

# Unimolecular Rectifiers and Prospects for Other Unimolecular Electronic Devices

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**ABSTRACT:** We briefly review the progress towards useful one-molecule electronic devices, toward the ultimate reduction in integrated circuit sizes, and then describe five unimolecular rectifiers, or one-way conductors of electrical current:  $\gamma$ -hexadecylquinolinium tricyanoquinodimethanide, an acetyl sulfoxide derivative of this compound, 2,6-di[dibutylamino-phenylvinyl]-1-butylpyridinium iodide, dimethylanilino-aza[C60]fullerene, and a new fullerene derivative. © 2004 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 4: 291–304; 2004; Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.20010

**Key words:** organic rectifiers; Langmuir–Blodgett films; unimolecular electronics

## Introduction

“Molecular electronics” (ME), or “molecular-scale” electronics, defined narrowly, is the very new study of electronic processes measured or controlled on the scale of a single molecule or a molecular cluster.<sup>1</sup> In contrast, the broadly defined “molecule-based” molecular electronics, is the study of bulk electronic properties of crystals or polymer aggregates: this mature area has established that the typical electrical properties of inorganic materials can also be found in organic crystals and polymers.<sup>1</sup>

We focus here on the former, much narrower definition: we emphasize processes that involve a single molecule, or small cluster of molecules, or molecules interrogated in parallel, for their single-molecule properties: we name this field “unimolecular electronics” (UE). Given the small scale of molecules (about 0.5 to 3 nm), UE may be thought as the *reductio ad absurdum* of standard electronics, and as a valid goal of nanotechnology.

Of course, the electronic properties of single molecules have been studied by spectroscopy for a long time, since photons can interrogate molecules in the gas phase, in the solid state, or in solution, without caring exactly where the mole-

cules are located within the medium; however, electrical circuits using photons as control elements cannot easily be reduced to nm dimensions. In contrast, UE implies “reaching out and touching” individual molecules with electrodes, and exploiting their chemical structure to control the flow of electrical signals.

UE may have been presaged indirectly by Feynman (“there is plenty of room at the bottom”), who, however, did not mention molecules.<sup>2</sup> UE started with the proposal by Aviram and Ratner (AR) that electrical rectification, or diode behavior, should be exhibited by a single molecule with suitable electronic asymmetry.<sup>3</sup>

The detection and understanding of unimolecular rectification will be the main subject of the present article, which updates a recent, extensive review.<sup>4</sup>

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Since 1996, UE developed, thanks to many direct measurements of the electronic behavior of single molecules, of monolayers of molecules assembled by the Langmuir–Blodgett (LB) method, or of “self-assembled monolayers” covalently bonded to an inorganic bulk substrate (e.g. organothiols on gold). We have finally learned how to “touch” molecules, and measure their individual electrical characteristics. A single molecule can be touched either on a bulk electrically conducting surface, by a scanning tunneling microscopy (STM) tip or by a conducting-tip atomic force microscopy (AFM) tip, or when placed between two Au tips, or else by making electrical contacts to sandwiches of organic monolayers placed between super-thin inorganic metal pads (with areas from  $1\ \mu\text{m}^2$  to  $1\ \text{cm}^2$ ). The current vs. voltage (IV) characteristics can be measured either for a single molecule, or, in parallel, for a monolayer of molecules, or many layers, either locally, by scanning tunneling spectroscopy (STS) or, as a macroscopic average, over a pad. The challenge is to fabricate the “metal | organic | metal” sandwiches or cells, while not over-heating or damaging the organic layer, and avoiding the interpenetration of the metal filaments and the organic layer.

UE is receiving attention in part, because of the recent interest in nanotechnology, but in greater part, because there is a hope that molecules could be used as active electronic devices. There are concerns about how much further silicon-based integrated circuits can be shrunk, to make components closer, and thus the speed of computing greater. These concerns are fed by the empirical correlation that, since the mid 1960s, the computing power of integrated circuits has doubled, at first every two years and now every 18 months or

so (Moore’s “law”).<sup>5</sup> This is driven by the steady decrease in the “design rules” for integrated circuits (i.e. the smallest distance between adjacent components).<sup>6</sup> Now, design rules below 100 nm are common. However, this shrinkage cannot reach, say, 1 nm. It is thought that, below design rules of 30 nm to 20 nm, huge technical hurdles may face silicon-based electronics, while molecules, with sizes 0.5 to 3 nm, can presumably do similar tasks with greater facility. Naturally, scientists and engineers advancing silicon-based electronics may find unexpected technical breakthroughs: this goal may be a “moving target” for UE. But it is fun to try to be both successful and, ultimately, useful.

Here is a brief and subjective list of recent advances in UE:

- (1) STS showed that electrical currents across alkanethiols are smaller than those across aromatic thiols.<sup>7</sup>
- (2) “Break junction”: a nanogap of about  $8\ \text{\AA}$  between two Au electrodes, fabricated by cracking reproducibly the silicon support onto which the Au wire was bonded, allows a single molecule of 1,4-benzenethiol, to bond to both Au shards; the measured resistance of this “Au | 1,4-benzenedithiolate | Au” sandwich is several  $\text{M}\Omega$ .<sup>8</sup>
- (3) Molecules of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-benzene-1-thiolate, attached to Au on one side and topped by a Ti electrode on the other, exhibit negative differential resistance (NDR).<sup>9</sup>
- (4) The Landauer quantum of resistance,<sup>10</sup>  $(h/2e^2) = 12.9\ \text{k}\Omega$  was measured at room temperature between a multi-walled carbon nanotube, glued to a conducting atomic force microscope (AFM) tip, and a pool of liquid Hg.<sup>11</sup>



► Robert Melville Metzger was born in Yokohama, Japan on 7 May 1940 of Hungarian parents, was educated in Paris (France), Merano (Italy), and Enfield (UK). He speaks, reads and writes five live languages. Emigrating to the US in 1959, he obtained his B. S. degree in Chemistry at UCLA in 1962 (research advisor: William F. Libby), his Ph.D. at Caltech in 1968 (research advisor: H. M. McConnell), did post-doctoral work at Stanford with the late Paul G. Simpson and Michel Boudart, and also taught Italian at Stanford. From 1971 to 1986 he was on the faculty in the Chemistry Department of the University of Mississippi (Asst. Prof., Assoc. Prof., Prof., Coulter Prof.). Since 1986 he has been at the University of Alabama as Professor of Chemistry, and is a member of the Tricampus Materials Science Ph.D. program. He has been a visiting professor at the Universities of Heidelberg, Bordeaux, Kyoto, Parma, Padova, Firenze, and Rennes. His research focus has been on electron transfer processes in organic crystals and monolayers. He has published 201 papers, edited 1 book and 5 volumes of symposium proceedings, directed 12 Ph.D. dissertations and 1 M. S. thesis. He has given 66 invited talks, 123 contributed talks, and 158 departmental seminars in 22 countries. For his research on unimolecular rectification he received the 8th Blackmon-Moody Award at the University of Alabama in 1998. ■

- (5) Field-effect transistor (FET) behavior was observed by STM for a single-walled carbon nanotube curled over parallel Au lines, with the STM acting as a gate electrode; the power gain was only 0.33.<sup>12</sup>
- (6) An LB monolayer of a bistable [3]catenane closed-loop molecule, with a naphthalene group as one “station”, and tetrathiafulvalene as the second “station”, and a tetracationic catenane hexafluorophosphate salt traveling on the catenane, like a train on a closed track, was deposited on polysilicon as one electrode, and topped by a 5 nm Ti layer and a 100 nm Al electrode. The current–voltage plot is asymmetric as a function of bias (which may move the train on the track), and a succession of read–write cycles shows that the resistance changes stepwise.<sup>13</sup>
- (7) The organometallic equivalent of a single-electron transistor (SET) has been realized at 0.1 K with an organometallic Co(II) complex.<sup>14</sup>
- (8) Unimolecular rectification across an LB monolayer of hexadecylquinolinium tricyanoquinodimethanide was first detected between Mg and Pt electrodes<sup>15,16</sup> and later thoroughly confirmed between Al electrodes<sup>17,18</sup> and, most recently, even between oxide-free Au electrodes,<sup>19,20</sup> to be a variant of the AR mechanism.<sup>3</sup> Most recently, we established rectification by LB monolayers of three new molecules between gold electrodes,<sup>21–23</sup> and also by a self-assembled thioacetate bonded onto Au.<sup>24</sup>

We first discuss metallic contacts; next, we present the AR proposal, followed by assembly techniques needed to study unimolecular rectification, and mechanisms that can cause rectification; then we describe the main experimental data for the confirmed unimolecular rectifiers; finally, we suggest some ideas for future progress.

