



## Nanosized starlike molecules. Synthesis and optical properties of tris- and tetrakis[oligo(disilanylenebithienylene)dimethylsilyl]benzene

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### ABSTRACT

The syntheses of two types of starlike molecules with the arms that extend to three and four directions have been reported. The molecules with the arms consisting of a regular alternating arrangement of a silicon–silicon bond and bithienylene unit that extend to three directions were synthesized by the reactions of 1,3,5-tris(chlorodimethylsilyl)benzene, which was chosen as a core, with the lithio[oligo(disilanylenebithienylene)] derivatives. The starlike molecules with extended arms to four directions were prepared by the reaction of 1,2,4,5-tetrakis(fluorodimethylsilyl)benzene used as a core, with lithio[oligo(disilanylenebithienylene)]s. UV–Vis absorption and fluorescence properties of these starlike molecules have been investigated in a dioxane solution. The present molecules showed absorption maxima in a range of 321–337 nm, and revealed higher fluorescence quantum yields than that of the corresponding linear polymer, poly[(tetraethylidisilanylene)bithiophene].

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### 1. Introduction

Three-dimensional, organometallic dendrimers containing  $\pi$ -conjugated system have attracted a great deal of attention owing to their unique physical and chemical properties and also to their potential application in organic photo- and electroluminescent devices, and many types of the dendrimers have been synthesized to date [1]. In the field of organosilicon chemistry, several types of dendrimers whose framework is composed of the silicon–silicon bonds, silicon–oxygen bonds, and silicon–carbon bonds, have been reported [2,3].

On the other hand, starlike compounds with the arms that extend to three directions have attracted much attention, because they show interesting properties, depending on their unique molecular structure, and may be used as functionality materials. Several types of the starlike molecules with conjugated  $\pi$ -electron system in their arms have been synthesized and their optical properties have been examined [4]. However, little interest has been shown in the chemistry of the starlike molecules including both silylene unit and  $\pi$ -electron system in their arms. Recently, Ponomarenko and his coworkers have reported the synthesis of the

starlike molecules bearing bithienylene–silylene units in the arms and investigated their optical properties [3e].

We have reported the synthesis of two types of the nano-sized, starlike molecules. One of them is the molecules bearing the arms consisting of a regular alternating arrangement of a silicon–silicon bond and bithienylene unit, which extend to three directions (see Chart 1). The other is silicon-containing starlike compounds with oligothienylene units (bithienylene to hexathienylene) [5]. As can be expected from the unique molecular structure, the starlike molecules display novel optical properties. For examples, they reveal high fluorescence quantum yields and long lifetimes of the excited state [5,6]. We also have reported that these molecules can be used as the functional devices such as optical recording materials [7] and semiconductors in field-effect transistors [8].

We have investigated so far optical properties of many types of the starlike molecules with the same core, tris(dimethylsilyl)methylsilane unit, but with different arms. We considered that the starlike molecules bearing aromatic ring system as a core might show better optical behavior than those with the tris(silyl)silane moiety reported previously. In this paper we report first synthesis of new types of the starlike molecules bearing a poly(silyl)-substituted benzene ring as a core, 1,3,5-tris- and 1,2,4,5-tetrakis[oligo(disilanylenebithienylene)dimethylsilyl]benzene, and their UV–Vis absorption and fluorescence spectra.

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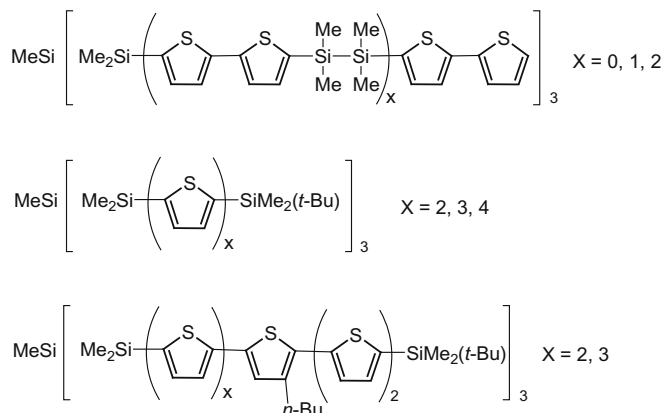


Chart 1.

## 2. Results and discussion

The method used for the synthesis of the present starlike molecules is based on the reaction of 1,3,5-tris(chlorodimethylsilyl)benzene (**1**) and 1,2,4,5-tetrakis(fluorodimethylsilyl)benzene (**2**) with the lithio[oligo(disilanyl)enebithienylene] derivatives. Compound, 1,3,5-tris(chlorosilyl)benzene (**1**), used as a core for the synthesis of the molecules with the extended arms to three directions, was prepared by the reaction of 1,3,5-tribromobenzene with chlorodimethylsilane in the presence of magnesium in a THF solution, followed by the reaction of the resulting 1,3,5-tris(dimethylsilyl)benzene with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride in high yield, as shown in Scheme 1. Similarly, the starting compound **2**, used for the synthesis of the starlike molecules consisting of four arms, was synthesized by the reaction of 1,2,4,5-tetrabromobenzene with dimethylchlorosilane in the presence of magnesium in THF, and then chlorination of the resulting tetrakis(dimethylsilyl)benzene with chlorine gas. Finally, treatment of 1,2,4,5-tetrakis(chlorodimethylsilyl)benzene with zinc fluoride afforded the core compound **2** in high total yield [9]. The structures of **1** and **2** were verified by mass and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis, as well as by elemental analysis (see Section 3).

