

Supporting Information

Fluorination, and Tunneling across Molecular Junctions

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Experimental Details

Materials. All monolayer precursors—*2H,2H,3H,3H*-perfluoroalkanoic acids ($\text{HO}_2\text{C}(\text{CH}_2)_2(\text{CF}_2)_{n-2}\text{CF}_3$), perfluoroalkanoic acids ($\text{HO}_2\text{C}(\text{CF}_2)_n\text{CF}_3$), ω -(4-trifluoromethyl-phenyl)-alkanoic acids ($\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_m\text{CF}_3$), ω -(4-fluorophenyl)-alkanoic acids ($\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_m\text{F}$), and (4-trifluoromethyl)-oligophenyl carboxylic acids ($\text{HO}_2\text{C}(\text{C}_6\text{H}_4)_m\text{CF}_3$)—are commercially available (Alfa Aesar; Wako Chemicals; Oakwood Chemical; Santa Cruz Biotechnology; Sigma-Aldrich; TCI), and all carboxylic acids (purities are equal or above 96%) were used as received. All organic solvents were analytical grade (99%, Sigma-Aldrich) and were used as supplied unless otherwise specified.

Eutectic Gallium-Indium (EGaIn) Top Electrode. EGaIn (eutectic Ga-In; 74.5% Ga, 25.5% In; 99.99%, Sigma-Aldrich) has shown to be a versatile material for making soft, ohmic contacts because of its properties (non-toxic, non-destructive, easy-to-handle) and availability.¹⁻⁷ The formation of a self-passivating oxide (mostly Ga_2O_3 ,) upon exposure of EGaIn to air makes it possible to fabricate electrodes with a range of useful shapes; in addition, the presence of the oxide skin increases the yield of working junctions.⁸ We use “selected” unflattened conical EGaIn⁹ to contact the surface of SAM-bound Ag^{TS} in a way that does not damage the SAM.^{10,11} The average geometrical contact area was $1800 \mu\text{m}^2$.

Template-Stripped Silver (Ag^{TS}) Substrates. Three hundred-nanometer thick silver films were deposited by electron-beam evaporation at $\sim 0.15 \text{ nm/second}$ onto a single-side polished n-doped silicon (Si) wafer with $\langle 111 \rangle$ orientation, and then attached to glass substrates (1 cm^2) using a photo-cured optical adhesive (Norland Optical Adhesive 61, Norland Products). The resulting Ag^{TS} films are smooth with an rms roughness of $\sim 0.65 \text{ nm}$. Using template-stripped substrates

significantly increases the yield of working junctions.^{10,12,13} The exact procedure used to prepare and characterize the film is detailed elsewhere.¹⁰

Preparation of SAMs. The preparation of SAMs of organic carboxylates on Ag follows published procedures:¹⁴⁻¹⁶ SAMs were formed by introducing freshly prepared Ag^{TS} substrates into 1-mM solutions of fluorinated carboxylic acids in *n*-hexadecane for 10 minutes; further immersion (up to 48 hours) did not change either the contact angle of water ($\sim 121 \pm 5^\circ$) on the SAMs, or the yields of working junctions. Following incubation at room temperature (and directly before electrical measurements), we rinsed the substrates three times with anhydrous hexane (1mL each time) to remove the residual hexadecane from the surface of R^F-bound silver and dried the substrates under a gentle stream of nitrogen.

Junction Measurements. These measurements were performed at room temperature using “selected” unflattened conical EGaIn top electrodes⁹ to make electrical contact with the SAM-bound Ag^{TS}.^{8,11,17,18} In order to extract the current density (J , in A/cm²), the EGaIn contact area ($1800 \pm 120 \mu\text{m}^2$) was determined from the diameter of the contact region estimated by the optical microscopy.^{1,8,17} For each monolayer, at least 300 J – V curves were measured (three junctions made by a fresh EGaIn tip, 21 traces measured on a junction) from three different substrates.^{8,16} The $J(V)$ measurements were collected in a voltage scan mode between +0.5 and -0.5 V, back and forth (0 V \rightarrow +0.5 V; +0.5 V \rightarrow 0 V; 0 V \rightarrow -0.5 V; -0.5 V \rightarrow 0 V), in steps of 0.05 V with a 0.02 second delay between scans.^{8,11,17-19} We calculate the yield of working junctions by dividing the number of non-shortening junctions by the total number of measured junctions ($\times 100$).¹⁸

