

Supporting Information

The Rate of Charge Tunneling in EGaIn Junctions is Insensitive to Halogen Substituents at the SAM//Ga₂O₃ Interface

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General Information

All reagents were used as supplied from the manufacturer unless otherwise specified. All organic solvents were purchased from Sigma-Aldrich (dichloromethane, hexanes and ethyl acetate) or Fisher (200 proof ethanol) while water was purified using a Milipore Q-POD water purification systems. All starting compounds for synthesis were purchased from Sigma-Aldrich, except 1,9-dibromononane (TCI) and iodoacetylchloride (Alfa Aesar). For the contact electrode, high-purity eutectic gallium-indium (EGaIn) was obtained from Sigma-Aldrich and used as supplied. All purified disulfide derivatives were stored at <4 °C. ¹H and ¹³C NMR spectra were recorded on a Varian INOVA 500 instrument using CDCl₃ as a solvent except when reported otherwise.

Synthetic Procedure

1,2-didodecyldisulfane (1):¹ To a stirred solution of 1-dodecanthiol (0.48 mL; 2 mmol) in ethyl acetate (5 mL) was added NaI (3.0 mg; 0.02 mmol) and H₂O₂ (30%; 0.44 mL; 4 mmol). The reaction mixture turned brown and was stirred at room temperature (~ 25 °C) for 1 h followed by addition of saturated aqueous Na₂S₂O₃ (30 mL). The aqueous phase was extracted with ethyl acetate (3 × 20 mL) and dried over sodium sulfate. Evaporation of the solvent afforded the product as a white solid (0.386 g) in 96% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.68 (t, *J* = 7.4 Hz, 4H), 1.67 (quint, *J* = 7.4 Hz, 4H), 1.36 (quint, *J* = 6.7 Hz, 4H), 1.25 (m, 32H), 0.88 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 39.2, 31.2, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 28.5, 22.7, 14.1.

N-(9-bromononyl)phthalimide (10):² A suspension of potassium phthalimide (2.4 g; 12.5 mmol) in DMF (12.5 mL) was added to 1,9-dibromoalkane (10.2 mL; 50 mmol) in DMF (5 mL) under N₂. After refluxing for 4h, the formed KBr was removed by filtration, and the DMF

was evaporated under reduced pressure. The crude product was purified by passing through a silica-gel column chromatography (eluent: hexanes/DCM 0%-30%). The product was obtained as a colourless oil (1.154 g) in 34% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.84 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.72 (dd, $J = 5.5, 3.0$ Hz, 2H), 3.69 (t, $J = 7.3$ Hz, 2H), 3.40 (t, $J = 6.9, 2\text{H}$), 1.85 (quint, $J = 7.2, 2\text{H}$), 1.68 (quint, $J = 7.2, 2\text{H}$), 1.42 (quint, $J = 8.0, 2\text{H}$), 1.42-1.27 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3): δ 168.5, 133.9, 132.2, 123.2, 38.0, 34.0, 32.8, 29.3, 29.0, 28.7, 28.6, 28.1, 26.8.

N-(9-thiononyl)phthalimide (11):² N-(9-bromononyl)phthalimide (1.150 g; 3.27 mmol) was dissolved in ethanol (20 mL) and thiourea (0.373 g; 4.9 mmol) was added. The reaction mixture was refluxed overnight. Evaporation of the solvent afforded a colourless oil. NaOH (0.144 g; 3.6 mmol) dissolved in water (20 mL) was purged with N_2 and subsequently added to the colourless oil. The reaction mixture was refluxed for 30 min and afterwards extracted by ethyl acetate (3×20 mL). The combined organic phases were dried over sodium sulfate. Evaporation of the solvent afforded the product as a white solid (0.849 g) in 85% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.85 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.71 (dd, $J = 5.5, 3.0$ Hz, 2H), 3.68 (t, $J = 7.3$ Hz, 2H), 2.51 (q, $J = 7.2$ Hz, 2H), 1.68 (quint, $J = 7.2, 2\text{H}$), 1.60 (quint, $J = 7.35$ Hz, 2H), 1.34-1.28 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3): δ 168.5, 133.8, 132.2, 123.2, 38.0, 34.0, 29.3, 29.1, 29.0, 28.6, 28.3, 26.8, 24.6.

