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Introducing Ionic and/or Hydrogen Bonds into the SAM//Ga₂O₃ Top-Interface of Ag^{TS}/S(CH₂)_nT//Ga₂O₃/EGaIn Junctions

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ABSTRACT. Junctions with the structure $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_n\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ (where $\text{S}(\text{CH}_2)_n\text{T}$ is a self-assembled monolayer, SAM, of *n*-alkanethiolate bearing a terminal functional group T) make it possible to examine the response of rates of charge transport by tunneling to changes in the strength of the interaction between T and Ga_2O_3 . Introducing a series of Lewis acidic/basic functional groups (T = $-\text{OH}$, $-\text{SH}$, $-\text{CO}_2\text{H}$, $-\text{CONH}_2$, and $-\text{PO}_3\text{H}$) at the terminus of the SAM gave values for the tunneling current density, $J(V)$ in A/cm^2 , that were indistinguishable (i.e., differed by less than a factor of 3) from the values observed with *n*-alkanethiolates of equivalent length. The insensitivity of the rate of tunneling to changes in the terminal functional group implies that replacing weak van der Waals contact interactions with stronger hydrogen- or ionic bonds at the T// Ga_2O_3 interface does not change the shape (i.e., the height or width) of the tunneling barrier enough to affect rates of charge transport. A comparison of the injection current, J_0 , for T = $-\text{CO}_2\text{H}$, and T = $-\text{CH}_2\text{CH}_3$ —two groups having similar extended lengths (in Å, or in numbers of non-hydrogen atoms)—suggests that both groups make indistinguishable contributions to the height of the tunneling barrier.

TEXT. Studies of the electrical behavior of junctions based on self-assembled monolayers, SAMs, and having the structure $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_n\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ have revealed several surprising insensitivities of the rates of charge transport across the SAM to the structure of the terminal group (T) of the SAM.¹⁻⁵ (Here, Ag^{TS} indicates a template-stripped silver substrate,⁶ EGaIn is eutectic gallium indium alloy, and Ga_2O_3 is a surface oxide that forms at the surface of EGaIn almost immediately upon exposure to air.⁷) One current interest in the interpretation of data for charge transport obtained with EGaIn top-electrodes is the contribution of the non-covalent van der Waals T// Ga_2O_3 top-interface to the shape of the tunneling barrier. When the group T is aliphatic, simple aromatic, or polar but not strongly Lewis-acidic or Lewis-basic—a range of

groups differing widely in electronic and molecular structure—details of the atomic/electronic structure of the group seems relatively unimportant, and the contribution of T to the rate of tunneling appears to come primarily from its contribution to the width of the barrier.^{4, 5, 8} In (possible) contrast, *n*-alkanethiolates show an odd/even effect⁹ (which might be a reflection of interface structure); T = ferrocene and its derivatives produce large rectification ratios ($R > 100$),¹⁰⁻¹⁴ and certain terminal groups (in other systems) have been reported to have large influences on tunneling currents.¹⁵⁻²⁰ To rationalize these results, this work systematically examined T groups capable of interacting with the surface of Ga₂O₃, with strengths between van der Waals and covalent bonds, and determined whether these groups (and the strengths of their interactions with the top Ga₂O₃/EGaIn electrode) changed rates of tunneling.

We have introduced a series of protic polar groups (T = -CO₂H, -SH, -PO₃H₂, -OH, -CONH₂) into the interface between the electrically conducting Ga₂O₃ layer⁸ and the insulating methylene -(CH₂)_n- portion of the SAM. These polar groups are capable, in principle, of interacting with the surface of the Ga₂O₃ either as Lewis acids or bases, and thus, more strongly than the aprotic polar T groups,⁴ and the nonpolar aromatic and aliphatic T groups we have studied before.⁵ We focused on two particular questions: i) Do these Lewis acidic or basic groups at the T//Ga₂O₃ interface change the current density (J in A/cm² at applied bias V) through these junctions? ii) How do these changes in structure affect the apparent dependence of the charge injection current density (J_0), and the tunneling decay constant (β) (as defined by the simplified Simmons equation²¹ for tunneling, eq. 1)?

