

## Supporting Information

### **The Rate of Charge Tunneling Is Insensitive to Polar Terminal Groups in SAMs in $\text{Ag}^{\text{TS}}\text{S}(\text{CH}_2)_n\text{M}(\text{CH}_2)_m\text{T}//\text{Ga}_2\text{O}_3/\text{EGaIn}$ Junctions**

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## Experimental Details

**Materials:** All reagents were used as supplied unless otherwise specified. All organic solvents were purchased from Sigma-Aldrich (dichloromethane and hexanes) or Fisher (200 proof ethanol) while water was purified using a Millipore Q-POD water purification system. HSC<sub>11</sub>Br (**3b**) and standards (HSC<sub>8</sub>, HSC<sub>10</sub>, HSC<sub>12</sub> and HSC<sub>14</sub>) were purchased from Sigma-Aldrich (the purity  $\geq 99\%$ ). All thiols were maintained under N<sub>2</sub> atmosphere and  $\leq 4$  °C, and purity was checked right before use (if <sup>1</sup>H NMR spectra showed impurities, thiols were purified by silica-gel column chromatography). All starting compounds for synthesis were also purchased from Sigma-Aldrich, except diethyl(aminoethyl)phosphonate oxalate (Acros Organics), 2-methylsulfonylethan-amine (Santa Cruz Biotechnology Inc.) and 11-bromoundecyltrimethoxysilane (Gelest, Inc.). 13-Bromotridecanenitrile was prepared following the method in the literature.<sup>1</sup> For the contact electrode, high-purity eutectic gallium-indium (EGaIn) was obtained from Sigma-Aldrich and used as supplied. All purified thiol derivatives were stored under N<sub>2</sub> atmosphere and  $< 4$  °C.

**Characterization:** <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra were recorded on a Bruker DPX 300, Bruker DPX 400 or a varian INOVA 500 instrument using CDCl<sub>3</sub> as a solvent and residual solvents as an internal standard. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF-Q at Harvard CCB.



29.4, 27.2, 25.0, 24.2, 16.9. (due to the lack of affinity to  $H^+$ ,  $Na^+$  or  $K^+$ , we were unable to obtain a HR-MS spectrum for this compound).

$HS(CH_2)_5CO_2CH_3$  (**2**). The method A.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  3.63 (s, 3H), 2.49 (q,  $J = 7.6$  Hz, 2H), 2.28 (t,  $J = 7.6$  Hz, 2H), 1.67 – 1.52 (m, 4H), 1.45 – 1.33 (m, 2H), 1.32 (t,  $J = 8$  Hz, 1H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  174.0, 51.5, 33.8, 33.5, 27.7, 24.32, 24.28. HRMS (m/z) calcd for  $[C_7H_{15}O_2S]^+$  ( $M+H^+$ ): 163.0793; found: 163.0744.

$HS(CH_2)_4CONH(CH_2)_2CF_3$  (**3**). This compound was synthesized following the method B. 2,2,2,-trifluoroethylamine (2.0 g, 17.69 mmol) and triethylamine (1.97 g, 19.46 mmol) in 100 mL of  $CH_2Cl_2$  was added dropwise to a 50 mL  $CH_2Cl_2$  solution of 5-bromovaleryl chloride (1.76 g, 17.69 mmol) at  $0^\circ C$ . The resulting solution was warmed to room temperature and stirred for 3 hrs. The reaction solution was then concentrated *in vacuo*, dissolved in  $CH_2Cl_2$  and washed with water. The combined organic layer was dried over anhydrous  $MgSO_4$ , filtered off and concentrated *in vacuo*. Without further purification, the crude compound was dissolved in 100 mL of EtOH, followed by addition of thiourea (1.48 g, 19.46 mmol). The resulting mixture was refluxed for 18 hrs. After removal of the ethanol *in vacuo*, sodium hydroxide (or potassium hydroxide) (0.78 g, 19.46 mmol) in 100 mL of degassed water was added to the crude mixture. The reaction mixture was again refluxed for 1 hr under  $N_2$  atmosphere. The reaction solution was cooled to room temperature and extracted with  $CH_2Cl_2$ . The combined organic layer was dried over anhydrous  $MgSO_4$ , filtered off, and concentrated *in vacuo*. The product was usually pure when analyzed by  $^1H$  NMR. If necessary, the produce was purified by passing through a silica-gel column chromatography (eluent was a mixture of ethyl acetate and  $CH_2Cl_2$ , 1:1,

