dithienosilole, DTS)¹ or a sulfur atom (dithienothiophene; for example, DTT in Chart 1)² as the bridging unit have been well studied as functionality materials in organic electroluminescent displays (OLEDs), charge transfer (CT) complexes, thin-film transistors (TFTs), nonlinear optical (NLO) chromophores, and other fields. Also, compounds with two thiophene rings doubly bridged by two heteroatoms at the α,α' - and β,β' -positions of the thiophenes have been reported.³ Rivière et al.^{3d} reported tricyclic derivatives having a group 14 atom (Si, Ge, and Sn) (DTTM; see Chart 1) and a sulfur atom bridging at the α,α' - and β,β' -positions of two thiophenes, respectively, and their characterization. However, little is known about their functionalities.

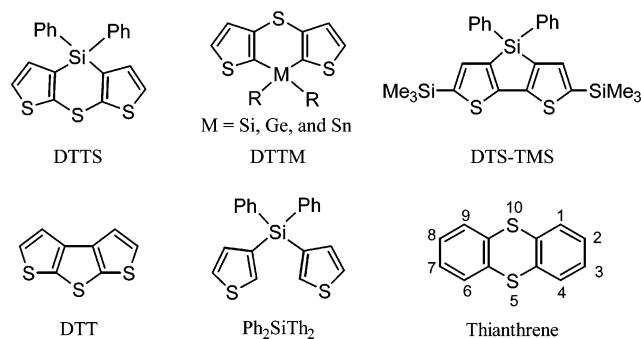
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Chart 1

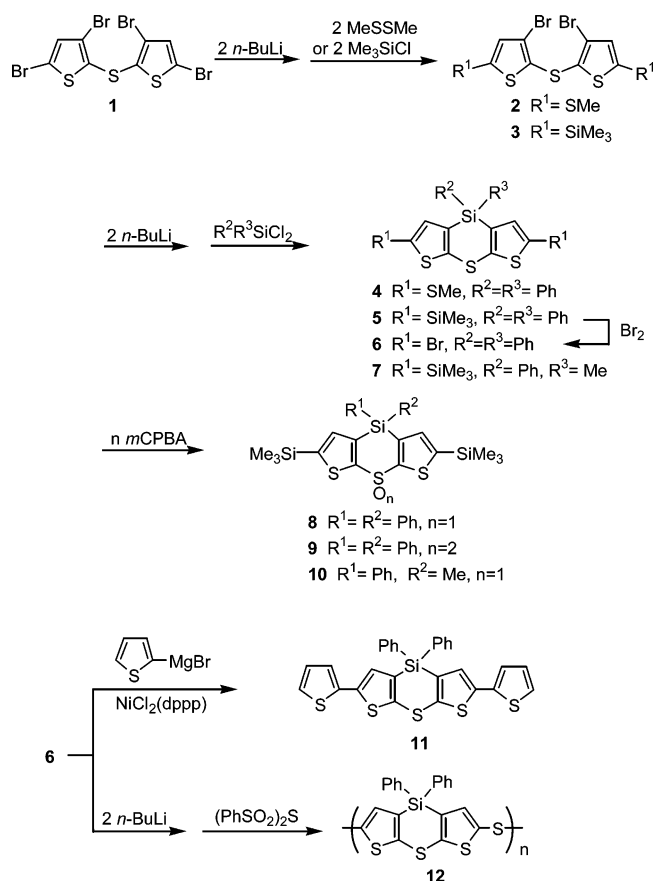


Here we report the synthesis of a new type of tricyclic system involving two thiophenes bridged by a sulfur atom at the α,α' -positions and by a silicon atom at the β,β' -positions, dithieno[2,3-*b*:3,2-*e*][1,4]thiasiline (DTTS; see Chart 1), by a novel synthetic route. DTTS derivatives substituted with trimethylsilyl, methylthio, and thienyl groups at the α,α' -positions of the thiophenes and a polymer containing DTTS and a sulfur atom as repeating components were prepared. The optical and electrochemical characteristics of DTTS derivatives and poly(DTTS sulfide) are discussed in comparison with DTTS oxides, prepared by oxidation of DTTS with *m*CPBA, and dithienosilole (DTS)^{1b} reported previously. The X-ray structure of DTTS **5** is also described. Finally, fabrication of EL devices with vapor-deposited DTTS films and a spin-coated poly(DTTS sulfide) film as hole-transporting materials and conducting and thermal properties of poly(DTTS sulfide) are introduced.

Results and Discussion

Synthesis of DTTS Derivatives. 2,2'-Bis(3,5-dibromothieryl) sulfide (**1**) was obtained in 69% yield by

Scheme 1



bromination of 2,2'-dithienyl sulfide⁴ with 4 equiv of *N*-bromosuccinimide (NBS). Reactions of 5,5'-dilithiated **1** with 2 equiv of dimethyl disulfide or trimethylsilyl chloride afforded 2,2'-bis(3-bromo-5-methylthiothienyl) sulfide (**2**; 80%) and 2,2'-bis(3-bromo-5-trimethylsilylthienyl) sulfide (**3**; 53%), respectively (Scheme 1). DTTs **4** (48%), **5** (62%), and **7** (61%) were readily prepared by ring closure reactions of 3,3'-dilithiated **2** and **3** with the corresponding dichlorosilanes. Treatment of 2,6-bis(trimethylsilyl) DTTs **5** and **7** with 1 or 2 equiv of *m*CPBA in CH_2Cl_2 afforded the monoxide **8** (64%), *S,S*-dioxide **9** (90%), and monoxide **10** (58%), respectively. The 2,6-dibromo DTTs **6** was readily prepared in 80% yield by replacement of Me_3Si groups of compound **5** with Br, by reaction with Br_2 . Successful bromination made the introduction of new substituents to DTTs and its polymerization possible. Thus, thienyl groups were readily introduced to the 2- and 6-positions of DTTs by the coupling reaction of the 2,6-dibromo DTTs **6** and thienylmagnesium bromide in the presence of a Ni catalyst, affording compound **11** in 40% yield. Polymerization between 2,6-dilithio DTTs, prepared from 2,6-dibromo DTTs, and bis(phenylsulfonyl) sulfide gave polymer **12** in 63% yield with $M_w = 5450$ (PD = 1.25).

