

**Supporting Information:**

**Comparison of SAM-Based Junctions with Ga<sub>2</sub>O<sub>3</sub>/EGaIn Top-Electrodes to other Large-Area Tunneling Junctions**

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**Nomenclature.** We studied four different SAMs of alkanethiolates on silver electrodes. We use the general notation Ag-SC<sub>n-1</sub>CH<sub>3</sub>//Ga<sub>2</sub>O<sub>3</sub>/EGaIn with n = the number of carbon atoms in the alkyl chain to describe the junctions: Here, Ag-SC<sub>n-1</sub>CH<sub>3</sub> is a silver thin-film electrode (with an area of about 1 cm<sup>2</sup>) supporting a SAM of SC<sub>n-1</sub>CH<sub>3</sub> with n = 12, 14, 16, or 18. We describe the interfaces with the symbols “-”, which indicates a chemisorbed contact, “/” which indicates the contact between Ga<sub>2</sub>O<sub>3</sub> and bulk EGaIn, and “//”, which indicates the presence of a non-covalent interface. The symbol *V* is defined as the difference in voltage between the two electrodes. We abbreviate polydimethylsiloxane as PDMS.

**Introduction.** Charge transport through organic matter that would normally be considered to be electrically insulating is important in fields from biology to electronics.<sup>1,2,3,4</sup> Junctions that incorporate SAMs seem to be good model systems with which to obtain fundamental information about the mechanisms of charge transport across electrical insulators having thicknesses of 1-5 nm, because SAMs are only one molecule thick, and have, in some cases, been well characterized structurally. Studies of charge transport across insulating SAMs (often considered to involve hole tunneling<sup>5</sup>) usually use one of two strategies: i) detailed physical-chemical measurements (usually carried out by a focused study of one or a few well-characterized simple systems), or ii) physical-organic studies (which infer mechanisms by examining the relationship between relevant processes and molecular structure over a wider range of structures). The main challenge with either strategy is to relate the electrical characteristics of the devices to the chemical and supramolecular structure of the SAMs.

Over the last 20 years, the measurement of tunneling currents through SAMs has been troublesome, and has suffered from a wide range of artifacts due to rough surfaces, thin or distorted regions in the SAMs,<sup>6</sup> damage to the SAMs during deposition of metal top-electrodes,<sup>7,8</sup> edge effects,<sup>9</sup> formation of metal filaments caused by electromigration,<sup>10,11</sup> effects of vapor transport and amalgamation (with mercury),<sup>6</sup> and use of structurally uncharacterized SAMs derived from thiols of complex structures.<sup>12,13,14</sup> Different techniques also address different numbers of molecules, from a few (for STM) to mm<sup>2</sup> of area (for mercury drop systems). As a result, there is still no method that is free of artifacts, experimentally convenient, and fully interpretable. The generation of statistically large numbers of data has been difficult or impossible to achieve, and definitions of what constitute a “working” junction and/or “representative” data remain matters of opinion rather than community agreement.<sup>15,16</sup>

While there is still no method that is free of artifacts, experimentally convenient, and fully interpretable, there are systems (top-electrodes of polymer,<sup>17</sup> Ga<sub>2</sub>O<sub>3</sub>/EGaIn,<sup>18,19</sup> .<sup>20,21</sup> or Hg-SAMs,<sup>22,23,24</sup> and monolayers on Si with Hg top- contacts<sup>25,26</sup>) that avoid many of the difficulties listed above. All of these systems yield data that meet the minimum requirements for a useful junction – reproducibility and statistically large numbers of data – but all have drawbacks. Comparisons of data generated by this range of experimental systems – each with different sources of error – will probably be the best approach to generating agreed-on characteristics of tunneling across SAMs making it possible to disentangle information related to mechanisms of charge transport from data primarily reflecting the electrodes.