## Metal Contacts

All-organic computers can be conceived, but at present the synthetic complexity of such a venture (making organic electronic components and also making organic or polymeric “backbone” interconnects) may seem overwhelming. At the present time, only two-terminal devices, such as resistors, insulators, or rectifiers have been studied: all these are interrogated by inorganic metal contacts (Au, Ti, Al, Mg, graphite, etc.).

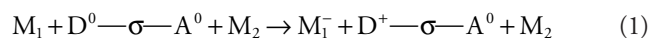
Three-terminal molecular devices do not exist at present (excluding the STM-probe interrogated FET<sup>12</sup> or the the SAT<sup>14</sup>). One can do some logic with two-terminal diodes, or with negative differential resistance devices, but the present semiconductor industry mostly uses three-terminal FET logic. This competition from industry suggests that somebody must first master the bringing of three terminal metal filaments within 1 nm of each other, without short circuits, then synthesize molecules with three terminations, to bridge and

connect across these gaps. The goal of bringing such electrodes together has interested several laboratories.<sup>14,25</sup> When that goal is reached, and power gain is demonstrated through three-terminal molecules, then all the necessary molecular electronic components will be present, and one can envision constructing all-organic backbones.

Another goal is to do with molecules what cannot easily be done with inorganic compounds: a me-too competition with proven commercial devices will always favor the existing technology.

## The Aviram–Ratner Proposal

The first concrete suggestion for UE was the AR proposal<sup>3</sup> that a one-molecule rectifier could be achieved with a D— $\sigma$ —A molecule, where D is a good one-electron donor with relatively low first ionization potential  $I_D$ , where  $\sigma$  is some saturated covalent “sigma” bridge, and where A is a good one-electron acceptor with relatively high electron affinity  $E_A$ , when this molecule is somehow placed between two appropriate metal contacts  $M_1$  and  $M_2$ . The purpose of  $\sigma$  is to decouple the molecular orbitals of the donor moiety D from the molecular orbitals of the acceptor moiety A. Of course, the molecular orbitals belong to the whole molecule, but they often are more localized on one moiety than the other.<sup>3</sup> If the decoupling between D and A is complete, then intramolecular electron transfer becomes impossible. The molecular ground state of D— $\sigma$ —A has a relatively lower dipole moment, and can be written as  $D^0$ — $\sigma$ — $A^0$ , while the first excited state is much more polar, has a higher dipole moment, and can be written as the zwitterionic or betaine state  $D^+$ — $\sigma$ — $A^-$ .<sup>3</sup> Given what is known about organic molecules, it is likely that resonant transfer would be possible (Figure 1) when the Fermi energy  $E_F$  of  $M_2$  is resonant with the lowest unoccupied molecular orbital (LUMO) of the A moiety or part (which is close to the negative of the electron affinity  $A_A$  of the A moiety), and the highest occupied molecular orbital (HOMO) of the D moiety (which is close to the negative of the ionization potential  $I_D$  of the D moiety), is in resonance with  $E_F$  of the metal  $M_1$  (upon the application of a positive bias  $V$  to  $M_1$ ). The intramolecular electron transfer would be an inelastic tunneling from the excited electronic state  $D^+$ — $\sigma$ — $A^-$  to the ground electronic state  $D^0$ — $\sigma$ — $A^0$ . The mechanism would consist of two resonant electron transfers across metal–organic interfaces:

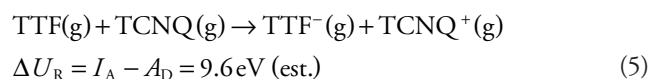
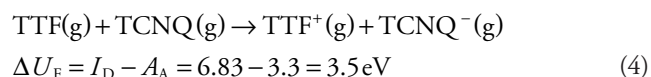


followed by (or simultaneous with) an inelastic downhill intramolecular electron transfer:



which achieves, overall, the migration of one electron from  $M_2$  to  $M_1$ .<sup>3</sup>

AR suggested, for  $D - \sigma - A$ ,  $D$  = tetrathiafulvalene (TTF),  $A$  = tetracyanoquinodimethan (TCNQ), because these were, respectively, a good organic donor  $D$ , and one of the best organic acceptors  $A$ , as evidenced by the following data (for the ions at infinite separation):



The AR proposal involves through-molecule tunneling, with two elastic metal-to-molecule electron transfers, requiring resonance between the metal Fermi levels and two molecular energy levels, plus one inelastic decay from the electronic excited state to the ground state (with either the creation of phonons, i.e. heat, or the emission of a photon): all these processes must be inherently fast (ps to ns), compared with translations,<sup>13</sup> conformational transitions, or molecular rearrangements (s to  $\mu$ s).

Rectification must involve a large change in the molecular dipole moment  $\mu$  (which is much larger for  $D^+ - \sigma - A^-$  than for  $D^0 - \sigma - A^0$ ) and a significant coupling (Mulliken transfer integral  $\langle D^+ - \sigma - A^- | \mu | D^0 - \sigma - A^0 \rangle$ ) between the two electron states. These requirements are the same for a molecule to possess a large second-order nonlinear optical polarizability  $\beta$ : there is a logical connection between molecular rectification and second-order optical susceptibility.

### Conditions for Rectification by Organic Monolayers

There are three distinct processes for asymmetrical conduction, i.e. rectification, in “metal | organic | metal” assemblies. The first process is due to Schottky barriers at the “metal | organic” interfaces: a surface dipole will be formed at one or both interfaces, and, if these dipoles differ in size, then the currents at positive bias will differ from those at negative bias.<sup>26</sup> We shall call molecules that rectify by this process “S” (for Schottky) rectifiers.<sup>27,28</sup>

The second process arises, if the “chromophore” (i.e. the part of the molecule whose molecular orbital must be accessed during conduction) is placed asymmetrically within a “metal | molecule | metal” sandwich, e.g. because of the presence of a

long alkyl “tail”.<sup>29,30</sup> We shall call molecules that rectify by this process “A” (for asymmetric) rectifiers.<sup>31,32</sup>

The third process occurs when the current passing through a molecule, or monolayer of molecules, involves electron transfers between molecular orbitals, whose significant probability amplitudes are asymmetrically placed within the chromophore: this third process we think of as true “unimolecular rectification”, and we shall call this process “U” (for unimolecular) rectification;<sup>3,29</sup> these “U” rectifiers are what we endeavor to achieve.

The practical requirements for assembling organic molecules between two inorganic metal electrodes may mean that the monolayer may behave simultaneously as an “A”, or “S”, or “U” rectifier: thus, pure “U” rectifiers are rare.<sup>30</sup>

### Current and Resistance in a Metal–Molecule–Metal System

The electron transport from metal to organic material to metal has received much theoretical attention; we single out some of our recent contributions.<sup>29,33</sup> First of all, asymmetries in current–voltage plots (usually ascribed to rectification) also occur if a chromophore is placed asymmetrically within the electrode gap (“A” rectifiers).<sup>29</sup> This has been seen in early STM experiments.<sup>34</sup> Second, an analytic expression for elastic electron transfer between a metal and a single molecular orbital of a molecule is:<sup>20,33,35</sup>

$$I = I_0 \{ \tan^{-1} [\theta(E_0 + peV)] - \tan^{-1} [\theta(E_0 - (1-p)eV)] \} \quad (6)$$

Here  $E_0$  is the energy of the molecular orbital,  $V$  is the applied potential, and  $p$  is the fractional distance of the molecule from, say, the left electrode (if the molecule is centered in the gap,  $p = 1/2$ ). One question is whether rectification must involve two levels, as in the AR proposal,<sup>3</sup> or only one level,<sup>20,33,35</sup> as in eq. 6.