The structures of DTTs derivatives and their oxides thus obtained were verified spectroscopically (see Experimental Section). The ^{29}Si NMR spectra of DTTs **5** revealed the ring silicon signal at -31.16 ppm, which was shifted upfield from that of Ph_2SiTh_2 (-24.15 ppm; see Chart 1). One might consider the possibility that a through-space interaction between the silicon atom and

sulfur lone pair orbital had taken place to make the coordination number of the silicon higher than 4, leading to a higher field shift of the silicon NMR signal. However, oxidation of a sulfur atom to the monoxide and the dioxide led to even larger upfield shifts of the silicon signal (-32.97 ppm for **8** and -33.77 ppm for **9**). These results clearly indicate that such an interaction was not important, if at all present, although the X-ray structure analysis of **5** (vide infra) showed an Si–S distance of 3.585(3) Å that was slightly shorter than the sum of van der Waals radii (3.90 Å). This high-field shift, therefore, is likely to be due to the ring constraint. Similar upfield shifts by ring constraints have been observed for 9,10-dihydro-9-silaanthracene derivatives^{5a} whose ^{29}Si signals appear upfield by about 10 ppm from the corresponding diphenylsilanes,^{5b} although the origins of such upfield shifts are still unclear.

Stereochemistry of DTTs Monoxides. The ^1H and ^{13}C NMR spectra of monoxide **8** indicated that the two phenyl groups attached to the bridging silicon were magnetically nonequivalent. In the ^1H NMR spectrum, the ortho proton signals of the two phenyl rings appeared at different chemical shifts, 7.50 and 7.57 ppm, respectively, with an integration ratio of 1:1 and the ^{13}C NMR spectrum gave 10 peaks (2 peaks may overlap) in the aromatic region, including those of the thiasilene ring carbons. These spectroscopic results may be derived from the fixed stereochemistry of the S=O group; that is, a conformation change of the sulfur atom does not occur on the NMR time scale. It was reported by Morita et al.⁶ that oxidation of the sulfur atom (S10) in thianthrene (see Chart 1) can be controlled stereochemically by introducing a bulky substituent on the sulfur atom (S5). We prepared thiasilene **7**, substituted with methyl and phenyl groups at the bridging silicon atom, and carried out its oxidation with 1 equiv of *m*CPBA, to examine the stereochemistry of the formation of the S=O group. However, the resulting sulfoxide was a *cis/trans* mixture in a ratio of 1:1. The lack of selectivity may be due to the fact that the steric difference between methyl and phenyl groups is not sufficient to realize it. In addition, the conformation of the thiasilene ring seems to affect the selectivity. Thus, DTTs would have a relatively planar conformation, as suggested by the optimized geometries based on MO calculations and the crystal structure of compound **5** (see below). In fact, the interplane angle of two thiophene rings in **5** is 171° and both of the the substituents on the ring silicon are too distant from the sulfur atom. In contrast, thianthrene has a butterfly-type conformation with an angle of benzene rings of 128° .⁷ This makes it possible to locate the S5 atom close to an axial substituent (S=O or *N-p*-toluenesulfonyl) on the S10 atom. The axial substituent would cover the sulfur to prevent the oxidizing reagent from approaching from this side.

Optical and Electrochemical Properties of DTTs Derivatives. Table 1 summarizes the results of UV and CV measurements and theoretical calculations for the

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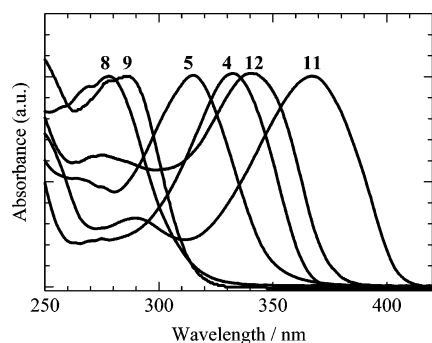
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Table 1. Results of UV and CV Measurements and Calculations for DTTs on Models

