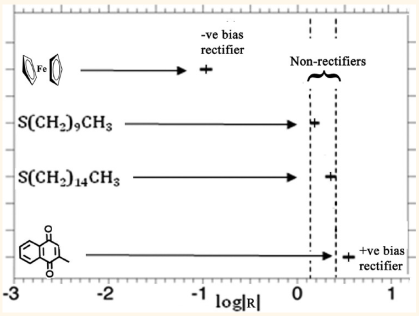
The SAM, Not the Electrodes, Dominates Charge Transport in Metal-Monolayer//Ga_2O_3/Gallium–Indium Eutectic Junctions

William F. Reus,[†,‖] Martin M. Thuo,[†,‖] Nathan D. Shapiro,[†] Christian A. Nijhuis,[†,‡,§] and George M. Whitesides[†,⊥,*]

[†]Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States, [‡]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, [§]Graphene Research Centre, Faculty of Science, National University of Singapore, 6 Science drive 2, Singapore 117546, and [⊥]Kavli Institute for Bionano Science & Technology, Harvard University, School of Engineering and Applied Sciences, Pierce Hall, 29 Oxford Street, Cambridge, Massachusetts 02138, United States. [‖]These authors contributed equally to this work.

ABSTRACT



The liquid–metal eutectic of gallium and indium (EGaIn) is a useful electrode for making soft electrical contacts to self-assembled monolayers (SAMs). This electrode has, however, one feature whose effect on charge transport has been incompletely understood: a thin (approximately 0.7 nm) film—consisting primarily of Ga_2O_3—that covers its surface when in contact with air. SAMs that rectify current have been measured using this electrode in Ag^{TS}-SAM//Ga_2O_3/EGaIn (where Ag^{TS} = template-stripped Ag surface) junctions. This paper organizes evidence, both published and unpublished, showing that the molecular structure of the SAM (specifically, the presence of an accessible molecular orbital asymmetrically located within the SAM), not the difference between the electrodes or the characteristics of the Ga_2O_3 film, causes the observed rectification. By examining and ruling out potential mechanisms of rectification that rely either on the Ga_2O_3 film or on the asymmetry of the electrodes, this paper demonstrates that the structure of the SAM dominates charge transport through Ag^{TS}-SAM//Ga_2O_3/EGaIn junctions, and that the electrical characteristics of the Ga_2O_3 film have a negligible effect on these measurements.

KEYWORDS: molecular electronics · self-assembled monolayers · molecular rectification · junctions · charge transport

In the decades since Aviram and Ratner first proposed a design for a molecular diode,[1] many experiments have been claimed to demonstrate rectification of current in systems involving molecular components.[2−11] Many of these reports involved experimentally difficult systems, and it has not always been clear that the rectification is either statistically significant or due to the molecules in the junctions (rather than, say, processes involving redox reactions or metal filaments). These ambiguities have been sufficiently disquieting that there has developed a substantial, and understandable, skepticism about interpretation of *all* reports of molecular rectification involving asymmetric or oxidizable electrodes.[12]

Since we report measurements of charge transport and rectification using a system with both asymmetric and oxidizable electrodes, we are interested in demonstrating that our system yields reliable information about SAMs. Our shorthand for the structures of these junctions is Ag^{TS}-SAM//Ga_2O_3/EGaIn: Ag^{TS} is so-called "template-stripped" (*e.g.*, smooth) silver (the fabrication of which we[13,14]and others[15,16] have described elsewhere), SAMs are those generated under carefully specified controlled conditions (and especially using freshly prepared thiols), "//" indicates a van der Waals interface, and Ga_2O_3/EGaIn denotes the eutectic alloy of gallium and indium with its ∼0.7 nm thick, self-passivating, surface layer of metal oxide[17] (with composition approximately Ga_2O_3, but with small amounts of indium oxide and nonstoichiometric gallium oxide).[18] This gallium oxide film is analogous to the oxide films that form on the surface of Al, Ti, and Si, but with—of course—its own physical and chemical properties. The characteristics of all the components of this system are relatively well-documented (although sometimes still incompletely understood), with the exception of the "Ga_2O_3" film (which we write henceforth simply as Ga_2O_3, but

* Address correspondence to gwhitesides@gmwgroup.harvard.edu.

Received for review December 27, 2011 and accepted May 2, 2012.

10.1021/nn205089u

understanding that its surface—if prepared in ambient conditions—is contaminated with adsorbed organic materials and contains small amounts of indium and other oxidation states of gallium).[18]

Since *all* experimental systems have the potential for artifacts, we suggest that—rather than including some systems and/or excluding others due to the potential for redox activity—it is more appropriate that every experimental system, and every claim of molecular rectification, be appropriately qualified. That is, the experimental results must be reproducible and amenable to statistical analysis and be backed by controls that rule out, or bound, all plausible nonmolecular mechanisms. The goal of this paper is to focus on the major sources of uncertainty in our junctions—the influence of the Ga_2O_3 film and the differences between the Fermi levels of the two metal electrodes (Ag ≈ -4.5 eV and EGaIn ≈ -4.2 eV)[19−21]—and to assemble all the currently available evidence (published and unpublished) that we interpret to indicate that they do not significantly affect our results.

The presence of this Ga_2O_3 film on the surface of "conical tip" electrodes is essential for their function, but the film itself raises three concerns: (i) *Electrical Conductivity*. The electrical conductivity of pure Ga_2O_3 depends on its method of preparation, and in principle, it might contribute substantial resistance to the junction. In fact, experimental measurements suggest that the resistance of the oxide film ($\sim 10^5$ to 10^6 Ω) is approximately 3 orders of magnitude smaller than the resistance of the most conductive alkanethiolate SAM that we have measured (for $S(CH_2)_9CH_3$, $\sim 10^9$ Ω) (on ~ 1 cm of the respective material). Temperature-dependent measurement data indicated that this barrier is not a tunneling barrier, but likely behaves as an n-type semiconductor.[24] (ii) *Adsorbed Organic Contaminants*. Experiments with X-ray photoelectron spectroscopy and time of flight secondary ion mass spectrometry (ToF-SIMS) indicate that the surface of the Ga_2O_3 film on EGaIn (as with most other surfaces exposed to the ambient environment and even some prepared in controlled atmospheres) supports a layer of adsorbed organic material that probably comprises volatile organic compounds, such as hydrocarbons and carboxylic acids.[18] This layer is probably a discontinuous network of organic islands and probably forms slowly on the time scale of the lifetime of a junction (>10 min), rather than a continuous sheet,[22] and while it is a poorly understood component of our system, it has not prevented us from observing even molecular effects that are quite subtle (*e.g.*, odd *vs* even alternation in *n*-alkanethiolates).[23] (iii) *Potential for Redox Behavior or for Other Processes That Might Cause Electrical Artifacts*. The reduction potential of Ga(III) and Ga(I) in the environment of the surface film is not known. Table S1 (in the Supporting Information) gives the reduction potentials of these species in aqueous solution, along with reduction potentials for other relevant species of Ga, In, Sn, Al, Ti, and Ag. Gallium(III) is, thus, probably easier to reduce than Al(III) but more difficult to reduce than Ag(I).

Objective. The objective of this paper is to examine Ag^{TS}-SAM//Ga_2O_3/EGaIn junction's behavior, using rectification as a probe, in order to establish whether the electrical characteristics of these systems—and especially *rectification* in a specific system (Ag^{TS}-$S(CH_2)_{11}$-Fc//Ga_2O_3/EGaIn)—are determined by the organic/organometallic molecules in the SAMs or by other components and/or characteristics of the systems (*e.g.*, the difference in work function between the electrode, the interfaces in the junction, or the Ga_2O_3 film). We particularly wished to understand if this gallium oxide film strongly influences charge transport through these junctions, especially in ways that could be mistaken for molecular rectification.

Rectification as a Model System. We have selected rectification—rather than the more commonly studied measurement of current density (J, A/cm^2) as a function of voltage (V, amps)—as the electrical characteristic to use as a probe in these junctions since it is particularly insensitive to some types of artifacts. Many of the experimental results we describe were obtained using a conical tip electrode.[23] This electrode has the advantage of convenience, but the disadvantage that several of its characteristics—and especially the contact area—are not completely defined (we discuss this issue in a following section). Rectification eliminates or reduces many artifacts, such as those from uncertainty in contact area: because the same junction provides J at positive and negative bias, many characteristics of the junction (contact area, distribution of defects, density and distribution of organic contaminants, thickness and topography of the Ga_2O_3 film) are constants for any specific junction. All of these characteristics ultimately must be studied independently by comparing rectification in different junctions, but the ability to compare $J(+V)$ and $J(-V)$ in exactly the *same* junction is an invaluable asset in a basic scientific inquiry into the relative contributions of the SAM (or the molecules in it—not necessarily exactly the same thing) and the Ga_2O_3 layer.

In addition to providing a system that is self-referencing, the study of rectification lends itself to testing clearly defined hypotheses. For example, we[24−27] and others[35−39] have falsified (and continue to show evidence against) the hypothesis that molecular rectification requires a D-σ-A structure (but proof is needed as metal filaments have been misinterpreted as molecular rectification before).[40−41] In a previous publication,[24] we have measured rectification in a series of compounds incorporating ferrocene (Fc) moieties, placed in different positions between the Ag^{TS} and Ga_2O_3/EGaIn electrodes, and were able to test three different theoretical predictions about the relationship of the rectification ratio to the structure of the rectifier (we summarize these results in the Background section). In a field that has often struggled to correlate theory with experiment, molecular rectification has been a rare example of success in this regard.

The Structure of this Paper. Information relevant to various electrical characteristics of the Ag^{TS}-SAM//Ga_2O_3/EGaIn junction, and especially the Ga_2O_3 layer, is distributed in a number of papers already published, including several describing rectification in SAMs containing Fc groups.[23−26] Because this information is scattered, and because its discussion has not always focused on understanding the Ga_2O_3 layer, it is currently understandably difficult for someone currently not active in the field to build a coherent picture of this critical component of the Ag^{TS}-SAM/Ga_2O_3/EGaIn junction. In this paper, we first review (in the Background section) our published work on rectification, emphasizing SAMs containing Fc groups. We then describe (in the Results section) new experimental studies of rectification in SAMs containing polar and redox-active terminal groups *other than* Fc. Finally, we discuss (in the Discussion section) these data, and relevant data from the literature, in terms of two concerns: the electrical characteristics of the Ga_2O_3 layer, and the mechanism of rectification. The Discussion section is divided into seven subsections, with the first subsection supporting the molecular origin of rectification, and with each following subsection addressing a hypothesis for how the Ga_2O_3 layer or the electrodes might exert unwanted influence over charge transport. Briefly, the hypotheses are (i) the difference between the Fermi levels of the electrodes causes rectification. (ii) Dipoles embedded in the SAM, the Ga_2O_3 layer, or the Ag−S interface cause rectification. (iii) Redox processes in the Ga_2O_3 layer significantly affect charge transport. (iv) Redox processes involving *both* the Ga_2O_3 layer *and* the SAM significantly affect charge transport. (v) The Ga_2O_3 layer forms a Schottky barrier (with either the bulk EGaIn or the SAM) and causes rectification. (vi) Mobile or variable dopants in the Ga_2O_3 layer cause memristor[27]-like behavior. Within each subsection, we summarize the hypothesis in question, give the relevant evidence that confirm or counter it, and draw a conclusion from that evidence. This format helps to organize the discussion.

To anticipate our conclusions, we find that (i) artifacts due to the Ga_2O_3 layer do *not* cause rectification; instead, rectification is due to the molecules incorporated in the SAMs. (ii) The mechanism of rectification requires the asymmetric placement of an accessible molecular orbital (that due to the Fc group which provides a HOMO that is slightly offset with respect to the E_F of both metals) between the electrodes, such that the orbital can undergo redox reactions at one bias, but not the opposite bias. (iii) The other characteristics of the junctions (the topography of the interfaces, surface contamination, the contact area, the composition of the Ga_2O_3 layer) do contribute to $J(V)$: rectification within a single junction is, however, more reproducible than rectification in different junctions, which is more reproducible than $J(V)$ in different junctions. All are, however, usefully diagnostic of the contribution of the structure of the SAM to the rates of charge transport across the junction. (iv) Rectification does *not* require an embedded electrical dipole, but rather (in our system) correlates with an accessible molecular orbital or orbitals.