Tunneling currents across molecules are expected to be approximately exponential to some power of the potential, so a sigmoidal curve is usually seen, symmetrical about  $I = 0$  and  $V = 0$ . The various models have been discussed in some detail.<sup>20</sup> It is only when the connection across the metal electrodes is macroscopic, i.e. involves a very large number  $N$  of channels ( $N \rightarrow \infty$ ), or if scattering occurs during the electron transport<sup>36</sup> that Ohm’s law becomes applicable:

$$V = IR \quad (7)$$

In rectification measurements the rectification ratio (RR) is defined as the current at a positive bias  $V$  divided by the

absolute value of the current at the corresponding negative bias  $-V$ :

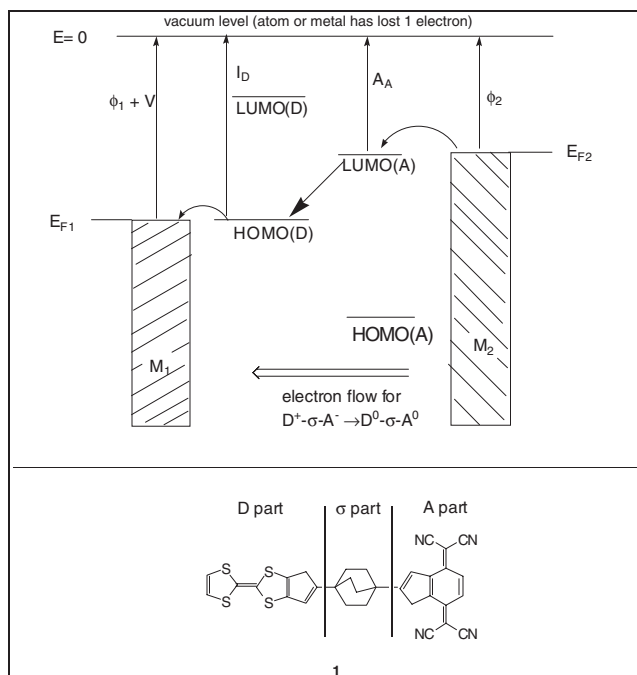
$$RR(V) = |I(V)|/I(-V) \quad (8)$$

### Assembly Techniques: Physisorption Versus Chemisorption

As one designs molecules for unimolecular rectifiers or, some day, for unimolecular amplifiers, one must decide how the designed molecules will be assembled and measured. One must “go out and touch a molecule”. For putting a molecule on a metal electrode, two techniques are available, physisorption and chemisorption.

Physisorption, or physical adsorption, includes the random deposition from a vapor onto a solid substrate, or the organized transfer of an ordered monolayer (Langmuir film) from the air–water interface to a solid substrate, forming an LB monolayer or, if the transfer is repeated, an LB multilayer. LB physisorption has two advantages: one is that the percent coverage of the surface at the moment of transfer can be measured directly as the film transfer ratio; the other is that Schottky barriers, or surface dipoles formed during chemisorption, are avoided. Physisorption has two inherent limitations: first, after transfer, the structure of the vapor-deposited film, or of the LB monolayer or multilayers, may change over time, as the film tends towards a thermodynamic steady state; second any other adsorbates already present on the metal electrode (e.g. the adsorbates that descend from air onto gold surfaces within 15 minutes after exposure to ambient air) are not displaced, but covered by the LB layer(s).

Chemisorption includes the formation of a covalent bond of thiols and similar compounds to gold and similar metals, or of chlorosilanes to hydroxyl-covered silicon surfaces: these have been labeled as “self-assembled monolayers” (SAMs). Chemisorption involves large heats of bond formation, and has two advantages: first, the chemical reaction displaces from the surface any previously physisorbed adsorbates; second, the adsorbed species, once bonded, are difficult to remove. There are three disadvantages: the uncertain degree of coverage, the possibility of further chemical reactions, and the formation of surface dipoles. One can hope that by exposing a surface long enough (e.g. a few days) to the adsorbate, the heat of reaction will help drive the reaction to produce “full coverage” of a Langmuir, or monolayer, on the solid surface. There are spectroscopic techniques to monitor this deposition, but they are accurate to only maybe  $\pm 0.1$  Langmuir. For thiolates, the bonding to gold is partially ionic, so one creates a surface dipole (1 or 2 debyes): i.e. an “S” rectifier. The polarity of silane links on silicon is much less, but there is also less known about how ordered the silanes can be on silicon.



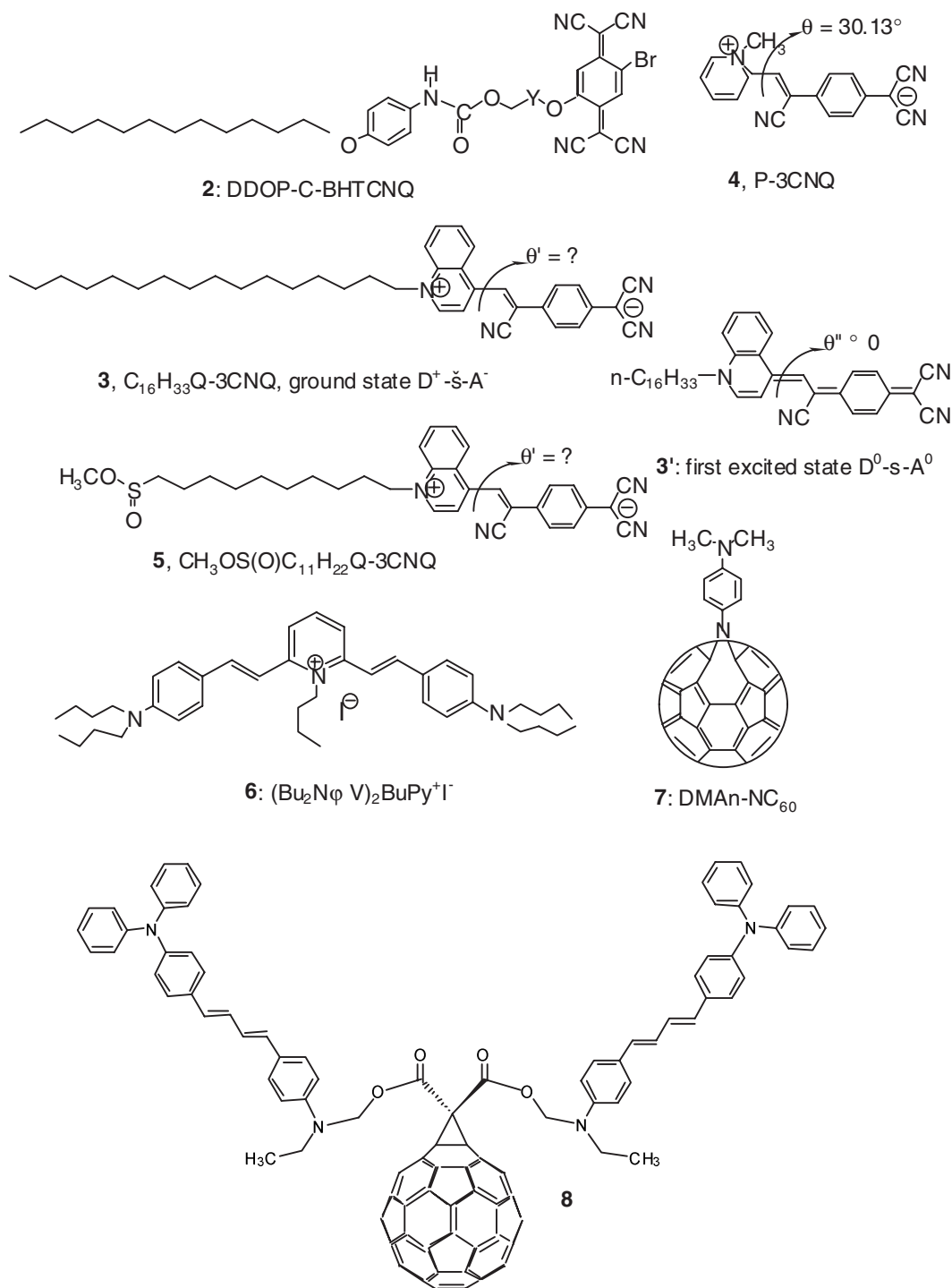
**Fig. 1.** The AR proposal,<sup>3</sup> showing a proposed D— $\sigma$ —A molecule (or “Gedankenmolekül”) **1** (which was never synthesized) and the through-molecule electron flow from the excited zwitterion state  $D^+-\sigma-A^-$  to the undissociated ground state  $D^0-\sigma-A^0$  when the molecule is placed between two metal electrodes  $M_1$  and  $M_2$ . Here  $E=0$  is the vacuum level,  $\phi$  is the work function of the metal electrodes,  $V$  is the potential applied on the left electrode (the right electrode is grounded),  $I_D$  is the ionization potential of the donor moiety D,  $A_A$  is the electron affinity of the acceptor moiety A, and  $E_{F1}$  and  $E_{F2}$  are the Fermi levels of the metal electrodes, and the HOMO and LUMO levels are the highest occupied molecular orbitals or lowest unoccupied molecular orbitals of the D and A moieties.

