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Nanosized, Starlike Silicon Compounds. Synthesis and Optical Properties of Tris[(*tert*-butyldimethylsilyl)oligothienylenedimethylsilyl]methylsilanes

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Starlike molecules with arms consisting of a *tert*-butyldimethylsilyloligothienylenedimethylsilyl unit, $\mathrm{MeSi[SiMe_2(T)_{\it n}SiMe_2(\it t\text{-}Bu)]_3}$ (**7**−**11**; $n = 2-6$, T = thienylene) were prepared by the reactions of tris(chlorodimethylsilyl)methylsilane, which was chosen as a core, with the *tert*-butyldimethylsilyl-substituted lithiooligothienylenes used for construction of the arms. UV−visible absorption and fluorescence properties of **7**−**11** have been studied in a dioxane solution. The molecules **7**−**11** showed high fluorescence quantum yields with respect to the corresponding oligothiophenes. Compounds **7** and **8** revealed longer lifetimes than those of bi- and terthiophene. The results of X-ray crystallographic analysis of the bromo derivative **12** are described. The density functional theoretical calculations were also carried out to compare the geometrical structures and the excitation energies with the available experimental data.

Introduction

Three-dimensional, metal-containing molecules, organometallic dendrimers, are attracting considerable attention as functionality materials with new and potentially useful properties.[1] In the field of organosilicon chemistry, mainly three types of dendrimers, whose frameworks are composed of silicon−silicon bonds,[2] silicon−oxygen bonds,[3] and silicon−carbon bonds,[4] have been reported to date. However, little interest has been shown in the chemistry of the dendrimers that involve both a silyl unit and a π-electron system in their arms. To our knowledge, the synthesis and some properties of two types of the dendrimers, silylthiophene dendrimers[5] and silylacetylene dendrimers,[6] have been reported so far.

Recently, we have reported the first synthesis of nanosized, starlike molecules bearing arms that have a regular alternating arrangement of an Si−Si bond and bithienylene unit that extends to three directions.[7] We also demonstrated that the nanosized, starlike mol-

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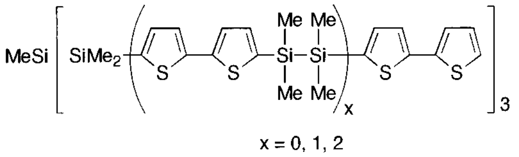
ecules showed high fluorescence quantum yields and long lifetimes of the exited state.[7,8]



To get more information on the chemistry of nanosized, starlike silicon compounds, we initiated systematic investigation concerning the synthesis and properties of the starlike molecules bearing the arms that are composed of an Si unit and π-electron system. In this paper we report the synthesis and optical properties of tris[(*tert*-butyldimethylsilyloligothienylene)dimethylsilyl]methylsilanes, MeSi[SiMe$_2$(T)$_n$SiMe$_2$(*t*-Bu)]$_3$ (n = 2−6, T = thienylene). We also report the results of theoretical calculations of the related starlike molecules.

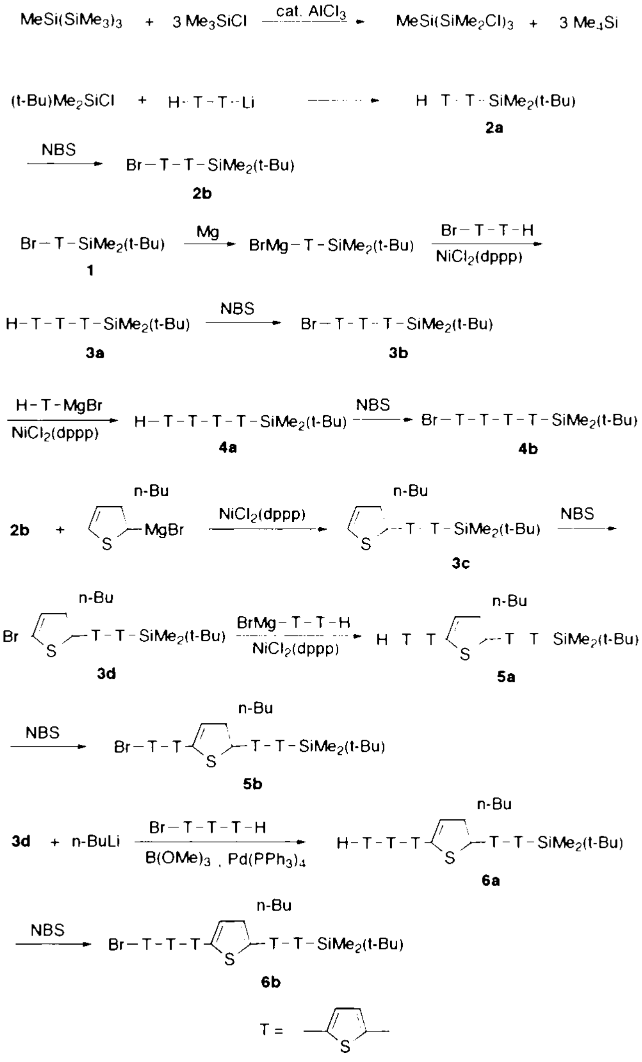
Results and Discussion

The method used for the synthesis of starlike compounds is based on the reaction of tris(chlorodimethylsilyl)methylsilane,[2d] which was chosen as a core, with *tert*-butyldimethylsilyl-substituted lithiooligothienylenes. Tris(chlorodimethylsilyl)methylsilane used as a core was prepared by the Me−Cl exchange reaction of tris(trimethylsilyl)methylsilane with a large excess of chlorotrimethylsilane in the presence of a catalytic amount of anhydrous aluminum chloride,[9] as shown in Scheme 1. The synthesis of compounds used as the arms is also shown in Scheme 1.

5′-Bromo-5-*tert*-butyldimethylsilyl(2,2′-bithiophene) (**2b**) was prepared by treating 5-*tert*-butyldimethylsilylbithiophene (**2a**), which was obtained by the reaction of *tert*-butyldimethylchlorosilane with 2-lithiobithiophene in 56% yield, with 1 equiv of NBS in chloroform in 93% yield. 5″-Bromo-5-*tert*-butyldimethylsilyl(2,2′; 5′,2″-terthiophene) (**3b**) was prepared in 96% yield by bromination of *tert*-butyldimethylsilylterthiophene (**3a**, 75% yield) obtained from the nickel-catalyzed Grignard coupling of *tert*-butyldimethylsilylthienylmagnesium bromide with 5-bromobithiophene. Similarly, the nickel-catalyzed reaction of **3b** with 2-thienylmagnesium bromide afforded *tert*-butyldimethylsilylquaterthiophene (**4a**, 21% yield), which can readily be transformed into the corresponding 5‴-bromo-5-*tert*-butyldimethylsilylquaterthiophene (**4b**) in 84% yield.

Introduction of a 3-butyl-substituted thiophene group to the oligothiophene unit was carried out by using the nickel-catalyzed reactions of a Grignard reagent prepared from 2-bromo-3-*n*-butylthiophene with **2b**. Thus, treatment of **2b** with 2-(3-*n*-butylthienyl)magnesium bromide in the presence of a catalytic amount of NiCl$_2$(dppp) in THF gave 5-*tert*-butyldimethylsilyl-3″-*n*-butylterthiophene (**3c**) in 89% yield. The reaction of **3c** with NBS in chloroform readily afforded 5″-bromo-3″-*n*-butyl-5-*tert*-butyldimethylsilylterthiophene (**3d**) in 90% yield.

Scheme 1



The nickel-catalyzed reaction of **3d** with a Grignard reagent prepared from 2-bromobithiophene produced 5-*tert*-butyldimethylsilyl-3″-*n*-butyl-2:2′,5′:2″,5″:2‴,5‴:2⁗-quinquethiophene (**5a**) in 13% yield, while the reaction of **3d** with *n*-butyllithium and trimethoxyborane, followed by treatment of the resulting solution with 5-bromoterthiophene and tetrakis(triphenylphosphine)palladium(0), produced 5-*tert*-butyldimethylsilyl-3″-*n*-butylsexithiophene (**6a**) in 65% yield. The bromination of **5a** and **6a** with the use of NBS in chloroform afforded the respective bromo derivatives **5b** and **6b** in 87% and 88% yields.

The bromo−lithium exchange reaction of **2b**, **3b**, **4b**, **5b**, and **6b** with *n*-butyllithium, followed by treatment of the resulting lithium compounds with tris(chlorodimethylsilyl)methylsilane, gave the respective nanosized, starlike molecules, tris[(*tert*-butyldimethylsilyloligothienyl)dimethylsilyl]methylsilanes (Scheme 2; **7**, 51% yield; **8**, 43% yield; **9**, 37% yield; **10**, 28% yield; and **11**, 29% yield).

