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Synthesis of π-Conjugated Oligomers Containing Dithienosilole Units

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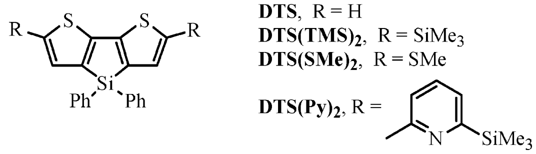
π-Conjugated oligomers having a dithienosilole unit(s) in the backbone were prepared, and their optical properties were examined. Their UV−vis absorption spectra and the emission spectra display maxima at 395−498 nm and at 498−576 nm, respectively, which are at longer wavelength than the oligomers that do not contain silole units with the same π-conjugated chain length. This clearly demonstrates the influence of silole segments in enhancing the conjugation in the oligomer backbone. The crystal structure of a bi(dithienosilole) derivative was determined by X-ray crystallographic analysis, showing high coplanarity of the two dithienosilole rings. One of the present dithienosilole-containing oligomers was found to be FET active in its vapor-deposited film as well as spin-coated film with a hole mobility of $\mu = 2.6 \times 10^{-5}$ cm^2/V s and $\mu = 1.2 \times 10^{-7}$ cm^2/V s, respectively.

Introduction

π-Conjugated polymers and oligomers are of importance as functional materials, such as organic semiconductors, luminescent materials, and chromic materials. Recently, we have demonstrated that introduction of an intramolecular organosilanylene bridge at the β,β'-position of a bithiophene unit leads to enhanced conjugation in the resulting tricyclic system (dithienosilole: DTS in Chart 1).[1] This is due not only to the high coplanarity of two thiophene rings fixed by the bridge but also to the interaction between the silicon σ^*-orbital and the π^*-orbital of the bithiophene unit, namely, $\sigma^*-\pi^*$ conjugation.[2,3] The conjugation lowers the LUMO energy level of the DTS system, leading to a reduced HOMO−LUMO energy gap, which is evident from both the experimental and theoretical studies. The low-lying LUMOs of DTS derivatives make it possible to apply them to electroluminescent (EL) devices as electron-transporting materials. For example, it was found that the device with a structure of ITO/TPD/Alq3/DTS(Py)$_2$/Mg−Ag, where Alq3 is an emitting layer, and TPD and DTS(Py)$_2$ (Chart 1) are hole- and electron-transporting layers, respectively, emitted a strong green light with the maximum luminance of 16 000 cd/m^2.[4] The $\sigma^*-\pi^*$ conjugation is operative even in the polymeric system.[5,6] Thus, a polymer derived from electropolymerization of 2,6-bis(trimethylsilyl)dithienosilole shows a red-shifted absorption maximum of about 30 nm from those of soluble poly(alkylthiophene)s, although the polymer contained some decomposed units, in addition to the dithienosilole-2,6-diyl major units.[6]

Chart 1



In this paper, we report the synthesis of oligomers that contain a DTS unit(s) in the conjugated linkage, using 2-bromo-6-methylthiodithienosilole as the key starting compound. The methylthio group, which would be the end-capping group of the resulting oligomers, is expected to raise the HOMO energy level because of its high electron-donating properties, thus leading to even smaller HOMO−LUMO energy gaps of the oligomers.[7,8] The electronic states of the oligomers were examined by UV absorption and emission spectra. The crystal structure of a bi(dithienosilole) was determined by X-ray crystallography. Applications of the oligomer films to field effect transistors (FETs) were also studied.

Results and Discussion

Preparation of Starting Compounds 3b and 4c. 3,3′,5-Tribromo-5′-trimethylsilyl-2,2′-bithiophene (**2a**) was obtained in 63% yield by the reaction of *N*-bromosuccinimide (NBS) and bis(trimethylsilyl)dibromobithiophene (**1**). 3,3′-Dibromo-5-methylthio-5′-trimethylsilyl-2,2′-bithiophene (**2b**) was ob-

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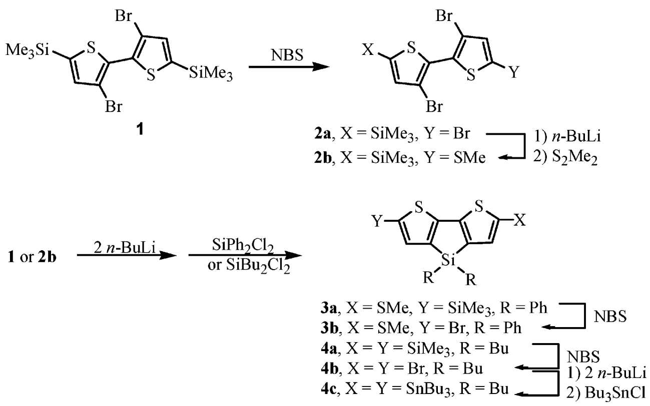
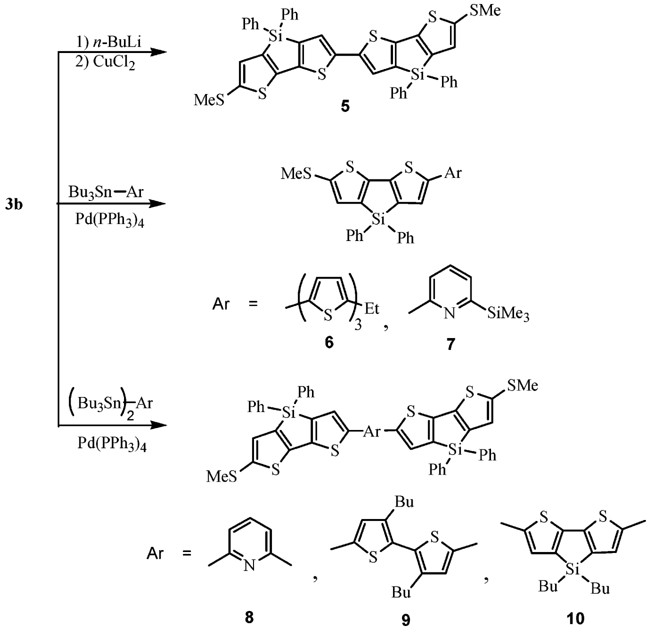
10.1021/om0510122 CCC: $33.50