### The Organic Rectifier Project

As mentioned above, the AR proposal requires that one couple a strong donor D with a strong acceptor A in the same molecule by some covalent bridge, preferably saturated (Figure 1). The synthesis requires that a strong oxidizing agent be coupled covalently to a strong reducing agent, not an easy synthetic challenge, but a challenge also met by researchers in artificial photosynthetic systems. In addition, the rectifier must include appropriate terminations for the molecule, to allow its assembly between metal electrodes for electrical measurements.

The assembly technique chosen by the Organic Rectifier Project at the University of Mississippi (1982–1991) was the LB method.<sup>37,38</sup> Many molecules were made which did indeed form LB films<sup>37,38</sup> (one of the many<sup>39</sup> is given as structure **2** in Figure 2). They were all obtained by using the carbamate coupling reaction (or an ester coupling) as the last synthetic step (it was not possible to convert a weak acceptor into a strong acceptor in the presence of a strong donor after the covalent





**Fig. 2.** Chemical structures of unimolecular rectifiers. The Schottky-barrier or “S” rectifier DDOP—C—BHTCNQ, **2** [refs 39,48]. The first confirmed molecular rectifier, **3** [refs 16–20], a related zwitterionic or betaine molecule **4** [ref 50]. The twist angle  $\theta = 30.13^\circ$  in the crystal structure of **4** is caused by steric hindrance.<sup>50</sup> A similar twist angle  $\theta'$  must exist in **3**. If this twist angle  $\theta'$  were somehow reduced to zero, despite the steric hindrance, then structures **3** and **3'** would be degenerate resonance states. Since the twist angle must be sufficiently far from zero, therefore either **3** is the ground state and **3'** is the first electronic excited state, or vice versa (but see text). Molecule **5** is a version of **3** that was chemisorbed onto an Au surface.<sup>24</sup> Molecules **6** [ref 21], **7** [ref 22], and **8** [ref 23] are new unimolecular rectifiers. For molecule **8**, rectification is persistent.<sup>23</sup>

bridge has been built; rather, the coupling reaction must strongly favor the bridge building over the competing formation of an ionic charge-transfer salt).<sup>37,38</sup> However, early rectification experiments failed, because of primitive techniques.<sup>37,38</sup>

## Electrical Properties of Monolayers and Multilayers

It is easy enough to transfer an organic monolayer or multilayer atop a sufficiently flat metal layer by the LB method,<sup>40,41</sup> or by chemisorption.<sup>42</sup> It is much more difficult to then deposit a second metal electrode atop the organic layer without damaging the organic layer. The electrical properties of LB multilayers have been studied for decades.<sup>43–46</sup> The method of making “metal | LB layers | metal” sandwiches was improved dramatically by J. Roy Sambles and co-workers at Exeter University, who found that Mg vapor and thin Mg films would damage the LB films least, and studied molecular rectification.<sup>15,47</sup> The first molecule studied was DDOP-C-BHTCNQ, **2**:<sup>39</sup> it had an asymmetric current-voltage curve.<sup>47</sup> However, it was shown later<sup>48</sup> that a Schottky barrier between Mg and the BHTCNQ termination of **2** (i.e. an interfacial  $\text{Mg}^{++}\text{TCNQ}^-$  or  $\text{Mg}^{++}(\text{TCNQ}^-)_2$  salt) was probably responsible for the rectification, rather than asymmetric conduction through the molecule, as in the AR proposal:<sup>3</sup> the LB multilayer of **2** was an “S” rectifier.<sup>48</sup>

The second molecule studied by Sambles was  $\gamma$ -hexadecylquinolinium tricyanoquinodimethanide,  $\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}$ , **3** (Figure 2).<sup>16</sup> Molecule **3** is one of a series of zwitterionic molecules synthesized by the group of Geoffrey J. Ashwell at Cranfield University for nonlinear optics;<sup>49</sup> it resembles the first member of that series,  $\alpha$ -picolinium tricyanoquinodimethanide or picolyl tricyanoquinodimethan, P-3CNQ, **4**, a crystalline ground-state zwitterion with a dihedral angle of  $30.13^\circ$  (between two least-squares planes of the pyridinium ring and the phenyl ring) and a calculated dipole moment of 26 debyes.<sup>50</sup> The rectification measured for LB monolayers and multilayers of **3** sandwiched between a Pt electrode on one side and a Mg electrode on the other (with an overcoat of Ag)<sup>16</sup> was at first put into some doubt;<sup>38,51,52</sup> but it was confirmed, when insulating LB layers of tricosenoic acid were added between the electroactive layers of **3** and the electrodes, and yet the rectification persisted.<sup>17</sup>

The work at the University of Alabama aimed at confirming unimolecular rectification by eliminating asymmetries in the current-voltage plots due to electrodes of dissimilar metals, and at clarifying the molecular mechanism for those asymmetries. This was done by again studying molecule **3**, using the *same* metallic electrode on both sides on an LB

monolayer or multilayer (at first Al [refs 18,19], and more recently Au [refs 19–23]), by concentrating on “metal | LB monolayer | metal” sandwiches, rather than “metal | LB multilayer | metal” sandwiches, and by resorting to a thorough chemical and spectroscopic characterization of the molecular species responsible for rectification.<sup>21,53</sup>

## General Properties of $\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}$

The first improvement was synthetic: a two-fold molar excess of the salt LiTCNQ was needed to give  $\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}$ , **3** in good yield.<sup>18</sup> Molecule **3** is slightly soluble in polar solvents and not at all in non-polar solvents. It does crystallize, but in very small crystallites so intertwined that a unit cell could not be indexed.<sup>18</sup> The cyclic voltammogram of **3** showed a reversible reduction at  $E_{1/2} = -0.54$  vs. SCE, a potential similar to that of p-benzoquinone; **3** has a second irreversible reduction, and a single irreversible oxidation.<sup>18</sup> The molecular ground-state static electric dipole moment of **3** is  $\mu_{\text{GS}} = 43 \pm 8$  debyes at infinite dilution in  $\text{CH}_2\text{Cl}_2$ .<sup>18</sup> The absorption spectrum in solution shows a relatively narrow and hypsochromic band, peaked between 600 and 900 nm; this band is an intervalence transfer (IVT) or internal charge-transfer band.<sup>18,53</sup> This band fluoresces in the near-IR region.<sup>53</sup> From the Stokes shift, the experimental value of  $\mu_{\text{GS}}$ , and also from a theoretical treatment of the solvation of ellipsoidal molecules in polar solvents, the excited-state dipole moment was estimated as  $\mu_{\text{ES}} = 3$  to 9 debyes.<sup>53</sup> The molecule is clearly zwitterionic in the ground state **3** ( $\text{D}^+-\pi-\text{A}^-$ ), and less dissociated **3'** ( $\text{D}^0-\pi-\text{A}^0$ ) in the first excited state. The twist angle  $\theta = 30^\circ$  in structure **4**, and a presumably similar twist angle  $\theta'$  in structure **3**, are non-zero for steric reasons, which prevent complete mixing of the quinolinium or pyridinium electrons with the electrons on the 3CNQ part. The short  $\pi$  bridge in **3** allows for a strong IVT between the D and A ends of the molecule.