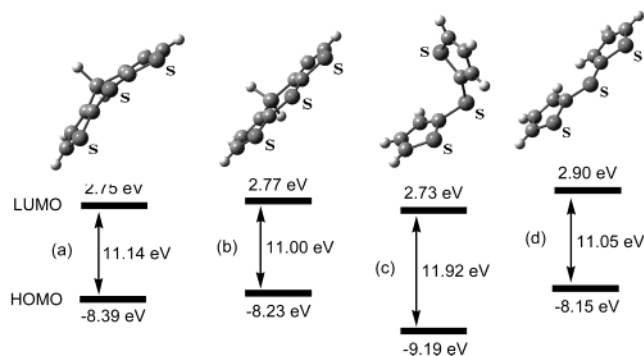
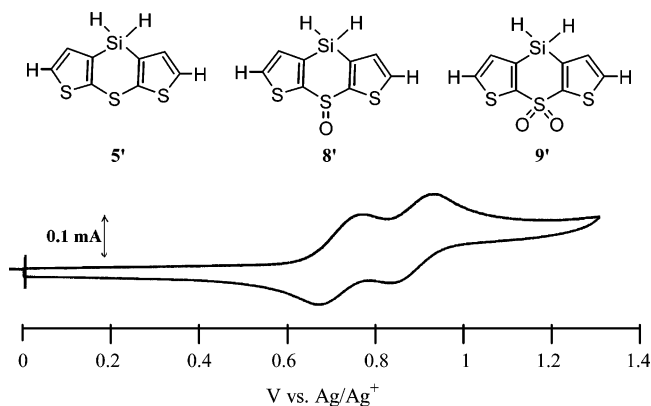
compd	UV/nm ^a		peak potential ^{b,c/} V vs Ag/Ag ⁺	calcd level/eV ^{e,f}		
	λ_{\max} (ϵ)	λ_{edge}		HOMO	LUMO	band gap
4	331 (16 800)	375	0.78			
5	318 (11 900)	370	0.91	-8.39	2.75	11.14
8	277 (18 900)	345	1.48	-9.69	1.76	11.45
9	282 (12 600)	330	1.56	-10.16	1.31	11.47
11	362 (36 700)	425	0.73 ^d			

^a In THF. ^b Determined by CV in acetonitrile containing 100 mM of LiClO₄ as the supporting electrolyte and 2 mM of the substrate at the scan rate of 100 mV/sec. ^c First oxidation potential. ^d 1 mM of the substrate was used due to low solubility in acetonitrile. ^e Carried out on models **5'**, **8'**, and **9'** (see Chart 2). ^f RHF/6-31G.

**Figure 1.** UV spectra of DTTs derivatives.

present DTTs derivatives and their models. The absorption spectra of DTTs and polymer **12** are shown in Figure 1. The UV λ_{\max} value of DTTs **5** (318 nm) was blue-shifted by 38 nm relative to that of DTS-TMS (356 nm), indicating that introduction of the sulfur atom between thiophenes negatively affects the conjugation length of the present system. However, the UV λ_{\max} value of DTTs **5** was red-shifted by about 50 and 70 nm, respectively, as compared with those of 2,2'-dithienyl sulfide (λ_{\max} 268 nm in CHCl₃)⁸ and dithieno-[2,3-*b*:3',2'-*d*]thiophene (DTT; see Chart 1) (λ_{\max} 250 nm),⁴ implying that the conjugation length was lengthened by introducing a silicon atom linking two thiophenes. When the trimethylsilyl groups of DTTs **5** were replaced with methylthio (compound **4**) and thienyl groups (compound **11**), the UV λ_{\max} values were red-shifted by 13 and 44 nm, respectively. It was also found that the UV λ_{\max} value was shifted to higher energy regions (λ_{\max} 277 nm for **8** and 282 nm for **9**), as the bridging sulfur of DTTs **5** was oxidized. The order of the calculated band gaps was in agreement with those estimated from UV λ_{edge} values. Polymer **12** showed the UV λ_{\max} at 339 nm, red-shifted by about 40 nm from that of oligo(thio-2,5-thienylenes), reported previously.⁸

To explain the role of the silicon bridge of DTTs, molecular orbital (MO) calculations based on the planar fixed and fully optimized structures of DTTs **5'** and 2,2'-dithienyl sulfide were carried out. Figure 2 shows the energy diagram of DTTs **5'** and 2,2'-dithienyl sulfide, together with their optimized geometries. The results showed that the HOMO–LUMO gap of planar fixed 2,2'-dithienyl sulfide (Figure 2d) is larger than that of a planar DTTs **5'** (Figure 2b) by 0.05 eV, whereas the

**Figure 2.** Energy diagrams of (a, b) **5'** and (c, d) 2,2'-dithienyl sulfide. Parts a and c stand for fully optimized structures and b and d for planar fixed structures.**Chart 2****Figure 3.** CV diagram of compound **4**.

planar fixed 2,2'-dithienyl sulfide gave a band gap much smaller (by 0.87 eV) than that of the fully optimized geometry (Figure 2c). These results show that the red shift of the UV λ_{\max} values for DTTs derivatives relative to 2,2'-dithienyl sulfide is mainly derived from retention of the planarity of the 2,2'-dithienyl sulfide moiety by linking with the silicon atom and less from an electronic interaction between the silicon atom and the thienyl moiety.

The cyclic voltammograms (CVs) of DTTs **5** and **11** and oxides **8** and **9** showed irreversible anodic peaks, whereas that of DTTs **4** exhibited a reversible couple. The peak potentials moved to higher voltages in the order **5** (0.91 V) < **8** (1.48 V) < **9** (1.56 V), indicating that the HOMO energy level of thiasiline **5** is lowered as the bridging sulfur is oxidized step by step, as predicted by theoretical calculations on model compounds (**5'**, **8'**, and **9'**; see Chart 2). On the other hand, the oxidation potential of thienyl DTTs **11** was lower than that of DTTs **5**, implying that π -electron substituents elevate the HOMO energy level of the DTTs system. For DTTs **4**, two pairs of reversible peaks appeared clearly at 0.72 V ($E_{1/2}^1$) and 0.92 V ($E_{1/2}^2$) in the range of 0–1.3 V (Figure 3). The electron-donating properties of methylthio groups would make the DTTs system electrochemically stable.⁹

