Supporting Information:

In-Place Modulation of Rectification in Tunneling Junctions Comprising Self-Assembled Monolayers

Yong Ai,‡† Andrii Kovalchuk,‡†‡ Xinkai Qiu,‡† Yanxi Zhang,‡†‡ Sumit Kumar,‡†‡ Xintai Wang,¶ Martin Kühnel,¶ Kasper Nørgaard,¶ and Ryan C. Chiechi*,†‡†

*Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
‡Zernike Institute for Advanced Materials, Nijenborgh 4, 9747 AG Groningen, The Netherlands
¶Nano-Science Center & Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

E-mail: r.c.chiechi@rug.nl
Contents

1 Methods. S-3
2 Experimental platform. S-3
   2.1 EGaIn/Ga$_2$O$_3$/SAM/Au Junction measurement . . . . . . . . S-3
   2.2 Conducting probe atomic force microscopy, CP-AFM . . . . . . . . S-4
   2.3 Kelvin probe force microscopy, KPFM . . . . . . . . . . S-5
   2.4 Reduced graphene oxide, rGO device . . . . . . . . . . S-5
   2.5 X-ray photoelectron spectroscopy, XPS . . . . . . . . . . S-6
3 Robustness of SAMs in the rectifying state. S-8
4 Individual J/V traces. S-10
5 Alkanethiols do not respond to treatment with H$_2$O. S-11
6 The Magnitude of Rectification is Sensitive to pH. S-12
7 Measurement and Calculation of Level-shifts S-13
References S-15
1 Methods.

**Chemicals:** 8-Mercaptooctanoic acid, 12-Mercaptododecanoic acid, 16-Mercaptohexadecanoic acid and 2,2-dimethoxypropane were purchased from Sigma-Aldrich and used as-received. Extra-dry ethanol (Acros) was used as the solvent.

**Substrates:** Template-striped Au was prepared according to literature procedures;\[S1\] Au (100 nm) was vapor-deposited onto technical grade Si wafers in a thermal evaporator. Typical evaporation rates were 0.5 nm s\(^{-1}\). Glass substrates (1 cm × 1 cm) were cleaned by Piranha solution (3:1 H\(_2\)SO\(_4\):H\(_2\)O\(_2\) by volume) and then glued onto the Au film with Norland optical adhesive. The glass/Au/Si sandwich substrates were cured under UV lamp for 300 s. The Au/glass was mechanically peeled off separate from the silicon wafer, exposing the ultra-smooth, buried Au interface.

**Self-assembled monolayers:** Self-assembled monolayers (SAMs) used in EGaIn and CP-AFM junctions was prepared inside a nitrogen-filled glovebox with both humidity and O\(_2\) in the sub-ppm level. Au\(^{TS}\) substrates were immersed in 1 mM ethanolic solutions overnight. SAMs were sonicated for 1 minute then rinsed sequentially with extra dry ethanol, followed by drying in a stream of dry N\(_2\).

**Tuning rectification:** To put a SAM in the rectifying state, it was either immersed in liquid water or exposed to water vapor produced by heating water in a round-bottom flask equipped with a glass tube. To turn off the rectification, the SAMs were immersed a 1:1 by volume mixture of 2,2-dimethoxypropane and ethanol for 30 min to 60 min.

2 Experimental platform.

2.1 EGaIn/Ga\(_2\)O\(_3\)//SAM/Au Junction measurement

The EGaIn tip was formed by extruding a droplet from a 15 μl syringe, placing it in contact with a sacrificial substrate and withdrawing it slowly. A conical EGaIn tip is created when
the EGaIn break down into two parts. Using a micromanipulator, the syringe was moved towards the SAMs until the tip contacted the Au surfaces supporting SAM. A Keithley 6430 electrometer was employed for the electronic and transport current measurement. The Au substrate was grounded while the EGaIn tip was biased. All current density measurements were carried out inside a flowbox with 1% to 3% O₂ in N₂ and relative humidity (RH) < 10%. Tunneling junctions comprising SAMs were formed by contacting the SAMs with a sharp tip of EGaIn.⁸²

