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D-σ-A unimolecular rectifiers

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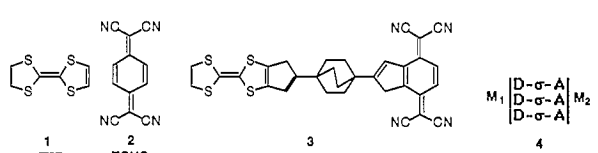
Abstract

Unimolecular devices can be defined as devices which manipulate the energy levels or the conformations of either a single molecule or a very small cluster of molecules. When made practical, these devices, the "advanced guard" of molecular electronics, should leapfrog conventional inorganic microelectronics, which should be limited to "design rules" of components no closer than 10 nm. Fast organic rectifiers and transistors should be addressable by scanning tunneling microscopy. The quest for the proposed Aviram–Ratner D-σ-A unimolecular rectifier is reviewed, where D is a good one-electron donor, σ is a covalent, saturated "sigma" bridge and A is a good one-electron acceptor. Under gentle bias, D-σ-A should more easily form the zwitterion D^+-σ-A^- than the zwitterion D^--σ-A^+ (by fast intramolecular downhill tunneling, the state D^+-σ-A^- reverts quickly to D-σ-A). Many D-σ-A molecules form Langmuir–Blodgett films. Sambles' group has observed Schottky barrier rectification in D-σ-A molecules and in D^+-π-A^- zwitterions; the groups of Kuhn, Sugi and Roth and von Klitzing have observed rectification by Langmuir–Blodgett multilayers. Intramolecular electron tunneling through a single D-σ-A molecule has not yet been confirmed.

Keywords: D-σ-A molecule; Unimolecular rectifier; Aviram–Ratner

1. The Aviram–Ratner Ansatz of unimolecular rectification

In 1974, Aviram et al. [1–3] proposed that a single organic molecule of the type D-σ-A could be a rectifier of electrical current. This D-σ-A molecule acts 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). The Aviram–Ratner ansatz [2–4] is inspired by the chemistry of highly conducting, lower dimensional, organic charge transfer systems based on good one-electron donors (D), such as tetrathiafulvalene (TTF, **1**), and good organic one-electron acceptors (A), such as 7,7,8,8-tetracyanoquinodimethane (TCNQ, **2**).



1 TTF 2 TCNQ 3 4

Good donor molecules (i.e. molecules with relatively low gas phase first ionization potentials I_D) are, at the same time, 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 (they have high I_A); thus the gas phase energy ΔT_F required for charge transfer (both components at infinite separation) is about 3.5 eV (Eq. (1)), while the energy ΔT_R required for the reverse reaction is greater than 9 eV (Eq. (2))

$$TTF(g) + TCNQ(g) \longrightarrow TTF^+(g) + TCNQ^-(g) \quad (1)$$

$$\Delta T_F = I_D - A_A = 6.83 - 3.3 = 3.5 \text{ eV}$$

$$TTF(g) + TCNQ(g) \longrightarrow TTF^-(g) + TCNQ^+(g) \quad (2)$$

$$\Delta T_R = I_A - A_D = 9.6 \text{ eV(est)}$$

The "Gedankenmolekül" D-σ-A (**3**), if assembled between two metal electrodes M_1 and M_2, as in **4** or in Fig. 1(b) (we will call it the device M_1|D-σ-A|M_2), will exhibit easy electron transfer from M_1 to M_2 because the relatively accessible zwitterionic state D^+-σ-A^- is used (while the electron flow from M_1 to M_2 would be inefficient because the barrier to form the zwitterion D^--σ-A^+ would be several electronvolts higher). The Aviram–Ratner device will work if the tunneling of electrons from A to D is assisted "through the bond system" [4], and will fail if the electron transfer between the metal electrodes M_1 and M_2 is predominantly by direct, unassisted, ordinary "through space" tunneling. Molecule **3** was never synthesized.

The interest in such a D-σ-A rectifier is its small size: its working thickness should be about one or two molecular lengths, i.e. about 5 nm; this is smaller than the most opti-

