The Rate of Charge Tunneling Is Insensitive to Polar Terminal Groups in Self-Assembled Monolayers in Ag TS S(CH 2) n M(CH 2) m T//Ga 2 O 3 /EGaIn Junctions

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The Rate of Charge Tunneling Is Insensitive to Polar Terminal Groups in SAMs in $Ag^{TS}S(CH_2)_nM(CH_2)_mT//Ga_2O_3/EGaIn$ Junctions

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Supporting Information Placeholder

ABSTRACT: This paper describes a physical-organic study of the effect of uncharged, polar, functional groups on the rate of charge transport by tunneling across self-assembled monolayer (SAM)-based large-area junctions of the form $Ag^{TS}S(CH_2)_nM(CH_2)_mT//Ga_2O_3/EGaIn$. Here Ag^{TS} is a template-stripped silver substrate, -M- and -T are "middle" and "terminal" functional groups, and EGaIn is eutectic gallium-indium alloy. A range of uncharged polar groups (-T), having permanent dipole moments in the range $0.5 < \mu < 4.5$, were incorporated into the SAM. A comparison of the electrical characteristics of these junctions with junctions formed from n-alkanethiolates led to the conclusion that the rates of charge tunneling are insensitive to the replacement of terminal alkyl groups with terminal polar groups. The current densities measured in this work suggest that the tunneling decay parameter (β) and injection current (J_o) for SAMs terminated in non-polar n-alkyl groups, and polar groups, are statistically indistinguishable.

A central goal in the field of molecular electronics is to understand relationships between rates of charge transport and molecular structure.[1-12] One current focus for inquiries is the importance of the two interfaces: Ag^{TS}-SR and $T//Ga_2O_3$, where Ag^{TS} is a template-stripped silver substrate, and T is a terminal functional group. This paper focuses on the latter interface, and examines the influence of the group T on the rate of charge transport. Our results[7,13-15] (and those obtained using other types of junctions[9,11,16-24]) have not led to a single, broad conclusion about this matter: some groups T seem to change the rate of charge transport (relative to a methyl group); some do not (Table S1 in the Supporting Information). Using self-assembled monolayer (SAM)-based large-area junctions having the structure $Ag^{TS}S(CH_2)_nM(CH_2)_mT//Ga_2O_3/EGaIn$, we have explored the influence of the terminal group, T, of the SAM on the tunneling current. We have observed odd-even effects[13] for n-alkanethiolates on silver, and rectification[14,15] in ferrocene-terminated n-undecanethiolates. We have also, rather surprisingly, observed that the tunneling current is insensitive

(within the precision of our measurements) to the structures of a range of nonpolar terminal aromatic and aliphatic groups with different geometries and electronic structures.[7] We have no single mechanistic picture that includes all of these results.[7,13-15]

This paper focuses on a specific physical-organic question: Do molecular dipoles, particularly when placed at the top-interface between a thin, electrically insulating organic film (a SAM) and a conducting top-electrode, influence the rates of charge transport by tunneling? [25,26] To answer this question, we examined the electrical characteristics of SAM-based large-area junctions of the form $Ag^{TS}S(CH_2)_nM(CH_2)_mT//Ga_2O_3/EGaIn$, where -M- (either -CONH- or $-CH_2CH_2-$) and -T (polar groups) are middle and terminal functional groups, and $Ga_2O_3/EGaIn$ is the top electrode we have described previously.[7,13-15,27,28] The interface, which exists between the top of the SAM and the rough Ga_2O_3 film that covers the EGaIn in the "conical tip" electrode, is a van der Waals contact. We systematically modified the terminal portion of the SAM with polar groups (-T, Figure 1) that are uncharged, but have significant group dipole moments ($0.5 < \mu < 4.5$), and measured the current density (J A/cm^2) at low bias ($\pm 0.5V$). We targeted a wide range of polar groups, regardless of molecular length; and compared their
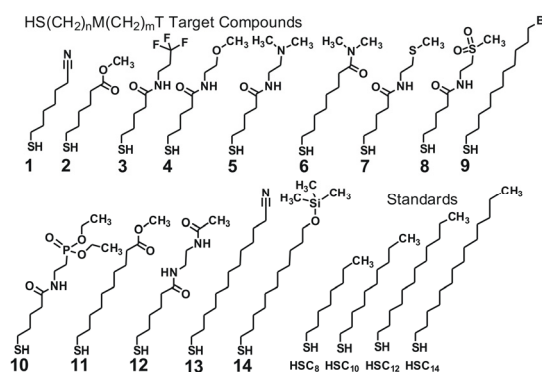