$$J(V) = J_0(V)e^{-\beta d} = J_0(V)10^{-\beta d/2.303} \quad (1)$$

A tunneling junction of the form Ag^{TS}/A(CH₂)_nT//Ga₂O₃/EGaIn has two different interfaces:

i) a covalent or ionic so-called “bottom” interface between the anchoring atom A and the Ag^{TS} and ii) a van der Waals interface between T and the Ga_2O_3 . The structure of the anchoring group (A) has little influence on the rate of tunneling (for example, replacing $\text{Ag}^{\text{TS}}\text{S}(\text{CH}_2)_n\text{CH}_3$ with $\text{Ag}^{\text{TS}}\text{O}_2\text{C}(\text{CH}_2)_{n-1}\text{CH}_3$ does not significantly change this rate).² The effect of structural variations at the top interface—where the strength of the interaction between the T and Ga_2O_3 could, in principle, change from a weak physical interaction (i.e., van der Waals interaction) to a much stronger chemical bond—is a question relevant to the relationship between the molecular-level structure of the SAM and its properties as a tunneling barrier.

This paper follows a physical-organic design in studying charge transport across EGaIn-based junctions: that is, we varied only the structure of the terminal group T, while keeping other components of the SAM (i.e., its thiolate anchoring group and polymethylene backbone $(-\text{CH}_2)_n-$) and the electrodes the same. This strategy minimized changes in the structure of the SAM unrelated to the group T and the T// Ga_2O_3 interface. (It cannot, of course, entirely eliminate them, since the structure of the group T may influence the structure of the polymethylene unit). We incorporated various terminal groups T into these junctions, and analyzed trends in $J(V)$ with T, assuming that the contributions of all other components of the junction remained consistent with those well-established for *n*-alkanethiolates. We chose the Lewis acidic/basic groups ($-\text{SH}$, $-\text{OH}$, $-\text{CONH}_2$, $-\text{CO}_2\text{H}$ and $-\text{PO}_3\text{H}_2$) based on their ability, in principle, to interact chemically (i.e., using interactions beyond electrostatic contacts, by hydrogen bonding, coordination, or formation of covalent bonds) with the gallium oxide of the top-electrode. The relevant values of pKa, in water, for these groups are: $-\text{PO}_3\text{H}_2 = 2.4$ (pKa₁), 7.1 (pKa₂); $-\text{CO}_2\text{H} = 4.8$; $-\text{SH} = 10.3$; $-\text{OH} = 18$; $-\text{CONH}_2 = 25$.²²

The structural and electrical characteristics of the $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_n\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junction are, by now, generally well-established.^{7, 8, 10, 23-26} In prior work, we concluded that i) the resistance of the Ga_2O_3 film does not contribute significantly to the resistance of the junction;^{7, 8, 23, 24, 27} ii) the surface of the film in contact with the SAM in the “conical tip”²⁴ electrode we use is rough, and only a small (although reproducible) fraction ($\sim 10^{-4}$) of the apparent area of contact between $\text{Ga}_2\text{O}_3/\text{EGaIn}$ tip and the SAM (as estimated by microscopy) is in effective electrical contact.⁸

The rate of charge transport in these junctions is compatible with a model based on hole transport through a potential barrier provided by the electrically insulating SAM, and the interfaces between top- and bottom-electrodes.^{19, 28} We have roughly estimated the shape of this potential barrier using known values of work functions for silver (-4.5 eV relative to vacuum),²⁹ and EGaIn (-4.3 eV).⁷ For a cluster of *n*-alkanethiolates (*n*-decanethiolate, SC_{10}) bound to Ag, we used density functional theory (DFT) to estimate the values of the frontier orbital energies—the highest occupied molecular orbital, HOMO (-4.89 eV), and lowest unoccupied molecular orbital, LUMO (-2.92 eV). Table S1 (in the Supporting Information) summarizes the potentials calculated for *n*-alkanethiolates and ω -carboxyl-alkanethiolates on Ag.

