Rectification of current responds to incorporation of fullerenes into mixed-monolayers of alkanethiols in tunneling junctions†

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This paper describes the rectification of current through molecular junctions comprising self-assembled monolayers of decanethiolate of fullerene moieties leading eutectic Ga-In (EIn) and Au conducting probe AFM (CP-AFM) top-contacts. The degree of rectification increases with increasing exposure of the decanethiolate monolayers to the fullerene moieties, going through a maximum after 24 h. We ascribe this observation to the resulting mixed-monolayer achieving an optimal packing density of fullerene cages sitting above the alkane monolayer. Thus, the degree of rectification is controlled by the amount of fullerene present in the mixed-monolayer. The voltage dependence of R varies with the composition of the top-contact and the force applied to the junction and the energy of the lowest unoccupied π-state determined from photoelectron spectroscopy is consistent with the direction of rectification. The maximum value of rectification R = |J(+)/J(−)| = 940 at ±1 V or 617 at ±0.95 V is in agreement with previous studies on pure monolayers relating the degree of rectification to the volume of the head-group on which the frontier orbitals are localized.

1 Introduction

Molecular rectification is the asymmetric current response to an external voltage bias of equal magnitude but opposite sign mediated by the electronic structure of individual molecules. In contrast to comparisons of current (I) or current-density (J), rectification has the advantage that it is self-referencing, which eliminates the resistance of the contacts in studies comparing the electronic structure of molecular tunneling junctions. Molecular diodes are, therefore, interesting both for functionality and fundamental, phenomenological study. Rectification can be controlled to some degree by tailoring molecules and/or altering the contacts.5–23 While the details of the mechanism can vary between experimental platforms, Nijhuis and co-workers have elucidated unambiguously for AgTS/S(CH2)11Fc//Ga2O3/EGaIn junctions, where EGaIn is eutectic GaIn alloy24,25 and Fc is either ferrocene or biferrocene incorporated into a self-assembled monolayer (SAM) supported by template-stripped Ag (AgTS) and ‘/’ and ‘\’ denote covalent and non-covalent interfaces, respectively.26–32 Depending on the sign of the applied bias, the difference in energy between the Fermi level (Ef) and the highest-occupied π-state (HOPS) of the Fc increases or decreases, increasing or decreasing the relative rate of charge-transfer.24,25

Yoon and Whitesides have shown rectification that is mediated instead by the lowest-unoccupied π-state (LUPS) of bipyridine (Bp) and naphthoquinone (Nq) moieties in AgTS/S(CH2)11Bp//Ga2O3/EGaIn junctions, though the degree of rectification was significantly lower in the latter.29,35 In these junctions, the sign of the applied bias at which the current is higher is reversed compared to Fc because Ef lies closer to the LUPS than the HOPS. In both cases, the magnitude of rectification, defined as R = |J(+)/J(−)| (measured at ±1 V) depends both on the structure of the SAM and on the volume of the π-system (i.e., Fc or Bp), thus it can be tuned by altering the substrate26 or through dilution with disulfides (to introduce defects)37 or non-rectifying alkanethiols38 and, in principle, by increasing the size of the π-system.27,28 These studies demonstrated a decrease in R either through the introduction of defects into the substrate or by introducing non-rectifying (or defect-inducing) compounds into the solution from which the SAMs were formed, establishing the sensitivity of R to the packing of the π-systems that mitigates rectification.

Fullerenes, due to their spherical geometry and unique optical and electronic properties, are widely studied for potential applications ranging from sensors and photovoltaic cells to nanostructured devices.40–43 Their high affinity for noble metals and large surface area available for contact also make them...
attractive candidates for applications in Molecular Electronics (ME), both in single-molecule (e.g., break-junctions) and large-area (e.g., GaIn) platforms. Fullerene-based anchoring groups have been demonstrated in single-molecule junctions and several studies on functionalized fullerene-based SAMs have shown that the electronic structure of [60]fullerene (C_{60}) remains intact even when the carbon cages are confined to a surface. Thus, the low-lying lowest-unoccupied molecular orbital (LUMO) of C_{60} (~4.5 eV) should translate into an accessible LUPS in SAM-based junctions and, therefore, rectification via the mechanism described above.

The preparation of SAMs of fullerene derivatives functionalized with thiols on metal surfaces has been extensively studied. Contrary to simple systems such as alkanethiols, the self-assembly of fullerene derivatives on gold is complicated by the formation of multilayers and head-to-tail assemblies due to competition from the strong fullerene–fullerene and fullerene–gold interactions. (The same complexities are expected on Ag.) These problems can be mitigated by pre-passivating the substrate with a SAM of decanethiol (SC10) and then forming a mixed-monolayer by incubating this SAM in a solution containing the fullerene derivatives (see Experimental).

