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ARTICLE

The Rate of Charge Tunneling in EGaIn Junctions Is Not Sensitive to Halogen Substituents at the Self-Assembled Monolayer//Ga_2O_3 Interface

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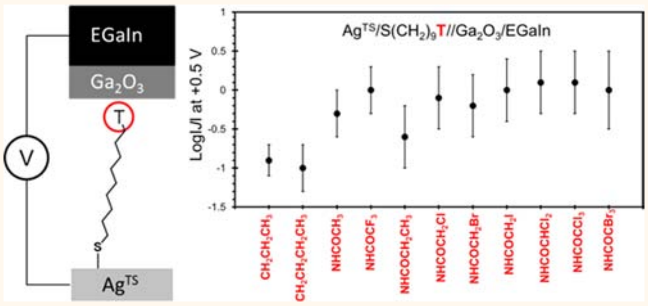
S Supporting Information

ABSTRACT: **This paper describes experiments that are designed to test the influence of terminal groups incorporating carbon−halogen bonds on the current density (by hole tunneling) across self-assembled monolayer (SAM)-based junctions of the form $M^{TS}/S\text{-}(CH_2)_9NHCOCH_nX_{3-n}//Ga_2O_3/EGaIn$ (where M = Ag and Au and X = CH_3, F, Cl, Br, I). Within the limits of statistical significance, these rates of tunneling are insensitive to the nature of the terminal group at the interface between the SAM and the Ga_2O_3. The results are relevant to the origin of an apparent inconsistency in the literature concerning the influence of halogen atoms at the SAM//electrode interface on the tunneling current density.**



KEYWORDS: *EGaIn junction, interface, self-assembled monolayers, molecular electronics, polarizability, charge tunneling*

One of the goals in molecular electronics is to understand the correlation between the structures of insulating organic molecules sandwiched between two electrodes and the rate of charge tunneling through them.[1−8] How the properties of functional groups present at the interface interact with the electrodes (either in single molecule- or self-assembled monolayer (SAM)-based junctions)[9−12] and influence the tunneling barrier and the rate of tunneling remains one of the specific problems in this area. To study the effect of polarizability at the SAM//Ga_2O_3 interface on tunneling barrier, this paper examines the relative rates of charge tunneling (*e.g.*, current density) across a series of junctions with structures of Au^{TS} and $Ag^{TS}/S\text{-}(CH_2)_9NHCOCH_nX_{3-n}//Ga_2O_3/EGaIn$ with X = H, CH_3, F, Cl, Br, and I (Figure 1, here Ag^{TS} is a template-stripped silver substrate and EGaIn is eutectic gallium−indium alloy). It demonstrates that the rate of charge tunneling across these molecular junctions is *not* sensitive to the presence of halogen-containing groups at the SAM//Ga_2O_3 interface and confirms that the polarizability and dipole moment of the terminal group do not influence the rate of charge tunneling.

Studying the influence of metal/molecule interfaces on charge transport has been an active area in molecular electronics.[13−22] Using a junction of the form $M^{TS}/A\text{-}(CH_2)_nT//Ga_2O_3/EGaIn$ (A is the anchoring group and T is the terminal group) we,[23−29] Nijhuis,[30−33] Chiechi,[34−37] Yoon,[38] Thuo,[39−41] and others[42] have examined the relationships between the structure of the organic molecule and the tunneling current. With exceptions that are largely understood,[28,43−45] most derivatives of *n*-alkyl-based SAMs are not sensitive to the nature of T: similar rates are observed for structurally simple terminal groups (*i.e.*, H, CH_3, and many polarizable functionalities).[25−27] In a few specific cases, however, the rates of tunneling respond in unexpected ways

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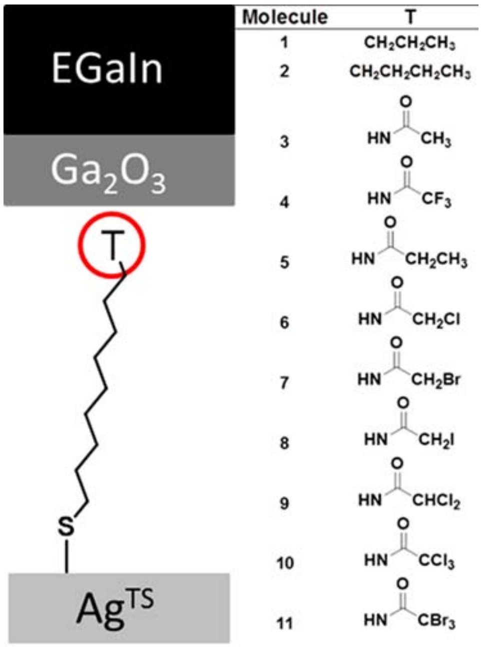

Figure 1. Cartoon representation of the EGaIn junction with the structure of $Ag^{TS}/S(CH_2)_9T//Ga_2O_3/EGaIn$.

to the structure of the T group.[24,27] Among the exceptions are significant decreases in current density by about a factor of 20 when the terminal group is CF_3 or F[46] and more complex behaviors (especially rectification) when T = ferrocene and its derivatives,[43,45] bipyridyl,[28] and other groups with accessible HOMOs or LUMOs (highest occupied molecular orbital or lowest unoccupied molecular orbital).

