

## Supporting Information for

### ***“Sulfonation of Alkyl Phenyl Ether Self-Assembled Monolayers”***

*Irit Katash, Xianglin Luo and Chaim N. Sukenik\**

Department of Chemistry and Institute of Nanotechnology and Advanced Materials

Bar Ilan University, Ramat Gan 52900, ISRAEL

*Section 1) Syntheses of trichlorosilanes and of the small molecule phenyl ether model compounds*

*Section 2) Representative spectral and kinetic data*

#### **Section 1) Syntheses of trichlorosilanes and of the small molecule phenyl ether model compounds:**

**Materials.** All reagents and solvents were obtained (unless otherwise specified) from the Sigma-Aldrich Chemical Company. 2-Methoxy benzene thiol was obtained from Acros Organics. Ethanol was obtained from BioLab.

Tetrahydrofuran (THF) was dried by distillation under N<sub>2</sub> from Na/ benzophenone. CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were dried by distillation under N<sub>2</sub> from P<sub>2</sub>O<sub>5</sub>. Toluene was dried over Na. Water was deionized and distilled in an all-glass apparatus.

**Equipment and Methods.** NMR spectra were recorded on a Bruker DPX 300 Spectrometer (units  $\delta$ , ppm). In CDCl<sub>3</sub> solvent they are referenced to TMS for <sup>1</sup>H-NMR and to CDCl<sub>3</sub> (77.16 ppm) for <sup>13</sup>C-NMR. In D<sub>2</sub>O solvent, they are referenced to H<sub>2</sub>O (4.79 ppm). Mass spectra were recorded as follows: direct chemical ionization (DCI) was done on an AutoSpec Premier instrument (Waters U.K.) using CH<sub>4</sub> as the reagent gas; electrospray ionization (ESI) was done on a QToF Micro instrument (Waters, U.K.) and FAB<sup>+</sup> was done on a VG AutoSpec instrument (Waters U.K.) using a glycerol matrix. UV spectra were obtained using quartz cuvettes in a Cary Model 100 (Varian) spectrophotometer ( $\lambda_{\text{max}}$  reported in nm and  $\epsilon$  reported in M<sup>-1</sup>·cm<sup>-1</sup>). Distillation conditions are reported as the pot-temperature of the Kugelrohr oven and the measured pressure in the system. Column chromatography used silica gel 60 (230-240 mesh) and was done under a positive pressure

of nitrogen. Ion exchange chromatography was performed on an Isco UA-6 LC system, using a DEAE Sephadex<sup>®</sup> (40-125  $\mu$ ) column.

**10-(Phenoxy)-decyl trichlorosilane (1)** was prepared in three steps:

***$\omega$ -Decenyl mesylate*** was prepared from 9-decen-1-ol (5.93 g, 38 mmol), using conditions identical to those previously reported.<sup>8</sup> The product was obtained as a yellow liquid and used without further purification. Yield: 8.41 g, 94%. **<sup>1</sup>H-NMR:** 1.30-1.42 (m, 10H), 1.69-1.79 (m, 2H), 2.00-2.07 (m 2H), 2.99 (s, 3H), 4.21 (t, J = 6.6 Hz, 2H), 4.90-5.03 (m, 2H), 5.73-5.82 (m, 1H). **<sup>13</sup>C-NMR:** 25.4, 28.84, 28.97 (2C), 29.11, 29.25, 33.75, 37.30, 70.32, 114.24, 139.10. **MS (DCI<sup>+</sup>):** C<sub>11</sub>H<sub>22</sub>O<sub>3</sub>S; 234.36 (M<sup>+</sup>) (calculated), 234.13 (found).

**10-Phenoxy-dec-1-ene** was prepared from  *$\omega$ -decenyl mesylate* (11.25 g, 48 mmol) and phenol (4.51 g, 48 mmol) using conditions identical to those previously reported.<sup>9</sup> Yield: 10.37 g, 93%. **<sup>1</sup>H-NMR:** 1.26-1.47 (m, 10H), 1.72-1.82 (m, 2H), 2.00-2.08 (m, 2H), 3.94 (t, J = 6.6 Hz, 2H), 4.91-5.02 (m, 2H), 5.74-5.87 (m, 1H), 6.87-6.94 (m, 3H), 7.23-7.29 (m, 2H). **<sup>13</sup>C-NMR:** 26.19, 29.05, 29.20, 29.43, 29.49, 29.55, 33.93, 67.98, 114.29, 114.62 (2C), 120.57, 129.52 (2C), 139.31, 159.26. **UV** (hexane or ethanol):  $\lambda_{\text{max}}$  = 220, 271, 279 nm. **MS (DCI<sup>+</sup>):** C<sub>16</sub>H<sub>24</sub>O; 232.18 (M<sup>+</sup>) (calculated), 232.18 (found).