Data Analysis. Figures S1 contains a summary of the histograms of $\log|J(-0.5 \text{ V})|$ for $\text{Ag}^{\text{TS}}\text{O}_2\text{C}(\text{CH}_2)_n(\text{CF}_2)_m\text{T//Ga}_2\text{O}_3/\text{EGaIn}$ junctions (where $n, m = 0, 2, 4, 6, 8$; $\text{T} = \text{CH}_3$ or CF_3); they exhibit approximately log-normal distributions. Fitting each histogram with a Gaussian curve, we obtained mean values of log-current density ($\log|J|_{\text{mean}}$) and standard deviation (σ_{\log}) of the corresponding Gaussian fits. Mean and median values of $\log|J|$ were indistinguishable and values of σ_{\log} ranged from 0.06 to 0.3. As expected from the simplified Simmons equation, the rate of charge transport across junction containing fluorinated SAMs followed an exponential decrease in current density with an increasing length of the alkyl chain.

The thickness of R^{F} SAMs is $\sim 20\%$ thinner than that of homologous R^{H} SAMs; the tilt angles for R^{F} and R^{H} SAMs are $\sim 28^\circ$ and $\sim 14^\circ$.^{14,20,21} If we consider the mechanism of tunneling transport from a through-bond to a through-space pathway, the attenuation factor β changes from 0.91 \AA^{-1} ($1.15 n_{\text{CF}_2}^{-1}$) to 1.36 \AA^{-1} for R^{F} SAMs and from 0.83 \AA^{-1} ($1.05 n_{\text{CH}_2}^{-1}$) to 1.01 \AA^{-1} for R^{H} SAMs; the difference between the values of β for R^{F} and R^{H} SAMs increases from 10% (the width of the tunneling barrier, d , is defined by the number of the repeating units or the length of the molecules) to 35% (d is the thickness of the SAMs). However, we know neither the exact conformation (helices or gauche-type conformations) of R^{F} SAMs nor the mechanism of tunneling transport (through-bond and/or –space). Therefore, we assume that the mechanism of hole tunneling is a through-bond transport, and define d by the number of CH_2 and/or CF_2 groups.

Previous Studies of EGaIn-based Junctions. Our recent studies have shown that the rate of charge transport across a $\text{Ag}^{\text{TS}}/\text{A}(\text{CH}_2)_n\text{M}(\text{CH}_2)_m\text{T//Ga}_2\text{O}_3/\text{EGaIn}$ junction is insensitive (within the precision of our measurements) to many functional groups inserted either at the SAM/electrode interfaces ($\text{Ag}^{\text{TS}}/\text{A}$ and $\text{T//Ga}_2\text{O}_3$) or in the backbone of the SAM ($-\text{M}-$), where A is a carboxylate or thiolate;¹⁶ M is an amide ($-\text{CONH}-$ and $-\text{HNCO}-$) or urea;²² the series of

functional groups T includes aromatics and heteroaromatics,¹⁹ acids and bases,⁹ amide and ester,²² cyanide and halogens.²³ The exceptions are redox active groups, such as ferrocene,²⁴⁻²⁶ quinones,²⁷ and 2,2'-bipyridine,²⁸ which result in the rectification of current.

Junction Measurements and Analytical Procedure. We measured $J(V)$ for junctions of the form $\text{Ag}^{\text{TS}}\text{O}_2\text{C}(\text{CH}_2)_n(\text{CF}_2)_m\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ over the range of ± 0.5 V as a function of the number of CH_2 and/or CF_2 units (where $n, m = 0, 2, 4, 6, 8, n + m = 8$, and $\text{T} = \text{CH}_3$ or CF_3). Each $\log|J|$ versus V curve was generated with more than 300 J - V scans from at least 15 different junctions on three samples, and the yields of working junctions were $\geq 90\%$. We did not observe rectification of current across the junctions. Figure S1 summarizes histograms of $\log|J(-0.5 \text{ V})|$ derived from the measurements. Fitting each histogram with a Gaussian curve, we found that mean and median values of $\log|J|$ were indistinguishable, and that values of σ_{\log} ranged from 0.06 to 0.3 which are similar to those measured for junctions having n -alkanethiolates and n -alkanoates.^{8,16}

Figure S1. Histograms of $\log|J|$ data derived from (a) $\text{HO}_2\text{C}(\text{CH}_2)_2(\text{CF}_2)_{n-2}\text{CF}_3$ and (b) $\text{HO}_2\text{C}(\text{CF}_2)_n\text{CF}_3$, ($n = 2, 4, 6, 8$) at -0.5 V. Each histogram is fitted with a Gaussian curve (black curve).