Different research groups (using *different* SAM-based junctions) are in qualitative agreement on specific features (especially the attenuation coefficient β of the simplified Simmons equation) and (as expected) disagree on values of the extrapolated current densities (*e.g.*, J_0).[12] Many of these latter disagreements stem from an inability to measure the electrical contact areas (and thus the current density in A/cm^2) of different types of SAM-based junctions.[23,47] When T = Br or I, there is a striking disagreement.[46,48−52] This disagreement may depend on the junction, the structure of the molecule, or the details of the experimental procedure; however, the literature of tunneling (not necessarily with EGaIn top electrodes) suggests real discrepancies, with no obvious rationalization for them. For example, for measurements of current densities for comparable systems, differences by as much as 8 orders of magnitude have been reported.[50,51] Some of these studies involved only one or two molecules and—without structurally similar molecules to provide calibration—are difficult to compare with others. The introduction of a carbon−halogen bond at the terminal position of the SAM might affect the local dipole moment, polarizability, and frontier molecular orbital, and this change has the potential to change the structure of the SAM, the junction, or the mechanism of charge transport, all in unrecognized ways.[48,49,53−55] Replacement of H with Br or I may also influence reactivity (*i.e.*, rates of electrochemical reduction with possible formation of carbon−metal bonds, S_N2 displacement, or coordination to Lewis acidic sites). Halogenation in the T group is, thus, interesting as a possible method of altering the shape (height, topography, and width) of the tunneling barrier and changing the nature of the interface of group T with the electrode that contacts it. Replacement of H by Br or I is also a possible source of artifacts, since these carbon−halogen bonds are reactive in ways carbon−hydrogen bonds are not.

This paper summarizes a study of the $T//Ga_2O_3$ interface, based on comparing the tunneling current densities across SAMs of $S(CH_2)_9T$ for a number of different T (T = $HNCOCH_nX_{3-n}$; X = H, CH_3, F, Cl, Br, and I, Figure 1).

We used molecules with an amide functional group for three reasons: (i) to minimize the difficulty in synthesis, (ii) to provide a new type of functional group to compare with prior work,[50−52] and (iii) to use a center that provides new (and greater) reactivity in certain types of reactions. In particular, the halogen atoms in groups of the structure $-NHCOCH_nX_{3-n}$ are more reactive than the halogen atoms in groups with the structure $-(CH_2)_nX$ and $-ArX$ in both electrochemical and free-radical reduction and in S_N2 reactions (a reaction potentially important in molecules also containing thiol groups).[56]

We have previously demonstrated that at the low voltages normally used with the EGaIn junction ($V = \pm 0.5$ V) replacement of CH_2CH_2 in the interior of the backbone of a SAM with a single amide group NHCO does not significantly influence the rate of charge tunneling, and we have demonstrated that rates of tunneling across junctions with structures $HS(CH_2)_{11}NHCOCH_3$ and $HS(CH_2)_{11}CH_2CH_2CH_3$ are indistinguishable.[27,57−59] Thus, comparisons of rates of charge tunneling across ordered SAMs with structures M/SAM//electrode, with SAM = $S(CH_2)_9NHCOCH_nX_{3-n}$, are instructive and appropriate.

We also intend for this study to allow us to consider the large increase in current density observed by two groups: by Cahen[50] for junctions having the structure $Si/CH_2(p\text{-}C_6H_4)X//Hg$ (X = CH_3, Br) (about 8 orders of magnitude for reducing potentials at the electrode contacting the halogen-containing group, $V = -1.0$ V, but not for oxidizing potentials) and of about 3 orders of magnitude by Nijhuis[51] at ±0.5 V for junctions having the structure $Ag^{TS}/S(CH_2)_{11}X//EGaIn$. Our comparison is between those literature values, our new values (Figure 2), and values reported by Yoon[33] (with the structures

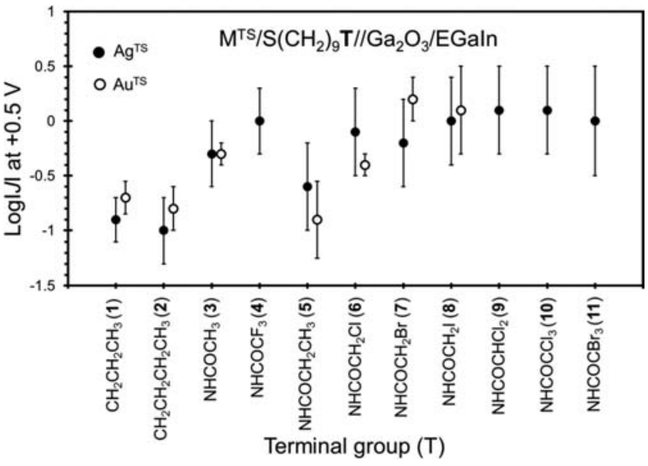

Figure 2. Charge transport through the SAMs of molecules examined in this study (molecules 1−11). The measurements were obtained with a junction of the structure $M^{TS}/S(CH_2)T//Ga_2O_3/EGaIn$. The error bars reported are of the standard deviation of the mean values of the log |*J*| at +0.5 V.