The visible-ultraviolet (VUV) spectrum of LB multilayers of **3** on quartz exhibits a strong IVT peak at 570 nm;<sup>18</sup> this peak was measured at  $565 \pm 5$  nm for a monolayer at the air–water interface [54]; there is a long absorbance tail that extends into the IR.<sup>18,54</sup> A second peak can appear at the air–water interface, at 670 nm, which fades with time.<sup>54</sup> The HOMO of **3** shows a delocalized charge density, spread on both the  $\text{D}^+$  part and the  $3\text{CNQ}^-$  part, while the LUMO is localized on the  $\text{A}^-$  part.<sup>18</sup>

Molecule **3** forms good amphiphilic Pockels–Langmuir monolayers at the air–water interface, with a collapse pressure of  $34 \text{ mN m}^{-1}$  and collapse areas of  $50 \text{ \AA}^2$  at  $20^\circ\text{C}$ .<sup>18</sup> It transfers well on the upstroke, with transfer ratios around 100% onto hydrophilic glass, quartz, or aluminum<sup>18,55</sup> or fresh hydrophilic Au.<sup>19,20</sup> It transfers poorly on the downstroke onto

graphite, with a transfer ratio of about 50%.<sup>55</sup> Thereafter, the monolayers transfer only on the upstroke, with 100% transfer ratios, onto all surfaces, forming Z-type LB multilayers<sup>18,49,55</sup> (except for that first poorly transferred layer on HOPG<sup>55</sup>). The LB monolayer thickness of **3** was determined by X-ray diffraction (23 Å [ref 18] and 29 Å [ref 20]), spectroscopic ellipsometry (23 Å) [ref 20], surface plasmon resonance (22 Å) [refs 18,56], and by X-ray photoelectron spectrometry (XPS) (25 Å) [ref 56]. Given an average monolayer thickness of 23 Å and a calculated molecular length of 33 Å (with an all-trans geometry for the C<sub>16</sub>H<sub>33</sub> “tail”), one deduces a tilt angle of 46° from the surface normal.<sup>18</sup> The XPS spectrum of one monolayer of **3** on Au shows two N(1s) peaks.<sup>56</sup> An angle-resolved XPS spectrum shows that the cyano N atoms lie closer to the Au substrate, than does the quinolinium N atom.<sup>56</sup> The valence-band portion of the XPS spectrum agrees roughly with the density of molecular energy states.<sup>53</sup> The contact angle of a drop of water on “hydrophilic Au” is 40° (it should be zero if the gold were perfectly free of hydrophobic adsorbates); this angle increases to 92° if a monolayer of **3** is transferred atop fresh hydrophobic Au.<sup>56</sup>

The molecules of **3** adhere somewhat by the two terminal CN groups onto a hydrophilic substrate, are tilted maybe 45° from the surface normal, and present alkyl chains to the air. This is confirmed by a grazing-angle FTIR study of **3** on Al [ref 18] or on Au [ref 56]. Since a monolayer survives in the ultra-high vacuum of an XPS instrument, it must adhere rather well to it, i.e. it does not desorb very rapidly. The absorption spectrum of an 11-layer LB film shows an intense IVT band at 570 nm or 2.17 eV.<sup>18</sup> LB multilayers of **3** have a strong second harmonic signal  $\chi_{zz}^{(2)} = 180 \text{ pm V}^{-1}$ , whose strength is partly due to resonance enhancement at 532 nm from the tail of the absorption band.<sup>57</sup> The STM image of **3** on HOPG shows an unresolved image of the molecule seen from the dicyanomethylene end.<sup>18</sup>

### Unimolecular Rectification by C<sub>16</sub>H<sub>33</sub>Q—3CNQ

To perform rectification measurements, LB monolayers and multilayers of **3** were sandwiched between macroscopic Al electrodes,<sup>18</sup> and most recently using the “cold gold” technique (Figure 3), between Au electrodes.<sup>19,20</sup> First, the bottom electrode (either Al [ref 18], or an adhesion layer of Cr followed by Au [ref 20]) is evaporated onto a glass or quartz or Si substrate; second, the LB monolayer or multilayer of **3** is transferred above it; third, the structure is dried for 2 days to remove any adventitious water; fourth, the second electrode is deposited through a shadow mask<sup>18</sup> or a contact mask<sup>19,20</sup>, to make 30 to 48 pads per substrate (most recently of area of 0.283 mm<sup>2</sup> each<sup>20</sup>); fifth, a droplet of either Ag paste or Ga/In eutectic is put above the bottom electrode and (very gently)

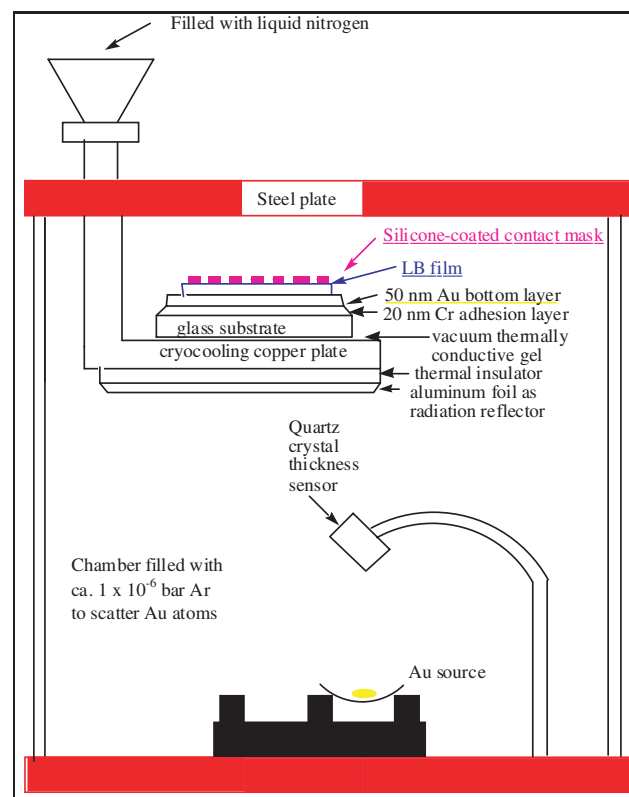


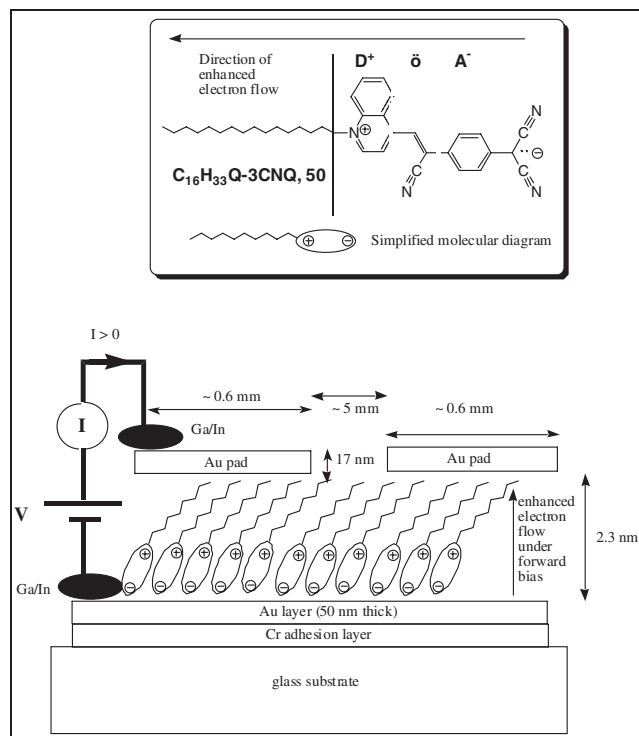
Fig. 3. Geometry of “cold gold” evaporation.<sup>20</sup>

sequentially on one of the pads of the top electrode, and electrical measurements are made. During the evaporation of the top electrode, a copper plate holding the sample is cooled by a liquid nitrogen bath; this is enough for an Al deposition<sup>18</sup> but not for an Au deposition. For Au deposition (Figure 3), two extra precautions are taken, one, to add 10<sup>−3</sup> torr of Ar gas to the evaporation chamber,<sup>58</sup> the other, to shield the substrate from direct thermal radiance from the heated Au source by hiding the sample on the opposite side of the copper plate (always cooled to liquid nitrogen temperatures). This “cold gold” deposition<sup>58</sup> forces the Au atoms to undergo multiple scattering by Ar atoms and cool down to room temperature before they reach the substrate.<sup>19,20</sup> The final metal–LB film–metal geometry is shown in Figure 4 for Au electrodes<sup>19,20</sup> (the geometry is similar for Al electrodes).

The Al layers are covered by the oxide, as is the Ga/In eutectic drop, while the Au electrodes have no oxide covering.