v/v).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.98 (s, 1H), 3.48 (q,  $J = 6.4$  Hz, 2H), 2.50 (t,  $J = 8.0$  Hz, 2H), 2.42 – 2.26 (m, 2H), 2.18 (t,  $J = 7.6$  Hz, 2H), 1.80 – 1.54 (m, 4H), 1.34 (t,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.8, 126.4 (d,  $J = 275$  Hz), 35.7, 33.6 (d,  $J = 27$  Hz), 33.3, 32.9 (d,  $J = 3.7$  Hz), 24.15, 24.08. HRMS (m/z) calcd for  $[\text{C}_8\text{H}_{14}\text{F}_3\text{NaOS}]^+$  ( $\text{M}+\text{Na}^+$ ): 252.0640; found: 252.0650.

$\text{HS}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_2\text{OCH}_3$  (**4**). The method B.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.92 (s, 1H), 3.46 – 3.35 (m, 4H), 3.32 (s, 3H), 2.50 (q,  $J = 7.2$  Hz, 2H), 2.17 (t,  $J = 7.2$  Hz, 2H), 1.79 – 1.55 (m, 4H), 1.34 (t,  $J = 7.5$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.6, 71.2, 58.7, 39.1, 35.9, 33.5, 24.30, 24.28. HRMS (m/z) calcd for  $[\text{C}_8\text{H}_{17}\text{NO}_2\text{SNa}]^+$  ( $\text{M}+\text{Na}^+$ ): 214.0878; found: 214.0879.

$\text{HS}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$  (**5**). The method B.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.06 (s, 1H), 3.31 (q,  $J = 5.7$  Hz, 2H), 2.53 (q,  $J = 6.9$  Hz, 2H), 2.39 (t,  $J = 5.7$  Hz, 2H), 2.22 – 2.16 (m, 8H), 1.82 – 1.56 (m, 4H), 1.36 (t,  $J = 6.9$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.6, 57.8, 45.1, 36.7, 35.9, 33.6, 24.4, 24.3. HRMS (m/z) calcd for  $[\text{C}_9\text{H}_{21}\text{N}_2\text{OS}]^+$  ( $\text{M}+\text{H}^+$ ): 205.1375; found: 205.1383.

$\text{HS}(\text{CH}_2)_7\text{CON}(\text{CH}_3)_2$  (**6**). This compound was synthesized following the modified procedure reported in literature.<sup>2</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.00 (s, 3H), 2.94 (s, 3H), 2.51 (q,  $J = 7.2$  Hz, 2H), 2.30 (t,  $J = 7.2$  Hz, 2H), 1.67 – 1.52 (m, 4H), 1.52 – 1.26 (m, 7H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  173.1, 37.3, 35.3, 33.9, 33.3, 29.3, 28.8, 28.2, 25.0, 24.6. HRMS (m/z) calcd for  $[\text{C}_{10}\text{H}_{22}\text{NOS}]^+$  ( $\text{M}+\text{H}^+$ ): 204.1417; found: 204.1426.

