

# Supporting Information

for

## Bidentate Aromatic Thiols on Gold: New Insight Regarding the Influence of Branching on the Structure, Packing, Wetting, and Stability of Self-Assembled Monolayers on Gold Surfaces

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## **EXPERIMENTAL SECTION**

**Materials and Methods.** Gold shot (99.99%) was purchased from Americana Precious Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Polished single-crystal Si(100) wafers were purchased from Silicon Inc. and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. The contacting liquids used for wettability measurements were of the highest purity available from Aldrich Chemical Co. and were used without purification. The materials and chemicals used in the syntheses of all adsorbates were purchased from Aldrich Chemical Co. Solvents used in the syntheses were distilled over calcium hydride and stored under argon. Column chromatography was performed using silica gel (40-64  $\mu\text{m}$ ) and thin-layer chromatography (TLC) was carried out using 200  $\mu\text{m}$ -thick silica gel plates, which were purchased from Sorbent Technologies Inc. Nuclear magnetic resonance (NMR) spectra were collected using JOEL ECX-400 and ECA-500 spectrometers operating at 400 MHz and 500 MHz, respectively. The solvent used was deuterated chloroform ( $\text{CDCl}_3$ ) and the spectra were referenced to  $\delta$  7.26 and 77.00 ppm for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, respectively.

**Synthetic Procedures.** The procedures used to prepare the 2-phenylpropane-1,3-dithiols having single (**R1ArDT**), double (**R2ArDT**), and triple (**R3ArDT**) octadecyloxy substituent chains are outlined in Scheme S1 and detailed below. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra associated with the final compounds (**R1ArDT**, **R2ArDT**, **R3ArDT**) follow the synthetic procedures outlined below, and can be found in Figures S1-S6.

The reaction scheme shows the synthesis of thiol compounds from substituted benzyl alcohols. The starting materials are substituted benzyl alcohols with substituents  $R_1$ ,  $R_2$ , and  $R_3$  on the benzene ring. The reaction proceeds through several steps:

- Starting Materials:**
  - 1a:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$
  - 2a:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$
  - 3a:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$
- Reaction 1:** Starting materials are reacted with  $\text{NaH}$ ,  $\text{CO}(\text{OCH}_3)_2$  in THF to form methyl ester intermediates.
  - 1b:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$ ; 86%
  - 2b:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$ ; 80%
  - 3b:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$ ; 77%
- Reaction 2:** Intermediates are reacted with  $\text{LiAlH}_4$  in THF to form diols.
  - 1c:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$ ; 96%
  - 2c:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$ ; 96%
  - 3c:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$ ; 90%
- Reaction 3:** Diols are reacted with  $\text{Et}_3\text{N}$ ,  $\text{MsCl}$  in THF to form dimethylsulfonate (OMs) intermediates.
  - 1d:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$ ; 80%
  - 2d:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$ ; 80%
  - 3d:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$ ; 76%
- Reaction 4:** OMs intermediates are reacted with  $\text{KSCN}$  in DMF to form dithiolane (S-S) intermediates.
  - 1e:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$ ; 69%
  - 2e:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$ ; 58%
  - 3e:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$ ; 61%
- Reaction 5:** Dithiolane intermediates are reacted with  $\text{LiAlH}_4$  in THF to form the final thiol products.
  - R1ArDT:**  $R_1, R_3 = \text{H}$ , and  $R_2 = -\text{OC}_{18}\text{H}_{37}$ ; 74%
  - R2ArDT:**  $R_1, R_3 = -\text{OC}_{18}\text{H}_{37}$ , and  $R_2 = \text{H}$ ; 84%
  - R3ArDT:**  $R_1, R_2$ , and  $R_3 = -\text{OC}_{18}\text{H}_{37}$ ; 90%

S3

to the solution to obtain a white precipitate of **1b** (4.93 g, 10.3 mmol, 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.57 (s, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.73 (s, 6H), 1.75 (m, 2H), 1.25-1.44 (m, 30H), 0.86 (t, *J* = 6.9 Hz, 3H).

**2-(4-(Octadecyloxy)phenyl)propane-1,3-diol (1c).** To a suspension of LiAlH<sub>4</sub> (0.80 g, 21 mmol) in THF (15 mL) was added slowly a solution of **1b** (2.00 g, 4.19 mmol), via addition funnel under argon. The reaction mixture was refluxed for 6 h, cooled down to rt, quenched with ethanol (25 mL), and acidified to pH ~1 with 2 M HCl. The mixture was extracted with diethyl ether (3 x 150 mL). The combined organic layers were subsequently washed with a dilute HCl solution (1 x 100 mL), brine (1 x 100 mL), and water (1 x 100 mL), and then dried over MgSO<sub>4</sub>. Removal of the organic solvent under vacuum gave the crude product, which was purified by co-solvent recrystallization with CH<sub>2</sub>Cl<sub>2</sub> and MeOH to afford **1c** as a white powder (1.70 g, 4.04 mmol, 96%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.95 (m, 7H), 3.15 (m, 2H), 1.76 (m, 2H), 1.24-1.45 (m, 30H), 0.87 (t, *J* = 6.5 Hz, 3H),

**2-(4-(Octadecyloxy)phenyl)propane-1,3-dimethanesulfonate (1d).** To a stirred solution of **1c** (2.00 g, 4.76 mmol), and triethylamine (3.98 mL, 28.5 mmol) in anhydrous THF (25 mL) was added dropwise methanesulfonyl chloride (2.22 mL, 28.5 mmol) over 5 min under argon atmosphere. After the addition was completed, stirring was continued for 4 h at rt. Ice-cold water was poured into the reaction mixture to destroy any excess methanesulfonyl chloride. The mixture was extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with dilute HCl (1 x 100 mL), brine (1 x 100 mL), and water (1 x 100 mL). The organic phase was dried over MgSO<sub>4</sub> and removed under vacuum to give the crude mesylate of **1d**. The crude product was dissolved with a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and then cold MeOH was added to the solution to obtain the white precipitate of **1d** (2.2 g, 3.8 mmol, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.17 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.50 (t, *J* = 6.3 Hz, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.45 (m, 1H), 2.96 (s, 9H), 1.77 (m, 2H), 1.25-1.44 (m, 30H), 0.88 (t, *J* = 6.8 Hz, 3H).

