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Citation

Published Version
doi:10.1021/ja509110a

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Rectification in Tunneling Junctions: 2,2'-Bipyridyl-terminated \textit{n}-Alkanethiolates

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ABSTRACT

Molecular rectification is a particularly attractive phenomenon to examine in studying structure-property relationships in charge transport across molecular junctions, since the tunneling currents across the same molecular junction are measured, with only a change in the sign of the bias, with the same electrodes, molecule(s), and contacts. This type of experiment minimizes the complexities arising from measurements of current densities at one polarity using replicate junctions. This paper describes a new organic molecular rectifier: a junction having the structure $\text{Ag}^\text{TS}/\text{S(CH}_2\text{)}_{11}-4\text{-methyl-2,2'}\text{-bipyrindyl}//\text{Ga}_2\text{O}_3/\text{EGaIn}$ ($\text{Ag}^\text{TS}$: template-stripped silver substrate; EGaIn: eutectic gallium-indium alloy) which shows reproducible rectification with mean $r^+ = |J(+1.0\text{V})|/|J(-1.0\text{V})| = 85 \pm 2$. This system is important because rectification occurs at a polarity opposite to that of the analogous but much more extensively studied systems based on ferrocene. It establishes (again) that rectification is due to the SAM, and not to redox reactions involving the Ga$_2$O$_3$ film, and confirms that rectification is not related to the polarity in the junction. Comparisons among SAM-based junctions incorporating the Ga$_2$O$_3$/EGaIn top-electrode and a variety of heterocyclic terminal groups indicate that the metal-free bipyridyl group, not other features of the junction, is responsible for the rectification. The paper also describes a structural and mechanistic hypothesis that suggests a partial rationalization of values of rectification available in the literature.
INTRODUCTION

One goal of the field of molecular electronics is to relate the electrical behavior of molecular junctions to the chemical structure of the molecules they incorporate. Molecular rectification—the asymmetric response of currents to applied potentials of equal magnitude but opposite sign in electrode-molecule(s)-electrode junctions—was an early justification for the study of molecular electronics.\textsuperscript{1} The potential to control rectification by designing molecule(s), and/or their contacts with the electrodes in these junctions, has been the subject of a number of theoretical and experimental studies.\textsuperscript{1-20}

Interpreting ostensible examples of rectification, and understanding the mechanism of rectification in these examples, has been difficult because some of the reported data have not been independently validated. One system that has been thoroughly studied, and reproduced in several laboratories\textsuperscript{18-21} uses the well-described “EGaIn-junction”\textsuperscript{18,20-28} with the form $\text{Ag}^{TS}/\text{S(CH}_2\text{)}_{11}\text{Fc}_n//\text{Ga}_2\text{O}_3/\text{EGaIn}$ (where Fc$_n$ is either ferrocene or biferrocene). These junctions give rectification ratios of $|I(-1.0\text{V})|/|I(+1.0\text{V})| = \sim 150$ for Fc,\textsuperscript{20} and $\sim 500$ for Fc$_2$.\textsuperscript{21} The higher current is at negative polarity (e.g., the electrode close to the Fc group is oxidizing). The mechanism of this rectification is well defined (the detailed energy diagrams for rectification are discussed elsewhere\textsuperscript{20,21}): it involves a change in mechanism—from tunneling across the entire molecule at one bias, to hopping (from the Fc to the electrode due to energetic proximity of HOMO of Fc (-5.0 eV) to the Fermi level of the Ga$_2$O$_3$/EGaIn electrode (–4.3 eV) at zero bias)\textsuperscript{29} followed by tunneling at the opposite polarity. The generality of rectification in SAM-based junctions remains unclear, as does the range of mechanisms that can produces rectification.

This work had three objectives. i) It was intended to use the Ga$_2$O$_3$/EGaIn top-electrode to search for compositionally well-defined junctions—other than the Fc-containing systems—to
study rectification. ii) It was particularly concerned with finding examples of molecules that
correct at polarity opposite to that required for rectification in Fc and Fc2, in order to demonstrate
that redox reactions involving the Ga2O3 film on the surface of the EGaIn electrode do not play a
role in rectification. iii) It was designed to examine examples of rectification reported in the
literature, and to search for common conceptual threads to correct them.

This paper describes a molecular rectifier (Figure 1a) that shows a large, reproducible,
unambiguous rectification ratio \(|J(+1.0V)|/|J(-1.0V)| = \sim 85\) having polarity opposite to that of
the Fc\(_n\)-based junctions; this junction has the structure Ag\(^{TS}/S(CH_2)_{11}BIPY//Ga_2O_3/EGaIn\)
(Figure 1a), where TS denotes a template-stripped substrate;\(^{30}\) BIPY is a 4-methyl-2,2'-bipyrid-
4'-yl group; and Ga2O3/EGaIn is the eutectic gallium-indium alloy (EGaIn) top-electrode
(specifically, what we call an “unflattened” conical tip)\(^{22,24,26}\) covered with a self-limiting thin
film of gallium oxide (Ga2O3, ostensibly \sim 0.7 nm, but undoubtedly thicker in portions of the
junctions where it is buckled)\(^{24,31}\). We determined experimentally that rectification (Figure 1b, c)
in this system stems from the BIPY terminal groups in the SAM, and not from other features of
the EGaIn-based junction.

