Characterizing the Metal–SAM Interface in Tunneling Junctions

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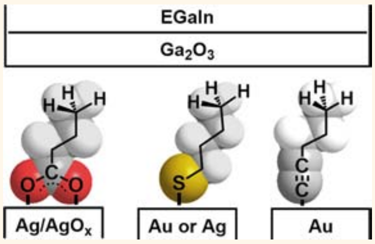
ABSTRACT This paper investigates the influence of the interface between a gold or silver metal electrode and an *n*-alkyl SAM (supported on that electrode) on the rate of charge transport across junctions with structure Met(Au or Ag)^{TS}/A(CH$_2$)$_n$H//Ga$_2$O$_3$/EGaIn by comparing measurements of current density, *J*(*V*), for Met/AR = Au/thiolate (Au/SR), Ag/thiolate (Ag/SR), Ag/carboxylate (Ag/O$_2$CR), and Au/acetylene (Au/C≡CR), where R is an *n*-alkyl group. Values of J_0 and β (from the Simmons equation) were indistinguishable for these four interfaces. Since the anchoring groups, A, have large differences in their physical and electronic properties, the observation that they are indistinguishable in their influence on the injection current, J_0 ($V = 0.5$) indicates that these four Met/A interfaces do not contribute to the shape of the tunneling barrier in a way that influences *J*(*V*).



KEYWORDS: charge transport · EGaIn · molecular electronics · alkynes · self-assembled monolayer

Understanding the relationship between the structure of the insulating organic molecules in junctions of the form Met^{TS}/A(CH$_2$)$_n$T//Ga$_2$O$_3$/EGaIn (TS, template-stripped; EGaIn, eutectic gallium indium), and rates of charge transport across these junctions by tunneling, requires understanding the influences of the interfaces between the electrodes and the self-assembled monolayer (SAM).[1−4] (Here, Met is the "metal" electrode and A and T are "anchoring" and "terminal groups.") The Supporting Information summarizes previous studies of this and other relevant systems of SAM-bound tunneling junctions, generally organized in terms of the injection current, $J_0(V)$, and the attenuation parameter, β, of the simplified Simmons equation,[5] eq 1.

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

Determining the influence of the interface between the SAM and electrode on the shape (for a simple rectangular barrier, the height and width) of the tunneling barrier, and of the current density across that barrier, has motivated a number of investigations.[6−18] Recent studies of single-molecule break junctions have been interpreted to indicate that the presence of covalent Au−C σ-bonds—formed using trimethyltin (−SnMe$_3$)-terminated *n*-alkyl groups,[19,20] and SnMe$_3$-terminated aromatics[19−21] or trimethylsilyl (TMS)-terminated conjugated systems[22]—increases rates of charge transport across these junctions by approximately a factor of 10−100, relative to amine or thiolate anchoring groups. One possible inference from the increase is that the Au−C σ-bond, and the absence of resistive anchoring heteroatoms, increases "conductivity" (although the meaning of this word is not entirely clear for tunneling junctions). Other reports have suggested that the strength of the interaction between the anchoring atom and the metal electrodes influences rates of charge transport, with stronger binding interactions (*i.e.*, Au/SR and Au/NH$_2$R) leading to higher measurements of conductance than weaker interactions (*i.e.*, Au/O$_2$CR and Au/NCR).[23,24] In contrast, using a large-area junction, Cahen and coworkers established that a substantial difference between two types of bonds between the electrode and the SAM did *not* influence rates of tunneling.[25] Using *n*-alkyl-SAMs on silicon, and Hg top electrodes, they demonstrated that a change in the interaction at the SAM-Hg interface—from a

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Received for review October 16, 2014
and accepted January 9, 2015.

