Supplemental Information:

Molecular Rectification in Metal-SAM-Metal Oxide-Metal Junctions

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Nomenclature. We denote the ferrocene (Fc) terminated SAMs of $HS(CH_2)_{11}Fc$ as $SC_{11}Fc$ and SAMs of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{14}CH_3$ as $SC_{10}CH_3$ and $SC_{14}CH_3$, respectively. We use the notation Ag^{TS}-$SC_{11}Fc$//Ga_2O_3/EGaIn to describe the junctions: here, Ag^{TS}-$SC_{11}Fc$ is an electrode of template-stripped silver (with an area of about 1 cm^2) supporting a SAM of $SC_{11}Fc$. We describe the interfaces with the symbols "-", which indicates a chemisorbed contact, "/" which describes the contact between Ga_2O_3 and EGaIn, and "//", which indicates a non-covalent (here a van der Waals) interface.[1] The difference in voltage between the two electrodes is *V*.

Experimental

SAM-Ga_2O_3/EGaIn Tunneling Junctions. We formed ultraflat Ag surfaces by a template-stripping (TS) procedure published previously.[1] Details can be found in reference 1, but we give a brief description here. We deposited a layer of 500 nm of Ag by electron-beam (e-beam) evaporation at 2-3 × 10^{-6} Torr at a rate of 8-10 Å/s on silicon wafers with their native SiO_2 layer present. Glass slides (typically 1 cm^2), which were cleaned by washing with EtOH, and subsequent exposure to oxygen plasma for 5 min, were glued at the Ag-surface using an optical adhesive (Norland, No. 61). The optical adhesive was cured by exposure to ultraviolet light for 2 h. The glass substrates were cleaved off the Si-wafer using a razor blade. After cleavage, the Ag^{TS} substrates were immersed in the ethanolic solutions containing the thiols under argon within 5 s.

The $SC_{10}CH_3$ and $SC_{14}CH_3$ (Sigma-Aldrich) were recrystallized from three times from ethanol before use. The $SC_{11}Fc$ was synthesized according to a literature procedure.[2]

SAMs of $SC_{10}CH_3$, $SC_{11}Fc$ and $SC_{14}CH_3$ were formed for 18-24 hours on the Ag^{TS} surfaces at room temperature (R.T., under argon) in 1-2 mM ethanolic solutions.

We used conical shaped eutectic indium-gallium (EGaIn, 75.5 % Ga 24.5 % by weight, 15.7 °C melting point) alloy as top-electrodes. A detailed description of the formation of the SAMs and the procedures used to contact them by Ga_2O_3/EGaIn top-electrodes has been reported by our group.[3] The Ga_2O_3/EGaIn behaves as a non-Newtonian fluid.[4] When sheer-pressure is applied, Ga_2O_3/EGaIn behaves as a liquid. The Ga_2O_3/EGaIn will flow until the shear is relieved. This behavior allows EGaIn, unlike mercury, to adopt non-spherical shapes. A drop of EGaIn hanging from a 26S-guage needle was brought into contact with a surface that is wettable by Ga_2O_3/EGaIn (PDMS, glass, or Ag). The Ga_2O_3/EGaIn adheres to both the surface and to the needle. Slowly retracting the needle from the drop of Ga_2O_3/EGaIn-drop, using a micromanipulator, deformed the Ga_2O_3/EGaIn drop in such a way that two conically-shaped Ga_2O_3/EGaIn structures, connected head-to-head, formed. Further retraction of the needle resulted in separation of the conically-shaped Ga_2O_3/EGaIn structures, one attached to the needle and the other attached to the surface. Subsequently, the substrate was discarded and replaced by a Ag^{TS} surface with the SAM of interest, and the conically-shaped Ga_2O_3/EGaIn at the needle was brought into contact with the SAM.

Wet Electrochemistry. The $SC_{11}Fc$ SAMs were characterized at Au^{TS} electrodes by wet electrochemistry. Electrochemical measurements were performed with an AUTOLAB PGSTAT10. A custom built three-electrode setup equipped with a platinum counter electrode, a Ag/AgCl reference electrode, and a screw cap to hold the gold working electrode (area exposed to the solution = 0.44 cm^2) was used. Cyclic voltammograms were recorded in an aqueous solution 1 M $HClO_4$, between –0.1 and 0.9 V at scan rates of 0.050, 0.10, 0.20, 0.50, 1.0, 2.0 and 5.0 V/s.

