Selective Electrochemical Mono- and Polysilylation of Halothiophenes

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Electrochemical trimethylsilylation of mono- and polyhalothiophenes (hal = Cl, Br) has been examined. In order to predict the selectivity of the reaction in accordance with the halogen position on the ring, the reduction potentials of the commercially available halothiophenes have been determined by cyclic voltammetry. Thus, as expected, the bromo derivatives are more easily reduced than the chloro analogs, and the 2-position is more reactive than the 3-position. We obtained 2- and 3-(trimethylsilyl)thiophenes, 2-(trimethylsilyl)-3 (or 5)-halothiophenes, 2-(trimethylsilyl)-3,4,5-trihalothiophenes, 2,5-bis(trimethylsilyl)thiophene, 2,5-bis(trimethylsilyl)-3,4-dihalothiophenes, and 2,3,5-tris(trimethylsilyl)-4-halothiophenes with an excellent selectivity. In contrast, the silylation of 2-(trimethylsilyl)-3-halo- and 2,3,5-tris(trimethylsilyl)-4-halothiophenes occurred with ring opening and afforded 1,1,4,4-tetrakis(trimethylsilyl)-1,2-butadiene and hexakis(trimethylsilyl)-2-butyne, respectively. A coherent interpretation of the synthetic results is proposed in correlation with the measured potential values.

Introduction

Silylthiophenes are useful synthons for a regiospecific access to functionalized thiophenes. The presence of a trimethylsilyl group at the second position of the ring acts as a protective group toward metalation[1] and radical reactions,[2] which are specifically restricted to the third position. Recently, silylthiophenes have received attention as the starting materials for the preparation of polythiophenes.[3] These polymers, resulting from the electropolymerization of silylated thiophene monomers, have greater conductivity properties than those from the nonsilylated monomers. The high conductivity encountered results from a highly structured polymer, exclusively linked through the 2- and 5-positions of the thiophene ring. The regularity of the formation of polythiophenes during the electropolymerization is due to the directing effects of the silyl group, which increases the selectivity of carbon−carbon bond formation (Scheme 1).

Although many chemical methods to accede to thienylsilanes or halothienylsilane thiophenes are known,[3−13] they are not general and often require an extreme temperature[4,5,8−12] (Table 1). Having to work at low temperatures is not a drawback in the research laboratory, but it would be a major disadvantage on the industrial scale. Commonly, bromothiophenes as the starting materials are necessary (except for the cases of silylation of tetrachlorothiophene[10,13] and disilylation of thiophene[11]). Thus, the organomagnesium route gives only mono- and disilylation, generally with medium yields.[3d-5,7] Organolithium compounds (BuLi or tBuLi) are utilized to carry out mono-, di-, and trisilylations, in good yields, but at low temperatures (*e.g.* −80 to −70 °C).[4,5,8−12] Lithium diisopropylamine (LDA), a stronger base, reacts well with C−H bonds, but when two bromine atoms are present, it reacts on both C−H and C−Br bonds promoting isomerizations called "base-catalyzed halogen dance reactions".[9]

Scheme 1. Electropolymerization of α-Silylated Thiophene Monomers

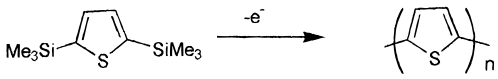

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Table 1. Preparation of (Trimethylsilyl)thiophenes and Halo(trimethylsilyl)thiophenes by Chemical Routes

