Synthesis of Novel Alkyl- and Aryl Sulfides and Thiols as Precursors for Self-Assembled Monolayers on Gold

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Received 13 April 2004

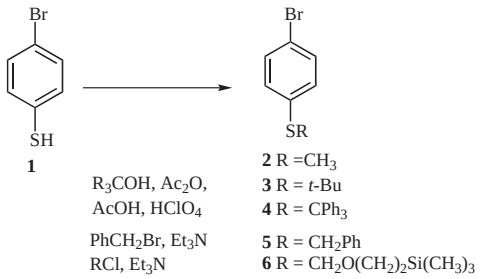
Abstract: A series of 4-alkyl-1-bromosulfanylbenzenes having *S*-methyl **2**, *S*-*t*-butyl **3**, *S*-trityl **4**, *S*-benzyl **5**, and *S*-silylethoxymethyl **6** substituents were prepared and evaluated for their ability to form a monolayer consisting of an *S*-aryl adsorbate on Au (111) surface. The monolayer was formed via the selective hydrolytic removal of an alkyl group protecting the sulfur functionality upon adsorbtion onto the gold surface. Thiols having variable carbon chain length and a peripheral thiophene moiety **9**, **10**, **17**, **18** and **23**–**26** were also prepared.

Key words: 4-alkyl-1-bromosulfanyl benzenes, 4-thienylthiophenols, thienylalkanethiols, self-assembled monolayers on gold

Conjugated organic materials have the potential to serve as molecular components for electronic devices.[1–4] The broad applicability of conjugated thiol compounds in molecular electronics is based on their unique ability to form well-ordered monolayers via a self-assembly process onto gold or other metal surfaces.[5–8] Unfortunately, it has recently been shown that this property is not general for all aromatic thiol compounds.[8] Characterization of the self-assembled monolayer molecular arrays which do serve as active layers in electronic devices is an important step in the search to understand and control molecular-scale electronics.

The substituents most suitable for adsorption onto a metal surface include thiols (RSH),[9] disulfides (RSSR), thioacetyls ($RSCOCH_3$),[10] and symmetric sulfides (RSR).[11,12] Thiols and disulfides are found to adsorb dissociatively on gold and form densely packed layers.[13] Sulfides are found to adsorb either molecularly or dissociatively into a thiolate on gold. However, sulfides are simpler to synthesize as no deprotection of the thiol is needed. An appropriate protecting group for the sulfur-bearing moiety must be robust enough to remain intact throughout the various organometallic coupling reactions and must also be selectively removable with formation of the monolayer. Hence, we imagined the use of an asymmetric sulfide that would promote the selective dissociation upon adsorption. Herein, we report an efficient synthesis of, and subsequent formation of, the monolayers from various alkyl aryl sulfides **3**–**6**, derived from 4-bromothiophenol (**1**). We also discuss the spectroscopic studies that were undertaken to address issues that arose concerning the composition and regularity of the monolayers, which resulted from the electrodeposition of these sulfides.

In addition to synthesizing sulfides using mercurial thiolates complexes in combination with symmetrical disulfides[14] as well as those involving the coupling of a thiol with a chloride or bromide catalyzed by Pd[15,16] or Ni,[16] we developed an efficient method for the protection of the thiol function of **1** as an *S*-*t*-butyl or *S*-trityl group from their corresponding alcohols. Typically, formation of the former involved the use of either isobutylene gas in an acidic medium or the corresponding *tert*-butyl halide in the presence of an organic base or a Lewis acid.[17] Both methods provided variable yields of **3**. The use of *tert*-butyl alcohol, with acetic anhydride as a dehydrating agent, led to good, reproducible yields of **3** (Scheme 1). This method is general for the preparation of *S*-*t*-butyl aromatic sulfides such as 4-nitro-*tert*-butylsulfanylbenzene[18] and 2-*tert*-butylsulfanylnaphthalene.[18a] This method was used to efficiently prepare *S*-trityl derivative **4** from triphenylcarbinol. In all cases the yields were equal to, or higher than, those obtained from the substitution using the corresponding *t*-butyl or trityl chloride.



Scheme 1

However, the use of a secondary or benzylic alcohol in the same reaction with acetic anhydride leads to the formation of the corresponding acetate. This occurs because these alcohols are more nucleophilic and, thus are able to react directly with acetic anhydride. Therefore, for this study, the *S*-benzyl **5** and *S*-SEM **6** protecting groups were introduced via a substitution reaction with benzyl bromide and SEM chloride, respectively.

