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

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The Concept of Unimolecular Electronics

In 1959, the late Richard P. Feynman proposed, in his usual witty way, that there was "plenty of room at the bottom", i.e., that atomic and molecular dimensions had not yet been exploited in information storage.[1] In electronic technology, what was initially called "micro-miniaturization" did provide fantastic economies of scale, cost, and speed: the integrated circuits (IC) introduced by Noyce and Kilby were the beginning of this trend. It was observed that the scale of ICs or "computer chips" has halved, at first every 2 years, then every 18 months;[2] this brought a concomitant increase in computing speed ("VAX on a chip", then "Cray on a chip") and an astonishing decrease in unit cost. However, there is trouble ahead. Circuit designers talk about "design rules", the closest distance between adjacent electronic components in the IC. These design rules define the clock cycle, which is the time required to travel between the furthest components on the chip: shorter cycles mean faster computing. These design rules have now crept down to about 180 nm commercially. If photolithography is used, the design rules are limited, by Rayleigh's criterion,[3] to about one-half the wavelength of light used. Capacitative coupling between components and heat dissipation are perennial headaches. Three-dimensional integration (rather than planar integration) has remained an elusive goal. To achieve better performance, i.e., going to design rules of 100 nm or below, requires abandoning UV radiation and resorting to X-ray or electron beam lithography, with much higher error rates. At 50 nm, an even more drastic limit sets in: one can no longer "dope" Si uniformly. Present projections are that this 50 nm "silicon wall" will be reached by the year 2005.[4]

The idea of using molecules as electronic devices has gained attention and respectability in the past quarter century. By chemical insertion of electron-donating or electron-withdrawing groups, molecules can become one-electron donors (D) or one-electron acceptors (A). To work properly, the oxidation or reduction of these molecules must be chemically reversible. In group IV chemistry (today, group 14: Si, Ge), one dopes a crystal of Ge or Si with dilute concentrations of interstitial or substitutional electron-rich elements (group V, or 15: N, P, As, etc.) to achieve an "n-doped" material. To make a "p-doped" crystal, one dopes with group III (or 13: Al, Ga, In, etc.). Thus, "D" corresponds to "n", and "A" corresponds to "p".

By accosting a micrometer-thick film of organic D molecules to a micrometer-thick film of an organic A molecules, one gets a microscopic DA rectifier (one-way conductor) of electrical current, equivalent to an inorganic pn rectifier.[5] In the 1960s, and particularly in the early 1970s, organic charge-transfer crystals and conducting polymers yielded organic equivalents of inorganic electronic systems: semiconductors, metals, superconductors, batteries, etc.[6] But this wave of "me-too-ism" did not create a new technology: the organic systems did not perform better, or less expensively, than their inorganic counterparts. The two niche areas that survived are liquid crystal displays and (maybe) light-emitting diodes based on conducting polymers.

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

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

Milestones in Unimolecular Electronics

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

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

(2) The electrical resistance of a single molecule (1,4-benzenedithiol) bonded to two Au electrodes was mea-

