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The unimolecular rectifier: unimolecular electronic devices are coming …

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Unimolecular electronic devices use the energy levels, or conformations, of one molecule or a very few molecules, and are contacted electrically from the outside. When made practical, these devices, the 'advanced guard' of unimolecular electronics, should leapfrog below the 50 nm limit of conventional inorganic microelectronics. Aviram and Ratner proposed in 1974 rectification of electrical current through a single molecule D–σ–A, 1, where D = good one-electron donor, σ = covalent, saturated 'sigma' bridge, A = good one-electron acceptor, because, from the undissociated ground state D^0–σ–A^0, the first zwitterionic excited state D^+–σ–A^- is accessible under electrical bias. Many such D–σ–A molecules were prepared. We found unimolecular rectification in a molecule, γ-hexadecylquinolinium tricyanoquinomethanide, 2, in which the ground state is zwitterionic: D^+–π–A^-, while the first excited state is undissociated: D^0–π–A^0.

The concept of unimolecular electronics

The proposal of using molecules as electronic devices has gained attention and respectability in the last quarter century. In the 1960's, and particularly in the early 1970's, it became clear that certain molecules can act as electron donors (as can atoms of the inorganic metals), while other molecules can act as electron acceptors (as do atoms of non-metals).[1] That is, with such constituents, organic semiconductors, *e.g.* (TMPD)(TCNQ), **3**,[2], organic metals, *e.g.* (TTF)(TCNQ), **4**,[3], and organic superconductors, *e.g.* (BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl, **5**,[4], and conducting polymers can do what their inorganic brethren have done: they can, at least conceptually, be harnessed as macroscopic, or even mesoscopic, organic 'wires', as organic pn or np junction rectifiers,[5] capacitors,[6] batteries,[7] field-effect transistors,[8] and most recently as electroluminescent devices.[9] Some of these applications smack of 'me-too-ism': the electrical conductivity of organic metals and conducting polymers can match that of copper or silver wires only at cryogenic temperatures[10] or when the conducting polymer is purified to an extreme degree.[11] Organic crystalline superconductors have reached a critical temperature $T_c = 12.8$ K with (BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl,[4] while their competitors, the inorganic layered perovskite-based cuprates[12] reached $T_c = 150$ K,[13] and alkali fullerides[14] reached $T_c = 40$ K at 15 kbar in Cs_3C_{60}.[15] Photoelectric devices[16] and batteries[7] based on organic conducting polymers proved to be kinetically unstable, and therefore impractical. Light-emitting diodes based on conducting polymers[9] seem to have a fighting chance at commercialization.

In the early 1980's, 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.[17–19] Since Mother Nature does some highly efficient computing of her own in our brains, the heralding of molecular electronics quickly begat a collateral interest in biological applications. Some scientists, viewing the vast genetic information storage in deoxyribonucleic acid (DNA), promoted 'biomolecular electronics'.[20] The popular press unfortunately caught this drift, and the term 'biochip' was coined in 1983 for 'biomolecules which can compute'. Since the scientific basis did not exist at the time, the biochip hoopla and concomitant ridicule by the scientific community almost buried the term 'molecular electronics' altogether. This term, or the term 'molecule-based electronics'[21] was extended to 'macroscopic' organic metals, semiconductors, and superconductors, which consist of molecules and their anions and cations.

A persistent minority view has been that unimolecular, or oligomolecular, or molecular-scale electronics, have a very bright future,[22] just as the new millennium begins. The fantastic advance of Si-based integrated circuits has been plotted by an empirical correlation due to Moore: in the last 20 years the speed of integrated circuits (IC) doubled, at first every two years, by now every 18 months.[23] However, this increased performance is mainly due to the linear decrease over time of the 'design rules', the linear distance between adjacent components and wires in an IC. These design rules of photolithography define the clock speed, which is set by how far a signal must travel between the furthest components in an IC. The design rules were 3 μm when the first IBM PC was introduced in 1982, using visible light photolithography; they have been gradually reduced to 150 or 100 nm today, by using hard UV radiation; clock speeds of 600 MHz have been reached commercially. Below 100 nm, one must resort to X-ray or electron beam lithography: both techniques are at present very error-prone. Below 50 nm, another, more sinister limitation sets in: one can not 'dope' Si uniformly. These two limitations have been called the 'silicon wall', which may be reached by the year 2005.

Molecules, with their 1 to 3 nm sizes, can then step in where inorganic chemistry finally fails. Thus, unimolecular electronics will come to the rescue: they will have finally found an essential niche in electronic technology.

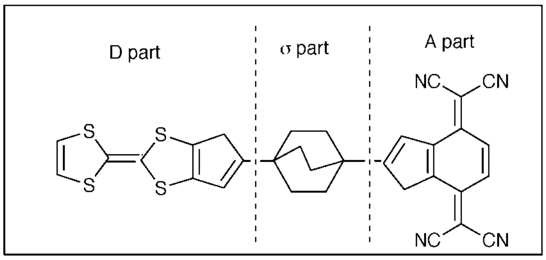
Milestones in unimolecular electronics

In the last three years the following milestones have been reached:

(1) differences in tunneling current through aliphatic and aromatic chains were measured.[24]

(2) the electrical resistance of a single molecule (benzene-1,4-dithiol) covalently bonded to two Au electrodes was measured: it was a few MΩ, because the work function of Au and the LUMO of the molecule were mismatched.[25]

(3) the quantum of electrical resistance (12 kΩ) was meas-



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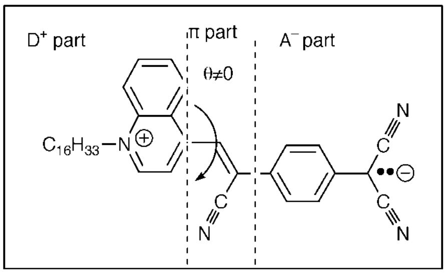
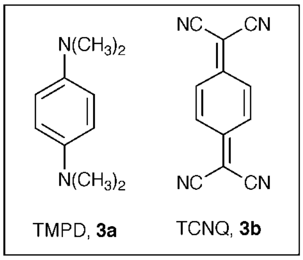
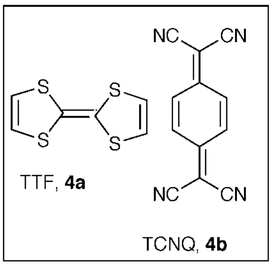


