# Supporting Information for

## Inhibiting Reductive Elimination as an Intramolecular Disulfide Dramatically Enhances the Thermal Stability of SAMs on Gold Derived from Bidentate Adsorbents

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#### **EXPERIMENTAL PART A**

**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 the highest purity available from Aldrich Chemical Co. and were used without purification. The starting material, dimethyl 5-hydroxyisophthalate, and other chemicals used in the syntheses of the adsorbates were purchased almost exclusively 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  $\mu$ m), and thin-layer chromatography (TLC) was carried out using 200  $\mu$ m-thick silica gel plates, which were purchased from Sorbent Technologies. Inc. Nuclear magnetic resonance (NMR) spectra were recorded on JOEL ECX-400 and ECA-500 spectrometers operating at 400 MHz and 500 MHz, respectively. The data were obtained in CDCl<sub>3</sub> and referenced to  $\delta$  7.26 and 77.00 ppm for <sup>1</sup>H NMR and <sup>13</sup>C NMR, respectively.

**Synthesis of (5-(Octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT):** Scheme S1 shows the synthetic strategy used to prepare **R1ArmDT**; the experimental details are provided in the following paragraphs.

Scheme S1. Synthesis of (5-(Octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT)



**Dimethyl 5-(octadecyloxy)isophthalate (2):** A mixture of 1-bromooctadecane (4.12 g, 12.4 mmol), compound **1** (2.00 g, 9.52 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.63 g, 19.0 mmol) in DMF (150 mL) was stirred at 120 °C overnight. After cooling, K<sub>2</sub>CO<sub>3</sub> was filtered away, and the filtrate was diluted with H<sub>2</sub>O and acidified with 2 M HCl. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 250 mL). The organic layers were combined and washed with H<sub>2</sub>O (3 × 50 mL), dried over MgSO<sub>4</sub> and concentrated to dryness to afford the crude product. The crude product was chromatographed on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane (3:2) as the eluent to give **2** as a white powder (3.52 g, 7.61 mmol, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (s, 2H), 7.73 (s, 2H), 4.02 (t, *J* = 6.9 Hz, 2H), 3.94 (s, 6H), 1.80 (m, 2H), 1.26-1.46 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H).

(5-(Octadecyloxy)-1,3-phenylene)dimethanol (3): A solution of 2 (3.00 g, 6.48 mmol) in THF (20 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (0.62 g, 16.0 mmol) in THF (25 mL) under argon. The mixture was stirred and heated to reflux for 6 h and then quenched with H<sub>2</sub>O and acidified with 2 M HCl. The reaction mixture was extracted with diethyl ether (3 × 150 mL). The combined organic layers were washed with brine (1 × 100 mL) and H<sub>2</sub>O (1 × 100 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness. The crude product was taken up in CH<sub>2</sub>Cl<sub>2</sub>, and then cold MeOH was added to precipitate **3** as a white powder (2.54 g, 6.25 mmol, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.93 (s, 2H), 6.81 (s, 2H), 4.66 (d, *J* = 4.6 Hz, 4H), 3.96 (t, *J* = 6.9 Hz, 2H), 1.77 (m, 2H), 1.63 (t, *J* = 4.6 Hz, 2H), 1.26-1.45 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H).

(5-(Octadecyloxy)-1,3-phenylene)bis(methylene) dimethanesulfonate (4): Methanesulfonyl chloride (1.15 mL, 14.8 mmol) was added dropwise over 5 min to a stirred solution of **3** (2.00 g, 4.92 mmol) and triethylamine (2.06 mL, 14.8 mmol) in anhydrous THF (25 mL). The mixture was stirred for 4 h at rt under argon. To destroy excess methanesulfonyl chloride, ice cold water was added to the reaction flask. The mixture was extracted with diethyl ether ( $3 \times 100$  mL). The organic layers were washed successively with 2M HCL ( $1 \times 100$  mL) and H<sub>2</sub>O ( $1 \times 100$  mL), dried over MgSO<sub>4</sub> and concentrated to dryness to yield the crude mesylate. The crude product was dissolved with a minimum volume of CH<sub>2</sub>Cl<sub>2</sub>, and then MeOH was subsequently added to obtain 4 as a white precipitate (2.19 g, 3.73 mmol, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.00 (s, 2H), 6.94 (s, 2H), 5.19 (d, *J* = 4.6 Hz, 4H), 3.96 (t, *J* = 6.4 Hz, 2H), 2.97 (s, 6H), 1.77 (m, 2H), 1.63 (t, *J* = 4.6 Hz, 2H), 1.25-1.45 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H).