**10-(phenoxy)-decyl trichlorosilane (1).** Into a 20 mL pressure tube containing a magnetic stirring bar was placed *10-phenoxy-dec-1-ene* (1 g, 4 mmol), 5 mL of HSiCl<sub>3</sub>, and 10-20  $\mu$ L of a 4% solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in i-PrOH. All transfers were done under N<sub>2</sub>. The tube was sealed and the mixture was stirred overnight at R.T. The progress of the reaction was followed by monitoring the disappearance of vinyl protons in the <sup>1</sup>H-NMR. After the reaction was complete, the contents of the tube were transferred (under N<sub>2</sub>) to a 25 mL round-bottom flask. Excess HSiCl<sub>3</sub> was distilled off and the product was isolated by Kugelrohr distillation at 145 °C (pot temperature) and 0.08 mm Hg. Yield: 0.97 g, 65%. **<sup>1</sup>H-NMR:** 1.30-1.47 (m, 14H), 1.55-1.60 (m, 2H), 1.72-1.79 (m, 2H), 3.93 (t, J = 6.3 Hz, 2H), 6.86-6.94 (m, 3H), 7.21-7.29 (m, 2H). **<sup>13</sup>C-NMR:** 22.38, 24.43, 26.18, 29.12, 29.41 (2C), 29.47, 29.62, 31.92, 67.94, 114.60 (2C) 120.58, 129.51 (2C), 159.24.

**11-Phenoxy-undecyl trichlorosilane (2)** was obtained as previously reported.<sup>9</sup>

**Sodium 2-methoxy benzene sulfonate (3a).** In a screw-capped vial were placed 2-methoxy benzenethiol (1.03 g, 7 mmol) and H<sub>2</sub>O<sub>2</sub> 30% (20 mL). The reaction was vigorously stirred at room temperature for 3 days. It was transferred to a separatory funnel and washed twice with diethyl ether to remove un-reacted thiol. The aqueous phase was neutralized with 1 M NaOH and the water was removed under vacuum at 65-70 °C to yield *sodium 2-methoxy benzene sulfonate*. Yield: 0.81 g, 55%. <sup>1</sup>H-NMR (D<sub>2</sub>O): 3.92 (s, 3H), 7.07 (td, J = 7.2 and 0.9 Hz, 1H), 7.17 (dd, J = 8.4 and 0.9 Hz, 1H), 7.57 (ddd, J = 8.4, 7.2 and 1.8 Hz, 1H), 7.78 (dd, J = 7.2 and 1.8 Hz, 1H). <sup>13</sup>C-NMR (D<sub>2</sub>O): 55.73, 112.57, 120.29, 128.20, 129.68, 133.72, 156.29. FTIR (KBr): 1661 (m), 1590 (m), 1480 (m), 1278 (s). UV (H<sub>2</sub>O): λ<sub>max</sub>(ε) = 220 (6489), 269 (1673), 278 (2515), 283 (2231). MS (FAB<sup>-</sup>): C<sub>7</sub>H<sub>7</sub>O<sub>4</sub>S<sup>-</sup>; 187.01 (M<sup>-</sup>) (calculated), 187.01 (found).

**Sodium 3-methoxy benzene sulfonate (3b).** NaOH (0.6 g, 15 mmol) was dissolved in water (6 mL) in a screw-capped vial and 3-methoxy benzene sulfonyl chloride (0.72 g, 3 mmol) was added. The mixture was vigorously stirred overnight at room temperature, transferred to a separatory funnel, and washed twice with diethyl ether to remove un-reacted sulfonyl chloride. The aqueous phase was neutralized with 1 M NaOH and the water was removed under vacuum at 65-70 °C. Yield: 0.56 g, 78%. <sup>1</sup>H-NMR (D<sub>2</sub>O): 3.88 (s, 3H), 7.14-7.18 (m, 1H), 7.36-7.51 (m, 3H). <sup>13</sup>C-NMR (D<sub>2</sub>O): 55.67, 110.78, 117.60, 118.08, 130.44, 143.69, 159.11. FTIR (KBr): 1625 (s), 1598 (s), 1487 (s), 1325 (m). UV (H<sub>2</sub>O): λ<sub>max</sub>(ε) = 219 (7361), 269 (1613), 277 (2341), 282 (2105). MS (FAB<sup>-</sup>): C<sub>7</sub>H<sub>7</sub>O<sub>4</sub>S<sup>-</sup>; 187.01 (M<sup>-</sup>) (calculated), 187.01 (found).