substrate	silylation method[a]	product	yield (%)	refs
2-bromothiophene	a	2-(trimethylsilyl)thiophene	*b*	4b
	d	2-(trimethylsilyl)thiophene	78	5
	h	2-(trimethylsilyl)-5-bromothiophene	85	6
3-bromothiophene	e	3-(trimethylsilyl)thiophene	50	4b
	f	3-(trimethylsilyl)thiophene	75	4g
	g	3-(trimethylsilyl)thiophene	80	5
2,3-dibromothiophene	a	2-(trimethylsilyl)-3-bromothiophene	87	9
	h	2-(trimethylsilyl)-3,5-dibromothiophene	75	9
2,4-dibromothiophene	d	2,4-bis(trimethylsilyl)thiophene	60	3d
2,5-dibromothiophene	e	2-(trimethylsilyl)-5-bromothiophene	50	7
	h	2-(trimethylsilyl)-3,5-dibromothiophene	*b*	9
	a	2,5-bis(trimethylsilyl)thiophene	89	12
	f	2,5-bis(trimethylsilyl)thiophene	65	3d
3,4-dibromothiophene	c	3-(trimethylsilyl)-4-bromothiophene	*b*	8
2-bromo-3-chlorothiophene	e	2-(trimethylsilyl)-3-chlorothiophene	70	3a
thiophene	a	2,5-bis(trimethylsilyl)thiophene	40	4b, 11
3-(trimethylsilyl)thiophene	a	2,4-bis(trimethylsilyl)thiophene	96	8
2-(trimethylsilyl)-3-bromothiophene	b	2,3-bis(trimethylsilyl)thiophene	35	8
3-(trimethylsilyl)-4-bromothiophene	c	3,4-bis(trimethylsilyl)thiophene	74	8
2,4-bis(trimethylsilyl)thiophene	a	2,3,5-tris(trimethylsilyl)thiophene	65	8
tetrachlorothiophene	c	2-(trimethylsilyl)-3,4,5-trichlorothiophene	53	10
	a	2,5-bis(trimethylsilyl)-3,4-dichlorothiophene	80	13

[a] Methods: (a) (1) BuLi/Et_2O/−80 °C, (2) Me_3SiCl; (b) (1) BuLi/Et_2O, (2) Me_3SiI; (c) (1) tBuLi/THF/−70 °C, (2) Me_3SiCl; (d) Me_3SiCl/Mg/HMPA; (e) (1) Mg/Et_2O, (2) Me_3SiCl; (f) Mg/THF/Me_3SiCl; (g) Me_3SiCl/Na/dioxane; (h) (1) LDA/THF/−80 °C, (2) Me_3SiCl. [b] Not given.

Considering the experience of our laboratory in the electrochemical trimethylsilylation of arenes and chloroarenes,[14,15] it appeared to us that the inexpensive, industrially feasible electrochemical technique involving a sacrificial anode (a massive metallic bar such as aluminum), an undivided cell, and a constant current density[16] could offer a competitive method, with much better selectivity. In this paper we report our results in electrochemical mono- and polysilylation of halothiophenes.

Results and Discussion

1. Cyclic Voltammetry of Chloro- and Bromothiophenes. As previously established by us from another aromatic series,[15] a 200 mV potential difference between the peak potentials of two carbon−halogen bonds accounts for chemoselectivities of the electrochemical silylation reaction and provides sites for attack in the molecules. However, up to now, no reduction potential determination of halogenothiophenes has been reported. Consequently, parallel to the development of methods for the synthesis of thienyl- and halothienylsilanes, reduction potentials of chloro- and bromothiophenes were determined. For this, the reduction peak potentials of commercially available chloro- and bromothiophenes, at a platinum electrode, were investigated under protonation conditions in THF−0.1 M Bu_4NBF_4 (Tables 2 and 3) instead of preparative electrosilylation conditions in a more complex medium containing Me_3SiCl, THF, HMPA, and NBu_4Br. This resulted in a bad resolution of the voltammograms. Nevertheless, as previously observed, the values of the potentials measured under protonation conditions, for a given halogenated compound, can constitute a good estimate for silylation conditions.[15]

Table 2. Peak Potentials[a] of Chlorothiophenes and Silylated Intermediates

chlorothiophenes	E_p[b] (V)	$E_{pn} - E_{pn-1}$ (mV)
2-chlorothiophene	−2.81	
3-chlorothiophene	−2.87	
2,3-dichlorothiophene	−2.60	
	−2.88	280
2,5-dichlorothiophene	−2.51	
	−2.81	300
tetrachlorothiophene	−2.06	
	−2.35	290
	−2.62	270
	−2.88	260
2-(trimethylsilyl)-5-chlorothiophene	−2.82	
2,5-bis(trimethylsilyl)-3,4-dichlorothiophene	−2.61	
	−2.86	250
tris(trimethylsilyl)-3-chlorothiophene	−2.86	

[a] Cyclic voltammetry in THF−0.1 M Bu_4NBF_4, at a 1-mm-diameter Pt disk; sweep rate, 0.1 V/s; voltage scan (V), 0/1.0/−2.93/0. [b] $E_p \pm 0.01$ V, vs SCE.