The syntheses of two types of the arms having an alternative arrangement of a silicon–silicon bond and bithienylene unit were carried out as shown in Scheme 2. One of them is the arms that have a terminal disilanyl group, while the other is the arms bearing

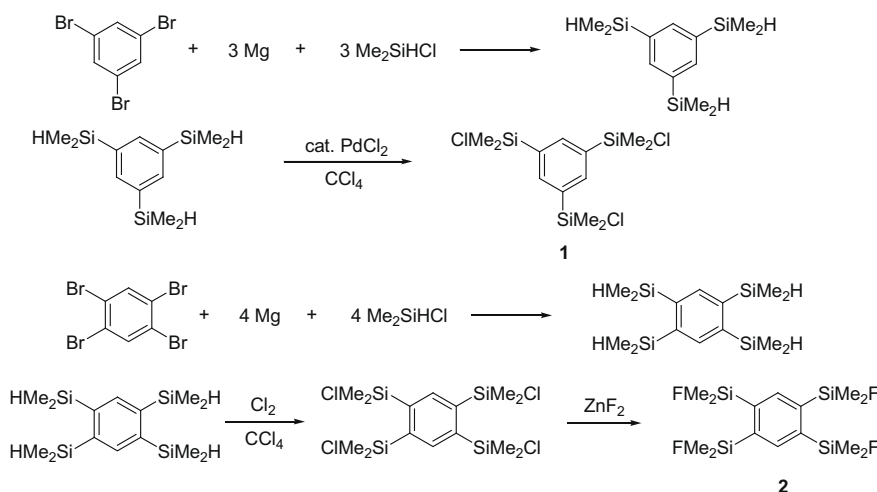
a bithienyl unit as an end-group. As reported previously, the reaction of chloropentamethylidisilane with 5'-bromo-5-lithiobithiophene in diethyl ether afforded (5'-bromo-2,2'-bithiophen-5-yl)pentamethylidisilane (**3**) in 70% yield [5a]. Similarly, 1-(5'-bromo-2,2'-bithiophen-5-yl)-2-[5'-(pentamethylidisilanyl)-2,2'-bithiophen-5-yl]tetramethylidisilane (**6**) was prepared by the reaction of 5'-bromo-5-lithiobithiophene with 1,2-dichlorotetramethylidisilane, followed by treatment of the resulting chloro compound **5** with a lithio derivative **4** prepared from **3** and *n*-butyllithium in 73% yield. Bromo compound **8** with a longer disilanylenebithienylene unit than **6** was obtained by the reaction of lithio compound **7**, generated from **6** and *n*-butyllithium, with **5** in 73% yield.

Similar methods were used for the syntheses of the arms with a bithienylene end-group. Thus, treatment of compound **5** with lithiobithiophene in diethyl ether gave 1-(2,2'-bithiophen-5-yl)-2-(5'-bromo-2,2'-bithiophen-5-yl)tetramethylidisilane (**10**) in 81% yield. Treatment of lithio compound **11**, prepared by the reaction of **10** with *n*-butyllithium, with compound **5** produced 1-(2,2'-bithiophen-5-yl)-2-[5'-(2-(5'-bromo-2,2'-bithiophen-5-yl)tetramethylidisilanyl)-2,2'-bithiophen-5-yl]tetramethylidisilane (**12**) in 82% yield. The structures of compounds **3**, **6**, **8**, **10**, and **12**, used for constructing the arms were confirmed by spectrometric analysis, as well as by elemental analysis.

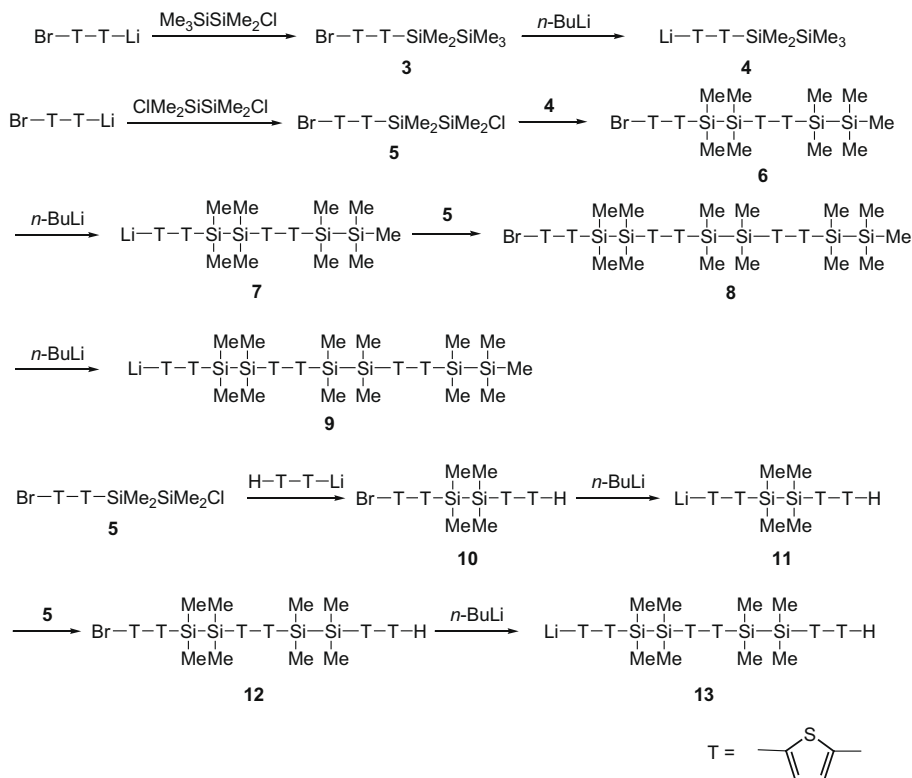
### 2.1. 1,3,5-Tris[oligo(disilanyl)enebithienylene]dimethylsilyl]benzenes