Starlike silicon compound **7** is a pastelike yellow liquid, while compound **8** (light yellow), **9** (dark yellow), **10** (orange), and **11** (red) are solids and soluble in common organic solvents such as benzene, chloroform, and THF, but hardly soluble in ethanol. The structures of compound **7**−**11** were verified by mass and ^{1}H, ^{13}C,

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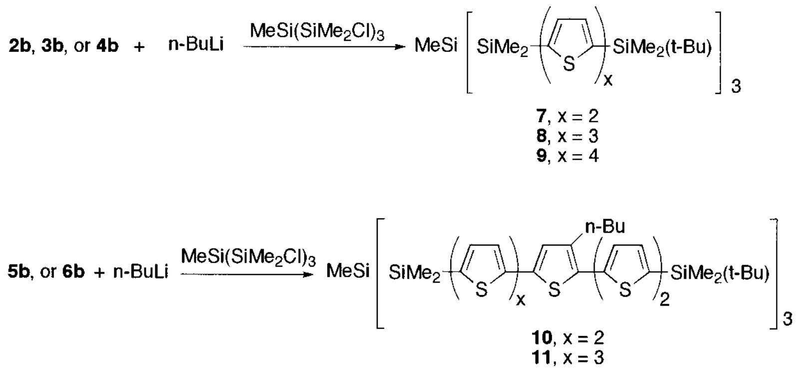
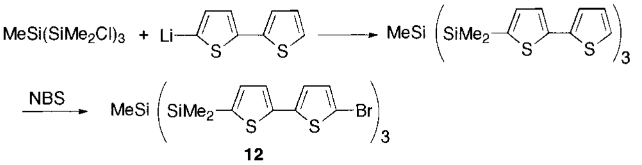
Scheme 2



and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis (see the Experimental Section).

We have interest in the molecular structure of the starlike molecules and attempted to carry out X-ray crystallographic analysis. However, all attempts to obtain single crystals that can be used for X-ray analysis by recrystallization of compound **8**−**11** were unsuccessful. Therefore, we attempted to prepare the starlike molecule bearing a bromine atom as a terminal group, instead of the *tert*-butyldimethylsilyl group, tris[(5′-bromo-2,2′-bithiophen-5-yl)dimethylsilyl]methylsilane (**12**). Thus, the reaction of tris(chlorodimethylsilyl)methylsilane with lithiobithiophene in ether produced tris[(2,2′-bithiophen-5-yl)dimethylsilyl]methylsilane in 89% yield, as a bright yellow viscous liquid. Treatment of this compound with 3 equiv of NBS in chloroform produced the starlike molecule **12** in 92% yield as a colorless solid (Scheme 3). Fortunately, we could obtain crystals of **12** suitable for X-ray crystallographic analysis by recrystallization from chloroform.

Scheme 3



Crystal Structure of MeSi(SiMe$_2$T$_2$Br)$_3$. A single crystal of **12** was obtained and the crystal structure was determined by an X-ray diffraction study. Cell dimensions, data collections, and refinement parameters are listed in Table 1. Figure 1 depicts the ORTEP drawing of **12**. Two of the bromobithienyl units are located in a parallel fashion to adopt π-stacking in the crystal structure, although there is no direct evidence for the existence of intramolecular through-space $\pi\angle\pi$-interaction. The adjacent thiophene rings in each of the bithienyl units are slightly rotated but still retain high coplanarity, as indicated by the torsion angles of S−C$\alpha\angle$C$\alpha\angle$S ranging from −168.0(5)° to −170.8(4)°, as listed in Table 2. Furthermore, the Si−Si bond is arranged to be almost perpendicular with respect to the thiophene rings to permit the $\sigma\angle\pi$-conjugation between the Si−Si σ-orbitals and the thiophene π-orbitals, similar to the crystal structure of (BrTT)SiEt$_2$SiEt$_2$(TTBr) reported previously.[10] These structural parameters clearly indicate that the intramolecular orbital interaction may take place efficiently, providing the extended conjugation in the molecule, by the through-space $\pi\angle\pi$-interaction, π-conjugation, and $\sigma\angle\pi$-conjugation.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for MeSi(SiMe$_2$T$_2$Br)$_3$

mol formula	$C_{31}H_{33}Br_3S_6Si_4$
mol wt	950.02
space group	$P2_1/n$ (No. 14)
cell dimens	
a, Å	14.996(2)
b, Å	13.565(3)
c, Å	19.386(1)
β, deg	92.546(7)
V, Å^3	3939.8(9)
Z	4
D_{cacld}, Mg/m^3	1.602
F_{000}	1904.00
cryst size, mm^3	0.4 × 0.4 × 0.3
cryst color	green
μ, cm^{-1}	81.14
diffractometer	Rigaku AFC-6
temp, K	298
wavelength, Å	1.5418 (Cu Kα)
monochromator	graphite cryst
scan type	$\omega-2\theta$
scan speed, deg/min	4
scan width, deg	$6 \leq 2\theta \leq 125.8$
no. of unique reflns	6046
no. of obsd reflns ($I > 3\sigma(I)$)	4232
corrections	Lorentz−polarization absorption (trans. factors: 0.5950−0.9994)
refln/parameter ratio	10.66
R	0.066
R_w[a]	0.082

[a] Weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

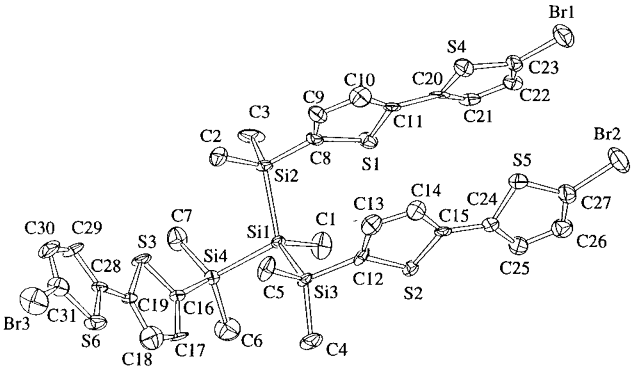


Figure 1. ORTEP diagram for **12** showing thermal ellipsoids at the 50% level; hydrogen atoms were omitted for clarity.

Table 2. Selected Torsion Angles of $MeSi(SiMe_2T_2Br)_3$ (deg)

S1−C11−C20−S4	−170.8(4)	S1−C8−Si2−Si1	53.4(5)
S2−C15−C24−S5	−169.8(4)	S2−C12−Si3−Si1	−74.3(5)
S3−C19−C28−S6	−168.0(5)	S3−C16−Si4−Si1	82.5(5)

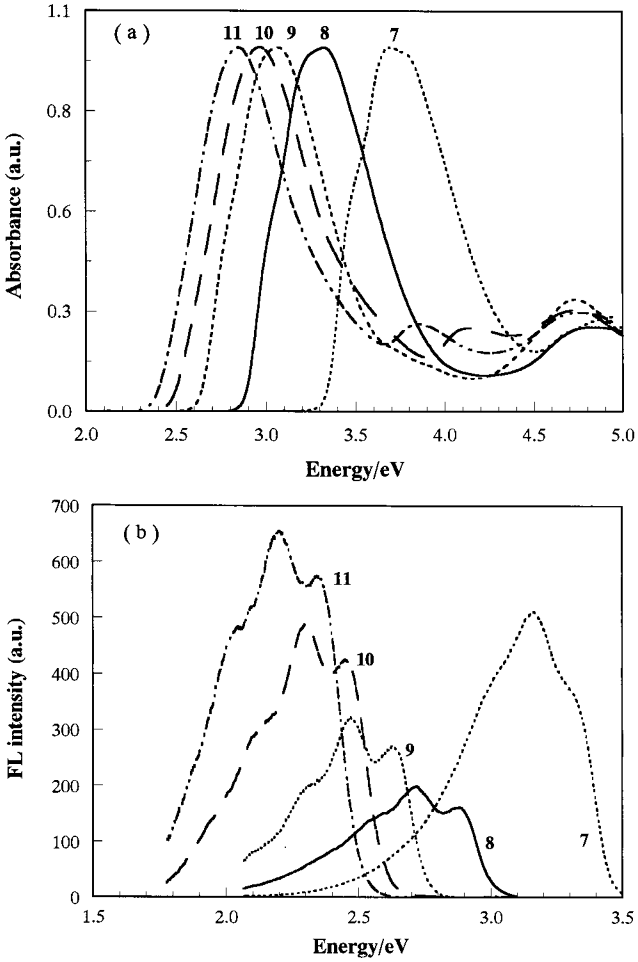


Figure 2. (a) Absorption and (b) emission spectra of compounds **7**−**11** in dioxane. The absorption spectra were normalized to unity at the maxima. The emission spectra were obtained with excitation at 366 nm, where the sample solution showed an absorbance of ca. 0.05.

