Supporting Information

Monolayer Films Prepared by the Spontaneous Self-Assembly of Symmetrical and Unsymmetrical Dialkyl Sulfides from Solution onto Gold Substrates: Structure, Properties, and Reactivity of Constituent Functional Groups",

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General. Physical constants for all compounds described here are given in Table I in the journal text. 5-585-11

11-Methylthioundecanoic acid was prepared using the procedure of method A. The product was purified by passing through a column containing silica gel using a solution of acetone-hexane (1/10). Removal of the eluent by rotoevaporation afforded a white solid.

11-Hexylthioundecanoic acid was prepared as described in method B using 1-hexanethiol (1.00 g, 8.46 mmol), 11-bromoundecanoic acid (2.24 g, 8.46 mmol), and sodium metal (428 mg, 18.6 mg-atom) in degassed methanol. The product was recrystallized from hexanes. The product was purified by passing through a column containing silica gel with a solution of acetone-hexane (1/5), collecting 50~ mL fractions. Recrystallization of the product from hexanes afforded a white solid.

11-Decylthioundecanoic acid was prepared as described in method A using 1-bromodecane (1.02 g, 4.61 mmol), sodium metal (193 mg, 8.38 mg-atom), and 11-mercaptoundecanoic acid (0.915 g, 4.19 mmol) in degassed methanol. The product was recrystallized from hexanes and purified by passing a solution in acetone-hexane (1/9) through a column containing silica gel. Concentration of the eluent by rotoevaporation followed by recrystallization from hexanes afforded a white solid.

11-Undecylthioundecanoic acid was prepared as described in method A using 1-bromoundecane (1.08 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recystallization from hexane afforded a white solid.

11-Dodecylthioundecanoic acid was prepared exactly as described in method B. Recrystallization from hexanes afforded a white solid.

11-Tridecylthioundecanoic acid was prepared as described by method A using 1-bromotridecane (1.21 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Tetradecylthioundecanoic acid was prepared as described by method A using 1-bromotetradecane (1.27 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Pentadecylthioundecanoic acid was prepared as described in method A using 1-bromopentadecane (1.34 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Hexadecylthioundecanoic acid was prepared as described in method B using 1-hexadecanethiol (1.00 g, 3.87 mmol), sodium metal (178 mg, 7.74 mg-atom), and 11-bromoundecanoic acid (1.03 g, 3.87 mmol) in degassed methanol. Recrystallization from hexanes afforded a white solid.

11-Heptadecylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (0.500 g, 2.29 mmol), 1-bromoheptadecane (0.733 g, 2.29 mmol), and sodium metal (105 mg, 4.59 mg-atom). The product was recrystallized from hexanes and then passed through a column of silica gel with a solution of ethylacetate-hexanes (25/75). After chromatography,

the product was recrystallized from hexanes to afford a white solid.

1-Bromoheptadecane was prepared by the addition of 1-heptadecanol (10 g, 39 mmol) to a 250-mL round-bottomed flask. Acetic acid (50 mL) and 48% hydrobromic acid (50 mL) were added to the reaction flask and the mixture was refluxed for 72 h. The mixture was cooled to room temperature and hexanes (250 mL) were added to the mixture. The hexanes layer was separated and extracted with saturated aqueous sodium chloride (3 X 100 mL), dried over anhydrous sodium sulfate, and filtered. The bromide was separated easily from the starting alcohol by filtration through silica gel followed by rinsing the silica gel with hexanes (150 mL). Removal of the hexanes by rotoevaporation afforded a white solid: mp 29-31 ^{o}C.

11-Octadecylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (1.00 g, 9.16 mmol), 1-bromooctadecane (1.53 g, 4.58 mmol), and sodium metal (211 mg, 9.16 mg-atom). The product was recrystallized from hexanes and passed through a column of silica gel with a solution of ethyl acetate-chloroform (1/9) collecting 50 mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid. 11-Octadecylthioundecanoic acid was also prepared as described in method B using octadecanethiol (1.00 g, 3.49 mmol), sodium metal (160.5 mg, 6.98 mg-atom), and 11-bromoundecanoic acid (0.925 g, 3.49) in methanol. The product was recrystallized from hexanes and

passed through a column of silica gel (R_f = 0.4) with a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid.

