

**Supplemental Information**

**Formation of Monolayer Films by the Spontaneous Assembly  
of Organic Thiols from Solution onto Gold**

Colin D. Bain, E. Barry Troughton; Yu-Tai Tao; Joesph Evall;  
George M. Whitesides, and Ralph G. Nuzzo

**1-Undecanethiol.** To 50 mL of ice-cold, degassed methanol were added sodium (0.69 g, 30 mg-atom), hiolacetic acid (2.15 mL, 30 mmol) and 1-bromoundecane (4.5 mL, 20 mmol). The reaction mixture was refluxed under N<sub>2</sub> for 1 h, NaOMe (1.1 g, 20 mmol) was added and reflux was maintained for a further hour. The reaction mixture was then cooled to room temperature and quenched with 50 mL of degassed, half-saturated ammonium chloride solution and 50 mL of ether. The aqueous layer was extracted with ether (2 x 20 mL) and the combined organic fractions were washed with water (2 x 30 mL). Filtration through MgSO<sub>4</sub> and Norit, and evaporation of the solvent yielded 3.8 g of a pale yellow liquid. Kugelrohr distillation (0.1 Torr, 60 °C; lit.<sup>1</sup> bp 3 Torr, 103-104 °C) afforded 3.37 g of 1-undecanethiol (18 mmol, 90%). Part of the product was purified further by flash chromatography using hexane as eluant: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.49 (q, 2 H), 1.55 (m, 2 H), 1.3 (t, 1 H), 1.2-1.4 (m, 16 H), 0.85 (t, 3 H).

**1-Heptadecanethiol.** 1-Bromoheptadecane was prepared by refluxing a mixture of 1-heptadecanol (10.0 g, 39 mmol), 48% hydrobromic acid (50 mL) and glacial acetic acid (50 mL) for 72 h. The mixture was cooled to room temperature and 250 mL of hexane added. The hexane layer was separated and washed with sat NaCl solution (3 x 100 mL), dried over anhyd Na<sub>2</sub>SO<sub>4</sub>, and filtered. Filtration through silica gel to remove the starting alcohol, and evaporation of the solvent yielded 1-bromoheptadecane as a white solid (mp 29-31 °C). To prepare the

thiol, sodium metal (237 mg, 10.3 mg-atom), thiolacetic acid (784 mg, 10.3 mmol) and bromoheptadecane (3 g, 9.3 mmol) were dissolved in 100 mL of degassed ethanol and refluxed for 3 h under argon. After cooling to room temperature, 5 mL of conc. HCl was added and the reaction mixture was refluxed overnight. Recrystallization of the product from ethanol yielded 1-heptadecanethiol as a white solid: mp 31.5-33 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.49 (q, 2 H), 1.59 (m, 2 H), 1.24 (m), 0.86 (t, 3 H). Anal. Calcd (Found) for  $\text{C}_{17}\text{H}_{36}\text{S}$ : C, 74.92 (74.71); H, 13.31 (13.34).

1-Eicosanethiol was prepared from 1-bromoeicosane in a manner analogous to that for 1-heptadecanethiol. Recrystallization from ethanol yielded 1-eicosanethiol as white crystals: mp 39-41 °C (lit.<sup>2</sup> mp 37.5-38.5 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.49 (q, 2 H), 1.58 (m, 2 H), 1.23 (m), 0.86 (t, 3 H).

1-Docosanethiol was prepared from 1-bromodocosane in a manner analogous to that for 1-heptadecanethiol. Recrystallization from hexane yielded white crystals of docosanethiol: mp 48-49 °C (lit.<sup>2</sup> mp 42.5-43.0 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.52 (q, 2 H), 1.61 (m, 2 H), 1.25 (m), 0.86 (t, 3 H). Exact Mass (EI): Calcd 342.1355 ( $\text{C}_{22}\text{H}_{44}\text{S}$ ), Found 342.1359.

