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2,3,4,5-Tetrakis(dimethylsilyl)thiophene: The First 2,3,4,5-Tetrasilylthiophene

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2,3,4,5-Tetrakis(dimethylsilyl)thiophene (**1**), the first 2,3,4,5-tetrasilylthiophene, was synthesized by the reaction of 2,3,4,5-tetrabromothiophene with chlorodimethylsilane in the presence of magnesium and a catalytic amount of copper(I) cyanide. The dimethylsilyl groups of **1** considerably affect the structure and the electronic properties of the thiophene ring, which was revealed by molecular orbital calculations and UV spectroscopy.

Introduction

Silylthiophenes have attracted much attention as useful reagents for organic synthesis,[1,2] the precursors of polythiophene and related polymers,[3−5] and the precursors of silylene−thienylene copolymers.[6] Many studies on the synthesis of silylthiophenes have been reported. The synthetic methods include (1) the reactions of organolithium[2a,4a,b,e,f,i,5,7] or Grignard reagents[4e,g,6b−d,7b,8] with chlorosilanes, (2) the coupling of halothiophenes and chlorosilanes with magnesium[2b,4a,g,i,6a,9] or sodium,[9a] (3) the electrochemical coupling of halothiophenes and chlorosilanes,[10] and (4) other methods.[2b] By these methods, mono-, di-, and trisilylthiophenes have so far been synthesized. However, tetrasilylthiophenes have not yet been reported, despite much effort. For example, Gilman and co-workers studied the silylation of 2,3,4,5-tetrachlorothiophene with chlorosilanes.[7e−g,8b,11] They obtained mono- and disilylthiophenes, but the attempt at persilylation of 2,3,4,5-tetrachlorothiophene with excess chlorotrimethylsilane and lithium resulted in the formation of a ring-opening product, hexakis(trimethylsilyl)-2-butyne.[11] More recently, Bordeau, Biran, and co-workers have reported the electrochemical silylation of halothiophenes.[10a] They carried out the silylation of tetrachloro- and tetrabromothiophenes with excess chlorotrimethylsilane. They obtained 2-chloro- and 2-bromo-1,3,4-tris(trimethylsilyl)thiophenes, but further silylation gave hexakis(trimethylsilyl)-2-butyne.

As part of our studies on organosilicon compounds containing aromatic rings,[12] we have synthesized 2,3,4,5-tetrakis(dimethylsilyl)thiophene as the first 2,3,4,5-tetrasilylthiophene. We report herein the synthesis and structural features of 2,3,4,5-tetrakis(dimethylsilyl)thiophene. Also, we discuss the electronic effects of the dimethylsilyl groups on the thiophene π system.

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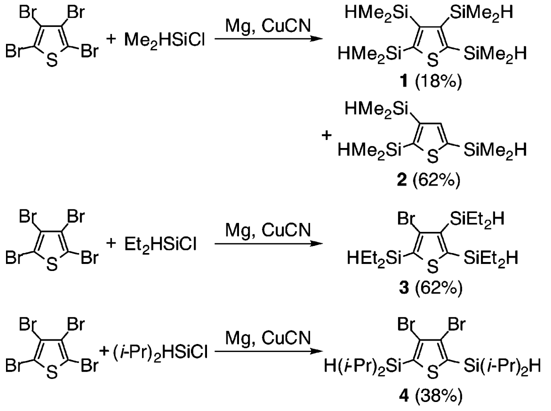
Scheme 1



