

Experimental

Reagents and Materials. Reagents were purchased from commercial sources and used as received. 9-anthrylmethyl(2-mercaptoethyl)ammonium bromide and its disulfide [3]-rotaxane were prepared, with some modifications, from a published procedure (Kolchinski, A.G.; Alcock, N.W.; Roesner, R.A.; Busch, D.H. *Chem. Commun.* **1998**, 1437). Au(111) on mica substrates were purchased from Molecular Imaging. Other Au(111) substrates formed by evaporating 5 nm Ti and 100nm Au on Si(100) were also used. All gold substrates were hydrogen flame annealed immediately before use following Molecular Imaging's procedure.

Instrumentation. NMR measurements were run at ambient conditions on a Bruker DRX-500 11.7T spectrometer equipped with a Bruker 5 mm inverse HCN probe. An observe pulse of approximately 7 microseconds was used and chemical shifts were referenced to the solvent resonance. Mass spectra were collected using an Applied Biosystems Voyager DE-STR Matrix-assisted laser desorption ionization time-of-flight mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as the matrix. Elemental analysis was performed by Galbraith Laboratories, Inc.

X-ray absorption spectra were taken at VUV BL 8.2 of The Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center. The beamline uses bend magnet radiation and a spherical grating monochromator (Tirsell, G. K.; Karpenko, V.P.; *Nucl. Instrum. Methods* **1990**, A291, 511). XAS experiments were conducted with an energy resolution of ~ 0.2 eV at the carbon K-edge. Absorption spectra were recorded using the total electron yield method, as the total current leaving the sample is proportional to the absorption signal. The sample current was normalized to the incident beam via the current from a clean grid with a freshly evaporated coat of gold. Care was taken to limit X-ray flux to minimize damage to the samples during data collection. All spectra were recorded at a base pressure of less than 1×10^{-9} torr. The degree of linear polarization of the beam was measured with highly-oriented pyrolytic graphite (HOPG) by rotating about two different axes and monitoring the intensity of the C 1s to π^* feature in the C K-edge spectra. A few days prior to these measurements, this method measured the polarization at $\sim 88\%$ in the plane of the storage ring. The energy scale of carbon XAS spectra were calibrated to the π^* resonance of HOPG set to 285.38 eV.

X-ray photoelectron spectra were obtained at SSRL using a PHI 15-255G CMA electron energy analyzer and its associated OEM electronics. The pass energy was set to 25 eV. S2p spectra were obtained at a photon energy of 280eV; C1s spectra were obtained at a photon energy of 400eV. The spectra *were not* normalized to the beam current. Spectra of the Au4f peaks of the substrates were taken immediately after every sulfur spectra and most of the carbon spectra to calibrate the binding energy scales. The Au 4f_{7/2} photoelectron at 84.01 ± 0.05 eV was used to convert the kinetic energy scales to binding energy scales. Additional X-ray photoelectron spectra were obtained using a Physical Electronics Quantum 2000 scanning XPS system with a focused monochromatic Al K α X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. A 1 mm diameter X-ray beam was used for analysis. The X-ray beam is incident normal to the sample and the X-ray detector is at 45° away from the normal. The pass energy was 23.5 eV, giving an

overall energy resolution of 0.3 eV. The collected data were referenced to an energy scale with binding energies for Cu 2p_{3/2} at 932.72 ± 0.05 eV and Au 4f_{7/2} at 84.01 ± 0.05 eV. All spectra were recorded at a base pressure of 5 × 10⁻¹⁰ torr. Low energy electrons and argon ions were used for specimen neutralization.