HS(CH<sub>2</sub>)<sub>4</sub>CONH(CH<sub>2</sub>)<sub>2</sub>SCH<sub>3</sub> (**7**). The method B. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.90 (s, 1H), 3.45 (q, *J* = 6.3 Hz, 2H), 2.63 (q, *J* = 6.6 Hz, 2H), 2.53 (q, *J* = 6.3 Hz, 2H), 2.20 (t, *J* = 6.9 Hz, 2H), 2.10 (s, 3H), 1.84 – 1.55 (m, 4H), 1.36 (t, *J* = 6.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 172.7, 37.5, 35.9, 33.8, 33.4, 24.3 (two different carbon signals are overlapped), 14.9. HRMS (m/z) calcd for [C<sub>8</sub>H<sub>18</sub>NOS<sub>2</sub>]<sup>+</sup> (M+H<sup>+</sup>): 208.0824.; found: 208.0831.

HS(CH<sub>2</sub>)<sub>4</sub>CONH(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub> (**8**). The method B. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.56 (s, 1H), 3.70 (q, *J* = 6.4 Hz, 2H), 3.23 (t, *J* = 6.4 Hz, 2H), 2.93 (s, 3H), 2.48 (q, *J* = 7.2 Hz, 2H), 2.17 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.49 (m, 4H), 1.34 (t, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 173.2, 53.8, 41.5, 35.6, 33.3, 33.1, 24.2, 24.1. HRMS (m/z) calcd for [C<sub>8</sub>H<sub>17</sub>NNaO<sub>3</sub>S<sub>2</sub>]<sup>+</sup> (M+Na<sup>+</sup>): 262.0542; found: 262.0540.

HS(CH<sub>2</sub>)<sub>4</sub>CONH(CH<sub>2</sub>)<sub>2</sub>PO(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (**10**). The method B. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.64 (s, 1H), 4.14 – 3.90 (m, 4H), 3.41 (dq, *J*<sub>H-H</sub> = 6.8 Hz; *J*<sub>P-H</sub> = 19.2 Hz, 2H), 2.42 (q, *J* = 7.6 Hz, 2H), 2.08 (t, *J* = 7.6 Hz, 2H), 1.88 (dt, *J*<sub>H-H</sub> = 6.8 Hz; *J*<sub>H-P</sub> = 17.6 Hz, 2H) 1.70 – 1.43 (m, 4H), 1.33 – 1.14 (m, 7H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 172.6, 61.8 (d, *J*<sub>C-P</sub> = 6.1 Hz), 35.8, 33.4, 33.3 (d, *J*<sub>C-P</sub> = 4.5 Hz), 26.2, 24.8, 24.1, 16.4 (*J*<sub>C-P</sub> = 6.1 Hz). <sup>31</sup>P (CDCl<sub>3</sub>): δ 29.6. HRMS (m/z) calcd for [C<sub>11</sub>H<sub>24</sub>NNaO<sub>4</sub>PS]<sup>+</sup> (M+Na<sup>+</sup>): 320.1061; found: 320.1092.

HS(CH<sub>2</sub>)<sub>9</sub>CO<sub>2</sub>CH<sub>3</sub> (**11**). The method A. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.63 (s, 3H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.48 (m, 4H), 1.42 – 1.14 (m, .11H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 174.2, 51.4, 34.03, 33.97, 29.13, 29.06, 28.9, 28.3, 24.9, 24.6. HRMS (m/z) calcd for [C<sub>11</sub>H<sub>22</sub>NaO<sub>2</sub>S]<sup>+</sup> (M+Na<sup>+</sup>): 241.1238; found: 241.1236.

HS(CH<sub>2</sub>)<sub>4</sub>CONH(CH<sub>2</sub>)<sub>2</sub>NHCOCH<sub>3</sub> (**12**). The method B. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.27 (br, s, 1H), 3.38 – 3.37 (m, 4H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.98 (s, 3H), 1.67 – 1.56 (m, 4H), 1.46 – 1.37 (m, 2H), 1.33 (t, *J* = 7.6 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 174.1., 171.4, 40.3, 40.2, 36.4, 35.5, 27.8, 25.0, 24.4, 23.2. HRMS (m/z) calcd for [C<sub>10</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>+</sup> (M+H<sup>+</sup>): 233.1324; found: 233.1320.