2 Results and discussion

The preparation of SAMs of fullerene derivatives functionalized with thiols on metal surfaces has been extensively studied. Contrary to simple systems such as alkanethiols, the self-assembly of fullerene derivatives on gold is complicated by the formation of multilayers and head-to-tail assemblies due to competition from the strong fullerene–fullerene and fullerene–gold interactions.

We measured the J/V characteristics of Ag\textsuperscript{TS}/FSC11/Ga_{2}O_{3}/EGaln and Au\textsuperscript{TS}/FSC11/Ga_{2}O_{3}/EGaln junctions (Fig. 2A) by acquiring 1016 (650 on Ag and 366 on Au) sweeps between ±0.5 V for 61 (37 on Ag and 24 on Au) junctions across 7 (4 on Ag and 3 on Au) substrates (Table 1). The frequency of shorts increased dramatically above 0.5 V precluding the extraction of meaningful statistics above 0.5 V. We also measured Ag\textsuperscript{TS}/SAM/ Ga_{2}O_{3}/EGaln junctions based on SAMs of pure FSC11 and SC10 for comparison. We calculated R by dividing each value of J at positive bias into the corresponding value at negative bias for each value of |V| and then fitting a Gaussian to the resulting histogram of log|R| and expressing the error as the confidence interval of the fit. Histograms comparing log|R| for SAMs of pure FSC11 and mixed-monolayers of FSC11 SAMs on Ag\textsuperscript{TS} are shown in the ESI. Although both monolayers show comparable peak values of log|R|, the histogram of the pure SAM is broad and possibly multi-modal, while that of the mixed-monolayer is a single, log-normal distribution. We ascribe this difference to the strong fullerene–metal interactions competing with thiol–metal interactions to form mixed phases of upright (thiol-down) and upside-down (fullerene-down) molecules. Despite these differences, the yields of working junctions for the pure SAMs of FSC11 versus the mixed-monolayers are comparable (Table 1), which underscores the utility of using statistics and observables such as log|R| to characterize tunneling junctions comprising SAMs.

Fig. 2B shows the J/V curves of the junctions before and after exchanging FSC11 into the passivating SAM of SC10 as described above (see ESI for details of the data acquisition and processing). The J/V curve of SC10 is almost perfectly symmetric (log|R| = 0.07), reaching a maximum of log|J| ≈ −1 at ±0.5 V (the units of J throughout this paper are A cm\textsuperscript{-2}). After exchange, however, the maximum value of log|J| at −0.5 V drops below −3, while the value at +0.5 V remains almost equal to that of SC10. This asymmetry results in a value of log|R| = 1.46 ± 0.018 and is characterized by a suppression of leakage current (at negative bias) compared to the SAM of pure SC10 caused by the increase in tunneling distance imposed by the C_{60} cage.
The low yield is due to the high bias. The value was obtained for the highest one at ±0.95 V. Junction comprising pure SAMs formed directly from FSC11.

To exclude the possibility that the increase in log|R| after exposure of SC10 to FSC11 is due to electrochemical reactions between the AgTS electrode and the C60 cage, we measured AuTS/FSC11//Ga2O3/EGaIn junctions where AuTS is template-striped Au prepared identically to AgTS. The lower work function of AuTS compared to AgTS has two potential consequences on log|R|: (i) the rectification of current is due to redox reactions taking place at the AgTS electrode, which will be pushed out of the experimental bias window; (ii) the lower (more negative) Ef of AuTS will increase the bias required to move the LUPS of FSC11 close enough to resonance to induce rectification. The corresponding observables are log|R| = 1 (i) and a decrease in log|R| at ±0.5 V (ii). We observe the latter: log|R| decreases from 1.46 ± 0.018 on AgTS to 0.92 ± 0.017 on AuTS from which we conclude that the origin of rectification in mixed SAMs of FSC11/SC10 is indeed the onset of a hopping as the LUPS comes close to Ef and not electrochemistry at the AgTS.