Crystal Structure of DTTs 5. The structure of DTTs **5** was determined by an X-ray single-crystal diffraction study. The asymmetric unit has two crystallographically independent but essentially identical

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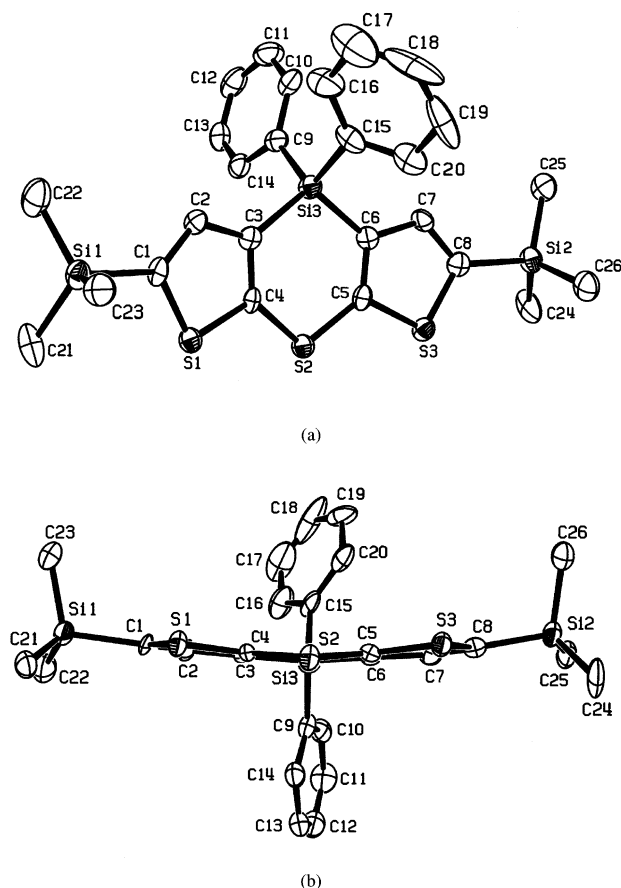


Figure 4. ORTEP drawing (50% probability ellipsoids) of compound **5**: (a) top view; (b) side view. Protons are omitted for clarity.

Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for Compound 5

mol formula	C ₂₆ H ₃₀ S ₃ Si ₃
mol wt	522.96
space group	<i>P</i> 1̄ (No. 2)
cell dimens	
<i>a</i> , Å	11.422(2)
<i>b</i> , Å	15.828(3)
<i>c</i> , Å	17.115(2)
α , deg	109.296(8)
β , deg	104.180(4)
γ , deg	93.11(1)
<i>V</i> , Å ³	2800.2(7)
<i>Z</i>	4
<i>D</i> _{calcd} , g/cm ³	1.240
<i>F</i> ₀₀₀	1104.00
cryst size, mm ³	0.50 × 0.30 × 0.10
cryst color	colorless
μ , cm ⁻¹	4.06
diffractometer	Rigaku RAXIS-RAPID
temp, °C	-150
wavelength, Å	0.710 69 (Mo K α)
monochromator	graphite
no. of unique rflns	11760
no. of obsd rflns (<i>I</i> > 3 σ (<i>I</i>))	8889
rfln/param ratio	13.93
<i>R</i>	0.071
<i>R</i> _w ^a	0.050

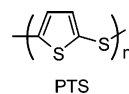
^a The weighting scheme is $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

molecules. The ORTEP drawing of one of the molecules is presented in Figure 4. Table 2 shows the crystal data, experimental conditions, and summary of structure refinement for DTTS **5**. Selected bond distances and

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 5 with Their Esd's in Parentheses

Si(3)–C(3)	1.865(6)	Si(3)–C(6)	1.869(7)	Si(3)–C(9)	1.857(7)
Si(3)–C(3)	1.865(6)	Si(3)–C(6)	1.869(7)	Si(3)–C(9)	1.857(7)
S(1)–C(1)	1.711(7)	S(1)–C(4)	1.715(6)	S(2)–C(4)	1.780(6)
S(2)–C(5)	1.753(6)	S(3)–C(5)	1.737(6)	S(3)–C(8)	1.730(7)
C(1)–C(2)	1.359(8)	C(2)–C(3)	1.419(8)	C(3)–C(4)	1.372(8)
C(5)–C(6)	1.358(8)	C(6)–C(7)	1.453(8)	C(7)–C(8)	1.396(8)
C(1)–S(1)–C(4)	91.2(3)	C(4)–S(2)–C(5)	103.2(3)		
C(5)–S(3)–C(8)	94.3(3)	C(3)–Si(3)–C(6)	104.8(3)		
S(1)–C(1)–Si(2)	118.8(4)	S(1)–C(1)–C(2)	111.1(5)		
Si(1)–C(1)–C(2)	130.0(5)	C(1)–C(2)–C(3)	114.9(6)		
Si(3)–C(3)–C(2)	127.8(5)	Si(3)–C(3)–C(4)	122.8(5)		
C(2)–C(3)–C(4)	109.4(6)	S(1)–C(4)–S(2)	114.4(4)		
S(1)–C(4)–C(3)	113.5(5)	S(2)–C(4)–C(3)	132.1(5)		
S(2)–C(5)–S(3)	116.2(4)	S(2)–C(5)–C(6)	131.5(5)		
S(3)–C(5)–C(6)	112.3(5)	Si(3)–C(6)–C(5)	124.3(5)		
Si(3)–C(6)–C(7)	126.0(5)	C(5)–C(6)–C(7)	109.7(6)		
C(6)–C(7)–C(8)	116.9(6)	S(3)–C(8)–Si(3)	123.1(4)		
S(3)–C(8)–C(7)	106.8(5)	Si(2)–C(8)–C(7)	129.7(5)		

Chart 3



angles are given in Table 3. The sums of bond angles for sp² carbons C3, C4, C5, and C6 at a thiasiline frame are all 360°. The structure of DTTS **5** is slightly folded on the Si–S center line, so that the two thiophene rings lie in two planes at an angle of 171°.