Results and Discussion

Synthesis of 2,3,4,5-Tetrakis(dimethylsilyl)thiophene and Related Compounds. Since 2,3,4,5-tetrasilylthiophene could not be synthesized by the common conditions as mentioned above, we used other reaction conditions, which were previously used in the synthesis of 1,2,4,5-tetrakis(diisopropylsilyl)-benzene.[12f] When 2,3,4,5-tetrabromothiophene was allowed to react with chlorodimethylsilane in the presence of magnesium and a catalytic amount of copper(I) cyanide, 2,3,4,5-tetrakis-(dimethylsilyl)thiophene (**1**) was formed in 18% yield together with a large amount of 2,3,5-tris(dimethylsilyl)thiophene (**2**) (Scheme 1). The formation of a large amount of **2** shows that three dimethylsilyl groups can be introduced into the thiophene ring relatively easily, but the fourth dimethylsilyl group cannot be easily attached, probably due to the steric hindrance by the adjacent two dimethylsilyl groups. We also attempted similar reactions of 2,3,4,5-tetrabromothiophene with chlorodiethylsilane or chlorodiisopropylsilane. In the case of chlorodiethylsilane, 2-bromo-1,3,4-tris(diethylsilyl)thiophene (**3**) was formed in 62% yield, but 2,3,4,5-tetrakis(diethylsilyl)thiophene was not detected.[13] The reaction of 2,3,4,5-tetrabromothiophene with chlorodiisopropylsilane gave 3,4-dibromo-2,5-bis(diisopropylsilyl)thiophene (**4**) in 38% yield, but no tri- and tetrasilylthiophenes were obtained.[13] Apparently, the maximum number of silyl groups on the thiophene ring is determined by the bulkiness of the silyl groups. Although the dimethylsilyl group seems relatively small, the fact that the fourth dimethylsilyl group is not easily introduced into the thiophene ring implies that **1** is a crowded molecule. Therefore, we studied the structure of **1**.

Optimized Structure of 1. Unfortunately, we could not analyze the structure of **1** by X-ray crystallography, because **1** was obtained as an oil. Instead, the structure of **1** was calculated and compared with the structure of thiophene. Although the structure of thiophene has already been studied by electron diffraction[14] and microwave techniques,[15] we calculated the structures of **1** and thiophene at the B3LYP/6-31G* level for comparison.[16] In Figure 1, the optimized structures of **1** and thiophene are shown. The optimized structures of **1** and thiophene have C_2 and C_{2v} symmetry, respectively. Compound **1** has a distorted structure compared with thiophene. The thiophene ring of **1** has a planar structure, but the Si(2)−C(2) and Si(3)−C(3) bonds are oriented above and below the thiophene plane. The deviation angles of these Si−C bonds from the thiophene plane are both 5.8°. The Si(1)−C(1) and Si(4)−C(4) bonds exist in the thiophene plane, but the S(1)−C(1)−Si(1) and S(1)−C(4)−Si(4) bond angles (116.62°) are smaller and the Si(1)−C(1)−C(2) and Si(4)−C(4)−C(3) bond angles (133.20°) are larger than the corresponding angles of thiophene (120.06 and 128.40°, respectively). The bond lengths of the thiophene ring of **1** (S(1)−C(1) and S(1)−C(4) = 1.745 Å, C(1)−C(2) and C(3)−C(4) = 1.391 Å, C(2)−C(3) = 1.460 Å) are significantly larger than those of thiophene (S(1)−C(1) and S(1)−C(4) = 1.735 Å, C(1)−C(2) and C(3)−C(4) = 1.367 Å, C(2)−C(3) = 1.430 Å). These structural features clearly indicate that **1** is a crowded molecule with four dimethylsilyl groups, and its structure is distorted to reduce the steric repulsion among the dimethylsilyl groups.