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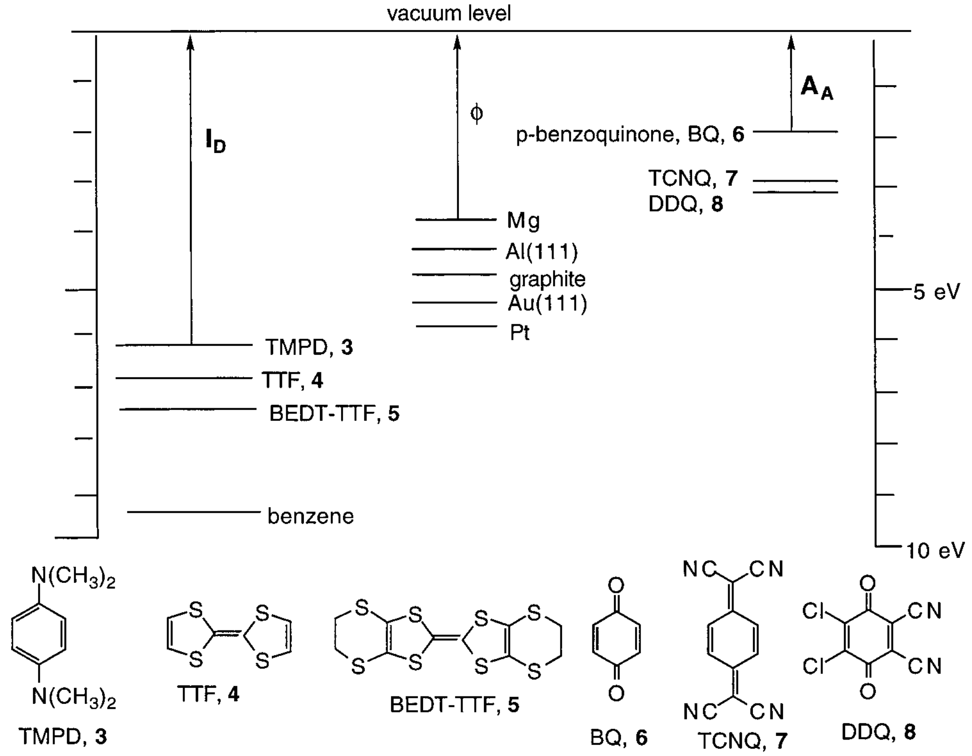
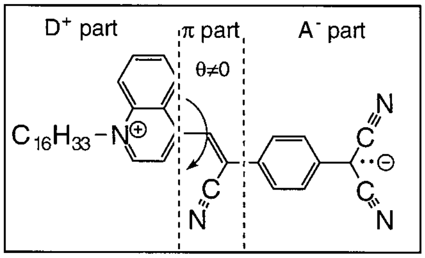


FIGURE 1. Energy levels relevant to potential unimolecular electronic devices: HOMOs and ionization potentials I_D of some organic one-electron donors D (left), work functions ϕ of some metals (middle), and LUMOs and electron affinities A_A of some organic one-electron acceptors A (right).

sured: it was a few megaohms, because the work function of Au and the LUMO of the molecule were mismatched.[14]

(3) The quantum of electrical resistance (12 kΩ) was measured at room temperature when a carbon nanotube, glued to a conducting AFM tip, was lowered into liquid Hg.[15]

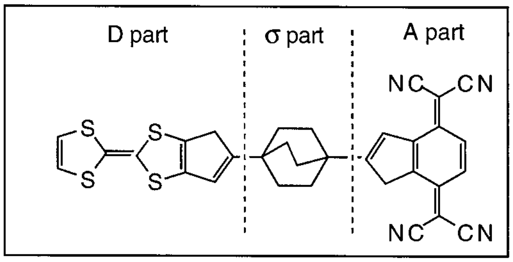
(4) The Aviram–Ratner mechanism,[16] slightly modified, was confirmed in both macroscopic and nanoscopic conductivity measurements through a monolayer of γ-hexadecyl-quinolinium tricyanoquinomethanide, **1**: this is the first proven two-terminal molecular device.[17] This result is reviewed in some detail below.



$C_{16}H_{33}$Q-3CNQ, **1**

The Aviram–Ratner Ansatz of Unimolecular Rectification

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



Gedankenmolekül, **2**

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

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

(1) I_D for the D end must be small and match as closely as possible the work function ϕ_1 of the metal layer M_1 (Figure 1), but if I_D is too small, the molecule would oxidize in air.

(2) A_A for the A end must be as large as possible and match if possible the work function ϕ_2 of the metal layer M_2. Figure 1 shows that this is not easy.