A consensus in data will also benefit from comparisons with approaches of a different class: break junctions (originally introduced by Tour and Reed,<sup>27</sup> improved by Ralph et al.,<sup>28</sup> and applied successfully in physical-organic studies by, for instance, Park et al.,<sup>29,30</sup> Venkataraman et al.,<sup>31</sup> and Bjørnholm et al.<sup>32</sup>) and scanning tunneling microscopy (STM) -based junctions.<sup>33,34</sup> STM measurements have the intrinsic bias that the operator selects “bright” molecules to study.<sup>35</sup> Break junctions have – in the hands of an experienced operator – given statistically significant results (see, for example, Venkataraman et al.<sup>31</sup>), but uncertainties about the structure of the actual junction, the origin of the breadth of the distributions of data, the conformations of the molecules inside the junctions, the nature of the contacts to the metal, and the substantial instrumental equipment needed to achieve these measurements, make them inconvenient for physical-organic studies.

**Characteristics of Successful Tunneling Junctions.** We have concluded that measurements of charge transport through preformed SAMs, in junctions with finite areas (100 - 1000  $\mu\text{m}^2$ ), in static systems with the potential (at least in principle) for incorporation into real devices are the best (or at minimum, a good) subject for fundamental physical-organic studies of charge transport through organic matter. As we note above, it seems that four different types of methods generate SAM-based junctions with sufficiently high stabilities to conduct physical-organic studies of charge transport across SAMs. These four methods all seem to require one common element: that is, all have a protective layer located between the SAM and one of the metal electrodes.

Akkerman *et al.*<sup>17</sup> and Rampi *et al.*<sup>36</sup> described a method for fabricating large-scale SAM-based tunneling junctions of the type Au-SAM//polymer/Au. The polymer

(PEDOT:PSS) protects the SAM during the deposition of the top-contact of gold by e-beam evaporation; it serves as a physical barrier to incoming metal atoms, or clusters of atoms, and preventing them from reacting with, or penetrating, the SAM. This system is the most attractive one now available to fabricate large arrays of devices (especially for possible use in applications), but is still severely limited as a tool for performing physical-organic studies. There exist four uncertainties in these PEDOT:PSS-based devices: i) the conductive polymer is not annealed (the solvent – DMSO – must be removed in vacuum under empirically evolved conditions), ii) the conductive polymer contains a complex mixture of additives, iii) the conductive polymer forms an ill-defined contact with the SAM, and iv) the conductive polymer may intercalate with, partially dissolve, dissolve in, or displace the SAM. Intercalation of the polymer with the SAM may alter the mechanism of charge transport across the junctions, and may be responsible for the anomalously low values of  $\beta$  ( $0.59 \text{ nC}^{-1}$ , or  $0.47 \text{ \AA}^{-1}$ ) reported for these junctions. Akkerman et al.<sup>17</sup> reported that the characteristics of their devices did not change over 2.5 years (when stored under ambient conditions at R.T.). It has been reported that the metal-thiolate bond of SAMs of n-thiolates on Au oxidize within one day and produce disordered SAMs.<sup>37,38</sup> Molecular oxygen ( $\text{O}_2$ ) diffuses through the layer of PEDOT:PSS; the layer of conductive polymer does not protect the SAM from oxidation by molecular oxygen.<sup>39,40</sup> Thus, either Akkerman's devices are not sensitive to the oxidation state of the SAMs they incorporate, or the SAMs have been removed or transformed into something else.

Our group,<sup>22,41</sup> Majda,<sup>24</sup> Slowinski,<sup>23,42</sup> Rampi,<sup>22</sup> and others<sup>25,43</sup> have used Hg as a “soft” liquid-metal electrode for investigating junctions of the form Ag-SAM//SAM-Hg.

In these junctions, a second SAM between the Hg top-electrode and the SAM serves as protective barrier against the diffusion of mercury vapor. Despite the protective layer, measurements have had to be carried out in hydrocarbon solvents containing thiol to increase the stability of the junctions. The yields of these junctions (~ 25%) are only modest, and the data they produce contain substantial numbers of outliers.<sup>6</sup> These junctions also have limited lifetimes (on the order of minutes) and are unstable to cycling (5-15 cycles are usually the maximum sustainable number). Additionally, measurements as a function of temperature are not possible using these junctions.

