Supporting Information

for

Robust Thick Polymer Brushes Grafted from Gold Surfaces Using Bidentate Thiol-Based Atom-Transfer Radical Polymerization Initiators

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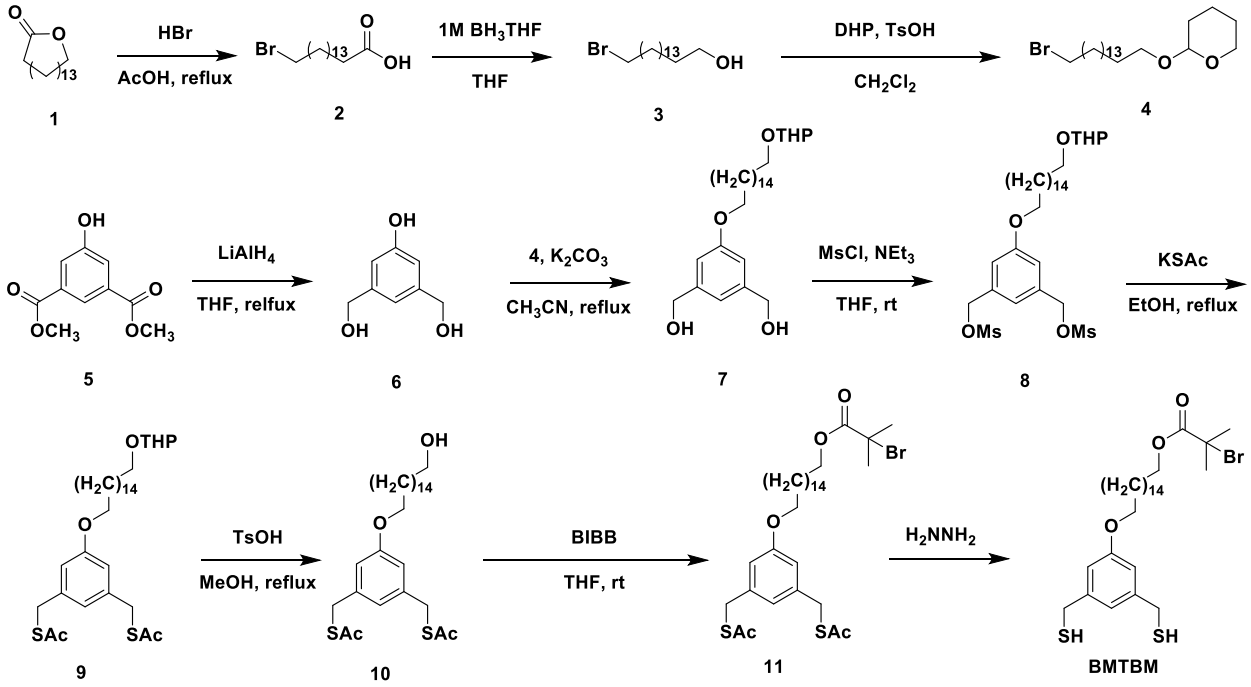
SYNTHETIC PROCEDURES

Synthesis of 16-(3,5-Bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methyl-propanoate (BMTBM). Scheme S1 shows the synthetic strategy used to prepare **BMTBM**; the experimental details are provided in the following paragraphs.

Scheme S1. Synthesis of 16-(3,5-Bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methyl-propanoate (**BMTBM**)



16-Bromohexadecanoic acid (2). ω-Hexadecalactone **1** (5.0 g, 20 mmol), 48% hydrobromic acid in water (10 mL), and acetic acid (250 mL) were introduced into a 500 mL round-bottomed flask and refluxed for 24 h. After the reaction mixture was cooled to rt, water (100 mL) was added to the flask containing the reaction mixture. The heterogeneous mixture was placed in an ice bath for 1 h and allowed to form a precipitate. The precipitate was filtered, washed extensively with water (5 × 100 mL) to remove traces of acetic acid, and recrystallized from hexanes to give the pure product (5.1 g, 15 mmol) as a white solid (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.40 (t, J = 6.8 Hz, 2H), 2.34 (t, J = 7.3 Hz, 2H), 1.84–1.21 (m, 26H).

16-Bromohexadecan-1-ol (3). A mixture of 16-bromohexadecanoic acid (5.1 g, 15 mmol) and THF (200 ml) were added to a 500 mL round-bottomed flask suspended in an ice bath. 1M

BH_3-THF (40 mL, 40 mmol) was then carefully added to the reaction flask using a syringe. After stirring for 30 min, the ice bath was removed. The reaction mixture was further stirred at room temperature for 5 hours. The reaction was quenched with 200 mL water and the mixture was extracted with 200 mL ether. The organic phase was concentrated in vacuo to produce 4.0 g (12 mmol) of a white solid product (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.86–1.24 (m, 28H).

2-((16-Bromohexadecyl)oxy)tetrahydro-2H-pyran (4). An aliquot of 4.0 g (12 mmol) of **3** and *p*-toluenesulfonic acid (0.23 g, 1.2 mmol) were introduced into a 200 mL round-bottomed flask with 200 mL CH_2Cl_2, and 3,4-dihydropyran (0.58 mL, 6.4 mmol) was added to the mixture dropwise while the flask was suspended in an ice bath. The ice bath was removed after 30 min, and the reaction mixture was stirred for 4 hours. The reaction was then quenched with 200 mL water, and the mixture extracted with 200 mL CH_2Cl_2, and concentrated in vacuo to give 4.2 g (10 mmol) of a brown liquid product (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 (t, J = 4.0 Hz, 1H), 3.86 (m, 2H), 3.73 (m, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.87–1.20 (m, 34H).

(5-Hydroxy-1,3-phenylene)dimethanol (6). A THF solution (25 mL) of dimethyl 5-hydroxyisophthalate (3.00 g, 14.2 mmol) was added to a THF (40 mL) suspension of $LiAlH_4$ (2.0 g, 53 mmol) dropwise at 0 °C. After 30 min, the ice bath was removed, and the reaction mixture was refluxed for 6 h. After completion of the reaction, 5M HCl solution was carefully added at 0 °C to deactivate any residual reducing agent. The reaction mixture was filtered, and the filtrate was condensed via rotary evaporation to give (5-hydroxy-1,3-phenylene)dimethanol (1.4 g, 9.0 mmol) as a white solid (63% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 6.79 (s, 1H), 6.71 (s, 2H), 4.50 (s, 4H).