Optical Properties. Figure 2 shows UV−visible absorption and fluorescence spectra of compounds **7**−**11** in dioxane. Spectroscopic characteristics of these compounds are summarized in Table 3, where the data for relevant oligothiophenes (T_n)[11−13] are also given for comparison. A considerable red shift is clearly noted in absorption and fluorescence maximum wavelengths when *n* increases from 2 to 6. The *n* dependence of the absorption and fluorescence maximum wavelengths for these compounds is very similar to that for the T_n series, indicating that the spectroscopic characteristics of these starlike compounds are primarily dependent on the π-conjugated oligothiophene part.[8] As shown in Table 3, quantum yields of compounds **7**−**11** do not increase monotonically with *n*, and a minimum appears at $n = 3$. These results are related to the $\sigma\angle\pi$-interaction between the σ-part and the π-part in the molecule, arising from the lowering of the energy of the π-system of the oligothiophene block with respect to the available electronic levels of the oligosilanylene moiety.[14,15] The $\sigma\angle\pi$-interaction in compounds **7**−**11** appears to increase as *n* decreases and becomes the strongest for the disilanylene−bithienylene combination, being similar to that observed for oligosilanylene−oligothienylene copolymers.[15] Kinetics for the decay of the first singlet excited state of compounds **7**−**11** was also investigated. Compounds **10** and **11** exhibited a single exponential decay, leading to lifetimes of 0.72 and 0.89 ns, respectively. The decay profiles were possibly fitted roughly with a single-exponential curve for compounds **7**−**9**, giving lifetimes in parentheses of Table 3 only for comparison with T_ns. Strictly speaking, these decay profiles were not single exponential. Two decay components were observed: a fast component varied from 0.4 to 0.5 ns and a slow one from 2.0 to 2.6 ns. We noted that Suto and co-workers[16] observed that some silanylene−biphenylene $\sigma\angle\pi$-conjugated polymers showed two components in the decay profile in tetrahydrofuran at room temperature, while the others exhibited only a single exponential. These authors suggested the existence of two stable conformation between the σ- and π-conjugated units to account for the two components observed in the decay.[16] Our results are very similar to theirs, possibly due to the same reason.

Table 3. Spectroscopic Characteristics (in dioxane) of Compounds 7−11 in Comparison with Oligothiophenes[8,12−14]

compd	$\lambda_{max,Abs}$[a] (nm)	$\lambda_{max,F}$ (nm)	ϕ_F	τ_F (ns)	k_R[b] (ns^{-1})	k_{NR}[b] (ns^{-1})
7[c]	335	374	0.50	(0.74)		
8[c]	373	430	0.20	(0.48)		
9[c]	404	472	0.27	(0.53)		
10	417	506	0.43	0.72	0.60	0.78
11	435	529	0.61	0.89	0.69	0.44
T_2	303	362	0.018	0.046	0.39	21.34
T_3	354	407	0.066	0.21	0.31	4.45
T_4	391	446	0.18	0.49	0.37	1.67
T_5	419	482	0.28	0.84	0.33	0.86
T_6	435	507	0.36	1.04	0.33	0.63

[a] See ref 17. [b] The radiative and nonradiative rate constants are calculated from $k_R = \phi_F/\tau_F$ and $k_{NR} = (1 - \phi_F)/\tau_F$. [c] See text for τ_F.

Structures and Electronic States of Starlike Compounds. Geometrical structures and excitation energies of the starlike molecules have been investigated using the plane wave (PW) and Gaussian type function (GTF) density functional theory (DFT) programs CASTEP[18] and Gaussian98.[19] In the plane wave

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(17) UV data in THF, λ_{max} nm (ϵ, M^{-1} cm^{-1}): 336 (86 000) for **7**; 374 (106 000) for **8**; 406 (140 000) for **9**; 419 (150 000) for **10**; 436 (180 000) for **11**.

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DFT calculations, the ultrasoft core potentials were used, and only the valence electrons were explicitly treated. The kinetic cutoff energy was set to 200 eV. In case of molecular calculations with the GTF DFT method, the Becke[20] and Lee−Yang−Parr functionals[21] were used for geometry optimization with the Los Alamos model core potentials.[22] The excitation energy was estimated by the single excitation configuration interaction (SECI) method, where the all-electron 6-31G basis set and the hybrid DFT (B3LYP) methods were employed.[23]

The molecules (in unit cells) investigated are MeSi-$(SiMe_2T_xH)_3$ (T = thiophene) (x = 1−4) and **12**. The X-ray crystal structure analysis data is available only for **12**. The structures of five crystals (unit cells and lattice parameters) are optimized using the PW DFT method. Figure 3 shows the side and top views of compound **12** and the top view of $MeSi(SiMe_2T_4H)_3$. These structures have an interesting character. Two of three T−T arms extend in a parallel rather than "fan" shaped structure, and we refer to this as a "fork" shape. Using **12**, the calculated structure parameters were compared with the X-ray structure analysis data. The largest discrepancies were 0.046 Å, 4.7°, and 1.1° for bond lengths, bond angles, and torsion angles, respectively. Agreement in the torsion angles is especially good. Relatively large differences in the bond angle come from the Si−Si−Si moiety, and it may be ascribed to a very weak bending force constant. Most of structure parameters agree with much smaller differences.

The stable structures were also investigated for an isolated molecule using the GTF DFT method. The relative stability was compared between the fork-shaped and fan-shaped structures for $MeSi(SiMe_2T_xH)_3$ (x = 1−3) and **12**. Figure 4 shows the optimized structures of the fork- and fan-shaped molecule $MeSi(SiMe_2T_2H)_3$. The fork-shaped molecular structure is considerably different from that optimized for the crystalline state, and the discrepancy between the calculation and X-ray structure data becomes bigger. The energies are shown in Table 4. The fan-shaped structures were found to be as stable as the fork-shaped structures or only slightly more stable. In these model compounds, the peripheral *tert*-butyldimethylsilyl groups were replaced by hydrogen or bromine atoms, and the steric repulsion was thought to be underestimated. We tried to simulate the repulsion with real molecules. Two conformations of the compound $MeSi[SiMe_2T_2SiMe_2(t\text{-}Bu)]_3$ were constructed by replacing the bromine atoms with the *tert*-butyldimethylsilyl groups in compound **12**. The optimized structures of **12** were used intact, and the *tert*-butyldimethylsilyl moiety was separately optimized by the force field implemented in Cerius2 software. The single point energy was calculated and is also shown in the last row of Table 4. The fan-shaped structure was found to be more stable by 12 kcal/mol. This large difference may be partly responsible for the single point calculation; however, it is true that the steric repulsion becomes large with bulky substituent groups. Thus the superior stability for fork-shaped structures is limited to the crystalline state, and it may be ascribed to the more dense stacking and the resulting extra stabilization caused by the van der Waals interactions in the crystalline state.

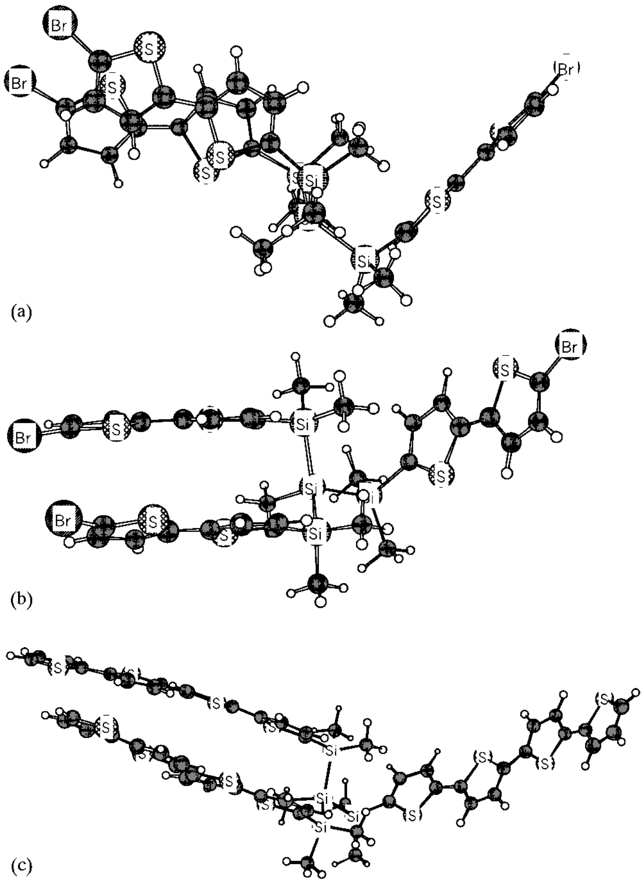

Figure 3. Optimized structures of dendrimers with the PW DFT method: (a) side view of $MeSi(SiMe_2T_2Br)_3$, (b) top view of $MeSi(SiMe_2T_2Br)_3$, and (c) top view of MeSi-$(SiMe_2T_4H)_3$.