11-Eicosylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol), 1-bromoeicosane (1.66 g, 4.59 mmol,), and sodium metal (211 mg, 9.18 mg-atom) in methanol. The addition of 50 mL of chloroform to the ethereal layer was necessary to improve solubility during work-up. The product was recrystallized from hexanes and passed through a column of silica gel (R_f= 0.5) with a solution of ethyl acetate-chloroform (1/9), collecting 50 mL fractions. Removal of the eluent by rotoevaporation followed by recrystallization from hexanes afforded a white solid.

11-Docosylthioundecanoic acid was prepared as described in method B from 1-docosanethiol (1.00g, 2.92 mmol), 11-bromoundecanoic acid (0.77 g, 2.92 mmol), and sodium metal (246 mg, 10.7 mg-atom) in methanol. The addition of chloroform to the ethereal layer was necessary to improve solubility during work-up. The product was recrystallized from hexanes (mp 87.5-89.0 ^{o}C) and passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9) and collecting 50 mL fractions. Removal of the eluent by rotoevaporation from fractions 5-12 followed by recrystallization from hexanes afforded a white solid. Docosanethiol was prepared by mixing 1-bromodocosane (18 g, 46.2 mmol), thiolacetic acid (6.6 mL, 92.4 mmol), and sodium metal

(2.12 g, 92.4 mg-atom) in a 500-mL round-bottomed flask containing 250 mL of degassed ethanol. The reaction mixture was refluxed under argon for 5 h. After cooling to room temperature, conc. HCl (25 mL) was added to the reaction vessel and the mixture was refluxed overnight. The thiol was purified by recrystallization from hexane to yield a white solid: mp 46-48 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 2.52 (q, 2 H); 1.61 (m); 1.25 (m).

16-Hexadecylthiohexadecanoic acid. 16-Bromohexadecanoic acid was prepared by refluxing a mixture of 16-hydroxyhexadecanoic acid (15 g), 48% hydrobromic acid (75 mL), and glacial acetic acid (75 mL) in a 500-mL round-bottomed flask for 2 days. After cooling the reaction mixture to room temperature, the bromide was isolated by filtration using a Buchner funnel and the product was rinsed with deionized water to remove excess hydrobromic acid and acetic acid. The product was recrystallized from hexanes: mp 68.5-70.3 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 3.39 (t, 2 H), 2.34 (t, 2 H), 1.84 (m, 2 H), 1.63 (m), 1.27 (m). To a 500 mL round-bottomed flask were added 16-bromohexadecanoic acid (5 g, 14.9 mmol), anhydrous methanol (250 mL), and concentrated sulfuric acid (3 mL). The reaction mixture was refluxed 24 hours. After cooling to room temperature, diethyl ether (300 mL) was added followed by the addition of enough water to form two phases. The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl solution (100 mL). The ethereal layer was dried with anhydrous sodium sulfate, filtered, and the ether was removed by rotoevaporation to afford a slightly yellow residue. Purification

of methyl 16-bromo- hexadecanoate (4 g) was accomplished by flash chromatography using silica gel and ether-hexanes (1/9) as the eluent, collecting 125-mL fractions. The product was recovered by rotoevaporation of fractions 5-8. After recrystallization from hexanes, white crystals were recovered.

16-Hexadecyl-thiohexadecanoic acid was prepared as described in method B using hexadecanethiol (0.37 g, 1.43 mmol), methyl 16-bromohexadecanoate (0.5 g, 1.43 mmol), sodium metal (250 mg, 10.9 mg-atom), and degassed ethanol as the solvent. The ester was isolated by the addition of diethyl ether (300 mL), water (200 mL), and concentrated hydrochloric acid (5 mL) to the reaction mixture. The ethereal layer was separated and extracted with water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. Removal of the ether by rotoevaporation afforded a white solid. The ester was hydrolyzed by refluxing in a solution of THF (100 mL), water (100 mL), and concentrated hydrochloric acid (5 mL) for 4 days. The product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. The solid residue was rinsed with water using suction filtration, dried, and recrystallized from THF, affording a white solid: mp 84-86 ^{o}C. The product was passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent from fractions 4-10 followed by recrystallization for hexanes afforded a white solid.

11-Hexadecyl-d_{33}-thioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (0.310 g, 1.42 mmol) and d_{33}-bromohexadecane (0.50 g, 1.48 mmol). The product was recrystallized from hexanes and passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid.

