JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
Cite This: J. Am. Chem. Soc. 2019, 141, 8969−8980
pubs.acs.org/JACS

Dipole-Induced Rectification Across Ag^{TS}/SAM//Ga_2O_3/EGaIn Junctions

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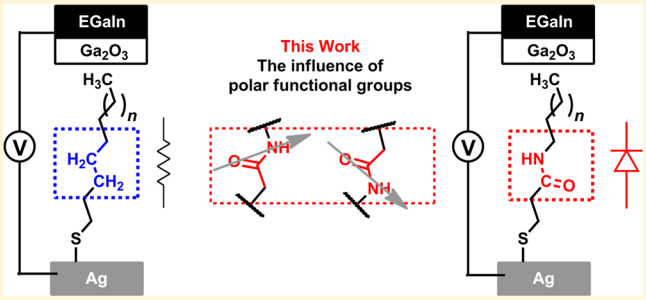
Supporting Information

ABSTRACT: This Article describes the relationship between molecular structure, and the rectification of tunneling current, in tunneling junctions based on self-assembled monolayers (SAMs). Molecular dipoles from simple organic functional groups (amide, urea, and thiourea) were introduced into junctions with the structure $Ag^{TS}/S(CH_2)_nR(CH_2)_mCH_3//Ga_2O_3$/EGaIn. Here, R is an *n*-alkyl fragment $(-CH_2-)_{2\text{ or }3}$, an amide group (either −CONH− or −NHCO−), a urea group (−NHCONH−), or a thiourea group (−NHCSNH−). The amide, urea, or thiourea groups introduce a localized electric dipole moment into the SAM and change the polarizability of that section of the SAM, but do not produce large, electronically delocalized groups or change other aspects of the tunneling barrier. This local change in electronic properties correlates with a statistically significant, but not large, rectification of current (r^+) at ±1.0 V (up to $r^+ \approx 20$). The results of this work demonstrate that the simplest form of rectification of current at ±1.0 V, in EGaIn junctions, is an interfacial effect, and is caused by a change in the work function of the SAM-modified silver electrode due to the proximity of the dipole associated with the amide (or related) group, and not to a change in the width or mean height of the tunneling barrier.



■ INTRODUCTION

Interest in molecular electronics has developed, in part, on the basis of the proposition that organic synthesis would enable so-called "wave-function engineering", and that current−voltage characteristics of junctions containing organic compounds could be tailored through modifications of molecular structure.[1−7] One of the original stimuli in this field was a paper by Aviram and Ratner,[8] which proposed that a single organic molecule with a π-donor and a π-acceptor separated by an insulating sigma bridge—a so-called donor−sigma−acceptor (D−σ−A) system—could, under an applied field, rectify current. This proposal—based on a general consideration of rectification in terms of a favorable molecular orbital framework—has been interpreted to be in agreement with results obtained in a number of studies using molecular rectifiers,[9−17] although not with systems incorporating ferrocene[13,18−26] and bipyridyl[27] groups, where rectification seems to reflect a combination of hopping and tunneling. The mechanisms of rectification in most systems involving tunneling are still being established.

Molecular orbital theory formed the basis of the Aviram−Ratner proposal for rectification. In this model, the alignment of donor and acceptor energy levels in the molecule, in addition to those of the electrodes, contributes to the passage of current. This model suggested that the internal energetic topography of the molecule is capable of influencing the tunneling barrier, and that effect is dependent on the sign of the applied bias. The design of an Aviram−Ratner-type rectifier proved to be difficult to implement experimentally, but many (and many types of) molecular rectifiers and diodes have been demonstrated in Langmuir−Blodgett films,[28,29] in SAMs,[20,21,23,27,30−34] and in single-molecule devices.[35−37] Rectification is also possible in a purely tunneling system

Received: March 15, 2019
Published: May 9, 2019

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

(e.g., not a combination of hopping and tunneling[21]) if the energy barrier is sufficiently asymmetric.[17,37−39]

Our objective for this work was to understand if the presence of a simple dipolar group within a SAM—in the absence of accessible delocalized molecular orbitals—would alter the shape of the tunneling barrier (and perhaps the work function of the electrodes) sufficiently to induce the rectification of current, and/or to alter tunneling current density (Figure 1). We also wished to test the influence of the

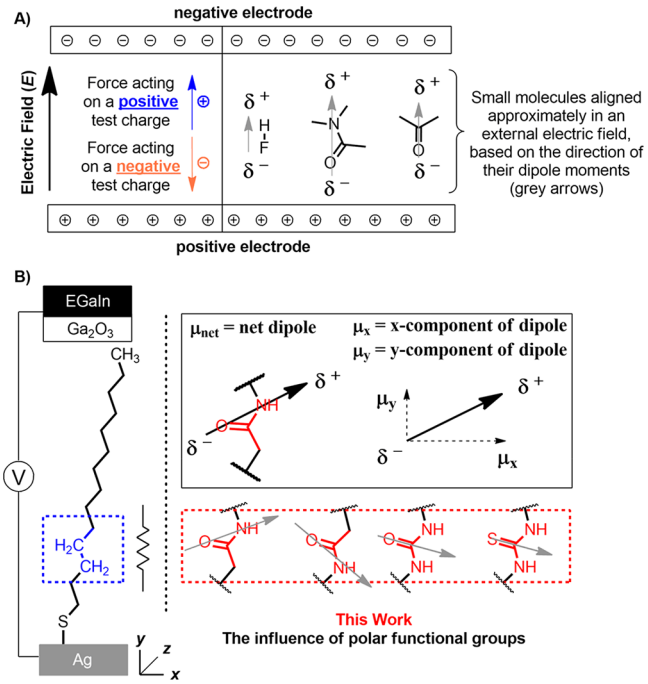


Figure 1. (A) Representation of small molecules aligned in an external electric field, based on the direction of their dipole moments. (B) Schematic representation of an alkanethiol SAM, within an electrical circuit made from the EGaIn junction, where the $-CH_2CH_2-$ groups (blue) act as resistive elements in the circuit. The red box shows the dipolar functional groups used in this work. Approximations of their associated dipole moments are represented by gray arrows. The black box (above) shows the convention that we use for drawing a dipole moment. The net dipole moment (μ_{net}) can be decoupled into its x- and y-components (μ_x and μ_y) relative to the mean plane of the surface of the electrode, and points toward the region of positive electrical charge.

position of this polar group in the SAM—relative to each electrode—using junctions of the form Ag^{TS}/SAM//Ga_2O_3/EGaIn (here, Ag^{TS} is a template-stripped silver substrate, and EGaIn is eutectic gallium−indium alloy, with its surface film of electrically conducting Ga_2O_3).[40−42]

Among the possible dipolar groups that can generate permanent dipole moments in SAMs, we chose amide, urea, and thiourea groups.[43] These functional groups are relatively redox-inert, and will not strongly perturb the structure of the HOMO or LUMO, but have a substantial dipole moment (∼4−5 D).[44−49] We incorporated these groups systematically in place of $-(CH_2)_2-$ or $-(CH_2)_3-$ groups in the SAM, while keeping both interfaces (Metal/SAM and SAM//Ga_2O_3) unaltered. We examined tunneling currents through two homologous series of molecules (Figure 2) with structures (i) $HS(CH_2)_mXY(CH_2)_nH$, where −XY− is $-CH_2CH_2-$, −CONH−, and −HNCO−, and $m + n = 12$ such that $1 \leq m \leq 11$, and (ii) $HS(CH_2)_2XYZ(CH_2)_6CH_3$, where −XYZ− is $-CH_2CH_2CH_2-$, $-CH_2CONH-$, −NHCONH−, −NHCSNH−, or $-NHCOCH_2-$.

Dipole Moment Convention. This Article uses the convention used by physicists for drawing dipole moments. That is, we draw the dipole as an arrow that points toward the region of positive electrical charge; this arrow represents the direction with which a polar molecule will align in an external electric field (Figure 1A). Chemists, in contrast (and despite the IUPAC definition), usually draw dipole moments in the opposite direction, where the arrowhead points toward the region of negative electrical charge.[50]

■ BACKGROUND

Definition of the Rectification Ratio. We define the rectification ratio (r) as the absolute value of the larger current density at a particular voltage divided by the absolute value of the current density at the opposite bias but the same magnitude of voltage. We also include an indication of polarity: $r^+ = |J(+V)|/|J(-V)|$ or $r^- = |J(-V)|/|J(+V)|$; in this definition, r is always ≥1. In EGaIn junctions, the bottom electrode (Ag^{TS} in this study) is always grounded, and the sign of the voltage is defined by the polarity of the EGaIn electrode; "+V" means the polarity of EGaIn is positive and it (or, more precisely, its electrically conducting Ga_2O_3 surface film) is oxidizing relative to the Au or Ag electrode, and "−V" means the polarity of the Ga_2O_3/EGaIn electrode is negative and it is reducing, relative to that electrode.

Factors unrelated to the molecular structure might—in principle—induce rectification, due perhaps to (i) the presence of oxides or contaminants on the surface of the electrodes; (ii) a difference in the work function of the electrodes; (iii) asymmetric contact at electrode-molecule interfaces; or (iv) experimental uncertainty. Junctions composed of SAMs of n-alkylthiolates on gold and silver surfaces, and using EGaIn as the top electrode, seem to produce r^+ values of up to 3 ± 2. We attribute these values to differences between the bottom and top electrodes, including differences in the interfaces between the SAM and the Au or Ag junction and the SAM and the Ga_2O_3/EGaIn electrode, and the polarizability of the sulfur atom, which is covalently bound to the Ag or Au (bottom) electrode.[51] We do not consider a value of this size to demonstrate the occurrence of rectification due to electronic features of the SAM. We use this value of $|r|$—a value generated for SAMs of n-alkanethiolates—as a threshold for determining significant r values in other molecular systems. In practice, and with a degree of subjectivity, we consider any value of $r < 5$ to be too small to be reliably assigned to (or mechanistically interpreted in terms of) molecular rectification,[40] although smaller values of r are routinely observed (and reported) even with the structurally simplest SAMs.

