

## Rectification between 370 and 105 K in Hexadecylquinolinium Tricyanoquinodimethanide

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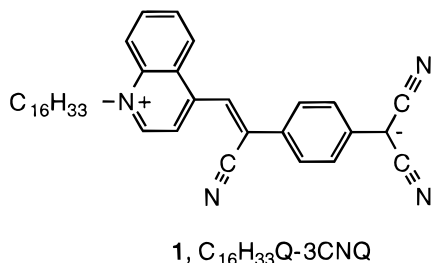
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The through-film electrical conductivity of Langmuir–Blodgett monolayer films of hexadecylquinolinium tricyanoquinodimethanide was studied as a function of temperature. The current is usually smaller at low temperature. Electrical rectification, probably due to an intramolecular electron transfer, was observed between 370 and 105 K, with a rectification ratio as large at 105 K as it is at room temperature.

## Introduction

We recently demonstrated unimolecular electrical rectification, i.e., asymmetric electrical conductivity (or large asymmetries in the plots of direct current  $I$  versus applied potential  $V$ ) through a single molecule of hexadecylquinolinium tricyanoquinodimethanide,  $C_{16}H_{33}Q-3CNQ$  (**1**), by macroscopic means (monolayer between Al electrodes) and by nanoscopic means (scanning tunneling spectroscopy) at room temperature.<sup>1</sup> This molecule rectifies by a modification of the proposed Aviram–Ratner mechanism.<sup>2</sup> We present here the temperature dependence (370 to 80 K) of this rectification.



$C_{16}H_{33}Q-3CNQ$  (**1**) is blue in  $CH_3CN$  solution,<sup>3</sup> has a dipole moment of  $43 \pm 8$  D at infinite dilution in  $CH_2Cl_2$ ,<sup>1</sup> has a second-order nonlinear optical susceptibility of  $180 \text{ pm V}^{-1}$ ,<sup>4</sup> makes green Langmuir–Blodgett (LB) monolayers and multilayers ( $\lambda_{\text{max}} = 570 \text{ nm}$ ), and is a rectifier in LB monolayers<sup>1</sup> and multilayers sandwiched between Al electrodes.<sup>5,6</sup> From X-ray diffraction measurements, the film thickness is  $23 \text{ \AA}$ ,<sup>1</sup> in agreement with earlier estimates by ellipsometry and surface plasmon resonance.<sup>3</sup> The molecule lies with its dicyanomethylene swallowtail (negative) end closest to the bottom Al film, but is tilted  $48 \pm 5^\circ$  from the normal to the monolayer plane.<sup>1</sup> The ground state of **1** is zwitterionic, of the type  $D^+-\pi-A^-$ , where  $D^+$  is the positively charged quinolinium ring,  $A^-$  is the negatively tricyanoquinodimethanide moiety, and  $\pi$  is the double bond bridge.<sup>1,4</sup>

From the strong negative solvatochromism of the visible spectrum of **1** and the shift between absorption and fluorescent emission, the first excited state of **1** is found to be less polar, undissociated, i.e.,  $D^0-\pi-A^0$ , with an estimated dipole moment of only  $8.7 \text{ D}$ .<sup>7</sup> It is therefore thought that the color, the frequency doubling, and the rectification are all due to a transition from a zwitterionic state to an undissociated excited-

state  $D^+-\pi-A^- \rightarrow D^0-\pi-A^0$ , which is made possible because the molecule is nonplanar and the conjugation between the two ends is broken by a nonzero twist angle.<sup>1,4,6</sup>

