

An Exciting Aspect of Nanotechnology: Unimolecular Electronics

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Abstract. This is a brief update on our experimental work towards better one-molecule-thick monolayer rectifiers of electrical current, and on theoretical progress towards a one-molecule amplifier of electrical current. This program aims to provide electronic devices at the 2 to 3 nm level, as a dramatic advance towards practical integrated circuits of the future.

1 Introduction

The field of unimolecular electronics started with a 1974 paper by Arieh Aviram and Mark Ratner (AR) [1]. As reviewed elsewhere [2, 3] eleven rectifiers have been completely characterized in our laboratory, and several others have been reported by others [4, 5]. For strictly one-molecule two-probe measurements, mechanical break junctions (MBJ) [6, 7], electromigration break junctions (EMBJ) [8], scanning tunnelling microscopy (STM) [9] and scanning probe break junctions (SPBJ) [10] permit the measurement of the electrical current through a single molecule that bridges, say, a 1 nm gap between electrodes. Alas, at present nobody can fabricate three nanoelectrode tips that are about 2 nm from each other (the challenge is getting insulating oxides between electrodes that are as thin as 2 nm). Here we summarize older measurements, report on on-going work on several new candidate rectifier molecules, and discuss a recent theory on how a three-terminal molecule could act as an electrical power amplifier [11].

2 Monolayer rectifiers

AR proposed that a single-molecule rectifier (or diode) of the type D- σ -A, where D is a strong electron donor moiety, A is a strong electron acceptor moiety, and σ is a saturated (or twisted aromatic) covalent link between D and A. By definition, a D moiety has a relatively low ionization potential, while the A moiety has a relatively large electron affinity. The experimental verification of AR rectification involved at first Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) monolayers measured between macroscopic metal electrodes (Al, Mg, Pt [12], and later Au), then chemisorbed monolayers tapped by a macroscopic Au electrode [13], and finally MBJ [4] and

scanning tunnelling microscopy [5] for single molecules. **Fig. 1** shows the chemical structures of eleven rectifiers, and **Table 1** shows their electrical characteristics.

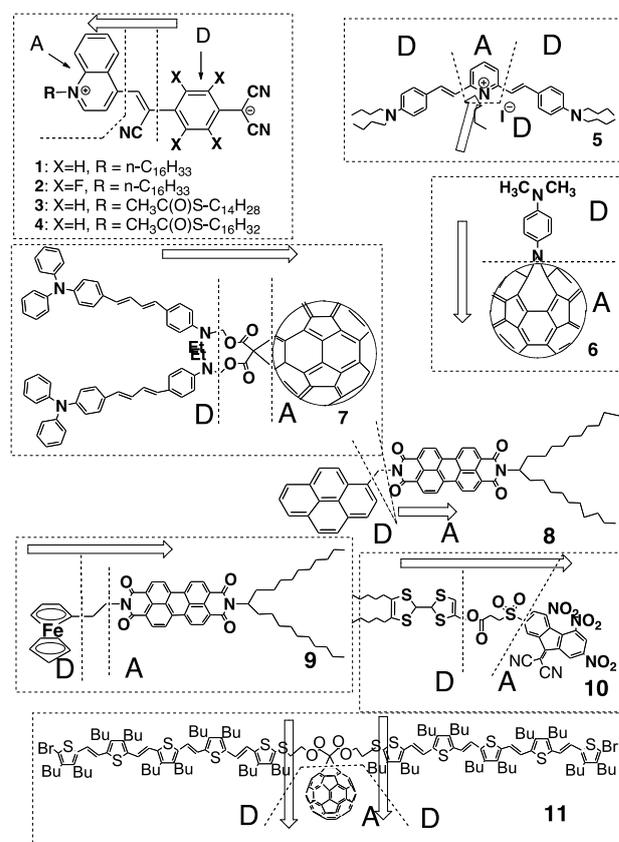


Fig. 1. Structures of the eleven rectifiers (1-11) characterized at the University of Alabama.

The AR rectification, or asymmetric conduction model, is ascribed to resonant transfer of electrons across the two metal/molecule junctions when the Fermi levels of the

electrodes match the HOMO or LUMO energies of the molecule.