Defining the Rectification Ratio. Before discussing possible mechanisms for rectification, we wish to give a cumbersome but unambiguous definition of the rectification ratio. For most diodes, researchers have chosen a particular voltage, V, and measured the current (or current density, J) at V and $-V$. Of the two applied voltages, the one that gives the greater $|J|$ is considered forward bias (V_{fwd}), while the one that gives the lesser $|J|$ is the reverse bias ($V_{rev} = -V_{fwd}$). The rectification ratio, then, is the magnitude of the ratio of current density at forward bias to that at reverse bias. We (and others) have used this definition eq 1 in all of our reports of rectification thus far.

$$\text{rectification ratio} \equiv \left|\frac{J(V_{fwd})}{J(V_{rev})}\right| \qquad (1)$$

This definition functions adequately when (i) one is reporting single measurements, rather than analyzing a statistical ensemble of measurements, and (ii) all that is important is the *magnitude* of rectification, and not the *direction* of rectification, that is, the polarity of the electrodes, with respect to the structure of the rectifying junction, at forward bias. For example, the statement that “SAMs of $S(CH_2)_{11}Fc$ show rectification ratios of 100, while SAMs of $S(CH_2)_{10}CH_3$ yield rectification ratios around 1.5”, informs the reader that the former is a much better rectifier than the latter, but it does not reveal that forward bias for the $S(CH_2)_{11}Fc$ occurs when the EGaIn electrode is biased negatively, while forward bias for $S(CH_2)_{10}CH_3$ occurs when EGaIn is biased positively. Knowing the direction of rectification is crucial to characterizing the mechanism of rectification.

For this reason, we began by measuring a statistical ensemble of rectification ratios, where each ratio was defined without regard to forward or reverse bias. This definition of r (eq 2), by itself, is not very informative: all values of r are negative, and most values of r for the best rectifiers ($S(CH_2)_{11}Fc_2$ and $S(CH_2)_{11}Fc$) are less than unity because forward bias is negative for these rectifiers.

$$r \equiv \frac{J(+V)}{J(-V)} \qquad (2)$$

This definition of r is, however, consistent across all rectifiers, and statistical analysis of distributions of $\log|r|$ is useful (r is approximately log-normally distributed, so $\log|r|$ is approximately normally distributed).[24,26] The average of log|r|, ⟨log|r|⟩, conveys both the magnitude and direction of rectification: ⟨log|r|⟩ takes on the sign of V_{fwd}, where V_{fwd} is the bias at which rectification is observed, that is, a positive or negative applied bias in which the "diode" allows current to flow through. The diode in our case is the rectifying molecule making up the SAM. Furthermore, the standard deviation (σ) of log|r| accurately quantifies the error in the measurement of the rectification ratio.

The field of molecular electronics is, however, accustomed to evaluating rectification ratios using a linear, rather than a logarithmic, scale. In order to report a value, on a linear scale, that conveys both the magnitude and the direction of rectification, we use the definition of rectification ratio, *R*, given by eq 3.

$$R \equiv sign(\langle \log|r| \rangle) 10^{|\langle \log|r| \rangle|} \tag{3}$$

This definition of *R* conveys the *direction* of rectification by taking the sign of V_{fwd}, while also having the same *magnitude* as the traditional definition of rectification (eq 1), without depending on shifting definitions of V_{fwd} and V_{rev}. The downside of using *R* is that there is no accurate and convenient way to report error: because *R* is not normally distributed, it cannot be reported as value ± error, whereas this format is appropriate for ⟨log|r|⟩ since it is approximately normally distributed. In our opinion, both ⟨log|r|⟩ ($\pm\sigma$) and *R* are informative—the former for giving a sense of the error or statistical uncertainty in the value, and the latter for communicating the magnitude of the value. As such, we have reported both quantities in Table 1 and will reference both in this paper. For a background on rectification in organic monolayers, see the Supporting Information.

Background: Evidence for Our Proposed Mechanism. We briefly describe here all of our relevant, published results on rectification in SAMs containing Fc and SAMs of alkanethiols (used as controls). We previously published a detailed study of the mechanism of rectification[24] in which we synthesized and measured several compounds containing Fc, including $S(CH_2)_{11}Fc_2$ (where Fc_2 is bis-ferrocene), $S(CH_2)_{11}Fc$, $S(CH_2)_9Fc$, and $S(CH_2)_6Fc(CH_2)_5CH_3$. Since we wish to discuss aspects of these experiments and data we have not discussed previously, and since the quality of the data is relevant to these discussions, we have included those (previously published) data in this paper: Figure 1A–D shows histograms of log|r| for these compounds; their values of ⟨log|r|⟩ and *R* appear in the same figure and in Table 1. We also measured junctions containing SAMs of alkanethiols ($S(CH_2)_{10}CH_3$ and $S(CH_2)_{14}CH_3$; Figure 1E,F) as controls to show that rectification was due to the SAM and not to other characteristics of the junction (for example, the Ga_2O_3/EGaIn electrode).

TABLE 1. Magnitude and Sign of the Rectification Ratio Depends on the Terminal Moiety of the SAM

compound	r (eq 2)	⟨log|r|⟩	R (eq 3)	molecular diode?[a]
$S(CH_2)_{11}Fc_2$	−0.0020	−2.70 ± 0.54	−500	yes
$S(CH_2)_{11}Fc$	−0.0093	−2.03 ± 0.49	−100	yes
$S(CH_2)_9Fc$	−0.11	−0.97 ± 0.65	−10	yes
$S(CH_2)_6Fc(CH_2)_5CH_3$	-1.2	0.10 ± 0.23	1.2	no
$S(CH_2)_{10}CH_3$	−1.5	0.18 ± 0.17	1.5	no[b]
$S(CH_2)_{14}CH_3$	−2.3	0.35 ± 0.40	2.3	no[b]
$S(CH_2)_{10}$S-trimethylbenzoquinone	−1.9	0.29 ± 0.22	1.9	no
$S(CH_2)_{10}$S-methylnaphthoquinone	−3.5	0.54 ± 0.34	3.5	yes[c]
$S(CH_2)_{10}CH_2OH$	−2.5	0.40 ± 0.32	2.5	no
$S(CH_2)_{10}COOH$	−2.4	0.38 ± 0.25	2.4	no

[a] The text discusses whether the value of *R* is statistically distinguishable, according to a multiple comparison test, from both alkanethiolate controls. [b] These compounds are controls and are, therefore, defined *not* to be molecular diodes. [c] Although the value of *R* for this compound was statistically distinguishable from those of both alkanethiolate controls, it is not as large as that of the ferrocenes but at the opposite V_{fwd}; that is, rectification is observed when a positive bias is applied.

We used these data to support our proposed mechanism of rectification, shown schematically in Figure 2A for $S(CH_2)_{11}Fc$.[26] According to this mechanism, the placement of the highest occupied molecular orbital (HOMO) of ferrocene (Fc) adjacent to the Ga_2O_3/EGaIn electrode, but separated from the Ag electrode by a C_{11} alkyl chain, fixes the position of the HOMO relative to the Fermi level of the Ga_2O_3/EGaIn electrode. When the EGaIn is biased positively, the HOMO of Fc remains below the Fermi levels of both electrodes and is unable to participate in charge transport. When the EGaIn is biased negatively, however, the Fc HOMO rises to a position between the Fermi levels of the two electrodes and is able to participate in charge transport. At negative bias, when the Fc HOMO participates in charge transport, the width of the tunneling barrier is approximately the length of the C_{11} alkyl chain (∼14.5 Å). At positive bias, however, when the Fc HOMO cannot participate in charge transport, the width of the tunneling barrier is defined by the length of the entire molecule (∼19 Å), including both the alkyl chain and the Fc moiety. Because the tunneling current density decreases exponentially as the width of the tunneling barrier increases, *J* at negative bias is significantly greater than *J* at positive bias; indeed, Ag^{TS}-$S(CH_2)_{11}Fc//Ga_2O_3$/EGaIn junctions rectify with $R \cong -100$ (Figure 1B). The difference between $J(-1.0\ \mathrm{V})$ and $J(+1.0\ \mathrm{V})$ can be modeled quantitatively, using the simplified Simmons model, adapted to the composite structure of the rectifier. The Simmons model predicts different values for $J(-1.0\ \mathrm{V})$ (eq 4) and $J(+1.0\ \mathrm{V})$ (eq 5), due to the necessity of tunneling through the Fc moiety at the latter bias, but not the former.

$$J(-1.0\ \mathrm{V}) = J_0 e^{-\beta_{\mathrm{alk}} d_{\mathrm{alk}}} \tag{4}$$

$$J(+1.0\ \mathrm{V}) = J_0 e^{-(\beta_{\mathrm{alk}} d_{\mathrm{alk}} + \beta_{\mathrm{Fc}} d_{\mathrm{Fc}})} \tag{5}$$

Here, β_{alk} is the tunneling constant for the C_{11} alkyl chain (approximately 0.8 $\mathrm{Å}^{-1}$, although this value does

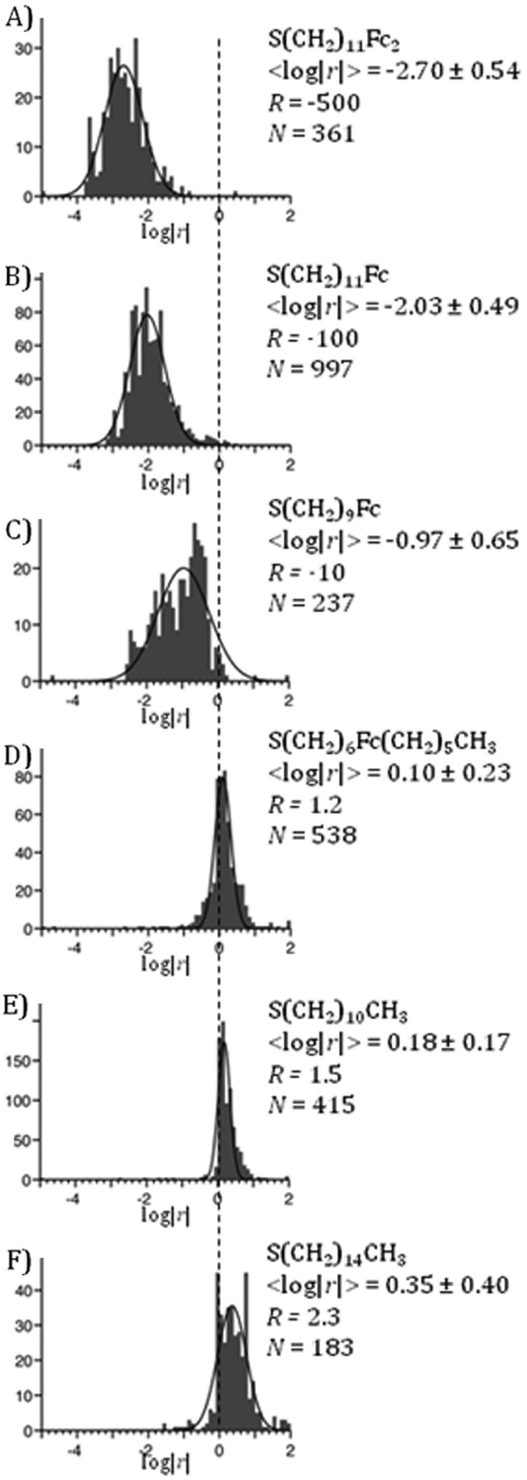


Figure 1. Histograms of log|*r*| (eq 2) for Ag^{TS}-$S(CH_2)_{11}Fc_2$//Ga_2O_3/EGaIn (A), Ag^{TS}-$S(CH_2)_{11}Fc$//Ga_2O_3/EGaIn (B), Ag^{TS}-$S(CH_2)_9Fc$//Ga_2O_3/EGaIn (C), Ag^{TS}-$S(CH_2)_6Fc(CH_2)_5CH_3$//Ga_2O_3/EGaIn (D), Ag^{TS}-$S(CH_2)_{10}CH_3$//Ga_2O_3/EGaIn (E), and Ag^{TS}-$S(CH_2)_{14}CH_3$//Ga_2O_3/EGaIn (F) junctions. Gaussian functions fitted to each histogram appear as black curves, and the values of ⟨log|*r*|⟩ and *R* (eq 3) determined from these functions, as well as the number of data (*N*), are given beside each histogram. The dashed line is a guide for the eye placed at log|*r*| = 0 (*R* = 1). The data in this figure were originally published in ref 22; here, they have been plotted differently, in accordance with the definitions of log|*r*| and *R* used in this paper.

not affect log|*r*|), and d_{alk} is the length (in Å) of the C_{11} alkyl chain. Similarly, β_{Fc} is the tunneling constant for the Fc moiety (when the HOMO is not in resonance with the electrodes), and d_{Fc} is the length of the Fc moiety along the axis perpendicular to the planes of the electrodes. Given these relationships, and assuming that J_0 is the same at -1.0 V and $+1.0$ V, it is possible to rewrite log|*r*|, using eq 6, in a way that depends only on β_{Fc} and d_{Fc}.

$$\log|r| = -\log(e)\beta_{Fc}d_{Fc} \qquad (6)$$

If we use the value of $d_{Fc} = 4.5$ Å and assume that $\beta_{Fc} = \beta_{alk}$ (=0.8 $Å^{-1}$; a questionable assumption because the heights of the two tunneling barriers posed by the C_{11} alkyl chain and the Fc moiety are probably not the same), then eq 6 predicts that log|*r*| = -1.6. The observed ⟨log|*r*|⟩ of -2.0 has a slightly greater magnitude than the predicted value but is within plausible agreement given the several assumptions made. The direction of disagreement implies that either $d_{Fc} > 4.5$ Å or $\beta_{Fc} > \beta_{alk}$. Of the two options, the latter is more likely. Setting log|*r*| = -2.0 and $d_{Fc} = 4.5$ Å and solving for β_{Fc} yields a value of 1.02 $Å^{-1}$.