The starlike compounds whose arms extend to three directions were synthesized by the reaction of 1,3,5-tris(chlorosilyl)benzene (**1**) with the respective lithio derivatives obtained by treatment of compounds **3**, **6**, and **8**, with *n*-butyllithium. Thus, the reaction of **1** with lithio compound **4**, generated from **3** and *n*-butyllithium in diethyl ether, afforded 1,3,5-tris[dimethyl(5'-pentamethylidisilanyl)-2,2'-bithiophen-5-yl]benzene (**14**) as shown in Scheme 3. The product **14** was isolated from the reaction mixture, using a silica gel column in 62% yield. The structure of **14** was confirmed by mass and,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis. In fact, mass spectrometric analysis for **14** indicates the presence of a molecular ion at  $m/z$  1134, corresponding to the calculated value for  $\text{C}_{51}\text{H}_{78}\text{Si}_9\text{S}_6$ . The  $^{29}\text{Si}$  NMR spectrum reveals three signals at  $-24.1$ ,  $-19.3$ , and  $-11.3$  ppm, due to three different kinds of the silicon atoms. These results are wholly consistent with the structure proposed for **14**.

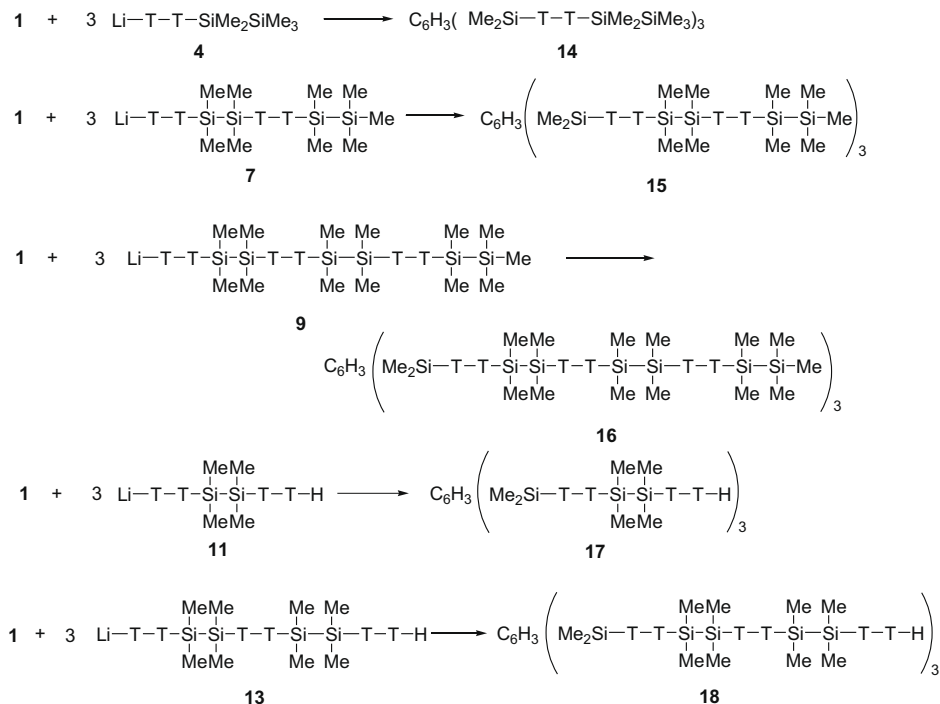
Treatment of **1** with the lithio derivative **7** generated from bromo compound **6** gave starlike molecule **15** in 62% isolated yield. Mass spectrometric analysis for **15** shows a parent ion at  $m/z$



Scheme 1.



Scheme 2.



Scheme 3.

1974, which is consistent with the calculated molecular weight of the proposed structure. Its  $^{29}\text{Si}$  NMR spectrum reveals five signals at  $-24.6$ ,  $-24.5$ ,  $-24.1$ ,  $-19.3$ , and  $-11.3$  ppm, attributable to five different kinds of the silicon atoms, as expected. Likewise, the core compound **1** reacted with the lithio derivative produced from **8**

and *n*-butyllithium in diethyl ether, to give starlike compound **16** in 13% isolated yield. Mass spectrometric analysis for **16** indicates a molecular ion at  $m/z$  2814, which is consistent with the calculated molecular weight for **16**. Its  $^{29}\text{Si}$  NMR spectrum reveals an overlapping signal at  $-24.6$  ppm, due to four silicon atoms, and

three signals at  $-24.1$ ,  $-18.3$ , and  $-11.3$  ppm. These results are wholly consistent with the structure proposed for **16**.

The starlike compounds bearing a bithienyl moiety as an end-group were prepared by the similar methods to those used for the synthesis of **14–16**. Thus, the reaction of **1** with lithio compound **11**, derived from treatment of bromo compound **10** with *n*-butyllithium in diethyl ether, afforded starlike molecule **17**, while with the lithio derivative **13**, arising from the reaction of **12** with *n*-butyllithium, compound **1** reacted to give the product (**18**) in 31% yield. The structures of **17** and **18** were verified by mass and,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis, as well as by elemental analysis (see Section 3).

### 2.2. 1,2,4,5-Tetrakis[oligo(disilanylnebithienylene)dimethylsilyl]benzenes

For the synthesis of starlike molecule **19**, we first carried out the reaction of 1,2,4,5-tetrakis(chlorodimethylsilyl)benzene with lithio compound **11**. However, no starlike molecule was obtained at all. We thought that the bulky chlorine atoms in the starting compound would prevent the coupling reaction with the lithio compound. Therefore, we used the fluoro derivative **2** as the starting compound. Thus, treatment of **2** with the lithio derivative **11** in diethyl ether afforded starlike molecule **19**, with the extended arms to four directions, in 27% isolated yield, as shown in Scheme 4.