N,N'-(Dithiodinonane-9,1-diyl)bis[phthalimide] (12):² To a stirred solution of N-(9-mercaptononyl)phthalimide (0.305 g; 1 mmol) in ethyl acetate (3 mL) was added NaI (1.5 mg; 0.01 mmol) and H_2O_2 (30%; 0.22 mL; 2 mmol). The reaction mixture turned brown. It was stirred at room temperature (~ 25 °C) for 0.5-1 h and subsequently saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) was added. The aqueous phase was extracted with ethyl acetate (3×15 mL) and dried

over sodium sulfate. Evaporation of the solvent afforded the product as a yellow oil (0.273 g) in 90% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.85 (dd, $J = 5.4, 3.0$ Hz, 4H), 7.72 (dd, $J = 5.4, 3.1$ Hz, 4H), 3.86 (t, $J = 7.3$, 4H), 2.67 (t, $J = 7.4$, 4H), 1.66 (quint, $J = 7.4$, 8H), 1.42-1.23 (m, 20H); ^{13}C NMR (125 MHz, CDCl_3): δ 168.5, 133.8, 132.2, 123.2, 39.2, 38.0, 29.3, 29.2, 29.1, 29.1, 28.6, 28.5, 26.8.

9,9'-Dithiobis[nonan-1-amine](13):² N,N'-(Dithiodinonane-9,1-diyl)bis[phthalimide] (0.304 g; 0.5 mmol) was refluxed under N_2 with hydrazine (49 μL ; 1.55 mmol) in ethanol (5 mL) for 1.5 h. While cooling down to room temperature (~ 25 $^\circ\text{C}$), a white precipitate starts to form. The solvent was evaporated and the residue was refluxed in HCl (1M; 5 mL) for 2 h. Afterwards, ethanol (10 mL) was added and a white precipitate was filtered off. The solvents were evaporated and to the remaining white precipitate an aq. solution of NaOH (10 mL) was added. The aqueous solution was extracted with ethyl acetate (2×15 ml). Evaporation of the solvent affords the product as a white solid (0.123 g) in 70% yield. ^1H NMR (500 MHz, DMSO): δ 2.69 (t, $J = 7.2$ Hz, 4H), 1.61 (quint, $J = 7.3$, 4H), 1.33-1.25 (m, 12H); ^{13}C NMR (125 MHz, DMSO): δ 42.1, 40.4, 38.3, 33.9, 29.4, 29.0, 29.0, 28.2, 26.9.

Method A

General procedure for the synthesis of compounds 3, 6, and 7: 9,9'-Dithiobis[nonan-1-amine] (87.5 mg; 0.25 mmol) was dissolved in THF (3 ml) while in an icebath. Acetylchloride (0.5 mmol) was added while stirring. The icebath was removed and triethylamine (0.14 mL; 1 mmol) in THF (1.5 mL) was added dropwise and the solution was stirred at room temperature (~ 25 $^\circ\text{C}$) for 4 h. Afterwards, ethyl acetate (30 mL) was added and it was washed with respectively 1M HCl (20 mL), saturated aqueous NaHCO_3 solution (20 mL) and brine (20 mL). The organic phase was dried over sodium sulfate. Evaporation of the solvent yields the product.

N,N'-{Dithiodinonane-9,1-diyl}bis[2-chloroacetamide] (3): Yield: 0.100 g (80%);
White powder; ¹H NMR (500 MHz, CDCl₃): δ 6.59 (s, 2H), 4.07 (s, 4H), 3.32 (q, *J* = 6.8 Hz, 4H), 2.69 (t, *J* = 7.4 Hz, 4H), 1.69 (quint, *J* = 7.4 Hz, 4H), 1.57 (m, 4H), 1.41-1.33 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): δ 165.7, 42.7, 39.9, 39.1, 29.3, 29.3, 29.1, 29.1, 29.1, 28.4, 26.8.

N,N'-{Dithiodinonane-9,1-diyl}bis[2,2-dichloroacetamide] (6): Yield: 0.110 g (55%);
White powder; ¹H NMR (500 MHz, CDCl₃): δ 6.51 (s, 2H), 5.94 (s, 2H), 3.34 (q, *J* = 6.6 Hz, 4H), 2.69 (t, *J* = 7.4 Hz, 4H), 1.69 (quint, *J* = 7.4 Hz, 4H), 1.59 (quint, *J* = 7.1 Hz, 4H), 1.43-1.29 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): δ 164.0, 66.5, 40.4, 39.1, 29.3, 29.1, 29.1, 29.1, 28.4, 26.6.

N,N'-{Dithiodinonane-9,1-diyl}bis[2,2,2-trichloroacetamide] (7): Yield: 0.110 g (100%); Yellow/orange solid; ¹H NMR (500 MHz, CDCl₃): δ 6.82 (s, 2H), 3.36 (q, *J* = 6.5 Hz, 4H), 2.67 (t, *J* = 7.4 Hz, 4H), 1.67 (quint, *J* = 7.4 Hz, 4H), 1.60 (quint, *J* = 6.9 Hz, 4H), 1.41-1.25 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): δ 161.9, 92.7, 41.5, 39.1, 29.3, 29.2, 29.1, 29.1, 28.9, 28.4, 26.6.

