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# Electrochemical Stepwise Synthesis of Poly[2,5-(silanylene)thiophene] Precursors

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The easy control of the electrochemical parameters involved in the intensiostatic sacrificial anode technique was applied to the stepwise synthesis of silanylene-2,5-thiophenylene backbones with high selectivity and versatility not accessible by purely chemical routes. 2,5-Bis(chlorodiorganosilyl)thiophenes and related linear poly[2,5-(silanylene)thiophene] oligomers with one to three silicon atoms were synthesized by electrochemical reduction of 2,5-dibromo- or 2,5-dichlorothiophene in the presence of a diorganodichlorosilane.

## Introduction

Silicon-containing polymers which possess a regular alternating arrangement of silanylenes and $\pi$-electron systems in a polymer backbone are of great interest[1−13] as photoresists,[14] semiconducting materials,[5,10,11,15,16] and precursors of silicon carbide.[17,18] When the $\pi$-electron system is a thienylene unit, poly[2,5-(silanylene)thiophene]s are convenient precursors of polythiophene films (which are sought after for their conductive and nonlinear optical properties[19]) by oxidative electropolymerization.[20] Such compounds usually are synthesized by coupling dilithio derivatives of thiophene,[10,11] bis(2-thienyl)dialkylsilanes,[21] and bis(5-bromo-2-thienyl)dialkylsilanes[15] with dichlorosilanes at low temperature (−80 °C) or by Wurtz type condensations with sodium of 2,5-bis(chlorodialkylsilyl)thiophenes.[1] However, these reactions are not selective and lead to mixtures of oligomers in moderate to low yield.

In a previous work,[22] we found that $(\mathrm{Th}-)_2\mathrm{SiR}_1\mathrm{R}_2$ ($\mathrm{Th}-$ = 2-thienyl) and $(\mathrm{Br}-\mathrm{Th}-)_2\mathrm{SiR}_1\mathrm{R}_2$ ($-\mathrm{Th}-$ = 2,5-thienylene) could be prepared selectively by cathodic reduction of 2,5-dihalothiophenes in the presence of a dichlorosilane. In the present work, the cathodic coupling has been extended successfully to the preparation of longer oligomers of poly[2,5-(silanylene)thiophene]s and of 2,5-bis(chlorosilyl)thiophenes in up to a 5−15 g scale. The technique used is the versatile intensiostatic sacrificial anode process (massive Al or Mg bar)[23] carried out at room temperature in an undivided cell.

## Results and Discussion

For a stepwise synthesis of poly[2,5-(silanylene)thiophene]s, our strategy was based on the initial selective synthesis of bis(2-halo-5-thienyl)]diorganosilanes. We shall examine successively the results of the electrochemical coupling using either a 2/1 dihalothiophene/dichlorosilane molar ratio or a large excess of dichlorosilane.

**1. Electrochemical Coupling of 2,5-Dihalothiophenes with Dichlorosilanes in a 2:1 Molar Ratio.** We have previously shown[22] (Scheme 1) that

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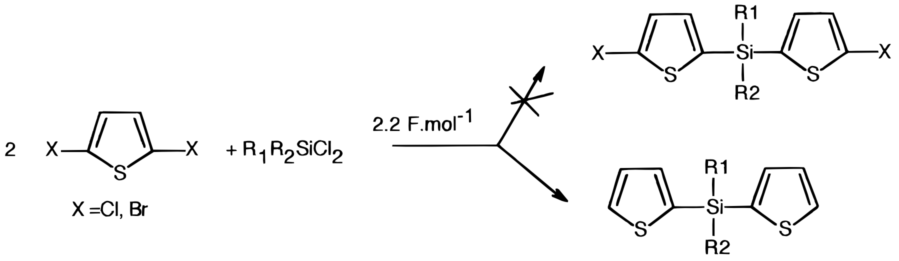
**Scheme 1. Electrochemical Coupling of 2,5-Dihalothiophenes with Dichlorosilanes in a 2:1 Molar Ratio**



the electroreductive coupling of 2,5-dibromo- or 2,5-dichlorothiophene with a dichlorodiorganosilane did not afford the expected bis(2-halo-5-thienyl)diorganosilane but rather (Th−)$_2$SiR$_1$R$_2$, after having passed 2.2 faradays mol$^{-1}$ of 2,5-dihalothiophene, under specified conditions, with THF/HMPA (70/10 v/v) as the solvent (HMPA = hexamethylphosphoramide), a magnesium anode, a stainless steel cathode, $i = 0.1$ A, $j = 0.1 \pm 0.05$ A dm$^{-2}$, and 0.02 M Bu$_4$NBr as the supporting electrolyte.

Theoretically, the reduction of both halogen−carbon bonds in 2,5-dibromothiophene requires 4 faradays mol$^{-1}$.[24] To understand the origin of the undesired (Th−)$_2$SiR$_1$R$_2$ in the electrochemical process, the composition of the electrolytic medium has been determined by dynamic gas chromatography (GC) throughout the electrolysis.

### 1.1. Product Analysis during the Electrocoupling of 2,5-Dichlorothiophene with Me$_2$SiCl$_2$.

Figure 1 shows that the reaction is more complex than expected. During the passage of 2.2 faradays mol$^{-1}$ of charge, three alternating silanylene/thienylene unit oligomers appeared and disappeared, finally leading to Th−SiMe$_2$−Th (**T$_2$Si**).

For a charge of 0.5 faraday mol$^{-1}$ of 2,5-dichlorothiophene the substrate conversion was 60%, instead of the 25% maximum expected for a two-electron per C−Cl bond process. At this stage of the reaction, the major product was bis(2-chloro-5-thienyl)]dimethylsilane (Cl−Th−)$_2$SiMe$_2$ in 52% GC yield, and **T$_2$Si**, the hydrogenated analogue, just began to appear (8%). At 1.1 faradays mol$^{-1}$, the substrate conversion was nearly quantitative and (Cl−Th−)$_2$SiMe$_2$ was completely transformed into Th−SiMe$_2$−Th−SiMe$_2$−Th−SiMe$_2$−Th (**T$_4$Si$_3$**) in 52% GC yield (43% isolated) and Th−SiMe$_2$−Th−SiMe$_2$−Th (**T$_3$Si$_2$**) in 24% GC yield. At this stage of the reaction, the amount of **T$_2$Si** had still increased (20%) and the anodic faradaic yield was 147%.[25] At 1.6 faradays mol$^{-1}$, **T$_4$Si$_3$** had totally disappeared and **T$_3$Si$_2$** had decreased, whereas **T$_2$Si** increased to 83% (GC yield). At 2 faradays mol$^{-1}$, the sole remaining product was **T$_2$Si** (63% isolated yield) and the anodic faradaic yield was then 168%. During the electrolysis, the maximum yields for **T$_3$Si$_2$** and **T$_4$Si$_3$** were obtained at 0.8 and 1.1 faradays mol$^{-1}$, respectively.

