

## Odd–Even Effects in Charge Transport across *n*-Alkanethiolate-Based SAMs

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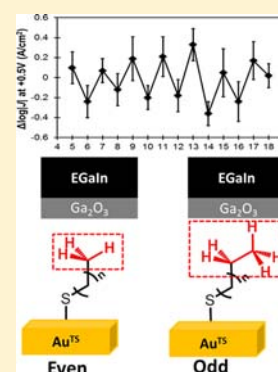
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### Supporting Information

**ABSTRACT:** This paper compares rates of charge transport across self-assembled monolayers (SAMs) of *n*-alkanethiolates having odd and even numbers of carbon atoms ( $n_{\text{odd}}$  and  $n_{\text{even}}$ ) using junctions with the structure  $M^{\text{TS}}/\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$  ( $M = \text{Au}$  or  $\text{Ag}$ ). Measurements of current density,  $J(V)$ , across SAMs of *n*-alkanethiolates on  $\text{Au}^{\text{TS}}$  and  $\text{Ag}^{\text{TS}}$  demonstrated a statistically significant odd–even effect on  $\text{Au}^{\text{TS}}$ , but not on  $\text{Ag}^{\text{TS}}$ , that could be detected using this technique. Statistical analysis showed the values of tunneling current density across SAMs of *n*-alkanethiolates on  $\text{Au}^{\text{TS}}$  with  $n_{\text{odd}}$  and  $n_{\text{even}}$  belonging to two separate sets, and while there is a significant difference between the values of injection current density,  $J_0$ , for these two series ( $\log|J_{0,\text{Au,even}}| = 4.0 \pm 0.3$  and  $\log|J_{0,\text{Au,odd}}| = 4.5 \pm 0.3$ ), the values of tunneling decay constant,  $\beta$ , for  $n_{\text{odd}}$  and  $n_{\text{even}}$  alkyl chains are indistinguishable ( $\beta_{\text{Au,even}} = 0.73 \pm 0.02 \text{ \AA}^{-1}$ , and  $\beta_{\text{Au,odd}} = 0.74 \pm 0.02 \text{ \AA}^{-1}$ ). A comparison of electrical characteristics across junctions of *n*-alkanethiolate SAMs on gold and silver electrodes yields indistinguishable values of  $\beta$  and  $J_0$  and indicates that a change that substantially alters the tilt angle of the alkyl chain (and, therefore, the thickness of the SAM) has no influence on the injection current density across SAMs of *n*-alkanethiolates.



## INTRODUCTION

Understanding charge tunneling through thin molecular films is important to understand the movement of charge in organic insulators and more broadly in nanoscience.<sup>1–7</sup> Using self-assembled monolayer (SAM)-based large-area junctions with the structure  $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_n\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$  (one type of so-called “EGaIn junction”),<sup>8,9</sup> we were able to study the influence of the changes in the structure of the SAM on the tunneling current density across it.<sup>10–14</sup> (Here  $\text{Ag}^{\text{TS}}$  is a template-stripped silver substrate,  $\text{S}(\text{CH}_2)_n$  is the *n*-alkanethiolate SAM covalently bonded to the  $\text{Ag}^{\text{TS}}$  substrate, T is the terminal functional group, and EGaIn is the liquid alloy of gallium and indium, covered with a thin, electrically conductive surface oxide—mostly  $\text{Ga}_2\text{O}_3$ —that forms spontaneously upon exposure to air.<sup>15,16</sup>) Those studies showed that alterations in the structure of the insulating organic layer,  $\text{S}(\text{CH}_2)_n\text{T}$ , for example, changing the anchoring group of the SAMs<sup>10</sup> or introducing polar organic groups either into the backbone of a polyethylene chain<sup>11</sup> or at the van der Waals  $\text{T}/\text{Ga}_2\text{O}_3$  interface,<sup>12–14</sup> do not influence the rates of charge transport at a level that is statistically significant (less than a factor of 3). In surprising contrast, we and others observed that the addition of one  $\text{CH}_2$  group to the alkyl chain—a change that, in essence, simply interchanges an exposed terminal methyl group for an ethyl group—appears to be sufficient to make a small but statistically

significant difference in the electronic properties of the junction.<sup>17–20</sup> This phenomenon is one manifestation of the so-called odd–even effect,<sup>21</sup> and its origin is a continuing puzzle in understanding SAM-based tunneling junctions.

In this work, we focused on three specific questions about the odd–even effect: (i) Is there indeed, when examined using current technology, a systemic difference in the rate of charge transport across SAMs of *n*-alkanethiolates ( $\text{SC}_n$ ) with an odd number of carbons ( $n_{\text{odd}}$ ) and SAMs with an even number of carbons ( $n_{\text{even}}$ )? (Much of the historical evidence for odd–even effects in charge transport has come from earlier and less accurate studies<sup>17</sup> and from studies of phenomena such as wetting, which are of unknown relevance to quantum tunneling.<sup>21</sup>) (ii) If there is an odd–even effect, then, mechanistically, how can such a small change in the structure of a SAM influence tunneling probabilities? (iii) How does changing the substrate supporting the SAM from Au to Ag—a change that also changes the tilt angle of *n*-alkanethiolates as well as properties such as wetting and work function of electrode—influence tunneling current density across SAM-based large-area junctions?

