

Rectification in Tunneling Junctions: 2,2'-Bipyridyl-Terminated *n*-Alkanethiolates

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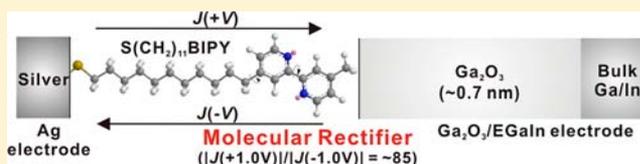
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Supporting Information

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 Ag^{TS}/S(CH₂)₁₁-4-methyl-2,2'-bipyridyl//Ga₂O₃/EGaIn (Ag^{TS}: template-stripped silver substrate; EGaIn: eutectic gallium–indium alloy) which shows reproducible rectification with a mean $r^{\pm} = |J(+1.0\text{ V})|/|J(-1.0\text{ V})| = 85 \pm 2$. 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 Ga₂O₃ film, and confirms that rectification is not related to the polarity in the junction. Comparisons among SAM-based junctions incorporating the Ga₂O₃/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.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.^{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,^{18–21} uses the well-described “EGaIn-junction”^{18,20–28} with the form Ag^{TS}/S(CH₂)₁₁Fc_n//Ga₂O₃/EGaIn (where Fc_n is either ferrocene or biferrocene). These junctions give rectification ratios of $|J(-1.0\text{ V})|/|J(+1.0\text{ V})| = \sim 150$ for Fc²⁰ and ~ 500 for Fc₂.²¹ 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 (detailed energy diagrams for rectification are discussed elsewhere^{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 Ga₂O₃/EGaIn electrode (–4.3 eV) at zero bias)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 produce rectification.

This work had three objectives. (i) It was intended to use the Ga₂O₃/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 rectify at polarity opposite of 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

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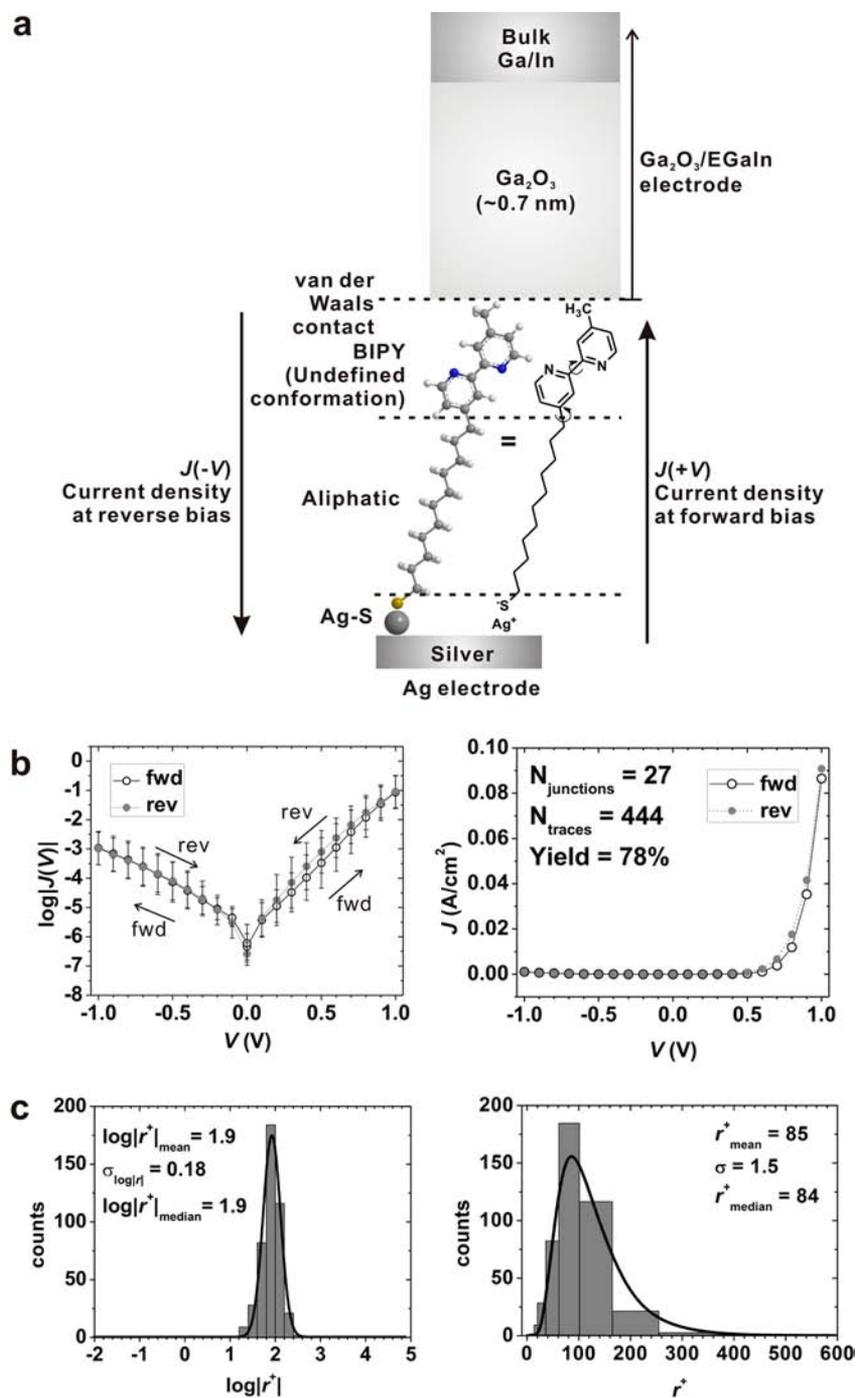