SYNTHESIS 2004, No. 14, pp 2283–2288
Advanced online publication: 23.08.2004
DOI: 10.1055/s-2004-831163; Art ID: M02504SS

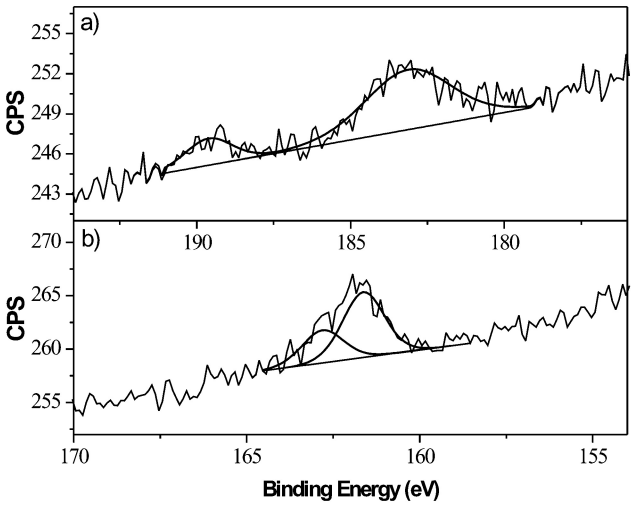
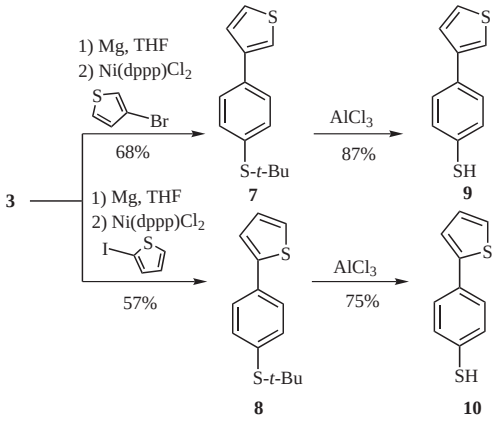


Figure 1 XPS spectra of **3** adsorbed on a gold substrate (a) Br 3d orbital region, (b) S 2p orbital region

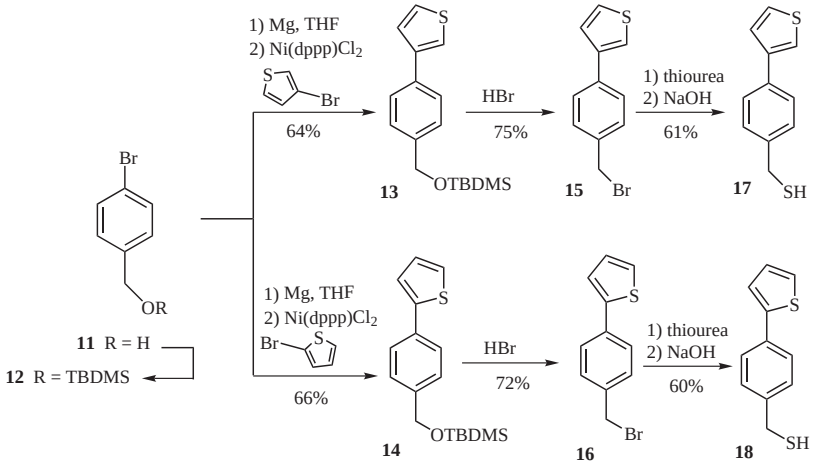


Scheme 2

Five *p*-bromothiophenolate derivatives were tested as precursors for monolayer self-assembly onto a gold substrate. Adsorption was achieved by immersing a previously cleaned gold film[19] in a dilute solution (1 mM) of the compound to be tested in 0.1 M ethanolic KOH. The film was left in the solution for three days, after which the surface composition was analyzed using X-Ray photoelectron spectroscopy (XPS). The 2p level of the sulfur and 3p level of the bromine, shown in Figure 1, were used to quantify the amount of *p*-bromothiophenolate adsorbed onto the surface. Quantification of the amount of adsorption for those R groups of the compounds shown in Scheme 1 relative to *p*-bromothiophenolate moiety, following dissociative adsorption, was calculated from their XPS intensities. For example, an atomic ratio for I (Br)/I (S) of **1** indicates that only the *p*-bromothiophenolate (100%) is adsorbed onto the gold whereas a ratio of 0 means that this compound is not present at the surface (0%). Hence, this allowed us to evalutate and compare the relative efficiencies of the leaving groups (*t*-butyl, benzyl, triphenylmethyl, methyl, hydrogen and SEM). We found that a complete (100%) monolayer of thiophenolate was formed by the *p*-bromothiophenol. An almost complete (60%) monolayer of thiophenolate was also formed by the *t*-butyl derivative **3** (Figure 1), although some *tert*-butylthiolate was also adsorbed. A partial monolayer was formed by the SEM derivative (10%) and no *p*-bromothiophenolate (0%) was adsorbed in the case of the triphenylmethyl, benzyl and methyl derivatives. Preliminary results showed higher coverage for the electro-deposition of most of the thiophenolate derivatives. These results will be reported elsewhere.

We have also used a *t*-butyl protecting group for the synthesis of an aromatic thiol. The syntheses of **9** and **10**, as shown in Scheme 2, were successful.