Factors That May Lead To Rectification of Current in a Tunneling Junction. The proposal of Aviram−Ratner for D−σ−A rectifiers[8] is based on a specific molecular orbital framework in which the frontier molecular orbitals of the D/A system align energetically with the Fermi levels of the electrodes at one particular bias; application of the opposite bias does not lead to such alignment of energy levels, with the result of asymmetry in the I/V trace. Experimental evidence for this type of rectifier (with r^+ of ∼5) was claimed by Metzger and co-workers[52] using a D−π−A system (γ-hexadecylquinolinium tricyanoquinodimethanide). The authors suggested two origins for rectification: (i) the position of the frontier

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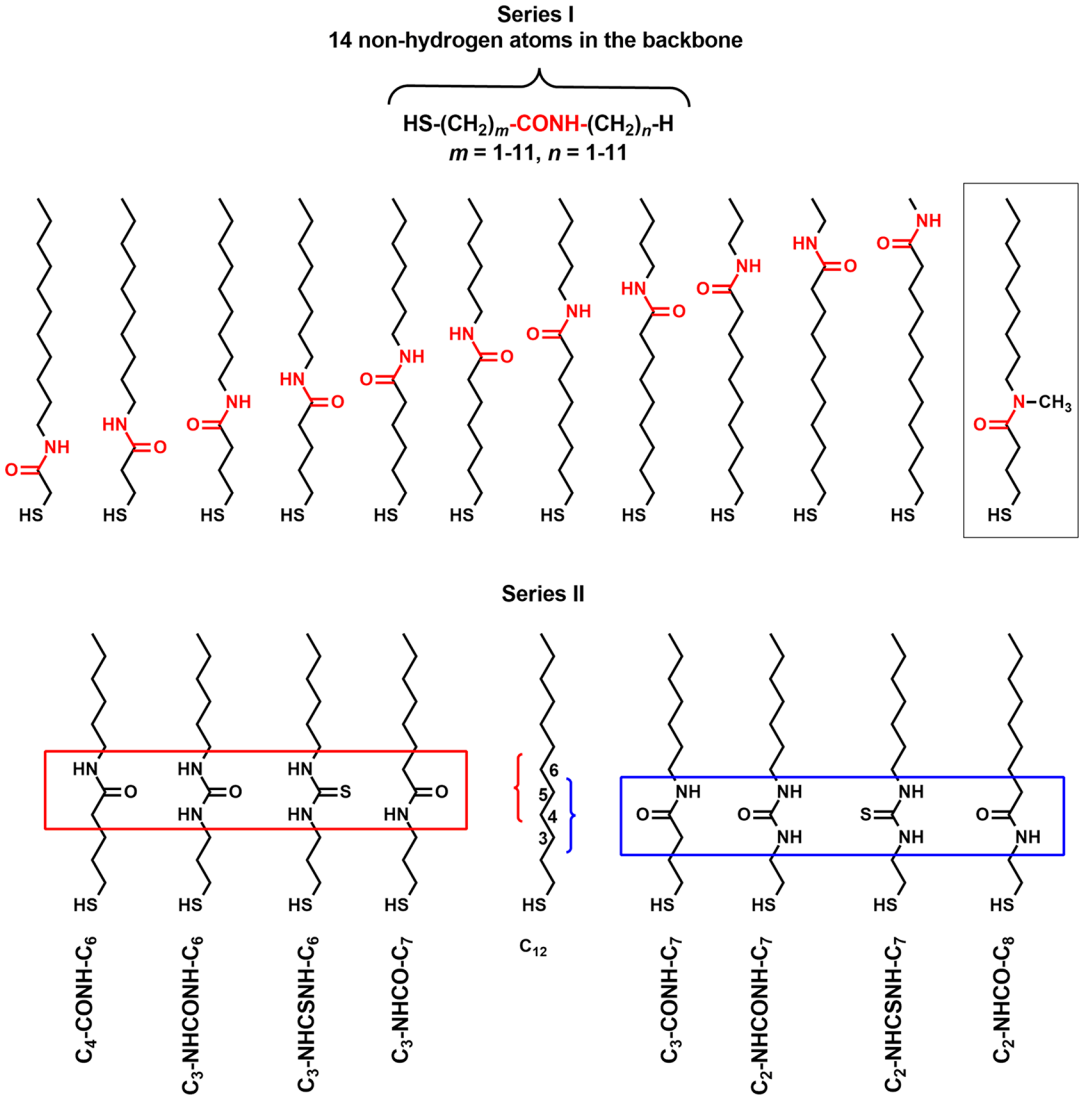

Figure 2. Schematic representation of the structural variations upon the inclusion of the amide group in the backbone of C_{14}-alkanethiol (Series I) and the inclusion of the amide, the urea, and the thiourea groups in the backbone of C_{12}-alkanethiol (Series II). "*m*" indicates the number of methyl groups between the sulfur anchoring atom and the amide group, and "*n*" indicates the number of methyl groups between the amide group and the terminal hydrogen atom in contact with the top electrode.

molecular orbitals relative to the Fermi levels of the electrodes, and (ii) an asymmetric drop in the electrostatic potential across the molecule due to the presence of a large dipole moment.[52,53]

Ratner and co-workers suggested,[54] as an alternative source of rectification, that asymmetry in I/V curves could be achieved from perturbations in the electrostatic potential profile of a molecular junction; these changes in electrostatic potential could take place across the molecular bridge or at the metal/molecule interfaces.[17,38,51,55] For this type of rectification, two mechanisms have been suggested: (i) A dipole-induced mechanism. In this mechanism, the profile of the potential generated by the applied bias is perturbed by an electrical dipole (permanent or induced) localized in a molecule or group.[29,35,55−57] Accordingly, the energy levels of the molecular orbitals (especially the HOMO for hole tunneling) change with the bias. Bias in one direction might bring a molecular orbital closer to resonance with the Fermi level, E_F, of an electrode, and reduce the tunneling barrier, while a bias of the same magnitude in the opposite direction would have an inverse effect and increase the tunneling barrier. (ii) Molecular asymmetry. Rectification might appear in a molecular orbital structure that is coupled differently to the two electrodes. Such asymmetric couplings might lead to an asymmetric electric potential profile along the molecule, and lead to rectification (although a detailed mechanism of rectification has not been clearly identified).[38,51,55]

■ EXPERIMENTAL DESIGN

Structural Design of Dipole-Embedded Alkylthiolates. To determine the influence of an embedded dipole moment (that is, a dipole in an otherwise nonpolar SAM) on the rectification of current, we compared two series of compounds (Series I and II; Figure 2). In Series I, we placed an amide group, −CONH−, at each position along the backbone of a C_{14}-alkylthiolate chain to determine if the position of the dipole, and (perhaps) the interchain H-bonding between amide groups, has an effect on the rate of tunneling currents at either positive or negative bias. We designed the structural perturbations to include a minimum of at least one methylene group ($-CH_2-$) as spacer between the amide group and the electrodes; this spacer serves to isolate (at least by direct conjugation[58]) the amide/urea group and

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its dipole from the sulfur atom and the electrode.[27,59−62] The mixture of interactions between HOMOs is, however, apparently more delocalized than anticipated by direct interaction of π-orbitals, and we have not quantified this interaction.

In the second series of molecules (Series II, Figure 2), we embedded different functional groups and changed the orientation of the amide group by replacing −CONH− with −NHCO−.

We also changed the chemical structure, polarizability, and dipole moment of the polar group by introducing urea (−NHCONH−), and thiourea groups (−NHCSNH−), and compared their charge-transport characteristics. To understand the influence of a urea or thiourea moiety on charge transport, we kept the overall length of the molecule equivalent to dodecanethiol (C_{12}) (Figure 2); that is, we kept the width of the tunneling barrier very close to the same, so the change in current density, if any, should allow us to recognize a change in tunneling current that correlates with the chemical (or electronic) structure of the molecule or the dipole groups embedded in it.

Electronic Influence of Dipolar Groups. Amide ($\mu \approx 4$ D),[44−46] urea ($\mu \approx 4$−5 D),[47−49] and thiourea ($\mu \approx 4$−5 D)[47,63] groups have large dipole moments and high polarizabilities, relative to those associated with the $-(CH_2)_{n=2,3}-$ groups ($\mu \approx 0$ D) they replace.[64] This change in electronic structure can, in principle, induce changes in rates of charge transport.[54] Amide and urea/thiourea groups also introduce a different orientation of the dipole vector relative to the (assumed) direction of charge tunneling (Figure 1B). Thus, the inclusion of an amide/urea/thiourea group in the structure of a tunneling junction might result in a significant change in the electrostatic potential along the charge-transport pathway, and change either the rate of charge tunneling through the junction or the rectification ratio (r) (that is, relative to the rates of tunneling in opposite directions at the same absolute value of voltage |V|).

Structure of SAMs Containing Amide and Urea Groups. We[65] and others[66−68] observed that the replacement of $-CH_2CH_2-$ by an amide group (either a −CONH− or a −NHCO−) enhances the stability of the SAM, possibly through interchain H-bonding. Structural studies on amide[66−68]- and urea[69−71]-containing SAMs have shown that the C═O and N−H of the H-bonded amides or ureas are oriented approximately parallel to the metal surface (Figure 2). The formation of intermolecular hydrogen bonding between the chains in the SAM causes a change in the tilt angle[72] (the tilt angle decreases from ∼24° to 18° on gold) to accommodate a conformation favorable for formation of the C═O---H−N H-bond between molecules. This change in the tilt angle—concurrent with a change in the interchain distance caused by the H-bonding networks—leads to a change in the order and conformation of the alkyl chains in the SAM.[65] The change in the tilt and twist angles is also dependent on the position of the amide group relative to the metal−thiol interface, and on the overall length of the alkyl chain in the overlayer.[65−68] The structure of SAMs containing a urea group is slightly more complicated; each urea group has been suggested to form four hydrogen bonds—two acceptors and two donors—with neighboring urea groups.[69−71]

■ EXPERIMENTAL METHODS

Synthesis of Urea- and Thiourea-Containing Alkylthiolates. Amide-, urea-, and thiourea-based compounds were synthesized using a previously reported protocol (see the Supporting Information for details).[73] For convenience, we abbreviated the names of the compounds using the assignments in Figure 1.