(5-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)-1,3-phenylene)dimethanol (7). A mixture of (5-hydroxy-1,3-phenylene)dimethanol (1.4 g, 9.0 mmol), K_2CO_3 (1.4 g, 10 mmol), and **4** (3.0 g, 7.3 mmol) in acetonitrile (150 mL) was refluxed for 12 h. After cooling to rt, water (100 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (300 mL). The organic layer was concentrated using rotary evaporation to obtain 2.5 g (5.2 mmol) of a pale brown solid (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H), 6.84 (s, 2H), 4.66 (s, 4H), 4.56 (t, J = 4.0, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.86 (m, 2H), 3.72 (m, 2H), 3.38 (m, 2H), 1.74–1.21 (m, 34H).

(5-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)-1,3-phenylene)bis(methylene) dimethanesulfonate (8). Compound **7** (2.5 g, 5.2 mmol) was introduced into a 250 mL round-bottomed flask containing 100 mL of THF, and then triethylamine (0.7 mL, 12 mmol) was added to the solution. The reaction flask was placed in an ice bath, and methanesulfonyl chloride (1.2 mL, 16 mmol) was added slowly into the flask during stirring. After 2 h, the ice bath was removed, and then water (100 mL) was added to destroy the remaining methanesulfonyl chloride. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the organic layer was washed with 3 M HCl solution (50 mL) and water (2 × 100 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated using a rotary evaporator to produce compound **8** (3.0 g, 4.7 mmol), which was used in the next step without further purification (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 1H), 6.94 (s, 2H), 5.19 (s, 4H), 4.56 (t, J = 4.0, 1H), 3.95 (t, J = 6.4 Hz, 2H), 3.88 (m, 2H), 3.71 (m, 2H), 3.35 (m, 2H), 2.97 (s, 6H), 1.80–1.23 (m, 34H).

(5-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)-1,3-phenylene)bis(methylene)) diethanethioate (9). Compound **8** (3.0 g, 4.7 mmol) and potassium thioacetate (1.35 g, 11.7 mmol) were introduced into a 500 mL round-bottomed flask containing 200 mL of ethanol under nitrogen. The reaction mixture was refluxed for 8 h. After cooling to rt, the precipitate was removed by vacuum filtration, and the organic phase was condensed by rotary evaporation. The residue was taken up in a blend of dichloromethane (100 mL) and water (100 mL), and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layers were washed with brine (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated via rotary evaporation. The crude product was purified by column chromatography (in hexanes:ethyl acetate = 9:1) to give 1.2 g (2.0 mmol) of **9** as a transparent liquid (42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (s, 1H), 6.72 (s, 2H), 4.56 (t, J = 4.0, 1H), 4.03 (s, 4H), 3.90 (m, 2H) 3.73 (m, 2H), 3.36 (m, 2H), 2.32 (s, 6H), 1.73–1.18 (m, 34H).

((5-((16-Hydroxyhexadecyl)oxy)-1,3-phenylene)bis(methylene)) diethanethioate (10). *p*-Toluenesulfonic acid (0.38 g, 2.0 mmol) and **9** (1.2 g, 2.0 mmol) were added to a 250 mL round-bottomed flask containing methanol (100 mL), and this mixture was refluxed for 2 h. After completion of the reaction, saturated $NaHCO_3$ solution was added to the reaction vessel, and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layer was dried over

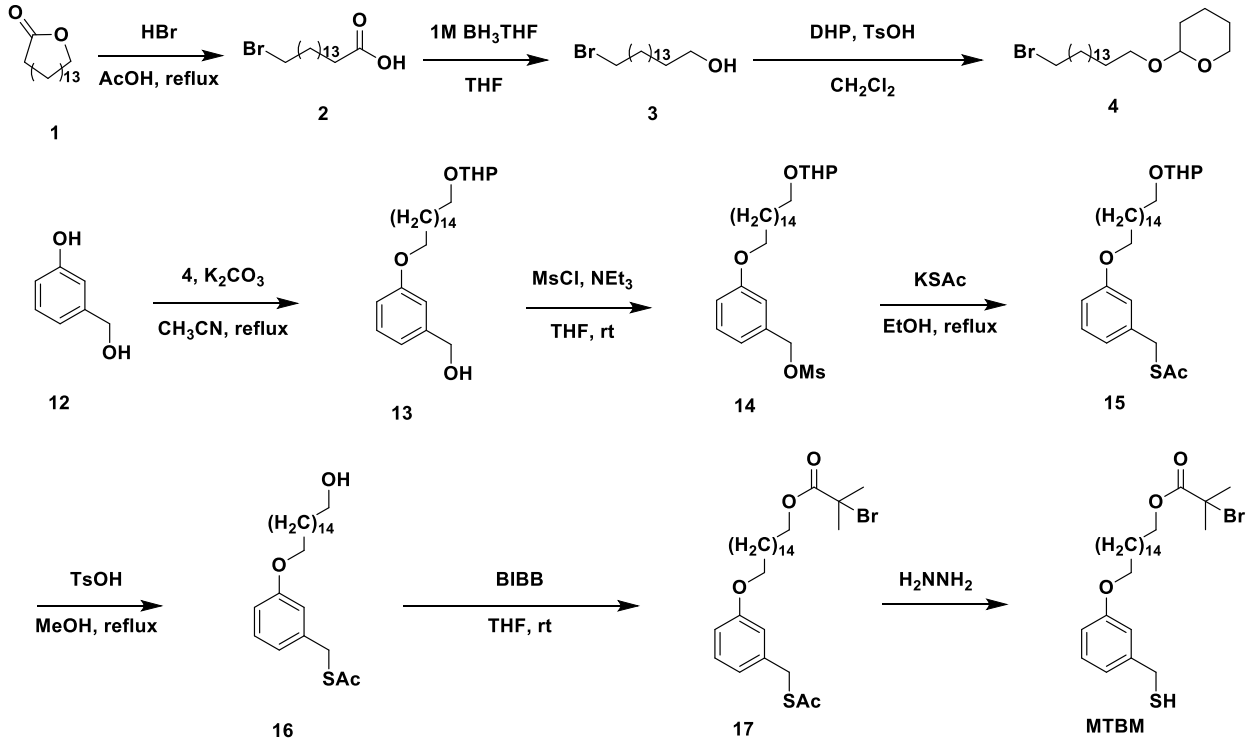
sodium sulfate, filtered, and concentrated using a rotary evaporator to give **10** (0.71 g, 1.4 mmol), which was used in the next step without further purification (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (s, 1H), 6.69 (s, 2H), 4.03 (s, 4H), 3.87 (t, *J* = 6.4 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 6H), 1.73–1.23 (m, 28H).