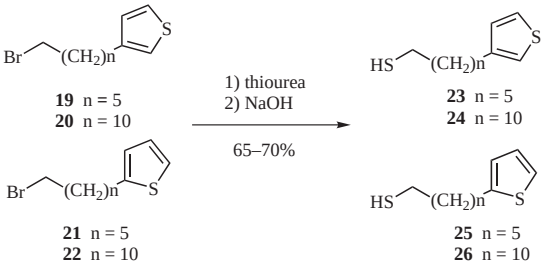
We were able to couple 1-bromo-4-*tert*-butylsulfanylbenzene (**3**), with 3-bromothiophene and 2-iodothiophene, assisted by nickel,[20] via a reaction of the in situ prepared 4-*tert*-butylthiophenylmagnesium bromide. This process led to sulfides **7** and **8,** respectively. Then the S-*t*-butyl moiety was selectively removed by treatment with aluminum trichloride followed by hydrolysis,[18b] providing 4-(thien-3-yl)- (**9**)[21] and 4-(thien-2-yl)benzenethiol (**10**), respectively. Derivative **9** was found to form a polymerizable monolayer on gold surface.[21]



Scheme 3

We were particularly interested in those thiols and other sulfides having more flexibility at the anchoring position as this would enhance their utility to material science. To this end, benzyl sulfides **17** and **18** were prepared as shown in Scheme 3. Here, the known TBDMS ether **13**[22] was directly transformed into the corresponding benzyl bromide **15** with HBr in acetic acid while subsequent substitution by thiourea, followed by hydrolysis, gave the desired thiol **17**. The isomeric 2-thienyl derivative **18** was obtained from the same coupling reaction, this time with 2-bromothiophene.

Thiols with C-5 and C-10 chains and having a peripheral 2- or a 3-thienyl heterocycle were prepared using an adapted literature procedure, which provided intermediates bromides **19**–**22**.[23–26] Substitution of the bromide function by a thiol was accomplished as described above providing thienylalkane thiols **23**–**26** (Scheme 4).



Scheme 4

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 FTIR instrument. 1H NMR spectra were recorded using a Varian 300 MHz or on a Bruker AMX 2-500 MHz spectrometer. ^{13}C NMR spectra were recorded at 75 or 125 MHz respectively. Chemical shifts are reported in parts per million (δ). ^{1}H Chemical shifts in $CDCl_3$ were referenced to the residual $CHCl_3$ (7.27 ppm); ^{13}C chemical shifts were referenced to the solvent ($CDCl_3$, 77.03 ppm). Mass spectra were obtained using a GC-MS (GCD plus gas chromatography-electron ionization detector, HPG 1800A GCD system) equipped with a 5% cross-linked Ph Me silicone HP 19091 J-433 column. Elemental analyses were carried out at the chemistry department of the Université de Montréal, Montréal, P.Q., Canada, on a Fisons Instrument SPA, model EA1108. TLC was performed on silica gel F254 (E. Merck precoated glass plates and visualized by UV irradiation or subjecting the plates to a 5% H_2SO_4–EtOH solution followed by heating. Separations were carried out on silica gel (7749 Merck) using circular chromatography (chromatotron®, model 7924, Harrison Research). 2-, 3-Bromothiophene, 4-bromobenzenethiol (**1**), 4-bromothioanisole (**2**), (2-trimethylsilyl)ethoxymethyl chloride, triphenylmethanol, and 4-methoxyphenol were obtained from Aldrich Chemical Co. and were used without further purification. 2-*tert*-Butylsulfanylnaphthalene was obtained from AsInEx Express Gold Collection. 4-Nitro-*tert*-butylsulfanylbenzene,[18b] compounds **12** and **13**[22]as wells as the bromides **19**, **20**[23] and **21**, **22**[26] were synthesized as previously reported. Solvents were dried by distillation from drying agents as follows: THF and Et_2O (sodium/benzophenone), CH_2Cl_2 (P_2O_5), Et_3N and pyridine (CaH_2). Petroleum ether used had bp 35–60 °C. All reactions involving organometallic reagents and liquid salt syntheses were carried out under dry N_2. After reaction work-up, solutions were dried using Na_2SO_4 and solvents were subsequently removed by rotary evaporation.

1-Bromo-4-*tert*-butylsulfanylbenzene (3)

To a 100 mL flask containing glacial AcOH (46 mL) was added 60% $HClO_4$ (10 mL), followed by Ac_2O (8 mL). The stirred solution was cooled in an ice bath and 4-bromothiophenol (**1**; 6.03 g, 31.89 mmol) was added with stirring. This was followed by the addition of *t*-BuOH (6 mL, 63.79 mmol). The TLC (eluent: petroleum ether) indicated the reaction was complete after 3 h, nonetheless the reaction mixture was stirred overnight. However, H_2O (60 mL) and Et_2O (60 mL) were added to the mixture and the phases separated. The aqueous phase was extracted with Et_2O (2 × 60 mL) and the combined organic phases were washed with 20% aq NaOH until alkaline and then were washed with H_2O until neutral. The organic layers were dried (Na_2SO_4) and were rota-evaporated, leaving a yellow oil. The crude oil was vacuum distilled under vacuum to give a colorless liquid; bp 140–145 °C/10 mm Hg; yield: 6.4 g (82%).