Table 1. Results for eleven monolayer rectifiers (structures in Fig. 1): IVT=maximum of intervalence transfer band; RR=rectification ratio at maximum measured voltage $V \equiv -I(V)/I(-V)$; "Survives cycling?" \equiv if "yes", then rectification ratio persists upon repeated measurement of the same metal | monolayer | metal "sandwich".

Mole-cule	LB or LS?	IVT/nm	RR	Survives Cycling?	Ref.
1	LB	530	2-27	No	[14]
2	LS	530	5	Yes	[13]
3	LS	530	5	Yes	[13]
4	LB	504	3-64	No	[15]
5	LB	480	8-60	No	[16]
6	LB	720	2	No	[17]
7	LS	---	10	Yes	[18]
8	LB	---	2-5	No	[19]
9	LB	595	30	Yes	[19]
10	LB	1220	13	No	[20]
11	LS	---	6-60	Yes	[21]

The rectification measurements in the period 1997-2007 showed that: (1) a single monolayer of molecules **1** through **11** between macroscopic metal electrodes (at first Al, then Au) moderate rectification ratios $RR \equiv I(V_{max})/I(-V_{max})$ were found at $V_{max} = \pm 1$ V or larger; (2) the RR values do vary from pad to pad, and are moderate; (3) for molecules **1**, **4**, **5**, **6**, **8**, and **10** RR decreases progressively as the same "sandwich" or "pad" is measured repeatedly; (4) RR stays constant (no decrease) for monolayers of **2** and **3** because the molecules were transferred as an LB monolayer and immediately chemisorbed onto the Au bottom electrode, and for **7** and **10** because the monolayer is very space-filling and rigid (so rigid that LS rather than LB transfer was necessary; (5) the molecules rectify in the direction opposite [3] to what was predicted by AR; (6) inelastic electron tunnelling spectroscopy of **10** at 4.2 K showed a broad and asymmetric signal that is characteristic of orbital-mediated tunnelling [21]: this probably means that the current really does travel through (and not around) the molecules of **10** [21].

3 Newer rectifiers

A newly designed molecule **12** (Fig. 2) does rectify electrical current (Fig. 3) [22].

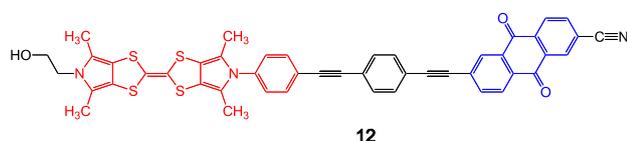


Fig. 2. Structure of a new rectifier (**12**) [22].

Molecule **12** chemisorbs quantitatively onto Au, and also forms a Pockels-Langmuir monolayer at the air-water interface (presumably with the hydroxyl group closer to

the water); under compression and over time molecules of **12** do slide past each other, quasi-reversibly, to create an aggregate multilayer (this was confirmed by atomic force microscopy) [22]. The IV curves show a rectification ratio RR at ± 1 V of about 80 (Fig. 3); RR increases considerably if the IV curve is studied between -2 and +2 Volts [22]. The orientation (tilt) of **12** in the monolayer is under study.

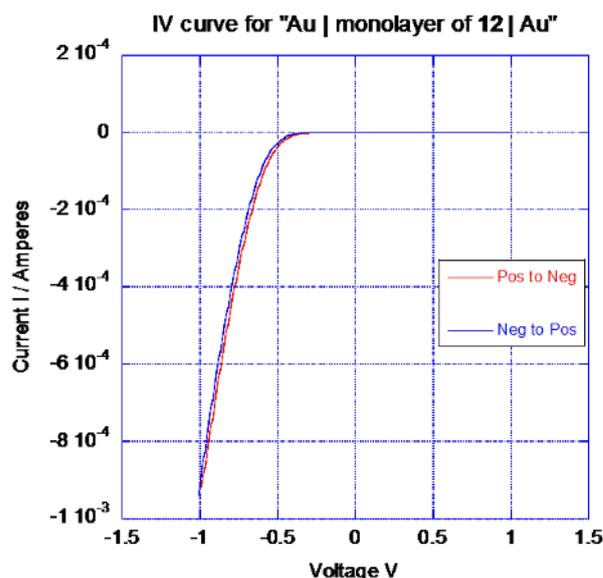


Fig. 3. IV curve for LB monolayer of new rectifier (**12**) [22].