**4-(4-(Octadecyloxy)phenyl)-1,2-dithiolane (1e).** A mixture of **1d** (1.50 g, 2.60 mmol) and KSCN (5.06 g, 52.0 mmol) in a mixture solution of EtOH (10 mL) and DMF (10 mL) was stirred at 140 °C for 24 h. The resulting brownish solution was poured into cold water to precipitate the crude product of **1e**. The precipitate was filtrated, washed with water, and then dissolved in

CH<sub>2</sub>Cl<sub>2</sub> (250 mL). The organic layer was washed with saturated brine (1 x 50 mL), water (1 x 50 mL), dried over MgSO<sub>4</sub>, and concentrated to dryness. The crude product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to afford **1d** (0.81 g, 1.79 mmol, 69%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.12 (d, *J* = 9.1 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.26-3.42 (m, 5H), 1.78 (m, 2H), 1.25-1.46 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H).

**2-(4-(Octadecyloxy)phenyl)propane-1,3-dithiol (R1ArDT).** A solution of **1e** (2.00 g, 4.43 mmol) in THF (25 mL) was added dropwise into a suspension of LiAlH<sub>4</sub> (0.84 g, 22.2 mmol) in THF (10 mL) through an addition funnel under argon. The reaction mixture was stirred at rt for 6 h, quenched with ethanol (25 mL), and then acidified with 2 M HCl (previously degas by bubbling with argon). After stirred for 10 min, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The combined organic layers were washed subsequently with brine (1 x 100 mL) and water (1 x 100 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness to give **R1ArDT** (1.50 g, 3.31 mmol, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.15 (d, *J* = 9.1 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 3.93 (t, *J* = 6.8 Hz, 2H), 2.90-2.82 (m, 5H), 1.77 (m, 2H), 1.25-1.48 (m, 32H), 0.87 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 158.55, 132.74, 128.90, 114.71, 68.07, 51.37, 32.02, 29.78, 29.70, 29.53, 29.45, 29.39, 26.16, 22.79, 14.22.

**Dimethyl 2-(3,5-bis(octadecyloxy)phenyl)malonate (2b).** Following the reaction procedure described for **1b**. To a reaction mixture of **2a** (1.00 g, 1.45 mmol) and sodium hydride (0.21 g, 8.7 mmol) in THF (20 mL) was added dropwise dimethyl carbonate (30 mL) to obtain **2b** (0.87 g, 1.2 mmol, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.51 (s, 2H), 6.40 (s, 1H), 4.54 (s, 1H), 3.91 (t, *J* = 6.3 Hz, 4H), 3.74 (s, 6H), 1.74 (pent, *J* = 8.0 Hz, 4H), 1.24-1.43 (m, 60H), 0.87 (t, *J* = 6.9 Hz, 6H).

**2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-diol (2c).** Following the reaction procedure described for **1c**. To a suspension of LiAlH<sub>4</sub> (0.38 g, 10.0 mmol) in THF (10 mL) was added a solution of **2b** (1.50 g, 2.01 mmol) in THF (15 mL) to obtain **2c** (1.34 g, 1.94 mmol, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.34 (s, 2H), 3.95-3.90 (m, 6H), 3.05 (b, 2H), 1.74 (pent, *J* = 7.8 Hz, 4H), 1.24-1.43 (m, 60H), 0.87 (t, *J* = 6.8 Hz, 6H).

**2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-diyl dimethanesulfonate (2d).** Following the procedure described for **1d**. A mixture of **2c** (1.50 g, 2.17 mmol) and triethylamine (1.82 mL, 13.1 mmol) in THF (30 mL) was reacted with methanesulfonyl chloride (1.02 mL, 13.1 mmol) to

obtain the crude mesylate product of **2d** (1.48 g, 1.75 mmol, 80%) as a white powder product. The crude product was directly used in the next step without any further purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.39 (s, 2H), 6.34 (s, 2H), 4.54-4.49 (m, 4H), 3.90 (t, *J* = 6.9 Hz, 4H), 3.36 (m, 1H), 2.97 (s, 6H), 1.77 (pent, *J* = 7.4 Hz, 4H), 1.25-1.49 (m, 60H), 0.87 (t, *J* = 6.8 Hz, 6H).

**4-(3,5-Bis(octadecyloxy)phenyl)-1,2-dithiolane (2e).** Following the procedure described for **1e**. The mesylate product of **2d** (1.50 g, 1.77 mmol) was treated with KSCN (3.45 g, 35.5 mmol) in a solution of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>:hexanes, 3:2, as the eluent to afford **2e** (0.74 g, 1.02 mmol, 58%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.42 (s, 2H), 6.31 (s, 2H), 3.90 (t, *J* = 6.9 Hz, 4H), 3.26-3.43 (m, 5H), 1.77 (pent, *J* = 8.2 Hz, 4H), 1.25-1.49 (m, 60H), 0.87 (t, *J* = 7.3 Hz, 6H).

