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THE QUEST FOR UNIMOLECULAR RECTIFICATION FROM OXFORD TO WALTHAM TO EXETER TO TUSCALOOSA

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THE QUEST FOR UNIMOLECULAR RECTIFICATION FROM OXFORD TO WALTHAM TO EXETER TO TUSCALOOSA

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Dedicated to the memory of Professor Sukant K. Tripathy,
who did so much and died so young.

ABSTRACT

A unimolecular electronic device should perform active electronic functions by exploiting the energy levels, or conformations, of a singlemolecule, or a very few molecules, and should be addressable electrically by macroscopic electrodes. We found unimolecular rectification in a molecule, γ-hexadecylquinolinium tricyanoquinomethanide, **4**, in which the ground state is Zwitterionic: D^+-π-A^-, while the first excited state is undissociated: D^0-π-A^0. This 2.3 nm long unimolecular device, measured three years ago between Al electrodes and now between Au electrodes, confirms a 1974 proposal by Aviram and Ratner.

HISTORICAL INTRODUCTION

Unimolecular electronics started with a seminal paper by Arieh Aviram and Mark A. Ratner in 1974 [1]. This paper was born during the frenzy of metallic conductivity [2] and possible high-temperature superconductivity in single crystals of TTF TCNQ (**1**) [3] (later dismissed [4], and found, instead, by Klaus

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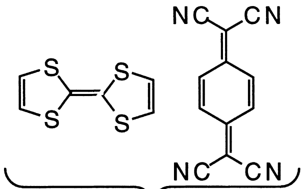
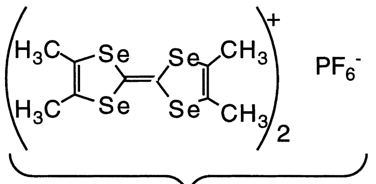
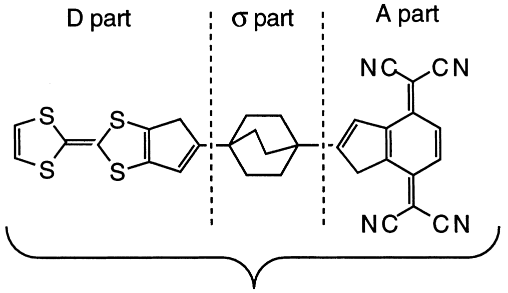


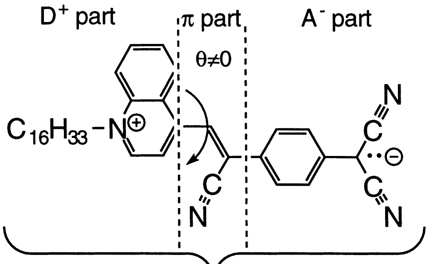
TTF TCNQ, **1**



TMTSF$_2$PF$_6$, **2**



Gedankenmolekül, **3**



C$_{16}$H$_{33}$Q-3CNQ, **4**

Bechgaard and Denis Jérome and co-workers, at much lower temperatures in other ion-radical salts, the first of which was TMTSF$_2$PF$_6$, 2 [5]). The proposal of Aviram and Ratner was that a single molecule 3, which we can style D-s-A, would rectify because its covalently bonded components are a good one-electron donor, D, like TTF, with a relatively low ionization potential, a "sigma" bridge s of sp^3-hybrizied saturated carbon atoms, and a good one-electron acceptor, A, like TCNQ, with a relatively large electron affinity. The synthesis of molecule 3 was not undertaken, nor were the considerable problems of device assembly considered [1]. Intellectually, this seminal paper responded to the 1959 challenge by Richard P. Feynman that there was "plenty of room at the bottom", i.e., that information storage had not yet reached atomic or molecular dimensions [6].

This review will focus on the practical realization of unimolecular rectification, which (1) started with the Organic Rectifier Project, led by the present author and Charles A. Panetta at the University of Mississippi (Oxford, MS, 1981-1992). [7-41], This project was (2) aided by a collaboration with Dr. Sukant K. Tripathy, then at General Telephone and Electronics (GTE) (Waltham, MA, 1986) [10], (3) and by a funded collaboration between GTE and Nippon Telephone and Telegraph (1987). The quest continued (4) in a collaboration between Daniel J. Sandman of GTE and Professor John Roy Sambles of the University of Exeter (Exeter, UK, 1987-1989) [88-90], (5) in a further collaboration between Sambles, and Professor Geoffrey J. Ashwell of Cranfield University (Cranfield, UK, 1989-1993) [82, 91, 92]. Finally, (6) a team consisting of the present author and Professor Michael P. Cava of the University of Alabama (Tuscaloosa, AL, 1995-present) [42- 64] confirmed beyond any reasonable doubt that molecular rectification is a reality, for molecule **4**. In the meantime, two other rectifiers have appeared [65, 66].