The rectification ratio \(r\) is the quotient of current density \(J, \text{A/cm}^2\) measured at applied
biases of opposite polarities \(+V\) and \(-V\). We define \(r\) with two different equations (Eq. 1 and 2),
\[
r^+ = \frac{|J(+V)|}{|J(-V)|}\quad \text{Eq. 1}
\]
\[
r^- = \frac{|J(-V)|}{|J(+V)|}\quad \text{Eq. 2}
\]
which convey information about both the magnitude and the polarity of rectification. We use Eq.
1 when \(|J(+V)|\) is larger than \(|J(-V)|\), and the rectification is positive \(r^+\); we use Eq. 2 when
\(|J(+V)|\) is smaller than \(|J(-V)|\), and the rectification is negative \(r^-\).
Figure 1. (a) Schematic representation of the tunneling junction with the structure Ag^{TS}/SC_{11}BIPY//Ga_{2}O_{3}/EGaIn. We do not know the conformation(s) of the BIPY group in these junctions. The positive bias (+1.0V) shows higher current density (J A/cm^2) than the negative bias (-1.0V); the rectification ratio $r^+$ ($r^+ = |J(+1.0V)|/|J(-1.0V)|$) is ~85. (b) Traces of current density and log|J| as a function of applied voltage (V). N_{junctions} is the number of junctions; N_{traces} is the number of J-V traces; and Yield (%) is the ratio of working junctions to the total number of junctions. (c) Histograms of log|r^+| and $r^+$ measured at ±1.0V for these junctions. Log|r^+|_{mean} and $r^+_{mean}$ are mean values of log|r^+| and $r^+$; log|r^+|_{median} and $r^+_{median}$ are median values of log|r^+| and $r^+$; $\sigma_{\log|r^+|}$ and $\sigma_{r^+}$ are standard deviations of log|r^+| and $r^+$. 
A number of SAM-based systems have been claimed to show significant rectification ratios ($r = 15 – 3000$). A number of smaller values ($r < 5$) have also been reported but are different to evaluate, since it is not straightforward to separate contributions from the SAM from those due to differences in work functions of the two electrodes, from the asymmetric contact modes in top and bottom interfaces, or other unknown factors. Table S1 in the SI summarizes previous studies of molecular rectifiers whose rectification ratios are ‘large’ and have a value of $r^+ > 5$ (or $r^- > 5$).

As we use EGaIn-based junctions, the bottom electrode (here, AgTS) supporting the SAM is grounded. At positive bias (+1.0V), the Ga$_2$O$_3$/EGaIn electrode is oxidizing; at negative bias (−1.0V) this electrode is reducing. In case of Fc-terminated SAM, at negative bias, Fc would undergo oxidation (to Fc$^+$)—a process that would enable hopping at the Fc-Ga$_2$O$_3$ interface. At positive bias (+1.0V) BIPY might undergo reduction to a radical anion, BIPY$^{−−}$.

**EXPERIMENTAL DESIGN**

We chose 2,2'-bipyridyl as a relatively easily reduced heterocycle, and one with potential for other uses (e.g., as a chelating agent). We attached it to an 11-undecanethiol (R(CH$_2$)$_{11}$SH). We used this polymethylene chain as the basis for the SAM because Nijhuis and coworkers have demonstrated that HS(CH$_2$)$_{11}$Fc gave the largest value of $r$ among a series of Fc-terminated $n$-alkanethiolates HS(CH$_2$)$_n$Fc ($n = 6 – 15$).

We performed three separate types of experiments, focusing on trends in $r$ with the structure of the SAM.

i) *Examination for Formation of BIPY Complexes with Ga$^{3+}$ or In$^{3+}$.* The BIPY terminal groups in the SAM are strong $\sigma$-donating ligands. After assembly of the junction they might, in
principle, form complexes with Ga$^{3+}$ and/or In$^{3+}$ cations in the EGaIn top-electrode and then contribute to the rectification. Using X-ray photoelectron spectroscopy (XPS), we explored the influence of formation (if it occurs) of metal complexes on the rectification by analysis of the surfaces of the SAMs using XPS before and after assembly of the junction (see the SI for detailed experimental description).

ii) Examination for Redox Behavior Involving Ag(I). The silver bottom-electrode oxidizes easily in air, and forms a thin layer of silver oxide (AgO$_x$)$_3$; although the thiols probably reduce the Ag(I) to Ag(0), the redox electrochemistry of this layer might also be involved in rectification. To examine the possible role of silver ions in rectification, we replaced the silver bottom-electrode with a gold electrode. Gold does not oxidize under our experimental conditions, and we would expect redox processes involving the silver electrode to be reflected in a difference in rectification on electrodes of gold and silver.

iii) Survey of Nitrogen-Containing Heterocycles as Terminal Groups in Place of BIPY. To probe the role of structure of BIPY terminal group in the rectification, we characterized tunneling junctions having SAMs terminated in four aromatic groups that are related to BIPY in conformation or composition, and that test the influence of conformation and composition (Figure 2).