Formation of the SAMs on Silver Bottom Electrodes. SAMs of amide-, urea-, and thiourea-based compounds were formed on the template-stripped surface of silver (Ag^{TS})[74] using a thiol anchoring group. We immersed the surface in a nitrogen-purged ethanolic solution of the thiol (3 mM). After 12 h of incubation under a nitrogen atmosphere, we rinsed the SAMs with ethanol (30 mL) and dried them by evaporation under a gentle stream of nitrogen. We used SAMs for electrical measurements immediately after drying.

Measurements of Work Function (WF). We performed measurements of work function using a K-Alpha XPS system. This system is equipped with an X-ray source with energy 1486.6 eV. A biasing stage held the samples in electrical contact with the analyzer; −30 V applied to the stage accelerated the secondary electrons and helped to detect their cutoff. We recorded the secondary electron cutoff from 32 to 38 eV (kinetic energy), and the Fermi edge from −35 to −25 eV (binding energy). We extrapolated the secondary electron cutoff to the x-axis to determine the vacuum level (E_v). Using the vacuum energy and Fermi level (E_f), we calculated the WF (WF = $E_v - E_f$) of the SAM-modified Ag surfaces, which is the energy required to eject a photoelectron from the surface of the metal−sulfur interface, through the monolayer, to the detector located within a vacuum chamber at 1×10^{-8} mbar. Work functions calculated in this way are generally used to represent the Fermi level of the modified metal surface: that is, the energy level of the electrons in the highest energy occupied states at the SAM-modified metal surface.

Measurement of Current Density. We measured the current density along SAMs of the molecules (Series I and II; Figure 2) on Ag^{TS} surfaces in steps over a range from +1.0 to −1.0 V (the Ag electrode was always grounded, and potentials are referenced to ground potential). For each SAM, the values of $\log|J(V)|$ are approximately normally distributed and could be fit to Gaussian curves. (We thus assume—incorrectly, at some level—no systematic error in the experiments—that is, only random noise—and a single peak. In fact, although a majority of the data are compatible with this assumption, some compounds seem to yield data with intrinsic heterogeneity; see the Supporting Information for the raw data.) Figures S1−S6 show the histograms for the values of $\log|J(V)|$ (J, A/cm^2) for SAMs of n-alkylthiolates and amide-containing compounds on Ag^{TS}. The Supporting Information summarizes details of electrical measurements.

Statistics. For every molecule used in this work, we collected data on three separate chips (separately prepared SAMs). We analyzed at least 10 (and maximum 20 three) junctions for each chip and collected 21 $J(V)$ traces per junction. Each $J(V)$ trace involves a forward-bias sweep and a reverse-bias sweep; see the Supporting Information for details. This procedure provides a minimum of 420 measured values of current density (J) for each applied voltage. The histograms take into account every measured value of J at a given voltage. We fit the histograms with Gaussian curves to obtain the log-mean and log-standard deviations. The plots of $\log|J|-V$ are derived from the average of all traces. We calculate the values of rectification (r^+) for each molecule by averaging the values at $|J(+V)|/|J(-V)|$ for every measured $J(V)$ trace (i.e., the reported value of r^+ is an average of all values of r^+ that we measured). The corresponding histograms of r^+ were fitted to Gaussian functions to obtain the log-mean and the log-standard deviation.

■ RESULTS AND DISCUSSION

At ±0.5 V the Presence of an Amide, Urea, or Thiourea Bond Does Not Influence Rates of Charge Tunneling. We reported previously that the inclusion of an amide group (−CONH− or −NHCO−) in place of an ethylene group ($-CH_2CH_2-$), in alkylthiolates, 11 or 12 atoms from the sulfur anchoring group, has no statistically significant effect on the rate of charge tunneling at ±0.5 V.[73,75−77] Here, we made systematic substitutions along the backbone of a C_{14}-alkylthiolate (Figure 2, Series 1) by replacing an ethylene group ($-CH_2CH_2-$) with an amide group (−CONH−) at each position. The values of J (±0.5 V) for the n-alkylthiolates and amide-containing compounds examined here are not distinguishable (at the precision of our measurements; Figures S1, S7, and Table S1); that is, the values of $\langle\log|J(V)|\rangle$ for amide-containing compounds are not distinguishable from that of a C_{14}-alkylthiolate. Similarly, the values of J (±0.5 V) for the amide-, urea-, and thiourea-

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

Table 1. Current Density (log|*J*|) Values and Rectification Ratios Observed for SAMs Composed of Series I Compounds in a Ag/SAM//Ga_2O_3/EGaIn Junction

compound	+1.0 V		−1.0 V				
	log|*J*|	σ_{log}	log|*J*|	σ_{log}	log|r^+|[a]	σ_{log}	|r^+|
C_{14}	−1.6	0.1	−2.2	0.5	0.5	0.2	3.6
SC_1-CONH-C_{11}	−1.2	0.1	−2.0	0.2	0.88	0.25	7.9
SC_2-CONH-C_{10}	−1.1	0.1	−2.4	0.2	1.26	0.04	18.1
SC_3-CONH-C_9	−0.9	0.2	−2.1	0.3	1.18	0.29	15.1
SC_4-CONH-C_8	−0.8	0.1	−1.5	0.3	0.58	0.31	3.8
SC_5-CONH-C_7	−1.3	0.1	−1.7	0.2	0.33	0.12	2.1
SC_6-CONH-C_6	−1.2	0.3	−1.8	0.2	0.49	0.09	3.2
SC_7-CONH-C_5	−1.0	0.3	−1.4	0.4	0.46	0.20	3.0
SC_8-CONH-C_4	−1.4	0.1	−1.9	0.2	0.49	0.20	3.1
SC_9-CONH-C_3	−1.6	0.4	−1.7	0.3	0.20	0.20	1.6
SC_{10}-CONH-C_2	−1.2	0.2	−1.8	0.5	0.47	0.33	3.0
SC_{11}-CONH-C_1	−1.2	0.1	−1.4	0.2	0.20	0.08	1.6
SC_{10}-NHCO-C_2	−1.0	0.4	−1.5	0.3	0.26	0.21	1.8
SC_3-CONMe-C_9	−1.3	0.2	−1.4	0.1	0.11	0.51	1.3

[a] $r^+ = \langle |J(+1.0\ V)|/|J(-1.0\ V)| \rangle$.

containing C_{12}-alkylthiolates of Series II are not distinguishable from that of an C_{12}-alkylthiolate standard (Table 1, Figures S2, S3, and S7; see the Supporting Information for additional details, including apparent trends in log|*J*| at ±0.5 V).

Measurements of *J*(*V*) at an applied bias of ±0.5 V resulted in almost symmetric voltage profiles at forward and reverse biases for all compounds; that is, none of the compounds measured showed a rectification ratio larger than 2.5 (Tables S1 and S3). In our judgment, rectification ratios that are <5.0 should not, in the absence of other information, be interpreted to originate from the SAM and its molecular orbitals or electrical characteristics.[53] These data indicate that incorporation of chemical linkages such as amide or urea groups—even with large dipoles ($\mu \approx 5$ D)—into SAMs across the pathway of a tunneling current does not cause rectification of current at ±0.5 V.

At ±1.0 V, the Presence of an Amide, Urea, or Thiourea Bond Can Influence the Current Density, and Result in Rectification. Increasing the applied voltage to ±1.0 V produced rectification of current; the magnitude of rectification depended on the location and direction of the dipolar group (Table 1, Figures S2, S3, S7, and S8). For the molecules in Series I, we observed a small (relative to that observed with Fc and BIPY terminal groups at the SAM/Ga_2O_3 interface) but statistically significant rectification ratio ($r^+ = |J(+1.0\ V)|/|J(-1.0\ V)| > 5$) when the dipole—the amide group—was located close to the bottom (Ag^{TS}) electrode, and, in particular, when the aliphatic spacer between the sulfur anchoring atom and the dipole group was no more than three carbon atoms in length.

By comparing the molecules in Series I that rectify current, and those that do not, we conclude that rectification is caused predominantly by a larger increase in tunneling current at positive bias (EGaIn is oxidizing) than at negative bias (EGaIn is reducing).

For the amides that rectify, at positive bias, the increase in tunneling current from +0.5 to +1.0 V is larger (average log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 1.5 A/cm^2) than the increase observed for C_{14} (average log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 0.8 A/cm^2). The amides that do not rectify, however, show an increase in current at positive bias that is approximately the same as that observed for C_{14} (log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 0.9 A/cm^2). At negative bias, the increase in tunneling current observed from −0.5 to −1.0 V for both rectifying amides (average log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 0.8 A/cm^2) and nonrectifying amides (average log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 0.6 A/cm^2) is nearly the same as that observed for C_{14} (log|*J*(+1.0 V)| − log|*J*(+0.5 V)|) = 0.6 A/cm^2). Clearly, these results (displayed graphically in Figure S11) demonstrate that rectification is the result of an increased rate of tunneling at positive bias.

The molecules in Series II were designed to preserve the length of the aliphatic spacer (between the sulfur anchoring atom and the dipole) that results in (or is correlated with) rectification (*m* = 2, 3), while changing the dipolar group. We observed that urea and thiourea groups at all rectified current (Figures 3, S9, S10, and Tables 2 and S2). Amide groups oriented in the opposite direction of those in Series I (i.e., C_3-NHCO-C_7 and C_2-NHCO-C_8), however, did not rectify current. The only obvious difference in polarity between the C_m-NHCO-C_n amides and the C_m-CONH-C_n amides is that the *y*-component of their dipoles must be aligned in opposing directions. Although the conformation of the chains and the exact orientations of the amide groups and of the associated dipoles are not known, no plausible configuration of the SAM (for a *trans*-extended conformation of the organic molecule, but independent of the tilt angle) reverses the direction of the component of the amide dipole relative to the mean plane of the surface.