Di-n-dodecyl sulfide. To a 100-mL round-bottomed flask containing 50 mL of degassed ethanol were added 1-bromododecane (1.23 g, 4.94 mmol), dodecanethiol (1.0 g, 4.94 mmol.) and sodium metal (228 mg, 9.92 mg-atom). The reaction mixture was stirred at room temperature under argon for 18 h. The mixture was worked up by extraction with ether. The product was purified by repeated recrystallization from ethanol.

Bis-(1-carboxymethyl)sulfide was obtained from Aldrich and was recystallized from deionized water to afford a white crystalline solid.

Bis-(2-carboxyethyl)sulfide was obtained from Aldrich and was recrystallized from deionized water to afford a white crystalline solid.

Bis-(6-carboxyhexyl)sulfide was prepared by dissolving methyl-6-iodohexanoate[1] (5.6 g, 22 mmol) in 50 mL of anhydrous methanol (degassed by bubbling argon through the liquid with stirring for at least 1 h) in a 250-mL round-bottomed flask. Lithium sulfide (0.5 g, 11 mmol) was added and the reaction mixture

stirred overnight under argon. The reaction was poured, with stirring, into a 500-mL beaker containing diethyl ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL), and sat aq NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a colorless liquid. The liquid (bis-(6-carbomethoxyhexyl)sulfide) was hydrolyzed by adding the ester to a 250 mL round-bottomed flask containing degassed 1 N aqueous NaOH (25 mL, 25 mmol) and degassed methanol (50 mL). After refluxing for 5 h, the product was isolated by neutralizing with cold, dilute HCl and extracting with ether. The ethereal layer was extracted with deionized water (3 X 100 mL), dried over anhydrous sodium sulfate, and filtered. After removal of the ether, a white solid was recovered. Recrystallization from deionized water gave white crystals.

Bis-(11-carboxyundecyl)sulfide was prepared by dissolving lithium sulfide (1.38 g, 30.2 mmol) in 50 mL of anhyd. methanol (degassed by bubbling argon gas through the liquid with stirring for at least 1 h) in a 100-mL flask. 11-Bromoundecanoic acid (2.00 g, 7.54 mmol) was added and the reaction mixture stirred for 4 h under argon. The reaction was poured, with stirring, into a 500-mL beaker containing diethyl ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a white solid. Recrystallization from hexanes gave white crystals: mp 109-110 ^{o}C Further purification was accomplished by flash chromatography using

silica gel and acetone/chloroform (1/3) as eluent, collecting 50-mL fractions. The product was recovered from fractions 5-12 and recrystallized from acetone.

Bis-(16-carbomethoxyhexadecyl)sulfide. Methyl 16-bromohex-adecanoate was prepared from 16-hydroxyhexadecanoic acid as described previously in the procedure for the preparation of 16-hexadecylthiohexadecanoic acid. To a 100-mL round-bottomed flask containing 50 mL of degassed methanol were added methyl 16-bromo-
hexadecanoate (1.0 g, 3.0 mmol) and lithium sulfide (154 mg, 3.1 mmol) and the reaction mixture was stirred under argon overnight at room temperature. The reaction was poured with stirring into a 500-mL beaker containing THF (300 mL). The ethereal layer was extracted with deionized water (2 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation and the residue was recrystallized from hexanes to afford a white solid. Further purification was accomplished by flash chromatography through silica gel using chloroform as the eluent and collecting 50-mL fractions. The product was recovered from fractions 6-10. After removal of the chloroform by rotoevaporation, the product was recrystallized from hexanes to afford white crystals.

Bis-(16-carboxyhexadecyl)sulfide was prepared by the hydrolysis of bis-(16-carbomethoxyhexadecyl)sulfide. The ester was hydrolyzed by refluxing the ester in a solution of THF (100 mL), water (100 mL), and conc. HCl (5 mL) for 4 days. After cooling the

reaction mixture to room temperature, the product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. The solid residue was rinsed with water under suction filtration, dried, and recrystallized from THF, affording a white solid.

