

Monolayer Rectifiers

Robert M. Metzger¹

Laboratory for Molecular Electronics, Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487-0336

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Molecular-scale electronics has now been enriched by the discovery that molecules, studied singly by scanning tunneling spectroscopy, or a large array of those molecules, studied in parallel as a Langmuir–Blodgett monolayer between metal electrodes, exhibit rectification, i.e., an asymmetric current as a function of applied voltage.

This asymmetry can come, first, from work function differences between two dissimilar metals or the metal–molecule interfaces (Schottky barriers), second from an asymmetric placement of the chromophore between the two metal electrodes, and third, from an asymmetry of the molecular orbitals of the molecule.

This third, electronic origin of rectification, first proposed by Aviram and Ratner in 1974, and confirmed in the work reported here, gives us hope that, not too many years from now, molecules can form the basis of ultra-small yet ultra-fast electronic devices and integrated circuits. © 2002 Elsevier Science (USA)

Key Words: unimolecular rectifiers; molecular devices; hexadecylquinolinium tricyanoquinodimethanide; Aviram–Ratner proposal; asymmetric current–voltage plots; Langmuir–Blodgett films; monolayers; through-bond tunneling.

INTRODUCTION

The research area “molecular electronics” has received two definitions (1): the narrower one (*sensu stricto*), as the electronic properties of either a single molecule or very few molecules, and the wider definition (*sensu lato*) of electronics based on charge-transfer single crystals or organic conducting polymers (1). The more narrow definition, discussed here (1), was presaged by Richard P. Feynman’s 1959 suggestion (published in 1961) that “there is plenty of room at the bottom,” even though molecules were not explicitly mentioned (2). The first concrete proposal of molecular electronics *sensu stricto* was the 1974 Ari Aviram – Mark A. Ratner “Ansatz” of electrical rectification by a single asymmetric molecule (3). This Ansatz was inspired in

part from the use of organic one-electron donors and acceptors in quasi-one-dimensional metallic charge-transfer crystals, such as $\text{TTF}^{+0.59}\text{TCNQ}^{-0.59}$. The practical embodiment of this Ansatz is discussed here.

Molecular electronics was first publicized by three conferences chaired by the late Carter (4–6), which brought together some seminal ideas and results. Researchers in artificial photosynthetic systems, or in intramolecular electron transfer, have studied the electron transfer within a large molecule for a very long time. Henry Taube established that electron transfer across organic bridges between two dissimilar metal ions occurs more slowly across saturated “sigma” bridges than across conjugated “pi” bridges (7). Fluorescence spectroscopy, or by time-decay spectroscopy, of solutions of the molecule of interest avoids the problem of “touching a molecule,” because fluorescent emission can be monitored by single-photon counting detectors wherever the molecule happens to be within a solution (8). Intramolecular electron transfer, adiabatic or non-adiabatic, by direct exchange or by superexchange, has been scrutinized closely, because a large body of experimental data has accumulated (9, 10). There have been thrusts into “supramolecular chemistry (11), and into “nanotechnology.”

Since about 1995 unimolecular electronics seems to have matured, thanks to a burst of new direct measurements of the electronic behavior of single molecules, of Langmuir–Blodgett (LB) monolayers, or of thiols covalently bound on gold. The key to success was to touch a molecule either by a scanning tunneling microscopy (STM) tip, by a conducting-tip atomic force microscopy (AFM) tip, or by making delicate sandwiches between inorganic metals and organic monolayers (or self-assembled monolayers).

Unimolecular electronics is of interest because molecules may become useful electronic devices when it will become too difficult to get further reductions in size of silicon-based integrated circuits. There has been an empirical correlation that computing power doubled, at first every 2 years (12) and by now every 18 months or so (Gordon E. Moore’s “law”). This occurs as the “design rules” for integrated circuits (i.e., the smallest distance between

¹To whom correspondence should be addressed. Fax: +1 205-348-9104. E-mail: rmetzger@bama.ua.edu.

adjacent components) get smaller and smaller (and the circuits get faster and faster). However, this shrinkage cannot go on forever. Below design rules of 50 nm, huge technical hurdles may face silicon-based electronics, while molecules, with sizes 0.5–3 nm, can presumably do similar tasks with great facility.

It should be remembered that diode-to-diode logic is possible, but impractical for integrated circuits based on Ge, Si and GaAs rectifiers. Therefore, the work presented here on organic rectifiers is only a first step to molecular logic. Indeed, molecular computing will become practical only if “molecular transistors,” i.e., molecules or oligomolecular assemblies with power gain, are demonstrated.

It is appropriate to summarize here some recent advances in unimolecular electronics:

(1) It was found, by scanning tunneling spectroscopy, that currents across organic thiols bonded to an Au (111) surface are larger for aromatic thiol molecules than for aliphatic thiols (13); this result confirms the earlier work by Taube (7).

(2) By a novel “break junction” technique, a thin gold film, placed above a thinned out silicon wafer, was broken in a reproducible manner by cracking the silicon wafer between two static wedged and a piston moved with a piezoelectric scanner: the crack in silicon forces the gold to crack as well; the resulting gap between the gold shards can be controlled. When a solution of 1,4-benzenedithiol is poured on this break junction, some bithiols will presumably bond to both shards, and establish a one-molecule path for conductivity. The resistance of 1,4-benzenedithiol was measured as several $M\Omega$ (14), i.e., much larger than Landauer’s quantum of resistance $h/2e^2 = 12.9\text{ k}\Omega$ (15), either because of mismatch between the Fermi level of Au and the relevant molecular orbital of the molecule, or because of other effects. Unfortunately, longer bithiols could not be studied by this technique (16).

(3) Molecules of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-2'-nitro-1-benzenethiolate topped by a Ti electrode show negative differential resistance effects (17); this was also followed by STM (18); these molecules, assembled on a gold electrode, with a titanium electrode on top, have low- and high-conductivity states, with an exponential decay of the high-conductivity state of 800 s at 260 K: this was publicized as a molecular random access memory cell (19).

(4) The Landauer quantum of resistance, 12.9 k Ω (15) was measured at room temperature in a single-walled carbon nanotube, glued to a conducting AFM tip, and dipped into a pool of liquid Hg (20).

(5) A single-walled carbon nanotube curled over parallel Au lines, with an STM tip acting as a gate electrode, shows field-effect transistor (FET) behavior; the power gain is only 0.33 (21). More recently, single electron transistor

effects were seen in metallic carbon nanotubes with kinks introduced into them by an AFM tip (22). A single-walled semiconducting carbon nanotube made to bridge a K-doped region (thus getting an n-type FET), and also an undoped region (forming a p-type FET), forms an intramolecular voltage inverter with an output/input voltage gain of 1.6 (23). FET behavior in LB multilayers of conducting polymers was observed (24), as was FET behavior in thin films organic semiconductors, such as sexithiophene (25,26). One can control the conductivity of a C_{60} molecule studied by STM by controlling the mechanical force with which it is squeezed by the tip (27). Very recently a monolayer of bithiols attached to an Au electrode, accosted by an n-type Si gate region, and topped by another Au electrode (to which the other end of the bithiols may have become bonded), also exhibited FET behavior (28), but this dramatic result is yet to be reproduced elsewhere.

(6) An L–B monolayer of a bistable (3) catenane, with a naphthalene group as one “station” and tetrathiafulvalene as the second “station”, and a tetracationic catenane hexafluorophosphate salt traveling on it like a “train” on a closed track, was deposited on poly silicon as one electrode, and topped by a 5 nm Ti layer followed by a 100 nm Al electrode. The current–voltage plot is asymmetric as a function of bias (which moves the train on the track), and a succession of read–write cycles shows that the resistance changes stepwise as the train(s) move from the lower-conductivity station(s) to the higher-conductivity station(s) (29).