At room temperature the best rectifying results for the sandwich



had a resistance of  $3.5 \text{ M}\Omega$  and a maximum forward current of  $0.4 \text{ }\mu\text{A}$ , corresponding to a current density of about  $0.33$  electrons per molecule per second; the rectification ratio was  $26:1$  at  $\pm 1.3 \text{ V}$ , but this ratio decreases upon repeated cycling from positive to negative voltages.<sup>1</sup> The molecules, exposed to electric fields  $\pm 1.3 \text{ V}/23 \text{ \AA} = 0.56 \text{ GV m}^{-1}$ , probably reorder within the monolayer to avoid such high fields.<sup>1</sup> The samples for which rectification was seen had higher resistivities of  $3$  to  $40 \text{ M}\Omega$ , while other samples, with lower resistivities ( $10$ – $100 \text{ k}\Omega$ ) had no rectification (symmetric  $IV$  curves).<sup>8</sup> By cryocooling the LB substrate while evaporating the top Al electrode, the thermal damage to the LB films was reduced.<sup>1</sup> Given the residual oxygen pressure in the evaporator ( $10^{-6}$  Torr vacuum), thin layers ( $10$ – $20 \text{ nm}$ ) of  $\text{Al}_2\text{O}_3$  probably form on both sides of the LB monolayer. No asymmetries in the electrical conductivity were seen when Y-type LB multilayers of arachidic acid ( $C_{19}H_{39}\text{COOH}$ ) were deposited in a similar manner.<sup>1</sup> Therefore, the rectification (asymmetries in the  $I$  versus  $V$  plot) seen for **1** must not be due to the two  $\text{Al} | \text{Al}_2\text{O}_3$  couples, which are most likely symmetrical on both sides of the organic layer,<sup>1</sup> but to the organic layer. Naturally, because the  $C_{16}H_{33}$  alkyl termination presents a smaller cross-section than the quinolinium ring, the organic film is not as compact as a simple alkyl fatty acid, e.g., arachidic acid. Therefore, some sample-to-sample variability in  $\text{Al}_2\text{O}_3$  penetration into the monolayer is possible, thereby giving some variation in electrical conductivities. Much larger currents per molecule ( $0.1$  to  $1 \text{ nA}$ ) are measured in the STM experiments.<sup>1</sup>

The voltage dependence<sup>9</sup> of through-film conductivity of fatty acids is either  $j \propto V^{1/2}$  (Sommerfeld–Bethe tunneling, Poole–Frenkel, or Schottky barrier mechanisms)<sup>10</sup> or  $j \propto V^{1/4}$  (Au atom migration or disclinations).<sup>11,12</sup>

To avoid the pesky oxide problem, many efforts have been made to measure the DC and AC conductivity of LB films between noble metal electrodes.<sup>13</sup> Short circuits were seen very often, either because the LB monolayers physisorb onto noble metal substrates with smaller binding energies than they do onto

Al substrates, causing many defects,<sup>13</sup> or because the hot noble metal atoms, deposited atop the LB film to form the top electrode, damage the LB film.<sup>13</sup> Mg overlayers have been deposited onto LB films atop noble metal electrodes,<sup>14</sup> and good contacts were formed because the temperature of the metal vapor is relatively low. The claim that MgO is absent between the Mg electrode and the LB films<sup>13</sup> is open to question: Mg is a very active metal, and the residual gas pressure in the evaporator is not low enough to exclude the usual monolayer of oxygen adsorbed on every surface, including the LB film.

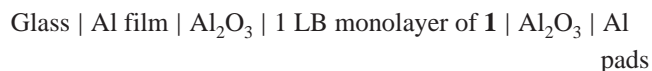
Another important issue is whether metals with low work functions  $\phi$  (4.24 eV for Al(111)<sup>15</sup> and 3.66 eV for Mg<sup>16</sup>) can reduce the organic molecule in the LB layer, either by direct contact or across an intervening oxide layer. This oxidation/reduction would form an additional, unwanted Schottky barrier, or layer of dipoles. Such a Schottky barrier was adduced for conductivity measurements on multilayers of a D- $\sigma$ -A molecule, BDDOP-C-BHTCNQ,<sup>17</sup> sandwiched between Ag or Pt electrodes and a Mg pad electrode. Indeed, the acceptor (A = TCNQ) end of BDDOP-C-BHTCNQ is a powerful one-electron acceptor, with electron affinity  $E_A = 3.3$  eV,<sup>18</sup> i.e., only 0.36 eV higher than  $\phi(\text{Mg})$ . A salt between the Mg and the TCNQ could easily form, maybe even across an insulating MgO barrier. A similar criticism was voiced about the previous multilayer work on **1**.<sup>19</sup> When insulating monolayers of fatty acid were inserted between the metal electrodes and the organic multilayers, asymmetries in the conductivity of **1** persisted.<sup>6</sup> The electrochemical reduction potential of **1** is only  $-0.51$  V vs SCE,<sup>1</sup> i.e., comparable to benzoquinone, whose electron affinity  $E_A = 1.91$  eV<sup>20</sup>  $\ll \phi(\text{Mg}) = 3.66$  eV.<sup>16</sup> Therefore, a reduction of **1** in the presence of Mg or Al can be discounted.