HS(CH<sub>2</sub>)<sub>12</sub>CN (**13**). The method A. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.43 (q, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 1.61 – 1.19 (m, 21H). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 119.8, 34.0, 29.4, 29.3, 29.2, 29.04, 28.98, 28.7, 28.6, 28.3, 25.3, 24.5, 17.0. (due to the lack of affinity to H<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>, we were unable to obtain a HR-MS spectrum for this compound)

HS(CH<sub>2</sub>)<sub>11</sub>OSi(CH<sub>3</sub>)<sub>3</sub> (**14**). This compound was synthesized following the procedure in literature.<sup>3</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.54 (t, *J* = 7.2 Hz, 2H), 2.50 (q, *J* = 7.8 Hz, 2H), 1.69 – 1.43 (m, 4H), 1.43 – 1.17 (m, .15H), 0.09 (s, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 62.7, 34.0, 32.7, 29.53, 29.46, 29.44, 29.38, 29.0, 28.3, 25.8, 24.6, -0.505. HRMS (m/z) calcd for [C<sub>14</sub>H<sub>32</sub>NaOSSi]<sup>+</sup> (M+Na<sup>+</sup>): 299.1841; found: 229.1836.

### Experimental designs

*EGaIn-based junctions.* A variety of methods are available for fabricating SAM-based, large-area junctions.<sup>4-6</sup> These methods may suffer from low yields of working junctions (0.1 – 30%) due to i) aggressive reaction conditions during fabrication, ii) diffusion of metal ions across the SAMs (for Hg drop junctions), or iii) the formation of filaments through

electromigration. In addition, the technical complexity of the fabrication and the difficulty in collecting large numbers of data, make it difficult to obtain statistically valid data. To bypass this problem, Lovrinčić *et al.*<sup>7</sup> recently developed a novel large-area junction, using directly deposited lead as a top-electrode. The thermal evaporation of lead requires a relatively low temperature, thereby minimizing damage to the SAM and generating working junctions in almost quantitative yields.

In this work, we incorporated target molecules into large-area junctions formed with conical Ga<sub>2</sub>O<sub>3</sub>/EGaIn tips as the top-electrode. EGaIn is a liquid metal at room temperature, and forms a self-passivating, thin layer of Ga<sub>2</sub>O<sub>3</sub> (nominally ~1 nm) upon exposure to air. This thin film of oxide enables the formation of a conical (i.e., non-spherical) Ga<sub>2</sub>O<sub>3</sub>/EGaIn tip, and serves as a protective layer in assembling junctions on the surface of SAMs. A conical Ga<sub>2</sub>O<sub>3</sub>/EGaIn tip is appropriate for performing physical-organic studies for three reasons. i) Its fabrication does not require harsh reaction conditions, expensive equipment, or difficult experimental techniques; forming fresh tips is simple and fast. ii) Its geometrical area of contact with the surface of a SAM is relatively small (~50 μm<sup>2</sup>)—due to its conical shape; the small area reduces the possibility of shorting junctions (due to the defect of SAM). iii) It generates working junctions in high yields (usually ≥ 80%), and allows rapid collection of large numbers of data (~10<sup>3</sup> current density-voltage, *J-V*, traces per day). These statistically valid sets of data allow comparisons between compounds with a high degree of confidence.

We note that we have recently developed a new conical tip the so-called “flattened” conical tip.<sup>8</sup> At present we believe that these two tips (flattened and unflattened) yield the same values of tunneling decay constant ( $\beta$ ); however we do not know the difference in the nature of top-metallic contact between these two tips, which is related to the injection parameter ( $J_0$ ).



*Measurement protocol.* We used the same protocol to measure the rate of charge transport across all samples: a conical Ga<sub>2</sub>O<sub>3</sub>/EGaIn tip was used to build three junctions, and 21 *J-V* traces were collected per junction. The use of the same protocol for all measurements minimizes experimental errors resulting from contamination of the top-electrode by adventitious organic contaminants.