(7) Last, but not least, unimolecular rectification across an L–B monolayer of hexadecylquinolinium tricyanoquinodimethanide was first detected between Mg and Pt electrodes (30,31), and later thoroughly confirmed between Al electrodes (32–34) most recently even between oxide-free Au electrodes (35,36), to be a variant of the Aviram–Ratner (3) mechanism. The original proposal suggested a D– σ –A molecule, with an electron donor moiety (D) connected to an electron acceptor moiety (A) through an insulating saturated “sigma” bridge σ (3); the mechanism would involve inelastic tunneling through the molecule from its first electronic excited state $D^+ - \sigma - A^-$ to the less polar ground state $D^0 - \sigma - A^0$ (3). The first confirmed rectifier was, instead, a ground-state zwitterion $D^+ - \pi - A^-$, connected by a twisted pi bridge, rather than a sigma bridge, and used inelastic tunneling from the lower-polarity excited state $D^0 - \pi - A^0$ to the higher-polarity ground state (37). Most recently, two new monolayer rectifiers have been found, when sandwiched between gold electrodes (38,39). The first is a pyridinium salt, in which the rectification seems to be due to interionic back-charge transfer from the anion to the pyridinium ion (38). The second is dimethylaminophenylazafullerene, which has a tremendous rectification ratio (as high as 20,000): here,

however, the bulk of the forward current seems to be due to the formation of stalagmites of gold, which do not pierce the monolayer totally, but behave ohmically (39).

The slow progress towards organic rectifiers has been reviewed often before (40–70). The first many years were dedicated to the study of D– σ –A systems, and were afflicted by lack of good experimental techniques to measure rectification for a monolayer (40–58). The last few years have seen good rectification results from a ground-state D⁺– π –A[–] zwitterion system (59–70). The present review updates what was known and reviewed 2 years ago (62,63,65), but adds to that knowledge the results obtained with new technique of “cold gold” evaporation (35,36) and two new rectifiers (38,39). The contributions from our laboratories have been published over almost a score years (71–97).

This review will first discuss why at present, and for several more years, we will still need metallic contacts; then it will review the Aviram–Ratner proposal, and electron transport through monolayers, and assembly techniques. The asymmetrical current–voltage plots for the three recently confirmed unimolecular rectifiers will then be presented. The review will finally address sources of asymmetric conduction, and suggest avenues for future work.

METAL CONTACTS

An all-organic computer may have been dreamt about, but at present the daunting synthetic complexity of such a project (making organic electronic components and making organic or polymeric interconnects for them) may deter even the most optimistic “futurists”. At present, only two-terminal devices (resistors, insulators, or rectifiers) have been proven, and interrogated by inorganic metal contacts (Au, Ti, Al, Mg, etc.). Three-terminal molecular devices or device assemblies do not exist yet (with one unconfirmed exception (26)). One can, of course, perform digital logic operations with two-terminal diodes, but the semiconductor industry now uses preponderately three-terminal FET logic, with design rules down to 120 nm or so. This strongly suggests that three-terminal metal filaments within 1 nm of each other must first be fabricated, without short circuits. Then molecules with three terminations can be synthesized, to bridge and connect across these gaps. When power gain is seen through such molecules, and when a reasonable “zoo” of organic molecular devices (resistors, capacitors, rectifiers, and transistors) exists, the metal contacts can be abandoned, and plans for an all-organic backbone for the all-organic computer can be initiated.

Another practical imperative is that we must seek to do with molecules what cannot easily be done with inorganic devices (Si- or GaAs-based). Otherwise, a self-defeating “me-too” competition with proven and improvable com-

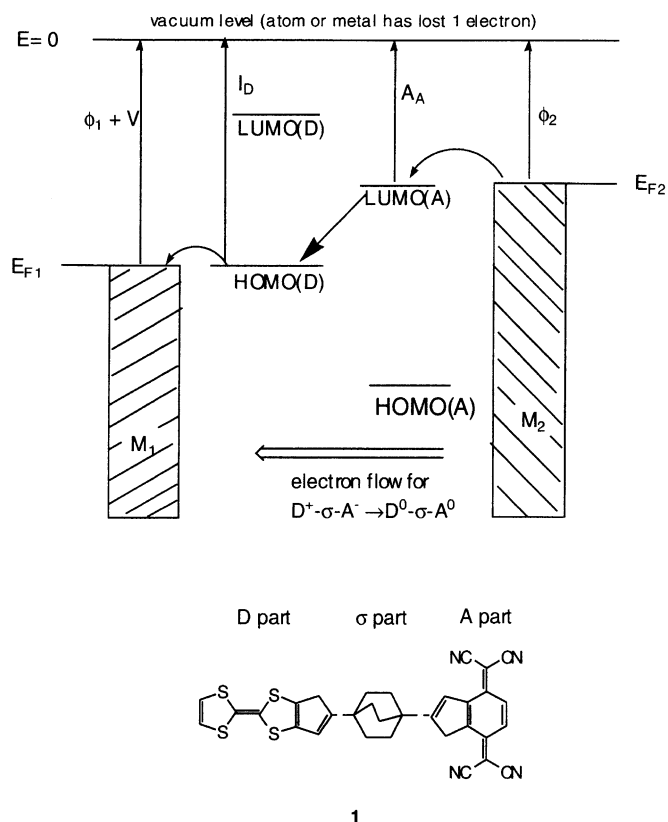


FIG. 1. The Aviram–Ratner Ansatz, showing a proposed D– σ –A molecule (or “Gedankenmolekül”) **1** (which was never synthesized) and the through-molecule electron flow from the excited zwitterionic state D⁺– σ –A[–] to the undissociated ground state D⁰– σ –A⁰, when the molecule is placed between two metal electrodes. Here $E = 0$ is the vacuum level, ϕ 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 of D– σ –A, A_A is the electron affinity of the acceptor moiety A of D– σ –A, E_{F1} and E_{F2} are the Fermi levels of the metal electrodes, and the HOMO (LUMO) levels are the highest occupied (lowest unoccupied) molecular orbitals of the D and A moieties.

mercial devices will ensue, since the latter will prove to be an ever-shifting target.

The field of molecular electronics received its first sensible and practical suggestion in the 1974 proposal by Aviram and Ratner (Fig. 1) that a D– σ –A molecule (D = good one-electron donor with relatively first low ionization potential I_D , σ = saturated covalent “sigma” bridge, A = a good one-electron acceptor with relatively high electron affinity E_A) would function as a unimolecular rectifier when placed between two appropriate metal contacts M_1 and M_2 . The function of σ 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 end than the other; also, if the decoupling between D and A is complete, then there would be no intramolecular electron transfer, or

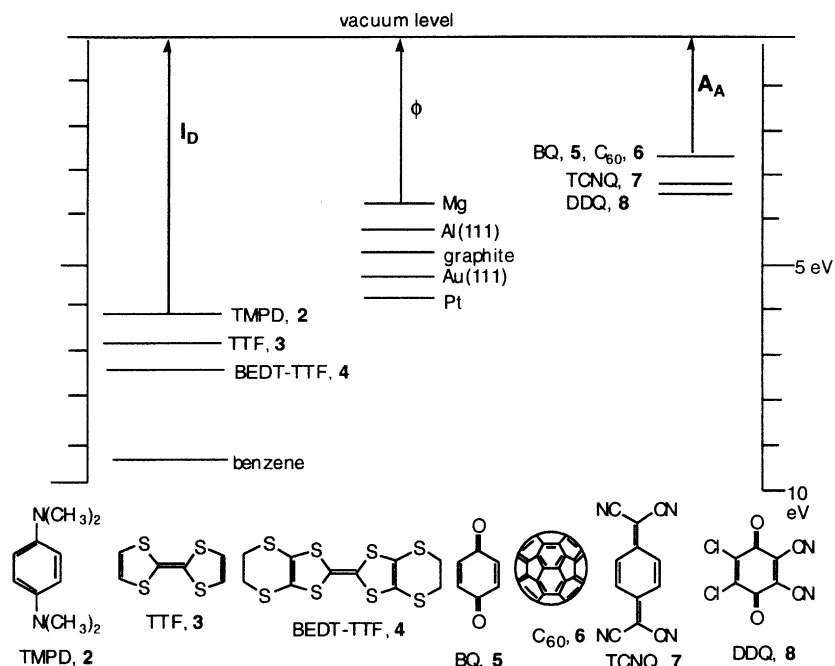
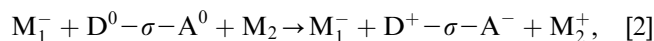


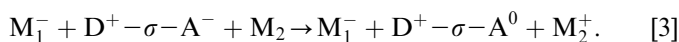
FIG. 2. Energy levels: HOMOs of some organic donors (left), work functions ϕ of some metals (center), LUMOs of some cross metal-organic acceptors (right).

intervalence transfer (IVT). The molecular ground state would then have a relatively lower dipole moment, and can be written as $D^0-\sigma-A^0$, while the first excited state is much more polar, with a much higher moment, and can be written as the zwitterion $D^+-\sigma-A^-$. Given what is known about the energy levels of organic molecules (Fig. 2), it is likely that resonant transfer would be possible (Fig. 1) when the Fermi energy of the metal electrode M_2 is resonant with the LUMO of the A part, and the HOMO of the D part is on resonance with the Fermi energy of the metal electrode M_1 (maybe upon applying some small positive bias V onto 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:

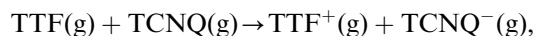


followed by an inelastic down-hill intramolecular electron transfer to restore the ground state:

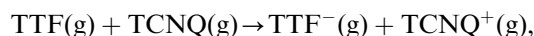


This transfer could be accompanied by the emission of light, or more probably, by non-radiative phonon emission.