Before going into details, a brief history of molecular electronics should be given. The field of molecular electronics, and bio-electronics, received intense, if premature, attention in the early 1980's, with three conferences organized by Forrest L. Carter[67-69]. Many molecular processes could potentially lead to electronic applications: the emphasis should be placed on the dangerous adverb "potentially": one must actually reach out and touch (measure) a molecule effectively to utilize its electronic properties, and this has rarely been done. The term "molecular electronics" was in part co-opted by the growing field of conducting organic and metal-organic crystals, and even by researchers of conducting polymers, which was initiated in 1977 by the Nobel-prize winning paper by Hideki Shirakawa, Alan MacDiarmid, and Alan J. Heeger [70]. The term "unimolecular electronics" came to signify the use of the electronic properties of a single molecule or small cluster of molecules [28].

In the 1990's, some seminal advances in unimolecular electronics have been made:

1. The electrical resistance of a single 1,4-benzenedithiol, bonded covalently as the dithiolate to two Au electrodes, was measured by the group headed by Mark A. Reed [71].
2. The quantum of electrical resistance (12 kΩ) was measured by Walt de Herr and his group at room temperature, when a carbon nanotube, glued to a conducting AFM tip, was lowered into liquid Hg [72].
3. The Aviram-Ratner mechanism [1], slightly modified, was confirmed in both macroscopic and nanoscopic conductivity measurements through a monolayer of γ-hexadecyl-quinolinium tricyanoquinomethanide, **4**: this is the first proven two-terminal molecular device [42].

Why does unimolecular electronics hold promise for electronic technology? In electronic integrated circuits (IC), the drive to achieve faster computers is a drive to reduce the "design rule", the closest distance between adjacent electronic components in the IC. The design rule sets the clock cycle, which is the time required for an electron to travel between the furthest components on the chip: shorter cycles mean faster computing. These design rules have now been reduced to about 180 nm commercially. If photolithography is used, the design rules are limited, by Rayleigh's criterion [73], to about one-half the wavelength of light used. To achieve design rules below 120 nm, UV photolithography must be replaced by X-ray or electron beam lithography, with much higher error rates. At 50 nm, an even more drastic limit appears: one can no longer "dope" Si uniformly. It is thought that this 50 nm "silicon wall" will be reached in a few years [74].

At the heart of all computers lie rectifiers and transistors. The first rectifiers, based on group-IV (or 14) semiconductors like ultra-pure Ge or Si, were pn junction rectifiers, where a region of p-doped Ge or Si was accosted to a region of n-doped Ge or Si. "doped" material. To make a "p-doped" crystal, one dopes the group IV matrix interstitially or subtitutionally with group III (or 13: Al, Ga, In, etc.), thus creating a semiconductor with an excess of "holes". To create an n-doped region, one dopes a group IV crystal with group V (or 15: P, As, etc.), creating a region that has an excess of electron carriers.

A connection must be made between the p,n terminology of solid state physics and with the organic chemical terminology of an electron donor D (a molecule that can be oxidized to the radical cation D^+ with relative ease), and of an electron acceptor A (a molecule which can easily be reduced, to the radical anion A^- fairly easily). The n-region has an excess of electrons, or is an electron donor (D) region; a p-region has an excess of holes, or is an electron acceptor (A) region. Thus, "D" corresponds to "n", and "A" corresponds to "p".

By accosting a μm-thick film of organic D molecules to a μm-thick film of an organic A molecules, one gets a DA rectifier (one-way conductor) of electrical current, equivalent to an inorganic pn rectifier [75]. In the 1960's, and particularly in the early 1970's, organic charge-transfer crystals and conducting polymers yielded organic equivalents of inorganic electronic systems: semiconductors, metals, superconductors, batteries, etc. [76].

