Rectification by a Monolayer of Hexadecylquinolinium Tricyanoquinodimethanide between Gold Electrodes[**]

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In memory of Sukant Kishore Tripathy

Rectification by Langmuir–Blodgett (LB) monolayers and multilayers of the ground-state zwitterionic molecule hexadecylquinolinium tricyanoquinodimethanide ($C_{16}H_{33}Q$-3CNQ, **1**) was first reported by Sambles, Ashwell, and coworkers between a Pt electrode on one side and a Mg pad (protected by Ag) on the other side,[1] and also with intervening monolayers of insulating aliphatic acids.[2] The rectification was confirmed with Al electrodes on both sides of monolayers and multilayers.[3] The mechanism of rectification was clarified,[3] and it was suggested that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1** were involved in the enhanced current observed in the forward direction.[3] Not all junctions rectify.[4] The rectification was measured in the temperature range 370 to 105 K,[5] and ancillary spectroscopic and electrochemical data were secured.[6]

In accordance with the seminal paper in this field of Aviram and Ratner,[7] it was suggested[3] that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1** were involved in the asymmetric shape of the observed current–voltage characteristics.[3] The asymmetry can be ascribed to the intervalence transfer band between the HOMO and LUMO, appropriately shifted by the applied electrical potential, and coupled to levels in the Al electrodes. The optical absorption at 570 nm (2.17 eV) in films of **1** can be ascribed to the HOMO–LUMO gap, or in slightly different language, to the transition from the ground state (dipole moment 43 ± 8 D)[3] to the first electronic excited state (dipole moment between 3 and 9 D).[6] The results have been reviewed elsewhere.[8, 9]

A persistent question was whether the oxides of Al or Mg were in any way involved in the rectification process.[8, 9] We now present experimental proof that rectification occurs also when monolayers or multilayers of **1** are placed between oxide-free gold electrodes.

Working with organic monolayers sandwiched between metal electrodes is difficult. It is easy to transfer one or more monolayers onto a metal electrode, but it is not simple to deposit a metal layer on top of an organic layer without damaging it. Sambles' original method was to use Mg vapor, which, in his experience, damaged an organic film the least. Our improvement was to cryocool the glass | Al | LB film assembly to 77 K, and thus prevent, or at least reduce, damage to the organic film when Al was evaporated on top of it.[3] The technique did not work in our laboratory with Au. Recently, Okazaki and Sambles showed that, by letting a low pressure of Ar (4×10^{-3} Torr) into the evaporator during Au deposition and by blocking the direct path from the Au source to the target with baffles, only Au atoms that had scattered off Ar atoms several times could reach the organic multilayer.[10]

Two glass samples (A and B; $50 \times 50 \times 0.4$ mm) with a root-mean square (r.m.s.) roughness of 2.3 Å (measured by X-ray reflectivity) were washed with isopropanol and then xylene. A thickness of 50 nm of Au was evaporated onto the hydrophobic glass from a Mo boat in an Edwards E306 evaporator. To ensure that the Au surface stayed hydrophilic, the samples were immediately placed under pure water (resistivity 18 MΩ cm), and left under water until a monolayer (for sample A) or a nine-layer multilayer (for sample B) of freshly prepared $C_{16}H_{33}Q$-3CNQ was transferred (Z-type, with transfer ratios of 100% or even above) from a monolayer of $C_{16}H_{33}Q$-3CNQ held at the air–water interface at a surface pressure of 25 mN m^{-1} in a NIMA Model 622 film balance at 12 °C in a HEPA-filtered room in darkness. As before,[3] the LB layers were dried in a vacuum desiccator over P_2O_5 for three days to remove any entrapped water between the layers.

