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Ferrocenes as One-Electron Donors in Unimolecular Rectifiers

Robert Melville Metzger

Abstract

Ferrocene is a good electron donor, and as such has been used to test asymmetric conduction (rectification) in molecules that contain ferrocene. Of the five ferrocene-containing molecules that rectify (structures 11, 15, 19, 20, and 22), the last (22) exhibits a record rectification ratio, which should be a dramatic incentive for searching for more high-efficiency rectifiers.

Keywords: ferrocene, unimolecular electronics, rectification ratio, highest occupied molecular orbital, Aviram-Ratner proposal of 1974

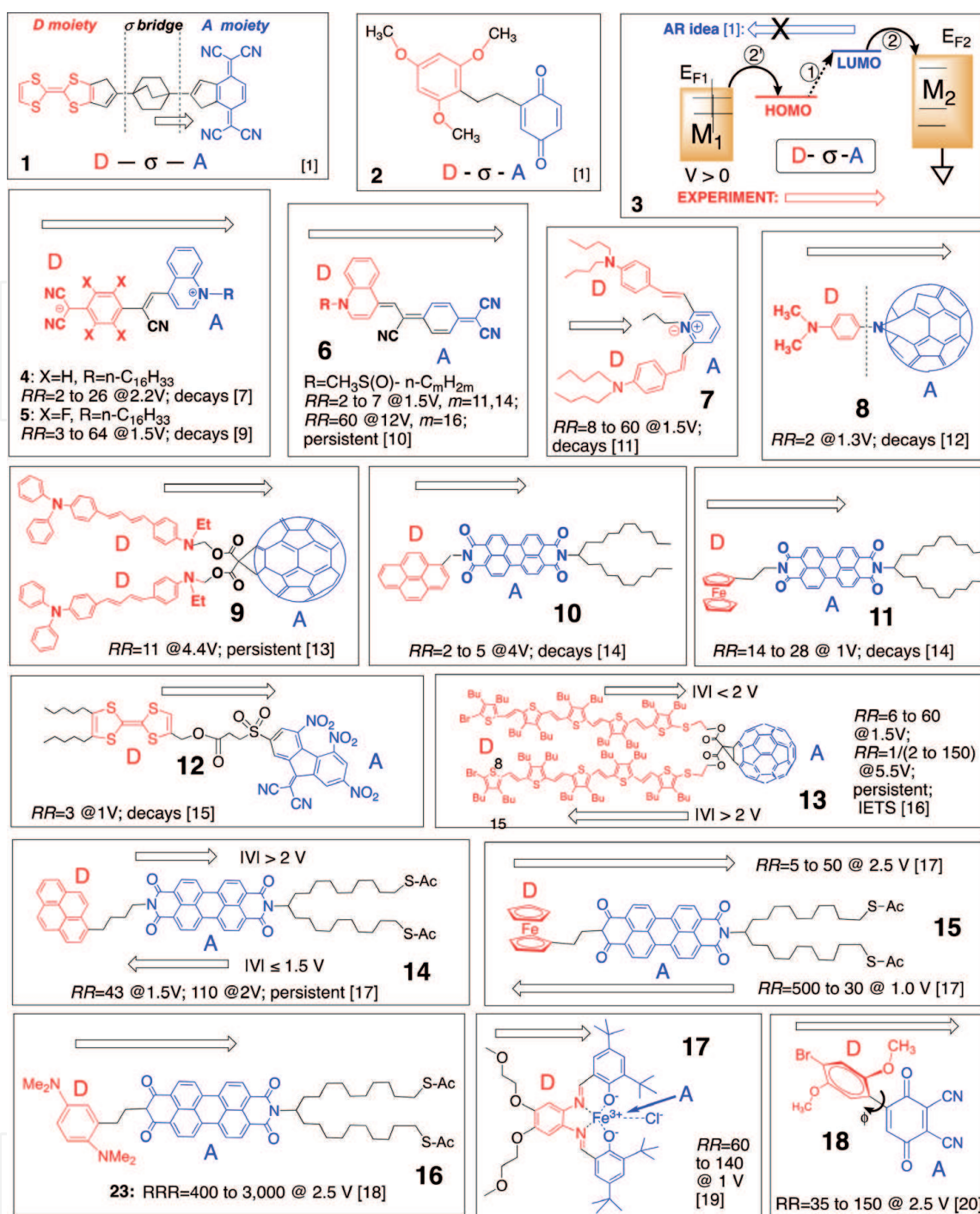
1. Introduction

“Unimolecular electronics” (UME) [1] was born in 1974 with a theoretical proposal by Arieh Aviram and Mark Ratner (AR) for a one-molecule rectifier (or diode) of electrical current donor-bridge-acceptor (D- σ -A) [1] (**Figure 1**, structures 1 and 2): within that molecule D represents a π -electron-rich one-electron donor (D) moiety, σ is a short and saturated bridge of sp^3 -hybridized C atoms (between two and maybe eight C atoms long), and A is the electron-poor moiety that can act a one-electron acceptor. One small correction, AR had suggested that the first mechanistic step would move electron and hole from metal electrodes to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the second step would involve the relaxation of the excited-state zwitterion [1]. The experimental direction of rectification for D- σ -A molecules has been shown to be “anti-AR” (**Figure 1** structure 3): in step (1), under applied electric field, the neutral ground-state molecule D- σ -A forms an excited-state zwitterion $D^+-\sigma-A^-$; in step (2) the electron and hole are transferred to the metal electrodes [2].