Table 3. Peak Potentials[a] of Bromothiophenes

bromothiophenes	E_p[b] (V)	$E_{pn} - E_{pn-1}$ (mV)
2-bromothiophene	−2.58	
3-bromothiophene	−2.76	
2,3-dibromothiophene	−1.57	
	−2.76	1190
2,5-dibromothiophene	−1.67	
	−2.58	910
tetrabromothiophene	*c*	

[a] Cyclic voltammetry in THF−0.1 M Bu_4NBF_4, at a 1-mm-diameter Pt disk; sweep rate, 0.1 V/s; voltage scan (V), 0/1.0/−2.93/0. [b] $E_p \pm 0.01$ V, vs SCE. [c] Not sufficiently soluble.

Tables 2 and 3 highlight the following results: (1) As expected, bromo derivatives are more easily reduced than the chloro analogs (smaller cathodic potentials); nonetheless, the higher cathodic potential found (−2.88 V for 3-chlorothiophene) is still smaller than the electroactivity limit of the electrolytic solution. Therefore, easy

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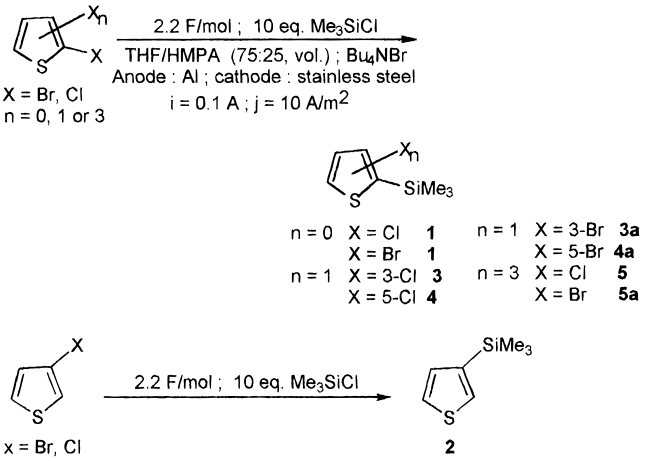
Scheme 2. Electrochemical Monosilylation of Chloro- and Bromothiophenes



reductive silylation reactions for chlorothiophenes can be envisaged. (2) Polyhalothiophenes undergo stepwise reduction; the more halogen atoms present in a molecule, the easier is the reduction of the first carbon−halogen bond. The observed potential differences between two consecutive peaks ($E_{pn} - E_{pn-1}$) are in the order of 280 mV for X = Cl and 1000 mV for X = Br. Thus, excellent chemoselectivity for successive silylations of polyhalogenothiophenes can be anticipated. (3) The potentials measured for the 2-halothiophene are 60 mV less cathodic than those for the corresponding 3-halothiophene for X = Cl, and 180 mV less for X = Br, showing a marked activation of the 2-position that can be attributed to the −I effect of sulfur; moreover, when 2,3-dichloro- and tetrachlorothiophenes were considered, the second potential of 2,3-dichlorothiophene matched well with that of 3-chlorothiophene showing that the 2-carbon−chlorine bond (2-Cl) is reduced first. Similarly the fourth reduction potential of tetrachlorothiophene matches with that of 3-chlorothiophene, showing that the 2- and 5-Cl are first reduced. As a verification, it can also be observed that the second potential of 2,5-dichlorothiophenes matches with that of 2-chlorothiophenes; consequently, good regioselectivity in the 2- or 5-positions for the monosilylation of 2,3-dihalogenothiophenes and in the 2,5-positions for the disilylation of trihalogeno- and tetrahalogenothiophenes can be expected. (4) Replacing one or more hydrogen(s) in an intermediate product by one or more trimethylsilyl group(s) has a very weak effect on the peak potentials. The preparative electrochemical monosilylation of several chloro- and bromothiophenes was examined next, in order to verify the previsions made from the measured potentials.

2. Monosilylation of Chloro- and Bromothiophenes. First, when 2.2 F/mol of substrate was passed under the conditions mentioned in Scheme 2, monosilylation occurred almost quantitatively and was always selective, as expected. It was chemoselective, as the chlorine or bromine atom was only replaced by the trimethylsilyl group without side reactions, such as ring opening or protonation of the relatively basic intermediate anion. Actually, protonation could be avoided using a large excess of Me_3SiCl (10 equiv). This was verified for monohalogenated thiophenes in the 2-position as well as in the 3-position (Scheme 2) and for symmetrical 2,5-dihalogenothiophenes (Scheme 2, Tables 3 and 4). Moreover, for 2,3-dihalogeno and tetrahalogeno derivatives, the expected regioselectivity for the 2-position was observed (Scheme 2, Tables 3 and 4).