RESULTS AND DISCUSSION
The SI summarizes the syntheses, purification, characterization of the molecules used, the preparation of SAMs, and the collection of $J-V$ data. We used selected, unflattened conical tips (i.e., those not having observable filaments after formation of tips; see the SI for detailed information). These procedures repeat those used previously.$^{22,24}$
**Figure 2.** Structurally similar thiol derivatives to BIPY-terminated \( n \)-alkanethiol: molecular structures of BIPY-, PHE-, PHEPY-, BIPY-, and PYR-terminated \( n \)-alkanethiols (T: terminal group; M: middle backbone of SAM, either \(-\text{CH}_2\text{CH}_2-\) or \(-\text{CONH}-\)).
Figure 3. (a, b) Histograms of current densities of Ag\textsuperscript{TS}/S(CH\textsubscript{2})\textsubscript{11}T//Ga\textsubscript{2}O\textsubscript{3}/EGaIn junctions, where T = BIPY (SC\textsubscript{11}BIPY) or -(CH\textsubscript{2})\textsubscript{6}CH\textsubscript{3} (SC\textsubscript{18}) at +1.0V and -1.0V. (c) Histograms of log|\(r^+\)| at ±1.0V of the same junctions.
Histograms of current density at opposite polarities (Figure 3) were approximately log-normally distributed; from these data we determined the log-mean ($\log|J(V)|_{\text{mean}}$), log-median ($\log|J(V)|_{\text{median}}$), and log-standard deviation ($\sigma_{\log|J|}$) values. At +1.0V $\log|J(V)|_{\text{mean}}$ and $\sigma_{\log|J|}$ were -1.1 ($\log|J(V)|_{\text{median}} = -1.1$) and 0.56; at -1.0V $\log|J(V)|_{\text{mean}}$ and $\sigma_{\log|J|}$ were -3.0 ($\log|J(V)|_{\text{median}} = -3.0$) and 0.56. The similarity of the mean and median values indicates that outliers do not influence the values of the means.

We measured tunneling current densities (at ±1.0V) in a SAM whose length is similar in the number of non-hydrogen atoms to SC$_{11}$BIPY (18 non-hydrogen atoms in linear connection from the sulfur to the distal atom closest to the EGaIn electrode): $n$-octadecanethiol, HSC$_{18}$. We compared the tunneling current densities measured for both molecules, and found the differences in $J(V)$ were significant at +1.0V but not at -1.0V (Figure 3): the $|J(+1.0V)|_{\text{mean}}$ of SC$_{11}$BIPY was approximately a factor of 30 higher than SC$_{18}$, but $|J(-1.0V)|_{\text{mean}}$ is only a factor of two lower than SC$_{18}$. (The averaged standard deviation of $\log|J(V)|$ in the EGaIn-based junctions is $\sigma_{\log|J|} \approx 0.3$, and thus variations in $J(V)$ that are $\leq 2 \times \sigma_{\log|J|}$ (~0.6 in $\log|J|$; a factor of four in $J$) are statistically indistinguishable.) The higher current density for SC$_{11}$BIPY at positive bias (relative to $n$-alkanethiolate of similar length (SC$_{18}$)) leads to rectification with positive polarity, and suggests that the charge transport process through SC$_{11}$BIPY at positive bias does not purely rely on a tunneling mechanism (but, presumably, on hopping plus tunneling). The rates of charge transport at negative bias for SC$_{11}$BIPY and SC$_{18}$, are indistinguishable, and this observation suggests that the charge transport at negative bias is based on a pure-tunneling regime.

A plot of $r^+$ versus the magnitude of applied bias (Figure S1 in the SI) showed an approximately exponential increase; $\log|r^+|$ was directly proportional to applied voltage $V$. The $\log|r^+|-V$ relation indicates that the difference in $\log|J(V)|$ at opposite biases ($\Delta \log|J(V)|$ =
\( \log|J(+V)| - \log|J(-V)| \) is in direct proportion to applied voltage. Significant rectification ratios \((r^+>5)\) appeared from \(V = +0.5V\) to \(V = +1.0V\). We did not examine higher voltages, because the junctions often failed.

