Electrical Rectification by a Molecule: The Advent of Unimolecular Electronic Devices

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Received April 12, 1999

The Concept of Unimolecular Electronics

In 1959, the late Richard P. Feynman proposed, in his usual witty way, that there was “plenty of room at the bottom”, i.e., that atomic and molecular dimensions had not yet been exploited in information storage.1 In electronic technology, what was initially called “microminiaturization” did provide fantastic economies of scale, cost, and speed: the integrated circuits (IC) introduced by Noyce and Kilby were the beginning of this trend. It was observed that the scale of ICs or “computer chips” has halved, at first every 2 years, then every 18 months;2 this brought a concomitant increase in computing speed (“VAX on a chip”, then “Cray on a chip”) and an astonishing decrease in unit cost. However, there is trouble ahead. Circuit designers talk about “design rules”, the closest distance between adjacent electronic components in the IC. These design rules define the clock cycle, which is the time required to travel between the furthest components on the chip: shorter cycles mean faster computing. These design rules have now crept down to about 180 nm commercially. If photolithography is used, the design rules are limited, by Rayleigh’s criterion,3 to about one-half the wavelength of light used. Capacitative coupling between components and heat dissipation are perennial headaches. Three-dimensional integration (rather than planar integration) has remained an elusive goal. To achieve better performance, i.e., going to design rules of 100 nm or below, requires abandoning UV radiation and resorting to X-ray or electron beam lithography, with much higher error rates. At 50 nm, an even more drastic limit sets in: one can no longer “dope” Si uniformly. Present projections are that this 50 nm “silicon wall” will be reached by the year 2005.4

The idea of using molecules as electronic devices has gained attention and respectability in the past quarter century. By chemical insertion of electron-donating or electron-withdrawing groups, molecules can become one-electron donors (D) or one-electron acceptors (A). To work properly, the oxidation or reduction of these molecules must be chemically reversible. In group IV chemistry (today, group 14: Si, Ge), one dopes a crystal of Ge or Si with dilute concentrations of interstitial or substitutional electron-rich elements (group V, or 15: N, P, As, etc.) to achieve an “n-doped” material. To make a “p-doped” crystal, one dopes with group III (or 13: Al, Ga, In, etc.). Thus, “D” corresponds to “n”, and “A” corresponds to “p”. By accosting a micrometer-thick film of organic D molecules to a micrometer-thick film of an organic A molecules, one gets a microscopic DA rectifier (one-way conductor) of electrical current, equivalent to an inorganic pn rectifier.5 In the 1960s, and particularly in the early 1970s, organic charge-transfer crystals and conducting polymers yielded organic equivalents of inorganic electronic systems: semiconductors, metals, superconductors, batteries, etc.6 But this wave of “me-too-ism” did not create a new technology: the organic systems did not perform better, or less expensively, than their inorganic counterparts. The two niche areas that survived are liquid crystal displays and (maybe) light-emitting diodes based on conducting polymers.

In the early 1980s, sparked by three scientific conferences organized by the late Forrest L. Carter, the idea of “molecular electronics”, that is, electronic devices consisting solely of molecules, gained large-scale interest.7–9 Aficionados of biological processes started talking about “biomolecular electronics”. The term “molecular electronics” was extended to all electronic properties of polymers, crystals, etc.—what we might call “large-scale molecular electronics”. This field, as outlined above, has not fared well in the marketplace.

A persistent view has been that unimolecular, or “oligomolecular”,10,11 or “molecular-scale”12 electronics have a very bright future, just as the new millennium begins. Molecules, with their 1–3 nm sizes, should step in where inorganic chemistry finally fails. Thus, unimolecular electronics will come to the rescue: they will finally find a central role in electronic technology.