Scheme 1



Scheme 2



tained in 67% yield in the reaction of dimethyl disulfide and 3,3′-dibromo-5-lithio-5′-trimethylsilyl-2,2′-bithiophene, prepared by lithiation of **2a** (Scheme 1). The reaction of dichlorodiphenylsilane and 3,3′-dilithio-5-bromo-5′-trimethylsilyl-2,2′-bithiophene obtained from **2b** afforded 2-methylthio-6-trimethylsilyl-4,4′-diphenyldithienosilole (**3a**) in 30% yield. 2-Bromo-6-methylthio-4,4′-diphenyldithienosilole (**3b**) was obtained in 86% yield by bromination of **3a**. Similarly, 2,6-bis(trimethylsilyl)-4,4′-dibutyldithienosilole (**4a**) was obtained in 71% yield. 2,6-Bis(tributylstannanyl)-4,4′-dibutyldithienosilole (**4c**) was prepared in 95% yield by the reaction of tributyltin chloride and 2,6′-dilithio-4,4′-dibutyldithienosilole prepared by lithiation of **4b** that had been obtained in 99% yield by bromination of **4a** with NBS.

Synthesis of Compounds 5−10. Bi(dithienosilole) **5** was obtained in 40% isolated yield by oxidative coupling of 2-lithio-6-methylthio-4,4′-diphenyldithienosilole with copper chloride (Scheme 2). Compound **6** was readily prepared by the Stille cross-coupling reaction of 2-bromo-6-methylthio-4,4′-diphenyldithienosilole (**3b**) and 5″-ethyl-5-(tributylstannyl)terthiophene using tetrakis(triphenylphosphine)palladium as the catalyst in 78% yield as a red solid. Compound **7** was obtained in 75% yield as an orange solid by a similar Pd-catalyzed reaction of **3b** and 2-trimethylsilyl-6-(tributylstannyl)pyridine. We next synthesized the compounds of structure DTS−Ar−DTS (Ar = aromatic linker) using the reactions of 2 equiv of **3b** and the corresponding bis(tributylstannyl)arenes (**8**: pale yellow solid, 46% yield; **9**: bright brown solid, 26%; **10**: dark red solid, 31%).

Table 1. Properties of 3a, 4a, and 5−10

compound	λ_{max} (nm) UV abs[a]	λ_{max} (nm) emission[a]	$(\Phi)_f$[b]	mp/°C
3a	365	454	*c*	oil
4a	351	415	*c*	oil
5	453	533	0.15	>300
6	451	520	0.15	265−266
7	400	500	0.20	205−206
8	395	498	0.22	182−184
9	436	544	0.02	125−126
10	498	576	0.08	293−295

[a] In THF, with [substrate] = 2.0×10^{-5} M. [b] Fluorescence quantum yield was measured in THF using 9,10-diphenylanthracene as a standard. [c] Not determined.

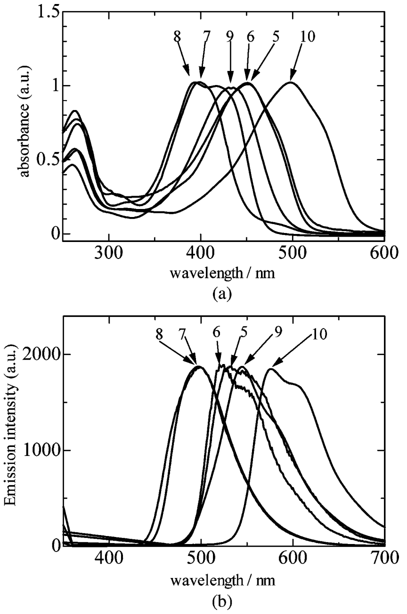
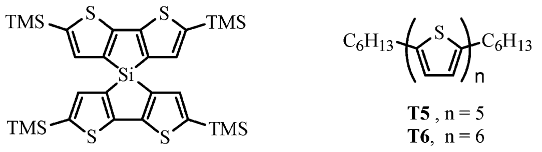


Figure 1. UV (a) and emission (b) spectra of compounds **5**−**10** in THF.