Properties of Polymer 12. It is known that some poly(arylene sulfides) yield highly conducting complexes when doped with AsF₅.¹⁰ When a film of polymer **12** prepared by spin casting was treated with FeCl₃ vapor as a dopant, a conductivity of 1.6 × 10⁻³ S/cm was achieved, which is 2 orders of magnitude higher than that of poly(thienylene sulfide) (PTS; Chart 3) doped with AsF₅ (2.6 × 10⁻⁵ S/cm).^{10c} The planarity of the DTTS unit of polymer **12** may give an increase of conductivity relative to PTS, making it easier to transfer charge carriers intramolecularly.

A CV diagram of polymer **12** revealed an irreversible oxidation peak in the anodic region, different from the case of DTTS **4**. The spin-coated film of polymer **12** on ITO (indium tin oxide) 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 (1.25 V) of polymer **12** shifted to a region more positive than that of DTTS **4**, it seems difficult to compare the values, due to the different measurement conditions (see Experimental Section).

The thermal property of polymer **12** was examined by thermogravimetric analysis (TGA) under a nitrogen atmosphere at a rate of 10 °C/min. The initial 5% weight loss (Td₅) occurred at 216 °C, and the weight loss at 1000 °C was 78% (Table 4). These values are very close to those of PTS (Td₅ = 215 °C and weight loss at 1000 °C of 80%).¹¹ However, the polymer decomposition occurred

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Table 4. Properties of Polymer 12

mol wt ^a		UV λ_{\max} / nm (ϵ) ^c	conductivity ^d (S/cm)	peak potential ^e / V vs Ag/Ag ⁺	TGA ^f	
M_w	PD ^b				Td ₅ /°C	wt loss/% ^g
5450	1.25	339 (16 100)	1.6×10^{-3}	1.25	216	78

^a Determined by GPC, relative to polystyrene standards. ^b Polydispersity. ^c In THF. ^d Doped by FeCl₃. ^e On an acetonitrile solution containing 100 mM of LiClO₄ as the supporting electrolyte and a spin-coated polymer on ITO at a scan rate of 100 mV/s. ^f Measured under N₂ at a rate of 10 °C/min. ^g Weight loss at 1000 °C.

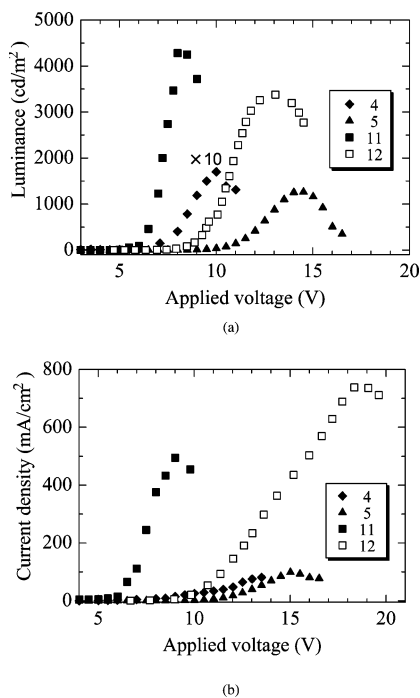


Figure 5. Plots of the applied voltage vs (a) luminance and (b) current density, derived from the EL devices, ITO/(DTTSs or polymer)/Alq₃/Mg–Ag.

in a manner different from that of PTS. For PTS, the decomposition occurred rapidly with a relatively large weight loss of 50% at 310 °C. On the other hand, for polymer **12**, the initial decomposition step was slow and the weight loss at 370 °C was only 20%. This was followed by a rapid weight loss up to 580 °C, indicating that the silicon bridge of polymer **12** plays a role in increasing the thermal stability to an extent.

Fabrication of EL Devices with DTTSs and Polymer 12. The high-lying HOMO energy level of DTTS derivatives, estimated from the electrochemical experiments and the theoretical calculations for their model compounds, inspired us to utilize them as hole-transporting materials in EL devices. Poly(DTTS sulfide) was also introduced in an EL device as a hole-transporting material. The structure of prepared EL devices that we employed was ITO/DTTS (40 nm)/Alq₃ (50 nm)/Mg–Ag and ITO/polymer (30 nm)/Alq₃ (60 nm)/Mg–Ag, where Alq₃ (tris(8-quinolinolato)aluminum(III)) was used as an emitting electron transport layer. Figure 5 summarizes the luminance–voltage and current–voltage plots of EL devices with DTTS derivatives and poly(DTTS sulfide). Of those, the EL device containing compound **11** exhibited superior results compared to the others with respect to the EL strength and the threshold voltage. The maximum luminance and current density