**Sodium 4-methoxy benzene sulfonate (3c).**<sup>10</sup> A round-bottomed flask was charged with anisole (5.0 mL, 46 mmol) and heated to 50 °C on a hot water bath. Conc. H<sub>2</sub>SO<sub>4</sub> (2.5 mL, 47 mmol) was added drop-wise with vigorous stirring. The mixture was heated at 100 °C for an additional 2 h. Upon cooling to room temperature the mixture solidified. Water (15 mL) was added to the solid and it was allowed to completely dissolve before any further workup. Saturated NaHCO<sub>3</sub> solution was added to bring the pH to ~8. The mixture was saturated with solid NaCl until a white solid

precipitated which was filtered and dried. Yield: 2.12 g, 22%. <sup>1</sup>H-NMR (D<sub>2</sub>O): 3.87 (s, 3H), 7.07 (m, 2H), 7.76 (m, 2H). <sup>13</sup>C-NMR (D<sub>2</sub>O): 55.72, 114.32 (2C), 127.54 (2C), 134.98, 161.37. FTIR (KBr): 1601 (s), 1580 (m), 1503 (vs), 1300 (m). UV (H<sub>2</sub>O): λ<sub>max</sub>(ε) = 231 (13031), 265 (883), 270 (945), 278 (700). MS (FAB<sup>+</sup>): C<sub>7</sub>H<sub>7</sub>O<sub>4</sub>S<sup>+</sup>; 187.01(M<sup>+</sup>) (calculated), 187.01 (found)

*Ammonium 4-methyl-1,3-benzene disulfonate (3d)* was prepared in two steps:

*Sodium 4-oxidobenzene-1,3-disulfonate.*<sup>11</sup> In a 50 mL round bottom flask were placed phenol (1 g, 11 mmol) and concentrated sulfuric acid (4 mL), and the mixture was heated on a boiling water bath for 3 h with constant mechanical stirring. The water bath was replaced by an ice bath. When the reaction mixture had cooled to room temperature, it was made alkaline by the careful addition of a solution of 10 M NaOH. A white solid salt (3.45 g, crude yield 98%) was filtered and used without any purification. <sup>1</sup>H-NMR (D<sub>2</sub>O): 7.12 (d, J = 8.7 Hz, 1H), 7.81 (dd, J = 8.7 and 2.4 Hz, 1H), 8.1 (d, J = 2.4 Hz, 1H). <sup>13</sup>C-NMR (D<sub>2</sub>O): 118.18, 126.27, 128.42, 131.12, 134.30, 156.48. MS (FAB<sup>+</sup>): C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>S<sub>2</sub><sup>+</sup>; 252.95 (M<sup>+</sup>) (calculated), 252.98 (found).

*Ammonium 4-methyl-1,3-benzene disulfonate (3d).*<sup>12</sup> In a 50 mL round bottom flask, a solution of NaOH (0.8 g, 20 mmol) in water (47 mL) was cooled to 0 °C, and sodium 4-oxidobenzene-1,3-disulfonate (3.2 g, 10 mmol) was added with stirring. Dimethyl sulfate (1 mL, 6 mmol) was quickly added while cooling, and the mixture was heated at 35 °C for 20 min. An additional 1 mL of dimethyl sulfate was added and the mixture was heated to 95-100 °C for 2 h. A solution of 5 M NaOH (2 mL) was added, and the mixture was stirred at 100 °C for additional 2 h. The mixture was cooled to room temperature, and transferred to a separatory funnel where it was extracted with diethyl ether to remove excess dimethyl sulfate. The water was removed under vacuum at 65-70 °C. Based on the <sup>1</sup>H-NMR analysis of the mixture, 88% conversion into *4-methoxy-1,3-benzene sulfonate* was obtained.