A persistent view has been that unimolecular, or "oligomolecular" [28, 38], or "molecular-scale" [77] electronics have a very bright future, just as the new millennium begins. Molecules, with their 1 to 3 nm sizes, should step in where inorganic chemistry may fail. Thus, unimolecular electronics will come to the rescue: they will finally find a central role in electronic technology.

The Aviram-Ratner Ansatz of Unimolecular Rectification

The Aviram-Ratner proposal [1] is based on a single molecule acting as a pn junction. The highest occupied molecular orbital, or HOMO, of the D part is 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 from the high-lying LUMO of A through the σ "bridge" 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-σ-A$|M_2$, with easy electron transfer from M_2 to M_1 because of the "down-hill" tunneling from the excited state D^+-σ-A^- to the ground state D^0-σ-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 such 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.

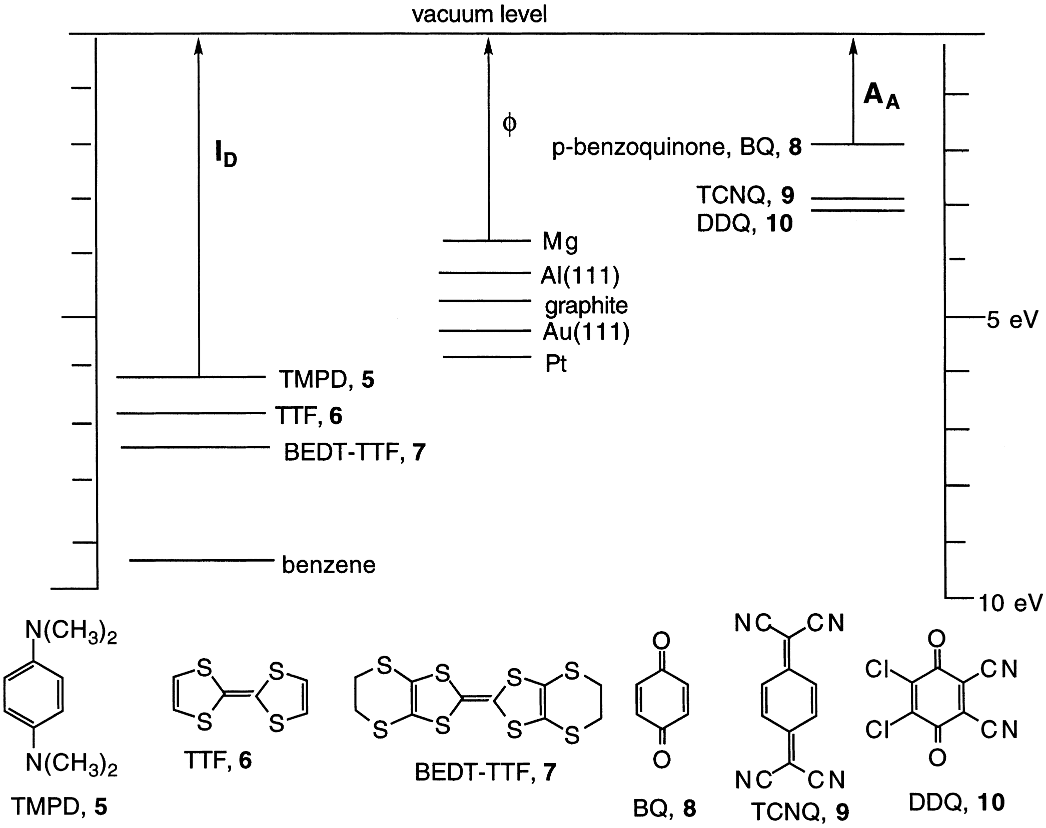


Figure 1. Energy levels of interest to unimolecular rectifiers: HOMOs and ionization potentials ID of some organic one-electron donors D (left), work functions f of some metals (middle), LUMOs and electron affinities A_A of some organic one-electron acceptors A (right).

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. The coupling reaction to form the bridge σ between D and A must be the last step of the synthesis, and must prevail over forming an intermolecular D^+A^- salt.
4. Efficient assembly as a monolayer on a metal electrode. 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. Other choices are self-assembled films bridging two electrodes, e.g., a bithiol attached to two Au electrodes, or a disilane, bonded to two Si electrodes. Efficient contact to electrodes is crucial.