Method B

General procedure for the synthesis of compounds 4, 5, and 9: 9,9'-Dithiobis[nonan-1-amine] (87.5 mg; 0.25 mmol) was dissolved in THF (3 ml) while in an icebath and [x]acetylchloride (0.5 mmol) was added. Triethylamine (0.07 mL; 0.5 mmol) in THF (1.5 mL) was added dropwise and the reaction mixture was stirred at 0 °C for 1h. Afterwards, ethyl acetate (30 mL) was added and it was washed with respectively 1M HCl (20 mL), saturated aqueous Na₂S₂O₃ solution (20 mL), saturated aqueous NaHCO₃ solution (20 mL) and brine (20 mL). The organic phase was dried over sodium sulfate. Evaporation of the solvent yields the product.

N,N'-{Dithiodinonane-9,1-diyl}bis[2-bromoacetamide] (4): The crude product was further purified by passing through a silica-gel column chromatography (eluent: DCM/MeOH 0%-5%). Yield: 0.048 g (33%); White solid; ^1H NMR (500 MHz, CDCl_3): δ 6.48 (s, 2H), 3.88 (s, 4H), 3.28 (q, $J = 7.2$ Hz, 4H), 2.67 (t, $J = 7.4$ Hz, 4H), 1.67 (quint, $J = 7.3$ Hz, 4H), 1.54 (quint, $J = 7.2$ Hz, 4H), 1.40-1.26 (m, 20H); ^{13}C NMR (125 MHz, CDCl_3): δ 165.2, 40.2, 39.1, 29.4, 29.3, 29.2, 29.1, 29.1, 29.1, 28.4, 26.7.

N,N'-{Dithiodinonane-9,1-diyl}bis[2-iodoacetamide] (5): The crude product was further purified by passing through a silica-gel column chromatography (eluent: DCM/MeOH 0%-5%). Yield: 0.106 g (62%); Pale yellow solid; ^1H NMR (500 MHz, CDCl_3): δ 6.13 (s, 2H), 3.72 (s, 4H), 3.28 (q, $J = 6.6$ Hz, 4H), 2.69 (t, $J = 7.4$ Hz, 4H), 1.68 (quint, $J = 7.4$ Hz, 4H), 1.51 (quint, $J = 7.1$, 4H), 1.39-1.25 (m, 20H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.8, 40.5, 39.2, 29.3, 29.2, 29.2, 29.1, 29.1, 28.4, 26.7, -0.2.

N,N'-{Dithiodinonane-9,1-diyl}bis[2,2,2-tribromoacetamide] (9): The crude product was further purified by passing through a silica-gel column chromatography (eluent: DCM/MeOH 0%-5%). Yield: 0.090 g (20%); Brownish solid; ^1H NMR (500 MHz, CDCl_3): δ 6.86 (s, 2H), 3.39 (q, $J = 6.5$ Hz, 4H), 2.69 (t, $J = 7.3$ Hz, 4H), 1.69 (quint, $J = 7.2$ Hz, 4H), 1.63 (quint, $J = 7.2$ Hz, 4H), 1.45-1.29 (m, 20H); ^{13}C NMR (125 MHz, CDCl_3): δ 162.3, 41.9, 39.1, 36.9, 29.3, 29.1, 29.1, 28.9, 28.4, 26.6.

Method C

General procedure for the synthesis of compounds 2, and 8: 9,9'-Dithiobis[nonan-1-amine] (87.5 mg; 0.25 mmol) was dissolved in THF (3 mL) while in an icebath. [x]anhydride (0.5 mmol) was added while stirring. The icebath was removed and triethylamine (0.14 mL; 1 mmol) in THF (1.5 mL) was added dropwise and the solution was stirred at room temperature (~

25 °C) for 4 h. Afterwards, ethyl acetate (30 mL) was added and it was washed with respectively 1M HCl (20 mL), saturated aqueous NaHCO₃ solution (20 mL) and brine (20 mL). The organic phase was dried over sodium sulfate. Evaporation of the solvent yields the product.