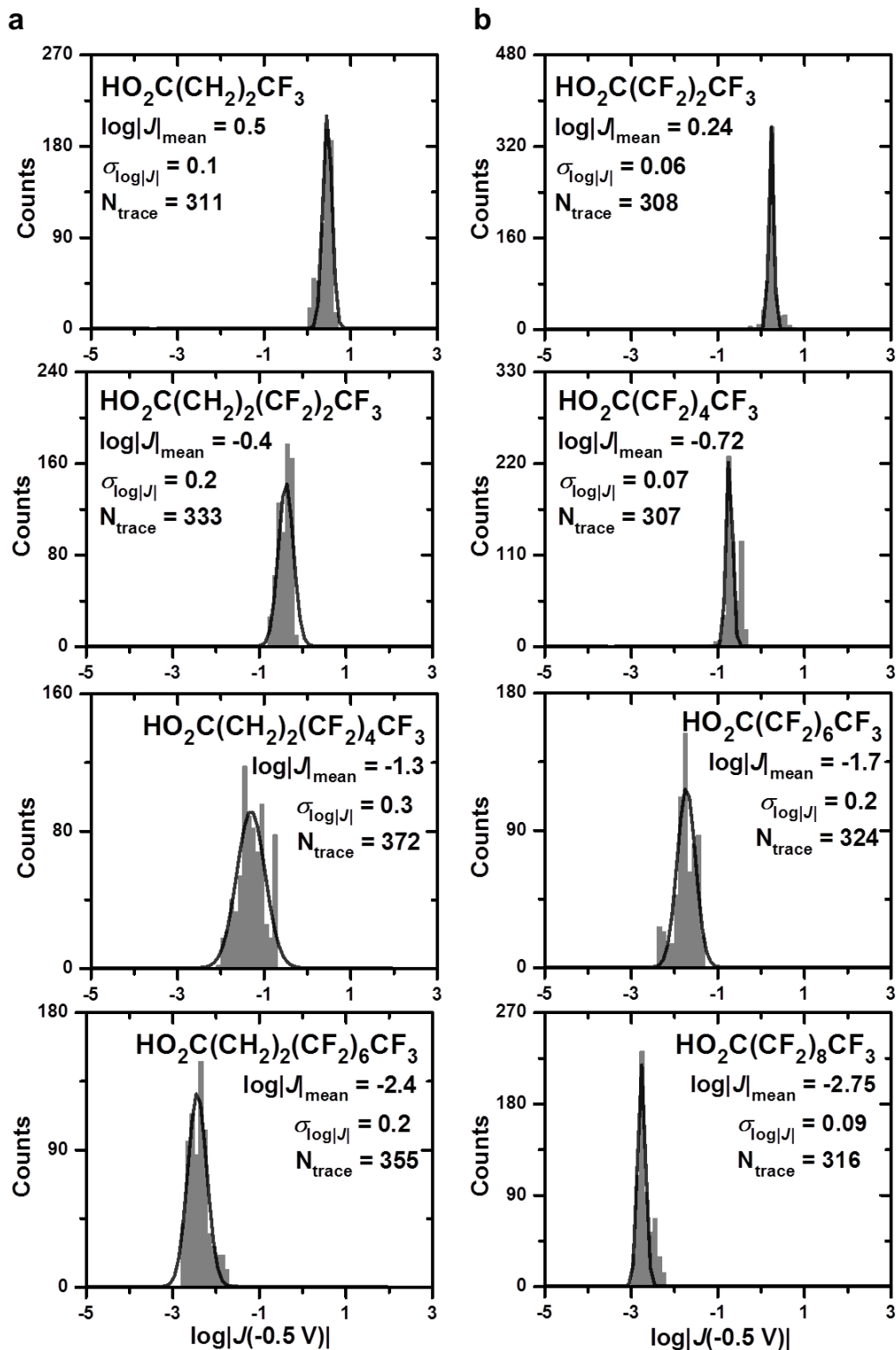


Figure S2. Histograms of $\log|J|$ data derived from (a) $\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_m\text{CH}_3$ and (b) $\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_m\text{CF}_3$ ($n = 0$ and 2 ; $m = 1$ and 2) at -0.5 V. Each histogram is fitted with a Gaussian curve (black curve).