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$Ag^{TS}/S(C_6H_4)X//EGaIn$ and $Ag^{TS}/SCH_2(C_6H_4)X//EGaIn$), with our previous studies (using junctions with structures of $Ag^{TS}/S(CH_2)_nM(CH_2)_mT//Ga_2O_3/EGaIn$[27] and Ag^{TS}/O_2C-$(CH_2)_n(CF_2)_mT//Ga_2O_3/EGaIn$[46]), and with several different halogen-containing groups T.[27,46] In all these reports, only small or statistically insignificant (less than a factor of 3) difference were observed between halogenated and non-halogenated T groups.

Effect of Halogens in the Terminal Group on Charge Transport across SAMs. Using a junction with the structure $Si/(CH_2)_2(p\text{-}C_6H_4X)//Hg$, where X = H, CH_3, or Br,[48−50] the Cahen group reported an increase in the rate of tunneling current for similar SAMs containing (or not containing) terminal hydrogen atoms. Performing one scan per junction, they observed an 8 orders of magnitude increase in current density for the bromo-substituted molecule (J (−1.0 V, X = Br) ≈ 10 $A{\cdot}cm^2$) relative to the methyl-substituted molecule (J (−1.0 V, X = CH_3) ≈ 10^{-7} $A{\cdot}cm^2$).[50] This large increase was observed only when a negative bias was applied (*i.e.*, when the Hg electrode had a negative charge and was the reducing electrode). Measurements at positive bias showed that the bromo-substituted molecule had only a slightly higher current density (about an order of magnitude) than the analogous methyl-terminated junction. The higher current density in the (phenyl)brominated molecule was attributed to the modest changes in the dipole moment (typically $\Delta\mu \approx 1.7$ D)[60] introduced by the addition of the bromine; this dipole might increase the potential step and compensate for the difference in work function between the two electrodes.[50]

Nijhuis and co-workers also report a smaller increase of 3 orders of magnitude in the rate of charge tunneling when carbon−halogen bonds are incorporated into SAMs of alkanethiolates in junctions with the structure Ag^{TS}/S-$(CH_2)_{11}X//EGaIn$, with X = H, F, Cl, Br, or I. Their studies suggest that as the polarizability of the T group increased, so did the current density. They attributed the apparent increase in current density observed across this series to two effects, both correlating with an increase in polarizability and size: (i) an increase in the van der Waals force between the top electrode and the SAM, an increase that would lower the contact resistance, and (ii) a decrease in the HOMO−LUMO gap, and therefore a decrease in the height of the tunneling barrier, which would increase the possibility of superexchange-based tunneling.[51]

In contrast, Yoon and co-workers observed that replacing hydrogen or a methyl group[61] with a halogen for molecules $HS(p\text{-}C_6H_4X)$ in a junction of the form $Ag^{TS}/S(p\text{-}C_6H_4)X//EGaIn$, where X = H, F, Cl, Br, or I, led only to a small *decrease* of the current density by a factor of 13 at ±0.5 V (they performed 20 scans per junction). When they used $HSCH_2(p\text{-}C_6H_4X)$ to form SAMs in the same type of junction changing hydrogen with halogens, it decreased the current density by a factor of 50 (Figure 5). The current densities measured by Yoon *et al.* were indistinguishable for X = F, Cl, Br, or I[52] and indicate that the polarizability and introduction of a dipole moment in the SAM did not influence the current density within this system.

RESULTS AND DISCUSSION

Formation of SAMs of Halogen-Terminated Alkanethiolates. We synthesized the molecules shown in Figure 1 following reported procedures (for details see Supporting Information).[62,63] For the formation of SAMs, we followed a procedure of the type we currently use and have described elsewhere in detail.[24]