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

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

Multilayer LB Organic Rectifiers and LB Photodiode

LB multilayer rectifiers have been made by Kuhn and co-workers,[18] Sugi and co-workers,[19] and Roth, von Klitzing, and co-workers;[20] these results could not be extended down to the monolayer level. Fujihira and co-workers demonstrated an LB monolayer photodiode, which is probably the first unimolecular electronic device.[21]

Getting Electrons to and from a Unimolecular Device

How does one make electrical contact to a molecule? Single-molecule detection is possible in fluorescence, but that experiment does not make an electrical contact. Scanning tunneling microscopy (STM) does allow us to "talk" to a single molecule. However, moving the STM tip amidst large arrays of molecules is impractical for information storage applications, because the piezoelectric distortions that control the tip position are too sluggish for rapid access to a new distant location on a surface. To address a single molecule electrically, one could think of a "molecular wire" (e.g., a polyacetylene strand) or a "molecular antenna" (e.g., the conjugated portion of β-carotene), but one must still make a connection to an external potential source. For macroscopic connections, two techniques seem promising: (1) the LB physisorption technique used to transfer molecules onto a pre-chosen macroscopic electrode and (2) the technique of covalent "self-assembly", or covalently bonding molecules to electrode surfaces. The former technique requires adding long "greasy chains" to enable ordering at the air−water interface before transfer to a solid substrate; the latter requires mostly thiols, disulfides, or silanes at one or both ends of a molecule. Self-assembly was used ingeniously to measure the conductivity of 1,4-benzenedithiol bonded to Au shards atop a Si break junction.[14] For both techniques, all electrical connections ultimately involve matching, possibly under bias, the Fermi levels of an inorganic metal to the HOMOs and/or LUMOs of organic molecules and avoiding unnecessary Schottky barriers (e.g., at the partially ionic Au−thiolate interface). Excessive bias will, of course, lead to dielectric breakdown. Excessive heating can lead to chemical decomposition.

Potential Unimolecular Rectifiers

As reviewed elsewhere, collaborations with C. A. Panetta at the University of Mississippi and M. P. Cava at the University of Alabama netted several candidates for unimolecular rectification, i.e., D−σ−A and D^+−π−A^- molecules designed to form physisorbed LB films.[11,22−29] Some of these are molecules **1** and **9**−**17** (Chart 1); molecule **1** became the first confirmed unimolecular rectifier.[17]

The various D−σ−A molecules that formed insoluble Pockels−Langmuir (PL) films[35] at the air−water interface and can be mostly transferred as LB films onto solid substrates were the carbamates **9**−**13**, and triptycene-quinone linked to TTF derivatives **14** and **15**. The D^+−π−A^- zwitterions were **1**,[30] which formed a rectifier, and its benzochalcogenazolium analogues **16** and **17**, which did not.[31] The monofunctionalized strong acceptors BHTCNQ and HETCNQ could only be produced in low yields. The very interesting strong donor−strong acceptor TTF−C−BHTCNQ (**9**) was difficult to purify.[22] The strongest films (highest collapse pressure) were obtained with **10b**.[34] As predicted, the triptycenequinone (weak A) in **14** and **15** could not be converted to triptycene-dicyano-quinodiimine (strong A) as the last synthetic step.[32]

