The Rate of Charge Tunneling through Self-Assembled Monolayers is Insensitive to Many Functional Group Substitutions

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Experimental Details

Materials: All reagents were purchased from Sigma-Aldrich and Alfa Aesar, and were used as supplied unless otherwise specified. All organic solvents were purchased from Sigma-Aldrich (dichloromethane, hexanes) or Fisher (200 proof ethanol) while water used in the synthesis was purified using a Millipore Q-POD water purification system. For the contact electrode, high purity eutectic gallium-indium (EGaIn) was obtained from Sigma-Aldrich and used as supplied. 2-(2-Norbornyl)ethylamine and 2-(2-cycloheptyl)ethylamine were purchased from J&W PharmLab (Levittown, PA) and ChemBridge (San Diego, CA), respectively. 2-(2-Nitrophenyl)ethylamine and 2-(1-adamantyl)ethylamine were synthesized through reactions of the corresponding acetonitriles with a $BH_3 \cdot THF$ complex by following a known method.[1] All compounds (synthesized or commercially available) were purified by silica gel column

chromatography. All purified thiol derivatives were maintained under N_2 atmosphere and <4 °C, and purity was checked right before use (These precautions were necessary as primary thiols readily react in an O_2 atmosphere to give disulfides, sulfonates and sulfonic acids). To ensure purity, all stored compounds were checked by ^1H NMR before use.

Characterization: ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 or a varian INOVA 500 instrument using $CDCl_3$ as solvent and residual solvent as an internal standard.

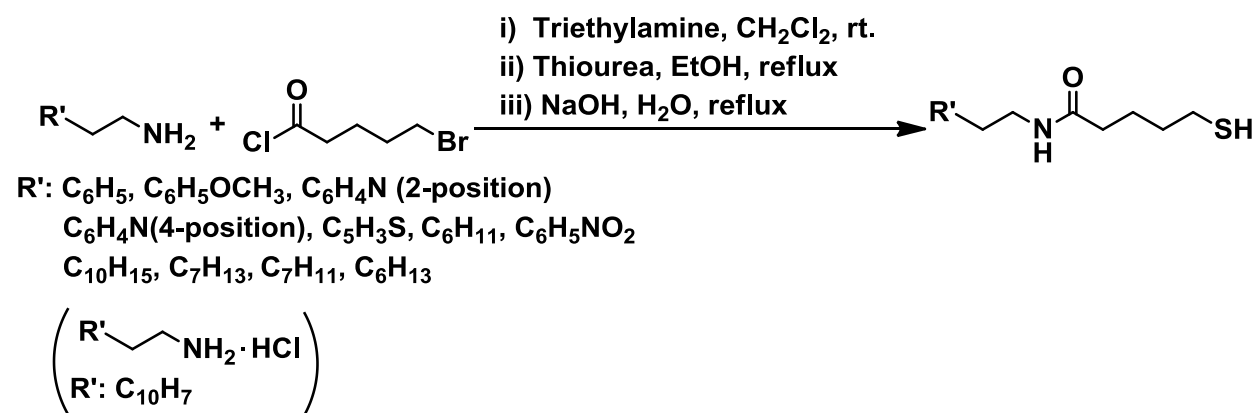**Preparation of Alkanethiols Derivatives.**

Figure S1. Synthetic scheme for the preparation of amide derivatives.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-C$_6$H$_{11}$ (8): 2-Cyclohexylethylamine (2.0 g, 15.7 mmol) in 50 mL CH_2Cl_2 was added to a 50 mL CH_2Cl_2 solution of 5-bromovaleryl chloride (1.74 g, 15.7 mmol) and triethylamine (1.74 g, 17.3 mmol) at room temperature. The reaction solution was then stirred for 3 hrs at room temperature. The solvent was removed *in vacuo*, and the residue was dissolved in 50 mL ethanol, followed by addition of thiourea (1.32 g, 17.3 mmol). The resulting solution was refluxed for 12 hrs. After removal of the ethanol *in vacuo*, sodium hydroxide (692 mg, 17.3 mmol) and water (50 mL) were added to the crude mixture. The reaction mixture was

again heated to reflux for 2 hrs. The solution was then cooled to room temperature and extracted with 3 x 30 mL CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, solvent was removed *in vacuo*, and the crude product was purified by passing through a silica-gel column eluting with a mixture of ethyl acetate and CH_2Cl_2 (1:1, v/v). After purification, the product was store under nitrogen at <4 °C. ^{1}H NMR (CDCl$_3$): δ 5.85 (br, 1H), 3.20 (q, 2H, J = 7.2 Hz), 2.48 (q, 2H, J = 6.8 Hz), 2.12 (t, 2H, J = 7.2Hz), 1.56-1.46 (m, 10H), 1.40-0.79 (m, 8H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.4, 37.2, 36.9, 35.9, 35.2, 33.4, 33.0, 26.3, 26.1, 24.3, 24.1.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-C$_6$H$_5$ (1). Reaction of 2-phenylethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 7.32-7.24 (m, 5H), 5.69 (br, 1H), 3.49 (q, 2H, J = 7.2 Hz), 2.80 (t, 2H, J = 6.8 Hz), 2.49 (q, 2H, J = 7.6 Hz), 2.13 (t, 2H, J = 7.2 Hz), 1.74-1.52 (m, 4H), 1.32 (t, 1H, J = 8.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.8, 139.1, 129.0, 128.9, 126.7, 40.8, 36.2, 35.9, 33.7, 24.6, 24.5.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(o-C$_6$H$_4$NO$_2$) (2). Reaction of 2-(2-nitrophenyl)ethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 7.90-7.87 (m, 1H), 7.61-7.48 (m, 1H), 7.45-7.32 (m, 2H), 5.95 (br, 1H), 3.57 (q, 2H, J = 8.0 Hz), 3.08 (t, 2H, J = 8.0 Hz), 2.49 (q, 2H, J = 8.0 Hz), 2.14 (t, 2H, J = 8.0 Hz), 1.72-1.53 (m, 4H), 1.32 (t, 1H, J = 8.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 173.0, 149.8, 134.2, 133.5, 132.8, 128.0,125.0, 40.3, 36.1, 33.4, 33.0, 24.5.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(o-C$_6$H$_4$OCH$_3$) (3). Reaction of 2-(2-methoxyphenyl)ethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 7.30-7.18 (m, 1H), 7.15-7.09 (m, 1H), 6.95-6.84 (m, 2H), 5.76 (br, 1H), 3.83 (s, 3H), 3.48 (q, 2H, J = 8.0 Hz), 2.82 (t, 2H, J = 8.0 Hz), 2.49 (q, 2H, J = 8.0 Hz), 2.11 (t, 2H, J = 8.0 Hz), 1.72-1.55 (m, 4H),