*Ag<sup>TS</sup> bottom electrode.* All SAMs were formed on ultraflat Ag<sup>TS</sup> substrates.<sup>9</sup> The use of Ag<sup>TS</sup> substrates as a bottom-electrode has several advantages in performing physical-organic studies, as we have discussed previously,<sup>10,11</sup>: e.g., Ag<sup>TS</sup> enables high yields of working junctions, and minimizes variation of data in tunneling currents due to surface roughness of the bottom-electrode.

#### Experimental details for preparation of SAMs

We prepared SAMs following the procedure reported previously.<sup>10</sup> EtOH (200 proof) solution (3 mM) of each of thiol derivatives was added to an amber-colored vial. The solution was sealed and degassed by bubbling N<sub>2</sub> through the solution for *ca.* 30 s. A silver substrate (Ag<sup>TS</sup>) was washed with pure EtOH, and placed in the solution of the thiol with the exposed metal face up. The vial was then filled with N<sub>2</sub>. After 3 h incubation at room temperature, the Ag<sup>TS</sup> film with the SAM on it was removed from solution and rinsed by repeatedly dipping the chip into clean EtOH (3 × 1 mL). The solvent on the SAM was then evaporated by blowing gently a stream of nitrogen over chip.

#### Experimental Details for Electrical Measurements

*Tip formation:* EGaIn tip was formed following a method reported previously by our group.<sup>11</sup> To generate a fine conical tip of EGaIn for use as a top contact, a 10 μL gas-tight syringe was filled with EGaIn (≥99.99%, Aldrich). A drop of EGaIn was then pushed to the tip

of the syringe needle and the hanging drop was brought into contact with a surface on which the EGaIn would stick (e.g. an oxidized Ag surface) and the needle gently pulled away from the drop using a micromanipulator. Upon breaking from the bulk EGaIn on the surface, a fine conical shaped tip is obtained. We prepared a new tip every three junctions.

*Junction formation and measurements:* Junction formation and measurements were done following the known method reported by our group.<sup>11</sup> The SAM is gently brought into contact first with the gold metal electrode. Then using a micromanipulator, the EGaIn tip is gently brought into contact with its own reflection on the Ag surface, at which point a conformal contact has been established between the SAM and the EGaIn tip. The contact area is derived from measuring the diameter of the contact area at high magnification. Assuming a circular contact, the area is derived from the measured diameter from which the current densities are calculated. The contact and presence of a SAM is confirmed by running a single scan after which 20 more scans are run if there is indication of contact and tunneling. The total number of working junctions versus those that shorted was used to calculate the yield.

**Table S1.** Summary of the previous results on the role of top-metallic interfaces in charge transport across large-area junctions. We only considered the results validated statistically in the literature. “No significant effect” indicates that the difference in tunneling current is  $\leq \times 10$ .