The structure of **19** was confirmed by mass and,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis, and also by elemental analysis. Mass spectrometric analysis for **19** shows a parent ion at  $m/z$  2086, corresponding to the calculated value for  $\text{C}_{94}\text{H}_{110}\text{Si}_{12}\text{S}_6$ . The  $^{29}\text{Si}$  NMR spectrum indicates a signal consisting of the two silicon atoms at  $-24.4$  and a signal at  $-9.0$  ppm.

Similarly, treatment of **2** with lithio compound **13** gave starlike molecule **20** in 7% isolated yield. The mass spectrum of the product **20** indicates a parent ion at  $m/z$  3206, which is consistent with the calculated molecular weight for the product **20**. Its  $^{29}\text{Si}$  NMR spectrum reveals an overlapping signal consisting of the four silicon atoms at  $-24.5$  ppm, and a signal at  $-9.8$  ppm. These results and also other NMR spectral data described in Section 3 are wholly consistent with the structures proposed for **19** and **20**.

### 2.3. Optical properties of starlike molecules

The UV–Vis absorption spectra and fluorescence spectra of compounds **14–20** are summarized in Table 1, where the data for bithiophene, the starlike molecules having the arms consisting of a regular alternating arrangement of a silicon–silicon bond and bithienylene unit and a tris(dimethylsilyl)methylsilane moiety as a core, **21–23**, and a linear polymer with an alternative arrangement of a disilanylne–bithienylene unit, poly[(tetraethylidisilanylne) bithiophene] (**24**) reported previously, are also included for comparison.

**Table 1**

Absorption and emission data (in dioxane) for compounds **14–20** in comparison with related compounds.

Compound	$\lambda_{\text{max,Abs}}$ (nm)	$\lambda_{\text{max,F}}$ (nm)	$\Phi\text{F}(\text{ns})^a$
<b>14</b>	321	388	0.39
<b>15</b>	337	384, 396	0.68
<b>16</b>	333	397	0.73
<b>17</b>	335	381, 394	0.41
<b>18</b>	328	380, 391	0.74
<b>19</b>	334	397	0.46
<b>20</b>	336	398	0.74
$\text{SiSiTTSiSi}^b$	325	390	0.23
<b>21</b> <sup>c</sup>	336	381, 398	0.68
<b>22</b> <sup>d</sup>	329	398	0.71
<b>23</b> <sup>e</sup>	332	386, 398	0.75
<b>24</b> <sup>f</sup>	343	383, 397	0.33

<sup>a</sup> Based on quinine sulfate ( $\Phi_{366} = 0.546$ ) as a standard.

<sup>b</sup>  $\text{Me}_2\text{SiMe}_2\text{SiTTSiMe}_2\text{SiMe}_3$  T = thienylene.

<sup>c</sup>  $\text{MeSi}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_3)_3$  T = thienylene.

<sup>d</sup>  $\text{MeSi}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTH})_3$  T = thienylene.

<sup>e</sup>  $\text{MeSi}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTH})_3$  T = thienylene.

<sup>f</sup> Poly[(tetraethylidisilanylne) bithiophene].

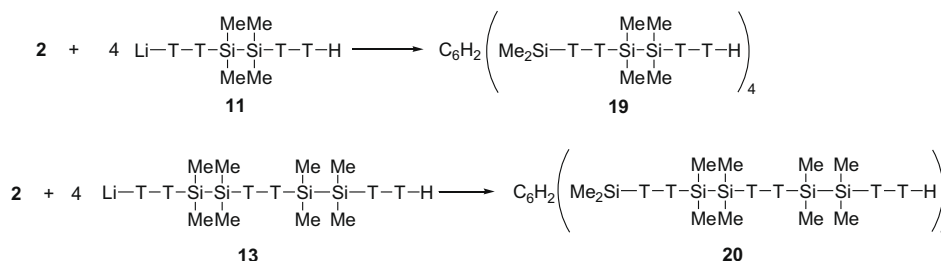
The present starlike molecules **14–20** show absorption maxima in the range of 321–337 nm. These results are similar to those of the starlike molecules **21–23**, reported previously [5a]. In their fluorescence spectra, a similar tendency is also observed. The quantum yields of compounds **14–20** are somewhat lower than those of the starlike compounds **21–23**, but much higher than those of bithiophene and poly[(tetraethylidisilanylne) bithiophene] (**24**). The higher quantum yields are probably due to the starlike structure. The absorption and fluorescence maximum wavelengths for 1,3,5-tris- and 1,2,4,5-tetrakis[oligo(disilanylnebithienylene)dimethylsilyl]benzene are very close to each other. The fluorescence quantum yields for these molecules also show a striking resemblance to each other as shown in Table 1.

In conclusion, the starlike molecules with the arms consisting of a regular alternating arrangement of a silicon–silicon bond and bithienylene unit were readily synthesized by the reactions of 1,3,5-tris(chlorodimethylsilyl)benzene and 1,2,4,5-tetrakis(fluorodimethylsilyl)benzene with the respective lithio[oligo(disilanylnebithienylene)] derivatives. The starlike molecules whose arms extend to three and four directions showed absorption maxima in the range of 321–337 nm, and high fluorescence quantum yields.

## 3. Experimental

### 3.1. General procedures

All reactions were performed under an atmosphere of dry nitrogen. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Low-resolution mass spectra were



**Scheme 4.**

measured on a JEOL Model JMS-700 instrument. UV–Vis absorption spectra were measured with a JASCO V-560 spectrometer in dioxane. Fluorescence spectra were measured with a JASCO FP-777 spectrometer in dioxane. Melting point was measured with a Yanco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Diethyl ether and THF used as a solvent were distilled from sodium/benzophenone ketyl, just before use.