Two hydrophobic contact masks were prepared from thin perforated sheets, in one case an Al/Mg alloy, and in the other case a phenolic resin. After removing gross asperities by polishing, the masks were coated with an approximately 50 μm layer of partially methoxylated poly(dimethylsiloxane) resin (General Electric Cat. No. GE 5060) by immersion in a 3% w/w solution in toluene, followed by removal of excess liquid, and evaporation of the solvent on a perfectly level surface. Samples A (with a single monolayer of $C_{16}H_{33}Q$-3CNQ) and B (bearing nine monolayers of $C_{16}H_{33}Q$-3CNQ) were placed in the Edwards evaporator on top of a Cu cryosurface; sample A faced the gold evaporation boat, but the direct trajectory of Au atoms was blocked by a copper strip, while sample B faced away from the boat. The cryosurface was cooled to 77 K using liquid nitrogen. Gold from a Mo boat was evaporated under an Ar pressure of between 8×10^{-4} and 2×10^{-3} Torr, at a rate of 0.02 nm s^{-1} for the first 200 nm, and then 0.1 nm s^{-1} for the next 400 nm, until the quartz thickness monitor recorded a nominal Au thickness of 600 nm. The Au pads that formed through the holes in the mask were much thinner: they were measured to be 17 nm thick by using a Sloan Dektak II profilometer. The r.m.s. roughness was measured by atomic force microscopy as 1 nm for the top of a pad and 0.4 nm for the bottom Au layer.

The measuring electronics were modified from the earlier procedure.[3] The same voltage source (Hewlett–Packard Model 3245A) and multimeter (Hewlett–Packard Model 3245A) were connected by a National Instruments IEEE-488 GPIB interface board to a Gateway 2000 Model P5-60 microcomputer. The computer control program was written using a Borland Delphi (Inprise Corp.) compiler. The multimeter, sample, and all signal lines, except for some low-impedance high-level lines, were enclosed in a Faraday cage. Selected Au pads were contacted through a terminal droplet of Ga/In eutectic, which did not wet the gold (Figure 1). All

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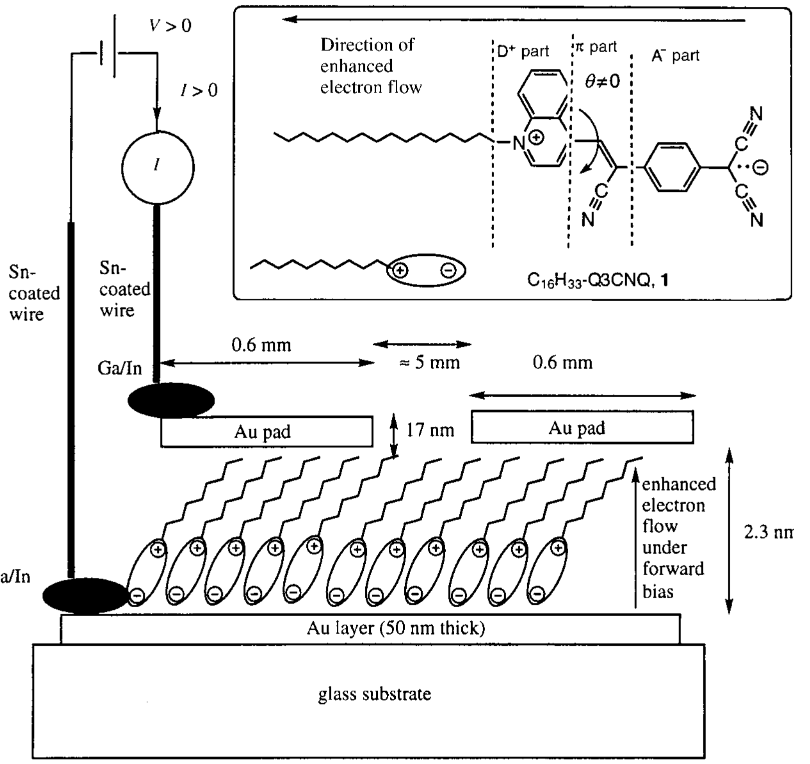

Figure 1. Depiction of a LB monolayer of **1** sandwiched between Au electrodes (top pad area: 0.6 to 1 mm^2) and with electrical contacts attached to the Au electrodes. Inset: Chemical structure of the ground-state zwitterionic molecule $C_{16}H_{33}$Q-3CNQ (**1**) and a diagrammatic depiction. The direction of the enhanced electron flow is also shown.

measurements were performed at room temperature. The procedures followed here preclude the formation of any oxide on the Au electrodes.