Figure 1c shows histograms of values of \(\log|r^+|\) and \(r^+\) at ±1.0 V for the SC\(_{11}\)BIPY SAM. The histogram of values of \(\log|r^+|\) approximately fit a Gaussian curve. The rectification ratio \((r^+ = 85)\) in the BIPY-terminated SAM was statistically significant, and reproducible. Current density was higher when the EGaIn electrode was reducing than when it was oxidizing. The polarity of rectification was opposite to the polarity observed in Fc-based junctions.\(^{18,21}\) At positive bias, the Ga\(_2\)O\(_3\)/EGaIn electrode is reducing relative to the silver bottom-electrode, and the current density is higher \((\times85)\) than at negative bias, where the Ga\(_2\)O\(_3\)/EGaIn electrode is oxidizing relative to the silver electrode.

We measured the XPS spectrum of a SAM of SC\(_{11}\)BIPY before and after we assembled a junction (Figure S2 in the SI). The XPS spectra of a pristine SC\(_{11}\)BIPY SAM and a SC\(_{11}\)BIPY SAM contacted with the Ga\(_2\)O\(_3\)/EGaIn top-electrode are indistinguishable, and indicate that there is no evidence—at the precision of the XPS instrument we used—of the formation of complexes of BIPY with gallium or indium.

**Comparisons of Junctions with Different Bottom-electrodes (Ag vs. Au).** We replaced the silver bottom-electrode with gold, and fabricated Au\(^{TS}\)/SC\(_{11}\)BIPY/Ga\(_2\)O\(_3\)/EGaIn junctions using the same procedure used with Ag\(^{TS}\). Electrical measurements of these junctions (Figure 4) showed a rectification ratio with similar polarity and magnitude \((\log|r^+_\text{mean} \sim 1.6; \ r^+_{\text{mean}} \sim 40)\) similar to that of the Ag\(^{TS}\)/SC\(_{11}\)BIPY/Ga\(_2\)O\(_3\)/EGaIn junctions \((\log|r^+_\text{mean} \sim 1.9; \ r^+_{\text{mean}} \sim 85)\). These results establish that the rectification is caused neither by redox behavior of an Ag/AgO\(_x\) layer on the Ag\(^{TS}\) electrode, nor by the chelation of silver ions by the BIPY group.
Figure 4. Comparison of histograms of $\log|r'|$ of SC$_{11}$BIPY SAM on $\text{Ag}^{\text{TS}}$ and $\text{Au}^{\text{TS}}$ substrates at $\pm 1.0\text{V}$. 

![Graph showing comparison of histograms](image-url)
The small difference \((\Delta \log |r^+|_{\text{mean}} = 0.3; \text{a factor of two in } r^+_{\text{mean}})\) in the rectification ratio of SC\(_{11}\)BIPY SAMs on gold and silver bottom-electrodes may be due to the difference in the structure (packing density and tilt angle)\(^{35,36}\) of SAMs on gold and silver surfaces, factors such as the difference in the work function between gold and silver, or weak intermolecular interactions.\(^{20}\)

**Comparisons of Different Terminal Groups.** We measured current densities for junctions having different T groups that are structurally similar to BIPY (T = PHE, PHEPY, PYR, or BIPH; Figure 2) at ±1.0V. These terminal groups were chosen to provide a bicyclic aromatic structure with no nitrogen atoms (BIPH), a monocyclic aromatic structure with two nitrogen atoms (PYR), a bicyclic aromatic structure with a nitrogen atom (PHEPY), and a non-rotating planar aromatic structure (PHE) with two nitrogen atoms. We chose the internal amide for the BIPH-terminated SAM for ease of synthesis; no difference in \(J(V)\) between an internal amide (-CONH-) and ethylene unit (-CH\(_2\)CH\(_2\)-) has been demonstrated in previous studies.\(^{22,26,27}\)

SAMs of SC\(_{11}\)PYR, SC\(_7\)CONHC\(_2\)BIPH, and SC\(_{11}\)PHEPY do not rectify currents at ±1.0V on Ag\(^{TS}\) substrates (Figure S3): Table 1 summarizes the values for rectification for those compounds. In contrast, a SAM composed of SC\(_{11}\)PHE on Ag\(^{TS}\) showed a rectification ratio \((\log |r^+|_{\text{mean}} = \sim 1.8; r^+ = \sim 64)\) similar to that of (and with the same polarity as) the SAM of SC\(_{11}\)BIPY (Figure 1). This comparative study indicates, *inter alia*, that any conformational changes (e.g., *syn*-coplanar versus *anti*-coplanar isomers in two pyridine groups) induced by the applied electric field (up to \(\sim 1 \text{ GV/m}\)) are not responsible for the rectification in the SC\(_{11}\)BIPY SAM.\(^9\)
Table 1. Rectification ratios at ±1.0V for Ag^{TS}/S(CH\textsubscript{2})\textsubscript{2}M(CH\textsubscript{2})\textsubscript{7}-T//Ga\textsubscript{2}O\textsubscript{3}/EGaIn junctions having different terminal groups (T); M is -CH\textsubscript{2}CH\textsubscript{2}- in each molecule except BIPH, where M is -CONH-). Histograms of the current density and the rectification of each junction are located in the SI.