The software used for the gathering and analysis of the data comprise homemade LabView scripts for acquiring raw data. The raw data, consist of five traces per junction, were filtered through a pruning algorithm (written in Python using the SciPy package) to remove shorted traces, no-contact traces, and other anomalous traces. A repeated cycling bias of 0→1.5V→0→-1.5V was applied to the SAMs. The measured potential was limited at 1.5V to avoid the short circuit. The traces are filtered by defining shorts as I/V curves where I>10 mA (J ≈ 103 A/cm²) at 0.2 V and no-contact traces where I is in the noise level (0.1 pA) at 0 V, or in which dI/dV changes sign five or more times during a forward or reverse trace. A trace that shorts or converts to no-contact at any point is entirely discarded.

2.2 Conducting probe atomic force microscopy, CP-AFM

CP-AFM I-V measurements were performed on a Bruker AFM Multimode MMAFM-2 equipped with a PeakForce TUNA Application Module (Bruker). The SAMs were contacted with a Au-coated silicon nitride tip with a nominal radius of 130 nm (NPG-10, Bruker; tip A, resonant frequency = 65 kHz, spring constant = 0.35 N/m; tip B, resonant frequency = 23 kHz, spring constant = 0.12 N/m; tip C, resonant frequency = 56 kHz, spring constant 0.24 N/m; tip D, resonant frequency = 18 kHz, spring constant 0.06 N/m; tip A was chosen in this work) in TUNA mode. The AFM tip was grounded and all samples were prepared on AuTS and biased from -1.5 V to +1.5 V and from +1.5 V to -1.5 V to record the I-V
curves: a max of 10 trace/retrace cycles per junction were performed and the top electrode was removed from SAMs between junctions.

2.3 Kelvin probe force microscopy, KPFM

KPFM measurements were performed on a Bruker AFM Multimode MMAFM-2 model in amplitude modulated KPFM. Pt/Ir coated conductive probes (SCM-PIT-V2, spring constant 3 N/m, resonant frequency 75 kHz, Bruker) were calibrated on freshly cleaved highly oriented pyrolytic graphite (HOPG) before the measurements. All samples were scanned at a rate of 0.5 Hz with a scan size of 500 nm and 512 samples per line over three different regions. The potential shifts were calculated by fitting the raw data into Gaussian distribution and were later translated into workfunctions based on the workfunction of the probe.

2.4 Reduced graphene oxide, rGO device

**Micro-pore device fabrication:** 5 nm Cr and 100 nm Au was evaporated on the UV-lithography patterned substrate via thermal evaporation under optimized condition for ultra-flatness to produce micro-chips. A 30 nm Al$_2$O$_3$ layer was then grown via atomic layer deposition (ALD) to serve as an isolating layer. Electron Beam lithography was used to pattern micro-pores with radius $\sim$1 µm on the chips. The micro-pores were characterized by AFM for pore size and Au flatness, only the ones with root-mean-square roughness less than 0.5 nm was selected for SAMs grow.

**SAMs:** The micro-pore device was cleaned by acetone, methanol and iso-propanol, blown dry nitrogen and immersed in the SAMs forming solution (100 µmol dm$^{-3}$ in 99 % ethanol) overnight in nitrogen atmosphere. After SAM formation, the device was rinsed by ethanol to eliminate physisorbed molecules.

**rGO film:** High quality chemically derived graphene oxide solution was prepared by modified Eigler’s method followed by centrifugation. The refined solution was spin coated
on oxygen plasma treated SiO$_2$ wafer (285 nm) to make GO film. The thickness of the film was characterized by AFM. The GO film was reduced by treatment in HI at 120°C for 2 hours, and then thermally treated in a tube-furnace at 650°C for 1 hour under a continuous nitrogen flow. A few drops of 1 M NaOH solution was dropped onto the corner of the rGO film to release the film from the wafer. The film was floated onto a water surface and transferred to the SAM device. A shadow mask and oxygen plasma was used to etch away the undesired rGO to avoid current leakage.