Figure 2 shows the results for pad g1 on top of a single monolayer of $C_{16}H_{33}$Q-3CNQ: the rectification lasts for six cycles, with the enhanced currents under positive bias decreasing in cycles three to six, and the currents at maximum negative bias becoming more negative in cycles two to six. Given the measured cross-sectional area of 50 Å^2 molecule^{-1}[3] and a pad area of 0.283 mm^2, the maximum forward current (4.08 mA at 2.2 V) for the first cycle corresponds to a current of 4.5×10^4 electrons molecule^{-1} s^{-1}. This maximum current is much larger than the 0.33 electrons molecule^{-1} s^{-1} reported between Al electrodes (with their partial oxide covering)[3] or the 35 electrons molecule^{-1} s^{-1} reported for an improved Al electrode design.[11] The rectification ratio at 2.2 V is RR = [I(at 2.2 V)/ | I(at −2.2 V) |] = 4.08 mA/0.759 mA = 5.39. The minimum nominal resistance is 2.2/0.004088 = 538 Ω at 2.2 V and 2900 Ω at −2.2 V.

Pad g2 of sample A (Figure 3) gave a higher *RR* value of 0.747 mA/0.0628 mA = 11.9; the current was somewhat smaller; the nominal resistance was 2945 Ω at 2.0 V; and short circuits developed in the third cycle.

Multilayers yielded, as expected, much smaller currents. Pad g22 of sample B (Figure 4) with nine Z-type monolayers gave an initial rectification ratio *RR* = 1.0305 μA/0.0523 μA = 19.7 for the first cycle, which decreased to *RR* = 0.6032 μA/0.3727 μA = 1.61 in the fifth cycle. Another pad (not shown) gave an initial rectification ratio of 4.34, which decreased to 0.85 on the third cycle.

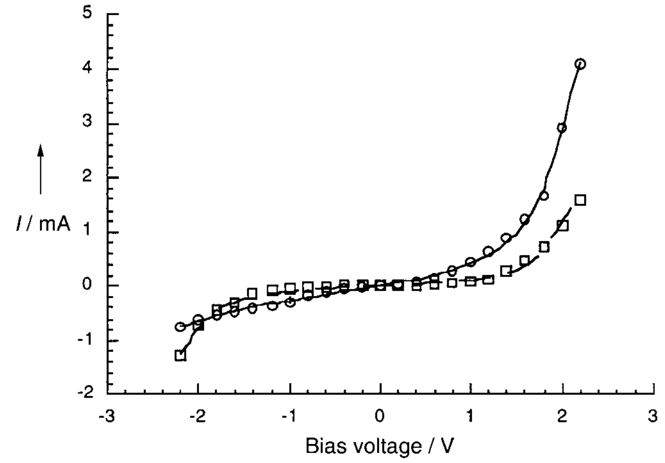

Figure 2. Current–voltage plots for sample A (pad g1) covering one monolayer of $C_{16}H_{33}$Q-3CNQ, and fitted to equation: $I = a\{\tan^{-1}[bc + bdV] - \tan^{-1}[bc - b(1-d)V]\}$,[15, 16] where I and a are in mA, V and c are in V, and R = Pearson's coefficient of fit. Cycle 1: circles and solid line; $a = 2.24 \pm 0.11$, $b = 4.52 \pm 0.22$, $c = 1.31 \pm 0.03$, $d = 0.37 \pm 0.01$, $R = 0.9991$. Cycle 6: squares and dashed line; $a = -0.68 \pm 0.04$, $b = 7.80 \pm 0.54$, $c = 1.01 \pm 0.01$, $d = 0.48 \pm 0.00$, $R = 0.9970$.