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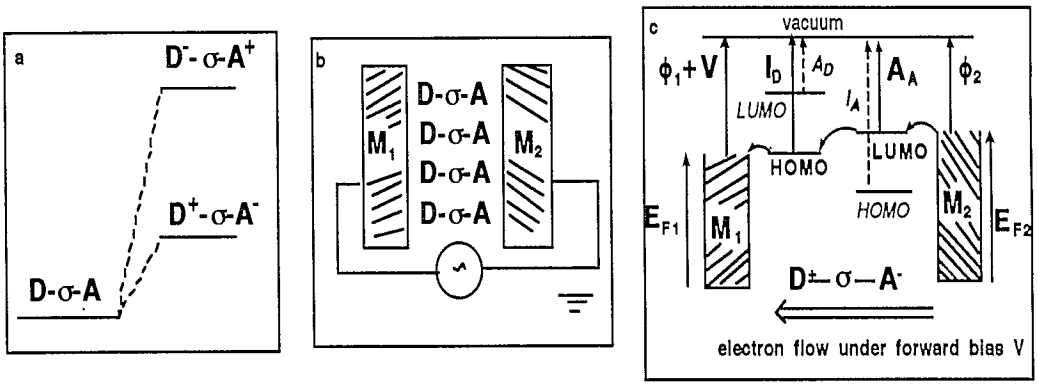
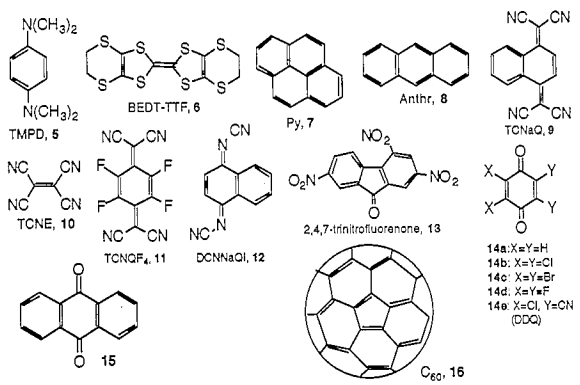


Fig. 1. The Aviram–Ratner ansatz [1]. (a) The zwitterion D^+-σ-A^- is many electronvolts lower in energy than D^--σ-A^+. (b) An oriented monolayer is sandwiched between two macroscopic metal electrodes M_1 and M_2; this is the device $M_1|D\text{-}\sigma\text{-}A|M_2$, grounded at M_2. (c) Under moderate forward bias V, the work function ϕ_2 of the macroscopic metal electrode M_2 will match the electron affinity A_A of the LUMO of the A side of D-σ-A (distance from the vacuum level to the LUMO of A), and the work function ϕ_1 plus the applied voltage V of the metal electrode M_1 will match the ionization potential I_D of the HOMO of the D side of D-σ-A (distance from the vacuum level to the HOMO of D). Then (I_D is typically larger than A_A) the tunneling through the barrier is assisted only in the direction shown, and rectification of the electrical current is achieved. (In italics are shown the HOMO of the acceptor, the LUMO of the donor and the energies I_A and A_D). The mechanism for forward bias is $M_1|D\text{-}\sigma\text{-}A|M_2 \rightarrow M_1^-|D^+\text{-}\sigma\text{-}A^-|M_2^+ \rightarrow (IT_F) \rightarrow M_1^-|D\text{-}\sigma\text{-}A|M_2^+$. For reverse bias, $M_1|D\text{-}\sigma\text{-}A|M_2 \rightarrow X \rightarrow M_1^+|D^-\text{-}\sigma\text{-}A^+|M_2^-$ does not occur, but autoionization can happen: $M_1|D\text{-}\sigma\text{-}A|M_2 \rightarrow (IT_R) \rightarrow M_1|D^+\text{-}\sigma\text{-}A^-|M_2 \rightarrow M_1^+|D\text{-}\sigma\text{-}A|M_2^-$. The Aviram–Ratner mechanism works if, and only if, the probability $IT_F \gg IT_R$, and if tunneling through bond is much greater than tunneling through space.

mistic forecast for the ultimate minimum working length ("design rule") in silicon or gallium arsenide devices (100 Å = 10 nm); present Si design rules are well above that.

There are several criteria for the rational synthesis of suitable D-σ-A systems

(1) I_D for the donor end D must be as small and as close as possible to the work function ϕ of the metal layer M_1. Typical values are given in Table 1 and Fig. 2.



(2) A_A for the acceptor end A (Table 1) must be as large and as close as possible to the work function ϕ of the metal layer M_2. Table 1 and Fig. 2 show that requirements (1) and (2) can be met only approximately.