Bis-(21-carboxyhenoicosyl)sulfide. Ethyl 21-docosenoate was

prepared as described previously[1] from 11-bromoundecene and ethyl 11-iodoundecanoate. The procedure of Brown[2] was followed using ethyl 21-docosenoate (10.0 g, 27.3 mmol) and 1.0 M borane in THF (10 mL, 10.0 mmol, Aldrich). Subsequently, 1 M sodium hydroxide (30.3 mL, 30.3 mmol) and 30% H_2O_2 (10.4 mL, 30.3 mmol) were added to the borane. The THF layer of the reaction mixture was washed with sat. aq. NaCl (3 X 100 mL) dried over anhydrous Na_2SO_4, and filtered. The solvent was removed by rotoevaporation to afford 8.4 g (80% yield) of white solid. ^1H NMR ($CDCl_3$) δ 4.11 (Q, 2 H), 3.63 (t, 2 H), 2.27 (t, 2 H); 1.59 (m); 1.27 (m). Ethyl 22-tosyldocosanoate was prepared following a procedure described previously[3] by adding ethyl 22-hydroxydocosanoate (8.4 g, 21.8 mmol) to a 100-mL round-bottomed flask containing pyridine (60 mL). The solution was warmed until the alcohol dissolved completely and then cooled to 20 °C to form a turbid solution. Tosyl chloride (4.58 g, 24.0 mmol) was added to the flask while keeping the temperature of the mixture below 20 °C. The reaction mixture was allowed to stand in a refrigerator overnight. The crude tosylate was poured into a 1000-mL beaker containing ice-water (400 mL) and conc. HCl (5 mL)

and the mixture was stirred with a spatula. The white precipitate was collected by suction filtration and excess water removed by pressing the product against the Buchner funnel with a spatula. The tosylate was purified further by dissolving it in ether (250 mL) (stirring for several hours at room temperature was necessary), washing the ethereal layer with 0.1 N HCl (100 mL) and with ice-cold deionized water (3 X 100 mL) and drying with anhydrous Na_2SO_4. The ethereal solution was decolorized with Norit, filtered, and the ether removed by rotoevaporation to afford a white solid: mp 67.5-69.6 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (AA'BB', 4 H), 4.12 (Q, 2 H), 4.01 (t, 2 H), 2.44 (s, 3 H), 2.27 (t, 2 H), 1.60 (m, 4 H), 1.24 (m). Ethyl 22-iododocosanoate was prepared as described previously for ethyl 11-iodoundecanoate by dissolving ethyl 22-tosyldocosanoate (3.5 g, 6.51 mmol) and NaI (1.95 g, 13.0 mmol) in 150-mL of acetone in a 250-mL round-bottomed flask and heating the mixture at reflux for 24 h. The reaction mixture was allowed to cool to room temperature and 250 mL of diethyl ether were added to the flask. The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous Na_2SO_4, and filtered. After removal of the ether by rotoevaporation, a white solid was obtained that was purified further by passing through a column of silica gel using ether-hexanes (1/9) as the eluent.

Bis-(21-carboethoxyheneicosyl)sulfide was prepared by adding ethyl 22-iododocosanoate (2.2 g, 4.5 mmol) to 100 mL of degassed, anhydrous methanol in a 250-mL round-bottomed flask.

Lithium sulfide (102 mg, 2.2 mmol) was added and the reaction mixture was heated at reflux under argon overnight. The mixture was cooled to room temperature, filtered and rinsed with deionized water. The white solid was recrystallized from hexanes to afford white crystals of bis-(carboethoxydocosyl)sulfide and bis-(21-carbomethoxyheneicosyl)sulfide. The esters were hydrolyzed in a solution of THF (100 mL), water (100 mL), and conc. HCl (5 mL) for 4 days. The product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. This residue was rinsed with deionized water under suction filtration, dried, and recrystallized from THF, affording a white solid.

Bis-(11-hydroxyundecyl)sulfide was prepared by dissolving lithium sulfide (0.95 g, 20.8 mmol) in 200 mL of degassed anhydr methanol in a 500-mL round-bottomed flask, adding 11-bromo-1-undecanol (5.22 g, 20.8 mmol, 98%, Aldrich, purified by recrystallization from hexanes) and stirring under argon for 24 h. The reaction mixture was poured, with stirring, into a 500-mL beaker containing ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a white solid. Recrystallization from hexanes gave a white solid. Further purification was accomplished by flash chromatography (R_f = 0.4) using silica gel and acetone/chloroform (1/3) as eluent. The product was recrystallized from hexanes.

References

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3) Marvel, E.S.; Sekera, V.C. In Organic Syntheses; Horning, E.C., Ed.; Wiley: New York, 1955; Collected Vol. 3, p 366.