Aviram and Ratner suggested a molecule where D represents tetrathiafulvalene (TTF) and 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):



$$\Delta U_F = I_D - A_A = 6.83 - 3.3 = 3.5 \text{ eV}, \quad [4]$$



$$\Delta U_R = I_A - A_D = 9.6 \text{ eV (est)}. \quad [5]$$

The disymmetry in energies between Eqs. (4) and (5) is at the heart of this rectifier Ansatz. The Aviram-Ratner proposal involves electronic transitions which are inherently fast, compared with translations (29) or with conformational transitions or molecular rearrangements.

However, Landauer studied the scattering from a single tunneling barrier and showed that any one-dimensional device between macroscopic electrodes has a *minimum* intrinsic resistance of 12.9 k Ω (15); the current is given by (98)

$$I = (2e/h) \int_{-\infty}^{\infty} [f_L(\epsilon) - f_R(\epsilon)] \text{Tr}\{G^a(\epsilon)\Gamma^R(\epsilon)G^t(\epsilon)\Gamma^L(\epsilon)\} d\epsilon, \quad [6]$$

where I is the current, e is the charge on one electron, h is Planck's constant of action, ε is the energy, $f_L(\varepsilon)$ and $f_R(\varepsilon)$ are the Fermi–Dirac distributions in the left and right electrodes, respectively, $G^a(\varepsilon)$ and $G^r(\varepsilon)$ are the advanced (and retarded) Green's function for the molecule, $\Gamma^R(\varepsilon)$ and $\Gamma^L(\varepsilon)$ are the matrices that describe the coupling between molecule and the metal electrodes, and $\text{Tr}\{\}$ is the trace operator. The quantum of resistance is given by

$$e^2/2h = 12.9 \text{ k}\Omega. \quad [7]$$

This resistance can be reduced by a factor N if N elementary wires, or N molecules, bridge the gap in parallel between the two metal contacts. However, recently, it was shown experimentally that a degenerate quasi-one-dimensional electron gas in a GaAs/GaAl_{1-x}As_x system, when interrogated in a geometry with four in-line probes, has zero resistance drop between probes 2 and 3 (in contrast to the expected 12.9 k Ω between probes 1 and 4), because the transport within the gas is ballistic (99).

The electron transport from metal to organic material to metal has also received theoretical attention from this laboratory (94,96). First, asymmetries in current–voltage plots can also occur if a chromophore is placed asymmetrically within the electrode gap (96) as observed in early STM experiments (100). Second, an analytic equation for elastic electron transfer between a metal and a single molecular orbital of a molecule is (94)

$$I = I_0 \{ \tan^{-1}[\theta(E_0 + peV)] - \tan^{-1}[\theta(E_0 - (1-p)eV)] \}, \quad [8]$$

which has also been obtained independently (101). Here E_0 is the energy of the molecular orbital, V is the applied potential, e is the electronic charge, and p is the fractional distance of the molecule from, say, the left electrode (if the molecule is centered in the gap, $p = 1/2$).

ASSEMBLY: PHYSISORPTION VERSUS CHEMISORPTION

As one designs molecules for unimolecular rectification or, in the future, for unimolecular transistors, one must decide how the electrical properties will be measured: indeed we must “reach out and touch a molecule.” STM, one can select an atomically flat but conducting substrate (graphite, Au(111) on mica, MoS₂, and a few others), deposit the molecule “somehow” on this substrate, and interrogate it with a Pt/Ir or W or single-walled carbon nanotube tip. However, control over individual molecules physisorbed on a surface can be difficult, except when their motion is inhibited at low temperatures.

For attaching molecules to any metal electrode, two choices are available, physisorption and chemisorption.

Physisorption includes the random deposition from a vapor onto a solid substrate (“chemical vapor deposition”), and the ordered transfer of an amphiphilic monolayer (Langmuir or Pockels–Langmuir monolayer) from the air–water interface onto a solid substrate (forming an LB monolayer, or, if 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 (transfer ratio); the other is that the surface dipoles that can form during chemisorption are avoided. However, physisorption has two limitations: one is that, 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; the second is that any other adsorbates already present on the metal electrode (e.g., on gold electrodes 15 min after exposure to ambient air) are not displaced, but merely covered by the physisorbed layers.

Chemisorption includes the bonding of thiols and similar compounds to gold and similar metals (often called “self-assembled monolayers”), or of chlorosilanes to hydroxyl-covered silicon surfaces. Chemisorption involves direct chemical bonding, with heats of bonding approaching 40–80 kJ mol⁻¹, and has two advantages. The first advantage is that the chemical reaction that occurs upon chemisorption will displace from the surface any previously formed physically attached adsorbates. The other advantage is that the adsorbate, once bonded, is difficult to remove from the surface. There are three disadvantages, the uncertain degree of coverage, the possibility of further chemical reactions, and the formation of surface dipoles. One usually hopes that, by exposing a surface long enough (e.g., 1 day) 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 ± 0.05 Langmuir. Whereas physical rearrangement of the film is less of a problem, a slow chemical transformation of a thiolate on gold to a sulfoxide on gold is known to occur. For either thiolates or sulfoxides, the bonding to gold is partially ionic, so one creates a surface dipole of maybe 1 or 2 Debyes per molecule every time a thiol is attached to gold: this would be a Schottky barrier that “comes with” chemisorption. Silane links on silicon are much less polar, but less is known about how ordered the silanes are on silicon.

The work on unimolecular rectifiers has been done mostly using LB films.

THE ORGANIC RECTIFIER PROJECT

The Aviram–Ratner proposal, or “Ansatz”, requires that one can couple a strong donor D and a strong acceptor A in the same molecule by some covalent bridge,

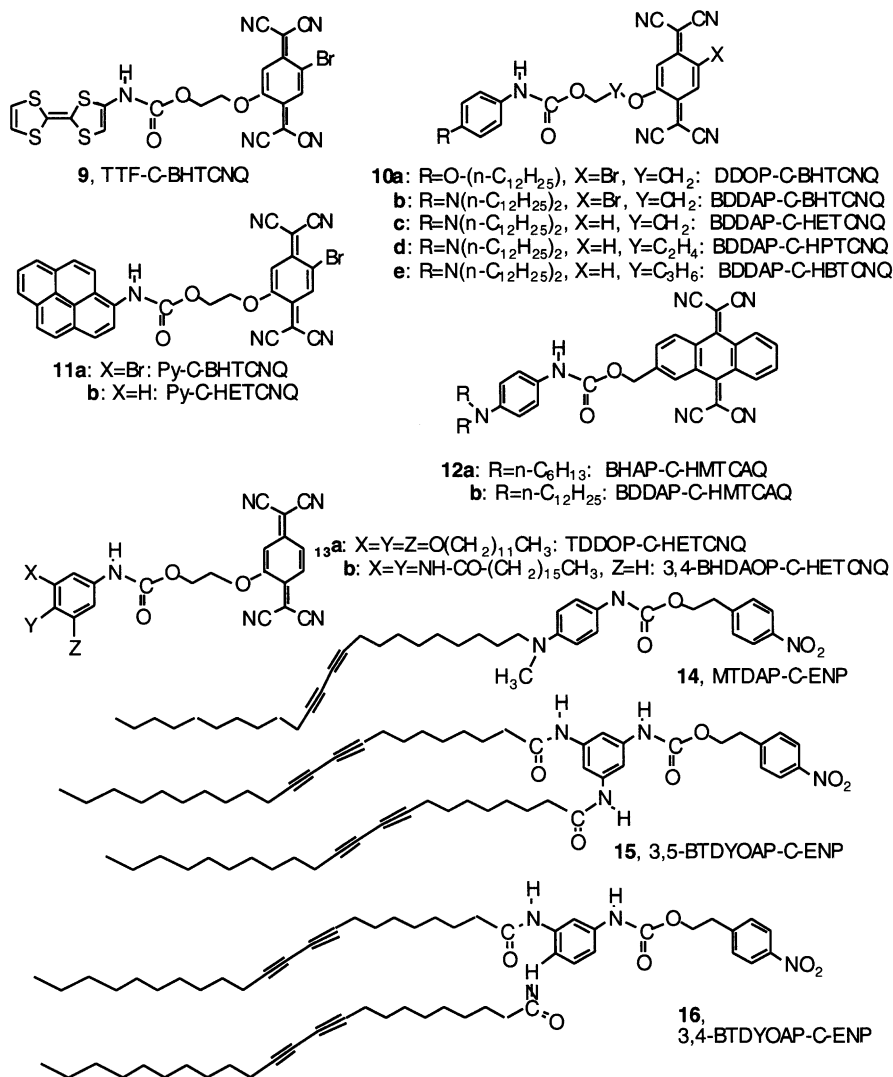


FIG. 3. D- σ -A molecules 9–16 synthesized at the University of Mississippi (1982–1991).