Cahen et al.<sup>25,26,43</sup> described junctions based on monolayers of alkenes covalently bound to hydrogen-passivated Si bottom-electrodes and contacted with Hg-drop top-electrodes. These Si-alkyl/Hg junctions are useful for studying charge transport for two reasons. i) They are more stable than junctions with SAMs of n-alkanethiolates chemisorbed on Au or Ag, partly because the Hg drop does not damage the monolayer (by penetration through pinholes or diffusion of mercury vapor through the SAM) and does not alloy with the Si bottom-electrode. ii) They support measurements of charge-transport over a limited range of temperature<sup>25,26</sup> ( $T = 250 - 330$  K) – measurements which have yielded valuable information on the mechanism of charge transport in these junctions.<sup>43,44,45,46,47</sup> These junctions also have two disadvantages. i) The monolayers covalently bound to Si are less well-ordered than SAMs of n-alkanethiolates on Au or Ag, and it is difficult synthetically to achieve large variations in the structure of the organic R group. ii) In addition to a tunneling barrier defined by the monolayers, these junctions incorporate a Schottky barrier defined by the electrodes and the monolayer.<sup>48</sup>

## Experimental

**Fabrication of the Ag<sup>TS</sup>-Electrodes.** We published the procedure for the fabrication of ultra-flat Ag<sup>TS</sup> electrodes embedded in an optical adhesive (OA, Norland No. 61) before in reference 19. Briefly, we fabricated electrodes of 10  $\mu\text{m}$  wide (Fig. S1), a feature length that is conveniently made using photolithography, and 50 to 100 nm thick (thicker layers of Ag were difficult to lift-off).<sup>49</sup> We formed arrays of 50 nm thick Ag electrodes on Si/SiO<sub>2</sub> wafers (used as received) using photolithography, e-beam evaporation (1-2  $\text{\AA}/\text{s}$ ,  $1 - 2 \times 10^{-6}$  bar), and a standard lift-off process (Figure S1A-D). The Ag electrodes were 10  $\mu\text{m}$  wide and 5000  $\mu\text{m}$  long, and incorporated  $3000 \times 3000 \mu\text{m}^2$  square pads at their ends to facilitate addressing the electrodes with microneedles.

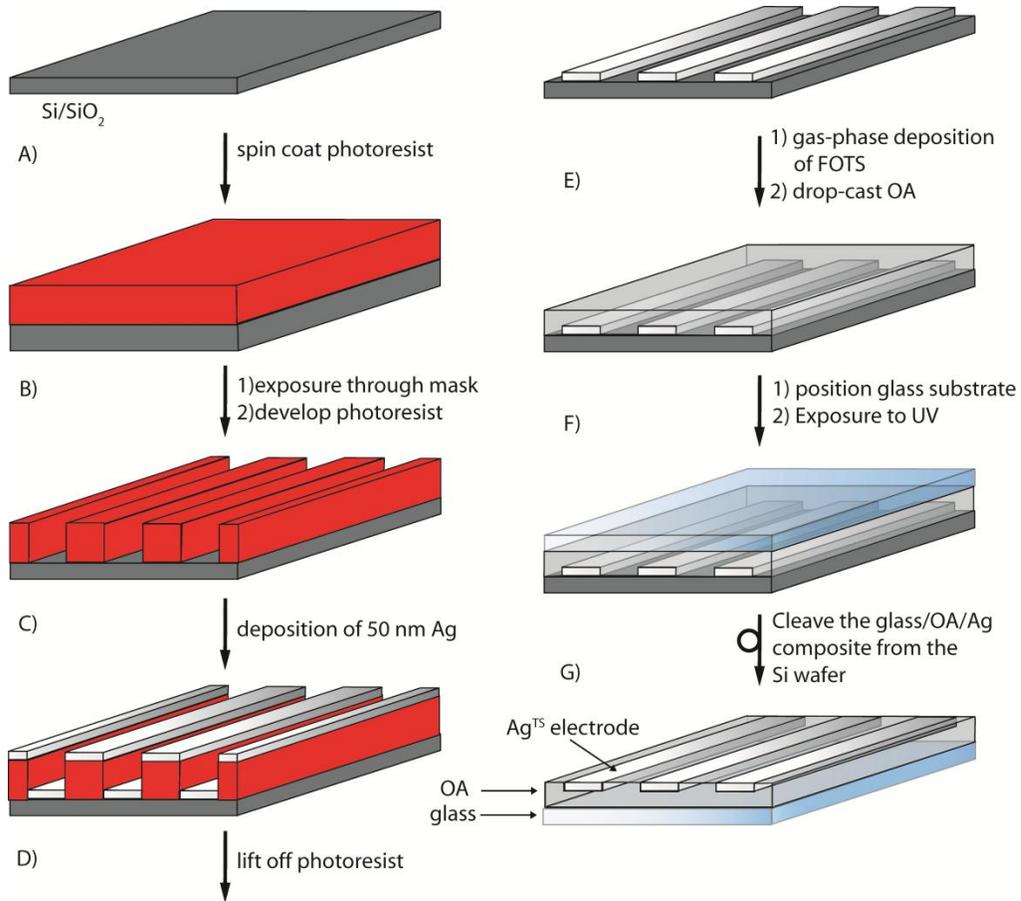
The OA adheres strongly to the Si/SiO<sub>2</sub> once cured. To reduce the interaction of the OA with the Si/SiO<sub>2</sub>, and to make template-stripping of the Ag-electrodes possible, we formed a monolayer of 1H,1H,2H,2H-perfluorooctyl-trichlorosilane ( $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_5(\text{CF}_3)$ , FOTS) on the SiO<sub>2</sub> by gas phase deposition (Figure S1E). We placed the Si/SiO<sub>2</sub> surfaces with the Ag-electrodes and a vial with 2 – 3 drops of the FOTS in a dessicator and reduced the pressure to 50 – 100 Torr for 1 h after which we restored the pressure to that of ambient, and removed the wafer from the dessicator. We applied a drop of OA on the electrodes, which were in turn covered with a glass slide (VWR microslides, 1 mm thick, cleaned with a plasma of air (5 min, 500 mTorr, Fig. S1F)). We cured (UV, 2 h) the OA between the substrate supporting the arrays of Ag electrodes and the glass slide, which served as a mechanical support. Using a razor blade, we removed the glass/OA/Ag composite from the wafer. The sharp side of the razor blade was (almost) orientated in the plane of Si-wafer and positioned at one of the