1.32 (t, 1H, $J = 8.0$ Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 172.7, 157.7, 130.9, 128.1, 127.6, 121.0, 110.7, 55.6, 40.0, 36.3, 33.7, 30.4, 24.6.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(2-C$_5$H$_4$N) (4). Reaction of 2-(2-pyridyl)ethylamine according to the previous procedure gave the title compound. ^1H NMR (CDCl$_3$): δ 8.60-8.49 (m, 1H), 7.75-7.65 (m, 1H), 7.32-7.32 (m, 2H), 3.70 (q, 2H, $J = 8.0$ Hz), 3.06 (t, 2H, $J = 8.0$ Hz), 2.56 (q, 2H, $J = 8.0$ Hz), 2.25 (t, 2H, $J = 8.0$ Hz), 1.81-1.61 (m, 4H), 1.46 (t, 1H, $J = 8.0$ Hz) (amide proton was too broad to be observable). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 172.5, 159.0, 148.6, 136.3, 123.1, 121.2, 38.5, 36.7, 35.5, 33.0, 24.0, 23.9.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(4-C$_6$H$_4$N) (5). Reaction of 2-(4-pyridyl)ethylamine according to the previous procedure gave the title compound. ^1H NMR (CDCl$_3$): δ 8.48 (dd, 2H, $J = 6.0, 1.6$ Hz), 7.07 (dd, 2H, $J = 6.0, 1.6$ Hz), 6.34 (br, 1H), 3.47 (q, 2H, $J = 6.8$ Hz), 2.78 (t, 2H, $J = 7.2$ Hz), 2.45 (q, 2H, $J = 7.6$ Hz), 2.11 (t, 2H, $J = 7.2$ Hz), 1.72-1.48 (m, 4H), 1.30 (t, 1H, $J = 7.6$ Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 172.7, 149.4, 148.3, 124.1, 39.5, 35.7, 34.9, 33.2, 24.2, 24.1.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(2-C$_4$H$_3$S) (6). Reaction of 2-(2-thiophenyl)ethylamine according to the previous procedure gave the title compound. ^1H NMR (CDCl$_3$): δ 7.21-7.12 (m, 1H), 7.00-6.89 (m, 1H), 6.89-6.80 (m, 1H), 6.19 (br, 1H), 3.52 (q, 2H, $J = 8.0$ Hz), 3.04 (t, 2H, $J = 8.0$ Hz), 2.52 (q, 2H, $J = 8.0$ Hz), 2.18 (t, 2H, $J = 8.0$ Hz), 1.66-1.59 (m, 4H), 1.36 (t, 1H, $J = 8.0$ Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 172.7, 141.3, 127.0, 125.3, 123.8, 40.8, 35.9, 33.4, 29.8, 24.29, 24.25.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(1-C$_{10}$H$_7$) (7). Reaction of 2-(1-naphthyl)ethylamine hydrochloride according to the previous procedure gave the title compound (two equiv of triethylamine was used instead of one equiv). ^1H NMR (CDCl$_3$): δ 8.07 (d, 1H, $J = 8.4$ Hz), 7.85 (d, 1H, $J = 8.4$ Hz), 7.74 (d, 1H, $J = 8.0$ Hz), 7.58-7.36 (m, 3H), 7.30 (d, 1H, $J = 6.8$ Hz), 5.68 (br, 1H), 3.61 (q, 2H, $J = 6.8$ Hz), 3.28 (t, 2H, $J = 6.8$ Hz), 2.49 (q, 2H, $J = 7.2$ Hz), 2.10 (t, 2H, $J = 7.2$ Hz), 1.76-

1.50 (m, 4H), 1.32 (t, 1H, J = 8.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.6, 135.0, 133.8, 131.9, 128.7, 127.2, 126.7, 126.1, 125.7, 125.4, 123.6, 40.1, 35.9, 33.4, 32.7, 24.2.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(1-C$_{10}$H$_{15}$) (9). Reaction of 2-(1-adamantyl)ethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 5.51 (br, 1H), 3.28-3.18 (m, 2H), 2.51 (q, 2H, J = 7.2 Hz), 2.13 (t, 2H, J = 7.2 Hz), 1.92 (br, 3H), 1.79-1.54 (m, 12H), 1.48 (br, 8H), 1.33 (t, 1H, J = 8.0 Hz), 1.35-1.30 (m, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.6, 43.8, 42.3, 36.9, 36.0, 34.5, 33.8, 33.5, 31.9, 28.5, 24.3, 24.2.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-C$_7$H$_{13}$ (10). Reaction of 2-cycloheptylethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 5.58 (br, 1H), 3.23 (q, 2H, J = 5.6 Hz), 2.52 (q, 2H, J = 7.6 Hz), 2.15 (t, 2H, J = 7.6 Hz), 1.78-1.25 (m, 20H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.4, 37.2, 36.9, 35.9, 35.2, 33.4, 33.0, 26.3, 26.1, 24.3, 24.1.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-C$_8$H$_{15}$ (11). Reaction of 2-cyclooctylethylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 5.72 (br, 1H), 3.22 (m, 2H), 2.50 (q, 2H, J = 6.8 Hz), 2.14 (t, 2H, J = 7.2 Hz), 1.79-1.18 (m, 22H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.4, 37.7, 37.6, 35.9, 34.8, 33.4, 32.0, 27.1, 26.1, 25.2, 24.3, 24.2.

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_2$-(2-C$_7$H$_{11}$) (12). Reaction of 2-(2-norbornyl)ethylamine according to the previous procedure gave the title compound. (Note that an enantiomerically undefined starting material was used). ^{1}H NMR (CDCl$_3$): δ 5.67 (br, 1H), 3.26-3.12 (m, 2H), 2.51 (q, 2H, J = 7.6 Hz), 2.20-2.03 (m, 4H), 1.82-0.96 (m, 14H), 0.66-0.52 (m, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.3, 39.8, 39.7, 39.0, 37.5, 36.89, 36.87, 36.0, 33.44, 32.7, 30.0, 24.3, 24.2, 22.3. (minor ^{13}C{^{1}H} peaks observed: 41.0, 39.6, 38.1, 38.0, 36.5, 36.4, 35.2, 28.6)

HS-(CH$_2$)$_4$-CONH-(CH$_2$)$_5$-CH$_3$ (13). Reaction of 1-hexylamine according to the previous procedure gave the title compound. ^{1}H NMR (CDCl$_3$): δ 5.91 (br, 1H), 3.17 (q, 2H, J = 6.8 Hz),

2.48 (q, 2H, J = 6.8 Hz), 2.13 (t, 2H, J = 6.8 Hz), 1.76-1.16 (m, 13H), 0.82 (t, 3H, J = 6.8 Hz).