The first rectifier (4 in **Figure 1**) was measured in 1990–1993 as a Langmuir-Blodgett (LB) multilayer between dissimilar metal electrodes by J. Roy Sambles (University of Exeter) and Geoffrey J. Ashwell (Cranfield University) [3, 4]. The asymmetric electrical current was confirmed at the University of Alabama (UA) as a LB monolayer of 4 between Al electrodes in 1997 [5] and then between oxide-free Au electrodes in 2001 [6, 7].

As of 2015, 53 unimolecular rectifiers had been measured worldwide [8], 15 of which at the UA (**Figure 1**, structures 4–18 [7–20]). Also, 169 molecular wires were measured around the world [8]. Several more rectifiers have been published worldwide since and many review articles on this subject have appeared [21–32].

The present article focuses on the use of one particular powerful one-electron donor in rectifiers: ferrocene.

**Figure 1.**

The Aviram-Ratner proposal of unimolecular rectification [1] with two specific molecules suggested (1, 2). Structure 3 shows the rectification direction (direction of larger and favored electron flow) seen (i) experimentally (bottom arrow from left to right, see Ref. [16]) and (ii) the rectification direction predicted by Aviram and Ratner (top arrow from right to left crossed out). Structures 4–18 are the unimolecular rectifiers studied at the University of Alabama (1997–2018) [7–20]: listed are the direction of enhanced current (hollow arrow), the rectification ratio $RR = -I(V_{max})/I(-V_{max})$, and the maximum bias V_{max} (Volts) measured; the word “decays” means that RR decreases monotonically as the measurement is repeated, while “persistent” means that RR does not decrease. The electron donor regions are shown in red, and the electron acceptor regions are shown in blue.

2. Results

In the 1980s, UME had hoped to develop useful molecular-scale ($\sim 2 \text{ nm}^3$) devices for ultrahigh-density and high-speed industrial electronics. To interrogate such molecules (or monolayers of molecules), metal electrodes or nanoelectrodes (Al, Ag, Au, etc.) are used: this is sketched below and explained in detail in many