2, $C_{16}H_{33}Q$-3CNQ



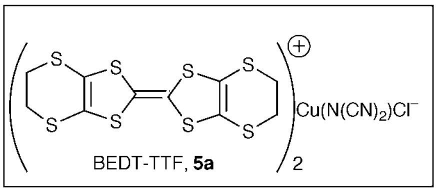
TMPD, **3a** TCNQ, **3b**

(TMPD)(TCNQ), **3**



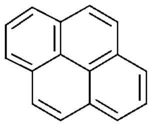
TTF, **4a** TCNQ, **4b**

(TTF)(TCNQ), **4**

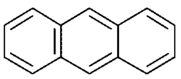


BEDT-TTF, **5a**

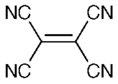
$(BEDT\text{-}TTF)_2Cu(N(CN)_2)Cl$, **5**



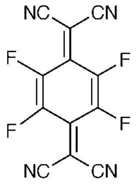
Py, **6**



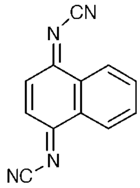
Anthr, **7**



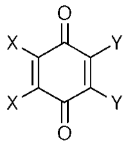
TCNE, **8**



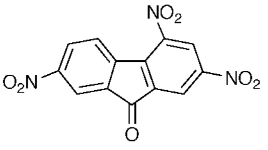
$TCNQF_4$, **9**



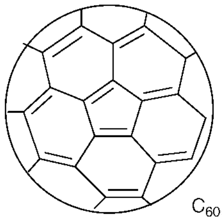
DCNNaQI, **10**



11a:X=Y=H
11b: X=Y=Cl
11c: X=Y=Br
11d: X=Y=F
11e: X=Cl, Y=CN (DDQ)



2,4,7-trinitrofluorenone, **12**



C_{60}, **13**

ured when a carbon nanotube, glued to a conducting AFM tip, was lowered into liquid Hg.[26]

(4) the Aviram–Ratner mechanism,[27–29] slightly modified, was confirmed in both macroscopic and nanoscopic conductivity measurements through a monolayer of γ-hexadecylquinolinium tricyanoquinomethanide: this is the first proven two-probe molecular electronic device.[30]

We summarize here the progress made by us[30–78] and by the group of J. R. Sambles[79–84] in achieving this fourth, important milestone.

The Aviram–Ratner Ansatz of unimolecular rectification

In 1974 Ari Aviram, Mark A. Ratner and coworkers[27–29] proposed that a single organic molecule of the type D–σ–A could be a rectifier of electrical current. This molecule D–σ–A 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). 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 through the sigma bonding network, as shown in Fig. 1. The device is asymmetric, because the HOMO of D is relatively low, and the LUMO of A is relatively high, as shown in Fig. 1. Also, the device will work if the inelastic through-bond tunneling is more likely than the elastic through-space tunneling,[85] which is unaffected by molecular orbitals.

Good donor molecules (*i.e.* molecules with relatively low gas-phase first ionization potentials I_D) are, at the same time,

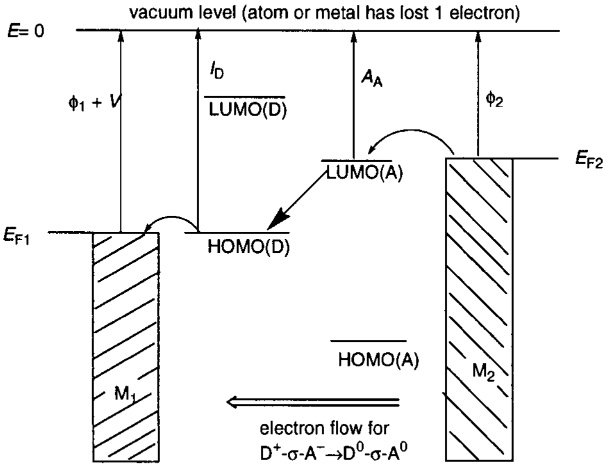


Fig. 1 The Aviram–Ratner Ansatz, showing the through-molecule electron flow from the excited zwitterion state D^+–σ–A^- to the undissociated ground state D^0–σ–A^0.

poor acceptors (they have low electron affinity A_D); good acceptors (*i.e.* molecules with a relatively high first electron affinity A_A) are, at the same time, rather poor donors (have high I_A). Thus the gas-phase energy ΔU_F required for charge transfer (both components at infinite separation) is about 3.5 eV (eqn. (1)), while the energy ΔU_R required for the reverse reaction would need over 9 eV (eqn. (2)).

$$\mathrm{TTF(g)+TCNQ(g)\rightarrow TTF^{+}(g)+TCNQ^{-}(g)} \tag{1}$$
$$\Delta U_F = I_D - A_A = 6.83 - 3.3 = 3.5\ \mathrm{eV}$$

$$\mathrm{TF(g)+TCNQ(g)\rightarrow TTF^{-}(g)+TCNQ^{+}(g)} \tag{2}$$
$$\Delta U_R = I_A - A_D = 9.6\ \mathrm{eV\ (est)}$$

The 'Gedankenmolekül' D–σ–A (**1**, never synthesized), 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 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 (Table 1 and Fig. 2), but if I_D is too low, 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. Table 1 and Fig. 2 show that this is not easy.

(3) In a molecule in which the 'sigma' bridge σ has already been built, it is very difficult to chemically convert a weak donor into a stronger donor, or a weak acceptor into a stronger acceptor. Therefore a coupling reaction must be found which joins D to A by forming the bridge σ as the last step, instead of forming an ionic 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. 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.

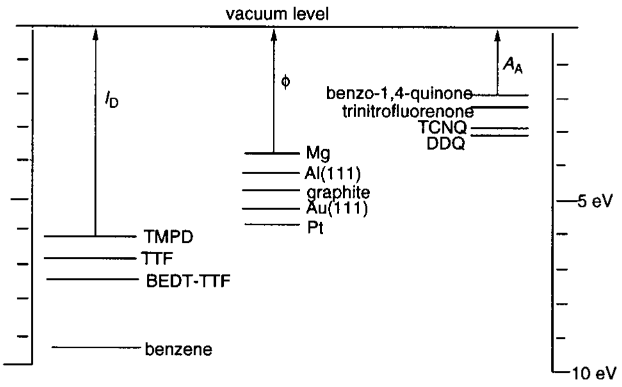


Fig. 2 Energy levels: HOMOs of some donors (left), work functions ϕ of some metals (middle), LUMOs of some acceptors (right).