Figure 1. Molecules with polar terminal groups and n-alkanethiols (as standards) used to form SAMs.

current densities with those of hypothetical *n*-alkanethiolates of the same lengths (estimated by a well-defined model: the simplified Simmons equation, *vide infra*). Surprisingly, we found that the presence of a range of molecular dipoles of different structures at the SAM//Ga$_2$O$_3$ top-interface does not significantly change the rate of charge tunneling.

The simplified Simmons equation (Eq. 1) is commonly

$$J(V) = J_o(V)e^{-\beta d} \qquad \text{Eq. 1}$$

used to summarize measurements of rates of charge transport through molecular junctions. The assumption underlying in this equation is that the tunneling barrier is rectangular (or approximately so). This assumption certainly does not describe a SAM exactly, but the extent to which the obvious differences between theory and reality are important in rationalizing trends in $J(V)$ with structure remains undefined. In Eq. 1, $J(V)$ is current density (current divided by the geometrical area determined by a microscopy; A/cm^2) at an applied voltage V. The injection current at an applied voltage V is $J_o(V)$: it is the current density for a hypothetical junction in which the SAM has no thickness but the interfaces are those characteristic of a SAM-contacting junction. The tunneling decay parameter (Å^{-1}) is β, which contains information about the height of the barrier; it is determined by the molecular structure of the backbone in the SAM. The width of the barrier across which charges traverse is d (Å).

Our study on the rates of charge transport is a physical-organic study: that is, one focusing on *trends* in current densities as a function of variations in the structures of molecules, rather than on absolute values of these measurements. We focus on trends of current densities as a function of molecular structure in the SAMs, rather than on absolute values. Values of β for *n*-alkanethiolates have been widely reproduced (across many users and different research groups) and provide a reproducible internal standard.

Molecular dipoles, introduced into the SAMs by molecules having polar functional groups, are readily dissipated or cancelled by disorder in the SAMs and by interactions with the electrodes and/or with neighboring molecules. Several studies[29-34] previously reported depolarization in SAMs formed with dipolar molecules: for example, Gershevitz et al.[33] reported that changes in molecular dipoles in the SAM are due to changes in molecular conformation and order of the molecular layers.

We emphasize that the association of a dipole moment with a terminal group T does not translate into an electrostatic field perpendicular to the SAM at the top interface. Antiparallel orientation of the polar groups can result in an effective cancellation of dipolar fields. The effect of the imposed electrostatic field on this orientation of polar groups in the SAM is also not known.

Figure 1 shows the polar molecules we examined. The choice of the polar terminal groups allowed us to avoid the complexity of ionization state (e.g., CO$_2$H versus CO$_2^-$) and ambiguities arising from the counter-ions (e.g., CO$_2^-$Na$^+$ versus CO$_2^-$H$_3$O$^+$). For the backbone, the electrical equivalence (insignificant differences in the rates of charge transport) between internal (the M region) -CH$_2$CH$_2$- and -CONH- groups allowed us to use synthetically-accessible, amide-containing compounds.[7,27]