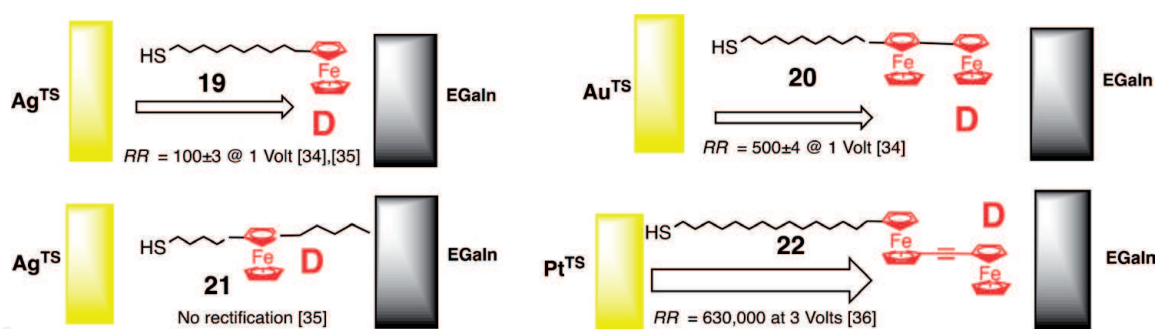


Figure 2. Ferrocene-containing unimolecular rectifiers studied by the groups of Whitesides [33–35] and Nijhuis [36]: all are “asymmetry-type A” rectifiers; the hollow arrow denotes the preferred direction of electron flow through the “metal | molecule | metal” sandwich (from electrode far from the electron donor part to the nearest electrode). **Corrigenda for Ref. [8]:** (i) the arrows for **19** (i.e., “molecule 193”) and **20** (i.e., “molecule 196”) are drawn in the wrong direction: they would apply to D-σ-A rectifiers; (ii) for **20** (i.e., “molecule 196”), the reference in Ref. [8] should be [124] instead of [122], [123]; and (iii) for **21** (i.e., “molecule 197”), the reference in Ref. [8] should be [125] instead of [122], [123].

review articles [8, 21–32]. UME learned how inorganic metals couple (associate with or bond to) single organic molecules and how one can reliably exchange electrons and photons with these molecules.

In the meantime the much wealthier and commercially driven electronic industry has made gigantic strides and has developed high-speed almost-nanoscale electronic circuits using inorganic semiconductors (Si, Ge, and GaAs). Therefore the original hope and promise of UME have been defeated. Nevertheless, UME has learned to interrogate and control individual molecules, and its present challenge is how to combine and exploit electronic, photonic, and spintronic functions in new ways.

The present review looks at how ferrocene-containing molecules have contributed valid and promising and most recently also very dramatic UME rectifiers: in particular molecules **11** [14] and **15** [17] already mentioned in **Figure 1** and four other molecules shown in **Figure 2**, **19** [33, 34], **20** [33, 34], and **21** [33, 34] studied by the Whitesides group at Harvard University and **22** [36] studied by the Nijhuis group at Singapore National University. As discussed below, molecule **21** should not, and does not, rectify.

Electrical measurements of rectifiers. Rectification can be measured with some difficulty at the single-molecule level, but more conveniently as a monolayer between macroscopic metal electrodes as a “metal | molecule | metal” sandwich [32]. All molecules discussed here were studied either as a Langmuir-Blodgett monolayer (**11** [14]) or as self-assembled monolayers (SAMs) with thiol terminations that could be bound covalently to either super-flat “template-stripped” Ag^{TS} or A^{TS} electrodes (**15** [17], **19** [33, 34], and **20** [34]) or Pt^{TS} electrodes (**22** [37]). Most (but not all) rectifier measurements have been done with direct current [8, 32].

Candidate unimolecular rectifiers can be (i) electron donor molecules, (ii) electron acceptor molecules, or (iii) D-σ-A molecules [8, 32]. The search for organic rectifiers started in the era of quasi-one-dimensional organic metals with an enduring synthetic emphasis toward strong (easily oxidized) donor moieties D and strong (easily reduced) acceptor moieties A, connected by a covalently saturated and electrically insulating “sigma” (σ) bridge, forming a D-σ-A molecule. For instance, the proposed tetrathiafulvalene (TTF)-σ-tetracyanoquinodimethane molecule (**Figure 1**, structure **1**) would have a presumed low barrier to form the corresponding excited zwitterion D⁺-σ-A⁻. Yet in 1974, a (weak donor)-σ-(weak acceptor) molecule (**Figure 1**, structure **2**) was also proposed [1]. Surprisingly, the recently studied (and dimensionally very tiny) molecule **18** (that resembles molecule **2**) incorporates a weak electron donor D and a moderate electron acceptor