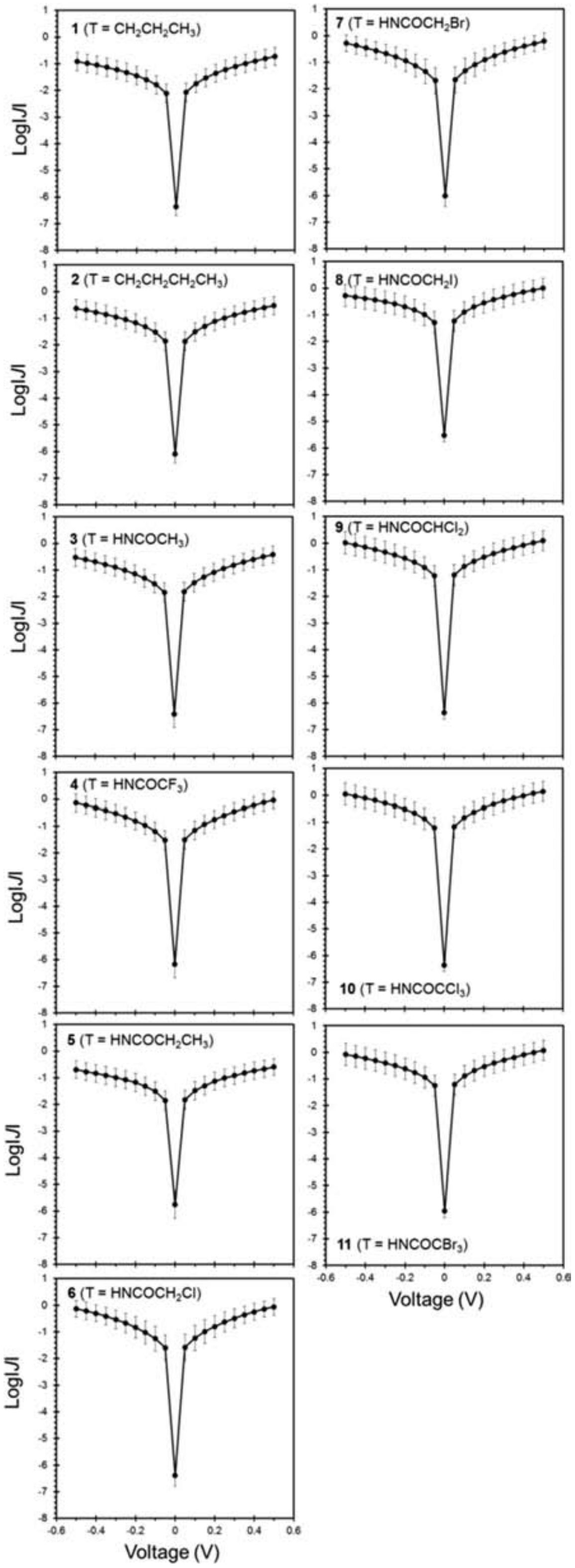

Figure 3. Log|J|-V plots of SAMs of compounds 1-11 on Ag^{TS}. The error bars represent the standard deviation of the mean values.

We chose to use Ag^{TS} for the majority of our work, rather than Au^{TS}, because it allows direct comparison with some of the data that have already been reported (the data from Yoon *et al.*, Nijhuis *et al.*, and us were all reported on Ag^{TS}; those by

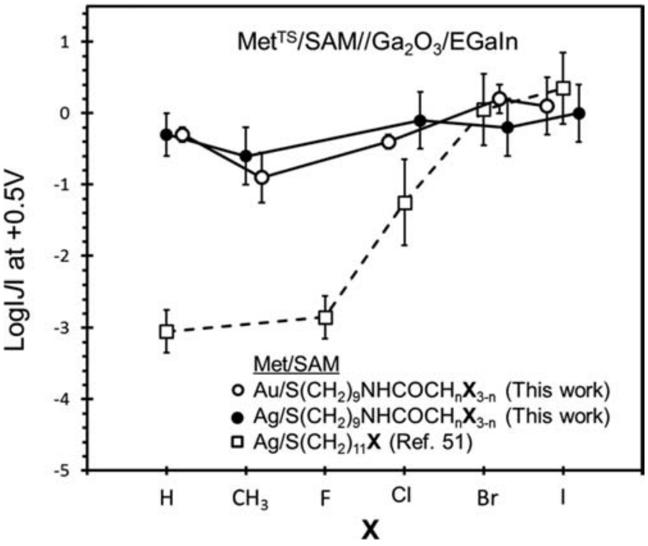

Figure 4. Graphical summary of the data reported for halogenated SAMs. The open black squares (□) are data reported by Nijhuis *et al.* and represent SAMs of the form S(CH$_2$)$_{11}$X.[51] The circles (● and ○) are the data that we are reporting. All data points are log |*J*| collected at +0.5 V, and the error bars are the standard deviation of the mean. The values of all points are slightly displaced laterally for clarity.

Cahen used a related but different junction). For a few selected molecules we also performed a comparison study on Au^{TS} because the tilt angle for alkanethiolates normal to the surface is about 30° for Au^{TS}, whereas for Ag^{TS} the tilt angle is about 10°.[64] This difference in tilt angle makes the molecules more vertical on Ag^{TS} than Au^{TS} and could, in principle, result in a slightly different geometry for contacts at the T//Ga$_2$O$_3$ interface.

We used disulfides (RSSR) rather than thiols (RSH) in preparing the SAMs because they are substantially less reactive than thiols (RSH especially thiolates RS$^-$) in S$_N$2 reactions with $-$HNCOCH$_2$X (X = Cl, Br, or I) and $-$CH$_2$CH$_2$CH$_2$X (X = Cl, Br, or I).[56] (X = F is unreactive, as are C$_6$H$_4$X, X = F, Cl, Br, and I.) SAMs formed from disulfides are similar in structure to those formed from thiols.[64,65] Prior studies by us[65] and others[66] have compared SAMs formed from thiols and disulfides using X-ray photon spectroscopy and contact angle measurements. Contact angle measurements ($\theta_{H_2O}^{a}$) were 3−5° lower for SAMs formed from disulfides than from thiols. This difference was interpreted to support the inference that SAMs formed from disulfides may be slightly less organized than those from thiols.[65] The small difference in contact angle should not, so far as we understand the correlation between these properties, correlate with a significant difference in the tunneling current densities.