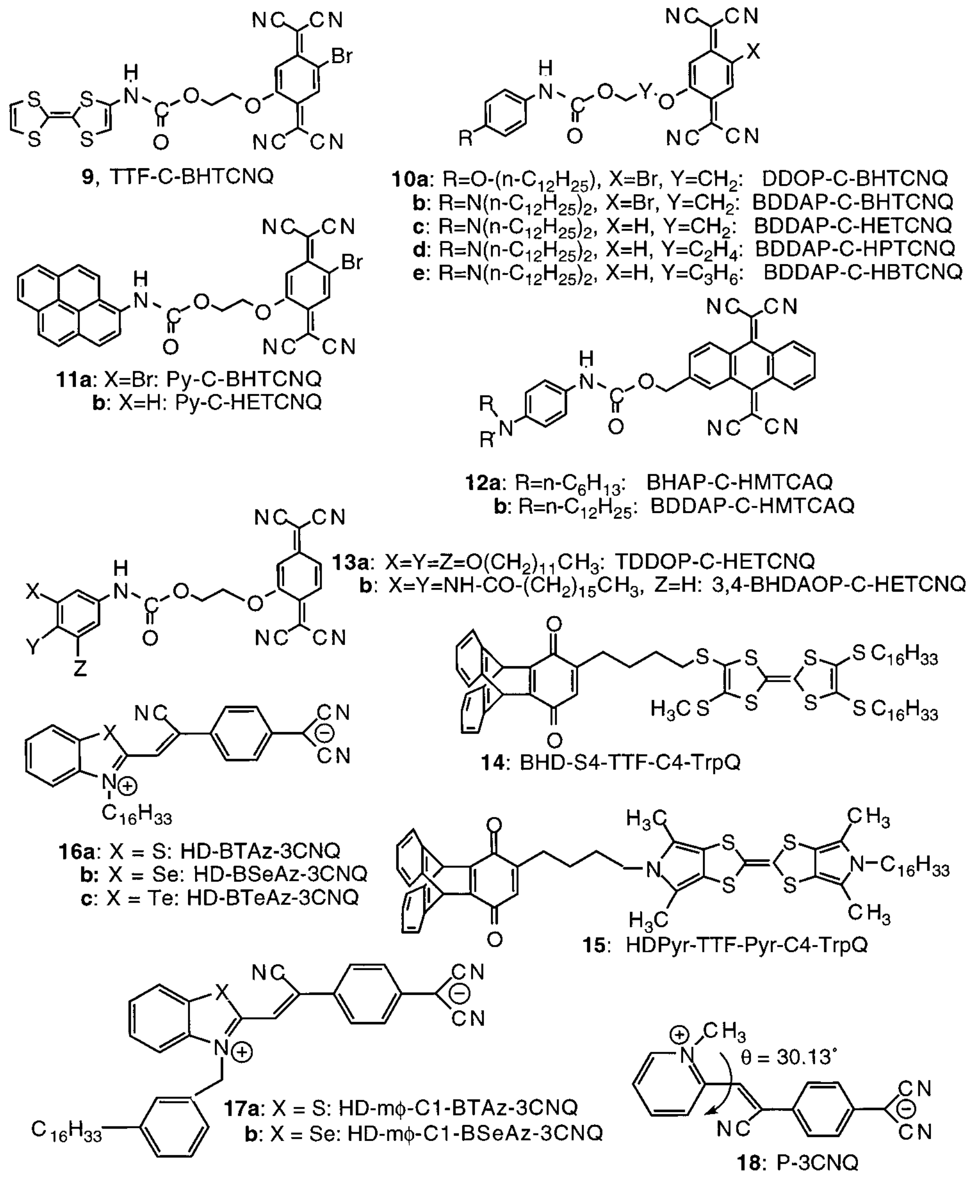
Initial Rectification Reports

The first rectification attempts, macroscopic[33,34] or nanoscopic (using an STM)[35,36] using mostly molecules **10a** and **10b**, were unsuccessful. Several asymmetric current−voltage (I−V) curves were reported in STM experiments on other systems: Cu tetraazaporphyrin bonded to carboxylated HOPG,[37] an alkylated hexabenzocoronene,[38] and an oligophenylethynyl-benzenethiol.[39] Electrochemical rectification at a monolayer-modified electrode was reported.[40,41]

Rectification in Pt|LB Film|Mg|Ag Sandwiches

Sambles and co-workers found that an LB multilayer of DDOP−C−BHTCNQ, **10a**, sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film:[42] they succeeded in making macroscopic defect-free LB multilayers and depositing atop the organic layer a metal film of magnesium (shadowed with Ag) without shorting the device. However, **10a** does not contain a strong donor moiety, i.e., I_D is probably too large for an Aviram−Ratner rectifier. The observed rectifying behavior of **10a** was later

Chart 1



9, TTF-C-BHTCNQ

10a: R=O-(n-$C_{12}H_{25}$), X=Br, Y=CH_2: DDOP-C-BHTCNQ
b: R=N(n-$C_{12}H_{25}$)$_2$, X=Br, Y=CH_2: BDDAP-C-BHTCNQ
c: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=CH_2: BDDAP-C-HETCNQ
d: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=C_2H_4: BDDAP-C-HPTCNQ
e: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=C_3H_6: BDDAP-C-HBTCNQ