Molecule	$I_D(g)$	$A_A(g)$
Benzene	9.24	-1.15 ^a
Pyrene	7.37	0.56
Perylene	6.90	0.97
Pc	6.41	—
TMPD	6.20	—
TTF	6.83	—
Fc = Cp ₂ Fe	6.81 ^b	—
1,4-benzoquinone	9.99	1.91
TCNQ	9.50	3.30
PBI	—	3.93 ^c

^aFrom Ref. [42].
^bFrom Ref. [43].
^cCalculated from Ref. [18].

Table 1.
Gas-phase ionization potentials I_D (eV) and gas-phase electron affinities A_A (eV), updated from [8], except where noted.

A, yet is an excellent rectifier [20]. We have also seen that a strong, easily oxidized donor like tetramethyl-*para*-phenylenediamine in molecule **16** blocks the current across the monolayer between -0.5 and +0.5 Volts (Coulomb blockade) [18].

Table 1 shows some relevant gas-phase ionization potentials I_D for electron donors D and gas-phase electron affinities A_A for electron acceptors A [8]. It should be noted that ferrocene (Fc or Cp₂Fe, where Cp is cyclopentadienyl) is as good an electron donor (i.e., has a relatively small I_D value) as tetrathiafulvalene TTF, but not as good as N,N,N',N'-tetramethyl-*para*-phenylenediamine (TMPD). Perylenebisimide (PBI) is as good an electron acceptor (i.e., has a similarly large A_A value) as 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Four mechanisms for rectification. Four potential mechanisms for electrical rectification in molecules have been discussed [38–40]:

1. Schottky barriers (“S” rectifier) [38, 40].
2. Asymmetric placement of the electrophore in the electrode gap (“A” rectifier) [38].
3. Unimolecular processes depending on molecular energy levels (“U” rectifier) [38].
4. A recent fourth mechanism for rectification is asymmetric polarization (“AP” rectifier), when highly polar solvents can induce an asymmetric conductance of a symmetrical molecule between very asymmetric electrodes in a scanning break junction (SBJ) [41].

Purists would prefer pure-“U” rectifiers, requiring “S” = 0 and “A” = 0. For many molecules, for reasons of assembly, “U” and “A” effects are combined [39] (e.g., **Figure 1** for structures **4**, **5**, **6**, **10**, **11**, **14**, **15**, **16**). For molecules **19**, **20**, and **22** in **Figure 2**, only the “A” effect is operative: the chromophore donor moiety (indicated as “D” and shown in red) yields rectifiers because it is **asymmetrically placed** within the “metal | monolayer | metal” sandwich. When the D moiety is in the middle of molecule **21**, there can be and is no rectification [33, 34], as predicted [38].

Reversal of rectification: “Janus effect.” The molecules studied routinely at the UA rectify in the “anti-AR” direction, that is, intramolecular electron flow occurs from D to A (e.g., **Figure 1** structure 3) [2, 8]. However, D-σ-A rectifiers **13**, **14**, **15**, and **16** also show an additional “Janus effect”: at lower bias they rectify one way, and at higher bias (e.g., at ±2.5 V), they rectify the other way [17, 18]! At lower bias, AR rectification may involve only one energy level (e.g., LUMO); at higher bias, anti-AR rectification may involve both HOMO and LUMO. Such bias-switchable rectifiers may be useful!