To support this conclusion, we compared the LUPS energies of SAMs of FSC11 and Bp and Nq using a combination of optical and photoelectron spectroscopy. The LUPS of FSC11 is approximately 3.72 eV (see ESI†), which is nearly identical to Bp.
(3.7 eV) and $N_{q}$ (3.9 eV) close to the assumed $E_{f}$ of Ga$_2$O$_3$/EGaIn electrode (approximately 4.3 eV). Thus, it is plausible that the mechanism of rectification for FSC11 is the same as Bp since the electrodes and substrates are identical. We also measured the $I/V$ characteristics of SAMs of FSC11 using conductive probe atomic force microscopy (CP-AFM) which replaces a conformal, liquid-metal electrode (EGaIn) with a rigid Au electrode. Fig. 3 compares log($R$) as a function of voltage for Ag$^{TS}$/FSC11/EGaIn and Ag$^{TS}$/FSC11/Au. (Note that the wiring is reversed, thus we use the convention of EGaIn junctions to express log($R$) as we have done previously.\textsuperscript{65}) Interestingly, log($R$) rises much faster with EGaIn, crossing 1.0 only above ±1.25 V with CP-AFM. The sudden onset with CP-AFM is due to the low-current limit (our CP-AFM module only above 1.25 V with CP-AFM). The variance (shown in the ESI) is much higher for pure and mixed FSC11 SAMs from EGaIn measurements show an identical trend; however, the variance (shown in the ESI) is much higher for the pure SAMs. CP-AFM measurements gave values of log($R$) > 1 at loading forces of 0.24 nN, 0.48 nN and 1.4 nN, but with opposite polarity from that of EGaIn due to the difference in wiring (as is described in ref. 65). The original curves with error bars are shown in ESI. The onset of rectification occurs at higher bias (2 V and 1.5 V) for CP-AFM than (0.5 V) for EGaIn, at least some of which is due to the low-current detection limit of CP-AFM at low bias.

Fig. 3 Comparison of log($R$)–$|V|$ plots of EGaIn (black squares and red dots) and CP-AFM (blue, green and magenta symbols) measurements. The Gaussian mean values for junctions based on pure and mixed FSC11 SAMs from EGaIn measurements show an identical trend; however, the variance (shown in the ESI) is much higher for the pure SAMs. CP-AFM measurements gave values of log($R$) > 1 at loading forces of 0.24 nN, 0.48 nN and 1.4 nN, but with opposite polarity from that of EGaIn due to the difference in wiring (as is described in ref. 65). The original curves with error bars are shown in ESI. The onset of rectification occurs at higher bias (2 V and 1.5 V) for CP-AFM than (0.5 V) for EGaIn, at least some of which is due to the low-current detection limit of CP-AFM at low bias.

An interesting consequence of using log($R$) as an observable is that the dynamics of the exchange between FSC11 and the passivating SAM of SC10 by observing the evolution of log($R$) in time. (Assuming the magnitude of log $R$ corresponds directly to the amount of FSC11 incorporated into the SAM.) Fig. 4 shows log($R$) versus exchange time (the amount of time a SAM of SC10 was exposed to a solution of FSC11). Following a relatively rapid increase, log($R$) saturates after 24 h, implying that the mixed-monolayer reaches an equilibrium structure past which it becomes energetically unfavorable to incorporate any more FSC11. We interpret this saturation as the point at which the fullerene head-groups (which rise above the SAM of SC10) have reached maximum packing density as is depicted in Fig. 2A. We recently observed similar kinetics by following the on/off ratio of SAMs of spiropyran switches as a function of exposure time to hexanethiol.\textsuperscript{66} This timescale is also normal for place-exchange between adsorbed thiolates.\textsuperscript{67,68} Thus, EGaIn can be used to follow the dynamics of exchange in mixed-monolayers by observing the changing characteristics of the commensurate tunneling junctions.

If FSC11 does indeed rectify current via the mechanism described above, the maximum observed rectification should relate to the volume of the C$_{60}$ cage because the LUPS is localized to the C$_{60}$ π-system that is in contact with and (partially) pinned to the Ga$_2$O$_3$/EGaIn electrode. As is hypothesized for Bp, positive bias decreases $E_{f}$ (relative to vacuum) at that electrode, which also decreases the LUPS and brings it into resonance with $E_{f}$ at the Ag$^{TS}$ electrode. At this point the LUPS becomes energetically accessible and charges tunnel from Ag$^{TS}$ onto the C$_{60}$ cage instead from Ag$^{TS}$ to Ga$_2$O$_3$/EGaIn (or Au in the case of CP-AFM). Assuming a rectangular tunneling barrier, $J = J_{0} \exp(−βd)$ where $β$ is the tunneling decay coefficient, $d$ is the barrier width and $J_{0}$ is the extrapolated value of $J$ when $d = 0$. Using this equation we can estimate log($R$) by calculating $J$ using the value of $d$ corresponding to the end-to-end lengths of

![Fig. 4](image-url)
FSC11 and $d_{\text{CH}}$ corresponding that value with the volume of the LUPS removed (that is, the red arrows in Fig. 1). This methodology in turn allows a direct comparison to Bp. The results are summarized in Table 2.