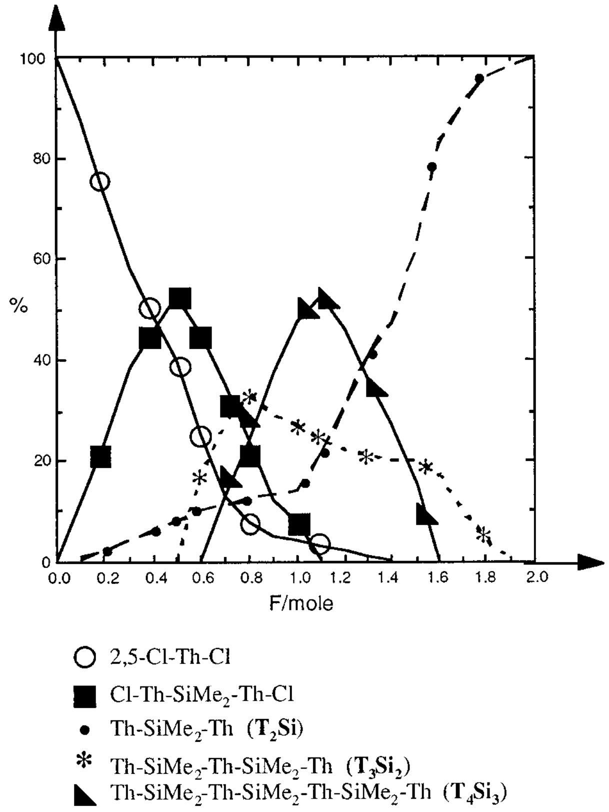


**Figure 1.** Dynamic GC analysis of 2,5-dichlorothiophene and Me$_2$SiCl$_2$ electrocoupling.

When the same electrolysis was carried out with 2,5-dibromothiophene as the substrate and stopped at 0.5 faraday mol$^{-1}$, all of the substrate was converted and the sole products formed were **T$_2$Si**, **T$_3$Si$_2$**, and **T$_4$Si$_3$**. No (Br−Th−)$_2$SiMe$_2$ was detected. Here again the anodic faradaic yield reached 172%. These high values of the anodic faradaic yields in these two experiments revealed a chemical reductive role of the anodically scoured magnesium, stronger and faster with the dibromo compound. At this stage, we could imagine that **T$_3$Si$_2$** and **T$_4$Si$_3$** are electroactive under our conditions, likely by reduction of the silicon-thiophene bond. To verify this hypothesis, we carried out a voltammetric study of these compounds.

### 1.2. Cyclic Voltammetric Study of Moieties with Alternating Silicon−Thiophene Units.

In a previous study,[26a] we determined the reduction peak potentials of a series of mono- and polychlorothiophenes (or their bromo analogues) by cyclic voltammetry. We showed that, in THF, polyhalothiophenes undergo stepwise reduction, due to sufficiently large differences between two consecutive peaks on the order of 280 mV

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[24] For additional details of the mechanism of the electrochemical reduction of alkyl and aryl halides, see for example: Savéant, J.-M. *Bull. Soc. Chim. Fr.* **1988**, 225.

[25] The anodic faradaic yield is the amount of metal consumed compared with the charge passed: 100% means a pure faradaic process, whereas higher values are the result of metal overconsumption due to a by-chemical process.

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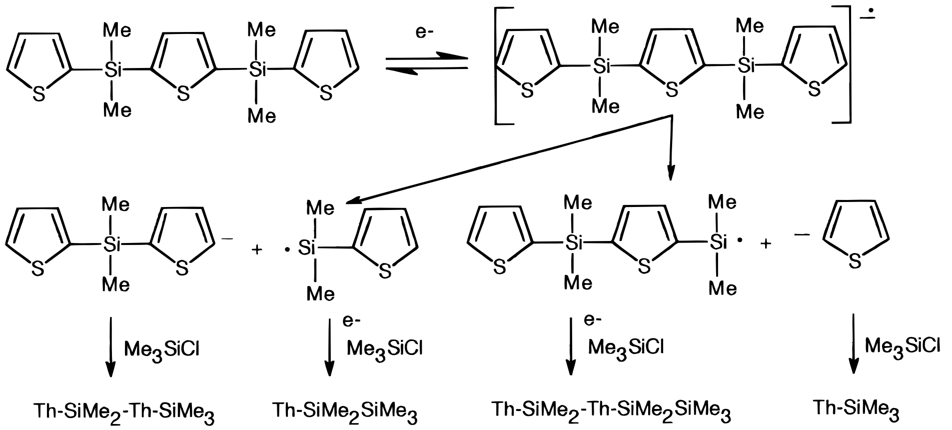
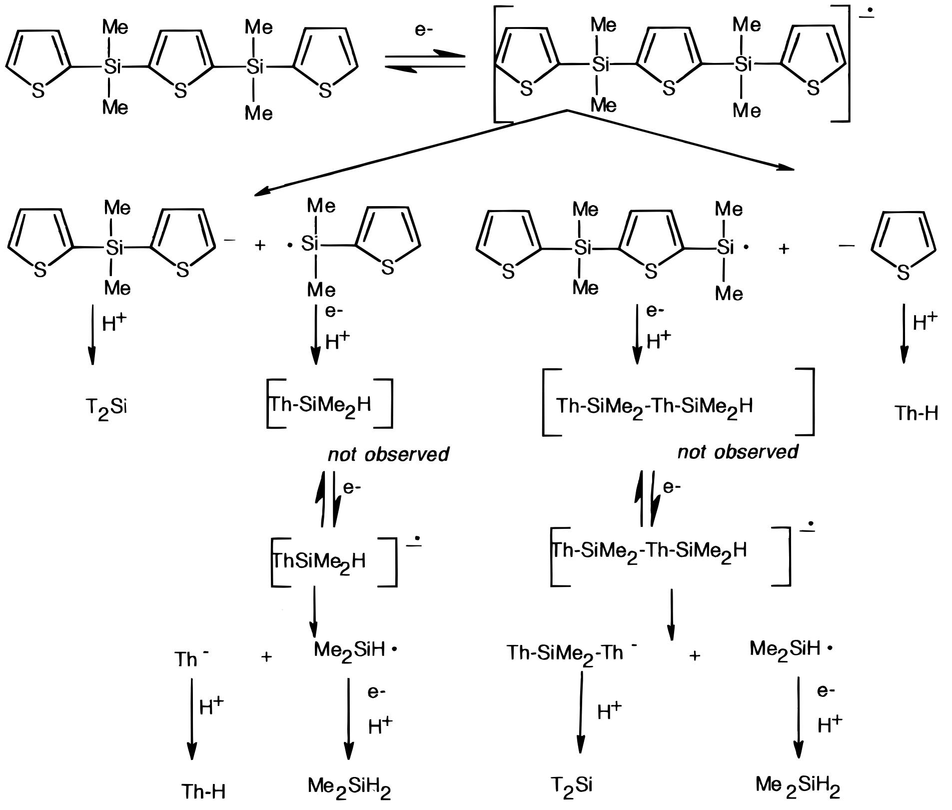
**Scheme 2. Mechanism for the Electroreduction of $T_3Si_2$ with Addition of $Me_3SiCl$**