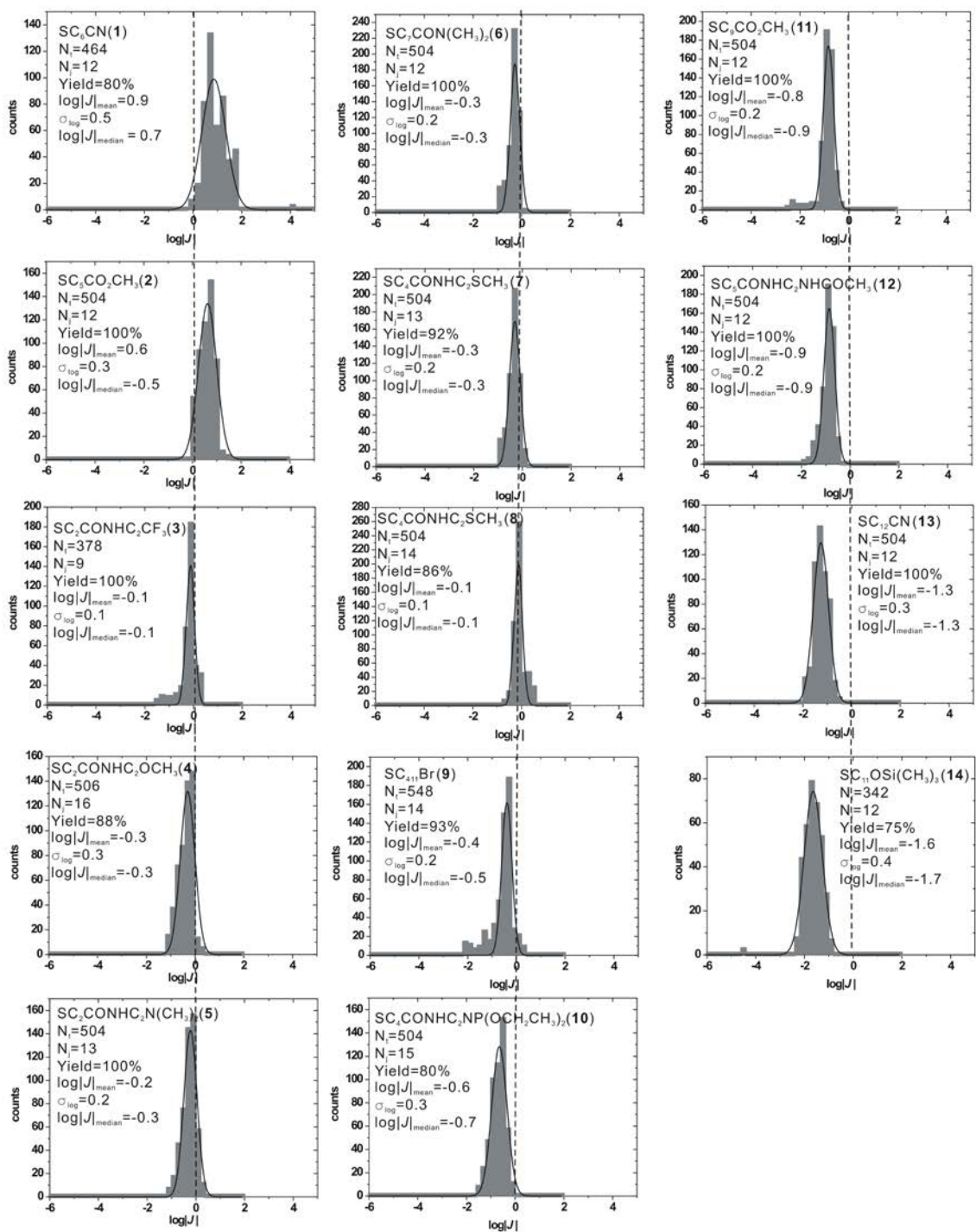
Junction Type <sup>a</sup>	Ref.	T	Experimental Result
Ag <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>11</sub> T//Ga <sub>2</sub> O <sub>3</sub> /EGaIn	12-14	Fc or Fc <sub>2</sub>	Strong molecular rectification
Ag <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>n</sub> T//Ga <sub>2</sub> O <sub>3</sub> /EGaIn	11	CH <sub>3</sub>	Odd-Even effect ( $\sim \times 10$ )
<i>n</i> -Si/styrene-T//Hg	15	CH <sub>3</sub> or Br	Significant effect ( $\sim \times 10^8$ )
<i>n</i> -Si/styrene-T//Pb	7	CH <sub>3</sub> or Br	Significant effect ( $\sim \times 10^5$ )
<i>n</i> -Si/styrene-T//Z <sup>b</sup>	7	CH <sub>3</sub> (Z: Ti or Pb)	Significant effect ( $\sim \times 10^5$ )
Ag <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>4</sub> CONH(CH <sub>2</sub> ) <sub>2</sub> T//Ga <sub>2</sub> O <sub>3</sub> /EGaIn	10	aromatic, aliphatic groups	No significant effect
Ag <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>n</sub> M(CH <sub>2</sub> ) <sub>m</sub> T//Ga <sub>2</sub> O <sub>3</sub> /EGaIn (M= CH <sub>2</sub> CH <sub>2</sub> or CONH)	this work	polar, uncharged groups	No significant effect
Au <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>n</sub> (phenylene) <sub>m</sub> T//Ga <sub>2</sub> O <sub>3</sub> /EGaIn	16	phenyl or 4-pyridiyl	No significant effect
Au <sup>TS</sup> /S(CH <sub>2</sub> ) <sub>15</sub> T//Au	17	CH <sub>2</sub> S or CO <sub>2</sub> (H)	No significant effect
Au/S(CH <sub>2</sub> ) <sub>7</sub> T//Au	18	CH <sub>3</sub> or CH <sub>2</sub> S	No significant effect
<i>n</i> -Si/(CH <sub>2</sub> ) <sub>11</sub> T//Hg	19	OH or Br	No significant effect
Si/S(CH <sub>2</sub> ) <sub>2</sub> T//Ag	20	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> or (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	No significant effect
<i>n</i> -Si/(CH=CH)(CH <sub>2</sub> ) <sub>14</sub> -T//Hg	21	H or F	No significant effect
PPF/ <i>p</i> -phenyl(triazole)-T//e-C <sup>b,c</sup>	22	(CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub> or (CH <sub>2</sub> )Fc	No significant effect