Figure 1. (a) Schematic representation of the tunneling junction with the structure Ag^{TS}/SC₁₁BIPY//Ga₂O₃/EGaIn. We do not know the conformation(s) of the BIPY group in these junctions. The positive bias (+1.0 V) shows higher current density (J A/cm²) than the negative bias (-1.0 V): the rectification ratio r^+ ($r^+ = |J(+1.0 \text{ V})|/|J(-1.0 \text{ V})|$) is ~ 85 . (b) Traces of current density and $\log|J|$ as a function of applied voltage (V). $N_{\text{junctions}}$ 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 ± 1.0 V for these junctions. $\log|r^+|_{\text{mean}}$ and r^+_{mean} are mean values of $\log|r^+|$ and r^+ ; $\log|r^+|_{\text{median}}$ and r^+_{median} are median values of $\log|r^+|$ and r^+ ; $\sigma_{\log|r^+|}$ and σ_{r^+} are standard deviations of $\log|r^+|$ and r^+ .

to examine examples of rectification reported in the literature and to search for common conceptual threads to connect them.

This paper describes a molecular rectifier (Figure 1a) that shows a large, reproducible, unambiguous rectification ratio ($|J(+1.0 \text{ V})|/|J(-1.0 \text{ V})| = \sim 85$) having polarity opposite to that of the Fc_{*n*}-based junctions; this junction has the structure Ag^{TS}/S(CH₂)₁₁BIPY//Ga₂O₃/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 “un attenuated” conical tip)^{22,24,26} covered with a self-limiting thin film of gallium oxide (Ga₂O₃, ostensibly ~ 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 , A/cm²) measured at applied biases of opposite polarity ($+V$ and $-V$). We define r with two different equations (eqs 1 and 2):

$$r^+ = |J(+V)|/|J(-V)| \quad (1)$$

$$r^- = |J(-V)|/|J(+V)| \quad (2)$$

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^-).

A number of SAM-based systems have been claimed to show significant rectification ratios ($r = 15\text{--}3000$).^{3,4,6,8,10–14,19–21} A number of smaller values ($r < 5$) have also been reported but are difficult 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.³² Table S1 in the SI summarizes previous studies^{3,4,6,8,10–14,19–21} 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, Ag^{TS}) supporting the SAM is grounded. At positive bias (+1.0 V), the Ga₂O₃/EGaIn electrode is oxidizing; at negative bias (−1.0 V), 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-Ga₂O₃ interface. At positive bias (+1.0 V) 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).³³ We attached it to an 11-undecanethiol (R(CH₂)₁₁SH). We used this polymethylene chain as the basis for the SAM because Nijhuis and co-workers have demonstrated that HS(CH₂)₁₁Fc gave the largest value of r among a series of Fc-terminated n -alkanethiolates HS(CH₂) _{n} Fc ($n = 6\text{--}15$).²⁰

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

Examination for Formation of BIPY Complexes with Ga³⁺ or In³⁺. The BIPY terminal groups in the SAM are strong σ -donating ligands.³³ After assembly of the junction they might, in principle, form complexes with Ga³⁺ and/or In³⁺ 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).

Examination for Redox Behavior Involving Ag(I). The silver bottom electrode oxidizes easily in air, and forms a thin layer of silver oxide (Ag₂O _{x});³⁴ 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.