**Scheme 3. Mechanism for the Electroreduction of $T_3Si_2$ without Addition of $Me_3SiCl$**



for Cl and 1000 mV for Br, and that, on an electrosynthesis scale, the successive trimethylsilylations presented excellent chemoselectivities. The peak potentials measured in THF−0.1 M $Bu_4NBF_4$ at a 1 mm diameter Pt disk for Br−Th−Br and Cl−Th−Cl were respectively (vs SCE) −1.67, −2.58 V (2 peaks) and −2.51, −2.81 V (sweep rate 0.1 V $s^{-1}$; voltage scan 0/1.0/−2.93/0 V). The first reduction peak potential of $Me_2SiCl_2$ (−2.54 V measured in MeCN−0.1 M $Bu_4NBPh_4$, other conditions being identical)[27] being more cathodic than that of Br−Th−Br or Cl−Th−Cl, it can be expected that the dihalothiophene is reduced first in the electrochemical process.

In the present work, the values obtained under the first conditions (Pt, THF) for the peak potentials of (Br−Th−)$_2$SiMe$_2$ and (Cl−Th−)$_2$SiMe$_2$ are respectively −2.4 and −2.45 V, showing that they can be easily reduced after the 2,5-dihalothiophene. Moreover, $\mathbf{T_3Si_2}$ and $\mathbf{T_4Si_3}$ exhibited a reduction peak at −2.3 V. This explains their observed decrease and disappearance by $C_{thienyl}$−Si bond cleavage during the electrolysis when they become sufficiently concentrated. On the other hand, at a glassy-carbon-disk electrode, no reduction wave was observed for these oligomers. This interesting analytical result, that the reduction overpotential of the $C_{thienyl}$−Si bond strongly depends on the cathode material, will be exploited below to improve the $\mathbf{T_4Si_3}$ synthesis.

**1.3. Chemical Evidence for C−Si Cleavage and the Related Anions Which Are Formed.** During the electrochemical reduction of 2,5-dibromo- or 2,5-dichlorothiophene in the presence of $Me_2SiCl_2$, we noticed gas evolution of $Me_2SiH_2$ (identified by IR spectroscopy)

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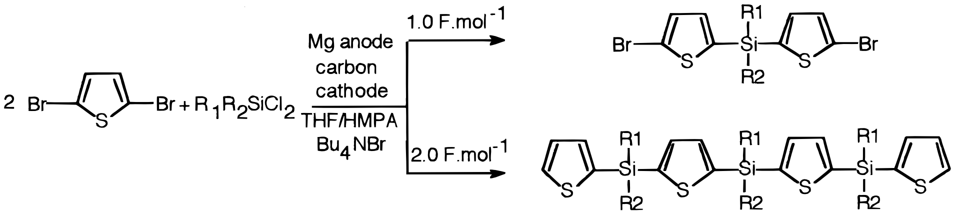
**Table 1. Electroreductive Coupling of 2,5-Dibromothiophene with a Dichlorosilane at a Carbon Cloth Cathode in a 2:1 Molar Ratio**

| | | | yield (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $(Br-Th-)_2SiR_1R_2$ | | $(Th-)_2Si\ R_1R_2$ | product A[b] | product B[c] | |
| $R_1R_2SiCl_2$ | *n* (faradays $mol^{-1}$) | Br−Th−Br $\tau$,[a] (%) | GC | isolated | GC | GC | GC | isolated |
| $Me_2SiCl_2$ | 2.0 | 100 | 0 | | 15 | 0 | 85 | 78 |
| | 1.0 | 60 | 43 | 36 | 3 | 0 | 14 | |
| $PhMeSiCl_2$ | 2.0 | 100 | 0 | | 19 | 0 | 81 | 75 |
| | 1.0 | 58 | 44 | 34 | 2 | 0 | 12 | |

[a] $\tau$ = conversion rate. [b] A = $Th-SiR_1R_2-Th-SiR_1R_2-Th$. [c] B = $Th-SiR_1R_2-Th-SiR_1R_2-Th-SiR_1R_2-Th$.

**Scheme 4. Electroreductive Coupling of 2,5-Dibromothiophene with a Dichlorosilane at a Carbon Cloth Cathode in a 2:1 Molar Ratio**



and an equivalent formation of thiophene. To supplement the electrochemical process during the electrolysis, the intermediate anionic species have been trapped by addition of 7 mL of $Me_3SiCl$ after having passed 1.1 faradays $mol^{-1}$. At this stage $Me_2SiCl_2$ was used up; the electrolysis then was pursued up to 2.2 faradays $mol^{-1}$. Four compounds were detected by GC/MS analysis at the end of the reaction: $Th-SiMe_3$ (*m/z* 156), $Th-SiMe_2-Th-SiMe_3$ (*m/z* 296), $Th-SiMe_2SiMe_3$ (*m/z* 214), and $Th-SiMe_2-Th-SiMe_2SiMe_3$ (*m/z* 354). According to these observations, we propose an electrochemical reductive cleavage of both inner and outer $C_{thienyl}-Si$ bonds according to the mechanism depicted in Schemes 2 and 3, taking $\mathbf{T_3Si_2}$ as an example.