of the EL device with **11** were 4280 cd/m² at 8.0 V and 490 mA/cm² at 9.0 V, respectively. The EL λ_{\max} appeared at 536 nm, consistent with the Alq₃ emission. On the other hand, the devices containing DTTSs **4** and **5** showed drastic decreases of the maximum luminances and current densities, compared with those of the device with **11**. The maximum luminances of the EL devices with **4** and **5** were 180 cd/m² at 13.0 V and 1260 cd/m² at 14.5 V, respectively. Also, their turn-on voltages increased by 1.0 and 3.5 V, respectively, relative to that of **11** (5.0 V) in the plots of the applied voltage vs luminance (Figure 5). The EL device having polymer **12** afforded the sufficiently high maximum luminance of 3380 cd/m² at 13.0 V and the quite high current density of 740 mA/cm² at 18.0 V. Although the EL performance of the device with polymer **12** is inferior to that of the device containing **11** with respect to the maximum luminance and turn-on voltage, the device with **12** displayed an increase of current density up to 18 V, indicating the thermal stability of the amorphous polymer film against the Joule heat derived from the high applied voltage as compared with DTTS compounds. The higher EL efficiency of the device with **11** as compared to those of the devices having **4** and **5** could be explained by the relatively higher HOMO energy level and elongated π conjugation of **11** compared with those of **4** and **5**, as confirmed by the CV and UV absorption data described above (Table 1).

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. Methylene chloride and acetonitrile were dried over CaH₂ and P₂O₅, respectively. 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. IR spectra were measured with a Shimadzu FTIR Model 8700 spectrometer. The molecular weight of polymer **12** was determined with Shodex GPC columns, using THF as the eluent, and is relative to polystyrene standards. Bis(phenylsulfonyl) sulfide¹² and 2,2′-dithienyl sulfide⁸ were prepared as described in the literature.

Preparation of 1. To a solution of 16.5 g (83.2 mmol) of 2,2′-dithienyl sulfide⁵ in 300 mL of chloroform/acetic acid (2:1) was added 66.6 g (374 mmol) of NBS at room temperature. After being stirred overnight, the mixture was poured into 500 mL of aqueous NaHCO₃ (10%) and the organic layer was washed with water (100 mL \times 3); then the organic layer was dried over MgSO₄. The organic solvent was removed with rotary evaporation to give crude solids that were recrystallized from chloroform/*n*-hexane to give 29.5 g (69%) of **1** as pale yellow solids: mp 88–90 °C; MS m/z 510 (M⁺); ¹H NMR (δ in CDCl₃) 6.97 (s, 2H); ¹³C NMR (δ in CDCl₃) 116.51, 118.20, 129.92, 133.05. Anal. Calcd for C₈H₂Br₄S₃: C, 18.70; H, 0.39. Found: C, 18.47; H, 0.41.

Preparation of 2. To a solution of 5.0 g (9.7 mmol) of **1** in 60 mL of ether was added 12.5 mL (19.5 mmol) of 1.56 M *n*-butyllithium/hexane solution at –80 °C. After the mixture was stirred for 1 h at this temperature, 1.84 g (19.5 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 MgSO_4 , and the organic solvent was removed with rotary evaporation. The residue was chromatographed on a silica gel column with hexane as an eluent to give crude solids that were recrystallized from ethanol to afford 3.5 g (80%) of colorless solids: mp 88–90 °C; MS m/z 446 (M^+); ^1H NMR (δ in CDCl_3) 2.48 (s, 6H), 6.87 (s, 2H); ^{13}C NMR (δ in CDCl_3) 20.53, 117.46, 129.35, 131.39, 142.95. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{Br}_2\text{S}_5$: C, 26.79; H, 1.80. Found: C, 26.93; H, 1.90.

Preparation of 3. Compound **3** was prepared in a fashion similar to **2**, by using trimethylsilyl chloride in place of dimethyl disulfide in 53% yield as colorless solids: mp 60–62 °C; MS m/z 498 (M^+); ^1H NMR (δ in CDCl_3) 0.28 (s, 18H), 7.08 (s, 2H); ^{13}C NMR (δ in CDCl_3) –0.48, 118.31, 134.07, 136.67, 146.22; ^{29}Si NMR (δ in CDCl_3) –5.22. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{S}_3\text{Si}_2$: C, 33.60; H, 4.03. Found: C, 33.50; H, 4.07.

Preparation of 4. To a solution of 2,2'-bis(3-lithio-5-methylthiothienyl) sulfide, prepared from the reaction of 2.80 g (6.25 mmol) of **2** and 8.0 mL (12.5 mmol) of a 1.56 M *n*-butyllithium/hexane solution in 50 mL of ether at –80 °C, was added 1.58 g (6.25 mmol) of dichlorodiphenylsilane at this temperature. After being stirred overnight at room temperature, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over MgSO_4 , and the organic solvent was removed with rotary evaporation. The residue was chromatographed on a silica gel column with *n*-hexane/THF (4:1) as an eluent to afford crude solids that were recrystallized from chloroform/ethanol to give 0.21 g (48%) of **4**, as analytically pure colorless solids: mp 128–129 °C; MS m/z 470 (M^+); ^1H NMR (δ in CDCl_3) 2.45 (s, 6H), 7.05 (s, 2H, thiophene), 7.35–7.50 (m, 6H, *m*- and *p*-Ph), 7.51 (dd, 4H, $J = 1.2$ and 7.7 Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) 22.36, 128.15, 130.17, 130.64, 133.12, 135.51, 136.16, 136.72, 144.24; ^{29}Si NMR (δ in CDCl_3) –33.14. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{S}_5\text{Si}$: C, 56.13; H, 3.85. Found: C, 56.17; H, 3.82.