Chart 2



sDTS

T5, n = 5
T6, n = 6

Optical Properties of Compounds 5−10. Table 1 summarizes the optical properties of compounds **5**−**10**. Figure 1a shows the UV spectra. Bi(dithienosilole) **5** is greenish-yellow in a THF solution and shows a red shift of the absorption maximum by 72 nm relative to DTS(SMe)$_2$ (pale yellow in THF, $\lambda_{max} = 381$ nm; see Chart 1). The UV absorption maximum of quinquethiophene **6** appeares at 451 nm in a dark yellow THF solution. This is red-shifted by 25 nm from T5 (426 nm; see Chart 2), having the same number of thienylene units (Chart 2). Interestingly, it is red-shifted even from sexithiophene T6 (440 nm; see Chart 2). This clearly indicates the significant influence of the silole ring that leads to a largely reduced band gap as expected. Pyridyl-substituted compound **7** is bright blue in THF. Its UV maximum was red-shifted by 19 nm relative to DTS(SMe)$_2$,[8] but blue-shifted by 18 nm from DTS(Py)$_2$ (418 nm; see Chart 1).[4] Compound **7** was expected to be a push−

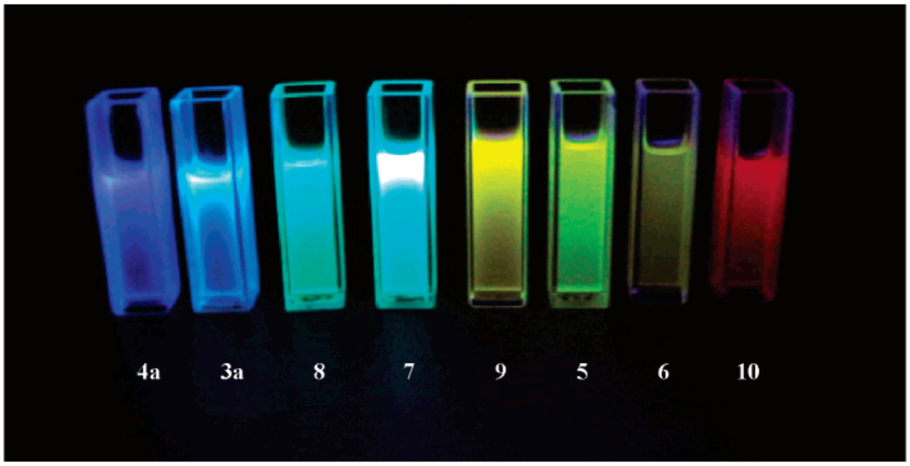
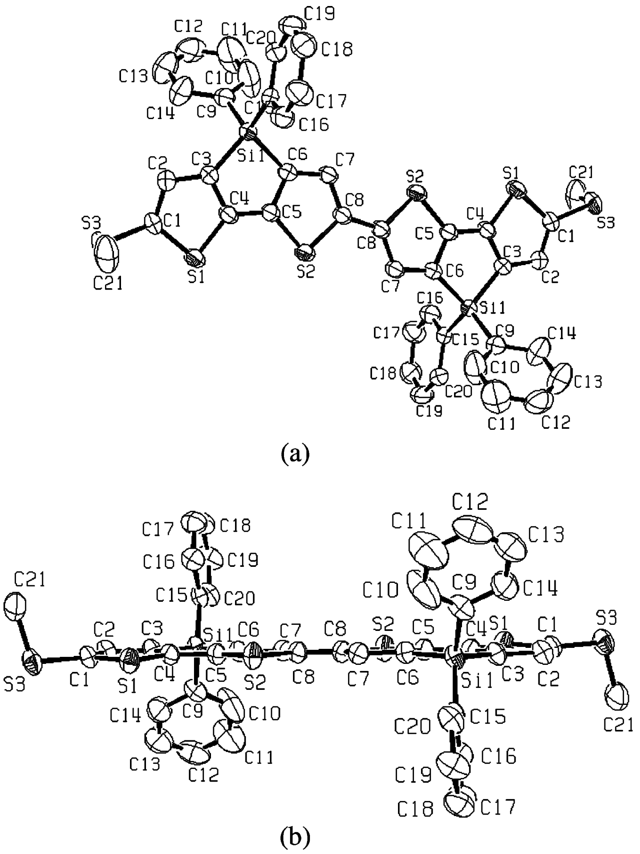


Figure 2. Luminescence color of THF solutions of DTS derivatives.

pull type DTS derivative. In fact, recently, we have reported that 2-(tricyanoethenyl)dithienosilole exhibits clear solvatochromic behavior.[9] However, no evident solvatochromic behaviors were observed for **7**.