**2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-dithiol (R2ArDT).** Following the procedure described for **R1ArDT**. To a suspension of LiAlH<sub>4</sub> (0.13 g, 3.5 mmol) in THF (10 mL) was added dropwise a solution of **2e** (0.50 g, 0.70 mmol) in THF (15 mL) to yield **R2ArDT** (0.42 g, 0.58 mmol, 84%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.34 (s, 1H), 6.30 (s, 2H), 3.91 (t, *J* = 6.3 Hz, 4H), 2.86-2.84 (m, 5H), 1.76 (pent, *J* = 8.0 Hz, 4H), 1.25-1.49 (m, 58H), 0.87 (t, *J* = 7.3 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.58, 143.46, 106.54, 99.80, 68.14, 52.66, 32.02, 29.79, 29.71, 29.68, 29.52, 29.46, 26.16, 22.78, 14.22.

**Dimethyl 2-(3,4,5-tris(octadecyloxy)phenyl)malonate (3b).** Following the reaction described for **1b**. To a reaction mixture of **3a** (2.00 g, 2.09 mmol) and sodium hydride (0.30 g, 12.6 mmol) in THF (20 mL) was added dropwise dimethyl carbonate (30 mL) to obtain **3b** (1.64 g, 1.62 mmol, 77%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.56 (s, 2H), 4.51 (s, 1H), 3.91-3.96 (m, 6H), 3.75 (s, 6H), 1.69-1.83 (m, 6H), 1.18-1.49 (m, 90H), 0.87 (t, *J* = 6.9 Hz, 9H).

**2-(3,4,5-Tris(octadecyloxy)phenyl)propane-1,3-diol (3c).** Following the reaction described for **1c**. To a suspension of LiAlH<sub>4</sub> (0.28 g, 7.40 mmol) in THF (10 mL) was added a solution of **3b** (1.50 g, 1.48 mmol) in THF (15 mL) to obtain **3c** (1.28 g, 1.33 mmol, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.39 (s, 2H), 3.91-3.93 (m, 9H), 1.69-1.80 (m, 6H), 1.25-1.49 (m, 90H), 0.87 (t, *J* = 6.9 Hz, 9H).

**2-(3,4,5-Tris(octadecyloxy)phenyl)propane-1,3-diyl dimethanesulfonate (3d).** Following the procedure described for **1d**. A mixture of **3c** (1.00 g, 1.04 mmol) and triethylamine (0.87 mL, 6.3 mmol) in THF (30 mL) was reacted with methanesulfonyl chloride (0.49 mL, 6.3 mmol) to

obtain the crude mesylate product of **3d** (0.89 g, 0.80 mmol, 76%) as a white powder product. The crude product was directly used in the next step without any further purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.40 (s, 2H), 4.54-4.47 (m, 4H), 3.90-3.94 (m, 6H), 3.35 (m, 1H), 2.95 (s, 6H), 1.70-1.80 (m, 6H), 1.25-1.49 (m, 90H), 0.87 (t, *J* = 7.4 Hz, 9H).

**4-(3,4,5-Tris(octadecyloxy)phenyl)-1,2-dithiolane (3e).** Following the procedure described for **1e**. The mesylate product of **3d** (1.00 g, 0.90 mmol) was reacted with KSCN (1.75 g, 18.0 mmol) in a mixture solution of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using hexanes:EtOAc, 4:1, as the eluent to afford **3e** (0.54 g, 0.55 mmol, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.34 (s, 2H), 3.90-3.94 (m, 6H), 3.27-3.40 (m, 5H), 1.70-1.80 (m, 6H), 1.25-1.49 (m, 90H), 0.87 (t, *J* = 6.9 Hz, 9H).

**2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-dithiol (R3ArDT).** Following the procedure described for **R1ArDT**. To a suspension of LiAlH<sub>4</sub> (0.10 g, 0.20 mmol) in THF (10 mL) was added dropwise a solution of **3e** (0.04 g, 1.0 mmol) in THF (15 mL) to yield **R3ArDT** (0.18 g, 0.18 mmol, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.33 (s, 2H), 3.97-3.88 (m, 6H), 2.77-2.88 (m, 5H), 1.82-1.68 (m, 6H), 1.48-1.24 (m, 90H), 0.87 (t, *J* = 6.3 Hz, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 153.30, 137.48, 136.18, 106.41, 73.47, 69.31, 52.46, 32.04, 30.44, 29.83, 29.76, 29.56, 29.48, 29.40, 26.22, 22.80, 14.24.

## **PREPARATION AND CHARACTERIZATION**

**Preparation of SAMs.** Under a vacuum  $\sim 10^{-5}$  Torr, a thin layer (100 Å) of chromium was first evaporated onto polished silicon (100) wafers to assist the adhesion of gold on the silicon substrate. Subsequently, the deposition of 1000 Å of gold onto the chromium-coated silicon wafers was performed. The freshly prepared gold-coated wafers were cut into slides (1 x 4 cm) and the slides were cleaned by rinsing with absolute ethanol and blown dry with ultra-pure nitrogen before collecting the optical constants of the substrates by ellipsometry. The glass vials used to store each thiol solution were previously cleaned with piranha solution (3:1 mixture of conc.  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ) and rinsed thoroughly with deionized water, followed by absolute ethanol. [*Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.*] The slides were then immersed in the appropriate 1 mM thiol solution and allowed to equilibrate for 72 hours at room temperature. Samples were rinsed with toluene, THF, methanol, and then ethanol, successively, and dried with a flow of ultra-pure nitrogen before characterization. The subsequent characterization techniques were repeated three times to ensure accuracy. The following sections describe procedures performed for each set of SAMs.