According to this mechanism, increasing the difference between the effective widths of the tunneling barriers at negative and positive bias should increase the magnitude of *R*. We tested this prediction by attaching a second Fc moiety, in conjugation with the first Fc moiety, to the end of the molecule to produce $S(CH_2)_{11}Fc_2$. Adding this second Fc moiety had only a small effect on the energy of the HOMO (increasing from -5.0 to -4.9 eV, still lower than the Fermi levels of both electrodes) but increased the total length of the molecule to ~23 Å ($d_{Fc} = 8.5$ Å, where in this case, d_{Fc} is the length of the Fc_2 moiety). In accordance with the qualitative prediction of our mechanism, we determined *R* = -500 (⟨log|*r*|⟩ = -2.70 ± 0.54) for this compound (Figure 1A). If we assume that the tunneling constant for Fc_2 is the same as that derived above for Fc (β_{Fc} = 1.02 $Å^{-1}$), eq 6 predicts that $S(CH_2)_{11}Fc_2$ should have ⟨log|*r*|⟩ = -3.78; that is, the predicted rectification is more than 1 order of magnitude greater than the observed rectification.

A plausible rationalization of this difference would start with the fact that the predicted value of ⟨log|*r*|⟩ = -3.78 assumes that the Fc_2 moiety adopts the most extended conformation possible—that is, the two Fc groups lie along the axis of the molecular backbone. Because SAMs are not perfect two-dimensional crystals, rotation probably occurs around the bond connecting the two Fc moieties to each other (*i.e.*, the Fc_2 group "folds over") or the bond connecting the Fc_2 group to the C_{11} alkyl chain (*i.e.*, the Fc_2 group tilts away from the axis of the molecular backbone). Either, or both, rotations would decrease the separation between the electrodes, relative to the conformation in which the Fc_2 group is maximally extended. In fact, if

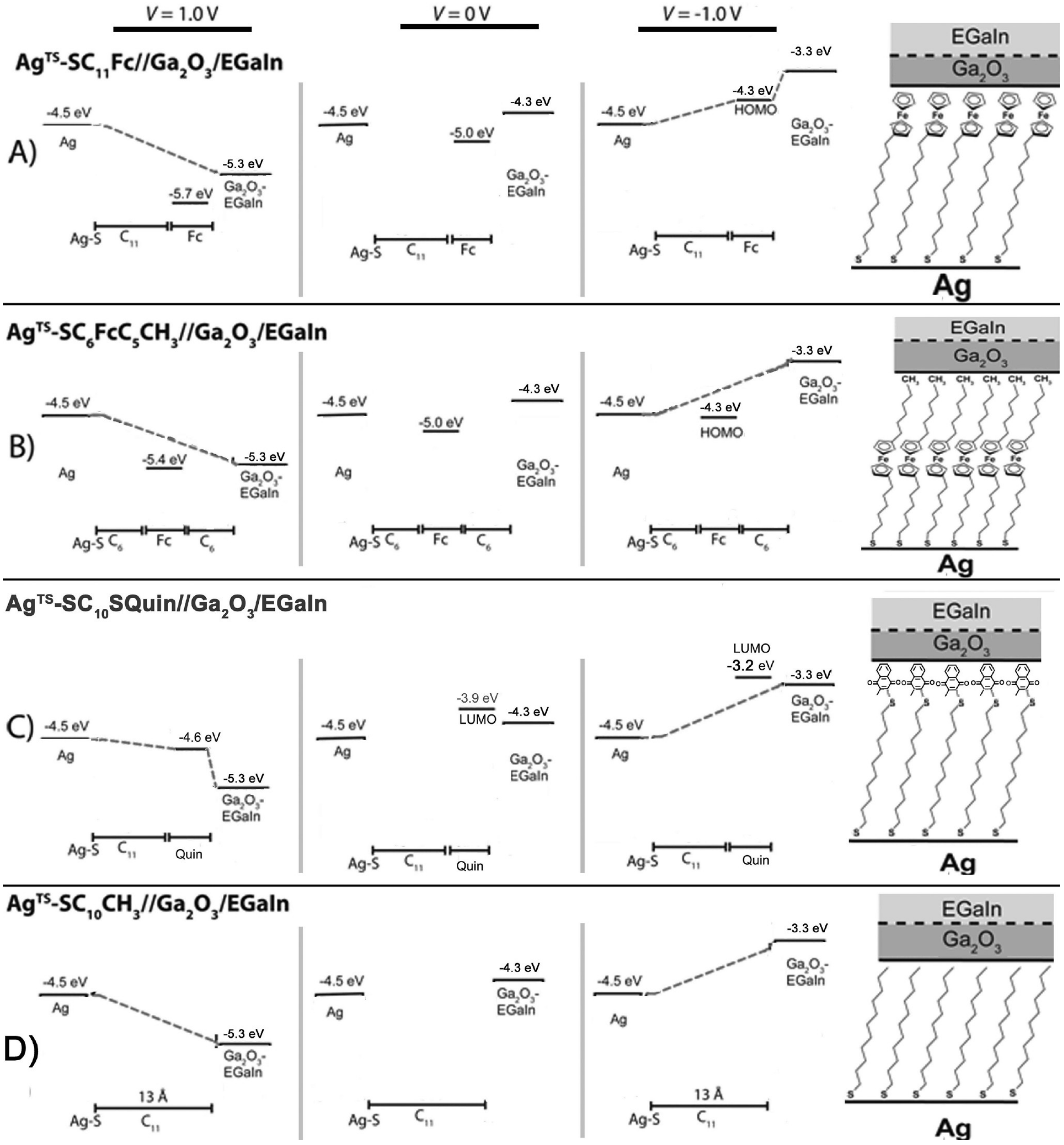
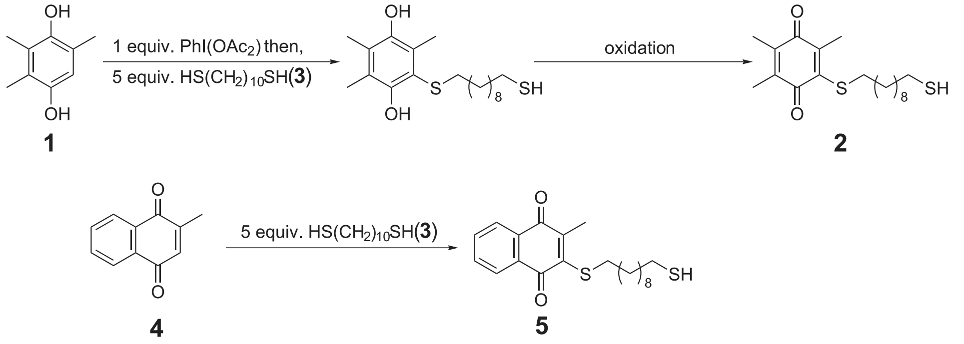


Figure 2. Energy level diagrams showing the proposed mechanism of rectification. (A) For SAMs of S(CH$_2$)$_{11}$Fc, the Fc HOMO couples to the Fermi level of EGaIn and remains below it over the range of applied bias. Our mechanism, therefore, predicts higher current when EGaIn is biased negatively than when it is biased positively because the Fc HOMO can participate in charge transport under the former condition, but not the latter. (B) For SAMs of S(CH$_2$)$_6$Fc(CH$_2$)$_5$CH$_3$, the Fc HOMO couples roughly equally to the Fermi levels of both electrodes and can, thus, participate in charge transport at both positive and negative bias. It does not rectify. (C) In SAMs of 5, the naphthoquinone LUMO lies *above* the Fermi levels of the electrodes and also couples to the EGaIn electrode. (D) SAMs of S(CH$_2$)$_{10}$CH$_3$ have no accessible molecular orbital to participate in charge transport and do not rectify. Idealized schematic representations of the corresponding tunneling junctions consisting of Ag^{TS} bottom electrodes, SAMs of S(CH$_2$)$_{11}$Fc (A), S(CH$_2$)$_6$Fc(CH$_2$)$_5$CH$_3$ (B), compound 5 (C), and S(CH$_2$)$_{10}$CH$_3$ (D), and Ga$_2$O$_3$/EGaIn top electrodes.

we substitute the observed value of ⟨log|*r*|⟩ into eq 6 and allow d_{Fc} to vary (with $\beta_{Fc} = 1.02$ Å^{-1}), we estimate $d_{Fc} = 6.07$ Å. This value lies between that of a single Fc moiety (4.5 Å) and a fully extended Fc$_2$ moiety (8.5 Å) and may represent the average length of the set of conformations adopted by the Fc$_2$ group.

On the other hand, the difference between the predicted and observed values of ⟨log|*r*|⟩ for S(CH$_2$)$_{11}$-Fc$_2$ may reflect a deficiency in the quantitative model (eqs 4–6); this deficiency nonetheless does not affect the integrity of the mechanism from which it is derived. For example, temperature-dependent measurements (described below in this section) establish that the mechanism of rectification involves a change, at sufficiently negative bias, from tunneling alone (through the entire S(CH$_2$)$_{11}$Fc molecule) to tunneling (through the C$_{11}$ alkyl chain) and hopping (between the Fc moiety and the Ga$_2$O$_3$/EGaIn electrode). Our proposed mechanism incorporates this observation, but the quantitative model in eqs 4–6 does not: it only



Scheme 1. Synthesis of benzo- and naphthoquinone-terminated alkane thiols. Trimethylhydroquinone 1 was oxidized to the corresponding *p*-quinone with (diacetoxyiodo)benzene. Addition of 1,10-decanedithiol (3) resulted in formation of quinone 2 after conjugate addition and reoxidation by another equivalent of starting material, as has been reported.[42,43] An excess of the dithiol was used to suppress the formation of *S,S*-bisarylated by-products (disulfides). The synthesis of naphthoquinone 5 was analogously performed beginning with commercially available menadione (4). Yields are given in the Supporting Information.

accounts for tunneling, not hopping. If hopping is not substantially faster than tunneling, or if the rate of hopping (*i.e.*, the activation energy) differs for the Fc and Fc_2 moieties, then the quantitative predictions of the model will fail, even though the underlying mechanism is correct. In any case, although our mechanism has yet to be vindicated by successful quantitative predictions, it does successfully rationalize trends qualitatively connecting values of R with the structure of the molecules making up the SAM.