Rectification ratio. The asymmetry in electrical current *I* is quantified by the rectification ratio:

$$RR(V_{\max}) \equiv -I(V_{\max})/I(-V_{\max}) \tag{1}$$

where *V* is the applied bias or voltage. Typical *RR* values span several orders of magnitude; for the rectifiers **4–18** studied at the UA, *RR*(*V*_{max}) is reported in **Figure 1**. The first rectifier, **4**, had *RR* = 26 [7]; **16** has a large *RR* = 3000 [19]. Why is the *RR* typically seen for unimolecular rectifiers (*RR* ≤ 10³) [8] so much smaller than the *RR* for commercial inorganic pn junction devices (*RR* = 10⁵–10⁶) [8]? If low *RR*s were intrinsic to UME rectifiers, then traditional Ge, Si, and Ga As semiconductor physicists could safely look down at UME as a harmless curiosity, not as a competitor. But, as discussed next, a huge increase in *RR*s was imminent.

We next discuss rectifier **16**, in which the electron donor moiety is the powerful electron donor TMPD instead of ferrocene (**Figure 5**). **Figure 6** shows a surprisingly large room temperature Coulomb blockade [18]: too much of a good thing, the

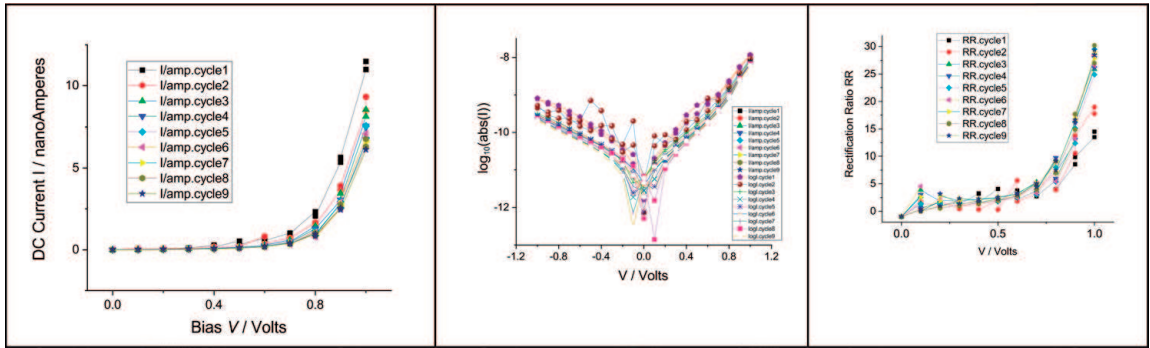


Figure 3. IV scans for a “Au | LB → SAM of **15** | Cold Au | Ga₂O₃ | EGaIn” sandwich in the bias range from −1.0 to +1.0 Volts for the bias *V* **increasing**: (left) *I* (ampères) vs. *V* (Volts). (Center) log₁₀*I* vs. *V*. (Right) *RR*(*V*) = −*I*(*V*)/*I*(−*V*) vs. *V*: (the average < *RR* > = 96.3 ± 36.7). The horizontal arrows indicate the scan direction; the vertical hollow arrows show how the ordinate values evolved with repeated scans [18].