It must be pointed out that thiophene itself exclusively underwent ring opening with formation of hexamethyldisilthiane and 1,1,4,4-tetrakis(trimethylsilyl)but-2-ene ($(Me_3Si)_2CHCH{=}CHCH(SiMe_3)_2$) on reaction with $Li/Me_3SiCl$ in THF.[26b] Thus, in our reaction, the cleavage of the $C_{thienyl}-Si$ bonds is faster than the reductive silylation of the thienyl ring. That is in agreement with the good leaving-group ability of the thienyl anion in nucleophilic substitutions.[28] For this reason, the silylation of the radical anion is not considered in the proposed mechanism.

When the electrolysis is carried out in the absence of $Me_3SiCl$, the sole electrophilic species able to trap the generated anions are protons derived from the solvent or the supporting electrolyte in the medium[29] (Scheme 3).

Moreover, we showed that such thienyl−silicon bonds also can be chemically reduced, even those of the less reactive 2,5-bis(trimethylsilyl)thiophene. Thus, stirring of the latter with lithium pellets in refluxing THF/HMPA, over 4 h, provided 2-(trimethylsilyl)thiophene in 37% yield by monodesilylation of the precursor. Very few examples of direct C−Si reductive cleavage have been reported.[28,30] Thus, sodium/potassium alloy is known to reduce the C−Si bond to give triphenylsilyl anions.[30]

**1.4. Synthesis of $\mathbf{Th-SiR_1R_2-Th-SiR_1R_2-Th-SiR_1R_2-Th}$.** Using common chemical routes, such linear oligomers are not easily synthesized. Thus, $\mathbf{T_4Si_3}$ had been prepared in tetramethylethylenediamine (TMEDA), at 0 °C, by reaction of 2,5-dilithiothiophene with $Me_2SiCl_2$ and isolated in only 7% yield.[21] Kauffmann et al. obtained this linear oligomer as a byproduct of the synthesis of its higher homologue with five silicon atoms.[31] It was obtained in 31% yield by coupling, at 0 °C in ether or THF, $\mathbf{T_2Si}$/BuLi (1 equiv/1 equiv) with $Me_2SiCl_2$. Moreover, these chemical routes often lead to tetra- or hexameric silylenethienylenes with cyclic structures[32] in THF. Such silicon-bridged macrocycles were never detected in our electrochemical medium.

Since our voltammetric study showed that $\mathbf{T_4Si_3}$ is not reduced at a glassy-carbon cathode, we investigated its preparation and that of $Th-SiMePh-Th-SiMePh-Th-SiMePh-Th$ by electrocoupling of 2,5-dibromothiophene with the corresponding diorganodichlorosilanes using a carbon-cloth cathode. As shown in Table 1, after having passed 2 faradays $mol^{-1}$, the expected products were obtained with excellent selectivity (85% for $\mathbf{T_4Si_3}$ and 81% for $R_1$ = Ph, $R_2$ = Me) and very high yield of isolated products (78% for $\mathbf{T_4Si_3}$ and 75% for $R_1$ = Ph, $R_2$ = Me) (Scheme 4). Here again, conversion was quantitative for a charge lower than theory (4 faradays $mol^{-1}$) due to the chemical participation of the anodic Mg(0).

For 1 faraday $mol^{-1}$ of charge, the conversion of Br−Th−Br (58−60%) was yet higher than theory (50% for one C−Br bond), but mostly one C−Br bond was effectively reduced (Table 1). $Br-Th-SiMe_2-Th-Br$ resulting from direct coupling of Br−Th−Br with $Me_2SiCl_2$ was mainly obtained. Such preservation of the external C−Br bonds can be assigned to the occur-

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[32] (a) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 661. (b) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G.; Thondorf, I. *J. Org. Chem.* **1995**, *60*, 7406.

**Scheme 5. Electrochemical Process of the Reaction at a Stainless Steel Cathode**

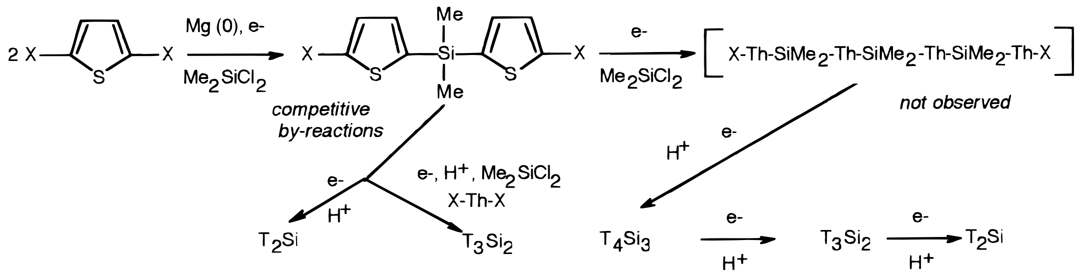


**Table 2. Comparison of Electrochemical and Chemical Routes to $Th-SiR_1R_2-Th-SiR_1R_2-Th-SiR_1R_2-Th$ Synthesis**

| | yield (%) | |
|---|---|---|
| R1, R2 | electrochemical route | best chemical route |
| Me, Me (**$T_4Si_3$**) | 78[a]<br>43[b] | 31[28] |
| Me, Ph | 75[a] | not described |

[a] For 2.0 faradays $mol^{-1}$ at a carbon-cloth cathode from 2,5-dibromothiophene. [b] For 1.1 faradays $mol^{-1}$ at a stainless steel cathode ($j = 0.1$ A/dm$^2$) from 2,5-dichlorothiophene.

rence of a much lower current density in the cloth than in our usual grid for the same current. We already showed the necessity of low current density for this reaction using a stainless steel grid of higher surface area.[22]

These results show that the electrochemical route to $Th-SiR_1R_2-Th-SiR_1R_2-Th-SiR_1R_2-Th$ is much more selective and effective than the chemical procedure (Table 2).