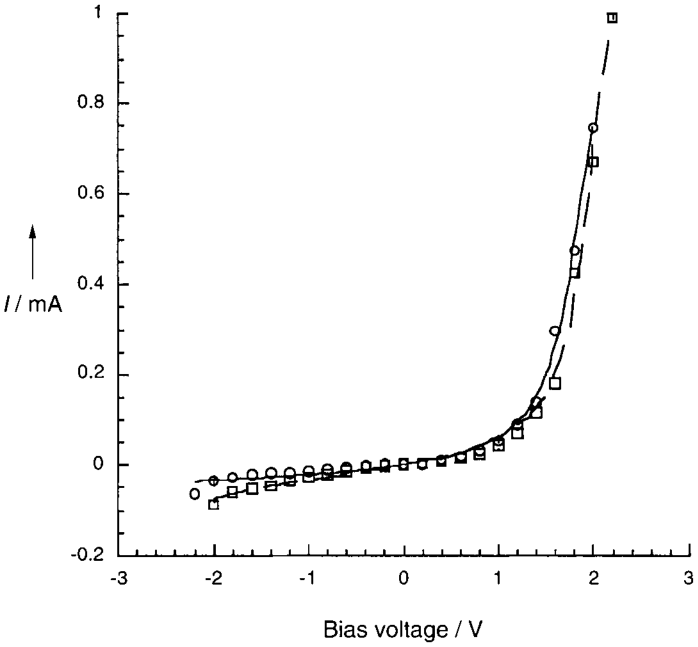

Figure 3. Current–voltage plots for sample A (pad g2) covering one monolayer of $C_{16}H_{33}$Q-3CNQ, and fit to the equation: $I = a\{\tan^{-1}[bc + bdV] - \tan^{-1}[bc - b(1-d)V]\}$,[15, 16] where I and a are in mA, V and c are in V, and R = Pearson's coefficient of fit. Cycle 1: solid line and circles: $a = 0.36 \pm 0.02$, $b = 4.17 \pm 0.70$, $c = 1.69 \pm 0.20$, $d = 0.08 \pm 0.10$, $R = 0.9981$. Cycle 2: dashed line and squares, $a = 0.43 \pm 0.02$, $b = 6.52 \pm 0.71$, $c = 1.32 \pm 0.08$, $d = 0.33 \pm 0.04$, $R = 0.9978$.

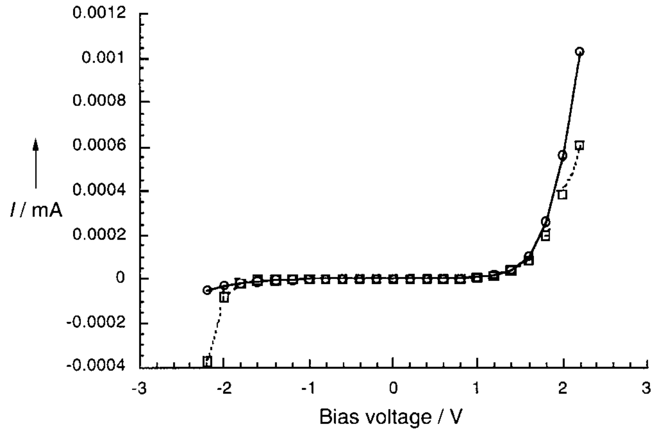

Figure 4. Current–voltage plots for sample B (pad g22) covering nine monolayers of $C_{16}H_{33}Q$-3CNQ. Cycle 1: solid line and circles; cycle 5: dashed line and squares.