This difference between $S(CH_2)_{2-3}CONHR$ and $S(CH_2)_{2-3}NHCOR$ provided clear evidence that the orientation of the dipole moment is important for current rectification. We do not know the exact orientation of the dipoles of the urea and thiourea groups, relative to the Ag^{TS} surface, and the differences in r^+ for these molecules when *m* = 2 and *m* = 3 may be a consequence of the distance between the dipole and the Ag surface, or changes in the orientation of the molecules (and thus net dipole moment). Thus, we interpret these results to indicate that different dipolar groups, when positioned close to the bottom electrode, can cause rectification of current.

A comparison within Series II, between the molecules that rectify current, and those that do not, indicates that, as observed in Series I, rectification is a result of an increased rate of tunneling at positive bias. At positive bias, the molecules

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

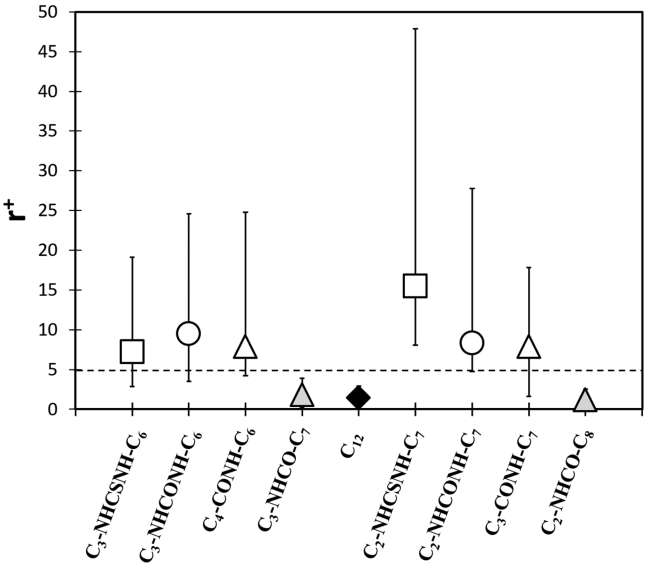

Figure 3. Plot of the rectification ratio ($r^+ = \langle|J(+1\ V)|/|J(-1\ V)|\rangle$) at ±1.0 V, for Series II compounds. The dashed line at $r^+ = 5$ indicates the minimum value of rectification that we believe is statistically significant and is not a consequence of artifacts. The error bars represent the standard deviation of the mean values, and are asymmetric about the mean because of the conversion from log scale to linear scale. The error bars are relatively large because their size scales with (a) the value of the log standard error and (b) the value of rectification with which the error is associated.

that rectify current showed larger increases in tunneling current from +0.5 to +1.0 V (average $\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 1.4\ A/cm^2$) than observed for C_{12} ($\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 0.7\ A/cm^2$), or for the molecules that do not rectify (average $\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 0.8\ A/cm^2$). At negative bias, the increase in tunneling current from −0.5 to −1.0 V was approximately the same for molecules that rectified (average $\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 0.8\ A/cm^2$), molecules that did not rectify (average $\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 0.7\ A/cm^2$), and C_{12} ($\log|J(+1.0\ V)| - \log|J(+0.5\ V)|) = 0.6\ A/cm^2$). Thus, the rectification observed with different dipolar groups is also the result of an increased rate of tunneling at positive bias. (These results are displayed graphically in Figure S12.)

Orientation of the Amide Bond Influences the Rectification. A comparison between the current densities at ±1.0 V across SAMs of C_4-CONH-C_6 ($r^+ = 7.9$), C_3-CONH-C_7 ($r^+ = 9.5$), C_3-NHCO-C_7 ($r^+ = 1.8$), and C_2-NHCO-C_8 ($r^+ = 1.2$) demonstrates that the ratio of rectification is sensitive to the orientation of the amide bond (Figure 3).

When the NH group is the group closer to the bottom (Ag^{TS}) electrode (e.g., $S(CH_2)_3NHCOR$ rather than $S(CH_2)_3CONHR$), the y-component of the dipole (μ_y) changes direction and is oriented toward the Ag^{TS} electrode (Figure 4b). This change in dipole moment orientation was accompanied by a decrease in the rectification ratio from $r^+ = 9.5$ (C_3-CONH-C_7) to $r^+ = 1.2$ (C_2-NHCO-C_8) and from $r^+ = 7.9$ (C_4-CONH-C_6) to $r^+ = 1.8$ (C_3-NHCO-C_7) (Figures 3 and 4b).

When we analyzed the effect of inverting the dipole close to the EGaIn electrode, however, by comparing the current density along C_{11}-CONH-C_1 and C_{10}-NHCO-C_2, at ±1.0 V (Figure 4c), we observed no rectification of either, and thus no influence of the orientation of the amide bond on the rectification ratio.

Rectification of Current Is Sensitive to the Supramolecular Structure of the SAM. Our results (Figure 4a–d) showed that, for Series I molecules, the observed rectification correlates with having a dipole moment close to the bottom electrode, with its y-component (μ_y) oriented perpendicular to (and away from) the mean plane of the Ag (bottom) electrode. Amide bonds, when embedded in the SAMs of alkanethiolates, form hydrogen bonds. This network of hydrogen bonds could help to order the molecules, and thus influence the magnitude and direction of the fixed dipole. In the absence of intermolecular hydrogen bonds, the structure of the SAM might, in principle, be disordered; disorder would undoubtedly influence the net dipole moment.[72,78] To examine the effect of hydrogen bonding on the rectification of current, we compared the current density across SAMs of C_3-CON**H**-C_9 and C_3-CON**Me**-C_9 (Figure 4d). These two compounds have (in principle) indistinguishable extended lengths, and differ only in the elimination of the potential for interchain hydrogen bonding and in the substitution of CH_3N for HN in the amide group.

Substituting a hydrogen atom for a methyl group—a change that converts C_3-CON**H**-C_9 to C_3-CON**Me**-C_9—eliminates the possibility of hydrogen bonding; it also has the potential to change local conformations in the SAM. Measurements of current density for these two compounds yielded very different values of r^+: C_3-CON**H**-C_9 ($r^+ = 15.1$) and C_3-CON**Me**-C_9 ($r^+ = 1.3$) (Figure 4d). (We do not know the conformation of the

Table 2. Current Density ($\log|J|$) Values and Rectification Ratios Observed for SAMs Composed of Compounds in Series II in a Ag/SAM//Ga_2O_3/EGaIn Junction

	+1.0 V		−1.0 V				
compound	$\log\|J\|$	σ_{log}	$\log\|J\|$	σ_{log}	$\log\|r^+\|$[a]	σ_{log}	$\|r^+\|$
SC_3-NHCSNH-SC_6	−0.8	0.4	−1.6	0.41	0.86	0.22	7.2
SC_3-NHCONH-SC_6	−0.7	0.4	−1.6	0.6	0.98	0.33	9.5
SC_4-CONH-C_6	−0.8	0.2	−1.6	0.33	0.90	0.20	6.3
SC_3-NHCO-C_7	−0.6	0.1	−0.9	0.16	0.27	0.07	1.8
SC_{12}	−0.7	0.1	−0.9	0.15	0.14	0.03	1.4
SC_2-NHCSNH-C_7	0.2	0.3	−1.0	0.39	1.18	0.04	15.5
SC_2-NHCONH-C_7	−0.2	0.5	−0.9	0.2	0.92	0.37	8.3
SC_3-CONH-C_7	−0.8	0.6	−1.7	0.28	0.90	0.32	7.9
SC_2-NHCO-C_8	−0.8	0.2	−0.9	0.27	0.10	0.10	1.2

[a] $r^+ = \langle|J(+1.0\ V)|/|J(-1.0\ V)|\rangle$.

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

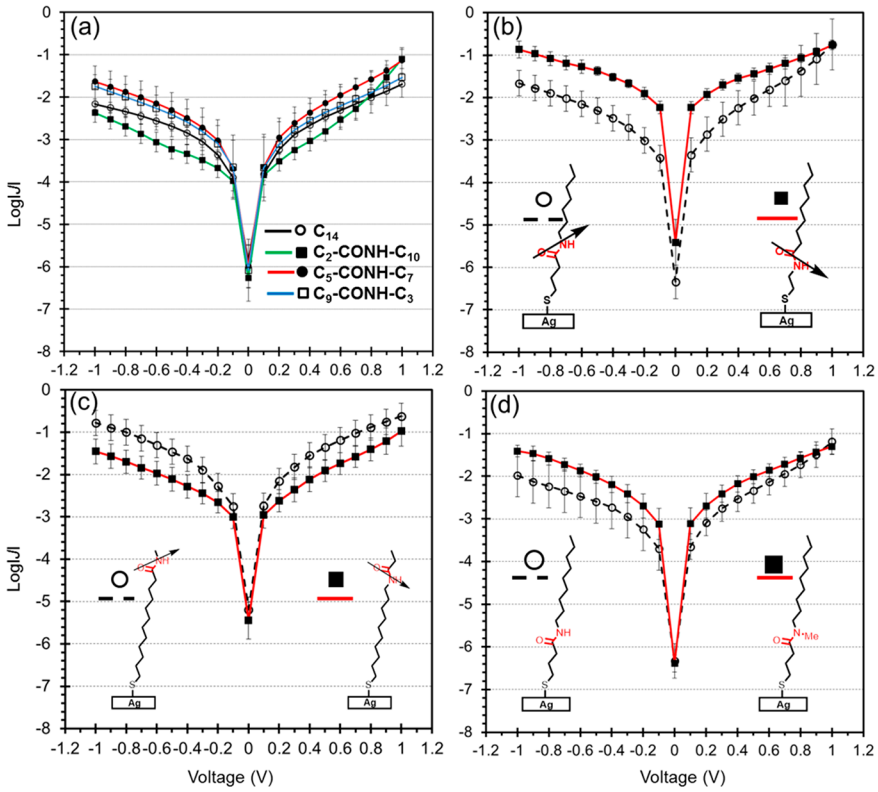

Figure 4. Log|J|−V responses for four compounds investigated in this study: (a) Position of dipole causes a rectification; C_{14} with an alkyl chain, C_2-CONH-C_{10} with the amide group close to the bottom interface, C_5-CONH-C_7 with an amide group in the middle of the backbone, and C_9-CONH-C_3 with an amide group close to the top interface. (b) The direction of dipole, when the dipole is close to the bottom electrode, is important in observing rectification in current. (c) The direction of dipole, when the dipole is close to the top electrode, does not influence the current density. (d) The presence of intermolecular hydrogen bonds is important for the observation of rectification.

individual molecules containing −CON**H**− or −CON**Me**− groups.)

