Supporting Information

Odd-Even Effects in Charge Transport across *n*-Alkanethiolate-Based SAMs

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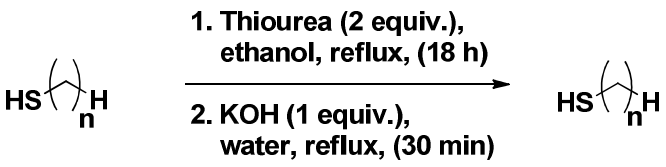
Experimental Details

Materials. All reagents were used as supplied from the manufacturer unless otherwise specified. Anhydrous toluene was purchased from Acros Organics and 200-proof ethanol was purchased from Fisher Scientific. Water was purified using a Millipore Q-POD water purification system. Alkanethiols (except SC_{13} and SC_{17}) and all starting compounds for synthesis were purchased from Sigma-Aldrich. For the contact electrode, high purity eutectic gallium-indium (EGaIn) was purchased from Sigma-Aldrich. All thiol derivatives were stored in a desiccator at room temperature to avoid decomposition.

General procedure for Synthesis of $HS(CH_2)_nH$. We followed a general procedure for the synthesis of alkanethiols.[1] A 25 mL ethanolic solution of $Br(CH_2)_nH$ (4 mmol) and thiourea (608 mg, 8 mmol) was heated under reflux for 18 hrs. The reaction was cooled to room temperature before removing the reaction solvent *in vacuo*. To the remaining residue, an aqueous solution of KOH (246 mg, 4.4 mmol in 20 mL of degassed water) was added and the resulting mixture was heated to 100 ˚C for 30 min under a N_2 atmosphere (Note: longer reaction times may result in adventitious oxidation of the thiol functional group). The reaction solution was allowed to cool to room temperature and the organic layer was extracted with 30 mL of cold CH_2Cl_2. The combined organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* (Note: the temperature of the water bath must be below 30 °C) to yield the final alkanethiol product ($HS(CH_2)_nH$. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ as a solvent.



Scheme S1. Synthesis of alkanethiols

Tridecane-1-thiol ($HS(CH_2)_{13}H$.[2]White solid, ^{1}H NMR ($CDCl_3$): δ 0.79 (t, 3H, J = 7.2 Hz), 1.17–1.26 (m, 20H), 1.52 (m, 2H), 2.44 (q, 2H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 24.7, 28.4, 29.1, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 34.1.

Heptadecane-1-thiol[2]($HS(CH_2)_{17}$ White solid, ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, J = 7.2 Hz), 1.26 (m, 28H), 1.58–1.66 (m, 2H), 2.53 (q, 2H, J = 7.2 Hz).

Purity of alkanethiols. We checked the purity of the *n*-alkanethiols by ^{1}H NMR. Figure S1 shows a sample ^{1}H NMR spectrum of heptanethiol with peak assignments.