**Contact Areas** Typical EGaIn contacts are 20 µm in diameter. The pore sizes of rGO devices is 1 µm. The contact-area of a typical CP-AFM junction contains about 100 molecules.

### 2.5 X-ray photoelectron spectroscopy, XPS

**Sample preparation for XPS.** All XPS measurements were carried out using freshly prepared samples on Au on mica (Au/mica) as substrates by immersing them anhydrous ethanol solutions containing 0.1 mM HS(CH$_2$)$_{11}$CO$_2$H overnight inside a nitrogen-filled glove box. The samples were removed from solution and rinsed with anhydrous ethanol and dried with dry N$_2$. The resulting SAMs were sealed in an Argon atmosphere and transferred to the antechamber of the instrument for XPS measurements. The SAMs were not exposed to ambient conditions even briefly.

**XPS measurements and Analysis.** XPS was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV). The constant chamber pressure was below $2 \times 10^{-9}$ mbar during data acquisition. The take-off angle of electrons with respect to the surface normal was 37°. XPS spectra optimized by using the least-squares curve fitting program Winspec (developed in the LISE laboratory of the Facultes Universitaires Notre-Dame de la Paix, Namur, Belgium). The diameter of the analyzed area was 1 mm yielding a total experimental energy resolution of 1.4 eV. Deconvolution of the spectra included a Shirley$^{[S3]}$ baseline subtraction and fitting with a minimum
number of peaks consistent with the structure of the molecules on a surface, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. Binding energies are reported 0.1 eV and referenced to the Au 4f\textsubscript{7/2} photoemission peak originating from the substrate, centered at a binding energy of 84 eV\textsuperscript{[S4]} (Figure S1). The uncertainty in the peak intensity determination is 1% for carbon. All measurements were carried out on freshly prepared samples as described above; on each surface 5 points were measured to check for reproducibility. We used statistical data acquisition process; in this processes we acquired 40 data point for each binding energy scan, with step size of 0.1 eV. A total of 200 data points were acquired for 5 measurement points in each sample. Therefore, each spectra is representative of statistical accumulation of 200 data points.

Table S1: C 1s XPS fitting parameters.

| SAMs   | peak position (eV) | mixing ratio | FWHM (eV) |
|--------|--------------------|--------------|-----------|
| Pristine | 285.1              | 0.78         | 1.9       |
|         | 286.6              | 0.78         | 1.9       |
|         | 288.8              | 0.78         | 2.5       |
| H\textsubscript{2}O(l) | 284.8              | 0.78         | 1.9       |
|         | 286.4              | 0.78         | 1.9       |
|         | 289.1              | 0.78         | 2.4       |
| DMP    | 285.1              | 0.78         | 1.9       |
|         | 286.6              | 0.78         | 1.9       |
|         | 288.8              | 0.78         | 2.5       |

Table S1 shows the fitting parameters of mixing ratio (a ratio of Gaussian to Lagrangian) and full width at half maximum (FWHM) of each main peak. All the fitting parameters of corresponding peak are kept as constant in all three cases (Pristine, water, Scavenger) to avoid the error in deconvolution.
Figure S1: Au 4f photoemission spectra of SAMs of S(CH₂)₁₁CO₂H grown on Au surface in pristine state (top), after exposure to water (middle) and subsequent treatment with scavenger (bottom). In all the cases binding energy of Au surface is not change. All the chemical changes observed by Figure 1 is real and free from surface or reference.