6-Mercaptohexanoic acid. Sodium metal (2.53 g, 110 mg-atom) was dissolved in 150 mL of degassed methanol and the resulting solution was cooled in an ice-bath. Thiolacetic acid (7.3 mL, 103 mmol) and 6-bromohexanoic acid (10.0 g, 51 mmol) were added and the solution was heated at reflux under argon for 6 h. After cooling to room temperature, 15 mL of conc. HCl were added and

reflux was continued for a further 15 h. The reaction mixture was cooled to room temperature and 300 mL of ether was added. The ethereal layer was extracted with water (3 x 100 mL) and sat aq NaCl solution (100 mL). Drying over  $\text{Na}_2\text{SO}_4$ , filtration and removal of the ether under vacuum yielded liquid methyl 6-mercaptohexanoate. A portion of the ester was hydrolysed by refluxing for 3 h with 50 mL of 1 N NaOH solution in 100 mL of degassed methanol. The product, 6-mercaptohexanoic acid, was purified by column chromatography using 9% ether in methylene chloride as eluant:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.49 (q, 2 H), 2.32 (t, 2 H), 1.59 (m, 4 H), 1.42 (m, 2 H), 1.30 (t, 1 H). Anal. Calcd (Found) for  $\text{C}_6\text{H}_{12}\text{O}_2\text{S}$ : C, 48.62 (48.68); H, 8.16 (8.06).

11-Mercaptoundecanoic acid was available from previous studies.<sup>3</sup>

16-Mercaptohexadecanoic acid. 16-Bromohexadecanoic acid was prepared from 16-hydroxyhexadecanoic acid by refluxing for 2 days in a 1:1 mixture of 48% hydrobromic acid and glacial acetic acid. Upon cooling, the bromide crystallized, was filtered through a Buchner funnel, washed with water, and recrystallized from hexanes: mp 68.5 - 70.3 °C (lit.<sup>4</sup> mp 68.5-69.0 °C). The bromide was converted to the thioacetate by adding sodium metal (0.96 g, 40.9 mg-atom), thiolacetic acid (2.9 mL, 40.9 mmol) and 16-bromohexadecanoic acid (7.0 g, 20.9 mmol) to 100 mL of methanol and refluxing for 15 h. After cooling to room temperature the thioester was hydrolysed by adding 50 mL of degassed 1N NaOH solution and refluxing for 3 h under argon. The reaction mixture

was then cooled with an ice-bath and poured, with stirring, into a 1-L beaker containing iced water (200 mL), conc. HCl (10 mL) and ether (300 mL). The ethereal layer was separated and washed with deionised water (3 x 150 mL) and sat aq NaCl solution (150 mL). The ethereal layer was dried over anhyd Na<sub>2</sub>SO<sub>4</sub>, filtered, and the ether removed by rotary evaporation. The resulting white solid was recrystallized from hexane and yielded 3.1 g of 16-mercaptohexadecanoic acid: mp 65 - 66 °C (lit.<sup>5</sup> mp 66-67 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.53 (q, 2 H), 2.35 (t, 2 H), 1.62 (m, 4 H), 1.28 (m).

**21-Mercaptoheneicosanoic acid.** Methyl 21-bromoheneicosanoate was prepared by electrolyzing a 1:1 mixture of 11-bromoundecanoic acid and methyl hydrogen dodecanoate in 150 mL of anhyd methanol with 0.1 equiv. of sodium metal for 12 h.<sup>6</sup> Methyl 21-bromoheneicosanoate precipitated from the solution at room temperature, was collected by filtration, and purified by column chromatography using 2% acetone in hexane as eluant. The first product eluted (dibromoeicosane) was discarded and the second product collected: mp 59.0 - 59.7 °C; NMR (CDCl<sub>3</sub>) δ 3.66 (s, 3 H), 3.40 (t, 2 H), 2.30 (t, 2 H), 1.84 (m, 2 H), 1.65 (m), 1.28 (m). Methyl 21-bromoheneicosanoate was converted to 21-mercaptoheneicosanoic by the method described above for the preparation of 16-mercaptohexadecanoic acid. The product was recrystallized from hexanes to yield a white solid: mp 81 - 82.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.51 (q, 2 H), 2.34 (t, 3 H), 1.61 (m), 1.25 (m). Exact Mass (CI, NH<sub>3</sub>): Calcd 376.3249 (C<sub>21</sub>H<sub>42</sub>O<sub>2</sub>S + NH<sub>4</sub><sup>+</sup>), Found

376.3243.