11a: X=Br: Py-C-BHTCNQ
b: X=H: Py-C-HETCNQ

12a: R=n-C_6H_{13}: BHAP-C-HMTCAQ
b: R=n-$C_{12}H_{25}$: BDDAP-C-HMTCAQ

13a: X=Y=Z=O$(CH_2)_{11}CH_3$: TDDOP-C-HETCNQ
b: X=Y=NH-CO-$(CH_2)_{15}CH_3$, Z=H: 3,4-BHDAOP-C-HETCNQ

14: BHD-S4-TTF-C4-TrpQ

16a: X = S: HD-BTAz-3CNQ
b: X = Se: HD-BSeAz-3CNQ
c: X = Te: HD-BTeAz-3CNQ

15: HDPyr-TTF-Pyr-C4-TrpQ

17a: X = S: HD-mϕ-C1-BTAz-3CNQ
b: X = Se: HD-mϕ-C1-BSeAz-3CNQ

18: P-3CNQ

reinterpreted to be due not to molecular rectification, but to Schottky barrier formation between Mg and TCNQ, i.e., to the formation of a salt, either $Mg^{2+}TCNQ^{2-}$ or $Mg^{2+}(TCNQ^-)_2$, at the metal–organic interface.[43,44]

Sambles's group also found asymmetries in an LB multilayer of the ground-state zwitterion $C_{16}H_{33}Q-3CNQ$, **1**, sandwiched between Pt and Mg electrodes;[30] there was also a slight $I-V$ asymmetry for an LB monolayer of **1**.[30] To partially alleviate doubts about a possible Schottky barrier, an insulating LB layer of ω-tricosenoic acid was next put between **1** and the electrodes; the $I-V$ asymmetry persisted.[45,46] It was thus claimed that molecular rectification had been observed, albeit between asymmetric metal electrodes.[45]

Rectification in Al|Al_2O_3|LB Monolayer|Al_2O_3|Al Sandwich

A very thorough repetition and major amplification of Sambles's pioneering work on $C_{16}H_{33}Q-3CNQ$, **1**, was carried out.[17,27,47–52] We review first the general physical and chemical properties of **1**. The synthesis of **1** was vastly improved.[17] Cyclic voltammetry reveals that **1** is a weak reversible one-electron acceptor, with a reduction half-wave potential (−0.513 V vs SCE in CH_2Cl_2) close to that of *p*-benzoquinone; the second reduction and the first oxidation of **1** are electrochemically irreversible.[17] If one holds the electrochemical potential at the first reduction potential and measures the electron paramagnetic resonance spectrum, the spin densities of the negative ion radical $\mathbf{1}^-$ are mostly localized on the 3CNQ ring;[50] therefore, the LUMO of **1** is mostly localized on the 3CNQ moiety. The dipole moment of **1** in CH_2Cl_2 solution is 43 ± 8 D, as befits a zwitterion with a 10.5-Å separation between the positive charge (on the quinolinium N) and the negative charge (on the dicyanomethylene bridge).[17] The intense blue or green color of a solution of **1** (depending on solvent) disappears at the first trace of acid but is recovered if the solution is exposed to ammonia