The excitation energy is estimated in two ways. Table 5 shows the band gap energy estimated from the energy difference between the top of the valence band and the bottom of the conduction band with the PW DFT method and the excitation energy evaluated by the SECI method, as well as the observed values. Usually the DFT calculations underestimate the band gap, and the estimated band gap energies are only ca. 60% of the observed excitation energy. The SECI calculation with the B3LYP hybrid functional gives good estimates of the experimental values. In both calculations, the excitation energy decreases with the length of thiophene chain, and this trend is consistent with the experimental finding.

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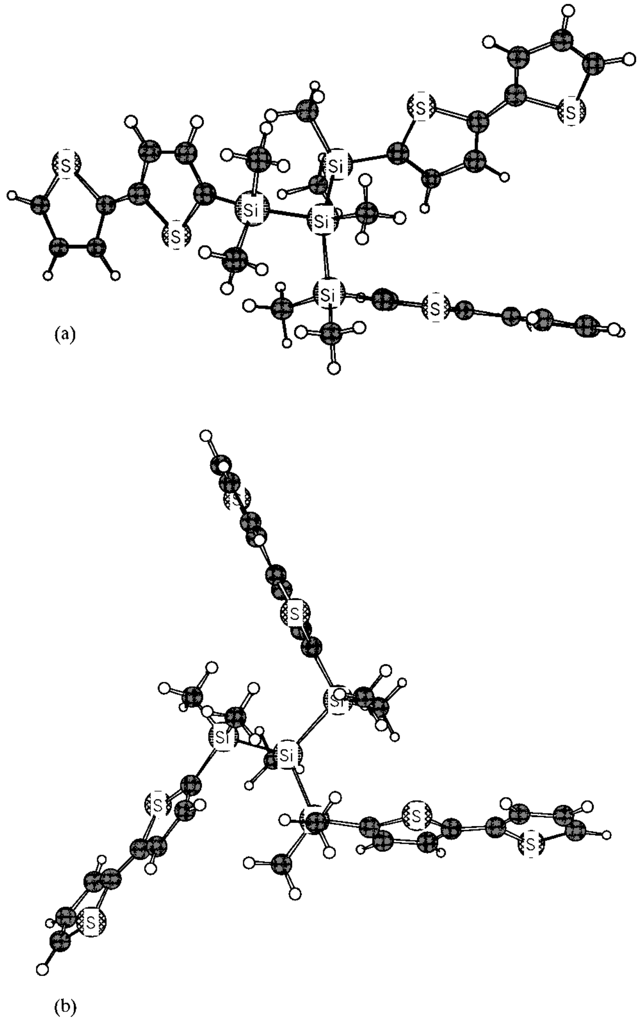

Figure 4. Two optimized structures of $MeSi(SiMe_2T_2H)_3$ with the GTF DFT method: (a) the "fork"-shaped structure and (b) the "fan"-shaped structure.

Table 4. Energy Difference between Two Optimized Structures for $MeSi(SiMe_2T_xH)_3$, $MeSi(SiMe_2T_2Br)_3$, and $MeSi[SiMe_2T_2SiMe_2(t\text{-}Bu)]_3$, as Free Molecules by the GTF DFT Method

compd	ΔE (kcal/mol)[a]
$MeSi(SiMe_2T)_3$	−1.4
$MeSi(SiMe_2T_2)_3$	−1.0
$MeSi(SiMe_2T_2Br)_3$	−1.2
$MeSi(SiMe_2T_3)_3$	−0.8
$MeSi[SiMe_2T_2SiMe_2(t\text{-}Bu)]_3$[b]	−12.2

[a] ΔE is defined as $\Delta E = E$(fan shaped) − E(fork shaped). A negative value means there is a larger stability for the fan-shaped structure. [b] Single point calculation. Optimized structure of $MeSi(SiMe_2T_2Br)_3$ is employed. The Br atom is replaced by $SiMe_2(t\text{-}Bu)$ group. The structure of $SiMe_2(t\text{-}Bu)$ group is optimized by the force field.

The several orbital density maps for the frontier orbital regions are illustrated in Figure 5, which are important to learn what orbitals are related to the photoexcitation. For the PW DFT calculation of $MeSi(SiMe_2T_2H)_3$, the highest occupied (HO) and lowest unoccupied (LU) crystal orbitals are the 106th and 107th orbitals. For simplicity, we refer, for example, to the 105th and 109th orbitals as [HO − 1] and [LU + 2], respectively. The SECI calculation shows that almost all excitation occurs from the [HO − 1] and [HO] orbitals to the [LU], [LU + 1], and [LU + 2] orbitals. The electron density maps for these orbitals are shown in Figure 5b,c, and most of electron density is localized in the thiophene rings. This means the $\pi\angle\pi^*$-transition. A still lower energy orbital [HO − 3] and still higher energy orbital [LU + 3] are also illustrated in Figure 5a,d, where the larger amount of electron density is localized at the Si−Si bonds. It is said that, for the shorter π-chain systems including Si−Si bonds, the excitation generally occurs with the $\sigma\angle\sigma^*$-transition of Si−Si bonds. However, in the present systems, the thiophene ring π- and π^*-orbitals are responsible for the photoexcitation.

Table 5. Observed and Calculated Excitation Energies for $MeSi(SiMe_2T_x)_3$[a]

			GTF calculation	
x	obsd λ_{max}	PW calculation of band gap	excitation energy	oscillator strength
1	no data	3.67	4.97	0.164
			5.05	0.102
2	3.70	2.43	3.70	0.331
			3.88	0.047
3	3.32	1.99	3.16	0.514
			3.22	0.172
4	3.07	1.65	2.78	0.860
			2.79	0.053

[a] All quantities except for oscillator strength are units of eV.

In conclusion, the starlike molecules **7**−**11** were prepared by coupling reactions of tris(chlorodimethylsilyl)methylsilane with *tert*-butyldimethylsilyl-substituted lithiooligothienylenes. Compounds **7**−**11** showed high fluorescence quantum yields with respect to the corresponding oligothiophenes.

The X-ray crystallographic analysis of **12** showed that two of three arms extend in parallel as a fork-shaped structure. Theoretical treatment of $MeSi(SiMe_2T_xH)_3$ with $x = 1-4$ and **12** indicated that in the crystals these compounds show the fork-shaped structures as a stable form; however, in the isolated molecules, the fan-shaped structures are as stable as the fork-shaped ones.

The excitation energies calculated for the isolated molecules well reproduced the observed ones, and the lowest energy excitation is found to correspond to the $\pi\angle\pi^*$-transitions.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL model JNM-LA300 spectrometer and a JNM-LA500 spectrometer. Infrared spectra were measured on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Absorption and emission spectra were obtained on a Shimadzu UV-3101PC scanning spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Fluorescence quantum yields (ϕ_F) were measured at an absorbance of ca. 0.05 at the excitation wavelengths by using quinine sulfate as the standard.[24] Fluorescence lifetimes (τ_F) were determined with a Hamamatsu C4780 time-resolved spectrophotometer. The samples were excited by a N_2 laser ($\lambda_{ex} = 337$ nm, $E_{ex} = 70$ μJ, $\tau_p = 300$ ps).