**18-Nonadecene-1-thiol.** A solution of 50 mL of THF, 11 mL (16.3 g, 60 mmol) of 1,8-dibromooctane and 5 mL of 0.1 M  $\text{Li}_2\text{CuCl}_4$  in THF was cooled to 0 °C under  $\text{N}_2$ . A 0.47 M solution of 10-undecenyl magnesium bromide was prepared by reaction of magnesium with 11-bromo-1-undecene in THF and 85 mL of this solution was added to the reaction mixture over a period of 5 h. The solution was stirred at 0 °C for 1 h, allowed to warm to room temperature, quenched with 75 mL of sat ammonium chloride solution and allowed to stand for several h to let the copper salts pass into the aqueous phase. The clear organic layer was decanted and the aq layer extracted with ether (2 x 50 mL). The organic fractions were combined, washed with brine (2 x 50 mL), dried over  $\text{MgSO}_4$  and the solvent removed under vacuum. Distillation (0.1 Torr, 132-140 °C) yielded 7.45 g of impure 19-bromo-1-nonadecene. Sodium (140 mg, 6 mg-atom), thiolacetic acid (0.43 mL, 6 mmol) and 19-bromo-1-nonadecene (0.82 g, 2.4 mmol) were added to 20 mL of degassed methanol and refluxed under  $\text{N}_2$  for 2 h. Sodium methoxide (0.25 g, 5 mmol) was added and reflux continued for 1 h. The reaction mixture was then quenched with 50 mL of degassed, half-saturated, ammonium chloride solution and 20 mL of  $\text{CH}_2\text{Cl}_2$ . The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 20 mL) and the combined organic extracts were washed with 50 mL of distilled water. Drying over  $\text{MgSO}_4$ , removal of the solvent, and flash chromatography using hexanes as eluant yielded 18-nonadecenethiol as a colorless liquid (480 mg, 1.6 mmol, 67%): mp

27.7-29 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.8 (m, 1 H), 4.9 (m, 2 H), 2.5 (q, 2 H), 2.0 (q, 2 H), 1.6 (m, 2 H), 1.3 (t, 1 H), 1.2-1.4 (m, 28 H). Anal. Calcd (Found) for  $\text{C}_{19}\text{H}_{38}\text{S}$ : C, 76.43 (76.47); H, 12.83 (12.77).

**11-(t-Butyldimethylsiloxy)-1-undecanethiol.** 1-Bromo-11-(t-butyldimethylsiloxy)undecane was prepared by adding 10 g (40 mmol) 11-bromo-1-undecanol to a solution of 8.23 g (80 mmol) of NaBr, 6.53 g (96 mmol) of imidazole, and 7.2 g (48 mmol) of TBDMS chloride in 20 mL of DMF. After stirring for 1 h, the reaction was quenched with 20 mL of half-saturated aq sodium bicarbonate solution to yield a pale yellow supernatant (product) and an aqueous layer. The aqueous layer was extracted with hexane (2 x 10 mL) and the combined organic fractions were washed with ammonium chloride solution (2 x 20 mL) to remove imidazole and DMF. Filtration through anhyd  $\text{MgSO}_4$  and removal of the solvent on a rotary evaporator yielded ca. 15 mL of a pale yellow liquid. Drying overnight under vacuum afforded 14 g (38.7 mmol, 97%) of 1-bromo-11-TBDMS-undecane:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.57 (t, 2 H), 3.38 (t, 2 H), 1.83 (m, 2 H), 1.26 (m), 0.87 (s, 9 H), 0.02 (s, 6 H).

Sodium (0.184 g, 8 mg-atom), thiolacetic acid (0.57 mL, 8 mmol) and 2 mL (2.15 g, 5.9 mmol) of 1-bromo-11-TBDMS-undecane were dissolved in 25 mL of dry, degassed methanol and refluxed under  $\text{N}_2$  for 3 h. Sodium methoxide (0.43 g, 8 mmol) was added and reflux maintained for a further 1 h. After cooling to room temperature the reaction was quenched with 50 mL of half-saturated ammonium chloride solution and 20 mL of ether. The aq phase

was extracted with ether (2 x 20 mL) and the combined organic phases washed with distilled water (2 x 25 mL). The ethereal solution was filtered through Norit and anhyd  $\text{MgSO}_4$  and the solvent removed on a rotary evaporator to leave a pale yellow oil (1.75 g, 5.5 mmol, 93%). The 11-(*t*-butyldimethylsilyl)-1-undecanethiol was purified further by flash chromatography using 40:1 hexane/ether as eluant:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.6 (t, 2 H), 2.5 (q, 2 H), 1.3 (t, 1 H), 0.9 (s, 9 H), 0.05 (s, 6 H). Anal. Calcd (found) for  $\text{C}_{17}\text{H}_{38}\text{OSSi}$ : C, 64.08 (64.07); H, 12.02 (12.01).