<sup>a</sup>Some of top-metallic interfaces may be covalent contacts, or coordination contacts, rather than van der Waals contacts; <sup>b</sup>Z is the top-electrode. This junction was included for completeness although it is not directly compatible to some of the others; <sup>c</sup>PPF is pyrolyzed photoresist film; e-C is e-beam deposited carbon.

### Minor discussion about Table S1

Table S1 summarizes previous studies showing results on the role of the top interface in large-area junction measurements, in particular, validated statistically. Most of the studies done by our group<sup>10</sup> and others<sup>14,16-22</sup> present no significant effects ( $\Delta J \leq \times 10$ ) on modifying the terminus of SAMs. We previously found significant effects resulting from ferrocene-terminated SAMs<sup>12-14</sup> and the odd-even effect<sup>11</sup> from a range of *n*-alkanethiolates; Cahen and colleagues<sup>7,15</sup> found a significant increase in current density resulting from Br-terminated styrene monolayer on *n*-Si with a mercury top electrode, but this increase might also reflect electrochemical reactions such as electroreduction of the C-Br bond (We do not see a corresponding effect for the aliphatic compound<sup>19</sup>).

**Figure S1.** Histograms of  $\log|J|$  at  $-0.5V$ . Dotted lines represent  $\log|J| = 0$ .  $N_t$  is the number of  $J$ - $V$  traces;  $N_j$  is the number of junctions; Yield is the ratio of working junctions to all junctions measured.