| T     | M       | $r^+_{\text{mean}}$ | $\log|r^+|_{\text{mean}}$ | $\sigma_{\log|r|}$ |
|-------|---------|---------------------|---------------------------|-------------------|
| PHEPY | -CH\textsubscript{2}CH\textsubscript{2}- | 1.3                 | 0.14                      | 0.10              |
| PYR   | -CH\textsubscript{2}CH\textsubscript{2}- | 1.9                 | 0.27                      | 0.26              |
| BIPH  | -CONH-  | 2.8                 | 0.44                      | 0.18              |
| PHE   | -CH\textsubscript{2}CH\textsubscript{2}- | 64                  | 1.8                       | 0.32              |
| BIPY  | -CH\textsubscript{2}CH\textsubscript{2}- | 85                  | 1.9                       | 0.18              |

\(^a\text{Mean value of } r^+\)
\(^b\text{Mean value of } \log|r^+|\)
\(^c\text{Standard deviation of } \log|r^+|\)
Correlations of Structure and Rectification Ratio. This work—combined with data from the literature—suggests a correlation between the magnitude of rectification and the structure of the terminal group. We assume that \( J(-V) \) for SC\(_{11}\)BIPY and \( J(+V) \) for SC\(_{11}\)Fc are based on a pure-tunneling regime; \( J(+V) \) for SC\(_{11}\)BIPY and \( J(-V) \) for SC\(_{11}\)Fc are based on the combination of hopping (due to BIPY and Fc) and tunneling, but the tunneling current is dominated by the tunneling barrier provided by the SC\(_{11}\) group. Using the simplified Simmons model\(^{22-24}\) \( J(V) = J_0(V)e^{-\beta d} \) where \( J_0 \) is an injection tunneling current density A/cm\(^2\), and \( \beta \) is a tunneling decay coefficient Å\(^{-1}\)) we are able to estimate, approximately, rectification ratios for SC\(_{11}\)BIPY, SC\(_{11}\)PHE, SC\(_{11}\)Fc, and SC\(_{11}\)Fc\(_2\): i) \( \tilde{J}(V) = J_0(V)e^{(-\beta CH_2 d_{CH_2} - \beta_{RM} d_{RM})} \) at a polarity, where charges tunnel through both the aliphatic spacer and the rectifying moiety (denoted as RM; e.g., BIPY and Fc); and ii) \( \tilde{J}(V) = J_0(V)e^{-\beta CH_2 d_{CH_2}} \) at the opposite polarity, where charges tunnel only through the aliphatic spacer, and hopping takes place through the RM region. (We assumed that the efficiency for hopping is the same for all of the systems examined.) Since, for rectification, the number of methylene groups in the S(CH\(_2\))\(_n\) group is the same for tunneling in both directions, we can, therefore, approximate the ratio of rectification by Eq. 3, where \( \tilde{J}(V) \)

\[
|r|_{\text{calcd}} = \tilde{J}(V)/\tilde{\tilde{J}}(V) = \exp(\beta_{RM} d_{RM})
\]

Eq. 3

and \( \tilde{J}(V) \) are current densities at opposite biases. The value of \( |r|_{\text{calcd}} \) in Eq. 3 depends on the “length” \( d_{RM} \) (that is the contribution to the thickness of the tunneling barrier in the polarity where the barrier includes the rectifying moiety) and the tunneling decay constant \( \beta_{RM} \) of the rectifying moiety.

The value of \( d_{RM} \) represents the width of the tunneling barrier for a rectifying moiety (e.g., BIPY, PHE or Fc\(_n\)), but is not a value we can define accurately, since we do not know what conformation (or mixture of conformations) this group has in the regions of contact between the
SAM and the top electrode. To test the hypothesis that there might be a relationship between rectification and “size” (as measured by some molecular dimension or metric) of the rectifying moiety, we estimated values of $d_{RM}$ based on two limiting, simplifying approximations. i) In one, we assume an extended *trans* structure (as presented in Figure S5 in the SI), and calculate $d_{RM}$ using Chem 3D or Spartan. ii) In the second, we treat the terminal groups as spheres in order to estimate values of $d_{RM}$. This latter assumption is roughly equivalent to assuming that the terminal groups are randomly oriented relative to the plane of the surface of the SAM. In this approximation, we estimate $d_{RM}$ for a group with a molecular volume ($V=4/3\pi(d_{RM}/2)^3$, Å$^3$; values of $V$ were calculated from Molinspiration Property Calculation Service at http://www.molinspiration.com, or obtained from the literature$^{37-39}$). Table 2 summarizes estimated values of $d_{RM}$ for PHE, BIPY, Fc and Fc$_2$. We also assume (lacking any other information) that the tunneling decay constant ($\beta_{RM}$) for the rectifying moieties are the same, and equal to those for either oligophenylenes ($\beta = \sim 0.6$ Å$^{-1}$) or polymethylenes ($\beta = \sim 0.7$ Å$^{-1}$)$^{23,24}$ These values of $\beta$ were determined at ±0.5V for both oligophenylenes and polymethylenes and are almost certainly not accurate at ±1.0V; to determine if difference in the size of the T group were, at least, compatible with the observed values of rectification, these values of $\beta$ are, however, sufficient. The values of $|r|_{calcd}$ approximated with $\beta \sim 0.6$ Å$^{-1}$ based on the two structural approximations are in rough accord with the empirical results (Table 2).