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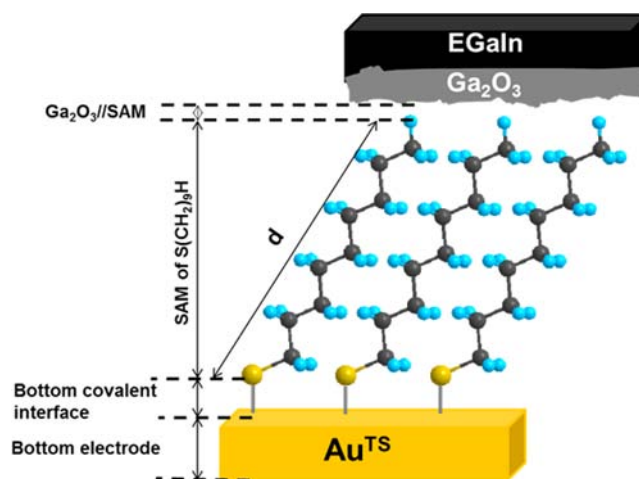
There are three plausible explanations for the observed odd–even effect in the rates of charge transport: (i) Changes in the nature of the van der Waals interface between the SAM and the top electrode—changes that are presumed to be responsible for the odd–even effect in wetting<sup>21</sup>—might also influence the ability of the SAM and the Ga<sub>2</sub>O<sub>3</sub> to “wet” and conform to one another, or to condense a water film, or to adsorb adventitious contaminants at the interface. (ii) Differences in rates of charge transport might reflect the differences in the orientation of the terminal group at the interface of the SAM with the Ga<sub>2</sub>O<sub>3</sub> (e.g., CH<sub>2</sub>CH<sub>3</sub> vs CH<sub>3</sub>, Figure S2), which might influence the strength of electronic coupling between the HOMOs of the *n*-alkyl groups and the Ga<sub>2</sub>O<sub>3</sub>. (iii) There might be a systematic difference in the thickness of the SAM between odd and even *n*-alkanethiolates. (The tunneling path might have a through-space component and thus be sensitive to the thickness, independently of the length of the *n*-alkyl chain.) A fourth (in principle) possibility, i.e., differences in the electric dipole moment along the surface normal, which would be induced by the odd–even differences in the orientation of the terminal ethyl (–CH<sub>2</sub>CH<sub>3</sub>) group, seems unlikely to be important since the difference is undoubtedly small, and introducing even large dipoles into the interface has little or no effect.<sup>12,13</sup>

In our previous studies, although we were able to identify an odd–even effect in tunneling current density,  $J$  (A/cm<sup>2</sup>) at  $\pm 0.5$  V (i.e., the results from SAMs with  $n_{\text{even}}$  and  $n_{\text{odd}}$  belonged to separate data sets and demanded separate fits to eq 1), we were not able, because the log-standard deviation ( $\log$ ) in those studies was large ( $\log = 0.6\text{--}1.4$ ) relative to those we now generate ( $\log = 0.3\text{--}0.6$ ), to determine the mechanism of the odd–even effect or to establish whether there was a statistically significant difference in the two parameters,  $\beta$ , and,  $J_0$ , of the simplified Simmons equation (eq 1).<sup>17</sup> In eq 1,  $J(V)$  is current density (current divided by the geometrical contact area; A/cm<sup>2</sup>) at an applied voltage  $V$ :<sup>22,23</sup>

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

In this study, as in prior work, we have focused on trends in current densities as a function of the number of methylene (–CH<sub>2</sub>–) units in SAMs of structure M(Au or Ag)/SC<sub>*n*</sub>//Ga<sub>2</sub>O<sub>3</sub>/EGaIn, rather than on absolute values of these measurements. We have described previously details of the procedure we used.<sup>15</sup> Here we used so-called “flattened” EGaIn tips,  $V = \pm 0.5$  V and template-stripped (TS) Ag and Au substrates (Figure 1).<sup>8,9,15</sup> The fabrication of the conical tip—a process that stretches the EGaIn until it breaks—results in a rough Ga<sub>2</sub>O<sub>3</sub> surface. Using “selected”<sup>14</sup> or “flattened”<sup>15</sup> tips yield data with slightly narrower distribution than tips with rougher surfaces. We do not know if flattening influences the thickness of the oxide.

Surfaces of Au and Ag have similar work functions ( $\Phi_{\text{Au}} = 4.9$  eV and  $\Phi_{\text{Ag}} = 4.4$  eV).<sup>24</sup> The tilt angle of the backbone from the surface normal for *n*-alkanethiolate monolayers on Au(111) (30°) is larger than that on Ag(111) (10°) (Figure S2).<sup>25</sup> Accordingly, comparing the rate of charge transport across the *n*-alkanethiolate SAMs on Au and Ag substrates makes it possible to separate the influence of several characteristics of a SAM, especially the tilt angle (and thus the relative thickness of the SAM along the surface normal) of the SAM and the SAM packing density (21.7 Å<sup>2</sup>/molecule on Au and 19.1 Å<sup>2</sup>/molecule on Ag),<sup>26</sup> on rates of tunneling. In particular, we hoped to answer two questions in this comparative study: (i)



**Figure 1.** Schematic structure of a Au<sup>TS</sup>/SAM//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junction. Here,  $d$  represents the length of the tunneling barrier established by the alkyl chains in the SAM. Assuming a through-bond mechanism,  $d$  coincides with the length of the alkyl chain.  $J_0$  is defined as the current density across a hypothetical junction where  $d = 0$ .

Does the charge move along the shortest distance between the two electrodes (a through-space path)? or (ii) does the charge follow the molecular orbitals along the backbone, regardless of the tilt of the *n*-alkyl group (a through-bond path)?<sup>27,28</sup> Density of chains, tilt angle, and the properties of the interface (T//Ga<sub>2</sub>O<sub>3</sub>, T = –CH<sub>3</sub>, –CH<sub>2</sub>CH<sub>3</sub>) are obviously convoluted, and no simple comparison of SAMs on Au and Ag will distinguish them all unambiguously; our results do, nonetheless, both allow some possibilities to be excluded and help to frame questions for future study.