Preparation of 5. Compound **5** was synthesized as described for **4** by using **3** as colorless crystals in 62% yield: mp 128–129 °C; MS m/z 522 (M^+); ^1H NMR (δ in CDCl_3) 0.28 (s, 18H), 7.20 (s, 2H, thiophene), 7.35–7.44 (m, 6H, *m*- and *p*-Ph), 7.54 (d, 4H, $J = 7.2$ Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) 0.00, 128.01, 129.83, 130.55, 134.33, 135.64, 138.67, 139.91, 147.82; ^{29}Si NMR (δ in CDCl_3) –6.41 (–SiMe₃), –31.16 (bridging Si). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{S}_3\text{Si}_3$: C, 59.71; H, 5.78. Found: C, 59.55; H, 5.81.

Preparation of 7. Compound **7** was synthesized as described for **4** by using **3** and dichloromethylphenylsilane as colorless solids in 61% yield: mp 111–112 °C; MS m/z 460 (M^+); ^1H NMR (δ in CDCl_3) 0.30 (s, 18H, –SiMe₃), 0.80 (s, 3H, –SiMe(Ph)), 7.19 (s, 2H, thiophene), 7.32–7.38 (m, 4H, *m*- and *p*-Ph), 7.52 (dd, 2H, $J = 7.2$, and 2.2 Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) –2.73 (–SiMe), –0.01 (–SiMe₃), 127.98, 129.60, 132.51, 134.41, 136.59, 138.08, 139.97, 147.08; ^{29}Si NMR (δ in CDCl_3) –6.45 (–SiMe₃), –26.83 (bridging Si). Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{S}_3\text{Si}_3$: C, 54.72; H, 6.12. Found: C, 54.59; H, 6.03.

Preparation of 6. To a solution of 0.267 g (0.51 mmol) of **5** in 30 mL of ether was added 0.163 g of (1.02 mmol) of bromine at –80 °C. After the mixture was stirred for 30 min at room temperature, the solvent was removed with rotary evaporation to give crude solids. The crude solids were washed with ethanol (20 mL \times 2) to give 0.22 g (80%) of **6** as colorless solids: mp 189–190 °C; MS m/z 534 (M^+); ^1H NMR (δ in CDCl_3) 7.01 (s, 2H, thiophene), 7.39 (t, 4H, $J = 7.13$ Hz, *m*-Ph), 7.43–7.51 (m, 6H, *o*- and *p*-Ph); ^{13}C NMR (δ in CDCl_3) 111.12, 128.30, 130.45, 131.82, 132.27, 134.33, 135.49, 142.81; ^{29}Si NMR (δ in CDCl_3) –33.27. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{S}_3\text{Si}$: C, 44.87; H, 2.25. Found: C, 44.50; H, 2.36.

Preparation of 8. To a solution of 200 mg (0.382 mmol) of **5** in 2 mL of CH_2Cl_2 was added at room temperature 92 mg (0.43 mmol) of *m*CPBA (80%) with several portions. The resulting mixture was poured into 30 mL of aqueous NaHCO_3 (10%) and extracted with CHCl_3 . The organic phase was washed once with water and dried over MgSO_4 . After the

organic solvent was removed with rotary evaporation the residue was recrystallized from chloroform/*n*-hexane to afford 130 mg (64%) of colorless solids: mp 142–144 °C; MS m/z 538 (M^+); ^1H NMR (δ in CDCl_3) 0.32 (s, 18H), 7.31 (s, 2H, thiophene), 7.36–7.47 (m, 6H, *m*- and *p*-Ph), 7.50 (dd, 2H, $J = 1.5$ and 8.0 Hz, *o*-Ph), 7.57 (dd, 2H, $J = 1.5$ and 8.0 Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) –0.09, 128.32 (2C), 130.45, 130.58, 131.70, 132.14, 135.27, 135.49, 135.92, 139.06, 148.0, 160.19 (two carbons may overlap); ^{29}Si NMR (δ in CDCl_3) –5.08 (–SiMe₃), –32.97 (bridging Si); IR (KBr) 1074 cm^{-1} (S=O). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{OS}_3\text{Si}_3$: C, 57.94; H, 5.61. Found: C, 57.88; H, 5.57.

Preparation of 9. Compound **9** was prepared as colorless solids in 90% yield, similar to preparation of monoxide **8** by using 2 equiv of *m*CPBA: mp 138–140 °C; MS m/z 554 (M^+); ^1H NMR (δ in CDCl_3) 0.32 (s, 18H), 7.19 (s, 2H, thiophene), 7.39–7.52 (m, 6H, *m*- and *p*-Ph), 7.56 (dd, 4H, $J = 1.2$ and 8.0 Hz); ^{13}C NMR (δ in CDCl_3) –0.16, 128.31, 128.43, 130.80, 135.76, 138.47, 140.70, 147.55, 155.18; ^{29}Si NMR (δ in CDCl_3) –4.53 (–SiMe₃), –33.77 (bridging Si); IR (KBr) 1137 and 1305 cm^{-1} (SO₂). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{O}_2\text{S}_3\text{Si}_3$: C, 56.27; H, 5.45. Found: C, 56.53; H, 5.40.

Preparation of 10. Compound **10** was prepared as described for monoxide **8** by reaction of **7** and 1 equiv of *m*CPBA as a colorless powder consisting of a *cis* and *trans* mixture in 58% yield: MS m/z 476 (M^+); ^1H NMR (δ in CDCl_3) 0.32 (s, 9H), 0.33 (s, 9H), 0.80 (s, 1.5H), 0.90 (s, 1.5H), 7.30 (s, 1H, thiophene), 7.32 (s, 1H, thiophene), 7.34–7.47 (m, 3H, *m*- and *p*-Ph), 7.67 (dd, 2H, $J = 1.7$ and 7.7 Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) –3.51, –2.96 (–SiMe), –0.13, –0.14 (–SiMe₃), 128.26, 128.28, 130.27, 130.28, 133.00, 133.97, 134.39, 134.89, 137.39, 138.49, 138.65, 143.21, 147.79, 148.09, 158.10, 159.58; ^{29}Si NMR (δ in CDCl_3) –5.09, –5.12 (–SiMe₃), –27.26, –28.12 (bridging Si); IR (KBr) 1078 cm^{-1} (SO). Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{OS}_3\text{Si}_3$: C, 52.89; H, 5.92. Found: C, 52.43; H, 5.93.