### 3.2. 1,3,5-Tris(dimethylsilyl)benzene

In a 200 mL two-necked flask was placed 2.81 g (0.12 mol) of magnesium and 12.99 g (0.14 mol) of chlorodimethylsilane in 60 mL of THF. To this was added 10.26 g (32.6 mmol) of 1,3,5-tribromobenzene in 40 mL of THF. After the mixture was stirred for 5 h at room temperature, it was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was distilled under reduced pressure to give 5.41 g (66% yield) of pure 1,3,5-tris(dimethylsilyl)benzene. Anal. Calc. for  $C_{12}H_{24}Si_3$ : C, 57.06; H, 9.58. Found: C, 57.06; H, 9.50%. B.p. 56 °C/1 torr; MS  $m/z$  252 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.40 (d, 18H,  $Me_2Si$ ,  $J = 3.7$  Hz), 4.48 (sep, 3H, SiH,  $J = 3.7$  Hz), 7.77 (s, 3H, phenylene ring protons);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) –3.7 ( $Me_2Si$ ), 135.9, 140.5 (phenylene ring carbons);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) –16.7.

### 3.3. Preparation of compound 1

In a 100 mL two-necked was placed 0.350 g (1.97 mmol) of palladium chloride and 70 mL of carbon tetrachloride. To this was added 5.41 g (21.46 mmol) of 1,3,5-tris(dimethylsilyl)benzene. The mixture was heated to reflux for 5 h. After the solvent was evaporated, the residue was distilled under reduced pressure to give 5.27 g (69% yield) of **1**. Anal. Calc. for  $C_{12}H_{21}Si_3Cl_3$ : C, 40.50; H, 5.95. Found: C, 40.36; H, 5.90%. B.p. 146 °C/1 torr; MS  $m/z$  354 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.74 (s, 18H,  $Me_2Si$ ), 7.96 (s, 3H, phenylene ring protons);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) 2.1 ( $Me_2Si$ ), 135.6, 139.4 (phenylene ring carbons);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) 20.6.

### 3.4. Preparation of compound 2

In a 50 mL two-necked was placed 2.15 g (20.8 mmol) of zinc fluoride and 30 mL of THF. To this was added 2.12 g (4.73 mmol) of 1,2,4,5-tetrakis(chlorodimethylsilyl)benzene [10]. The mixture was heated to reflux for 5 h. After the solvent was evaporated, the residue was distilled under reduced pressure to give 1.73 g (96% yield) of **2**. Anal. Calc. for  $C_{14}H_{26}Si_4F_4$ : C, 43.94; H, 6.85. Found: C, 43.66; H, 6.90%. B.p. 120 °C/1 torr; MS  $m/z$  382 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.52 (d, 24H,  $Me_2Si$ ,  $^3J_{HF} = 9.0$  Hz), 7.91 (s, 2H, phenylene ring protons);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) 0.37 (d,  $Me_2Si$ ,  $^2J_{HF} = 19.0$  Hz), 138.1 (phenylene ring carbons), 143.0 (d, phenylene ring carbons,  $^2J_{HF} = 14.0$  Hz);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) 21.7 (d,  $SiMe_2$ ,  $^1J_{SiF} = 279$  Hz).

### 3.5. Preparation of compound 3

In a 500 mL three-necked flask was placed 30.00 g (0.09 mol) of 5,5'-dibromo-2,2'-bithiophene in 400 mL of diethyl ether. To this was added 58.8 mL (0.09 mol) of a 1.58 M *n*-butyllithium–hexane solution at –80 °C. After the mixture was stirred for 3 h at –80 °C, it was warmed to room temperature and stirred for 12 h. The resulting mixture was slowly added to 15.42 g (0.093 mol) of chloropentamethyldisilane at room temperature. After the addition was completed, the solvent was removed by distillation and hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous magne-

sium sulfate. After the solvent was evaporated, compound **3** (24.31 g, 70% yield) was isolated by a silica gel column eluting with hexane as a yellow viscous liquid. Anal. Calc. for  $C_{13}H_{19}Si_2S_2Br$ : C, 41.58; H, 5.10. Found: C, 41.53; H, 5.00%. MS  $m/z$  374 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.12 (s, 9H,  $SiMe_3$ ), 0.38 (s, 6H,  $SiMe_2$ ), 6.91 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.95 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.05 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.15 (d, 1H,  $J = 3.7$  Hz, thienylene proton);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) –2.9, –2.5 ( $Me_3Si$ ,  $Me_2Si$ ), 110.8, 123.6, 125.3, 130.6, 134.7, 139.0, 139.5, 141.3 (thienylene carbons);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) –19.3, –23.9.

### 3.6. Preparation of compound 5

To a solution of 10.01 g (0.03 mol) of 5,5'-dibromo-2,2'-bithiophene in 100 mL of diethyl ether was added 20.0 mL (0.031 mol) of a 1.54 M *n*-butyllithium–hexane solution at –40 °C over a period of 20 min. The resulting mixture was stirred at room temperature for 5 h, and then 5.70 g (0.030 mol) of 1,2-dichlorotetramethyldisilane was added at –20 °C over a period of 30 min. After filtration of the mixture, the solvent was evaporated, and the residue was distilled under reduced pressure to give 7.24 g (61% yield) of **5**, as a bright yellow viscous liquid. Anal. Calc. for  $C_{12}H_{16}Si_2S_2ClBr$ : C, 36.40; H, 4.07. Found: C, 36.10; H, 3.99%. B.p. 172–178 °C/1 torr; MS  $m/z$  394 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.10 (s, 6H,  $SiMe_2$ ), 0.12 (s, 6H,  $SiMe_2$ ), 6.53 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.56 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.74 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.78 (d, 1H,  $J = 3.7$  Hz, thienylene proton);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) –3.5, 1.9 ( $Me_2Si$ ), 111.1, 123.9, 125.5, 130.6, 135.7, 136.0, 138.6, 142.1 (thienylene carbons);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) –24.5, –21.2.

