

**Supporting Information for**  
**A Molecular Half-Wave Rectifier**

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**Nomenclature.** We denote the ferrocene (Fc) terminated SAMs of HS(CH<sub>2</sub>)<sub>11</sub>Fc as SC<sub>11</sub>Fc, the biferrocene terminated SAMs of HS(CH<sub>2</sub>)<sub>11</sub>Fc<sub>2</sub> as SC<sub>11</sub>Fc<sub>2</sub>, and SAMs of S(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> as SC<sub>11</sub>. We use the general notation Ag<sup>TS</sup>-SC<sub>11</sub>Fc//Ga<sub>2</sub>O<sub>3</sub>/EGaIn to describe the junctions: here, Ag<sup>TS</sup>-SC<sub>11</sub>Fc is a silver template stripped thin-film electrode (with an area of about 1 cm<sup>2</sup>) supporting a SAM of SC<sub>11</sub>Fc. We describe the interfaces with the symbols “-”, which indicates a chemisorbed contact, “/”, which indicates the presence of a non-covalent interface, and “/”, which indicates the interface of Ga<sub>2</sub>O<sub>3</sub> and EGaIn. The symbol *V* is defined as the difference in voltage between the two electrodes.

## Experimental

Detailed descriptions of the experimental procedures for the preparation of the template-stripped Ag electrodes,<sup>1</sup> the formation and characterization of the SAMs,<sup>2</sup> and formation of the tunneling junctions with cone-shaped tips of Ga<sub>2</sub>O<sub>3</sub>/EGaIn have been reported before.<sup>3,4</sup>

**Purification of HSC<sub>10</sub>CH<sub>3</sub>.** We purified the HSC<sub>10</sub>CH<sub>3</sub> (Aldrich). We recrystallized the thiol from ethanol by dissolving the thiol in ethanol at room temperature under an atmosphere of N<sub>2</sub>. We filtered the ethanolic solution after slowly cooling the solution to 0 °C. Crystals of the thiol formed overnight after the mother liquor was further cooled to -20 °C; these crystals were collected by filtration. This procedure was repeated three times.

**Formation of the SAMs.** We immersed the Ag<sup>TS</sup> surfaces within 5 s after removal from the wafer in the ethanolic solutions of the corresponding thiols (R.T., under argon) to minimize contamination of the metal surface. We formed the SAMs over 12 hours after which we rinsed the surfaces with ethanol to remove physisorbed materials.

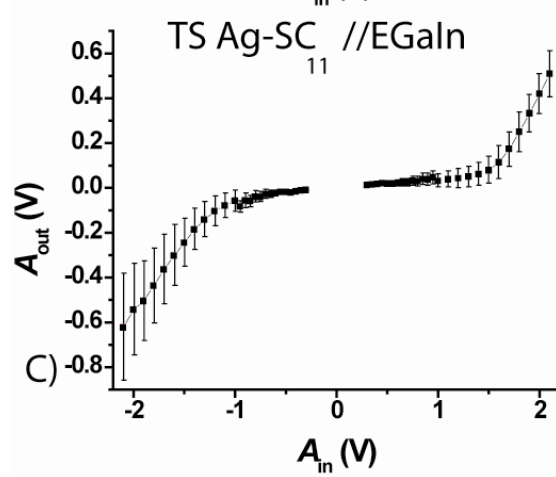
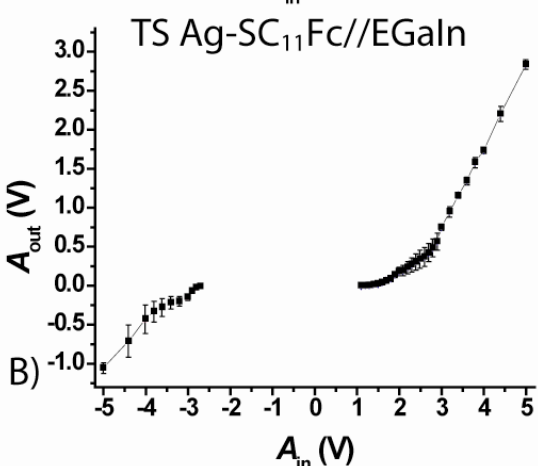
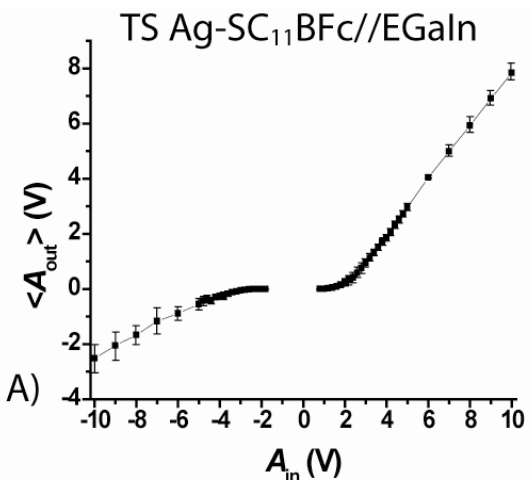
**Ag<sup>TS</sup>-SAM//Ga<sub>2</sub>O<sub>3</sub>/EGaIn Junctions.** We formed ultra-flat Ag surfaces by a template-stripping (TS) procedure published previously.<sup>1</sup> We give a brief description here. We deposited a layer of 500 nm of Ag by electron-beam (e-beam) evaporation at  $2-3 \times 10^{-6}$  Torr at a rate of 8-10 Å/s on silicon wafers with their native SiO<sub>2</sub> layer present. We glued glass slides of  $\sim 1$  cm<sup>2</sup> – cleaned by washing with EtOH, and subsequent exposure to oxygen plasma (500 Torr, 5min) – at the Ag-surface using an optical adhesive (Norland, No. 61). We cured the optical adhesive by exposure to ultraviolet light (100 W; the light source was kept at a distance of 50 cm to prevent heating of the wafer) for 2 h. The glass substrates were cleaved off the Si-wafer using a razor blade. To minimize contamination of the Ag<sup>TS</sup> substrates after cleavage, we immersed the Ag<sup>TS</sup> substrates in the ethanolic solutions containing the thiols under argon within 5 s.