Milestones in Unimolecular Electronics

In the past 3 years, the following milestones have been reached:

(1) Differences in tunneling current across aliphatic vs aromatic chains were measured.13

(2) The electrical resistance of a single molecule (1,4-benzenedithiol) bonded to two Au electrodes was mea-
sured: it was a few megohms, because the work function of Au and the LUMO of the molecule were mismatched.\textsuperscript{14}

(3) The quantum of electrical resistance ($12 \text{k} \Omega$) was measured at room temperature when a carbon nanotube, glued to a conducting AFM tip, was lowered into liquid Hg.\textsuperscript{15}

(4) The Aviram–Ratner mechanism,\textsuperscript{16} slightly modified, was confirmed in both macroscopic and nanoscopic conductivity measurements through a monolayer of $\gamma$-hexadeyl-quinolinium tricyanomethanide, $1$; this is the first proven two-terminal molecular device.\textsuperscript{17} This result is reviewed in some detail below.

The Aviram–Ratner Ansatz of Unimolecular Rectification

In 1974, Aviram and Ratner proposed that a single organic molecule of the type $D-\sigma-A$ could be a rectifier of electrical current.\textsuperscript{16} This $D-\sigma-A$ "Gedankenmolekül" \textsuperscript{2} (never synthesized) would act as a rectifier, because the $D$ end is a good organic one-electron donor (but poor acceptor), $\sigma$ is a covalent saturated ("sigma") bridge, and $A$ is a good organic one-electron acceptor (but poor donor).

Equivalently, the highest occupied molecular orbital, or HOMO, of the $D$ part is relatively high, i.e., close to the "vacuum" state, and in resonance, possibly at a small applied bias $V$, with the Fermi level of one metallic contact (say, $E_{F1}$), while the LUMO of the $A$ part is relatively low and in resonance with the Fermi level of the other contact, $E_{F2}$; the electron then tunnels inelastically (i.e., with release of energy) through the $\sigma$ bonding network from the high-lying LUMO of $A$ to the low-lying HOMO of $D$. The device is asymmetric, because the HOMO of $A$ is relatively low, and the LUMO of $A$ is relatively high (Figure 1).

The "Gedankenmolekül" $D-\sigma-A$, when assembled between two metal electrodes $M_1$ and $M_2$, should form the rectifier $M_1[D-\sigma-A]M_2$, with easy electron transfer from $M_2$ to $M_1$ because of the "down-hill" tunneling from the excited-state $D^+-\sigma-A^-$ to the ground-state $D^0-\sigma-A^0$. Since the working thickness is about 2 or 3 nm, this should
be the world’s smallest electronic device. There are several criteria for the rational assembly of suitable D—a–A systems:

(1) \(I_D\) for the D end must be small and match as closely as possible the work function \(\phi_d\) of the metal layer \(M_1\) (Figure 1), but if \(I_D\) is too small, the molecule would oxidize in air.

(2) \(A_A\) for the A end must be as large as possible and match if possible the work function \(\phi_A\) of the metal layer \(M_2\). Figure 1 shows that this is not easy.

(3) It is very difficult to chemically convert a weak D into a stronger D, or a weak A into a stronger A, after the bridge \(\sigma\) is built. The coupling reaction forming the bridge between D and A is the last step, which must prevail over forming an intermolecular D–A salt instead.

(4) The assembly as a monolayer on a metal electrode must be efficient. The Langmuir–Blodgett (LB) technique transfers a physisorbed monolayer onto a solid substrate, but the molecules often need a long aliphatic chain, which may retard electron flow. Thiols and disulfides bind covalently to Au, but with a partially ionic Au–thiolate bond, which is an extra unwanted dipolar layer, or Schottky barrier. Silane attachment to silicon is less polar and preferable. The molecules should form compact and defect-free films.

**Multilayer LB Organic Rectifiers and LB Photodiode**

LB multilayer rectifiers have been made by Kuhn and co-workers, Sugi and co-workers, and Roth, von Kiltzing, and co-workers; these results could not be extended to Au, but with a partially ionic Au–thiolate interface. Excessive bias will, of course, lead to dielectric breakdown. Excessive heating can lead to chemical decomposition.

**Potential Unimolecular Rectifiers**

As reviewed elsewhere, collaborations with C. A. Panetta at the University of Mississippi and M. P. Cava at the University of Alabama netted several candidates for unimolecular rectification, i.e., D—a–A and D—π–A: molecules designed to form physisorbed LB films. Some of these are molecules 1 and 9–17 (Chart 1); molecule 1 became the first confirmed unimolecular rectifier.