### 3.7. Preparation of compound 6

Compound **6** was prepared from 6.10 g (0.016 mol) of **3**, 10.3 mL (0.016 mol) of a 1.58 M *n*-butyllithium–hexane solution, and 6.40 g (0.016 mol) of **5** in diethyl ether, as described above. Compound **6** (7.70 g, 73% yield) was isolated by a silica gel column eluting with hexane–chloroform (5:1). Anal. Calc. for  $C_{25}H_{35}Si_4S_4Br$ : C, 45.77; H, 5.38. Found: C, 45.77; H, 5.33%. M.p. 94–95 °C; MS  $m/z$  654 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.09 (s, 9H,  $SiMe_3$ ), 0.35 (s, 6H,  $SiMe_2$ ), 0.40 (s, 12H,  $Me_2Si$ ), 6.89 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.93 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.02 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.03 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.05 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.13 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.22 (d, 2H,  $J = 3.7$  Hz, thienylene proton);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) –2.89, –2.88, –2.84, –2.4 ( $Me_2Si$ ,  $Me_3Si$ ), 110.9, 123.8, 125.1, 125.2, 125.4, 130.6, 134.8, 135.3, 135.4, 136.9, 138.1, 138.86, 138.87, 141.6, 142.3, 142.9 (thienylene carbons);  $^{29}Si$  NMR ( $\delta$   $CDCl_3$ ) –24.5, –24.4, –24.1, –19.3.

### 3.8. Preparation of compound 8

Compound **8** was prepared from 4.08 g (6.22 mmol) of **6**, 4.0 mL (6.32 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 2.42 g (6.11 mmol) of **5** in diethyl ether. Compound **8** (4.18 g, 73% yield) was isolated by a silica gel column eluting with hexane–chloroform (5:1). Anal. Calc. for  $C_{37}H_{51}Si_6S_6Br$ : C, 47.45; H, 5.49. Found: C, 45.73; H, 5.30%. M.p. 151–153 °C; MS  $m/z$  934 ( $M^+$ );  $^1H$  NMR ( $\delta$   $CDCl_3$ ) 0.10 (s, 9H,  $SiMe_3$ ), 0.36 (s, 6H,  $SiMe_2$ ), 0.41 (s, 24H,  $Me_2Si$ ), 6.90 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 6.94 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.02–7.06 (m, 5H, thienylene proton), 7.14 (d, 1H,  $J = 3.7$  Hz, thienylene proton), 7.20–7.23 (m, 4H, thienylene proton);  $^{13}C$  NMR ( $\delta$   $CDCl_3$ ) –2.88, –2.87, –2.84 (3C), –2.5 ( $Me_2Si$ ,  $Me_3Si$ ), 110.9, 123.8, 125.1, 125.15, 125.24, 125.3, 125.4, 130.6, 134.8, 135.30 (2C), 135.34, 135.36, 135.37,

137.1, 137.5, 138.1, 138.8, 138.9, 141.7, 142.3, 142.7, 142.8, 142.9 (thienylene carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.6, –24.5 (2Si), –24.4, –24.1, –19.3.

### 3.9. Preparation of compound **10**

Compound **10** was prepared from 10.87 g (0.044 mol) of 5-bromo-2,2'-bithiophene, a 1.58 M *n*-butyllithium–hexane solution, and 17.55 g (0.02 mol) of **5**. Compound **10** (18.88 g, 81% yield) was isolated using a silica gel column eluting with a mixed solvent of hexane–chloroform (5:1), as a colorless solid. Anal. Calc. for  $\text{C}_{20}\text{H}_{21}\text{Si}_2\text{S}_4\text{Br}$ : C, 45.69; H, 4.03. Found: C, 45.64; H, 4.05%. M.p. 87–89 °C; MS  $m/z$  524 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.40 (br s, 12H,  $\text{SiMe}_2$ ), 6.89 (d, 1H,  $J=3.7$  Hz, thienylene proton), 6.94 (d, 1H,  $J=3.7$  Hz, thienylene proton), 6.99 (t, 1H,  $J=3.7$  Hz, thienylene proton), 7.02 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.03 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.13 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.16 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.19 (d, 1H,  $J=5.2$  Hz, thienylene proton), 7.21 (d, 1H,  $J=3.7$  Hz, thienylene proton);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.9 (2C) ( $\text{Me}_2\text{Si}$ ), 110.9, 123.8 (2C), 124.4, 125.2, 125.4, 127.8, 130.6, 135.30, 135.32, 137.2, 137.3, 138.0, 138.9, 141.7, 142.8 (thienylene carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.5, –24.3.

### 3.10. Preparation of compound **12**

Compound **12** was prepared from 6.79 g (12.9 mmol) of **10**, 8.2 mL (13.0 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 5.11 g (12.9 mmol) of **5**. Compound **12** (8.62 g, 82% yield) was isolated using a silica gel column eluting with a mixed solvent of hexane–chloroform (5:1), as a yellow green solid. Anal. Calc. for  $\text{C}_{32}\text{H}_{37}\text{Si}_4\text{S}_6\text{Br}$ : C, 47.65; H, 4.63. Found: C, 47.54; H, 4.63%. M.p. 120–122 °C; MS  $m/z$  804 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.40 (br s, 24H,  $\text{SiMe}_2$ ), 6.89 (d, 1H,  $J=3.7$  Hz, thienylene proton), 6.93 (d, 1H,  $J=3.7$  Hz, thienylene proton), 6.99 (t, 1H,  $J=3.7$  Hz, thienylene proton), 7.01 (d, 2H,  $J=3.7$  Hz, thienylene protons), 7.13 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.15 (d, 2H,  $J=3.7$  Hz, thienylene protons), 7.16 (d, 1H,  $J=3.7$  Hz, thienylene proton), 7.18 (d, 1H,  $J=5.2$  Hz, thienylene proton), 7.21 (d, 3H,  $J=3.7$  Hz, thienylene protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.9 (2C), –2.84 (2C) ( $\text{Me}_2\text{Si}$ ), 110.9, 123.76, 123.78, 124.3, 125.19, 125.23, 125.3, 125.4, 127.8, 130.6, 135.3 (2C), 135.4 (2C), 137.1, 137.29, 137.34, 137.4, 138.0, 138.9, 141.7, 142.7, 142.76, 142.78 (thienylene carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.5 (2Si), –24.3 (2Si).