(3) In a molecule in which the "sigma" bridge σ has already been built, it is extremely difficult to convert chemically a weak donor into a strong donor or a weak acceptor into a strong acceptor. Therefore we must first synthesize a monosubstituted strong donor (D-X) and a monosubstituted strong acceptor (Y-A) and join them by a coupling reaction (Eq. (3a)) which somehow avoids the undesirable, but probable, formation of ionic charge transfer complexes (Eq. (3b))

$$\text{D-X} + \text{Y-A} \longrightarrow \text{D-}\sigma\text{-A} \quad (3a)$$

$$\text{D-X} + \text{Y-A} \longrightarrow \text{D}^+\text{-X} + \text{Y-A}^- \quad (3b)$$

(4) The molecules must pack efficiently into self-assembling monolayers, or bind covalently to a substrate. If the designed D-σ-A molecule does not form Pockels–Langmuir (PL) [33,34] self-assembling monolayers at the air–water interface, then either long aliphatic "greasy tails" must be added to form a hydrophobic tail, or an ionic, hydrophilic "head" should be added to either the D end or the A end. The molecules should be fairly flat so as to form compact PL films, yet flexible enough so as to transfer well as Langmuir–Blodgett (LB) films (by the vertical or LB dipping method [35,36], or by the horizontal or Langmuir–Schaefer (LS) method [37]).

(5) The electron transfer through the D-σ-A molecule, and through its hydrophobic or hydrophilic tails, must be fast: a molecular device that is small but slow is predicted to be useless. That electron transfer is fast through properly designed molecules, e.g. the photosynthetic reaction center, is well known. The work of Miller and coworkers [38–40] shows that electron transfer through σ-bonded androstane skeletons can be faster than 1 ns for optimal $I_D - A_A$, but it slows down for either very small $I_D - A_A$ or very large $I_D - A_A$ (where a large Franck–Condon reorganization slows down the electron transfer rate: Marcus "inverted region" [41]).

(6) The device will have a limited tolerance for high voltages or for heating. A monolayer 2 to 3 nm thick will probably tolerate no more than 1 V external bias across it before dielectric breakdown occurs [1–3].

Ionization potentials for all-organic donors range from 6.25 eV for a "strong" donor such as TMPD (**5**) to 9.38 eV

Table 1
Solution cyclic voltammetric half-wave potentials $E_{1/2}$ (V vs. SCE), and gas phase ionization potentials I_D (eV) and electron affinities A_A (eV) for donors D and acceptors A ($E_{1/2}=E_{ox,p}-0.03$ or $E_{1/2}=E_{red,p}+0.03$). A_A for TCNQ has shifted from 2.8 eV [5] to 3.3 eV [6]; this affects A_A for $TCNQF_4$ and DCNQI

Molecule	Soln. oxidation		Soln. reduction		Reference	Gas phase		Reference
	(1) $D \rightarrow D^+ E^1_{1/2}$ (V)	(2) $D^+ \rightarrow D^{2+} E^2_{1/2}$ (V)	(1) $A \rightarrow A^- E^1_{1/2}$ (V)	(2) $A^- \rightarrow A^{2-} E^1_{1/2}$ (V)		Oxid. $D \rightarrow D^+ I_D$ (eV)	Red. $A \rightarrow A^- A_A$ (eV)	
Donors D								
TMPD (**5**)	0.10	0.66	–	–	[7]	6.25	–	[8]
TTF (**1**)	0.35	0.75	–	–	[9]	6.83	–	[10]
BEDT-TTF (**6**) [a]	0.54	0.96	–	–	[9]	6.21	–	[11]
Pyrene (**7**) [a]	1.16	–	–	–	[12]	7.41	0.58	[13]
Anthracene (**8**) [a]	1.09	–	–	–	[12]	7.55	0.60	[14]
Benzene [a]	2.30	–	–	–	[12]	9.38	−1.0	[15,16]
Acceptors A								
TCNQ (**2**) [a]	–	–	0.127	−0.291	[17]	–	3.3	[5,6]
TCNaQ (**9**) [c]	–	–	0.060	−0.425	[18]			
TCNE (**10**) [a]	–	–	0.152	−0.568	[17]	–	2.3, 2.9	[19,20]
$TCNQF_4$ (**11**) [c]	–	–	0.53	0.02	[21]	–	3.72	[22]
DCNNaQI (**12**) [b]	–	–	0.19	−0.35	[23]	–	≈3.3	[24]
Trinitrofluorenone (**13**) [a]	–	–	−0.42	−0.67	[25]	–	2.2	[26]
p-Benzoquinone (**14a**) [a]	–	–	−0.481	−1.030	[27]	–	1.95	[14,28]
Chloranil (**14b**) [a]	–	–	+0.01	−0.71	[29]	–	2.76	[14]
Bromanil (**14c**) [a]			0.00	−0.72	[29]			
Fluoranil (**14d**) [a]	–	–	−0.04	−0.82	[29]	–	2.92	[14]
DDQ (**14d**) [a]	–	–	0.51	−0.30	[27]	–	3.13	[26]
Anthraquinone (**15**) [a]	1.21	–	−0.98	−1.50	[30]	–	1.59	[28]
C_{60} (**16**) [b]	–	–	−0.18	−0.58, −1.07	[31]		2.6–2.8	[32]

[a] Solvent CH_3CN. Reference electrode SCE.
[b] Solvent CH_2Cl_2. Reference electrode Ag|AgCl. Offset = 0.15 V [33].
[c] Solvent BuCN. Reference electrode SCE.
[d] Solvent CH_2ClCH_2Cl. Reference electrode Ag|AgCl. Offset = 0.15 V [33].