Multilayer Lb Organic Rectifiers and Lb Photodiode

LB multilayer rectifiers have been made by doping arachidic acids with either electron donors (for a few monolayers of D) or nothing or electron acceptors (a few monolayers of A) by Kuhn and coworkers [78], and also by Sugi and co-workers [79]. Roth, von Klitzing, and co-workers used pure donor layers and pure acceptor layers [80]. However, these results could not be extended down to the monolayer level. Fujihira and co-workers discovered an LB monolayer photodiode, which may be the first unimolecular electronic device [81].

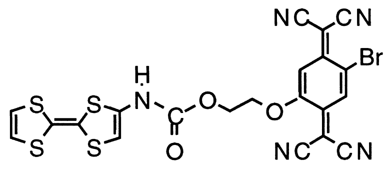
Potential Unimolecular Rectifiers

Collaborations of the present author with Professor C. A. Panetta at the University of Mississippi in Oxford, MS and Professor M. P. Cava at the University of Alabama in Tuscaloosa, AL netted several candidates for unimolecular rectification, i.e. D-σ-A and D^+-π-A^- molecules designed to form physisorbed LB films [11, 8, 27, 30, 34, 40, 48, 55, 56, 59. Some of these are molecules **4** and **11-19**. Molecule **4** is the first confirmed unimolecular rectifier [42].

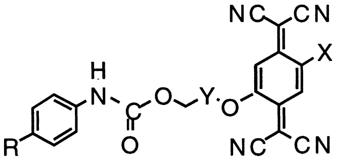
The various D-σ-A molecules that formed insoluble Pockels-Langmuir (PL) films [22] at the air-water interface and can be mostly transferred as LB films onto solid substrates were the carbamates **11-15**, and triptycenequinone linked to TTF derivatives **16** and **17**. The D^+-π-A^-Zwitterions were **4** [82], which formed a rectifier, and its benzochalcogenazolium analogs **18** and **19**, which did not [54]. The monofunctionalized strong acceptors BHTCNQ and HETCNQ could only be produced in low yields. The very interesting strong donor-strong acceptor TTF-C-BHTCNQ, **11**, was difficult to purify [8]. The strongest films (highest collapse pressure) were obtained with **12b** [21]. As predicted, the triptycenequinone (weak A) in **16** and **17** could not be converted to triptycene-dicyanoquinodiimine (strong A) as the last synthetic step [44].

Initial Rectification Reports

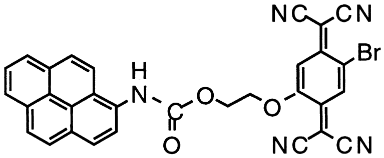
The first rectification attempt was macroscopic, in a collaboration between this author, Panetta, and Dr. S. K. Tripathy at GTE Laboratories, Waltham, MA [10]. It failed, as did the next attempt in Tuscaloosa [21]. Nanoscopic STM experiments, in collaboration with Dr. M. Pomerantz of IBM Watson Research Laboratory Yorktown Heights, NY [22, 23], using molecules **12a** and **12b**, failed, despite some initial excitement. Other investigators reported asymmetric current-voltage (I-V) curves in STM experiments on Cu tetraazaporphyrin bonded to carboxylated HOPG [83], an alkylated hexabenzocoronene [84] and an oligo-phenylethynyl)-benzenethiol [85]. Electrochemical rectification at a monolayer-modified electrode was also reported [86, 87].



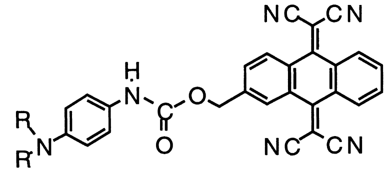
11, TTF-C-BHTCNQ



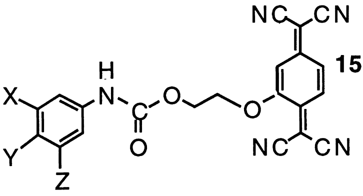
12a: R=O-(n-$C_{12}H_{25}$), X=Br, Y=CH_2: DDOP-C-BHTCNQ
b: R=N(n-$C_{12}H_{25}$)$_2$, X=Br, Y=CH_2: BDDAP-C-BHTCNQ
c: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=CH_2: BDDAP-C-HETCNQ
d: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=C_2H_4: BDDAP-C-HPTCNQ
e: R=N(n-$C_{12}H_{25}$)$_2$, X=H, Y=C_3H_6: BDDAP-C-HBTCNQ