Statistical Analysis of the Junctions

In total, we recorded 997 *J*(V) traces (1 trace = 0V → +1V → -1V → 0V) from 53 Ag^{TS}-$SC_{11}Fc$//Ga_2O_3/EGaIn junctions assembled on ten different Ag^{TS} substrates (five to six junctions per substrate). The Ag^{TS} substrates on glass were obtained from three different Ag coated wafers. Of the 53 junctions examined, three junctions (5%) failed on the first trace: that is, they showed either no electrical contact or a short circuit. During subsequent measurement two junctions suffered from excessive noise, one from a loss of contact, and one from a short-circuit (defined as a sudden increase in current density of more than two orders of magnitude). The remaining 46 junctions continued to rectify for 21 traces, after which the experiment was terminated so that every junction would weigh equally in the statistical analysis. Thus, the yield of stable junctions is 87% and the number of traces recorded on the junctions is 997, from which the <log|*J*|> values and *R* were determined.

A total of 23 Ag^{TS}-$SC_{10}CH_3$//Ga_2O_3/EGaIn junctions were characterized. The junctions were measured at four different Ag^{TS} substrates (three to seven junctions per substrate) obtained from two different Ag coated wafers. Of the 23 junctions, four short-circuited on the first trace and three junctions short-circuited during data acquisition. Thus, the yield of stable junctions was 74%, giving a total of 415 traces from which the <log|*J*|> values and *R* were determined.

In total 14, Ag^{TS}-$SC_{14}CH_3$//Ga_2O_3/EGaIn junctions were characterized. The junctions assembled at five different Ag^{TS} substrates (three to five junctions per substrate) obtained from two different Ag-coated wafers. Of the 14 junctions, none failed on the first trace, though two junctions short-circuited during the course of measurement and one became an open circuit (presumably due to a loss of contact between Ga_2O_3/EGaIn and the SAM). Thus, the yield of stable junctions was 79%, and yielded a total of 287 traces.

We used a linear least-squares fitting algorithm (the curve-fitting tool in MATLAB R2007a)[5] to fit Gaussians to the histograms of current densities and rectification ratios. Since *R* and *J* were log-normally distributed, the normally-distributed variables log(*R*) and log(*J*) served as the input to the fitting algorithm, so that the algorithm always fit

Gaussians to normally-distributed data.[6] The mean (μ) and standard deviation (σ) extracted from each Gaussian fit were transformed to the log-mean ($\mu_{\log}$) and log-standard deviation ($\sigma_{\log}$) according to the formulae: $\mu_{\log} = 10^{\mu}$ and $\sigma_{\log} = 10^{\sigma}$.

We stress that every measurement, without exception, collected for each type of junction was included in both the corresponding histogram and the input to the fitting algorithm that determined the Gaussian fit. Thus, in plotting and fitting the data, we neither excluded nor omitted any value. In some figures, the Gaussian fit appears not to conform to a region of the histogram, as if the data in that region had been excluded from the fitting process; however, no data were excluded. Though a particular Gaussian fit may be visually unsatisfying, all fits are reproducible because they result from the minimization of error by the fitting algorithm without interference from the operator. We believe that the community should adopt this approach – or another similarly straightforward and unbiased strategy – concerning the presentation and fitting of data.

Junctions of Ag^{TS}-$SC_{11}Fc$//Au^{TS}.

We used Scotch tape to template-strip a thin layer of Au (500 nm, electron-beam evaporation with a speed of 0.5 Å/s at 2.2×10^{-6} bar) from the Si/SiO_2 wafer (Fig. S1). We applied the Scotch tape to the Au on a Si/SiO_2 wafer; removal of the Scotch tape effectively template-stripped the layer of gold from the Si/SiO_2. Apparently, the interaction of the gold with the Scotch tape is stronger than the interaction of the gold with the Si/SiO_2 wafer. Larger areas of gold than defined by the contact area of the Scotch tape could be template-stripped. Thus, at the edges of the Scotch tape with a layer of template-stripped gold, a layer of Au^{TS}-foil, as indicated in Fig. S1, was present that was not supported by the Scotch tape. We used this thin layer of gold-foil to contact SAMs of $SC_{11}Fc$ on Ag^{TS} bottom-electrodes. Out of 40 junctions, five junctions were not shorting, or did not short during the measurement. Figure S2 shows the *I*(V) characteristics of two of those junctions. The junctions show characteristics similar to those obtained with the Ag^{TS}-$SC_{11}Fc//Ga_2O_3/EGaIn$ junctions, and rectified currents. The junctions shown in Fig. S2 had rectification ratios of 12 and 1.1×10^2 at ± 1.0 V; the other three junctions had rectification ratios of 11, 20, and 40. The contact area of the Au^{TS} top-contact with the SAM could not be exactly determined using the camera in our setup since the Au is not transparent, but the width of the junctions were smaller than 50 μm.

Figure S1: Optical micrographs of the Scotch tape with Au^{TS} and Au^{TS}-foil at the edges of the Scotch tape after template-stripping (A), and the Ag^{TS}-$SC_{11}Fc//Au^{TS}$ junctions (B and C).