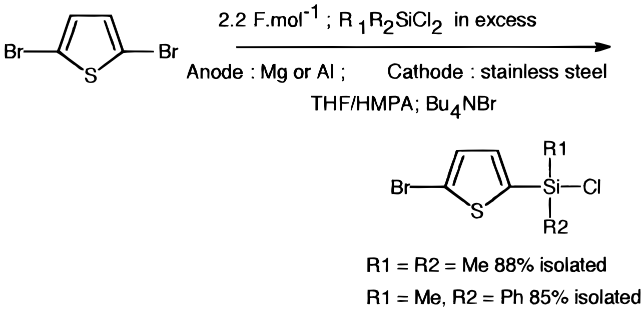
**1.5. Proposed Mechanism for the Electrocoupling of 2,5-Dihalothiophenes with $Me_2SiCl_2$ at a Stainless Steel Cathode in a 2:1 Molar Ratio.** The above data show that mechanisms at glassy-carbon and stainless steel cathodes are different.

Using a stainless steel cathode and starting from Cl−Th−Cl (Figure 1), we can propose (Scheme 5) that, as expected, $Me_2Si(-Th-Cl)_2$ is formed at the beginning of the electrolysis and, when its concentration becomes higher than that of the substrate, it is reduced and couples with the remaining $Me_2SiCl_2$, leading to $Cl-Th-SiMe_2-Th-SiMe_2-Th$ $SiMe_2-Th-Cl$. The latter then is promptly reduced and protonated to give **$T_4Si_3$**, the dichlorosilane being used up. Minor byproducts, **$T_2Si$** and **$T_3Si_2$**, also are formed under 0.5 faraday $mol^{-1}$ likely due to competitive by-protonation for the former and by-protonation, silylation, and reaction with the remaining substrate for the latter. **$T_4Si_3$**, when sufficiently concentrated, then is reduced to **$T_3Si_2$**, which itself gives **$T_2Si$** as the final product. Such a mechanism also is expected for Br−Th−Br, but reactions are faster because of the higher reactivity of C−Br bonds.

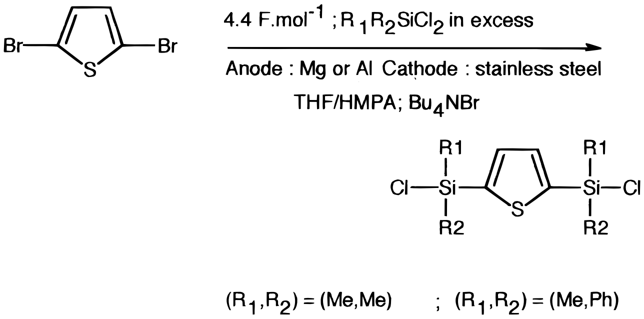
Using a carbon cloth cathode, on the other hand, and starting from Br−Th−Br, all kinetics are slower, and **$T_4Si_3$**, not reduced, is the final product.

**2. Electrochlorodiorganosilylation of 2,5-Dihalothiophenes with a Large Excess of Dichlorosilane. 2.1. Synthesis of 2-(Chlorodiorganosilyl)-5-bromothiophenes.** We have previously shown[22] that only one C−Br bond of 2,5-dibromothiophene is selectively reduced and silylated by $Me_2SiCl_2$ when it is present in large excess (20 equiv) after the passage of 2.2 faradays $mol^{-1}$ of charge, under our standard electrolysis conditions (Scheme 6).

**Scheme 6. Electrochemical Coupling of 2,5-Dibromothiophene with Excess $Me_2SiCl_2$ for 2.2 faradays $mol^{-1}$ of Charge**



**Scheme 7. Electrochemical Synthesis of 2,5-Bis(chlorodiorganosilyl)thiophenes**



**2.2. Synthesis of 2,5-Bis(chlorodiorganosilyl)thiophenes.** The passage, under the same experimental conditions, of a charge of 4.4 faradays $mol^{-1}$ of Br−Th−Br led to the expected 2,5-bis(diorganochlorosilyl)thiophenes in excellent selectivity and isolated yield (Scheme 7).

These compounds are key intermediates in the synthesis of long alternating $SiR_1R_2$−thiophene backbones, which are useful as polythiophene precursors.[1,33] Their chemical syntheses generally necessitate two steps,[1] and the yields are markedly lower than those obtained with our electrochemical method (Table 3), which is proving to be a better alternative.

**2.3. Syntheses of $Th-SiR_1R_2-Th-SiR_1R_2-Th$ and $Br-Th-SiMe_2-Th-SiMe_2-Th-Br$.** 2,5-Bis(chlorodiorganosilyl)thiophenes have been used as electrophiles in electrochemical coupling reactions. Thus, $Th-SiR_1R_2-Th-SiR_1R_2-Th$ compounds were selectively obtained in high yields from 2-bromothiophene using our usual 2/1 Th−Br/chlorosilane molar ratio after

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[33] Oshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, Y. *Macromolecules* **1991**, *24*, 2106.

**Table 3. Comparison of Electrochemical and Chemical Routes for 2,5-Bis(chlorodiorganosilyl)thiophenes**

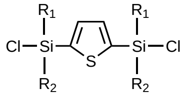
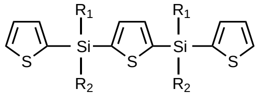
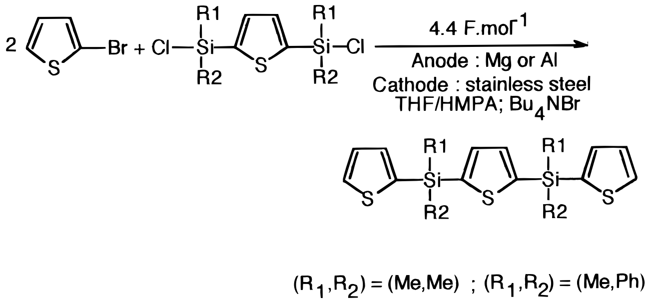
|  | yield (%) | |
|---|---|---|
| | electrochemical route | chemical route |
| R1, R2 = Me, Me | 85 | 51 |
| R1, R2 = Me, Ph | 77 | 57 |

**Table 4. Comparison of Electrochemical and Chemical Routes to Th−SiR$_1$R$_2$−Th−SiR$_1$R$_2$−Th**

|  | isolated yield (%) | |
|---|---|---|
| | electrochemical route | chemical route |
| R1, R2 = Me, Me (**T$_3$Si$_2$**) | 80 | 15[21] |
| R1, R2 = Me, Ph | 67 | not described |

**Scheme 8. Electrochemical Synthesis of Th−SiR$_1$R$_2$−Th−SiR$_1$R$_2$−Th**



having passed 2.2 faradays mol$^{-1}$ of charge (Scheme 8 and Table 4).