The various D—a–A molecules that formed insoluble Pockels–Langmuir (PL) films at the air–water interface and can be mostly transferred as LB films onto solid substrates were the carbamates 9–13, and triptycene-quinone linked to TTF derivatives 14 and 15. The D—π–A zwitterions were 1, which formed a rectifier, and its benzachalcogenazolium analogues 16 and 17, which did not. The monofunctionalized strong acceptors BHTCNQ and HETCNQ could only be produced in low yields. The very interesting strong donor–strong acceptor TTF–C–BHTCNQ (9) was difficult to purify. The strongest films (highest collapse pressure) were obtained with 10a. As predicted, the triptycenequinone (weak A) in 14 and 15 could not be converted to triptycene-dicyano-quinodimine (strong A) as the last synthetic step.

**Initial Rectification Reports**

The first rectification attempts, macroscopic or nanoscopic using an STM, were unsuccessful. Several asymmetric current–voltage (I–V) curves were reported in STM experiments on other systems: Cu tetrazazoporphrin bonded to carboxylated HOPG, an alkylated hexabenzocoronene, and an oligophenylethynyl-benzenthioil. Electrochemical rectification at a monolayer-modified electrode was reported.

**Rectification in Pt|LB Film|Mg|Ag Sandwiches**

Samples and co-workers found that an LB multilayer of DDOP–C–BHTCNQ, 10a, sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film; they succeeded in making macroscopic defect-free LB multilayers and depositing atop the organic layer a metal film of magnesium (shadowed with Ag) without shorting the device. However, 10a does not contain a strong donor moiety, i.e., \(I_A\) is probably too large for an Aviram–Ratner rectifier. The observed rectifying behavior of 10a was later
reinterpreted to be due not to molecular rectification, but
to Schottky barrier formation between Mg and TCNQ, i.e.,
to the formation of a salt, either Mg$^{2+}$TCNQ$^{-}$ or
Mg$^{2+}$((TCNQ$^{-}$))$_2$, at the metal–organic interface.43,44

Sambles’s group also found asymmetries in an LB
multilayer of the ground-state zwitterion C$_{16}$H$_{33}$Q
$^{-}$3CNQ, 1, sandwiched between Pt and Mg electrodes;30 there was
also a slight I–V asymmetry for an LB monolayer of 1.30

To partially alleviate doubts about a possible Schottky
barrier, an insulating LB layer of $\omega$-tricosenoic acid was
next put between 1 and the electrodes; the I–V asymmetry
persisted.45,46 It was thus claimed that molecular rectifica-
tion had been observed, albeit between asymmetric metal
electrodes.45

Rectification in Al|Al$_2$O$_3$|LB Monolayer|Al$_2$O$_3$|Al
Sandwich

A very thorough repetition and major amplification of
Sambles’s pioneering work on C$_{16}$H$_{33}$Q–3CNQ, 1, was
carried out.17,27,47–52 We review first the general physical
and chemical properties of 1. The synthesis of 1 was vastly
improved.17 Cyclic voltammetry reveals that 1 is a weak
reversible one-electron acceptor, with a reduction half-
wave potential (−0.513 V vs SCE in CH$_2$Cl$_2$) close to that
of $p$-benzoquinone; the second reduction and the first
oxidation of 1 are electrochemically irreversible.17 If one
holds the electrochemical potential at the first reduction
potential and measures the electron paramagnetic reso-
nance spectrum, the spin densities of the negative ion
radical 1 are mostly localized on the 3CNQ ring;50
therefore, the LUMO of 1 is mostly localized on the 3CNQ
moiety. The dipole moment of 1 in CH$_2$Cl$_2$ solution is 43
(8 D, as befits a zwitterion with a 10.5-Å separation
between the positive charge (on the quinolinium N) and
the negative charge (on the dicyanomethylene bridge).17
The intense blue or green color of a solution of 1
(depending on solvent) disappears at the first trace of acid
but is recovered if the solution is exposed to ammonia
vapor. This blue or green absorption, probably due to an intervalence transition (IVT) band or intramolecular charge-transfer transition, is narrow, intense, and hypsochromic: this peak shifts from \( \lambda_{\text{max}} = 838 \text{ nm in CHCl}_3 \) (least polar solvent) to \( \lambda_{\text{max}} = 711 \text{ nm in CH}_3\text{CN} \) (most polar solvent). There are two fluorescence emissions, one in the visible region (corresponding to UV absorption bands) and the other in the near-infrared region. The excited-state dipole moment is calculated at between 3 and 9 D. The IVT transition is probably to an excited singlet state, rather than to a biradical state, and may not involve a large change in the torsion angle \( \theta \) (shown in structure 1); i.e., it is probably not of the twisted internal charge transfer (TICT) type.