IR (film): 3072, 2961, 1468, 1384, 1363, 730 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.28 [(s, 9 H, $(CH_3)_3C$], 7.46 (dd, 2 H, *J* = 6.3, 2.1 Hz, H-2,6), 7.39 (dd, 2 H, *J* = 6.6, 2.1 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 30.84 [$(CH_3)_3C$], 46.09 [$(CH_3)_3C$], 123.42 (C-1), 131.61 (C-2,6), 131.80 (C-4), 138.88 (C-3,5).

GC/MS: *m*/*z* (%) = 190 (95), 189 (12), 188 (93), 109 (42), 108 (35), 57 (100), 41 (34) 29 (18).

1-Bromo-4-triphenylmethylsulfanylbenzene (4)

Compound **4** was prepared from triphenylmethanol (390 mg, 1.5 mmol) and **1** (189 mg, 1 mmol) using the procedure for the synthesis of **3**. Purification by chromatography (dissolved in a minimal amount of CH_2Cl_2 and eluted with petroleum ether) gave **4** (88% 378 mg) as a white solid; yield: 378 mg (88%); mp 190 °C.

IR (film): 3049, 747, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.13 (dd, 2 H, *J* = 6.8, 1.5 Hz, H-2,6), 6.80 (dd, 2 H, *J* = 6.8, 1.5 Hz, H-3,5), 7.42–7.38 (m, 6 H, H-2′,6′), 7.26–7.20 (m, 9 H, H-3′,5′).

^{13}C NMR ($CDCl_3$): δ = 70.91 [$(Ph)_3C$], 122.16 (C-1), 126.82 (3 C, C-4′), 127.75 (6 C, C-2′,6′), 129.90 (C-3,5), 131.16 (6 C, C-3′,5′), 133.62 (C-4), 135.79 (C-2,6), 144.17 (3 C, C-1′).

Anal Calcd for $C_{25}H_{19}BrS$: C, 69.61; H, 4.44; S, 7.43. Found: C, 69.66; H, 4.18; S, 7.05.

[2-(4-Bromophenylsulfanylmethoxy)ethyl]trimethylsilane (6)

4-Bromothiophenol (**1**; 486 mg, 2.57 mmol) and (2-trimethylsilyl)ethoxymethyl chloride (442.7 mg, 2.66 mmol) were dissolved in anhyd Et_2O (30 mL). Et_3N (470 μL, 3.37 mmol) was then added, and the solution was stirred at r.t. After 2 h, the solvent was evaporated, H_2O (25 mL) and CH_2Cl_2 (25 mL) were added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined extracts were washed with H_2O (3 × 10 mL), dried (Na_2SO_4) and rota-evaporated leaving a colorless viscous liquid. Purification by chromatography (eluent: petroleum ether) gave **6** as a colorless oil; yield: 697 mg (88%).

IR (film): 2951, 2891, 1248, 834, 811 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 0.95 (t, 2 H, *J* = 8.2 Hz, CH_2Si), 3.69 (t, 2 H, *J* = 8.2 Hz, CH_2O), 4.98 (s, 2 H, SCH_2O), 7.41 (dd, 2 H, *J* = 6.6, 2.2 Hz, H-2,6), 7.34 (dd, 2 H, *J* = 6.6, 2.2 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = –1.14 [$Si(CH_3)_3$], 17.69 (CH_2Si), 66.05 (CH_2O), 75.29 (SCH_2O), 120.43 (C-1), 131.38 (C-2,6), 131.89 (C-3,6), 135.61 (C-4).

GC/MS: *m*/*z* (%) = 103 (15), 122 (11), 73 (100).

Anal Calcd for $C_{12}H_{19}BrOSSi$: C, 45.14; H, 5.95. Found: C, 45.23; H, 6.16.

3-(4-*tert*-Butylsulfanylphenyl)thiophene (7)
1-Bromo-4-*tert*-butylsulfanylbenzene (**3**; 400 mg, 1.63 mmol) and anhyd THF (2 mL) were added, under N_2, to a vessel containing Mg turnings (47.6 mg, 1.96 mmol) and THF (10 mL) and the mixture was refluxed for 6 h. The Grignard solution was subsequently transferred dropwise (over 30 min) to a second flask containing Ni(dppp)Cl_2 (26.5 mg, 3 mol%) and 3-bromothiophene (320.2 mg, 1.79 mmol), which was then refluxed for 12 h. After this, the reaction mixture was hydrolyzed by adding it to 10% aq HCl (10 mL) combined with ice water (10 mL), which was followed by the addition of Et_2O (10 mL). The phases were separated and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with H_2O until neutral and dried (Na_2SO_4). The solvent was removed under reduced pressure leaving a yellow residue which was purified by chromatography (dissolved in a minimal amount of CH_2Cl_2 and eluted with petroleum ether to give **7** as a white solid; yield: 275 mg (68%); mp 96 °C.

