Supporting Information
for
Molecular Voltammetric Determination of the Electrical Properties of Self-Assembled Monolayers of Compounds of Interest in Molecular Electronics

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Additional References on Molecular Electronics

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7. Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
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General References on Scanning Probe Methods

1. (a) *Scanning Tunneling Microscopy and Spectroscopy*, 2nd ed.; Bonnell, D. A., Ed.; VCH: New York, 2000. (b) *Scanning Probe Microscopy: Analytical Methods*; Wiesendanger, R., Ed.; Springer-Verlag: Berlin, 1998. (c) *Scanned Probe Microscopy*; Wickramasinghe, H. K., Ed.; AIP Conference Proceedings, *241*, American Institute of Physics: New York, 1992.

Synthesis and SAM Preparation

The syntheses of the molecular wires were described elsewhere [Jones, L., II; Schumm, J. S.; Tour, J. M. "Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene-ethynylene)s With Thioester Termini: Molecular Scale Wires With Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support," *J. Org. Chem.* **1997**, *62*, 1388-1410.] The compounds were purified by chromatography and/or recrystallization. Au substrates were prepared by depositing a 50-nm layer of chromium, followed by a 120-nm layer of Au onto a clean surface of a single crystal silicon wafer. These two metal layers were vacuum-deposited sequentially (Auto 306, Edwards High Vacuum International), without breaking the vacuum. The evaporation rate was ~ 1 Å/s and the vacuum was ~ 4×10^{-6} Torr. Immediately before use, the Au substrates were cleaned by placing them in an aqueous solution of H_2O_2/NH_4OH (H_2O_2:NH_4OH:H_2O = 1:1:5 by volume) for 15 min, followed by a thorough washing with de-ionized water and ethanol. Acetonitrile (Fisher Scientific) was distilled over calcium hydride under nitrogen and was used immediately after being distilled. Tetrabutylammonium tetrafluoroborate (Aldrich) and other chemicals were used without further purification.

Self-assembly of thiolacetates on Au was carried out in a vial which contained a piece of the Au substrate, the conjugated compound (1.0 mg), ethanol (20 mL), and saturated NH_4OH (20 μL). The sample was removed after 24 h and washed with acetone, THF and ethanol, [Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. S.; Burgin, T. P.; Whitesides, G. W.; Allara, D. L.; Parikh, A. N.; Atre, S. "Self-Assembled Monolayers and Multilayers of Conjugated Thiols, α,ω-Dithiols, and Thioacetyl-Containing Adsorbates. Understanding Attachments Between Potential Molecular Wires and Gold Surfaces," *J. Am. Chem. Soc.* **1995**, *117*, 9529-9534.]. Self-assembly of diazonium salts on Au was carried out in an Al foil covered vial which contained a piece of metal substrate, the diazonium salt of a molecular wire (1.0 mg), acetonitrile (20 mL). The sample was removed after 24 h and washed with acetonitrile, and ethanol. After drying the sample was stored in a nitrogen-filled zip lock plastic bag. Ellipsometry measurement was carried out in a nitrogen atmosphere.

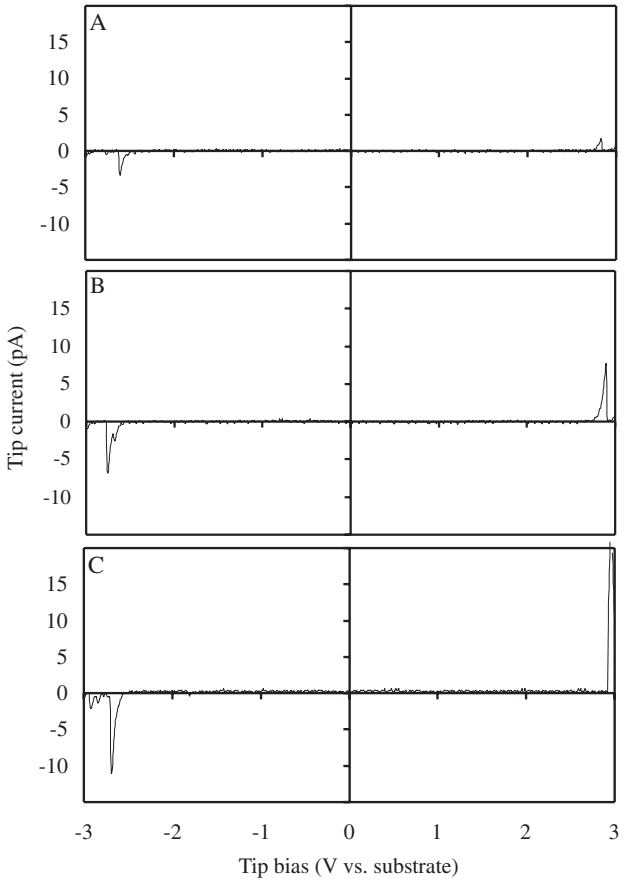

Figure S1. Three voltammetric curves recorded as the tip approaches in 2 Å steps to the surface (from frame A to frame C) of a SAM of 2'-ethyl-4,4'-bis(phenylethynyl)-1-benzenethiolate (II) on gold.