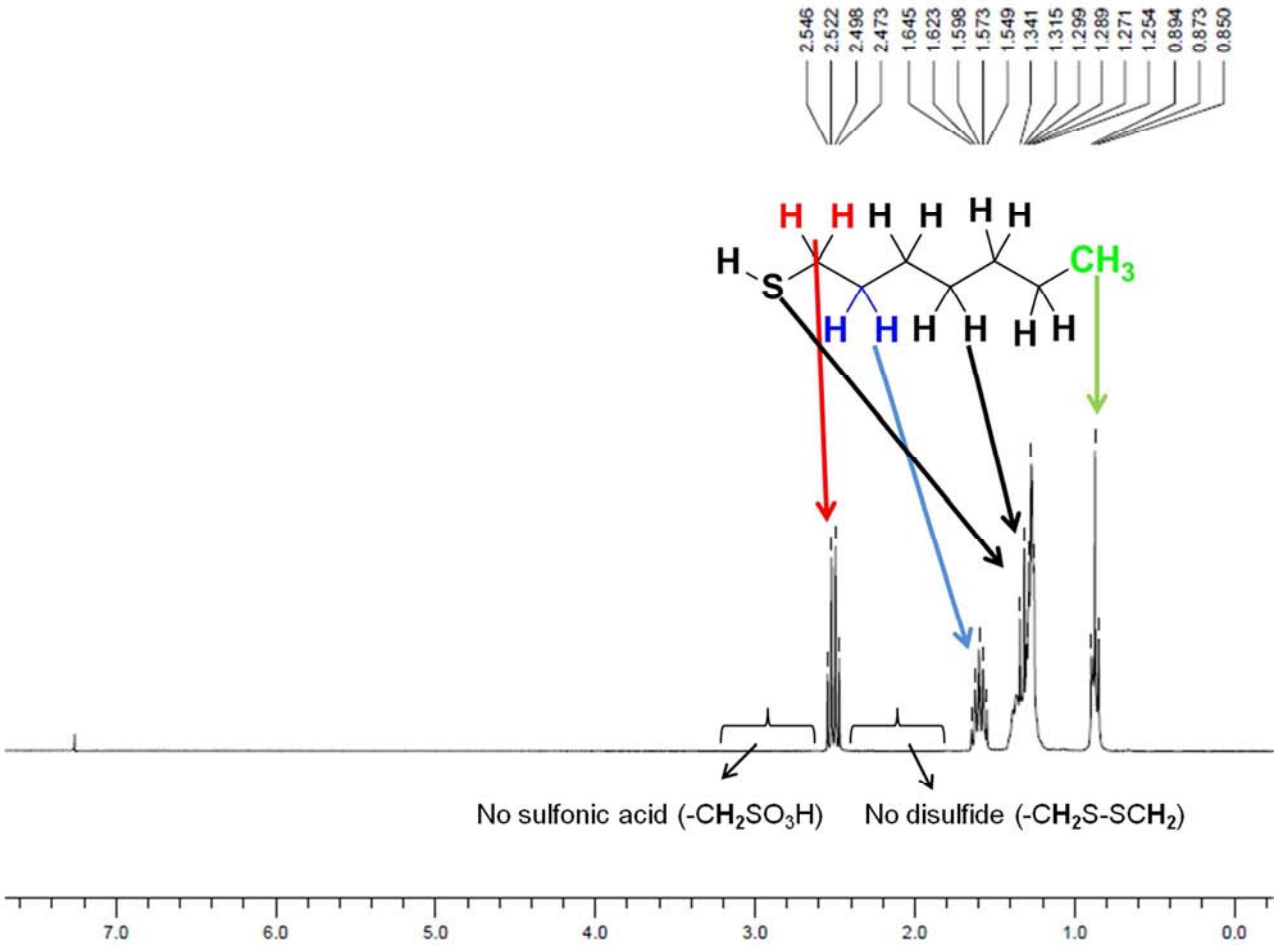


Figure S1. ^{1}H NMR spectrum (with peak assignments) of pure heptanethiol. No peaks are observed in the regions assigned to oxidized thiols and disulfides.

Formation of SAMs of *n*-alkanethiolates on gold and silver substrate. Following previously reported protocols,[3] SAMs of *n*-alkanethiolates were prepared on Ag^{TS} and Au^{TS} substrate. After cleaning the backside of the M^{TS} chips with pure ethanol, we stripped the M^{TS} substrates[2] and transferred them to a 1 mM solution of thiol in anhydrous toluene. After 3 h of incubation at ambient conditions and under a N_2 atmosphere, we removed the substrate from the solvent, and cleaned it by immersing, for three minutes each, in three vials containing 3 mL of pure toluene. Residual toluene was allowed to evaporate in air. We collected *J*−*V* data for SAMs composed of SC_n with n = 5 to n = 18.

Electrical measurements using EGaIn. We formed a "flattened" conical EGaIn tip following a protocol reported previously by our group.[3] (For detailed information on the formation of flattened conical tips, please see the video in the supporting information of ref. 3). Flattened tips[3] allowed the collection of data with a narrower distribution compared to unselected tips (i.e. tips having surface asperities visible by optical microscopy).[2] After forming a flattened tip, we moved the tip slowly down to the substrate to make a gentle contact between the EGaIn tip and substrate.[3] Assuming a circular contact, we measured the contact area between the tip and substrate using optical microscopy.[3]

Protocol for collection of data. We followed a standard "1/3/20" protocol for the collection of *J*(V) data; that is, we used each tip for three different junction measurements (i.e., three contacts on three different places on the substrate) and acquired 20 scans per junction.[2,4,3] To check the stability of the junction, we first recorded one trace, and after a successful measurement (i.e. no shorting) we recorded 20 *J*−*V* traces at a positive and negative bias (V = 0 V→V = −0.5 V →V = 0 V→V = +0.5 V →V = 0 V). (For additional details see reference 3).