DTS−Ar−DTS type compounds **8**, **9**, and **10** show blue, yellow, and red luminescence in THF solutions, respectively, and their UV spectra show the absorption bands between 395 and 498 nm, as shown in Table 1 and Figure 1a. It is noted that ter(dithienosilole) **10** exhibits a band red-shifted by about 45 nm from that of dimeric DTS **5** (453 nm) and by about 117 nm from that of DTS(SMe)$_2$ (Chart 1).[8] When the absorption maximum of compound **10** is compared with that of sexithiophene derivatives, it is red-shifted by 58 nm. This, again, indicates the electronic effect of the silicon bridge, which enhances the conjugation. The emission spectra of the present DTS derivatives are shown in Figure 1b. As shown in Figure 1b, the emission maxima of compounds **5**−**10** are between 498 and 576 nm. The photoluminescence quantum yields Φ_f were determined using 9,10-diphenylanthracene as the standard to be $\Phi_f = 0.02-0.22$, which are a little lower than that of DTS(TMS)$_2$ ($\Phi_f = 0.69$; Chart 1)[1] and thiophene oligomer T5 ($\Phi_f = 0.43$).[10] Photoluminescence colors from the present DTS derivatives are readily controlled by introduction of π-conjugated substituents from blue to red, as shown in Figure 2.

Field Effect Mobilities of 6. Field effect transistors (FETs) were fabricated using compounds **5**−**10** as the active layer. Although compounds **5**, **7**, **8**, **9**, and **10** were not active for FET, a vapor-deposited film of **6** showed FET activity with the field effect mobility μ of 2.6×10^{-5} cm^2/V s and I_{on}/I_{off} ratio of 1.0×10^2. Interestingly, compound **6** was found to be FET active even in the form of a spin-coated film, and a μ_{FET} of 1.2×10^{-7}cm^2/V s and I_{on}/I_{off} ratio of 2.4×10 were obtained. Accordingly, μ_{FET} of the vapor-deposited film of **6** is higher than that of sDTS ($\mu_{FET} = 1.4 \times 10^{-6}$ cm^2/V s; Chart 2).[11] However, these values are not as high as those of the crystalline oligothiophene films, investigated previously.[12] We measured X-ray diffraction in order to examine the molecular arrangement of compounds **5**−**10** as vacuum-deposited films. However, no clear diffraction peaks were observed. The lack of molecular orientation would be responsible for the low FET mobility.



(a)

(b)

Figure 3. ORTEP drawing (50% probability ellipsoids) of **5**: top view (a) and side view (b). Protons are omitted for clarity.

Crystal Structure of Compound 5. The crystal structure of **5** was determined by an X-ray single-crystal diffraction study. An ORTEP drawing of **5** is presented in Figure 3. Table 2 shows the crystal data, experimental conditions, and summary of structural refinement for **5**, and selected bond distances and angles are given in Table 3. Two methyl groups are located in a trans fashion with respect to the bi(dithienosilole) unit. This structure has a C_i center between C(8) atoms, indicating complete coplanarity of the DTS units.

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

molecular formula	$C_{42}H_{30}S_6Si_2$
molecular weight	783.23
cryst style	triclinic
space group	$P\bar{1}$ (#2)
cell dimens	
a, Å	9.3886(5)
b, Å	10.5077(1)
c, Å	12.4065(6)
α, deg	68.413(2)
β, deg	81.359(5)
γ, deg	83.288(3)
V, Å^3	1122.64(8)
Z	1
D_{calcd}, g/cm^3	1.158
F_{000}	406.00
cryst size, mm^3	0.35 × 0.35 × 0.15
cryst color	red
μ, cm^{-1}	3.84
diffractometer	Rigaku RAXIS-RAPID
temp, °C	−50
wavelength, Å	0.71069 (Mo Kα)
monochromator	graphite
no. of obsd rflns ($I > 3\sigma(I)$)	8452
R	0.079
R_w[a]	0.157

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

Table 3. Selected Distances (Å) and Angles (deg) for 5 (esd's in parentheses)

S(1)−C(1)	1.740(6)	S(1)−C(4)	1.722(7)	S(2)−C(5)	1.728(6)
S(2)−C(8)	1.743(7)	S(3)−C(1)	1.741(7)	S(3)−C(21)	1.760(1)
Si(1)−C(3)	1.876(7)	Si(1)−C(6)	1.872(6)	Si(1)−C(9)	1.859(7)
Si(1)−C(15)	1.862(8)	C(1)−C(2)	1.360(1)	C(2)−C(3)	1.408(9)
C(3)−C(4)	1.380(9)	C(4)−C(5)	1.434(8)	C(5)−C(6)	1.380(1)
C(6)−C(7)	1.396(8)	C(7)−C(8)	1.383(8)		