10.1021/nn5059216

van der Waals interaction ($-CH_3$//Hg) to a covalent bond (S/Hg)—did not change rates of charge transport.[25]

This paper summarizes a study of the so-called "bottom" (Met^{TS}-AR) interface, based on characterizing $J_0(V)$ and β for three groups, A, chosen to be very different in their electronic and geometrical structure. We measured $J_0(V)$ and β for five SAMs formed by allowing terminal alkynes (1-hexyne, 1-octyne, 1-decyne, 1-dodecyne, 1-tetradecyne) to react with gold, and compared the rates of charge tunneling through these alkyne-based junctions to those through junctions composed of *n*-alkanethiolates[26] and *n*-alkanecarboxylates[27] of comparable lengths on gold and silver. SAMs with composition AuSR and AuC≡CR (R = *n*-alkyl) have very similar geometrical structure.[28]

We conclude that the rate of tunneling transport through Ag/(AgO_x)/O_2CR, Ag/SR, Au/SR, and Au/C≡CR interfaces are—using an "EGaIn" top electrode (that is, Ga_2O_3/EGaIn)—indistinguishable. This work indicates that in these large-area junctions, the details of the chemical binding at the Met/A interface do not significantly influence the injection current or current density: remarkably, the total variation in J_0 across the four systems examined (Figure 1) is no more than a factor of 2. This result does not imply definitively that there are *no* differences in the electronic structure of the interface, or that differences in the Met/A interfaces do not influence the shape of the tunneling barrier associated with those interfaces; rather, they demonstrate that these differences—whatever their nature—do not influence tunneling currents.

RESULTS AND DISCUSSION

In contrast to the ionic interaction of Ag/O_2CR[27,29−31] and the covalent but weak (~30 kcal/mol,[32] estimated by density functional theory, DFT) interaction of Ag(Au)/SR, acetylenes form strong covalent bonds with Au. McDonagh and co-workers calculated, using DFT analysis of ethynylbenzene on Au(111), a bond strength of 70 kcal/mol for Au−C. In SAMs, the Au/C≡CR group orients perpendicularly to the surface;[32−37] Cyganik and co-workers characterized a lattice of $(\sqrt{3} \times \sqrt{3})R30°$ (using scanning tunnelling microscopy) for AuC≡C$(CH_2)_n$H on Au, with parameters similar to those of alkanethiols on Au(111).[28]

This study also demonstrated that these SAMs are susceptible to oxidation during (and possibly after) formation of the Au−C≡CR bond, and require careful handling (see the Supporting Information for more details). In this current work, SAMs were prepared by immersion of template-stripped gold substrates in an anhydrous solution of *n*-alkyne (~6 mM in hexadecane) for 48 h at room temperature under an atmosphere of nitrogen. We monitored the SAM for oxygen contamination using both X-ray photoelectron spectroscopy (XPS) and contact angles with water (Supporting Information Figure S1 and Table S1). Electrical measurements were performed using EGaIn (eutectic Ga−In; 74.5% Ga, 25.5% In) top electrodes over a potential window of ±0.5 V (Figure 2). We and others have described the EGaIn electrode extensively,[26,38−41] and have demonstrated that the ~0.7 nm thick Ga_2O_3 layer forms an ohmic contact with the SAM.[42]

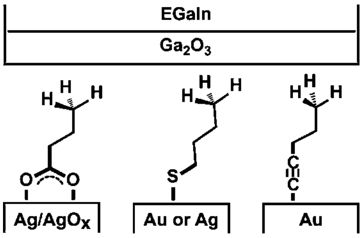


Figure 1. Structure of M^{TS}/A$(CH_2)_n CH_3$//Ga_2O_3/EGaIn junctions with A = $-O_2C-$, $-S-$, and $-C\equiv C-$ on Au^{TS} and Ag^{TS}.

Comparing the Electrical Properties of *n*-Alkyl SAMs Having A = −C≡C− and A =−S− on Gold Electrodes. Figure 2a summarizes values of log|J(0.5 V)| *versus* the length of molecules in Å (estimated for an all-*trans* extended conformation from the anchoring atom that binds to Au to the distal hydrogen atom in van der Waals contact with Ga_2O_3/EGaIn); we did not observe rectification of current (Supporting Information Figure S7). A linear least-squares fit of the data to eq 1 yielded log|J_0(0.5 V)| = 3.9 ± 0.1 and $\beta = 0.67 \pm 0.02$ Å^{-1}. Comparisons of $J(V)$ data between SAMs of *n*-alkynes and *n*-alkanethiolates on Au indicate that junctions comprising these two SAMs result in statistically indistinguishable values of the injection current (log|J_0(0.5 V)| = 3.9 ± 0.1 for *n*-alkynes; log|J_0(0.5 V)| = 4.2 ± 0.2 for *n*-alkanethiolates). Thus, replacing Au/SR with Au/C≡CR, a change that substantially alters the molecular and electronic structure of the Met/A interface, has no statistically significant influence (that we can detect) on the injection current across *n*-alkyl-based SAMs.