N,N'-(Dithiodinonane-9,1-diyl)bis[acetamide] (2): Yield: 0.030 g (28%); White powder; ¹H NMR (500 MHz, DMSO): δ 7.75 (s, 2H), 2.97 (q, *J* = 6.4 Hz, 4H), 2.67 (t, *J* = 7.2 Hz, 4H), 1.75 (s, 6H), 1.59 (quint, *J* = 7.1 Hz, 4H), 1.38-1.19 (m, 24H); ¹³C NMR (125 MHz, DMSO): δ 169.3, 38.9, 38.3, 29.6, 29.3, 29.1, 29.0, 29.0, 28.2, 26.9, 23.1.

N,N'-(Dithiodinonane-9,1-diyl)bis[2,2,2-trifluoroacetamide] (8): The crude product was further purified by passing through a silica-gel column chromatography (eluent: DCM/MeOH 0%-5%). Yield: 0.037 g (27%); White solid; ¹H NMR (500 MHz, CDCl₃): δ 6.75 (s, 2H), 3.34 (q, *J* = 6.8 Hz, 4H), 2.67 (t, *J* = 7.3 Hz, 4H), 1.66 (quint, *J* = 7.4 Hz, 4H), 1.57 (quint, *J* = 6.9 Hz, 4H), 1.42-1.24 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): δ 157.1 (q), 117.0, 40.0, 39.1, 29.3, 29.1, 29.1, 29.0, 28.8, 28.4, 26.6.

Charge Transport Measurements

Measurements of Tunneling Current Densities. We measured the rate of charge transport across SAMs of ω -halogen terminated alkanethiolates with the EGaIn junction, using a previously described procedure.³ Tips were formed by extruding a small droplet of EGaIn from a 10 μ L Hamilton syringe. The syringe was fixed to a micromanipulator to allow for precise movement. The syringe was lowered until the EGaIn drop meets a clean Ag^{TS} surface. The syringe was then slowly moved upward, this motion formed the EGaIn into an hourglass shape. As we continued to move the syringe upward, the hourglass shape separated into two conical structures; one hanging from the syringe needle. This tip was gently brought into contact with the SAM-modified surface. After the EGaIn tip and SAM contacted, the voltage was scanned across the junction.³ We follow the standard “1/20/1” protocol, for each junction we used a newly prepared tip and each tip was used for 20 scans. We make seven to nine junctions per substrate (e.g., per chip supporting the Ag^{TS} (or Au^{TS})/SAM) and use 3 different substrates for each molecule. We report the current density (J) at + 0.5 V for each molecule and plot the Gaussian mean values of $\log |J|$ with error bars representing the standard deviation of the mean value.