S(1)−C(1)−S(3)	121.4(4)	S(1)−C(1)−C(2)	110.9(5)
C(4)−S(1)−C(1)	91.2(3)	S(1)−C(4)−C(3)	112.1(5)
S(1)−C(4)−C(5)	131.3(5)	S(2)−C(5)−C(4)	130.6(5)
S(2)−C(5)−C(6)	112.1(4)	C(8)−S(2)−C(5)	91.4(3)
S(2)−C(8)−C(7)	110.3(4)	S(3)−C(1)−C(2)	127.7(5)
C(21)−S(3)−C(1)	103.3(4)	Si(1)−C(3)−C(2)	140.9(5)
Si(1)−C(3)−C(4)	107.5(4)	C(6)−Si(1)−C(3)	91.6(3)
C(9)−Si(1)−C(3)	112.3(4)	C(15)−Si(1)−C(3)	113.3(3)
Si(1)−C(6)−C(5)	107.0(4)	Si(1)−C(6)−C(7)	140.9(6)
C(9)−Si(1)−C(6)	115.4(3)	C(15)−Si(1)−C(6)	112.1(3)
C(15)−Si(1)−C(9)	111.0(3)	C(1)−C(2)−C(3)	114.3(6)
C(2)−C(3)−C(4)	111.5(6)	C(3)−C(4)−C(5)	116.5(6)
C(4)−C(5)−C(6)	117.3(5)	C(5)−C(6)−C(7)	111.9(5)
C(6)−C(7)−C(8)	114.3(6)		

Conclusion

On the basis of the results described above, we demonstrated that introduction of DTS system(s) into a π-conjugated linkage effectively reduces the HOMO−LUMO energy gap. The present oligomers showed clear color changes, tunable by the nature of π-conjugated units involved in the main chain. One of the oligomers was found to be usable as an active layer of a FET device in its vapor-deposited film as well as spin-coated film. Studies concerning other applications of the oligomers, such as to EL device materials, are underway.

Experimental Section

General Procedures. All reactions were carried out under a dry nitrogen atmosphere. THF, ether, and toluene were dried over sodium−potassium alloy and distilled just before use. 3,3′-Dibromo-5,5′-bis(trimethylsilyl)-2,2′-bithiophene,[1] 3,3′-dibutyl-2,2′-bithiophene,[12] and 5″-ethyl-5-bromo-2,2′:5′,2″-terthiophene[13] were prepared as reported in the literature. 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, and TOF-MS spectra were measured on a Shimadzu Kratos Kompact MALDI 2 V5.2.2. UV−Vis spectra were measured with a Shimadzu 3150 spectrometer, and emission spectra were recorded on a Hitachi F-4500 spectrophotometer.

Preparation of 2a. In a 50 mL two-necked flask were placed 12.6 g (26.9 mmol) of **1**, 60 mL of chloroform, and 100 mL of acetic acid. To this was added 4.79 g (26.9 mmol) of NBS at room temperature. The mixture was stirred for 5 h at room temperature, then hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on a silica gel column using hexane as an eluent to give 8.05 g (63% yield) of **2a** as a yellow oil: MS m/z 472 (M^+); ^1H NMR (δ in $CDCl_3$) 0.36 (s, 9H), 7.04 (s, 1H), 7.15 (s, 1H); ^{13}C NMR (δ in $CDCl_3$) −0.42, 111.21, 113.63, 114.03, 130.80, 132.59, 132.90, 136.92, 143.67. Anal. Calcd for $C_{11}H_{11}Br_3S_2Si$: C, 27.81; H, 2.33. Found: C, 27.80; H, 2.27.

Preparation of 2b. To solution of 7.11 g (14.96 mmol) of **2a** in 100 mL of ether was added 9.47 mL (14.96 mmol) of a 1.58 M *n*-butyllithium−hexane solution at −78 °C. After the mixture was stirred for 0.5 h at −78 °C, 1.41 g (14.96 mmol) of dimethyl disulfide was added to the mixture. After the mixture was stirred for 1 h at room temperature, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous magnesium sulfate, and the organic solvent was removed with rotary evaporation. The resulting residue was chromatographed on a silica gel column with *n*-hexane as an eluent to give 4.43 g (67% yield) of **2b** as a yellow oil: MS m/z 440 (M^+); ^1H NMR (δ in $CDCl_3$) 0.33 (s, 9H, $SiMe_3$), 2.53 (s, 3H, SMe), 6.89, (s, 1H, thiophene ring protons), 7.13 (s, 1H, thiophene ring protons); ^{13}C NMR (δ in $CDCl_3$) −0.39, 20.95, 111.23, 113.24, 130.26, 132.41, 133.29, 136.94, 139.85, 143.20. Anal. Calcd for $C_{12}H_{14}Br_2S_3Si$: C, 32.58; H, 3.19. Found: C, 32.62; H, 3.18.

Preparation of 3a. In a 50 mL two-necked flask fitted with a dropping funnel were placed 2.95 g (6.67 mmol) of **2b** and 20 mL of ether. To this was added 8.45 mL (12.34 mmol) of a 1.58 M solution of *n*-butyllithium-hexane at −78 °C. After the resulting mixture was stirred for 1 h at this temperature, 1.43 g (6.67 mmol) of dichlorodiphenylsilane and 10 mL of THF were added to the mixture. The mixture was then warmed to room temperature and hydrolyzed with water. The resulting mixture was chromatographed on a silica gel column with *n*-hexane as an eluent to give 0.93 g (30% yield) of **3a** as a yellow oil: MS m/z 464 (M^+); ^1H NMR (δ in $CDCl_3$) 0.32 (s, 9H, $SiMe_3$), 2.50 (s, 3H, SMe), 7.19 (s, 1H, thiophene ring proton), 7.29 (s, 1H, thiophene ring proton), 7.34−7.44 (m, 6H, *m*- and *p*-Ph), 7.62 (dd, 4H, J = 7.9 Hz, and 1.3 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 0.04, 22.81, 128.18, 130.33, 131.67, 134.66, 135.41, 136.34, 138.00, 140.47, 140.92, 142.54, 152.48, 155.50 Anal. Calcd for $C_{24}H_{24}S_3Si_2$: C, 66.91; H, 5.39. Found: C, 66.86; H, 5.26.