Proposed Origin of Dipole-Induced Rectification. Figure 5 shows a schematic of a SC_2-CONH-C_{10} SAM on a Ag^{TS} surface, the polarity of the electrodes, and the directions of the dipole moments of the amides within the SAM. The y-component of the dipole (μ_y) generates a local electric field along the y-axis (perpendicular to the electrode surface). When the direction of μ_y is aligned with the polarity of the electrodes, the rate of the tunneling current is larger (Figure 5a) than when the applied electric potential is reversed (Figure 5b; cathodic top (EGaIn) electrode to anodic bottom (Ag^{TS}) electrode), and the direction of the electrostatic field generated by the dipole opposes the polarity of the electrodes. We make these empirical observations from these results. (i) Rectification occurs only when the dipole of the amide (or urea/thiourea) is close to the silver electrode. (ii) Rectification reflects primarily an increase in $J(V)$ at positive bias (that is, with Ga_2O_3 oxidizing). (iii) There is no rectification when the direction of the y-component of the dipole moment (perpendicular to the plane of the electrode surface) is reversed, and points toward the Ag surface.

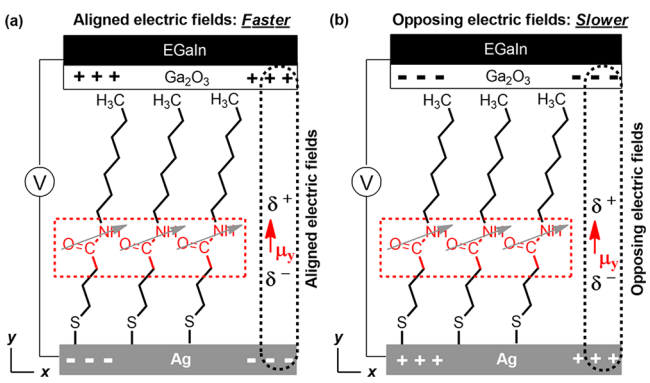

Figure 5. A schematic representation of a Ag^{TS}/SC_2CONHC_7//EGaIn junction: (a) At +1.0 V applied voltage (EGaIn is oxidizing), the polarity of the electrodes is aligned with the y-component of the electric field generated by the dipole moment (μ_y) of the amide bond. The tunneling current is faster. (b) At −1.0 V applied voltage (Ag is oxidizing), the polarity of the electrodes is misaligned with the y-component of the electric field generated by the dipole moment (μ_y) of the amide bond. The tunneling current is slower.

Thus, in the absence of a suitable detailed theory, we attribute the position-dependent rectification of current to alignment between the electric field of the electrodes and a configuration of the molecules in the SAM, such that the perpendicular component of the dipole (μ_y) of the amide group points toward the EGaIn electrode. Rectification does not occur when the dipolar group is separated from the bottom electrode by more than three carbon atoms.

Other groups have also reported a similar influence of the dipole moment on charge transport using single molecule junctions (using peptides)[79] and/or large area junctions (with 1,2-diazine[38] and phenyl bromide[80]). The reported rectifications (r > 8) in those studies were similar in size (although slightly smaller) than those we observe in this study. The

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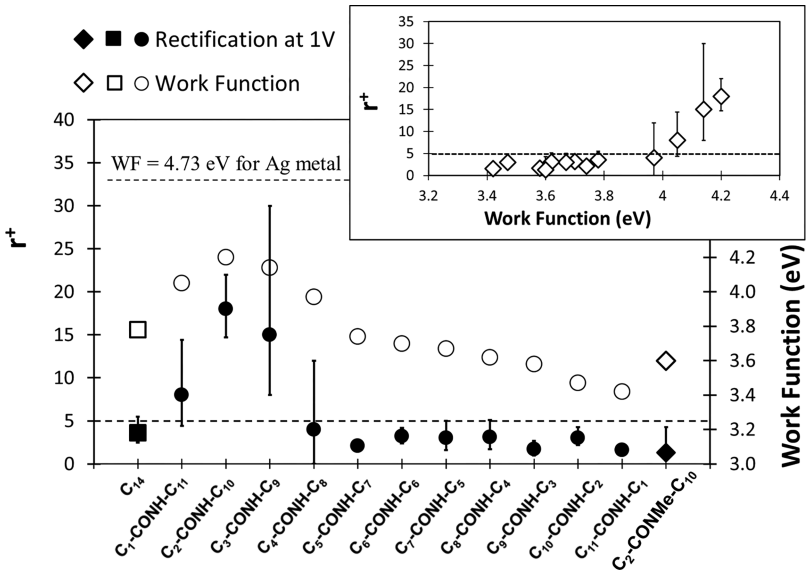

Figure 6. Main plot: Plot of r^+ ($r^+ = \langle |J(+1\ \mathrm{V})|/|J(-1\ \mathrm{V})| \rangle$) at 1.0 V of Series I compounds (amides) and the work function of the silver substrate when covered with SAMs of these amides. Inset plot; upper right: Plot of r^+ and work function. The dashed line at $r^+ = 5.0$ indicates the minimum value of rectification that we consider statistically significant (not resulting from artifacts unrelated to the molecules). The error bars represent the standard deviation of the mean values, and are asymmetric about the mean because of the conversion from log scale to linear. The error bar for C_2-CONH-C_9 is relatively large because its size scales with (i) the value of the log standard error and (ii) the value of rectification with which the error is associated. The uncertainties in the measured work function values are 0.1 eV and are determined by the resolution of the XPS spectra.

rectification ratios in these reports are also dependent on the magnitude of applied voltage.

Analysis of Work Function Indicates That the Position of the Dipole Moment Contributes to the Rectification of Current. Previous work has shown that collective electrostatic properties of SAMs, such as net dipole moment, can modify the work function of the surface, relative to that of the bare metal.[80−83] To rationalize the mechanism of molecular rectification, we measured the work function (WF) of the SAM-modified bottom-electrodes using XPS (Table S3). We note here that our measurements of the vacuum level (E_v) and the Fermi level (E_f), which we used to calculate the WF (WF = $E_v - E_f$), are performed on the SAM-modified Ag-electrodes. Thus, the values that we obtain are those of the SAM-modified Ag-surface, and they represent the energy of the emitted photoelectron outside of the surface of the SAM and not just outside the Ag/S interface. Figure 6 summarizes the values of the WF as a function of m (the number of methylene groups between S and the −CONH− group) for Series I. Our measurements indicate that the WF of the SAM-modified surface changes (relative to C_{14}-alkylthiolate SAM) as a function of the position of the −CONH− group. In particular, when −CONH− is positioned away from the bottom electrode ($m > 5$), the WF is less than that of a C_{14}-alkylthiolate SAM (3.78 eV), and when it is close to the bottom electrode ($m = 1-4$), the WF is larger (by 0.21−0.42 eV) than that of a C_{14}-alkanethiolate SAM. The molecules in Series I have similar chemical structures and surface coverage, and the amides are not expected to alter the Ag−S bonding energy (because they are separated by at least one $-CH_2-$ group).[84] Nevertheless, molecules with a net dipole moment in the same direction as −CONH− are known to decrease the WF relative to alkanethiolate-modified Ag. Our observation that −CONH−, when positioned close to the Ag/S interface, increases the WF relative to a C_{14}-alkanethiolate SAM suggests that polarizable dipole moments, such as an imbedded amide group, can interact electrostatically with the metal/organic interface. In this instance, the positional dependence could be caused by the amide group withdrawing charge from the highly polarizable $Ag^{\delta+}-S^{\delta-}$ surface dipole (~0.6 D[85]) when they are in close proximity.

Although the amide (−CONH−) groups embed a large dipole moment into individual molecules (Table S5) and, we assume, into the SAM, the orientation of molecules within a SAM might cause some cancellation of dipole moments,[86,87] and lead to SAMs with a lower net-dipole moment (μ_{net}) than expected by considering only isolated molecules. The influence of orientation on the net dipole is supported by the difference in WF measurements and rectification ratios between C_3-CON**H**-C_9 (WF = 4.2 eV, $r^+ = 15.1$), which we expect to be more conformationally ordered and have better alignment of dipoles, and C_3-CON**Me**-C_9 (WF = 3.6 eV, $r^+ = 1.3$), which we expect to be less ordered and have poorer alignment of dipoles (we expect both molecules to have group dipole moments that are similar in magnitude and direction). This premise, that conformation influences dipole alignment (and thus WF and r^+), may also explain why the rectification ratio of C_2-CON**H**-C_{10} ($r^+ \approx 18$) is higher than that of C_1-CON**H**-C_{11} ($r^+ \approx 8$), although its dipole is closer to the Ag^{TS} electrode (Figure 4a). That is, the orientation of SAMs is influenced by the location of hydrogen bonds between adjacent amide groups.[88,89]

An even number of methylene ($-CH_2-$) groups between the sulfur anchoring atom and the hydrogen-bond acceptor (the carbonyl of the amide) produces more crystalline SAMs (which presumably have better aligned dipoles) than an odd number of methylene ($-CH_2-$) groups. Changes in WF correlate well with changes in the rectification ratio (r^+) (Figure 6).