The values of β are, perhaps, marginally distinguishable across *n*-alkynes and *n*-alkanethiolates ($\beta = 0.67 \pm 0.02$ Å^{-1} for *n*-alkynes; $\beta = 0.76 \pm 0.02$ Å^{-1} for *n*-alkanethiolates); we note, however, that the standard deviation ($\sigma_{log} \sim 0.5$) in $J(V)$ for each point results in overlap between the linear least-squares fits for the *n*-alkynes and *n*-alkanethiolates. Figure 2b considers the distance of the barrier only in terms of the number of methylene (CH_2) units. This plot demonstrates that the current densities measured for alkynes and alkanethiolates on gold having an equivalent number of methylene units are superimposable, with the exception of hexyne ($n = 4$). SAMs of hexyne and hexanethiol could plausibly become less ordered with shorter chain lengths than SAMs composed of longer chains;[43]

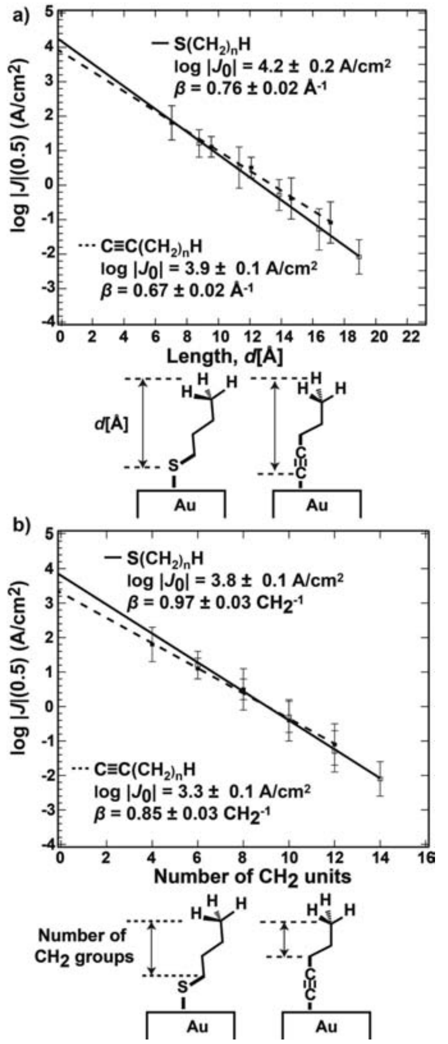


Figure 2. (a) Plot of the Gaussian mean values of log|*J*| at +0.5 V *versus* molecular length (calculated in Å for an all *trans*-extended conformation) for *n*-alkynes (dashed linear−least-squares fit) and *n*-alkanethiolates (solid linear−least-squares fit) on Au^{TS}. The distance is calculated from the anchoring atom (S or C) to the distal hydrogen atom. (b) Plot of the Gaussian mean values of log|*J*| at +0.5 V *versus* number of methylene units (CH$_2$).