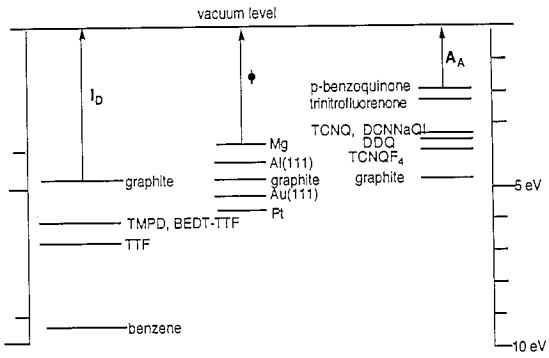


Fig. 2. Energy levels: HOMO of donors (left); work functions of metals (middle); LUMO of acceptors (right).

for a "weak" donor such as benzene; electron affinities have a much more limited range: from 1.9 eV for a relatively "weak" acceptor (*p*-benzoquinone, **14a**) to 3.7 eV for the strongest acceptor $TCNQF_4$ (**11**). The ionization potentials (electron affinities) of condensed aromatic hydrocarbons decrease (increase) with increasing molar mass to meet "at infinity" the work function of graphite, which can be considered as an "infinite" hermaphroditic two-dimensional ideal donor and acceptor [42,43]: $I_D = A_A = \phi = 4.40$ eV [44], 4.45 eV [45] or 4.62 eV [46]. The match with metal work functions is not optimal.

For the Aviram–Ratner unimolecular rectifier, we need $\Delta T_F = I_D - A_A > 0$ to ensure "downhill" through-bond-assisted inelastic electron tunneling from A^- to D^+; this condition is trivially realized.

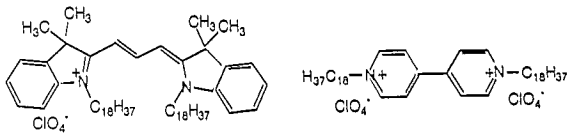
The energy levels shown in Fig. 2 suggest that a good combination for the device $M_1|D\text{-}\sigma\text{-}A|M_2$ is $M_1 \equiv Pt$, $D \equiv TMPD$, $A \equiv TCNQ$ and $M_2 \equiv Mg$ or Al); the former should allow the zwitterion $D^+\text{-}\sigma\text{-}A^-$ to form at about 0.5 V bias, the latter at 1 V bias. As a rough guide for the synthetic chemist, we would prefer $I_D < 7$ eV (TMPD, TTF, BEDT-TTF) and $A_A > 2.5$ eV (TCNQ, $TCNQF_4$, DCNQI, chloranil, bromanil, fluoranil, TCNE, C_{60}). Since gas phase ionization potentials, and particularly gas phase electron affinities, are not easily accessible to the organic chemist, a more convenient, if approximate, measure is the voltammetric half-wave oxidation or reduction potential $E_{1/2}$. Using the $E_{1/2}$ values in CH_3CN solution, relative to the standard calomel electrode (SCE), for strong donors and acceptors and the correlations of I_D and $E_{1/2}$ and A_A and $E_{1/2}$ [11,26,47–51] ($E_{1/2} = 0.89 I_D - 5.70 \pm 0.2$ and $E_{1/2} = 0.64 A_A - 1.86 \pm 0.2$), the criteria become $E_{1/2} < 0.50$ V vs. SCE for the donor D and $E_{1/2} > -0.18$ V vs. SCE for the acceptor A.

2. Bulk organic rectifiers

After the discovery of the pn junction diode (p = hole-rich region, n = electron-rich region) and the npn transistor, 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 (which becomes a p region) were brought into contact with that of an organic electron acceptor (n region). This was indeed verified in the 1960s [52].