We estimated the molecular length in angstroms of the target molecules through modeling using ChemDraw 3D software, assuming an extended, all-trans conformation (Figure 1). The lengths of the molecules were calculated from the sulfur head-group to the distal atom (hydrogen or other elements) closest to the top-electrode. The central strategy in this study is to compare electrical characteristics of molecules with different structures, regardless of length. The well-defined values of β and J_o of *n*-alkanethiolates in the EGaIn-based tunnel junctions make it possible to estimate the current density for a hypothetical *n*-alkanethiolate of the same length as the target molecule (with a length ranging from methyl to *n*-octadecyl), and thus to compare current densities of target molecules with hypothetical *n*-alkanes of the same length. This strategy makes it possible to compare a number of molecules with different structures and lengths, and SAMs of different thicknesses, and avoids (or minimizes) laborious synthesis of molecules with constant lengths.

We prepared SAMs on Ag^{TS} substrates, and formed and characterized the molecular junctions with an "unflattened" conical Ga$_2$O$_3$/EGaIn tip[7,27] (See the Supporting Information for more detail). Histograms (based on 342 – 548 *J-V* scans) of values of $J(V)$ exhibited approximately log-normal distributions (Figure S1 in the Supporting Information); fitting Gaussian curves to these histograms yielded mean values and standard deviations (σ_{log}) of log$|J(V)|$. Table S2 in the Supporting Information summarizes the data from the junction measurements. Mean and median values for the histograms of $J(V)$ were indistinguishable (this observation indicates that outliers do not distort the mean values calculated using Gaussian curve fit to the data[35]).

Comparisons of the tunneling rates of SAMs with the structure S(CH$_2$)$_n$M(CH$_2$)$_m$T, and of standards with T = -CH$_3$ in Figure 2A, led to the surprising conclusion that current densities (log$|J_{polar}|$) for the S(CH$_2$)$_n$M(CH$_2$)$_m$T were statistically indistinguishable from current densities (log$|J_{CH3}|$) for *n*-alkanethiolates standards of the same (hypothetical) thicknesses; log$|J_{CH3}|$ was estimated through substitution of the estimated length (Å) of polar molecule, S(CH$_2$)$_n$M(CH$_2$)$_m$T, into the algebraic equation of the linear least squares fit for *n*-alkanethiolate standards. The difference in log$|J|$ (Δlog$|J|$ = log$|J_{polar}|$ - log$|J_{CH3}|$) was ≤ 0.5, or less than a factor of three in $|J|$. The typical range of σ_{log} observed in the EGaIn-based junctions is ~0.1 – 0.5, which corresponds to $\Delta|J|$ ≤ ×3: two values of $J(V)$ less than ×6 apart (Δlog$|J(V)|$≤0.8) cannot therefore be distinguished without other information.

The rate of charge tunneling through Ag^{TS}S(CH$_2$)$_n$M(CH$_2$)$_m$T//Ga$_2$O$_3$/EGaIn junctions was independent of the structure of polar functional groups T (**1** – **14** in Figure 1), and there was no correlation between the molecular dipole of T and variations in the values of log$|J|$ (Figure 2B). The polar functional groups T also had no effect on the symmetry of *J-V* curves: the rectification ratios (r, r = $|J(+V)|/|J(-V)|$) were ~1.0 – 1.3 (Table S2 in the Supporting Information), regardless of the structure or dipole moment of T. Similar values are observed for *n*-alkanethiolates. We regard these values as indicating "no rectification".