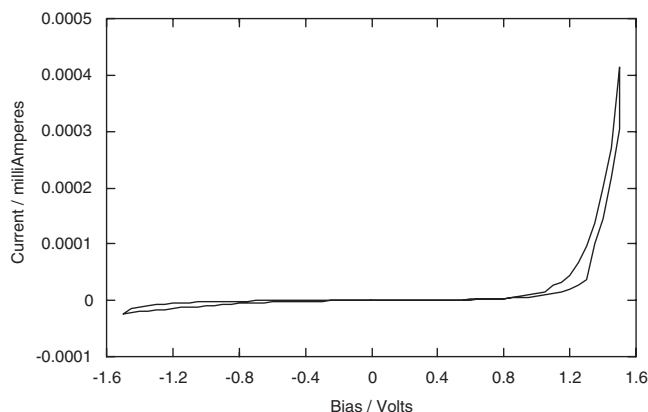
A monolayer or multilayer of arachidic acid, C<sub>19</sub>H<sub>39</sub>COOH, sandwiched between Al electrodes as in Figure 4, has a sigmoidal and almost symmetrical curve under both positive bias and negative bias, as expected;<sup>18</sup> ditto for Au electrodes.<sup>20</sup> When a monolayer of **3** is placed between Al electrodes (with their inevitable patchy and defect-ridden covering





**Fig. 4.** Molecular structure and geometry of LB monolayer of  $C_{16}H_{33}Q-3CNQ$ , **3** sandwiched between Au electrodes, with an arrow showing the direction of enhanced electron flow under positive, or forward bias. The glass substrate, 50 mm  $\times$  50 mm  $\times$  0.4 mm, covered either by a Cr adhesion layer, or by a hydrophobic xylene covering, followed by an evaporated Au film 50 mm  $\times$  50 mm  $\times$  50 nm, then the LB monolayer or multilayer, then by 48 cylindrical Au pads, 17 nm thick and with an area of 0.283 mm<sup>2</sup> each.<sup>20</sup>

of oxide), then a dramatically asymmetric current is seen (Figure 5). For **3**, the rectification ratio (eq. 8) is  $RR = 26$  at 1.5 volts.<sup>18</sup> Assuming a molecular area of 50 Å<sup>2</sup>, the total current at 1.5 volts corresponds to 0.33 electrons molecule<sup>-1</sup> s<sup>-1</sup>.<sup>18</sup> The rectification ratios vary somewhat from pad to pad, as does the total current, because these are all two-probe measurements, with all electrical resistances (Al, Ga/In or Ag paste, wires, etc.) in series. As high potentials are scanned repeatedly, the IV curves show progressively less asymmetry; the rectification ratios decrease gradually with measurement, i.e. with repeated cycling of the bias across the monolayer. One should remember that putting 1.5 volts across a monolayer of thickness 2.3 nm creates an electrical field of 0.65 GV m<sup>-1</sup>, which is very large; under such fields, many zwitterionic molecules in the monolayer may turn around, end over end, to minimize the total energy. The more “liquid”-like the monolayer, the easier this process would be. Measurements of the temperature-dependence of rectification of **3** between Al electrodes, in the range 105 K <  $T$  < 390 K, established that the asymmetry



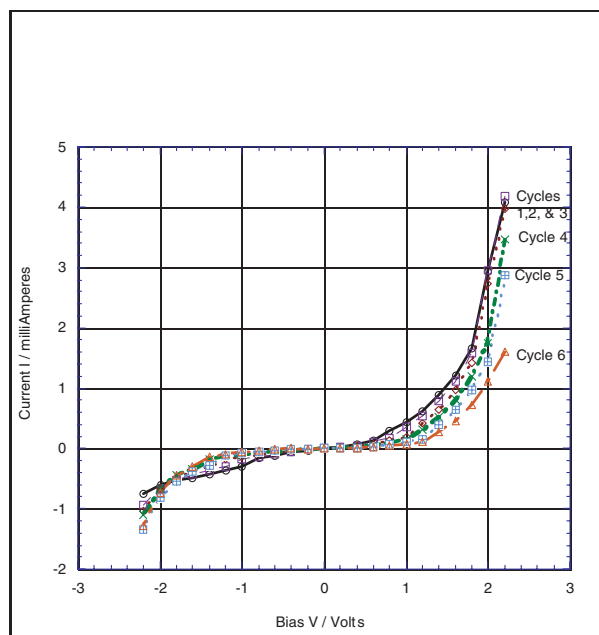
**Fig. 5.** Plot of the DC current  $I$  versus the DC applied voltage  $V$  ( $I$ - $V$  plot) through a single monolayer of  $C_{16}H_{33}Q-3CNQ$ , **3** sandwiched between Al electrodes (top Al pad area 4.5 mm<sup>2</sup>, thickness 100 nm), using Ga/In eutectic and Au wires. The DC voltage is swept at a rate of 10 mV s<sup>-1</sup> [ref 18].

is not temperature-dependent, but that the currents increase with temperature; this may be due to temperature effects across the several metal-oxide-metal junctions.<sup>18</sup>

Although the experiments with Al electrodes measured the rectification of several molecules in parallel, or unimolecular rectification, this conclusion rested on the assumption that the oxide covering of the Al electrodes was sufficiently defective to allow “ohmic” contact with the molecules, in other words, that no substantial electrical contact was made wherever the oxide coverage was thick, and that the current measured flowed mostly through those sites, where the oxide coating was very thin or non-existent. This conclusion may not have been completely convincing to all readers. With Au electrodes the current through the pads increased dramatically, as expected, but the asymmetry persisted: this confirmed that the same asymmetric conduction through the molecules could be measured using either Au or Al electrodes.<sup>19,20</sup>

Figure 6 shows the results obtained for one cell “Au | LB monolayer of **3** | Au”: the rectification ratio decreases from 5.39 to 1.0 in cycles 1 to 6.<sup>20</sup> For other “cells” (not shown here), the best rectification ratio was 27.53 at 2.2 volts; the highest current was 90,400 electrons molecule<sup>-1</sup> s<sup>-1</sup>; some cells exhibit a saturation in the forward current; in other cells, the current increases until breakdown occurs; in some cells this breakdown happens at 5.0 volts, i.e. the cells suffer dielectric breakdown only at a field close to 2 GV m<sup>-1</sup> [ref 20]. Rectification by a one-molecule thick layer of **3** is an established fact.

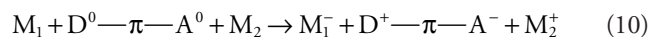
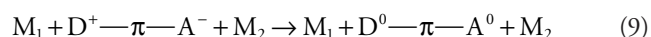
The AR proposal suggested a D— $\sigma$ —A molecule; the mechanism of action involves inelastic tunneling through the molecule from its first electronic excited state D<sup>+</sup>— $\sigma$ —A<sup>-</sup> to the less polar ground state D<sup>0</sup>— $\sigma$ —A<sup>0</sup> [ref 3]. The first confirmed rectifier **3**<sup>16–20</sup> is, instead, a ground-state zwitterion D<sup>+</sup>— $\pi$ —A<sup>-</sup>, connected by a twisted  $\pi$ -bridge, rather than a



**Fig. 6.**  $I$ - $V$  plot for a cell "Au | monolayer of  $C_{16}H_{33}Q-3CNQ$ , **3** | Au", showing the decrease in rectification ratio. At 2.2 V in the first cycle,  $R = 538 \Omega$ ,  $I = 4.09 \text{ mA} = 4.5 \times 10^4 \text{ electrons molecule}^{-1} \text{ s}^{-1}$ , and  $RR = 5.39$ . Cycle 1: circles  $\circ$ ; cycle 2: squares  $\square$ ; cycle 3: diamonds  $\diamond$ ; cycle 4: crosses  $\times$ ; cycle 5: squares with crosses  $\oplus$ ; cycle 6: triangles  $\triangle$  [20].

$\sigma$ -bridge, and presumably uses inelastic tunneling between the lower-polarity excited state  $D^0-\pi-A^0$  and the higher-polarity ground state  $D^+-\pi-A^-$  [ref 53].