We observed a statistically significant odd–even effect in the rates of tunneling across SAMs of *n*-alkanethiolate on Au<sup>TS</sup>, where *n*-alkanethiolates with  $n_{\text{odd}}$  gave higher current densities ( $J(V)$ ) than did SAMs of *n*-alkanethiolate with  $n_{\text{even}}$ . We show that the tunneling current densities across SAMs of *n*-alkanethiolates with  $n_{\text{odd}}$  and  $n_{\text{even}}$  on Au<sup>TS</sup> fit in separate sets of data when analyzed using the simplified Simmons model (eq 1); i.e., analyzing the two series separately led to more consistent interpretations of the results than analyzing them together. In contrast, charge tunneling across SAMs of *n*-alkanethiolates on Ag<sup>TS</sup> does not show an odd–even effect that we can detect in either  $\beta$  or  $J_0$ .

## ■ BACKGROUND

**Odd–Even Effects in Tunneling across SAMs.** The odd–even effect in SAMs has been observed (and reviewed<sup>21</sup>) in a number of properties, including wetting by liquids,<sup>29–32</sup> molecular packing,<sup>33</sup> and electronic,<sup>19</sup> frictional,<sup>34</sup> and electrochemical behaviors.<sup>35</sup> Odd–even effects have been studied in the surface treatment of dielectric materials for pentacene-based field-effect transistors<sup>36</sup> and in the rate of charge transport across carbon-chain-based molecular devices.<sup>20</sup> Odd–even alternation in rectification of tunneling current density has also been reported.<sup>18</sup> Using EGaIn-based top electrodes in molecular junctions, we have studied odd–even effects in charge transport across *n*-alkanethiolate SAMs on Ag<sup>TS</sup> substrates.<sup>17,11</sup> Using statistical tools, we showed that the data for current densities for SAMs with  $n_{\text{even}}$  and  $n_{\text{odd}}$  belong to separate data sets.<sup>37</sup>

**Theory of Charge Tunneling across SAMs.** SAMs of alkanes are considered to be good electrical insulators for current transport at low bias (we use  $\pm 0.5$  V), and charge transport takes place by hole tunneling.<sup>38,39</sup> When such molecules are placed between two electrodes, the charge transport has usually been interpreted (in the absence of a more detailed model) in terms of a rectangular barrier using eq 1.<sup>22</sup> The injection current density at an applied voltage  $V$ ,  $J_0(V)$ , gives, ideally, the current flowing across a hypothetical junction in which the SAM has zero ( $d = 0$ ) thickness, but the characteristic of the interfaces between the SAM and the electrodes remain the same as those when there is a SAM. The tunneling decay constant  $\beta$  ( $\text{\AA}^{-1}$ ) contains, according to the Simmons model, information about the shape of the tunneling barrier, which, in principle, is determined by the molecular/electronic structure of the backbone in the SAM. The width of the barrier across which charges move is  $d$  ( $\text{\AA}$ ) and is usually assumed to be determined by the molecular structure, not the shortest path between the two electrodes, but this assumption is not based either on solid empirical or theoretical grounds.

## RESULTS AND DISCUSSION

We collected  $J(V)$  using “flattened” conical tips. The procedures for formation and use of these flattened tips are described in detail elsewhere.<sup>15</sup> See the Supporting Information for details of experimental design.

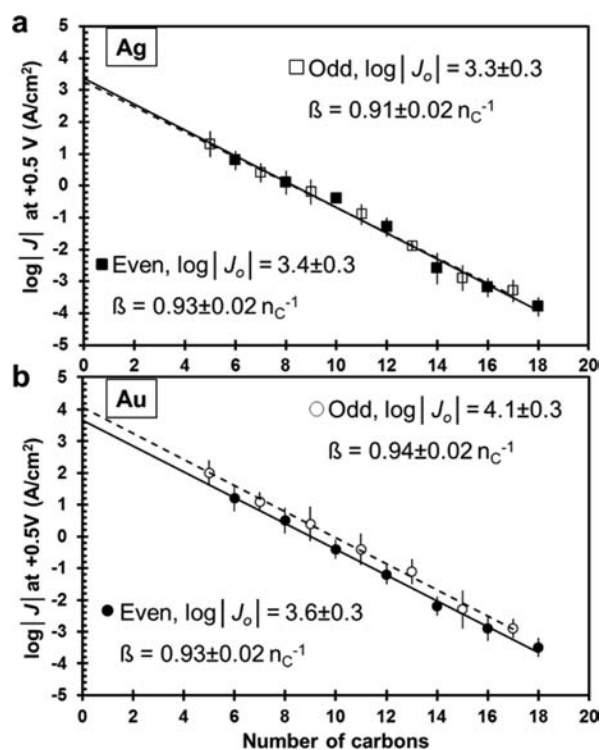
**Charge Transport across  $n$ -Alkanethiolates on  $\text{Ag}^{\text{TS}}$  and  $\text{Au}^{\text{TS}}$  Substrates.** Values of  $J$  are approximately log-normally distributed (Figures S3 and S4). For each SAM, we could fit, by nonlinear least-squares fitting,<sup>37</sup> Gaussian curves to the distributions of  $\log|J|$ . Figures S3 and S4 show the histograms for the values of  $\log|J|$  ( $J$ ,  $\text{A cm}^{-2}$ ) for SAMs of  $n$ -alkanethiolates on  $\text{Ag}^{\text{TS}}$  and  $\text{Au}^{\text{TS}}$ . Table S1 summarizes the values of  $\log|J|$  at  $V = +0.5$  V for SAMs of  $n$ -alkanethiolates ( $\text{SC}_n$ ) on  $\text{Ag}^{\text{TS}}$  and  $\text{Au}^{\text{TS}}$  with both odd and/or even numbers of carbons ( $n_{\text{odd}}$  and  $n_{\text{even}}$ ). Table 1 summarizes the values for

**Table 1. Values for Injection Current Density,  $\log|J_0|$ , and Tunneling Decay Coefficient,  $\beta$ , for the  $n$ -Alkanethiolates with  $n_{\text{even}}$  and  $n_{\text{odd}}$  on Both  $\text{Ag}^{\text{TS}}$  and  $\text{Au}^{\text{TS}}$  Substrates**