Although 1 is not a strong donor—strong acceptor molecule, it has a spectroscopically allowed transition between a ground state with a high dipole moment and an excited state with a low dipole moment. In contrast, in molecule 16a, the loss of vibronic structure, as the dielectric constant of the solvent increases, masks any solvatochromic shift in the absorbance maximum; this lack of strong solvatochromism may help explain why LB films of 16 or 17 do not rectify. Simple semiempirical MO calculations (AM1, PM3) do not yield a large ground-state dipole moment for 1, unless \( \theta \approx 90^\circ \). Larger dipole moments are obtained in LDA calculations. There is no evidence of a proposed TICT transition in 1 due to a large internal rotation, the \( ^1\text{H} \) NMR of the H bonded to the ring carbon attached to the quinolinium N atom shows a large chemical shift (relative to what is expected from neutral quinoline) due to the zwitterionic ground state; there is no change in the NMR spectrum as a function of temperature. Evidently, 1 has some non-zero twist angle \( \theta \) between the quinolinium ring and the phenyl ring, due to a steric hindrance, which guarantees that the ground state is not that of a cyanine dye (where the zwitterion state \( D^+ - \pi - A^- \) would be degenerate) but rather that of a zwitterion. 1 forms multiply twinned crystals, whose unit cell could not be indexed. However, the crystal structure of a related compound, picolytricyanoquinodimethan, or picolinium tricyanoquinodimethanide, 18 (Chart 1), exhibits a twist angle \( \theta = 30^\circ \) (dihedral angle between the pyridinium ring and the phenyl ring of 3CNQ).

When left in air and intense sunlight for weeks, a solution of 1 can discolor, by some unknown mechanism. Most manipulations of 1 were thereafter carried out with minimum exposure to light. 1 forms PL films at the air–water interface; by using a darkened room, a collapse area of 50 Å\(^2\) at a collapse pressure of 34 mN m\(^{-1}\) was seen. The monolayer thickness (X-ray diffraction, ellipsometry) is 23 Å, which means that this 30 Å long molecule is inclined by about 45° to the film normal. Z-type multilayers form on Al, as depicted in Figure 2b. A grazing-angle Fourier transform infrared spectrum of a monolayer of 1 on Al shows two CN peaks at 2139 and 2175 cm\(^{-1}\). The X-ray photoelectron spectrum of a multilayer shows three N 1s peaks; the valence band onset is at -7.8 eV vs vacuum, close to the calculated (PM3) HOMO at -7.8 eV. The intense IVT band is at \( \lambda_{\text{max}} = 565 \text{ nm in the LB monolayer} \) and also in the LB multilayer.