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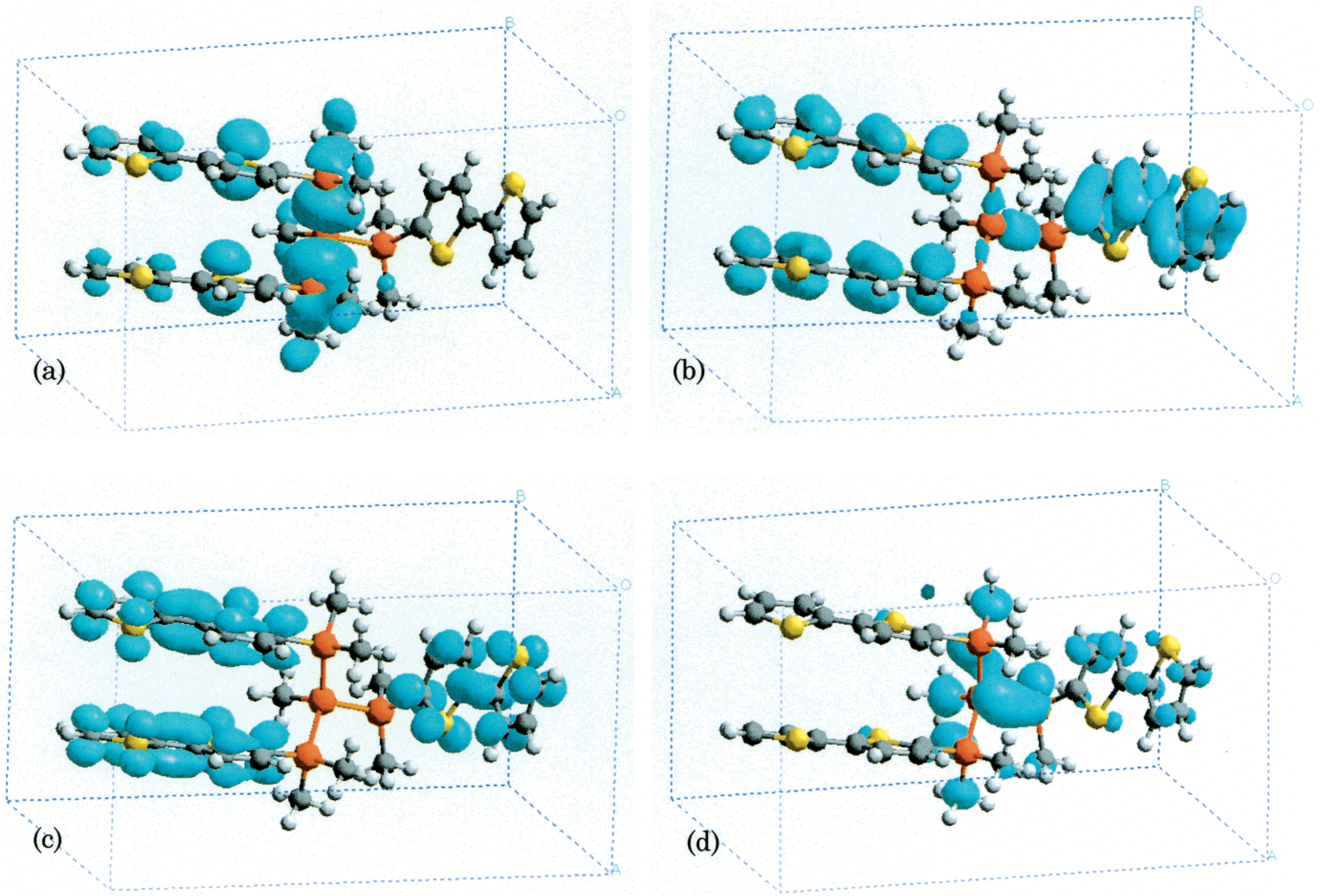

Figure 5. Orbital density maps for the frontier orbital regions of MeSi(SiMe$_2$T$_2$H)$_3$ calculated by the PW DFT method: (a) Density map for the [HO − 3] orbital, (b) collected density map for the [HO − 2] to [HO] orbitals, (c) collected density map for the [LU] to [LU + 2] orbitals, (d) density map for the [LU + 3] orbital.

Tetrahydrofuran and ether used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use.

Preparation of 1. In a 200-mL, two-necked flask was placed 30 g (0.12 mol) of 2,5-dibromothiophene on 100 mL of ether. To this was added 81 mL (0.12 mol) of a 1.53 M *n*-butyllithium−hexane solution at −40 °C over a period of 1 h. The mixture was stirred at room temperature for 5 h, and then 18.6 g (0.12 mol) of *tert*-butylchlorodimethylsilane was added at −20 °C. The reaction mixture was allowed to stir overnight at room temperature and filtered. The filtrate was concentrated and the residue was distilled under reduced pressure to give 22.3 g (65% yield) of **1**: bp 121−123 °C/4 Torr; MS *m/z* 276 (M^+); ^1H NMR δ ($CDCl_3$) 0.19 (s, 6H, Me_2Si), 0.84 (s, 9H, *t*-Bu), 6.90 (d, 1H, $J = 3.4$ Hz, thienyl ring proton), 6.99 (d, 1H, $J = 3.4$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.86 (Me_2Si), 16.80 (CMe_3), 26.42 (Me_3C), 116.84, 131.02, 135.46, 140.21 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 1.13. Anal. Calcd for $C_{10}H_{17}SiSBr$: C, 43.31; H, 6.18. Found: C, 43.24; H, 6.27.

Preparation of 2a. In a 100-mL, three-necked flask was placed 11.7 g (0.048 mol) of 2-bromobithiophene in 40 mL of dry ether. To this was added 31.3 mL (0.05 mol) of an *n*-butyllithium−hexane solution at −40 °C. After the mixture was stirred at room temperature for 5 h, 7.2 g (0.048 mol) of *tert*-butylchlorodimethylsilane in 20 mL of dry ether was added at room temperature. The mixture was heated to reflux for 5 h and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was distilled under reduced pressure to give 7.5 g (56% yield) of **2a**: bp 122−124 °C/3 Torr; MS *m/z* 280 (M^+); IR ^1H NMR δ ($CDCl_3$) 0.29 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-Bu), 6.99 (dd, 1H, $J = 5.2$ Hz, 3.6 Hz, thienyl ring proton), 7.11 (d, 1H, $J = 3.6$ Hz, thienyl ring proton), 7.17 (d, 1H, $J = 3.6$ Hz, thienyl ring proton), 7.18 (d, 1H, $J = 5.2$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.6$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.98 (Me_2Si), 16.89 (CMe_3), 26.32 (Me_3C), 123.73, 124.36, 124.84, 127.76, 135.82, 136.73, 137.39, 142.53 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 0.91. Anal. Calcd for $C_{14}H_{20}SiS_2$: C, 59.94; H, 7.19. Found: C, 60.09; H, 7.22.

Preparation of 2b. In a 200-mL, three-necked flask was placed 7.46 g (0.027 mol) of **2a** in 100 mL of chloroform. To this was added 4.74 g (0.027 mol) of NBS with ice cooling, and the mixture was stirred for 15 h at room temperature. The mixture was hydrolyzed and a chloroform layer was separated, washed with water, and dried over calcium chloride. After evaporation of chloroform, the residue was chromatographed on silica gel using hexane as the eluent to give 8.72 g (93% yield) of **2b**: mp 62−63 °C; MS *m/z* 358 (M^+); ^1H NMR δ ($CDCl_3$) 0.29 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-Bu), 6.91 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.94 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.11 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.15 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.49 (Me_2Si), 16.87 (CMe_3), 26.30 (Me_3C), 110.88, 123.79, 125.07, 130.59, 135.83, 137.44, 138.92, 141.47 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 1.07. Anal. Calcd for $C_{14}H_{19}SiS_2Br$: C, 46.78; H, 5.33. Found: C, 46.61; H, 5.20.

Preparation of 3a. In a 200-mL, three-necked flask was placed a Grignard reagent prepared from 10 g (36.1 mmol) of **1** and 0.88 g (36.2 mmol) of magnesium in 100 mL of dry THF. To this was added a mixture of 8.85 g (36.1 mmol) of 5-bromo-2,2′-bithiophene and 100 mg (0.18 mmol) of $NiCl_2$(dppp) in 50 mL of THF at room temperature. The mixture was heated to reflux for 15 h and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over calcium chloride. The solvent was evaporated and the residue was chromatographed on silica gel using hexane as the eluent to give 9.8 g (75% yield) of **3a** as a yellow-brown solid: mp 88−89 °C/3 Torr; MS *m/z* 362 (M^+); ^1H NMR δ ($CDCl_3$) 0.30 (s, 6H, Me_2Si), 0.94 (s, 9H, *t*-Bu), 7.01 (dd, 1H, $J = 4.9$ Hz, 3.7 Hz, thienyl ring proton), 7.07 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.08 (d, 1H, $J = 3.7$ Hz, thienyl ring protons), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.16 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.20 (d, 1H, $J = 4.9$ Hz, thienyl ring proton), 7.23 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.98 (Me_2Si), 16.90 (CMe_3), 26.32 (Me_3C), 123.60, 124.31, 124.33, 124.39, 124.76, 127.84, 135.90, 136.17, 136.20, 137.01, 137.20, 142.20 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 0.99. Anal. Calcd for $C_{18}H_{22}SiS_3$: C, 59.62; H, 6.11. Found: C, 59.56; H, 6.22.