A sample of the product was subjected to ion-exchange chromatography on a Sephadex® column, which was swelled in 1 M NaHCO<sub>3</sub> in the cold for 1 day. Elution was preformed using a gradient 0 - 0.7 M NH<sub>4</sub>HCO<sub>3</sub>, total volume ~ 2000 mL. Several different fractions as detected by a

UV detector at 250 nm were collected. The excess  $\text{NH}_4\text{HCO}_3$  buffer-water solution mixture was removed under vacuum at 65-70 °C to yield **3d** as the ammonium salt.  **$^1\text{H-NMR}$**  ( $\text{D}_2\text{O}$ ): 4.00 (s, 3H), 7.14 (d,  $J = 8.7$  Hz, 1H), 7.97 (dd,  $J = 8.7$  and 2.4 Hz, 1H), 8.18 (d,  $J = 2.4$  Hz, 1H).  **$^{13}\text{C-NMR}$**  ( $\text{D}_2\text{O}$ ): 56.83, 113.48, 126.52, 130.63, 131.53, 134.80, 159.11. **FTIR** (KBr): 1596 (vs), 1486 (vs), 1395 (m), 12786 (vs). **UV** ( $\text{H}_2\text{O}$ ):  $\lambda_{\text{max}}(\epsilon) = 234$  (10993), 279 (2316), 284 (2047). **MS** ( $\text{FAB}^+$ ):  $\text{C}_7\text{H}_6\text{O}_7\text{S}_2^{2-}$ ; 266.25 ( $\text{M}^{2-}$ ) (calculated), 266.01 (found).

***S-4-(11-undecyloxy) phenyl ethanethioate trichlorosilane (4)*** was prepared in five steps:

***4-(2-(4-hydroxyphenyl) disulfanyl) phenol***. In a 500 mL round bottom flask equipped with a magnetic stirrer were placed 45 mL ethanol and 5 mL water.  $\text{I}_2$  was added (22 g, 87 mmol) and solution turned deep red. 4-Mercaptophenol (10 g, 79 mmol) was added, and the solution was stirred at R.T. for 20 h. Freshly prepared aqueous sodium thiosulfate solution (10%) was added until the red solution turned bright yellow (~ 300 mL) and the *4-(2-(4-hydroxyphenyl) disulfanyl) phenol* precipitated out. The solid was filtered and dried under vacuum. The product was obtained as a light-yellow solid. Yield: 9.91 g, 99%.  **$^1\text{H-NMR}$**  (acetone- $\text{d}_6$ ): 6.81-6.58 (m, 4H), 7.30-7.35 (m, 4H), 8.82 (bs, 2H).  **$^{13}\text{C-NMR}$**  (acetone- $\text{d}_6$ ): 117.05 (4C), 127.43 (2C), 134.09 (4C), 159.20 (2C). **MS** ( $\text{DCI}^+$ ):  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_2$ ; 250.01 ( $\text{M}^+$ ) (calculated), 250.01 (found).

***1,2-bis(4-(undec-10-enyloxy) phenyl) disulfane***. A dry 500 mL flask equipped with a magnetic stirring bar, a reflux condenser and drying tube, was charged with *4-(2-(4-hydroxyphenyl) disulfanyl) phenol* (4.45 g, 18 mmol) and 400 mL of acetone. Potassium carbonate (7.80 g, 56 mmol) and  $\omega$ -undecenyl mesylate<sup>8</sup> (14.89 g, 60 mmol) were added and the reaction mixture was heated at reflux for 4 days and monitored by TLC (hexane: ether 90:10). It was cooled to room temperature and the resulting suspension concentrated to a solid on a rotary evaporator. The material was suspended in diethyl ether and transferred to a separatory funnel. The ether solution was washed with cold water, 10% NaOH and saturated aqueous NaCl. It was then dried with  $\text{MgSO}_4$ , filtered, and concentrated on a rotary evaporator. *1,2-bis(4-(undec-10-enyloxy) phenyl) disulfane* was obtained as a bright-yellow solid and used after purification by flash chromatography

(silica gel/ hexane/ ether 90:10). Yield: 8.44 g, 86%. <sup>1</sup>H-NMR: 1.19-1.42 (m, 24H), 1.69-1.79 (m, 4H), 1.99-2.06 (m, 4H), 3.89 (t, J = 6.6 Hz, 4H), 4.89-5.01 (m, 4H), 5.73-5.87 (m, 2H), 6.77-6.80 (m, 4H), 7.34-7.37 (m, 4H). <sup>13</sup>C-NMR: 22.76 (2C), 29.01 (2C), 29.21 (2C), 29.29 (2C), 29.47 (2C), 29.52 (2C), 29.61 (2C), 33.90 (2C), 68.15 (2C), 114.25 (2C), 115.16 (4C), 128.25 (2C), 132.76 (4C), 139.18 (2C), 159.56 (2C). MS (DCI<sup>+</sup>): C<sub>34</sub>H<sub>50</sub>O<sub>2</sub>S<sub>2</sub>; 554.32 (M<sup>+</sup>) (calculated), 554.32 (found).