We first calculated $d_{\text{BM}}$ (the width of the tunneling barrier for the rectifying moiety) based on two different approximations used in ref. 35 to be 10.9 Å for a spherical volume and 11.2 Å for the volume of an extended structure, respectively. Not surprisingly, the two different methods of calculating volume give very similar values for FSC11 because the C60 cage is nearly spherical. To compare observed values of rectification it is necessary to pick a value of $|V|$ at which to compute $|R|_{\text{obsd}}$. Thus far we have used $0.5\,\text{V}$ because the junctions were not sufficiently stable above this value to collect sufficient data for a robust statistical analysis. However, the standard value in ME is $1.0\,\text{V}$. Fig. 5 shows a linear dependence of $\log|R|$ on $|V|$ from which we extrapolated a value of $R = 676$ at $0.95\,\text{V}$. We compared this value to $R = 617$ from a ‘hero junction’ that survived sweeping to $0.95\,\text{V}$ (which most junctions did not) and gave qualitatively similar curves to the more robust and reproducible curves acquired at $0.5\,\text{V}$. This very close agreement and the fact that plots of $\log|R|$ versus $|V|$ for SAMs of FSC11 at different exchange time (24, 36 and 60 h) gave the same slope (see ESI†) validates the extrapolated value of $|R|_{\text{calcd}}$ to $940$ at $1.0\,\text{V}$. Fig. 6 compares values of $|R|_{\text{obsd}}$ and $|R|_{\text{calcd}}$ to several other rectifiers, including Fe and Bp; FSC11 lies almost exactly on the diagonal, further validating the presumed mechanism.

### 3 Conclusions

We have shown that FSC11 SAMs composed of decanethiolate (SC10) and functionalized C60 bearing undecanethiol groups (FSC11) reproducibly rectify current in AgTS/SAM/EGaIn.
junctions at ±0.5 V. The mechanism is identical to those of SAMs containing bipyridyl (Bp) and Nq since the LUMO of these compounds lie at nearly the same energy, translating into an accessible π-state in SAM-based junctions under positive bias. Further, we show unambiguously that rectification is the result of the electronic structure of C60 because it persists with AuTS bottom electrode and with Au top-contact. We circumvented the difficulties of growing SAMs from C60 derivatives by preparing mixed-monolayers via exchange into substrates pre-passivated with SAMs of SC10 such that the C60 cages are never exposed to bare metal surfaces.

Among the molecular rectifiers included in Fig. 6, the fullerene head group of FSC11 is the second largest behind the copper phthalocyanine salt complex from ref. 19 measured by scanning tunneling microscopy (STM). Not only does FSC11 show the second-highest magnitude of rectification, it shows rectifying behavior with a large-area, conformal EGaIn top-contact and a nanoscopic, rigid Au top-contact. Moreover, the spherical symmetry of C60 and the use of mixed-monolayers mitigates the extreme sensitivity of molecular rectifiers to the details of packing and supramolecular structure. The magnitude of rectification for ferrocene moieties, for example, is sensitive to tilt angle and the purity of the thiol-precursor is also crucial; less than 5% of disulfide disrupts the packing and causes a drop in R and rectification vanishes completely at 15%.7 Similarly, forming mixed monolayers of Bp with π-alkanethiolates only decreases R from that of pure Bp and phase separation makes binary SAMs with relatively uniform composition difficult to achieve.8 Since we begin from non-rectifying SAMs of SC10 into which FSC11 is incorporated, R increases to a saturation point.

The magnitude of log|R| at ±0.5 V is 1.46 ± 0.018, which can reach as high as 940 at ±1 V in a few hero junctions (too few for statistical analysis). This value (940) is consistent with calculations assuming the proposed rectification mechanism, further supporting the proposed relationship between the volume and energy of the accessible π-state and the magnitude and direction of rectification. Future work will focus on stabilizing junctions containing C60 above ±1 V to utilize the large magnitude of rectification in the hero junctions in device platforms.