Here also, the electrochemical route for **T$_3$Si$_2$** is a better alternative than the chemical route (Table 4).[21] On the other hand, the synthesis of Th−SiMePh−Th−SiMePh−Th had not been previously described.

The electrochemical coupling of 2,5-dibromothiophene with 2,5-bis(chlorodimethylsilyl)thiophene as the electrophile, in a 2/1 molar ratio, has also been investigated for 2.2 faradays mol$^{-1}$ according to Scheme 9.

Two compounds were obtained: Br−Th−SiMe$_2$−Th−SiMe$_2$−Th−Br as the major product and **T$_3$Si$_2$** as the minor product. The selectivity of this reaction depended on the nature of the metal anode (Table 5). Use of aluminum avoided the reduction of the second C−Br bond, retaining the terminal bromine atoms since Al is not chemically involved, in contrast to the case for magnesium, as we already reported in previous studies in which monochlorosilanes were the electrophiles used.[34]

## Conclusion

The results collected in Schemes 1, 4, and 6−9 show the versatility of the electrochemical route for the coupling of 2,5-dihalothiophenes with dichlorosilanes, according to the experimental conditions. This method provides an efficient tool for monitoring the stepwise synthesis of linear alternating silanylene−thienylene unit oligomers while the terminal bromines are or are not retained. In each case, conversion is 100% and the yield of isolated product generally is higher than those obtained by chemical routes. Moreover, dilithio derivatives of thiophene often give rise to four-unit cyclic oligomers.

The conductivities of the films obtained by electropolymerization of the nonbrominated oligomers have been evaluated and correlated to their Raman and photoluminescence spectra. These oligomers are also interesting for their nonlinear optic properties for the third-generation harmonic at the excited state and constitute a good compromise between superior physical performance and good transparency, attributed to the presence of the silicon atom.[35] These last results are reported elsewhere.[36,37]

## Experimental Section

**Materials.** Halothiophenes (Acros) and Bu$_4$NBr (Aldrich) were used without purification. THF (SDS) and HMPA (Aldrich) were dried by distillation over sodium benzophenone ketyl and CaH$_2$, respectively, while dichlorosilanes were distilled over Mg powder just before use.

**General Methods.** Gas chromatography was performed with a temperature-programmable Hewlett-Packard 5890A apparatus equipped with a 25 m × 0.25 $\mu$m CP-Sil 5CB capillary column. $^1$H NMR spectra were recorded in CDCl$_3$ at 250 MHz on a Bruker AC 250 spectrometer, using residual CHCl$_3$ ($\delta$ 7.27 ppm) as the internal standard. *J* values are given in Hz. $^{13}$C NMR spectra were obtained at 62.86 MHz on a Bruker AC 250 using CDCl$_3$ ($\delta$ 77.70 ppm) as the internal standard. $^{29}$Si NMR spectra were recorded in CDCl$_3$ at 39.73 MHz on a Bruker AC 200 spectrometer. Electron impact mass spectra were measured at 70 eV on a VG Micromass 16F mass spectrometer coupled with a gas chromatograph equipped with a 25 m × 0.25 $\mu$m CP-Sil 5CB capillary column. IR spectra were recorded with a Perkin-Elmer 1420 spectrophotometer with pure liquid films (NaCl or KBr plates). Elemental analyses were performed by the Service Central de Microanalyse du CNRS (France).

**Voltammetry.** Cyclic voltammetry was carried out under argon in THF (20 mL) solutions containing the substrate (2 mM) and 0.1 M−Bu$_4$NBF$_4$, using a 1 mm diameter Pt or glassy-carbon disk as the working electrode and an aqueous saturated calomel reference electrode (Tacussel XR 110) separated from the medium by a Tacussel AL 120 junction filled with the same electrolytic solution. For measurements with a Pt-disk working electrode, ferrocene (10$^{-3}$ M) was used as the internal standard ($E_{p,a}$ = 0.63 V, $E_{p,c}$ = 0.56 V). The solution resistance was compensated for with a positive feedback device. The potentiostat used (Sirius) was previously described.[23b] The sweep rate was 0.5 V s$^{-1}$ and the voltage scan 0/1.0/−3/0 V.

**General Procedure for Electrolysis.** Electrolysis was performed in an undivided cell (100 mL) described elsewhere[22,23b,34] equipped with a sacrificial cylindrical aluminum or magnesium bar (1 cm diameter) as the anode and a concentric stainless steel grid or carbon (1.0 ± 0.2 dm$^2$) as the cathode. A constant current (0.1 A, density 0.1 ± 0.05 A dm$^{-2}$)

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[34] (a) Pons, P.; Biran, C.; Bordeau, M.; Dunoguès, J. *J. Organomet. Chem.* **1988**, *358*, 31. (b) Léger-Lambert, M.-P. Thesis, Université Bordeaux I, Bordeaux, France, 1991; No. 646.

[35] (a) Mignani, G.; Krämer, A.; Puccetti, G.; Ledoux, I.; Zyss, J.; Soula, G. *Organometallics* **1991**, *10*, 3656. (b) Mignani, G.; Krämer, A.; Puccetti, G.; Ledoux, I.; Soula, G.; Zyss, J.; Meyrveix, R. *Organometallics* **1990**, *9*, 2640. (c) Mignani, G.; Barzoukas, M.; Zyss, J.; Soula, G.; Balegroune, F.; Grandjean, D.; Josse, D. *Organometallics* **1991**, *10*, 3660.

[36] Moreau, C. Thesis, Université Bordeaux I, Bordeaux, France, 1996; No. 1565.

[37] Moreau, C.; Serein-Spirau, F.; Létard, J.-F.; Lapouyade, R.; Jonusauskas, G.; Rullière, C. *J. Phys. Chem. B* **1998**, *102*, 1487.