Compound **4a** was prepared in a fashion similar to that for **3a**, by using dibutyldichlorosilane in place of dichlorodiphenylsilane, in 71% yield as a yellow oil: TOF-MS m/z 449 (M^+); ^1H NMR (δ in $CDCl_3$) 0.33 (s, 18H, $SiMe_3$), 0.84−0.90 (m, 10H, CH_2CH_3), 1.29−1.41 (m, 8H, CH_2CH_2), 7.12 (s, 2H, thiophene ring protons); ^{13}C NMR (δ in $CDCl_3$) 0.14, 11.66, 13.67, 26.28, 26.40, 136.56, 141.01, 143.83, 154.48. Anal. Calcd for $C_{22}H_{38}S_2Si_3$: C, 58.60; H, 8.49. Found: C, 58.86; H, 8.40.

Compounds **3b**, **4b**, and 3,3′-dibutyl-5,5′-dibromo-2,2′-bithiophene were prepared in a fashion similar to that for **2a**. Data for **3b**: 86% yield; yellow solids; mp 185−186 °C; TOF-MS m/z 470 (M^+); ^1H NMR (δ in $CDCl_3$) 2.49 (s, 3H, SMe), 7.17 (s, 1H, thiophene ring proton), 7.19 (s, 1H, thiophene ring proton), 7.35−7.46 (m, 6H,

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m- and *p*-Ph), 7.59 (d, 4H, *J* = 6.50 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 22.79, 112.29, 128.29, 130.62, 130.70, 131.29, 132.13, 134.43, 135.31, 138.55, 139.63, 150.58, 151.67. Anal. Calcd for $C_{21}H_{15}BrS_3Si$: C, 53.49; H, 3.21. Found: C, 53.30; H, 3.14. Data for **4b**: 99% yield; yellow oil; MS *m/z* 462 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.83−0.88 (m, 10H, CH_2CH_3), 1.29−1.32 (m, 8H, CH_2-CH_2), 6.99 (s, 2H, thiophene ring protons); ^{13}C NMR (δ in $CDCl_3$) 11.36, 13.26, 26.14, 26.15, 111.40, 132.13, 140.93, 148.92. Anal. Calcd for $C_{16}H_{20}Br_2S_2Si$: C, 41.38; H, 4.34. Found: C, 41.41; H, 4.00. Data for 3,3′-dibutyl-5,5′-dibromo-2,2′-bithiophene: 97% yield; lime-colored oil; MS *m/z* 434 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.85 (t, 6H, *J* = 7.56, CH_3), 1.22−1.31 (m, 4H, CH_2), 1.44−1.52 (m, 4H, CH_2), 2.43 (t, 4H, *J* = 7.84, CH_2), 6.90 (s, 2H); ^{13}C NMR (δ in $CDCl_3$) 13.85, 22.36, 28.43, 32.66, 112.37, 128.85, 131.39, 143.78. Anal. Calcd for $C_{21}H_{15}BrS_3Si$: C, 44.05; H, 4.62. Found: C, 44.09; H, 4.59.

Preparation of 4c. In a 100 mL two-necked flask was placed 0.386 g (0.83 mmol) of **4b** in 50 mL of ether. To this was added 1.05 mL (0.83 mmol) of a 1.58 M hexane solution of *n*-butyllithium at −78 °C. The mixture was warmed slowly to room temperature with stirring. Then the mixture was again cooled to −78 °C and 0.54 g (0.83 mmol) of tributyltin chloride in 10 mL of diethyl ether was added to the mixture over a period of 30 min. The mixture was stirred for 12 h at room temperature and hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 0.7 g (95% yield) of **4c**, as a light brown liquid: TOF-MS *m/z* 883 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.84−0.93 (m, 28H, CH_3 of $SnBu_3$ and CH_3 of $SiBu_2$), 1.07−1.12 (m, 12H, CH_2 of $SnBu_3$), 1.29−1.38 (m, 20H, CH_3CH_2 of $SiBu_3$, CH_2 of $SnBu_3$), 1.54−1.64 (m, 12H, CH_2 of $SnBu_3$), 7.03 (s, 2H, thiophene ring protons); ^{13}C NMR (δ in $CDCl_3$) 10.91, 11.82, 13.66, 17.52, 26.10, 26.50, 27.24, 29.00, 136.58, 137.94, 142.85. One carbon may be overlapped. This compound was used for the following dehalostannylation without further purification.