$M^a$ /odd or even	Length ( $\text{\AA}$ ) <sup>b</sup>		Length ( $n_c$ ) <sup>c</sup>	
	$\log J_0 $	$\beta$ ( $\text{\AA}^{-1}$ )	$\log J_0 $	$\beta$ ( $n_c^{-1}$ )
$\text{Ag}^{\text{TS}}$ /even	$3.7 \pm 0.3$	$0.73 \pm 0.02$	$3.4 \pm 0.3$	$0.93 \pm 0.02$
$\text{Ag}^{\text{TS}}$ /odd	$3.6 \pm 0.3$	$0.71 \pm 0.02$	$3.3 \pm 0.3$	$0.91 \pm 0.02$
$\text{Au}^{\text{TS}}$ /even	$4.0 \pm 0.3$	$0.73 \pm 0.02$	$3.6 \pm 0.3$	$0.93 \pm 0.02$
$\text{Au}^{\text{TS}}$ /odd	$4.5 \pm 0.3$	$0.74 \pm 0.02$	$4.1 \pm 0.3$	$0.94 \pm 0.02$

<sup>a</sup>The metal substrate. <sup>b</sup>Molecular length from the sulfur atom to the distal hydrogen atom of the final methyl group in contact with  $\text{Ga}_2\text{O}_3$  (Figure 1). <sup>c</sup>Length based on the number of carbons of  $\text{SC}_n$ .

injection current density,  $\log|J_0|$ , and tunneling decay coefficient,  $\beta$ , for the  $n$ -alkanethiolates with  $n_{\text{even}}$  and  $n_{\text{odd}}$  on both Ag and Au substrates. Figure 2 shows plots of linear regression of  $\log|J|$  versus molecular length (number of carbons) for SAMs of  $n$ -alkanethiolate on Ag (Figure 2a) and Au (Figure 2b) with  $n_{\text{even}}$  and  $n_{\text{odd}}$ . Figure S5 shows plots of  $\log|J|$ , at  $V = +0.5$  V, versus  $d$  ( $\text{\AA}$ ) for different lengths of  $n$ -alkanethiolates on both  $\text{Ag}^{\text{TS}}$  and  $\text{Au}^{\text{TS}}$  substrates. We calculated the molecular length from the sulfur atom to the distal hydrogen atom of the final methyl group in contact with  $\text{Ga}_2\text{O}_3$  (Figure 1). Despite the potential for differences in the structural order for SAMs with short ( $n < 9$ ) and long chains ( $n$

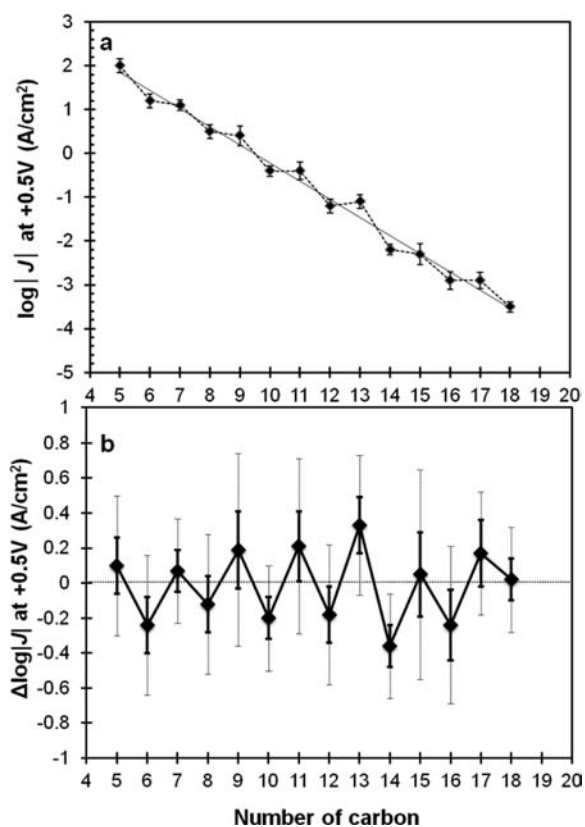


**Figure 2.**  $\log|J|$  at  $V = +0.5$  V versus number of carbons for SAMs of  $n$ -alkanethiolates ( $\text{SC}_n$ ) on (a)  $\text{Ag}^{\text{TS}}$  and (b)  $\text{Au}^{\text{TS}}$ . Solid line (for  $n$ -alkanethiolate SAMs with  $n_{\text{even}}$ ) and dashed line (for  $n$ -alkanethiolate SAMs with  $n_{\text{odd}}$ ) represent the linear regression analyses which gives  $\beta/2.303$  (slopes) and  $\log|J_0|$  (intercepts at  $d = 0$ ). Error bars represent the standard deviation for the  $\log|J|$  values (0.1 <sub>log</sub> 0.6).

$> 9$ ),<sup>40</sup> we do not detect these differences in the current density or the yields of working junctions. The values of  $J_0$  and  $\beta$  for SAMs of alkanethiolate on  $\text{Ag}^{\text{TS}}$  with  $n_{\text{even}}$  are in agreement with our report using flattened  $\text{Ga}_2\text{O}_3/\text{EGaIn}$  conical tips.<sup>15</sup> The  $\beta$  value ( $0.74 \text{ \AA}^{-1}$ ) for  $n$ -alkanethiolates with  $n_{\text{even}}$  on  $\text{Au}^{\text{TS}}$  is in good agreement with reported values of  $\beta$  ( $0.6\text{--}1 \text{ \AA}^{-1}$ ) across a wide range of measurement techniques.<sup>2</sup>