$^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 172.4, 39.4, 35.9, 33.4, 31.3, 29.4, 26.5, 24.3, 24.1, 22.4, 13.9.

Experimental Design

We prepared template-stripped Ag substrates, liquid-metal (EGaIn) top electrodes, and self-assembled monolayers by following the procedure for fabrication, reported previously.[2]

Use of Template-Stripped Silver Substrates (Ag^{TS}): We used template-stripped silver substrate (Ag^{TS}) instead of Au^{TS} or the top surface of evaporated Ag due to three reasons: i) Ag^{TS} substrates are flatter than as-deposited substrates.[3] These surfaces, therefore, reduce errors caused by defects in the SAM and the interface between the SAM and the top electrode. ii) The smaller tilt-angle (~10˚ to the surface normal) of alkanethiolates on Ag produces SAMs with denser packing than SAMs on Au. (Alkanethiolates on gold are tilted at an angle of ~30˚ to the surface normal. SAMs on Ag (111) have ~26% more alkyl chains per unit area than do those on Au (111),[4] and better packing is believed to correlate with increases in the yield of working junctions in SAM-based devices.[3, 5])

Use of a Liquid Metal Electrode (Eutectic Gallium-Indium alloy, EGaIn): We used the Ga$_2$O$_3$/EGaIn electrode[6] for three reasons: i) It forms a reproducible, soft contact with the SAM. EGaIn forms a thick (~2 nm) gallium (III) oxide film on exposure to ambient air; this film both makes it possible to form and maintain non-equilibrium shapes (e.g. cones) that limit the contact area of the junction to ~100 μm^2. ii) It is a soft liquid metal, and allows repeated non-damaging physical contact with the surface of the SAM. We and others have used the Ga$_2$O$_3$/EGaIn electrode to study odd-even effects in *n*-alkanethiolates[6c], rectification[6b, 6d], and quantum interference in SAMs on charge tunneling[7]. iii) EGaIn is commercially available, easy to use, non-volatile, and non-toxic.

Statistical Analysis: The availability of large numbers of data (>200 $J(V)$ traces per sample) from this system enables us to analyze data statistically, using technique described previously.[6b-d, 8]

Use of Calibration Standards: Various experimental approaches have been explored to measure charge transport through organic molecules.[9] Measurements have, however, been notoriously difficult to reproduce for reasons that are, at least in part, understood (roughness in the electrode surface, errors due to "this" regions, formation of filaments by electromigration, structural defects in the SAMs, uncertainties in estimating areas across which tunneling occurred, surface contamination, various types of mechanical or electrical damage to the SAMs, etc.). It is helpful to use calibration standards: that is, compounds taken as reference values, to which all other measurements are compared. In this work, we have used two compounds either as "internal" or "calibrating" standards (depending on definitions).

Throughout the measurements reported in this study, we have intermittently measured $J(V)$ plots for 1-dedecanethiol (n-$C_{12}H_{23}SH$, **C12**) and 1-octadecanethiol (n-$C_{18}H_{37}SH$, **C18**) as calibration standards. The standards were collected throughout the study. (e.g. The sequence of experiments was: calibration standards ➔ samples ➔ calibration standards ➔ samples ➔ calibration standards.) We chose these two alkanethiols as standards for two reasons: i) The alkanethiols are commercially available. ii) They have been extensively studied in the area of molecular electronics, and their behavior is as understood as is that for any compound.

For Ag^{TS}/SAM//Ga_2O_3/EGaIn junctions, using these standards helps to correct for two major sources of error that accompany the measurement of a $J(V)$ trace: i) the *user* who brings the top-electrode into contact with the SAM and, ii) the *shape* of the Ga_2O_3/EGaIn top-electrode. These variables are minimized through familiarity with proper technique and a practiced hand.

In our program, a system was deemed ready to study, and a user *qualified* to make the measurements, after the operator reproduced the population means and standard deviations of log|J| in a statistically acceptable range for both **C12** and **C18** thiols. The statistically acceptable range is defined by comparison to previously reported value[6c].

Preparation and Measurement of the SAM

Experimental details for preparation of SAMs

SAMs were prepared following the reported method by our group.[2] HS-$(CH_2)_4$-CONH-$(CH_2)_2$-C_6H_{11} (3.7 mg, 0.015 mmol) in 5 mL EtOH (200 proof) was added to a scintillation vial. The solution was sonicated for 5 mins, sealed and further degassed by bubbling N_2 through the solution for *ca*. 3 mins. Glass supported template stripped silver film (Ag^{TS}) was placed to the solution of the thiol derivative with the exposed metal face up. The solution was then degassed by bubbling N_2 for 2 mins and allowed to stand under an inert atmosphere for a further 3 hrs. The Ag^{TS} film with the SAM on it was removed from solution and rinsed by repeatedly dipping the chip into clean EtOH. The solvent on the SAM was then evaporated by blowing a stream of nitrogen over chip. Measurements on the chip were then taken in less than 2.5 hrs after the SAM formation. All other SAMs were prepared in a similar manner.

Experimental Details for Electrical Measurements

Tip formation: EGaIn tip was formed following the known method reported by our group.[2] To generate a fine conical tip from 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. Every newly formed tip was used after 10 mins.

Junction formation and measurements: Junction formation and measurements were done

following the known method reported by our group.[2] 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. At least 10 junctions were

formed per molecule studied and each SAM was randomly sampled. The total number of

working junctions versus those that shorted was used to calculate the yield.

The Use of Calibration Standards: We deliberately took measurements on two molecules,

1-dodecanethiol and 1-octadecanethiol, as calibration standards, and measured the difference in β

and current density ($\Delta J = \log(|J_{C12}|) - \log(|J_{C18}|)$) between these two molecules to calibrate our

system. These data are used to confirm that the system is within the limits of acceptable variation,

and is therefore ready for further study. Broadly distributed data and/or unreasonably low/high

current densities occasionally arise; this is likely due to either the shape of tip or the user who

brings the EGaIn tip into contact with the SAM. These variables are minimized thorough

familiarity with proper technique and a practiced hand. After the operator reproduces J and σ_J in

a statistically acceptable range for both **C12** and **C18** thiols, the system is ready for measuring

charge transport through novel SAMs. Periodically, throughout data collection charge transport

through the calibration standards (**C12** and **C18**) was measured to confirm that the system remained well collaborated. A typical procedure is as follow: (i) Five to ten junctions of **C12** and **C18** first are first measured. (ii) If the data from these standards are reliable, target sample(s) are then measured (at least 10 junctions).(iii) At intervals between samples, the standard thiols are measured randomly to confirm the system works properly.