The ability to estimate rectification ratios for several systems described in Table S1 allowed us to compare calculated values ($|r|_{calcd}$; see Figure S5 and Table S3 in the SI for structures used for calculations and summary of calculations) with experimentally observed values ($|r|_{obsd}$), and qualitatively to reconcile the previous systems with systems based on SC$_{11}$T (T=BIPY, PHE or Fc$_a$). A plot of $|r|_{obsd}$ against $|r|_{calcd}$ (estimated based on the two structural
Table 2. Summary of calculated molecular lengths \((d)\) and ratios of current rectification \((r)\) for SC\(_{11}\)PHE, SC\(_{11}\)BIPY, and SC\(_{11}\)Fc\(_n\) (\(n = 1\) or \(2\)).

<table>
<thead>
<tr>
<th>Assumed structure of T group</th>
<th>Molecular Rectifiers</th>
<th>(d_{RM} (\text{Å})^a)</th>
<th>Rectification ratio ((r))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated(^{e,f})</td>
<td>Calculated(^{e,f})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>((\beta \sim 0.6 \text{Å}^{-1}))</td>
<td>((\beta \sim 0.7 \text{Å}^{-1}))</td>
</tr>
<tr>
<td>Spherical shape</td>
<td>SC(_{11})PHE</td>
<td>7.0(^b)</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>SC(_{11})BIPY</td>
<td>6.8(^b)</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>SC(_{11})Fc</td>
<td>7.2(^c)</td>
<td>73</td>
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<tr>
<td></td>
<td>SC(_{11})Fc(_2)</td>
<td>8.9(^c)</td>
<td>210</td>
</tr>
<tr>
<td>Extended trans structure</td>
<td>SC(_{11})PHE</td>
<td>6.9(^d)</td>
<td>64</td>
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<tr>
<td></td>
<td>SC(_{11})BIPY</td>
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<td>75</td>
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<tr>
<td></td>
<td>SC(_{11})Fc</td>
<td>6.0(^d)</td>
<td>36</td>
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<tr>
<td></td>
<td>SC(_{11})Fc(_2)</td>
<td>11.4(^d)</td>
<td>954</td>
</tr>
</tbody>
</table>

\(^a\)Calculations were based on the assumptions that i) terminal groups Fc\(_n\), BIPY, and PHE are spherical in shape, and the width of tunneling barrier of terminal group \((d_{RM})\) is \(d_{RM} = 2\times(3V/4\pi)^{3/2}\); or ii) the terminal groups are in extended trans structure.

\(^b\)The width was estimated by including the methyl substituents in the BIPY and PHE group. We do not know the role of the methyl substituent in hopping; if the methyl groups are excluded, the values of \(d_{RM}\) are 6.6Å for BIPY and 6.8Å for PHE, and the values of \(|r|_{\text{calcd}}\) for \(\beta = \sim 0.6\text{Å}^{-1}\) and \(\sim 0.7\text{Å}^{-1}\) are 51 and 98 for BIPY, and 59 and 116 for PHE.

\(^c\)Calculations were based on the literature values of volumes for Fc and Fc\(_2\).\(^{37-40}\)

\(^d\)See Figure S5 in the SI for detailed molecular structures.

\(^e\)Values of \(|r|_{\text{calcd}}\) were calculated with Eq. 3, assuming that the tunneling decay constants characteristic of attenuation through PHE and BIPY are equal to that either of oligophenylenes \((\beta \sim 0.6 \text{Å}^{-1})\) or of polymethylenes \((\beta \sim 0.7 \text{Å}^{-1})\).