16-(3,5-Bis((acetylthio)methyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (11). Compound **10** (0.71 g, 1.4 mmol) was introduced into a 250 mL round-bottomed flask containing 100 mL of THF under nitrogen. Subsequently, α-bromoisobutyryl bromide (0.24 mL, 2.0 mmol) was added carefully to the reaction vessel at 0 °C. After 4 h, the reaction was quenched by adding 100 mL of water at 0 °C, and the volatiles were removed by rotary evaporation. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9:1) to obtain the pure compound **11** (0.82 g, 1.2 mmol) as a transparent liquid (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (s, 1H), 6.69 (s, 2H), 4.15 (t, *J* = 6.4 Hz, 2H), 4.03 (s, 4H), 3.89 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 6H), 1.92 (s, 6H), 1.81–1.21 (m, 28H).

16-(3,5-Bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (BMTBM). Compound **11** (0.82 g, 1.2 mmol) was introduced into a 100 mL round-bottomed flask with 10 mL of THF, and after 20 min, 12 mL of 1 M NH_2NH_2 in THF was introduced carefully to the reaction flask. After 3 h of stirring, 3 mL of 4 M hydrogen chloride in dioxane was carefully added to the reaction solution. The crude product was purified by column chromatography (in hexanes:ethyl acetate = 9.7:0.3) to obtain pure **BMTBM** (0.25 g, 0.49 mmol) as a transparent liquid (40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 1H), 6.74 (s, 2H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.66 (d, *J* = 7.3 Hz, 4H), 1.77–1.25 (m, 28H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.83, 159.71, 142.98, 119.88, 112.97, 68.11, 66.26, 56.12, 30.88, 29.76, 29.73, 29.70, 29.68, 29.64, 29.58, 29.27, 29.10. ESI-MS: 575 $[C_{28}H_{47}O_3S_2{}^{79}Br+H]^+$, 577 $[C_{28}H_{47}O_3S_2{}^{81}Br+H]^+$, 592 $[C_{28}H_{47}O_3S_2{}^{79}Br+NH_4]^+$, 594 $[C_{28}H_{47}O_3S_2{}^{81}Br+NH_4]^+$, 597 $[C_{28}H_{47}O_3S_2{}^{79}Br+Na]^+$, 599 $[C_{28}H_{47}O_3S_2{}^{81}Br+Na]^+$.

Synthesis of 16-(3-(Mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (MTBM). MTBM was prepared according to Scheme S2. The experimental details are provided in the following paragraphs.

Scheme S2. Synthesis of 16-(3-(Mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methyl-propanoate (**MTBM**)



(3-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)phenyl)methanol (13). A mixture of (5-hydroxy-1,3-phenylene)dimethanol (1.1 g, 9.0 mmol), K_2CO_3 (1.4 g, 10 mmol), and **4** (3.0 g, 7.3 mmol) in acetonitrile (150 mL) was refluxed for 12 h. After cooling to rt, water (100 mL) was added to the reaction, and the mixture was extracted with CH_2Cl_2 (300 mL). The combined organic layers were concentrated using a rotary evaporator to obtain 3.1 g (7.0 mmol) of a pale brown solid (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 7.4 Hz, 1H), 6.92 (m, 2H), 6.82 (d, J = 8.2 Hz, 1H), 4.66 (s, 2H), 4.55 (t, J = 4.0 Hz, 1H), 3.95 (t, J = 6.8 Hz, 2H), 3.88 (m, 2H), 3.73 (m, 2H), 3.38 (m, 2H), 1.82–1.38 (m, 34H).

3-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)benzyl methanesulfonate (14). Compound **13** (3.1 g, 7.0 mmol) was introduced into a 250 mL round-bottomed flask containing 100 mL of THF, and then trimethylamine (0.61 mL, 10 mmol) was added to the solution. The reaction flask was placed in an ice bath, and methanesulfonyl chloride (0.75 mL, 10 mmol) was added slowly into the flask with stirring. After 2 h, the ice bath was removed, and water (100 mL) was added to destroy any remaining methanesulfonyl chloride. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and then the organic layer was washed with 3 M HCl solution (50 mL) and water (2 × 100 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated using a rotary evaporator to give **14** (2.9 g, 5.6 mmol), which was used in the next step without further purification (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, J = 7.4 Hz, 1H), δ 6.97 (m, 2H), 6.72 (m, 1H), 5.20 (s, 2H), 4.55 (t, J = 4.0 Hz, 1H), 3.94 (t, J = 6.8 Hz, 2H), 3.84 (m, 2H), 3.74 (m, 2H), 3.38 (m, 2H), 2.90 (s, 3H), 1.85–1.24 (m, 34H).

(3-((16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl)oxy)benzyl) ethanethioate (15). Compound **14** (2.9 g, 5.5 mmol) and potassium thioacetate (0.67 g, 5.7 mmol) were introduced into a 500 mL round-bottomed flask containing 200 mL of ethanol under nitrogen. The reaction mixture was then refluxed for 8 h. After cooling to rt, the precipitate was removed using vacuum filtration, and the organic phase was concentrated using a rotary evaporator. The residue was taken up in a blend of dichloromethane (100 mL) and water (100 mL), and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layers were washed with brine (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated via rotary evaporation. The crude product was purified by column chromatography (in hexanes:ethyl acetate = 9:1) to give 1.5 g (3.0 mmol) of **15** as a transparent liquid (54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, J = 7.8 Hz, 1H), 6.86 (m, 2H), 6.76 (d, J = 7.8 Hz, 1H), 4.56 (t, J = 4.0 Hz, 1H), 4.03 (s, 2H), 3.91 (t, J = 6.8 Hz, 2H) 3.86 (m, 2H), 3.73 (t, J = 6.8 Hz, 2H), 3.36 (m, 2H), 2.33 (s, 3H), 1.86–1.23 (m, 34H).