**1-(Octadecyloxy)-3,5-bis(thiocyanatomethyl)benzene (5):** A mixture of dimesylate **4** (2.00 g, 3.55 mmol) and KSCN (3.45 g, 35.5 mmol) in a mixture of ethanol (15 mL) and DMF (15 mL) was stirred at 140 °C for 24 h. The product was poured into cold water, and the resulting precipitate was collected by filtration and washed with H<sub>2</sub>O to yield the crude dithiocyanate. The crude product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to obtain **5** (1.35 g, 2.76 mmol, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.00 (s, 2H), 6.94 (s, 2H), 4.10 (d, *J* = 4.6 Hz, 4H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.78 (m, 2H), 1.63 (t, *J* = 4.6 Hz, 2H), 1.25-1.45 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H).

(5-(Octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT) (6): A solution of 5 (1.00 g, 2.05 mmol) in THF (20 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (0.19 g, 5.1 mmol) in THF (15 mL) under argon. The mixture was stirred at rt for 6 h, and then quenched with H<sub>2</sub>O and acidified with 2 M HCl. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 100$  mL). The combined organic layers were washed with brine and H<sub>2</sub>O ( $1 \times 100$  mL), dried over MgSO<sub>4</sub> and evaporated to dryness to give the crude compound. Finally, the crude dithiol was dissolved in dichloromethane and crystallized after adding methanol to give pure **R1ArmDT** (0.83 g, 1.9 mmol, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.84 (s, 2H), 6.74 (s, 2H), 3.95 (t, *J* = 6.3 Hz, 2H), 3.68 (d, *J* = 7.5 Hz, 4H), 1.77 (m, 2H), 1.25-1.45 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>): 159.77, 142.98, 119.87, 112.97, 68.13, 32.02, 29.79, 29.70, 29.46, 29.35, 29.01, 26.14, 22.78, 14.22. ESI HR-MS: calculated for C<sub>26</sub>H<sub>46</sub>OS<sub>2</sub> 438.2990; found 438.2984.

#### **EXPERIMENTAL PART B**

**Preparation of Substrates and SAMs.** The gold substrates were prepared by evaporation of *ca*. 100 Å of chromium on polished Si(100) wafers to promote the adhesion of gold, followed by evaporation of *ca*. 1000 Å of gold. The freshly prepared gold-coated on chromium-primed Si wafers were cut into slides of ca. 1 cm  $\times$  4 cm. The slides were subsequently rinsed with methanol and absolute ethanol and then dried with ultra-pure nitrogen blown from a needle. Typical solutions of a 1 mM concentration of **R1ArDT** and **R1ArmDT** in THF, and **C18SH** in ethanol were prepared in 25 mL glass vials, which were previously cleaned with piranha solution (3:1 mixture of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) and rinsed thoroughly with deionized water and then absolute ethanol before use. [*Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.*] The gold slides were incubated in a 1 mM solution of the respective adsorbates for at least 72 h to allow full monolayer development and equilibration at rt. Before characterization, the resultant slides were rinsed with toluene, THF, methanol, and ethanol, and then dried with ultra-pure nitrogen.