The absence of rectification is an interesting result. We imagined that the application of a strong applied electric field (*ca.* 250MV/m, assuming that the distance between top and bottom electrodes is 2 nm at ±0.5V) might orient (at

least partially) the dipoles at the top-interface at one polarity, and lead to the generation of a local electric field and a decrease in the net electric field gradient, and thus, perhaps, to rectification. The lack of rectification, regardless of the polarity of dipole, suggests that such a local electric field (if it is generated) at the top-interface has no detectable influence (by our measure) on r.
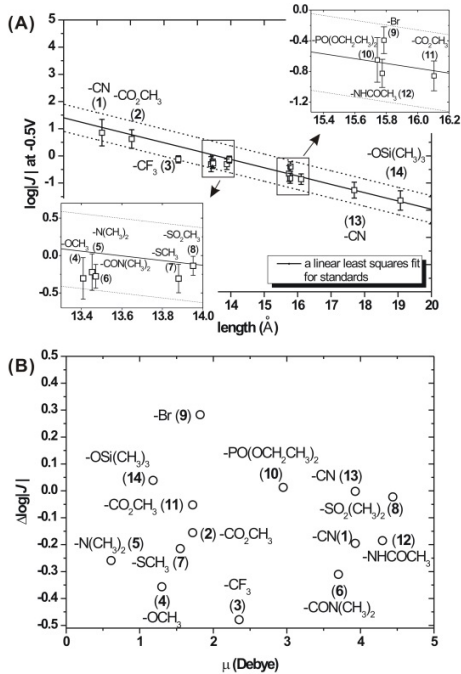

Figure 2. (A) A plot of log|J| at -0.5V for compounds with the structure $S(CH_2)_nM(CH_2)_mT$ as a function of calculated length (from sulfur to the distal hydrogen atom closest to the EGaIn top-electrode). (B) A plot of the difference in log|J| (Δlog|J| = log|J_{polar}| - log|J_{CH_3}|) between $S(CH_2)_nM(CH_2)_mT$ and hypothetical n-alkanethiolate (estimated from the simplified Simmons equation, Eq. 1) at -0.5V as a function of molecular dipole for the model structure (CH_3T or CH_3CH_2T). The solid line in the plot (a) represents a linear square fit of mean values of log|J| for n-alkanethiolates (standards in Figure 1) and the values of β and J_o for the standards was ~0.71 ±0.04 Å^{-1} and $10^{4.0±0.3}$ A/cm²; the dotted lines represent the range of Δlog|J| = ±0.5 (corresponding to about a factor of three variation in J). Dipole moments were obtained from the CRC Handbook of Chemistry and Physics 94th edition, 2013-2014 (See the Supporting Information).

The current density measurements for the cyano- (CN, **1** and **13**) and methyl ester- (CO_2CH_3, **2** and **11**) terminated compounds (Figure 2A) give approximate (because of the small numbers of points) information about the response of the tunneling decay parameter, β, and the injection current, J_o, to the presence of terminal polar groups. Mean values of $J(V)$ for two different lengths of the cyano compound and two different lengths of the methyl ester compound provided approximate values of β and J_o (β = ~0.7 ± 0.2 Å^{-1}, and J_o = ~$10^{3.8\ ±1.5}$ A/cm²). For comparison, n-alkanethiolates (M= -CH_2CH_2-, T= -CH_3) showed β =0.71 ± 0.04 Å^{-1}, and J_o = $10^{4.0±0.3}$ A/cm². Values of β and J_o for SAMs terminated in alkanes and polar groups were thus statistically indistinguishable.

The similarity in J_o between polar and non-polar (-CH_3) terminal groups indicates that seemingly large changes in the composition and electrostatic character at the SAM//Ga_2O_3 top-interface (a van der Waals interface) do not change the shape of the tunneling barrier associated with SAM-based junction sufficiently to influence the rate of charge transport.