IR (KBr): 3098, 2962, 1670, 1457, 1363, 1168, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 [s, 9 H, $(CH_3)_3C$], 7.41 (d, 2 H, *J* = 2.2 Hz, H-4′,5′), 7.50 (t, 1 H, *J* = 2.2 Hz, H-2′), 7.57 (br s, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 30.94 [$(CH_3)_3C$], 46.05 [$(CH_3)_3C$], 120.77 (C-2′), 126.17 (C-4′), 126.34 (C-3,5), 126.42 (C-5′), 131.39 (C-1), 136.10 (C-4), 137.86 (C-2,6), 141.52 (C-3′).

GC/MS: *m*/*z* (%) = 248 (M^+, 12), 193 (14), 192 (100), 191 (22), 147 (22), 57 (14).

2-(4-*tert*-Butylsulfanylphenyl)thiophene (8)
Compound **8** was prepared from 2-iodothiophene (1.18 g, 5.6 mmol) and **3** (1.25g, 5.1 mmol) using the procedure for the synthesis of **7**. Purification by chromatography (dissolved in a minimum amount of CH_2Cl_2 and eluted with petroleum ether) gave **8** (58% 0.74 g) as a yellow solid; mp 105 °C.

IR (KBr): 3010, 2961, 1592, 1399, 1363, 1166, 696 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 [s, 9 H, $C(CH_3)_3$], 7.10 (dd, 1 H, *J* = 5.0, 3.7 Hz, H-4′), 7.32 (dd, 1 H, *J* = 5.0, 0.8 Hz, H-5′), 7.36 (dd, 1 H, *J* = 3.7, 0.8 Hz, H-3′), 7.54 (d, 2 H, *J* = 8.5 Hz, H-2,6), 7.59 (d, 2 H, *J* = 8.5 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 30.94 [$(CH_3)_3C$], 46.19 [$(CH_3)_3C$], 123.54 (C-3′), 125.30 (C-5′), 125.73 (C-3,5), 128.13 (C-4′), 131.77 (C-1), 134.70 (C-4), 137.89 (C-2,6), 143.56 (C-2′).

GC/MS: *m*/*z* = 248 (M^+, 12), 193 (14), 192 (100), 191 (22), 147 (18), 57 (14).

4-(Thien-3-yl)benzenethiol (9)
To a 25 mL ice-cooled flask containing a solution of $AlCl_3$ (88.7 mg, 0.67 mmol) in toluene (10 mL), was added dropwise a solution of 3-(4-*tert*-butylsulfanylphenyl)thiophene (**7**; 275 mg, 1.11 mmol) in toluene (3 mL). The resultant red reaction mixture was stirred at r.t. for 30 min and then poured into ice (20 g). The aqueous phase was extracted with toluene (2 × 20 mL) and the combined organic phases were treated with 20% aq NaOH (3 × 15 mL) until alkaline and then with 12 N HCl until a white precipitate had formed. This solid was filtered and washed with cold H_2O to afford **9** as a white solid; yield: 185 mg (87%), which was then recrystallized from Et_2O; mp 138 °C.

IR (KBr): 3357, 3100, 2554, 1106, 760 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.49 (br s, 1 H, SH), 7.31 (dd, 2 H, *J* = 6.8, 1.8 Hz, H-2,6), 7.36 (dd, 1 H, *J* = 4.9, 1.4 Hz, H-5′), 7.39 (dd, 1 H, *J* = 4.9, 2.7 Hz, H-4′), 7.42 (dd, 1 H, *J* = 2.7, 1.4 Hz, H-2′), 7.48 (dd, 2 H, *J* = 6.8, 1.8 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 120.09 (C-2′), 126.06 (C-4′), 126.34 (C-5′), 127.04 (C-3,5), 129.34 (C-4), 129.86 (C-2,6), 133.45 (C-1), 141.50 (C-3′).

GC/MS: *m*/*z* (%) = 193 (M^+ + 1, 16), 192 (M^+, 100), 191 (47), 160 (14), 147 (42), 115 (20).

Anal Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19. Found: C, 62.24; H, 4.05.

4-(Thien-2-yl)benzenethiol (10)
Compound **10** was prepared from **8** (250 mg, 1.01 mmol) following the same protocol as for **9** which gave **10** as a yellow solid; yield: 125 mg (65%). This solid was then recrystallized from Et_2O; mp 110 °C.

IR (KBr): 3451, 3066, 2551, 1104, 811, 691 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.49 (br s, 1 H, SH), 7.07 (dd, 1 H, *J* = 5.0, 3.7 Hz, H-4′), 7.28 (s, 2 H, H-3′,5′), 7.29 (d, 2 H, *J* = 8.5 Hz, H-2,6), 7.49 (d, 2 H, *J* = 8.5 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 122.95 (C-3′), 124.71 (C-5′), 126.50 (C-3,5), 128.04 (C-4′), 129.82 (C-2,6 + C-1), 132.02 (C-4), 143.65 (C-2′).

GC/MS: *m*/*z* (%) = 192 (M^+, 100), 191 (47), 160 (14), 147 (42) 115 (20), 96 (15).

Anal Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19. Found: C, 62.82; H, 3.64.

[(4-Bromobenzyl)oxy](*tert*-butyldimethyl)silane (12)
Compound **12** was prepared, as previously described, in 93% yield.[22]

IR (film): 2950, 2928, 2856, 1593, 1486, 1257, 1087, 1011, 838, 776 cm^{-1}.