**Ellipsometric Thicknesses.** The thicknesses of the monolayer films were measured using a Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser with a single wavelength of 632.8 nm at an angle of incidence of 70°. Immediately after the evaporation of gold, the optical constants of bare substrates were collected. The film thicknesses were evaluated by using an approximate value of the film refractive index of 1.45 and the predetermined optical constants of the uncoated substrate. The data were averaged over the collections from two separate slides with three spots for each slide. The reported values are an average of 9 data points obtained from 3 gold slides.

**X-ray Photoelectron Spectroscopy (XPS).** XPS spectra were collected using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source (hv = 1486.7 eV) incident at 90° relative to the axis of hemispherical energy analyzer. The spectrometer was operated at high resolution with a pass energy of 23.5 eV, a photoelectron taken off angle of 45° from the surface, and analyzer spot diameters of 1.1 mm. The base pressure in the chamber during the measurements was ~4 x 10<sup>-8</sup> Torr. After collection of the data, the binding energy scales was adjusted by setting the Au 4f<sub>7/2</sub> peak to 84 eV as a reference peak. Analysis of the XPS spectra were obtained from three independent sets of SAMs.

**Contact Angle Measurements.** A Ramé-Hart model 100 contact angle goniometer was employed to measure the contact angles of the probe liquids on the monolayer films. The contacting liquids, water (H<sub>2</sub>O), hexadecane (HD), and decalin (DEC) were dispensed and withdrawn on the film surfaces with a Matrix Technologies Micro-Electrapipet 25 at the slowest speed (1  $\mu$ L/s) to measure advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) contact angles, respectively. For a given sample, the data were averaged over three separate slides using three drops per slide and measuring angles from both edges of each drop. The measurements were performed at 293 K with the pipet tip in contact with the drop.

**Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS).** Infrared reflection-adsorption spectra of monolayer films were collected using a Nicolet NEXUS 670 Fourier transform spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photo elastic modulator operating at 37 Hz. A continuous flow of nitrogen gas was maintained in the chamber during the measurements. The spectra were collected for 512 scans at 2 cm<sup>-1</sup> spectral resolution with a grazing angle for the reflected infrared beam aligned at 80° to the surface normal. Analysis by PM-IRRAS was obtained from three independent sets of SAMs.

### SPECTRAL DATA



Figure S1. <sup>1</sup>H NMR spectrum of (5-(octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT)



Figure S2. <sup>13</sup>C NMR spectrum of (5-(octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT)



Figure S3. Structural representations of (a) R1ArDT, (b) R1ArmDT (flat orientation), and (c) R1ArmDT (upright orientation).<sup>S1</sup>



**Figure S4.** X-Ray photoelectron spectra (XPS) of the S 2p region for the monolayers derived from **R1ArmDT** in various solvents.

	C18SH	<b>R1ArDT</b>	R1ArmDT
Ns	0.172	0.172	0.166
	0.159	0.166	0.172
	0.160	0.166	0.160
	0.171	0.171	0.178
	0.172	0.172	0.161
	0.172	0.171	0.172
Average	0.168	0.170	0.168
Ks	3.476	3.476	3.474
	3.457	3.474	3.473
	3.474	3.468	3.471
	3.462	3.462	3.479
	3.468	3.482	3.480
	3.470	3.465	3.468
Average	3.468	3.471	3.474

Table S1. Ns and Ks Values of Bare Gold Surfaces



**Figure S5.** Peak fitting for the S 2p spectral region of the XP spectra of the films derived from (A) **C18SH**, (B) **R1ArDT**, and (C) **R1ArmDT**. For all samples, chi-squared was less than 0.4.

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Table S2. Percentage of Bound and Unbound Sulfur Derived fromthe S 2p Peak Fitting Data

#### References

(S1) Molecular models were performed using the GaussView 03, revision 3.07; Gaussian, Inc., Pittsburgh, PA. We assumed that the alkyl chains were fully extended and tilted ~30° from the surface normal. The following data were used: C-C ~1.5 Å, C-O ~1.4 Å, <CCC ~109.5°>.