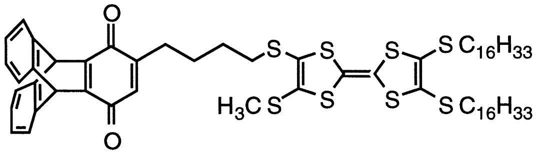
13a: X=Br: Py-C-BHTCNQ
b: X=H: Py-C-HETCNQ



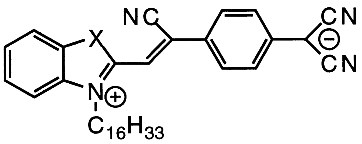
14a: R=n-C_6H_{13}: BHAP-C-HMTCAQ
b: R=n-$C_{12}H_{25}$: BDDAP-C-HMTCAQ



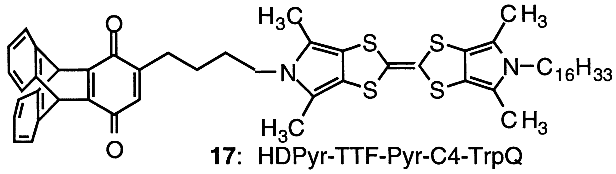
15a: X=Y=Z=O$(CH_2)_{11}CH_3$: TDDOP-C-HETCNQ
b: X=Y=NH-CO-$(CH_2)_{15}CH_3$, Z=H: 3,4-BHDAOP-C-HETCNQ



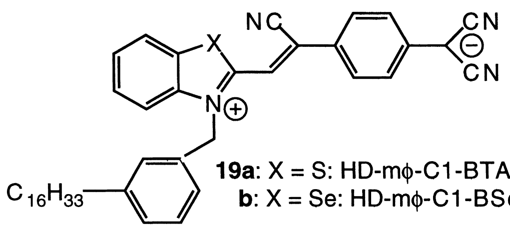
16: BHD-S4-TTF-C4-TrpQ



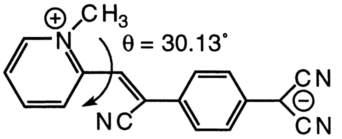
18a: X = S: HD-BTAz-3CNQ
b: X = Se: HD-BSeAz-3CNQ
c: X = Te: HD-BTeAz-3CNQ



17: HDPyr-TTF-Pyr-C4-TrpQ



19a: X = S: HD-mϕ-C1-BTAz-3CNQ
b: X = Se: HD-mϕ-C1-BSeAz-3CNQ



20: P-3CNQ

Rectification in Pt | LB FILM | Mg | Ag Sandwiches

Funds received by GTE from NTT first supported the work of Panetta, the present author, and Tripathy, but, after the departure of Dr. Tripathy for what is now the University of Massachusetts at Lowell, GTE management diverted those funds to support Dr. D. J. Sandman of GTE, who in turn collaborated with Professor J. R. Sambles of Exeter University. Sandman and Sambles and co-workers found that an LB multilayer of DDOP-C-BHTCNQ, **12a**, sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film [88]: 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, **12a** 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 **12a** was later reinterpreted to be due, not to molecular rectification, but to Schottky barrier formation between Mg and TCNQ, i.e. to the formation of a salt, either $Mg^{++}TCNQ^{--}$ or $Mg^{++}(TCNQ^{-})_2$, at the metal-organic interface [89, 90].

Sambles, collaborating with Professor G. J. Ashwell of Cranfield University, also found asymmetries in an LB multilayer of the ground state Zwitterion $C_{16}H_{33}$Q-3CNQ, 4, sandwiched between Pt and Mg electrodes [82]; there was also a slight I-V asymmetry for an LB monolayer of 4 [82]. To partially alleviate doubts about a similar possible Schottky barrier, an insulating LB layer of ω-tricosenoic acid was next put between 4 and the electrodes; the I-V asymmetry persisted [91, 92]. It was thus claimed that molecular rectification had been observed, albeit between asymmetric metal electrodes [91].