Survey of Nitrogen-Containing Heterocycles as Terminal Groups in Place of BIPY. To probe the role of the structure of BIPY

terminal group in rectification, we characterized tunneling junctions having SAMs terminated in four different aromatic groups that are related to BIPY in conformation or composition and that test the influence of conformation and composition (Figure 2).

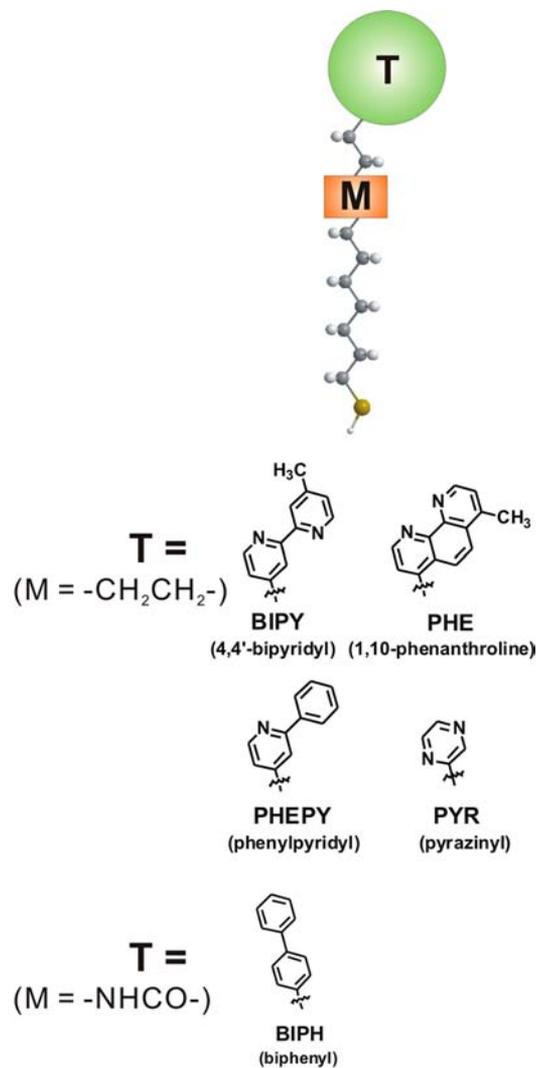


Figure 2. Structurally similar thiol derivatives to BIPY-terminated n -alkanethiol: molecular structures of BIPY-, PHE-, PHEPY-, BIPH-, and PYR-terminated n -alkanethiols (T: terminal group; M: middle backbone of SAM, either $-\text{CH}_2\text{CH}_2-$ or $-\text{CONH}-$).

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, unattened 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}

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 +1.0 V $\log|J(V)|_{\text{mean}}$ and $\sigma_{\log|J|}$ were -1.1 ($\log|J(V)|_{\text{median}} = -1.1$) and 0.56 ; at -1.0 V $\log|J(V)|_{\text{mean}}$ and $\sigma_{\log|J|}$ were -3.0 ($\log|J(V)|_{\text{median}} = -3.0$) and 0.56 . The similarity of the mean and