Although a monolayer rectifier is now established,<sup>1</sup> it is less certain whether the asymmetrical current passes through the molecule by "through-bond" tunneling,<sup>21</sup> rather than around the molecules by "through-space" tunneling,<sup>21</sup> or whether the Aviram-Ratner mechanism is the correct interpretation. The measurements reported here were performed as a function of temperature, to see whether there is any thermally activated current-voltage behavior.

## Experimental Details

Hexadecylquinolinium tricyanoquinodimethanide, C<sub>16</sub>H<sub>33</sub>Q-3CNQ (**1**), was synthesized as described elsewhere.<sup>1</sup> A glass microscope slide was cut into small pieces and treated with "piranha" solution (Caro's acid or peroxymonosulfuric acid) at 90 °C for 30 min, then an Al film of 100 nm was evaporated atop these pieces in an Edwards E308A coater. Molecule **1** was dissolved in CH<sub>2</sub>Cl<sub>2</sub> by using an ultrasonic bath for 20 min, with a final concentration of less than 0.1 mg mL<sup>-1</sup>. The solution was carefully spread, using a syringe, onto a purified water subphase (Millipore Milli-Q, resistivity > 14 M $\Omega$  cm) in a microcomputer-controlled Nima model 622D2 trough in a vibration-isolated room with HEPA-filtered air. The spreading solution was compressed immediately at a barrier speed of 200 cm<sup>2</sup> min<sup>-1</sup> to a constant pressure of 25 mN m<sup>-1</sup>. Monolayers were transferred on the upstroke onto the Al-coated microscope slide, at a speed of 15 mm min<sup>-1</sup> under a green safelight, with a transfer ratio of 100%. The subphase temperature was controlled thermostatically by a Lauda constant-temperature bath at 14 °C. To remove any traces of moisture trapped under the monolayer, the substrate bearing the monolayer was dried for 2 days in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. The sample was then returned to the evaporator, placed on a holder cooled by liquid N<sub>2</sub>, and 12 cylindrical Al "pads", 100 nm thick (4 each of areas

1.5, 2.0, 2.5 mm<sup>2</sup>), were evaporated through a mask at a rate of 0.4 nm sec<sup>-1</sup>, to finally form the sandwich:



Contact was made to the Al pads and the Al film by using Au wires (0.0127 mm diameter) through a Ga/In eutectic. The eutectic makes good ohmic contact with the Au wires. If enough defects are found on the oxide-laden Al surface to cause complete wetting, then the Ga/In eutectic dissolves the small Al pad completely. The results presented here were obtained for those samples for which the aluminum oxide on the Al surface was sufficiently defect-free and impervious to prevent dissolution of the pad; the penalty paid was two additional resistances in series across the Ga/In eutectic | oxide | Al junction on both sides of the sandwich. Using Ag paint contacts instead of the Ga/In eutectic<sup>1</sup> caused very many short circuits, probably because the organic thinner leaked into the LB film before evaporating. Using Hg contacts directly without Al pads severely damaged the monolayer.

The sample was mounted in a Janis Varitemp 100R dewar, fitted with a Lakeshore 330 dual temperature heater/controller, controlled by a Gateway 2000 P5/60 microcomputer. A two-probe *IV* measurement was performed using a Hewlett-Packard model 3245A universal source (DC mode), a Hewlett-Packard model 3457A multimeter, and an IEEE-488 link to the microcomputer program.

In the cryostat cooled with liquid nitrogen, many measurements were made at various temperatures between 295 and 78 K. A heater was used to measure the sample at 370 K.