(3-((16-Hydroxyhexadecyl)oxy)benzyl) ethanethioate (16). *p*-Toluenesulfonic acid (0.55 g, 2.9 mmol) and **15** (1.5 g, 3.0 mmol) were added to a 250 mL round-bottomed flask containing methanol (100 mL), and the mixture then was refluxed for 2 h. After completion of the reaction, saturated $NaHCO_3$ solution was added to the reaction vessel, and the mixture was extracted with

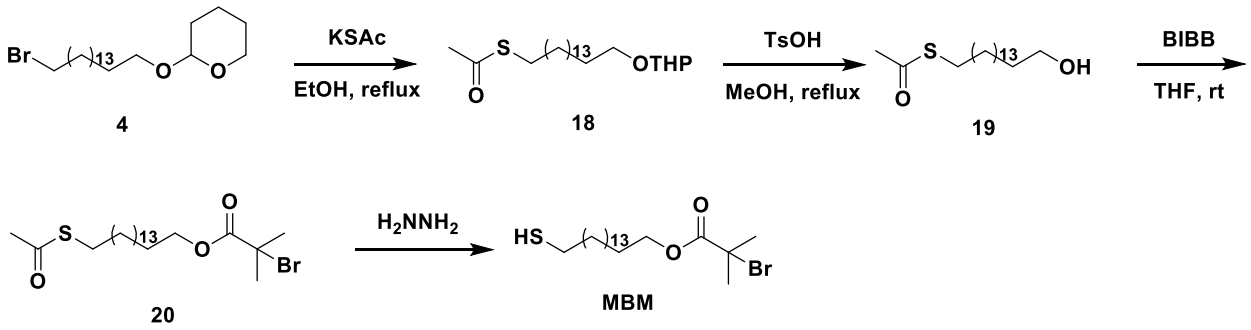
dichloromethane (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated with a rotary evaporator to give compound **16** (0.9 g, 2 mmol), which was used in the next step without further purification (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.82 (m, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.07 (s, 2H), 3.91 (t, *J* = 6.8 Hz, 2H), 3.62 (m, 2H), 2.34 (s, 3H), 1.80–1.19 (m, 28H).

16-(3-((Acetylthio)methyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (17). Compound **16** (0.9 g, 2 mmol) was introduced into a 250 mL round-bottomed flask containing 100 mL of THF under nitrogen. α-Bromoisobutyryl bromide (0.26 mL, 2.0 mmol) was then added carefully to the reaction vessel at 0 °C. Subsequently, the reaction flask was warmed to rt. After 4 h of stirring at rt, the reaction was quenched by adding 100 mL of water at 0 °C, and the resulting solution was concentrated using a rotary evaporator. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9:1) to obtain pure compound **17** (0.78 g, 1.3 mmol) as a transparent liquid (61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.81 (m, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 4.07 (s, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H) 1.92 (s, 6H), 1.81–1.23 (m, 28H).

16-(3-(Mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (MTBM). Compound **17** (0.78 g, 1.3 mmol) was introduced into a 100 mL round-bottomed flask along with 10 mL of THF. A 13 mL portion of 1 M NH_2NH_2 in THF was then introduced carefully into the reaction flask over a period of 20 min. After 3 h, 3.2 mL of 4 M hydrogen chloride in dioxane was carefully added to the reaction solution. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9.7:0.3) to obtain pure **MTBM** (0.24 g, 0.45 mmol) as a transparent liquid (33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 8.2 Hz, 1H), 6.86 (m, 2H), 6.76 (dd, *J* = 8.2, *J* = 2.1, Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.69 (d, *J* = 7.3 Hz, 2H), 1.92 (s, 6H), 1.81–1.20 (m, 28H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.85, 159.46, 142.69, 129.73, 120.17, 114.31, 114.16, 68.04, 66.27, 56.12, 30.88, 29.76, 29.73, 29.70, 29.64, 29.58, 29.38, 29.27. ESI-MS: 529 $[C_{27}H_{45}O_3S^{79}Br+H]^+$, 531 $[C_{27}H_{45}O_3S^{81}Br+H]^+$, 546 $[C_{27}H_{45}O_3S^{79}Br+NH_4]^+$, 548 $[C_{27}H_{45}O_3S^{81}Br+NH_4]^+$, 551 $[C_{27}H_{45}O_3S^{79}Br+Na]^+$, 553 $[C_{27}H_{45}O_3S^{81}Br+Na]^+$.

Synthesis of 16-Mercaptohexadecyl 2-bromo-2-methylpropanoate (MBM). **MBM** was prepared according to Scheme S3. The experimental details are provided in the following paragraphs.

Scheme S3. Synthesis of 16-Mercaptohexadecyl 2-bromo-2-methylpropanoate (**MBM**)



S-(16-((Tetrahydro-2H-pyran-2-yl)oxy)hexadecyl) ethanethioate (18). Compound **4** (2.0 g, 3.8 mmol) and potassium thioacetate (0.54 g, 4.5 mmol) were introduced into a 500 mL round-bottomed flask containing 200 mL of ethanol under nitrogen. The reaction mixture was then refluxed for 8 h. After cooling to rt, the precipitate was removed using vacuum filtration, and the organic phase was concentrated using a rotary evaporator. The residue was taken up in a blend of dichloromethane (100 mL) and water (100 mL), and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layers were washed with brine (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated via rotary evaporation. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9:1) to give 1.4 g (3.5 mmol) of compound **18** as a transparent liquid (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.55 (t, J = 4.0 Hz, 1H), 3.86 (m, 2H), 3.72 (m, 2H), 3.38 (m, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 1.88–1.17 (m, 34H).

S-(16-Hydroxyhexadecyl) ethanethioate (19). *p*-Toluenesulfonic acid (0.66 g, 3.5 mmol) and **18** (1.4 g, 3.5 mmol) were added to a 250 mL round-bottomed flask containing methanol (100 mL), and the reaction mixture was refluxed for 2 h. After completion of the reaction, saturated $NaHCO_3$ solution was added to the reaction vessel, and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered, and

concentrated with a rotary evaporator to give compound **19** (0.81 g, 2.5 mmol), which was used in the next step without further purification (69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, J = 6.8 Hz, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 1.79–1.19 (m, 28H).