Molecular dipoles at the SAM//Ga_2O_3 top-interface do not seem to influence the rates of charge tunneling. The empirical correlation between "length" and tunneling current in Figure 2 demonstrates that the rate of charge tunneling is insensitive to the presence of molecular dipoles in terminal organic groups in junctions of the form Ag-$^{TS}S(CH_2)_nM(CH_2)_mT$//Ga_2O_3/EGaIn. The *interpretation* of this observation is ambiguous, for at least three reasons.

i) *Complicated structural features of SAMs make it difficult to relate rates of charge transport to the conformation of dipoles at the SAM//Ga_2O_3/interface.* Although it is straightforward to estimate the magnitude of the dipole moment of an isolated functional group, understanding the electrostatic character of the interface between the SAM-bound dipole group and the surface of the Ga_2O_3 is complicated (especially when the magnitude of the applied electrical field—250MV/m—is high). The fact that the direction of the group dipole is constrained (if not fixed) by the structure of the molecule, but the magnitude of the tunneling current is unchanged by reversing the polarity of the field (i.e., the junction does not rectify), suggests both that the local dipoles (in the range of 0.5 < μ < 4.5) do not influence tunneling currents, and that any ordering of them by intermolecular or external field effects are not reflected in changes in charge tunneling that we can detect.

ii) *The physical/mechanical structure of the SAM//Ga_2O_3 interface is not established.* Another factor that complicates the analysis of interfacial phenomena in these (and other) junctions is an incomplete understanding of the nature of the path followed by the charge. In the junctions we use, the evidence indicates that only a small fraction (perhaps 10^{-4}) of the apparent *geometrical* area of contact of the top (Ga_2O_3/EGaIn) junction is in *electrical* contact with the SAM. Although this number is compatible with measures of contact from other solid-solid electrical and mechanical interfaces,[36] and although it is quite reproducible (as judged by the values of σ_{log} in Table S2 in the Supporting Information), it leaves open the detailed atomic-level nature of these electrically effective regions.

iii) *The contribution of the SAM//Ga_2O_3 interface to the topography of the tunneling barrier remains undefined.* A final question about the interpretation of the data in Figure 2 concerns theoretical expectations. The hypothesis on which this work was based is that a change in the magnitude of molecular dipoles placed at the terminus of the SAM *might* influence the shape of the tunneling barrier, and hence the magnitude of the tunneling current. We infer experimentally that there is no observable change using our technique. We cannot, however, infer that there is no change in the tunneling barrier, only that any change in it does not influence observed tunneling currents.

The absence of an atomically detailed theory to guide the design and interpretation of measurements is presently a limitation in the field of molecular electronics. Early efforts to add local detail to simple barriers (for example, the early, very stimulating prediction of Aviram and Ratner[26] concern-

ing the role of embedded molecular dipoles on rectification) so far have no experimental support. Authentic rectification has been observed across SAMs terminated in ferrocene groups,[14,15] but the origin of the rectification involves a change in mechanism (from tunneling to not electrostatic influences due to molecular dipoles. At present, we simply have no theory that would predict what kind of change—in either the body of the SAM or on the interfaces—would lead to enough of a change in the shape of the tunneling barrier to change the tunneling current.

The conclusion from this work is that dipoles from a number of functional groups at the terminus (T in this paper), and from amides (-CONH- or -NHCO-) in the interior (M)[7,27] of a SAM have no (or small) effect on the magnitude of experimental tunneling currents. This result adds to a number of observations about the relations between molecular structure and tunneling (particularly previous studies on the effect of the structure of the top-interface on J(V) summarized in Table S1) which suggest that the structure of this interface influences rates of tunneling only when reactions (e.g., redox reactions, or "hopping" for Fc[9,14,15]) are possible. From these and previous studies, however, we infer that: i) Familiar organic terminal groups linked at the terminal (T) position to aliphatic chains have too small an influence on the shape of the tunneling barrier to change the rate of charge tunneling[7,18,19] (The mechanistic origin of the "odd/even effect" remains a puzzle[13]). ii) More exotic functional groups— e.g., metal complexes[9,14,15]—may influence J(V) significantly, but the mechanism may involve hopping rather than pure tunneling. iii) The composition of top-electrode seems not to be a primary determinant of the electrical characteristics of the junction.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectroscopic data for all new compounds, histograms of current densities and summary of junction measurements. 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 interests.

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