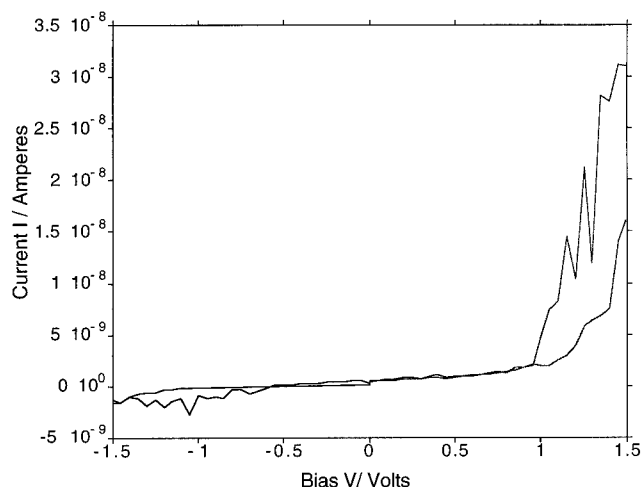
Because the organic monolayer, the barrier aluminum oxide, and the metals used in the contacts (Al, Ga/In, Au) all have different thermal expansivities, the monolayer thickness, the capacitance, and the electrical resistance of the sandwich change with temperature; defects and cracks occurred often, no matter how slowly the samples were cooled or warmed. The measurements were often plagued by intermittent short circuits at low temperatures, many of which would "heal" as the temperature was increased to room temperature; however, these samples would always thereafter show a "negative rectification ratio" and a very large current. These phenomena were ascribed to field-induced reordering within the LB monolayer, and the relevant data were removed from consideration. For samples which did not exhibit such anomalies, many repeated measurements on the same sample at several different temperatures could not be made easily, because the rectification ratios tend to decrease with repeated exposure of the sample to DC voltages over 1 V, as noted previously at room temperature.<sup>1</sup>

Capacitances were measured at room temperature in the range 100 Hz to 100 kHz at either 20 mV or 1 V bias, with a Hewlett-Packard model 4263B LCR meter. The AC measurements of capacitance were more reproducible and did not drift.

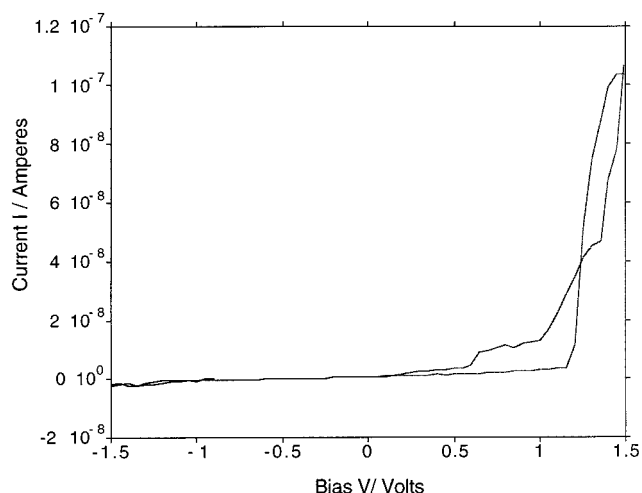
## Results

Many samples, which rectified at room temperature, were measured at decreasing temperature. Results could easily be obtained above 250 K. Below 250 K, either open circuits or permanent or intermittent short circuits happened often: only a few reliable results were obtained below 100 K. We discuss below four samples which rectified (samples A, B, C, and D) and one which did not rectify (sample E).

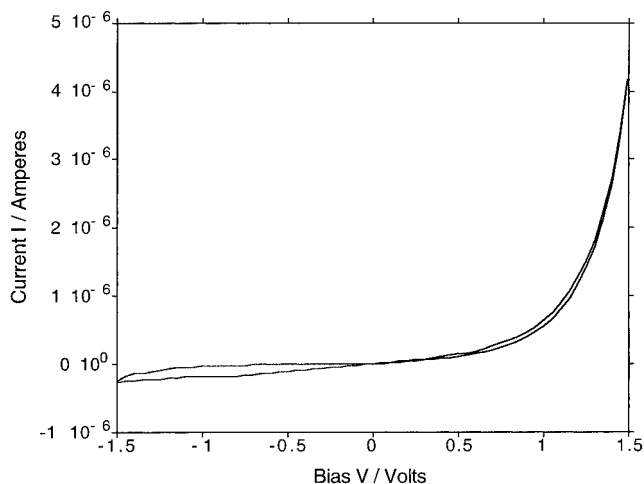
Figures 1 and 2 show the *I*-*V* plots for sample A at 195 and 105 K, respectively. The rectification ratio increased from 18