3,3′-Dibutyl-5,5′-bis(tributylstannyl)-2,2′-bithiophene and 5″-ethyl-5-(tributylstannyl)terthiophene were prepared in a fashion similar to that above. Data for 3,3′-dibutyl-5,5′-bis(tributylstannyl)-2,2′-bithiophene: 99% yield; light brown oil; MS *m/z* 856 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.83−0.94 (m, 24H, CH_3 of butylthiophene and CH_3 of $SnBu_3$), 1.07−1.11 (m, 12H, CH_2 of $SnBu_3$), 1.26−1.39 (m, 16H, CH_2 of butylthiophene and CH_2 of $SnBu_3$), 1.51−1.66 (m, 16H, CH_2 of butylthiophene and CH_2 of $SnBu_3$), 2.52 (t, 4H, *J* = 7.56, CH_2 of butylthiophene), 6.97 (s, 2H); ^{13}C NMR (δ in $CDCl_3$) 10.78, 13.67, 17.52, 22.57, 27.25, 28.42, 28.98, 33.13, 135.17, 136.11, 137.10, 142.53. This compound was used for the following dehalostannylation without further purification. Data for 5″-ethyl-5-(tributylstannyl)-2,2′:5′,2″-terthiophene: 99% yield; light brown oil; MS *m/z* 566 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.91 (t, 9H, CH_3 of $SnBu_3$), 1.06−1.11 (m, 6H, CH_2 of $SnBu_3$), 1.26−1.37 (m, 9H, CH_2 of $SnBu_3$ and CH_3 of ethyl), 1.48−1.67 (m, 6H, CH_2 of $SnBu_3$), 2.82 (q, 2H, *J* = 7.56 Hz, CH_2 of ethyl), 6.68 (d, 1H, *J* = 3.4 Hz, thienylene), 6.96−6.98 (m, 2H, thienylene), 7.04−7.05 (m, 2H, thienylene), 7.25 (d, 1H, *J* = 3.64 Hz, thienylene); ^{13}C NMR (δ in $CDCl_3$) 10.87, 13.65, 15.84, 23.52, 27.24, 28.92, 123.76, 123.38, 123.47, 123.54, 123.93, 124.10, 124.13, 124.26, 124.68, 127.82, 142.05, 147.36. This compound was used for the following dehalostannylation without further purification.

Preparation of 5. In a 50 mL two-necked flask was placed 100 mg (0.212 mmol) of **3b** in 20 mL of THF. To this was added 0.134 mL (0.212 mmol) of a 1.58 M solution of *n*-butyllithium−hexane at −78 °C for 1 h. After the mixture was warmed slowly to −10 °C, 34.2 mg (0.254 mmol) of copper chloride was added. The mixture was stirred overnight at room temperature and hydrolyzed with 4 N HCl(aq). The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on a silica gel column using hexane−$CHCl_3$ (10:1) as an eluent to give 54.8 mg (40% yield) of **5** as brown solids: mp >300 °C; TOF-MS *m/z* 782 (M^+); ^{1}H NMR (δ in $CDCl_3$) 2.51 (s, 6H, SMe), 7.20 (s, 2H, thiophene ring protons), 7.28 (s, 2H, thiophene ring protons), 7.35−7.45 (m, 12H, *m*- and *p*-Ph), 7.63 (dd, 8H, *J* = 8.06 Hz, and 1.48 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 22.84, 126.04, 128.29, 130.53, 131.10, 134.62, 135.37, 138.45, 138.96, 140.00, 140.89, 148.56, 152.17; HRMS (FAB+) calcd for $C_{42}H_{30}S_6Si_2$ 782.0210 (M^+), found *m/z* 782.0219.

Preparation of 6−10. In a 25 mL two-necked flask were placed 90 mg (0.19 mmol) of **3b** and 11 mg (0.010 mmol) of $Pd(PPh_3)_4$ in 5 mL of toluene. To this was added 0.12 g (0.21 mmol) of 5″-ethyl-5-(tributylstannyl)terthiophene with ice cooling. The mixture was stirred at 100 °C for 3 days. The solvent was evaporated, and the residue was chromatographed on a silica gel column using hexane−chloroform (10:1) as an eluent to give 0.10 g (78% yield) of **6** as red solids: TOF-MS *m/z* 666 (M^+); ^{1}H NMR (δ in $CDCl_3$) 1.32 (t, 3H, *J* = 7.56 Hz, CH_3), 2.51 (s, 3H, SMe), 2.82 (q, 2H, *J* = 7.56 Hz, CH_2), 6.69 (d, 1H, *J* = 3.4 Hz, thiophene ring proton), 6.98−7.05 (m, 5H, thiophene ring protons), 7.20 (s, 1H, thienylene), 7.27 (s, 1H, thienylene), 7.35−7.47 (m, 6H, *m*- and *p*-Ph), 7.64 (dd, 4H, *J* = 7.9 and 1.2 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 15.83, 22.82, 23.53, 123.51, 123.64, 124. 12, 124.20, 126.11, 128.29, 130.54, 131.08, 134.30, 134.59, 135.14, 135.39, 135.91, 136.95, 138.54, 138.78, 140.10, 140.39, 140.88, 147.26, 148.80, 152.17 (two thiophene ring carbons may be overlapped). Anal. Calcd for $C_{35}H_{26}S_6Si$: C, 63.02; H, 3.93. Found: C, 62.88; H, 3.76.