These results show that the electrochemical synthesis can be applied to the chlorinated derivatives even though, to date, only silylation of tetrachlorothiophene has been reported.[10,13]

3. Polysilylation of Polychloro- and Polybromothiophenes. As shown in Table 5, when 4.4 F/mol of substrate was passed under the same conditions, 2,5-disilylation was chemoselective for 2,5-dihalothiophenes and regioselective for tetrahalothiophenes. However, 2,3-disilylation was not observed in the case of 2,3-dichlorothiophene and 2,3-dibromothiophene, the latter leading to ring opening of thiophene, as described later. Under the same conditions, trisilylation of tetrahalogenothiophenes gave high yields of trisilylated compounds (Scheme 3) without any ring opening.

For these tetrahalo compounds, chemoselectivity is preserved beyond disilylation due to the first two steps being regioselective for the 2,5-positions allowing formation of only one silylated isomer in the final step (Scheme 4). A survey of the literature indicated that no equivalent reaction has been described by a chemical route.

On the other hand, when 8.8 F/mol was passed, tetrasilylation was not observed, but a ring-opening occurred. In order to supplement our study, it became necessary to investigate this phenomenon. In the case of 2,3-dichloro- and 2,3-dibromothiophenes, when 8.8 F/mol was passed, the allene, 1,1,4,4-tetrakis(trimethylsilyl)-1,2-butadiene (**9**), was exclusively formed. This constitutes a much better convenient and efficient synthesis of **9** than the palladium-catalyzed double silylation of 1,4-bis(trimethylsilyl)butadiyne with disilanes forming 1,1,4,4-tetrakis(trimethylsilyl)butatriene followed by Pd/C-catalyzed hydrogenation leading to a mixture of **9** and 1,1,4,4-tetrakis(trimethylsilyl)-but-2-ene.[20,21] In the case of tetrachloro- and tetrabromothiophenes, when 13.2 F/mol was passed, the final product was the hexakis(trimethylsilyl)-2-butyne (**10**) (90% yield). This hexasilylated acetylenic compound was also obtained by Gilman[17] from chemical persilylation of tetrachlorothiophene, in 13% yield.

In both cases, the electroreduction of the last carbon−halogen bond led to a ring opening and desulfurization took place giving $(Me_3Si)_2S$ (Scheme 5).

Thus, when two or more halogen atoms are present, they are activated and, therefore, reduced and silylated before the ring is affected; but when there is only one halogen in the 3-position, two types of reactions can occur: (i) If there is an H atom in the 2-position, the C−X bond is still reduced and silylated. (ii) If a silicon group is present in the 2-position, a preferential ring-opening occurs, producing **9** or **10**, respectively, until 6 electrons have been consumed, as shown by a kinetic study monitored by GC.

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Table 4. Electrochemical Monosilylation of Chloro- and Bromothiophenes

mono- and polyhalothiophenes	monosilylated product name	no.	GC yield (isolated) (%)	chem yield (%)[a]
2-chlorothiophene	2-(trimethylsilyl)thiophene	1	91 (73)	95
2-bromothiophene		1	97 (64)	97
3-chlorothiophene	3-(trimethylsilyl)thiophene	2	70 (65)	72
3-bromothiophene		2	75 (56)	76
2,3-dichlorothiophene	2-(trimethylsilyl)-3-chlorothiophene	3	95 (80)	99
2,3-dibromothiophene	2-(trimethylsilyl)-3-bromothiophene	3a	93 (88)	95
2,5-dichlorothiophene	2-(trimethylsilyl)-5-chlorothiophene	4	93 (88)	95
2,5-dibromothiophene	2-(trimethylsilyl)-5-bromothiophene	4a	91 (73)	95
tetrachlorothiophene	2-(trimethylsilyl)-3,4,5-trichlorothiophene	5	90 (83)	98
tetrabromothiophene	2-(trimethylsilyl)-3,4,5-tribromothiophene	5a	92 (85)	97

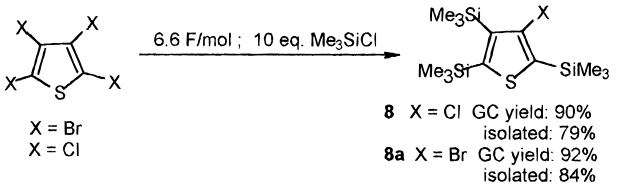
[a] Yield relative to the amount of reacted substrate (chemoselectivity).