**Figure 1.** DC current  $I$  versus applied voltage  $V$  for sample A (pad area  $2.0 \text{ mm}^2$ ) at 195 K.



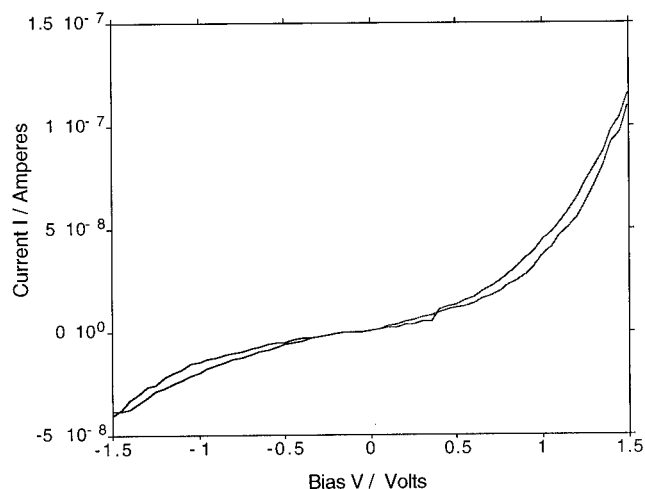
**Figure 2.** DC current  $I$  versus DC applied voltage  $V$  for sample A at 105 K.



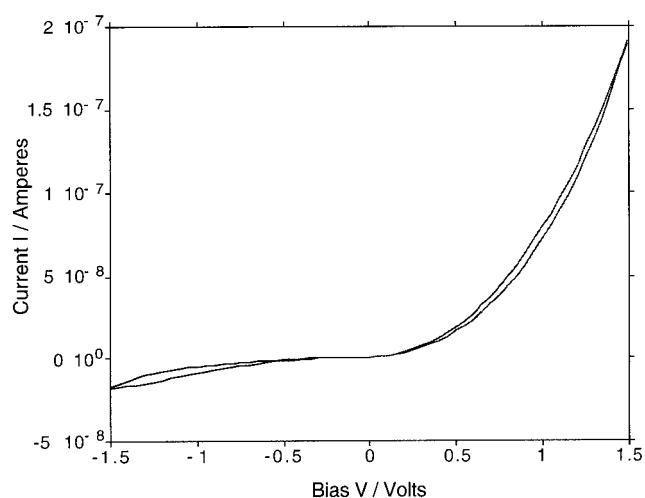
**Figure 3.** DC current  $I$  versus applied voltage  $V$  for sample B (pad area  $2.0 \text{ mm}^2$ ) at 290 K.

at 195 K to 48 at 105 K. There is a turning point at a positive bias of about 1 V, which means that the sample rectifies at the applied potential  $> 1 \text{ V}$  (at 295, 195, or 105 K). There is hysteresis in the enhanced forward current.

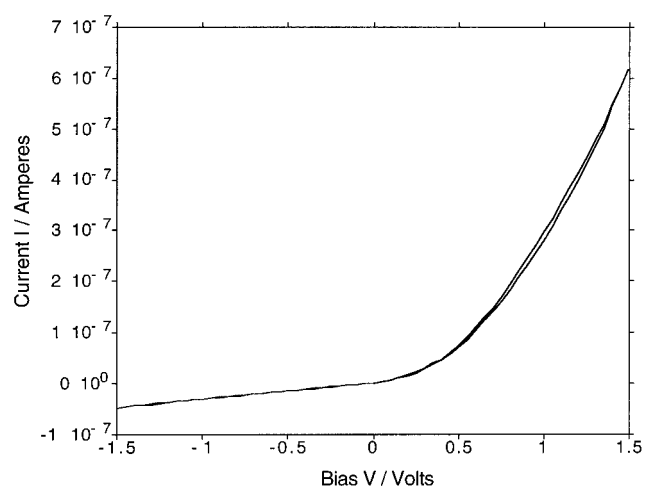
Figures 3 and 4 are  $I$ - $V$  plots of sample B at 290 and 150 K. At the lower temperature, the current at both positive and