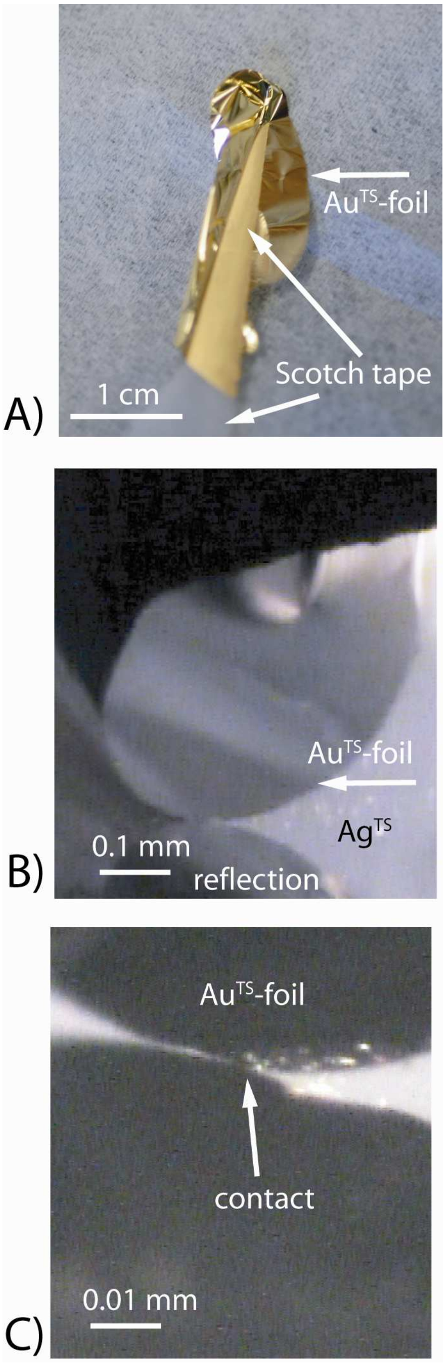
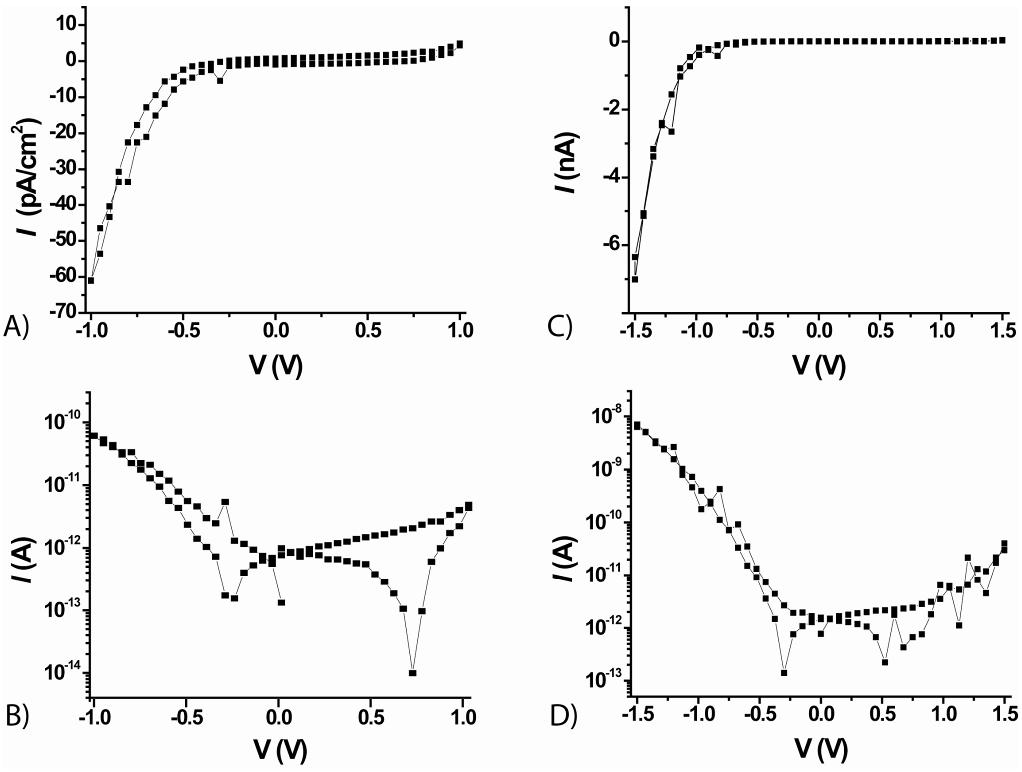

Au^{TS}-foil
Scotch tape
1 cm
A)
Au^{TS}-foil
Ag^{TS}
0.1 mm
reflection
B)
Au^{TS}-foil
contact
0.01 mm
C)

Figure S2: *I*(V) curves of two different Ag^{TS}-$SC_{11}Fc$//Au^{T} junctions (A and C) and the corresponding semi-log plots (C and D) of the absolute value of *I* as a function of potential.