The rectification work was performed both on macroscopic Al/LB film/Al sandwiches and by nanoscopic STM. Sambles found that Mg perturbs a physisorbed LB film the least. We decided to use Al on both sides of the LB film but cryocooled to 77 K the glass/Al/LB film assembly, to minimize the thermal load on the LB film as the Al pad electrode is deposited from the vapor phase. The LB films were thoroughly dried, to prevent any spurious effect due to moisture (which has a large effect on the electrical characteristics of Y-type centrosymmetric arachidic acid multilayers). A drop of Ga/In eutectic was used to make contact with Au wire electrodes, as shown in Figure 2. Asymmetric I–V curves were seen in a four-monolayer Z-type LB film, as well as in a four-monolayer film with a Mg electrode between the organic layer and the top Al pad, and even for a single monolayer (Figure 3). In a control experiment, no I–V asymmetry was seen for Y-type multilayers of arachidic acid after careful sample drying. Rectification for 1 was also seen, as a function of temperature, between 370 and 105 K (Figure 4). The maximum measured rectification ratio (at 1.5 V, Figure 2).
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I ∝ V (Figure 3b); past V = 0.8 – 1.3 V, sample-dependent, an enhanced current is observed (Figure 3a and 3b).\textsuperscript{17} The current measured amounts to about 0.33 electrons per molecule\textsuperscript{1 s}\textsuperscript{1}.\textsuperscript{17} Of course, not all Al/monolayer/Al “pads” rectify. After one discards the shorted junctions, or the junctions that short during the experiment, there are still several pads which exhibit either symmetrical I–V curves, or curves which “rectify the wrong way”; these “aberrant” junctions show lower currents and a characteristically different dependence on voltage.\textsuperscript{52} The direction of the current for forward bias, shown in Figure 2, indicates that the negative charges are “pushed” by the polarity of the electrode from the dicyanomethylene end, through the bridge, to the quinolinium end of the molecule. The Aviram–Ratner mechanism for D–σ–A molecules considered an undissociated ground-state D\textsuperscript{0}–σ–A\textsuperscript{0} and a zwitterionic excited-state D\textsuperscript{+}–σ–A\textsuperscript{+}; this mechanism can be trivially modified and inverted for the case where the ground state is mostly zwitterionic (D\textsuperscript{+}–π–A\textsuperscript{+}) and the excited state is mostly undissociated (D\textsuperscript{0}–π–A\textsuperscript{0}).\textsuperscript{17}

The rectification was also verified for a 15-layer film of \textbf{1} on HOPG by STM,\textsuperscript{17,47} and a small I–V asymmetry was even seen for monolayer of \textbf{1} on HOPG,\textsuperscript{17} but there is low adhesion of that first monolayer on HOPG.

The Aviram–Ratner mechanism\textsuperscript{16} for unimolecular rectification used an undissociated ground-state D\textsuperscript{0}–σ–A\textsuperscript{0} and a relatively low-lying zwitterionic excited-state D\textsuperscript{+}–σ–A\textsuperscript{+}. In the initial conception, this excited state could be a biradical,\textsuperscript{18} i.e., a state where D is oxidized and A is reduced. This is necessary if the length of the σ bridge makes the intramolecular charge-transfer transition moment very small. However, when there is appreciable intramolecular mixing of states, or an observable interference transition (IVT), then a biradical D\textsuperscript{+}–σ–A\textsuperscript{+} state is probably not necessary, provided that the change in dipole moment upon excitation is reversible: then D\textsuperscript{+}–σ–A\textsuperscript{+} could also be an excited singlet state. If the ground state is zwitterionic D\textsuperscript{+}–π–A\textsuperscript{+}, and the excited state is undissociated D\textsuperscript{0}–π–A\textsuperscript{0}, then the Aviram–Ratner mechanism can work... “backwards”:\textsuperscript{17} The direction of rectification, shown in Figure 2, agrees with this mechanism.

Thus, 25 years after it was proposed, the Aviram–Ratner ansatz has been unequivocally and finally verified, using either Al electrodes on both sides of a monolayer or an STM\textsuperscript{17,27} A 2.3 nm thick unimolecular device is now a reality.

### Puzzles

There are still some unsolved puzzles:

1. The sandwiches using Al or Mg electrodes bear an inevitable oxide layer. Al is a “valve” metal, and its thin covering with oxide is not defect-free, unless it is anodized.\textsuperscript{36,57} Control experiments using arachidic acid\textsuperscript{19} reduce the problem but do not eliminate it. Adhesion of LB films to hydrophilic Au is poor, and depositing oxide-free Au pads on an LB monolayer destroys it by heating, despite cryocooling the sample holder.

2. The Ga/In eutectic has, typically, a 100 kΩ contact resistance with the Al pads,\textsuperscript{51} which is 1–2 orders of
magnitude less than the resistance of the LB monolayer. When the eutectic wets the Al by piercing through the oxide layer, then the pad lifts off the monolayer. Ag paste has similar problems.