preferably saturated (see Figs. 2 and 3 and Table 1 for additional relevant data). The synthesis requires that a strong oxidizing agent be coupled covalently to a strong reducing agent. This is not easy, but this challenge has also been met by researchers in artificial photosynthetic systems, e.g., Gust, Moore and Moore, Paddon-Row, Mataga, and others. In addition, the synthetic plan for a rectifier must include appropriate terminations for assembly between metal electrodes. The assembly technique chosen by the Organic Rectifier Project at the University of Mississippi (1982–1991) was the LB method. Many molecules were made which formed LB films (structures 9–16 in Fig. 3). They were all obtained by a carbamate coupling reaction as the last synthetic step (an ester coupling would also work). It is essential that strong donors and strong acceptors be formed first, and linked

covalently in the last synthetic step. Once a bridged molecule is formed, it is probably almost impossible to transform, e.g., a weak electron acceptor into a strong electron acceptor, because of side reactions with the other end of the molecule.

Of the molecules that formed Pockels–Langmuir monolayers at the air–water interface and LB films on a solid substrate, only one (molecule 9) included the strong donor TTF and the strong acceptor TCNQ; there were two products, one seemingly zwitterionic in the ground state, the other neutral, but both difficult to purify. Most molecules in Fig. 3 were based on the strong monofunctionalized one-electron acceptors BHTCNQ (2-bromo, 5-hydroxyethoxyTCNQ) and HETCNQ (2-hydroxyethoxyTCNQ), whose synthesis never gave high yields. Two molecules (structures 12a and 12b) included the weak

two-electron acceptor HMTCAQ. Several (molecules **14–16**) used the weak acceptor ENP (ethylene-*p*-nitrophenol), but were made to include a polymerizable diacetylene chain to aid in the rigidity of the eventual LB monolayer (an idea of the late Sukant K. Tripathy). Most included a long “greasy tail” to aid in LB assembly, but two (structures **IIa** and **IIb**) formed films with no alkyl chain (here it was not clear whether they were head-to-head assemblies or head-to-tail assemblies). The methods of testing for rectification used by the Metzger group at that time were too crude (52,71) and no rectification was found. This does not say that all molecules in Table 3 were “failures”; rather, now that better techniques have become available (32,35,36), some of those molecules do deserve a second look. If the same research strategy is continued, then monosubstituted strong electron acceptors are necessary (52,57). So far, using the ester and carbamate coupling reactions can prevent the competing formation of charge-transfer anion radical-cation radical salts (52,57). The synthesis of monosubstituted strong acceptors needs vast improvement in yields (70).

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 (102), or by chemisorption (103) (the so-called “self-assembly method”) It is much more difficult to then put a second metal electrode atop the organic layer without damaging the organic layer. The electrical properties of LB monolayers and multilayers had been studied by the research groups of Mann and Kuhn (104), Handy and Scala (105), Tredgold *et al.* (106), and Roberts *et al.* (107). An important improvement in making “metal–LB layers–metal” sandwiches by J. Roy Sambles and co-workers at Exeter University, was that Mg vapor and thin Mg films with areas on the scale of a few square millimeters would damage the LB films least (30,108). (In a different application, Reed *et al.* found that nanopores formed in thinned Si substrates could be made small enough that a Ti adsorbate would not damage an organic monolayer (109). The first molecule studied for rectification was DDOP-C-BHTCNQ, **10a** (72), which had an asymmetric current–voltage curve (108), but later (110) rectification was attributed to a Schottky barrier between Mg and the BHTCNQ termination of **10a** (i.e., an interfacial $\text{Mg}^{++}\text{TCNQ}^{-}$ salt), rather than to asymmetric conduction through the molecule, as in the Aviram and Ratner (3) proposal. The second molecule studied was γ -hexadecylquinolinium tricyanoquinodimethanide, $\text{C}_{16}\text{H}_{33}\text{Q-3CNQ}$, **17** (Fig. 4) (30). Molecule **17** is part (111) of a series of zwitterionic molecules synthesized by the group of Geoffrey J. Ashwell at Cranfield University for their

nonlinear optics. Molecule **17** resembles the first member of that series, α -picolinium tricyanoquinodimethanide or picolyl tricyanoquinodimethan, **18**, which is a crystalline ground-state zwitterion with a dihedral angle of 30° (between the two least-squares planes of the pyridinium ring and the phenyl ring) and a calculated dipole moment of 26 Debyes (112). The rectification measured for LB monolayers and multilayers of **17** sandwiched between a Pt electrode on one side and an Mg electrode on the other (with an overcoat of Ag) was at first put into some doubt (54,56,57), but was confirmed by the following experiment: the rectification persistent even when insulating LB layers of tricosenoic acid were added between the electroactive layers of **17** and the electrodes (31). A further recent technical improvement by the Exeter group was the development of the “cold gold” deposition technique (113), which has been copied (35,36,38,39).

ELECTRICAL RECTIFICATION BY A SINGLE MOLECULE IS CONFIRMED

The work in Alabama confirmed unimolecular rectification by using identical metals on both sides of organic monolayers, thus eliminating asymmetries in the current–voltage plots due to dissimilar metal electrodes; thus Al was used at first (32–34), then Au (35,36,38,39). Also, **17** was thoroughly characterized (37,38).

MOLECULAR PROPERTIES OF $\text{C}_{16}\text{H}_{33}\text{Q-3CNQ}$, **17**

A two-fold molar excess of the salt LiTCNQ afforded $\text{C}_{16}\text{H}_{33}\text{Q-3CNQ}$, **17** in improved yield: the first mole of TCNQ radicals creates a methylene radical on the quinolinium and the next mole carries through the coupling with loss of HCN (32). Molecule **17** is insoluble in apolar solvents, and not very soluble in polar solvents. It does crystallize, but in several attempts gave several unit cells that were so intertwined that indexing proved impossible (32). The cyclic voltammogram of **17** showed that the molecule can be reduced reversibly at a potential $E_{1/2} = -0.54$ versus SCE (akin to that of *p*-benzoquinone, **5**); **17** has a second irreversible reduction and a single irreversible oxidation (32). The molecular dipole moment of **17** is $\mu_{\text{GS}} = 43 \pm 8$ Debyes at infinite dilution in CH_2Cl_2 . The absorption spectrum of **17** in solution shows a relatively narrow, hypsochromic band peaked between 600 and 900 nm, with a loss of vibrational structure in the more polar solvents; this is an IVT or internal charge-transfer band (32,37). It fluoresces in the near IR region (37). From the Stokes shift, the value of μ_{GS} , and from a theoretical treatment of the solvation of ellipsoidal molecules in polar solvents, the excited state dipole moment was estimated as $\mu_{\text{ES}} = 3-9$ Debyes (37). The molecule is zwitterionic in the ground state ($\text{D}^+\pi\text{-A}^-$) and