Characterization of SAMs. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) confirmed that the calculated thicknesses (*d*) of all the SAMs were similar to those reported previously for alkanethiolate SAMs with same number of atoms (see Table 1 for details). We infer that all SAMs were similarly densely packed. We also conclude that SAMs formed from compounds **1−11** have ordered supramolecular struc-

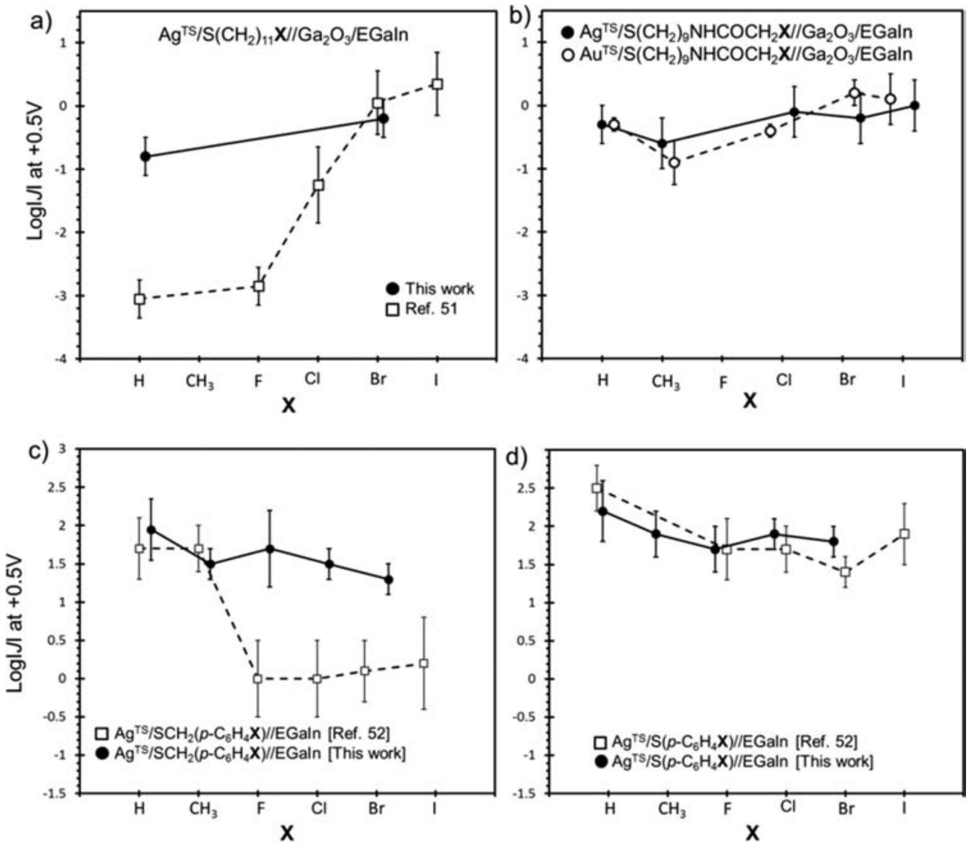

Figure 5. Graphical summary of the data reported for halogenated SAMs reported by Nijhuis[51] and Yoon *et al.*[52] The open red squares are the data that we are reporting. All data points are log|*J*| collected at +0.5 V, and the error bars are the standard deviation of the mean.

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Table 1. Summary of the Results We Obtained in This Study with a Junction of the Form $Ag^{TS}/S(CH_2)_9T//Ga_2O_3/EGaIn$

	thickness (nm)[a]			log |J| at +0.5 V[d]	
T (compound)	estimated[b]	measured	work function (eV)[c]	Ag^{TS}	Au^{TS}
$CH_2CH_2CH_3$ (**1**)	1.61	1.56	4.0 ± 0.2	−0.9 ± 0.2	−0.7 ± 0.2
$CH_2CH_2CH_2CH_3$ (**2**)	1.73	1.80	4.0 ± 0.2	−1.0 ± 0.3	−0.8 ± 0.2
$NHCOCH_3$ (**3**)	1.58	1.50	4.0 ± 0.2	−0.3 ± 0.3	−0.3 ± 0.1
$NHCOCF_3$ (**4**)	1.61	1.54	4.8 ± 0.2	0.0 ± 0.3	
$NHCOCH_2CH_3$ (**5**)	1.71	1.62	4.0 ± 0.2	−0.6 ± 0.4	−0.9 ± 0.4
$NHCOCH_2Cl$ (**6**)	1.66	1.60	4.4 ± 0.2	−0.1 ± 0.4	−0.4 ± 0.1
$NHCOCH_2Br$ (**7**)	1.68	1.54	4.0 ± 0.2	−0.2 ± 0.4	0.2 ± 0.2
$NHCOCH_2I$ (**8**)	1.70	1.79	3.9 ± 0.2	0.0 ± 0.4	0.1 ± 0.4
$NHCOCHCl_2$ (**9**)	1.63	1.53	4.0 ± 0.2	0.1 ± 0.4	
$NHCOCCl_3$ (**10**)	1.66	1.71	3.8 ± 0.2	0.1 ± 0.4	
$NHCOCBr_3$ (**11**)	1.65	1.52	4.0 ± 0.2	0.0 ± 0.5	

[a] Thickness measurements were done for SAMs on Ag^{TS} (for details see SI). [b] The calculated thickness is based on the assumption that SAMs on the Ag^{TS} surface have a tilt angle of 10°.[64] For our calculations we calculate the length in nm for an all trans-extended conformation from the anchoring sulfur atom that chemically contacts the surface of metal substrates to the distal hydrogen atom. [c] Work function measurements were done for SAMs on Ag^{TS}. [d] The error bars reported are of the standard deviation of the mean values of log |J| at +0.5 V.

tures that are similar to those of SAMs of alkanethiolates. We do not, however, have information relevant to the detailed structure (especially the geometry of the $CH_2NHCOCH_{3-n}X_n$ groups at the interface between the SAM and Ga_2O_3/EGaIn).