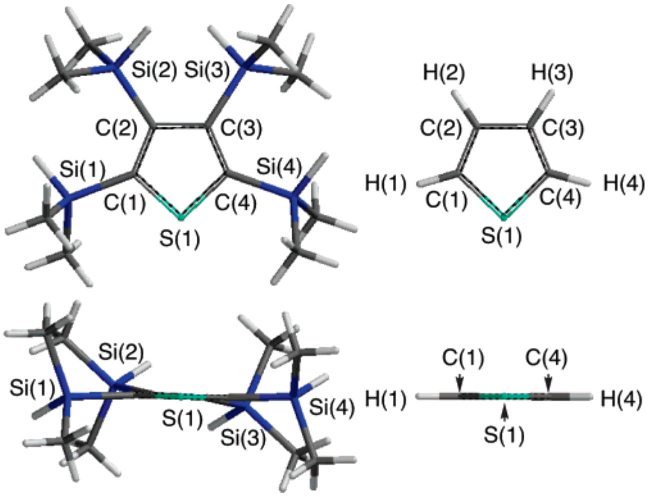


Figure 1. Optimized structures of **1** (top and side views, left) and thiophene (top and side views, right) calculated at the B3LYP/6-31G* level. Selected bond lengths (Å) and angles (deg) of **1**: S(1)−C(1) = 1.745, Si(1)−C(1) = 1.889, Si(2)−C(2) = 1.902, C(1)−C(2) = 1.391, C(2)−C(3) = 1.460; C(1)−S(1)−C(4) = 93.70, S(1)−C(1)−Si(1) = 116.62, S(1)−C(1)−C(2) = 110.14, Si(1)−C(1)−C(2) = 133.20, Si(2)−C(2)−C(1) = 123.53, Si(2)−C(2)−C(3) = 123.32, C(1)−C(2)−C(3) = 112.98. Selected bond lengths (Å) and angles (deg) of thiophene: S(1)−C(1) = 1.735, C(1)−C(2) = 1.367, C(2)−C(3) = 1.430; C(1)−S(1)−C(4) = 91.49, S(1)−C(1)−C(2) = 111.53, S(1)−C(1)−H(1) = 120.06, C(2)−C(1)−H(1) = 128.40, C(1)−C(2)−C(3) = 112.73, C(1)−C(2)−H(2) = 123.33, C(3)−C(2)−H(2) = 123.94.

UV Spectra of 1 and Related Compounds and Electronic Effects of Dimethylsilyl Groups. In Figure 2, the UV spectra of **1**, **2**, 2,5-bis(dimethylsilyl)thiophene (**5**), and thiophene are shown. Thiophene shows an absorption band at 230 nm. As the number of dimethylsilyl groups on the thiophene ring progressively increases, the absorption band shifts bathochromically: the absorption maxima of **5**, **2**, and **1** exist at 245, 252, and 254 nm, respectively. In the cases of **1** and **2**, another absorption band, which might be in the vacuum-ultraviolet region in the cases of **5** and thiophene, appears in the UV region by the bathochromic shift. The extinction coefficients of the lowest energy absorption bands of **5** (ϵ 13 700), **2** (ϵ 11 700),

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(13) The remaining bromine atom of **3** did not react with magnesium under prolonged reaction conditions, probably due to steric hindrance by the adjacent diethylsilyl groups. On the other hand, **4** was gradually decomposed under prolonged reaction conditions to give 2,5-bis(diisopropylsilyl)thiophene and an unidentified product which was different from tri- and tetrasilylthiophenes.

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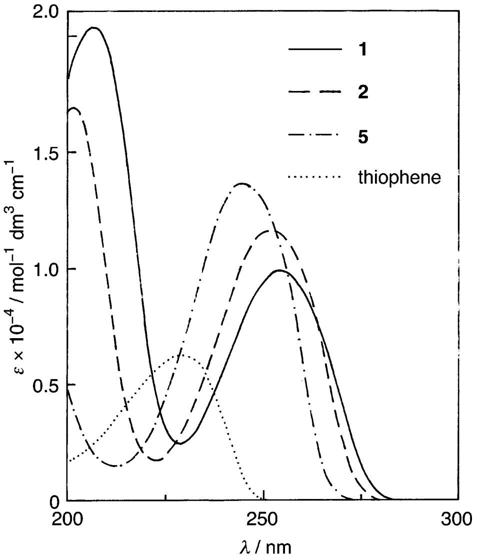

Figure 2. UV spectra of **1**, **2**, **5**, and thiophene in hexane at room temperature.

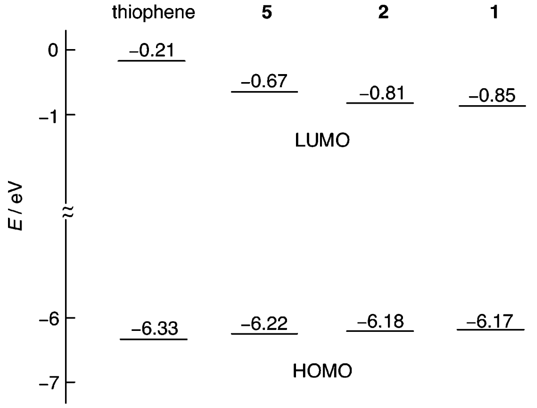

Figure 3. Energy levels of the HOMO's and the LUMO's of **1**, **2**, **5**, and thiophene calculated at the B3LYP/6-31G* level.

and **1** (ϵ 9900) are much larger than that of thiophene (ϵ 6300), although the values of the extinction coefficients have irregular orders of magnitude (thiophene $\ll$ **5** > **2** > **1**). These results indicate that the π electron system of thiophene is considerably perturbed by the dimethylsilyl groups.