One plausible mechanism for rectification by  $C_{16}H_{33}Q-3CNQ$ , **3** is a minor change in the AR proposal, so that eqs. 1, 2, and 3 are replaced by:



where the first step is the electric field-driven excitation from ground to excited state, followed by electron transfers across the two "molecule | metal" interfaces.<sup>18</sup>

Independently, it was confirmed that Z-type 30-layer films of **3** rectify between Au electrodes.<sup>54</sup> The currents for the multilayer<sup>54</sup> were three orders of magnitude smaller than those reported for the monolayer,<sup>20</sup> either because of inefficient electron transport between adjacent layers, or because of current contributions from Au filaments within the LB monolayer.<sup>54</sup>

Some promise was shown by **5**, a derivative of **3** with  $R = \text{undecylthioacetyl}$ .<sup>24</sup> the idea was to combine the advantages of LB assembly with those of self-assembly, where, if a monolayer of **5** is covalently bonded to Au as a thiolate  $-S-C_{11}H_{22}Q-3CNQ$ , (with loss of an acetate group),

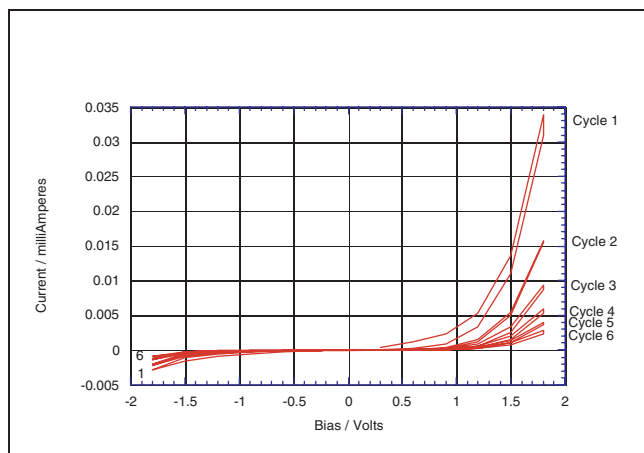
then "sturdy" rectification conditions will be found, with no decay of the RR. What happened instead is that the Langmuir isotherm was not very "vertical", i.e. the monolayer at the air-water interface was more fluid-like than solid-like, and the LB monolayer was disordered, in that some of the molecules probably adhered with the  $C(CN)_2$  portion closest to Au, while others adhered with the  $-S-C_{11}H_{22}Q$  portion closest to Au.<sup>24</sup> As a result, the RR for all pads was close to 1 [ref 24]. Molecules of **5** dissolved in basic solution and chemisorbed to an Au substrate also exhibited such a competition: some molecules had enhanced electron currents flowing from the bottom Au through the molecule to the STM Pt/Ir tip (indicating that the thiolate was closest to the bottom Au), while others had enhanced electron flow from tip to molecule to bottom Au electrode (indicating that the molecule was attached to Au by the dicyanomethanide end).<sup>24</sup>

### Three New Rectifiers

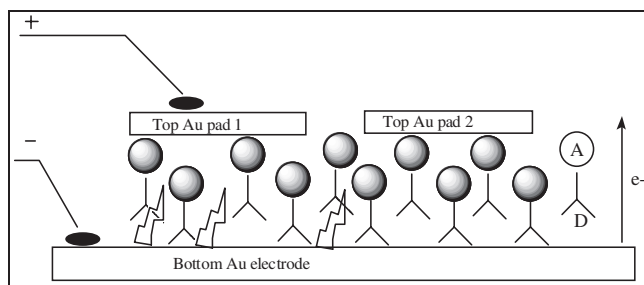
Recently, three more molecules (Figure 2) were studied at the University of Alabama, 2,6-di[dibutylamino-phenylvinyl]-1-butylpyridinium iodide  $[(Bu_2N\phi V)_2BuPy^+I^-]$ , **6**, [ref 21], dimethyl-anilino-aza[C60]fullerene  $[DMA-NC_{60}]$ , **7**, [ref 22], and the fullerene derivative **8**: all three are unimolecular rectifiers.

$(Bu_2N\phi V)_2BuPy^+I^-$ , **6** forms a Pockels-Langmuir film at the air-water interface, and transfers to hydrophilic substrates as a Z-type multilayer.<sup>21</sup> The monolayer thickness was estimated as 0.7 nm by spectroscopic ellipsometry, and 1.15 nm by surface plasmon resonance (at  $\lambda = 532 \text{ nm}$ ) or 1.18 nm (at  $\lambda = 632.8 \text{ nm}$ ); X-ray diffraction suggests a layer thickness of 1.3 nm.<sup>21</sup> The films exhibit an absorption maximum at 490 nm (which is slightly hypsochromic in solution), attributable to iodide-to-pyridinium back-charge-transfer, and a second harmonic signal  $\chi^{(2)} = 50 \text{ pm V}^{-1}$  at normal incidence ( $\lambda = 1064 \text{ nm}$ ) and  $150 \text{ pm V}^{-1}$  at  $45^\circ$  [21]. X-ray photoelectron spectroscopy of a multilayer of **6** on a gold substrate finds only 30% of the expected signal from the iodide; it is likely that the iodide anion is partially replaced by a more abundant hydroxide anion during LB transfer.<sup>21</sup> The rectification is shown in Figure 7: once again, there is a decrease of rectification upon successive cycles. Some cells have initial rectification ratios as high as 60. The favored direction of electron flow is from the gegenion to the pyridinium ion, i.e. in the direction of "back charge transfer", and the rectification in  $(Bu_2N\phi V)_2BuPy^+I^-$ , **6** can be attributed to an interionic electron transfer, rather than to an intramolecular electron transfer.<sup>22</sup>

The azafullerene  $DMA-NC_{60}$ , **7** consists of a weak electron donor (dimethylaniline) bonded to a moderate electron acceptor (N-capped  $C_{60}$ ). It is a blue compound, with a significant IVT peak at 720 nm.<sup>22</sup> The Langmuir film is very



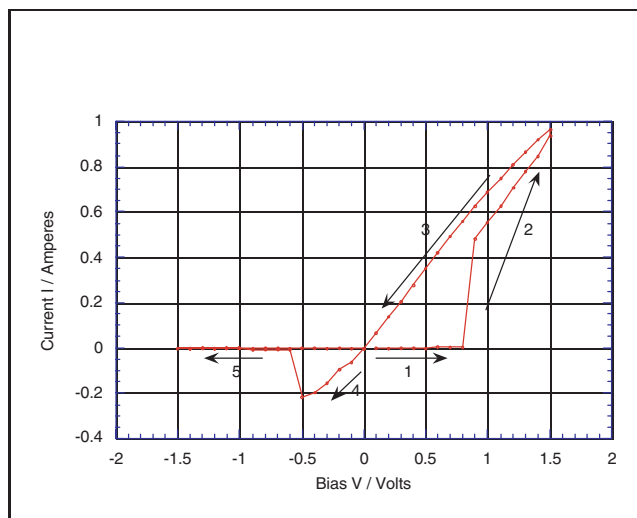
**Fig. 7.**  $I$ - $V$  plots for  $(\text{Bu}_2\text{N}\phi\text{V})_2\text{BuPy}^+\text{I}^-$ , **6** measured in a "Au | LB monolayer of **6** | Au" cell, for six successive cycles of measurement. The rectification ratios are  $\text{RR} = 12, 7, 5, 4, 3, 3$ , for cycles 1 through 6, respectively.<sup>21</sup>



**Fig. 8.** Schematic of LB monolayer of DMAAn- $\text{NC}_{60}$ , **7** on gold substrate, including top Au pads and Au stalagmites. The direction of preferred electron flow under forward bias is also shown as an arrow from the bottom gold electrode to top gold electrode pads.<sup>22</sup>

rigid, i.e. the slope of the isotherm is relatively large.<sup>22</sup> However, the molecular areas are  $70 \text{ \AA}^2$  at extrapolated zero pressure, and  $50 \text{ \AA}^2$  at the chosen LB film transfer pressure of  $22 \text{ mN m}^{-1}$  [ref 22], whereas the true molecular area of  $\text{C}_{60}$  is close to  $100 \text{ \AA}^2$ . Therefore, maybe molecules of **7**, transferred onto Au on the upstroke, are somewhat staggered, as shown in Figure 8, with the more hydrophilic dimethylamino group closer to the bottom Au electrode. The film thickness is estimated by XPS to be  $2.2 \text{ nm}$ .<sup>22</sup> The monolayer is covered, as previously,<sup>19–21</sup> with  $17 \text{ nm}$ -thick Au pads deposited by the "cold gold" technique. The dimethylamino groups in the LB film are probably not as close-packed as the azafullerenes. Angle-resolved  $\text{N}(1s)$  XPS spectra confirm that the two N atoms are closer to the bottom Au electrode than is the  $\text{C}_{60}$  cage.<sup>22</sup>

The current-voltage plot shown in Figure 9 is a dramatic but unwelcome surprise.<sup>22</sup> The top pads have an area of  $0.283 \text{ mm}^2$ , as before,<sup>20,22</sup> and the cell now supports 1 ampere of



**Fig. 9.**  $I$ - $V$  plots for DMAAn- $\text{NC}_{60}$ , **7** measured in a "Au | LB monolayer of **7** | Au" cell, with numbers indicating the measuring sequence. This is filamentary conduction through Au stalagmites and **7** [ref 22].