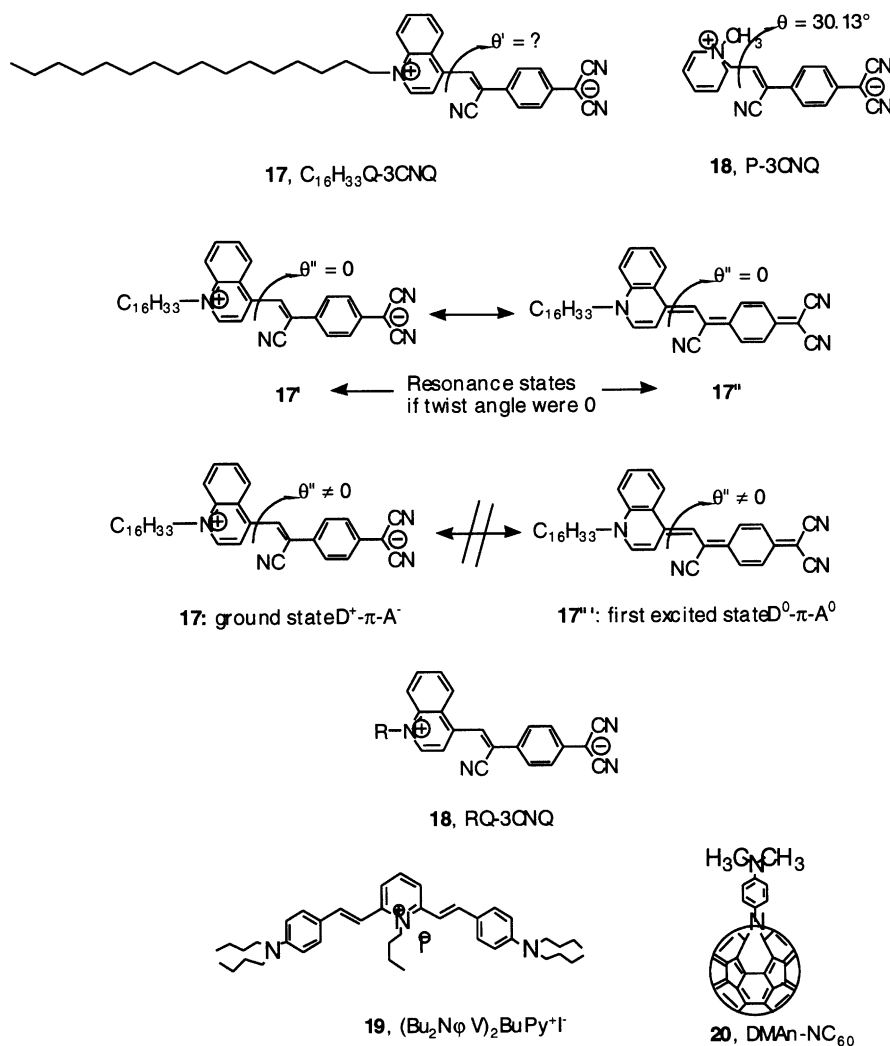


FIG. 4. The first molecular rectifier, **17** (30–36), a related zwitterionic molecule **18** (112), a generalized depiction **19** of analogs of **17** with different alkyl terminations, and two new rectifiers, molecules (Bu₂N ϕ V)₂BuPy⁺I⁻, **19** and DMAn-NC₆₀, **20**. The very important twist angle $\theta = 30.13^\circ$ in the crystal structure of **18** is caused by steric hindrance between a hydrogen on the pyridinium ring and the N atom of the closest cyano group (112). A similar twist angle θ' must exist in **17** (for which no crystal structure is available). If this twist angle θ' could be reduced to zero despite the steric hindrance, then structures **17'** and **17''** would be degenerate resonance states. Since the twist angle must be sufficiently far from zero, therefore **17** is the ground (or excited) state and **17''** is the first electronic excited (or ground) state, respectively.

less dissociated ($D^0-\pi-A^0$) in the first excited state. The twist angle $\theta = 30^\circ$ in structure **18** (and a presumably similar twist angle θ' in structure **17**) is non-zero for steric reasons, and prevents the pi electron bridge in structure **17** or **18** from allowing complete mixing of the quinolinium or pyridinium electrons with the electrons on the 3CNQ part. Since the molecule is hypsochromic, the ground state must be **17** ($D^+-\pi-A^-$), and the first electronically excited state must be **17''** ($D^0-\pi-A^0$). The shortness of the π bridge in **17** allows for a strong IVT between the D and A ends of the molecule. We now turn to the theoretical estimates of the molecular dipole moment μ_{GS} . If a full positive charge in **17** is placed on the quinolinium N atom and a full negative charge is localized on the central C atom of the

dicyanomethylene bridge, one estimates 50 Debyes for the dipole moment μ_{GS} (32). Molecular orbital analyses will yield such high dipole moments only if the phenyl ring is perpendicular to the quinolinium ring, i.e., if the twist angle θ' is 90° (114). For intermediate values of this twist angle, semiempirical molecular orbital theories provide lesser values of μ_{GS} , closer to 25 Debyes (32,93), possibly because of the parametrization of the theoretical method. The HOMO of **17** shows a delocalized charge density, spread on both the D^+ part and the 3CNQ⁻ part, while the LUMO is localized on the A^- part. An EPR spectrum of the anion radical of **17** shows a hyperfine spectrum for the $S = \frac{1}{2}$ species (37), whose spin densities can be simulated very well with significant densities localized on only the

3CNQ part of the molecule (32). No evidence was found for a twisted internal charge transfer transition in **17** within reasonable temperatures (32).

FILM PROPERTIES OF $C_{16}H_{33}Q$ -3CNQ, **17**

Molecule **17** forms amphiphilic Pockels–Langmuir monolayers at the air–water interface (collapse pressure = 34 mN m^{-1} , collapse area = 43 \AA^2 at 14°C and 50 \AA^2 at 20°C) (32). It transfers well on the upstroke, with transfer ratios around 100% onto hydrophilic glass, quartz, or aluminum (32, 87) or fresh hydrophilic Au (35, 36). It transfers poorly on the downstroke onto graphite, with a transfer ratio of about 50%. Thereafter, the monolayers transfer only on the upstroke, with 100% transfer ratios, onto all surfaces, forming Z-type LB multilayers (32, 87, 111) (except for that first poorly transferred layer on HOPG (87)). The monolayer thickness was determined by X-ray diffraction (2.3 nm (32), 2.9 nm (36)), spectroscopic ellipsometry (2.3 nm) (36), surface plasmon resonance (2.2 nm) (32, 97), and by X-ray photoelectron spectrometry (XPS) (2.5 nm) (97). Assuming a monolayer thickness of 2.3 nm and a calculated molecular length of 3.3 nm (with an all-trans geometry for the $C_{16}H_{33}$ “tail”), the tilt angle is $\cos^{-1}(2.3/3.3) = 46^\circ$ from the surface normal (32). The XPS spectrum of one monolayer of **17** on Au shows two N(1s) peaks, one at 401.7 eV (attributable to the quinolinium N), and the other at 399.4 eV (attributable to the three CN species) (97). An earlier XPS spectrum of a multilayer of **17** on Al was deconvoluted into three peaks, one at 402.3 eV (quinolinium N), one at 400.3 eV (neutral CN) and one at 398.8 eV (negatively charged CN) (37). An angle-resolved XPS spectrum shows that, as the take-off angle increases, the quinolinium N signal decreases, while the CN signal stays relatively constant: the cyano nitrogens lie closer to the Au substrate than does the quinolinium N atom (97). The valence band portion of the XPS spectrum agrees approximately with the density of molecular energy states (37). The contact angle of a drop of water on “hydrophilic Au” is measured to be 40° (it should be zero if the gold were perfectly free of hydrophobic adsorbates from laboratory air); this angle increases to 92° if a monolayer of **17** is transferred atop fresh hydrophobic Au: the hydrophobic alkyl chains are closer to the water surface than the hydrophilic quinolinolium or phenyl rings (97).

Thus, **17** adheres by the two terminal CN groups onto a hydrophilic substrate, is tilted maybe 45° from the surface normal, and shows alkyl chains to the air. This is confirmed by a grazing-angle FTIR study of **17** either on Al (32) or Au. Since **17** survives in the ultra-high vacuum of an XPS instrument, it must not desorb very rapidly from the substrate. The absorption spectrum of **17** of an 11-layer LB film has an intense IVT band peaked at 575 nm or 2.17 eV

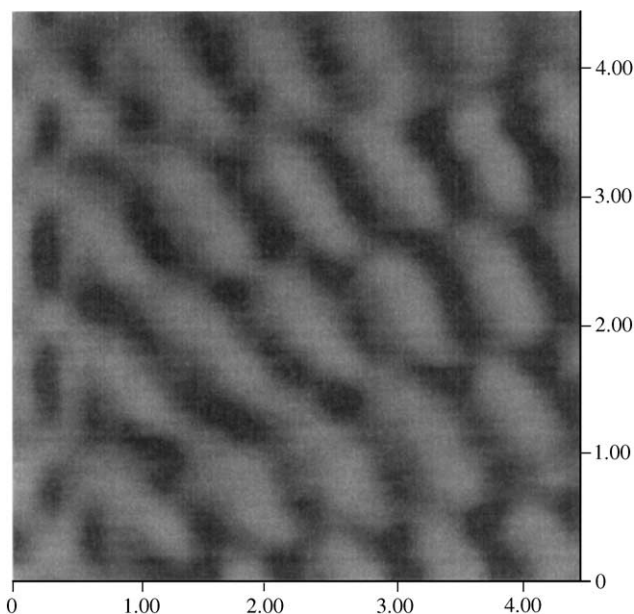


FIG. 5. STM image of an LB monolayer of $C_{16}H_{33}Q$ -3CNQ, **17** on HOPG, with Pt/Ir tip (Nanoscope III). Scan size = $4.5 \text{ nm} \times 4.5 \text{ nm}$, Z-range = 2.3 pA, bias = -316 mV ; setpoint current = 3.2 pA (32).