**Figure 4.** DC current  $I$  versus applied voltage  $V$  for sample B at 150 K.



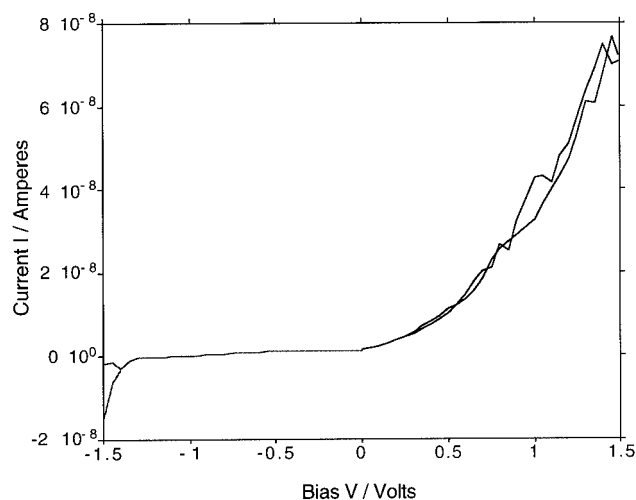
**Figure 5.** DC current  $I$  versus applied voltage  $V$  for sample C (pad area  $2.5 \text{ mm}^2$ ) at 290 K.



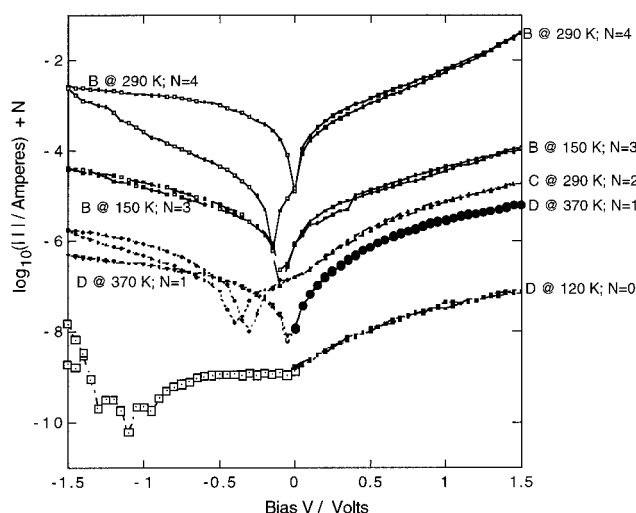
**Figure 6.** DC current  $I$  versus applied voltage  $V$  for sample C at 370 K.

negative bias is much smaller than that at room temperature, and the rectification ratio drops from 14.9 to 2.7.

We also studied the  $I$ - $V$  dependence of temperature when the temperature was increased. Figures 5 and 6 show the  $I$ - $V$  plots of sample C at 290 and 370 K: the current at higher temperature increased as much as 3.2 times at 1.5 V and 2.8



**Figure 7.** DC current  $I$  versus applied voltage  $V$  for sample D (pad area 1.5 mm<sup>2</sup>) at 120 K.

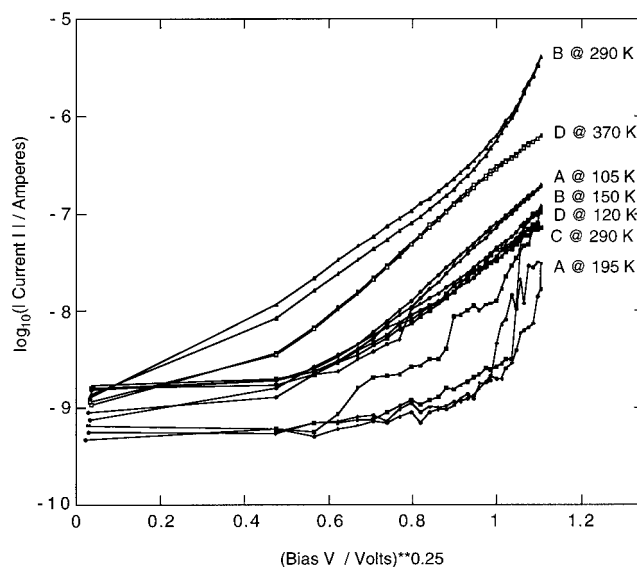


**Figure 8.** Logarithm of the current  $I$  versus bias  $V$ , for samples B, C, and D, displaced vertically by  $N = 4, 3, 2, 1$ , or 0 for clarity.