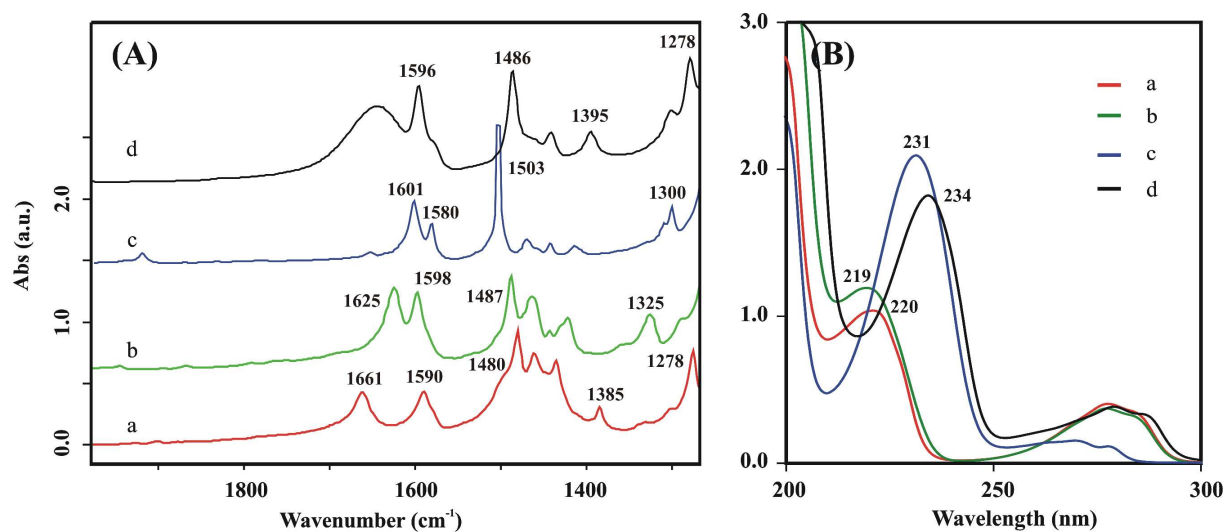
**4-(undec-10-enyloxy) benzenethiol.**<sup>13</sup> In a two-necked 500 mL round bottom flask equipped with a magnetic stirrer were placed *1,2-bis(4-(undec-10-enyloxy) phenyl) disulfane* (7.55 g, 14 mmol), 70 mL dry THF and 70 mL dry MeOH. This mixture was degassed by successive freeze-thaw cycles. NaBH<sub>4</sub> (5.45 g, 144 mmol) was added to the solution portion-wise over 40 min under a positive pressure of N<sub>2</sub>. The reaction mixture was stirred overnight at R.T. The progress of the reaction was followed by monitoring the appearance of the thiol proton peak in the <sup>1</sup>H-NMR. The solvents were then evaporated and water was added to the residue. The aqueous layer was acidified using HCl to achieve pH ~ 2-3 and this aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined and dried over MgSO<sub>4</sub> and filtered. The solvent was removed by rotary evaporator to afford a clear liquid. The material was used without further purification. <sup>1</sup>H-NMR: 1.23-1.45 (m, 12H), 1.70-1.85 (m, 2H), 1.99-2.07 (m, 2H), 3.34 (s, 1H), 3.88 (t, J = 6.6 Hz, 2H), 4.90-5.02 (m, 2H), 5.73-5.87 (m, 1H), 6.74-6.80 (m, 2H), 7.19-7.25 (m, 2H). <sup>13</sup>C-NMR: 26.09, 28.99, 29.19, 29.28, 29.44, 29.50, 29.58, 33.88, 68.16, 114.23, 115.17 (2C), 132.50 (2C), 132.79, 139.23, 158.13. MS (DCI<sup>+</sup>): C<sub>17</sub>H<sub>26</sub>OS; 278.17 (M<sup>+</sup>) (calculated), 278.17 (found).