Compounds **7**, **8**, **9**, and **10** were prepared in a fashion similar to that above. Data for **7**: TOF-MS *m/z* 541 (M^+); ^{1}H NMR (60 °C) (δ in $CDCl_3$) 0.36 (s, 9H, $SiMe_3$), 2.52 (s, 3H, SMe), 7.20 (s, 1H, thienylene), 7.30−7.44 (m, 10H, *m*-and *p*-Ph, 5-pyridyl), 7.50−7.56 (m, 2H, 3,4-pyridyl), 7.65 (dd, 4H, *J* = 8.0 and 1.48 Hz, *o*-Ph), 7.71 (s, 1H, thienylene); ^{13}C NMR (δ in $CDCl_3$) −1.76, 22.66, 117.89, 126.59, 127.02, 128.29, 130.43, 131.62, 134.26, 134.40, 134.59, 135.48, 139.16, 140.62, 140.95, 147.87, 152.25, 152.76, 168.37. Anal. Calcd for $C_{29}H_{27}NS_3Si_2$: C, 64.28; H, 5.02; N, 2.58. Found: C, 64.08; H, 4.97; N, 2.39. Data for **8**: TOF-MS *m/z* 859 (M^+); ^{1}H NMR (δ in $CDCl_3$) 2.53 (s, 6H, SMe), 7.22 (s, 2H, thienylene), 7.36−7.46 (m, 14H, *m*- and *p*-Ph, 3,5-pyridyl), 7.62 (t, 1H, *J* = 8.0 Hz, 4-pyridyl), 7.66 (dd, 8H, *J* = 8.0 and 1.5 Hz, *o*-Ph), 7.74 (s, 2H, thienylene); ^{13}C NMR (δ in $CDCl_3$) 22.72, 116.34, 127.36, 128.27, 130.49, 131.22, 134.32, 135.42, 137.08, 139.13, 140.47, 140.85, 146.58, 152.11, 152.43, 152.49. Anal. Calcd for $C_{47}H_{33}NS_6Si_2$: C, 65.61; H, 3.87; N, 1.63. Found: C, 65. 74; H, 3.97; N, 1.47. Data for **9**: TOF-MS *m/z* 1058 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.85 (t, 6H, *J* = 7.32 Hz, CH_3), 1.30 (sext, 4H, *J* = 7.56 Hz, CH_2), 1.51−1.59 (m, 4H, CH_2), 2.48−2.54 (m, 10H, CH_2 and SMe), 7.04 (s, 2H, thienylene), 7.20 (s, 2H, thienylene), 7.27 (s, 2H, thienylene), 7.35−7.46 (m, 12H, *m*-and *p*-Ph), 7.63 (dd, 8H, *J* = 8.1 and 1.48 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 13.95, 22.46, 22.86, 28.69, 32.77, 125.11, 126.04, 127.18, 128.27, 130.52, 131.07, 134.65, 135.39, 136.85, 138.28, 138.99, 139.98, 140.75, 143.40, 148.63, 152.27. Anal. Calcd for $C_{58}H_{50}S_8Si_2$: C, 65.74; H, 4.76. Found: C, 65.69; H, 4.52. Data for **10**: TOF-MS *m/z* 1086 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.84−0.92 (m, 10H, CH_2CH_3), 1.30−1.39 (m, 8H, CH_2CH_2), 2.50 (s, 6H, SMe), 7.11 (s, 2H, thienylene), 7.21 (s, 2H, thienylene), 7. 27 (s, 2H, thienylene), 7.35−7.46 (m, 12H, *m*- and *p*-Ph), 7.64 (dd, 8H, *J* = 8.6 and 1.2 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) 11.54, 13.68, 22.87, 26.23, 26.26, 125.70, 126.27, 128.28, 130.51, 131.15, 134.68, 135.38, 138.07, 138.23, 139.34, 139.85, 140.91, 143.06, 147.54, 148.22, 152.38; HRMS (FAB +) calcd for $C_{58}H_{50}S_8Si_3$ 1086.0986 (M^+), found *m/z* 1086.0977.

Fabrication of FET Device with 6. FETs based on compound **6** were fabricated on the insulator, both a bottom contact and a top contact type. The drain-source channel length and width are 50 μm and 1.5 mm, respectively. The organic films were prepared by spin-coating of the solution (3.6 g/L in chloroform) at 2000 rpm as the bottom type semiconductor and depositing of the solid (10^{-3} Pa at 25 °C) with 500 Å thickness as the top type semiconductor. Field effect characteristics of the device were measured under vacuum at room temperature. The field effect mobility μ was calculated in the saturation regime as reported in a previous paper.[14]

X-ray Crystallographic Analysis of 5. The structure of **5** was solved by SIR92 direct methods[15] and expanded using DIRDIF94 Fourier techniques.[16] Hydrogen atoms were refined using the riding model. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and MaAuley.[19] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[20] All calculations were performed using the Crystal-Stucture[21,22] crystallographic software package.

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Supporting Information Available: Data in CIF format for **5**. ^{1}H and ^{13}C NMR spectra of **5** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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