In a molecular junction, the width of the tunneling barrier (d , eq.1) is commonly approximated by the length of the molecules comprising the SAM that separates the two electrodes, but it is still unclear which components of the molecule should be considered to belong to the insulating tunneling barrier. The tunneling barrier certainly includes all of the insulating $-(\text{CH}_2)_n-$ units, but it might also include the anchoring atom (S), and the terminal group T in van der Waals contact with Ga_2O_3 . We do not know, with precision, the shape (height and width of the energy profile) of the barrier associated with a van der Waals interface between

group T and Ga₂O₃ (Figure S7); we assume that it is the highest potential in the barrier (potentially close to vacuum at 0 eV). As a starting point in the analysis of the width of the barrier, we defined the injection current for $d = 0 \text{ \AA}$ to be that obtained by extrapolation of a series of *n*-alkanethiolates S(CH₂)_nH ($n = 16$ to $n = 0$), and included both the anchoring atom and the distal hydrogen atom (Figure 1b).

We fabricated “unflattened” conical-tip EGaIn electrodes and selected those that were free of visible surface asperities (using procedures described elsewhere,⁸ and in the Supporting Information) to measure current density, $J(V)$, across T-terminated alkanethiolates on Ag^{TS}. Figure 2 shows $J(V)$ data for T being either a methyl group (T = -CH₃)—represented by the dashed reference line—or a Lewis acid/base functional group. We do not know the ionization state of the protic groups T in the SAM, and arbitrarily assume a protonated state for each SAM when calculating the total molecular length (from the anchoring atom to the very distal hydrogen atom). In order to account for uncertainty associated with protonation state and molecular length, the horizontal bar for each point in Figure 2 includes estimated lengths of both protonated and deprotonated states. The Supporting Information (Figure S5) contains a summary of the histograms describing all measurements of $\log|J|$ ($V = +0.5 \text{ V}$). The values of J ($V = +0.5 \text{ V}$) for alkanethiolates terminated with protic groups T were not significantly different from the methyl-terminated alkanethiolates (i.e., they differ by less than a factor of 3). This result suggests that introducing Lewis-acidic or -basic groups that have the potential to coordinate gallium oxide or hydroxide in the T//Ga₂O₃ interface does not change the shape of the barrier enough to affect the tunneling conductance of the junctions.

Although we have no quantitative measure of the strength of the interaction between EGaIn and the surface of the SAM, we have one clear qualitative indication that the interaction is stronger for $T = -\text{CO}_2\text{H}$ than for $T = -\text{CH}_3$. Upon retraction of the EGaIn conical tip electrode from the surface (for $T = -\text{CO}_2\text{H}$, Figure S2), the tip adhered to the SAM. Although this tip is “sticky” (and thus, we infer, interacts more strongly with the surface of the SAM than other surfaces we have examined; for example, the surface of *n*-alkanethiolates on Ag), the measured current density is indistinguishable from *n*-alkanethiolate standards of the same length. Moreover, the adhesion does not result in electrically “shorted” junctions. This observation suggests qualitatively that terminal CO_2H groups form, at least in part, hydrogen or coordination bonds with the gallium oxide, but that these bonds do not change the rate of charge transport detectably. The inference that Ga_2O_3 can act as a base (i.e., a hydrogen bond acceptor) agrees with work by Ito and coworkers.³⁰ We infer that a terminal $T = -\text{CO}_2\text{H}$ group forms bonds with the Ga_2O_3 of the top-electrode that are stronger than van der Waals interactions involving $T = -\text{CH}_3$ and other groups, but that these bonds do not increase observably the tunneling current relative to a top interface having the weak van der Waals interaction of a $T = -\text{CH}_3$ group.^{31, 32}

To investigate further the influence of the interaction between $T = -\text{CO}_2\text{H}$ and the Ga_2O_3 of the EGaIn top electrode on the rate of charge transport, we investigated a range of lengths of ω -carboxyl-alkanethiolates (Figure 3). The Supporting Information contains histograms of data for $\log |J|$ for carboxyl-terminated molecules. Yields of working junctions for the carboxyl-terminated SAMs (100%) were as high or higher than those composed of *n*-alkanethiolates. Standard deviations of measured currents for ω -carboxyl-alkanethiolates were smaller than those of the *n*-alkanethiolates: the σ_{\log} calculated from the Gaussian fitting was ~ 0.3 for SAMs bearing terminal carboxyl groups, but ~ 0.5 for SAMs of *n*-alkanethiolates on Ag^{TS} (Figure S5 and S6).