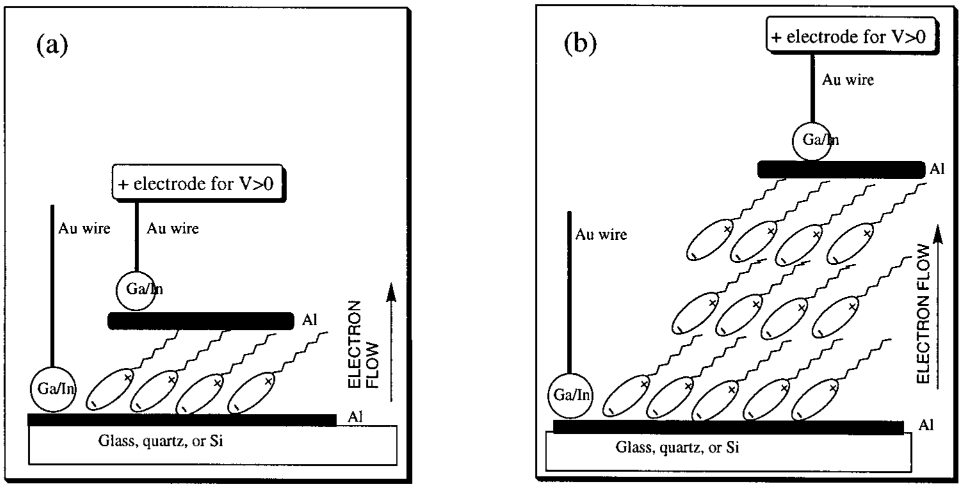


FIGURE 2. Orientation of the LB monolayer (a) or multilayer (b) of **1** on a glass, quartz, or Si substrate. The electrode (+) for positive bias and the direction of "easy" electron flow for $V > 0$ are marked. Reprinted from ref 17. Copyright 1997 American Chemical Society.

vapor. This blue or green absorption, probably due to an intervalence transition (IVT) band or intramolecular charge-transfer transition, is narrow, intense, and hypsochromic:[17,50] this peak shifts from $\lambda_{max} = 838$ nm in $CHCl_3$ (least polar solvent) to $\lambda_{max} = 711$ nm in CH_3CN (most polar solvent). There are two fluorescence emissions, one in the visible region (corresponding to UV absorption bands) and the other in the near-infrared region.[50] The excited-state dipole moment is calculated at between 3 and 9 D.[50] The IVT transition is probably to an excited singlet state, rather than to a biradical state, and may not involve a large change in the torsion angle θ (shown in structure **1**); i.e., it is probably not of the twisted internal charge transfer (TICT) type.

Although **1** is not a strong donor−strong acceptor molecule, it has a spectroscopically allowed transition between a ground state with a high dipole moment and an excited state with low dipole moment. In contrast, in molecule **16a**, the loss of vibronic structure, as the dielectric constant of the solvent increases, masks any solvatochromic shift in the absorbance maximum;[31] this lack of strong solvatochromism may help explain why LB films of **16** or **17** do not rectify.[31] Simple semiempirical MO calculations (AM1, PM3) do not yield a large ground-state dipole moment for **1**,[17] unless $\theta \approx 90°$.[53] Larger dipole moments are obtained in LDA calculations.[54] There is no evidence of a proposed TICT transition in **1** due to a large internal rotation:[53] the ^1H NMR of the H bonded to the ring carbon attached to the quinolinium N atom shows a large chemical shift (relative to what is expected from neutral quinoline) due to the zwitterionic ground state;[17] there is no change in the NMR spectrum as a function of temperature.[50] Evidently, **1** has some non-zero twist angle θ between the quinolinium ring and the phenyl ring, due to a steric hindrance, which guarantees that the ground state is not that of a cyanine dye (where the zwitterion state $D^+{-}\pi{-}A^-$ and the undissociated ("neutral") state $D^0{-}\pi{-}A^0$ would be degenerate) but rather that of a zwitterion. **1** forms multiply twinned crystals, whose unit cell could not be indexed.[17] However, the crystal structure of a related compound, picolyltricyanoquino-dimethan, or picolinium tricyanoquinodimethanide, **18** (Chart 1), exhibits a twist angle $\theta = 30°$ (dihedral angle between the pyridinium ring and the phenyl ring of 3CNQ).[55]

When left in air and intense sunlight for weeks, a solution of **1** can discolor, by some unknown mechanism. Most manipulations of **1** were thereafter carried out with minimum exposure to light. **1** forms PL films at the air−water interface; by using a darkened room, a collapse area of 50 $Å^2$ at a collapse pressure of 34 $mN\ m^{-1}$ was seen.[17,47] The monolayer thickness (X-ray diffraction, ellipsometry) is 23 Å, which means that this 30 Å long molecule is inclined by about 45° to the film normal.[17] Z-type multilayers form on Al, as depicted in Figure 2b. A grazing-angle Fourier transform infrared spectrum of a monolayer of **1** on Al shows two CN peaks at 2139 and 2175 cm^{-1}.[17] The X-ray photoelectron spectrum of a multilayer shows three N 1s peaks; the valence band onset is at −7.8 eV vs vacuum, close to the calculated (PM3) HOMO at −7.8 eV.[50] The intense IVT band is at $\lambda_{max} = 565$ nm in the LB monolayer[50] and also in the LB multilayer.[17]