Table 5. Electrochemical Disilylation of Polychloro- and Polybromothiophenes

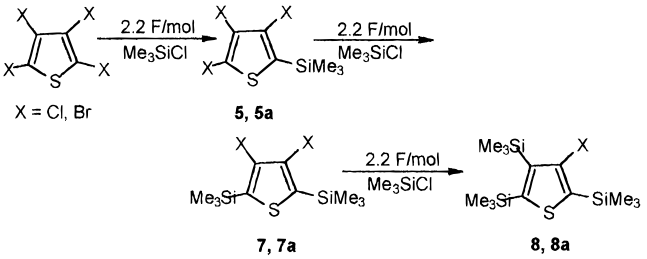
polychlorothiophene	disilylated product name	no.	GC yield (isolated) (%)	chem yield (%)[a]
2,5-dichlorothiophene	2,5-bis(trimethylsilyl)thiophene	6	96 (76)	98
2,5-dibromothiophene		6	98 (81)	100
2,3-dichlorothiophene	*b*			
2,3-dibromothiophene	*b*			
tetrachlorothiophene	2,5-bis(trimethylsilyl)-3,4-dichlorothiophene	7	96 (78)	98
tetrabromothiophene	2,5-bis(trimethylsilyl)-3,4-dibromothiophene	7a	97 (75)	98

[a] Yield relative to the amount of reacted substrate (chemoselectivity). [b] Ring-opening product.

Scheme 3. Electrochemical Trisilylation of Tetrachloro- and Tetrabromothiophenes



Scheme 4. Regio- and Chemoselectivities of the Electrochemical Silylation Steps



Conclusion

The present study opens the possibility of regioselective construction of the various mono- and polysilylated thiophenes. The knowledge of the reduction potentials of the various carbon−halogen bonds allows a good prevision of the possible reactions. However, when a trimethylsilyl group is present in the 2-position, a univocal ring opening occurs preferentially to the reduction of the carbon−halogen bond in the 3-position. The high-yield formation of the polysilylated allene (**9**) and acetylene (**10**) is noteworthy. Convenient methods for the synthesis of various acetylene- and allene-containing molecules could be envisaged on the basis of these results.

Experimental Section

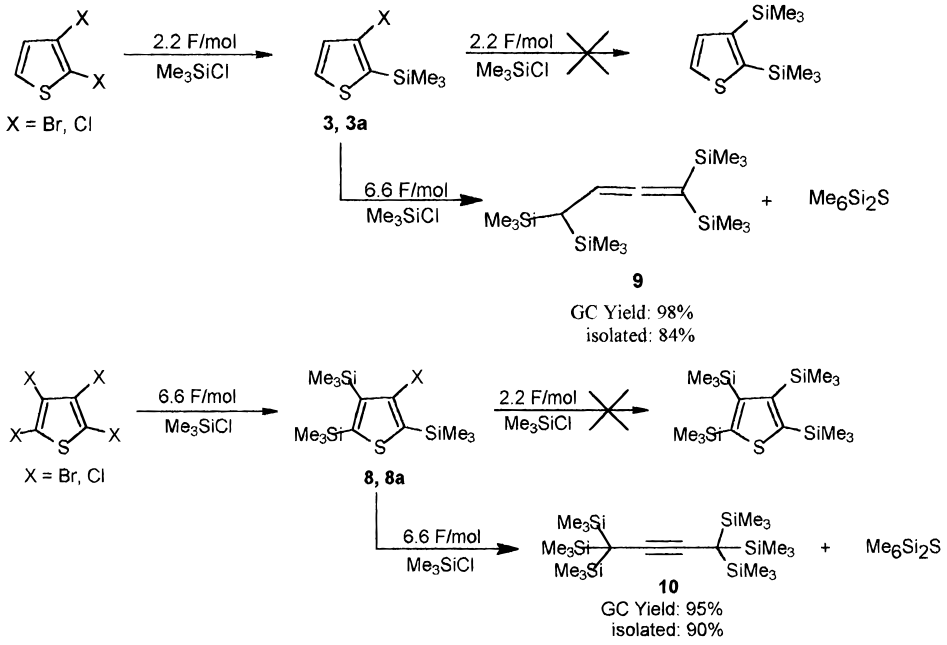
Materials. Halothiophenes (Lancaster) and Bu_4NBr (Janssen) were used without purification. THF (SDS) and HMPA (Aldrich) were dried by distillation over sodium benzophenone ketyl and CaH_2, respectively. Me_3SiCl, a generous gift from Rhône-Poulenc Co., was distilled over Mg powder just before use.