### 3.11. Preparation of compound **14**

In a 200 mL two-necked flask was placed 15.82 g (42.2 mmol) of (5'-bromo-2,2'-bithiophen-5-yl)pentamethyldisilane **3** in 150 mL of diethyl ether. To this was added 26.7 mL (42.2 mmol) of a 1.58 M *n*-butyllithium–hexane solution at –40 °C. The mixture was added to 5.00 g (14.1 mmol) of **1** in 50 mL of ether at room temperature. The solvent was evaporated, and the residue was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Compound **14** (9.89 g, 62% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{51}\text{H}_{78}\text{Si}_9\text{S}_6$ : C, 53.91; H, 6.92. Found: C, 53.51; H, 6.95%. M.p. 104–105 °C; MS  $m/z$  1134 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.11 (s, 27H,  $\text{SiMe}_3$ ), 0.38 (s, 18H,  $\text{SiMe}_2$ ), 0.59 (s, 18H,  $\text{SiMe}_2$ ), 7.06 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.11 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.20 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.21 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.84 (s, 3H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.8 ( $\text{Me}_2\text{Si}$ ), –2.4 ( $\text{Me}_3\text{Si}$ ), –1.3 ( $\text{Me}_2\text{Si}$ ), 125.0, 125.3, 134.8, 135.9, 136.2, 137.0, 138.9, 140.5, 142.3, 143.2 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.1, –19.3, –11.3.

### 3.12. Preparation of compound **15**

Compound **15** was prepared from 3.32 g (5.06 mmol) of **6**, 3.2 mL (5.06 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 5.00 g (14.1 mmol) of **1**. Compound **15** (2.07 g, 62% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{87}\text{H}_{126}\text{Si}_{15}\text{S}_{12}$ : C, 52.83; H, 6.42. Found: C, 52.43; H, 6.49%. M.p. 123–124 °C; MS  $m/z$  1974 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.09 (s, 27H,  $\text{SiMe}_3$ ), 0.35 (s, 18H,  $\text{SiMe}_2$ ), 0.40 (s, 36H,  $\text{SiMe}_2$ ), 0.57 (s, 18H,  $\text{SiMe}_2$ ), 7.02–7.04 (m, 9H, thienylene protons), 7.10 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.15–7.21 (m, 12H, thienylene protons), 7.82 (s, 3H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.8 (3C) ( $\text{Me}_2\text{Si}$ ), –2.4 ( $\text{Me}_3\text{Si}$ ), –1.3 ( $\text{Me}_2\text{Si}$ ), 125.1 (2C), 125.2, 125.4, 134.8, 135.3, 135.4, 135.9, 136.2, 137.1, 137.2, 137.5, 138.8, 140.5, 142.3, 142.7, 142.9, 143.1 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.6, –24.5, –24.1, –19.3, –11.3.

### 3.13. Preparation of compound **16**

Compound **16** was prepared 2.45 g (2.62 mmol) of **8**, 1.7 mL (2.69 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 0.313 g (0.88 mmol) of **1**. Compound **16** (0.323 g, 13% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{123}\text{H}_{174}\text{Si}_{21}\text{S}_{18}$ : C, 52.39; H, 6.22. Found: C, 52.44; H, 6.20%. M.p. 124–125 °C; MS  $m/z$  2814 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.11 (s, 27H,  $\text{SiMe}_3$ ), 0.37 (s, 18H,  $\text{SiMe}_2$ ), 0.41 (s, 72H,  $\text{SiMe}_2$ ), 0.59 (s, 18H,  $\text{SiMe}_2$ ), 7.03–7.06 (m, 15H, thienylene protons), 7.11 (d, 3H,  $J=3.4$  Hz, thienylene protons), 7.19–7.23 (m, 18H, thienylene protons), 7.84 (s, 3H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.84 (2C), –2.83 (2C), –2.82, –2.4, –1.3, ( $\text{Me}_3\text{Si}$ ,  $\text{Me}_2\text{Si}$ ), 125.12, 125.13, 125.2, 125.3 (2C), 125.4, 134.8, 135.3, 135.4 (2C), 135.9, 136.2, 137.16, 137.19, 137.3, 137.4, 137.5, 138.8, 140.5 (2C), 142.3, 142.66, 142.70, 142.73, 142.9, 143.1 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.6 (4Si), –24.1, –19.3, –11.3.