Bulk organic rectifiers

After the discovery of the pn junction diode (p = hole-rich region, n = electron-rich region),[86] it was of interest to see whether macroscopic films of organic molecules could function as bulk pn rectifiers (diodes) or as npn transistors. The former would occur if a film or crystal of an organic electron donor (p region) were brought in contact with that of an organic electron acceptor (n region). This was indeed verified in the 1960's.[5] Bulk rectifiers were also formed recently by accosting two films of different phthalocyanine derivatives,[87] or by doping *in situ* different parts of a single crystal of perylene with electron donors and with electron acceptors.[88]

Table 1 Solution cyclic voltammetric half-wave potentials $E_{1/2}$ (V *vs.* SCE), gas-phase ionization potentials I_D (eV), electron affinities A_A (eV) for donors D and acceptors A. ($E_{1/2}=E_{\mathrm{ox,p}}$, −0.03 or $E_{1/2}=E_{\mathrm{red,p}}+0.03$), and metal work functions ϕ from Ref. 61

	Soln. oxidation		Soln. reduction		Gas-phase		
Molecule	(1) $D\rightarrow D^+$ $E_{1/2}{}^1$/V	(2) $D^+\rightarrow D^{++}$ $E_{1/2}{}^2$/V	(1) $A\rightarrow A^-$ $E_{1/2}{}^1$/V	(2) $A^-\rightarrow A^{--}$ $E_{1/2}{}^2$/V	Oxid. $D\rightarrow D^+$ I_D/eV	Red. $A\rightarrow A^-$ A_A/eV	Metal work function ϕ/eV
Donors (D):							
TMPD (**3a**)	0.10	0.66	—	—	6.25		
TTF (**4a**)	0.35	0.75	—	—	6.83		
BEDT-TTF (**5a**)	0.54	0.96	—	—	6.21		
Pyrene (**6**)	1.16	—	—	—	7.41	0.58	
Anthracene (**7**)	1.09	—	—	—	7.55	0.60	
Acceptors (A):							
TCNQ (**3b**)	—	—	0.127	−0.291	—	3.3	
TCNE (**8**)	—	—	0.152	−0.568	—	2.3, 2.9	
$TCNQF_4$ (**9**)	—	—	0.53	0.02	—	3.72	
DCNNaQ (**10**)	—	—	0.19	−0.35			
p-BQ (**11a**)	—	—	−0.481	−1.030	—	1.95	
Chloranil (**11b**)	—	—	+0.01	−0.71	—	2.76	
Bromanil (**11c**)			0.00	−0.72			
Fluoranil (**11d**)	—	—	−0.04	−0.82	—	2.92	
DDQ (**11e**)	—	—	0.51	−0.30	—	3.13	
TNF (**12**)	—	—	−0.42	−0.67	—	2.2	
C_{60} (**13**)	—	—	−0.18	−0.58, −1.07	—	2.6–2.8	
Metals							
Mg	—	—	—	—	—	—	3.66
Al(111)	—	—	—	—	—	—	4.24
Au(111)	—	—	—	—	—	—	5.31
Pt(111)	—	—	—	—	—	—	5.7
Graphite	—	—	—	—	—	—	4.40

Multilayer LB organic rectifiers

Kuhn and co-workers[89] obtained a 'pn' (or DA) rectifier in an LB multilayer sandwich Al|$(CA–D)_r$|$(CA)_s$|$(CA–A)_t$|Al, where $(CA–D)_r$ denotes the electron donor system D [*r* LB monolayers of cadmium arachidate (CA) randomly doped in the ratio 5:1 with an organic π electron donor D, a cyanine dye]; $(CA)_s$ denotes a spacer layer of *s* undoped monolayers of CA; $(CA–A)_t$ denotes the electron acceptor system A [*t* LB monolayers of CA randomly doped with an organic π electron acceptor A, paraquat]. This work was repeated and confirmed by Sugi and co-workers,[90] who observed rectification properties, but only if $r \geqslant 3$, $s \geqslant 1$, and $t \geqslant 3$, *i.e.* if there are at least seven monolayers. In these LB films, the registry and intermolecular approach between D and A dissolved in adjacent cadmium arachidate monolayers cannot be controlled.

Roth, von Klitzing, and co-workers found rectification at 5 K in an LB multilayer of 6 layers of D molecules (Pd octakis(pentyloxy)benzophthalocyanine) and 6 layers of A molecules (a substituted perylene-3,4,9,10-tetracarboxydiimide); Coulomb blockades were seen.[91]

Molecule-based field effect transistors

Wrighton and co-workers developed a 'molecule-based transistor' which uses conducting polymers: chemically doped polyaniline layers deposited on Au interdigitated electrodes[92] or a 50–100 nm 'gate' polyaniline polymer between two Au electrodes shadowed with SiO_2; this device still has a gain of almost 1000, but also a slow switching rate (10 kHz), limited by ionic conduction rates.[8] Stubb and co-workers used a single Langmuir–Blodgett monolayer as a 'molecule-based' transistor.[93] Garnier used sexithiophene in a field-effect transistor.[94]

Fujihira's LB photodiode

Fujihira and co-workers demonstrated an LB monolayer photodiode,[95] which is probably the first unimolecular electronic device. They synthesized a D–σ_1–A–σ_2–S molecule, where D = electron donor = ferrocene, $\sigma_1 = (CH_2)_{11}$ chain, A = final electron acceptor = viologen, $\sigma_2 = (CH_2)_6$ chain, S = sensitizer = pyrene. This molecule was transferred as an LB monolayer onto a semitransparent Au electrode (with the viologen part of molecule closest to Au). The electrode was the side of an electrochemical cell containing a 0.1 M KCl solution and a Pt counter electrode. Under bias, an electron is transferred from solution to the ferrocene end of the LB film, and then to the ground state of the pyrene molecule. Ultraviolet light at 330 nm excites the pyrene radical cation from the ground state to an excited state, from which the electron is transferred to the viologen, thus completing the circuit. A photocurrent of 2 nA at 0.0 V *vs.* the standard calomel electrode (SCE) is observed only whenever the light is turned on.[95]