\(^f\)Note that our calculations for determining \(d_{RM}\) do not include information about the supramolecular structure of groups in a SAM.
**Figure 5.** A plot of reported, experimentally observed rectification ratios ($|r_{\text{obsd}}|$) (on a logarithmic scale) for systems taken from the literature and described in Table S1 (in the SI), against rectification ratios ($|r_{\text{calcd}}|$) calculated using Eq. 3, and values of the width of the barrier for rectifying moiety ($d_{\text{RM}}$). Values of $d_{\text{RM}}$ were estimated using the molecular volume of terminal groups—those assigned as a rectifying moiety—(□: based on the approximation that the terminal groups are spherical in shape; ●: based on the approximation that the terminal groups are in extended *trans* conformations). For ref. 14 (see Figure S5 for assumed, detailed molecular structures in the SI) we calculated $d_{\text{RM}}$ by using one quarter of the volume or width of Cu(II)phthalocyanine group (as reported in the reference).
approximations described above) in Figure 5 suggests that our hypothesis—that the terminal group T for SC_nT system is conducting at one polarity and insulating at the other polarity—roughly accounts for the rectifications in the previously described systems. We used a log/log plot here for convenience to summarize the broad range of data. We recognize that such a plot tends to convert a range of data into linear relationships, but point out that the greatest deviation (ref. 6 by McCreery et al. in Figure 5) differs in calculated and observed values by only a factor of eight. The fact that the azo compound (Figure S5 in the SI) described by McCreery et al. does not follow the expected trend (Figure 5) for the “spherical” approximation but does for the “extended” hypothesis is easily rationalized: this group could be trans-extended, and therefore ordered, at the surface of the SAM. Correspondingly, the compound reported by Ashwell et al. is composed of the bulky terminal group and the thin alkyl backbone (Figure S5 in the SI), and plausibly disordered.

Figure 5 focuses on the structures of known molecular rectifiers, and includes the data we could find in the literature; we did not intentionally include or reject data based on our assessment of the validity of the reported rectification ratios. Previous work showed that junction characteristics (e.g., the topography of the bottom electrode, the supramolecular structure of molecules within the SAM, the presence of impurities, and the structure of the HOMO and LUMO of the presumed electroactive groups) influence rectification in molecular junctions, but there is little usefully detailed information about the influence of these characteristics on rectification for most of the rectifiers reported previously. There is also no information on junctions that might have been expected to rectify based solely on Figure 5, but did not (and were thus not reported).
CONCLUSIONS

SAMs composed of S(CH$_2$)$_{11}$BIPY (BIPY = 4-methyl-2,2'-bipyrid-4'-yl) show values of rectification of the same magnitude that has been observed with SAMs of S(CH$_2$)$_{11}$Fc, but of the opposite polarity. SAMs of 2,2'-bipyridyl-terminated $n$-undecanethiolate on AgTS rectify statistically significantly ($\sigma_{\text{log}|r|}$~0.18) at ±1.0V. Mean (~85) and median (~84) values of $r^+$ are statistically indistinguishable (Figure 1). The magnitude of rectification for SAMs of SC$_{11}$BIPY is similar to that reported previously for SAMs composed of similar thiolates terminated in Fc ($r^+$~150); Fc-terminated SAMs rectify with polarity opposite to that of BIPY-terminated SAMs.

Rectification is due to the SAM, not to the redox behavior of Ga$_2$O$_3$, Ga, In, or Ag components of the Ag$^{TS}$S(CH$_2$)$_{11}$BIPY//Ga$_2$O$_3$/EGaIn junction. XPS analysis of the composition of the surface of a SAM of SC$_{11}$BIPY SAM that had been brought into contact with Ga$_2$O$_3$/EGaIn shows that there is no detectable transfer of Ga or In components from the electrode to the surface. This observation suggests that the metal complexation between BIPY and Ga$_2$O$_3$/EGaIn is not substantial enough to influence rates of charge transport. Junctions with the form Au$^{TS}$S(CH$_2$)$_{11}$BIPY//Ga$_2$O$_3$/EGaIn also rectified current with the same magnitude and polarity as the Ag$^{TS}$S(CH$_2$)$_{11}$BIPY//Ga$_2$O$_3$/EGaIn junction. This similarity demonstrates that rectification is not a result of the BIPY terminal group chelating silver ions from the bottom electrode. Replacing the T = BIPY in Ag$^{TS}$/S(CH$_2$)$_{11}$T//Ga$_2$O$_3$/EGaIn junctions with T = PYR, PHEPY, or BIPH does not lead to rectification. The response of the rectification ratio to the structural variation in the terminal group T indicates that the SC$_{11}$BIPY molecules, not non-molecular characteristics of the junction such as redox phenomena in the Ga$_2$O$_3$ film$^{43}$ nor the composition of the bottom-electrode, are responsible for the rectification observed in the Ag$^{TS}$/SC$_{11}$BIPY//Ga$_2$O$_3$/EGaIn junctions.
The rectification of BIPY-terminated SAM is dominated by a change in current in one direction. When the electrode proximal to the BIPY is reducing, the current is higher than that for a length-matched \( n \)-alkanethiolate. When that electrode is oxidizing, the currents are the same and indistinguishable statistically. This observation is compatible with a basic mechanistic hypothesis that Fc and BIPY follow similar mechanisms, but with opposite redox behaviors. The SAM of S(CH\(_2\))\(_{11}\)Fc has been established to rectify by a process in which the current density in one direction (at +1.0V) is rate-limiting tunneling across the (CH\(_2\))\(_{11}\) moiety, and in the other direction (at -1.0V) involves an initial step of hopping (that is, electron transfer to convert Fc to Fc\(^+\)) followed by rate-limiting tunneling across the insulating (CH\(_2\))\(_{11}\) moiety.\(^{18-21}\) The difference in the tunneling distances—the thickness of the tunneling barrier, which we take to be the distance between the bottom sulfur and the distal atom closest to the top electrode—determines the differences in current densities, and thus the rectification. In the case of BIPY, we postulate that the same mechanism—tunneling at negative bias, versus hopping plus tunneling at positive bias—occurs at the opposite polarity, and thus implies that the hopping step is the reduction of BIPY to BIPY\(^-\) by one-electron reduction.\(^{44}\)