We note that $\sigma_{\log} \sim 0.3$ indicates that $\sim 67\%$ of the junctions give values of J ($V = +0.5V$) that fall within a range differing by a factor of 4 (across multiple junctions, tips, and users). This narrow distribution indicates that EGaIn-based junctions based on a T//Ga₂O₃ contact is reproducible and replicable, and suggests that the formation of a weak bond at the SAM//Ga₂O₃ interface increases the stability of the junction on measurements of $J(V)$.

To determine the contribution of a terminal carboxyl group ($T = -CO_2H$) to the shape—the height and width—of the tunneling barrier, we compared the tunneling current densities with length-matched *n*-alkanethiolates ($T = -CH_3$). We estimated the width, d , of the tunneling barrier using three different assumptions (Figure 4 and 5): i) $d[\text{Å}]$ = the total length of the molecular SAM in Å, from the center of the anchoring atom (sulfur) to the center of the distal atom assumed to be closest to the top electrode. Thus, for example, $d[\text{Å}]$ for S(CH₂)₁₀H would be 12.9 Å for the S to C distance of the (CH₂)₁₀ unit, plus 1.0 Å for the terminal hydrogen; that for S(CH₂)₉CO₂H would be 11.8 Å for the S to C distance of the (CH₂)₉ unit, plus 3.1 Å for $T = -CO_2H$; ii) $d[S(CH_2)_nT]$ = the sum of the number of methylene (CH₂) units, the anchoring atom (here S), and the non-hydrogen atoms of the terminal functional group, (thus, for example, $d[S(CH_2)_nT]$ for S(CH₂)₁₀H would be 10 methylene units and 1 sulfur atom; that for S(CH₂)₉CO₂H would be 9 methylene units, 1 sulfur atom, and 2 non-hydrogen atoms, C and O, from T) and iii) $d[(CH_2)_n]$ is determined only by the number of methylene (CH₂) units, (thus, for example, $d[(CH_2)_n]$ for S(CH₂)₁₀H would be 10 methylene and that for S(CH₂)₉CO₂H would be 9 methylene units).

Figure 4 shows a plot of $\log|J(+0.5 V)|$ vs. $d[\text{Å}]$ for different lengths of carboxyl-terminated alkanethiolates, and for *n*-alkanethiolate standards (dashed line). The linear-least square fit ($R^2 =$

0.99) of $\langle \log|J(+0.5V)| \rangle$ to equation 1^{21, 33} yielded the injection current ($\log|J_0(+0.5V)|$) and the tunneling attenuation coefficient (β (in \AA^{-1})). The injection current for the carboxyl-terminated alkanethiolates ($\log|J_0(0.5V)| = 3.6 \pm 0.2 \text{ A/cm}^2$) was indistinguishable from that of the methyl terminated *n*-alkanethiolate standards ($\log|J_0(0.5V)| = 3.7 \pm 0.2 \text{ A/cm}^2$) when considering the entire length (measured in \AA) of the SAM from the sulfur atom to the distal hydrogen atom of the carboxyl group in contact with Ga_2O_3 .

The Simmons equation (eq. 1) fits the experimental observations (Figure 4) qualitatively in this experiment (as in many other experiments).^{8, 34, 35} There are, however, unresolved questions in most of these experiments about the interpretation of the parameters J_0 , β , and d . The attenuation parameter β describes the falloff in tunneling current with distance, and is remarkably consistent ($\beta = 0.73\text{-}0.89 \text{ \AA}^{-1}$ or $0.9\text{-}1.1 \text{ nC}^{-1}$) for a large number of studies of *n*-alkanethiolates on gold and silver, and of *n*-alkyl groups bonded directly to silicon.^{28, 34-38} The value of the injection current, J_0 , is interpreted to be characteristic of a hypothetical junction in which the SAM has zero length d , but in which the characteristics of the Ag/S and T// Ga_2O_3 interfaces is preserved. For all compounds (other than those with $(\text{CH}_2)_n$ groups so short that the AgS and T groups interact directly), we expected the contribution to J_0 from the Ag-S interface to be the same for all experimental junctions of the form Ag/S $(\text{CH}_2)_n$ T// Ga_2O_3 /EGaIn. For compounds where T is not a methyl group, however, there is a question about the meaning of d (a parameter which defines the width of the tunneling barrier): *viz.*, should T be considered as part of the insulating tunneling barrier, or a part of the electrically conducting Ga_2O_3 interface, or as some hybrid between the two? To address this question, we have plotted $J(V)$ as a function of the number of non-hydrogen atoms (here, S and C and/or O) and as a function only of the number of methylene groups in the molecules of the junction. Figure 5a shows that the former plot yields