16-(Acetylthio)hexadecyl 2-bromo-2-methylpropanoate (20). Compound **19** (0.81 g, 2.5 mmol) was introduced into a 250 mL round-bottomed flask containing 100 mL of THF under nitrogen. α-Bromoisobutyryl bromide (0.33 mL, 2.5 mmol) was added carefully to the reaction vessel at 0 °C. Subsequently, the reaction flask was warmed to rt. After 4 h of stirring at rt, the reaction was quenched by adding 100 mL of water at 0 °C, and the resulting solution was concentrated using a rotary evaporator. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9:1) to obtain the pure compound **20** (0.68 g, 1.4 mmol) as a transparent liquid (59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (t, J = 6.8 Hz, 2H), 2.83 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 1.92 (s, 6H), 1.72–1.18 (m, 28H).

16-Mercaptohexadecyl 2-bromo-2-methylpropanoate (MBM). Compound **20** (0.68 g, 1.4 mmol) was introduced into a 100 mL round-bottomed flask along with 10 mL of THF. An aliquot of 14 mL of 1 M NH_2NH_2 in THF was introduced carefully into the reaction flask over a period of 20 min. After 3 h, 3.5 mL of 4 M hydrogen chloride in dioxane was carefully added to the reaction solution. The crude product was purified by column chromatography (hexanes:ethyl acetate = 9.7:0.3) to obtain pure **MBM** (0.46 g, 1.0 mmol) as a transparent liquid (71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (t, J = 6.8 Hz, 2H), 2.50 (q, J = 4.5 Hz, 2H), 1.92 (s, 6H), 1.72–1.18 (m, 28H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.86, 76.85, 66.27, 56.11, 30.88, 29.75, 29.68, 29.63, 29.61, 29.57, 28.48, 28.43, 25.87. ESI-MS: 423 $[C_{20}H_{39}O_2S^{79}Br+H]^+$, 425 $[C_{20}H_{39}O_2S^{81}Br+H]^+$, 440 $[C_{20}H_{39}O_2S^{79}Br+NH_4]^+$, 442 $[C_{20}H_{39}O_2S^{81}Br+NH_4]^+$,445 $[C_{20}H_{39}O_2S^{79}Br+Na]^+$, 447 $[C_{20}H_{39}O_2S^{81}Br+Na]^+$.

INSTRUMENTAL PROCEDURES

Ellipsometric Measurements of Film Thickness. The thicknesses of the organic monolayers were measured with a Rudolph Research Auto EL III ellipsometer operating with a He-Ne laser at a wavelength of 632.8 nm, reflecting off the slides at a fixed angle of incidence of 70°. Thickness measurements were obtained from three different regions on two slides for each of the organic films. The reported ellipsometric thicknesses for the SAMs were observed to be reproducible within ± 2 Å.

Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) Measurements. Surface IR spectra were collected with a Nicolet NEXUS 670 FT-IR spectrophotometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM 90 photoelastic modulator running at 37 kHz. The p-polarized light was reflected from the sample at an angle of incidence of 80º with respect to the surface normal. We collected the spectra over 256 scans at a spectral resolution of 2 cm^{-1}.

X-Ray Photoelectron Spectroscopy (XPS) Measurements. A PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer was used to obtain X-ray photoelectron spectra for all monolayer samples. The spectrometer was set up with a pass energy of 23.5 eV and a photoelectron takeoff angle of 45° from the surface. Spectra were collected at rt and at a base pressure of 2×10^{-8} Torr. The binding energy of the Au $4f_{7/2}$ peak at 84.0 eV was used as a reference peak for the collected data.

SPECTRAL DATA

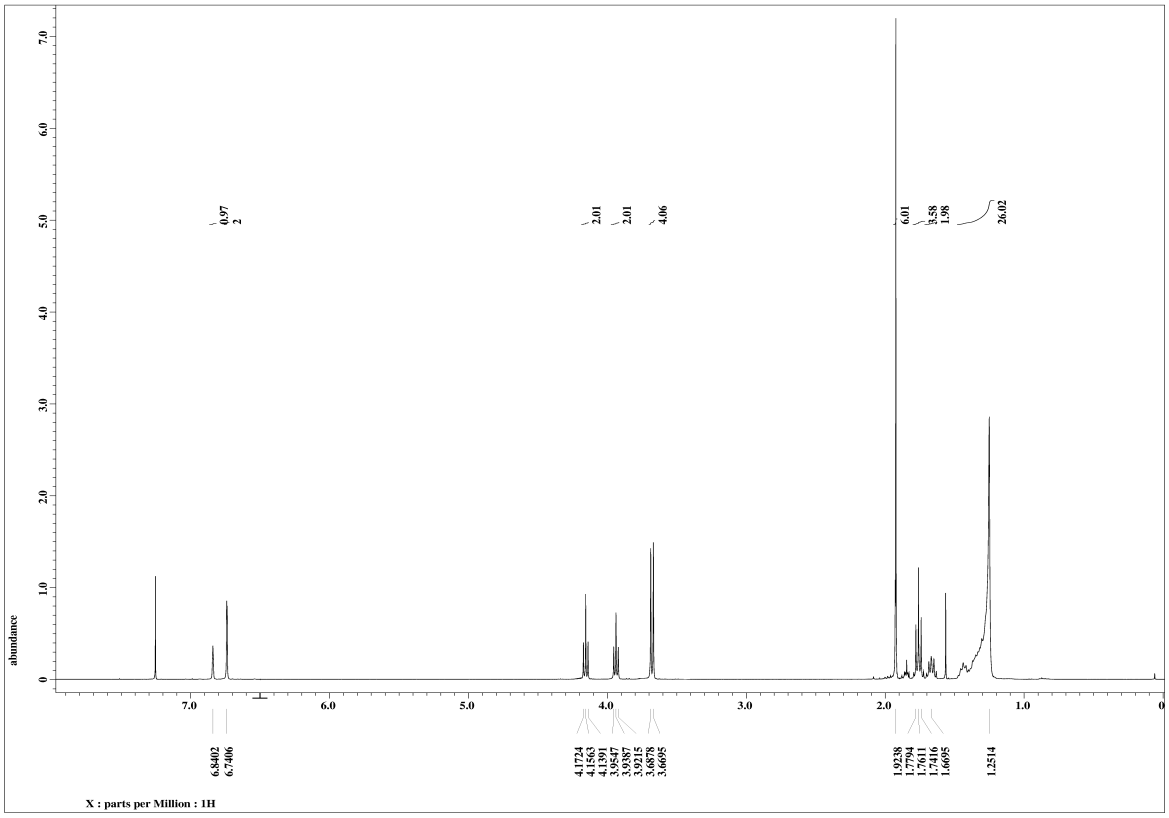


Figure S1. ^{1}H NMR spectrum of 16-(3,5-bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (**BMTBM**).