Tunneling Current Densities. Figure 2 summarizes the tunneling current collected for the molecules identified in Figure 1 at V = +0.5 V. Figure 3 shows log |J|−V plots for SAMs of molecules **1**−**11** on Ag^{TS}. As controls, we used SAMs prepared from C_{12} and C_{13} disulfides. These SAMs are approximately the same length as the halogenated species we were primarily interested in examining (as measured by XPS).

The current density measurements across SAMs of molecules **1** and **3** are statistically indistinguishable (Figures 2 and 3). This control experiment shows that the presence of an amide bond does not significantly influence the current density and agrees with our previous results.[59]

Tunneling Current Is Not Sensitive to the Presence of Halogen Atoms at the $T//Ga_2O_3$/EGaIn Interface. Addition of a single halogen atom also does not significantly influence current density across the SAMs used in this study (Figures 2 and 3 and Table 1). Changing the T from CH_3 (molecule **5**) to I (molecule **8**) produced the largest change in current density at ±0.5 V, but this change was only a factor of 3 (Δlog |J| = 0.5) and at the edge of statistical significance. Considering the typical magnitude of the standard deviation of mean values in EGaIn measurements ($\sigma_{\log}$ = 0.2−0.5), we consider any changes smaller than a factor of 3 to be too small to be assigned reliably to a significant change in tunneling current. Nonoverlap of standard deviations assumes a specific statistical model for the distribution of difference from the mean value and ignores systematic errors. (For more details on factors that influence the current density in EGaIn junctions see refs 23, 24, 33, and 47.) We observed similar results running current density measurements across SAMs of ω-halogenated alkanethiolates on Au^{TS} (Figure 2, Table 1).

Addition of two or three chlorine atoms to the terminal group also does not influence the current density. We also obtained similar results when we used three bromine atoms—in $-NHCOCBr_3$—in the terminal group (log |J| = 0.0 ± 0.5, Figure 2). The change in current density we observed (about a factor of 3) also appears to be much smaller than similar structural changes that have been reported by the Nijhuis group (about 3 orders of magnitude) (Figure 4).[51] We emphasize that this apparent difference—if substantial by further analysis—does not necessarily imply an "error" in either measurement, since all of these junctions, although similar, are different in small but possibly important ways, both in structure and in the procedures used to measure tunneling current.

Our results establish that large changes in the polarizability at the $T//Ga_2O_3$ interface in our junction do not significantly (less than a factor of 3) change the current density, and we infer the details of the tunneling barrier. This result agrees with our previous conclusions that terminal groups with a range of dipole moments (μ = 0.5−4.5 D) and polarizabilities were similar in their current densities.[27] Current density measurements across SAMs of ω-halogenated alkanethiolates (shown in Figure 1) at ±0.5 V result in no significant rectification (Figure 3, $r^+(J(+0.5\ V)/J(-0.5\ V)) \leq 2$).

Measurements of work function (WF) of Ag surfaces covered by SAMs of molecules **1**−**11** showed that except for SAMs of molecule **6** (T = HNCOCl, WF = 4.4 ± 0.2 eV) and **4** (T = $HNCOCF_3$, WF = 4.8 ± 0.2 eV) changing the CH_2 units to amide, or the top interface from H to Br or I, does not significantly change the work function (Table 1). This observation could be explained by the fact that the work function of metal surfaces is influenced by the surface coverage of the SAM and the *net* dipole moment of the SAM.[67] Our XPS results suggest SAMs of molecules **1**−**11** are packed in similar surface coverage. The net dipole moment of the SAM depends on the dipole moment of individual molecules that make up the SAM and the conformation of the molecules in the SAM (*i.e.*, how molecules and/or polar groups oriented).[14,67−70] In this series of molecules (**1**−**11**), although replacing an ethyl (CH_2CH_2) group with amide (HNCO) group and/or replacing a methyl group with halogens introduces a dipole moment ($\mu_{amide} \approx 4$ D, $\mu_{C\text{-halogen}} \approx 1.7$−1.9 D) in individual molecules, when they form SAMs on Ag^{TS} surfaces, the orientation of amide and/or carbon−halogen bonds in molecules might not be uniform and dipole moments of individual molecules might cancel each other out.

To expand our study, we compared the current density across SAMs of $HS(p\text{-}C_6H_4)X$ and $HSCH_2(p\text{-}C_6H_4)X$ (X = H, CH_3, F, Cl, Br) series. The results of our measurements showed that replacing CH_3 with halogen atoms at $T//Ga_2O_3$ does not influence the current density significantly (Figure 5).

This conclusion is in qualitative agreement with the observation of the Yoon group.[51] Our results show a good agreement with their measured current densities across SAMs of HS(p-C_6H_4)X. Measurements across SAMs of $HSCH_2$(p-C_6H_4)X, however, did not show the factor of 50 decrease in current density on changing X from CH_3 to halogen atoms that was reported by the Yoon group (Figure 5).