Preparation of 3b. In a 200-mL, three-necked flask was placed 9.71 g (26.8 mmol) of **3a** in 100 mL of chloroform. To this was added 4.78 g (26.8 mmol) of NBS with ice cooling. The mixture was stirred at room temperature for 15 h and then hydrolyzed with water. The chloroform layer was separated, washed with water, and dried over calcium chloride. After evaporation of chloroform, the residue was chromatographed on silica gel using hexane as the eluent to give 11.3 g (96% yield) of **3b**: mp 105−107 °C; MS *m/z* 440 (M^+); ^1H NMR δ ($CDCl_3$) 0.29 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-Bu), 6.88 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.95 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.99 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.05 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.12 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.98 (Me_2Si), 16.90 (CMe_3), 26.31 (Me_3C), 110.96, 123.63, 124.31, 124.61, 124.97, 130.67, 135.02, 135.92, 136.73, 137.41, 138.70, 141.90 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 1.04. Anal. Calcd for $C_{18}H_{21}SiS_3Br$: C, 48.96; H, 4.79. Found: C, 48.77; H, 4.75.

Preparation of 3c. In a 100-mL, two-necked flask was placed a mixture of 6.55 g (18.2 mmol) of **2b** and 60 mg of $NiCl_2$(dppp) in 50 mL of THF. To this was added a Grignard reagent prepared from 4.0 g (18.2 mmol) of 2-bromo-3-*n*-butylthiophene and 0.45 g (18.5 mmol) of magnesium in 20 mL of THF at room temperature. The mixture was heated to reflux for 15 h and hydrolyzed with dilute hydrochloric acid. The organic layer was separated and aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 6.86 g (89% yield) of **3c** as a viscous liquid: MS *m/z* 418 (M^+); ^1H NMR δ ($CDCl_3$) 0.29 (s, 6H, Me_2Si), 0.91 (t, 3H, $J = 7.3$ Hz, CH_3), 0.93 (s, 9H, *t*-Bu), 1.38 (sext, 2H, $J = 7.3$ Hz, CH_2), 1.61 (quint, 2H, $J = 7.3$ Hz, CH_2), 2.76 (t, 2H, $J = 7.3$ Hz, CH_2), 6.91 (d, 1H, $J = 5.2$ Hz, thienyl ring proton), 6.99 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.11 (d, 1H, $J = 3.7$ Hz, thienyl ring protons), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.15 (d, 1H, $J = 5.2$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.93 (Me_2Si), 13.95, 16.90, 22.60, 26.33, 28.95, 32.80 (*n*-Bu, *t*-Bu), 123.74, 123.95, 124.70, 129.49, 130.03, 130.42, 135.22, 135.89, 136.89, 137.03, 139.69, 142.27 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 0.96. Anal. Calcd for $C_{22}H_{30}SiS_3$: C, 63.10; H, 7.22. Found: C, 63.17; H, 7.23.

Preparation of 3d. In a 50-mL, two-necked flask was placed 4.54 g (10.8 mmol) of **3c** in 30 mL of chloroform. To this was added 1.94 g (10.8 mmol) of NBS with ice cooling. The mixture was stirred at room temperature for 15 h and hydrolyzed with water. The chloroform layer was separated, washed with water, and then dried over calcium chloride. After evaporation of chloroform, the residue was chromatographed on silica gel using hexane as the eluent to give 4.86 g (90% yield) of **3d** as a viscous liquid: MS *m/z* 496 (M^+); ^1H NMR δ ($CDCl_3$) 0.29 (s, 6H, Me_2Si), 0.91 (t, 3H, $J = 7.3$ Hz, CH_3), 0.93 (s, 9H, *t*-Bu), 1.36 (sext, 2H, $J = 7.3$ Hz, CH_2), 1.58 (quint, 2H, $J = 7.3$ Hz, CH_2), 2.70 (t, 2H, $J = 7.3$ Hz, CH_2), 6.87 (s, 1H, thienyl ring proton), 6.93 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.10 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.15 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ ($CDCl_3$) −4.98 (Me_2Si), 13.90, 16.87, 22.49, 26.31, 28.89, 33.16 (*n*-Bu, *t*-Bu), 110.45, 123.89, 124.87, 126.88, 131.92, 132.62, 133.70, 135.88, 137.16, 137.58, 140.20, 141.95 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 1.02. Anal. Calcd for $C_{22}H_{29}SiS_3Br$: C, 53.10; H, 5.87. Found: C, 52.98; H, 5.83.

Preparation of 4a. In a 50-mL, two-necked flask was placed a mixture of 6.0 g (13.6 mmol) of **3b** and 100 mg of NiCl$_2$(dppp) in 100 mL of dry THF. To this was added a Grignard reagent prepared from 2.70 g (16.6 mmol) of 2-bromothiophene and 0.40 g (16.5 mmol) of magnesium in 20 mL of THF at room temperature. The resulting mixture was heated to reflux for 14 h and hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 1.02 g (21% yield) of **4a** as a yellow solid: mp 178−180 °C; MS *m*/*z* 444 (M^+); ^{1}H NMR δ (CDCl$_3$) 0.29 (s, 6H, Me$_2$Si), 0.93 (s, 9H, *t*-Bu), 7.01 (dd, 1H, $J = 5.2$ Hz, 3.7 Hz, thienyl ring proton), 7.05−7.09 (m, 5H, thienyl ring protons), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.16 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.97 (Me$_2$Si), 16.91 (CMe$_3$), 29.32 (Me$_3$C), 123.71, 124.17, 124.29, 124.38 (2C), 124.53, 124.83, 127.89, 135.83, 135.93, 135.98, 136.26, 136.34, 137.08, 137.19, 142.13 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 1.00. Anal. Calcd for $C_{22}H_{24}SiS_4$: C, 59.41; H, 5.44. Found: C, 59.37; H, 5.21.

Preparation of 4b. In a 30-mL, two-necked flask was placed 1.0 g (2.25 mmol) of **4a** in 20 mL of chloroform. To this was added 0.4 g (2.25 mmol) of NBS with ice cooling. The resulting mixture was stirred at room temperature for 15 h and then hydrolyzed with water. The chloroform layer was separated, washed with water, and dried over calcium chloride. Solvent chloroform was evaporated and the residue was chromatographed on silica gel using hexane as the eluent to give 0.99 g (84% yield) of **4b**: mp 205−207 °C; MS *m*/*z* 522 (M^+); ^{1}H NMR δ (CDCl$_3$) 0.29 (s, 6H, Me$_2$Si), 0.93 (s, 9H, *t*-Bu), 6.89 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.96 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.99 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.03 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.05 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.08 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.97 (Me$_2$Si), 16.91 (CMe$_3$), 26.32 (Me$_3$C), 110.10, 123.75, 124.16, 124.42, 124.53, 124.66, 124.91, 130.71, 135.07, 135.52, 135.96, 136.49, 136.63, 137.34, 138.55, 142.02 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 1.01. Anal. Calcd for $C_{22}H_{23}SiS_4Br$: C, 50.46; H, 4.43. Found: C, 50.28; H, 4.23.

Preparation of 5a. In a 50-mL, two-necked flask was placed a mixture of 4.86 g (9.80 mmol) of **3d** and 100 mg of NiCl$_2$(dppp) in 30 mL of THF. To this was added a Grignard reagent prepared from 3.03 g (13.8 mmol) of 2-bromobithiophene and 0.335 g (13.8 mmol) of magnesium in 20 mL of THF at room temperature. The resulting mixture was heated to reflux for 6 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 0.74 g (13% yield) of **5a**: mp 103−105 °C; MS *m*/*z* 582 (M^+); ^{1}H NMR δ (CDCl$_3$) 0.30 (s, 6H, Me$_2$Si), 0.94 (br s, 12H, *t*-Bu, CH$_3$), 1.41 (sext, 2H, $J = 7.8$ Hz, CH$_2$), 1.64 (quint, 2H, $J = 7.8$ Hz, CH$_2$), 2.74 (t, 2H, $J = 7.8$ Hz, CH$_2$), 6.97−7.01 (m, 4H, thienyl ring proton), 7.03 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.10 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.12 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.17 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.22 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.98 (Me$_2$Si), 13.94, 16.89, 22.64, 26.32, 29.19, 32.57 (*n*-Bu, *t*-Bu), 123.61, 124.03, 124.13, 124.34, 124.42, 124.76, 126.35, 126.54, 127.84, 129.63, 134.74, 134.79, 135.90 (2C), 136.17, 137.01, 137.08, 137.12, 140.35, 142.15 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 1.00. Anal. Calcd for $C_{30}H_{34}SiS_5$: C, 61.80; H, 5.88. Found: C, 61.76; H, 5.77.