Statistical analysis of data for current density across SAMs. We estimated J_0 ($A \cdot cm^{-2}$) and β ($Å^{-1}$; n_C^{-1}) by least-squares linear regression analysis of values of log|*J*| versus the length of the molecule. The length of the molecule was calculated based on the number carbon atoms and/or the distance between the sulfur and most distal hydrogen atom (assuming all-trans configuration, the distance was calculated using ChemDraw software). Log|*J*| is the Gaussian mean value of data for log|*J*|, where *J* is the current density (measured in $A \cdot cm^{-2}$ at V = +0.5 V, and defined for the geometrical contact area.[4] (For details see ref 3)

Calculation of confidence interval (CI)*:* The formula for confidence intervals (for the Gaussian mean value based on the Z-test) is given by equation S1, in which σ represents the standard deviation of the Gaussian mean.[4,5]

$$\mathrm{CI} = 1.96\frac{\sigma}{\sqrt{\mathrm{N}}} \qquad \text{S1}$$

In equation S1, N is a number of independently measured current densities. Since values of log|*J*| measured using the same junction are probably correlated, we consider N as a number of individual junctions (not the whole data points).[4]

Statistical analysis of data for SAMs on Au^{TS}. We assume that SAMs of alkanethiolates having n_{odd} and n_{even} result in two different data sets and determined, using statistical analysis (see below), if these two lines are distinguishable. We note that this analysis does not confirm *necessarily* the significance of the alternation in the odd and even data set (Figure 3b), but shows a difference between two regression lines.

Application of the Simmon's equation to the data yields two regression lines:

$$\log|J| = \log|J_{0\,odd}| - \beta_1 d \qquad (2)$$

$$\log|J| = \log|J_{0\,even}| - \beta_2 d \qquad (3)$$

Equation (2) represents the regression line fitted to the odd number of carbons and equation (3) represents the regression line fitted to even number of carbons; we estimated their parameters previously (Figure 4).In order to determine a statistical difference between (2) and (3), we tested for the significant difference ($\alpha = 0.01$) between intercepts ($\log|J_{0\ odd}|$ and $\log|J_{0\ even}|$), and slopes (β_1 and β_2). To generate sufficient data to fit the regression lines, we used a resampling method called bootstrap.[6] This method constructs a number of resamples of the observed dataset (and of equal size to the observed dataset), each of which is obtained by random sampling with replacement from the original dataset. We iterated resampling 10,000 times and obtained four vectors, $\boldsymbol{\beta_1}$, $\boldsymbol{\beta_2}$, $\mathbf{log}|\boldsymbol{J_{0odd}}|$, and $\mathbf{log}|\boldsymbol{J_{0even}}|$ (vectors appear in bold), each having 10,000 rows.

To test for the significant difference we have the following tests: $\psi_{11} = \begin{cases} H_{10}: \mu_{\boldsymbol{\beta_1}} = \mu_{\boldsymbol{\beta_2}} \\ H_{11}: \mu_{\boldsymbol{\beta_1}} \neq \mu_{\boldsymbol{\beta_2}} \end{cases}$ and $\psi_{12} = \begin{cases} H_{20}: \mu_{\mathbf{log}|\boldsymbol{J_{0odd}}|} = \mu_{\mathbf{log}|\boldsymbol{J_{0even}}|} \\ H_{21}: \mu_{\mathbf{log}|\boldsymbol{J_{0odd}}|} \neq \mu_{\mathbf{log}|\boldsymbol{J_{0even}}|} \end{cases}$, where μ is the population mean, H_{10} and H_{20} are null hypotheses and H_{11} and H_{21} are alternative hypotheses. In order to use a t-test to compare means of two vectors, three fundamental assumptions must be considered: i) vectors should follow a normal distribution; ii) vectors should have same variances; iii) vectors should be independent. We tested the vectors for normality, using the Shapiro-Wilk test,[7] which showed that all vectors are normally distributed. The vectors ($\boldsymbol{\beta_1}$, $\boldsymbol{\beta_2}$, $\mathbf{log}|\boldsymbol{J_{0odd}}|$, and $\mathbf{log}|\boldsymbol{J_{0even}}|$) were tested ($\psi_{21} = \begin{cases} H_{10}: \sigma^2_{\boldsymbol{\beta_1}} = \sigma^2_{\boldsymbol{\beta_1}} \\ H_{11}: \sigma^2_{\boldsymbol{\beta_1}} \neq \sigma^2_{\boldsymbol{\beta_1}} \end{cases}$ and $\psi_{22} = \begin{cases} H_{20}: \sigma^2_{\mathbf{log}|\boldsymbol{J_{0odd}}|} = \sigma^2_{\mathbf{log}|\boldsymbol{J_{0even}}|} \\ H_{21}: \sigma^2_{\mathbf{log}|\boldsymbol{J_{0odd}}|} \neq \sigma^2_{\mathbf{log}|\boldsymbol{J_{0even}}|} \end{cases}$ where σ^2 is the population variance) subsequently for variance equality using the F- test,[8] which determined that we had populations with unequal variances. For the third assumption, according to the sampling method we know that data points are independent. Under these conditions (normality, unequal variances, and

independency), we implemented a Welch's *t*-test.[9] For ψ_{11}, according to its p-value = 0.0491, we cannot reject null hypothesis at the significance level of $\alpha = 0.01$ (and any α smaller than p-value=0.049). For ψ_{12} we obtain p-value= 0.000, which means we can reject the null hypothesis and say there is a significant difference between the intercepts (J_0). This analysis suggests that while we cannot reject the hypothesis of the equality of slopes of the two regression lines, we can say that SAMs of alkanethiolates with n_{odd} have a higher injection current value, J_0, than alkanethiolates with n_{even}.