Several conclusions can be drawn:

1) The rectification, first reported between unsymmetrical electrodes[1] and confirmed between symmetrical Al pads,[3] is definitely molecular in origin, and not attributable to oxide effects.
2) The currents through an oxide-free gold pad of macroscopic dimensions are large, because most molecules under the Au pad may be involved in the rectification.
3) Although LB films develop conducting defects when vacuum-coated with hot Au vapor, this is mediated by temperature-induced changes of structure.[12, 13]
4) Mechanical damage to LB films, which arise from the use of a contact mask, is avoided by the use of a hydrophobic elastomer.
5) The currents decrease during successive cycles, presumably as the molecules reorient in the monolayer;[3] this may be related to the damage known to occur in monolayers of long aliphatic chains as a result of the passage of hot electrons.[14]
6) We should consider a chemical basis for the change in film conductivity: since the first reduction is electrochemically reversible in solution, no damage occurs on adding one electron to the LUMO (which is concentrated on the 3CNQ part of the molecule),[6] however, oxidizing the molecule in solution is electrochemically irreversible.[3] The large current at negative bias in the last cycle suggests that the number of molecules conducting is not decreasing dramatically; therefore the molecular reorientation mentioned above is more likely (and may be prevented if a polymerized monolayer were fabricated).
7) Multilayers show rectification but the currents are smaller, because the current must somehow cross the several insulating hexadecyl tails required for LB film assembly.
8) The bias at which enhanced electron flow occurs can be estimated visually from Figure 2 as around 2 V, while this bias was estimated as between 1 and 1.3 V with Al electrodes (Table 1 of ref. [3]); this difference in bias agrees with the difference of 1.1 eV between the work functions of Au (5.3 eV) and Al (4.2 eV).
9) The direction of larger conductivity in the forward direction agrees with what was established with monolayers of $C_{16}H_{33}Q$-3CNQ sandwiched between Al electrodes,[3] and therefore with a modification[3] of the two-level Aviram–Ratner model.[7]
10) Recent theoretical analyses of molecular conduction,[15, 16] have suggested that conduction asymmetry of the type observed may also arise from processes dominated by a single molecular level. The current I as a function of the bias voltage V is given, approximately, by:[15]

$$I = (2I_0/\pi)\{\tan^{-1}[\theta^{-1}(pV-V_0)] - \tan^{-1}[\theta^{-1}((1-p)V+V_0)]\} \quad (1)$$

where I_0 is the saturation current, θ is a tunneling gap coupling parameter, eV_0 is the zero-bias energy difference between the dominant level and the Fermi level, and the parameter p gives the fractional position of the "center of gravity" of the molecular energy level within the gap.[15] Equation (1) closely resembles a similar equation derived independently (Equation (21) of ref. [16]). Figures 2 and 3 show excellent fits to Equation 1. The fits yield $V_0 = 1.31$ and 1.01 V (Figure 2), and 1.69 and 1.32 V (Figure 3). The average over many data sets (more than reported here) is $V_0 = 1.31 \pm 0.25$ eV.[17] These curve-fit estimates are smaller than the $V_0 = 2.0$ V estimated visually (see point 8 above).
11) The $I-V$ curves change upon successive cycles: the forward current at $V > 0$ becomes smaller, and the current at $V < 0$ becomes more negative. These observations seem to argue against some irreversible chemical reaction, and suggests that the molecules "turn around" with increased exposure to large potentials ($V = 2.3$ V across a monolayer 2.3 nm thick[3] corresponds to an electric field of 1 GV m^{-1}).
12) The Aviram–Ratner proposal assumes enhanced current beyond a certain threshold voltage, and a constant current plateau, or saturation, somewhat above this threshold voltage: this enhanced current involves inelastic tunneling.[7] In contrast, the current through an appropriately substituted triphenylenebithiol at low temperatures was recently found at Yale University to have a relatively narrow peak at the threshold voltage: the device Au | bithiol | Au thus exhibits negative differential resistance over a narrow range above the threshold voltage.[18] This enhanced current occurs only at potentials close to resonance with a localized excited state, and may be the result of elastic tunneling at resonance. Thus, the Aviram–Ratner proposal[7] allows inelastic tunneling at and above the threshold voltage and a current plateau; in contrast, the Yale results[18] suggest elastic tunneling at the threshold voltage, and a narrow peak. In the data reported here, no maximum in the current (peak or plateau) was found within the potential ranges used, but a plateau was seen in subsequent work.[17]