If the data shows unusual J(V), all parts of experiments including freshness of EGaIn, tip (e.g. shape), SAM formation, electrometer, connection of electric wires and experimental environment (e.g. unusual humidity, temperature, etc) should be carefully examined. If all equipments and experimental setup are in working order, the J(V) of the junction is again measured to confirm that the unexpectedly high/low J(V) originated from the target molecule, and not just noise. This process, including the use of calibration standards allows one to study J(V) of new compounds in reliable way.

For experimental details, experiments using the standard alkanethiols were carried out based on the following procedures: i) Several junctions (5 – 10) of **C12** and **C18** were first measured to confirm that reasonable J, σ_J and β for both **C12** and **C18** were being acquired (The confirmation should be done using the t test if you are not convinced for the results you obtain.). This data was used to confirm that the system is within the limits of acceptable variation. ii) One of the target samples (here, we chose an amide molecule with phenyl tail group, **1** in Figure 1) was randomly chosen, and measurements of J(V) from several junctions (5 – 10) of the target sample were made. iii) Again, several junctions (5 – 10) of **C12** and **C18** were measured. This set of experiments (i – iii) was repeated until sufficient data for statistical analysis were obtained. After confirming the system produces highly reliable data, we reduced the frequency of the

measurements of **C12** and **C18** gradually (e.g. five junctions of each standard were measured per two days).

Figure S2. Comparison of calibration standards with the previous work[2]; β (per carbon) is the tunneling decay constant from the Simmons equation ($J=J_o\,e^{-\beta d}$).
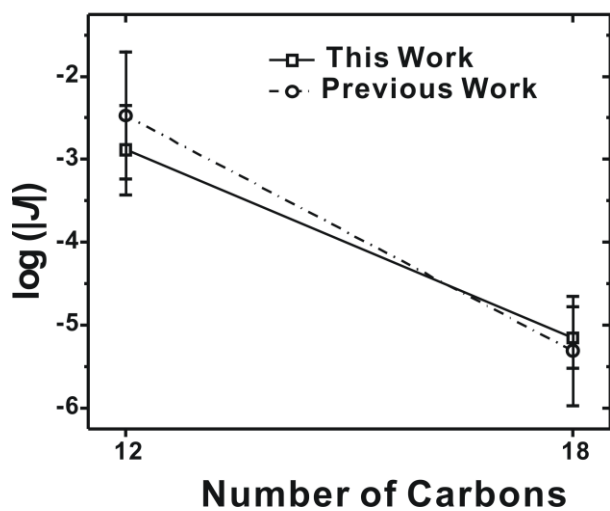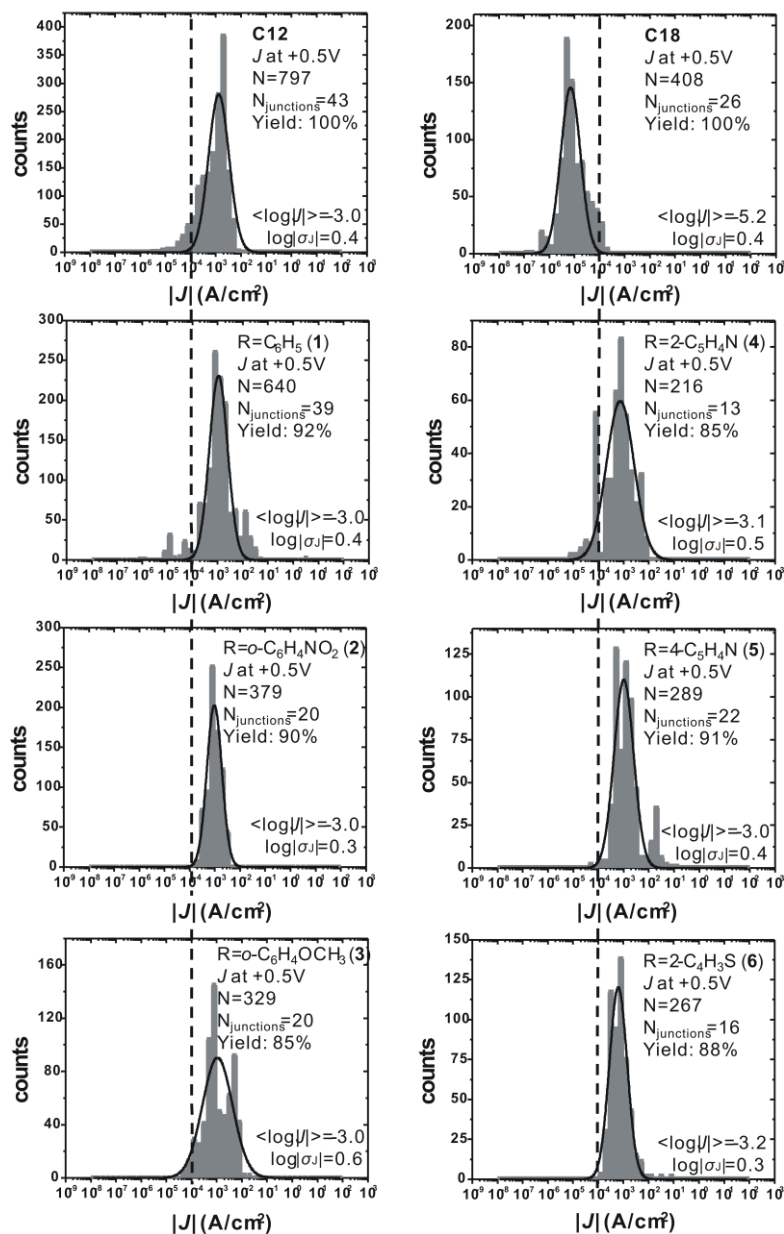
Figure S3. Histograms of current densities (at +0.5V) of amide derivatives (**1 – 13** in Figure 1,

HS-($CH_2)_4$-CONH-$(CH_2)_2$-R) and two calibration standard molecules (HS-$(CH_2)_{11}CH_3$, **C12** and

HS-$(CH_2)_{17}CH_3$, **C18**). (R: tail group of amide derivatives; N: number of data; $N_{junctions}$: number

of junctions; $<\log|J|>$: population mean of $\log|J|$; $\log|\sigma_J|$: log scale of standard deviation of *J*.