For SAMs on  $\text{Au}^{\text{TS}}$ , junctions comprising SAMs of  $n$ -alkanethiolates with  $n_{\text{odd}}$  consistently showed higher values of current densities than their analogs with  $n_{\text{even}}$  (Figures 2b and 3). Based on a careful statistical analysis, we concluded, with 95% probability, that there is a significant difference between two regression lines (Figure 2b). We determined that the difference in the values of the intercepts ( $\log|J_0|$ ) of the two lines is statistically significant, but the slopes ( $\beta$ ) are indistinguishable (for details of statistical analysis; see Supporting Information). We did not, however, observe any significant difference in the trends of  $\log|J|$  (i.e., odd–even alternation) for SAMs of  $n$ -alkanethiolates with  $n_{\text{even}}$  or  $n_{\text{odd}}$  on  $\text{Ag}^{\text{TS}}$  (Figure 2a). Statistical analysis, similar to that carried out for SAMs on  $\text{Au}^{\text{TS}}$ , for SAMs of  $n$ -alkanethiolates with  $n_{\text{even}}$  or  $n_{\text{odd}}$  on  $\text{Ag}^{\text{TS}}$  showed that the two lines are indistinguishable and values of the injection current density,  $\log|J_0|$ , and of tunneling decay coefficient,  $\beta$ , for the  $n$ -alkanethiolates with  $n_{\text{even}}$  were indistinguishable from  $\log|J_0|$  and  $\beta$  for  $n$ -alkanethiolates with  $n_{\text{odd}}$ .

For SAMs on  $\text{Au}^{\text{TS}}$ , values of  $\log|J|$  of most of the  $n$ -alkanethiolate SAMs with  $n_{\text{even}}$  ( $\text{SC}_n$ ) were within 0.1 of the values of  $\log|J|$  of their next homologue with  $n_{\text{odd}}$  ( $\text{SC}_{n+1}$ ) (Figure 3a). Figure 3b shows that the  $\Delta\log|J|$  ( $\Delta\log|J| = \log|J|$



**Figure 3.** Odd–even effect in charge transport across *n*-alkanethiolates on Au<sup>TS</sup>. (a) Plot of  $\log|J|$  at  $V = +0.5$  V versus number of carbons for SAMs of *n*-alkanethiolates on Au<sup>TS</sup> ( $SC_n$ ,  $n = 5$ – $18$ ). The solid line represents the linear regression analysis to all the data. Error bars represent 95% CI for the  $\log|J|$  values. (b) Difference ( $\Delta\log|J|$ ) between the observed current density ( $\log|J|_{\text{observed}}$ ) and the calculated current density ( $\log|J|_{\text{fitted}}$ ) based on the regression line ( $\Delta\log|J| = \log|J|_{\text{observed}} - \log|J|_{\text{fitted}}$ ). Error bars represent standard deviation (light dotted) and 95% CI (solid) for the  $\log|J|$  values.

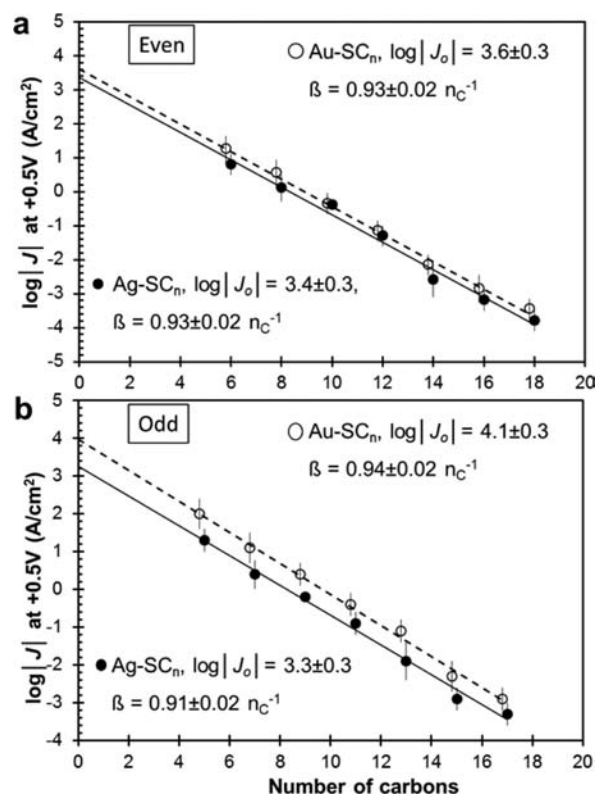
$J_{\text{observed}} - \log|J|_{\text{fitted}}$ ) for SAMs with  $n_{\text{odd}}$  is constantly 0, while  $\Delta\log|J|$  for SAMs with  $n_{\text{even}}$  is constantly 0.

To examine the statistical difference between the tunneling current density values,  $\log|J|$ , of SAMs of *n*-alkanethiolates on Au<sup>TS</sup>, we calculated the 95% confidence intervals (CI) for the whole set of  $\log|J|$  values (for details see Supporting Information). Error bars in Figure 3 show the 95% CI for the  $\log|J|$  values on Au<sup>TS</sup> substrate (i.e., the smaller the overlap of bars or the larger the gap between bars, the stronger the evidence for a true difference).<sup>41</sup> Figure 3b shows an interesting phenomenon; i.e., although the odd–even alternation can be observed for the whole series of  $SC_n$  ( $n = 5$ – $18$ ), it is only statistically significant for  $10 \leq n \leq 14$ . We rationalize this difference as a reflection of the conclusion—drawn largely from spectroscopic studies<sup>42</sup>—that SAMs with longer SAMs ( $n \geq 10$ ) are crystalline and well ordered, while those with  $9 \leq n$  are disordered, probably because of weak interactions between the shorter alkyl chains. The SAMs with long chains ( $n \geq 15$ ) may be less ordered and have chains with gauche configurations (similar observations have been reported for some other types of odd–even effect).<sup>18,43</sup> Our data are consistent with suggestions that the magnitude of odd–even effect depends on the degree of order of the SAM.