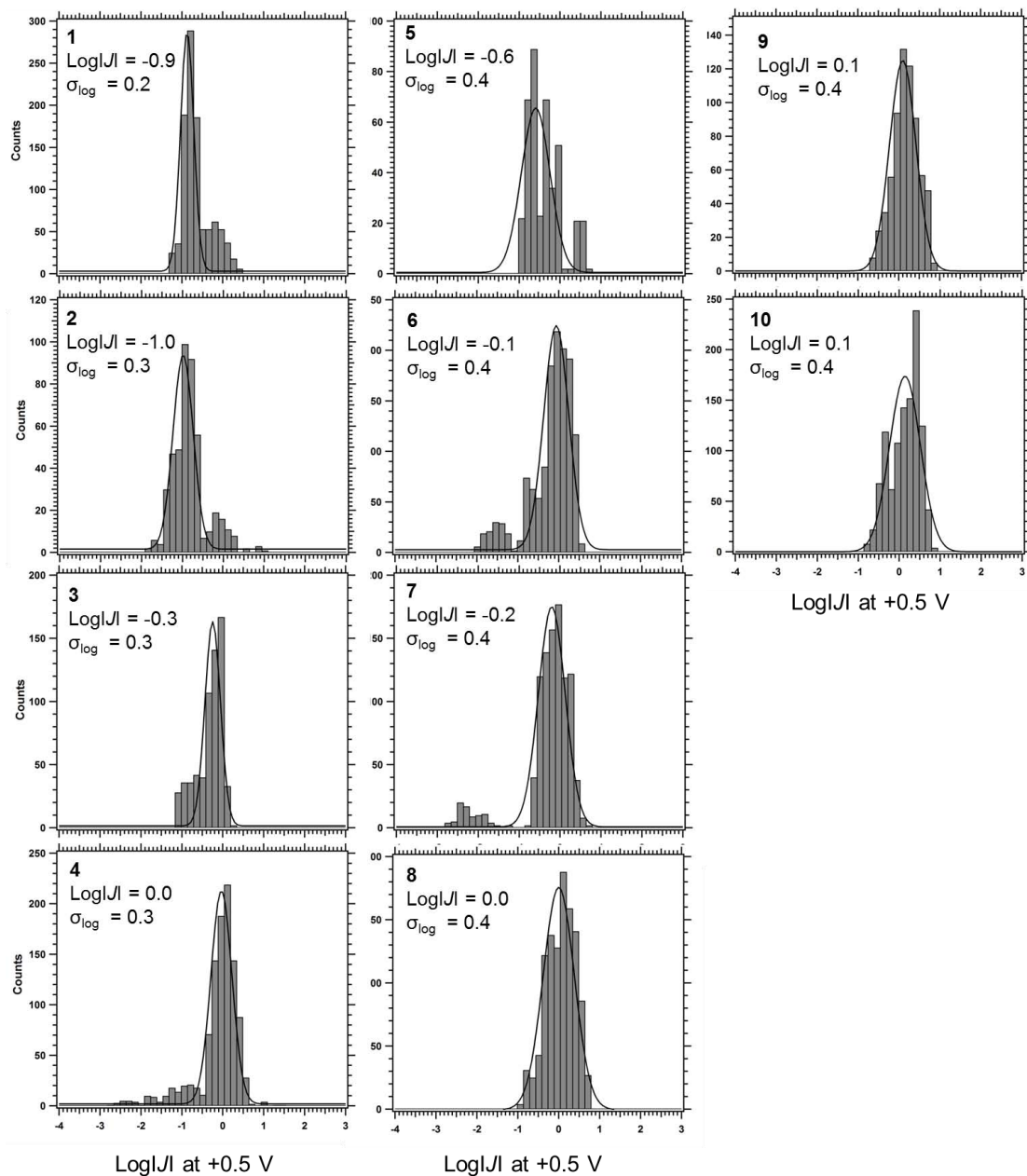


Figure S1. Histograms of the distribution of the values of $\log|J|$ at $V = +0.5$ V for ω -halogenated alkanethiolate SAMs on Ag^{TS} .

SAM Formation

Formation of SAMs of Halogen Terminated Alkanethiolates. We followed a procedure of the type currently used in preparing SAMs.⁴ In short, a template-stripped silver substrate (Ag^{TS}) was immersed in a 5 mL of a 1-mM solution of $[\text{S}(\text{CH}_2)_9\text{T}]_2$ ($\text{T} = \text{NHCOCH}_{3-n}\text{X}_n$) solution in anhydrous ethanol under N_2 (atmospheric pressure). The substrate was incubated, in the dark, overnight. After incubation, the substrate was removed and washed with 30 mL of ethanol and dried under a gentle stream of N_2 .

Surface Characterization

Thickness Measurements. We used angle-resolved X-ray photoelectron spectroscopy (ARXPS) to characterize the SAMs of ω -halogen terminated alkanethiolates. The energy of the incident X-ray beam used by the Thermo Scientific K-Alpha XPS system is at 1486.6 eV. We recorded the high-resolution XPS spectra at four incident angles: 90° , 75° , 60° , and 45° . We used the least-square peak fit analysis with Voigt functions (Lorentzian (30%) and Gaussian (70 %)) to fit the XPS spectra with XPSpeak software, and the sloping background was modeled using Shirley plus linear background correction.⁵⁻⁶ We used Voigt functions to obtain best-fits because it is well-known that instrumental factors (e.g., resolution of the analysed or monochromator) and experimental factors (e.g., surface roughness of the samples, vibrational effect, and polarization effects) manifest themselves as Gaussian broadening of the ideally Lorentzian signals of photoelectrons.

Work Function Measurements. We measured work functions (WF) using the same XPS system. The samples were held on a specially designed biasing stage that is in electrical contact with the analyzer. The WF of SAM-modified Ag^{TS} surfaces were calculated by recording two sets of spectra: the peak of secondary electron (free electrons with low kinetic energy (<50 eV)

generated by photoelectron)^{5, 7} and the slope of the Fermi-edge (see all spectra in SI, Figures S2 and S3). The cut-off of the secondary electron peak is the lowest energy of a free electron to escape to vacuum from a metal surface. We applied -30 V to the stage to accelerate the secondary electrons with sufficient kinetic energy to see the secondary electron cut-off. The secondary electron cut-off spectra were recorded in the range of 32 to 38 eV kinetic energy and we extrapolated the secondary electron cut-off to the x-axis to determine the energy position of the vacuum (E_v). The Fermi edge spectra were recorded in the range of -35 to -25 eV binding energy. We referenced the measured binding energy of the Fermi edge to E_v to determine the WF of SAM-modified Ag^{TS} surfaces.