The formation of the cone-shaped tips of Ga<sub>2</sub>O<sub>3</sub>/EGaIn and detailed descriptions of the procedures used to contact these SAMs by Ga<sub>2</sub>O<sub>3</sub>/EGaIn top-electrodes have been reported by our group.<sup>3</sup> We have reported that the Ga<sub>2</sub>O<sub>3</sub>/EGaIn (Aldrich) behaves as if it were a non-Newtonian fluid:<sup>5</sup> when shear-pressure is applied, Ga<sub>2</sub>O<sub>3</sub>/EGaIn behaves as a liquid and will flow until the shear-pressure is relieved. This behavior makes it possible to shape Ga<sub>2</sub>O<sub>3</sub>/EGaIn, unlike mercury, into non-spherical shapes (here cones). A drop of Ga<sub>2</sub>O<sub>3</sub>/EGaIn hanging from a 26S-gauge needle was brought into contact with a surface that is wettable by Ga<sub>2</sub>O<sub>3</sub>/EGaIn (PDMS, glass, or Ag). The Ga<sub>2</sub>O<sub>3</sub>/EGaIn adheres to both the surface and to the needle. Slowly retracting the needle from the drop of Ga<sub>2</sub>O<sub>3</sub>/EGaIn-drop, using a micromanipulator, deformed the Ga<sub>2</sub>O<sub>3</sub>/EGaIn drop in such a way that two conically-shaped Ga<sub>2</sub>O<sub>3</sub>/EGaIn structures, connected head-to-head, formed. Further retraction of the needle resulted in separation of the conically-shaped Ga<sub>2</sub>O<sub>3</sub>/EGaIn structures, one attached to the needle and the other attached to

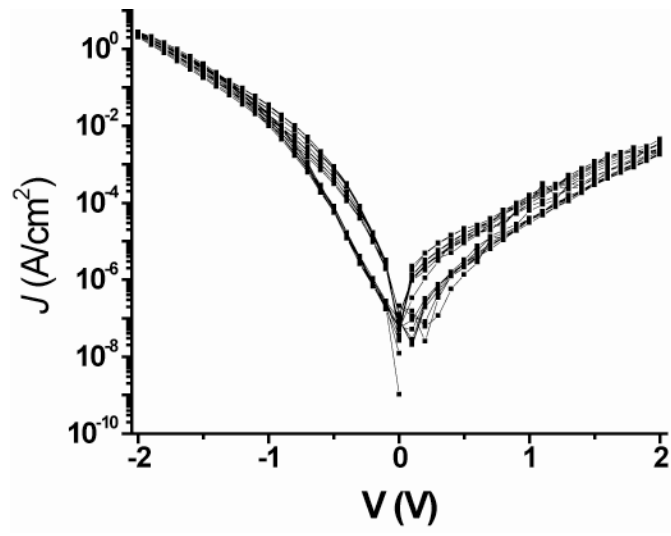
the surface. Subsequently, we discarded the substrate and replaced it by a  $\text{Ag}^{\text{TS}}$  surface with the SAM of interest, and contacted the SAM with the conically-shaped  $\text{Ga}_2\text{O}_3/\text{EGaIn}$  at the needle.