To confirm the molecular origin of rectification in these Fc-terminated rectifiers, we employed three compounds as controls: $S(CH_2)_{10}CH_3$, $S(CH_2)_{14}CH_3$, and $S(CH_2)_6Fc(CH_2)_5CH_3$. The first two controls—alkanethiols having the same length as the C_{11} alkyl chain and the entire $S(CH_2)_{11}Fc$ molecule, respectively—tested the prediction that SAMs without an accessible molecular orbital should not rectify. For $S(CH_2)_{10}CH_3$, we measured $R = 1.5$ (Figure 1E), and for $S(CH_2)_{14}CH_3$, we measured $R = 2.3$ (Figure 1F). We found that these values do differ slightly, but statistically significantly,[24] from unity and from each other. We note, however, that whatever unknown factor causes slight rectification in SAMs of alkanethiols produces values of R that are *positive*, whereas R is *negative* for Fc-terminated SAMs. The third control, $S(CH_2)_6Fc(CH_2)_5CH_3$, was designed to test the prediction of our mechanism that a compound incorporating a Fc moiety but lacking any asymmetry (*i.e.*, with the Fc moiety placed in the middle of the SAM, flanked by alkyl chains of equal length) should not rectify because rectification arises from the preferential coupling of the Fc moiety to one electrode over the other. Indeed, we determined that, for $S(CH_2)_6Fc(CH_2)_5CH_3$, $R(1.0\text{ V}) = 1.2$ (Figure 1D); this value is quite close to unity and has the opposite sign from those of $S(CH_2)_{11}Fc$ and $S(CH_2)_{11}Fc_2$. These controls established that (i) a molecular orbital is required for rectification, and (ii) a single molecular orbital must be located asymmetrically within the junction in order to rectify.

In another prior publication,[25] we used measurements of $J(V)$ as a function of temperature (T, in K) in order to elucidate the mechanism of rectification in SAMs of $S(CH_2)_{11}Fc$. These experiments yielded two important results. (i) Charge transport through junctions of the form Ag^{TS}-$S(CH_2)_{n-1}CH_3$//Ga_2O_3/EGaIn showed negligible temperature dependence for n = 12, 14, 16, and 18. This observation indicates that tunneling, as expected, is the dominant mechanism of charge transport through junctions incorporating SAMs of alkanethiols. (ii) At sufficiently negative bias ($V < -0.6$ V), the rate of charge transfer through SAMs of $S(CH_2)_{11}Fc$ decreased with decreasing temperature, whereas at all other biases ($V > -0.6$ V), charge transport was independent of temperature. The temperature-dependent charge transport at negative bias conformed to the Arrhenius relationship (a straight line on a plot of $\ln(J)$ *vs* $1/T$), and thus implied a hopping mechanism, with an activation energy of 78 meV. Our mechanism predicts that, at sufficiently negative bias, the Fc HOMO should become able to participate in classical charge transport (as opposed to tunneling). We interpreted the observation of thermally activated charge transport at $V < -0.6$ V as confirmation that Fc HOMO is involved in classical charge transport (*i.e.*, hopping) at negative bias but not at positive bias.

Our proposed mechanism of rectification—the asymmetric placement of a molecular orbital between two electrodes—successfully predicts the effect, on R, of several changes in the molecular structure of the rectifier. This mechanism finds further validation through temperature-dependent studies showing hopping (between the Fc moiety and the Ga_2O_3/EGaIn electrode) at negative bias but not at positive bias. While we believe that this evidence is enough to justify confidence in our mechanism, we present, in this paper, further experimental confirmation of this mechanism, as well as evidence against alternative mechanisms, especially those involving the Ga_2O_3 film.

EXPERIMENTAL DESIGN

Choice of Compounds. Our choice of molecules with Fc and Fc_2 moieties and our choice of alkanethiols are explained in a previous publication.[24] In addition to the compounds already reported previously, we chose to synthesize and measure two classes of compounds: (i) those with conjugated terminal groups having lowest unoccupied molecular orbitals (LUMOs) slightly above the Fermi levels of the electrodes (−4.3 to −4.5 eV),[19,20] and (ii) those with polar terminal groups (COOH and OH).

SAMs terminated by conjugated moieties with accessible HOMOs ($S(CH_2)_{11}Fc_2$, $S(CH_2)_{11}Fc$, and $S(CH_2)_9Fc$) slightly below the Fermi levels of the electrodes exhibit large negative values of *R*. Our mechanism of rectification predicts that substituting a LUMO for the HOMO should change the sign of *R*. To test this prediction, we chose two molecules (Scheme 1) with terminal groups based on benzoquinone and modified with electron-withdrawing groups. Compound **2** is terminated by a trimethylbenzoquinone, and compound **5** is terminated by a methylnaphthoquinone. We attached each of these moieties, *via* a thioether, to an alkanethiol chain with a total length of 12 atoms (including both sulfur atoms) in order to mimic the structures of $S(CH_2)_{11}Fc$ and $S(CH_2)_{11}Fc_2$ as closely as possible.

We also desired to test the effect, on charge transport and rectification, of polar terminal groups *without* an accessible molecular orbital. For this reason, we selected a carboxylic acid and a primary alcohol. We designed the length of the alkanethiol tail so that we could compare three compounds of the form $S(CH_2)_{10}R$, where R = CH_3, COOH, and CH_2OH.

Statistical Analysis of Rectification. Because many statistical analyses presume normal distributions[44] and because *r* is approximately log-normally distributed,[24,26] we analyzed distributions of log|*r*| rather than *r*. We did not directly analyze distributions of *R* because *R* is discontinuous (*i.e.*, it is impossible to have values of *R* between −1 and 1) and therefore difficult to analyze statistically. Detailed descriptions of our procedure for plotting histograms of log|*r*| and fitting them with Gaussians are given elsewhere.[23,24,26]

RESULTS

SAMs with Redox-Active Terminal Groups. We synthesized two compounds (Scheme 1: **2** and **5**) having redox-active terminal groups with lowest unoccupied molecular orbitals (LUMOs) having energies close to, but greater than, the Fermi levels of the electrodes (EGaIn ≈ −4.3 eV, Ag ≈ −4.5 eV).[19−21] The synthesis of these compounds is described in the Supporting Information. We do not know the exact energies of the LUMOs of these compounds, but we do know that the LUMO of **2** is higher in energy than the LUMO of **5** because the addition of a second aromatic ring increases the electron affinity of the moiety. We estimated the orbital energies (E_{HOMO} and E_{LUMO}) to be ∼−5.0 and ∼−3.9 eV for the ferrocene and naphthoquinone, respectively, from cyclic voltammetric data[23,55] using the equation below, where $E_{abs,NHE}$ is the absolute potential of the normal hydrogen electrode (−4.5 eV), and $E_{1/2,NHE}$ is the formal half-wave potential *versus* normal hydrogen electrode (which is 0.47 eV for ferrocene and −0.60 eV for 2-methyl naphthoquinone):

$$E_{HOMO} = E_{abs,NHE} - eE_{1/2,NHE} \qquad (7)$$

These values cannot be related directly to the HOMO and LUMO energies (relative to vacuum) because of the importance of medium and solvation, but these numbers are a useful approximation of the energy levels at open circuit, not when a bias is applied.

Using procedures described previously,[23,24,26] we formed SAMs of these compounds and used conical tips of Ga_2O_3/EGaIn to fabricate and measure junctions of the form Ag^{TS}-SR//Ga_2O_3/EGaIn. We measured *J* through these junctions over a range of applied bias from *V* = −1.2 to 1.2 V. (Because a range of *V* = −1.0 to 1.0 V was insufficient to observe rectification for SAMs of **2** and **5**, we were forced to expand the range of applied bias slightly, from ±1.0 to ±1.2 V.) The values reported in the literature for the Fermi levels of Ag (∼−4.5 eV) and EGaIn (∼−4.3 eV) are slightly different, and the actual Fermi levels of the electrodes in the junctions might differ by either more or less than ∼0.3 eV, due to any number of factors (the presence of a Ga_2O_3 film on EGaIn, the van der Waals interface between Ga_2O_3/EGaIn and the SAM, the Ag−S bond).

If the Fermi level of the Ag^{TS} electrode in the actual junction was still lower than that of the Ga_2O_3/EGaIn electrode, then this difference would increase the positive voltage necessary to bring the LUMO of **2** or **5** into resonance with the Fermi levels of the electrodes (Figure 3). By contrast, this situation would actually reduce the negative voltage necessary to bring the HOMO of Fc into resonance. In any case, we note that, based on a small set of measurements of $S(CH_2)_{11}Fc$ over the range of *V* = −1.2 to 1.2 V, the value of *R* at ±1.2 V does not differ substantially from the value of *R* at 1.0 V. We believe, therefore, that comparisons between *R*(1.0 V) for $S(CH_2)_{11}Fc$ and *R*(1.2 V) for **2** and **5** are valid. Figure 4 contains histograms of log|*r*| for various compounds, including **2** and **5** (at a bias of ±1.2 V), as well as $S(CH_2)_{11}Fc$ and $S(CH_2)_{10}CH_3$ (at a bias of ±1.0 V), for comparison.

SAMs with Polar Terminal Groups. We have also formed junctions incorporating SAMs of two compounds with polar, non-redox-active terminal groups: $S(CH_2)_{10}$-CH_2OH (11-mercapto-1-undecanol) and $S(CH_2)_{10}COOH$ (11-thioundecanoic acid). Both compounds are

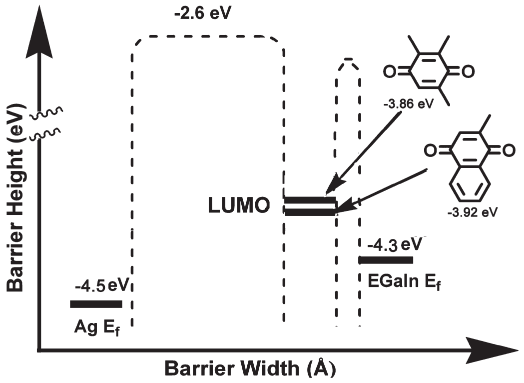


Figure 3. Energy-level diagram for junctions containing SAMs of compounds 2 and 5 (Scheme 1). Because the terminal moiety of 5 is more electron-withdrawing than that of 2, the LUMO of 5 lies closer to the Fermi levels of the electrodes than that of 2. The energies of the LUMOs of 2 and 5 are approximate, but their relative positions are accurate. The heights of the tunneling barriers for the alkyl chain and the van der Waals interface have not been measured in our junctions and may be quite different from what are shown.

commercially available (Sigma Aldrich). We measured J through these junctions over a range of applied bias from $V = -1.0$ to 1.0 V. Histograms of log|r|, at $V = \pm 1.0$ V, for these compounds appear in Figure 5, again with $S(CH_2)_{11}Fc$ and $S(CH_2)_{10}CH_3$ for comparison. The values of R(1.0 V) for $S(CH_2)_{10}CH_2OH$ and $S(CH_2)_{10}COOH$ were 2.5 and 2.4, respectively; these values are statistically distinguishable from R = 1, according to a t test[44] (see next section).

Statistical Significance of Rectification. It is necessary to assess the statistical significance of the values of R in Table 1 by asking two questions: (i) is each value of R statistically distinguishable from R = 1? and (ii) is each value of R statistically distinct from the values of R for other compounds (especially the controls that lack molecular asymmetry: $S(CH_2)_{10}CH_3$ and $S(CH_2)_{14}CH_3$)? Statistical tests exist to answer these questions,[44,46] and since these tests operate on variables with continuous probability distributions (*i.e.*, not R), we applied them to the values of log|r| for the various compounds. Finding a statistically significant value (or difference between values) of ⟨log|r|⟩ is, nonetheless, equivalent to finding a statistically significant result for R. A value of R that is statistically significant (*i.e.*, distinguishable from R = 1), in turn, implies an equivalent statistical significance for the sign of R.

To answer the first question, we performed t tests on the distributions of log|r| for each compound to determine the probability (p) of the null hypothesis: that a distribution was derived from a population with zero mean (*i.e.*, that the value of ⟨log|r|⟩ was zero).

All of these tests rejected the null hypothesis at well above the 95% confidence level (the highest p obtained was 7×10^{-6}, for $S(CH_2)_6Fc(CH_2)_5CH_3$; the rest were many orders of magnitude lower). This result implies that *junctions* containing every compound in Table 1 can be considered rectifying in the sense of giving rise to statistically significant rectification. We are primarily concerned with identifying which SAMs rectify; there are nonmolecular reasons that would make a junction rectify current, for example junction asymmetry, and we are not interested in this. For some types of junctions (*e.g.*, those containing alkanethiolates), the observed rectification, although statistically significant, almost certainly arises from something other than the SAM (we discuss several possible origins of the values of R between 1.2 and 2.5 in the Discussion section).