11-Bromo-1-undecanethiol. Triphenylphosphine (8.5 g, 32.4 mmol) was dissolved in 120 mL of dry, distilled THF in a 300-mL round-bottomed flask and cooled to 0 °C under  $\text{N}_2$ . Upon addition of 6.5 mL (33 mmol) of diisopropyl azodicarboxylate, a white precipitate rapidly formed. After stirring for 30 min at 0 °C, 7.53 g (30 mmol) of 11-bromo-1-undecanol was added as a 1 M solution in THF. Thiolacetic acid (20 mL of a 1.5M solution in THF) was added to the resulting slurry over a period of 10 min, and produced a clear solution. The solution was stirred at 0 °C for a further 15 min and then allowed to warm to room temperature. Two drops of water were added and the solvent was removed on a rotary evaporator. The product was extracted into ether and the triphenylphosphine oxide was removed by filtration. Kugelrohr distillation (1 Torr, 150 °C) yielded impure 11-bromo-1-undecyl thioacetate as a yellowish oil (7.2 g, 77%). A small part of this material was purified further by flash chromatography using 60% hexane/40% methylene chloride as eluant. Pure



11-bromo-1-undecyl thioacetate was obtained as a colorless oil.

A solution of dry HCl in methanol was prepared by the careful addition of 5 mL of acetyl chloride to 50 mL of ice-cold, degassed methanol. 11-Bromo-1-undecyl thioacetate (0.5 g) was added and the solution was stirred at room temperature for 3 h under N<sub>2</sub> to allow transesterification to take place. The reaction mixture was then poured into 50 mL of degassed, distilled water and the organic layer extracted into 30 mL of hexane. The aqueous layer was extracted with hexane (2 x 20 mL) and the combined organic phases were washed with water (2 x 50 mL). The hexane solution was dried over anhyd MgSO<sub>4</sub> and reduced to a volume of 3 mL on a rotary evaporator at room temperature. Flash chromatography using 2:1 hexane/methylene chloride as eluant yielded 11-bromo-1-undecanethiol as a colorless oil (0.4 g, 90%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.37 (t, 2 H), 2.50 (q, 2 H), 1.82 (m, 2 H), 1.58 (m, 2 H), 1.3 (t, 1 H). Anal. Calcd (Found) for C<sub>11</sub>H<sub>23</sub>SBBr: C, 49.43 (49.70); H, 8.67 (8.89).

11-Chloro-1-undecanethiol. 11-Chloro-1-undecene (1.89 g, 10 mmol, prepared by A. F. Sowinski) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a pyrex flask. Thiolacetic acid (1.07 mL, 15 mmol) and a small amount of AIBN were added and the reaction exposed to a 100 W, medium pressure, mercury lamp at 6-in. separation for 2h. The reaction mixture was quenched with 20 mL of NaHCO<sub>3</sub> solution and the aq layer extracted with ether (2 x 10 mL). The combined organic extracts were washed with brine (2 x 20 mL), dried over MgSO<sub>4</sub>, and the solvent removed. Kugelrohr distillation (90 °C,

0.05 Torr) yielded 2.65 g (10 mmol, 100%) of 11-chloroundecyl thioacetate. 11-Chloroundecanethiol was prepared by hydrolysing 0.8 mL (0.95 g, 3.6 mmol) of the thioacetate in 10 mL of degassed methanol containing about 0.5 g of  $K_2CO_3$ . After 30 min, the reaction was quenched with 0.25 mL of acetic acid, the solvent removed by evaporation and the potassium carbonate removed by filtration. Flash chromatography (3:1 hexane/ $CH_2Cl_2$ ) yielded 0.6 g (2.7 mmol, 74 %) of 11-chloroundecanethiol as a colorless oil:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.5 (t, 2 H), 2.5 (q, 2 H), 1.75 (m, 2 H), 1.6 (m, 2 H), 1.3 (t, 1 H), 1.2-1.5 (m, 14 H). Anal. Calcd (Found) for  $C_{11}H_{23}ClS$ : C, 59.30 (59.39); H, 10.40 (10.32).

**11-Methoxy-1-undecanethiol.** Sodium (350 mg, 15 mmol) was added to 50 mL of degassed methanol. Once effervescence had ceased, 2.3 g (10 mmol) of 11-bromo-1-undecene was added and the reaction was heated at reflux overnight. Removal of the solvent and Kugelrohr distillation (55 °C, 0.3 Torr) yielded 1.64 g (9 mmol) of 11-methoxy-1-undecene. 11-Methoxy-1-undecanethiol was prepared from 11-methoxy-1-undecene as described above for 11-chloro-1-undecanethiol. The product was purified by flash chromatography using 3:2 hexane/ $CH_2Cl_2$  as eluant:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.34 (t, 2 H), 3.31 (s, 3 H), 2.50 (q, 2 H), 1.4-1.7 (m, 4 H), 1.30 (t, 1 H), 1.2-1.4 (m, 14 H). Anal. Calcd (Found) for  $C_{12}H_{26}OS$ : C, 66.00 (66.05); H, 12.00 (11.80).