General Methods. ^1H NMR spectra were recorded in $CDCl_3$ at 250 MHz using residual $CHCl_3$ ($\delta = 7.27$ ppm) as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR spectra were obtained at 62.86 MHz using $CDCl_3$ ($\delta = 77.7$ ppm) as the internal standard. Electron impact mass spectra were performed at an ionization voltage of 70 eV. IR spectra were recorded in liquid films. Analysis of the products and monitoring of the reaction were performed by gas chromatography (GC). Elementary microanalyses were performed by the "Service Central de Microanalyse" of the CNRS (France).

Voltammetry. Cyclic Voltammetry was carried out under argon in 20 mL THF solutions containing the substrate (2 mM) and Bu_4NBF_4 (0.1 M), using a 1-mm diameter Pt 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. Ferrocene (10^{-3} M) was used as an internal standard ($E_{pa} = 0.63$ V, $E_{pc} = 0.56$ V). The solution resistance was compensated for with a positive feedback device. The potentiostat used (Sirius) was previously described.[15] The sweep rate was 0.1 V/s, and the voltage scan (V) was 0/1.0/−2.93/0.

General Procedure for Electrolysis. Electrolysis was performed in an undivided cell (100 mL) described elsewhere[15] fitted with a sacrificial cylindrical aluminum bar (1 cm diameter) as the anode and a concentric stainless steel grid (1.0 ± 0.2 dm^2) as the cathode. A constant current (0.1 A, density 0.1 ± 0.05 A·dm^{-2}) was provided by a Sodilec EDL 36-0.7 regulated DC power supply. To the dried cell, containing a magnetic spin bar, was added 0.5 g (1.6 mmol) of Bu_4NBr as the supporting electrolyte. The cell was then twice pumped out and flushed with argon. THF (40 mL), HMPA (7 mL), and Me_3SiCl, in large excess (25−30 mL), were introduced through a septum by means of a syringe. The solution was degassed by bubbling argon for 10 min. Any HCl that was produced by the reaction of Me_3SiCl with residual traces of water was removed by pre-electrolysis of the solution at room temperature under a controlled current of 0.1 A. The halothiophene (30 mmol) was then introduced. The electrolysis (0.1 A) was performed until the desired charge had been passed (18 h for 2.2 F/mol). The progress of the reaction was monitored by GC. After elimination of most of the salts from

Scheme 5. Ring Opening for 2-(Trimethylsilyl)-3-halo-Substituted Thiophenes



the resulting solution by adding anhydrous pentane and filtering and evaporating the Me_3SiCl and the solvents, the residue was extracted with Et_2O (3 × 50 mL) and washed with water (2 × 10 mL). The crude product was then purified by fractional distillation.

2-(Trimethylsilyl)thiophene (1): bp 149−151 °C; IR (neat) 3076, 2963, 2905, 1506, 1406, 1259, 1215, 1084, 993, 840, 763, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 9H), 7.25−7.67 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 0.0, 128.0, 130.3, 133.9, 139.9; MS, *m*/*z* (relative intensity) 156 (M^+, 14), 142 (12), 141 (100), 73 (6), 45 (9), 43 (16). The obtained data agree with those reported in the literature.[4f,9,18,19]

3-(Trimethylsilyl)thiophene (2): bp 168 °C; IR (neat) 2962, 2910, 1390, 1257, 1103, 904, 843, 759, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 7.03−7.36 (m, 3H); ^{13}C NMR ($CDCl_3$) δ -0.5, 125.3 (C5), 131.4 (C2), 131.4 (C4), 141.1 (C3); MS, *m*/*z* (relative intensity) 156 (M^+, 17), 142 (16), 141 (100), 126 (15), 73 (15), 43 (4). The obtained data are in agreement with those reported in the literature.[3e,9]

2-(Trimethylsilyl)-3-chlorothiophene (3): IR (neat) 2965, 2906, 1488, 1420, 1397, 1337, 1258, 1148, 1088, 998, 847, 762, 713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.43 (s, 9H), 7.06 (d, J = 5 Hz, 1H), 7.48 (d, J = 5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.7, 129.8, 130.1, 131.9, 132.0; MS, *m*/*z* (relative intensity) 192 (12), 190 (M^+, 26), 177 (28), 175 (100), 97 (48), 73 (16), 45 (5), 44 (30), 43 (19). Anal. Calcd for $C_7H_{11}SSiCl$: C, 44.08; H, 5.81; Cl, 18.58. Found: C, 43.87; H, 5.72; Cl, 18.69. The spectral data are in agreement with those reported in the literature.[3a]