### 3.14. Preparation of compound **17**

Compound **17** was prepared from 4.57 g (8.69 mmol) of **10**, 5.5 mL (8.69 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 1.02 g (2.87 mmol) of **1**. Compound **17** (2.64 g, 58% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{72}\text{H}_{84}\text{Si}_9\text{S}_{12}$ : C, 54.49; H, 5.33. Found: C, 54.46; H, 5.28%. MS  $m/z$  1584 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.397 (s, 18H,  $\text{SiMe}_2$ ), 0.401 (s, 18H,  $\text{SiMe}_2$ ), 0.57 (s, 18H,  $\text{SiMe}_2$ ), 6.97 (dd, 3H,  $J=5.1$  Hz, 3.7 Hz, thienylene protons), 7.01 (d, 3H,  $J=3.7$  Hz, thienylene protons), 7.02 (d, 3H,  $J=3.7$  Hz, thienylene protons), 7.09 (d, 3H,  $J=3.7$  Hz, thienylene protons), 7.14 (d, 3H,  $J=3.7$  Hz, thienylene protons), 7.16–7.20 (m, 12H, thienylene protons), 7.81 (s, 3H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.9, –2.8, –1.3, 123.8, 124.3, 125.1, 125.2, 125.4, 127.8, 135.3, 135.4, 135.9, 136.2, 137.2, 137.3, 137.4, 137.5, 140.5, 142.7, 142.8, 143.1 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –24.5 (2Si), –11.3.

### 3.15. Preparation of compound **18**

Compound **18** was prepared from 4.08 g (5.06 mmol) of **12**, 3.2 mL (5.06 mmol) of a 1.58 M *n*-butyllithium–hexane solution, and 0.601 g (1.69 mmol) of **1**. Compound **18** (1.27 g, 31% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{108}\text{H}_{132}\text{Si}_{15}\text{S}_{18}$ : C, 53.41; H, 5.48. Found: C, 53.63; H, 5.56%. M.p. 80–81 °C; MS  $m/z$  2424 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.41 (s, 72H,  $\text{SiMe}_2$ ), 0.58 (s, 18H,  $\text{SiMe}_2$ ), 6.98 (dd, 3H,  $J=5.1$  Hz, 3.7 Hz, thienylene protons), 7.02–7.05 (m, 12H, thienylene protons), 7.10 (d, 3H,  $J=3.7$  Hz, thienylene protons), 7.16–7.22 (m, 21H, thienylene protons), 7.83 (s, 3H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ ) –2.84 (2C), –2.83 (2C), –1.3, 123.8, 124.3, 125.1, 125.19, 125.24,

125.3, 125.4, 127.8 (2C), 135.3, 135.4, 135.9, 136.2, 137.2, 137.285, 137.294 (2C), 137.30, 137.34, 137.46, 137.50, 142.65, 142.70, 142.72, 142.3, 143.1 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ )  $-24.5$  (4Si),  $-11.3$ .

### 3.16. Preparation of compound 19

In a 100 mL two-necked flask was placed 2.66 g (5.07 mmol) of **10** in 50 mL of diethyl ether. To this suspension was added 3.3 mL (5.08 mmol) of a 1.54 M *n*-butyllithium–hexane solution at  $-80$  °C. The mixture was stirred over night at room temperature, and then it was added to 0.421 g (1.10 mmol) of **2** in 10 mL of ether. The solvent was evaporated, and the residue was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Compound **19** (0.63 g, 27% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{94}\text{H}_{110}\text{Si}_2\text{S}_6$ : C, 54.02; H, 5.30. Found: C, 53.88; H, 5.28%. MS  $m/z$  2086 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.39 (br s, 48H,  $\text{SiMe}_2$ ), 0.42 (s, 24H,  $\text{SiMe}_2$ ), 6.98–7.02 (m, 8H, thienyl ring protons), 7.05 (d, 16H,  $J = 3.4$  Hz, thienylene protons), 7.17–7.24 (m, 12H, thienylene protons), 7.80 (s, 2H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ )  $-2.8$  (2C), 1.0 ( $\text{Me}_2\text{Si}$ ), 123.7, 124.2, 124.9, 125.2, 125.4, 127.7, 135.3 (2C), 135.4, 136.2, 136.6, 136.8, 137.1, 137.3, 140.2, 142.6, 142.8, 143.0 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ )  $-24.4$  (2Si),  $-9.0$ .

### 3.17. Preparation of compound 20

Compound **20** was prepared from 3.00 g (3.72 mmol) of **12**, 2.5 mL (3.85 mmol) of a 1.54 M *n*-butyllithium–hexane solution, and 0.301 g (0.79 mmol) of **2**. Compound **20** (0.19 g, 7% yield) was isolated by column chromatography. Anal. Calc. for  $\text{C}_{142}\text{H}_{174}\text{Si}_{20}\text{S}_{24}$ : C, 53.10; H, 5.46. Found: C, 53.33; H, 5.10%. MS  $m/z$  3206 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$   $\text{CDCl}_3$ ) 0.41 (br s, 96H,  $\text{SiMe}_2$ ), 0.51 (s, 24H,  $\text{SiMe}_2$ ), 6.96 (d, 4H,  $J = 3.4$  Hz, thienylene protons), 6.98–7.00 (m, 4H, thienylene protons), 7.01–7.04 (m, 16H, thienyl ring protons), 7.14 (d, 4H,  $J = 3.4$  Hz, thienylene protons), 7.15–7.19 (m, 12H, thienylene protons), 7.21 (d, 12H,  $J = 3.4$  Hz, thienylene protons), 8.06 (s, 2H, phenylene ring protons);  $^{13}\text{C}$  NMR ( $\delta$   $\text{CDCl}_3$ )  $-2.85$ ,  $-2.83$ ,  $-2.81$  (2C), 1.5 ( $\text{Me}_2\text{Si}$ ), 123.8, 124.3, 125.1, 125.2, 125.26 (2C), 125.28 (2C), 125.4, 127.8, 135.3, 135.4 (3C), 136.4, 137.3, 137.35, 137.37 (2C), 137.39, 139.00, 142.7, 142.75, 142.77, 143.01, 143.04 (thienylene and phenylene ring carbons);  $^{29}\text{Si}$  NMR ( $\delta$   $\text{CDCl}_3$ )  $-24.5$  (4Si),  $-9.8$ .

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