Synthesis of 9-anthrylmethyl(2-mercaptoethyl)ammonium bromide (I). 9-Anthraldehyde (5.36 g, 26.0 mmol) and 2-aminoethanethiol (2.00 g, 26.0 mmol) were refluxed in 50 mL of toluene with an attached dean-stark trap until the amount of water in the trap was constant (ca. 1 hour). After cooling to room temperature, solvent was removed by rotary evaporation, and the residue was dissolved with light heating in 50 mL of 4:1 methanol/toluene. Sodium borohydride (1.97 g, 52.0 mmol) was added in portions over 30 minutes and the solution stirred for another hour at room temperature. Solvent was removed by rotary evaporation and the residue dissolved in 50 mL of 1:1 water/dichloromethane. The organic layer was collected and dried over sodium sulfate. The solution was filtered and solvent removed by rotary evaporation. The aminothiols were dissolved in 50 mL of 1:1 ethanol/diethyl ether under nitrogen and 0.35 g of sodium borohydride was added to reduce possible disulfides. About 3 mL of hydrogen bromide were added, and after standing for about 1 hour, the yellow precipitate was collected, washed with ethanol, ethanol/ether and ether then dried in vacuo to give 5.7 g of product (63% yield). (Note, some disulfide (5-10%) may be present in the final product, but the product can be used to prepare the [3]rotaxane.) ¹H-NMR spectrum (d₃-MeOD): 8.58 (s, 1H), 8.39 (d, 2H), 8.08 (d, 2H), 7.68 (t, 2H), 7.55 (t, 2H), 5.24 (s, 2H), 3.52 (t, 2H), 2.92 (t, 2H). ¹³C-NMR spectrum (d₃-MeOD): 132.94, 132.33, 131.85, 130.78, 129.05, 126.78, 124.48, 122.87, 52.11, 44.30, 21.17. Anal. Calcd for C₁₇H₁₈BrNS: C, 58.62; H, 5.21; N, 4.02. Found: C, 58.42; H, 5.46; N, 4.01. MALDI-TOF mass spectrum: 266.10 [M]⁺.

Synthesis of the hexafluorophosphate salt of the [3]rotaxane (II) from 9-anthrylmethyl(2-mercaptoethyl)ammonium bromide (I). Thiol (I) was used in 25% excess relative to remaining reagents to compensate for the possible presence of disulfide. The thiol (1.25 g, 3.59 mmol) was dissolved in 35 mL of methanol and filtered to remove a small amount of insoluble material (presumably disulfide). Three equivalents (based on ca. 2.87 mmol of thiol) of dibenzo-24-crown-8 (3.86 g, 8.61 mmol) were added followed by 45 mL of chloroform. The yellow solution was stirred for 20 min. Bromine (0.69 g, 4.31 mmol) was dissolved in 15 mL of chloroform and added to the thiol solution from a dropping funnel over ca. 1 hour. After stirring for 3 hours, the solvent was removed by rotary evaporation and the residue mixed with 50 mL of methanol. The mixture was filtered to remove excess crown ether and a 2-fold excess of ammonium hexafluorophosphate in 15 mL of methanol (0.94 g, 5.74 mmol) was added, giving an immediate precipitate. The precipitate was collected by vacuum filtration and dissolved in ca. 10 mL of acetonitrile. The [3]rotaxane was crystallized by adding ethanol to the acetonitrile solution and evaporating the solution on a rotary evaporator until a precipitate appeared. The microcrystalline powder was collected and dried to give 408 mg of product (16% yield). Elemental analysis and ¹H-NMR spectrum showed the product crystallized with ethanol and water present. ¹H-NMR spectrum (CD₃CN): 8.50 (d, 4H), 8.37 (s, 2H), 7.96 (d, 4H), 7.63 (t, 4H), 7.52 (t, 4H), 6.72 (m, 8H), 6.55 (m, 8H), 5.53 (t, 4H), 3.98-3.50 (m, 56H). ¹³C-NMR spectrum (CD₃CN): 148.55, 132.56, 132.36, 131.61, 130.55, 126.26, 125.23, 125.07, 123.09, 114.21, 113.16, 72.67, 71.85, 69.58, 50.61, 46.83, 34.32, (data excluding smaller peaks between 132 and 121 ppm from

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apparent dissymmetry in crown ethers). Anal. Calcd for $\text{C}_{82}\text{H}_{98}\text{F}_{12}\text{N}_2\text{O}_{16}\text{P}_2\text{S}_2 \cdot 2\text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}$: C, 56.39; H, 6.16; N, 1.53. Found: C, 56.32; H, 6.23; N, 1.78. MALDI-TOF mass spectrum: 1575.60 $[\text{M}+\text{PF}_6]^{+}$, 1429.68 $[\text{M}-\text{H}]^{+}$.