**Scheme 9. Electrochemical Synthesis of Br−Th−SiMe$_2$−Th−SiMe$_2$−Th−Br**

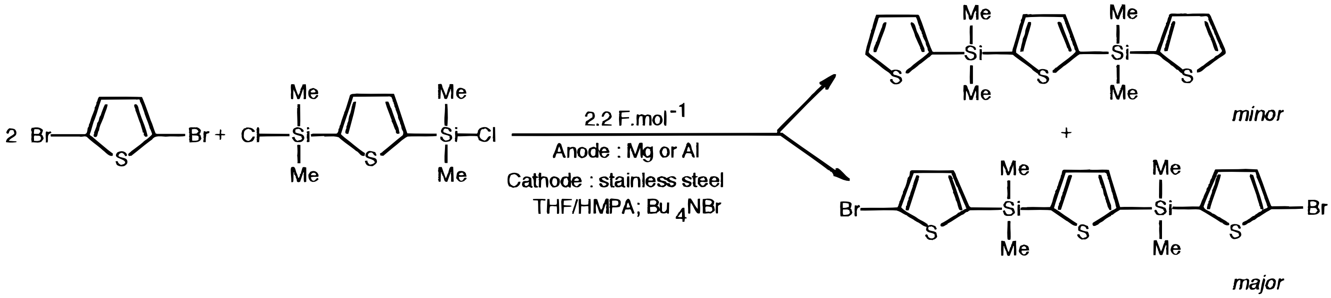

**Table 5. Selectivity of the Br−Th−SiMe$_2$−Th−SiMe$_2$−Th−Br Electrosynthesis Related to the Nature of the Anode**

| | | yield (%) of Br−Th−SiMe$_2$−Th−SiMe$_2$−Th−Br | | yield (%) of Th−SiMe$_2$−Th−SiMe$_2$−Th |
|---|---|---|---|---|
| anode metal | conversion[a] (%) | GC | isolated | GC |
| Al | 100 | 85 | 68 | 15 |
| Mg | 100 | 66 | 51 | 34 |

[a] For 2.2 faradays mol$^{-1}$.

was provided by a Sodilec EDL 36-07 regulated DC power supply. In the dried cell, containing a magnetic spin bar, was added $Bu_4NBr$ (0.5 g, 1.6 mmol) as the supporting electrolyte. The cell then was deaerated twice under vacuum and flushed with dry nitrogen. THF (70 mL), HMPA (10 mL), and a minimum excess of trimethylchlorosilane just sufficient for drying the medium (generally between 1 and 1.5 mL) were introduced through a septum by syringe. The solution was degassed by bubbling nitrogen for 10 min. The resulting HCl (from the reaction of $Me_3SiCl$ with traces of water) was removed by pre-electrolyzing the solution ($i$ = 0.1 A). The $(Me_3Si)_2O$ formed is electrochemically inert. When evolution of $H_2$ had ceased, the substrate (20 mmol) and dichlorosilane (10 mmol) for the synthesis of $(Th-)_nSi_{n-1}R_1R_2$ or 400 mmol for the synthesis of $[(ClR_1R_2Si)_2(-Th-)]$ were introduced by means of a syringe. The electrolysis ($i$ = 0.1 A) then was performed until the theoretically required charge had been passed. The reaction was monitored by gas chromatography. After precipitation of the major part of the salts from the resulting solution by addition of anhydrous pentane (2 × 50 mL), and subsequent filtration and evaporation of the solvents, the residue was extracted with $Et_2O$ (2 × 50 mL), and, when the product was $(Th-)_nSi_{n-1}R_1R_2$ (but not with $[(ClR_1R_2Si)_2(-Th-)]$, washed with an HCl solution (0.1 M, 2 × 20 mL). After drying over $MgSO_4$, the ether was evaporated. The crude product was analyzed by GC and distilled or purified with a silica gel column. For $[(ClR_1R_2Si)_2(-Th-)]$ synthesis, after ether extraction, the excess of dichlorosilane was evaporated and the residue then was distilled under vacuum.

**2,5-Bis(chlorodimethylsilyl)thiophene:** CAS Registry No. (RN) 4414-24-8; yield 85% (4.6 g, also prepared up to 10 g); bp 112−114 °C/14 mmHg; $^1$H NMR ($CDCl_3$) $\delta$ 0.33 (s, 12H, $SiMe_2$), 7.12 (s, 2H, thienyl); $^{13}$C NMR ($CDCl_3$) $\delta$ 1.4 (P), 136.3 (T), 142.8 (Q); $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.87; MS $m/z$ (relative intensity) 272 (1), 270 (6), 268 (8, $M^+$), 257 (10), 255 (27), 253 (30), 149 (42), 93 (32), 71 (100), 42 (90); IR (neat KBr) 2963, 1488, 1405, 1258, 1204, 1088, 1066, 1016, 991, 960, 837, 807, 793, 753, 744, 681, 643, 511, 468, 434 cm$^{-1}$. The spectral data agree with those reported in the literature.[1]

**2,5-Bis(chloromethylphenylsilyl)thiophene:** RN 132440-06-3; yield 77% (6.1 g); bp 207−210 °C/1 mmHg; $^1$H NMR ($CDCl_3$) $\delta$ 0.94 (s, 6H, SiMe), 7.2 (m, 8H, $CH_{arom}$), 7.87 (m, 4H, $CH_{arom}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 2.1 (P), 128.4 (T), 134.1 (T), 130.8 (T), 133.8 (T), 137.4 (T), 142.5 (Q); IR (neat KBr) 3072, 3053, 2962, 1959, 1887, 1819, 1768, 1591, 1429, 1404, 1326, 1261, 1216, 1123, 1086, 998, 791, 734, 696, 546, 502, 466 cm$^{-1}$. The spectral data agree with those reported in the literature.[1]

**2,5-Bis[(2-thienyl)dimethylsilyl]thiophene ($T_3Si_2$):** RN 141696-65-3; yield 80% (5.9 g, also prepared up to 8 g); bp 207−210 °C/1 mmHg; $^1$H NMR ($CDCl_3$) $\delta$ 0.85 (s, 12H, $SiMe_2$), 7.35 (dd, 2H, $C_4H$, $^3J_{H4H5}$ = 3.5, $^3J_{H4H3}$ = 4.6), 7.53 (dd, 2H, $C_5H$, $^3J_{H4H5}$ = 3.5, $^3J_{H5H3}$ = 0.5), 7.59 (s, 2H, $C_7H$); 7.76 (dd, 2H, $C_3H$, $^3J_{H3H5}$ = 0.5, $^3J_{H4H3}$ = 4.6); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.3 (P), 128.5 (T), 131.6 (T), 135.7 (T), 136.8 (T), 137.4 (T), 144.3 (Q); $^{29}$Si NMR ($CDCl_3$) $\delta$ −15.43; MS $m/z$ (relative intensity) 366 (5), 365 (8), 364 (30, M), 351 (24), 350 (25), 349 (100, M − $CH_3$), 209 (8), 167 (18), 151 (8), 141 (34), 83 (7), 75 (6); IR (neat NaCl) 2954, 1487, 1408, 1268, 1251, 1214, 1201, 1084, 1010, 850, 829, 807, 798, 792, 749, 707, 673 cm$^{-1}$. The spectral data agree with those reported in the literature.[21]