Rectification IN Al | Al_2O_3 | LB Monolayer | Al_2O_3 | Al | Sandwich

A very thorough repetition and major amplification of Sambles' pioneering work on $C_{16}H_{33}$Q-3CNQ, **4** was carried out [41, 42, 46, 48-50, 52, 53]. We review first the general physical and chemical properties of **4**. The synthesis of **4** was vastly improved [42]. Cyclic voltammetry reveals that **4** 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 **4** are electrochemically irreversible [42]. 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 $\mathbf{4}^{-}$ are mostly localized on the 3CNQ ring [50]; therefore, the LUMO of **4** is mostly localized on the 3CNQ moiety. The dipole moment of **4** in CH_2Cl_2 solution is 43 ± 8 Debyes, 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) [42]. The intense blue or green color of a solution of **4** (depending on solvent) disappears at the first trace of acid, but is recovered if the solution is exposed to ammonia vapor. This blue or green absorption, probably due to an intervalence transition

(IVT) band or intramolecular charge-transfer transition, is narrow, intense, and hypsochromic [42, 50]: this peak shifts from λ_{max} = 838 nm in $CHCl_3$ (least polar solvent) to λ_{max} = 711 nm in CH_3CN (most polar solvent). There are two fluorescence emissions, one in the visible region (corresponding to UV absorption bands), the other in the near-infrared region [50]. The excited-state dipole moment is calculated at between 3 and 9 Debyes [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 **4**), i.e., it is probably not of the twisted internal charge transfer (TICT) type.

Although **4** 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 **18a** the loss of vibronic structure, as the dielectric constant of the solvent increases, masks any solvatochromic shift in the absorbance maximum [54]: this lack of strong solvatochromism may help explain why LB films of **18** or **19** do not rectify [54]. Simple semiempirical MO calculations (AM1, PM3) do not yield a large ground-state dipole moment for **4** [42], unless $\theta \approx 90°$ [93]. Larger dipole moments are obtained in LDA calculations [57]. There is no evidence of a proposed TICT transition in **4** due to a large internal rotation [93]: the ^{1}H NMR of the H bonded to the ring carbon attached to the quinolinium N atom shows a large chemical shift (relative to what is expected from neutral quinoline) due to the zwitterionic ground state [42]; there is no change in the NMR spectrum as a function of temperature [50]. Evidently, **4** 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^+-π-A^- and the undissociated ("neutral") state D^0-π-A^0 would be degenerate), but rather that of a Zwitterion. **4** forms multiply twinned crystals, whose unit cell could not be indexed [42]. However, the crystal structure of a related compound, picolyltricyanoquino-dimethan, or picolinium tricyanoquinodimethanide, **20**, exhibits a twist angle θ = 30° (dihedral angle between the pyridinium ring and the phenyl ring of 3CNQ) [94].

When left in air and intense sunlight for weeks, a solution of **4** can discolor, by some unknown mechanism. Most manipulations of **4** were thereafter carried out with minimum exposure to light. **4** 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 [42, 41]. 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 [42]. Z-type multilayers form on Al, as depicted in Figure 2(b). A grazing-angle Fourier transform infrared spectrum of a monolayer of **4** on Al shows two CN peaks at 2139 and 2175 cm^{-1} [42]. 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 λ_{max} = 565 nm in the LB monolayer [50] and also in the LB multilayer [42].

The rectification work was performed both on macroscopic Al | LB film | Al sandwiches, and by nanoscopic STM [42]. 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 [42]. 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) [42]. 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 4-monolayer Z-type LB film, as well as in a 4-monolayer film with a Mg electrode between the organic layer and the top Al pad [42], and even for a single monolayer (Figure 3) [42]. In a control experiment, no I-V asymmetry was seen for Y-type multilayers of arachidic acid, after careful sample drying [42]. Rectification for **4** was also seen, as a function of temperature, between 370 K and 105 K [52]. The maximum measured rectification ratio (at 1.5 V, Figure 3) was 26:1. However, if one cycles the measurement, the rectification ratio for **4** 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 [42]. The current measured amounts to about 0.33 electrons per molecule per second [42]. 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