**Ellipsometric Measurements.** A Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser (632.8 nm) at angle of incidence of  $70^\circ$  was utilized to measure the film thicknesses. An approximate value for the film refractive index of 1.45 was used for all measurements. For each sample, optical constants were determined from six measurements from two separate slides using three different spots for each slide. Reported values of thicknesses were the average of the measurements over the experimental data collection made in triplicate on two slides.

**Contact Angle Measurements.** Contact angles for the SAMs were measured on a ramé-hart model 100 contact angle goniometer. The contacting liquids, water ( $\text{H}_2\text{O}$ ), hexadecane (HD), and decalin (DEC), were dispensed (advancing contact angle,  $\theta_a$ ) and withdrawn (receding contact angle,  $\theta_r$ ) on the surfaces using a Matrix Technologies micro-Electrapette 25 at the slowest speed (1  $\mu\text{L/s}$ ). The contact angle data were collected at room temperature while keeping the pipet tip in contact with the drop, the sessile drop technique. Contact angle values were reported by averaging the results from six independent drops from two separate slides with three drops per slide, including measurements for both drop edges.

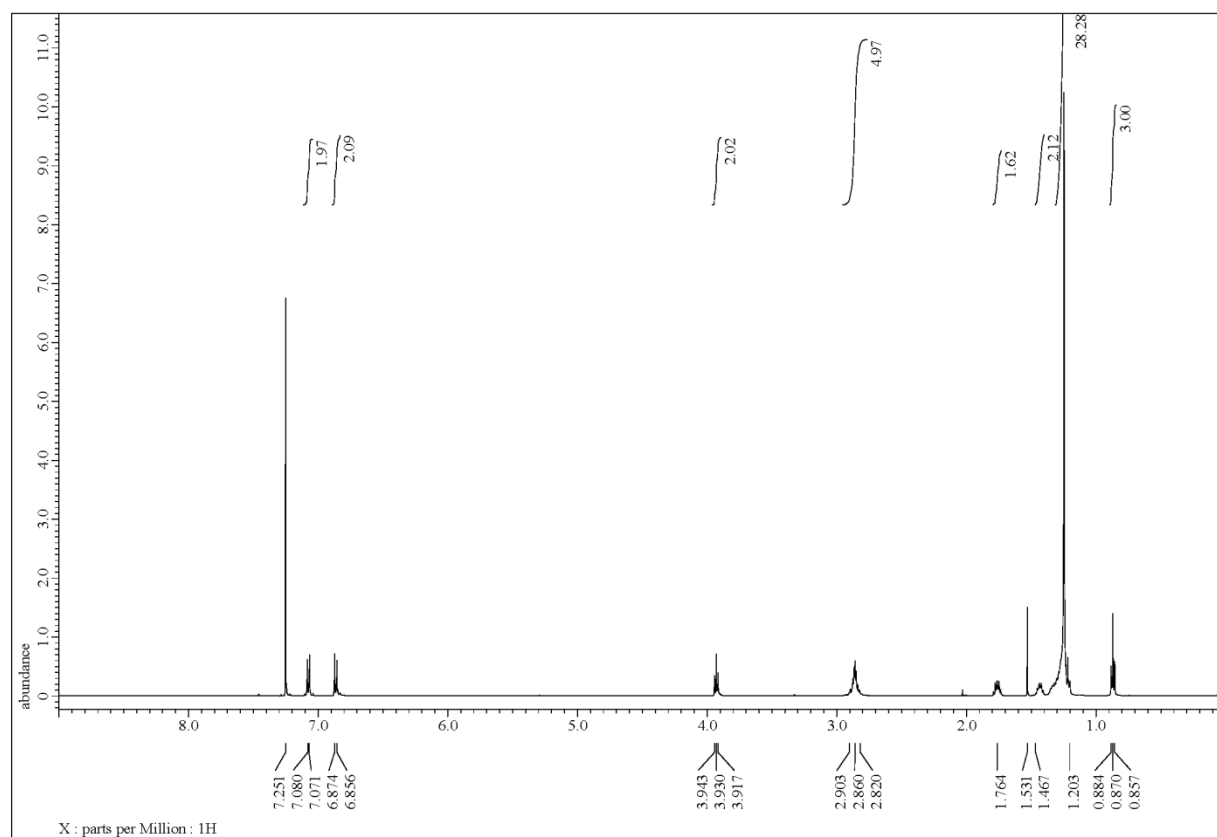


**X-ray Photoelectron Spectroscopy (XPS).** XPS spectra were recorded with a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.7$  eV) incident at 90° relative to the axis of a hemispherical energy analyzer. Spectra were taken at high resolution with a pass energy of 23.5 eV, a photoelectron taken off angle of 45° from the surface, and an analyzer spot diameter of 2.0 mm. The pressure in the chamber during the measurements was  $\sim 4 \times 10^{-8}$  Torr. The binding energy scales were referenced to the Au 4f<sub>7/2</sub> peak at 84.0 eV.