Comparison between current densities across SAMs of **3** (T = $NHCOCH_3$) and **4** (T = $NHCOCF_3$) showed that replacing CH_3 with CF_3 at the T//Ga_2O_3 interface does not significantly influence the current density. At first this observation seemed not to be consistent with our previous work illustrating that SAMs of fluorinated alkanes resulted in an up to 20 times decrease in current density relative to SAMs of alkanes.[46] In that study,[46] we related the decrease in current density across SAMs of fluorinated alkanes to very low polarizability of fluorine atoms that reduces the wettability of SAMs and eventually reduces the effective contact between the SAM and Ga_2O_3 (fluorinated SAMs are hydrophobic, but the Ga_2O_3 layer of the top EGaIn electrode is hydrophilic). Due to the presence of an amide bond next to CF_3, SAMs of molecule **4** (T = $NHCOCF_3$), however, could have different wettability or force enough interaction with the polar Ga_2O_3 surface.

We measured the static contact angles with water for SAMs of molecule **4**, with the result that the stationary water contact angle of SAMs of molecule **4** (θs = 73 ± 5°) is significantly smaller than what has been reported for SAMs of fluorinated alkanes (θs ≈ 121 ± 5°)[46] (*i.e.*, SAMs of molecule **4** were wet better by water than SAMs of fluorinated alkanes). These results are compatible with our reported hypothesis[46] that in fluorinated alkanes a weak physical contact (wetting or adhesion) of the C−F-containing surface by Ga_2O_3 at the CF_3//Ga_2O_3 interface might result in a lower area of effective electrical contact for a F//Ga_2O_3 interface than for a H//Ga_2O_3 interface.[46] For SAMs of molecule **4** (T = $NHCOCF_3$), the amide group (NHCO) underneath the CF_3 group could perhaps interact with Ga_2O_3 (*e.g.*, by hydrogen bonding), and we do not see a weak contact similar to SAMs of fluorinated alkanes (T = CF_2CF_3).[46]

We conclude that the presence of a polarizable group (*e.g.*, halogen atom) at the T//Ga_2O_3 does *not* significantly influence the tunneling current across the Ag^{TS}/S-$(CH_2)_9NHCOCH_nX_{3-n}$//Ga_2O_3/EGaIn junctions and see no sign of the large increase reported by Cahen (for a different type of junction). Our conclusion is also in contrast with that reported by the Nijhuis group, who observed a 3 orders of magnitude increase in the tunneling current on replacing a hydrogen atom with bromine and/or iodine in a junction with a structure of $Ag^{TS}/S(CH_2)_{10}CH_2$-X//Ga_2O_3/EGaIn (Figure 4).[51]

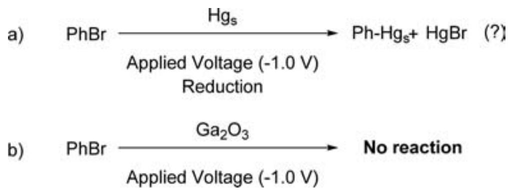
A comparison between the results of this study and molecules studied by the Nijhuis group (Figure 4) suggests that the difference in the conclusions of the two studies arises from the unexpected difference in current densities measured for SAMs when T = CH_3 rather than from current densities of halogenated and nonhalogenated groups (which are in good agreement). To look at this problem more carefully, we synthesized $HS(CH_2)_{10}CH_2\mathbf{Br}$ and, similar to their study, measured the current density across SAMs of $HS(CH_2)_{10}CH_2\mathbf{H}$ and $HS(CH_2)_{10}CH_2\mathbf{Br}$. When we measured the current density following their experimental procedure (which differs from ours in that it forms junctions using a smaller contact pressure for the junctions), we observed a higher current density for SAMs of $Ag^{TS}/S(CH_2)_{10}CH_2\mathbf{Br}$ ($\log |J_{Br}| = 1.1 \pm 1.1$) than SAMs of $Ag^{TS}/S(CH_2)_{10}CH_2\mathbf{H}$ ($\log |J_H| = -1.7 \pm 0.5$) (Figures S4 and S5; that is, a factor of about 600). We did not observe a significant change in current density when we used junctions with the higher contact pressure that we normally use (since this procedure yields more stable and reproducible results than those at lower pressure[47]) and which we have characterized in some detail.[47] The most relevant values from our work at high pressure are $\log |J_{Br}| = -0.2 \pm 0.4$ and $\log |J_H| = -0.8 \pm 0.3$.

CONCLUSION

This work shows that changing the polarizability of SAMs at the T//Ga_2O_3 interface in junctions with the structure of $Ag^{TS}/S(CH_2)_9NHCOCH_nX_{3-n}$//$Ga_2O_3$/EGaIn (with X = CH_3, F, Cl, Br, and I) has no (or small unobservable by our method) effect on the magnitude of tunneling current densities. This result is in agreement with our previous studies about the relations between molecular structure and tunneling (particularly previous studies on the effect of the structure of the top interface), which suggests that in most derivatives of *n*-alkyl SAMs, when measured using the EGaIn junction, the SAM seems to act primarily as a structurally homogeneous insulator and that many common organic functional groups do not modify the tunneling barrier sufficiently to influence the tunneling current density.[25−27,29,46,57,58,71] This work also demonstrates that in SAM-based molecular junctions a careful analysis of physical properties of the SAM and electrodes such as WF of the bottom electrode, wettability of SAM, and the nature of the contact between electrodes and SAM should take place to understand the origin of changes in tunneling conductivity of SAMs.