Electrical signals to and from a unimolecular device

How does one 'talk' to such single molecules or clusters, that is, how can one get electrical signals from the macroscopic world of electronics (>1 mm) to the 'nanoscopic' world of single molecules, and *vice versa*? To address a single molecule electrically, one could use a 'molecular wire' (*e.g.* a polyacetylene strand) or a 'molecular antenna' (*e.g.* the conjugated portion of β-carotene), neither of which is easily connected to an external potential source. For macroscopic connections, two techniques seem promising: (1) the LB physisorption technique and (2) the technique of covalent 'self-assembly', or covalently bonding molecules to electrode surfaces. Scanning tunneling microscopy (STM) allows the electronic addressing of a single molecule. All 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, such as exist, *e.g.*, at the Au^+thiolate$^-$ covalent/ionic interface. Excessive bias will, of course, lead to dielectric breakdown; excessive heating will lead to chemical decomposition.

Potential unimolecular rectifiers

Between 1981 and 1991 the groups of Panetta and Metzger at the University of Mississippi prepared several D–σ–A molecules as candidates for unimolecular rectification;[31–62] later, Cava and Metzger made two more D–σ–A molecules,[30,63–78] and several ground-state zwitterions, D^+–π–A^-, one of which (**2**) became the first confirmed unimolecular rectifier.[30] The LB technique of assembling compact but physisorbed monolayer films was chosen. The carbamate coupling reaction[96] can form a covalent bond between functionalized derivatives of even a strong donor, like TTF, **4a**, and a strong one-electron acceptor like TCNQ, **3b**.[31]

The various D–σ–A molecules that formed Pockels–Langmuir (PL) films at the air–water interface and can be mostly transferred as LB films onto solid substrates (Table 2) were the carbamates **14**–**19**, and triptycenequinone linked to TTF derivatives **20** and **21**. The D^+–π–A^- zwitterions were $C_{16}H_{33}Q$-3CNQ, **2**,[82] which formed a molecular rectifier[30,82] and its benzochalcogenazolium analogs **22**, which did not rectify.[77] Compounds **18a**–**18g** were prepared to incorporate D–σ–A molecules into polymerizable diacetylenes, as candidate non-linear optical materials. To explain the acronyms, molecule **15b**, BDDAP-C-BHTCNQ is the *N*,*N*-bis-dodecyl-*p*-aminophenyl carbamate of 2-bromo-5-hydroxyethoxyTCNQ. The strongest films (highest collapse pressure, most vertical pressure–area isotherm) were obtained with BDDAP-C-BHTCNQ, **15b**. For the Aviram–Ratner mechanism, one does need strong donors and strong acceptors in the same molecule. The monofunctionalized strong acceptors BHTCNQ and HETCNQ could only be produced in low yields. The very interesting strong donor–strong acceptor TTF-C-BHTCNQ, **14**, was difficult to purify. The conversion of the triptycenequinone of **20** and **21** to the corresponding triptycene-dicyanoquinodiimine as a last synthetic step failed.

Crystal structures were solved for a donor[40] and for three acceptors;[41,42,59] amphiphilic molecules that form LB films will not usually crystallize, because of the usual aliphatic 'tails' added to them. The crystal structures of two D–σ–A molecules which do not form PL or LB films, were solved.[34,49]

Initial rectification reports

The first rectification attempts, macroscopic[35,46] or nanoscopic (using an STM)[47,48] were unsuccessful. Several asymmetric current–voltage (*I*–*V*) curves were reported in STM experiments. An STM experiment on an H atom switch was initially encouraging,[97] but was later blamed on an artifact.[98] Cu tetraazaporphyrin bonded to carboxylated HOPG yielded asymmetric *I*–*V* curves.[99] Some *I*–*V* asymmetries, which were not very reproducible, were seen for BDDAP-C-HETCNQ, **15c** and Py-C-HETCNQ, **16b**[60] and for $C_{16}H_{33}Q$-3CNQ, **2**.[61] An unsymmetrical STM tunneling current was seen through an alkylated hexabenzocoronene deposited on graphite[100] and an oligo(phenylethynyl)benzenethiol on Au(111) and Ag(111).[101] Electrochemical rectification at a monolayer-modified electrode was reported.[102,103]

Rectification in Pt|LB film|Mg|Ag sandwiches

Sambles and co-workers found that an LB multilayer of DDOP-C-BHTCNQ, **15a**, sandwiched between Pt and Mg electrodes, behaved as a rectifier.[79] The great technical merit of this work was to have made macroscopic defect-free LB

Table 2 Pressure–area isotherm data for Pockels–Langmuir films of D–σ–A and D^+–π–A^- molecules. Π_c and A_c are the pressure and molecular area, respectively, at the collapse point