2-(Trimethylsilyl)-3-bromothiophene (3a): IR (neat) 2940, 1480, 1380, 1360, 1250, 1130, 1080, 990, 840, 770, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.41 (s, 9H), 7.09 (d, J = 5 Hz, 1H), 7.43 (d, J = 5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.7, 117.3, 127.1, 130.7, 132.6; MS, *m*/*z* (relative intensity) 236 (23), 234 (M^+, 22), 221 (72), 219 (66), 139 (14), 109 (9), 97 (100), 73 (8), 65 (12), 45 (13), 43 (18). Anal. Calcd for $C_7H_{11}SSiBr$: C, 35.75; H, 4.71; Br, 33.97. Found: C, 35.88; H, 4.67; Br, 34.06.

2-(Trimethylsilyl)-5-chlorothiophene (4): bp 157−9 °C; IR (neat) 3065, 2964, 2903, 1508, 1414, 1290, 1259, 1207, 1071, 968, 844, 794, 764, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9H), 6.98 (d, J = 5 Hz, 1H), 7.04 (d, J = 5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.2, 127.4, 133.4, 134.6, 140.3; MS, *m*/*z* (relative intensity) 192 (8), 190 (M^+, 21), 177 (47), 175 (100), 95 (11), 93 (30), 73 (6), 45 (1), 44 (16), 43 (7). Anal. Calcd for $C_7H_{11}SSiCl$: C, 44.08; H, 5.81; Cl, 18.58. Found: C, 43.95; H, 5.84; Cl, 18.46.

2-(Trimethylsilyl)-5-bromothiophene (4a): bp 218−9 °C; IR (neat) 2960, 1400, 1250, 1200, 1065, 1000, 980, 950, 840, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9H), 7.01(d, J = 3.5 Hz, 1H), et 7,10 (d, J = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.0, 116.9, 131.3, 134.5, 143.4; MS, *m*/*z* (relative intensity) 236 (23), 234 (M^+, 24), 221 (100), 219 (97), 139 (34), 137 (31), 109 (9), 73 (15), 45 (14), 43 (27). The spectral data are in agreement with those reported in the literature.[6,7]

2-(Trimethylsilyl)trichlorothiophene (5): IR (neat) 2958, 2900, 1521, 1498, 1407, 1308, 1280, 1253, 1064, 1032, 992, 908, 844, 792, 759, 742, 700, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9H); ^{13}C NMR ($CDCl_3$) δ −1.2, 125.0, 128.5, 129.5, 130.8; ^{29}Si NMR ($CDCl_3$) δ −3.7; MS, *m*/*z* (relative intensity) 264 (2), 262 (12), 260 (30), 258 (M^+, 30), 249 (6), 247 (38), 245 (100), 243 (99), 119 (2), 117 (14), 115 (53), 113 (51), 95 (66), 93 (37), 73 (23), 45 (21), 43 (24). Anal. Calcd for $C_7H_9SSiCl_3$: C, 32.38; H, 3.49; Cl, 40.96. Found: C, 32.84; H, 3.55; Cl, 40.33. The ^1H NMR spectrum agrees with ref 10.

2-(Trimethylsilyl)tribromothiophene (5a): IR (neat) 2950, 2895, 2870, 2800, 1485, 1465, 1390, 1290, 1270, 1250, 1205, 1095, 1010, 980, 970, 840, 785, 755, 720, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9H); ^{13}C NMR ($CDCl_3$) δ −1.1, 115.1, 119.4, 119.6, 137.5; MS, *m*/*z* (relative intensity) 396 (10), 394 (29), 392 (27), 390 (M^+, 9), 381 (38), 379 (97), 377 (100), 375 (31), 300 (10), 298 (17), 296 (8), 257 (4), 255 (7), 253 (3), 205 (10), 203 (19), 201 (10), 161 (14), 159 (12), 139 (13), 137 (13), 95 (38), 73 (31), 45 (19), 43 (22). Anal. Calcd for $C_7H_9SSiBr_3$: C, 21.39; H, 2.31; Br, 60.99. Found: C, 21.27; H, 2.36; Br, 60.65.