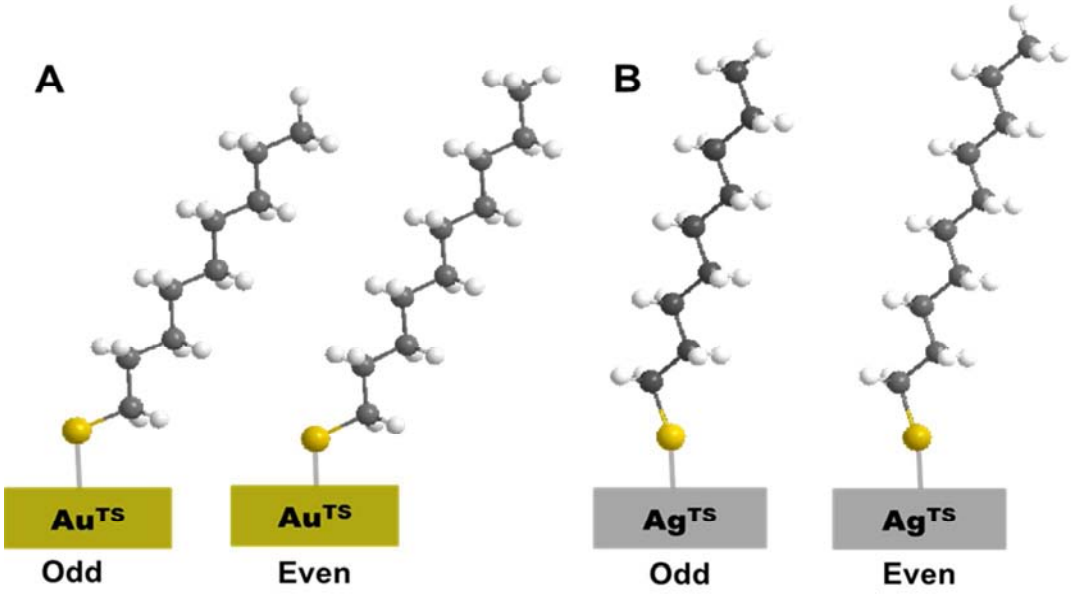


Figure S2. Structure of *n*-alkanethiolate SAMs with an even (SC_{10}) and odd (SC_9) number of carbons on the A) Au^{TS} and B) Ag^{TS} surfaces. Different tilt angles on Ag and Au cause different geometry for the top CH_2-CH_3 group and different thickness of SAMs; SAMs on Ag^{TS} surface form a ticker film than on Au^{TS} surface.