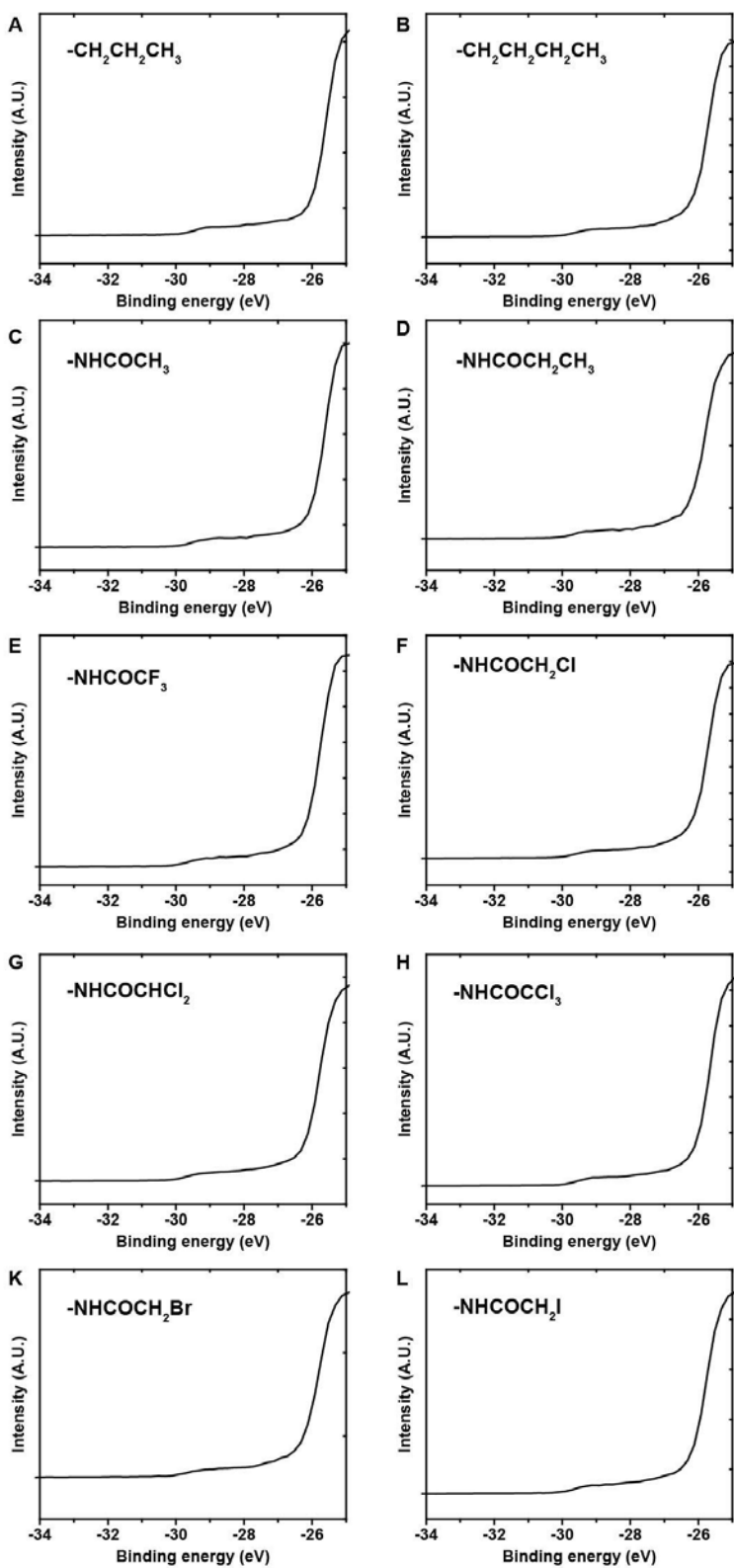


Figure S2. The Fermi edge spectra for ω -halogenated alkanethiolate SAMs on Ag^{TS} .