4 Unimolecular amplifier

Theoretical calculations [11] have determined the conditions under which a three-terminal molecule, connected to three inorganic metal electrodes (Fig. 4), will be a power amplifier.

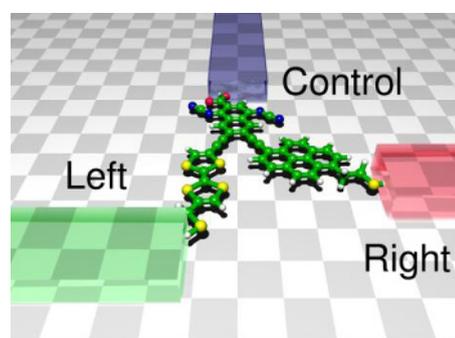


Fig. 4. Depiction of a candidate unimolecular amplifier attached to three metal electrodes (Left, Control, Right).

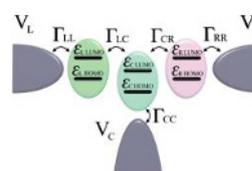


Fig. 5. The energy levels ϵ_a and the coupling energies Γ_i

The algorithm was based on Ref. [23]. The energy levels of the three moieties were ε_a ($a = \text{L HOMO, L LUMO, C HOMO, C LUMO, R HOMO, or R LUMO}$), estimated from a DFT calculation, with an assumed Lorentzian density of states (values for ε_a ranged between -2.5 to -5 eV). Γ_{ja} , the coupling energy to the electrodes j ($j = \text{L, C, R}$) and the moieties a , was set at 0.05 eV, but the coupling Γ_{CC} had to be smaller: 0.001 eV. The occupation number N_{ja} on each molecular level a due to electrode j depended on the energy ε_a and the chemical potential μ_j ; N_{ja} ranged between 0 to 2. The chemical potential μ_{j0} at zero bias was set to -5.0 eV for all j . The current I_{ja} between electrode j and level a was $I_{ja} = (\Gamma_j / \hbar) (N_{ja} - N_a)$ ($I_{ja} > 0$ if electrons were entering molecule). Within the molecule, levels could modify the occupations on each other. The current I_{ab} between levels a and b was $I_{ab} = (e \Gamma_{ab} / \hbar) (N_{ja} - N_b)$. At steady-state, the occupation of each level was constant, and the sum of all of the currents in and out of this level vanished. This model did not directly consider the geometry of the system. The equation for the molecular level energy was:

$$\varepsilon_a = \varepsilon_{a0} + U_a(N_a - N_{a0}) + U^{ee}_{ja}(\mu_j - \mu_{j0})$$

where U_a was energy by which the molecular level a changed when an electron was added to it or removed from it, while $U^{ee}_{ja} = 0.03$ eV was the energy by which the molecular level a changed in response to the electric field created by the voltage applied to electrode j . Calculations proceeded to self-consistency. The current between L and R electrodes shifted for a non-zero bias applied to the central electrode (**Fig. 6**): amplification was found both for when $U^{ee}_{ja} \neq 0$ (field-effect), and also when $U^{ee}_{ja} = 0$ (bipolar junction effect).

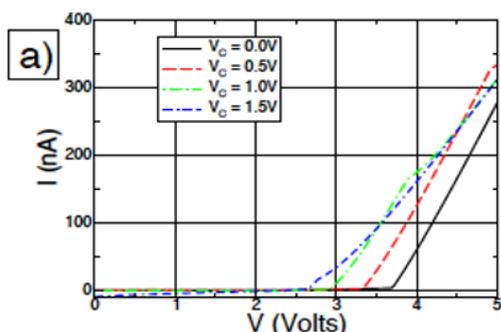


Fig. 6. Theoretical current (I)-voltage (V) plot for three-terminal molecule attached to three metal electrodes, which is displaced, as different potentials V_C are applied to the center (control) electrode: **this is amplification!**

Acknowledgments

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