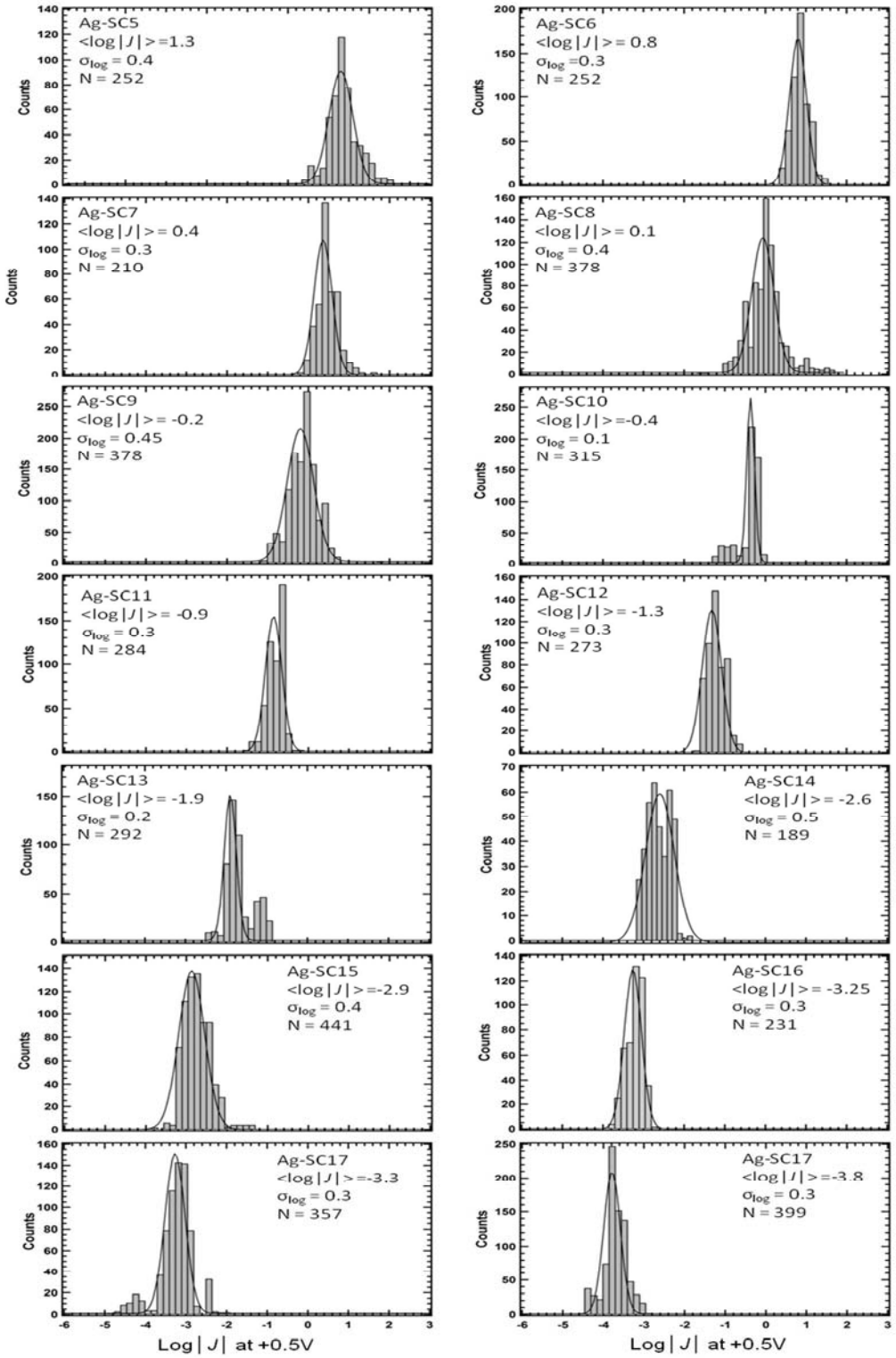


Figure S3. Histograms of the distribution of the values of log|*J*| at V = +0.5V for *n*-alkanethiolates SAMs on Ag^{TS}. Solid curves represent the best Gaussian fits. N is the number of data points. Values of log|*J*| and σ_{log} reported in the Figure were extracted from the fitting.