Molecular formulas describe the formula of the tail group, R. Dotted lines are fixed at 10^{-4} A/cm^2

for comparison.)

R=1-C$_{10}$H$_7$ (**7**)
J at +0.5V
N=593
N$_{junctions}$=31
Yield: 97%
<log|J|>=-2.9
log|σ_J|=0.4

R=C$_6$H$_{15}$ (**11**)
J at +0.5V
N=422
N$_{junctions}$=22
Yield: 100%
<log|J|>=-3.5
log|σ_J|=0.5

R=C$_6$H$_{11}$ (**8**)
J at +0.5V
N=213
N$_{junctions}$=10
Yield: 100%
<log|J|>=-3.6
log|σ_J|=0.2

R=2-C$_7$H$_{11}$ (**12**)
J at +0.5V
N=443
N$_{junctions}$=21
Yield: 100%
<log|J|>=-3.5
log|σ_J|=0.3

R=1-C$_{10}$H$_{15}$ (**9**)
J at +0.5V
N=433
N$_{junctions}$=21
Yield: 100%
<log|J|>=-3.5
log|σ_J|=0.1

R=C$_4$H$_9$ (**13**)
J at +0.5V
N=402
N$_{junctions}$=20
Yield: 100%
<log|J|>=-3.0
log|σ_J|=0.3

R=C$_7$H$_{13}$ (**10**)
J at +0.5V
N=422
N$_{junctions}$=20
Yield: 100%
<log|J|>=-3.4
log|σ_J|=0.2

|J| (A/cm^2)

S13

Figure S4. Histograms of rectification ratio (r, $r \equiv J(+V)/J(-V)$) of amide derivatives (**1** – **13** in Figure 1, HS-($CH_2)_4$-CONH-$(CH_2)_2$-R)) and two calibration standard molecules ($HS(CH_2)_{11}CH_3$, **C12** and $HS(CH_2)_{17}CH_3$, **C18**). (R: tail group of amide derivatives; N: number of data; $N_{junctions}$: number of junctions. Molecular formulas at Figure correspond to tail group, R. Dotted lines are fixed at 10^0 for comparison.)

R=1-$C_{10}H_7$ (**7**)
N=593
$N_{junctions}$=31
Yield: 97%
r = 1.3 at +0.5V
σ = 1.1

R=C_7H_{13} (**11**)
N=422
$N_{junctions}$=20
Yield: 100%
r = 1.2 at +0.5V
σ = 1.1

R=C_6H_{11} (**8**)
N=213
$N_{junctions}$=10
Yield: 100%
r = 1.4 at +0.5V
σ = 1.1

R=2-C_7H_{11} (**12**)
N=443
$N_{junctions}$=23
Yield: 100%
r = 1.3 at +0.5V
σ = 1.0

R=1-$C_{10}H_{15}$ (**9**)
N=433
$N_{junctions}$=21
Yield: 100%
r = 1.1 at +0.5V
σ = 1.1