2,5-Bis(trimethylsilyl)thiophene (6): IR (neat) 3056, 2962, 2904, 1459, 1263, 1203, 1007, 844, 763, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 18H), 7.54 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.3, 135.2, 145.9; MS, *m*/*z* (relative intensity) 228 (M^+, 15), 215 (13), 214 (20), 213 (100), 99 (24), 73 (48), 45 (20), 43 (19). The spectral data are in agreement with those reported in the literature.[3e]

2,5-Bis(trimethylsilyl)dichlorothiophene (7): bp 81 °C/1 mmHg; IR (neat) 2964, 2906, 1464, 1392, 1310, 1275, 1259, 1034, 846, 762, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s, 18H); ^{13}C NMR ($CDCl_3$) δ −1.2; 131.9; 137.8; MS, *m*/*z* (relative intensity) 300 (1), 298 (6), 296 (M^+, 8), 285 (5), 283 (22), 281 (29), 95 (12), 93 (34), 73 (100), 58 (2), 45 (29), 44 (12), 43 (16). The IR, ^1H NMR, and MS data are in agreement with those reported in the literature.[13]

2,5-Bis(trimethylsilyl)dibromothiophene (7a): IR (neat) 2940, 2880, 1440, 1400, 1380, 1240, 1000, 970, 830, 770, 740, 705, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 18H); ^{13}C NMR ($CDCl_3$) δ −1.1, 122.3, 140.7; MS, *m*/*z* (relative intensity) 388

(17), 386 (27), 384 (M^+, 14), 373 (31), 371 (51), 369 (26), 271 (51), 219 (13), 217 (9), 178 (16), 153 (25), 139 (23), 137 (23), 73 (100), 45 (12), 43 (5). Anal. Calcd for $C_{10}H_8SSi_2Br_2$: C, 31.09; H, 4.70; Br, 41.37. Found: C, 31.27; H, 4.76; Br, 41.12.

Tris(trimethylsilyl)-4-chlorothiophene (8): IR (neat) 2961, 2906, 1437, 1257, 1211, 1027, 973, 847, 766, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.47 (s, 9H), 0.50 (s, 9H), 0.51 (s, 9H); ^{13}C NMR ($CDCl_3$) δ -0.3, 1.9, 2.0, 136.2, 139.9, 147.0, 152.9; MS, *m/z* (relative intensity) 336 (4), 334 (M^+, 8), 321 (4), 319 (8), 212 (13), 211 (45), 121 (13), 95 (4), 93 (11), 73 (100), 45 (22), 43 (6). Anal. Calcd for $C_{13}H_{27}SSi_3Cl$: C, 46.59; H, 8.12; Cl, 10.58. Found: C, 46.48; H, 8.09; Cl, 10.65.

Tris(trimethylsilyl)-4-bromothiophene (8a): IR (neat) 2960, 2907, 1429, 1312, 1301, 1256, 1195, 1010, 968, 846, 766, 699 cm^{-1}; MS, *m/z* (relative intensity) 380 (9), 378 (M^+, 7), 365 (12), 363 (11), 277 (5), 275 (4), 211 (40), 121 (10), 73 (100), 45 (19), 44 (14), 43 (7). Anal. Calcd for $C_{13}H_{27}SSi_3Br$: C, 41.13; H, 7.17; Br, 21.05. Found: C, 41.36; H, 7.12; Br, 21.21.

1,1,4,4-Tetrakis(trimethylsilyl)-1,2-butadiene (9): IR (neat) 2960, 2905, 1891, 1348, 1254, 1162, 1032, 884, 848, 769, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 18H), 0.06 (s, 18H), 0.62 (d, J = 10.8 Hz, 1H), 4.24 (d, J = 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.2, 0.4, 15.3, 73.8, 143.0, 212.0; MS, *m/z* (relative intensity) 342 (M^+, 30), 269 (15), 239 (19), 182 (15), 181 (79), 157 (11), 155 (12), 73 (100), 45 (12), 43 (4). The ^1H NMR spectrum is in agreement with ref 21.

Hexakis(trimethylsilyl)-2-butyne (10): mp 276−7 °C; IR (neat) 2980, 2963, 2908, 1267, 1255, 1110, 858, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 54H); ^{13}C NMR ($CDCl_3$) δ 2.3, 6.0, 79.3; MS, *m/z* (relative intensity) 486 (M^+, 2), 471 (2), 229 (21), 228 (74), 155 (23), 73 (100), 45 (10), 43 (1). The melting point and ^1H NMR spectrum are in agreement with ref 17a.

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