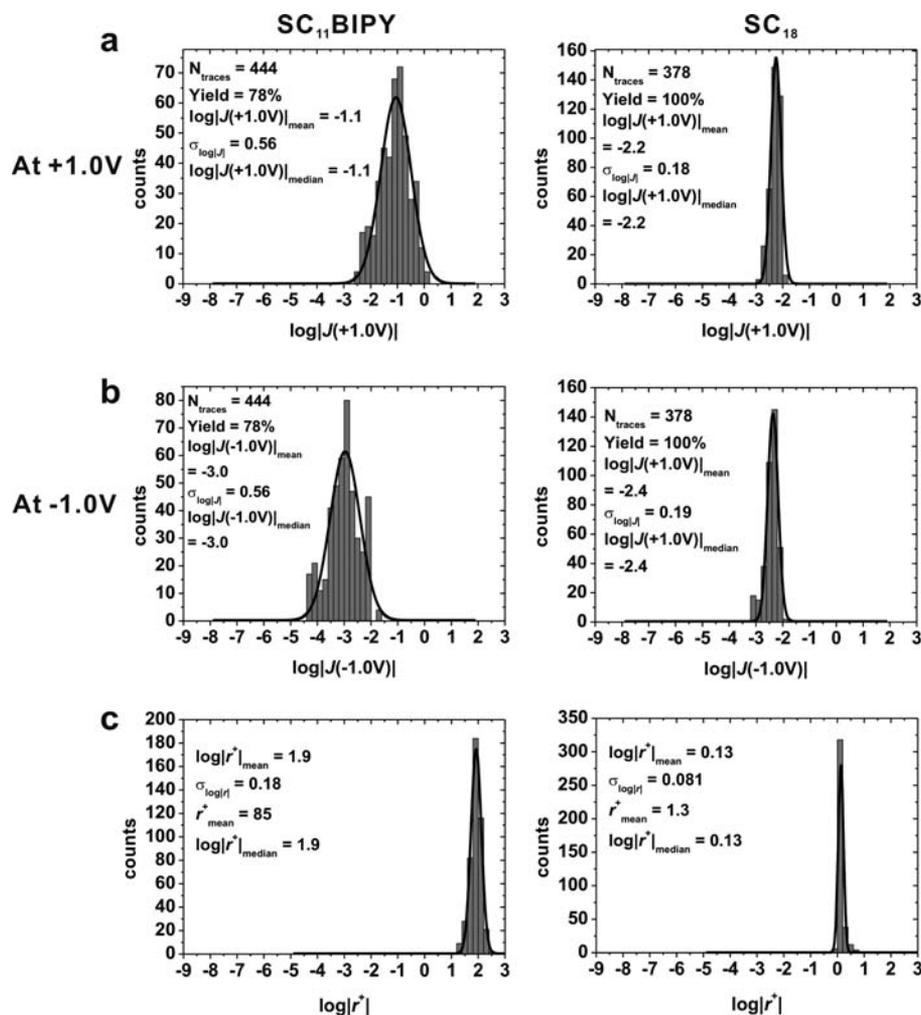


Figure 3. (a, b) Histograms of current densities of $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_{11}\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junctions, where T = BIPY (SC₁₁BIPY) or $-(\text{CH}_2)_6\text{CH}_3$ (SC₁₈) at +1.0 V and -1.0 V. (c) Histograms of $\log|r^+|$ at ± 1.0 V of the same junctions.

median values indicates that outliers do not influence the values of the means.

We measured tunneling current densities (at ± 1.0 V) in a SAM whose length is similar in the number of non-hydrogen atoms to SC₁₁BIPY (18 non-hydrogen atoms in linear connection from the sulfur to the distal atom closest to the EGaIn electrode): *n*-octadecanethiol, HSC₁₈. We compared the tunneling current densities measured for both molecules and found the differences in $J(V)$ were significant at +1.0 V but not at -1.0 V (Figure 3): the $|J(+1.0\text{ V})|_{\text{mean}}$ of SC₁₁BIPY was approximately a factor of 30 higher than SC₁₈, but $J(-1.0\text{ V})_{\text{mean}}$ is only a factor of 2 lower than SC₁₈. (The averaged standard deviation of $\log|J(V)|$ in the EGaIn-based junctions is $\sigma_{\log|J|} \sim 0.3$, and thus variations in $J(V)$ that are $2 \times \sigma_{\log|J|}$ (~ 0.6 in $\log|J|$; a factor of 4 in J) are statistically indistinguishable.) The higher current density for SC₁₁BIPY at positive bias (relative to *n*-alkanethiolate of similar length (SC₁₈)) leads to rectification with positive polarity, and suggests that the charge transport process through SC₁₁BIPY at positive bias does not rely purely on a tunneling mechanism (but, presumably, on hopping plus tunneling). The rates of charge transport at negative bias for SC₁₁BIPY and SC₁₈, 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 $V = +0.5$ V to $V = +1.0$ V. 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 SC₁₁BIPY 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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ electrode is reducing relative to the silver bottom electrode, and the current density is higher ($\times 85$) than at negative bias, where the $\text{Ga}_2\text{O}_3/\text{EGaIn}$ electrode is oxidizing relative to the silver electrode.

We measured the XPS spectrum of a SAM of SC₁₁BIPY before and after we assembled a junction (Figure S2 in the SI). The XPS spectra of a pristine SC₁₁BIPY SAM and a SC₁₁BIPY SAM contacted with the $\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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}/SC₁₁BIPY//Ga₂O₃/EGaIn junctions using the same procedure used with Ag^{TS}. Electrical measurements of these junctions (Figure 4) showed a

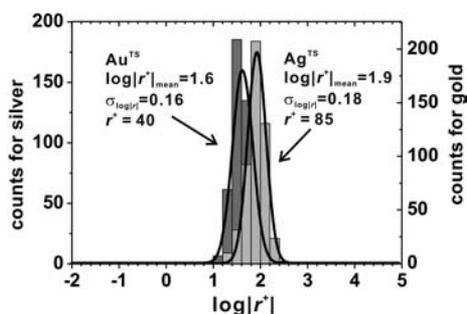


Figure 4. Comparison of histograms of $\log|r^+|$ of SC₁₁BIPY SAM on Ag^{TS} and Au^{TS} substrates at ± 1.0 V.

rectification ratio with polarity and magnitude ($\log|r^+|_{\text{mean}} \sim 1.6$; $r^+_{\text{mean}} \sim 40$) similar to that of the Ag^{TS}/SC₁₁BIPY//Ga₂O₃/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.