The electronic effects of dimethylsilyl groups on the thiophene ring were studied by molecular orbital calculations. The energy levels of the highest occupied molecular orbitals (HOMO's) and the lowest unoccupied molecular orbitals (LUMO's) of **1**, **2**, **5**, and thiophene are shown in Figure 3. As the number of dimethylsilyl groups progressively increases, the HOMO is more destabilized and the LUMO is more stabilized. The destabilization of the HOMO is caused by the $\sigma-\pi$ conjugation[12f] between Si−C(methyl) σ orbitals and a π orbital of thiophene (Figure 4). The LUMO of thiophene is stabilized by the $\sigma^*-\pi^*$ conjugation[17] between Si−C(methyl) σ^* orbitals and a π^* orbital of thiophene (Figure 4). As a result of these effects, the energy gap between the HOMO and the LUMO successively decreases as the number of dimethylsilyl groups progressively increases. The bathochromic shift of the lowest energy absorption band in the UV spectra is explained by this decreasing energy gap.

The $\sigma-\pi$ conjugation in the HOMO and the $\sigma^*-\pi^*$ conjugation in the LUMO also affect the extinction coefficients of the lowest energy absorption bands of the UV spectra. The molecular orbital calculations at the CNDO/S level considering configuration interaction showed that the lowest energy absorption bands of **1**, **2**, **5**, and thiophene are due to the transition from the HOMO to the LUMO. Therefore, the transition moment is expressed by

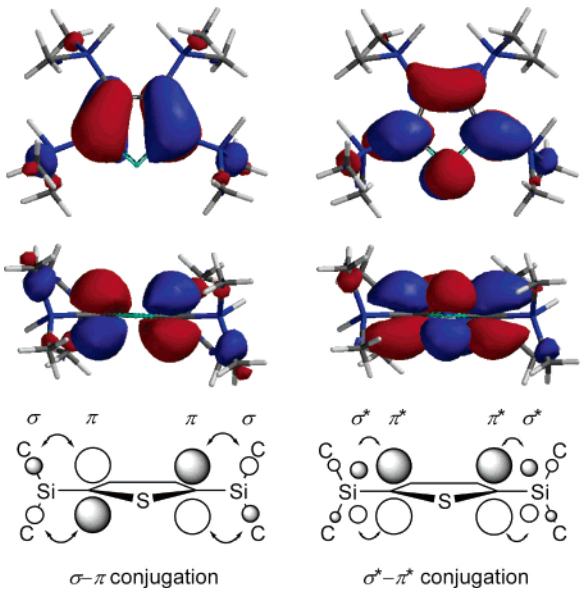

Figure 4. Top and side views of the HOMO (left) and top and side views of the LUMO (right) of **1** calculated at the B3LYP/6-31G* level.

$$\mu = \int \psi_{\mathrm{HOMO}} \boldsymbol{M} \psi_{\mathrm{LUMO}} \, d\tau$$

where ψ_{HOMO} and ψ_{LUMO} are the wave functions of the HOMO and the LUMO, respectively, and $\boldsymbol{M}$ is the operator of the dipole moment.[18]

According to this equation, we can assess the transition moment qualitatively by the following procedure. The multiplication of ψ_{HOMO} and ψ_{LUMO} of thiophene gives an alternating arrangement of positive and negative areas in the thiophene ring (Scheme 2). Substitution on the C(1) or C(4) atom by a dimethylsilyl group leads to the participation of the Si−C(methyl) σ and σ^* orbitals, expanding the negative area on the C(1) atom and the positive area on the C(4) atom. The similar expanding effect by a dimethylsilyl group also works at the C(2) and C(3) positions, but the effect is limited because the lobes of the Si−C(methyl) σ and σ^* orbitals are smaller than those at the C(1) and C(4) positions, as shown in Figure 4.