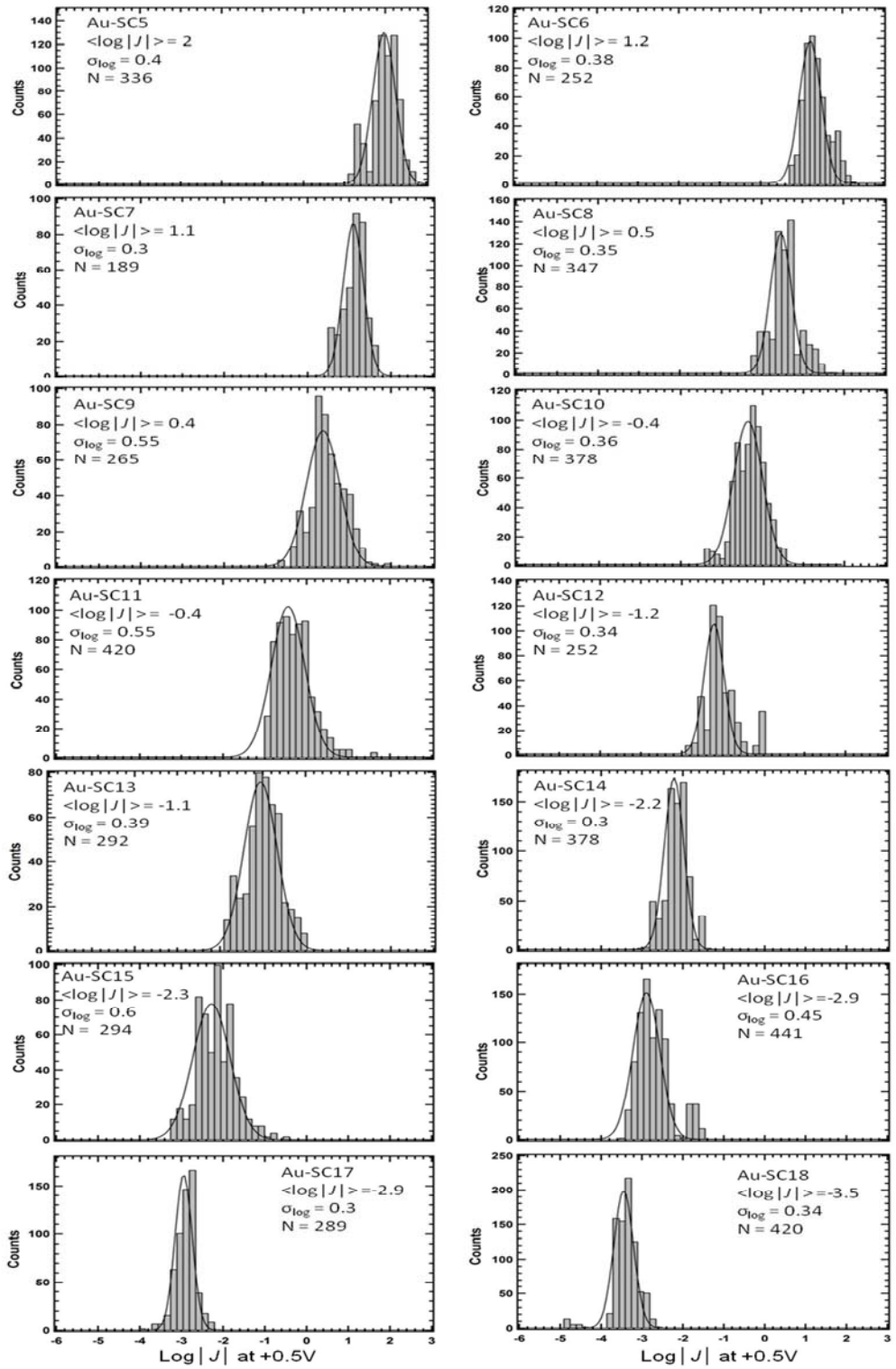


Figure S4. Histograms of the distribution of the values of log|*J*| at V = +0.5V for *n*-alkanethiolates SAMs on Au^{TS}. Solid curves represent the best Gaussian fits. N is the number of data points. Values of log|*J*| and σ_{log} reported in the Figure were extracted from the fitting.