The small difference ($\Delta \log|r^+|_{\text{mean}} = 0.3$; a factor of 2 in r^+_{mean}) in the rectification ratio of SC₁₁BIPY 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 ± 1.0 V. 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 nonrotating 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 (–CH₂CH₂–) has been demonstrated in previous studies.^{22,26,27}

SAMs of SC₁₁PYR, SC₇CONHC₂BIPH, and SC₁₁PHEPY do not rectify currents at ± 1.0 V on Ag^{TS} substrates (Figure S3): Table 1 summarizes the values for rectification for those compounds. In contrast, a SAM composed of SC₁₁PHE 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 SC₁₁BIPY (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 ~ 1 GV/m) are not responsible for the rectification in the SC₁₁BIPY SAM.⁹

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

Table 1. Rectification Ratios at ± 1.0 V for Ag^{TS}/S(CH₂)₂M(CH₂)₇-T//Ga₂O₃/EGaIn Junctions Having Different Terminal Groups (T)^a

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

^aM is –CH₂CH₂– 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. ^bMean value of r^+ . ^cMean value of $\log|r^+|$. ^dStandard deviation of $\log|r^+|$.

SC₁₁BIPY and $J(+V)$ for SC₁₁Fc are based on a pure-tunneling regime; $J(+V)$ for SC₁₁BIPY and $J(-V)$ for SC₁₁Fc 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 SC₁₁ 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/cm², and β is a tunneling decay coefficient Å⁻¹). We are able to estimate, approximately, rectification ratios for SC₁₁BIPY, SC₁₁PHE, SC₁₁Fc, and SC₁₁Fc₂: (i) $\bar{J}(V) = J_0(V) \exp(-\beta_{\text{CH}_2}d_{\text{CH}_2} - \beta_{\text{RM}}d_{\text{RM}})$ 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) $\bar{J}(V) = J_0(V) \exp(-\beta_{\text{CH}_2}d_{\text{CH}_2})$ 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(CH₂)_n group is the same for tunneling in both directions, we can, therefore, approximate the ratio of rectification by eq 3, where $\bar{J}(V)$

$$|r|_{\text{calcd}} = |\bar{J}(V)|/|\bar{J}(-V)| = \exp(\beta_{\text{RM}}d_{\text{RM}}) \quad (3)$$

and $\bar{J}(V)$ 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 (β_{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 ($V = 4/3[\pi(d_{\text{RM}}/2)^3]$, Å³; 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

Table 2. Summary of Calculated Molecular Lengths (d) and Ratios of Current Rectification (r) for SC₁₁PHE, SC₁₁BIPY, and SC₁₁Fc_{*n*} ($n = 1$ or 2)

assumed structure of T group	molecular rectifiers	d_{RM} (Å) ^a	calcd ^{e,f} ($\beta \sim 0.6$ Å ⁻¹)	rectification ratio (r)	
				calcd ^{e,f} ($\beta \sim 0.7$ Å ⁻¹)	obsd
spherical shape	SC ₁₁ PHE	7.0 ^b	67	135	$r_{\text{mean}}^+ = 64$
	SC ₁₁ BIPY	6.8 ^b	59	116	$r_{\text{mean}}^+ = 85$
	SC ₁₁ Fc	7.2 ^c	73	150	$r_{\text{mean}}^- = 150$
	SC ₁₁ Fc ₂	8.9 ^c	210	512	$r_{\text{mean}}^- = 500$
extended <i>trans</i> structure	SC ₁₁ PHE	6.9 ^d	64	129	$r_{\text{mean}}^+ = 64$
	SC ₁₁ BIPY	7.2 ^d	75	154	$r_{\text{mean}}^+ = 85$
	SC ₁₁ Fc	6.0 ^d	36	65	$r_{\text{mean}}^- = 150$
	SC ₁₁ Fc ₂	11.4 ^d	954	2994	$r_{\text{mean}}^- = 500$