Preparation of 11. To a mixture of 0.36 g (14.9 mmol) of magnesium and 5 mL of ether was added slowly 1.22 g (7.76 mmol) of 2-bromothiophene at room temperature. The resulting solution of 2-thienylmagnesium bromide was added dropwise into a solution of 1.00 g (1.86 mmol) of compound **6** and 0.02 g (0.037 mol) of $\text{NiCl}_2(\text{dppp})$ in 15 mL of ether/THF (2:1) at room temperature. The mixture was refluxed overnight, poured into water, and extracted with ether. The extract was dried over MgSO_4 , and the organic solvent was removed with rotary evaporation. The residue was chromatographed on silica gel with chloroform/*n*-hexane (1:5) as the eluent to give crude yellow solids that were recrystallized from chloroform/ethanol (1:3) to afford 0.40 g (40%) of yellow solids: mp 216–218 °C; MS m/z 542 (M^+); ^1H NMR (δ in CDCl_3) 6.99 (dd, 2H, $J = 3.6$ and 5.1 Hz, thiophene), 7.11 (dd, 2H, $J = 1.1$ and 3.6 Hz), 7.16 (s, 2H, thiophene), 7.20 (dd, 2H, $J = 1.1$ and 5.1 Hz, thiophene), 7.34–7.48 (m, 6H, *m*- and *p*-Ph), 7.61 (dd, 4H, $J = 1.6$ and 7.9 Hz, *o*-Ph); ^{13}C NMR (δ in CDCl_3) 124.31, 124.73, 127.82, 128.09, 128.21, 130.21, 130.72, 133.19, 135.60, 136.01, 136.86, 141.04; ^{29}Si NMR (δ in CDCl_3) –32.30. Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{S}_5\text{Si}$: C, 61.95; H, 3.34. Found: C, 61.93; H, 3.37.

Preparation of Polymer 12. To a solution of 2,6-dilithiated DTTS prepared from the reaction of 0.10 g (0.19 mmol) of **6** and 0.24 mL (0.37 mmol) of *n*-butyllithium/hexane (1.56 M) in 5 mL of THF at –80 °C was added 0.058 g (0.186 mmol) of bis(phenylsulfonyl) sulfide at the temperature. The mixture was stirred for 4 h at room temperature and poured into ethanol for reprecipitation. The precipitates were filtered and dissolved in a minimum amount of chloroform. Those were poured again into ethanol to give 0.052 g (63%) of colorless powder: GPC (THF) $M_w = 5450$ (PD = 1.25); ^1H NMR (δ in CDCl_3) 7.14 (s, 2H, thiophene), 7.34–7.50 (m, 10H, Ph); ^{13}C NMR (δ in CDCl_3) 128.24, 130.32, 131.13, 132.57, 134.55, 135.49, 137.54, 146.19; ^{29}Si NMR (δ in CDCl_3) –33.01. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{S}_4\text{Si}$: C, 58.79; H, 2.97. Found: C, 58.79; H, 3.26.

X-ray Crystallographic Analysis of DTTS 5. The structure of DTTS **5** was solved by SIR92 direct methods¹³ and expanded using DIRDIF94 Fourier techniques.¹⁴ Hydrogen atoms were refined using the riding model. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects were included in F_c ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁷ The values for the mass attenuation coefficients are those of Creagh and Hubbel.¹⁸ All calculations were performed using the CrystalStructure^{19,20} crystallographic software package.

CV Measurements. CV measurements for DTTS derivatives **4**, **5**, **8**, **9**, and **11** and polymer **12** were carried out using a three-electrode system in an acetonitrile solution containing 100 mM of LiClO₄ as the supporting electrolyte and Ag/Ag⁺ as the reference electrode with a sweep rate of 100 mV/s. For **4**, **5**, **8**, **9**, and **11**, 2 mmol of the substrate was dissolved in acetonitrile and Pt wires were used as the working and counter electrodes. For polymer **12**, 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.

Conductivity Measurement. The film of polymer **12** was prepared by spin coating of the polymer/chloroform solution on a glass plate, and the film was installed over FeCl₃ powder

placed on the bottom of a glass vessel. Doping was performed under reduced pressure (ca. 1 mmHg) at 150 °C until the conductivity reached the maximum value.

MO Calculations. Ab initio MO calculations on the model compounds **5'**, **8'**, and **9'** and on 2,2'-dithienyl sulfide were carried out at the level of RHF/6-31G.²¹ For the planar structures, the two dihedral angles C=C–S–C and C–S–C=C (S = bridging sulfur) at the inner ring systems of compound **5'** and 2,2'-dithienyl sulfide were fixed to be 0.00° and the other factors were all optimized. On the basis of the optimized geometries of compound **5'** and 2,2'-dithienyl sulfide the dihedral angles of C=C–S–C and C–S–C=C were 24.70° (compound **5'**) and 106.17° (2,2'-dithienyl sulfide), respectively.

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Supporting Information Available: CIF file and tables giving crystal data for **5** and figures giving NMR spectra of the selected products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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