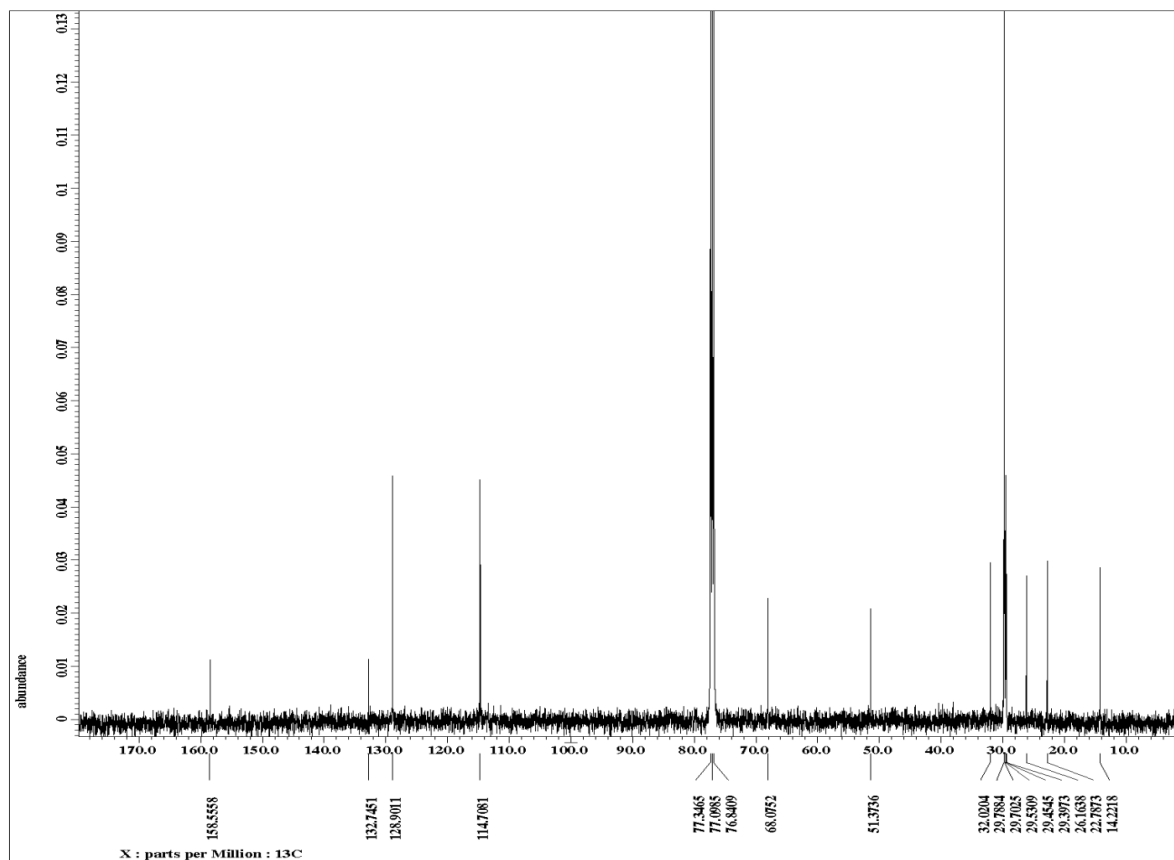
**Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS).** IR spectra were collected using a Nicolet Nexus 670 Fourier transform IR spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instrument PEM-90 photoelastic modulator. All measurements were performed in a sample compartment purged with nitrogen gas during the course of the experiments. The spectra were collected at 2 cm<sup>-1</sup> spectral resolution for 512 scans with a grazing angle for the infrared beam aligned at 80°.

**Thermal Desorption of SAMs at an Elevated Temperature.** Thermal stability experiments were performed in isooctane at  $80 \pm 2$  °C. SAM-coated gold slides were immersed in the stirred solvent and periodically removed at systematic intervals of time. The samples were subsequently rinsed with toluene, THF, methanol, and ethanol, in that order, and blown dry in a stream of ultra-pure nitrogen gas. The samples were immediately characterized by ellipsometry and PM-IRRAS, and then re-immersed in the heated solvent in the temperature-controlled bath.