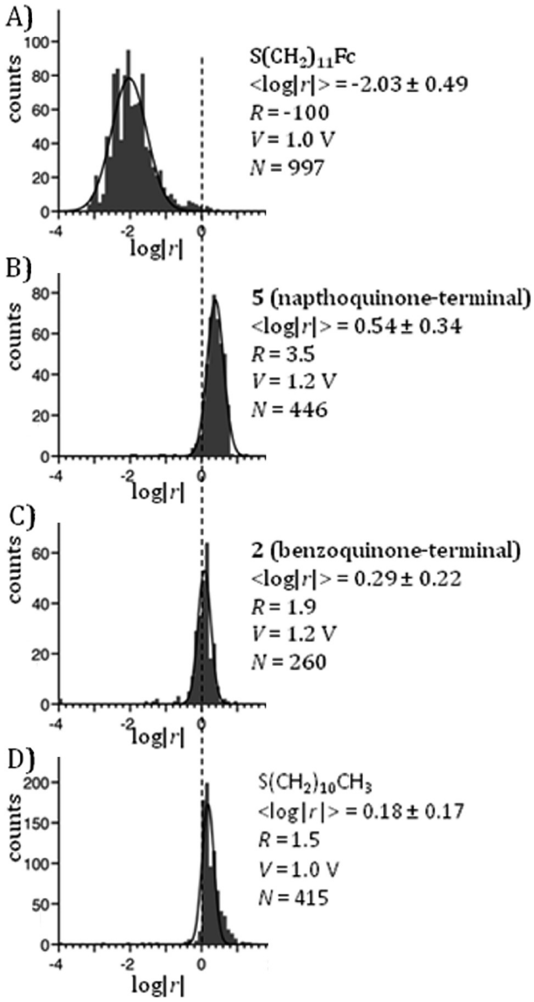


Figure 4. Histograms of log|r| (eq 2) for junctions containing (A) SAMs of $S(CH_2)_{10}CH_3$ and compounds with redox-active terminal groups: (B) naphthoquinone-terminated compound 5, (C) benzoquinone-terminated compound 2, and (D) $S(CH_2)_{11}Fc$. Definitions of log|r| (eq 2) and R (eq 3) appear in the text. Solid black curves give the Gaussian functions fitted to each histogram. We note that the SAMs of 2 and 5, whose histograms appear in (B and C), had to be measured at a bias range of ±1.2 V in order to observe rectification. SAMs of $S(CH_2)_{11}Fc$ were also stable up to ±1.2 V and continued to rectify at this bias range (R was roughly unchanged). The dotted line is a guide for the eye at log|r| = 0 (R = 1).

In determining which SAMs rectify, the second question—does the value of R for a compound differ

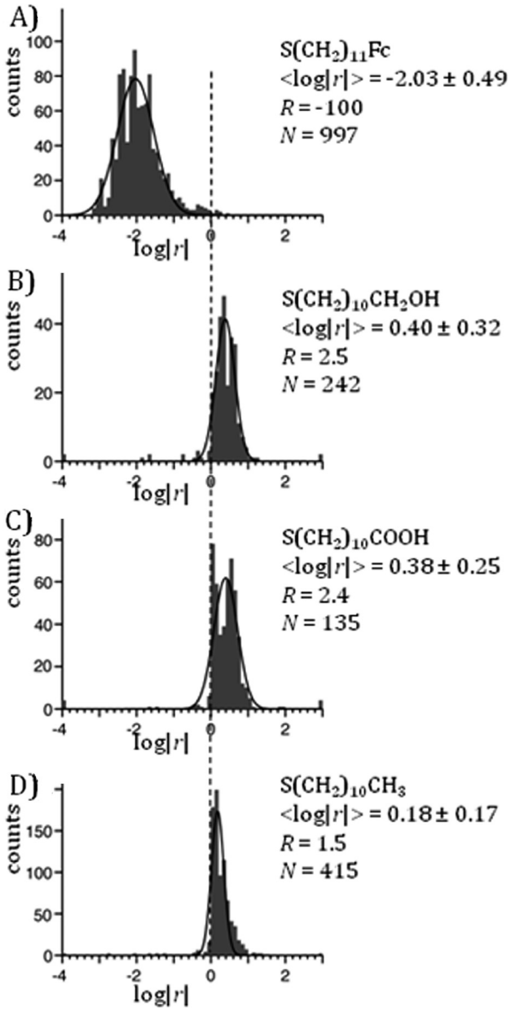


Figure 5. Histograms of log|*r*| (eq 2) for junctions containing SAMs of $S(CH_2)_{10}CH_3$ (A), two polar terminal groups: $S(CH_2)_{10}CH_2OH$ (B) and $S(CH_2)_{10}COOH$ (C), and $S(CH_2)_{11}Fc$ (D). Definitions of log|*r*| (eq 2) and *R* (eq 3) appear in the text. Solid black curves indicate Gaussian functions fitted to each histogram. The dotted line is a guide for the eye at log|*r*| = 0 (*R* = 1).

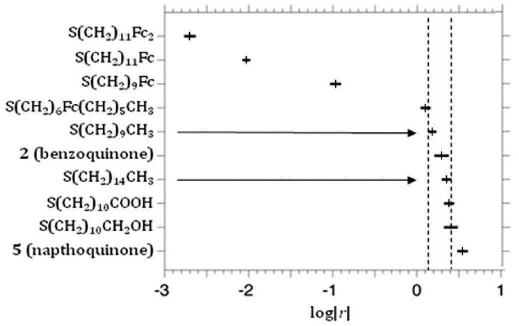


Figure 6. Results of a multiple comparison test, performed on the distributions of log|*r*| for all 10 compounds reported in this paper. For each compound, the vertical dash represents the value of ⟨log|*r*|⟩ (Table 1) determined from the Gaussian fit to the histogram of log|*r*|, and the horizontal bar represents the confidence interval for the value, calculated by the test. Arrows point to the confidence intervals of the two alkanethiolate controls, and vertical dotted lines indicate the range encompassing both confidence intervals of the alkanethiolate controls. The multiple comparison test is designed such that, if the confidence intervals of any two values of ⟨log|*r*|⟩ do not overlap, then the difference between those values is statistically significant.

from the values of *R* for other compounds, especially those of controls—is much more informative than the first. In order to answer this question, we used a multiple comparison test, which compares the distributions of log|*r*| for all compounds simultaneously, using a procedure similar to a *t* test.[44−46] The multiple comparison test shows (at the 95% confidence level) whether, for example, the value of *R* for $S(CH_2)_{11}Fc$ is statistically distinguishable from the values of *R* for other compounds.[46] Figure 6 graphically represents the results of the multiple comparison test. Each bar in Figure 6 gives the confidence interval for a particular compound; if the bars of two compounds overlap, then their values of *R* are not statistically distinguishable from one another. If two bars in Figure 6 do *not* overlap, however, then the values of *R* for the corresponding two compounds are statistically different, at the 95% confidence level. According to this test, four compounds—$S(CH_2)_{11}Fc_2$, $S(CH_2)_{11}Fc$, $S(CH_2)_9Fc$, and compound **5**—have values of *R* that are statistically distinct from those of every other compound, including both alkanethiolate controls ($S(CH_2)_{10}CH_3$ and $S(CH_2)_{14}CH_3$). This test confirms that the compounds terminated by Fc and Fc_2 are, indeed, molecular diodes. Compound **5** also rectifies in a manner that is statistically distinguishable from other compounds, and unlike the ferrocene containing SAMS, compound **5** rectifies when a positive bias is applied albeit with a lower rectification ratio (*R* = 3.5).

Comparison of Distributions of log|*J*| *versus* Those of log|*r*|. In the introduction, we discussed the advantages of using rectification, instead of *J*: rectification is a self-referencing measurement that is insensitive to factors that vary from junction to junction. Figure 7 compares histograms of log|*J*/(A/cm^2)| against histograms of log|*r*| for three compounds: $S(CH_2)_{11}Fc$, **5** (the naphthoquinone-terminated rectifier), and $S(CH_2)_{14}CH_3$.

The *x*-axes of all histograms span the same width on a log-scale: 13 orders of magnitude. Comparing histograms of the two quantities, we observe that (i) the variance (square of the standard deviation) of log|*r*| is typically less than or equal to the variance of log|*J*/(A/cm^2)|, and (ii) histograms of log|*r*| are less noisy and have fewer outliers (virtually none, in fact) than histograms of log|*J*/(A/cm^2)|. These observations are valid for the other compounds investigated in this paper, and they confirm the advantages of using rectification to study charge transport in SAMs. Values of log|*r*| represent the difference between values of log|*J*(1.0 V)| and log|*J*(−1.0 V)|. Ordinarily, when a variable *X* is the difference between variables *A* and *B*, the variance of *X* is greater than the variances of both *A* and *B*, assuming *A* and *B* are independent. When *A* and *B* are

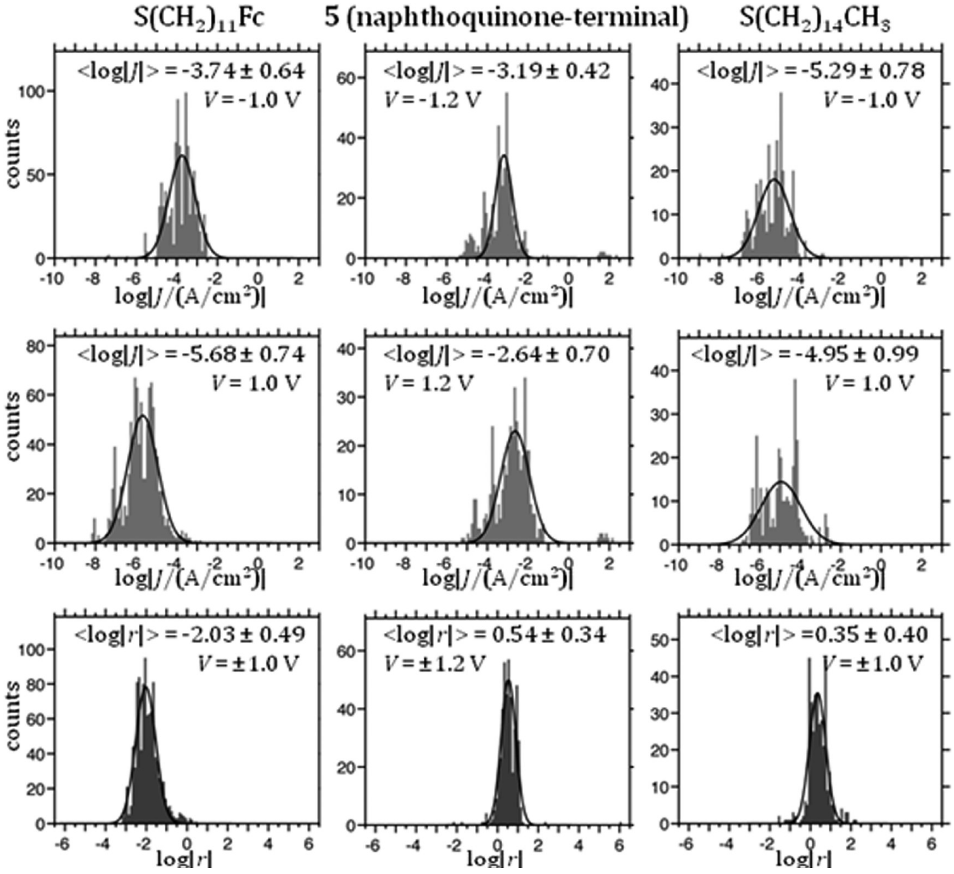


Figure 7. Comparison of log|J/(A/cm^2)| and log|r| for three compounds: $S(CH_2)_{11}Fc$ (left column), 5 ($S(CH_2)_8S$-naphthoquinone, center column), and $S(CH_2)_{14}CH_3$ (right column). Within each column, the top two histograms show log|J/(A/cm^2)| at $-V$ and V, respectively (where V is the bias at which R was determined). The bottom histogram (darkened for contrast) in each column shows log|r|, plotted on the same length of axis (13 orders of magnitude) to enable visual comparison of the distributions of log|J/(A/cm^2)| and log|r|. All histograms have been fitted with Gaussians (black lines), and the means and standard deviations determined from these Gaussians are shown above each histogram.

not independent, however, the variance of X can actually be less than the variances of A and B separately (in statistical terms, this decrease in variance occurs because the covariance of A and B is large). Because log|J(1.0 V)| and log|J(−1.0 V)| are measured across the same junction, they are highly correlated (*i.e.*, they have a large covariance). The fact that log|r| is a self-referencing measurement, therefore, explains why the error in log|r| is typically less than the error in log|J|, as seen in Figure 7.