The rectification work was performed both on macroscopic Al|LB film|Al sandwiches and by nanoscopic STM.[17] Sambles found that Mg perturbs a physisorbed LB film the least. We decided to use Al on both sides of the LB film but cryocooled to 77 K the glass|Al|LB film assembly, to minimize the thermal load on the LB film as the Al pad electrode is deposited from the vapor phase.[17] The LB films were thoroughly dried, to prevent any spurious effect due to moisture (which has a large effect on the electrical characteristics of Y-type centrosymmetric arachidic acid multilayers).[17] A drop of Ga/In eutectic was used to make contact with Au wire electrodes, as shown in Figure 2. Asymmetric $I{-}V$ curves were seen in a four-monolayer Z-type LB film, as well as in a four-monolayer film with a Mg electrode between the organic layer and the top Al pad,[17] and even for a single monolayer (Figure 3).[17] In a control experiment, no $I{-}V$ asymmetry was seen for Y-type multilayers of arachidic acid after careful sample drying.[17] Rectification for **1** was also seen, as a function of temperature, between 370 and 105 K (Figure 4).[51] The maximum measured rectification ratio (at 1.5 V, Figure

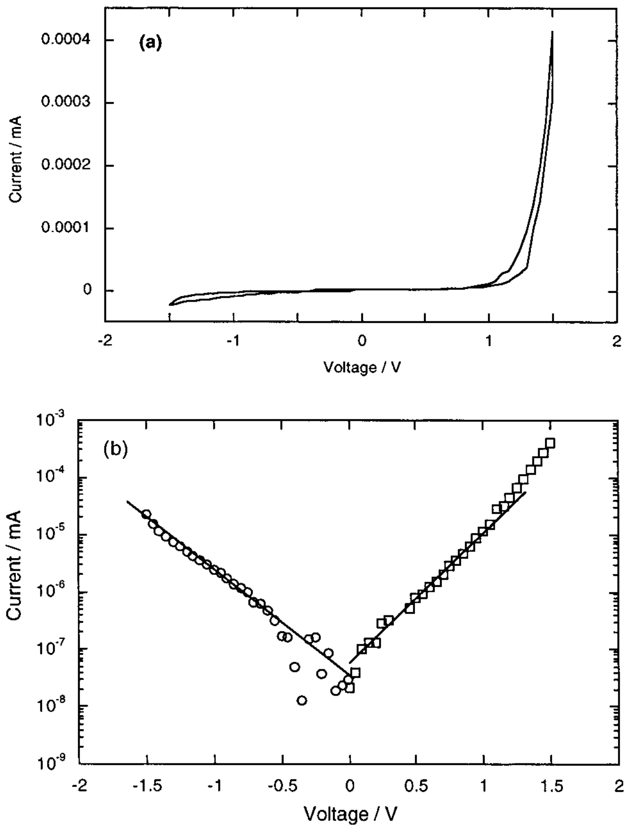


FIGURE 3. Rectification at 297 K through a single 2.3 nm thick monolayer of **1** sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using, as shown in Figure 2a, Ga/In eutectic and Au wires. (a) Plot of the dc current *I* versus the dc applied voltage *V*. (b) Plot of log *I* versus *V*. Reprinted from ref 17. Copyright 1997 American Chemical Society.

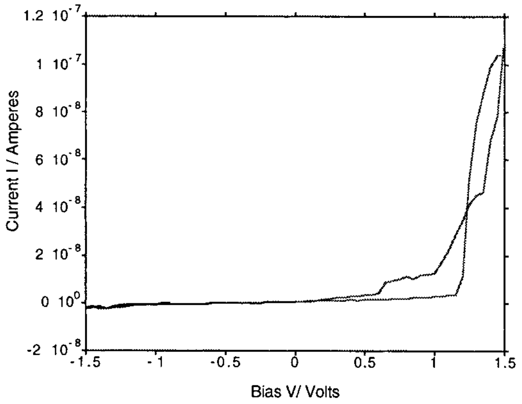


FIGURE 4. Rectification at 105 K (plot of dc current *I* versus dc applied voltage *V*) for a single 2.3 nm thick LB monolayer of **1**, sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using, as shown in Figure 2a, Ga/In eutectic and Au wires. Reprinted from ref 51. Copyright 1999 American Chemical Society.