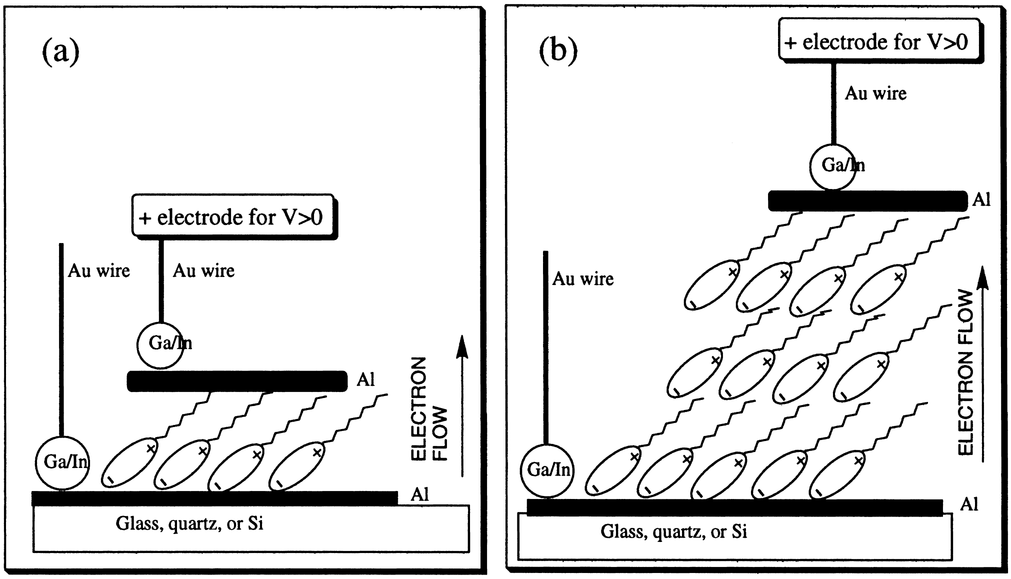


Figure 2. Orientation of the LB monolayer: (a) or multilayer; (b) of **4** on a glass, quartz, or Si substrate. The electrode (+) for positive bias, and the direction of "easy" electron flow for V > 0 are marked. From Reference [42].

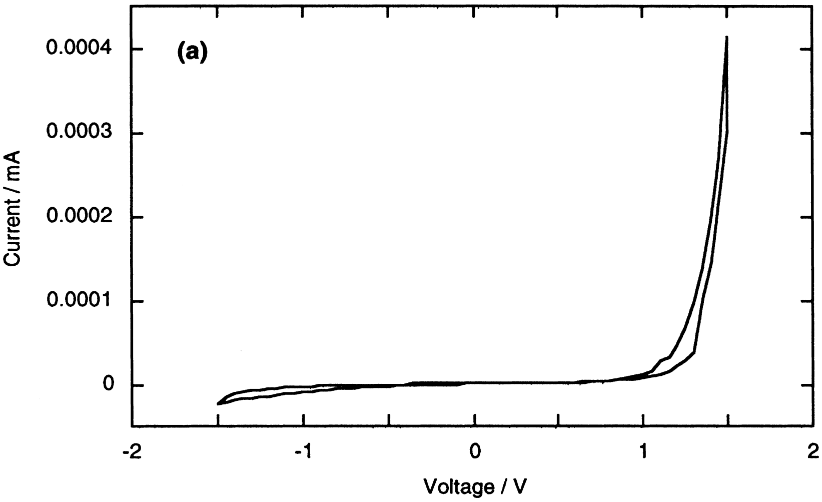


Figure 3. Rectification at 297 K through a single 2.3 nm thick monolayer of **4** sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using, as shown in Figure 2(a), Ga/In eutectic and Au wires. Plot of the DC current I versus the DC applied voltage V. From Reference [42].

the wrong way"; these "aberrant" junctions show lower currents, and a characteristically different dependence on voltage [53]. 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-σ-A^0 and a Zwitterionic excited state D^+-σ-A^-; this mechanism can be trivially modified and inverted for the case where the ground state is mostly zwitterionic (D^+-π-A^-), and the excited state is mostly undissociated (D^0-π-A^0)^{17}.

The rectification was also verified for a 15-layer film of **4** on HOPG by STM [41], [42], and a small I-V asymmetry was even seen for monolayer of **4** on HOPG [42], but there is low adhesion of that first monolayer on HOPG.

The Aviram-Ratner mechanism [1] for unimolecular rectification used an undissociated ground state D^0-σ-A^0 and a relatively low-lying Zwitterionic excited state D^+-σ-A^-. In the initial conception, this excited state could be a biradical [1], 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+-σ-A- state is probably not necessary, provided that the change in dipole moment upon excitation is reversible: then D+-σ-A- could also be an excited singlet state. If the ground state is zwitterionic D+-π-A-, and the excited state is undissociated D0-π-A0, then the Aviram-Ratner mechanism can work…"backwards" [42]: the direction of rectification, shown in Figure 2, agrees with this mechanism.