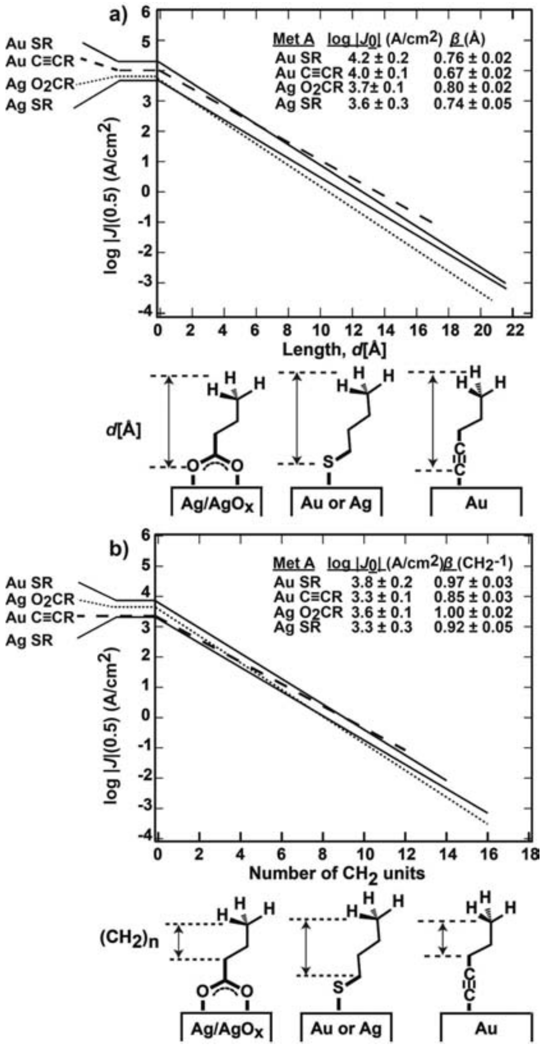


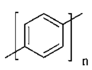
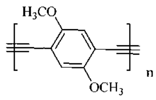
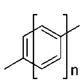
Figure 3. (a) Plot of the Gaussian mean values of log|*J*| at +0.5 V *versus* molecular length (calculated in Å for an all *trans*-extended conformation) for alkyl SAMs having A = −S−, −C≡C−, and −O$_2$C−;[27] the distance is calculated from the anchoring atom A that chemically contacts to the surface of metal substrates, to the distal hydrogen atom (A−(CH$_2$)$_n$−H). (b) Plot of the Gaussian mean values of log|*J*| at +0.5 V *versus* number of methylene units.

increasing disorder could lead to deviations from the Simmons equation for several reasons (especially, changes in conformation of the chains; see the Supporting Information for additional information). The conclusion that values of β do not depend on the Metal/A interface is in agreement with single-molecule studies.[17,44]

Comparing the Electrical Properties of *n*-Alkyl SAMs Having A = −C≡C−, A = −S−, and A = −O$_2$C− on Gold and Silver Electrodes. Comparisons of the results summarized in Figure 2 with those published previously[3,26,27,45] make it possible to compare the rate of charge transport across length-matched *n*-alkyl SAMs having three different anchoring groups, on two different metals (*i.e.*, Au/SR, Au/C≡CR, Ag/SR, and Ag/O$_2$CR). Values of J_0 and β for the *n*-alkyl SAMs having A = −S−, −C≡C−, and −O$_2$C− (Figure 3a) were indistinguishable when considering the entire length (measured in Å) of the SAM from the anchoring atom (that is, the atom in contact with the bottom metal electrode) to the distal hydrogen. The difference in J_0 observed between *n*-alkanethiolates SAMs on Au^{TS} and Ag^{TS} (log $|J_0|$ = 4.2 ± 0.2 for Au/SR and log $|J_0|$ = 3.6 ± 0.3 for Ag/SR) might be attributed to the difference in the work functions of the metals (~5.1 eV for Au and ~4.3 eV for Ag), and was reported previously by Frisbie and co-workers.[17]

Figure 3b provides a comparison of the rates of charge transport when we exclude the anchoring group as a contributor to the width of the tunneling barrier; that is, when we estimate the distance of the tunneling barrier to be only the number of CH$_2$ units in the *n*-alkyl group. Although this figure yields lower

TABLE 1. Comparison of Electrical Measurements from Literature Reports on Changes to the Met/A Interface