***tert*-Butyldimethyl[4-thien-3-ylbenzyl)oxy]silane (13)**
Compound **13** was prepared according to the literature[22] and the ^1H NMR, ^{13}C NMR and GC/MS were found to be identical to those reported; mp 64 °C.

IR (KBr): 3097, 2950, 2929, 2856, 1467, 1380, 1365, 1253, 1096, 1056, 839, 787 cm^{-1}.

***tert*-Butyldimethyl[(4-thien-2-ylbenzyl)oxy]silane (14)**
This compound was obtained as a white solid from the procedure established for **13**, this time using **12** (3.5 g, 11.6 mmol); yield: 2.1 g (66%); mp 50 °C.

IR (KBr): 3075, 2954, 2927, 2854, 1500, 1460, 1376, 1256, 1094, 852, 830, 776 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.13 (s, 6 H, 2 CH_3), 0.97 [s, 9 H, $C(CH_3)_3$], 4.77 (s, 2 H, CH_2), 7.09 (dd, 2 H, *J* = 5.0, 3.6 Hz, H-4′), 7.28 (dd, 1 H, *J* = 5.0, 1.2 Hz, H-5′), 7.31 (dd, 1 H, *J* = 3.6, 1.2 Hz, H-3′), 7.35 (dt, 2 H, *J* = 8.4, 1.9 Hz, H-3,5), 7.60 (dt, 2 H, *J* = 8.4, 1.9 Hz, H-2,6).

^{13}C NMR ($CDCl_3$): δ = –5.23 [$Si(CH_3)_2$], 18.42 [$SiC(CH_3)_3$], 25.95 [$SiC(CH_3)_3$], 64.68 (OCH_2), 122.83 (C-3′), 124.50 (C-5′), 125.80 (C-3,5), 126.65 (C-2,6), 127.94 (C-4′), 133.05 (C-4), 140.79 (C-1), 144.41 (C-2′).

GC/MS: *m*/*z* (%) = 304 (M^+), 247 (17), 175 (5), 174 (13), 173 (100).

3-[4-(Bromomethyl)phenyl]thiophene (15)
A solution of *tert*-butyldimethyl[4-thien-3-ylbenzyl)oxy]silane (**13**; 700 mg, 2.30 mmol) in glacial AcOH (5 mL) was added to a chilled vessel containing glacial AcOH (10 mL) and HBr (10 mL, 33% in AcOH). The resulting mixture was stirred at 5 °C for 1 h, diluted with H_2O (50 mL) and extracted with Et_2O (3 × 25 mL). The combined organic phases were washed to neutrality with 5% aq NaOH

(4 × 50 mL), dried (Na_2SO_4) and rota-evaporated. The residue was chromatographed with petroleum ether to yield **15** as white solid; yield: 438 mg (75%); mp 106 °C.

IR (KBr): 3100, 2932, 1655, 1565, 1426, 1383, 1203, 1122, 836, 817, 728 cm^{-1}.

The ^1H NMR, ^{13}C NMR and GC/MS were identical to those reported.[22]

2-[4-(Bromomethyl)phenyl]thiophene (16)

The use of **14** (500 mg, 1.64 mmol) in the procedure for **15** followed by purification of the crude product on silica gel gave **16** as a white solid; yield: 300 mg (72%); mp 62 °C.

IR (KBr): 3067, 2962, 1607, 1501, 1426, 1227, 1208, 816, 702 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.53 (s, 2 H, CH_2), 7.10 (dd, 1 H, *J* = 5.2, 3.6 Hz, H-4′), 7.31 (dd, 1 H, *J* = 5.2, 1.1 Hz, H-5′), 7.33 (dd, 1 H, *J* = 3.6, 1.1 Hz, H-3′), 7.41 (d, 2 H, *J* = 8.1 Hz, H-3,5), 7.60 (d, 2 H, *J* = 8.1 Hz, H-2,6).

^{13}C NMR ($CDCl_3$): δ = 33.28 (CH_2Br), 123.49 (C-3′), 125.21 (C-5′), 126.22 (C-3,5), 128.09 (C-4′), 129.61 (C-2,6), 134.54 (C-1), 136.84 (C-4), 143.60 (C-2′).

GC/MS: *m*/*z* (%) = 254 ($^{81}BrM^+$, 3) 252 ($^{79}BrM^+$, 3), 174 (24), 173 (100), 128 (9), 87 (10).

(4-Thien-3-ylphenyl)methanethiol (17)

A mixture of 3-[4-(bromomethyl)phenyl]thiophene (**15**; 583 mg, 2.30 mmol) and thiourea (351 mg, 4.60 mmol) in abs EtOH (20 mL) was refluxed with stirring overnight and then poured into 10% aq NaOH (15 mL). The resultant mixture was refluxed with stirring for 4 h, cooled to r.t., neutralized with 10% HCl (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with H_2O (3 × 10 mL), dried (Na_2SO_4) and rota-evaporated leaving a colorless viscous liquid. Purification by chromatography (eluant: petroleum ether) afforded **17** as a pungent white solid; yield: 289 mg (61%); mp 94 °C.