3. Multilayer LB organic rectifiers

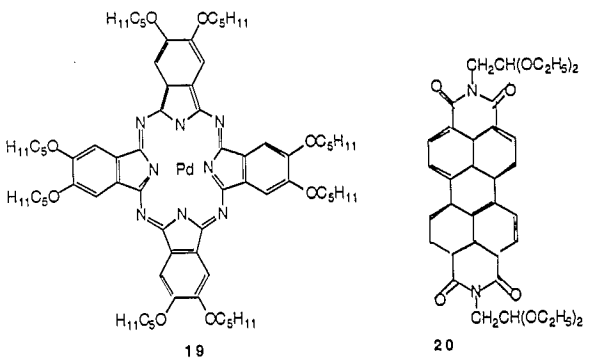
Kuhn and coworkers [53] obtained a "pn" (or DA) rectifier in an LB multilayer sandwich Al $(CA\text{-}D)_q$ $(CA)_r$ $(CA\text{-}A)_s$ Al. Here $(CA\text{-}D)_q$ denotes the electron donor system D (i.e. q LB monolayers of cadmium arachidate (CA) randomly doped in the ratio 5 : 1 with a suitable organic π- electron donor D, the cyanine dye **17**), $(CA)_r$ denotes a spacer layer of r undoped monolayers of CA and $(CA\text{-}A)_s$ denotes the electron acceptor system A (i.e. s LB monolayers of CA randomly doped with a suitable organic π-electron acceptor A, paraquat, **18**).



CY, 17 PQ, 18

This work was repeated and confirmed by Sugi et al. [54], who observed rectification properties, but only if $q \geq 3$, $r \geq 1$ and $s \geq 3$, i.e. if there are at least seven monolayers (below that, irreproducible data resulted). In these LB films, the registry and intermolecular approach between D and A dissolved in adjacent cadmium arachidate monolayers cannot be controlled.

Recently, the groups of Roth and coworkers have seen rectification at 5 K in an LB multilayer of six layers of D molecules (Pd octa(pentyloxy)benzophthalocyanine, **19**) and six layers of A molecules (a substituted perylene-3,4,9,10-tetracarboxyldiimide, **20**); evidence for Coulomb blockades was seen [55].



19 20

4. Molecule-based field effect transistor using conducting polymers or semiconductors

Wrighton and coworkers developed a "molecule-based transistor" which uses conducting polymers: chemically

doped polyaniline layers deposited on Au interdigitated electrodes [56] 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 [57]. Stubb and coworkers [58] showed that a single LB monolayer can be used in a "molecule-based" transistor. Garnier et al. [59] used sexithiophene as the active semiconductor in a field effect transistor.

5. Connections to a unimolecular electronic device

How does one "talk" to such single molecules or clusters, i.e. how can one get signals to and from the macroscopic world of electronics (greater than 1 μm) to the "nanoscopic" world of single molecules? Perhaps through an intermediate "mesoscopic" world of sizes of the order of 1 μm to 100 nm?

To address a single molecule electrically, we need a "molecular wire" (e.g. a polyacetylene strand) or a "molecular antenna" (e.g. the conjugated portion of β-carotene), neither of which can be easily connected to an external potential source at present. Until the recent advent of scanning tunneling microscopy (STM) [60], we could not connect a single molecule to an external circuit. For macroscopic connections, three techniques seem promising: (1) the LB technique [35–37], and the technique of covalently bonding molecules to electrode surfaces, either by (2) silanizing a hydroxyl-coated electrode then attaching molecules covalently [61], or (3) silanizing the molecule and attaching it directly by spin coating by the oleophobic method [62] to a hydroxyl-coated electrode [63].

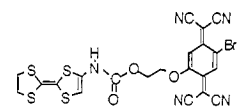
The recent advent of STM [60] as an affordable research technique should allow the electronic addressing of a single molecule. If this becomes easily controllable and reproducible, a real revolution in molecular electronic (ME) devices should be "just around the corner". Indeed, STM has been used to demonstrate tunnel diode behavior [64]. However, we must beware of false STM images, account for reconstructions of the conducting surface by the tip, and understand the distortions caused by the tip on a weakly chemisorbed species such as an LB or LS film.

6. Fujihira's LB photodiode

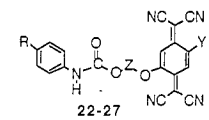
Fujihira et al. [65] have demonstrated that a single LB monolayer can function as a photodiode; this is probably the first truly unimolecular device. They synthesized a D-σ_1-A-σ_2-S molecule (**9**), where D is the electron donor (ferrocene), σ_1 is a $(CH_2)_{11}$ chain, A is the final electron acceptor (viologen), σ_2 is a $(CH_2)_6$ chain and S is a sensitizer (pyrene). This molecule was transferred as an LB monolayer onto a semitransparent Au electrode (with the viologen, or A, part of the molecule closest to Au). The electrode was the side of an electrochemical cell containing a 0.1 M KCl solution and a Pt counterelectrode. 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. UV light at 330 nm excites the pyrene radical cation from the ground state to the 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. SCE was observed only when the light was turned on [65].