**S-4-(undec-10-enyloxy) phenyl ethanethioate.** A dry 250 mL round bottom flask equipped with a magnetic stirring bar and N<sub>2</sub> inlet was charged with *4-(undec-10-enyloxy) benzenethiol* (1.42 g, 5 mmol), and 50 mL of dry THF. Triethylamine (6 mL, 43 mmol) was added at 0 °C. A solution of acetylchloride (4.1 mL, 47 mmol) in 10 mL of dry THF was added drop-wise with constant stirring. The mixture started turning orange-red. After addition was completed, the mixture was stirred at 0 °C for an additional 30 min after which 15 mL of water was added to decompose un-reacted

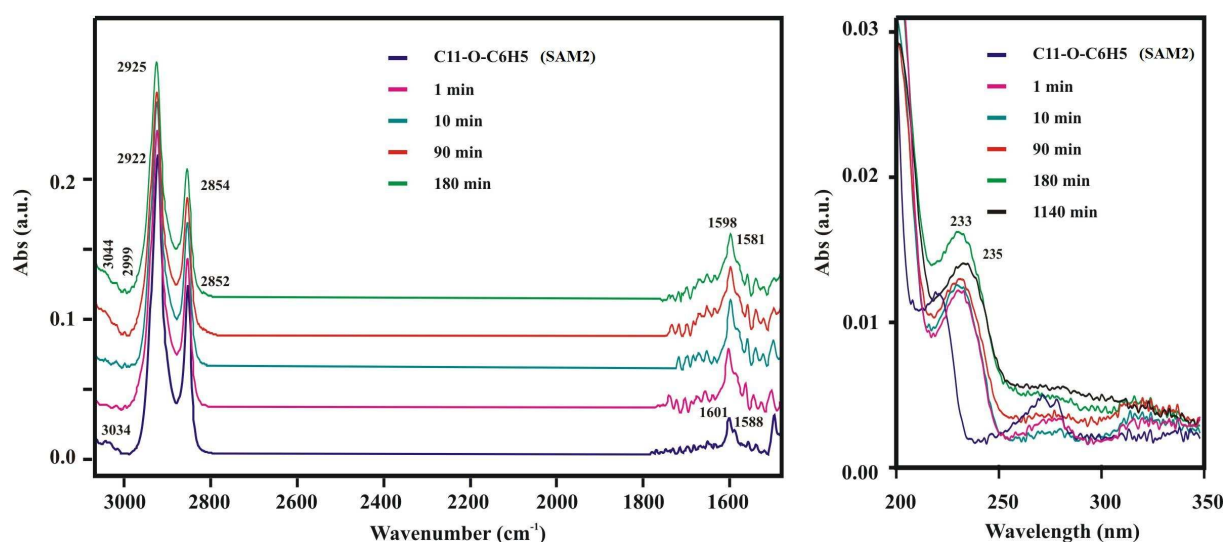
acetyl chloride. The mixture was concentrated under vacuum to remove the THF. The crude product was transferred to a separatory funnel and diluted with diethyl ether. The organic solution was washed with cold water, 40% NaHSO<sub>4</sub>, and saturated NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub>, and concentrated on a rotary evaporator. The product was purified by flash chromatography (silica gel/hexane: ether 90:10). Yield: 1.51 g, 92%. **<sup>1</sup>H-NMR**: 1.25-1.49 (m, 12H), 1.72-1.81 (m, 2H), 1.99-2.07 (m, 2H), 2.36 (s, 3H), 3.93 (t, J = 6.6 Hz, 2H), 4.90-5.02 (m, 2H), 5.73-5.87 (m, 1H), 6.88-6.93 (m, 2H), 7.26-7.31 (m, 2H). **<sup>13</sup>C-NMR**: 26.06, 28.97, 29.17, 19.21, 29.40, 29.47, 29.56, 29.95, 33.86, 68.10, 114.22, 115.39 (2C), 118.39, 136.08 (2C), 139.19, 160.32, 195.21. **UV** (hexane or ethanol):  $\lambda_{\text{max}}$  = 239, 271 (shoulder) nm. **MS** (DCI<sup>+</sup>): C<sub>19</sub>H<sub>28</sub>O<sub>2</sub>S; 320.18 (M<sup>+</sup>) (calculated), 320.18 (found).

