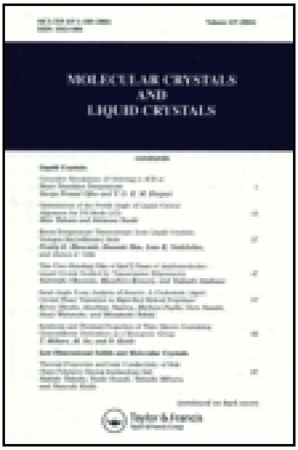

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Unimolecular Electrical Rectification by Hexadecylquinolinium Tricyanoquinodimethanide

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Unimolecular Electrical Rectification by Hexadecylquinolinium Tricyanoquinodimethanide

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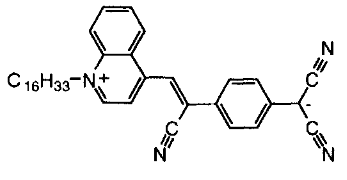
The asymmetrical DC electrical conductivity (macroscopic and also nanoscopic) through Langmuir-Blodgett multilayers, and even a monolayer, of γ-(n-hexadecyl)quinolinum tricyanoquinodimethanide, $C_{16}H_{33}Q$-3CNQ (**1**) is due to rectification of electrical current by a molecule.

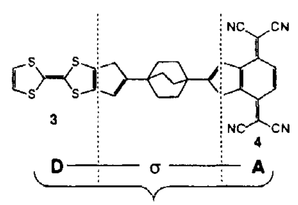
Keywords: unimolecular rectification; hexadecylquinolinium tricyanoquinodimethanide; through-molecule tunneling

INTRODUCTION

Aviram and Ratner proposed in 1974 that a single molecule can be a "nanoscopic" rectifier of electrical current if there is a strongly asymmetric flow of electrons through it, because the electrical conductivity in one direction through the molecule is much larger than the conductivity in the opposite direction[1]. We recently confirmed unimolecular rectification in hexadecylquinolinium tricyanoquinodimethanide $C_{16}H_{33}Q$-3CNQ, **1**[2-5].



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



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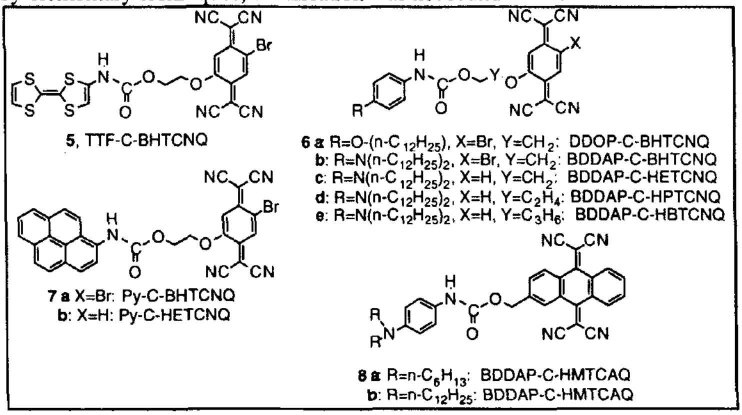
Electrical rectification was achieved in 1904 in vacuum diodes[6], in 1949 in junctions of p-doped semiconducting Ge accosted to n-doped Ge[7]. A layer of n-doped organic semiconductor atop a layer of p-doped organic semiconductor (both layers several μm thick) also produces a "mesoscopic" rectifier[8-10].

Kuhn[11] and others[12,13] found rectification in Langmuir-Blodgett (LB) multilayer sandwiches. Fujihira made an electrochemical LB monolayer photodiode[14]. Aviram and Ratner proposed for the unimolecular rectifier a D-σ-A molecule **2**, where D = good one-electron donor, like TTF, **3**, with low ionization potential but low electron affinity, A = good one-electron acceptor, like TCNQ, **4**, with high electron affinity but high ionization potential, and σ = insulating saturated covalent "bridge"[11]. From the undissociated ground state D-σ-A, the excited zwitterionic state D^+-σ-A^- should be accessible, but the zwitterion D^--σ-A^+ should lie 4 to 5 eV higher[11].

Many LB film-forming D-σ-A molecules (**5**-**8**) were synthesized, but, by elementary techniques, rectification was not found[15-17].



5, TTF-C-BHTCNQ

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

6 a 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

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

Sambles found asymmetries in DC current for forward versus reverse bias in sandwiches: "Pt | LB multilayer of **6a** | Mg | Ag"[18], but a Schottky barrier between Mg and TCNQ (**4**) may also explain these asymmetries[19].

Ashwell discovered new ground-state zwitterionic molecules of the type D^+-π-A^-[20]: among these is γ-(n-hexadecyl)quinolinum tricyanoquinodimethanide, $C_{16}H_{33}Q$-3CNQ (**1**) (here D^+ = quinolinium = Q^+, π = pi-electron bridge, A^- = tricyanoquinodimethanide = 3CNQ$^-$)[20]. A sandwich "Pt | LB multilayer of **1** | Mg | Ag" exhibited asymmetric currents, indicating electrical rectification[21], even when an insulating fatty acid monolayer was inserted between the metal electrodes and 3 monolayers of **1**[22]. We confirmed electrical rectification by LB monolayers and LB multilayers of **1** by both macroscopic and nanoscopic methods: **1** is a unimolecular rectifier; it may be the smallest molecular device[2].