In Figure 5, the results of the multiplication of ψ_{HOMO} and ψ_{LUMO} are summarized. In the case of thiophene, the partial transition moment in the C(1) to C(4) direction is partially compensated by the partial transition moment in the C(3) to C(2) direction, resulting in the total transition moment in the C(1) to C(4) direction. The partial transition moment in the C(1) to C(4) direction is enlarged by the expansion of the negative area on the C(1) atom and the positive area on the C(4) atom in the case of **5**. Therefore, the total transition moment of **5** is predicted to be much larger than that of thiophene. In the case of **2**, the partial transition moment in the C(3) to C(2) direction is increased by the slight expansion effect of the dimethylsilyl

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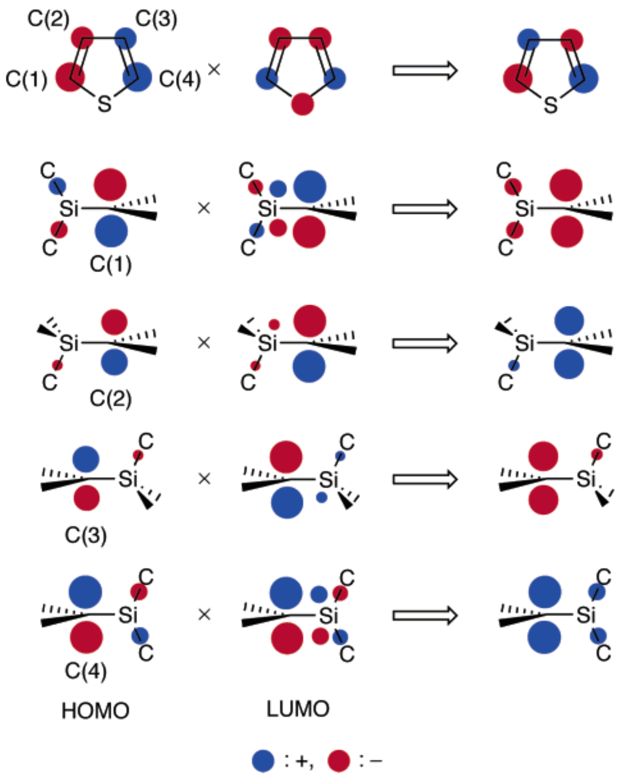
Scheme 2



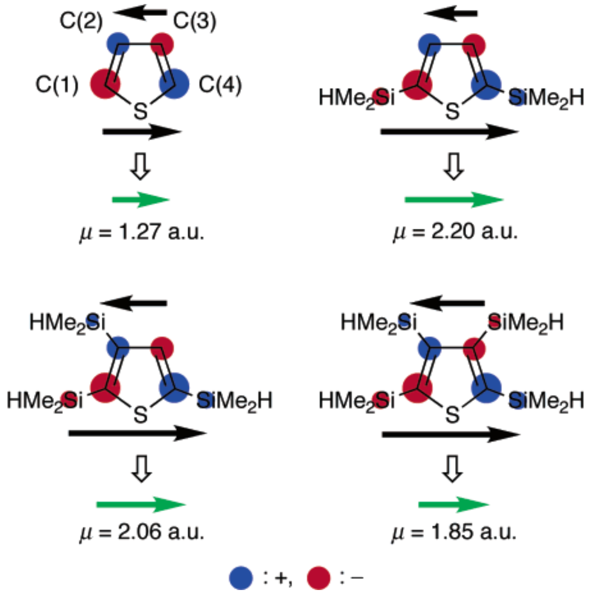


Figure 5. Transition moments of **1**, **2**, **5**, and thiophene calculated at the CNDO/S level considering configuration interaction. The black arrows denote the partial transition moments in the C(1) to C(4) direction and in the C(3) to C(2) direction. Total transition moments are shown by the green arrows.

group on the C(2) atom, and therefore, the total transition moment becomes smaller than that of **5**. Similarly, the total transition moment of **1** is presumed to be smaller than that of **2**. In fact, the transition moments calculated at the CNDO/S level considering configuration interaction are 1.27 (thiophene), 2.20 (**5**), 2.06 (**2**), and 1.85 atomic units (**1**). These results are in good accord with the extinction coefficients (thiophene $\ll$ **5** > **2** > **1**) observed in the UV spectra.

