4-Nitrophenyl Sulfenyl Chloride as a New Precursor for the Formation of Aromatic SAMs on Gold Surfaces

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I- Experimental Section

Chemicals and substrates. 4-nitrophenyl sulenyl chloride was purchased from Aldrich and used without further purification. Dimethyl formamide, DMF, (certified ACS from Fisher Scientific) was freshly distilled under argon just prior to use. Ethanol, EtOH, (anhydrous, Commercial Alcohols) was used as received.

Au (111) preparation. Au from a gold wire (0.762 mm dia, Premion ®, 99.999%, Alfa Aesar) was evaporated onto freshly cleaved mica (V1 Grade, Ted Pella) in a custom built evaporation system, consisting of a Kurt J. Lesker bell jar, Varian turbo pump, and operating at a pressure of 1 x 10^{-7} Torr. The base plate holding the mica was heated at 600 K for 12 hours prior to depositing the gold and was kept at 600 K for an additional 3 hours after the gold was deposited to help ensure the formation of high quality Au (111) surfaces. Upon removal from the evaporation chamber, the gold samples were cleaned with Chromic Sulfuric Acid, (Chromerge ®, Bel-Art), anhydrous ethanol (Commercial Alcohols), and ultra pure water (Millipore, 18.2 MΩ) and then dried under a nitrogen stream and stored in a dessicator until used. Au (111) substrates are routinely imaged using STM before modification to assess their quality. Examples are provided in Figure 1, showing large and atomic scale images.

STM. A 5500 SPM system (Agilent) was used for STM imaging. Images were obtained in air using a tungsten tip (0.25 mm dia, 99.95%, Alfa Aesar) electrochemically etched in 3 M NaOH (99.99%, Semiconductor Grade, Sigma Aldrich).

XPS. X-ray photoelectron spectroscopy (XPS) studies were conducted in an ultrahigh vacuum (UHV) system (Omicron) operating at a base pressure of 5 x 10^{-11} Torr. X-rays were generated from an Al Kα source (1486.6 eV). The system contains a hemispherical sector analyzer coupled to a multichannel electron detector. The analyzer was operated in constant analyzer energy (CAE) mode with a pass energy of 20 eV. A takeoff angle of 75° was used for all samples. All XPS spectra presented in the work were fitted using XPSPEAK 4.1 software.

For thickness determination, an attenuation length value of 33 Å was used. This value has been previously used (M. S. Boeckl, A. L. Bramblett, K. D. Hauch, T. Sasaki, B. D. Ratner, J. W. Rogers, Jr. Langmuir 2000, 16, 5644.) where it was estimated using the empirical formula of Seah and Dench (Seah, M. P.; Dench, W. A. Surf. Interface Anal. 1979, 1, 2.). A close value (30-31 Å) was also used (M. Zharnikov, and M. Grunze, J. Phys.: Condens. Matter, 2001, 13, 11333.).
**Supporting Information**

**PMIRRAS.** IR measurements were obtained using a commercial FT-IR system (Thermo Scientific Nicolet 8700) equipped with an external tabletop optical mount, a photoelastic modulator (PEM) (Hinds Instruments PM-90 with a II/ZS50 ZnSe 50 kHz optical head, Hillsboro, OR) and a demodulator (GWC Instruments Synchronous Sampling Demodulator, Madison, WI). Dry air (Balston 74-45) was purged through all atmospheric regions of the system. The angle of incidence of the IR beam was optimized to ~ 80° with respect to the surface normal and PEM was set for half wave retardation at 2900 cm⁻¹ (for CH stretch) and at 1300 cm⁻¹ (for NO₂ stretch). The spectrum was obtained using a liquid nitrogen cooled MCT-A detector with a resolution of 4.0 cm⁻¹ and 10,000 scans were recorded. The output signal was relative differential reflectivity ($\Delta R/R_a$). ($\Delta R/R_a=2(R_p-R_s)/(R_p+R_s)$). ($R_p$ and $R_s$ are the reflection coefficients for the p and s polarization, respectively). The spectrum was referenced against bare gold and spline interpolation technique was used for background correction.

**Cyclic Voltammetry.** Electrochemical measurements were conducted in a three electrode glass cell thermostated at 25 °C under dry nitrogen. A 2 mm diameter gold electrode ($\Omega$ Metrohm) was used. The electrode was carefully polished and ultrasonically rinsed with ethanol then electrochemically cleaned in a 0.5 M KOH aqueous solution. The reference electrode was a SCE. The counter electrode was a platinum wire. The electrochemical instrument used was an Autolab PGSTAT30 (Eco Chemie).

**II - STM Imaging of the Au(111) substrates**

STM images of Au(111) substrates prepared as described in the experimental part. (a) 200x200 nm² and (b) 5x5 nm².
III- STM Imaging of the 4-nitrophenyl thiolate SAM on a Au(111) substrate

STM Images of the 4-nitrophenyl thiolate SAMs on Au(111) obtained using the corresponding sulfenyl chloride precursor in DMF/EtOH (1/9). (a) 5x5 nm², (b) 15x15 nm², (c) 30x30 nm², (d) 45x45 nm² and (e) 54x54 nm². Tunnelling conditions: tunnelling current = 1.0 nA and bias voltage = 0.1V (a, b and c); tunnelling current = 0.8.0 nA and bias voltage = 0.1V (d and e).
Supporting Information

IV- IR spectrum of 4-nitrophenyl sulfenyl chloride.