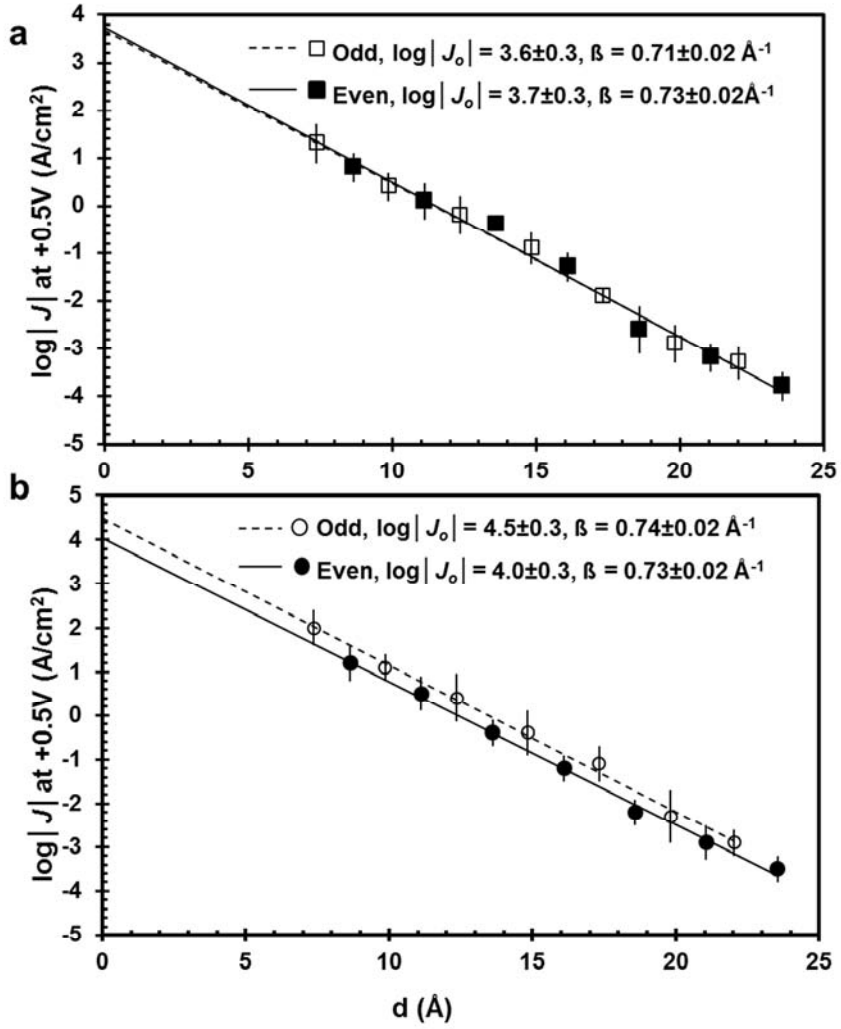


Figure S5. log|*J*| at V = +0.5V *versus* number of carbons for SAMs of *n*-alkanethiolates on a) Ag^{TS} and b) Au^{TS}. Solid line (for alkanethiolate SAMs with n_{even}) and dashed line (for alkanethiolate SAMs with n_{odd}) represent the linear regression analyses which gives β/2.303 (slopes) and log|J_0| (intercepts at d = 0).

Table S1. Junction performance for SAMs of alkanethiolates in a M^{TS}/SAM//Ga_2O_3/EGaIn junction where M^{TS} = Au^{TS} or Ag^{TS}.

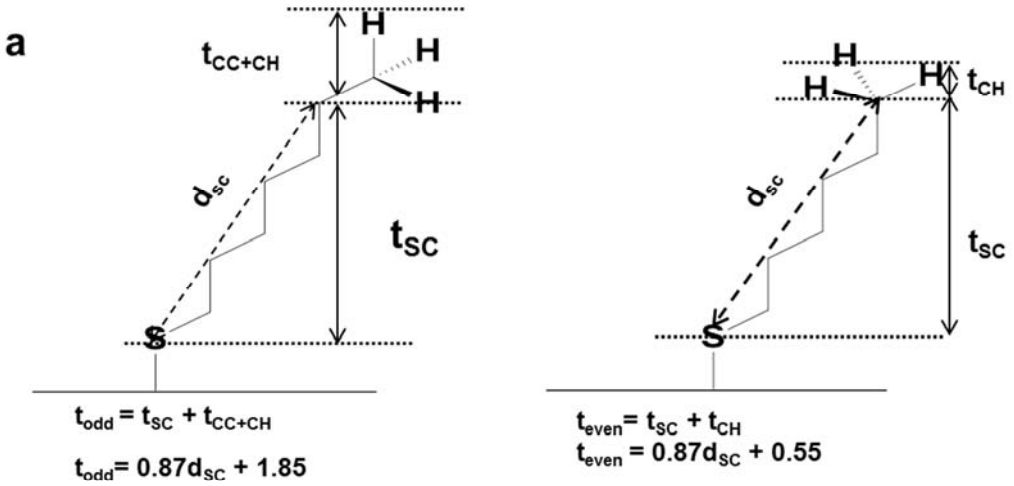
Compound	Ag^{TS}			Au^{TS}		
	N[a]	Yield (%)[b]	<log|J|>[c]	N[a]	Yield (%)[b]	<log|J|>[c]
SC_5	252	100	1.3	336	89	2.0
SC_6	252	100	0.8	252	100	1.2
SC_7	210	83	0.4	189	90	1.1
SC_8	378	100	0.1	347	89	0.5
SC_9	378	100	-0.2	265	80	0.4
SC_{10}	315	100	-0.4	378	95	-0.4
SC_{11}	284	87	-0.9	420	87	-0.4
SC_{12}	273	87	-1.3	252	80	-1.2
SC_{13}	292	100	-1.9	292	87	-1.1
SC_{14}	189	100	-2.6	378	86	-2.2
SC_{15}	441	100	-2.9	294	93	-2.3
SC_{16}	231	92	-3.25	441	88	-2.9
SC_{17}	357	95	-3.3	289	87	-2.9
SC_{18}	378	100	-3.8	420	95	-3.5

[a] Number of data points. [b] Percentage of non-shorting junctions out of the total junctions. [c] At V= +0.5 V.

Table S2. Junction performance for SAMs of SC_{10} and SC_{11} in a M^{TS}/SAM//Ga_2O_3/EGaIn junction where M^{TS} = Au^{TS} or Ag^{TS}.[a]

Time	SC_{10}			SC_{11}		
	M[b]	σ_{log}[c]	$\langle \log\lvert J\rvert \rangle$[d]	M[b]	σ_{log}[c]	$\langle \log\lvert J\rvert \rangle$[d]
3h	Ag	0.1	-0.4	Ag	0.3	-0.9
1d	Ag	0.3	-0.5	Ag	0.3	-0.8
2d	Ag	0.2	-0.5	Ag	0.4	-1
7d	Ag	0.3	-0.4	Ag	0.4	-0.9
3h	Au	0.4	-0.4	Au	0.6	-0.4
1d	Au	0.4	-0.4	Au	0.4	-0.3
2d	Au	0.4	-0.4	Au	0.6	-0.4
7d	Au	0.4	-0.4	Au	0.6	-0.5

[a] Number of data points for all junctions is 126. [b] Metal substrate. [c] Standard deviation of Gaussian mean. [d] At V= +0.5 V.