effectively indistinguishable least-square fits for the trend derived from SAMs of ω -carboxyl-alkanethiolates and from SAMs of *n*-alkanethiolates, with the same value of J_0 at 0.5 V; the latter yields parallel lines, but quite different values of J_0 . These data are compatible with the conclusion that the contribution of the carboxyl group to the width of the tunneling barrier is equivalent to that of an ethyl ($-\text{CH}_2\text{CH}_3$) group, and *not* to that of a group whose electronic properties make it part of the electronically conducting part of the interface, or one that changes the shape of the tunneling barrier (relative to T = $-\text{CH}_3$ of *n*-alkanethiolates) in a way that significantly (at the resolution of our experiments) influences tunneling currents.

The value of β for the carboxyl-terminated SAMs ($\beta = 0.74 \pm 0.02 \text{ \AA}^{-1}$, $0.94 \pm 0.05 \text{ n}_{\text{CH}_2}^{-1}$) is also indistinguishable from that of the *n*-alkanethiolate standards ($\beta = 0.78 \pm 0.03 \text{ \AA}^{-1}$, $0.92 \pm 0.04 \text{ n}_{\text{CH}_2}^{-1}$). This similarity in the tunneling decay coefficient suggests that the attenuation in tunneling current through the SAM is not substantially influenced by the chemical nature of the top interface, or of the electrical dipoles that we associate with these polar groups T, over the range of compounds summarized in Figures 2 and 3.

We conclude that replacing a terminal *n*-alkyl group (T) of an *n*-alkanethiolate of the same total length (e.g. T = $-\text{CH}_2\text{CH}_3$) at the SAM//Ga₂O₃ interface with a Lewis acid/base (e.g. T = $-\text{CO}_2\text{H}$), does not influence the tunneling current. Junctions of the same length ($d[\text{\AA}]$ or $d[\text{S}(\text{CH}_2)_n\text{T}]$) and with composition Ag^{TS}/S(CH₂)_nT//Ga₂O₃, where T = $-\text{CH}_3$, $-\text{OH}$, $-\text{SH}$, $-\text{CO}_2\text{H}$, $-\text{CONH}_2$, and $-\text{PO}_3\text{H}$, all have tunneling currents that are indistinguishable (e.g. within a factor of 3). The introduction of protic polar groups at the T//Ga₂O₃ interface by the group T does not change the shape (i.e., the height or width relative to *n*-alkanethiolates) of the tunneling barrier enough to influence the rate of charge tunneling observably (a conclusion that is

reinforced by data from studies of other organic groups, including a number of simple aromatics and uncharged polar groups).^{4,5} The similarity of the injection current (J_0) for junctions derived from data using SAMs terminated in $-\text{CH}_3$ or $-(\text{CH}_2)_n\text{CH}_3$ (depending on the size of the group to be compared) and for junctions from SAMs terminated in a variety of other functional groups (including simple aromatic groups,⁵ polar aprotic groups with large dipole moments,⁴ and the polar, protic groups studied here) indicates that these T//Ga₂O₃ interfaces are all very similar in their contribution to the tunneling barrier.

A comparison of J_0 for T = $-\text{CO}_2\text{H}$ and T = $-\text{CH}_2\text{CH}_3$ for similar extended lengths (Å) or number of non-hydrogen atoms is compatible with the hypothesis that both act primarily as (equivalent) contributors to the width of the tunneling barrier. Any difference in their contribution to the energetic topography of the tunneling barrier does not appear as differences in our experimental measurements.

ASSOCIATED CONTENT

Supporting Information. The experimental procedures, characterization of the SAMs, histograms of $J(V)$ data, and DFT computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

EGaIn, eutectic gallium indium; SAM, self-assembled monolayer; TS, template-stripped; HOMO, highest occupied molecular orbital; LUMO, lowest occupied molecular orbital.