(3) The measured current, 0.33 electrons molecule⁻¹ s⁻¹ (5.3 x 10⁻²⁰ A), is many orders of magnitude lower than the currents measured in an STM experiment (10 pA to 1 nA): maybe only one molecule in a million is “at work”.

(4) The reduction of the rectification ratio upon repeated cycling and the number of “aberrant” junctions could be partially eliminated by chemisorbing a suitably modified version of molecule 1 onto Si or Al. A thiol termination is incompatible with the acid-sensitive molecule 1. A silanized version of 1 was prepared but in initial experiments did not form a uniform layer on Si.

(5) The Volta, or Kelvin potential of about 0.5 V for a monolayer of 1 at the air–water interface or for a dry monolayer of 1 on Al is 1 order of magnitude lower than expected for a zwitterionic monolayer.

(6) Asymmetrical STM currents for molecules that have no rectifying moieties are puzzling; it is likely that the molecules, if placed asymmetrically within the potential field, can experience asymmetric tunneling currents.

(7) A theoretical calculation of the I–V asymmetry for 1 would be welcome.

(8) Can all ground-state zwitterions with a strong IVT band and a low-lying undissociated excited state rectify?

(9) How can we make an active electronic device (nþpþn transistor, or logic gate)?

Conclusion

The goal of Aviram–Ratner rectification through an oriented D⁻−→−Τ−−A− monolayer has been achieved. Much exciting work lies ahead, as we proceed toward making unimolecular electronics a practical reality in the 21st century.

I am indebted to Profs. C. A. Panetta, N. E. Heimer, M. P. Cava, and G. J. Ashwell and Dr. M. V. Lakshminanth for their help. I am grateful to Profs. J. R. Sambles and L. Brønchorst and Drs. A. Aviram and S. Roth for their suggestions. I was helped by many students and post-docs. The US National Science Foundation (DMR-94-20699) and DOE-EPSCoR (DE-FC02-91-ER-75678) supported this work.

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Keywords: Rectifiers Unimolecular electronic devices Single-molecule electronics IETS Monolayers Langmuir–Blodgett
Langmuir–Schaefer Self-assembled monolayers Break junctions Mooreâ€™s law Aviram–Ratner rectifier

1. Introduction

By a mechanically controlled âœœbreak junctionâ€ (MCBJ) technique a single benzene-1,4-bithiol was chemisorbed to two Au shards. Molecules either singly, or in parallel as a monolayer array (one with a measured resistance of several M [9], molecule thick), can be either passive or active electronic components. Scanning Tunneling Spectroscopy (STS) showed that the current in unimolecular reaction rate theory describes the isomerization, dissociation, or decomposition of a single reactant molecule or complex in the gas phase. Early work on unimolecular reactions was hampered by experimental difficulties and theoretical misconceptions. Some purportedly unimolecular reactions turned out to be multistep reactions, chain reactions, or reactions catalyzed by reactor walls. For truly unimolecular reactions, it was not initially clear why the rate should scale with the first power of concentration while the frequency of collisions scales with the square of concentration.

A unimolecular electronic device should perform active electronic functions by exploiting the energy levels, or conformations, of a single molecule, or a very few molecules, and should be addressable electrically by macroscopic electrodes. We found unimolecular rectification in a molecule, Î³-hexadecylquinolinium tricyanoquinodimethanide, 4, in which the ground state is Zwitterionic: D-Î€-A, while the first excited state is undissociated: D-Î€-A. This 2.3 nm long unimolecular device, measured three years ago between Al electrodes and now between Au electrodes, confirms a 1974 proposal by Aviram and

ChemInform Abstract: Electrical Rectification by a Molecule: The Advent of Unimolecular Electronic Devices. Article. Sep 1999. â€” The electronic properties of molecules can in some cases be elucidated by scanning tunneling microscopy and spectroscopy. The currentâ€“voltage characteristics through the aromatic core of a benzocoronene molecule (1), localized with submolecular resolution, are the same those of a diode, and are caused by the properties of a single molecule in contact with two electrodes. R = n-C12H25.