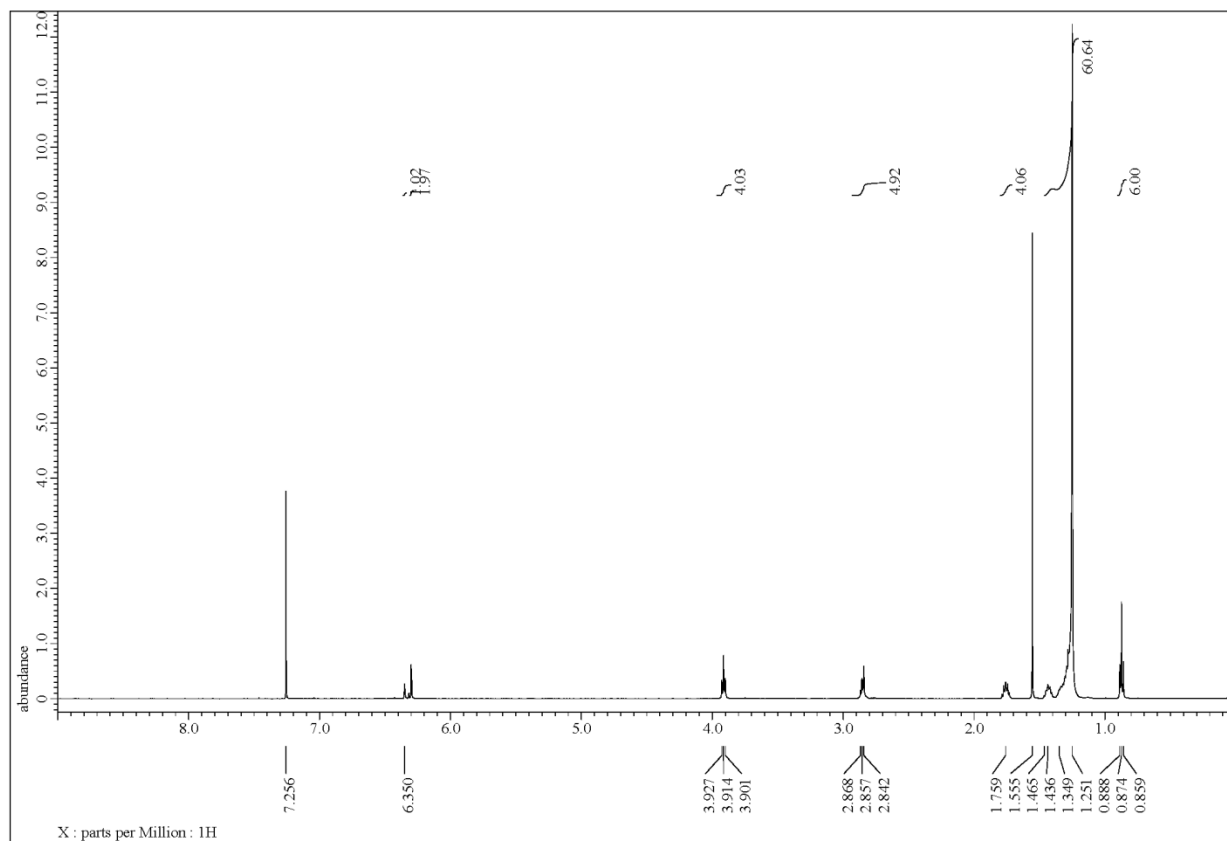
## SPECTRAL DATA



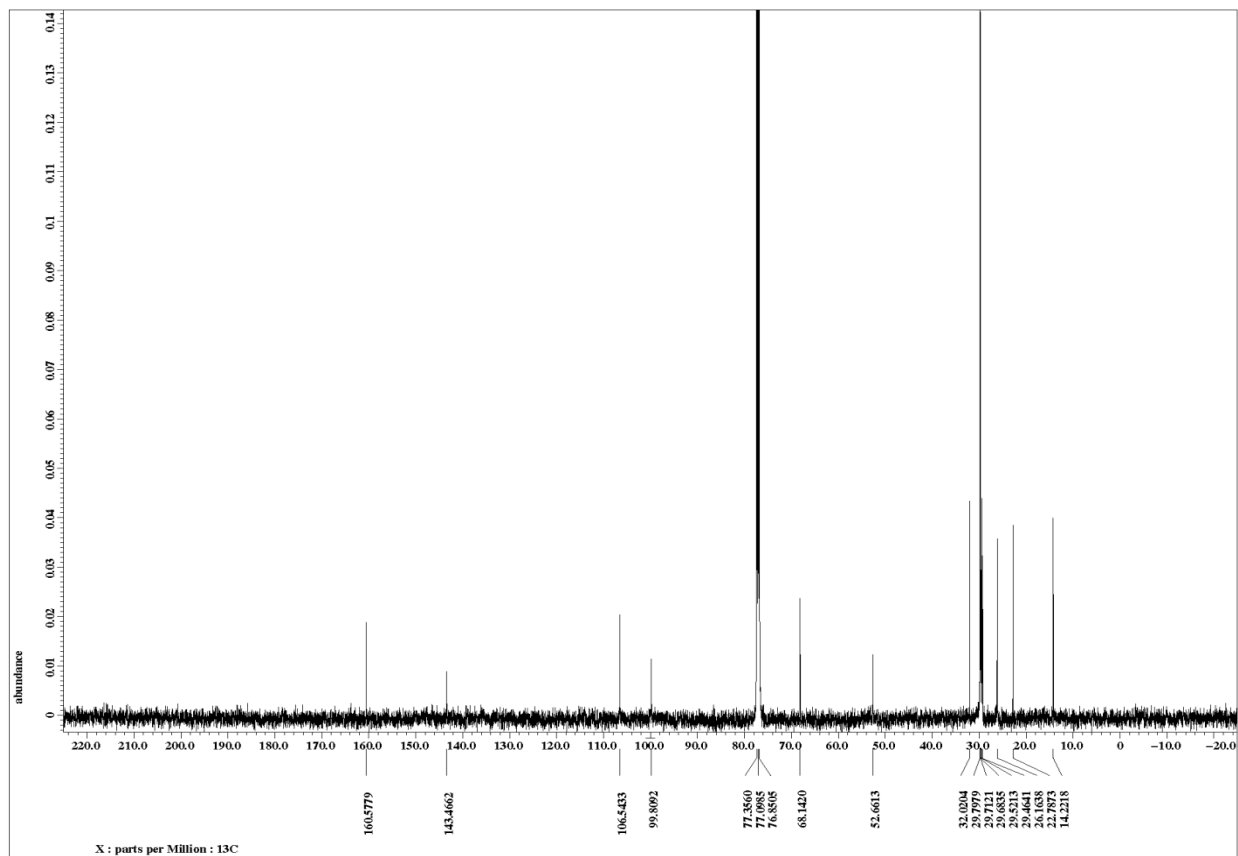
**Figure S1.** <sup>1</sup>H NMR spectrum of 2-(4-(octadecyloxy)phenyl)propane-1,3-dithiol (**R1ArDT**).