3a) was 26:1. However, if one cycles the measurement, the rectification ratio for **1** decreases over time: as the monolayer feels the immense electric fields (up to 6.5 MV cm^{-1}), the physisorbed molecules probably "flip" between the Al pads.[17] In the range from -0.5 to 0.5 V, the $I-V$ curve is ohmic; in reverse bias (from -1.8 to -0.5 V) and in forward bias (from 0.5 V to between 0.8 and 1.3 V), log $I \propto V$ (Figure 3b); past $V = 0.8-1.3$ V, sample-dependent, an enhanced current is observed (Figure 3a and 3b).[17] The current measured amounts to about 0.33 electrons molecule^{-1} s^{-1}.[17] Of course, not all Al|monolayer|Al "pads" rectify. After one discards the shorted junctions, or the junctions that short during the experiment, there are still several pads which exhibit either symmetrical $I-V$ curves, or curves which "rectify the wrong way"; these "aberrant" junctions show lower currents and a characteristically different dependence on voltage.[52] The direction of the current for forward bias, shown in Figure 2, indicates that the negative charges are "pushed" by the polarity of the electrode from the dicyanomethylene end, through the bridge, to the quinolinium end of the molecule. The Aviram–Ratner mechanism for D–σ–A molecules considered an undissociated ground-state $D^0-\sigma-A^0$ and a zwitterionic excited-state $D^+-\sigma-A^-$; this mechanism can be trivially modified and inverted for the case where the ground state is mostly zwitterionic ($D^+-\pi-A^-$) and the excited state is mostly undissociated ($D^0-\pi-A^0$).[17]

The rectification was also verified for a 15-layer film of **1** on HOPG by STM,[17,47] and a small $I-V$ asymmetry was even seen for monolayer of **1** on HOPG,[17] but there is low adhesion of that first monolayer on HOPG.

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

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

Puzzles

There are still some unsolved puzzles:

(1) The sandwiches using Al or Mg electrodes bear an inevitable oxide layer. Al is a "valve" metal, and its thin covering with oxide is not defect-free, unless it is anodized.[56,57] Control experiments using arachidic acid[17] reduce the problem but do not eliminate it. Adhesion of LB films to hydrophilic Au is poor, and depositing oxide-free Au pads on an LB monolayer destroys it by heating, despite cryocooling the sample holder.

(2) The Ga/In eutectic has, typically, a 100 kΩ contact resistance with the Al pads,[51] which is 1–2 orders of

magnitude less than the resistance of the LB monolayer. When the eutectic wets the Al by piercing through the oxide layer, then the pad lifts off the monolayer. Ag paste has similar problems.

(3) The measured current, 0.33 electrons molecule^{-1} s^{-1} (5.3×10^{-20} A),[17] is many orders of magnitude lower than the currents measured in an STM experiment (10 pA to 1 nA): maybe only one molecule in a million is “at work”.

(4) The reduction of the rectification ratio upon repeated cycling[17] and the number of “aberrant” junctions could be partially eliminated by chemisorbing a suitably modified version of molecule **1** onto Si or Al. A thiol termination is incompatible with the acid-sensitive molecule **1**. A silanized version of **1** was prepared but in initial experiments did not form a uniform layer on Si.

(5) The Volta, or Kelvin potential of about 0.5 V for a monolayer of **1** at the air—water interface[17] or for a dry monolayer of **1** on Al is 1 order of magnitude lower than expected for a zwitterionic monolayer.

(6) Asymmetrical STM currents for molecules that have no rectifying moieties[38,39] are puzzling; it is likely[38] that the molecules, if placed asymmetrically within the potential field, can experience asymmetric tunneling currents.

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

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

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

Conclusion

The goal of Aviram—Ratner rectification through an oriented $D^{+}-\pi-A^{-}$ monolayer has been achieved. Much exciting work lies ahead, as we proceed toward making unimolecular electronics a practical reality in the 21st century.

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