***S-4-(11-undecyloxy) phenyl ethanethioate trichlorosilane (4)***. *S-4-(undec-10-enyloxy) phenyl ethanethioate* was hydrosilylated overnight at R.T, to produce **4** using the same procedure described for **1**. The product was isolated by Kugelrohr distillation at 180 °C and 0.01 mm Hg. Yield: 0.87 g, 62%. **<sup>1</sup>H-NMR**: 1.28-1.42 (m, 16H), 1.53-1.61 (m, 2H), 1.73-1.82 (m, 2H), 2.39 (s, 3H), 3.96 (t, 6.3 Hz, 2H), 6.89-6.94 (m, 2H), 7.25-7.32 (m, 2H). **<sup>13</sup>C-NMR**: 22.38, 24.43, 26.13, 29.12, 29.28, 29.45 (2C), 29.62 (2C), 30.05, 31.93, 68.20, 115.49 (2C), 118.47, 136.17 (2C), 160.40, 195.47.

## Section 2) Representative spectral and kinetic data



**Figure S.1:** IR (left) and UV-Vis (right) spectra of methoxy benzene sulfonate model compounds (3): (a) 2-methoxy benzene sulfonate (3a); (b) 3-methoxy benzene sulfonate (3b); (c) 4-methoxy benzene sulfonate (3c); (d) 4-methoxy-1,3-benzene sulfonate (3d)



**Figure S.2:** ATR-FTIR (left) and UV-Vis (right) spectra for the sulfonation of phenyl ether terminated SAM2 by conc.  $\text{H}_2\text{SO}_4$  5 °C

The following tables detail the product distribution based on deconvolution of UV spectra collected *in-situ*, at the indicated conditions.



Time	Run No. 1			Run No. 2		
	<i>Ortho</i>	<i>Para</i>	<i>Di</i>	<i>Ortho</i>	<i>Para</i>	<i>Di</i>
<b>0</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>1</b>	0.40	0.28	0.32	0.42	0.29	0.29
<b>5</b>	0.39	0.27	0.34	0.41	0.29	0.30
<b>10</b>	0.39	0.26	0.35	0.39	0.28	0.33
<b>20</b>	0.38	0.26	0.36	0.38	0.26	0.36
<b>30</b>	0.37	0.26	0.37	0.37	0.26	0.37
<b>40</b>	0.36	0.26	0.38	0.36	0.26	0.38
<b>50</b>	0.35	0.26	0.39	0.36	0.25	0.39
<b>60</b>	0.34	0.26	0.40	0.35	0.25	0.40
<b>70</b>	0.34	0.25	0.41	0.34	0.25	0.41
<b>80</b>	0.33	0.25	0.42	0.33	0.25	0.42
<b>90</b>	0.32	0.24	0.44	0.32	0.24	0.44
<b>100</b>	0.32	0.23	0.45	0.31	0.23	0.46
<b>110</b>	0.31	0.23	0.46	0.31	0.23	0.46
<b>120</b>	0.30	0.23	0.47	0.30	0.22	0.48
<b>150</b>	0.30	0.22	0.48	0.29	0.21	0.50
<b>180</b>	0.28	0.20	0.52	0.28	0.20	0.52
<b>210</b>	0.27	0.19	0.54	0.27	0.19	0.54
<b>240</b>	0.26	0.20	0.54	0.25	0.20	0.55
<b>270</b>	0.24	0.19	0.57	0.24	0.19	0.57
<b>300</b>	0.23	0.18	0.59	0.22	0.19	0.59
<b>330</b>	0.22	0.19	0.59	0.21	0.20	0.60

**Table S.1:** Product distribution in the sulfonation reaction of **SAM1** by conc.  $H_2SO_4$  at 5 °C, as obtained from curve resolution after correction for relative extinction coefficients and normalization.

Time	Run No. 1			Run No. 2		
	<i>Ortho</i>	<i>Para</i>	<i>Di</i>	<i>Ortho</i>	<i>Para</i>	<i>Di</i>
<b>0</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>1</b>	0.34	0.28	0.38	-	-	-
<b>5</b>	0.33	0.27	0.40	-	-	-
<b>10</b>	0.32	0.27	0.41	0.33	0.28	0.39
<b>20</b>	0.31	0.27	0.42	0.32	0.27	0.41
<b>30</b>	0.31	0.26	0.43	0.31	0.26	0.43
<b>40</b>	0.30	0.25	0.45	0.30	0.25	0.45
<b>50</b>	0.29	0.25	0.46	0.29	0.25	0.46
<b>60</b>	0.29	0.23	0.48	0.28	0.25	0.47
<b>70</b>	0.28	0.23	0.49	0.28	0.24	0.48
<b>80</b>	0.26	0.23	0.51	0.26	0.24	0.50
<b>90</b>	0.25	0.22	0.53	0.25	0.22	0.53
<b>100</b>	0.22	0.22	0.56	0.24	0.22	0.54
<b>110</b>	0.22	0.20	0.58	0.22	0.20	0.58
<b>120</b>	0.20	0.19	0.61	0.20	0.20	0.60
<b>150</b>	0.20	0.20	0.60	0.20	0.20	0.60
<b>180</b>	0.19	0.18	0.63	0.19	0.18	0.63