One of the factors that, potentially, can influence the quality of the SAM is the incubation time (i.e., the time that metal

substrate stayed in a solution of the thiols (1 mM in toluene)). To examine the effect of incubation time, we prepared SAMs of  $SC_{10}$  and  $SC_{11}$  on both Ag<sup>TS</sup> and Au<sup>TS</sup> substrates with incubations of 3 h and 1, 2, and 7 days. The rate of charge tunneling for SAMs formed over 3 h is not distinguishable from the 7 day sample (Table S2).

**Comparison between Au and Ag.** To examine the influence of geometry of SAMs on tunneling transport, we compared  $J(V)$  of *n*-alkanethiolates on Au<sup>TS</sup> and Ag<sup>TS</sup>. Figure 4



**Figure 4.**  $\log|J|$  at  $V = +0.5$  V versus number of carbons for SAMs of *n*-alkanethiolates (a) with an even number of carbons on Au<sup>TS</sup> and Ag<sup>TS</sup> and (b) with an odd number of carbons on Au<sup>TS</sup> and Ag<sup>TS</sup>. Solid line (for *n*-alkanethiolate SAMs on Ag<sup>TS</sup>) and dashed line (for *n*-alkanethiolate SAMs Au<sup>TS</sup>) represent the linear regression analyses which give  $\beta/2.303$  (slopes) and  $\log|J|_0$  (intercepts at  $d = 0$ ). Error bars represent the standard deviation for the  $\log|J|$  values.

shows plots of  $\log|J|$  at  $V = +0.5$  versus molecular length (in number of carbons) for *n*-alkanethiolate SAMs with  $n_{\text{even}}$  and  $n_{\text{odd}}$  on both Au<sup>TS</sup> and Ag<sup>TS</sup>. Statistical analysis, similar to that which we have carried out for the odd–even effect, showed that SAMs with  $n_{\text{even}}$  on both Au<sup>TS</sup> and Ag<sup>TS</sup> result in indistinguishable values of  $\log|J|_0$  and  $\beta$  (Table 1, Figure 4a). When, however, we compared the tunneling current density between SAMs with  $n_{\text{odd}}$  on Ag<sup>TS</sup> and Au<sup>TS</sup>, we observed a significant difference in values of  $\log|J|_0$ , while the values of  $\beta$  were indistinguishable (Table 1, Figure 4b). These comparisons lead to two important conclusions: (i) They indicate that replacing Au/SR with Ag/SR (for SAMs with  $n_{\text{even}}$ ), a change that substantially alters the tilt angle of the alkyl chain (and, therefore, the thickness of the SAM),<sup>29</sup> had no influence (to the precision that we can measure) on the injection current density across these SAMs (Figure 4a). (ii) The odd–even effect in charge tunneling across the SAMs of *n*-alkanethiolates is related to the orientation of the terminal methyl group. This study

showed that SAMs of *n*-alkanethiolates with  $n_{\text{even}}$  on Au<sup>TS</sup> behave, in EGaIn junctions, similarly to the SAMs with  $n_{\text{even}}$  and  $n_{\text{odd}}$  on Ag<sup>TS</sup> and that only SAMs with  $n_{\text{odd}}$  on Au<sup>TS</sup> conduct differently (Figure 4 and Table 1). The significant structural difference between SAMs with  $n_{\text{odd}}$  on Au<sup>TS</sup> with the other SAMs studied in this comparison is the orientation of terminal ethyl group: for SAMs with  $n_{\text{even}}$  on Au<sup>TS</sup> and SAMs with  $n_{\text{even}}$  and  $n_{\text{odd}}$  on Ag<sup>TS</sup>, the surface consists predominantly of methyl groups. Based on high-resolution electron energy loss spectroscopy studies,<sup>43</sup> the terminal CH<sub>2</sub>–CH<sub>3</sub> moiety of the SAMs with  $n_{\text{odd}}$  on Au<sup>TS</sup> is tilted away from the surface normal, producing a surface that is composed of a mixture of methyl and methylene groups (i.e., an “ethyl” rather than “methyl” surface)<sup>29</sup> (Figure S2). The same behavior was reported in wetting properties of SAMs on Ag and Au; SAMs of *n*-alkanethiolate on Ag showed no<sup>29</sup> or slight<sup>44</sup> odd–even effect; the effect was more distinguishable on Au.<sup>45</sup>

An alternative hypothesis that might rationalize the fact that no odd–even effect is observed on Ag<sup>TS</sup> could be that there are differences in the order of the SAMs on these substrates, with SAMs on Ag<sup>TS</sup> being more disordered than SAMs on Au<sup>TS</sup>. Differences in these SAMs are due primarily to differences in the tilt angle of the monolayers and to the resulting differences in the density of molecules per unit area. Since the template-stripped metal substrates have similar values of surface roughness, we do not expect significant differences in the degree of order between SAMs on Ag<sup>TS</sup> and Au<sup>TS</sup> due to surface roughness. Moreover, the narrow distribution of data, high yields in nonshorting junctions, and good reproducibility<sup>46</sup> on Ag<sup>TS</sup> substrates provide empirical evidence that there is no difference between the order of the SAMs on Ag<sup>TS</sup> and Au<sup>TS</sup>.

## CONCLUSION

**The Odd–Even Effect in Charge Transport by Tunneling Is Real.** Our statistical analysis for SAMs of *n*-alkanethiolates on Au<sup>TS</sup> showed (i) the values of tunneling current density across SAMs of *n*-alkanethiolates with  $n_{\text{odd}}$  and  $n_{\text{even}}$  belong to two separate data sets, and (ii) while there is a significant difference between the values of  $J_0$  for these two series, the values of  $\beta$  for  $n_{\text{odd}}$  and  $n_{\text{even}}$  alkyl chains were indistinguishable. We conclude that there is an odd–even effect in tunneling transport across SAMs on Au<sup>TS</sup>; an odd–even effect, however, was *not* observable (at the precision that we could measure) for the series on Ag<sup>TS</sup>.