corners of the glass/OA/Ag composite. Pressing gently (in a direction parallel to the wafer) with the razor caused the glass/OA/Ag composite to separate from the Si/SiO<sub>2</sub> template exposing the surface of the Ag that had originally been in contact with the wafer.

The thiols, as received (Aldrich), were not pure: <sup>1</sup>H NMR indicated the presence of disulfides and other species (probably sulfonic acids). To obtain better quality SAMs, we purified the HSC<sub>n-1</sub>CH<sub>3</sub> (Aldrich; n = 12, 14, 16, or, 18) prior use by recrystallization from ethanol. The thiol (~5 – 10 g) was dissolved in ethanol (used as received from Pharmco-AAPER, ACS/USP grade) at room temperature under an atmosphere of N<sub>2</sub> (N<sub>2</sub> was flushed through the ethanol (~50 - 100 mL) for 15-20 min prior use). We filtered the solution after slowly cooling it to 0 °C. The filtered solution was cooled to -20 °C overnight, during this time crystals of the thiols formed. These crystals were collected by filtration under ambient conditions. This procedure was repeated three times. We could not detect any disulfides or sulfonic acids by <sup>1</sup>H NMR. We stored the purified thiolates under an atmosphere of N<sub>2</sub> at 0 or -10 °C (as a solid) to minimize oxidation of thiolates to their corresponding disulfides and used them within 1-2 days to form the SAMs.

We formed the SAM by immersion of the Ag<sup>TS</sup> substrates, within 5 s after removal from the wafer, in an ethanol solution of the corresponding thiol (2-3 mM; R.T.; under argon) to minimize contamination of the metal surface. We allowed the SAMs to form over 12 hours (R.T.; under argon), after which we rinsed the surfaces with ethanol to remove physisorbed materials.