7. Progress towards organic unimolecular rectifiers

Between 1981 and 1991, Panetta and Metzger prepared several D-σ-A molecules as candidates for unimolecular rectification. STM was not available initially, so there was a commitment to the LB technique. Hertler [66] coupled a bifunctional TTF to a bifunctional TCNQ alcohol via the urethane or carbamate coupling reaction, yielding a semiconducting copolymer $(-\sigma\text{-TTF-}\sigma\text{-TCNQ-})_x$, and also prepared a monofunctional alcohol. This led to the synthesis of monofunctionalized donors and acceptors, and the successful couping of strong donors and strong acceptors by the carbamate linkages: a representative list of D-σ-A molecules is given by **21–40**, most of which make LB films [7,33,34,67–96].

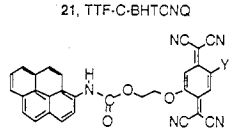


21, TTF-C-BHTCNQ



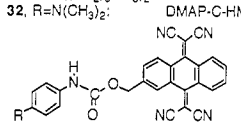
22-27

22: Y=Br, Z=$(CH_2)_2$, R=$N((CH_2)_{11}CH_3)_2$: BDDAP-C-BHTCNQ
23: Y=Br, Z=$(CH_2)_2$,R=$O(CH_2)_{11}CH_3$: DDOP-C-HETCNQ
24: Y=Br, Z=$(CH_2)_2$,R=$N((CH_2)_{11}CH_3)_2$: BDDAP-C-HETCNQ
25: Y=Br, Z=$(CH_2)_3$,R=$N((CH_2)_{11}CH_3)_2$: BDDAP-C-HPTCNQ
26: Y=Br, Z=$(CH_2)_4$,R=$N((CH_2)_{11}CH_3)_2$: BDDAP-C-HBTCNQ
27: Y=Br, Z=$(CH_2)_4$,R=H: Ph-C-BHTCNQ



28, Y=Br: Py-C-BHTCNQ
29, Y=H: Py-C-HETCNQ

30, R=$N((CH_2)_{11}CH_3)_2$: BDDAP-C-HMTCAQ
31, R=$N((CH_2)_5CH_3)_2$: BHAP-C-HMTCAQ
32, R=$N(CH_3)_2$: DMAP-C-HMTCAQ



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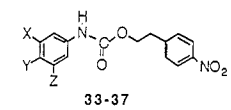
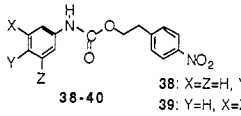


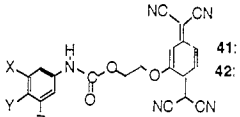
33-37

33: X=H, Y=$O(CH_2)_{11}CH_3$, Z=H: DDOP-C-ENP
34: X=Y=Z=$O(CH_2)_{11}CH_3$: TDDOP-C-ENP
35: X=Z=NH-CO-$(CH_2)_{15}CH_3$, Y=H: 3,5-BHDOAP-C-ENP
36: X=Y=NH-CO-$(CH_2)_{15}CH_3$, Z=H: 3,4-BHDOAP-C-ENP
37: X=Z=$O(CH_2)_{11}CH_3$, Y=H: BDDOP-C-ENP



38-40

38: X=Z=H, Y=$N(CH_3)(CH_2)_8C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_9CH_3$: MTDAP-C-ENP
39: Y=H, X=Z=$NHCO(CH_2)_7C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_9CH_3$: 3,5-BTDYOAP-C-ENP
40: Z=H, X=Y=$NHCO(CH_2)_7C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_9CH_3$: 3,4-BTDYOAP-C-ENP



41-42

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

The various D-σ-A molecules that form LB films are the carbamates **21–42**. Of these, **30–42** were prepared to incorporate D-σ-A molecules into polymerizable diacetylenes, which may yield promising non-linear optical materials, primarily for frequency doubling. To explain the acronyms, for structure **22**, BDDAP-C-BHTCNQ is the *N,N*-bis-dodecyl-

Table 2
Pressure–area isotherm data for Pockels–Langmuir films. Π_c and A_c are the pressure and molecular area respectively at the collapse point. Asterisk indicates that the film makes Z-type LB multilayers (substrate at 22 °C, film at 5 °C)