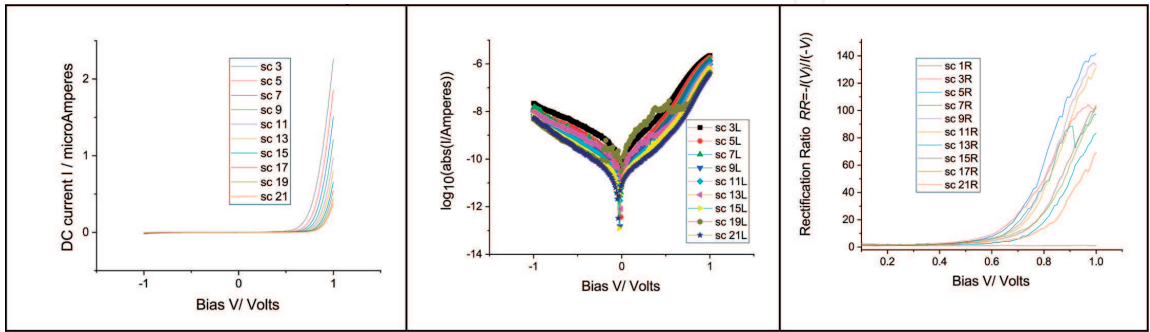


Figure 4. Current-voltage (IV) curves (*I*/ampères vs. *V*/Volts) for a “EGaIn | Ga₂O₃ | Au | Z-type LB monolayer of **11** | Cold Au | Ga₂O₃ | EGaIn” sandwich. (left) *I* vs. *V*. (Center) log₁₀*I* vs. *V*. (Right) *RR* = 14–28 vs. *V*. *RR* persists for up to 40 measurement cycles, with a minimal decrease in the currents (which are relatively small). Rectification was even seen for biases up to ±2 Volts [14].

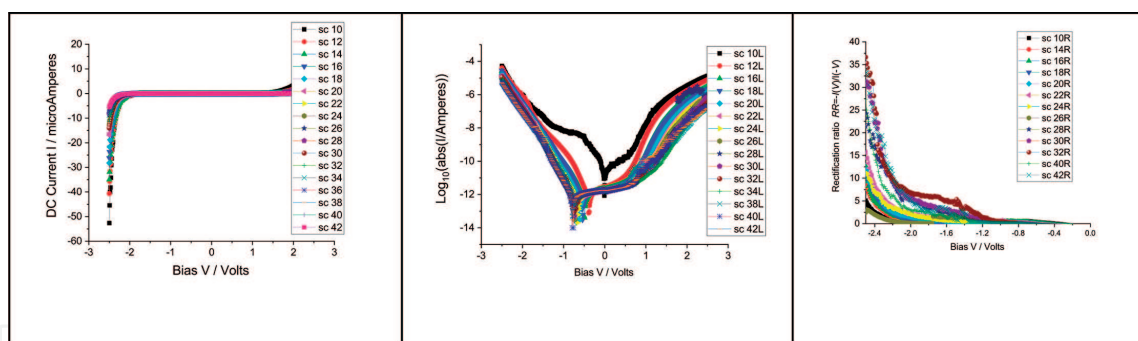


Figure 5.

IV scans for a “EGaIn | Au | LB → SAM of **15** | Cold Au | EGaIn” sandwich in the bias range from –2.5 to +2.5 Volts for the bias V **increasing**: (left) I (ampères) vs. V (Volts). (Center) $\log_{10}I$ vs. V . Note that the position of minimum current, which for normal tunneling curves of this type should occur at zero volt bias, as in **Figures 3** (center) and **4** (center) shown above, is displaced here very significantly to the left by about 0.8 Volts: This is **incipient Coulomb blockade**. (Right) $RR(V) = I(V)/I(-V)$ vs. V [18].

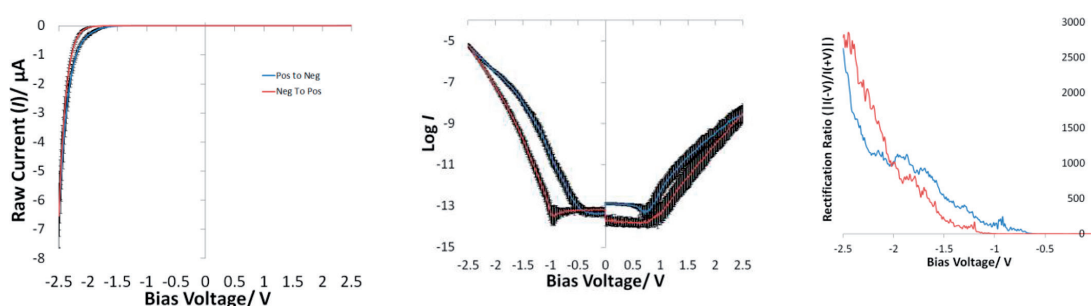


Figure 6.

IV scans for a “EGaIn | Au | LB → SAM of **16** | Cold Au | EGaIn” sandwich in the bias range from –2.5 to +2.5 Volts for the bias V **increasing**: (left) I (ampères) vs. V (Volts) (average of 50 scans). (Center) $\log_{10}I$ vs. V . **True Coulomb blockade**. (C) $RR(V) = I(V)/I(-V)$ vs. V . (right) RR vs. V [18].