Monolayer formation. Monolayers were formed by immersing the gold substrates in 1.0 mM solutions of the thiol (in methanol), thiol plus 3-fold excess of crown ether (in 1:1 methanol/chloroform) or [3]rotaxane (in acetonitrile) for 24 hours. The samples were rinsed thoroughly with clean solvent, dried in a nitrogen stream and stored in a closed vial to prevent oxidation of the sulfur.

Supporting Experimental Results

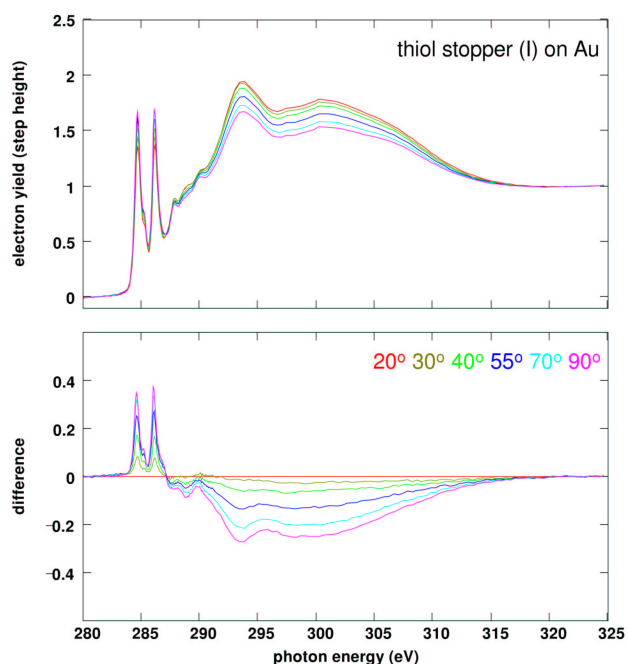


Figure 1 – supporting. Polarization dependence carbon XAS of thiol stopper (I) on gold.

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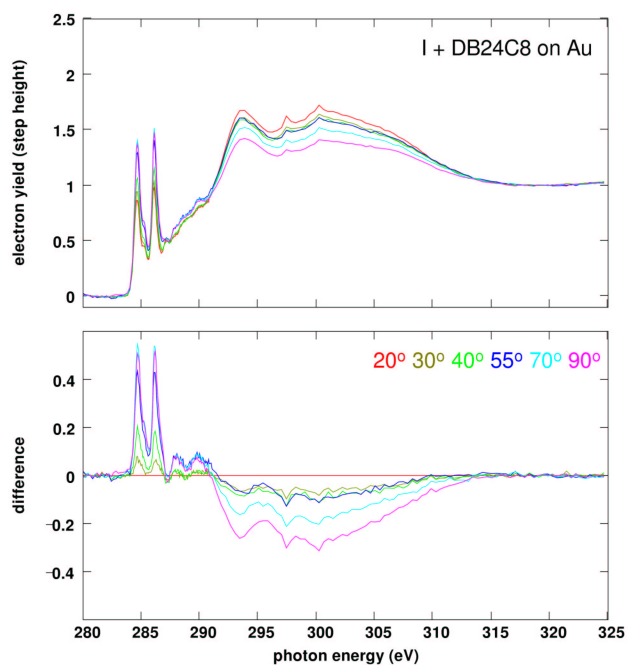


Figure 2 – supporting. Polarization dependence carbon XAS of thiol stopper (I) + DB24C8 on gold.