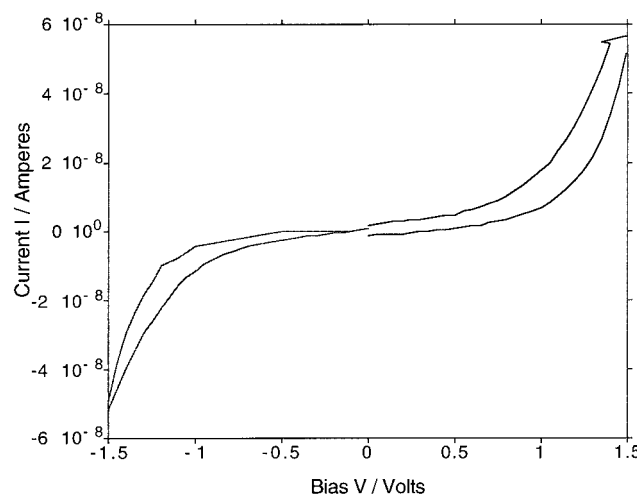
times at  $-1.5$  V, while the rectification ratio changed from 10.7 to 12.5. Finally, Figure 7 gives the rectification of sample D at 120 K. The enhanced current increases with increasing temperature (for samples B, C, D, but not for sample A). There is a fair variation in this current from sample to sample.

The plots of the logarithms of the current versus the applied voltage (Figure 8) are roughly linear with voltage far enough away from  $V = 0$ , but with steeper slopes at positive bias. The current drops to a minimum  $I_{\min}$  at  $V_{\min} = 0$  for sample D at 370 K, and for sample B at 290 K;  $I_{\min}$  is displaced to  $V_{\min} = -0.1$  to  $-0.4$  V for samples B at 150 K, D, and particularly C. There is some hysteresis for samples B and C. The data for sample A were too scattered to be included in Figure 8.

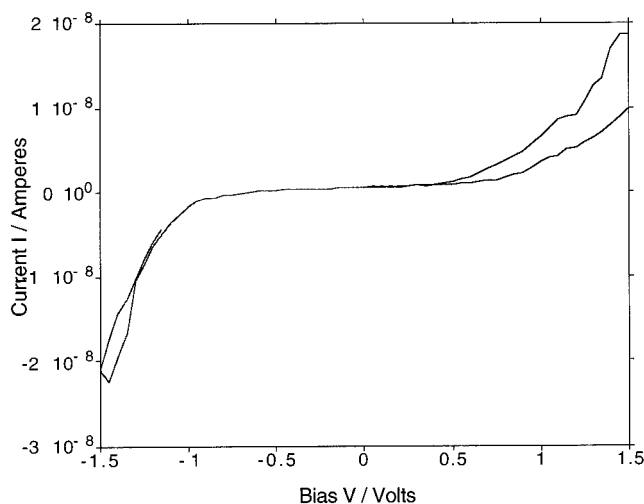
Plots of  $\log |I|$  versus both  $V^{0.5}$  and versus  $V^{0.25}$  show several regimes, a low-voltage regime, ( $0 < V < 0.5$ ) with almost zero slope, and a high-voltage regime with several large and varying slopes. The plot of  $\log |I|$  versus  $V^{0.25}$  (Figure 9) shows clearly that, above about 0.5 V bias, the current through a single monolayer of **1** is due neither to scattering by mobile defects ( $\log j \propto V^{0.25}$ ) nor to simple tunneling through vacuum nor to Poole–Frenkel nor to Schottky processes ( $\log j \propto V^{0.5}$ ). The current has a complicated dependence on bias  $V$ , which may be due to molecular processes.



**Figure 9.** Plot of  $\log I$  versus  $V^{0.25}$  in the forward regime ( $I > 0$ ) for samples A, B, C, and D: there are several regimes, with different slopes.



**Figure 10.**  $I$ – $V$  plot of sample E (pad area 1.5 mm<sup>2</sup>) at 295 K (no rectification).



**Figure 11.**  $I$ – $V$  plot of sample E at 80 K (no rectification).

Figures 10 and 11 show the  $I$ – $V$  plots of sample E at 295 and 80 K: this sample shows no rectification at either temperature; the current at 80 K was one-third that at 295 K.