(32). LB multilayers of **17** have a strong second harmonic signal $\chi_{zzz}^{(2)} = 180 \text{ pm V}^{-1}$ which is resonance-enhanced at 532 nm (115). The fluorescence lifetime of **17** in solution in the near infrared has been measured to be less than 20 ps (116). The STM image of **17** on HOPG has been measured (Fig. 5) (32): since **17** adheres (poorly) with the alkyl chains closest to the graphite, what one sees is an unresolved image of the molecule seen from the dicyanomethylene end, with a repeat distance of $6 \text{ \AA} \times 12 \text{ \AA}$ (32), somewhat larger than the collapse area per molecule of 50 \AA^2 . The poor adhesion to graphite and the low coverage means that the image seen in Fig. 5 tends to move over time (32).

Metal–LB Film–Metal Sandwiches of $C_{16}H_{33}Q$ -3CNQ, **17**

LB monolayers and multilayers of $C_{16}H_{33}Q$ -3CNQ, **17** were sandwiched between macroscopic Al electrodes (32), and recently between Au electrodes (35, 36). First, the bottom electrode (Al or an adhesion layer of Cr followed by Au) is evaporated onto a glass or quartz or Si substrate; second, the LB monolayer or multilayer of **17** 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 (32) or a contact mask (35, 36), to make 30–48 pads (most recently of an area of 0.283 mm^2 each (36)) per substrate; fifth, a droplet of either Ag paste or Ga/In eutectic is put above the bottom electrode and (very gently) sequentially on one of the pads of the top electrode, and electrical measurements are made.

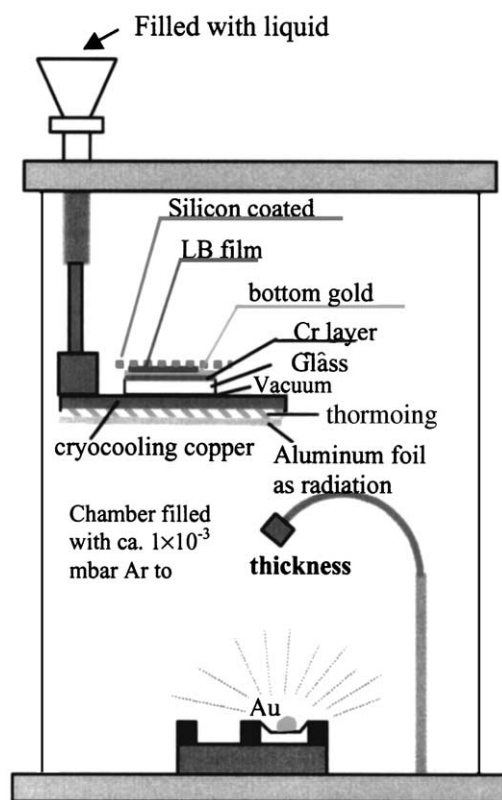


FIG. 6. Geometry of cold gold evaporation (36).

During the evaporation of the top electrode, a copper plate holding the sample is cooled by a liquid nitrogen bath; this suffices for Al deposition (32) but not for Au deposition. For Au deposition (Fig. 6), two additional and essential precautions were taken, one, to add 10^{-3} Torr of Ar gas to the evaporation chamber (113), the other, to protect 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 forces the Au atoms to undergo multiple scattering by Ar atoms before they reach the substrate (35, 36). The final metal–LB film–metal geometry is shown in Fig. 7 for Au electrodes (35, 36).

One should note that the Al layers have oxides on all sides, as does the GaIn eutectic drop, while the Au electrodes have no oxide covering.

UNIMOLECULAR RECTIFICATION BY $C_{16}H_{33}Q-3CNQ$, **17**

Arachidic acid, $C_{19}H_{39}COOH$, sandwiched as a monolayer or as a multilayer between Al electrodes, as in Fig. 7, has a sigmoidal and almost symmetrical IV curve under both positive and negative bias (as expected) for Al electrodes (32) and also for Au electrodes (36). When a monolayer of $C_{16}H_{33}Q-3CNQ$, **17** is placed between Al electrodes (with their inevitable patchy and defect-ridden

covering of oxide), a dramatically asymmetric current is seen (Fig. 8): the rectification ratio (RR) defined as the absolute value of the ratio of the current at a positive bias V to the current at the corresponding negative bias $-V$:

$$RR(V) = -I(V)/I(-V).$$

This RR is 26 at 1.5 V (32). Assuming a molecular area of 50 \AA^2 , the total current at 1.5 V corresponds to 0.33 electrons molecule $^{-1} \text{ s}^{-1}$ (32). The direction of enhanced electron flow is shown in Fig. 7. This same asymmetry is also seen for multilayers of **17**, for a four-layer film covered by Mg pads topped by Al pads (32) (as in the Sambles experiment (27, 31)), for monolayers and multilayers of **17** on graphite studied by scanning tunneling spectroscopy (32, 87), and even for a solution of **17** in dimethylsulfoxide (with some film of **17** on a graphite electrode) (32). The rectification ratios vary from pad to pad, as does the total current, in part because these are all two-probe measurements, with all electrical resistances (Al, Ga/In or Ag paste, wires, etc.) in series, and in part because any gentle pressure put manually on the top pad through the drop of Ag paste or eutectic to make electrical contact may vary between measurements. A review of all data suggested that any molecule which exhibits $RR(V) < 2$ at maximum bias V should not be taken as a rectifier (33). As high potentials are scanned repeatedly, the IV curves show progressively less asymmetry: the RR decreases gradually with repeated cycling of the bias across the monolayer. One should remember that putting 1.5 V across a monolayer of thickness 2.3 nm creates an electrical field of 0.65 GV m^{-1} ; many molecules in the monolayer may turn around, end over end, to minimize the total energy. Measurements of the temperature dependence of rectification of **17** between Al electrodes in the range $105 \text{ K} < T < 390 \text{ K}$ established that the asymmetry is not temperature dependent (34).

Despite using oxide-bearing Al electrodes, it seemed clear that the rectification of several molecules in parallel, or unimolecular rectification, had been measured. This conclusion rested on the assumption that the oxide covering of the Al electrodes was sufficiently defective to allow “ohmic” contact here and there 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 sites where the oxide coating was very thin or non-existent. This may not have been completely convincing to all readers. Luckily, the Sambles group showed how “cold gold” evaporation atop arachidic acid could be performed safely, without destroying the monolayer (113). Our implementation provided a dramatic increase of the current through the pads, and a gratifying confirmation that the same asymmetric conduction through the molecules could be