3 Robustness of SAMs in the rectifying state.

To better understand the robustness of the rectifying state of the SAM the samples were exposed to vacuum. Figure S2 shows that S(CH₂)₁₁COOH is non-rectifying in its pristine state (black). It changed to rectifying state after treatment with liquid water (red). After heating the SAMs to 80 °C in mild vacuum (Figure S2a, blue) no significant change in recti-
fication was observed. Figure S2b shows the stability of RR of S(CH$_2$)$_{11}$COOH SAMs after exposure to ultra-high vacuum ($10^{-8}$ mbar) for 2 h. As expected, the log $|R|$ vs $|V|$ curves before (red) and after (blue) exposure to vacuum are indistinguishable. Each experiment was repeated 3 times and yielded equivalent results. This test shows that water bound to the surface CO$_2$H groups is stable under heating and vacuum and, therefore, is not simply physisorbed.

Figure S2: Semilog plots of the rectification ratio (log $|R|$) vs absolute potential ($|V|$) of Au$^{+}$/S(CH$_2$)$_{11}$COOH//EGaIn junctions under various condition: i) pristine, non-rectifying (black); ii) after exposure to H$_2$O (l), rectifying (red); iii) after exposure to H$_2$O (l) and then (a) placed in a vacuum oven for 12 h at 80°C or (b) placed in a ultra-high vacuum for 2 h, rectifying (blue). The shaded areas represent the variance.

Figure S3 contextualizes the magnitude of the log $|R|$ with previous reports. While the magnitude of log $|R|$ is a contrived figure of merit because it is a function of $V$, it is nonetheless used as such. While our maximum value of log $|R|$ is not record-setting, it is very clearly amongst the highest reported. And it can be modulated by external inputs.
Figure S3: Plots of log $|R|$ of reported values (blue square) and carboxylic acid (red dot) versus publication years.

4 Individual J/V traces.

Figure S4 shows an example of individual traces of junctions comprising $\text{S(CH}_2\text{)}_{11}\text{COOH}$ in its non-rectifying and rectifying state. The cycling scans overlap each other perfectly, without hysteresis, indicating that no redox (or charge-trapping) occurs. For comparison, Ref. S5 shows the behavior of $J/V$ curves when water is trapped in a SAM in a tunneling junction. The curves are asymmetric and also hysteretic because $\text{H}_2\text{O}$ is being oxidized and reduced with the applied bias. The lack of these features in junctions comprising $\text{S(CH}_2\text{)}_{11}\text{COOH}$ coupled with the thermal stability (Figure S2a) indicate that there are no free $\text{H}_2\text{O}$ molecules in the junction and no redox chemistry is occurring; the rectification is the result of the changes to the electronic structure of the junction that are induced by protonation of the $\text{CO}_2\text{H}$ groups.
Figure S4: Exemplary forward and return $J/V$ traces of Au$^{TS}$/S(CH$_2$)$_{11}$COOH//EGaIn junctions in the pristine, non-rectifying state (a and b, black) and rectifying state after exposure to H$_2$O (l) (c and d, red). None of the $J/V$ traces recorded showed any hysteresis.

5 Alkanethiols do not respond to treatment with H$_2$O.

To exclude the possibility that water, alone can induce rectification, we treated junctions comprising SAMs of alkanethiols (S(CH$_2$)$_{11}$CH$_3$ and S(CH$_2$)$_{15}$CH$_3$) identically to the CO$_2$H SAMs. In their pristine state, log $|R|$ < 0.5 at 1.5 V (Figure S5). The small, non-zero value of log $|R|$ of these aliphatic SAMs is the result of the asymmetric electrodes/coupling of EGaIn junctions. It varies considerably between experiments, presumably due to subtle changes at the SAM//EGaIn interface, but is always < 0.5. Upon exposure to either H$_2$O(l) or H$_2$O(g)), no significant changes in log $|R|$ are observed.
6 The Magnitude of Rectification is Sensitive to pH.

To further elucidate the role of acidity versus neutral water, we treated SAMs of S(CH$_2$)$_{11}$COOH with solutions of varying pH and characterized their rectifying behavior. These data are shown in Figure S6. In the pristine state, log |R| is approximately 0.5 at 1.5 V. Upon exposure to either acidic (HCl and HAc) or basic (NH$_4$OH) aqueous solutions significant changes in log |R| are observed. However, exposure to anhydrous solution of NaOH in EtOH does not affect the rectification ratio. This observation supports the hypothesis that log |R|
is influenced by the adsorption of water—and the resulting dipoles—rather than a direct manipulation of the protonation state of the terminal CO₂H groups.