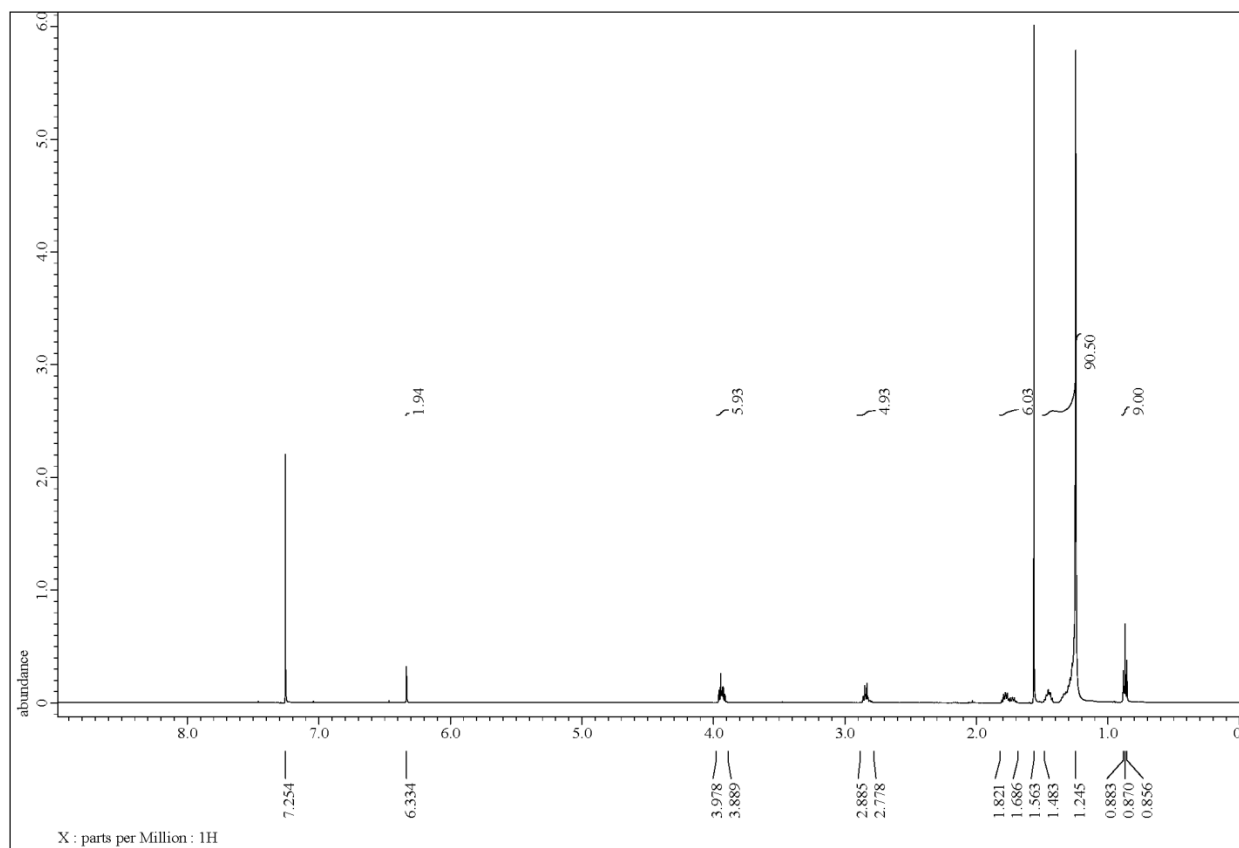
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of 2-(4-(octadecyloxy)phenyl)propane-1,3-dithiol (**R1ArDT**).



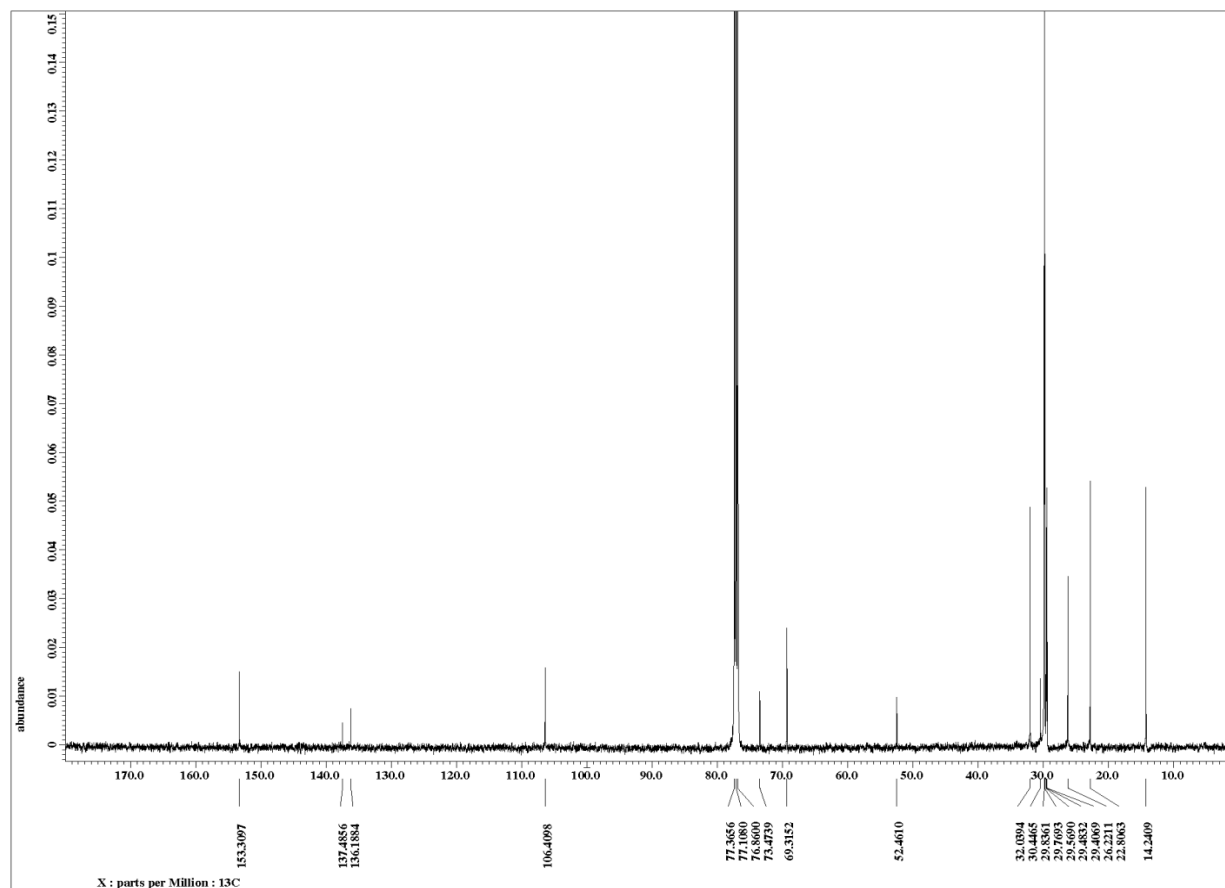
**Figure S3.**  $^1\text{H}$  NMR spectrum of 2-(3,5-bis(octadecyloxy)phenyl)propane-1,3-dithiol (R2ArDT).