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Nondestructive Data Processing Based on Chiroptical 1,2-Dithienylethene Photochromes[**]

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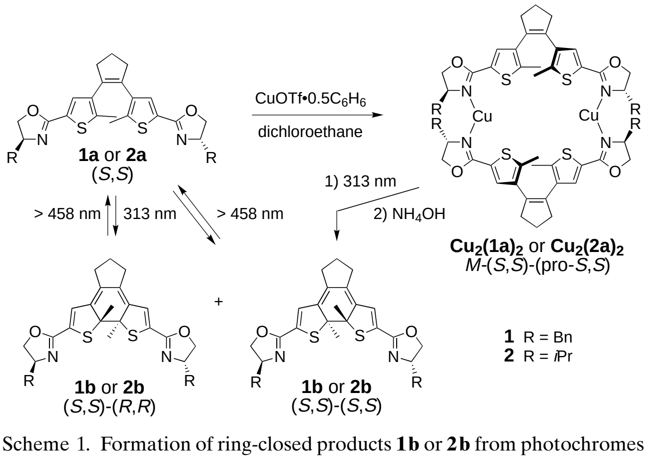
The viability of photochromic 1,2-dithienylethene derivatives in optical device applications stems from their striking display of advantageous photochromic properties such as thermal irreversibility and fatigue resistance.[1] Their application to erasable memory media requires that both photochromic states be detected in the readout event in a facile and noninvasive manner. Typically, the readout event relies on the use of UV/Vis spectroscopy to record the spectral changes near the absorption bands corresponding to the two photochromic states. However, these are the same absorptions that induce the ring-opening and ring-closing reactions. Thus, sampling near these photoactive absorption bands inevitably causes partial switching of the photochrome and erases the stored information. This problem can be circumvented by developing photochromic systems that employ gated mechanisms[2] or systems that, upon photoisomerization, display variations in their optical properties such as refractive index,[3] luminescence,[4] or optical rotation.[4f, 5] It is the detection of these accompanying changes that may ultimately lead to effective nondestructive information processing systems.

Recording changes in optical rotation is a particularly promising alternative for nondestructive readout, because the detection can often be performed outside the photoactive spectral regions. To enhance the readout signal in order to use this technique, two conditions must be satisfied: 1) the photochromes should exhibit significantly contrasting optical rotating strengths between their two states, and 2) the photochromic reactions should maximize the formation of only one stereoisomer.

The closed forms of 1,2-dithienylethene derivatives are chiral, making them excellent candidates for incorporation into chiroptical devices; however, the ring-closing reactions inevitably yield racemates. The presence of stereogenic centers appended to the thiophene rings can induce stereodifferentiation in the photocyclization reaction,[5d, 6] but the restrictive conditions needed to ensure high stereoselection limit the use of the existing systems.[5d, 6a] Inspired by several recent examples in which remote stereogenic centers guide the creation of metallohelicates in a stereochemically pure form,[7] we began to explore the unique properties of self-assembled helicates in stereoselective photochromic transformations, with the goal of realizing a nondestructive write – read – erase system.

Herein we report the self-assembly of double-stranded stereochemically pure copper(I) helicates from chiral ligands **1** and **2** (Scheme 1). The chiral discrimination event that occurs when the chiral oxazoline auxiliaries on the periphery of the individual strands are brought into close proximity translates through the 1,2-dithienylethene backbone and ultimately dictates the handedness of the helicates. This preorients the thiophene rings with respect to each other so that photocyclization yields a single diastereomer. The dramatic changes in optical rotation that accompany the stereoselective photochromic process can be recorded in a nondestructive manner.



Scheme 1. Formation of ring-closed products **1b** or **2b** from photochromes **1a** or **2a** and their complexes with copper.

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