**The Geometry of the *n*-Alkyl Chain Determines the Odd–Even Effect.** The contrast of junction measurements between SAMs of *n*-alkanethiolates on gold (where we observed an odd–even effect) and on silver (where we did not observe a significant trend) indicates that the odd–even effect in tunneling transport corresponds to the composition (“methyl” vs “ethyl”) of the surface of the SAM (Figure S2).

**The Tunneling Path Is along Single Molecule Rather than Across Multiple Molecules.** Our results demonstrate that although a SAM on gold is thinner than one on silver, the values of  $J_0$  and  $\beta$  for SAMs of *n*-alkanethiolates with  $n_{\text{even}}$  on Au<sup>TS</sup> and Ag<sup>TS</sup> are statistically indistinguishable (Figure 4a). We suggest—based on this observation—that charge carriers travel through the backbone of the alkyl chain in the SAM, rather than across the shortest (and thus across multiple molecules of *n*-alkanethiolate) distance between the two electrodes.

**The SAM//Ga<sub>2</sub>O<sub>3</sub> Interface Is Responsible for the Odd–Even Effect on Au<sup>TS</sup>.** Since the value of  $J_0$  reflects the characteristics of the interfaces between the SAM and the

electrodes, rather than the shape of the most insulating part of the tunneling barrier, significant differences in values of injection current densities,  $J_0$ , and indistinguishable values of tunneling decay,  $\beta$ , for SAMs of *n*-alkanethiolates with  $n_{\text{odd}}$  and  $n_{\text{even}}$  imply that the odd–even effect is influenced by some property of the interfaces (e.g., Au/S or SAM//Ga<sub>2</sub>O<sub>3</sub>). We suggest that a determining contribution of the SAM//Ga<sub>2</sub>O<sub>3</sub> interface to odd–even effects is more plausible than one for the Au/S interface for two reasons: (i) Our previous studies,<sup>10,47</sup> and the current study (Figure 4a), showed that changing the bottom interface does not significantly influence the tunneling current densities. (ii) Results of this study indicate that changing the terminal group from CH<sub>3</sub> to CH<sub>2</sub>CH<sub>3</sub> correlates with a change in the injection current density (Figures 2b and 4b).

**The Origin of the Odd–Even Effect Is not Completely Defined by Currently Available Data.** While we were able to identify the odd–even effect with respect to  $J$ ,  $\beta$ , and  $J_0$ , between *n*-alkanethiols with  $n_{\text{odd}}$  and  $n_{\text{even}}$ , we cannot pinpoint the origin of the observed odd–even effect on Au<sup>TS</sup>. We can, however, identify and assess four possibilities (although, based on our current and previous studies, some possibilities are less plausible than others).

**Differences in the Orientation of the Terminal (T) Group at the Ga<sub>2</sub>O<sub>3</sub> Interface (e.g., CH<sub>2</sub>CH<sub>3</sub> vs CH<sub>3</sub>).** A larger exposure of terminal CH<sub>2</sub>CH<sub>3</sub> group at the surface of the *n*-alkanethiolate SAMs with  $n_{\text{odd}}$  results in larger van der Waals interactions (by changing the polarizability of surface and increasing the area of contact) between the monolayer and the EGaIn tip and may consequently give rise to a difference in  $J(V)$  (similar to differences observed in wetting of SAMs on Au).<sup>21</sup> If the orientation of terminal CH<sub>2</sub>–CH<sub>3</sub> bonds is responsible for both the odd–even effect in charge transport and the odd–even effect in wetting, then increasing the van der Waals interactions as a result of different surface polarization is a possible origin of the former. (These changes in van der Waals interactions *could* influence the contact resistance at the SAM//Ga<sub>2</sub>O<sub>3</sub> interface; however, we did not observe this influence in the distribution of current density (Figures S3 and S4).) This hypothesis, that the odd–even effect in charge tunneling across SAMs terminating in ethyl and methyl groups reflects polarizability and van der Waals interactions, is not easily reconciled with the fact that introducing groups such as halogens or aromatics into this interface does *not* produce large differences in  $J_0$  in our experiments.<sup>12,13</sup> (Cahen and others have reported much larger differences with specific terminal halogen substituents when using a mercury top electrode.)<sup>48</sup>

Large exposure of terminal CH<sub>2</sub>CH<sub>3</sub> groups at the surface of the SAMs with  $n_{\text{odd}}$  on Au<sup>TS</sup> might also result in direct interaction between the EGaIn electrode and the CH<sub>2</sub> groups, which are adjacent to the terminal CH<sub>3</sub> groups. This direct interaction would reduce the length of the molecule between both electrodes effectively by one C–C bond (excluding the top CH<sub>3</sub>). This hypothesis would also explain why this effect is not observed on the Ag substrate where the surface consists predominantly of methyl groups, and the tilt is too little to expose CH<sub>2</sub> group to the molecule//EGaIn interface. We do not know if there is a van der Waals contact between the CH<sub>2</sub> of the terminal ethyl group and the Ga<sub>2</sub>O<sub>3</sub> and, thus, cannot accept or reject this hypothesis.

**Systematic Alternations in Energy of the Frontier Orbital Energies (i.e., HOMO/LUMO Levels) of Odd and Even *n*-Alkanethiolates.** Difference in the orientation of the terminal

group at the SAM interface between the Ga<sub>2</sub>O<sub>3</sub> (CH<sub>2</sub>CH<sub>3</sub> vs CH<sub>3</sub>, Figure S2) might influence the strength of electronic coupling between the HOMOs of the *n*-alkyl groups and the Ga<sub>2</sub>O<sub>3</sub>. This hypothesis seems less plausible when we consider the fact that the HOMO in these SAMs is concentrated at the Au/S interface, with little amplitude at the SAM//Ga<sub>2</sub>O<sub>3</sub> interface.<sup>49</sup> We do not, however, have a sound theoretical understanding of the CH<sub>3</sub> (or CH<sub>2</sub>CH<sub>3</sub>)//Ga<sub>2</sub>O<sub>3</sub> interface.