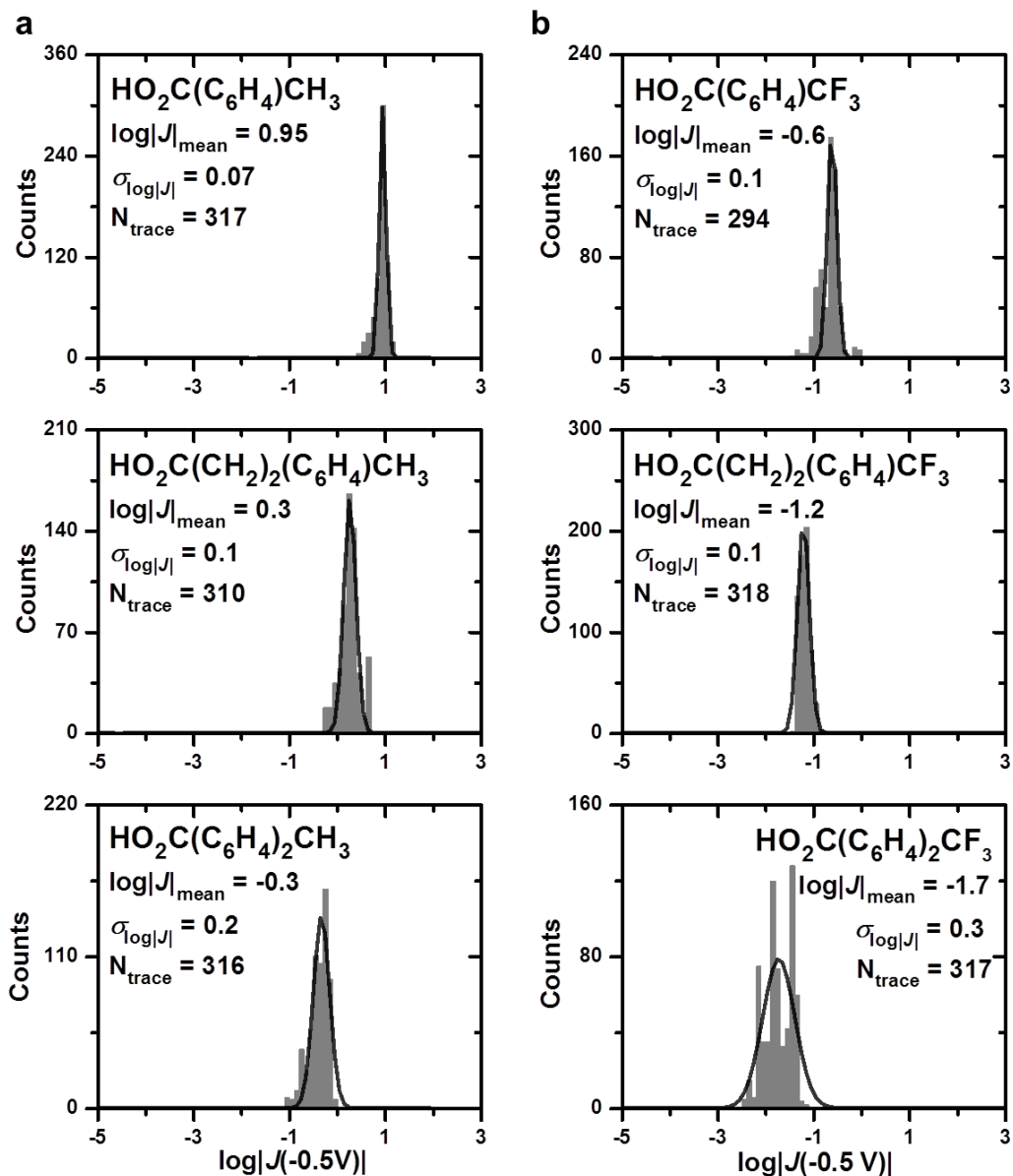
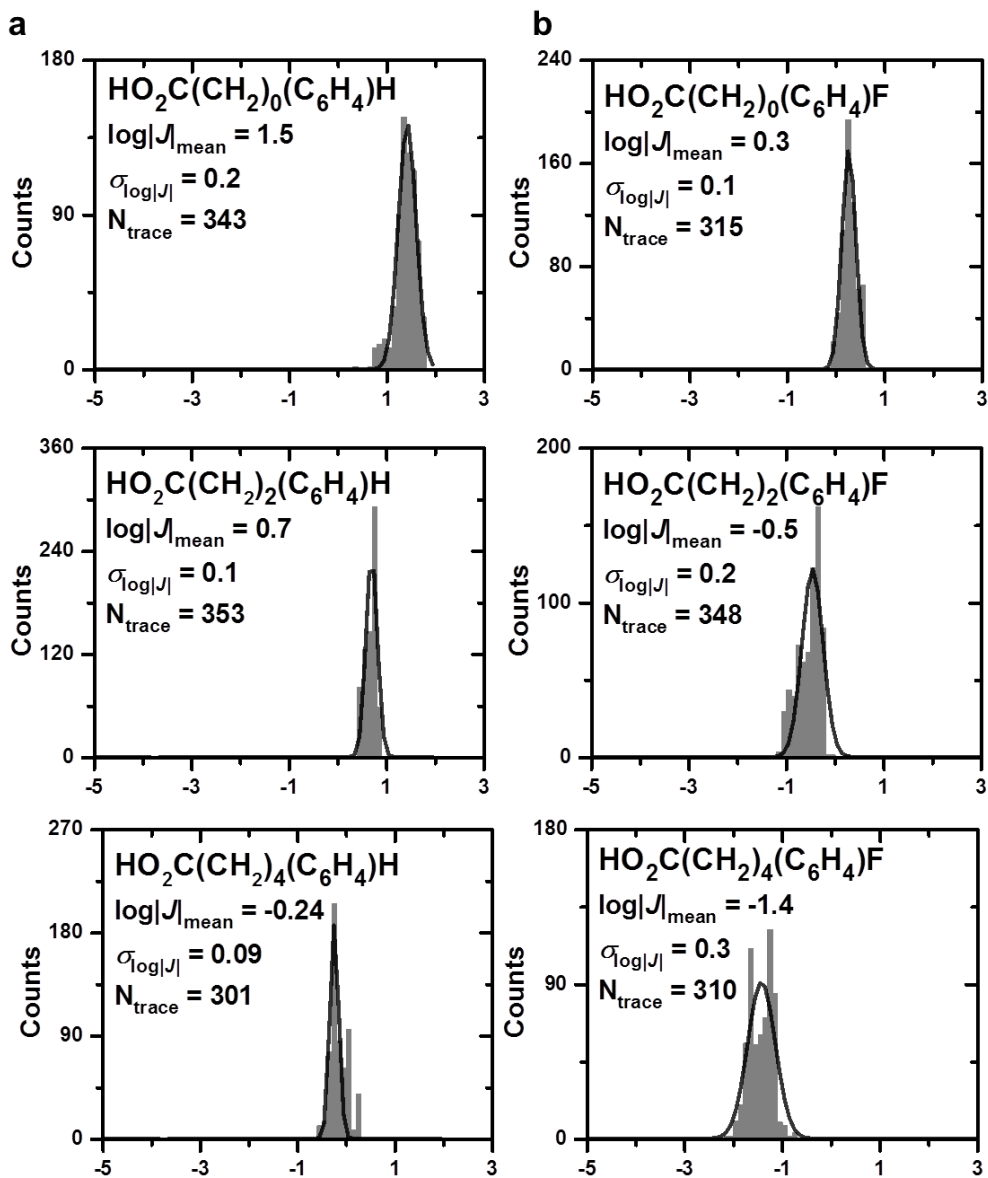


Figure S3. Histograms of $\log|J|$ data derived from (a) $\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)\text{H}$ and (b) $\text{HO}_2\text{C}(\text{CH}_2)_n(\text{C}_6\text{H}_4)\text{F}$ ($n = 0, 2, 4$) at -0.5 V. Each histogram is fitted with a Gaussian curve (black curve).



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