The relationship between WF and r^+ can be rationalized by an interaction between the dipole moments perpendicular to the SAM surface (μ_y) and electrons at the Fermi level. This interaction changes depending on the distance and orientation

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

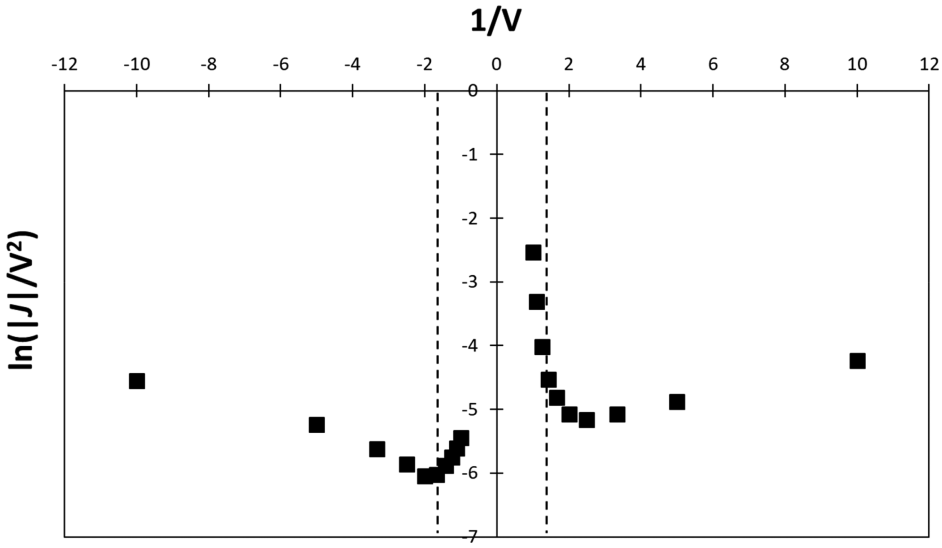

Figure 7. Plot of the tunneling current $\ln(J/V^2)$ as a function of $1/V$ for SC_3-CONH-C_9. A transition from exponential dependency on voltage to linear dependency is apparent at ∼0.6 V.

of the −CONH− group relative to the Ag^{TS} surface. When the amide bond (in S-$(CH_2)_m$-CONH-$(CH_2)_n$-H) is located close ($m \leq 4$) to the bottom (Ag^{TS}) electrode, the change in internal dipole increases the WF of the bottom electrode. This increase in WF lowers the current injection barrier at +1.0 V[82,90,91] (where the Ag^{TS} electrode is reducing) and leads to a higher tunneling rate across the SAM from the Ag^{TS} electrode to the EGaIn electrode, relative to the rate of tunneling at −1.0 V (where the EGaIn electrode is reducing). We conclude, regardless of the mechanism, that to observe rectification in current density, using EGaIn junctions, the internal dipole must be close to the metal−sulfur interface (Figures 4 and 6).

The relationship between work function and rectification (Figure 6, inset plot) indicates that only when the WF of the Ag-electrode is above a threshold of ∼4 eV do we observe rectification. We have not yet rationalized theoretically and quantitatively why (above a WF of > ∼4 eV) rectification increases linearly with the apparent WF (inset, Figure 6), because the thickness of the SAM does not change. This increase probably reflects a change in the electronic profile of the tunneling barrier. This observation must also be interpreted using a mechanism consistent with the absence of rectification below ±0.5 V. We speculate that the onset of rectification at WF ≈ 4 eV and voltage > 0.5 V might correspond to the onset of a new conduction mechanism: that is, from direct tunneling to field emission,[92] or from direct tunneling to Fowler−Nordheim tunneling.[93] Using SC_3-CONH-C_9 as an example, we plotted the tunneling current as $\ln(J/V^2)$ versus $1/V$ and observed a transition from logarithmic dependency on voltage to linear dependency on voltage; this transition took place at ∼0.6 V (Figure 7). This transition to a linear dependency correlates with the observed threshold voltage required for rectification, and could, in principle, arise from an asymmetric interfacial barrier height caused by the change in WF.[94,95] Using SC_3-CONH-C_9 as an example, we plotted the tunneling current as $\ln(J/V^2)$ versus $1/V$ and observed a transition from logarithmic dependency on voltage to linear dependency on voltage, which took place at ∼0.6 V (Figure 7). This transition to a linear dependency correlates with the observed threshold voltage required for rectification, and could, in principle, arise from an asymmetric interfacial barrier height caused by the change in WF.[94,95]

■ CONCLUSIONS

This study reaches the following main conclusions and/or inferences:

(i) The magnitude of rectification is sensitive to the direction of the dipole of the molecule, but only when that dipole is close to the silver electrode ($m \leq 4$).

(ii) The charge (e.g., the hole) tunnels along the SAM more rapidly when the direction of the amide dipole is aligned with the external electric field (e.g., Ga_2O_3 electrode is oxidizing relative to the grounded Ag electrode) generated by the electrodes, than when it is aligned against the external field.

(iii) The supramolecular structure of the SAM influences the magnitude of rectification, we infer, by controlling the orientation of the local dipole of the SAM.

(iv) The mechanism of rectification is based on a change in the work function of the bottom (Ag^{TS}) electrode, which is due to its electrostatic interaction with the local dipole (that, for example, from an amide group).

(v) Rectification occurs as a result of an increase in the rate of charge (hole) tunneling when the Ga_2O_3 electrode is oxidizing (positive bias). The rate of charge transport in the opposite direction (negative bias) remains unchanged.

(vi) The process that leads to an increase in tunneling current at positive bias occurs at ∼0.6 V and is visible in the $J(V)$ curves (in the inset in Figure 6, and the F−N plot in Figure 7).

This mechanism is different from the mechanism of rectification observed in SAMs with a redox-active component (e.g., ferrocene and derivatives: the mechanism is less clear with bipyridyl but also seems to be a redox process), and from the original—historically significant—theoretical suggestion of Aviram and Ratner. It does not indicate that the Aviram/Ratner suggestion (which described rectification in terms of the shape of the tunneling barrier rather than the energy of the work function) is necessarily incorrect, or inapplicable to SAM-based junctions, but extensive work suggests that tunneling through most SAMs is (with exceptions involving SAMs with low-lying HOMOs) not strongly influenced by the energetic

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

topography of the barrier, and that using this approach to control tunneling may not be generally achievable. (It is, however, possible with certain SAMs containing a number of amide or other linkages, with interacting HOMOs.)

This work, like many others in the field, originally set out to change the shape of the tunneling barrier by synthetic modification of its molecular structure (in this case, with localized dipole moments), and to use that change to study the mechanism of rectification. Instead of finding evidence that a change in barrier shape was responsible for rectification, however, we conclude that the underlying effect of synthetic modification was to change the WF across the Ag^{TS} electrode/SAM interface. This result is analogous to the operation of traditional semiconductor diodes, where rectification is caused by the Schottky barrier height.[94,95] Given the historical (and continued) significance in the semiconducting industry of controlling the Schottky barrier height, understanding this phenomenon in the context of molecule−electrode interfaces will be important for considering the potential (if any) of molecular electronics devices. (It does prove an important principal for design of passive electronic devices such as capacitors, where tunneling rates can contribute to rates of leakage of charge.)

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02891.

General information and details on materials and electronic measurements; additional data for charge transport measurements; trends in log|J| at ±0.5 V; surface characterization; and synthetic procedures (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF, CHE-1808361). We acknowledge the Materials Research and Engineering Center (MRSEC, DMR-1420570) at Harvard University for supporting XPS measurements, and providing access to the clean room facilities. Sample characterization was performed in part 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). L.B. acknowledges fellowship support from NSERC, Canada. M.H.A.-S. acknowledges the financial support of the American University of Sharjah, UAE (FRG13-02-04), Arab Fund Fellowship Program, Kuwait (Research Scholar Award: 2-1-72/1841), and ONRG, UK (VSP grant no. N62909-14-1-V17). We thank Dmitrij Rappoport, Martin M. Thuo, Philipp Rothemund, Kung-Ching Liao, and Mathieu Gonidec for useful discussion and input.

■ REFERENCES

(1) Armstrong, N.; Hoft, R. C.; McDonagh, A.; Cortie, M. B.; Ford, M. J. Exploring the performance of molecular rectifiers: Limitations and factors affecting molecular rectification. *Nano Lett.* **2007**, *7*, 3018.

(2) Ashkenasy, G.; Cahen, D.; Cohen, R.; Shanzer, A.; Vilan, A. Molecular engineering of semiconductor surfaces and devices. *Acc. Chem. Res.* **2002**, *35*, 121.

(3) Vilan, A.; Shanzer, A.; Cahen, D. Molecular control over Au/GaAs diodes. *Nature* **2000**, *404*, 166.

(4) Song, H.; Reed, M. A.; Lee, T. Single molecule electronic devices. *Adv. Mater.* **2011**, *23*, 1583.

(5) Metzger, R. M. Electrical rectification by a molecule: The advent of unimolecular electronic devices. *Acc. Chem. Res.* **1999**, *32*, 950.

(6) Vilan, A.; Aswal, D.; Cahen, D. Large-area, ensemble molecular electronics: motivation and challenges. *Chem. Rev.* **2017**, *117*, 4248.

(7) Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. Molecular-scale electronics: from concept to function. *Chem. Rev.* **2016**, *116*, 4318.

(8) Aviram, A.; Ratner, M. A. Molecular rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277.

(9) Pan, J. B.; Zhang, Z. H.; Deng, X. Q.; Qiu, M.; Guo, C. Rectifying performance of D-pi-A molecules based on cyanovinyl aniline derivatives. *Appl. Phys. Lett.* **2010**, *97*, 203104.

(10) Ho, G.; Heath, J. R.; Kondratenko, M.; Perepichka, D. F.; Arseneault, K.; Pezolet, M.; Bryce, M. R. The first studies of a tetrathiafulvalene-sigma-acceptor molecular rectifier. *Chem. - Eur. J.* **2005**, *11*, 2914.

(11) Zhou, K. G.; Zhang, Y. H.; Wang, L. J.; Xie, K. F.; Xiong, Y. Q.; Zhang, H. L.; Wang, C. W. Can azulene-like molecules function as substitution-free molecular rectifiers? *Phys. Chem. Chem. Phys.* **2011**, *13*, 15882.

(12) Zhao, J.; Zeng, C. G.; Cheng, X.; Wang, K. D.; Wang, G. W.; Yang, J. L.; Hou, J. G.; Zhu, Q. S. Single C59N molecule as a molecular rectifier. *Phys. Rev. Lett.* **2005**, *95*, 045502.