**AC Measurements.** We positioned the molecular junction in series with a large resistor ( $1.5 \text{ M}\Omega$ ) on a breadboard and measured the voltage drop across the resistor; the large value of  $R_1$  limits the current through the molecular junction and prevents breakdown. We used a waveform generator (Agilent 33120A) to generate the input signals, and an oscilloscope (Tektronix TDS 3014) to measure the input and output signals simultaneously. We biased the  $\text{Ag}^{\text{TS}}$  bottom-electrode and the  $\text{Ga}_2\text{O}_3/\text{EGaIn}$  top-electrode was connected to ground across the  $1.5 \text{ M}\Omega$  resistor. The area of the  $\text{Ga}_2\text{O}_3/\text{EGaIn}$  junctions, measured using a CCD camera, varied (in different preparations) from  $300$  to  $1000 \text{ }\mu\text{m}^2$ . In operation, a sinusoidal wave form with amplitudes between  $0.5 - 10.0 \text{ V}$  was applied to the circuit at a frequency of  $50 \text{ Hz}$ .

**Figure S1:** Same as Figure 8 but with expanded scales for the data of Fc and SC<sub>11</sub> junctions.

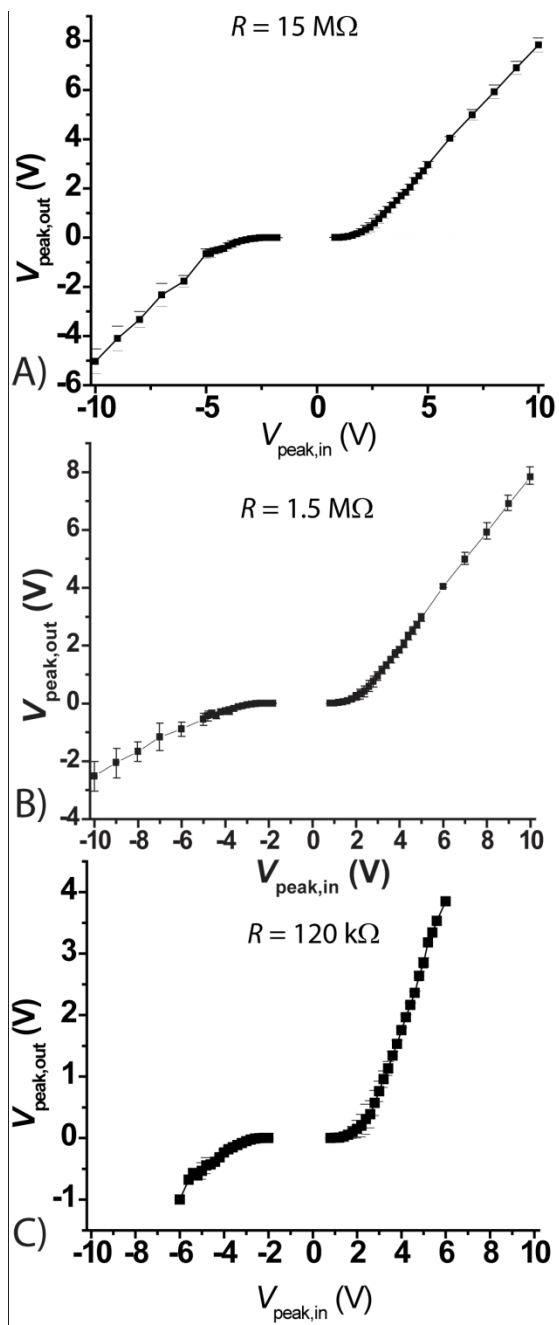


**Figure S2:** An example of  $\text{Ag}^{\text{TS}}\text{-SC}_{11}\text{Fc}_2//\text{Ga}_2\text{O}_3/\text{EGaIn}$  junction that was stable during  $J(V)$  measurement of  $\pm 2.0$  V for nine  $J(V)$  traces after which we terminated the experiment.





**Figure S3:** The  $V_{\text{peak,out}}$  as a function of  $V_{\text{peak,in}}$  for the  $\text{Ag}^{\text{TS}}\text{-SC}_{11}\text{Fc}_2//\text{Ga}_2\text{O}_3/\text{EGaIn}$  junctions with a resistor of 15 M $\Omega$  (A), 1.5 M $\Omega$  (B), or 120 k $\Omega$  (C) in the circuit. The error bars represent the standard deviation of four measurements. The junctions broke down (resulting in shorts) at lower input bias in the circuits with the 120 k $\Omega$  resistor than junctions in circuits with large resistors: none of the junctions survived input voltages of  $> 6.0$  V.



## References

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