DISCUSSION

In this section, we use the evidence introduced above in the Background and Results sections to evaluate the mechanism of rectification we propose against alternative mechanisms. The first subsection discusses our mechanism, while each subsequent subsection is devoted to one alternative mechanism.

Our Proposed Mechanism. *Asymmetric placement of a conducting molecular orbital within a tunneling junction allows the orbital to participate in redox reactions at one bias, but not the opposite bias.*

This mechanism is supported by a number of predictions borne out by experimental evidence, which we have reviewed in the Background section. In summary, our proposed mechanism of rectification—the asymmetric coupling of a molecular orbital to one electrode causing the orbital to participate in charge transport at one bias, but not the opposite bias—explains the signs and relative magnitudes of the values of R observed for $S(CH_2)_9Fc$, $S(CH_2)_{11}Fc$, and $S(CH_2)_{11}Fc_2$. This mechanism finds further validation through temperature-dependent studies of $S(CH_2)_{11}Fc$ that show hopping (between the Fc moiety and the Ga_2O_3/EGaIn electrode) at negative bias, but not at positive bias.[25] These data, collectively, are also incompatible, in our view, with mechanisms for rectification that depend on the properties of the metals in the electrodes (*e.g.*, Fermi levels) or of the oxide skin (*e.g.*, redox reactions); we elaborate these points in the following subsections.

Other Hypotheses. We evaluate alternative mechanisms of rectification using the following format: (i) a summary of the mechanism in question, (ii) a discussion of the evidence for or against it, (iii) our conclusion concerning the compatibility of the mechanism in question with the experimental data.

Hypothesis. Rectification is the result of asymmetries due to electrodes with different work functions, or to the presence of one chemisorbed contact (Ag−S) and one van der Waals contact (SAM//Ga_2O_3/EGaIn).

Summary. EGaIn and Ag have bulk work functions that are slightly different (Ag ≈ −4.5 eV, EGaIn ≈ −4.2 eV),[19−21] but the actual work functions at the surfaces of the Ag^{TS} and Ga_2O_3/EGaIn electrodes, in the environment of the Ag^{TS}-SAM//Ga_2O_3/EGaIn, may differ from the bulk values. The fact that we must use a potential range of $V = -1.2$ to 1.2 V when measuring compounds **2** and **5** may be evidence that the work functions of the electrodes differ (see the Results section). For example, if the actual work function of the Ag^{TS} electrode is indeed 0.3 eV greater (*i.e.*, if the Fermi energy[47] of Ag^{TS} electrode is 0.3 eV lower) than that of the Ga_2O_3/EGaIn electrode, then this difference in work functions causes the tunneling barrier posed by the SAM to change from an approximately flat (rectangular) barrier to a tilted (trapezoidal) barrier, sloping downward toward the Ga_2O_3/EGaIn electrode. The shape of the tunneling barrier would, therefore, be asymmetric, and electrons (or holes) approaching the barrier from opposite sides would tunnel at different rates.[48] In this way, the value of J at one applied bias would differ from that at the opposite applied bias. In addition, the asymmetry of having a chemisorbed contact and a van der Waals contact at opposite ends of the junction almost certainly would increase this asymmetry in the shape of the tunneling barrier and, in the same way, might cause rectification. In tunneling diodes, an inorganic insulator is sandwiched between two different metals, and the difference between the work functions of the metals causes rectification. Even in commercial tunneling diodes, it is a challenge to achieve values of $R > 6$.[49]

Evidence against. While we do believe that one or both of these mechanisms (perhaps combined with others) results in the slight rectification (R = 1.5−3.5) observed for a variety of SAMs, several control experiments rule out this mechanism as an explanation for the large rectification ($R(1.0\text{ V}) = -100$) observed with Fc-terminated SAMs.

(i) As mentioned previously and depicted in Figure 1E,F, SAMs of *n*-alkanethiols, lacking a conductive molecular orbital, show rectification ratios different from that of $S(CH_2)_{11}Fc$ ($R = -100$) by more than 2 orders of magnitude. For SAMs of $S(CH_2)_{10}CH_3$, $R(1.0\text{ V}) = 1.5$, whereas $R(1.0\text{ V}) = 2.3$ for SAMs of $S(CH_2)_{14}CH_3$. We note, in addition, that values of R for *n*-alkanethiols have the opposite sign to that of $S(CH_2)_{11}Fc$; that is, $|J|$ is higher at positive bias than at negative bias for *n*-alkanethiols, and *vice versa* for $S(CH_2)_{11}Fc$. This result is difficult to explain using only the asymmetry of the electrodes. Asymmetry in the electrodes and/or the interfaces may cause the slight rectification observed for *n*-alkanethiols, but not the large rectification observed for Fc-terminated SAMs, and not the change in the bias at which rectification occurs.

(ii) In addition to these two alkanethiols, we have also previously reported[23] measurements of a complete series of *n*-alkanethiols (n = 9−18) within a bias range of $V = \pm 0.5$ V. We did not observe any significant rectification, albeit at ±0.5 V applied bias, but one would expect that rectification due to junction asymmetry would not be dependent on the applied bias and, as such, we would observe the same rectification ration at all applied biases.[48] For these 10 alkanethiolates, we observed a range of values of $R(0.5\text{ V})$ from 1.1 to 2.2. These values match the values of $R(1.0\text{ V})$ reported here for $S(CH_2)_{10}CH_3$ and $S(CH_2)_{14}CH_3$ and strengthen the claim that the values of R observed for alkanethiolates are, indeed, much smaller than those observed for the three Fc-based molecular diodes discussed in this work. Again, this result is difficult to explain using only the difference between the electrodes.

(iii) Also mentioned previously, SAMs with the Fc in the middle of the alkyl chain, $S(CH_2)_6Fc(CH_2)_5CH_3$ (Figure 2B), are not molecular diodes ($R(1.0\text{ V}) = 1.2$). Changing the position of the Fc moiety probably does not change the work functions of the electrodes. While the position of the Fc moiety does affect the interface between the SAM and the electrodes, the difference in R between, say, $S(CH_2)_6Fc(CH_2)_5CH_3$ and $S(CH_2)_{11}Fc$ is too large to be explained simply by a change in the shape of the tunneling barrier since an asymmetric tunneling barrier can only produce $R < 6$.[49]

Conclusion. If electrodes having different Fermi levels, or having different contacts (chemisorbed *versus* van der Waals) with the SAM, were sufficient to cause the rectification ($R = -100$) observed with SAMs of $S(CH_2)_{11}Fc$, then one would expect to see the same magnitude of rectification for any SAM in the junction, including simple *n*-alkanethiol SAMs and SAMs having the Fc moiety in the middle. Since we do not observe significant rectification in these cases, we conclude that mechanisms based on asymmetry in the Fermi levels of the contact electrodes are not sufficient to explain either the magnitude or the sign of the observed rectification.

Hypothesis. Embedded dipoles in the SAM give the tunneling barrier an asymmetric shape.

Summary. Attaching functional groups to the end of the SAM (or incorporating them into the alkyl chain of the SAM) can change the dipole moment within the junction (see Table S2 in the Supporting Information for dipole moments of moieties relevant to this discussion and Figure S4 for a plot of the variation of the rectification ratio, $|R|$, with dipole moment). A dipole present in a tunneling junction induces an electrical field, which causes the tunneling barrier to tilt toward one electrode or the other and produces a tunneling barrier with an asymmetric shape. Either of these effects could result in rectification.

Evidence against. (i) As described in the Results section, we measured junctions incorporating SAMs of $S(CH_2)_{10}CH_2OH$ and $S(CH_2)_{10}COOH$ (11-mercaptoundecanoic acid), both of which present polar functional groups at the surface of the SAM. Figure 5B,C shows that these SAMs have small values of R: $S(CH_2)_{10}CH_2OH$ gives $R(1.0\ V) = 2.5$ ($\langle \log|r| \rangle = 0.40 \pm 0.32$) and $S(CH_2)_{10}COOH$ yields $R(1.0\ V) = 2.4$ ($\langle \log|r| \rangle = 0.38 \pm 0.25$). The multiple comparison test described in the Results section confirms that these compounds are not molecular diodes—their values of R are not statistically distinguishable from those of alkanethiols. These observations indicate that changing the dipole of the SAM from that of an alkanethiol to that of a hydroxyl- or carboxylic-acid-terminated alkanethiol changes R by less than a factor of 2. The dipole of the SAM, therefore, has only a minimal effect on rectification.

(ii) We have synthesized and measured several compounds containing secondary amide groups in the middle of the alkyl chain (these new results will be described in detail in forthcoming publications). SAMs of these molecules should have a significant internal dipole, and while we have only measured these SAMs over a potential window of $V = \pm 0.5$ V, we have not observed values of R significantly different from those of alkanethiols. The highest value of R that we observed was $R(0.5\ V) = 1.6$ ($\log|r| = 0.20 \pm 0.20$) for $S(CH_2)_{10}CONHCH_3$.

Conclusion. Several SAMs with dipoles in the interior and at the surface of the SAM do not rectify appreciably.[54] We conclude that a molecular dipole is not sufficient to cause the rectification we observe for SAMs of $S(CH_2)_{11}Fc$ (this conclusion does not preclude the possibility that a molecular dipole in another SAM might cause rectification).

Hypothesis. Electrochemical reactions that require both a redox-active SAM and the Ga_2O_3 film might occur at one bias, but not the opposite bias.

Summary. This mechanism would be similar to the previous one involving redox processes occurring inside the Ga_2O_3 film, except that the previous mechanism asserts that the Ga_2O_3 film is *sufficient* for rectification, while this mechanism asserts that the Ga_2O_3 film is *necessary*, but not sufficient, for rectification. In other words, this mechanism posits that the reaction of a redox-active Ga_2O_3 film with a redox-active SAM is responsible for rectification. This mechanism is close to our proposed mechanism of rectification in SAMs of $S(CH_2)_{11}Fc$: in both mechanisms, the Fc moiety at the SAM//Ga_2O_3 interface undergoes a redox reaction, The question, however, is whether this reaction couples with another redox reaction in the metal oxide layer (as in this hypothesis) or not (as in the mechanism we defend in this work).

Wrighton *et al.*[28] have demonstrated rectification in a micrometer-scale electrochemical junction between two redox-active polymers, one of which contained Fc groups. The mechanism of rectification in these junctions involves two redox reactions that couple in a specific order—electrons flow from the first redox couple to the second, but not in the opposite direction—resulting in the flow of current at one bias, but not the opposite bias. It is important to note that these junctions were assembled and tested in a wet electrochemical environment in the presence of a reference electrode (saturated calomel). Also, compared to SAM-based junctions (in which the electrodes are separated by 1−2 nm) these polymer-based junctions are large (~1 μm between electrodes), and charge transport through them cannot involve tunneling.

Evidence against. (i) Junctions of the form Ag^{TS}-$S(CH_2)_{11}Fc$//Au, with top electrodes of Au foil (Supporting Information of our previous paper[25]), rectify with approximately the same value of R ($R(1.0\ V) = -100$) as Ag^{TS}-$S(CH_2)_{11}Fc$//Ga_2O_3/EGaIn junctions, even without a metal oxide film. The metal oxide film is, therefore, not a necessary condition for rectification.

(ii) The results of Zandvliet *et al.*,[50] in which Au-$S(CH_2)_{11}Fc$-(vacuum)-Pt/Ir junctions give $R(2.0\ V) \approx -10$, show that a redox-active top electrode is not necessary for rectification. In these junctions, as in ours, a Fc group located asymmetrically within the SAM is sufficient for rectification.