Our results are in contrast with those reported by Cahen *et al.*,[50] who reported an increase of 8 orders of magnitude in current density on changing the terminal group (X) from CH_3 to Br in junctions with a structure of Si/$(CH_2)_2$(p-C_6H_4X)//Hg. This junction has the potential to be significantly different in its mechanism than ours. Cahen's group used a mercury drop as the top electrode; the change has the potential to change the chemical reactivity (especially in terms of electrochemical redox activity) at the top electrode when in contact with the same functional groups. It is possible that the results observed by Cahen's group reflect, in some part, an electrochemical reaction between the Hg electrode and Ph-Br-based SAM; the nature of the interaction between the SAM and the Hg electrode might thus change from an initial van der Waals contact for Ph-Br//Hg and (perhaps) to formation of a covalent bond between phenyl and mercury (Ph−Hg, Scheme 1) by one- or two-electron reduction.[72] Although we have no direct evidence to support this suggestion, two observations are

Scheme 1. (a) A plausible electrochemical reaction between PhBr and Hg under the applied voltage of −1.0 V. (b) Ga_2O_3 does not react with PhBr at −1.0 V. "Hgs" indicates the mercury surface.



consistent with this hypothesis: (i) the increase in current density was only observed when the Hg electrode was reducing (*i.e.*, at negative bias), and (ii) using a similar junction (Hg drop as the top electrode), the Cahen group also studied SAMs of terminally brominated alkanes using a junction with a structure of Si/$(CH_2)_{11}$Br//Hg and observed a significantly smaller increase of about an order of magnitude in the current density relative to SAMs of nonbrominated alkanes (Si/$(CH_2)_{11}$H//Hg).[49] This difference would be compatible with an electrochemical reaction process. Considering the very different surface chemistry and reactivity of Ga_2O_3 and mercury, we, thus, do not believe that our findings are directly comparable to Cahen's group's work. The results raise, however, the very interesting (but previously untested) possibility that direct interaction between reactive groups on the terminus of a SAM and an appropriately reactive metal (Hg, perhaps Au in evaporated Au top electrodes) might provide a new SAM-based tunneling junction in which the organic SAM is bonded to both the top and bottom electrode surfaces.

Our conclusion is different from the work of the Nijhuis group while using the Ga_2O_3/EGaIn top electrodes. In comparison with Cahen's group, the enhancement they observed in the current density is smaller and is about 3 orders of magnitude. It appears, however, to come from what appears to be an unexpectedly small value for T = H, rather than a high value for T = Br. In this work, using a so-called "low"-pressure contact, we have approximately reproduced their experiments for compounds $HS(CH_2)_{10}CH_2\mathbf{H}$ and $HS(CH_2)_{10}CH_2\mathbf{Br}$ (Figures S4 and S5) (we observed an enhancement of about a factor of 600). We tentatively conclude that the difference between the work of Nijhuis and the work we report is procedural; that is, they use a low contact pressure in the junction and we use (for reasons we have fully described elsewhere)[47] a higher pressure one. These two procedures may have different sensitivities and thus measure different phenomena in some cases. Also, in our hands, measurements at low contact pressures are significantly noisier and more variable than those at higher pressure and may thus be less reproducible.

METHODS

Formation of SAMs of Halogen-Terminated Alkanethiolates. We followed a procedure of the type currently used in preparing SAMs.[24,26] In short, a template-stripped silver substrate (Ag^{TS}) was immersed in 5 mL of a 1 mM solution of $[S(CH_2)_9T]_2$ (T = $NHCOCH_{3-n}X_n$) 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.

Thickness Measurements. We used ARXPS to characterize the SAMs of ω-halogen-terminated alkanethiolates. The energy of the incident X-ray beam used by the Thermo Scientifc 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-squares peak fit analysis with the pseudo-Voigt function (a linear combination of Lorentzian (30%) and Gaussian (70%) functions) to fit the XPS spectra with XPSpeak software, and the sloping background was modeled using Shirley plus linear background correction.[73,74] We used pseudo-Voight functions to obtain best fits because it is well known that instrumental factors (*e.g.*, resolution of the analyzer 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 Lorenzian signals of photoelectrons.

Work Function Measurements. We measured work functions using the same XPS system. The samples were held on a specially designed biasing stage that is in electrical contact with the analyzer. The WFs of SAM-modified Ag^{TS} surfaces were calculated by recording two sets of spectra: the peak of the secondary electron (free electrons with low kinetic energy (<50 eV) generated by a photoelectron)[73,75] and the slope of the Fermi edge (see all spectra in the SI, Figures S2 and S3). The cutoff 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 cutoff. The secondary electron cutoff spectra were recorded in the range of 32 to 38 eV kinetic energy, and we extrapolated the secondary electron cutoff 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.

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.[26] Tips were formed by extruding a small droplet of EGaIn from a 10 μL 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.[26] 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 made seven to nine junctions per substrate (*e.g.*, per chip supporting the Ag^{TS} (or Au^{TS})/SAM) and used three 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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b05217.

> Synthesis and characterization of molecules **1**−**11**, histograms of current density measurements for SAMs of molecules **1**−**11**, surface characterization, and the effect of contact pressure on current density (PDF)

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Notes

The authors declare no competing financial interest.

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