**Table S.2:** Product distribution in the sulfonation reaction of **SAMI** by conc.  $H_2SO_4$  at R.T, as obtained from curve resolution after correction for relative extinction coefficients and normalization.

Time	Run No. 1			Run No. 2		
	<i>Ortho</i>	<i>Para</i>	<i>Di</i>	<i>Ortho</i>	<i>Para</i>	<i>Di</i>
<b>0</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>0.5</b>	0.43	0.50	0.07	-	-	-
<b>1</b>	0.41	0.47	0.12	0.43	0.50	0.07
<b>2</b>	0.41	0.45	0.14	-	-	-
<b>3</b>	0.38	0.47	0.15	-	-	-
<b>5</b>	0.40	0.45	0.15	0.41	0.46	0.13
<b>10</b>	0.39	0.43	0.18	0.40	0.44	0.16
<b>20</b>	0.34	0.40	0.26	0.38	0.41	0.21
<b>30</b>	0.36	0.37	0.27	0.36	0.39	0.25
<b>40</b>	0.33	0.38	0.29	0.34	0.38	0.28
<b>50</b>	0.30	0.37	0.33	0.33	0.37	0.30
<b>60</b>	0.30	0.35	0.35	0.32	0.35	0.33
<b>70</b>	0.29	0.34	0.37	0.31	0.34	0.35
<b>80</b>	0.28	0.34	0.38	0.30	0.34	0.36
<b>90</b>	0.29	0.34	0.37	0.31	0.35	0.34
<b>110</b>	0.3	0.33	0.37	0.30	0.34	0.36
<b>120</b>	0.28	0.33	0.39	0.29	0.33	0.38
<b>150</b>	0.28	0.31	0.41	0.28	0.31	0.41
<b>180</b>	0.29	0.31	0.40	0.28	0.31	0.41
<b>210</b>	0.27	0.30	0.43	0.25	0.30	0.45
<b>1140</b>	0.19	0.20	0.61	0.20	0.20	0.60

**Table S.3:** Product distribution in the sulfonation reaction of **SAM2** by conc.  $H_2SO_4$  at 5 °C, as obtained from curve resolution after correction for relative extinction coefficients and normalization.

Time	Run No. 1			Run No. 2		
	<i>Ortho</i>	<i>Para</i>	<i>Di</i>	<i>Ortho</i>	<i>Para</i>	<i>Di</i>
0	0.00	0.00	0.00	0.00	0.00	0.00
1	0.3	0.43	0.27	-	-	-
2	0.31	0.4	0.29	-	-	-
3	0.29	0.39	0.32	-	-	-
5	0.29	0.37	0.34	0.31	0.39	0.3
10	0.26	0.38	0.36	0.29	0.38	0.33
20	0.23	0.39	0.38	0.26	0.37	0.37
30	0.25	0.35	0.4	0.25	0.35	0.4
40	0.22	0.36	0.42	0.22	0.36	0.42
50	0.21	0.36	0.43	0.22	0.35	0.43
60	0.22	0.35	0.43	0.21	0.35	0.44
70	0.22	0.34	0.44	0.21	0.34	0.45
80	0.21	0.34	0.45	0.2	0.34	0.46
90	0.2	0.34	0.46	0.2	0.34	0.46
110	0.18	0.31	0.51	0.18	0.31	0.51
120	0.19	0.29	0.52	0.18	0.29	0.53
150	0.19	0.25	0.57	0.19	0.24	0.57
180	0.19	0.22	0.59	0.19	0.22	0.59
210	0.18	0.22	0.6	0.18	0.22	0.6

**Table S.4:** Product distribution in the sulfonation reaction of **SAM2** by conc.  $H_2SO_4$  at R.T, as obtained from curve resolution after correction for relative extinction coefficients and normalization.