^aCalculations 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 $d_{RM} = 2 \times (3V/4\pi)^{-3}$; or (ii) the terminal groups are in extended *trans* structure. ^bThe 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 6.6 Å for BIPY and 6.8 Å for PHE, and the values of $|r|_{\text{calcd}}$ for $\beta = \sim 0.6$ Å⁻¹ and ~ 0.7 Å⁻¹ are 51 and 98 for BIPY and 59 and 116 for PHE. ^cCalculations were based on the literature values of volumes for Fc and Fc₂.^{37–40} ^dSee Figure S5 in the SI for detailed molecular structures. ^eValues of $|r|_{\text{calcd}}$ were calculated with eq 3, assuming that the tunneling decay constants characteristic of attenuation through PHE, BIPY and Fc_{*n*} ($n = 1$ or 2) are equal to that either of oligophenylenes ($\beta \sim 0.6$ Å⁻¹) or of polymethylenes ($\beta \sim 0.7$ Å⁻¹). ^fNote that our calculations for determining d_{RM} do not include information about the supramolecular structure of groups in a SAM.

estimated values of d_{RM} for PHE, BIPY, Fc and Fc₂. We also assume (lacking any other information) that the tunneling decay constant (β_{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 β were determined at ± 0.5 V for both oligophenylenes and polymethylenes and are almost certainly not accurate at ± 1.0 V; to determine if difference in the size of the T group were, at least, compatible with the observed values of rectification, these values of β are, however, sufficient. The values of $|r|_{\text{calcd}}$ 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 in the SI allowed us to compare calculated values ($|r|_{\text{calcd}}$; see Figure S5 and Table S3 in the SI for structures used for calculations and summary of calculations) with experimentally observed values ($|r|_{\text{obsd}}$) and qualitatively reconcile the previous systems with systems based on SC₁₁T (T=BIPY, PHE or Fc_{*n*}). A plot of $|r|_{\text{obsd}}$ against $|r|_{\text{calcd}}$ (estimated based on the two structural approximations described above) in Figure 5 suggests that our hypothesis that the terminal group T for SC_{*n*}T 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 8. The fact that the azo compound (Figure S5 in the SI) described by McCreery et al.⁶ does not follow the expected trend (Figure 5) for the “spherical” approximation but does for the “extended” approximation 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.¹⁰ 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

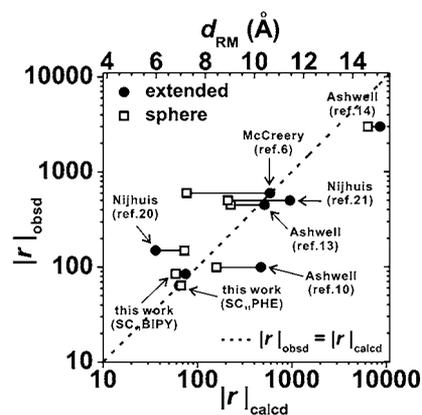


Figure 5. A plot of reported, experimentally observed rectification ratios ($|r|_{\text{obsd}}$) (on a logarithmic scale) for systems taken from the literature and described in Table S1 (in the SI), against rectification ratios ($|r|_{\text{calcd}}$) calculated using eq 3 and values of the width of the barrier for rectifying moiety (d_{RM}). Values of d_{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_{RM} by using one-quarter of the volume or width of Cu(II)phthalocyanine group (as reported in the reference).