(13) Ashwell, G. J.; Mohib, A.; Collins, C. J.; Aref, A. Molecular rectification: Confirmation of its molecular origin by chemical suppression of the electrical asymmetry. *Synth. Met.* **2009**, *159*, 2282.

(14) Ashwell, G. J.; Mohib, A. Improved molecular rectification from self-assembled monolayers of a sterically hindered dye. *J. Am. Chem. Soc.* **2005**, *127*, 16238.

(15) Ashwell, G. J.; Tyrrell, W. D.; Whittam, A. J. Molecular rectification: Self-assembled monolayers in which donor-(pi-bridge)-acceptor moieties are centrally located and symmetrically coupled to both gold electrodes. *J. Am. Chem. Soc.* **2004**, *126*, 7102.

(16) Metzger, R. M. Unimolecular rectifiers: Methods and challenges. *Anal. Chim. Acta* **2006**, *568*, 146.

(17) Van Dyck, C.; Ratner, M. A. Molecular Rectifiers: A New Design Based on Asymmetric Anchoring Moieties. *Nano Lett.* **2015**, *15*, 1577.

(18) Nerngchamnong, N.; Yuan, L.; Qi, D. C.; Li, J.; Thompson, D.; Nijhuis, C. A. The role of van der Waals forces in the performance of molecular diodes. *Nat. Nanotechnol.* **2013**, *8*, 113.

(19) 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.

(20) 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.

(21) 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.

(22) Yuan, L.; Breuer, R.; Jiang, L.; Schmittel, M.; Nijhuis, C. A. A molecular diode with a statistically robust rectification ratio of three orders of magnitude. *Nano Lett.* **2015**, *15*, 5506.

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

(23) Yuan, L.; Nerngchamnong, N.; Cao, L.; Hamoudi, H.; del Barco, E.; Roemer, M.; Sriramula, R. K.; Thompson, D.; Nijhuis, C. A. Controlling the direction of rectification in a molecular diode. *Nat. Commun.* **2015**, *6*, 6324.
(24) Jiang, L.; Yuan, L.; Cao, L.; Nijhuis, C. A. Controlling leakage currents: the role of the binding group and purity of the precursors for self-assembled monolayers in the performance of molecular diodes. *J. Am. Chem. Soc.* **2014**, *136*, 1982.
(25) Yuan, L.; Jiang, L.; Thompson, D.; Nijhuis, C. A. On the remarkable role of surface topography of the bottom electrodes in blocking leakage currents in molecular diodes. *J. Am. Chem. Soc.* **2014**, *136*, 6554.
(26) Chen, X.; Roemer, M.; Yuan, L.; Du, W.; Thompson, D.; Del Barco, E.; Nijhuis, C. A. Molecular diodes with rectification ratios exceeding 105 driven by electrostatic interactions. *Nat. Nanotechnol.* **2017**, *12*, 797.
(27) Yoon, H. J.; Liao, K. C.; Lockett, M. R.; Kwok, S. W.; Baghbanzadeh, M.; Whitesides, G. M. Rectification in tunneling junctions: 2,2 ′-bipyridyl-terminated n-alkanethiolates. *J. Am. Chem. Soc.* **2014**, *136*, 17155.
(28) Martin, A. S.; Sambles, J. R.; Ashwell, G. J. Molecular rectifier. *Phys. Rev. Lett.* **1993**, *70*, 218.
(29) Metzger, R. M. Unimolecular rectifiers: Present status. *Chem. Phys.* **2006**, *326*, 176.
(30) Qiu, L.; Zhang, Y.; Krijger, T. L.; Qiu, X.; Hof, P. v. t.; Hummelen, J. C.; Chiechi, R. C. Rectification of current responds to incorporation of fullerenes into mixed-monolayers of alkanethiolates in tunneling junctions. *Chem. Sci.* **2017**, *8*, 2365.
(31) Garg, K.; Majumder, C.; Gupta, S. K.; Aswal, D. K.; Nayak, S. K.; Chattopadhyay, S. A novel design for porphyrin based D-s-A systems as molecular rectifiers. *Chem. Sci.* **2016**, *7*, 1548.
(32) Bayat, A.; Lacroix, J.-C.; McCreery, R. L. Control of electronic symmetry and rectification through energy level variations in bilayer molecular junctions. *J. Am. Chem. Soc.* **2016**, *138*, 12287.
(33) Souto, M.; Yuan, L.; Morales, D. C.; Jiang, L.; Ratera, I.; Nijhuis, C. A.; Veciana, J. Tuning the rectification ratio by changing the electronic nature (open-shell and closed-shell) in donor−acceptor self-assembled monolayers. *J. Am. Chem. Soc.* **2017**, *139*, 4262.
(34) Duche, D.; Planchoke, U.; Dang, F.-X.; Rouzo, J. L.; Bescond, M.; Simon, J.-J.; Balaban, T. S.; Escoubas, L. Model of self assembled monolayer based molecular diodes made of ferrocenyl-alkanethiols. *J. Appl. Phys.* **2017**, *121*, 115503.
(35) Batra, A.; Darancet, P.; Chen, Q.; Meisner, J. S.; Widawsky, J. R.; Neaton, J. B.; Nuckolls, C.; Venkataraman, L. Tuning rectification in single-molecular diodes. *Nano Lett.* **2013**, *13*, 6233.
(36) Zuo, X.; Chu, L.; Zhang, G.-P.; Wang, C.-K. Rectifying enhancement induced by conjugation breaking in thiolated arylethynylene single-molecular diodes. *Chem. Phys. Lett.* **2016**, *663*, 74.
(37) Hihath, J.; Bruot, C.; Nakamura, H.; Asai, Y.; Díez-Pérez, I.; Lee, Y.; Yu, L.; Tao, N. Inelastic transport and low-bias rectification in a single-molecule diode. *ACS Nano* **2011**, *5*, 8331.
(38) Kovalchuk, A.; Egger, D. A.; Abu-Husein, T.; Zojer, E.; Terfort, A.; Chiechi, R. C. Dipole-induced asymmetric conduction in tunneling junctions comprising self-assembled monolayers. *RSC Adv.* **2016**, *6*, 69479.
(39) Mahmoud, A.; Lugli, P. Designing the rectification behavior of molecular diodes. *J. Appl. Phys.* **2012**, *112*, 113720.
(40) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. Defining the value of injection current and effective electrical contact area for egain-based molecular tunneling junctions. *J. Am. Chem. Soc.* **2013**, *135*, 18131.
(41) Rothemund, P.; Morris Bowers, C.; Suo, Z.; Whitesides, G. M. Influence of the contact area on the current density across molecular tunneling junctions measured with egain top-electrodes. *Chem. Mater.* **2018**, *30*, 129.
(42) Baghbanzadeh, M.; Pieters, P. F.; Yuan, L.; Collison, D.; Whitesides, G. M. The rate of charge tunneling in egain junctions is not sensitive to halogen substituents at the self-assembled monolayer//Ga_2O_3 interface. *ACS Nano* **2018**, *12*, 10221.
(43) Lee, H. J.; Jamison, A. C.; Lee, T. R. Surface dipoles: a growing body of evidence supports their impact and importance. *Acc. Chem. Res.* **2015**, *48*, 3007.
(44) Hoesterey, B.; Neely, W. C.; Worley, S. D. A semi-empirical mo study of a series of amide, imidic acid, and imidate isomers. *Chem. Phys. Lett.* **1983**, *94*, 311.
(45) Meighan, R. M.; Cole, R. H. Dielectric properties of alkyl amides.i. vapor phase dipole moments + polarization in benzene solution. *J. Phys. Chem.* **1964**, *68*, 503.
(46) Rodrigo, M. M.; Tarazona, M. P.; Saiz, E. Experimental-determination and analysis of the direction of the dipole-moments of some substituted amides. *J. Phys. Chem.* **1986**, *90*, 2236.
(47) Kumler, W. D.; Fohlen, G. M. The dipole moment and structure of urea and thiourea. *J. Am. Chem. Soc.* **1942**, *64*, 1944.
(48) Custelcean, R. Crystal engineering with urea and thiourea hydrogen-bonding groups. *Chem. Commun.* **2008**, 295.
(49) George, M.; Tan, G.; John, V. T.; Weiss, R. G. Urea and thiourea derivatives as low molecular-mass organogelators. *Chem. - Eur. J.* **2005**, *11*, 3243.
(50) Hovick, J. W.; Poler, J. C. Misconceptions in Sign Conventions: Flipping the Electric Dipole Moment. *J. Chem. Educ.* **2005**, *82*, 889.
(51) Zhang, G.; Ratner, M. A.; Reuter, M. G. Is molecular rectification caused by asymmetric electrode couplings or by a molecular bias drop? *J. Phys. Chem. C* **2015**, *119*, 6254.
(52) Krzeminski, C.; Delerue, C.; Allan, G.; Vuillaume, D.; Metzger, R. M. Theory of electrical rectification in a molecular monolayer. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *64*, 085405.
(53) Xu, T.; Peterson, I. R.; Lakshmikantham, M. V.; Metzger, R. M. Rectification by a monolayer of hexadecylquinolinium tricyanoquinodimethanide between gold electrodes. *Angew. Chem., Int. Ed.* **2001**, *40*, 1749.
(54) Gonzalez, C.; Mujica, V.; Ratner, M. A. Modeling the electrostatic potential spatial profile of molecular junctions - The influence of defects and weak links. *Ann. N. Y. Acad. Sci.* **2002**, *960*, 163.
(55) Ding, W. D.; Negre, C. F. A.; Vogt, L.; Batista, V. S. Single molecule rectification induced by the asymmetry of a single frontier orbital. *J. Chem. Theory Comput.* **2014**, *10*, 3393.
(56) Mujica, V.; Ratner, M. A.; Nitzan, A. Molecular rectification: why is it so rare? *Chem. Phys.* **2002**, *281*, 147.
(57) Lörtscher, E.; Gotsmann, B.; Lee, Y.; Yu, L.; Rettner, C.; Riel, H. Transport properties of a single-molecule diode. *ACS Nano* **2012**, *6*, 4931.
(58) Bowers, C. M.; Rappoport, D.; Baghbanzadeh, M.; Simeone, F. C.; Liao, K.-C.; Semenov, S. N.; Żaba, T.; Cyganik, P.; Aspuru-Guzik, A.; Whitesides, G. M. Tunneling across sams containing oligophenyl groups. *J. Phys. Chem. C* **2016**, *120*, 11331.
(59) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. Metal-molecule contacts and charge transport across monomolecular layers: Measurement and theory. *Phys. Rev. Lett.* **2002**, *89*, 086802.
(60) Kushmerick, J. G.; Whitaker, C. M.; Pollack, S. K.; Schull, T. L.; Shashidhar, R. Tuning current rectification across molecular junctions. *Nanotechnology* **2004**, *15*, S489.
(61) Reichert, J.; Ochs, R.; Beckmann, D.; Weber, H. B.; Mayor, M.; von Lohneysen, H. Driving current through single organic molecules. *Phys. Rev. Lett.* **2002**, *88*, 176804.
(62) Ashwell, G. J.; Stokes, R. J. Do alkyl tunnelling barriers contribute to molecular rectification? *J. Mater. Chem.* **2004**, *14*, 1228.
(63) Young, R. C.; Ganellin, C. R.; Graham, M. J.; Grant, E. H. The dipole moments of 1,3-dimethylthiourea, 1,3-dimethyl-2-cyanoguanidine and 1,1-bis-methylamino-2-nitroethene in a aqueous solution. *Tetrahedron* **1982**, *38*, 1493.
(64) Pal, S.; Manna, A. K.; Pati, S. K. The role of H bonding and dipole-dipole interactions on the electrical polarizations and charge mobilities in linear arrays of urea, thiourea, and their derivatives. *J. Chem. Phys.* **2008**, *129*, 204301.