MOLECULAR PROPERTIES

The cyclic voltammogram of **1** shows a one-electron quasi-reversible reduction ($E_{1/2}$ = -0.513 V vs SCE), close to that of p-benzoquinone[2]. The NMR spectrum of **1** indicates a dipolar ground state[2]. The dipole moment for **1** at infinite dilution in CH_2Cl_2 is 43 • 8 Debyes, i.e. 90% of the moment for a unit positive charge at the quinolinium N, and a unit negative charge at the bridgehead C of the C(CN)- group 10.5 Å away[2]. The long-wavelength absorption maximum of **1** is hypsochromic: the solvatochromism yields an excited-state dipole moment of 8.7 Debyes[24].

MONOLAYER PROPERTIES

The Π-A isotherm of **1** shows a collapse point at 50 Å^2 molecule^{-1} and 34 mN m^{-1}[2,3]. Monolayers and multilayers of **1** were transferred to solid substrates: **1** transfers on the downstroke onto hydrophobic HOPG, and on the upstroke onto a freshly cleaned hydrophilic Au(111) single crystal and onto Al . The hydrophobic hexadecyl group T is thought to be the end of the molecule closest to HOPG {HOPG |→}, while the hydrophilic $3CNQ^-$ (A^-) end should be closest to Al {Al |←}. On Al the multilayers are Z-type {Al | ← ← ... ←} ; on HOPG, the first layer is X-type, the others are Z-type {HOPG |→ ← ←... ←}. A sharp absorption band with peak at 570 nm is seen in LB films on quartz; this band disappears if the films are protonated, but returns when the film is exposed to NH_3[23]. The monolayer thickness (ellipsometry and surface plasmon resonance), is 22 ± 2 Å [2,23]; if **1** is 30 Å long, then **1** is tilted 48 ± 5° from the normal to the monolayer plane.

MACROSCOPIC CONDUCTIVITY OF LB FILMS

Macroscopic "metal | organic | metal" sandwiches were studied, using an Edwards 306A evaporator with a liquid nitrogen-cooled substrate holder and a multiple-source evaporator, and a DC conductivity system (HP 3245A

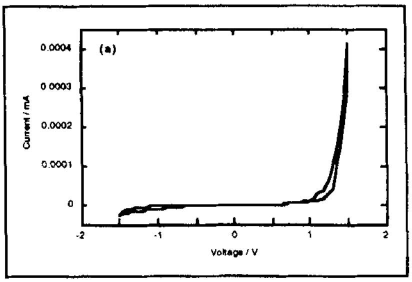


FIGURE 1. Rectification in "Al | LB monolayer of **1** | Al" sandwich[2].

universal source, HP 3457A multimeter). Glass, quartz, or Si substrates were covered by Al; the LB films were transferred under a green safelight; the sample was dried, then cylindrical pads of Al were evaporated atop the organic layer, with the substrate cooled to 77 K. Contact to the Al electrodes was made with Ga/In eutectic, or Ag paste. A very asymmetric I-V curve was found for a 4-monolayer film; reversing the electrode connections reversed this asymmetry[2]. A similar asymmetry occurred when a Mg layer was put between the multilayer and the Al[2]. The work with a single monolayer was more difficult: of 39 pads, 17 were electrical short circuits, either because of monolayer defects, or because the Ga/In or Ag created new defects. The 22 "good" junctions had DC resistances from 1 to 400 MΩ; of these, 4 exhibited rectifying behavior. Fig. 1 shows the best rectification curve. Above a threshold V_t = 0.8 to 1.3 V (sample-dependent, maybe junction-dependent), the monolayer shows larger currents for positive bias than for negative bias. The rectification ratio RR = (current at V_0) / (current at $-V_0$), where V_0 is the highest positive bias used, ranges from 2.4 to 26.4 the first time the film is measured; as the cycle is repeated, RR drops steadily, and disappears after 4 to 6 cycles: the dipoles probably re-orient to minimize energy[2].

NANOSCOPIC STRUCTURE OF LB FILMS

Using a Nanoscope III low-current scanning tunneling microscope (STM), an LB monolayer of **1** showed an image with a repeat of 6 Å × 12 Å (Fig. 2), consistent with the molecules viewed end-on[2].

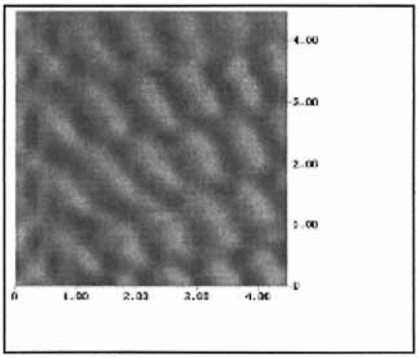


FIGURE 2. STM of an LB monolayer of **1** on HOPG (Pt/Ir nanotip)[2].

NANOSCOPIC CONDUCTIVITY OF LB FILMS

Multilayers of **1** on HOPG, studied using a Pt/Ir nanotip at 300 K in air by STM and scanning tunneling spectroscopy (STS) showed I-V asymmetries in a 15-layer film (Fig. 3)[2,3].

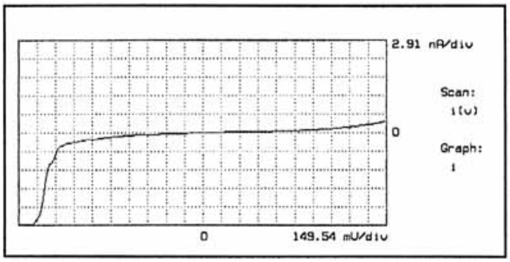


FIGURE 3. STS current across"Pt/Ir | 15 LB monolayers of **1** | HOPG"[2].

CONCLUSION

1 is not only a multilayer rectifier[21,22], but also a monolayer rectifier[2], in accord with the Aviram-Ratner Ansatz[1] (except that the relative placement of the undissociated state and the zwitterion is reversed), and dispelling doubts arising from using dissimilar metal electrodes.

ACKNOWLEDGMENTS

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