Molecule	No.	Type	T (K)	Π_c (mN m^{-1})	A_c (Å^2)	Reference
TTF-C-BHTCNQ	**21**	Strong D, strong A	292	12.7	134 ± 50	[69]
BDDAP-C-BHTCNQ	**22**	Medium D, strong A	293	47.3	57 ± 1	[34]
DDOP-C-BHTCNQ	**23**	Weak D, strong A	292	20.2	50 ± 1	[71]
BDDAP-C-HETCNQ	**24**	Medium D, strong A	293	40.0	44 ± 1	[89]
Py-C-BHTCNQ	**28**	Medium D, strong A	283	28.2	53 ± 1	[71]
Py-C-HETCNQ	**29**	Medium D, strong A	293	46	–	[89]
BDDAP-C-HMTCAQ	**30**	Medium D, weak A	293	22.3	58 ± 1	[34]
BHAP-C-HMTCAQ	**31**	Medium D, weak A	293	35.8	42 ± 1	[78]
DDOP-C-ENP *	**33**	Weak D, weak A	278	23.7	38 ± 1	[33]
TDDOP-C-ENP *	**34**	Weak D, weak A	278	34.0	76 ± 1	[33]
3,5-BHDOAP-C-ENP	**35**	Weak D, weak A	299	49.6	39 ± 2	[96]
3,4-BHDOAP-C-ENP	**36**	Weak D, weak A	300	54.5	35.8 ± 0.5	[90]
3,5-BTDYOAP-C-ENP	**39**	Weak D, weak A	298	18.7	58 ± 2	[90]
3,4-BTDYOAP-C-ENP	**40**	Weak D, weak A	300	49.4	50 ± 1	[90]
TDDOP-C-HETCNQ *	**41**	Weak D, strong A	282	47.5	54 ± 1	[33]
3,4-BHDOAP-C-HETCNQ	**42**	Weak D, strong A	300	55.2	51 ± 1	[90]

p-aminophenyl carbamate of 2-bromo-5-hydroxyethoxy-TCNQ. Donors, acceptors and several D-σ-A molecules were characterized by cyclic voltammetry (CV). Table 2 displays a catalog of molecules which form PL monolayers at the air–water interface, and which transfer well onto Al or glass or other slides as LB monolayers. Of these, TTF-C-BHTCNQ (**21**) was difficult to purify: the "neutral" form seemed to deposit "pancake-style" onto the water, and synthetic difficulties forced its abandonment. The strongest films (highest collapse pressure, most vertical pressure–area isotherm) were obtained with BDDAP-C-BHTCNQ (**22**). However, for the Aviram–Ratner mechanism, we need strong donors and strong acceptors in the same molecule!

Crystal structures were solved for a donor [75] and for three acceptors [76,77,93]; 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, **27** and **32**, which do not form PL or LB films were solved [70,84]. Semi-empirical molecular orbital (MO) calculations, using the MNDO algorithm with full geometry optimization, were performed on D-σ-A molecules to predict their geometry and also their highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) energies [82]. The MNDO structures are extended, as expected, and as favored by the MNDO parametrization [82].

8. Rectification experiments

We discuss here several attempts to detect unimolecular rectification.

8.1. Macroscopic test: metal LB monolayer Hg

In the first experiment [71], an Hg droplet (2 mm in diameter) probed the conductivity across a single monolayer LB film deposited on top of either Pt or conducting tin oxide (ITO) glass: the sandwiches (1) Pt|DDOP-C-BHTCNQ|Hg, (2) Pt|Py-C-BHTCNQ|Hg and (3) ITO|DDOP-C-BHTCNQ|Hg were tested: only the conductivity of the solid support was seen due to pinholes in the LB film [71].

8.2. Macroscopic test: Al|BDDAP-C-BHTCNQ|Al fingers with low overlap

An interleaved system of 0.5 mm wide Al electrodes, with low overlap, sandwiching a single monolayer of BDDAP-C-BHTCNQ (**22**) failed to find a rectifying junction [81]; the films had too many defects.

8.3. Nanoscopic test: STM on H atom switch

Rectification was reported to occur in a modified Digital Instruments Nanoscope I STM for a molecule which had been originally designed as an internal hydrogen atom transfer switch (and not as a rectifier) [97]; this claim was later retracted [98].

8.4. Nanoscopic test: STM on BDDAP-C-BHTCNQ

Wih the same Nanoscope I, Pomerantz studied an LB monolayer of BDDAP-C-BHTCNQ (**22**) deposited on an Au Ag mica substrate, using an atomically sharp W tip, as the couple W BDDAP-C-BHTCNQ Au. At first, large "rectification" currents were observed [82,83], but these were later found to be artifacts [82,83].