Molecule	No.	Type	T/K	Π_c/mN m^{-1}	A_c/Å^2	Ref.
D–σ–A molecules						
TTF-C-BHTCNQ	**14**	Strong D, strong A	292	12.7	134±50	33
DDOP-C-BHTCNQ	**15a**	Weak D, strong A	292	20.2	50±1	35
BDDAP-C-BHTCNQ	**15b**	Medium D, strong A	293	47.3	57±1	39
BDDAP-C-HETCNQ	**15c**	Medium D, strong A	293	40.0	44±1	55
Py-C-BHTCNQ	**16a**	Medium D, strong A	283	28.2	53±1	35
Py-C-HETCNQ	**16b**	Medium D, strong A	293	46	—	55
BHAP-C-HMTCAQ	**17a**	Medium D, weak A	293	35.8	42±1	43
BDDAP-C-HMTCAQ	**17b**	Medium D, weak A	293	22.3	58±1	39
DDOP-C-ENP	**18a**	Weak D, weak A	278	23.7	38±1	50
TDDOP-C-ENP	**18b**	Weak D, weak A	278	34.0	76±1	50
3,5-BHDOAP-C-ENP	**18c**	Weak D, weak A	299	49.6	39±2	62
3,4-BHDOAP-C-ENP	**18d**	Weak D, weak A	300	54.5	35.8±0.5	56
3,5-BTDYOAP-C-ENP	**18f**	Weak D, weak A	298	18.7	58±2	56
3,4-BTDYOAP-C-ENP	**18g**	Weak D, weak A	300	49.4	50±1	56
TDDOP-C-HETCNQ	**19a**	Weak D, strong A	283	47.5	54±1	50
3,4-BHDOAP-C-HETCNQ	**19b**	Weak D, strong A	300	55.2	51±1	56
BHD-S4-TTF-C4-TrpQ	**20**	Strong D, weak A	300	41	28±1	65
HDPyr-TTF-Pyr-C4-TrpQ	**21**	Strong D, weak A	300	37	38±1	65
D^+–π–A^- molecules						
$C_{16}H_{33}Q$-3CNQ	**2**	D^+–π–A^- (weak A)	287	34	50±1	30
HD-BTAz-3CNQ	**22a**	D^+–π–A^-	283	30.0	37.5±1	76
HD-BSeAz-3CNQ	**22b**	D^+–π–A^-	287	32.4	41.5±1	76
HD-BTeAz-3CNQ	**22c**	D^+–π–A^-	283	30.8	51±1	76
HD-mϕ-BTAz-3CNQ	**23a**	D^+–π–A^-	287	43.0	42.2±1	76
HD-mϕ-BSeAz-3CNQ	**23b**	D^+–π–A^-	283	40.0	42.3±1	76

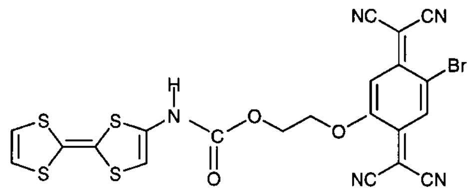
multilayers, and to have deposited atop the organic layer a metal film of magnesium (later shadowed with Ag) without shorting the device. However, **15a** does not contain a strong donor moiety, *i.e.* I_D is probably too large for an Aviram–Ratner rectifier. The observed rectifying behavior of **15a** was later ascribed, 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.[80,81]

Sambles' group also found asymmetries in an LB multilayer of the ground state zwitterion $C_{16}H_{33}Q$-3CNQ, **2**, sandwiched between Pt and Mg electrodes;[82] there was also a slight I–V asymmetry for an LB monolayer of **2**.[82] To respond to the self-criticism about a possible Schottky barrier,[80,81] an insulating LB layer was put between **2** and the electrodes; the I–V asymmetry persisted.[83,84] It was thus claimed that molecular rectification had been observed, albeit between asymmetric metal electrodes.[83] This result was well received;[104] some lingering questions are discussed below.

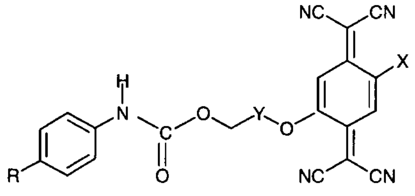
Asymmetric I–V curves were also seen[105,106] in a D–σ–A molecule **24**, but in a direction opposite from what was expected from the Aviram–Ratner mechanism of rectification.[107] The molecule contains a medium donor moiety (pyrene) and a weak acceptor moiety (dinitrobenzene). This result[105] and an equally puzzling STM result[100] suggest that electrical asymmetries in through-film conduction may have several explanations.

Rectification in Al|Al_2O_3|LB monolayer|Al_2O_3|Al sandwich

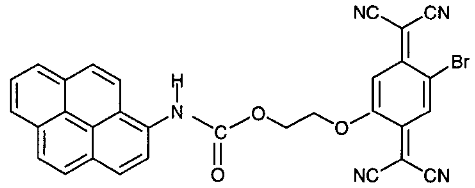
A very thorough repetition and major amplification of Sambles' pioneering work on $C_{16}H_{33}Q$-3CNQ, **2** was carried out.[30,65,68,70,71,73,75,76] We review first the general physical and chemical properties of **2**. The synthesis of **2** was vastly improved.[30] Cyclic voltammetry reveals that **2** 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*-benzo-1,4-quinone; the second reduction and the first oxidation of **2** are electrochemically irreversible.[30] 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 $\mathbf{2}^-$ are mostly localized on the 3CNQ ring;[73] therefore the LUMO of **2** is mostly localized on the 3CNQ moiety. The dipole moment of **2** 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).[30] The absorption band, probably due to an intervalence transition (IVT) band or intramolecular charge-transfer (CT) transition, is narrow, intense, and hypsochromic.[30,73] There are two fluorescence emissions, one in the visible region (corresponding to UV absorption bands), the other in the near infrared region.[73] The excited state dipole moment is estimated at between 3 and 9 D.[73] There is no evidence of a proposed twisted CT transition due to an internal rotation:[109] the NMR shows a large chemical shift due to the zwitterionic ground state[30] but no change in the temperature-dependent spectrum due to twisting/untwisting.[73] Evidently, the molecule has some 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 state would be degenerate), but rather that of a zwitterion. The molecule forms multiply twinned crystals, whose unit cell could not be indexed.[30] However, in the crystal structure of a related compound, picolyltricyanoquinodimethane, or picolinium tricyanoquinodimethanide [(*N*-methylpyridin-1-ium-2-ylmethylidene)tricyanoquinodimethanide], **25**, a twist angle $\theta = 30.13°$ (dihedral angle between the pyridinium ring and the phenyl ring of 3CNQ) was measured.[108] Simple semiempirical MO calculations (AM1, PM3) do not yield large ground-state dipole moments,[30] unless the twist angle becomes 90°.[1-9] Large dipole moments are obtained in LDA calculations.[78] The intense blue or green color of a solution of **2** (depending on solvent) disappears at the first trace of acid, but is recovered if the solution is exposed to ammonia vapor. When left in air and intense sunlight for weeks, a solution of **2** can discolor, by some unknown mechanism. Most manipulations of **2** were thereafter carried out with minimum exposure to light. **2** forms