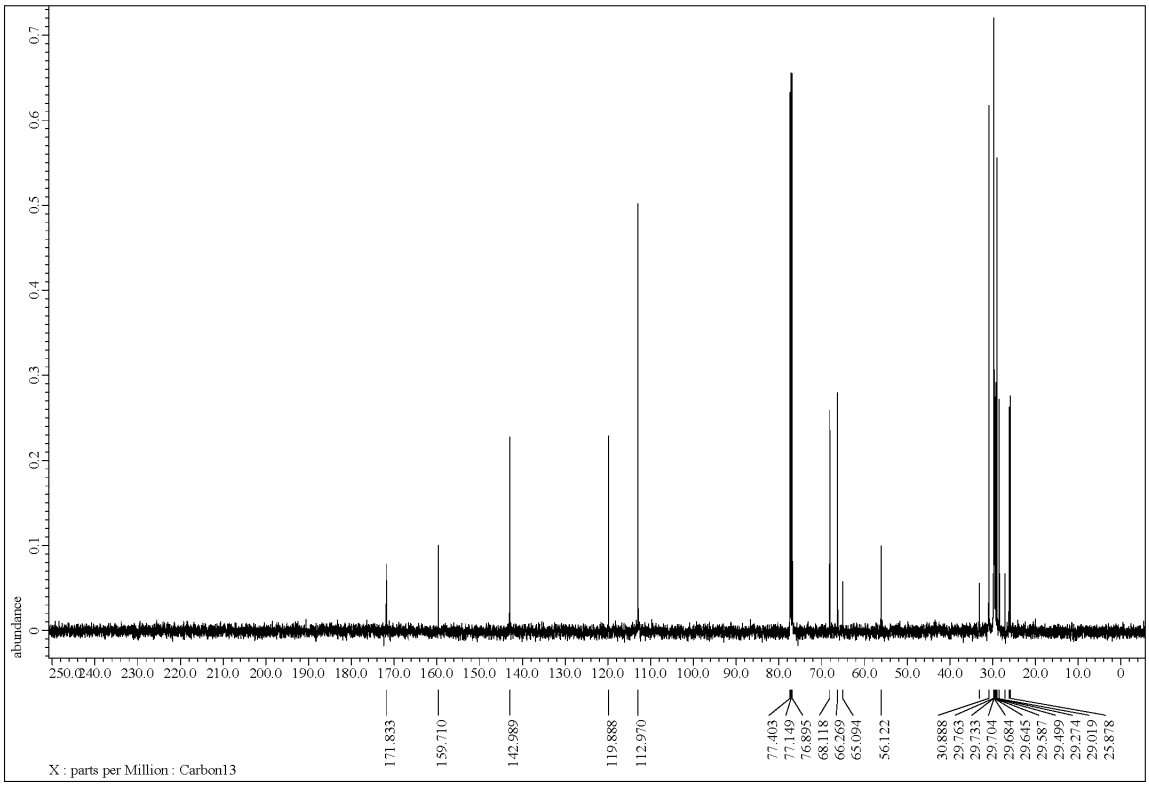


Figure S2. ^{13}C NMR spectrum of 16-(3,5-bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (**BMTBM**).

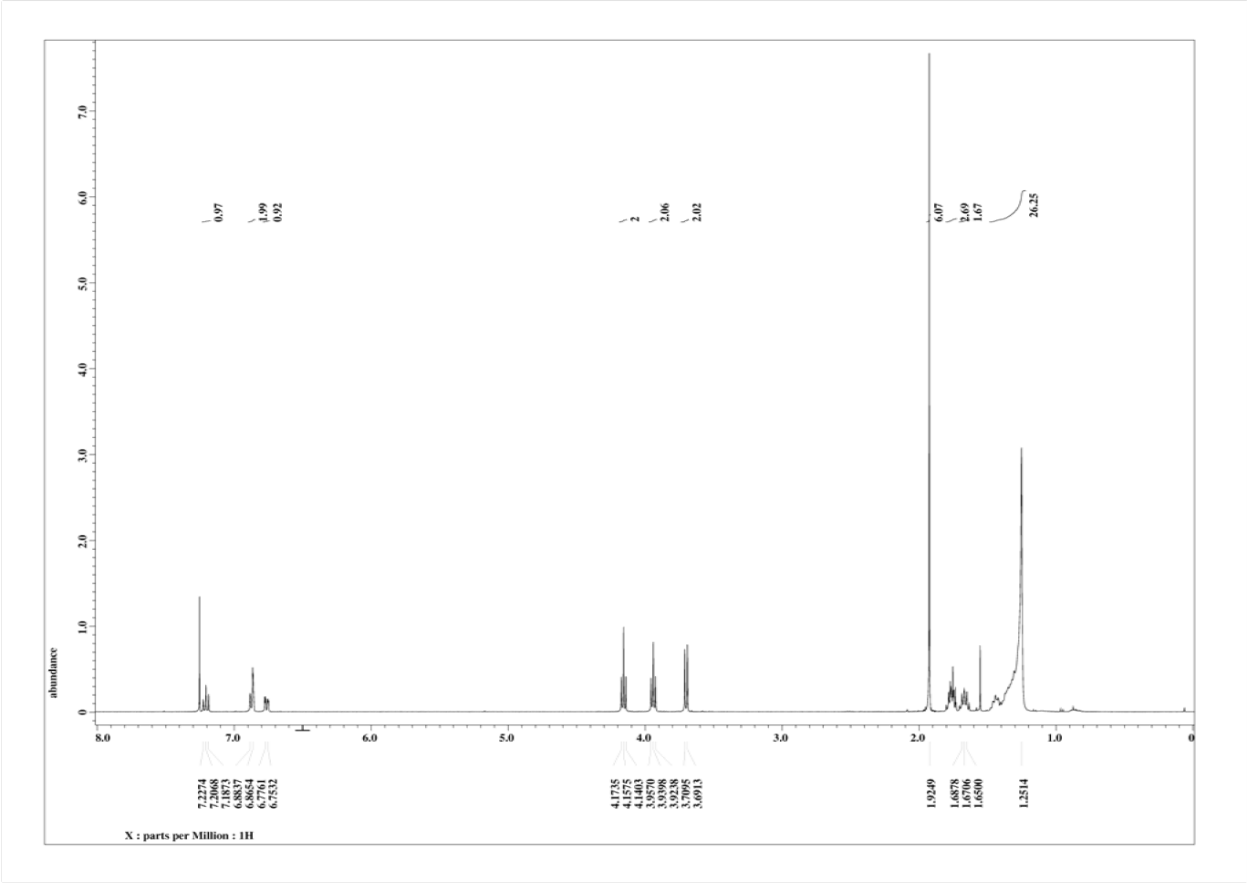


Figure S3. ^{1}H NMR spectrum of 16-(3-(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (**MTBM**).

