Supplementary Information

Replacing $Ag^{TS}SCH_2$–R with $Ag^{TS}O_2C$–R in EGaIn-Based Tunneling Junctions Does Not Significantly Change Rates of Charge Transport

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Experimental Details

Materials. All monolayer precursors: *n*-alkanoic acids ($CH_3(CH_2)_{2n}CO_2H$, n = 1 – 8), oligo(phenylene)carboxylic acids ($HO_2C(C_6H_4)_nH$, n = 1 – 3), and *n*-alkanethiols ($CH_3(CH_2)_{2n}CH_2SH$, n = 1 – 8) are commercially available (≥ 96%, Sigma-Aldrich), and all carboxylic acids were used as received. All organic solvents were analytical grade (99%, Sigma-Aldrich) and were used as supplied unless otherwise specified. All thiols used to make SAMs were purified by silica-gel column chromatography (using 15% ethyl acetate in hexane, and gravity elution). All purified alkanethiols were maintained under a N_2 atmosphere at < 4 °C. To ensure purity, all stored compounds were checked by ^{1}H NMR prior to use.

Template-Stripped Silver (Ag^{TS}) Substrates. Four hundred–nanometer thick Ag films were electron-beam evaporated onto a single–side polished n-doped silicon (Si) wafer with <111> orientation, and then attached to glass substrates using a photo–cured optical adhesive (Norland Optical Adhesive 61, Nortland Products). The resulting Ag^{TS} films are ultrasmooth with an rms roughness of 0.5 nm. The low surface roughness significantly increases the yield of working junctions. Exact film preparation and characterization is detailed elsewhere.[1-3]

Eutectic Gallium-Indium (EGaIn) Top Electrode. EGaIn is non-toxic, non-destructive, easy-to-handle, and commercially available (99.99%, Sigma-Aldrich). Upon exposure to air, EGaIn forms a thin, native gallium oxide film (Ga_2O_3, with thickness about 0.7 nm) which facilitates the fabrication of different shapes with high precision in contact area (50 μm^2 on average) and enhances the yield of working junctions.[4-6] In this study, we used conical-shaped EGaIn top electrodes to form electrical contacts in junction measurements.[4, 5, 7]

Monolayer Preparation. The preparation of SAMs of *n*-alkanoates and of *n*-alkanethiolates on Ag follows published procedures;[7-11] in brief, freshly prepared Ag^{TS} substrates were introduced into the solution of monolayer precursor for 3 hours (1mM of each of the *n*-alkanoic acids in hexadecane or *n*-alkanethiols in toluene). The preparation of SAMs of oligophenylene carboxylates follows the reports published by Tao and coworkers.[12, 13] Most of the SAM-bound Ag substrates emerged dry from the solution, but surfaces coated with shorter alkane-SAMs or aromatic SAMs emerged wet. We rinsed these substrates three times with anhydrous hexane/THF or toluene and dried these under a gentle stream of nitrogen.

Junction Measurements. These measurements were performed in ambient conditions, using conical EGaIn top electrodes to make electrical contacts to SAM-bonded Ag substrates.[5-7, 14] In order to extract the current density (J, in A/cm^2), the EGaIn contact area (50 ± 10 μm^2) was determined from the optically measured diameter. For each monolayer, at least 430 J—V curves were measured (3 junctions made by a fresh EGaIn tip, 21 traces measured on a junction) from 3—4 different substrates. The *J(V)* measurements were collected in a voltage scan mode between +0.5 and -0.5 V, back and forth (0 V→ +0.5 V→ 0 V →-0.5 V→ 0 V), in steps of 0.05 V with a 0.02 second delay between scans.[5-7, 10, 14]

Table S1. Summary of geometric information for SAMs of *n*-alkanethiolates,[15-17] *n*-alkanoates,[9, 18, 19] and oligophenylene carboxylates[12, 13] on Ag (111). The calculation of molecular footprint is based on the lattice spacing and SAM overlayer.

	n-alkanethiolates	*n*-alkanoates	oligophenylene carboxylates
Tilt angle (^{o})	11-13	15-25	0
Cell	$(\sqrt{7}x\sqrt{7})R10.9^{o}$	$p(2x2)^{a}$	$p(2x2)^{a}$
Lattice spacing (Å)	4.4^{b}	5.8	10
Molecular footprint ($Å^2$)	6	6	18

[a]Overlayer on Ag; [b]Nearest neighbor spacing.

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