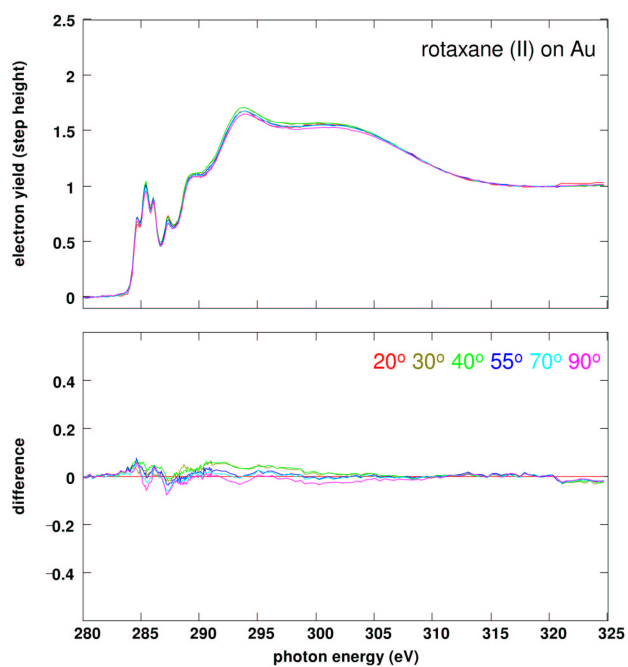


Figure 3 – supporting. Polarization dependence carbon XAS of rotaxane (II) on gold.

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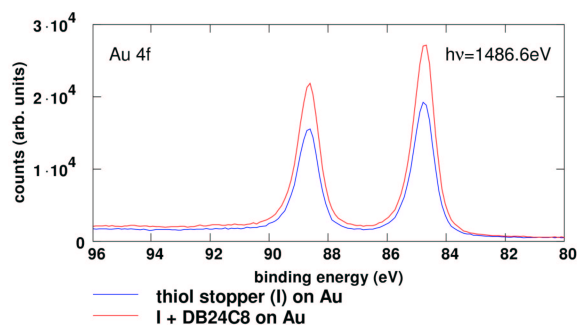


Figure 4 – supporting. Au 4f intensity using standard monochromatized Al K- α X-rays, second set of samples. Attenuation of Au4f electrons as they pass through the layer indicates coverage of the thiol stopper (I) only film is higher than thiol stopper + DB24C8 layer.

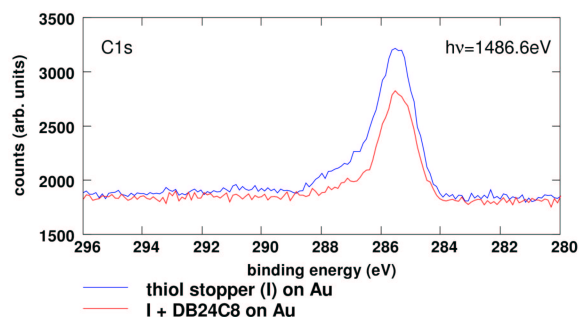


Figure 5 – supporting. C1s intensity using standard monochromatized Al K- α X-rays, second set of samples. Greater C1s intensity in the thiol stopper (I) film indicates higher coverage than I + DB24C8 layer. There is ~58% more intensity in the stopper only C1s peaks.

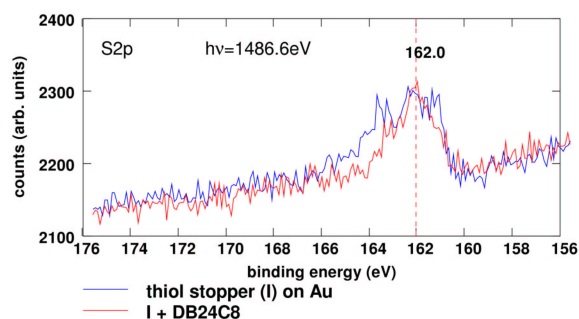


Figure 6 – supporting. S2p intensity from the second set of samples. Both show the same features as the synchrotron samples. Unbound features in thiol stopper (I) are larger than I + DB24C8. These unbound features are less intense than the synchrotron samples, partially due to the increased mean free path of the photoelectrons at ~25 Å compared to ~5 Å in the synchrotron data.