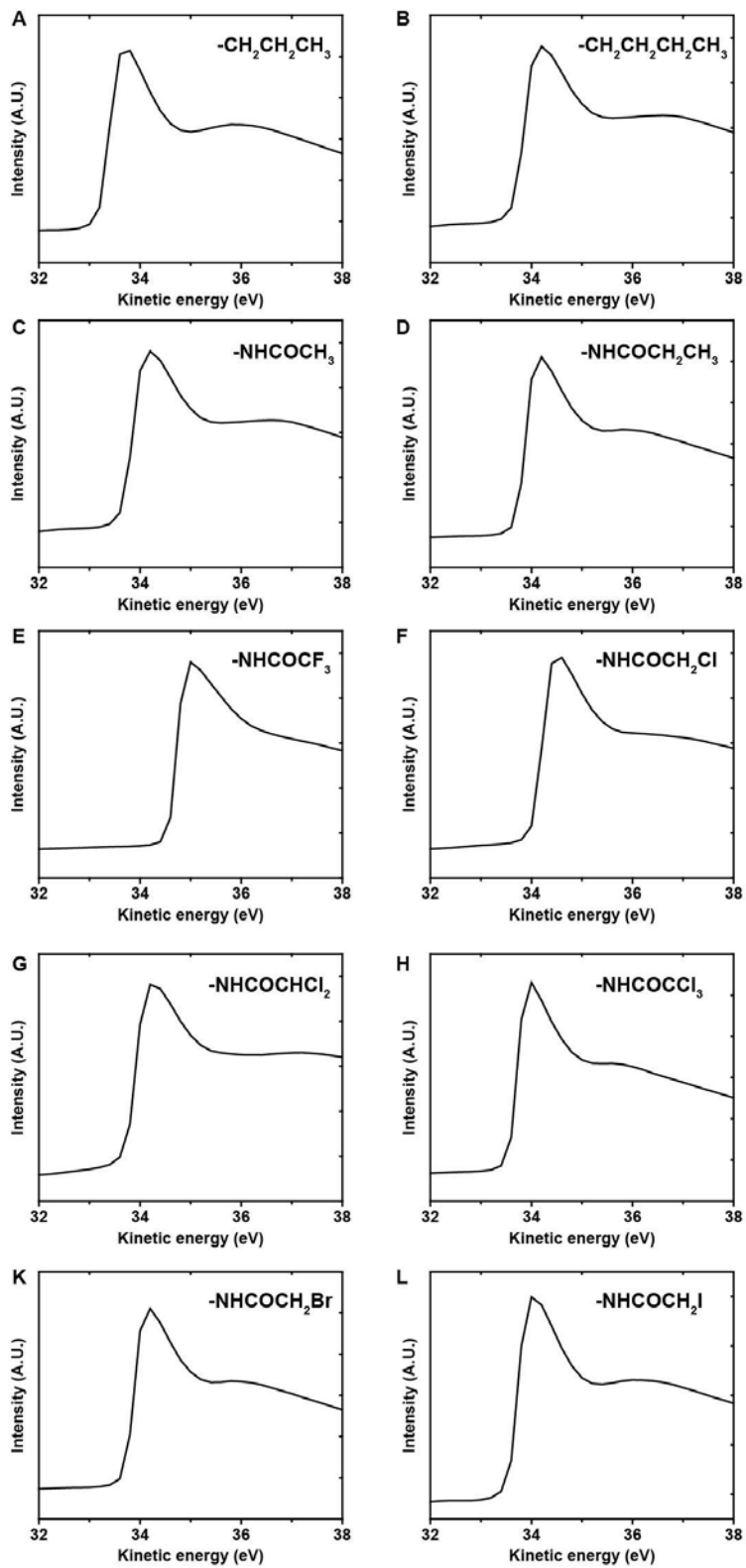


Figure S3. The Fermi edge spectra for ω -halogenated alkanethiolate SAMs on Ag^{TS} .