**Figure S1:** Schematic representation describing the fabrication of the Ag<sup>TS</sup>-electrodes. A) A silicon wafer with a 3 μm thick layer of positive photoresist. B) UV exposure of the photoresist through a mask, and subsequent development of the resist, produced a pattern onto which 50 nm of Ag was deposited (C). Lift-off of the resist with acetone produced the desired pattern of Ag electrodes (D). Optical adhesive (OA) was cast on the Ag patterns (E) and cured between the substrate and glass slide (F). Cleaving the glass/OA/Ag composite off the wafer exposed the Ag surface that had originally been in contact with the Si wafer (G).



**Fabrication of the Molecular Tunneling Junctions.** We fabricated microfluidic channels in polydimethylsiloxane (PDMS) using established methods.<sup>50</sup> The surface of the PDMS was oxidized in a plasma of air (60 s, 500 mTorr) prior to alignment to facilitate wetting by Ga<sub>2</sub>O<sub>3</sub>/EGaIn.<sup>50</sup>

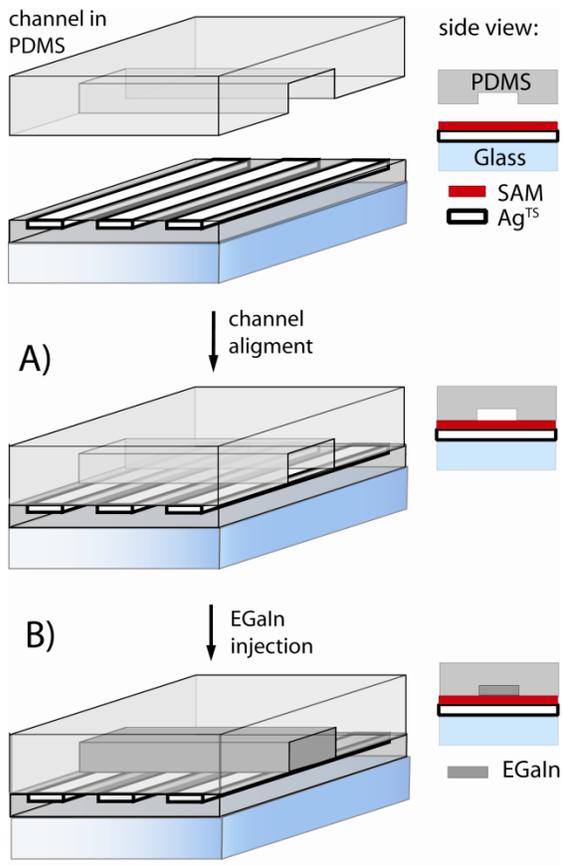
The long axis of the 30 μm wide × 50 μm deep × 8000 μm long microchannels were aligned perpendicular to the long axis of the Ag electrodes supporting SAMs (Fig. S2A). The PDMS formed a van der Waals contact with the Ag-SAM electrodes and the OA. This contact completed the channel, and could easily be disassembled to examine the component surfaces. It did not support pressure inside the channel.

We filled the PDMS channels with Ga<sub>2</sub>O<sub>3</sub>/EGaIn (Figure S2B) under ambient conditions by placing a drop of Ga<sub>2</sub>O<sub>3</sub>/EGaIn on the inlet of the channel and applying vacuum to the outlet. The vacuum was relatively low (just enough to pull the EGaIn through the channel) and as soon the channel was full, we removed the vacuum. This procedure minimized the pressure applied to the device. This procedure formed an array of seven Ag<sup>TS</sup>-SC<sub>n-1</sub>CH<sub>3</sub>//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions (in which each Ag<sup>TS</sup> electrode served as a bottom-electrode and the Ga<sub>2</sub>O<sub>3</sub>/EGaIn served as the top-electrode) with a surface area of 300 μm<sup>2</sup>. During filling, the channels did not leak Ga<sub>2</sub>O<sub>3</sub>/EGaIn. Forcing the Ga<sub>2</sub>O<sub>3</sub>/EGaIn through the channel by *elevating* the pressure resulted in leakage of the Ga<sub>2</sub>O<sub>3</sub>/EGaIn out of the channel, and caused the devices to become shorted.