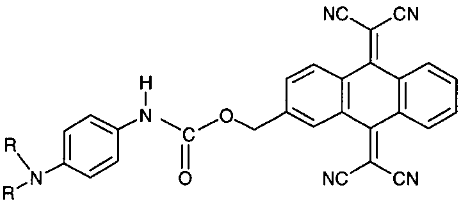
14, TTF-C-BHTCNQ



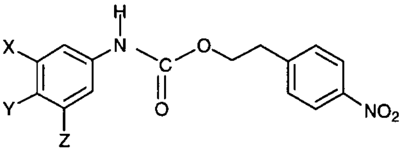
15a: $R=O\text{-}(n\text{-}C_{12}H_{25})$, $X=Br$, $Y=CH_2$: DDOP-C-BHTCNQ
b: $R=N(n\text{-}C_{12}H_{25})_2$, $X=Br$, $Y=CH_2$: BDDAP-C-BHTCNQ
c: $R=N(n\text{-}C_{12}H_{25})_2$, $X=H$, $Y=CH_2$: BDDAP-C-HETCNQ
d: $R=N(n\text{-}C_{12}H_{25})_2$, $X=H$, $Y=C_2H_4$: BDDAP-C-HPTCNQ
e: $R=N(n\text{-}C_{12}H_{25})_2$, $X=H$, $Y=C_3H_6$: BDDAP-C-HBTCNQ



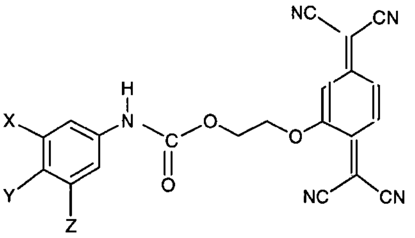
16a: X=Br: Py-C-BHTCNQ
b: X=H: Py-C-HETCNQ



17a: $R=n\text{-}C_6H_{13}$: BHAP-C-HMTCAQ
b: $R=n\text{-}C_{12}H_{25}$: BDDAP-C-HMTCAQ



18a: $X=H$, $Y=O(CH_2)_{11}CH_3$, $Z=H$: DDOP-C-ENP
b: $X=Y=Z=O(CH_2)_{11}CH_3$: TDDOP-C-ENP
c: $X=Z=NH\text{-}CO\text{-}(CH_2)_{15}CH_3$, $Y=H$: 3,5-BHDOAP-C-ENP
d: $X=Y=NH\text{-}CO\text{-}(CH_2)_{15}CH_3$, $Z=H$: 3,4-BHDOAP-C-ENP
e: $X=Z=O(CH_2)_{11}CH_3$, $Y=H$: BDDOP-C-ENP
f: $Y=H$, $X=Z=NHCO(CH_2)_7C\equiv C\text{-}C\equiv C\text{-}(CH_2)_9CH_3$: 3,5-BTDYOAP-C-ENP
g: $Z=H$, $X=Y=NHCO(CH_2)_7C\equiv C\text{-}C\equiv C\text{-}(CH_2)_9CH_3$: 3,4-BTDYOAP-C-ENP



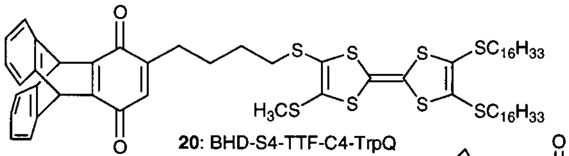
19a: $X=Y=Z=O(CH_2)_{11}CH_3$: TDDOP-C-HETCNQ
b: $X=Y=NH\text{-}CO\text{-}(CH_2)_{15}CH_3$, $Z=H$: 3,4-BHDOAP-C-HETCNQ

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.[30,65] The monolayer thickness (X-ray diffraction, ellipsometry) is 22 Å, which means that a 30 Å long molecule is inclined by about 45° to the film normal.[30] Z-type multilayers form on Al. A grazing-angle Fourier transform infrared spectrum of a monolayer of **2** on Al shows two CN peaks at 2139 and 2175 cm^{-1}.[30] 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.[73] The intense CT band peaks at 565 nm in the LB monolayer[73] and the LB multilayer.[30,73]

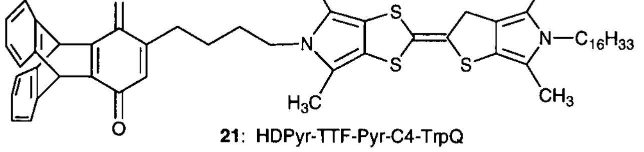
The rectification work was performed both on macroscopic Al|LB film|Al sandwiches, and by nanoscopic STM. Sambles found that Mg perturbs a physisorbed LB film the least. We decided to use Al on both sides of the LB film, but cryocooled to 77 K the glass |Al|LB film assembly, to minimize the thermal load on the LB film as the Al pad electrode is deposited from the vapor phase. The LB films were thoroughly dried, to prevent any spurious effect due to moisture (which has a large effect on the electrical characteristics of Y-type centrosymmetric arachidic acid multilayers). Ga/In eutectic was used to make contact with Au wire electrodes, as shown in Fig. 3. Asymmetric *I–V* curves were seen in a 4-monolayer Z-type LB film (Fig. 4), in a 4-monolayer film with a Mg electrode between the organic layer and the top Al pad,[30] and even for a single monolayer (Fig. 5).[30] Rectification was still seen, as a function of temperature, between 370 and 105 K (Fig. 6).[75] The maximum measured rectification ratio (at 1.5 V, Fig. 5a) was 26 : 1. However, if one cycles the measurement, the rectification ratio 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.[30] The current measured amounts to about 0.33 electrons per molecule per second.[30] 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.[76]

The direction of the current for forward bias, shown in Fig. 3, 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 $D^0\text{–}\sigma\text{–}A^0$, and a zwitterionic excited state $D^+\text{–}\sigma\text{–}A^-$; this mechanism is trivially modified and inverted for when the ground state is zwitterionic $D^+\text{–}\pi\text{–}A^-$, and the excited state is undissociated, $D^0\text{–}\pi\text{–}A^0$.[30]

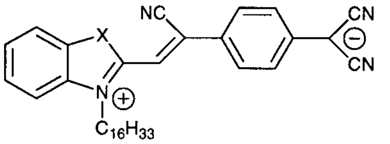
The Aviram–Ratner mechanism for unimolecular rectifi-