**Table S2.** Summary of junction measurements.

# in Fig. 1	-T in $S(CH_2)_nM(CH_2)_mT$	length <sup>a</sup> (Å)	$N_{\text{junctions}}$	$N_{\text{traces}}^b$	Yield (%)	$\log J _{\text{mean}} \pm \sigma_{\log}$ at -0.5V	$\log J _{\text{median}}$	$r^c$	$\log r  \pm \sigma_{\log}$
1	-C≡N	10.1	12	462	80	$0.9 \pm 0.5$	0.7	1.1	$0.04 \pm 0.01$
2	-CO <sub>2</sub> CH <sub>3</sub>	11.0	12	504	100	$0.6 \pm 0.3$	0.5	1.2	$0.08 \pm 0.03$
3	-CF <sub>3</sub>	12.4	9	378	100	$-0.1 \pm 0.1$	-0.1	1.1	$0.03 \pm 0.02$
4	-OCH <sub>3</sub>	13.4	16	506	88	$-0.3 \pm 0.3$	-0.3	1.3	$0.10 \pm 0.08$
5	-N(CH <sub>3</sub> ) <sub>2</sub>	13.5	13	504	100	$-0.2 \pm 0.2$	-0.3	1.1	$0.03 \pm 0.02$
6	-CON(CH <sub>3</sub> ) <sub>2</sub>	13.5	12	504	100	$-0.3 \pm 0.2$	-0.3	1.2	$0.07 \pm 0.01$
7	-SCH <sub>3</sub>	13.9	13	504	92	$-0.3 \pm 0.2$	-0.3	1.2	$0.08 \pm 0.03$
8	-SO <sub>2</sub> CH <sub>3</sub>	14.0	14	504	86	$-0.1 \pm 0.1$	-0.1	1.0	$0.0 \pm 0.03$
9	-Br	15.8	14	548	93	$-0.4 \pm 0.2$	-0.5	1.2	$0.09 \pm 0.03$
10	-PO(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	15.7	15	504	80	$-0.6 \pm 0.3$	-0.7	1.0	$0.0 \pm 0.03$
11	-CO <sub>2</sub> CH <sub>3</sub>	16.1	12	504	100	$-0.8 \pm 0.2$	-0.9	1.3	$0.12 \pm 0.08$
12	-NHCOCH <sub>3</sub>	15.8	12	504	100	$-0.9 \pm 0.2$	-0.9	1.1	$0.02 \pm 0.05$
13	-C≡N	17.7	12	504	100	$-1.3 \pm 0.3$	-1.3	1.1	$0.05 \pm 0.01$
14	-OSi(CH <sub>3</sub> ) <sub>3</sub>	19.1	12	342	75	$-1.6 \pm 0.4$	-1.7	1.2	$0.09 \pm 0.09$

<sup>a</sup>Length from sulfur to distal atom (hydrogen or other) in the terminus of the SAM; <sup>b</sup>Each trace corresponds to (0V→+0.5V→0V→-0.5V→0V, and contains two  $J$ - $V$  scans).  $r = |J(+V)|/|J(-V)|$

**Table S3.** Dipole moment for terminal group -Y and the difference in  $\log|J|$  ( $\Delta\log|J|$ ). Dipoles were obtained from the CRC Handbook of Chemistry and Physics 94<sup>th</sup> edition, 2013-2014.

# in Fig. 1	-T in $SC_nMC_mT$	Dipole ( $\mu$ in D) <sup>a</sup>	$\Delta\log J $ <sup>b</sup> at -0.5V
1	-C $\equiv$ N	3.93	0.028
2	-CO <sub>2</sub> CH <sub>3</sub>	1.72	-0.18
3	-CF <sub>3</sub>	2.35	-0.25
4	-OCH <sub>3</sub>	1.30	-0.078
5	-N(CH <sub>3</sub> ) <sub>2</sub>	0.61	0.0059
6	-CON(CH <sub>3</sub> ) <sub>2</sub>	3.70	-0.051
7	-SCH <sub>3</sub>	1.55	-0.080
8	-SO <sub>2</sub> CH <sub>3</sub>	4.44 <sup>c</sup>	0.090
9	-Br	1.82	0.19
10	-PO(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	2.95	0.28
11	-CO <sub>2</sub> CH <sub>3</sub>	1.72	0.10
12	-NHCOCH <sub>3</sub>	4.30	0.072
13	-C $\equiv$ N	3.93	0.020
14	-OSi(CH <sub>3</sub> ) <sub>3</sub>	1.18 <sup>d</sup>	-0.010

<sup>a</sup>Values of dipole moment for CH<sub>3</sub>-Y or CH<sub>3</sub>CH<sub>2</sub>-Y; <sup>b</sup> $\Delta\log|J| = \log|J_{\text{polar}}| - \log|J_{\text{CH}_3}|$ ; <sup>c</sup>Clark, T.;

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