**Systematic Differences in the Thickness of the SAM between Odd and Even *n*-Alkanethiolates.** Naively, it seemed that SAMs on gold with *n*<sub>odd</sub> might be thinner than SAMs with *n*<sub>even</sub>. Our calculation of thicknesses of odd and even SAMs suggests that there is no significant (<0.5 Å) systematic alternation in the thickness between *n*<sub>odd</sub> and *n*<sub>even</sub>. Figure S6b shows an essentially monotonic increase in the thickness for *n*-alkanethiolate monolayers with a tilt angle of 30° on Au<sup>TS</sup>. These calculations suggest that an odd–even variation in thickness is not the cause of the odd–even alternation in *J*(*V*) (Figure S7). In addition, by comparing the rate of tunneling across SAMs of *n*-alkanethiolates on Au and Ag, we have shown empirically that charge transport is insensitive to the thickness of the SAMs (as measured along the perpendicular to the mean plane of the surface of the metal). The value of β for SAMs of *n*-alkanethiolates on Au<sup>TS</sup> and Ag<sup>TS</sup> is indistinguishable; this observation indicates that tunneling current densities are insensitive to the difference in thickness. We conclude that there is no evidence to support a contribution of the thickness of the SAM to the existence of the odd–even effect.

**Difference in the Dipole along the Surface Normal, Which Might Correlate With Odd–Even Differences in the Orientation of the Terminal CH<sub>3</sub> Group (Figure S2).** Different orientations of the terminal methyl group in *n*<sub>odd</sub> and *n*<sub>even</sub> could cause an odd–even alternation in the dipole along the surface normal,<sup>50</sup> which might contribute to an odd–even effect through an influence on the work function of the surface.<sup>19,50</sup> Although we have no direct evidence to prove or exclude this hypothesis, our previous studies<sup>12,13</sup> showed that introducing even a group with a large dipole moment at the SAM//Ga<sub>2</sub>O<sub>3</sub> interface does not change the tunneling barrier enough to influence the rate of charge transport; thus, we think this very small difference in dipole along surface normal seems unlikely to be important. To be proved or excluded, this hypothesis, however, needs more investigation (e.g., using a series of odd and even SAMs having terminal polar groups such as CF<sub>3</sub> or OCH<sub>3</sub> that introduce a dipole at the interface but do not change the topography of the SAM).

**If There Is an Observable Odd–Even Effect for *n*-Alkanes, Why Was There No Detectable Difference in Much Larger Changes in Terminal Groups for SAMs?**

This paper confirms that there is an odd–even effect for *n*-alkanethiolates, but that it is small (a factor of 3 when appropriately compared, or Δlog *J*<sub>0</sub> = 0.5) and only reliably detectable given the availability of a substantial number of structurally related compounds, with measurements taken carefully, and in parallel. Previous papers have shown that a range of groups with quite different polarities, degrees of saturation, composition, and polarizability have a surprisingly small influence on tunneling current densities.<sup>13</sup> These two sets of observations seem at odds.

The problem in comparing these data is that they are not, strictly speaking, comparable. Most of our studies of terminal groups *did* show variability, but the variation (which might have been a factor of 10 across of series of groups) was not designed

to detect differences as small as those characterizing the odd–even effect and would require comparing groups known to have different sizes and shapes. In those studies, we compared the current densities of compounds having polar terminal groups (R) with those of hypothetical *n*-alkanethiolates of the same length. If those comparisons demonstrate that the difference in log|*J*| (Δlog|*J*| = log|*J*<sub>polar</sub>| – log|*J*<sub>CH<sub>3</sub></sub>|) was 0.5 or less than a factor of 3 in |*J*|, we considered the compound with polar terminal group and *n*-alkanethiol to be indistinguishable. In the current study, however, we did not compare two single data points but studied a series of compounds (S(CH<sub>2</sub>)<sub>*n*</sub>H, *n* = 5–18) and analyzed the results based on eq 1. Although the Δlog|*J*| for each adjacent pair of *n*-alkanethiolate was 0.4 (Figure 3b), analyzing the two series separately led to more consistent interpretations of the results than did analyzing them together (*n*<sub>even</sub> and *n*<sub>odd</sub> produce two statistically distinguishable sets of data).

The surprise in these studies was thus that substituting, for example, a terminal methyl group for an amide, or a terminal cyclohexyl group with a phenyl, produced a change in current density (*J*(*V*)) of approximately a factor of 4.0 (Δlog|*J*(0.5 V)| = 0.6)<sup>12</sup> and that this change was smaller than we had—perhaps naively—expected, while substituting a terminal methyl for a terminal ethyl produced a change of a factor of 2.5 (Δlog|*J*(0.5 V)| = 0.4), which was larger than we had expected. The precision of the former studies was, however, substantially less than the latter, and the studies of polar and aromatic groups, as they were designed, would not have been able to detect the subtle differences characterizing the odd/even effect. Differences in size, composition, and other factors restricted our ability to make meaningful comparisons of current densities with Δlog|*J*(0.5 V)| = 0.6.

So, what is the origin of the odd–even effect? Although this paper cannot answer the question unambiguously, it has eliminated a number of possibilities (differences in the thickness of the SAM, certain differences in the HOMOs for the SAMs) and leaves a focus on the contribution of the noncovalent interface between the SAM and the Ga<sub>2</sub>O<sub>3</sub> film on the EGaIn electrode. This interface has been characterized empirically by studies such as those described in this paper, but have not yet been included in relevant theoretical calculations. In particular, the height of the barrier to tunneling is probably high in the region where there is only physical contact (relative to the rest of the SAM), but the width of this region is small. Understanding the mechanism of charge transport across this interface, and its contribution to overall tunneling currents, remains an unresolved problem with this junction (and, in fact, with all junctions involving SAMs as insulating layers between two conducting electrodes).

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The experimental procedures, synthesis characterization of the alkanethiols, histograms of *J*(*V*) data, and statistical analysis 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.

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