(iii) Naphthoquinone, **5**, rectifies when a positive bias is applied but the analogous benzoquinone, **3**, does not rectify at all. Although both molecules bear a quinone moiety, in which case the interfacial redox chemistry would be similar, there is a significant difference in their rectification ratios. The small, but statistically significant, difference in rectification ratios of compounds **3** and **5** can be attributed to the differences in the orbital energies (3.8 *vs* 3.9 eV, respectively). Although there is only 0.1 eV difference in the orbital energies between compounds **3** and **5**, their placement only allows one of them to be placed asymmetrically between the two electrodes when a positive bias is applied. From our previous studies with Fc-terminated SAMs, we estimated a 0.3 V potential drop across the van der Waals interface. Revisiting Figure 2, one would then observe that for compound **5**, when a bias of +1 V is applied to the top electrode, the LUMO is placed at −4.6 eV. This places the LUMO of **5** closer to, and a bit lower than, the Ag electrode by 0.1 eV and higher than the shifted EGaIn by 0.7 eV. On the other hand, compound **3** would be placed at −4.5 eV, which is not between the two electrodes but at the same level as the Ag electrode and, as such, is not placed between the two electrodes. Comparing the quinones with Fc-terminated molecules, we observe that they rectify at opposite signs of the applied bias which supports our conclusion that they do so through accessible states with different electronic properties, such as LUMO *versus* HOMO, respectively.

Conclusion. We conclude that rectification in SAMs of $S(CH_2)_{11}Fc$ is the result of a redox reaction involving the Fc moiety. We further conclude that the evidence rules out the participation of the metal oxide film in this redox reaction (or at least demonstrates that it does not contribute appreciably to rectification).

Hypothesis. Depletion of charge carriers from the metal oxide creates a rectifying Schottky barrier.

Summary. The layer of Ga_2O_3 is semiconducting and might have a significant concentration of free charge carriers arising from interface states, nonstoichiometric regions, oxygen vacancies or excesses, *etc.*[51] Since this layer is adjacent to a bulk metal alloy (EGaIn) and a SAM containing an electron donor (Fc), these charge carriers might become depleted and form a Schottky barrier; generation of a Schottky barrier could lead to rectification (as in Schottky diodes).

Evidence against. (i) *R* switches sign when the accessible Fc HOMO is replaced by an accessible naphthoquinone LUMO. Therefore, if depletion of charge in the Ga_2O_3 occurs, it is due to the redox-active moiety in the SAM, and not the bulk EGaIn (which would produce a constant effect for all SAMs). Not all SAMs with a redox-active moiety qualify as molecular diodes, however, as an example $S(CH_2)_6Fc(CH_2)_5CH_3$, with Fc buried in the SAM, gives $R = 1.2$ and compound **2** (with trimethylbenzoquinone at the unbound surface of the SAM) gives $R = 1.9$. These rectification ratios are comparable to those derived from *n*-alkanethiolate SAMs or other molecules not having accessible frontier orbitals. Therefore, doping or depletion is either strongly dependent on the molecular structure of the SAM or not involved in rectification.

(ii) If a layer of oxide has significant free charge carriers, then it must be either n-type or p-type, but it cannot be both. An electron donor, such as the HOMO of Fc, can only deplete a p-type semiconductor, not an n-type semiconductor, in order to form a Schottky barrier. Ga_2O_3 grown under oxidizing conditions is an insulator (*i.e.*, it is neither n-type nor p-type), and although common defects in Ga_2O_3 can cause the material to become an n-type semiconductor, p-type Ga_2O_3 does not form under ambient conditions.[52,53] It is, therefore, unlikely that the Ga_2O_3 film would be the type of semiconductor that is able to form a Schottky barrier in the presence of Fc.

(iii) Finally, we have estimated the average thickness of the layer of oxides, using angle-resolved X-ray photoelectron spectroscopy, as $\sim$0.7 nm[18] (this value is consistent with that reported by Regan *et al.*).[17] In all but the most highly doped semiconductors, the formation of a depletion region requires a layer of material several micrometers thick. Without sufficient material to form a depletion layer, it is impossible to form a Schottky barrier.

Conclusion. Because of the ability to control the polarity of rectification using the SAM, and because the layer of oxides is too thin to form a depletion layer, we conclude that the observed rectification is not the result of a Schottky barrier.

CONCLUSIONS

Rectification and Charge Transport in Ag^{TS}-SAM//Ga_2O_3/EGaIn Junctions Are Determined by the SAM. Because charge transport in organic matter is still incompletely understood, we believe that claims of molecular rectification—or any claim related to molecular charge transport, for that matter—must be carefully examined, in order to rule out nonmolecular mechanisms involving metals, metal oxides, or other components of the system (organic adsorbates, atmospheric gases). While our junctions employ a top electrode with a metal (EGaIn) whose surface oxidizes spontaneously to a Ga_2O_3 film on contact with air, and while this Ga_2O_3/EGaIn electrode might have a different work function than the Ag^{TS} bottom electrode, this fact does not disqualify our junctions, *a priori*, from use in measuring charge transport through SAMs; it simply places the burden of proof on us to show that the results generated using these junctions are truly molecular, and not dominated by the electrodes.

This paper considers an exhaustive list of alternative mechanisms related to asymmetric and/or oxidizable electrodes, in light of experiments (both published and new) that test these alternative mechanisms by changing the structure of the SAM. From these results, we conclude that mechanisms involving the Ga_2O_3 film, or the asymmetry of the electrodes, are insufficient to explain the large values of *R* for our molecular diodes, or the dependence of both the magnitude and sign of *R* on molecular structure. The value of *R* is, essentially, a self-referencing measurement of charge transport—that is, current measure on one applied bias acts as a standard to current measured on the same but reverse bias, for example, $J_{0.5V}$ is an internal standard for $J_{-0.5V}$. Because *R* is sensitive to the SAM and not determined by the other components of the junction, charge transport through these junctions, therefore, reflects the structure and properties of the SAM, not only the electrodes or the Ga_2O_3 film.

Our understanding of rectification at the molecular level is growing but is not at a point that we can claim complete understanding. The conceptual approach we adopted here is qualitative and, hence, not fully exhaustive. A complete understanding of rectification requires more sophisticated analysis of the electronic behavior that is beyond our expertise.

One Accessible Molecular Orbital Located Asymmetrically between Two Electrodes Is Sufficient for Rectification. We are also convinced that, of the several possible mechanisms in which rectification has a molecular origin, the only one that fits our results posits that rectification occurs as the result of the asymmetric placement inside the junction of an accessible molecular orbital. The donor-bridge-acceptor structure of the molecular diode proposed by Aviram and Ratner[1] and realized by others[29−34] is, therefore, not required for rectification (contrary to the claims of Ashwell *et al.*[12]). While the donor-bridge-acceptor has been shown to rectify, no study has conclusively identified the mechanism of rectification, so it is unclear whether this structure is *sufficient* for rectification. We note that, in many studies of molecules of this sort, the donor and acceptor moieties were significantly offset from the center of the junction (closer to one electrode than the other). Since both moieties are potentially accessible molecular orbitals, it is possible that some of these junctions rectify due to the asymmetric placement of a molecular orbital(s) between the electrodes. Such an explanation needs to be ruled out before the community can conclude that, for a given molecule in a given type of junction, the donor-bridge-acceptor structure alone, and not any other asymmetry, is responsible for rectification.

***R* Is Statistically Significant.** Statistical tests demonstrate the significance of the values of R for the three ferrocene-based molecular diodes discussed here, when compared to those of alkanethiolate SAMs, and indicate (together with the other evidence discussed in this paper) that rectification in these diodes has a molecular origin. The largest of our values of R comes from $S(CH_2)_{11}Fc_2$, for which $R = -500$. While individual values of $|R|$ greater than 500 have been reported in the literature (*e.g.*, $R = 3000$ by Ashwell *et al.*[34]), our value of R is the log-average of an entire distribution of hundreds of discretely observed rectification ratios. Most publications on molecular rectification simply report individual values, without any statistical analysis of the *distribution* of observed values. If we followed the same procedure, we could claim the highest rectification ratio from a molecular rectifier to date: in the histogram of $\log|r|$ for our best rectifier, $S(CH_2)_{11}Fc_2$, ~20% of the measured values of $\log|r|$ are in the range of -3 to -4 (*i.e.*, $R = -1000$ to $-10\,000$), with a few values approaching -5 (*e.g.*, $R = -100\,000$; Figure 3A). We know that these high individual values are, however, outliers and may be artifacts or errors, and reporting them would obscure the fact that they are different, to a suspicious degree, from the average value, $\langle \log|r| \rangle$. Examining the entire distribution of $\log|r|$ and reporting the average, while less impressive than reporting single values, enables the identification of these extreme values as outliers and affords a representative and meaningful characterization of the results.

MATERIALS AND METHODS

Template Stripping. We prepared our surfaces as previously described.[14,23] On clean ultraflat silicon (111) wafers (with the native oxide), 450 nm Ag was evaporated using an e-beam (Temescal, base pressure 2×10^{-6} Torr). On the exposed surface of the metal film, plasma-cleaned glass supports were attached using a thin film of photocurable optical adhesive (Norland optical adhesive 81). The optical adhesive was then cured under broad-band UV light for 2 h after which the glass supports were well attached to the metal surface.

Preparation of the Self-Assembled Monolayer (SAM). SAMs were prepared as previously described.[23,26] To prepare SAMs, the ultraflat metal film template-stripped from the silicon wafer was detached by cutting around the support using a razor blade. The film and glued support were then lifted from the silicon wafer, rinsed with ethanol (200 proof), then immersed into a 3 mM thiol solution to form the SAM.

Measurement of Current Density through SAMs. We first prepared a cone shape Ga_2O_3/EGaIn tip by splitting a drop of EGaIn between a syringe needle and a dirty Ag surface as previously described.[23,24,26] We used the prepared SAMs to form junctions using procedures described previously: by bringing the cone-shaped tips of Ga_2O_3/EGaIn into contact with SAMs formed on ultraflat, template-stripped silver (Ag^{TS}) substrates.[23,26] We measured the current through the junction using a Keithley 6430 subfemtoamp source-meter and calculated the current density (J) using the area of the junction estimated by measuring the diameter, under 450× magnification, of the contact (assumed to be circular) between the cone-shaped tip and the SAM-bearing substrate.

Synthesis of Quinone-Terminated Thiols:. *Benzoquinone.* Hydroquinone **1** (0.76 g, 5.0 mmol, 1 equiv) was dissolved in methanol (30 mL) and treated with (diacetoxyiodo)benzene (1.61 g, 5.0 mmol, 1 equiv). After 5 min, TLC analysis revealed complete conversion to the quinone. 1,10-Decanedithiol (6.0 mL, 28 mmol, 5.5 equiv) was added, and the mixture was stirred overnight at 35 °C. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (CH_2Cl_2/hexanes) to yield thiol **2** (550 mg, 31% yield).

Naphthoquinone. Similarly, the naphthoquinone, **5**, was synthesized. Menadione **4** (400 mg, 2.32 mmol, 1 equiv) and 1,10-decanedithiol (2.5 mL, 12 mmol, 5 equiv) were heated to 35 °C in ethanol (30 mL) for 4 h. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (CH_2Cl_2/hexanes) to yield thiol **5** (100 mg, 11% yield). Characterization of the target compounds is summarized in the Supporting Information.

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

Acknowledgment. This research was supported by the U.S. Department of Energy, under Award No. DE-SC0000989 (synthesis of materials, partial support for measurements of charge transport, and support for W.R.), and by the National Science Foundation under Award Nos. CHE-05180055 (partial support for measurements of charge transport) and PHY-0646094. C.N. acknowledges support from The Netherlands Organization for Scientific Research (NWO) through a Rubicon grant and the Singapore National Research Foundation under NRF Award No. NRF-RF2010-03. M.T. was supported by a Mary-Fieser fellowship from Department of Chemistry, Harvard University. and a postdoctoral fellowship from the Nanoscale Science and Engineering Centre (NSEC) at Harvard University.