Preparation of 5b. In a 30-mL, two-necked flask was placed 0.74 g (1.27 mmol) of **5a** in 20 mL of chloroform. To this was added 0.23 g (1.29 mmol) of NBS with ice cooling. The resulting mixture was heated to reflux for 15 h and then hydrolyzed with water. The chloroform layer was separated, washed with water, and then dried over calcium chloride. The solvent was evaporated and the residue was chromatographed on silica gel using hexane as the eluent to give 0.73 g (87% yield) of **5b** as a yellow viscous liquid: MS *m*/*z* 660 (M^+); ^{1}H NMR δ (CDCl$_3$) 0.31 (s, 6H, Me$_2$Si), 0.95 (s, 9H, *t*-Bu), 0.96 (t, 3H, $J = 7.3$ Hz, CH$_3$), 1.42 (sext, 2H, $J = 7.3$ Hz, CH$_2$), 1.64 (quint, 2H, $J = 7.3$ Hz, CH$_2$), 2.75 (t, 2H, $J = 7.3$ Hz, CH$_2$), 6.70 (s, 1H, thienyl ring proton), 6.71 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.87 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.94 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.97 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.98 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.11 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.13 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 7.23 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.98 (Me$_2$Si), 13.94, 16.90, 22.64, 26.33, 29.19, 32.52 (*n*-Bu, *t*-Bu), 110.04, 123.66, 124.05, 124.13, 124.63, 124.81, 126.45, 126.77, 129.94, 130.69, 134.46, 134.68, 135.02, 135.92, 136.44, 137.14, 137.24, 138.62, 140.41, 142.14 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 0.99. Anal. Calcd for $C_{30}H_{33}SiS_5Br$: C, 54.44; H, 5.03. Found: C, 54.20; H, 5.12.

Preparation of 6a. In a 100-mL, two-necked flask was 4.00 g (8.10 mmol) of **3d** in 30 mL of THF. To this was added 5.5 mL (8.40 mmol) of *n*-butyllithium-hexane solution at −80 °C. The resulting mixture was stirred at room temperature for 1 h and added to a solution of 1.4 mL (12.55 mmol) of trimethoxyborane in 30 mL of THF at −80 °C. The mixture was stirred at −80 °C for 6 h and then warmed to −60 °C. The resulting solution was added to a mixture of 2.0 g (6.12 mmol) of 2-bromoterthiophene and 612 mg of tetrakis(triphenylphosphine)palladium in dioxane/water = 10/1 at refluxing temperature. The reaction mixture was heated to reflux for 15 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 2.24 g (65% yield) of **6a** as a orange-yellow solid: mp 126−128 °C; MS *m*/*z* 664 (M^+); ^{1}H NMR δ (CDCl$_3$) 0.30 (s, 6H, Me$_2$Si), 0.94 (br s, 12H, $J =$ 7.8 Hz, *t*-Bu, CH$_3$), 1.42 (sext, 2H, $J = 7.8$ Hz, CH$_2$), 1.63 (quint, 2H, $J = 7.8$ Hz, CH$_2$), 2.64 (t, 2H, $J = 7.8$ Hz, CH$_2$), 6.65−6.73 (m, 7H, thienyl ring protons), 6.82 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.85 (d, 2H, $J = 3.7$ Hz, thienyl ring protons), 6.90 (d, 1H, $J = 3.7$ Hz, thienyl ring proton), 6.94 (d, 1H, $J = 3.7$ Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.98 (Me$_2$Si), 13.94, 16.89, 22.65, 26.31, 29.20, 32.54 (*n*-Bu, *t*-Bu), 123.67, 124.03, 124.16, 124.19, 124.26, 124.33, 124.45, 124.75, 126.33, 126.57, 127.84, 129.73, 134.65, 134.78, 135.80, 135.85, 135.90, 135.98, 136.27, 137.00, 137.04, 137.06, 140.34, 142.15 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 0.99. Anal. Calcd for $C_{34}H_{36}SiS_6$: C, 61.40; H, 5.46. Found: C, 61.20; H, 5.49.

Preparation of 6b. In a 30-mL, two-necked flask was placed 2.24 g (3.37 mmol) of **6a** in 10 mL of chloroform. To this was added 0.60 g (3.37 mmol) of NBS with ice cooling. The resulting mixture was stirred at room temperature for 15 h and then hydrolyzed with water. The chloroform layer was separated, washed with water, and then dried over calcium chloride. The solvent was evaporated and the residue was chromatographed on silica gel using hexane as the eluent to give 2.20 g (88% yield) of **6b** as an orange-yellow solid: mp

168−170 °C; MS *m/z* 742 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.30 (s, 6H, Me$_2$Si), 0.94 (br s, 12H, *t*-Bu, CH$_3$), 1.43 (sext, 2H, J = 7.3 Hz, CH$_2$), 1.65 (quint, 2H, J = 7.3 Hz, CH$_2$), 2.75 (t, 2H, J = 7.3 Hz, CH$_2$), 6.89 (d, 1H, J = 4.0 Hz, thienyl ring proton), 6.95 (d, 1H, J = 4.0 Hz, thienyl ring proton), 6.99−7.07 (m, 6H, thienyl ring protons), 7.12 (d, 1H, J = 4.0 Hz, thienyl ring proton), 7.13 (d, 1H, J = 4.0 Hz, thienyl ring proton), 7.23 (d, 1H, J = 4.0 Hz, thienyl ring proton); ^{13}C NMR δ (CDCl$_3$) −4.96 (Me$_2$Si), 13.95, 16.91, 22.65, 26.33, 29.19, 32.59 (*n*-Bu, *t*-Bu), 111.14, 123.76, 124.06, 124.21, 124.25, 124.54, 124.66, 124.82, 126.44, 126.73, 129.88, 130.71, 134.58, 134.72, 135.16, 135.54, 135.93, 136.33, 136.40, 137.15, 137.22, 138.54, 140.44, 142.12 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 0.99. Anal. Calcd for $C_{34}H_{35}SiS_6Br$: C, 54.89; H, 4.74. Found: C, 54.71; H, 4.46.

Preparation of 7. In a 100-mL, three-necked flask was placed 6.35 g (17.7 mmol) of **2b** in 50 mL of dry ether. To this was dropwise added 11.6 mL (17.7 mmol) of a 1.53 M *n*-butyllithium-hexane solution at −40 °C. After the mixture was stirred at room temperature for 2 h, 1.72 g (5.32 mmol) of tris(chlorodimethylsilyl)methylsilane in 10 mL of dry ether was added to the resulting mixture at room temperature. The reaction mixture was stirred overnight at room temperature, heated to reflux for 20 h, and hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 2.84 g (51% yield) of **7** as a yellow viscous liquid: MS *m/z* 1054 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.29 (s, 18H, Me$_2$Si), 0.30 (s, 3H, MeSi), 0.33 (s, 18H, Me$_2$Si), 0.99 (s, 27H, *t*-Bu), 6.90 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.09 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.15 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.17 (d, 3H, J = 3.5 Hz, thienyl ring protons); ^{13}C NMR δ (CDCl$_3$) −11.80 (MeSi), −4.58 (Me$_2$Si), −0.37 (Me$_2$Si), 16.91 (CMe$_3$), 26.41 (Me$_3$C), 124.91, 125.16, 135.06, 135.87, 136.49, 138.92, 142.63 (2C) (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −84.66, −18.10, 0.94. Anal. Calcd for $C_{49}H_{78}Si_7S_6$: C, 55.72; H, 7.44. Found: C, 55.77; H, 7.48.