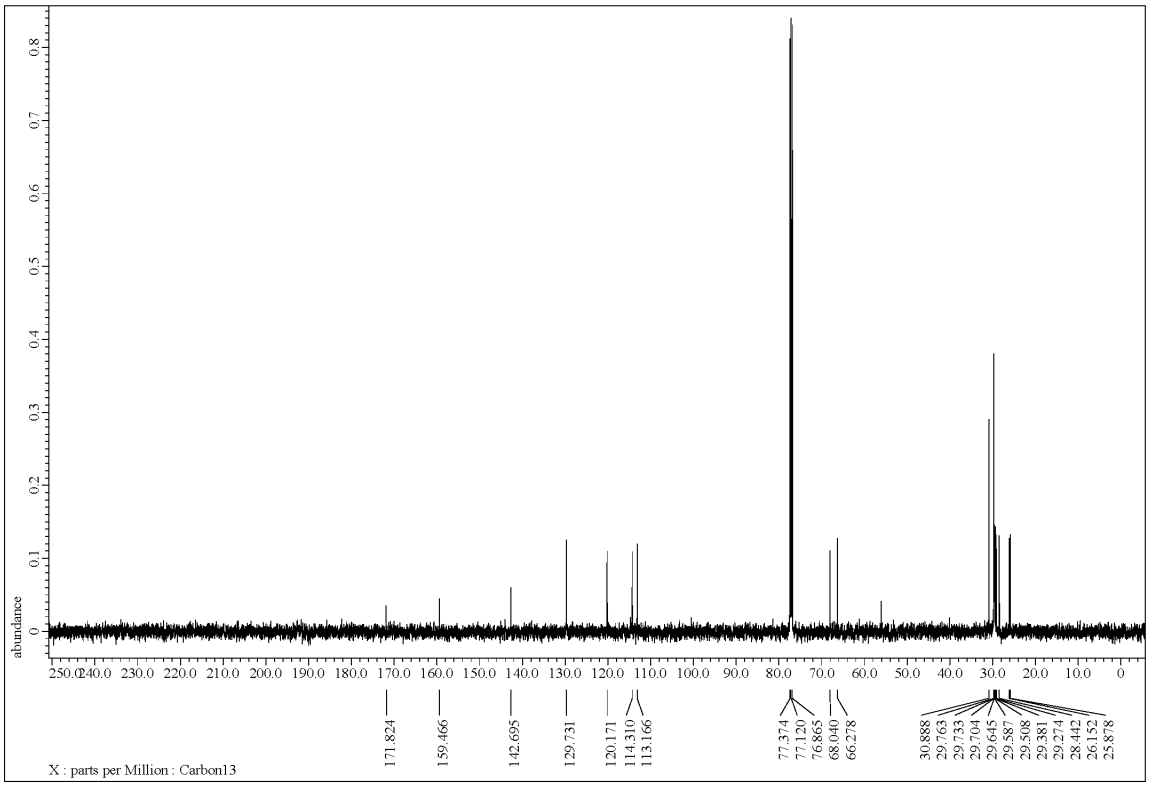


Figure S4. ^{13}C NMR spectrum of 16-(3-(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (**MTBM**).