Supporting Information Available: Experimental details, NMR spectra, and review of rectification in organic SAMs. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
2. Chabinyc, M. L.; Chen, X.; Holmlin, R. E.; Jacobs, H.; Skulason, H.; Frisbie, C. D.; Mujica, V.; Ratner, M. A.; Rampi, M. A.; Whitesides, G. M. Molecular Rectification in a Metal-Insulator-Metal Junction Based on Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2002**, *124*, 11730–11736.
3. Honciuc, A.; Jaiswal, A.; Gong, A.; Ashworth, K.; Spangler, C. W.; Peterson, I. R.; Dalton, L. R.; Metzger, R. M. Current Rectification in a Langmuir−Schaefer Monolayer of Fullerene-bis-[4-diphenylamino-4″-(*N*-ethyl-*N*-2‴-ethyl)amino-1,4-diphenyl-1,3-butadiene] Malonate between Au Electrodes. *J. Phys. Chem. B* **2005**, *109*, 857–871.
4. Kushmerick, J. G.; Whitaker, C. M.; Pollack, S. K.; Schull, T. L.; Shashidhar, R. Tuning Current Rectification Across Molecular Junctions. *Nanotechnology* **2004**, *15*, S489–S493.
5. Lenfant, S.; Guerin, D.; Van, F. T.; Chevrot, C.; Palacin, S.; Bourgoin, J. P.; Bouloussa, O.; Rondelez, F.; Vuillaume, D. Electron Transport through Rectifying Self-Assembled Monolayer Diodes on Silicon: Fermi-Level Pinning at the Molecule−Metal Interface. *J. Phys. Chem. B* **2006**, *110*, 13947–13958.
6. McCreery, R. L. Molecular Electronic Junctions. *Chem. Mater.* **2004**, *16*, 4477–4496.
7. Metzger, R. M. Unimolecular Electrical Rectifiers. *Chem. Rev.* **2003**, *103*, 3803–3834.
8. Troisi, A.; Ratner, M. A. Molecular Rectification through Electric Field Induced Conformational Changes. *J. Am. Chem. Soc.* **2002**, *124*, 14528–14529.
9. Twardowski, M.; Nuzzo, R. G. Molecular Recognition at Model Organic Interfaces: Electrochemical Discrimination Using Self-Assembled Monolayers (SAMs) Modified *via* the Fusion of Phospholipid Vesicles. *Langmuir* **2003**, *19*, 9781–9791.
10. Waldeck, D. H.; Beratan, D. N. Molecular Electronics: Observation of Molecular Rectification. *Science* **1993**, *261*, 576–577.
11. Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, K., II; Tour, J. M. Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures. *Appl. Phys. Lett.* **1997**, *71*, 611–613.
12. Ashwell, G. J.; Chwialkowska, A.; Hermann High, L. R. Au-S-C_nH_{2n}-Q3CNQ: Self-Assembled Monolayers for Molecular Rectification. *J. Mater. Chem.* **2004**, *14*, 2389–2394.
13. Weiss, E. A.; Chiechi, R. C.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Duati, M.; Rampi, M. A.; Whitesides, G. M. Influence of Defects on the Electrical Characteristics of Mercury-Drop Junctions. Self-Assembled Monolayers of *n*-Alkanethiolates on Rough and Smooth Silver. *J. Am. Chem. Soc.* **2007**, *129*, 4336–4349.
14. Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO_2-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.
15. Blackstock, J. J.; Li, Z.; Freeman, M. R.; Stewalt, D. R. Ultra-flat Platinum Surfaces from Template-Stripping of Sputter Deposited Films. *Surf. Sci.* **2003**, *546*, 87–96.
16. Hegner, M.; Wagner, P.; Semenza, G. Ultralarge Atomically Flat Template-Stripped Au Surfaces for Scanning Probe Microscopy. *Surf. Sci.* **1993**, *291*, 39–46.
17. Regan, M. J.; Tostmann, H.; Pershan, P. S.; Magnussen, O. M.; DiMasi, E.; Ocko, B. M.; Deutsch, M. X-ray Study of the Oxidation of Liquid-Gallium Surfaces. *Phys. Rev. B* **1997**, *55*, 10786–10790.
18. Cademartiri, L.; Thuo, M. M.; Nijhuis, C. A.; Reus, W. F.; Tricard, S.; Barber, J. R.; Sodhi, R. N. S.; Brodersen, P.; Kim, C.; Chiechi, R.; Whitesides, G. M. The Electrical Resistance of Ag^{TS}-$S(CH_2)_{n-1}CH_3$//Ga_2O_3/EGaIn Tunneling Junctions. *J. Phys. Chem. C* **2012**, DOI: 10.1021/jp212501s.
19. Chelvayohan, M.; Mee, C. H. B. Work Function Measurements on (110), (100) and (111) Surfaces of Silver. *J. Phys.: Condens. Matter* **1982**, *15*, 2305–2312.
20. Giesen, K.; Hage, F.; Himpsel, F. J.; Riess, H. J.; Steinmann, W.; Smith, N. V. Effective Mass of Image-Potential States. *Phys. Rev. B* **1987**, *35*, 975–978.
21. Monreal, R. C.; Guillemot, L.; Esaulov, V. A. On Auger Neutralization of He^+ Ions on a Ag(111) Surface. *J. Phys.: Condens. Matter* **2003**, *15*, 1165–1171.
22. Barr, T. L.; Seal, S. Nature of the Use of Adventitious Carbon as a Binding Energy Standard. *J. Vac. Sci. Technol., A* **1995**, *13*, 1239–1246.
23. Thuo, M. M.; Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Kim, C.; Schulz, M. D.; Whitesides, G. M. Odd-Even Effects in Charge Transport Across Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2011**, *133*, 2962–2975.
24. Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Mechanism of Rectification in Tunneling Junctions Based on Molecules with Asymmetric Potential Drops. *J. Am. Chem. Soc.* **2010**, *132*, 18386–18401.
25. Nijhuis, C. A.; Reus, W. F.; Barber, J. R.; Dickey, M. D.; Whitesides, G. M. Charge Transport and Rectification in Arrays of SAM-Based Tunneling Junctions. *Nano Lett.* **2010**, *10*, 3611–3619.
26. Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Molecular Rectification in Metal-SAM-Metal Oxide-Metal Junctions. *J. Am. Chem. Soc.* **2009**, *131*, 17814–17827.
27. Strukov, D. B.; Snider, G. S.; Stewart, D. R.; Williams, R. S. The Missing Memristor Found. *Nature* **2008**, *453*, 80–83.
28. Kittlesen, G. P.; White, H. S.; Wrighton, M. S. A Microelectrochemical Diode with Submicron Contact Spacing Based on the Connection of Two Microelectrodes Using Dissimilar Redox Polymers. *J. Am. Chem. Soc.* **1985**, *107*, 7373–7380.
29. Ashwell, G. J.; Sambles, J. R.; Martin, A. S.; Parker, W. G.; Szablewski, M. Rectifying Characteristics of Mg[($C_{16}H_{33}$-Q_3CNQ LB film)]Pt Structures. *J. Chem. Soc., Chem. Commun.* **1990**, 1374–1376.
30. Chen, B.; Metzger, R. M. Rectification between 370 and 105 K in Hexadecylquinolinium Tricyanoquinodimethanide. *J. Phys. Chem. B* **1999**, *103*, 4447–4451.
31. Metzger, R. M. Unimolecular Rectifiers and Prospects for Other Unimolecular Electronic Devices. *Chem. Rec.* **2004**, *4*, 291–304.
32. Ashwell, G. J.; Tyrrell, W. D.; Whittam, A. J. Molecular Rectification: Self-Assembled Monolayers in which Donor-(π-Bridge)-Acceptor Moieties Are Centrally Located and Symmetrically Coupled to Both Gold Electrodes. *J. Am. Chem. Soc.* **2004**, *126*, 7102–7110.
33. Ashwell, G. J.; Mohib, A. Improved Molecular Rectification from Self-Assembled Monolayers of a Sterically Hindered Dye. *J. Am. Chem. Soc.* **2005**, *127*, 16238–16244.
34. Ashwell, G. J.; Urasinska, B.; Tyrrell, W. D. Molecules that Mimic Schottky Diodes. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3314–3319.
35. Kornilovitch, P. E.; Bratkovsky, A. M.; Williams, R. S. Current Rectification by Molecules with Asymmetric Tunneling Barriers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 165436/1–11.
36. Larade, B.; Bratkovsky, A. M. Current Rectification by Simple Molecular Quantum Dots: An *Ab Initio* Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 235305.
37. Liu, R.; Ke, S.-H.; Yang, W.; Baranger, H. U. Organometallic Molecular Rectification. *J. Chem. Phys.* **2006**, *124*, 024718.
38. Zhou, Y.; Zheng, X.; Xu, Y.; Zeng, Z. Y. Current Rectification by Asymmetric Molecules: An *Ab Initio* Study. *J. Chem. Phys.* **2006**, *125*, 244701.
39. Chang, S.-C.; Li, Z.; Lau, C. N.; Williams, R. S. Investigation of a Model Molecular-Electronic Rectifier with an Evaporated Ti−Metal Top Contact. *Appl. Phys. Lett.* **2003**, *83*, 3198–3200.
40. McCreery, R.; Dieringer, J.; Solak, A. O.; Snyder, B.; Nowak, A. M.; McGovern, W. R.; DuVall, S. Molecular Rectification and Conductance Switching in Carbon-Based Molecular Junctions by Structural Rearrangement Accompanying Electron Injection. *J. Am. Chem. Soc.* **2003**, *125*, 10748–10758.
41. McCreery, R.; Dieringer, J.; Solak, A. O.; Snyder, B.; Nowak, A. M.; McGovern, W. R.; DuVall, S. Molecular Rectification

and Conductance Switching in Carbon-Based Molecular Junctions by Structural Rearrangement Accompanying Electron Injection. [Erratum to Document Cited in CA139:171867]. *J. Am. Chem. Soc.* **2004**, *126*, 6200.

42. Chen, C.; Liu, Y.-Z.; Shia, K.-S.; Tseng, H.-Y. Synthesis and Anticancer Evaluation of Vitamin K3 Analogues. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2729–2732.
43. Li, W. W.; Heinze, J.; Haehnel, W. J. Site-Specific Binding of Quinones to Proteins through Thiol Addition and Addition−Elimination Reactions. *J. Am. Chem. Soc.* **2005**, *127*, 6140–6141.
44. Casella, G.; Berger, R. L. *Statistical Inference*; Duxbury Press: Belmont, CA, 1990.
45. Galwey, N. W. A New Measure of the Effective Number of Tests, a Practical Tool for Comparing Families of Non-independent Significance Tests. *Genet. Epidemiol.* **2009**, *33*, 559–568.
46. Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Thuo, M. M.; Tricard, S.; Whitesides, G., M. Statistical Tools for Analyzing Measurements of Charge Transport. *J. Phys. Chem. C* **2012**, *116*, 6714–6733.
47. The term "work function" and "Fermi energy" are similar and are often used synonymously. Technically, the work function is the amount of energy required to remove an (average) electron from a material to vacuum, while Fermi energy is the energy (with respect to vacuum) at which 50% of the electronic states in the material are occupied. Although the two concepts are subtly different, their differences do not affect the present discussion.
48. Brinkman, W. F.; Dynes, R. C.; Rowell, J. M. Tunneling Conductance of Asymmetrical Barriers. *J. Appl. Phys.* **1970**, *41*, 1915–1921.
49. Krishnan, S.; Stefanakos, E.; Bhansali, S. Effects of Dielectric Thickness and Contact Area on Current−Voltage Characteristics of Thin Film Metal−Insulator−Metal Diodes. *Thin Solid Films* **2008**, *516*, 2244–2250.
50. Muller-Meskamp, L.; Karthauser, S.; Zandvliet, H. J. W.; Homberger, M.; Simon, U.; Waser, R. Field-Emission Resonances at Tip/α,ω-Mercaptoalkyl Ferrocene/Au Interfaces Studied by STM. *Small* **2009**, *5*, 496–502.
51. Spicer, W. E.; Lindau, I.; Skeath, P.; Su, C. Y.; Chye, P. Unified Mechanism for Schottky-Barrier Formation and III−V Oxide Interface States. *Phys. Rev. Lett.* **1980**, *44*, 420–423.
52. Lorenz, M. R.; Woods, J. F.; Gambino, R. J. Some Electrical Properties of the Semiconductor β-Gallium Oxide. *J. Phys. Chem. Solids* **1967**, *28*, 403–404.
53. Ueda, N.; Hosono, H.; Waseda, R.; Kawazoe, H. Synthesis and Control of Conductivity of Ultraviolet Transmitting β-Ga_2O_3 Single Crystals. *Appl. Phys. Lett.* **1997**, *70*, 3561–3563.
54. Wimbush, K. S.; Reus, W. F.; van der Wiel, W. G.; Reinhoudt, D. N.; Whitesides, G. M.; Nijhuis, C. A.; Velders, A. H. Control Over Rectification in Supramolecular Tunneling Junctions. *Angew. Chem., Int. Ed.* **2010**, *122*, 10374–10378.
55. Zhu, X.-Q.; Wang, C.-H. Accurate Estimation of the One-Electron Reduction Potentials of Various Substituted Quinones in DMSO and CH_3CN. *J. Org. Chem.* **2010**, *75*, 5037–5047.