Thus, the Aviram-Ratner Ansatz was verified, using either Al electrodes on both sides of a monolayer, or an STM [42, 48]. A 2.3 nm thick unimolecular device is now a reality. However, critics could still point at the oxide covering at least part of the Al electrodes (on both sides of the monolayer), and may wonder whether the oxide had any effect, i.e., presenting a barrier to conduction, and maybe also acting as an additional rectifier in series with the organic monolayer.

These doubts were very recently put to rest [64]. An experiment with "cold gold" gave a dramatic confirmation of unimolecular rectification: a monolayer of **4**, deposited atop an Au electrode, [64], was then covered by Au atoms pre-cooled to room temperature with a low pressure of Ar gas (following recent work by Professor J. R. Sambles). The thermalized Au atoms, cooled by scattering off several Ar atoms, ensures that the monolayer is not heated or destroyed by hot Au atom bombardment. Further, the direct path from Au source to target is blocked off by baffles, so radiant heating of the monolayer target is minimized. Finally, the target is cryocooled to 77 K with an external supply of liquid nitrogen (this last precaution was also used for the Al work). The result is shown in Figure 4: the

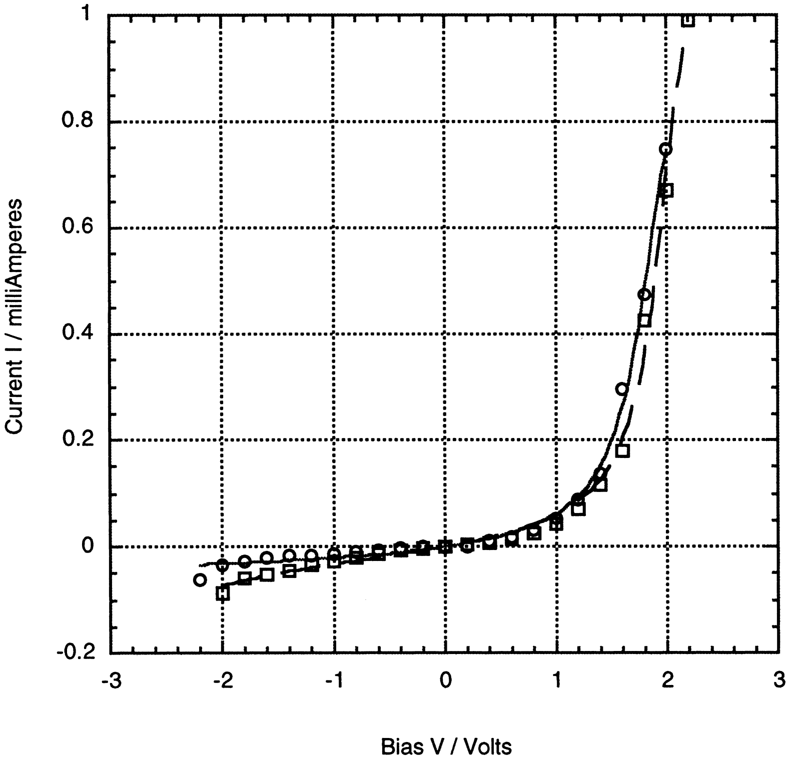


Figure 4. Rectification at room temperature [plot of DC current I versus DC applied voltage V] for a single 2.3 nm thick LB monolayer of 4, sandwiched between Au electrodes (top Au pad area 0.283 mm2, thickness 18 nm). Cycle 1: solid line and open circles: rectification ratio at 2.2 V is 11.9; nominal resistance 2945 W. Cycle 2: dashed line and squares. Device shorted in third cycle. From Reference [64].

same rectification phenomena occur as with Al electrodes (the rectification ratio decreases upon cycling). Another run (not shown here) with a rectification ratio of only 5.39, had a forward current of 4.08 mA across a pad area of 0.283 mm^2, corresponding to a forward current of 4.5 × 10^4 electrons $molecule^{-1}$ s^{-1} [64], a 100,000-fold improvement on the forward current seen with Al electrodes. Thus, rectification is assured with an oxide-free electrode, and exhibits very large currents [64].

CONCLUSION

The goal of Aviram-Ratner rectification through an oriented D^+-?-A^- monolayer has been achieved, using either oxide-covered Al electrodes [42] or, now, Au electrodes [64]. Much exciting work lies ahead, as we make measured progress towards unimolecular electronics as a practical reality in the 21st century.

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