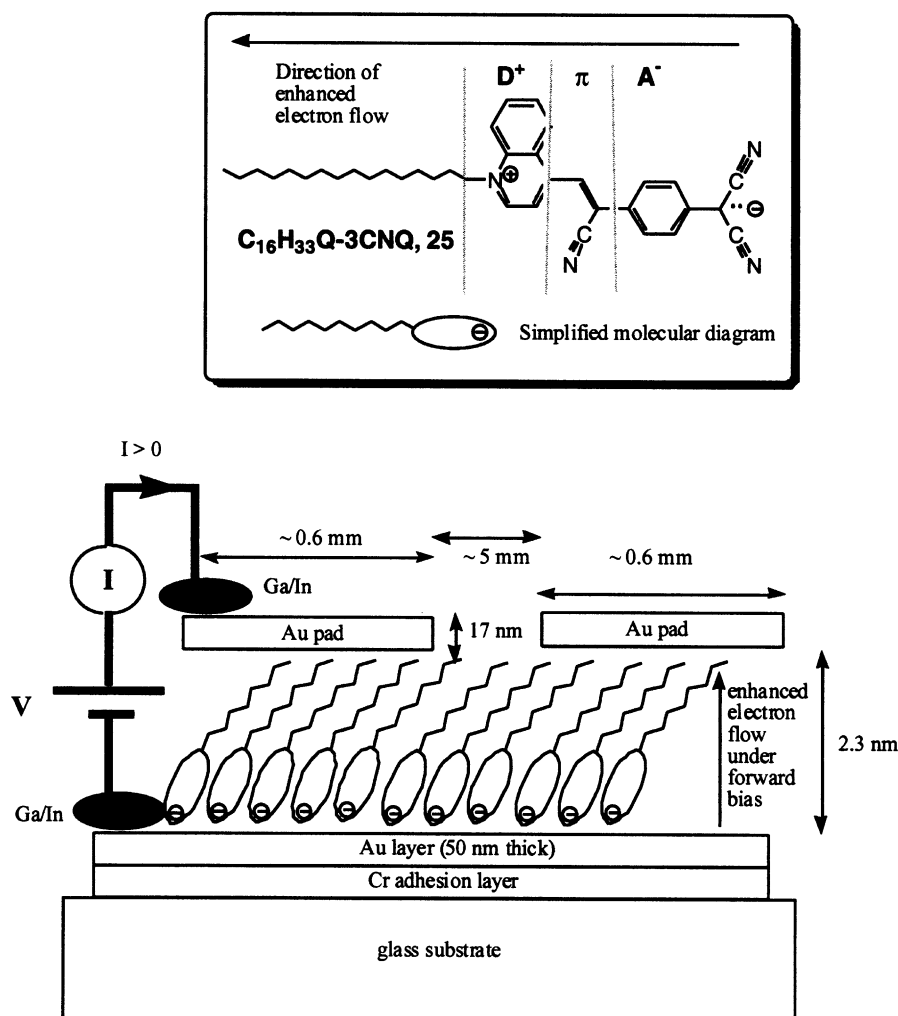


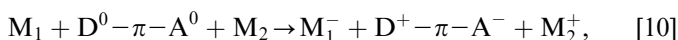
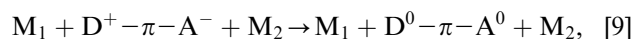
FIG. 7. Molecular structure and geometry of LB monolayer of $C_{16}H_{33}Q-3CNQ$, **17** sandwiched between Au electrodes, with the direction of enhanced electron flow indicated. The substrate was glass, $50\text{ mm} \times 50\text{ mm} \times 0.4\text{ mm}$, covered either by a Cr adhesion layer or by a hydrophobic xylene covering, followed by an evaporated Au film $50\text{ mm} \times 50\text{ mm} \times 50\text{ nm}$, then the LB monolayer or multilayer, then by 48 cylindrical Au pads, 17 nm thick and with an area of 0.283 mm^2 (36).

measured using Au electrodes (35, 36) as previously for Al electrodes.

Figures 9 and 10 give details of what was measured using Au electrodes. The best rectification ratio at 2.2 V was $RR = 27.53$ in the first cycle (36). Figure 9 shows how the rectification ratio decreases from cycles 1 to 6. Figure 10 shows that in some cells a saturation in the forward current is seen, as predicted by any physical model for conduction through a molecule, or a set of molecules measured in parallel. For some other cells, the current increases until breakdown occurs, and some cells do so only at 5.0 V, i.e., they break down only at a field close to 2 GV m^{-1} (36). It is quite clear that rectification by a one-molecule thick layer of $C_{16}H_{33}Q-3CNQ$, **17** is an established fact.

A plausible mechanism for rectification by $C_{16}H_{33}Q-3CNQ$, **17** is a minor change in the Aviram-Ratner

proposal, so that Eqs. [1]–[3] are replaced by



where the first step is the electric field-driven excitation from ground to excited state, followed by electron transfer across the two molecule-metal interfaces (32).

TWO NEW RECTIFIERS

Recently, two more molecules were studied, 2,6-di[dibutylamino-phenylvinyl]-1-butylpyridinium iodide, $(Bu_2N\phi V)_2BuPy^+I^-$, **19** (38) and dimethylanilinoaza

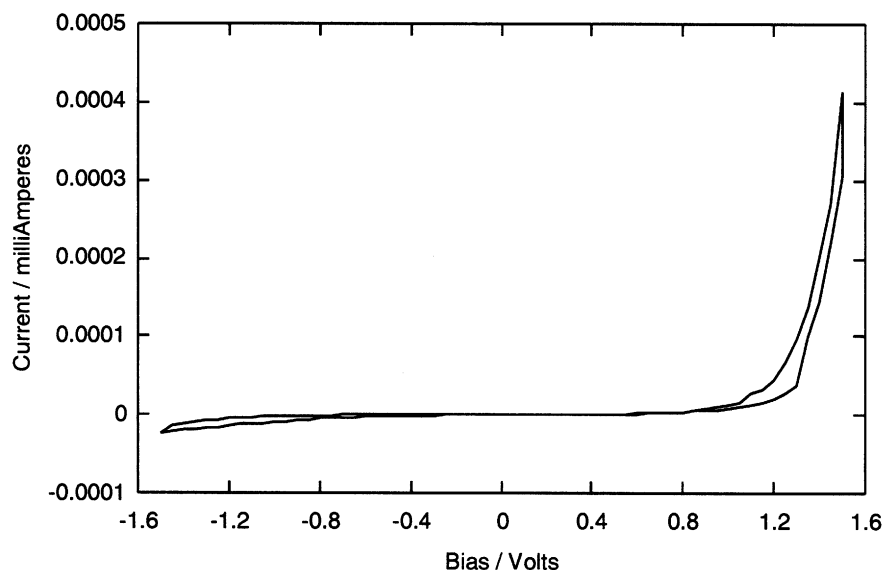


FIG. 8. Linear plot of the DC current I versus the DC applied voltage V through a single monolayer of $C_{16}H_{33}Q$ -3CNQ, **17** sandwiched between Al electrodes (top Al pad area 4.5 nm^2 , thickness 100 nm), using Ga/In eutectic and Au wires. The DC voltage is swept at a rate of 10 mV s^{-1} (32).

$[C_{60}]$ fullerene, DMan-NC₆₀, **20** (39) (Fig. 4): both are unimolecular rectifiers (the second one, barely).

$(Bu_2N\phi V)_2BuPy^+I^-$, **19** forms a Pockels–Langmuir film at the air–water interface, and transfers to hydrophilic

substrates as a Z-type multilayer. The monolayer thickness was estimated as 0.7 nm by spectroscopic ellipsometry, 1.15 nm by surface plasmon resonance (at $\lambda = 532 \text{ nm}$) or 1.18 nm (at $\lambda = 632.8 \text{ nm}$); and 1.3 nm by X-ray diffraction

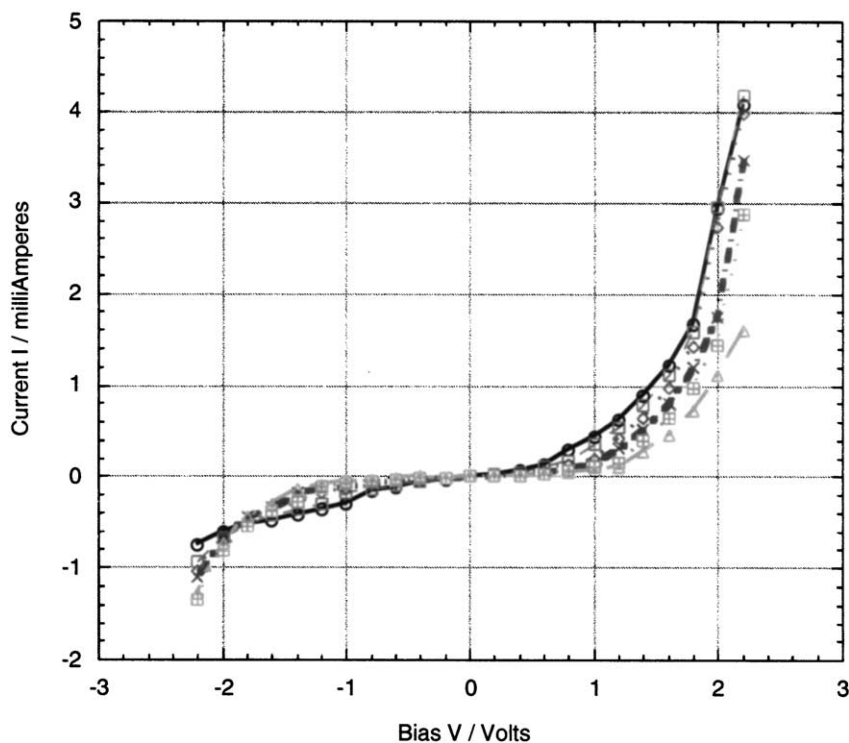


FIG. 9. IV plot for a cell “Au–monolayer of $C_{16}H_{33}Q$ -3CNQ, **17**–Au”, showing the decrease in rectification ratio. At 2.2 V in the first cycle, $R = 538 \Omega$, $I = 4.09 \text{ mA} = 4.5 \times 10^4 \text{ electrons molecule}^{-1} \text{ s}^{-1}$, and $RR = 5.39$. Cycle 1: \circ ; cycle 2: \square ; cycle 3: \diamond ; cycle 4: \times ; cycle 5: \oplus ; cycle 6: \triangle (36).