**Measurements of  $J(V)$  as a Function of Temperature.** We biased the Ga<sub>2</sub>O<sub>3</sub>/EGaIn top-electrodes and grounded the Ag<sup>TS</sup> bottom-electrode in all of our measurements. We selected junctions for measurements of  $J(V)$  as a function of temperature that had their  $J(V)$  characteristics within one log-standard deviation of the

mean value of  $J$  (see below). The temperature-dependent measurements were performed with a probe station (Desert Crygenics) in vacuum ( $1 \times 10^{-6}$  bar). We cooled the devices with liquid nitrogen from 293 to 110 K over three hours, and measured one  $J(V)$  curve at intervals of 20 K while keeping the temperature constant during measurement. Reducing the pressure, cooling the devices, or solidification of EGaIn (at 240-260 K) did not result in shorts or open circuits. The electrodes were not contacted with the probes during cooling or heating of the devices.

**Figure S2:** Schematic of the fabrication of the metal–SAM//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions. A) A micro-channel in PDMS is aligned perpendicularly to the Ag electrodes. B) Injection of Ga<sub>2</sub>O<sub>3</sub>/EGaIn by applying vacuum at the outlet of the micro-channel while a drop of Ga<sub>2</sub>O<sub>3</sub>/EGaIn is present at the inlet completes the fabrication of the tunneling junctions.



**Fitting Log-Normally Distributed Data with Gaussians.** Our data for  $J$  and  $R$  are log-normally distributed, thus  $\log(|J|)$  and  $\log(R)$  are both normally distributed. We analyzed the data for  $J$  and  $R$  by a similar procedure. We first created histograms of  $\log(|J|)$  at a certain voltage, and of  $R$  (at  $\pm 1.0$  V). We then used a trust-region algorithm (available in the curve-fitting toolbox of MATLAB 7.4.0.287, R2007a; Copyright The MathWorks, Inc. 1984-2007). No weighting or exclusion rules were applied to the data. To minimize the Gaussian function **S1** (nonlinear least-squares fitting) where  $\mathbf{x}$  is a vector representing the centers of the logarithmically-spaced bins in the histogram,  $\mathbf{y}$  is the vector of counts in the histogram (i.e.,  $y_i$  is the number values of  $\log(|J|)$  that fall within bin  $i$ , centered at  $\mathbf{x}_i$ ).

$$F(\mathbf{x}) = \|\mathbf{y} - G(\mathbf{x})\|^2 \quad (\text{S1})$$

The  $G(\mathbf{x})$  is the Gaussian function, given by **S2** where  $m$  is the mean and  $s$  is the standard deviation of  $\log(|J|)$ .

$$G(\mathbf{x}) = \frac{1}{s\sqrt{2\pi}} \exp\left(-\frac{(\mathbf{x} - m)^2}{2s^2}\right) \quad (\text{S2})$$

To report statistics for  $|J|$ , we calculate the log-mean,  $\mu_{\log} = 10^m$ , and log-standard deviation,  $\sigma_{\log} = 10^s$ , of  $|J|$ . Because  $\log(|J|)$  is normally distributed, 68% of its distribution lies within the interval  $(m-s, m+s)$ ; however, since  $|J|$  is log-normally distributed, 68% of its distribution lies within the interval  $(\mu_{\log}/\sigma_{\log}, \mu_{\log} \times \sigma_{\log})$ , or equivalently,  $(10^{m-s}, 10^{m+s})$ . Sometimes a fit looks to the eye unsatisfactory, and it seems that data have been excluded from the fit, but *none* of the data in this study have been excluded. The data that seem to be excluded do not weigh in the fitting as much as the data centered around the main peak.



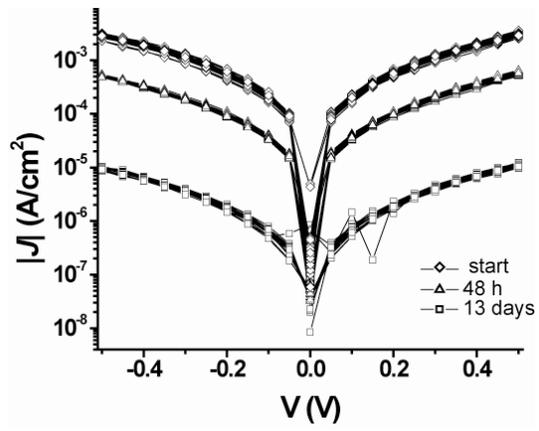
**Table S1:** Statistics of the Ag<sup>TS</sup>-SAM//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions.