A)
I (pA/cm2)
10
0
-10
-20
-30
-40
-50
-60
-70
-1.0
-0.5
0.0
0.5
1.0
V (V)
C)
I (nA)
0
-2
-4
-6
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
V (V)
B)
I (A)
10-10
10-11
10-12
10-13
10-14
-1.0
-0.5
0.0
0.5
1.0
V (V)
D)
I (A)
10-8
10-9
10-10
10-11
10-12
10-13
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
V (V)

Statistical Significance of the *R* Determined by the T-test

A one-sample *t*-test evaluates the null hypothesis that the mean of a normally-distributed population is equal to a specified value x_0.[6] The value of *t* is given by eq. **S1**.

$$t = \frac{(\mu - x_0)\sqrt{n}}{\sigma} \qquad \textbf{(S1)}$$

Here μ, σ, and *n* are the mean, standard deviation, and sample size of the population, respectively. This value of *t* is then used to calculate *p*, which is the probability of observing the measured distribution given that the null hypothesis is true, according to formula **S2**; where *B* is the beta function (**S3**):

$$p = 1 - \left[\frac{1}{B\left(\frac{1}{2}, \frac{1}{n-1}\right)\sqrt{n-1}} \int_{-t}^{t} \left(1 + \frac{y^2}{n-1}\right)^{-\frac{n}{2}} dy \right] \qquad \textbf{(S2)}$$

$$B(a,b) = \int_0^1 r^{a-1}(1-r)^{y-1}\,dr \qquad \textbf{(S3)}$$

To complete the test, one selects a confidence level (α, typically 95%, 99%, or 99.9%, such that if $p < 1 - \alpha$, one may reject the null hypothesis with a confidence of α.

For example, we examine the normally-distributed dataset consisting of log(*R*) for all junctions of the form Ag^{TS}-$SC_{10}CH_3$//Ga_2O_3/EGaIn. We cannot apply the *t*-test directly to *R* because those data are log-normally distributed, not normally distributed. We take as the null hypothesis that the mean of log(*R*) is equal to zero and set a confidence level of 99.9% which we must reach in order to reject this hypothesis. Using a statistical calculator, we calculate that $p < 0.0001$ and can, with 99.9% confidence, reject the null hypothesis. Thus, we conclude that the mean of log(*R*) is not zero, or equivalently that *R* is significantly greater than unity.

A two-sample *t*-test evaluates the null hypothesis that two populations have the same mean. The value of the statistic *t* is given by eq. **S4**, where the variables are defined in the same manner as above and the subscripts indicate to which population the variable belongs.

$$t = \frac{\mu_1 - \mu_2}{\sqrt{\frac{\sigma_1^2}{n_1^2} + \frac{\sigma_2^2}{n_2^2}}} \qquad \text{(S}\mathbf{4}\text{)}$$

Again, eq. **2** gives the value of *p*, though in the case of a two-sample *t*-test, one must calculate *n* according to the formula **S5**:

$$n = \frac{\left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}\right)^2}{\frac{(\sigma_1^2/n_1)^2}{(n_1 - 1)} + \frac{(\sigma_2^2/n_2)^2}{(n_2 - 1)}} \qquad \textbf{(S5)}$$

We apply the two-sample *t*-test to the two normally distributed datasets: i) log(*R*) for junctions of the form Ag^{TS}-$SC_{10}CH_3$//Ga_2O_3/EGaIn and ii) log(*R*) for junctions of the form Ag^{TS}-$SC_{14}CH_3$//Ga_2O_3/EGaIn. Again, we cannot treat *R* directly because it is log-normally distributed. In this case, the null hypothesis states that these two populations of log(*R*) have the same mean. We now apply the two-sample *t*-test with a confidence level of 99.9% for rejecting this hypothesis. We determine that $p < 0.0001$, so we reject the null hypothesis and conclude with 99.9% confidence that log(*R*) (and thus *R*) are different for these two junctions.

References

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[2] Creager, S. E.; Rowe, G. K. *J. Electroanal. Chem.* **1994**, *370*, 203.

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[4] Dickey, M. D.; Chiechi, R. C.; Larson, R. J.; Weiss, E. A.; Weitz, D. A.; Whitesides, G. M. *Adv. Funct. Mater.* **2008**, *18*, 1097.

[5] We obtained Gaussian fits using a least-squares, trust-region based algorithm: the 'gauss1' model (all options set to default) in the curve-fitting toolbox in MATLAB 7.4.0.287 (R2007a) Copyright The MathWorks, Inc. 1984-2007. No weighting or exclusion rules were applied to the data.

[6] Mendenhall, W.; Sincich, T. *Statistics for Engineering and Sciences* (5th Edition), Prentice Hall, **2006**.