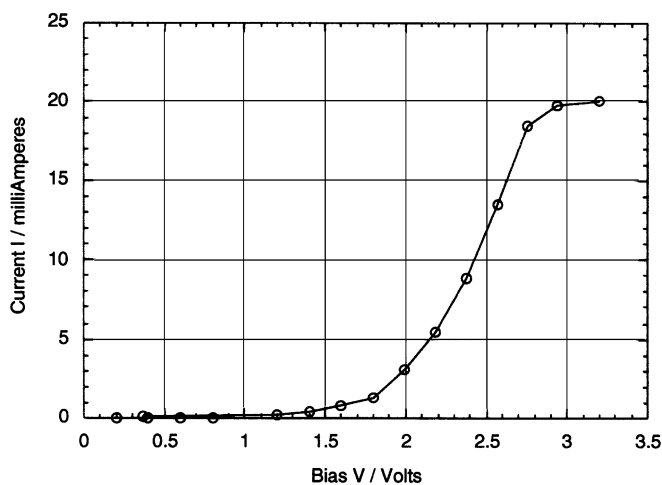


FIG. 10. *IV* plot for a cell "Au-monolayer of $C_{16}H_{33}Q-3CNQ$, **17**-Au," that shows saturation in the forward current $I = 20$ mA at 3.2 V (this cell broke down at 3.4 V) (36).

(38). The films have an absorption maximum at 490 nm (which is slightly hypsochromic in solution) attributable to back charge transfer from iodide to pyridinium, and a second harmonic signal $\chi^{(2)} = 50 \text{ pm V}^{-1}$ at normal incidence ($\lambda = 1064 \text{ nm}$) and 150 pm V^{-1} at 45° (38). X-ray photoelectron spectroscopy of a multilayer of **19** on a gold substrate finds only 30% of the expected signal from the iodide; it is likely that the iodide anion was partially replaced by a more abundant hydroxide anion during LB transfer (38). The rectification is shown in Fig. 11: once again, there is a decrease of rectification upon successive cycles. Some cells have initial rectification ratios as high as 60. The measurements of the molecular area at film transfer (100 \AA^2) and of the monolayer thickness (1.1–1.3 nm) are consistent with the molecule sitting above the bottom gold electrode with the iodide (or other gegenion) closer to the bottom Au electrode and the pyridinium ion above it; the

direction of enhanced electron flow is from the bottom Au electrode toward the top Au pad (as in Fig. 7). Therefore, 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 $(Bu_2N\phi V)_2BuPy^+I^-$, **19** is attributed to an interionic electron transfer, rather than to an intramolecular electron transfer (39). The azafullerene DMA-n-NCa, **20** 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 (39). The Pockels–Langmuir film is very rigid, but the molecular areas are 70 \AA^2 at extrapolated zero pressure, and 50 \AA^2 at the chosen LB film transfer pressure of 22 mN m^{-1} , whereas the true molecular area of C_{60} is close to 100 \AA^2 (117, 183). Therefore, it is thought that the molecules **20** transferred onto Au on the upstroke are actually somewhat staggered, with the more hydrophilic dimethylamino group closer to the bottom Au electrode. The film thickness is estimated by XPS to be 2.2 nm (39). The monolayer is covered, as previously (36, 37), with 17 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 $N(1s)$ XPS spectra confirm that the two N atoms are closer to the bottom Au electrode than is the C_{60} cage (39). The current–voltage plots are a dramatic and somewhat unwelcome surprise (39).

The top pads have an area of 0.283 mm^2 , as before (36, 37), but now the cell supports 1 A of current across it (per molecule, that would be an absurdly large number such as 5×10^{11} electrons per molecule per second)! Moreover, the high current between 1.5 and -0.5 V is ohmic. This asymmetry decreases upon cycling (39). 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. In contrast, some cells show no such large current, but a much smaller current, which is "marginally" rectifying (33) in the forward direction, with RR of about 2 (39).

OTHER RECTIFIER RESULTS

Several reports of asymmetric conduction through molecules have appeared in the literature over the past 40 years. It is well known that junctions of μm -thick layers of n-doped organic semiconductors with w -thick layers of p-doped organic semiconductors act as rectifiers (119–122). LB multilayers, "doped" with interspersed electron donors, then covered by insulating LB monolayers, then covered by LB multilayers "doped" with electron acceptors also form rectifiers, as was demonstrated by Kuhn and co-workers (123), and confirmed by others (124, 125). An electrochemical L–B photodiode has been produced (126). Electrochemical rectification at a monolayer-modified electrode

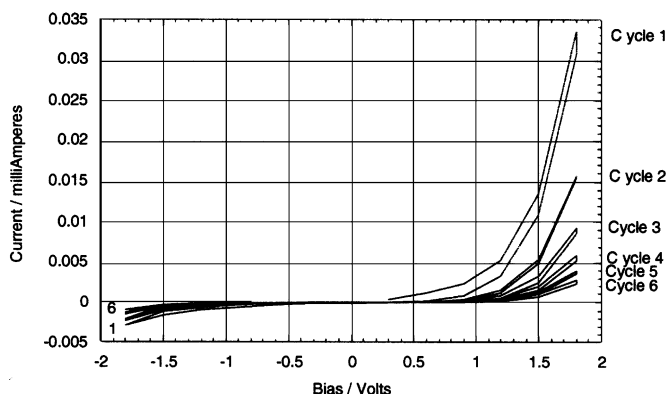


FIG. 11. Current–voltage plots for $(Bu_2N\phi V)_2BuPRy^+I^-$, **19** measured in an "Au-LB monolayer of **19**-Au" cell, for six successive cycles of measurement. The rectification ratios are $RR = 12, 7, 5, 4, 3, 3$, for cycles 1, 2, 3, 4, 5, 6, respectively (38).

has been reported (127,128). A porphyrin covalently bonded to a carboxylated highly oriented pyrolytic graphite (HOPO) surface, and studied by STM also rectifies (129). An unsymmetrical STM tunneling current was measured through an alkylated hexabenzocoronene deposited on graphite (100), and through an oligo(phenylethynyl)benzenethiol (130). Recently, two new multilayer rectifiers have been studied (131, 132).

Not all asymmetric currents seen in “metal–molecule–metal” cells are due to asymmetries in the molecular energy levels. At any “molecule–metal” interface, a set of dipoles may form, that become Schottky barriers (133). Furthermore, it has been pointed out that if a chromophore is placed asymmetrically within a metal–molecule–metal sandwich, a current asymmetry will be produced (96): this may explain the results of Ref. (100), for example, and also provide food for thought for researchers who to bond alkanethiol terminations to gold, or add long hydrocarbon tails to form LB films.

CHALLENGES FOR THE NEAR FUTURE

Although unimolecular rectification has been fully confirmed, there are still open questions:

- (1) How fast is the rectification?
- (2) Can inelastic electron tunneling spectroscopy confirm that the electron really does go through the bonds in the molecule (rather than tunnel through space)?
- (3) Can the device be made more sturdy?
- (4) What do the metal electrodes do during the measuring process? Can they form stalagmites and stalagmites within the monolayer?
- (5) Can one investigate optically what occurs during the electrical measurements?
- (6) Can unimolecular rectifiers and strands of conducting polymers be grafted together to form a molecular transistor with power gain?

CONCLUSION

We have presented here a review of unimolecular rectification, which, a quarter century after it was first proposed, 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.

ACKNOWLEDGMENTS

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