4 Experimental section

Materials

11-Bromoundec-1-ene, 4-hydroxybenzaldehyde, thioacetic acid, 1-decanethiol (SC10) were obtained from Sigma-Aldrich and used as received with the exception of SC10 which was purified by column chromatography (silica, hexane). The C60 used for the synthesis was of 99.5% purity (purchased from Solenne BV, Groningen, the Netherlands). All compounds were stored in nitrogen-flushed vials and in the dark. Their structures were verified by acquiring 1H-NMR and IR spectra immediately prior to use and comparing to the spectra acquired immediately after purification. FSC11 was prepared starting from 11-bromoundec-1-ene as described in the ESI.† All new compounds were all fully characterized by means of HRMS, NMR and IR. The AgTS and AuTS substrates used in this work were made by mechanistic template stripping as described elsewhere;24 we deposited 200 nm of Ag and 100 nm of Au (99.99%), respectively, by thermal vacuum deposition onto a 3¨ silicon wafer (with no-adhesion layer). Using the UV-curable optical adhesive (OA) Norland 61, we glued 1 cm² glass chips on the metal surfaces.

SAM formation

SAMs of FSC11 were prepared through exchange of SC10 from its SAMs with FSC11 through two steps. Firstly, SAMs of SC10 were formed by incubating freshly cleaved 1 × 1 cm² AgTS surfaces for 24 h in 2 mL of 2 mM solution of SC10 in degassed ethanol (100%; anhydrous) at room temperature. The substrates were then rinsed gently with 200 proof ethanol (3 × 1 mL) and residual solvent on surface was removed by gently blowing N₂. SAMs of FSC11 were then prepared by incubation of the resulting SAMs of SC10 (bared AgTS surfaces used directly for the pure SAMs) in 0.5 mM solutions of FSC11 in degassed toluene at room temperature for 24 h. After incubation, they were then rinsed with toluene and dried as previously described and then used for the measurements.

SAM characterization: contact angle measurement

The SAM of FSC11 was first evaluated with water contact angle measurements under ambient conditions on a SCA20 Data Physics instrument with software version 3.60.2. Equilibrium contact angles were obtained by applying 1 µL water droplets on SAMs using the sessile drop method. The contact angle was measured at three different locations on each surface and the results were averaged. The results showed an average contact angle of 68 ± 1°, which corresponds closely to values of C60/SAM reported by Tsukruk and co-workers.69 While, before the exchanging, the SAM of SC10 was determined to be more hydrophobic with a contact angle of 94 ± 1°, which also confirmed the formation of the fullerene SAM. See ESI† for a description of the EGaIn measurement setup.

XPS thickness measurement

To measure the thickness of the SAM, XPS measurements were performed using a VG Microtech spectrometer with a hemispherical electron analyzer (Clam 100), and a MgKα (1253.6 eV) X-ray source. The Ag3p3/2 and Ag3d peaks were acquired with the sample rotated under 0, 10, 20, 30, 40, and 50 degrees with respect to the electron analyzer. A Gaussian fit with background was made to the peaks to obtain their intensities. To correct for slow fluctuations in the X-ray source intensity we acquired the spectra for each peak at 0° in between the measurements where the sample is rotated. These measurements are used to obtain a correction factor γ1.

The corrected peak intensities I* are given by I* = γ1I and can be used to determine the thickness of the layer. The values are given in ESI† The measured electrons in the peaks are the electrons that make it from the silver through the layer without scattering. An expression for the intensity of the peaks for different lengths of the path that through the overlayer:
Estimation of LUMO of FSC11

The UV-vis absorption spectrum of FSC11 enables the estimation of optical band gap ($E_g$) to be 1.73 eV from the onset wavelength of 718.13 nm. Ultraviolet photoelectron spectroscopy (UPS) analysis of the SAM-bound Ag₃d and Ag₃p, from measurements on a SAM of SC10 on silver, whose thickness was well studied (12 ± 3 Å). The values were found to be 8 Å⁻¹ and 8.8 Å⁻¹ for Ag₃d and Ag₃p respectively. With these values of λ, we can make a fit to the corrected intensities to find the thickness of the FSC11 SAM, which was found to be $d = 1.8 ± 0.3$ nm. This treatment assumes the inelastic mean free path in the FSC11 SAM to be equal to that in the SC10 SAM. The lower packing density of FSC11 could lead to a slight underestimation of the thickness of the layer.

AFM measurement

AFM and CP-AFM measurements were performed on a Bruker AFM Multimode MMAFM-2 equipped with a Peak Force TUNA Application Module (Bruker). Pure SAMs of SC10 before exchange and mixed-monolayers of FSC11 were characterized by AFM. While individual C₆₀ cages could not be resolved, Fig. S16† shows clear qualitative differences before and after exchange, but low roughnesses ($R_m = 1$ nm) and no signs of aggregation or other irregularities. See ESI† for details.

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References