In summary, we synthesized **1**, the first 2,3,4,5-tetrasilylthiophene, and found that its structure is distorted to reduce the steric repulsion among the dimethylsilyl groups. Also, we found that the dimethylsilyl groups affect the electronic properties of thiophene and the features of UV absorption bands are clearly explained by the molecular orbital calculations.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. 2,5-Bis(dimethylsilyl)thiophene,[6b] 2,3,4,5-tetrabromothiophene,[19] chlorodiethylsilane,[20] and chlorodiisopropylsilane[21] were prepared by published procedures. Magnesium turnings (Sigma-Aldrich), copper(I) cyanide (Wako), and chlorodimethylsilane (Tokyo Kasei) were purchased.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained with a JEOL JNM-LA500 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8700 spectrophotometer. UV spectra were obtained with a JASCO V-570 spectrophotometer. Mass spectra were recorded on a JEOL JMS-SX102 mass spectrometer. Elemental analyses were performed by The Microanalytical Laboratory of Department of Chemistry, Graduate School of Science, The University of Tokyo, and Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Synthesis of 2,3,4,5-Tetrakis(dimethylsilyl)thiophene (1) and 2,3,5-Tris(dimethylsilyl)thiophene (2). A solution of 2,3,4,5-tetrabromothiophene (1.97 g, 4.93 mmol) in THF (6 mL) was added dropwise to a mixture of magnesium turnings (0.498 g, 20.5 mmol), copper(I) cyanide (0.097 g, 1.1 mmol), and chlorodimethylsilane (2.08 g, 22.0 mmol) at room temperature. The reaction mixture was refluxed for 3 days. Hexane was added to the reaction mixture, and insoluble materials were filtered out. The filtrate was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was separated by recycle-type HPLC (ODS, methanol) to give **1** (0.281 g, 18%) and **2** (0.790 g, 62%) as colorless oils.

1: ^{1}H NMR (CDCl$_3$) δ 0.41 (d, 12H, $J = 4.0$ Hz), 0.43 (d, 12H, $J = 3.7$ Hz), 4.76 (sept, 2H, $J = 3.7$ Hz), 4.79 (sept, 2H, $J = 4.0$ Hz); ^{13}C NMR (CDCl$_3$) δ −1.6, −1.4, 151.8, 154.2; ^{29}Si NMR (CDCl$_3$) δ −24.4, −23.8; IR (NaCl) 2960, 2150, 1400, 1250, 890, 840, 770 cm^{-1}; UV (λ_{max} in hexane) 207 (ϵ 20 400), 254 nm (9900); MS *m/z* 316 (M$^+$, 55), 315 (45), 314 (54), 301 (61), 299 (39), 73 (100). Anal. Calcd for $C_{12}H_{28}SSi_4$: C, 45.50; H, 8.91. Found: C, 45.65; H, 8.72.

2: ^{1}H NMR (CDCl$_3$) δ 0.58 (d, 6H, $J = 3.7$ Hz), 0.62 (d, 6H, $J = 3.7$ Hz), 0.64 (d, 6H, $J = 3.7$ Hz), 4.85 (sept, 1H, $J = 3.7$ Hz), 4.87 (sept, 1H, $J = 3.7$ Hz), 4.98 (sept, 1H, $J = 3.7$ Hz), 7.73 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −2.53, −2.45, −2.0, 141.5, 142.6, 147.2, 151.1; ^{29}Si NMR (CDCl$_3$) δ −24.8, −24.3, −23.7; IR (NaCl) 3040, 2960, 2130, 1460, 1250, 1020, 890, 870, 840, 770 cm^{-1}; UV (λ_{max} in hexane) 202 (ϵ 16 900), 252 nm (11 700); MS *m/z* 258 (M$^+$, 52), 243 (100), 199 (91), 73 (46). Anal. Calcd for $C_{10}H_{22}SSi_3$: C, 46.44; H, 8.57. Found: C, 46.68; H, 8.36.