R=C_4H_9 (**13**)
N=402
$N_{junctions}$=21
Yield: 100%
r = 1.4 at +0.5V
σ = 1.1

R=C_6H_{15} (**10**)
N=422
$N_{junctions}$=22
Yield: 100%
r = 1.1 at +0.5V
σ = 1.1
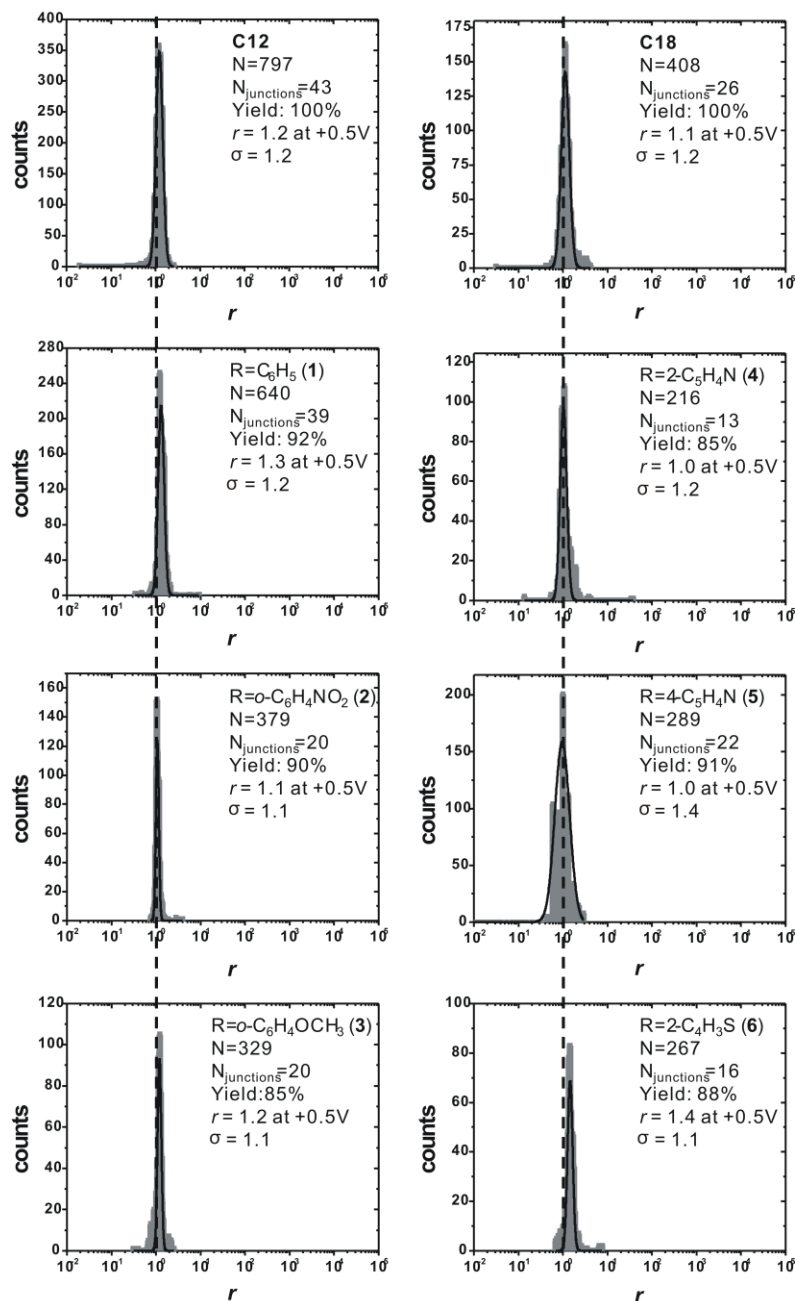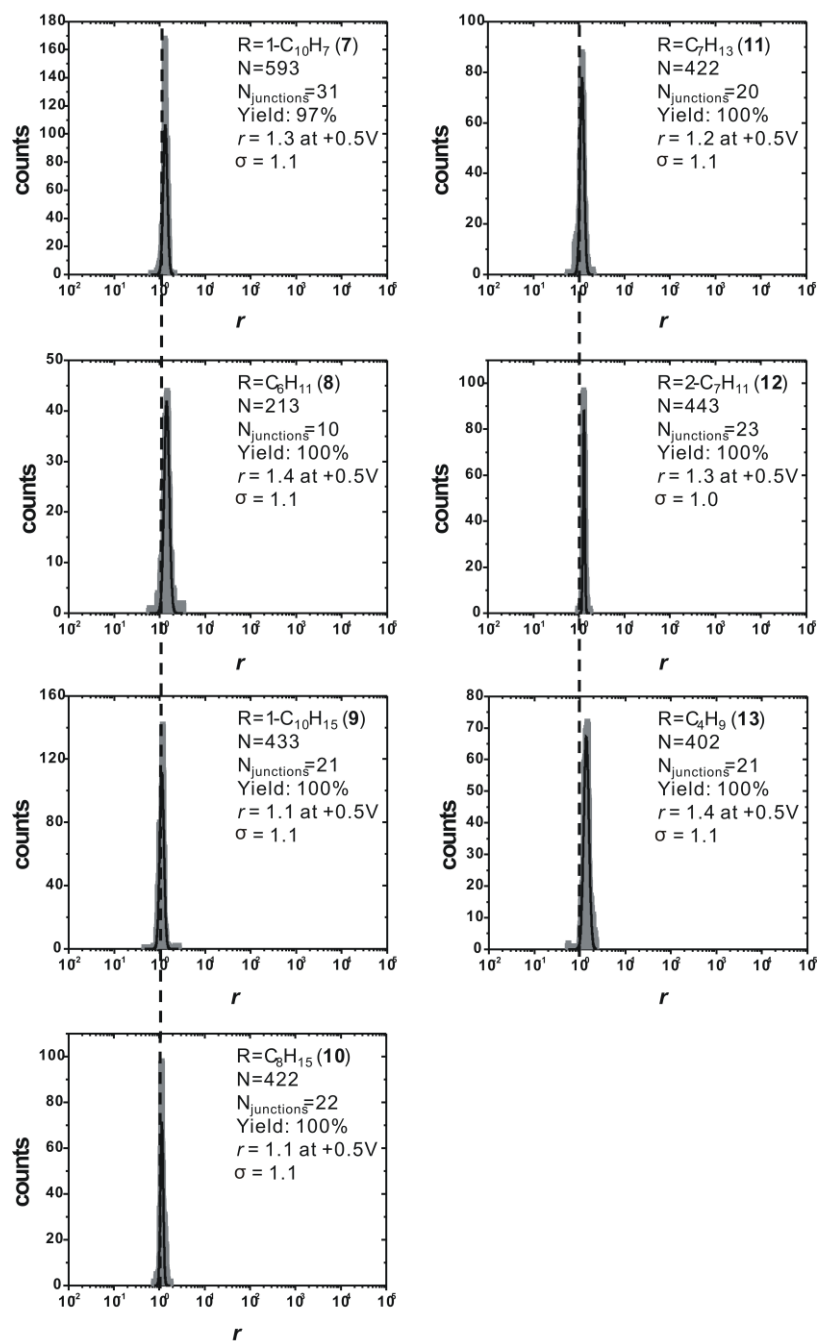
Figure S5. *J-V* responses of a series of HS-$(CH_2)_4$-CONH-$(CH_2)_2$-R and calibration standard molecules (HS-$(CH_2)_{11}CH_3$, **C12** and HS-$(CH_2)_{17}CH_3$, **C18**). (R: tail group)
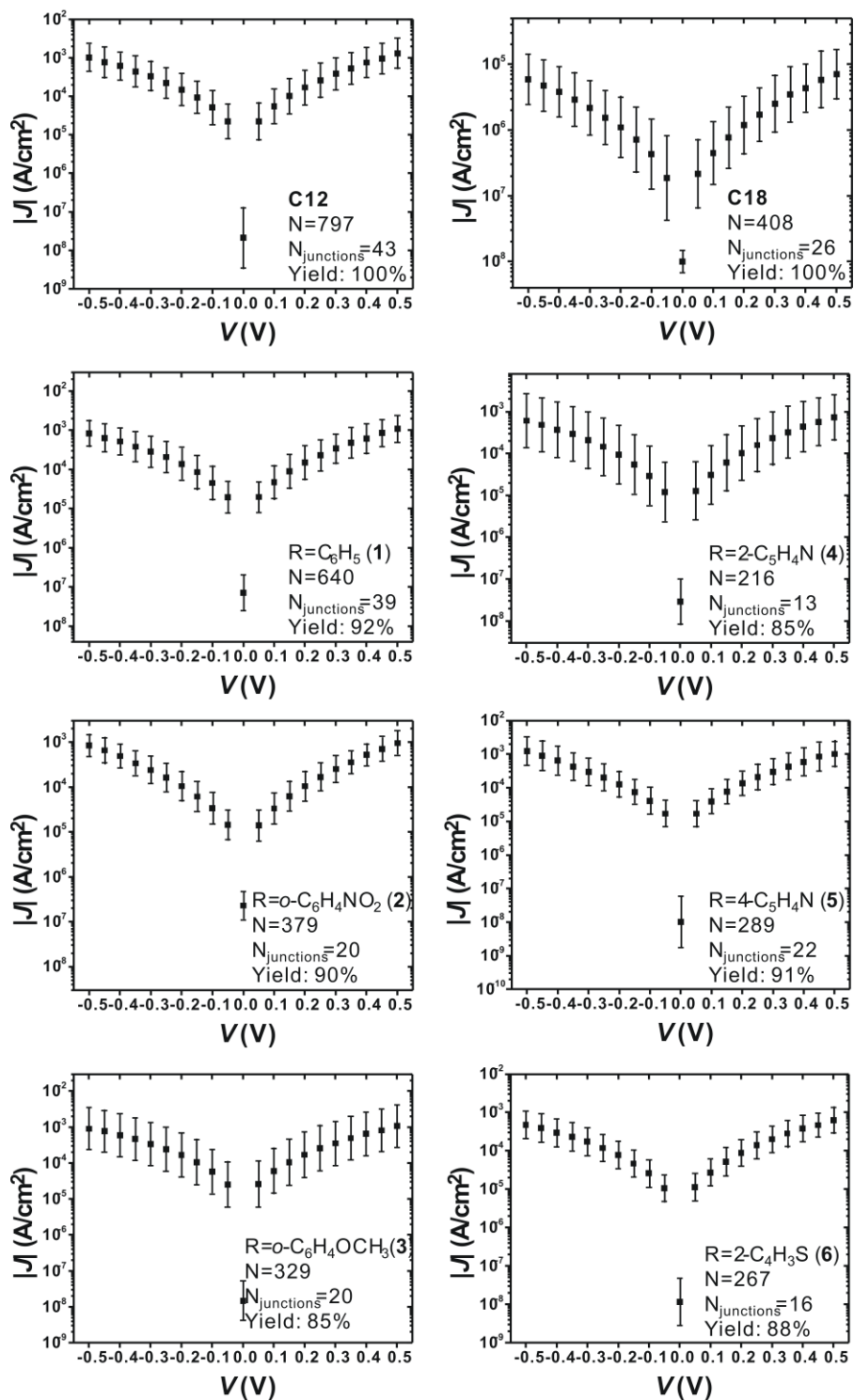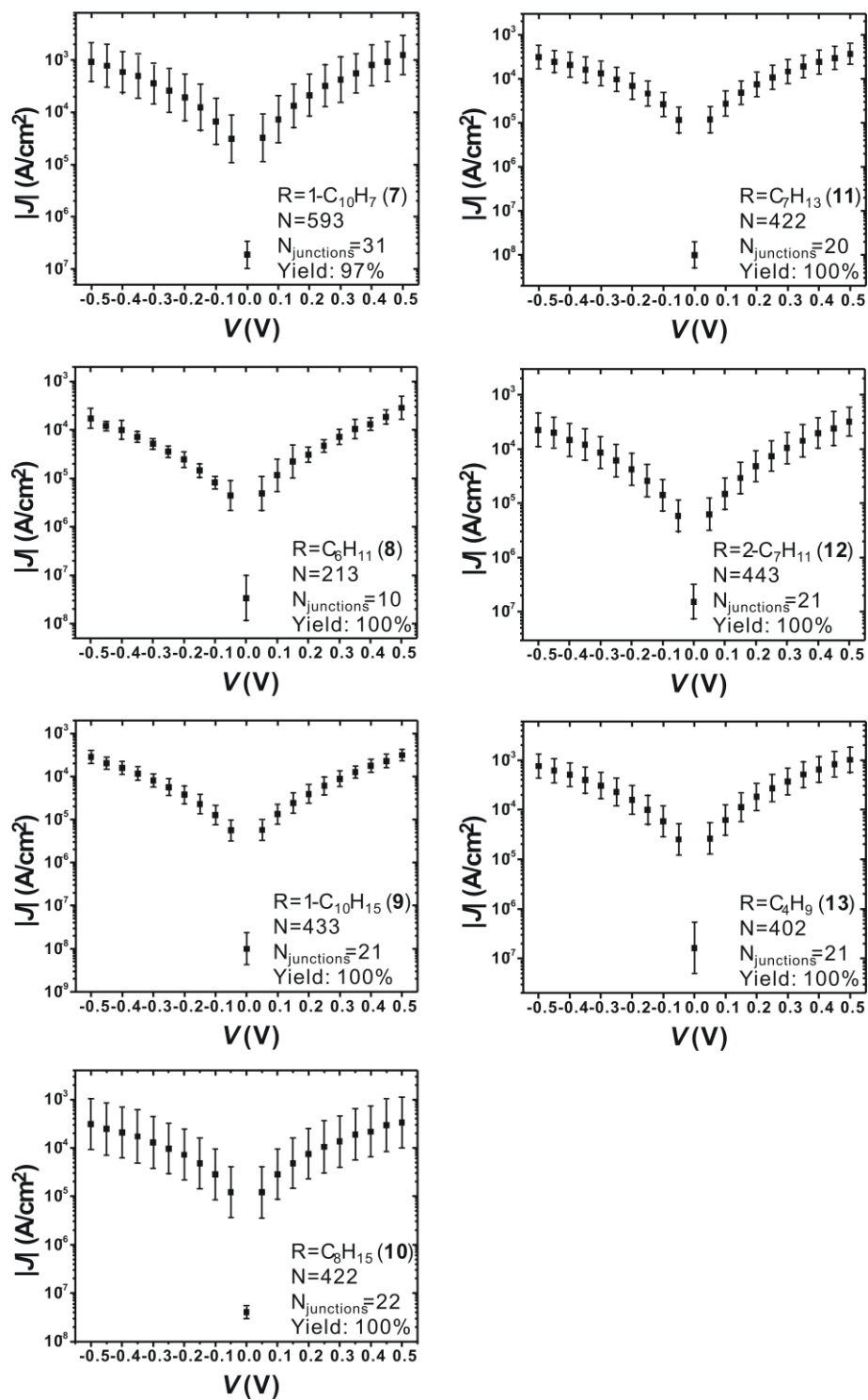
Table S1. Comparison of yield of junctions ($Ag^{TS}S(CH_2)_4CONH(CH_2)_2R//Ga_2O_3/EGaIn$).