**12-Mercapto-1-dodecyl thioacetate.** 1,12-dodecyl dithioacetate was prepared by adding sodium methoxide (6.9 g), thiol-acetic acid (9.15 mL) and 1,12-dibromododecane (13.13 g, 40 mmol)

to 100 mL of degassed methanol and refluxing overnight under  $N_2$ . The reaction mixture was allowed to cool and then poured into 200 mL of iced water. A yellow solid precipitated and was removed by filtration, washed with water and dried under vacuum.

Recrystallization from 150 mL of ethanol/water yielded 1,12-dodecyl dithioacetate (8.05 g, 25 mmol, 63%):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.85 (t, 4 H), 2.30 (s, 6 H), 1.65 (m, 4 H), 1.2-1.4 (m, 16 H).

A slurry of 0.5 g of 1,12-dodecyl dithioacetate in 30 mL of methanol was degassed with  $N_2$  and 1 mL acetyl chloride was added. The reaction mixture was then heated at 40 °C for 30 min, after which time TLC (9:1 hexane/ether) indicated that the monohydrolysed material was the major component. The reaction mixture was quenched by pouring into 150 mL of degassed, iced water and extracted with ether (2 x 50 mL). The organic extracts were washed with distilled water (2 x 50 mL), dried over  $MgSO_4$ , and evaporated to yield 0.45 g of a yellow oil. 12-Mercapto-1-dodecyl thioacetate was separated from the dithiol and the dithioacetate by flash chromatography using 4% ether in hexane as eluant. The fractions containing only the monothiol were collected, the solvent removed, and the resulting yellow oil recrystallized from degassed methanol to produce 80 mg of 12-mercapto-1-dodecyl thioacetate: mp 31-32 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.84 (t, 2 H), 2.50 (q, 2 H), 2.30 (3, 3 H), 1.5 (m, 4 H), 1.30 (t, 1 H), 1.2-1.4 (m, 16 H). Anal. Calcd (Found) for  $C_{14}H_{28}OS_2$ : C, 60.82 (60.76); H, 10.21 (10.14).

Methyl 11-mercaptoundecanoate Sodium methoxide (4.9 g, 90

mmol), thiolacetic acid (3.6 mL, 50 mmol) and 11-bromoundecanoic acid (10.6 g, 40 mmol) were refluxed in 100 mL of degassed methanol under  $N_2$  for 5 h. Addition of 10 mL of conc.  $H_2SO_4$  to the cooled solution and refluxing overnight under  $N_2$  converted the thioacetate to the thiol and the carboxylic acid to its methyl ester. The reaction mixture was then cooled to room temperature and quenched with 150 mL of degassed  $NaHCO_3$  solution and 100 mL of ether. The aqueous layer was separated and extracted with two 50-mL portions of ether. The ether extracts were combined with the organic layer, washed with degassed, distilled water, and dried over  $MgSO_4$ . Removal of the solvent yielded methyl 11-mercaptoundecanoate as a pale yellow oil. Contaminating disulfide was removed by distillation (0.1 Torr, 105 °C; lit.<sup>7</sup> 0.07 Torr, 93-94 °C) to produce 7.65 g (33 mmol, 82%) of a colorless liquid which solidified on cooling in a refrigerator: mp 10-13 °C. A small portion was purified further by flash chromatography using 9:1 hexane/ether as eluant:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.64 (s, 3 H), 2.48 (q, 2 H), 2.27 (t, 2 H), 1.6 (m, 4 H), 1.3 (t, 1 H), 1.2-1.4 (m, 12 H).

**9-Mercaptononanenitrile.** Sodium (0.95 g, 41 mg-atom), thiolacetic acid (3.0 mL, 37 mmol) and 1,8-dibromooctane (6.8 mL, 37 mmol) were added to 20 mL of dry, degassed methanol. The reaction mixture was refluxed under  $N_2$  for 4 h and then quenched with 20 mL of degassed, distilled water and 20 mL of hexane. The aqueous layer was separated and extracted with hexane (2 x 15 mL). The combined organic extracts were washed with sodium

bicarbonate solution (2 x 20 mL) and distilled water (20 mL), dried over  $\text{MgSO}_4$  and evaporated to a colorless oil. The monothioacetate was separated from the dithioacetate and residual starting material by column chromatography on silica gel 60 (Merck) using 19:1 hexane/ether as eluant to yield 4.5 g (17 mmol, 46%) of 8-bromooctyl thioacetate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.37 (t, 2 H), 2.83 (t, 2 H), 2.29 (s, 3 H), 1.82 (m, 2 H), 1.54 (m, 2 H).