Synthesis of 2-Bromo-1,3,4-tris(diethylsilyl)thiophene (3). A solution of 2,3,4,5-tetrabromothiophene (1.00 g, 2.50 mmol) in THF (8 mL) was added dropwise to a mixture of magnesium turnings (0.450 g, 18.5 mmol), copper(I) cyanide (0.100 g, 1.12 mmol), chlorodiethylsilane (2.21 g, 18.0 mmol), and THF (2 mL) at room temperature. The reaction mixture was refluxed for 3 days and 19 h. The reaction mixture was poured into a mixture of hexane and water. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was separated by recycle-type HPLC (ODS, methanol) to give **3** (0.656 g, 62%) as a colorless oil. ^{1}H NMR (CDCl$_3$): δ 0.89−1.06 (m, 30H), 4.39 (quin, 1H, $J = 3.5$ Hz), 4.41 (quin, 2H, $J = 3.5$ Hz). ^{13}C NMR (CDCl$_3$): δ 3.5,

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4.0, 4.9, 8.2, 8.3, 8.7, 126.0, 135.9, 146.2, 151.8. ^{29}Si NMR ($CDCl_3$): δ −12.8, −10.9, −9.7. IR (NaCl): 2950, 2870, 2130, 1460, 1440, 1410, 1230, 1030, 970, 870, 860, 810, 720 cm^{-1}. UV (λ_{max} in hexane): 208 (ϵ 19 700), 252 nm (9100). MS: m/z 422 (M$^+$(^{81}Br), 20), 393 (^{81}Br, 100), 365 (^{81}Br, 27), 225 (41), 197 (43). Anal. Calcd for $C_{16}H_{33}BrSSi_3$: C, 45.58; H, 7.89. Found: C, 45.38; H, 7.71.

Synthesis of 3,4-Dibromo-2,5-bis(diisopropylsilyl)thiophene (4). A solution of 2,3,4,5-tetrabromothiophene (0.500 g, 1.25 mmol) in THF (8 mL) was added dropwise to a mixture of magnesium turnings (0.137 g, 5.64 mmol), copper(I) cyanide (0.024 g, 0.27 mmol), chlorodiisopropylsilane (0.842 g, 5.59 mmol), and THF (2 mL) at room temperature. The reaction mixture was stirred for 4 h at room temperature. The reaction mixture was poured into a mixture of hexane and water. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was separated by recycle-type HPLC (ODS, methanol) to give **4** (0.224 g, 38%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.03 (d, 12H, J = 7.5 Hz), 1.10 (d, 12H, J = 7.5 Hz), 1.38 (sept of d, 4H, J = 7.5, 3.6 Hz), 4.15 (t, 2H, J = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ 11.1, 18.7, 18.8, 123.2, 136.7. ^{29}Si NMR ($CDCl_3$): δ −1.2. IR (NaCl): 2940, 2860, 2110, 1460, 1380, 1250, 1010, 880, 790 cm^{-1}. UV (λ_{max} in hexane): 258 nm (ϵ 9400). MS: m/z 470 (M$^+$(^{79}Br^{81}Br), 51), 427 (^{79}Br^{81}Br, 100), 399 (^{79}Br^{81}Br, 32), 385 (^{79}Br^{81}Br, 23). Anal. Calcd for $C_{16}H_{30}Br_2SSi_2$: C, 40.85; H, 6.43. Found: C, 40.62; H, 6.31.

Molecular Orbital Calculations of 1, 2, 5, and Thiophene. The optimized structures of **1** and thiophene and the HOMO's and the LUMO's of **1**, **2**, **5**, and thiophene were calculated at the B3LYP/6-31G* level by using Spartan '04[22] on a Dell Dimension XPSGEN4 computer. The transition moments of **1**, **2**, **5**, and thiophene were calculated at the CNDO/S level considering configuration interaction by using WinMOPAC[23] on a Dell Dimension 4500C computer.

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