# in Figure 1	Tail group (R)	Molecular Structure of R	Yield (%)[a]	$<\log|J|>$[b]	$\log|\sigma_J|$[c]	r[d]	$\log|\sigma_r|$[e]
1	C_6H_5		92	-3.0	0.4	1.3	0.1
2	$o\text{-}C_5H_4NO_2$		90	-3.0	0.3	1.1	<0.05
3	$o\text{-}C_6H_4OCH_3$		85	-3.0	0.6	1.2	<0.05
4	$2\text{-}C_5H_4N$		85	-3.1	0.5	~1.0	0.1
5	$4\text{-}C_5H_4N$		91	-3.0	0.4	~1.0	0.1
6	$2\text{-}C_4H_3S$		88	-3.2	0.3	1.4	<0.05
7	$1\text{-}C_{10}H_7$		97	-2.9	0.4	1.3	<0.05
8	C_6H_{11}		100	-3.6	0.2	1.4	<0.05
9	$1\text{-}C_{10}H_{15}$		100	-3.5	0.1	1.1	<0.05
10	C_7H_{13}		100	-3.4	0.2	1.2	<0.05
11	C_8H_{15}		100	-3.5	0.5	1.1	<0.05
12	$2\text{-}C_7H_{11}$		100	-3.5	0.3	1.3	<0.05
13	C_4H_9		100	-3.0	0.3	1.4	< 0.05
C12[f]	Standard	-	100	-3.0	0.4	1.2	0.1
C18[g]	Standard	-	100	-5.2	0.4	1.1	0.1

[a]Yield was calculated as the ratio of non-shorting junctions to the total number of junctions measured; [b]Population means of $\log|J|$; [c]Log standard deviation of J value; [d]Rectification ratio (r, $r \equiv J(+V)/J(-V)$); [e]Log standard deviation of r value; [f]$HS(CH_2)_{11}CH_3$; [g]$HS(CH_2)_{17}CH_3$. A value of "~1.0" in r indicates $1 < r < 1.05$.