**2,5-Bis[(2-thienyl)methylphenylsilyl]thiophene:** yield 67% (6.6 g); this compound was directly purified by silica gel column chromatography, with pentane/ethyl acetate (98/2 v/v) as the eluent; $^1$H NMR ($CDCl_3$) $\delta$ 0.75 (s, 6H, SiMe), 7.24 (m, 2H, thienyl), 7.36 (s, 2H, thienyl), 7.45 (m, 8H, $CH_{arom}$), 7.68 (m, 6H, $CH_{arom}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.7 (P), 127.9 (T), 128.0 (T), 128.2 (T), 130 (T), 131.7 (T), 133.5 (T), 136.0 (T), 137.8 (Q), 141.0 (Q), 147.2 (Q); MS $m/z$ (relative intensity) 488 (30, M), 473 (100, M − $CH_3$); IR (neat NaCl) 3070, 3023, 2089, 2928, 2871, 1958, 1886, 1820, 1591, 1497, 1428, 1405, 1325, 1259, 1215, 1118, 1088, 1061, 998, 852, 787, 734, 699 cm$^{-1}$. Anal. Calcd for $C_{16}H_{24}S_3Si_2$: C, 52.74; H, 6.59; S, 26.37. Found: C, 52.56; H, 6.51; S, 26.31.

**2,5-Bis[(5-bromo-2-thienyl)dimethylsilyl]thiophene:** yield 68% (7.1 g); this compound was directly purified by silica gel column chromatography, with pentane as the eluent; $^1$H NMR ($CDCl_3$) $\delta$ 0.38 (s, 12H, $SiMe_2$), 6.96 (q, 4H, thienyl), 7.18 (s, 2H, thienyl); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.0 (P), 117.6 (Q), 130.9 (T), 135.5 (T), 136.3 (T), 139.9 (Q), 143.0 (Q); MS $m/z$ (relative intensity) 524 (21), 522 (32), (18, M), 512 (15), 511 (20), 610 (63), 507 (100), 505 (43, M − $CH_3$), 449 (19), 259 (16), 258 (20), 222 (16), 221 (64), 219 (58), 215 (18), 213 (19), 199 (80), 149 (17), 147 (28), 141 (34), 137 (22), 83 (20), 73 (87), 59 (17), 44 (39), 40 (35); IR (neat NaCl) 2950, 1495, 1408, 1392, 1325, 1287, 1266, 1250, 1205, 1200, 1081, 1068, 996, 950, 850, 830, 800, 772, 707, 673 cm$^{-1}$. Anal. Calcd for $C_{16}H_{18}Br_2S_3Si_2$: C, 36.78; H, 3.85; S, 18.27. Found: C, 36.87; H, 3.74; S, 18.41.

**Bis{5-[(2′-thienyl)dimethylsilyl]-2-thienylene}-dimethylsilane ($T_4Si_3$):** RN 51384-58-8; yield 78% (7.9 g, also prepared up to 15 g); bp 248−250 °C/0.1 mmHg; $^1$H NMR ($CDCl_3$) $\delta$ 0.82 (s, 8H, $SiMe_2$), 7.32 (dd, 2H, $C_4H$, $^3J_{H4H5}$ = 3.5, $^3J_{H4H3}$ = 4.6), 7.50 (dd, 2H, $C_5H$, $^3J_{H4H5}$ = 3.5, $^4J_{H5H3}$ = 0.5), 7.56 (s, 4H, $C_{7-8}H$), 7.74 (dd, 2H, $C_3H$, $^3J_{H3H4}$ = 4.6, $^4J_{H5H3}$ = 0.5); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.4 (P), 128.5 (T), 131.5 (T), 135.7 (T), 136.9 (T), 137.0 (T), 137.4 (Q), 144.2 (Q), 144.3 (Q); $^{29}$Si NMR ($CDCl_3$) $\delta$ −15.42; MS $m/z$ (relative intensity) 506 (13), 505 (15), 504 (35, M), 492 (6), 491 (26), 490 (36), 489 (100, M − $CH_3$), 349 (6), 238 (7), 237 (33), 151 (7), 141 (68), 83 (13), 44

(7), 32 (20); IR (neat NaCl) 3057, 2958, 1483, 1408, 1325, 1268, 1251, 1214, 1202, 1083, 1010, 829, 799, 772, 707, 672 cm$^{-1}$. The spectral data agree with those reported in the literature.[21]

**Bis{5-[(2-thienyl)methylphenylsilyl]-2-thienylene}-methylphenylsilane:** yield 87% (12 g); this compound was directly purified by silica gel column chromatography, with pentane/ethyl acetate (98/2 v/v) as the eluent; $^1$H NMR (CDCl$_3$) $\delta$ 1.23 (s, 9H, SiMe), 7.43 (m, 2H, thienyl), 7.63 (s, 11H, CH$_{arom}$), 7.76 (s, 4H, thienyl), 7.85 (d, 2H, $^3J = 4.4$, thienyl), 7.92 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ $-0.5$ (P), 128.3 (T), 128.7 (T), 130.5 (T), 132.5 (T), 135.0 (T), 135.9 (T), 137.4 (Q), 138.5 (Q), 143.0 (Q); $^{29}$Si NMR (CDCl$_3$) $\delta$ $-19.96/-19.65$; IR (neat NaCl) 3070, 3025, 2961, 1955, 1884, 1819, 1589, 1486, 1429, 1405, 1269, 1254, 1215, 1203, 1111, 1085, 1010, 786, 726, 698, 686 cm$^{-1}$. Anal. Calcd for $C_{37}H_{34}S_4Si_3$: C, 62.3; H, 5.05; S, 18.55. Found: C, 62.30; H, 4.96; S, 18.55.

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