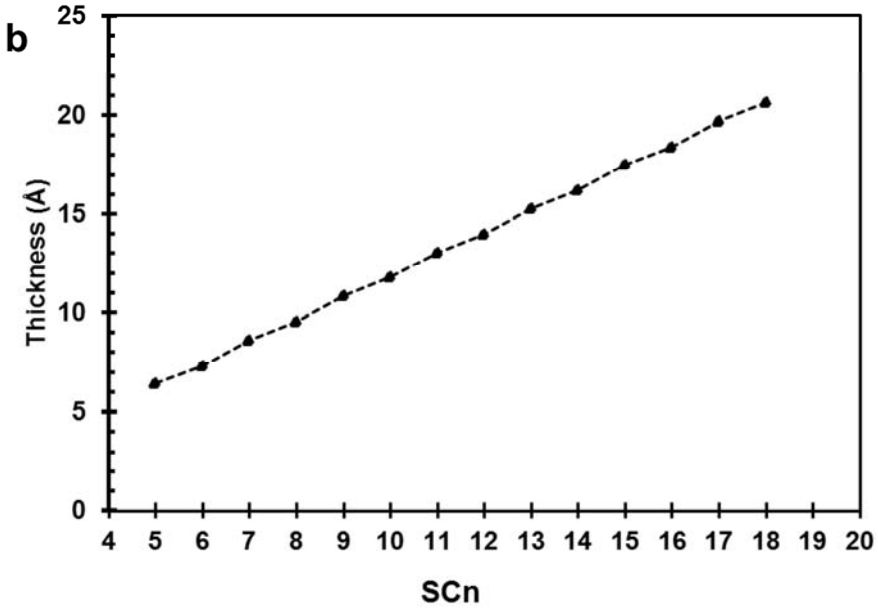


Figure S6. (A) Calculation of thickness (for n_{odd}: thickness = t_{SC} +tcc_{+CH}; for n_{even} thickness = t_{SC} +t_{CH}). We assumed the tilt angle is 30°. (B) The plot shows thickness *versus* number of carbons.

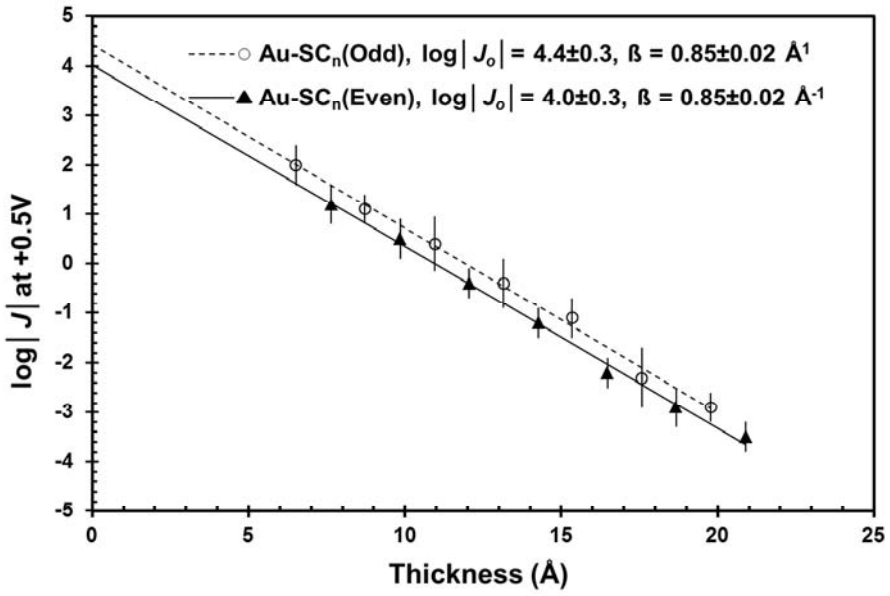


Figure S7. log|*J*| at V = +0.5V *versus* thickness of molecule for *n*-alkanethiolates on Au^{TS}. Solid line (for alkanethiolate SAMs with n_{even}) and dashed line (for alkanethiolate SAMs with n_{odd}) represent the linear regression analyses which gives β/2.303 (slopes) and log|J_0| (intercepts at d = 0).

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