Figure S6. Plots of current densities of amide derivatives **1 – 13** (in Figure 1) and two calibration standard alkanethiols, 1-dodecanethiol (HS-$(CH_2)_{11}CH_3$, **C12**) and 1-octadecanethiol (HS-$(CH_2)_{17}CH_3$, **C18**), as a function of number of atoms of the corresponding aliphatic and aromatic tail group (R for $HS(CH_2)_4CONH(CH_2)_2R$). The dashed lines represent the tunneling current for the calibration standards (**C12** and **C18** alkanethiols), and the solid lines are linear squares fits. The given molecular structures are those of the tail groups, R. The r_{coeff} is a correlation coefficient for each scatterplot. (○: Aromatics, ●: Aliphatics)
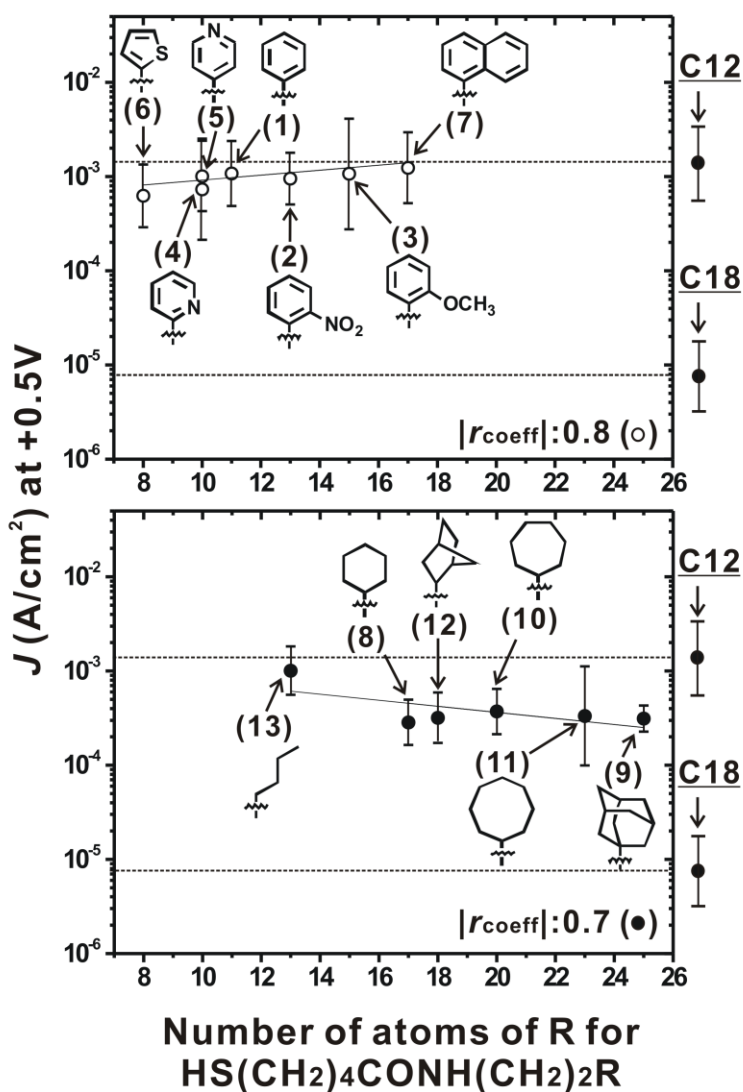
Statistical Analyses for the Slopes of the Linear Square Fits in Figure 2

After performing linear regression for the data on aromatic and aliphatic molecules, we can also calculate the 95% confidence intervals of the slopes of the regression by treating the slope as a statistical quantity.[10] For aromatics, the slope is 0.0037 with a 95% confidence interval of (-0.0005, 0.0079) and for aliphatics, the slope is -0.0057 with a 95% confidence interval of (-0.0142, 0.0028). Since zero is within the range of the confidence interval for both aromatics and aliphatics, we conclude that the slopes obtained are not significantly different from zero at 95% confidence level.

Additional Discussions

The comparisons of $<\log|J|>$, $\log|\sigma_J|$, r and $\log|\sigma_r|$ of molecules we studied provided two minor features: i) The distributions of r ($\log|\sigma_r|$) are much narrower than the corresponding distributions of J (see Table S1 and Figure S4 for the histograms of r of molecules **1 – 13**). ii) The adamantyl molecule **9** provided the junction with the narrowest distribution of J(V).

Distributions of r are narrower than those of J(V), as a reflection of the origin of rectification: Figure 2 and Table S1 summarize charge transport measurements of the molecules **1 – 13** and calibration standards, and histograms of the rectification ratio ($\log|r|$ at ±0.5 V). None of the molecules studied rectified significantly. The distributions of r ($\log|\sigma_r|$) were, however, much narrower than those of J(V) (the largest $\log|\sigma_r|$ is 0.1, see Table S1). The decrease in distribution reflects that fact that rectification is self-referencing: variations in the contact areas of from junction to junction, and in the distribution of the width of the barrier across the junction, cancel out since the same junction is used for measurements of both forward and reverse bias. The fact that all compounds studied here show statistically indistinguishable rectification

suggests that the rectification observed in other systems (e.g. ferrocene)[6b, 6d] is due to the

molecules comprising the SAM (more precisely from the particular ferrocene moieties), not to

features of the junction (e.g. redox reactions involving the Ga_2O_3 layer or differences in the work

function of Ag/AgSR and $R//Ga_2O_3$/EGaIn). On the other hand, the wider distributions of $\log|\sigma_J|$

than those of $\log|\sigma_r|$ probably reflect *junction-to-junction variations* (e.g. the differences in the

roughness of the Ag^{TS} electrode, or variations in the morphology, composition, or electrical

properties of the Ga_2O_3/EGaIn electrode), not to the SAM or the molecules comprising the SAM.

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