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Table 1-supporting. Sulfur 2p_{3/2} binding energies, assignments, and the percentage of the total S2p signal.

Sulfur 2p	bound	% intensity	unbound	% intensity	oxidized	% intensity	Other	% intensity
thiol	161.9	24	163.8	58	--	--	160.9	18
thiol/crown	161.9	38	163.8	5	167.8	6	161.0	51
rotaxane	161.9	52	163.8	30	167.9	13	160.9	5

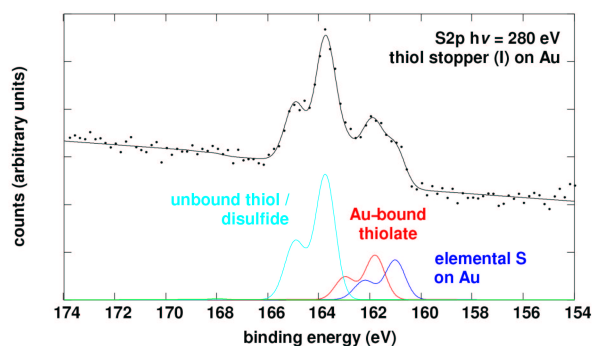


Figure 7 – supporting. S2p XPS spectrum of the film derived from thiol stopper (I) using a photon energy of 280eV. The figure includes data, fit, and the individual spin orbit split pairs from the fit. There is a dominant feature due to unbound thiol consistent with more than one monolayer on the surface.

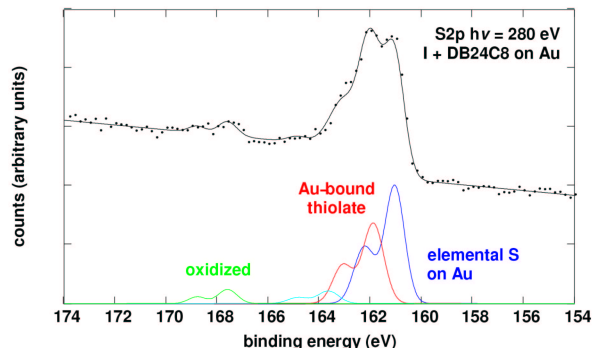


Figure 8 – supporting. S2p XPS spectrum of the monolayer derived from I + DB24C8 using a photon energy of 280eV. The figure includes data, fit, and the individual spin orbit split pairs from the fit. Although there is a significant amount of elemental sulfur on the gold surface, the molecule is mostly bound to the gold.

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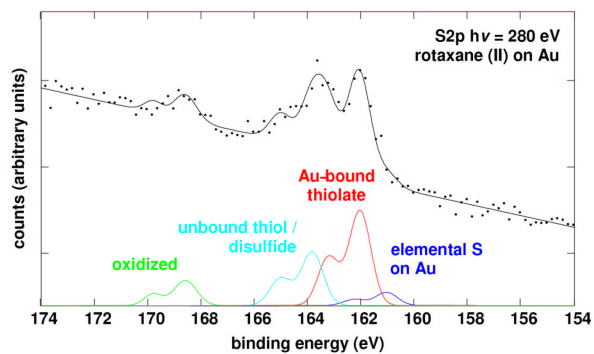


Figure 9 - supporting. S2p XPS spectrum of the monolayer derived from [3] rotaxane (II) using a photon energy of 280eV. The figure includes data, fit, and the individual spin orbit split pairs from the fit. In this sample, the most intense feature is from sulfur chemisorbed to the gold.