The redox potentials of the terminal (T) groups structurally related to the BIPY are in qualitative accord with the expectation that the more easily reduced compounds would rectify more than those that are less easily reduced. For example, the reduction potentials determined experimentally for both 2,2'-bipyridine and \( o \)-phenanthroline are -2.1V vs. SCE in 0.1 M acetonitrile solution of tetrabutylammonium tetrafluoroborate, while that for biphenyl it is -2.7V vs. SCE in the same conditions.\(^{44}\) The reported value of reduction potential for pyrazine is -1.25V vs. SCE, but the reduction involves proton-assisted two-electron reduction,\(^{45}\) which is mechanistically distinct from the one-electron process with BIPY, and of unknown relevance in
an environment with limited availability of protons. Note that the values of the reduction potential were determined in solution; the high electric field (~1 GV/m) in SAM-based junctions, and the difference in solvation, may cause shifts in redox potential.\textsuperscript{46}

Fc and Fc\textsubscript{2} show oxidation potentials, +0.38 V vs. SCE\textsuperscript{47} and +0.38 V vs. Ag/Ag\textsuperscript{+} (+0.33 V vs. SCE)\textsuperscript{48} in 0.1 M acetonitrile solution of tetrabutylammonium hexafluorophosphate. The low oxidation potential of Fc and Fc\textsubscript{2} supports the conclusion that the rectification of SC\textsubscript{11}Fc\textsubscript{n} relies on the oxidation of Fc\textsubscript{n}, and rationalizes the observation that the direction of rectification is opposite to that of rectification of SC\textsubscript{11}BIPY.

\textbf{This work proposes a model to rationalize rectifications of different magnitudes reported in the literature.} Eq. 3 (which we have shown to be compatible with rectification ratios reported in the literature, and summarized in Figure 5) in conjunction with the simplified Simmons model, is compatible with the hypothesis that most of rectifiers previously reported use a mechanism similar—at least in part—to that proposed for the SC\textsubscript{11}Fc system.\textsuperscript{21} In this approximation, for SAMs terminated in redox-active groups, the magnitude of rectification is related to the size or shape (by some metric, or combination of metrics) of the terminal group, and to the accessibility of a one-electron redox process allowing hopping to or from the Ga\textsubscript{2}O\textsubscript{3}/EGaIn electrode. (The approximations in this estimate—the geometry of the T group, the value of $\beta$ characterizing it, and the details of the shape of the tunneling barrier—were sufficient that this agreement indicates only mechanistic compatibility, and not mechanistic proof. It is, therefore, a mechanistic hypothesis at this point, and subject to further experimental testing.) A number of other factors—the energies and position of the HOMO or LUMO of the SAM, the energies of the HOMO and LUMO of the terminal group, the extent of coupling of this group to the orbitals of the electrodes, the details of the conformation(s) of the group T, and yet other
terms—may ultimately be demonstrated to be important in determining the magnitude of
rectification. The rough agreement suggested by Figure 5 is, nonetheless, stimulating, and
suggests a range of experiments testing the relationship between sign and magnitude of the
rectification ratio and the structure and conformation of the group T.

ASSOCIATED CONTENT
Supporting Information: full experimental details, summary of previous rectifier systems, and
other secondary discussions. This material is available free of charge via the Internet at
http://pubs.acs.org.

ACKNOWLEDGEMENT
This work was supported by a subcontract from Northwestern University from the Department of
Energy (DE-SC0000989). The DOE grant from Northwestern also supported the salary for
H.J.Y., K.-C.L., and M.B. Sample characterization (XPS analysis) was performed at the Center
for Nanoscale Systems (CNS) at Harvard University, a member of the National Nanotechnology
Infrastructure Network (NNIN), which is supported by the National Science Foundation (ECS-
0335765).
REFERENCES


Table of Content Graphic

Molecular Rectifier

$\frac{|J(+1.0\text{V})|}{|J(-1.0\text{V})|} = 85$