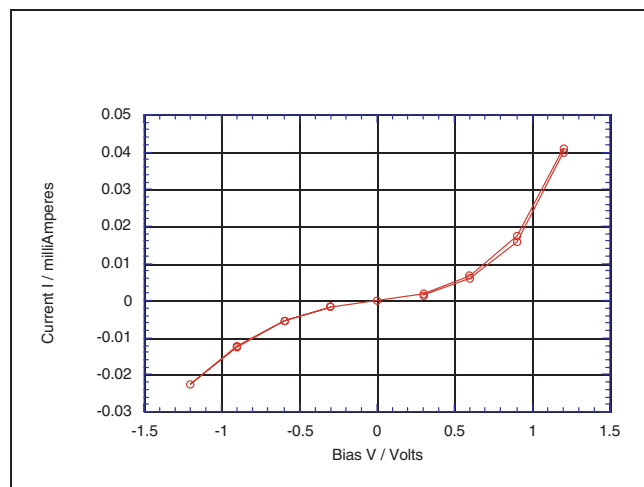
current across it! (that would be an absurdly large  $5 \times 10^{11}$  electrons molecule<sup>-1</sup> s<sup>-1</sup>). Moreover, the high current between  $1.5$  volts and  $-0.5$  volts in the "return" path (3 and 4 in Figure 9) is ohmic. The asymmetry decreases upon cycling (not shown here).<sup>22</sup> Probably, metallic Au filaments have formed within the monolayer, which do not pierce the fullerene ends of the monolayer, and are progressively destroyed by cycling the voltage: these Au stalagmites are shown in Figure 8 as jagged arrows or thunderbolts.

In contrast, some cells show no such large current, but a much smaller current, which is "marginally" rectifying in the forward direction, with a rectification ratio  $\text{RR}$  of about 2 (Figure 10).<sup>22</sup>

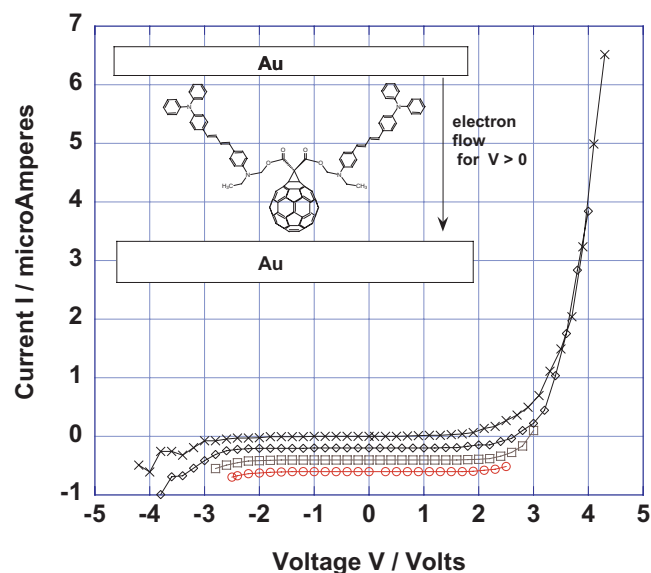
Molecule **8** is a new rectifier, based on two triphenylamines (one-electron donors) and the fullerene (weak one-electron acceptor), which has a very novel property: under conditions similar to those used for **3**, **6**, and **7**, a Langmuir-Schaefer monolayer of **8** rectifies (Figure 11), but the rectification ratio does *not* decrease upon successive cycling. The reason this current does not decay, may be that the monolayer is very dense and stiff, so stiff, in fact, that it cannot be transferred onto an Au substrate by the usual vertical LB process, but will adhere to Au if it is moved by horizontal, or Langmuir-Schaefer, transfer.<sup>23</sup>

## Challenges for the Near Future

Although unimolecular rectification has been fully confirmed, there are still open questions for the near term:

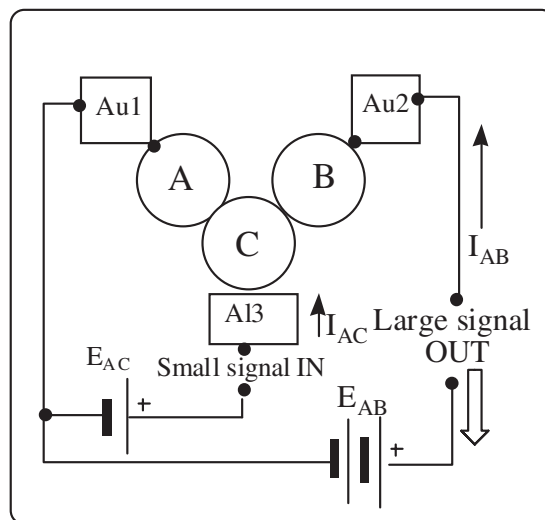


**Fig. 10.** Current-voltage plots for DMAAn-NC<sub>60</sub>, 7 measured in a "Au | LB monolayer of 7 | Au" cell, in which the current stays small: this should be the current due to the molecules 7 and not to the Au filaments.<sup>22</sup>



**Fig. 11.** Multiple  $I$ - $V$  scans for a LS monolayer of 8. Curve (a): circles ○: voltage range  $\pm 2.5$  V; the current is offset by  $-0.6 \mu\text{A}$ ; Curve (b): squares □: voltage range  $\pm 2.8$  volts; the current is offset by  $-0.4 \mu\text{A}$ ; Curve (c): diamonds ◇: voltage range  $\pm 3.8$  volts; the current is offset by  $-0.2 \mu\text{A}$ ; Curve (d): crosses ×: voltage range  $\pm 4.4$  volts, with zero current offset.<sup>23</sup>

- (1) Can inelastic electron tunneling spectroscopy confirm that the electron really does go through the molecule (instead of tunneling through space)? This has been accomplished recently.<sup>59</sup>
- (2) How fast is the rectification process?



**Fig. 12.** Proposed unimolecular amplifier, shown very schematically as molecule ABC, contacted by two Au electrodes (Au1 and Au2) and a third, different, electrode (Al3).<sup>63</sup>

- (3) What is the role of the metal electrodes during the measuring process? Do they indeed form stalagmites and stalagmites within the monolayer? Can this process be controlled? A recent admission by the Hewlett-Packard group<sup>60</sup> that their previously well-advertized work on self-assembled monolayers is plagued by metal filaments (similar to what we saw above in Figure 9) has helped to clarify what is intrinsic conduction through molecules and what is artifact.
- (4) Can one merge the complementary advantages of LB methods (better order) and self-assembly methods (sturdier bonds to the metal electrodes)?
- (5) Can one investigate optically what occurs during the electrical measurements? Can we "peek" under the monolayer?
- (6) What is the role of image dipoles induced in the metal electrodes by the molecular dipole moments in either the ground state or the excited state?

Can rectifiers and bridges and strands of conducting polymers be grafted together to form a molecular amplifier, or transistor, with power gain?<sup>61-63</sup> We show in Figure 12 one such idea:<sup>62</sup> if a molecule with three moieties A, B, and C covalently bonded together is such that either the electron mobility from A to B is much larger, than the mobility from C to B, then the molecule may function as a molecular amplifier, as an analog of an npn bipolar junction transistor. Alternately, if this mechanism does not work, perhaps a field effect would function between moieties C and B, thus narrowing the channel or conductivity of the main current from A to B. However, it is very hard to prepare three electrodes, say two of Au (Au1 and Au2, to bond thiol terminations of a molecule) and one

different one of Al (to bond a carboxylic acid termination) such that the gap between all the electrodes is molecule-sized, i.e. 1 to 2 nm. This goal is an ongoing effort in many laboratories.

## Conclusion

We have reviewed unimolecular rectification, which has now become an established reality. May this progress guide all of us to many new ideas for molecular devices to power the ultimate computers of the future.

*This work was made possible by the help of many colleagues, students, and post-doctoral fellows.*

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