assessment of the validity of the reported rectification ratios. Previous work showed that junction characteristics (e.g., the topography of the bottom electrode,⁴¹ the supramolecular structure of molecules within the SAM,²⁰ the presence of impurities,⁴² and the structure of the HOMO and LUMO of the presumed electroactive groups) influence rectification in molecular junctions, but there is little useful 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 $S(\text{CH}_2)_{11}\text{BIPY}$ ($\text{BIPY} = 4\text{-methyl-}2,2'\text{-bipyrid-}4'\text{-yl}$) show values of rectification of the same magnitude that has been observed with SAMs of $S(\text{CH}_2)_{11}\text{Fc}$ but of the opposite polarity. SAMs of $2,2'\text{-bipyridyl-terminated } n\text{-undecanethiolate}$ on Ag^{TS} rectify statistically significantly ($\sigma_{\log r} \sim 0.18$) at ± 1.0 V. Mean (~ 85) and median (~ 84) values of r^+ are statistically indistinguishable (Figure 1). The magnitude of rectification for SAMs of $\text{SC}_{11}\text{BIPY}$ is similar to that reported previously for SAMs composed of similar thioliates terminated in Fc ($r^- \sim 150$); 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_2O_3 , Ga , In , or Ag components of the $\text{Ag}^{\text{TS}}S(\text{CH}_2)_{11}\text{BIPY}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junction. XPS analysis of the composition of the surface of a SAM of $\text{SC}_{11}\text{BIPY}$ SAM that had been brought into contact with $\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ is not substantial enough to influence rates of charge transport. Junctions with the form $\text{Au}^{\text{TS}}S(\text{CH}_2)_{11}\text{BIPY}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ also rectified current with the same magnitude and polarity as the $\text{Ag}^{\text{TS}}S(\text{CH}_2)_{11}\text{BIPY}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junction. This similarity demonstrates that rectification is not a result of the BIPY terminal group chelating silver ions from the bottom electrode. Replacing the $\text{T} = \text{BIPY}$ in $\text{Ag}^{\text{TS}}S(\text{CH}_2)_{11}\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junctions with $\text{T} = \text{PYR}$, 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 $\text{SC}_{11}\text{BIPY}$ molecules, not nonmolecular characteristics of the junction such as redox phenomena in the Ga_2O_3 film⁴³ nor the composition of the bottom electrode, are responsible for the rectification observed in the $\text{Ag}^{\text{TS}}/\text{SC}_{11}\text{BIPY}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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 $S(\text{CH}_2)_{11}\text{Fc}$ has been established to rectify by a process in which the current density in one direction (at $+1.0$ V) is rate-limiting tunneling across the $(\text{CH}_2)_{11}$ moiety and in the other direction (at -1.0 V) involves an initial step of hopping (that is, electron transfer to convert Fc to Fc^+) followed by rate-limiting tunneling across the insulating $(\text{CH}_2)_{11}$ 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 -2.1 V vs SCE in 0.1 M acetonitrile solution of tetrabutylammonium tetra uoroborate,⁴⁴ while that for biphenyl is -2.7 V vs SCE 0.1 M DMF solution of tetrabutylammonium iodide.⁴⁵ The reported value of reduction potential for pyrazine is -1.25 V vs SCE, but the reduction involves proton-assisted two-electron reduction,⁴⁶ 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.⁴⁷

Fc and Fc_2 show oxidation potentials of $\sim +0.40$ V²⁰ and $\sim +0.25$ V²¹ vs Ag/Ag^+ ($\sim +0.36$ V and $\sim +0.21$ V vs SCE) in aqueous 1 M HClO_4 . The low oxidation potential of Fc and Fc_2 supports the conclusion that the rectification of $\text{SC}_{11}\text{Fc}_n$ relies on the oxidation of Fc_n and rationalizes the observation that the direction of rectification is opposite to that of rectification of $\text{SC}_{11}\text{BIPY}$.