8-Cyanooctyl thioacetate was prepared by the method of Friedman and Shechter.<sup>8</sup> Sodium cyanide (0.9 g, 18 mmol) was dissolved in 40 mL of DMSO at 60 °C and 8-bromooctyl thioacetate (4.5 g, 17 mmol) was added over a 5-min period to the stirred solution. After stirring at 60 °C for 30 min, the reaction mixture was cooled to room temperature, poured into 100 mL of water, and the product extracted with ether (3 x 20 mL). The ether extracts were combined, washed with brine (3 x 25 mL), dried over  $\text{MgSO}_4$  and evaporated to a yellow oil (3.2 g, 15 mmol, 89%).

Potassium carbonate (0.5 g) was dried and placed in 15 mL of degassed methanol. 8-Cyanooctyl thioacetate (1.1 g, 5.1 mmol) was added. The resulting slurry was stirred at room temperature under  $\text{N}_2$  for 3 h. The reaction mixture was quenched with 50 mL of aq ammonium chloride solution and 20 mL of ether. The aqueous layer was extracted with ether (2 x 20 mL), and the combined organic layers washed with distilled water (2 x 20 mL) and dried over  $\text{MgSO}_4$ . The solvent was evaporated to yield a colorless liquid (0.80 g, 4.7 mmol, 91%). Pure 8-cyano-1-octanethiol was

obtained by flash chromatography using 1:1 hexane/ether as eluant:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.49 (q, 2 H), 2.31 (t, 2 H), 1.5-1.7 (m, 4 H), 1.2-1.5 (m, 9 H). Anal. Calcd (Found) for  $\text{C}_9\text{H}_{17}\text{NS}$ : C, 63.11 (63.03); H, 10.00 (10.17).

**11-Mercapto-1-undecanol.** Sodium (0.23 g, 10 mg-atom), thiolacetic acid (0.71 mL, 10 mmol) and 11-bromo-1-undecanol (2 g, 8 mmol) were dissolved in 25 mL of degassed, anhyd methanol and refluxed under  $\text{N}_2$  for 5 h. Sodium methoxide (0.54 g, 10 mmol) was added and reflux maintained for a further 1.5 h. The reaction was allowed to cool to room temperature and then quenched with 30 mL of degassed, half-saturated ammonium chloride solution. An off-white solid precipitated. Recrystallization of this solid from 20 mL of hexane yielded 11-mercapto-1-undecanol (1.35 g, 83%) as white crystals. Traces of the disulphide were removed by flash chromatography (1:1 hexane/ethyl acetate) followed by recrystallization from hexane: mp 34-35 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.6 (q, 2 H), 2.5 (q, 2 H), 1.55 (m, 4 H), 1.2-1.4 (m, 15 H). Anal. Calcd (Found) for  $\text{C}_{11}\text{H}_{24}\text{OS}$ : C, 64.65 (64.72); H, 11.84 (11.75).

**Di(11-hydroxyundecyl) disulfide.** A solution of 11-hydroxyundecanethiol in ethanol was titrated with a 0.1 M solution of  $\text{I}_2$  in ethanol until a yellow color persisted. The reaction mixture was quenched with 10 mL of water and extracted twice with 10 mL of ether. The extracts were washed with water, dried over  $\text{MgSO}_4$ , and concentrated under vacuum. Recrystallization from hexane afforded a white solid: mp 81.5-82.5 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.62

(q, 4 H), 2.67 (t, 4 H), 1.5-1.7 (m, 8 H), 1.2-1.4 (m, 28 H).  
Anal. Calcd (Found) for  $C_{22}H_{46}O_2S_2$ : C, 64.97 (64.89); H, 11.39 (11.43).

**Diundecyl disulfide.** Undecanethiol was oxidised to diundecyl disulfide by the technique described for di(11-hydroxyundecyl) disulfide: mp 31.5-32 °C (lit.<sup>9</sup> mp 26-27 °C);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.67 (t, 4 H), 1.65 (m, 4 H), 1.2-1.4 (m, 32 H), 0.86 (t, 6 H).

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