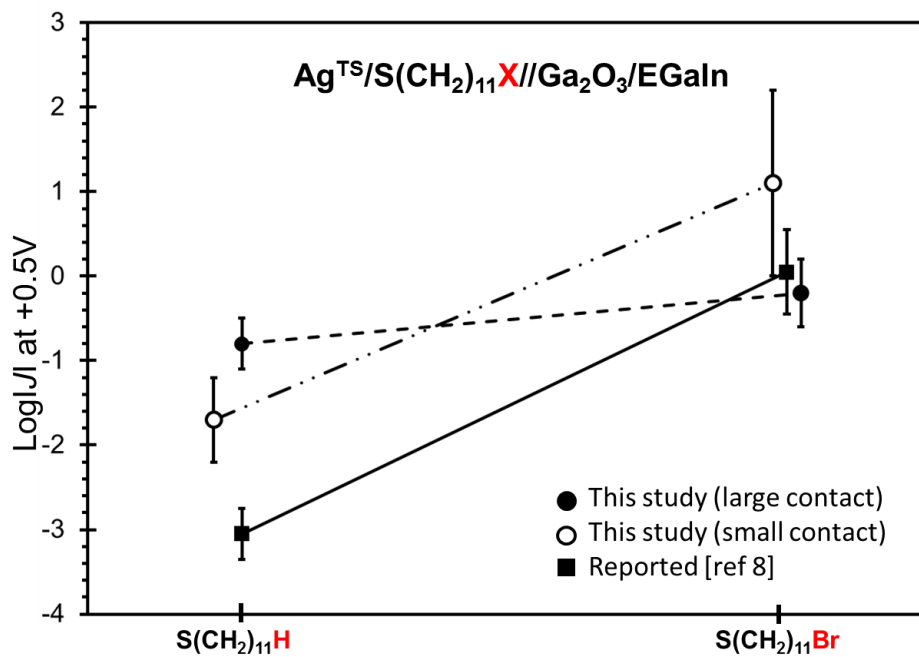


Figure S4. Effect of contact area on current density across SAMs of S(CH₂)₁₁X (X = H, Br).⁸ All data points are log|J| collected at + 0.5 V and the error bars are the standard deviation of the mean. All data points in this work are the results of more than 15 junctions (300 scans) (see Figure S5 for histograms).

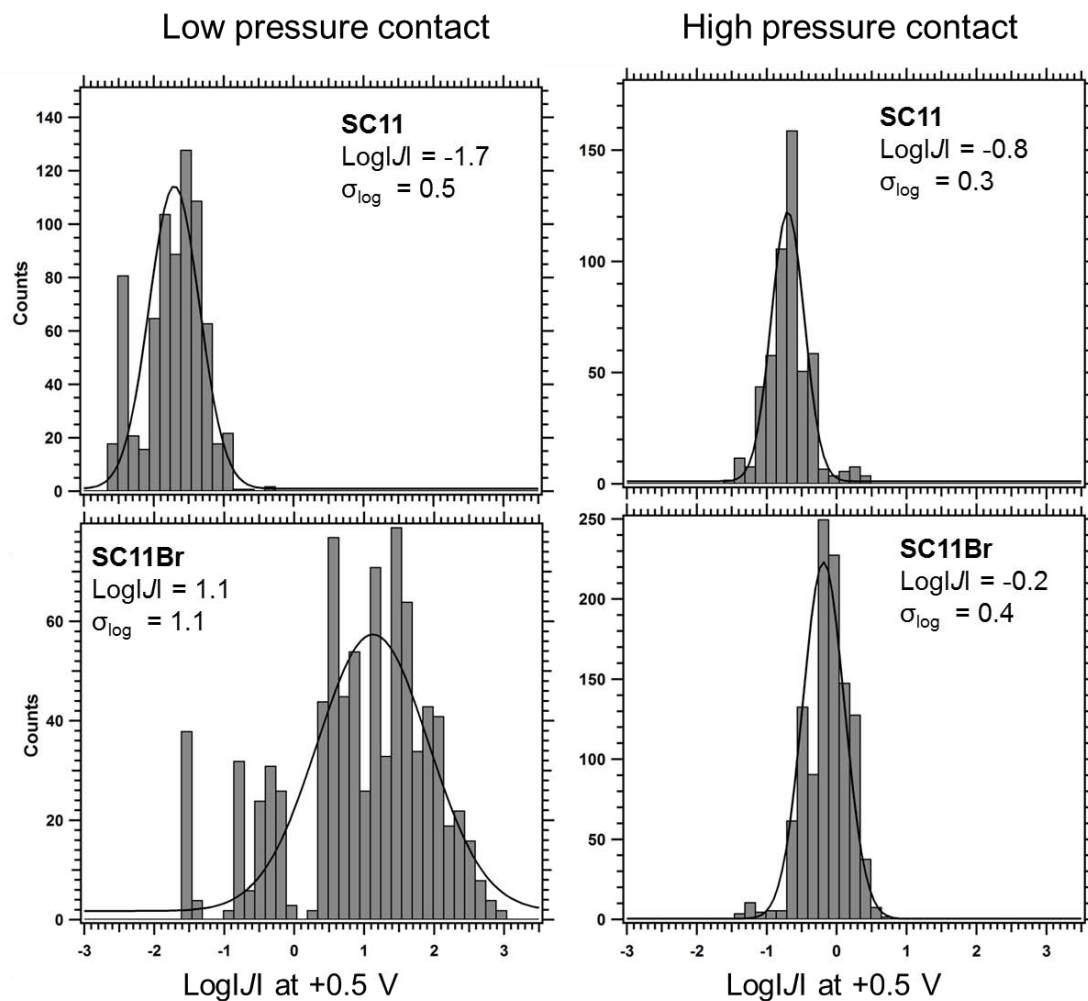


Figure S5. Histograms of the distribution of the values of $\log|J|$ at $V = +0.5\text{ V}$ for SAMs of SC11 and SC11Br using low and high pressure contacts on Ag^{TS} .

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