Measurement Technique	Insulating Barrier	Structure of the Junction[a,b]	Ratio of Measured Conductance	Ref
Hg top-electrode	*n*-alkyls -$(CH_2)_n$-	Si/$CH_2(CH_2)_n$**CH_3//Hg** Si/$CH_2(CH_2)_n$**S/Hg**	$\frac{S/Hg}{CH_3//Hg} \sim 1$	14
STM break junction	*n*-alkyls -$(CH_2)_n$-	**Au/CH_2**$(CH_2)_n$**CH_2/Au** **Au/NH_2**$(CH_2)_n$**NH_2/Au**	$\frac{CH_2/Au}{NH_2/Au} \sim 100$	19
	n-alkyls -$(CH_2)_n$-	**Au/S**$(CH_2)_n$**S/Au** **Au/H_2N**$(CH_2)_n$**NH_2/Au** **Au/O_2C**$(CH_2)_n$**CO_2/Au**	$\frac{S/Au}{NH_2/Au} \sim 18$ $\frac{S/Au}{CO_2/Au} \sim 95$	23
	Oligo-phenyls 	**Au/CH_2**$(C_6H_4)_n$**CH_2/Au** **Au/H_2N**$(C_6H_4)_n$**NH_2/Au**	$\frac{CH_2/Au}{NH_2/Au} \sim 100$	21
	Oligo-(phenylene ethynylene)s  (OPEs)	**Au/C≡C**(OPEs)**C≡C/Au** **Au/S**(OPEs)**S/Au**	$\frac{C≡C/Au}{S/Au} \sim 10$	22
CP-AFM	Oligoacenes 	**Au/CN**-oligoacene-**H//Au** **Au/S**-oligoacene-**H//Au**	$\frac{NC/Au}{S/Au} \sim 3$	44

[a] Bold text indicates the interface(s) changed. [b] The "/" indicates a covalent bond and "//" indicates a van der Waals contact.

values of J_0 than those in Figure 3a, a finding that is consistent with a reduction in the estimation of the tunneling barrier with the exclusion of the anchoring group, the values of the injection current for each A = −S−, $-O_2C-$, and −C≡C− are statistically indistinguishable. We conclude, then—based on the investigation of a wide range of anchoring groups—that the chemical identity of the anchoring group (and its chemical interactions with the electrodes) does not influence the rates of charge transport. We do not detect any difference in their contribution to the energetic topography of the tunneling barrier as differences in $J(V)$ or β.

Influence of the Met/A on the HOMO. Given the distinctions in the chemical and electronic properties of A = −S−, −C≡C−, and $-O_2C-$, the similarity in the rates of charge transport is surprising. Electronic structure calculations using DFT indicated differences of ∼0.5 eV in the highest occupied molecular orbital energy (HOMO, eV) for *n*-alkyls on gold clusters having A = −S− and A = −C≡C− (Supporting Information Table S3). (Since the HOMO is the closest orbital to the Fermi energy of the electrodes, we assume transport by hole tunneling.) The results indicate that the HOMO for these two types of junctions is localized on the anchoring atoms (here, −S− and −C≡C−); this observation is in agreement with DFT calculations by Mirjani *et al.* on amide-containing alkanethiolates.[46,47] A careful consideration of the MOs localized on the *n*-alkyl fragments revealed spatially and energetically indistinguishable MO patterns between *n*-alkynes and *n*-alkanethiolates, indicating that changes to the anchoring atom have littte or no influence on tunneling through the alkyl chain (Supporting Information Table S3). These orbital calculations, in combination with the measurements of charge tunneling, suggest that the height of the tunneling barrier is dominated by the orbital energies of the MOs localized on the *n*-alkyl groups, and although there may be differences in the orbital energies associated with Metal/SAM interface (when A = −S− or −C≡C−), these differences are not sufficient to alter the rate of charge transport across the junction.

A Comparison of the Influence of Met/A on Charge Tunneling across Techniques. To rationalize our results with those reported previously in the literature, we compare the conductance across several classes of insulating units having chemically distinct anchoring groups, A.[19,21−23,25,44] Table 1 summarizes some of the work using single-molecule and large-area junctions across saturated polymethylene and conjugated molecular systems having different anchoring groups. To simplify the comparison, we report a ratio of the electrical measurement values that arise from a change to the

Met/A interface. Measurements using single-molecule techniques ((*i.e.*, scanning tunneling microscope break-junction (STM-BJ) and conductive probe atomic force microscope (CP-AFM)) report a wide range in the factor of change in conductance (~3−100) following modifications to the Met/A interface. For example, Wandlowski and co-workers (ref 22 in Table 1) report a factor of 10 difference in the conductance between Au−C and Au−S contacts using STM, and Venkataraman and co-workers (ref 21 in Table 1) report a factor of 100 difference in conductance between Au−C and Au−NH_2 contacts using STM. It is not clear that one can extract a consensus from these data concerning the influence of the group A on tunneling across junctions having a Met/A interface.