TMPD oxidizes too easily and prevents current from flowing for a large bias range [18]! Beyond where the Coulomb blockade was operative, a relatively impressive $RR \approx 3000$ is reached.

The Whitesides group (including Nijhuis) studied the rectification of self-assembled monolayers of thiol-containing molecules **19** and **20** and the non-rectification of the symmetric **22** [35], in sandwich “Au | SAM | Ga₂O₃ | GaIn” with a thorough effort to isolate the potential influence of the disordered Ga₂O₃ oxide that forms at the surface of the GaIn eutectic (without completely covering it) [33–35] (**Figure 7**).

Recent huge rectification ratio. A very dramatic result was published recently for the (“A-type”) rectifying monolayer sandwich “Pt^{TS}-S-C₁₅H₃₀-Fc-C≡C-Fc | EGaIn” (**Figure 2**, structure **22**) consisting of a diad of ferrocene (Fc) donors (linked by an alkynyl-C≡C-), with a pentadecanethiol “tail” [36]. This sandwich was studied between a bottom template-stripped electrode M^{TS} (=Pt^{TS}, Au^{TS}, or Ag^{TS}) and an EGaIn droplet top electrode. The new record is a very dramatic $RR = 6.3 \times 10^5$ at ± 3 Volts for Pt^{TS} (but much less for Au^{TS} or Ag^{TS}) (**Figure 8**) [36]. Also, the conductance “plateaued” around –2 Volts when the Ag^{TS} electrode was used [36].

The key improvements in [36] were (i) using Pt as the “bottom” electrode, because Pt^{TS} tolerates a larger bias range than Au^{TS} or Ag^{TS}, (ii) a presumed efficient van der Waals contact between Fc-C≡C-Fc and EGaIn, and (iii) a “long enough alkyl tail” to get a very small reverse-bias current [38].

Also, light emission was measured (with blinking) for **22**, with a broad peak at 1.7 eV ($\lambda_{\max} = 730$ nm), but only at the large negative bias V that corresponds