IR (KBr): 3036, 2938, 2255, 1670, 1554, 1123, 855, 779 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.79 (t, 1 H, *J* = 7.6 Hz, SH), 3.78 (d, 2 H, *J* = 7.6 Hz, CH_2S), 7.37 (dt, 2 H, *J* = 8.5, 2.0 Hz, H-2,6), 7.39 (d, 1 H, *J* = 1.7 Hz, H-4′), 7.4 (d, 1 H, *J* = 2.7 Hz, H-5′), 7.45 (dd, 1 H, *J* = 2.6, 1.8 Hz, H-2′), 7.34 (dt, 2 H, *J* = 8.2, 2.0 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 28.69 (CH_2SH), 120.24 (C-2′), 126.24 (C-4′), 126.26 (C-5′), 126.72 (C-3,5), 128.48 (C-2,6), 134.70 (C-4), 140.00 (C-1), 141.90 (C-3′).

GC/MS: *m*/*z* (%) = 206 (M^+, 15), 174 (35), 173 (M^+ – SH, 100), 171 (10), 128 (13).

Anal Calcd for $C_{11}H_{10}S_2$: C, 64.04; H, 4.89; S, 31.08. Found: C, 63.83; H, 4.40; S, 30.41.

(4-Thien-2-ylphenyl)methanethiol (18)

Compound **18** was obtained using the procedure for **17**, this time with 2-[4-(bromomethyl)phenyl]thiophene (**16**; 1.55 g, 6.13 mmol) and thiourea (933 mg, 12.25 mmol). Product **18** was obtained as a pungent white solid; yield: 750 mg (60%); mp 162 °C.

IR (KBr): 3063, 2919, 2550, 1905, 1659, 1604, 1495, 1423, 1250, 1110, 820 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.79 (t, 1 H, *J* = 7.6 Hz, SH), 3.77 (d, 2 H, *J* = 7.6 Hz, CH_2), 7.09 (dd, 1 H, *J* = 5.0, 3.6 Hz, H-4′), 7.28 (dd, 1 H, *J* = 5.0, 1.1 Hz, H-5′), 7.31 (dd, 1 H, *J* = 3.6, 1.1 Hz, H-3′), 7.34 (dt, 2 H, *J* = 8.5, 2.1 Hz, H-2,6), 7.57 (dt, 2 H, *J* = 8.5, 2.1 Hz, H-3,5).

^{13}C NMR ($CDCl_3$): δ = 28.67 (CH_2SH), 123.07 (C-3′), 124.78 (C-5′), 126.21 (C-3,5), 128.0 (C-4′), 128.55 (C-2,6), 133.25 (C-4), 140.38 (C-1), 143.98 (C-2′).

GC/MS: *m*/*z* (%) = 206 (M^+, 19), 174 (17), 173 (100), 171 (9), 128 (11).

Anal Calcd for $C_{11}H_{10}S_2$: C, 64.04; H, 4.89; S, 31.08. Found: C, 63.86; H, 4.42, S, 30.85.

5-(Thien-3-yl)pentane-1-thiol (23)

This product was obtained using the same procedure as for **17**, this time with 3-(5-bromopentyl)thiophene (**19**; 1.16 g, 4.97 mmol) and thiourea (757 mg, 9.95 mmol) in abs EtOH as a pungent colorless oil; yield: 570 mg (62%).

IR (film): 3358, 3101, 2929, 2854, 2562, 1460, 1080, 834, 775 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.34 (t, *J* = 7.8 Hz, 1 H, SH), 1.39–1.50 (m, 2 H, H-3), 1.65 (quin, *J* = 7.6 Hz, 2 H, H-4 or 2), 1.66 (quin, *J* = 7.4 Hz, 2 H, H-2 or 4), 2.54 (q, *J* = 7.4 Hz, 2 H, H-1), 2.65 (t, *J* = 7.6 Hz, 2 H, H-5), 6.93 (dd, *J* = 5.0, 1.2 Hz, 1 H, H-5′), 6.95 (dd, *J* = 3.1, 1.2 Hz, 1 H, H-2′), 7.25 (dd, *J* = 5.0, 3.1 Hz, 1 H, H-4′).

^{13}C NMR ($CDCl_3$): δ = 24.52 (C-1), 27.96 (C-3), 29.95 (C-5), 30.08 (C-4), 33.81 (C-2), 119.92 (C-2′), 125.18 (C-5′), 128.16 (C-4′), 142.76 (C-3′).

GC/MS: *m*/*z* (%) = 186 (M^+, 32), 153 (11), 98 (55), 97 (100).

Anal Calcd For $C_9H_{14}S_2$: C, 58.01; H, 7.57; S, 34.41. Found: C, 57.93; H, 7.79; S, 34.27.

10-(Thien-3-yl)decane-1-thiol (24)

The final product was obtained by mixing 3-(10-bromodecyl)thiophene (**20**; 1.11 g, 3.66 mmol) with thiourea (557 mg, 7.32 mmol) in abs EtOH, using the procedure described for **17**; yield: 536 mg (57%); pungent colorless oil.