The conclusion from the work presented here—that a change in the Met/A interface does not influence rates of charge tunneling—is, however, in agreement with one other large-area junction measurement. Cahen and co-workers observed—using a Hg large-area junction (ref 14 in Table 1)—no change in tunneling when changing the top metal/SAM interaction from a van der Waals interaction (−RCH_3//Hg) to a chemical bond (−RS/Hg).

We offer three possible rationalizations for the differences in the sensitivity of single-molecule and large-area junctions to changes at the Met/A interface. (i) Large-area junctions probe an ensemble of molecules rather than one or a few molecules; structural defects in the SAM or the metal electrode could limit the ability of a large-area junction to detect differences at the interface. (ii) Single-molecule studies often change the anchoring atom at both electrode/molecule interfaces. One exception is the work by Frisbie and co-workers (ref 44 in Table 1); they changed the bottom electrode/SAM covalent contact (from Au-CNR to Au-SR, where R = oligoacenes), while keeping the van der Waals top contact unchanged, and reported just a factor of ~3 difference in conductance between the two interfaces using CP-AFM. (iii) The nature of the contacts between the molecules and the metal in break junctions is not defined, and the structure of the metal tip is also unclear. These uncertainties limit the ability to compare large-area and break-junction measurements.

CONCLUSIONS

The results from the measurements of tunneling currents of $Met^{TS}/A(CH_2)_nH//Ga_2O_3$/EGaIn show that the electronic properties of the four Met/A interfaces (AuSR, AgSR, AuC≡CR, AgO_2CR), which must be substantially different given the differences among them in binding, contribute similarly to the rate of charge transport. That is, empirically, the details of the chemical binding in the Met/A interface do not appear to influence the injection current (in a large-area EGaIn junction). One (of several) possible explanations for the insensitivity of the rates of charge transport to differences in the Met/A interface rests on the fact that the SAMs examined here were *n*-alkyl groups—polymethylene chains, $-(CH_2)_n-H$. These groups, although structurally simple, facilitating the systematic study of changes only at the Met/A interface, are characterized by large HOMO−LUMO gaps (~7−9 eV),[14] which lead to high tunneling barriers and high values of β. In this view, the rate of tunneling is dominated by transport through the *n*-alkyl chain (with perhaps a contribution from the noncovalent SAM//Ga_2O_3 interface), and differences in the electronic structure and orbital energy levels at the Met/A interface are not important in determining rates of charge tunneling across these junctions.[24,48] Analysis of SAMs having small HOMO−LUMO gaps (~3−5 eV, *i.e.*, highly conjugated systems)[14] may show a greater sensitivity to the details of the Met/A interface differences in rates of charge tunneling; that is, if the HOMO or the LUMO levels of the SAM are brought closer to the Fermi level of the electrode, differences in the strength and structure of the Met/A interface might then play a role in rates of charge transport.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Detailed experimental procedure, histograms of current densities, and summary of junction measurements. This material is available free of charge *via* the Internet at http://pubs.acs.org.

Acknowledgment. This work was supported by a subcontract from Northwestern University from the United States Department of Energy (DOE, DE-SC0000989) and by the National Science Centre Poland (Grant DEC-2013/10/E/ST5/00060). The DOE grant from Northwestern also supported the salary for C.M.B, K.-C.L, and M.B. The Cyberdiscovery Initiative Type II (CDI2) grant from the National Science Foundation (NSF, OIA-1125087) supported the salary for D.R. Sample characterization was performed at the Center for Nanoscale Systems (CNS) at Harvard University, a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation (ECS-0335765). In particular, we appreciate the assistance of Dr. Hao-Yu Lin at CNS with XPS analysis. We also thank Andreas Roetheli for helpful discussions concerning the oxidation of acetylene.

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