Although the barrier resistances are small for the Au | Ga/In

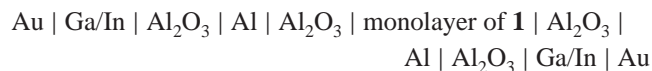


contact, an ohmic contact resistance of about 100 k $\Omega$  was measured in a separate experiment for a nonwetting Ga/In | Al<sub>2</sub>O<sub>3</sub> | Al | Al<sub>2</sub>O<sub>3</sub> | Ga/In couple. This contact resistance is many orders of magnitude smaller than the resistance across the organic monolayer.

The capacitance  $C$  (monolayer) and parallel AC resistance  $R_p$  were measured for monolayers of **1**, and also for monolayers of arachidic acid, as a function of frequency from 100 Hz to 100 kHz, with an applied potential of either 0.020 or 1 V. The measured  $C$  and  $R_p$  for the same sample remained steady over time: in contrast with the direct current measurements discussed above, during the AC measurements the monolayer of **1** probably did not reorient. The preliminary measured capacitances varied somewhat. The average values (for 3 pads) are  $C = 5 \pm 4$  nF at 100 Hz,  $6 \pm 4$  nF at 1000 Hz,  $5 \pm 2$  nF at 100 kHz for **1**, while  $C = 11 \pm 1$  nF at 100 Hz,  $9 \pm 0.5$  nF at 1000 Hz, and  $6 \pm 1$  nF at 100 kHz for arachidic acid. The latter values agree with a calculated value  $C = 8.20$  nF, obtained by using  $C = \epsilon_r \epsilon_0 A/d$ , where  $\epsilon_r$  = relative permittivity = 2.5,<sup>13</sup>  $\epsilon_0$  = permittivity of vacuum,  $A$  = capacitor area = 1 mm<sup>2</sup>, and  $d$  = arachidic acid monolayer thickness = 27 Å. The scatter in preliminary capacitance values for **1** is consistent with the variation in DC resistances seen in Figures 1–7.

## Discussion

The electrical characteristics of a metal | organic | metal sandwich are complicated. The AC capacitance and DC resistance measurements are for the electrode system:



We assume that in the present experiments Al<sub>2</sub>O<sub>3</sub> grows as a lossy amorphous layer<sup>22,23</sup> with equal ease between the base Al layer and the monolayer (where it is exposed to air for several days) as between the organic monolayer and the deposited Al metal, because at the pressures in our evaporator, a monolayer of oxygen is always present atop the organic layer. Because no rectification is seen with properly dried centrosymmetric arachidic acid bilayers, we can assume that there is no large asymmetry in the oxide layers in the two sides of the organic layer. The unavoidable Ga/In | Al<sub>2</sub>O<sub>3</sub> | Al ohmic contact resistance, and a further resistance between Al and the monolayer, probably vary from sample to sample and account for the variation in currents seen in Figures 1–7, 10, and 11. These resistances may also explain, in part, why the currents measured here (per molecule) are so much smaller than those measured in scanning tunneling microscopy (STM) between a monolayer of **1** and a graphite electrode on one side and an atomically sharp Pt/Ir nanotip on the other (there are also large geometry effects that make the STM current relatively large).

Of course, a single Al | Al<sub>2</sub>O<sub>3</sub> junction is also rectifying: Al is a “valve” metal<sup>22,23</sup> with a small barrier at 0.08 eV (within our range of measurement, but below the threshold for molecular asymmetries) and a very large photoelectric metal–insulator barrier at 2.3 eV (outside our range).<sup>24</sup> The present experiment is limited to a potential window of  $\pm 1.5$  V, beyond which the monolayer of **1** suffers dielectric breakdown.<sup>1</sup> The symmetrical arrangement of the various metal/oxide couples in the present

experiment allows the study of the electrical processes within the organic monolayer.

The conspicuous asymmetry, seen here for monolayers of **1** between symmetrical electrodes between 1 V and 1.5 eV in the temperature range 370 to 105 K, is most likely due to a molecular process. Because rectification by a single monolayer between symmetrical electrodes has now been observed as a function of temperature, the possibility that rectification is caused by some thermally activated mechanism can be discounted. A molecular explanation, such as a modification<sup>1</sup> of the Aviram–Ratner intramolecular electron-transfer mechanism,<sup>2</sup> is reinforced.

## Conclusion

The conductivities across a monolayer of **1** at different temperatures (370 to 105 K) buttress a molecular mechanism of rectification in hexadecylquinolinium tricyanoquinodimethanide.

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