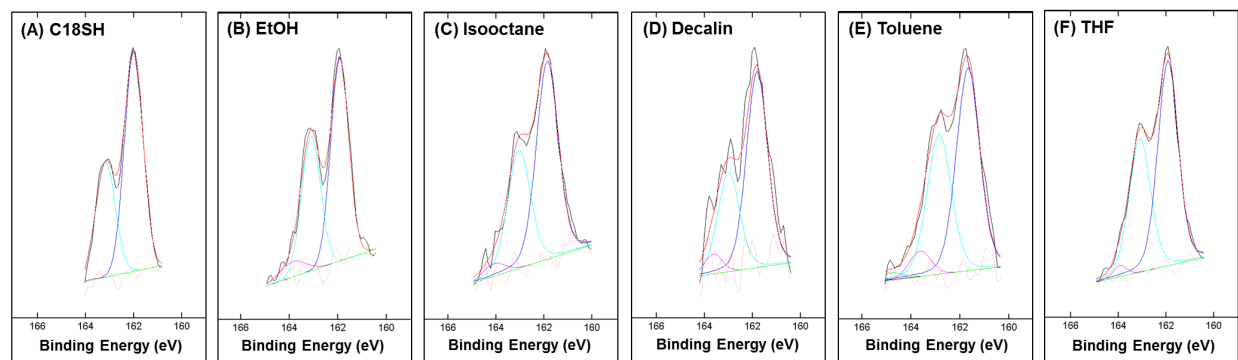
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of 2-(3,5-bis(octadecyloxy)phenyl)propane-1,3-dithiol (R2ArDT).



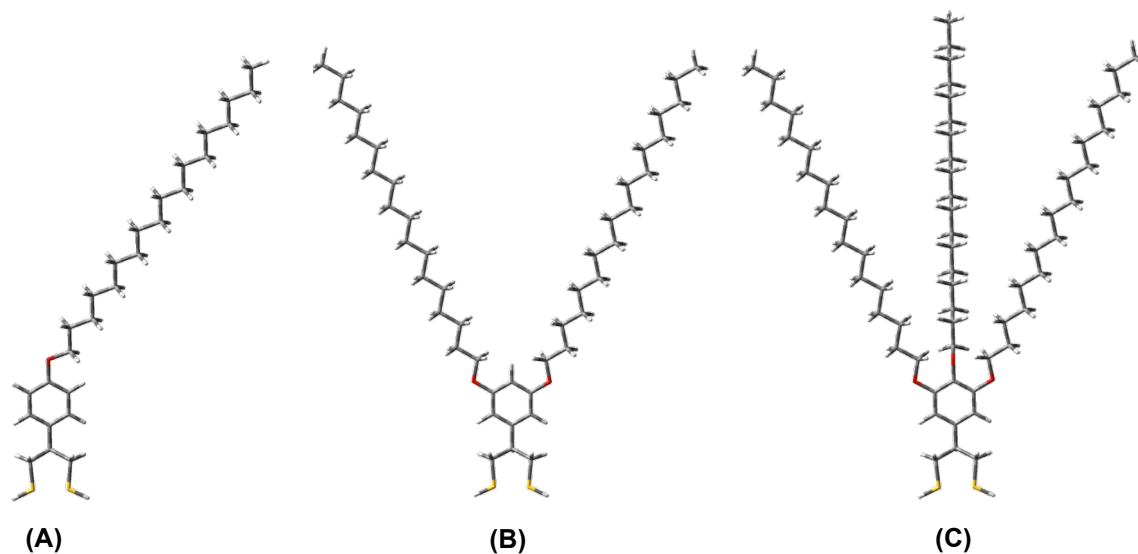
**Figure S5.**  $^1\text{H}$  NMR spectrum of 2-(3,5-bis(octadecyloxy)phenyl)propane-1,3-dithiol (**R3ArDT**).



**Figure S6.**  $^{13}\text{C}$  NMR spectrum of 2-(3,5-bis(octadecyloxy)phenyl)propane-1,3-dithiol (R3ArDT).



**Figure S7.** Peak fitting of the peaks for the S 2p spectral region of the XP spectra of the films derived from (A) **C18SH**, and (B) **EtOH**, (C) **Isooctane**, (D) **Decalin**, (E) **Toluene**, and (F) **THF** with R1ArDT. For all samples, chi-squared was less than 0.7.



**Figure S8.** Structural representations of (A) **R1ArDT**, (B) **R2ArDT**, and (C) **R3ArDT**. Molecular models were prepared using Gaussview 03, revision 3.07 (Gaussian, Inc., Pittsburgh, PA).



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

adsorbate (solvent)	percentage of bound sulfur (%)	percentage of unbound sulfur (%)
<b>C18SH (EtOH)</b>	99.8	0.2
<b>R1ArDT (EtOH)</b>	94.1	5.9
<b>R1ArDT( Isooctane)</b>	95.3	4.7
<b>R1ArDT (Decalin)</b>	95.0	5.0
<b>R1ArDT (Toluene)</b>	91.5	8.5
<b>R1ArDT (THF)</b>	97.9	2.1