8.5. Nanoscopic test: Cu tetraazaporphyrin bonded to carboxylated HOPG

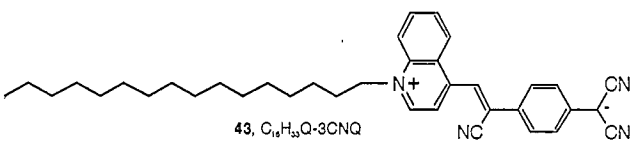
Pomerantz et al. [99] prepared a carboxylated surface on HOPG, anchored a Cu tetraazaporphyrin to this surface, and observed very asymmetric *I–V* curves by STM.

8.6. Macroscopic test: Pt|DDOP-C-BHTCNQ|Mg|Al

Sambles and coworkers [100] (University of Exeter) found that a monolayer of DDOP-C-BHTCNQ (**23**), sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film. The great merit of this work was to have made defect-free LB monolayers, but the molecule used does not contain a strong donor moiety, i.e. I_D is probably too high for an Aviram–Ratner rectifier. Indeed, the rectifying behavior has been ascribed to Schottky barrier formation between Mg and TCNQ [101,102].

8.7. Macroscopic test: Pt|$C_{16}H_{33}$-Q3CNQ|Mg|Al

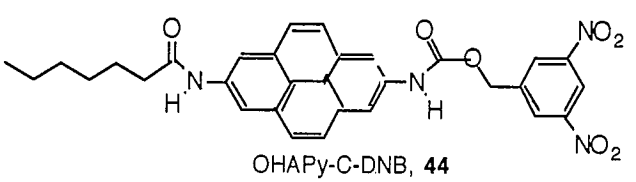
Ashwell et al. [103] found that an LB film of Z-β-(1-hexadecyl-4-quinolinium)-α-cyano-4-styryldicyanomethanide ($C_{16}H_{33}$-Q3CNQ, **43**), similarly sandwiched between Pt and Mg electrodes (the latter shadowed with Ag), also showed macroscopic rectification behavior. However, the observed *I–V* curves may also be due to a Schottky barrier (Mg 3CNQ salt) [102]. More recently, a layer of insulator was interspersed between the Pt|$C_{16}H_{33}$-Q3CNQ|Mg|Al and the Pt and Mg electrodes, yet asymmetric *I–V* curves persisted; this was claimed as proof of molecular rectification, rather than Schottky barrier effects [104].



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

8.8. Macroscopic test: Pt OHAPy-C-DNB Mg Al

Most recently, Sambles and coworkers [105] measured a sandwich involving a new molecule synthesized by Panetta: OHAPy-C-DNB (**44**), where the donor is a medium donor based on pyrene, but the acceptor is a very weak acceptor, dinitrobenzene. Despite the unfavorably low electron affinity of the acceptor, asymmetric *I–V* curves were seen. This result casts serious doubt on which mechanism predominates in the thin films studied by Sambles' group.



OHAPy-C-DNB, **44**

8.9. Nanoscopic test: STM on BDDAP-C-HETCNQ, Py-C-HETCNQ and $C_{16}H_{33}$-Q3CNQ

With a Digital Instruments Nanoscope II STM, we studied samples of BDDAP-C-HETCNQ (**24**) [90], Py-C-HETCNQ (**29**) [90] and $C_{16}H_{33}$-3CNQ (**43**) (the latter kindly supplied by Dr. G.J. Ashwell) [106]. The samples were transferred onto highly oriented pyrolytic graphite (Union Carbide grade ZYA and ZYH) by the LS horizontal transfer lifting technique, and were studied in air at room temperature using Pt/Ir "nanotips" (Digital Instruments) and the "A" head. At low set-point currents, some asymmetries in the current–voltage plots could be seen. The image of graphite is replaced by what seems to be an image of the film [90], sometimes with atomic resolution [106].

In preliminary work on freshly synthesized samples of **43**, hints of rectification (asymmetric *I–V* curves) are seen. Furthermore, for HOPG or Au(111) substrates covered by LB monolayers or bilayers of **43**, and then with an aqueous solution of $K_3Fe(CN)_6$, the oxidation wave is seen (the reduction wave is blocked). The $C_{16}H_{33}$-3CNQ monolayer thickness was measured to be 27 ± 1 Å, which argues for a 30° tilt of the molecule from the surface normal. Further work is in progress [107].

9. Conclusions

The progress towards the organic rectifier has been reviewed, together with the broader perspective of other related issues in unimolecular electronics. Rectification has been seen in LB films of D-σ-A and D^+-π-A^- molecules, probably by a Schottky process. The goal of Aviram–Ratner rectification through an oriented D-σ-A molecule has not yet been achieved.

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