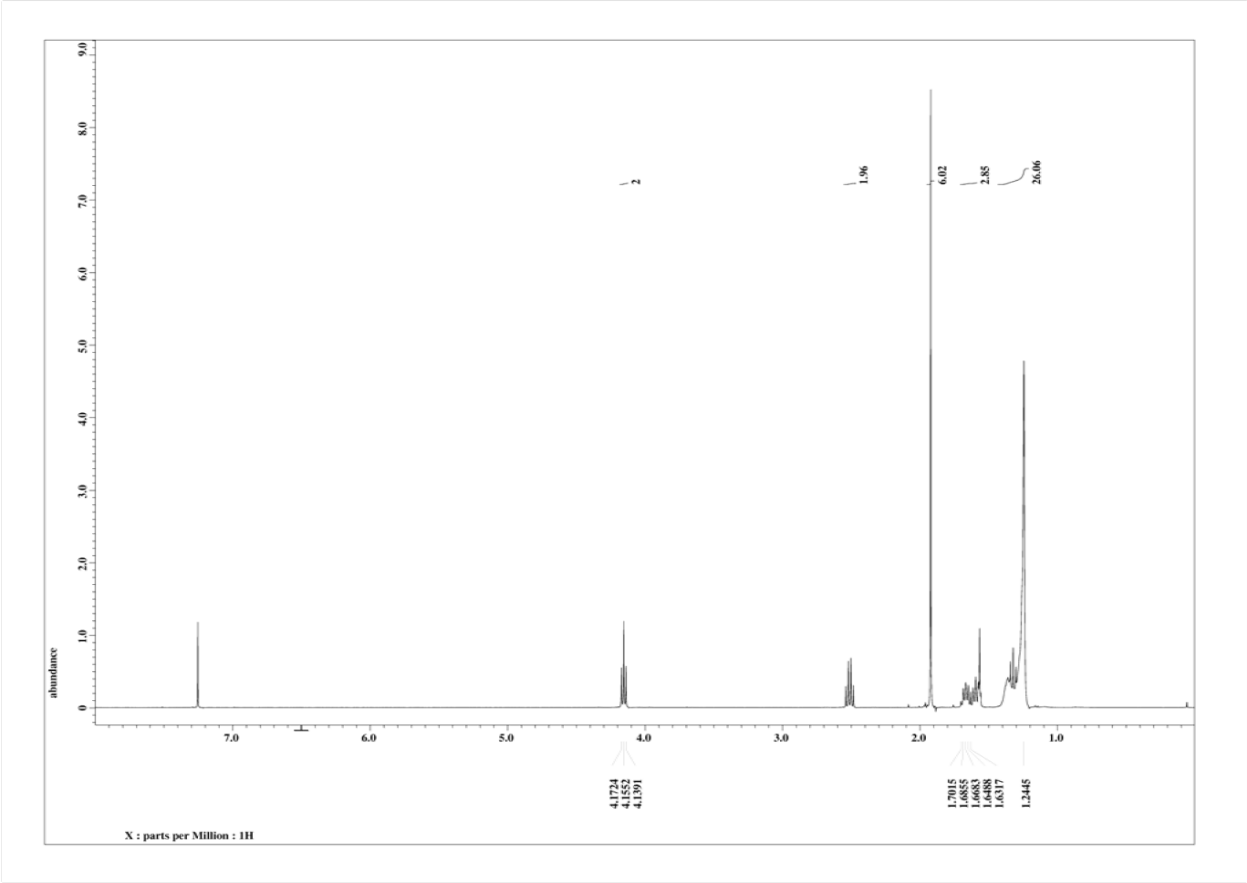


Figure S5. ^{1}H NMR spectrum of 15-mercaptohexadecyl 2-bromo-2-methylpropanoate (**MBM**).

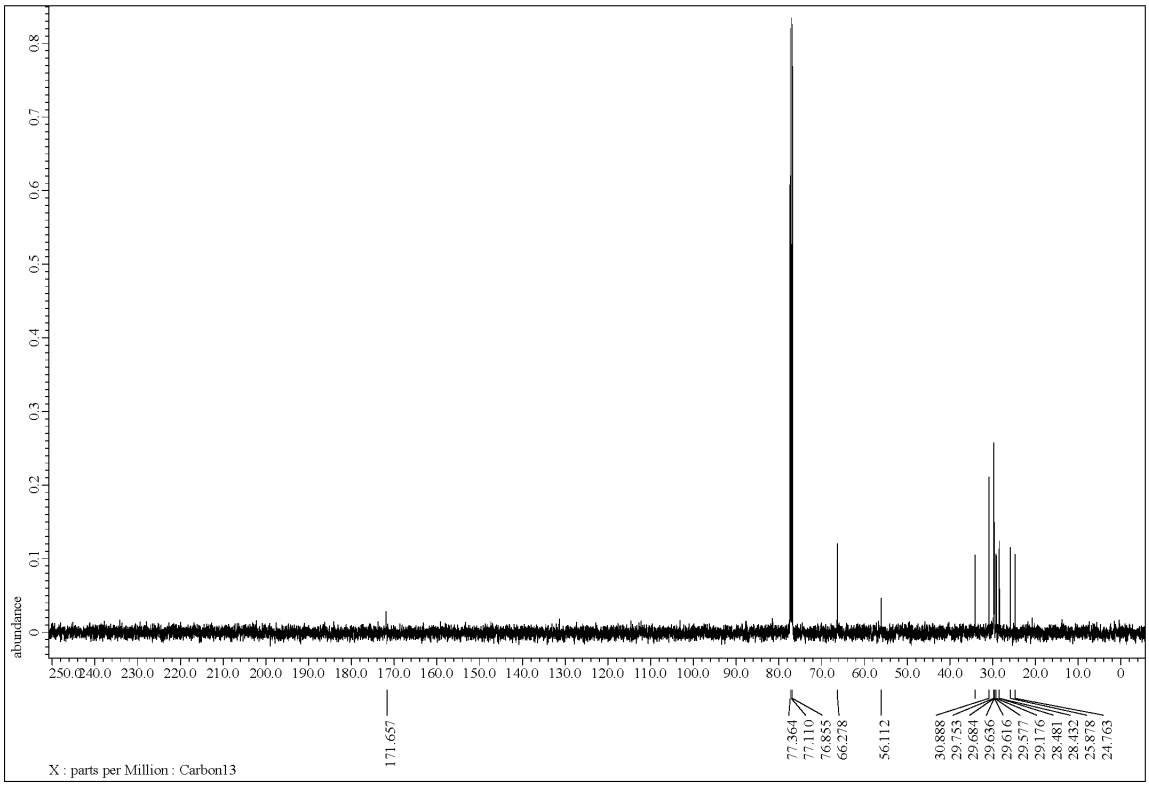


Figure S6. ^{13}C NMR spectrum of 15-mercaptohexadecyl 2-bromo-2-methylpropanoate (**MBM**).

Peak Fitting for the XPS Spectra

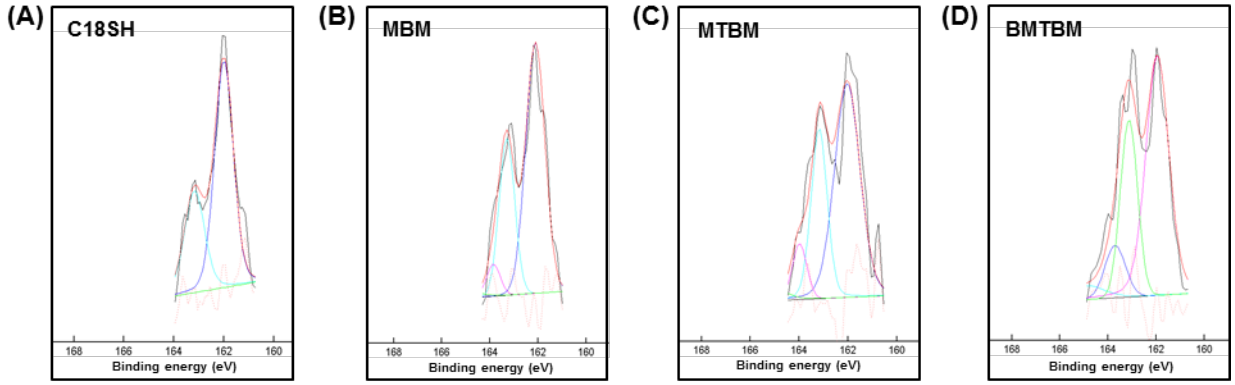


Figure S7. Peak fitting of the peaks for the S 2p spectral region of the XPS spectra of the films derived from (A) **C18SH**, (B) **MBM**, (C) **MTBM**, and (D) **BMTBM**. For all samples, chi-squared was less than 0.7.

Table S1. Percentage of Bound and Unbound Sulfur Derived from the S 2p Peak Fitting Data

adsorbate	percentage of bound sulfur (%)	percentage of unbound sulfur (%)
C18SH	99.4	0.6
MBM	94.1	5.9
MTBM	92.3	7.7
BMTBM	85.3	14.7