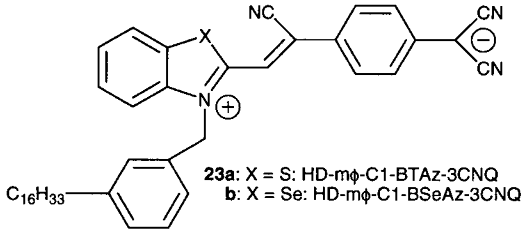
20: BHD-S4-TTF-C4-TrpQ



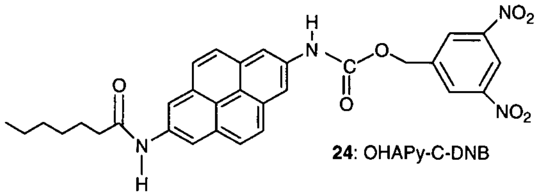
21: HDPyr-TTF-Pyr-C4-TrpQ



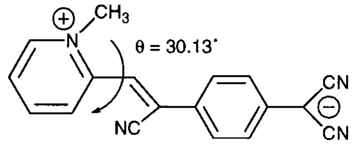
22a: X = S: HD-BTAz-3CNQ
b: X = Se: HD-BSeAz-3CNQ
c: X = Te: HD-BTeAz-3CNQ



23a: X = S: HD-mϕ-C1-BTAz-3CNQ
b: X = Se: HD-mϕ-C1-BSeAz-3CNQ



24: OHAPy-C-DNB



25: P-3CNQ

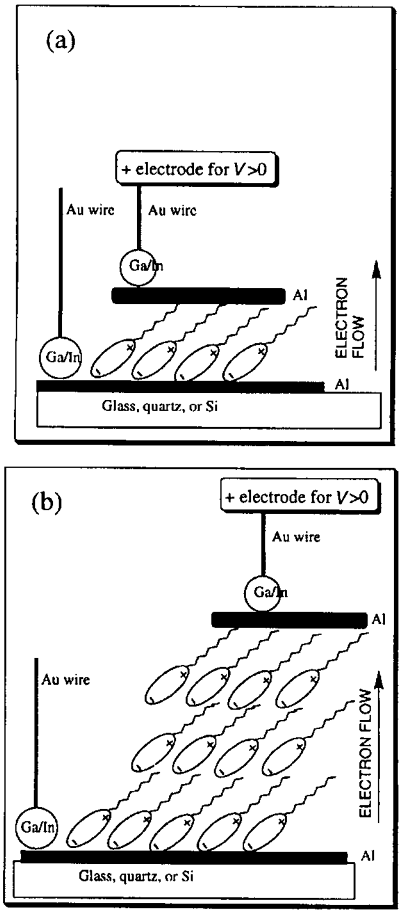


Fig. 3 Orientation of the LB monolayer (a) or multilayer (b) of **2** on a glass, quartz, or Si substrate; the electrode (+) for positive bias, and the direction of 'easy' electron flow for $V > 0$ are marked, from Ref. 30.

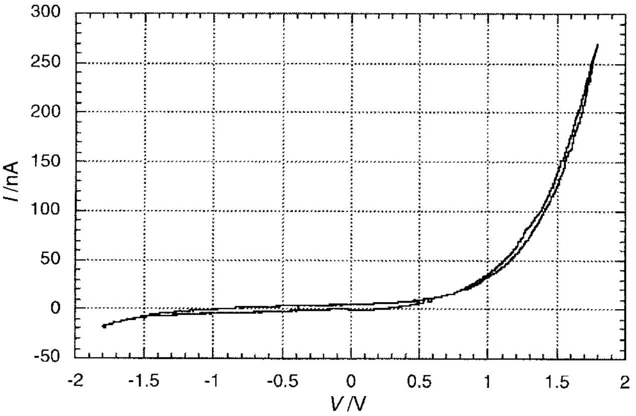


Fig. 4 Conductivity of a sandwich Ga/In eutectic|Al (100 nm)|4 LB monolayers of **2** (Z-type)|Al (100 nm)|Ga/In eutectic. The direction of easier electron flow ($I > 0$ for $V > 0$) is from the bottom electrode through the film to the top electrode, as in Fig. 3. From Ref. 30.

cation used an undissociated ground state D^0–σ–A^0 and a relatively low-lying zwitterionic excited state D^+–σ–A^-.[13] In the initial conception, this excited state could be a biradical,[13] *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.

The rectification was also verified for a 15-layer film of **2** on HOPG by STM,[30,65] and a small *I*–*V* asymmetry was even seen for a monolayer of **2** on HOPG,[30] but there is low adhesion of that first monolayer on HOPG.

Two dissenting interpretations should be discussed. The first is that the observed rectification is actually due to one rectifying Al|Al_2O_3 junction. The second is that the asymmetric current is due to the formation of a Schottky barrier between one end of **2** (presumably the 3CNQ end) and the Al electrode.

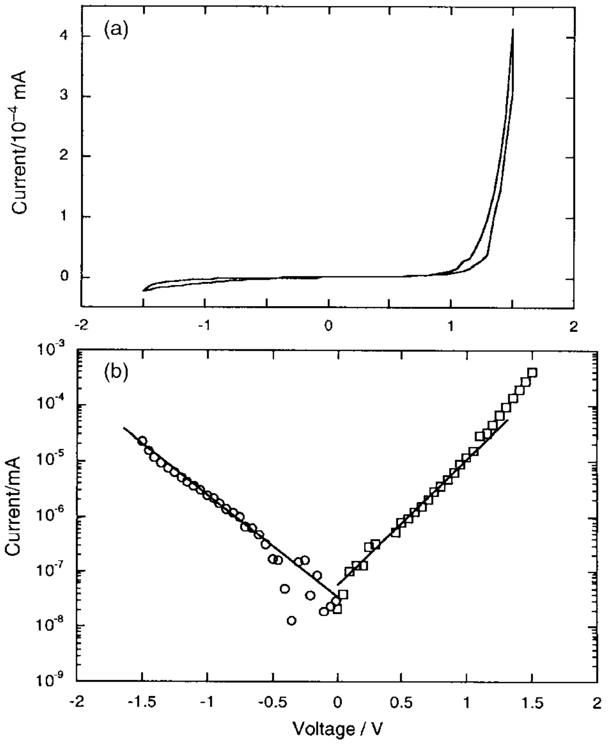


Fig. 5 Rectification through a single monolayer of **2** sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using Ga/In eutectic and Au wires. (a) Plot of the DC current *I versus* the DC applied voltage *V*; (b) plot of $\log_{10}I$ *versus V*. From Ref. 30.