<b>Junction</b>	<b>Number of devices</b>	<b>Number of junctions</b>	<b>shorts</b>	<b>Open circuits</b>	<b>Yield (%)</b>	<b>Total scans</b>
SC <sub>11</sub> CH <sub>3</sub>	3	21	9	2	48	400
SC <sub>13</sub> CH <sub>3</sub>	2	14	2	2	71	400
SC <sub>15</sub> CH <sub>3</sub>	4	28	5	1	79	631
SC <sub>17</sub> CH <sub>3</sub>	3	21	3	-	86	756
SC <sub>17</sub> CH <sub>3</sub> <sup>a</sup>	2 <sup>a</sup>	12 <sup>a,b</sup>	-	-	100 <sup>a,b</sup>	248 <sup>a</sup>

<sup>a</sup> 48 h old junctions

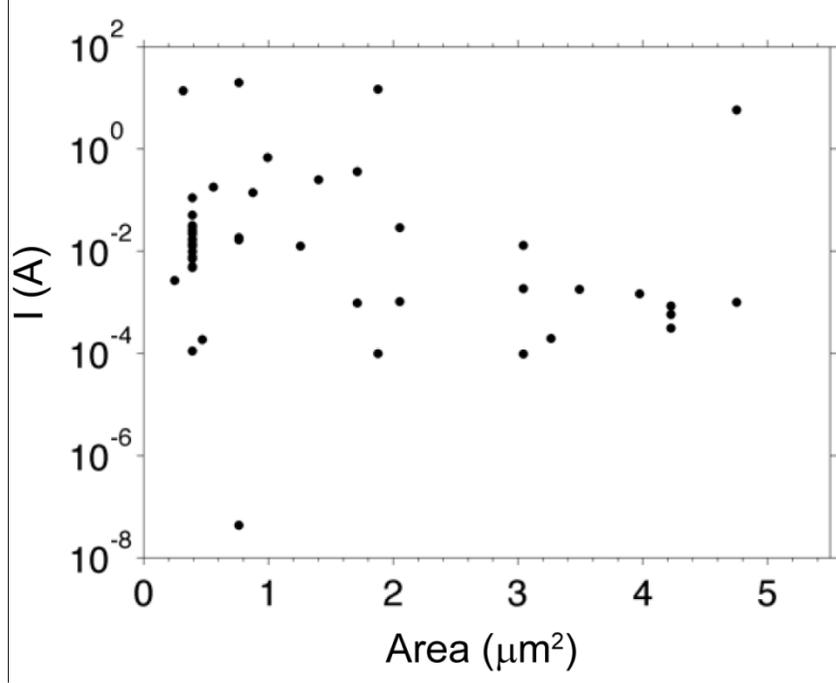
<sup>b</sup> Two out of the set of three devices prepared with a SC<sub>18</sub> SAM were selected to test their behavior upon aging (ambient conditions, room temperature). The two devices had 12 working junctions and two shorts at  $t = 0$ . At  $t = 48$  h all 12 junctions still worked resulting in a yield of 100%.

**Figure S3:**  $J(V)$  curves of one device with junctions of  $\text{Ag}^{\text{TS}}\text{-SC}_{11}\text{CH}_3//\text{Ga}_2\text{O}_3/\text{EGaIn}$  that was stable for 13 days. During this time period the current density decreased by a factor of  $\sim 200$ .



**Figure S4:** Current as a function of junction area for junctions of Ag<sup>TS</sup>-

SC<sub>11</sub>CH<sub>3</sub>//Ga<sub>2</sub>O<sub>3</sub>/EGaIn with cone-shaped top-electrodes of Ga<sub>2</sub>O<sub>3</sub>/EGaIn. The lack of correlation between the measured current and area of the junctions indicates that our junctions are dominated by thin area defects. This observation agrees with the observation that the measured values of  $J$  follow a log-normal distribution. Consequently, our value of  $J_0$  can not be compared directly to techniques involving single molecule experiments.



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