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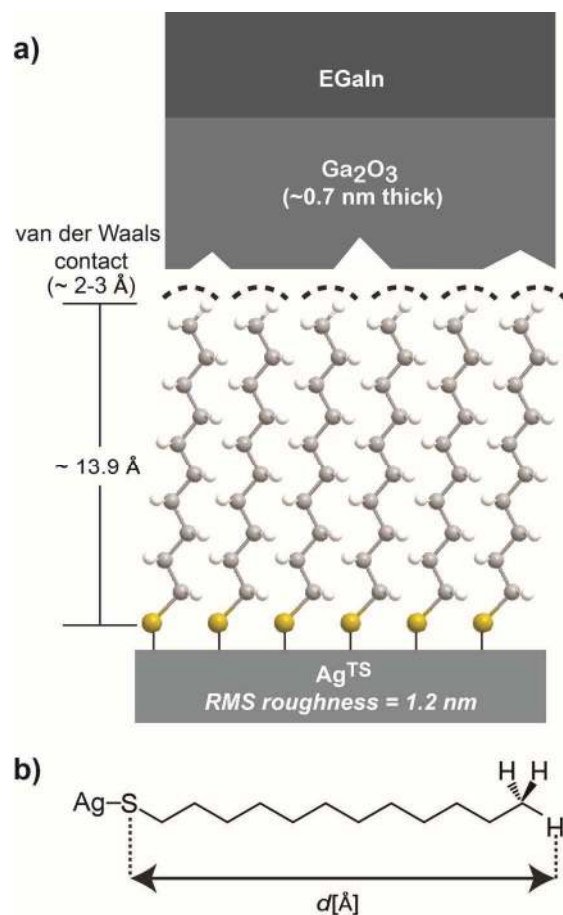


Figure 1. a) Components of the Ag^{TS}/S(CH₂)_nT//Ga₂O₃/EGaIn junction, where n is the number of methylene units (CH₂), and T is a terminal functional group; here n = 9 and T = CH₃. A tilt angle of 11° from the surface normal was applied to the SAM.³⁹ The inherent roughness of the Ga₂O₃ film and the SAM-bound Ag^{TS} substrate contributes to an effective electrical contact area that is ~10⁻⁴ the geometrical contact area.⁸ The van der Waals contact distance was estimated by adding the van der Waals radius of the terminal H atom of the SAM and the O atom of the Ga₂O₃ film. We do not know the height or width of the energy profile associated with the van der Waals interface. b) Definition of the molecular length in Å of the insulating molecular component from an all *trans*-extended configuration using Chem3D software. The distance is calculated from the center of the sulfur anchoring atom to the center of the distal hydrogen atom that is presumably closest to the EGaIn top electrode.

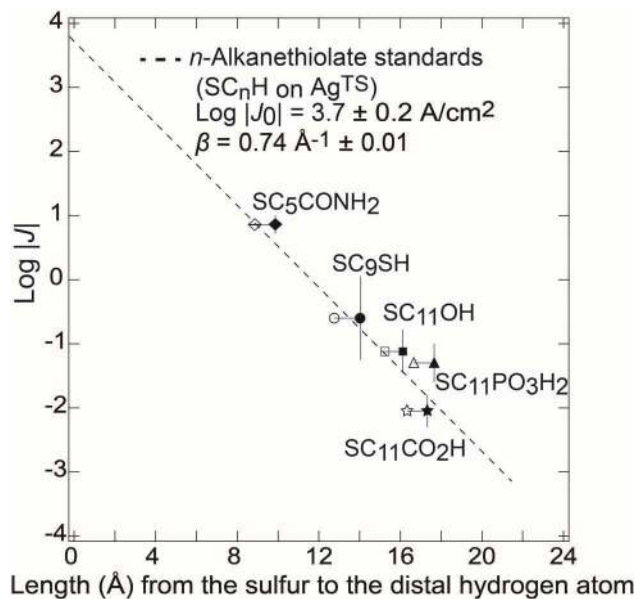


Figure 2. $\langle \log |J| \rangle$ at +0.5 V versus molecular length for n -alkanethiolate standards and alkanethiolates bearing terminal Lewis acidic or basic functional groups. The two points for protonated (\bullet) or deprotonated (\circ) ω -substituted -alkanethiolate SAM take into account the difference in the estimated molecular length associated with the protonation state of the SAM (right point, protonated state; left point, deprotonated). The molecular length was estimated using an all *trans*-extended configuration from the sulfur atom to the final hydrogen atom using Chem3D software.