This work proposes a model to rationalize rectifications of different magnitudes reported in the literature. Equation 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_{11}Fc system.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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ electrode. (The approximations in this estimate—the geometry of the T group, the value of β 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>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.
- (2) Ashwell, G. J.; Bonham, J. S.; Lyons, L. E. *Aust. J. Chem.* **1980**, *33*, 1619.
- (3) Xu, T.; Peterson, I. R.; Lakshminantham, M. V.; Metzger, R. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1749.
- (4) Ng, M.-K.; Yu, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 3598.
- (5) Troisi, A.; Ratner, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 14528.
- (6) McCreery, R.; Dieringer, J.; Solak, A. O.; Snyder, B.; Nowak, A. M.; McGovern, W. R.; DuVall, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 10748.
- (7) Metzger, R. M. *Chem. Rev.* **2003**, *103*, 3803.
- (8) Ashwell, G. J.; Tyrrell, W. D.; Whittam, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 7102.
- (9) Troisi, A.; Ratner, M. A. *Nano Lett.* **2004**, *4*, 591.
- (10) Ashwell, G. J.; Mohib, A. *J. Am. Chem. Soc.* **2005**, *127*, 16238.
- (11) Ho, G.; Heath, J. R.; Kondratenko, M.; Perepichka, D. F.; Arseneault, K.; Pezolet, M.; Bryce, M. R. *Chem.—Eur. J.* **2005**, *11*, 2914.
- (12) Honciuc, A.; Jaiswal, A.; Gong, A.; Ashworth, K.; Spangler, C. W.; Peterson, I. R.; Dalton, L. R.; Metzger, R. M. *J. Phys. Chem. B* **2005**, *109*, 857.
- (13) Ashwell, G. J.; Chwialkowska, A. *Chem. Commun.* **2006**, 1404.
- (14) Ashwell, G. J.; Urasinska, B.; Tyrrell, W. D. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3314.
- (15) McCreery, R. L.; Wu, J.; Kalakodimi, R. P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2572.
- (16) Armstrong, N.; Hoft, R. C.; McDonagh, A.; Cortie, M. B.; Ford, M. J. *Nano Lett.* **2007**, *7*, 3018.
- (17) Chen, X.; Yeganeh, S.; Qin, L.; Li, S.; Xue, C.; Braunschweig, A. B.; Schatz, G. C.; Ratner, M. A.; Mirkin, C. A. *Nano Lett.* **2009**, *9*, 3974.
- (18) Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **2009**, *131*, 17814.
- (19) Wimbush, K. S.; Reus, W. F.; van der Wiel, W. G.; Reinhoudt, D. N.; Whitesides, G. M.; Nijhuis, C. A.; Velders, A. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10176.
- (20) Nerngchamnong, N.; Yuan, L.; Qi, D. C.; Li, J.; Thompson, D.; Nijhuis, C. A. *Nat. Nanotechnol.* **2013**, *8*, 113.
- (21) Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **2010**, *132*, 18386.
- (22) Yoon, H. J.; Bowers, C. M.; Baghbanzadeh, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2014**, *136*, 16.
- (23) Liao, K.-C.; Yoon, H. J.; Bowers, C. M.; Simeone, F. C.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2014**, *53*, 3889.
- (24) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. *J. Am. Chem. Soc.* **2013**, *135*, 18131.
- (25) Fracasso, D.; Muglali, M. I.; Rohwerder, M.; Terfort, A.; Chiechi, R. C. *J. Phys. Chem. C* **2013**, *117*, 11367.
- (26) Yoon, H. J.; Shapiro, N. D.; Park, K. M.; Thuo, M. M.; Soh, S.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 4658.
- (27) Thuo, M. M.; Reus, W. F.; Simeone, F. C.; Kim, C.; Schulz, M. D.; Yoon, H. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **2012**, *134*, 10876.
- (28) Chiechi, R. C.; Weiss, E. A.; Dickey, M. D.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 142.
- (29) Nijhuis, C. A.; Reus, W. F.; Barber, J. R.; Dickey, M. D.; Whitesides, G. M. *Nano Lett.* **2010**, *10*, 3611.
- (30) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. *Langmuir* **2007**, *23*, 9686.
- (31) Cademartiri, L.; Thuo, M. M.; Nijhuis, C. A.; Reus, W. F.; Tricard, S.; Barber, J. R.; Sodhi, R. N. S.; Brodersen, P.; Kim, C.; Chiechi, R. C.; Whitesides, G. M. *J. Phys. Chem. C* **2012**, *116*, 10848.
- (32) Jin, Y.; Friedman, N.; Sheves, M.; Cahen, D. *Langmuir* **2008**, *24*, 5622.
- (33) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553–3590.
- (34) de Rooij, A. *Eur. Space Agency J.* **1989**, *13*, 363.
- (35) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.
- (36) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (37) Gražulis, S.; Daškevič, A.; Merkys, A.; Chateigner, D.; Lutterotti, L.; Quirós, M.; Serebryanaya, N. R.; Moeck, P.; Downs, R. T.; Le Bail, A. *Nucleic Acids Res.* **2012**, *40*, D420.
- (38) Gražulis, S.; Chateigner, D.; Downs, R. T.; Yokochi, A. T.; Quiros, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P.; Le Bail, A. *J. Appl. Crystallogr.* **2009**, *42*, 726.
- (39) Downs, R. T.; Hall-Wallace, M. A. *Mineral.* **2006**, *88*, 247.
- (40) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 1741.
- (41) Yuan, L.; Jiang, L.; Thompson, D.; Nijhuis, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 6554.
- (42) Jiang, L.; Yuan, L.; Cao, L.; Nijhuis, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 1982.
- (43) Wimbush, K. S.; Fratila, R. M.; Wang, D.; Qi, D.; Liang, C.; Yuan, L.; Yakovlev, N.; Loh, K. P.; Reinhoudt, D. N.; Velders, A. H.; Nijhuis, C. A. *Nanoscale* **2014**, *6*, 11246.
- (44) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.
- (45) Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1118.
- (46) Brolo, A. G.; Irish, D. E. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 419.
- (47) Rivas, L.; Soares, C. M.; Baptista, A. M.; Simaan, J.; Paolo, R. E. D.; Murgida, D. H.; Hildebrandt, P. *Biophys. J.* **2005**, *88*, 4188.