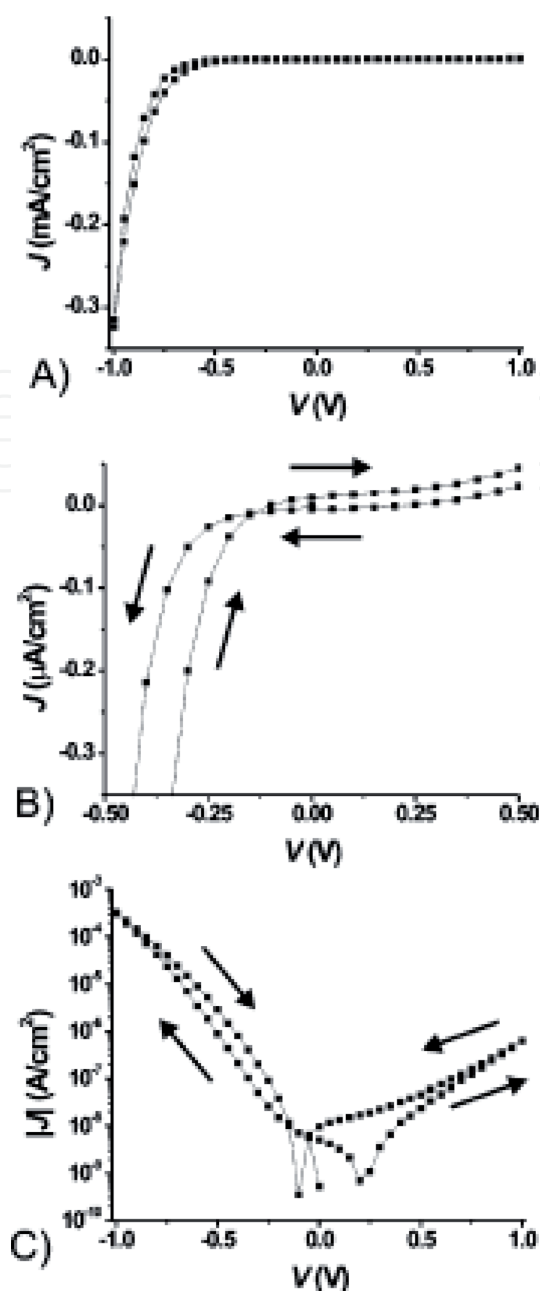


Figure 7. JV scans for “ $\text{Ag}^{\text{TS}} / \text{SAM of alkanethiol } \text{CH}_3(\text{CH}_2)_{11}\text{SH} / \text{Ga}_2\text{O}_3 / \text{EGaIn}$ ” sandwich in the bias range from -1.0 to +1.0 Volts, (A) J vs. V (B) detail of (A) showing hysteresis (C) $\log_{10} J$ vs. V . $\text{RR} \approx 100$. From Ref. [33, 34].

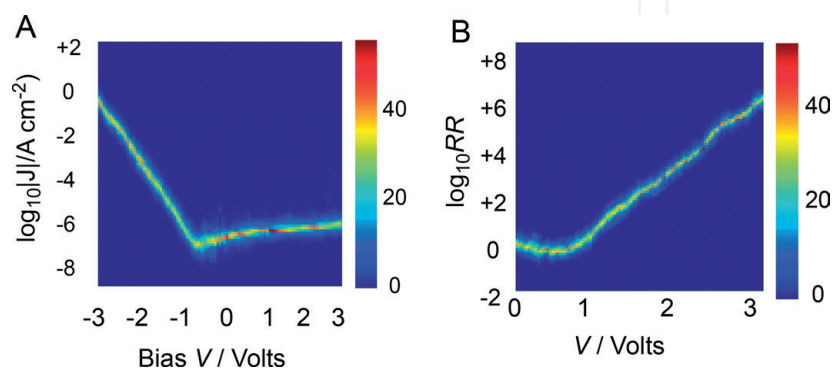


Figure 8. IV data for “ $\text{Pt}^{\text{TS}} / \text{SAM of } 22 / \text{Ga}_2\text{O}_3 / \text{EGaIn}$ ” sandwich: (A) $\log_{10} J$ vs. V and (B) rectification ratio $\text{RR}(V)$ vs. V . the current densities $J = I/A$ are calculated from the measured currents I and the estimated areas A of the EGaIn drops. The “heat map” shows in false color the number of times that any point in the xy plot was recorded (see color code on the right of each xy plot) From Ref. [36].

to rectification: this emission was attributed to surface plasma polaritons excited distally within the Pt electrode after tunneling. Thus, the electrical excitation at large negative bias may have accessed the HOMO and HOMO-1 of Fc, but the energy is emitted neither directly (electroluminescence from Fc⁺ with an expected narrow energy distribution) nor indirectly (as lattice phonons), but indirectly and effectively, as surface plasma polaritons with a wide spectral distribution [36].

3. Conclusion

The frustrating issue of historically low measured *RRs* [8] has thus been resolved experimentally [36]: organic monolayer rectifiers may finally challenge the *RR* of inorganic *pn* junction rectifiers.

However, the measured *RRs* for alkanethiols are hundreds of times smaller than expected from careful theoretical simulations [42]: this puzzle must be solved, so that measurements are not victims of unforeseen inefficiencies in the “metal | molecule” interface. The number of measured unimolecular rectifiers has grown dramatically, but their preselection as candidate rectifiers has been somewhat haphazard. Once the “metal | molecule” interface is brought under experimental control, better measurements may provide valid physical organic criteria to guide the design of the better unimolecular rectifiers of tomorrow.

There has also been a recent brief review on this exact topic [43]; for the sake of brevity, we refer the reader to the papers cited for other significant rectifiers containing the donor ferrocene [43–49].


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