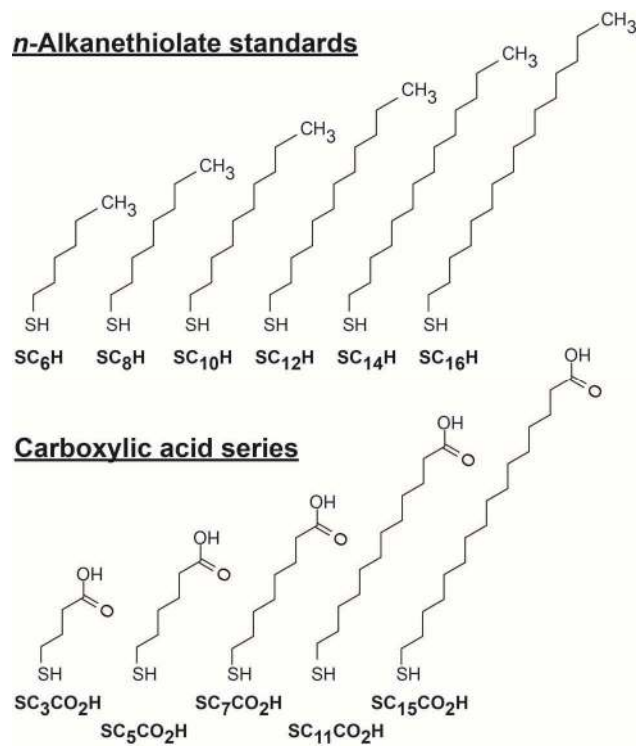


Figure 3. A series of methyl- and carboxyl-terminated alkanethiolates used to form SAMs for the determination of J_0 and β .

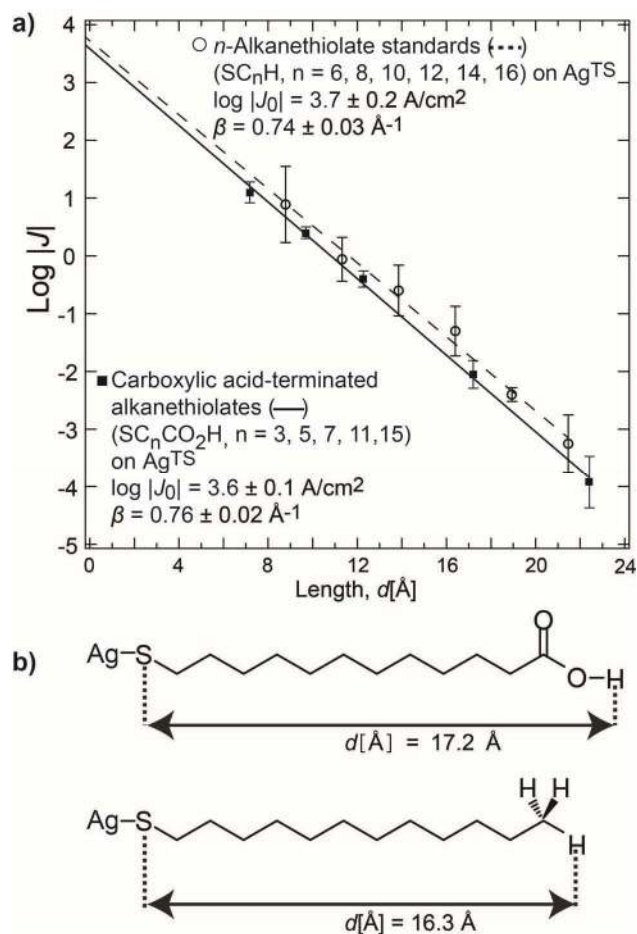


Figure 4. a) Plot of the Gaussian mean values of $\log |J|$ at +0.5 V versus molecular length (calculated in \AA for an all *trans*-extended conformation) for ω -carboxyl-alkanethiolates and *n*-alkanethiolate standards on Ag^{TS}. The least-squares lines are not distinguishable. b) The distance is calculated from the sulfur atom to the final hydrogen atom as shown.