Preparation of 8. In a 50-mL, two-necked flask was placed 4.75 g (10.8 mmol) of **3b** in 10 mL of dry ether. To this was added 7.0 mL (10.8 mmol) of a 1.54 M *n*-butyllithium−hexane solution at −80 °C. The mixture was stirred at room temperature for 1 h, and then 1.06 g (3.29 mmol) of tris(chlorodimethylsilyl)methylsilane in 10 mL of dry ether was added to the mixture. The reaction mixture was stirred overnight at room temperature and heated to reflux for 4 h. The mixture was hydrolyzed with water, and the organic layer was separated, washed with water, and dried over calcium chloride. After the solvents were evaporated, the residue was chromatographed on silica gel using hexane as the eluent to give 1.80 g (43% yield) of **8** as a yellow solid: mp 121−123 °C; MS *m/z* 1300 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.29 (s, 18H, Me$_2$Si), 0.33 (s, 3H, MeSi), 0.37 (s, 18H, Me$_2$Si), 0.93 (s, 27H, *t*-Bu), 6.90 (d, 3H, J = 3.3 Hz, thienyl ring protons), 6.98 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.01 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.10 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.12 (d, 3H, J = 3.5 Hz, thienyl ring protons), 7.17 (d, 3H, J = 3.3 Hz, thienyl ring protons); ^{13}C NMR δ (CDCl$_3$) −11.82 (MeSi), −4.95 (Me$_2$Si), −0.42 (Me$_2$Si), 16.29 (CMe$_3$), 26.35 (Me$_3$C), 124.36, 124.40, 124.70, 124.86, 135.02, 135.92, 136.09, 136.21, 136.87, 139.08, 142.33, 142.46 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −84.68, −18.17, 0.93. Anal. Calcd for $C_{61}H_{84}Si_7S_9$: C, 56.25; H, 6.50. Found: C, 56.30; H, 6.57.

Preparation of 9. In a 50-mL, two-necked flask was placed 1.90 g (3.60 mmol) of **4b** in 20 mL of dry ether. To this was added 2.4 mL (3.67 mmol) of a 1.53 M *n*-butyllithium-hexane solution at −80 °C. The resulting mixture was stirred at −80 °C for 1 h and then allowed to stand overnight at room temperature. A solution of 0.35 g (1.10 mmol) of tris(chlorodimethylsilyl)methylsilane in 10 mL of dry ether was added to the mixture. The reaction mixture was stirred overnight at room temperature and heated to reflux for 4 h. The mixture was hydrolyzed with water, and the organic layer was separated, washed with water, and dried over calcium chloride. After the solvents were evaporated, the residue was chromatographed on silica gel using hexane as the eluent to give 0.60 g (37% yield) of **9** as an orange-yellow solid: mp 211−213 °C; MS *m/z* 1546 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.30 (s, 18H, Me$_2$Si), 0.35 (s, 3H, MeSi), 0.40 (s, 18H, Me$_2$Si), 0.94 (s, 27H, *t*-Bu), 6.91 (d, 3H, J = 3.7 Hz, thienyl ring protons), 6.96 (d, 6H, J = 3.7 Hz, thienyl ring protons), 6.97 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.01 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.10 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.11 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.17 (d, 3H, J = 3.7 Hz, thienyl ring protons); ^{13}C NMR δ (CDCl$_3$) −11.78 (MeSi), −4.94 (Me$_2$Si), −0.39 (Me$_2$Si), 16.93 (CMe$_3$), 26.36 (Me$_3$C), 124.19 (2C), 124.36, 124.44, 124.79, 124.87, 134.97, 135.85, 135.94, 135.95, 136.15, 136.27, 137.01, 139.13, 142.22, 142.44 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −84.58, −18.20, 0.95. Anal. Calcd for $C_{73}H_{90}Si_7S_{12}$: C, 56.61; H, 5.86. Found: C, 56.61; H, 6.11.

Preparation of 10. In a 30-mL, two-necked flask was placed 1.62 g (2.45 mmol) of **5b** in 10 mL of dry ether. To this was added 1.6 mL (2.45 mmol) of a 1.53 M *n*-butyllithium−hexane solution at −80 °C. After the mixture was stirred at room temperature for 5 h, a solution of 0.24 g (0.73 mmol) of tris(chlorodimethylsilyl)methylsilane in 5 mL of dry ether was added to the mixture. The reaction mixture was stirred overnight at room temperature and heated to reflux for 12 h. The mixture was hydrolyzed with water and the organic layer was separated, washed with water, and dried over calcium chloride. After evaporation of the solvent, the residue was chromatographed on silica gel using hexane as the eluent to give 0.40 g (28% yield) of **10** as an orange solid: mp 139−140 °C; MS *m/z* 1960 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.31 (s, 18H, Me$_2$Si), 0.36 (s, 3H, MeSi), 0.40 (s, 18H, Me$_2$Si), 0.92 (t, 9H, J = 7.3 Hz, CH$_3$), 0.94 (s, 27H, *t*-Bu), 1.39 (sext, 6H, J = 7.3 Hz, CH$_2$), 1.62 (quint, 6H, J = 7.3 Hz, CH$_2$), 2.71 (t, 6H, J = 7.3 Hz, CH$_2$), 6.92−6.96 (m, 15H, thienyl ring protons), 7.06 (d, 3H, J = 3.7 Hz, thienyl ring protons), 7.11 (d, 6H, J = 3.7 Hz, thienyl ring protons), 7.20 (d, 3H, J = 3.7 Hz, thienyl ring protons); ^{13}C NMR δ (CDCl$_3$) −11.78 (MeSi), −4.94 (Me$_2$Si), −0.38 (Me$_2$Si), 13.94, 16.92, 22.66, 26.35, 30.08, 32.55 (*n*-Bu, *t*-Bu), 124.05 (2C), 124.19, 124.35, 124.75, 124.79, 126.26, 126.44, 129.57, 134.84, 134.92, 134.96, 135.83, 135.92, 136.19, 136.97, 139.08, 140.32, 142.22, 142.53 (thienyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −84.25, −18.20, 0.95. Anal. Calcd for $C_{97}H_{120}Si_7S_{15}$: C, 59.33; H, 6.16. Found: C, 59.25; H, 6.19.

Preparation of 11. In a 30-mL, two-necked flask was placed 0.80 g (1.08 mmol) of **6b** in 10 mL of dry ether. To this was added 0.7 mL (1.08 mmol) of a 1.53 M *n*-butyllithium−hexane solution at −80 °C. After the mixture was stirred at room temperature for 3 h, a solution of 0.10 g (0.30 mmol) of tris(chlorodimethylsilyl)methylsilane in 5 mL of dry ether was added to the mixture. The reaction mixture was heated to reflux for 10 h and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over calcium chloride. After evaporation of the solvent, the residue was chromatographed on silica gel using hexane as the eluent to give 0.20 g (29% yield) of **11** as a red solid: mp 107−108 °C; MS *m/z* 2206 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.31 (s, 18H, Me$_2$Si), 0.38 (s, 3H, MeSi), 0.45 (s, 18H, Me$_2$Si), 0.93 (t, 9H, J = 7.7 Hz, CH$_3$), 0.95 (s, 27H, *t*-Bu), 1.39 (sext, 6H, J = 7.7 Hz, CH$_2$), 1.61 (quint, 6H, J = 7.7 Hz, CH$_2$), 2.70 (t, 6H, J = 7.7 Hz, CH$_2$), 6.89−6.95 (m, 21H, thienyl ring protons), 7.05 (d, 3H, J = 3.4 Hz, thienyl ring protons), 7.08 (d, 3H, J = 3.4 Hz, thienyl ring protons), 7.11 (d, 3H, J = 3.4 Hz, thienyl ring protons), 7.19 (d, 3H, J = 3.4 Hz, thienyl ring protons); ^{13}C NMR δ (CDCl$_3$) −11.78 (MeSi), −4.97 (Me$_2$Si), −0.37 (Me$_2$Si), 13.95, 16.94, 22.64, 26.33, 29.34, 32.50 (*n*-Bu, *t*-Bu), 124.03, 124.10, 124.12, 124.18, 124.26, 124.71 (2C), 124.80, 126.21, 126.46, 129.63, 134.65, 134.84, 134.90, 135.79, 135.91 (2C), 136.25, 136.89, 138.96, 140.26, 140.44, 142.18, 142.45 (thienyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) −84.63, −18.26, 0.95. Anal. Calcd for $C_{109}H_{126}Si_7S_{18}$: C, 59.24; H, 5.75. Found: C, 59.18; H, 5.71.

X-ray Crystallographic Analysis of $MeSi(SiMe_2T_2Br)_3$. All unique diffraction maxima with $6 < 2\theta < 125.8°$ for $MeSi(SiMe_2T_2Br)_3$ were recorded on a Rigaku AFC-6 automated four-circle diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). Refractions with $I > 3\sigma(I)$ were used in the least-squares refinement. The structure was solved by SIR92 direct method[25] and expanded using DIRDIF94 Fourier techniques.[26] The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[27] Anomalous dispersion effects were included in Fcalc;[28] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[29] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[30] All calculations were performed using the teXsan[31] crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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