![Figure S6: Semilog plots of the rectification ratio ($\log |R|$) vs absolute potential ($|V|$) of AuTS/S(CH₂)₁₁COOH//EGaIn junctions under various pH environments. Pristine, non-rectifying state (black); exposure to (red): a) $10^{-4}$ M HCl; b) $10^{-4}$ M HAc; c) 3% NH₄OH aqueous solution and d) $10^{-4}$ M NaOH in anhydrous EtOH.](image)

7 Measurement and Calculation of Level-shifts

All geometry optimization and single-point energy calculations were performed using Gaussian 16. We followed Ref. S6 for the outer-valence Greens function (Stark shift) calculations; An example of the route section is `#p hf/6-311++g(d,p) nosymm ept=ovgf field=x-5 iop(9/11=100)` for a molecule projected along the x-axis. The molecular orbitals used in the
calculation must be listed at the end of the Z-matrix. All density function theory calculations were carried out using the def2 basis sets starting with geometry optimization using polarized valence double-zeta basis and increasing iteratively for a final single-point calculation at the B3LYP/Def2QZVPP level.

Figure S7: The gas-phase energies (eV) of the HOMO (left) and LUMO (right) calculated by hf/6-311++g(d,p) OVGF for SH(CH$_2$)$_{11}$CO$_2$H · H$_2$O versus an applied electric field (V nm$^{-1}$) showing a linear response for the former and a symmetric response for the latter. There was no difference between SH(CH$_2$)$_{11}$CO$_2$H and SH(CH$_2$)$_{11}$CO$_2$H · H$_2$O, however, the dipole moment present at the CO$_2$H · H$_2$O terminus of the SAM will shift the X-axis of the right-hand plot to the right (it adds a positive constant to the applied field).

Figure S8: Isoplots of the HOMO (left) and LUMO (right) calculated by hf/6-311++g(d,p) OVGF for SH(CH$_2$)$_{11}$CO$_2$H · H$_2$O at positive and electric fields corresponding to tip bias. Note that the positive of the LUMO is highly sensitive to the choice of functional and basis set because the LUMO and LUMO+1 are very close in energy; these isoplots are from the same calculations used to prepare Figure S7.
Figure S9: Left: Surface potentials measured by Kelvin-probe AFM for SAMs of $\text{S(CH}_2\text{)}_{11}\text{CH}_3$ (black), $\text{S(CH}_2\text{)}_{11}\text{CO}_2\text{H}$ (green), $\text{S(CH}_2\text{)}_{11}\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$ (blue) and $\text{S(CH}_2\text{)}_{11}\text{CO}_2\text{H}$ following exposure to the merocyanine photo-acid (cyan) and HOPG for reference (red). Right: Shifts in work function versus C12 reference showing that CO$_2$H raises the vacuum level, which increases further when H$_2$O binds.

References

(S1) 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, 9686–9694.

(S2) Chiechi, R. C.; Weiss, E. A.; Dickey, M. D.; Whitesides, G. M. Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers. *Angew. Chem. Int. Ed.* 2008, 120, 148–150.

(S3) Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* 1972, 5, 4709.

(S4) Moulder, J.; Stickle, W.; Sobol, P. Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Physical Electronics Division. 1993.

(S5) 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. Bias Induced Transition
From an Ohmic to a Non-Ohmic Interface in Supramolecular Tunneling Junctions With Ga2O3/EGaIn Top Electrodes. *Nanoscale* **2014**, *6*, 11246–11258.

(S6) Xie, Z.; Băldea, I.; Frisbie, C. D. Why one can expect large rectification in molecular junctions based on alkane monothiols and why rectification is so modest. *Chem. Sci.* **2018**, *9*, 4456–4467.