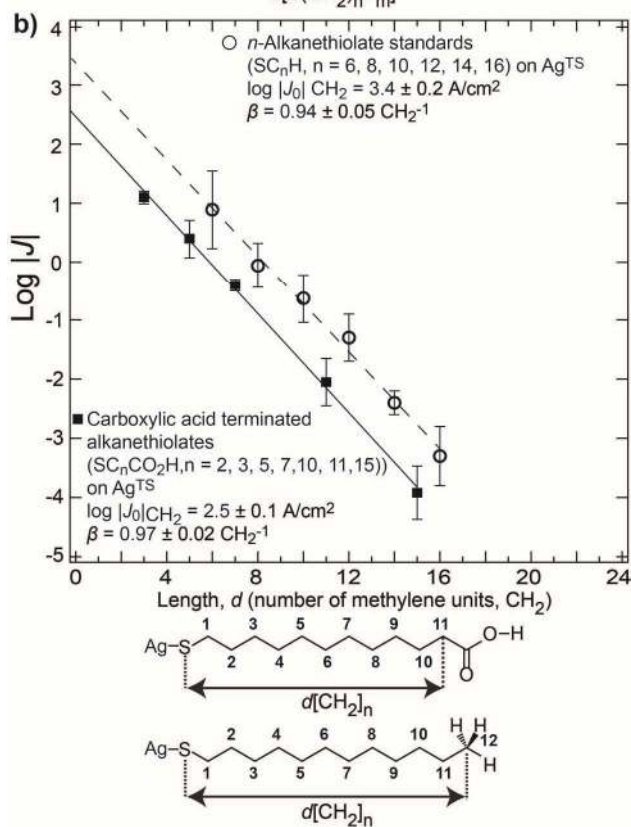
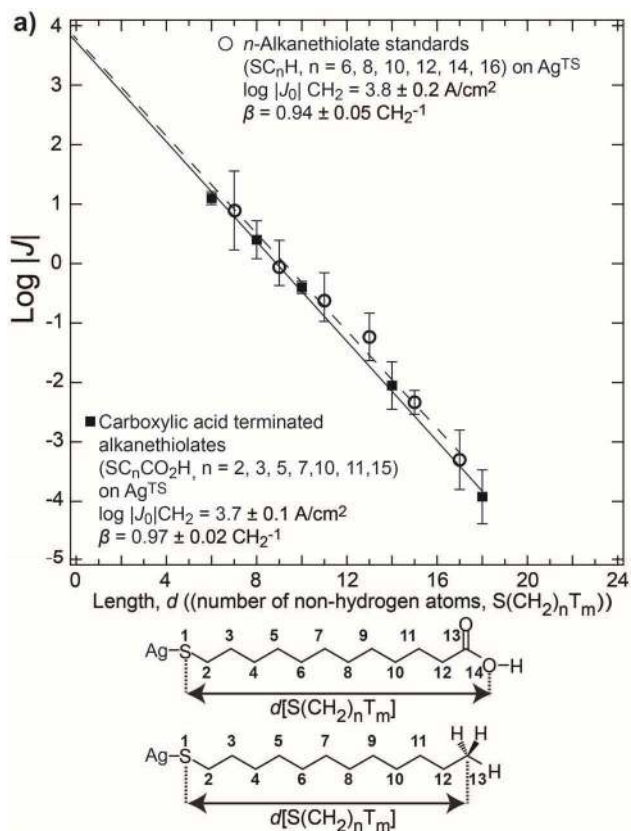


Figure 5. a) Plot of the Gaussian mean values of $\log|J|$ at +0.5 V *versus* molecular length in number of non-hydrogen atoms ($n + m$: n is the number of non-hydrogen atoms of the polymethylene chain and m is the number of non-hydrogen atoms (in linear connection) of T; here, n is 11 and m is 2 for T = $-\text{CO}_2\text{H}$) for carboxyl-terminated alkanethiolates and n -alkanethiolate standards of similar length on Ag^{TS} . b) Plot of the Gaussian mean values of $\log|J|$ at +0.5 V *versus* molecular length in number of methylene units (CH_2) for carboxyl-terminated alkanethiolates and n -alkanethiolate standards on Ag^{TS} . The final methylene unit of the terminal methyl group $-(\text{CH}_2)\text{H}$ group is included in the total number of methylene units.