IR (film): 3103, 2922, 2852, 2566, 1465, 1152, 772, 632 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.29–1.38 (m, 12 H, H-3 to H-8), 1.34 (t, *J* = 7.7 Hz, 1 H, SH), 1.63 (quin, *J* = 7.1 Hz, 4 H, H-2,9), 2.53 (q, *J* = 7.3 Hz, 2 H, H-1), 2.63 (t, *J* = 7.6 Hz, 2 H, H-10), 6.93 (dd, *J* = 3.0, 1.1 Hz, 1 H, H-2′), 6.94 (dd, *J* = 5.0, 1.1 Hz, 1 H, H-4′), 7.25 (dd, *J* = 5.0, 3.0 Hz, 1 H, H-5′).

^{13}C NMR ($CDCl_3$): δ = 24.64 (C-1), 28.35 (C-3), 29.04 (C-4), 29.29 (C-8), 29.41 and 29.47 (C-5, C-6, C-7), 30.26 (C-10), 30.53 (C-9), 34.03 (C-2), 119.74 (C-2′), 125.02 (C-5′), 128.26 (C-4′), 143.22 (C-3′).

GC/MS: *m*/*z* (%) = 256 (M^+, 15), 111 (15), 98 (100), 97 (47).

Anal Calcd for $C_{14}H_{24}S_2$: C, 65.57; H, 9.43; S, 25.00. Found: C, 65.39; H, 9.58; S, 24.77.

5-(Thien-2-yl)pentane-1-thiol (25)

Compound **25** was prepared from 2-(5-bromopentyl)thiophene (**21**; 1 g, 4.3 mmol) following the procedure for **17**. It was obtained as a pungent colorless oil; yield: 0.5 g (63%).

IR (film): 3068, 2928, 2853, 2564, 1459, 1439, 1254, 849, 822, 694 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7.8 Hz, 1 H, SH), 1.42–1.53 (m, 2 H, H-3), 1.62–1.76 (m, 4 H, H-2,4), 2.54 (q, *J* = 7.3 Hz, 2 H, H-1), 2.85 (td, *J* = 7.8, 0.6 Hz, 2 H, H-5), 6.79 (dq, 1 H, *J* = 3.4, 1.2 Hz, 1 H, H-3′), 6.93 (dd, 1 H, *J* = 5.1, 3.4 Hz, 1 H, H-4′), 7.12 (dd, 1 H, *J* = 5.1, 1.2 Hz, 1 H, H-5′).

^{13}C NMR ($CDCl_3$): δ = 24.80 (C-1), 27.74 (C-3), 29.72 (C-5), 31.17 (C-4), 33.70 (C-2), 122.84 (C-5′), 124.02 (C-3′), 126.65 (C-4′), 145.29 (C-2′).

GC/MS: *m*/z (%) = 186 (M^+, 16), 123 (16), 111 (12), 98 (18), 97 (100).

Anal Calcd for $C_9H_{14}S_2$: C, 58.01; H, 7.57; S, 34.41. Found: C, 57.76; H, 7.79; S, 34.31.

10-(Thien-2-yl)decane-1-thiol (26)

The synthetic procedure for **17**, this time from 2-(10-bromodecyl)thiophene (**22**; 620 mg, 2.04 mmol) gave **26** as a pungent colorless oil; yield: 350 mg (67%).

IR (film): 2923, 2851, 2359, 1458, 1438, 1236, 849, 818, 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.29–1.55 (m, 13 H, SH, H-3 to H-8), 1.68 (quin, *J* = 7.2 Hz, 4 H, H-2,9), 2.69 (t, *J* = 7.2 Hz, 2 H, H-1), 2.82 (t, *J* = 7.7 Hz, 2 H, H-10), 6.78 (dt, *J* = 3.3, 1.1 Hz, 1 H, H-3′), 6.92 (dd, *J* = 4.8, 3.3 Hz, 1 H, H-4′), 7.11 (dt, *J* = 4.8, 1.1 Hz, 1 H, H-5′).

^{13}C NMR ($CDCl_3$): δ = 28.50 (C-1), 29.09 (C-3), 29.20, 29.31 and 29.45 (4 CH_2, C4 to C-8), 29.90 (C-10), 31.78 (C-9), 39.17 (C-2), 122.70 (C-5′), 123.87 (C-3′), 126.61 (C-4′), 145.83 (C-2′).

GC/MS: *m*/*z* (%) = 256 (M^+, 10), 111 (29), 97 (100).

Anal Calcd for $C_{14}H_{24}S_2$: C, 65.57; H, 9.43; S, 25.00. Found: C, 65.18; H, 9.42; S, 25.06.

Acknowledgment

M.T. and L.B. acknowledge the financial contribution of UQAM for a fellowship. This work was also partially supported by Research Grants from the Natural Sciences and Engineering Research Council of Canada (NSERC). Special thanks to K. Walsh for providing assistance with the preparation of the manuscript.

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