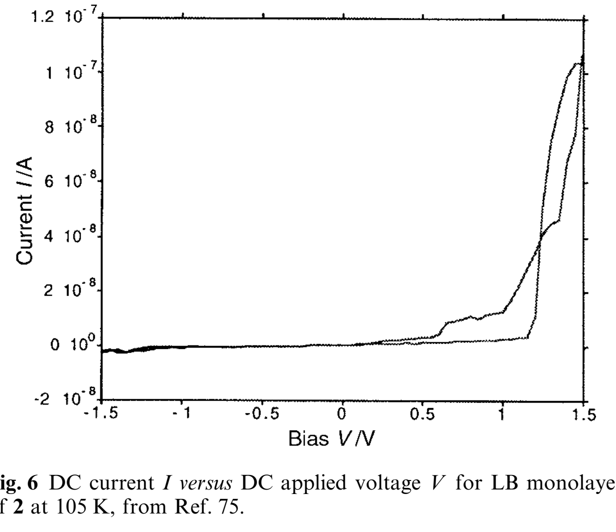


Fig. 6 DC current *I versus* DC applied voltage *V* for LB monolayer of **2** at 105 K, from Ref. 75.

The first dissenting view can dispelled by two observations: first, Al|Al$_2$O$_3$ couples occur naturally and symmetrically on both Al electrodes;[30] second, a centrosymmetric Y-type Langmuir–Blodgett multilayer of cadmium arachidate, after extensive drying, does not rectify, but exhibits symmetric current–voltage traces.[30]

The second dissenting view can be answered by considering the reduction potential of **2** and the work function of Al. The initial work on DDOP-BHTCNQ, **15a** accosted a Mg layer (work function $\phi = 3.66$ eV) to the BHTCNQ part of **15a**.[79] A later analysis suggested that the rectification was due not to a molecular process, but to a Schottky barrier at the interface between Mg and **15a**.[80,81] The first electrochemical reduction of BHTCNQ in acetonitrile solution is $E_{1/2} = 0.305$ V *vs.* SCE,[35] compared to $E_{1/2} = 0.127$ V *vs.* SCE for TCNQ (**3b**), whose gas-phase electron affinity is $A_A = 3.3$ eV. If the shifts of $E_{1/2}$ in solution correlate with A_A, then A_A (BHTCNQ)$\approx$3.1 eV, which is only 0.6 V higher in energy than the work function ϕ (Mg) = 3.66 eV. This makes it easy to form a Schottky barrier (salt) at the BHTCNQ|Mg interface; this Schottky barrier may be responsible for the observed rectification.[80,81] As a referee kindly pointed out, even the introduction of 'barrier monolayers' of cadmium arachidate[83] would not prevent the formation of such Schottky barriers. In contrast, for **2** the electrochemical $E_{1/2} = -0.513$ V *vs.* SCE[30] is close to $E_{1/2} = -0.481$ V *vs.* SCE for *p*-BQ (**11a**), which is a weak electron acceptor with $A_A = 1.95$ eV. Therefore, accosting Mg ($\phi = 3.66$ eV)[82] or Al ($\phi = 4.24$ eV)[30] to a monolayer of $C_{16}H_{33}$Q-3CNQ, **2** (estimated $A_A \approx 1.90$ eV) would form a Schottky barrier only if one supplies relatively large energies $\Delta E = 4.24 - 1.90 = 2.14$ eV (for Al electrode) or $\Delta E = 3.66 - 1.9 = 1.56$ V (for Mg electrode), *i.e.* enough energy to short-circuit the device. Despite earlier doubts about Schottky barriers,[64] the more recent electrochemical results[30] strongly indicate that in 'Al|oxide|monolayer of **2**|oxide|Al' sandwiches a Schottky barrier is unlikely to form. Also, no rectification was found even for Z-type multilayers of **22**.[77]

Further, centrosymmetric multilayers of cadmium arachidate sandwiched between Al electrodes did not provide rectification,[30] nor did monolayers and multilayers of **22**.[77]

The arguments given here buttress the claim that molecular rectification has been observed[30] in **2**. The 'sure proof' of molecular rectification would be inelastic electron tunneling peaks for **2**. Such experiments are presently in progress.

The 'ultimate direct proof' of molecular rectification may still be missing, but the evidence for a molecular rectification seems abundant.

Thus, 25 years after it was proposed, the Aviram–Ratner Ansatz has been unequivocally and finally verified.[70] This major result has received favorable attention.[110]

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.[112,113] Control experiments using arachidic acid[30] 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 of **2** 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,[75] which is 1 to 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 of 0.33 electrons per molecule per second (0.053 a A) is many orders of magnitude lower than the currents measured in an STM experiment (10 pA to 1 nA): maybe only one molecule in a million is 'at work'.

(4) The reduction of the rectification ratio upon repeated cycling[30] and the number of 'aberrant' junctions could be partially eliminated by chemisorbing a suitably modified version of molecule 2 onto Si or Al. A thiol termination is incompatible with the acid-sensitive molecule **2**. A silanized version of molecule **2** was prepared, but in initial experiments did not form a uniform layer on Si.

(5) The Volta potential of about 0.5 V for a monolayer of **2** at the air–water interface[30] or for a dry monolayer of **2** on Al is one order of magnitude less than expected for a zwitterionic monolayer.

(6) Asymmetrical STM currents for molecules that have no rectifying moieties[100,101] are not understood.

(7) The 'backward' *I–V* characteristics of molecule **24**[105–107] can be explained theoretically if one polarizes the molecule in an electrical field. Such polarization has been calculated for

2.[111] But the Aviram–Ratner mechanism is clearly not a polarization process ('pull'), but an electron transfer at resonance ('push').

(8) A theoretical calculation of the I–V asymmetry for **2** would be welcome.

(9) Can all ground-state zwitterions with a low-lying undissociated excited state rectify? Probably yes, if they also have a strong IVT band.

(10) 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^+–π–A^- monolayer has been achieved. Much exciting work lies ahead, as we proceed towards making unimolecular electronics a practical reality in the 21st century.

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