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980

(65) Tamchang, S. W.; Biebuyck, H. A.; Whitesides, G. M.; Jeon, N.; Nuzzo, R. G. Self-assembled monolayers on gold generated from alkanethiols with the structure RNHCOCH(2)SH. *Langmuir* **1995**, *11*, 4371.
(66) Clegg, R. S.; Hutchison, J. E. Hydrogen-bonding, self-assembled monolayers: Ordered molecular films for study of through-peptide electron transfer. *Langmuir* **1996**, *12*, 5239.
(67) Clegg, R. S.; Hutchison, J. E. Control of monolayer assembly structure by hydrogen bonding rather than by adsorbate-substrate templating. *J. Am. Chem. Soc.* **1999**, *121*, 5319.
(68) Clegg, R. S.; Reed, S. M.; Smith, R. K.; Barron, B. L.; Rear, J. A.; Hutchison, J. E. The interplay of lateral and tiered interactions in stratified self-organized molecular assemblies. *Langmuir* **1999**, *15*, 8876.
(69) Kim, J. H.; Shin, H. S.; Kim, S. B.; Hasegawa, T. Hydrogen-bonding networks of dialkyl disulfides containing the urea moiety in self-assembled monolayers. *Langmuir* **2004**, *20*, 1674.
(70) Ramin, M. A.; Le Bourdon, G.; Daugey, N.; Bennetau, B.; Vellutini, L.; Buffeteau, T. PM-IRRAS Investigation of Self-Assembled Monolayers Grafted onto SiO2/Au Substrates. *Langmuir* **2011**, *27*, 6076.
(71) Shin, H. S.; Kim, J. H.; Bin Kim, S.; Jung, Y. M. Thermal characterization of self-assembled monolayers of dialkyl disulfides containing the urea moiety. *Langmuir* **2007**, *23*, 10567.
(72) Thomas, J. C.; Goronzy, D. P.; Dragomiretskiy, K.; Zosso, D.; Gilles, J.; Osher, S. J.; Bertozzi, A. L.; Weiss, P. S. Mapping buried hydrogen-bonding networks. *ACS Nano* **2016**, *10*, 5446.
(73) Yoon, H. J.; Bowers, C. M.; Baghbanzadeh, M.; Whitesides, G. M. The rate of charge tunneling is insensitive to polar terminal groups in self-assembled monolayers in (AgS)-S-TS$(CH_2)(n)$M$(CH_2)(m)$-T//Ga_2O_3/EGaIn junctions. *J. Am. Chem. Soc.* **2014**, *136*, 16.
(74) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO2-templated formation of ultraflat metal surfaces on glass, polymer, and solder supports: their use as substrates for self-assembled monolayers. *Langmuir* **2007**, *23*, 9686.
(75) Mirjani, F.; Thijssen, J. M.; Whitesides, G. M.; Ratner, M. A. Charge transport across insulating self-assembled mono layers: non-equilibrium approaches and modeling to relate current and molecular structure. *ACS Nano* **2014**, *8*, 12428.
(76) Thuo, M. M.; Reus, W. F.; Simeone, F. C.; Kim, C.; Schulz, M. D.; Yoon, H. J.; Whitesides, G. M. Replacing -CH_2CH_2- with -CONH- does not significantly change rates of charge transport through Ag-TS-SAM//Ga_2O_3/EGaIn junctions. *J. Am. Chem. Soc.* **2012**, *134*, 10876.
(77) Baghbanzadeh, M.; Bowers, C. M.; Rappoport, D.; Zaba, T.; Gonidec, M.; Al-Sayah, M. H.; Cyganik, P.; Aspuru-Guzik, A.; Whitesides, G. M. Charge tunneling along short oligoglycine chains. *Angew. Chem., Int. Ed.* **2015**, *54*, 14743.
(78) Arndt, A. P.; Gerhard, M.; Koch, M.; Lemmer, U.; Howard, I. A. Identifying charge-transfer states in polymer: fullerene hetero-junctions by their emission polarization anisotropy. *J. Phys. Chem. C* **2017**, *121*, 6357.
(79) Uji, H.; Morita, T.; Kimura, S. Molecular direction dependence of single-molecule conductance of a helical peptide in molecular junction. *Phys. Chem. Chem. Phys.* **2013**, *15*, 757.
(80) Alloway, D. M.; Graham, A. L.; Yang, X.; Mudalige, A.; Colorado, R.; Wysocki, V. H.; Pemberton, J. E.; Lee, T. R.; Wysocki, R. J.; Armstrong, N. R. Tuning the effective work function of gold and silver using ω-functionalized alkanethiols: varying surface composition through dilution and choice of terminal groups. *J. Phys. Chem. C* **2009**, *113*, 20328.
(81) Obersteiner, V.; Egger, D. A.; Heimel, G.; Zojer, E. Impact of collective electrostatic effects on charge transport through molecular monolayers. *J. Phys. Chem. C* **2014**, *118*, 22395.
(82) Cabarcos, O. M.; Schuster, S.; Hehn, I.; Zhang, P. P.; Maitani, M. M.; Sullivan, N.; Giguère, J.-B.; Morin, J.-F.; Weiss, P. S.; Zojer, E.; Zharnikov, M.; Allara, D. L. Effects of embedded dipole layers on electrostatic properties of alkanethiolate self-assembled monolayers. *J. Phys. Chem. C* **2017**, *121*, 15815.
(83) Shu, A. L.; McClain, W. E.; Schwartz, J.; Kahn, A. Interface dipole engineering at buried organic−organic semiconductor heterojunctions. *Org. Electron.* **2014**, *15*, 2360.
(84) de Boer, B.; Hadipour, A.; Mandoc, M. M.; van Woudenbergh, T.; Blom, P. W. M. Tuning of metal work functions with self-assembled monolayers. *Adv. Mater.* **2005**, *17*, 621.
(85) Rusu, P. C.; Giovannetti, G.; Brocks, G. Dipole formation at interfaces of alkanethiolate self-assembled monolayers and Ag(111). *J. Phys. Chem. C* **2007**, *111*, 14448.
(86) Crispin, X.; Geskin, V.; Crispin, A.; Cornil, J.; Lazzaroni, R.; Salaneck, W. R.; Brédas, J.-L. Characterization of the interface dipole at organic/ metal interfaces. *J. Am. Chem. Soc.* **2002**, *124*, 8131.
(87) Dubi, Y. Transport through self-assembled monolayer molecular junctions: role of in-plane dephasing. *J. Phys. Chem. C* **2014**, *118*, 21119.
(88) Tao, F.; Bernasek, S. L. Understanding odd−even effects in organic self-assembled monolayers. *Chem. Rev.* **2007**, *107*, 1408.
(89) Schneider, J.; Messerschmidt, C.; Schulz, A.; Gnade, M.; Schade, B.; Luger, P.; Bombicz, P.; Hubert, V.; Fuhrhop, J.-H. Odd−even effects in supramolecular assemblies of diamide bolaamphiphiles. *Langmuir* **2000**, *16*, 8575.
(90) Kim, B.; Choi, S. H.; Zhu, X. Y.; Frisbie, C. D. Molecular tunnel junctions based on π-conjugated oligoacene thiols and dithiols between ag, au, and pt contacts: effect of surface linking group and metal work function. *J. Am. Chem. Soc.* **2011**, *133*, 19864.
(91) Heimel, G.; Romaner, L.; Zojer, E.; Bredas, J.-L. The interface energetics of self-assembled monolayers on metals. *Acc. Chem. Res.* **2008**, *41*, 721.
(92) Chiu, F.-C. A Review on conduction mechanisms in dielectric films. *Adv. Mater. Sci. Eng.* **2014**, *2014*, 18.
(93) Beebe, J. M.; Kim, B.; Gadzuk, J. W.; Daniel Frisbie, C.; Kushmerick, J. G. Transition from direct tunneling to field emission in metal-molecule-metal junctions. *Phys. Rev. Lett.* **2006**, *97*, 026801.
(94) Natan, A.; Kronik, L.; Haick, H.; Tung, R. T. Electrostatic properties of ideal and non-ideal polar organic monolayers: implications for electronic devices. *Adv. Mater.* **2007**, *19*, 4103.
(95) Tung, R. T. The physics and chemistry of the Schottky barrier height. *Appl. Phys. Rev.* **2014**, *1*, 011304.

DOI: 10.1021/jacs.9b02891
J. Am. Chem. Soc. 2019, 141, 8969−8980