# Molecular Rectifier

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Current density–voltage characteristics are presented for a molecular structure of the form metal/organic-multilayer/metal for which the rectifierlike forward bias current density dependence is unequivocally associated with *zwitterionic* molecules. By placing passive organic barriers between the metal layers and the active molecules we prove that Schottky barrier effects are not important. This is the clearest evidence so far for molecularly controlled rectification, the basis for molecular electronics.

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For almost two decades, since the seminal publication of Aviram and Ratner [1], there have been attempts to demonstrate that a suitably designed organic molecule deposited in a layer between two electrodes would give current density–voltage characteristics analogous to the behavior of a *p-n* junction. Such a demonstration constitutes a major advance in molecular electronics and bridges the gap between molecular structure and macroscopic electronic device behavior. Continuing from the work of Geddes *et al.* [2,3], electrically rectifying properties have been reported for such structures [4] using a monomolecular Langmuir-Blodgett film of a *zwitterionic* molecule, $C_{16}H_{33}$-$\gamma$Q3CNQ [5] (the structure of which is shown in Fig. 1), between platinum and magnesium electrodes. The electrical conduction mechanism may be conjectured to follow the Aviram and Ratner model with the forward bias behavior composed of resonant (elastic) electron tunneling from the Mg anode to the quinolinium cation ($D^+$) and from the phenyldicyanomethanide anion ($A^-$) to the Ag cathode followed by a reversion to the *zwitterionic* ground state via intramolecular inelastic tunneling, while under reverse bias, a high energy barrier to the $D^{2+}$-$\pi$-$A^{2-}$ state limits the electron flow:

$$\mathrm{Mg}/D^{+}\text{-}\pi\text{-}A^{-}/\mathrm{Ag} \rightarrow \mathrm{Mg}/D^{0}\text{-}\pi\text{-}A^{0}/\mathrm{Ag} \rightarrow \mathrm{Mg}/D^{+}\text{-}\pi\text{-}A^{-}/\mathrm{Ag}\,.$$

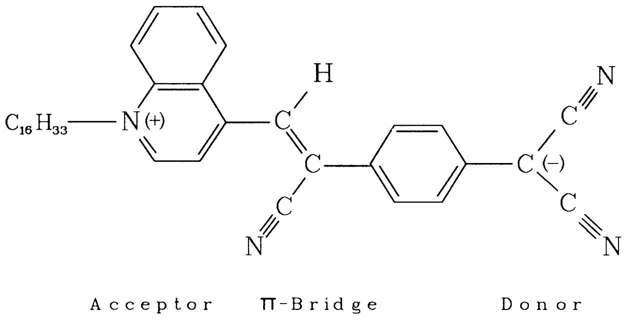

FIG. 1. Chemical composition of $C_{16}H_{33}$-$\gamma$Q3CNQ.

It is, however, clear that this may not be the only interpretation of the experimental observation of asymmetric conduction and thus these observations were not sufficient proof that the rectification is solely a molecular process. Interaction between the electrodes and the molecular headgroup producing a rectifying interfacial region is, clearly, an alternative explanation for the asymmetric $J/V$ curves [6,7]. In the present study we introduce for the first time passive organic spacer layers, $\omega$-tricosenoic acid multilayers, between the active molecules and the metal electrodes. The use of $\omega$-tricosenoic acid layers to space the metal from the rectifying molecule prevents Schottky barrier effects and thus provides conclusive evidence that the rectifierlike characteristics are attributable to molecular processes.

Initially, simple metal/Langmuir-Blodgett multilayer/metal (M/LB/M) junctions were fabricated using a similar planar geometry to that used by Geddes *et al.* [8–10]. They reported that $\omega$-tricosenoic acid multilayers interposed between silver and magnesium electrodes exhibited $J/V$ characteristics which were nonlinear at larger applied biases, obeying $\ln(J) \propto V^{1/4}$ for junctions of four monolayers thickness or less and $\ln(J) \propto V^{1/2}$ for more than six monolayers. All the $J/V$ data were symmetric with respect to the sense of the applied bias and, therefore, act as a convenient comparison for our subsequent work in which direction of the bias is important. It is partly for this reason and also because it is chemically relatively inert and has no oxide barrier that silver was chosen as the base electrode material. This base electrode was formed by thermal evaporation of 99.99% pure silver onto a thoroughly cleaned flame-polished glass coverslip. With minimal delay the LB film was transferred onto this fresh metallic surface. This was accomplished using a solution of $C_{16}H_{33}$-$\gamma$Q3CNQ in Aristar grade dichloromethane spread on a subphase of ultrapure water. The film transfer rate was 0.1 $\mathrm{mm\,s^{-1}}$ at a surface pressure of 25 $\mathrm{mN\,m^{-1}}$ using a rectangular single-compartment Teflon trough. The transfer ratios indicated a $Z$-type LB film (headgroups oriented towards the

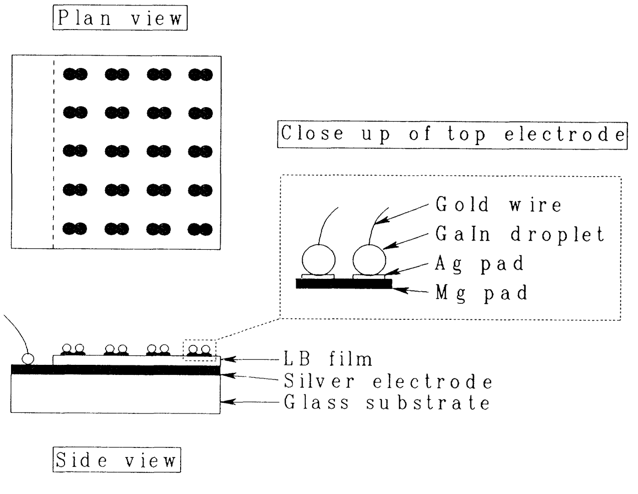

FIG. 2. Schematic of sample fabrication.

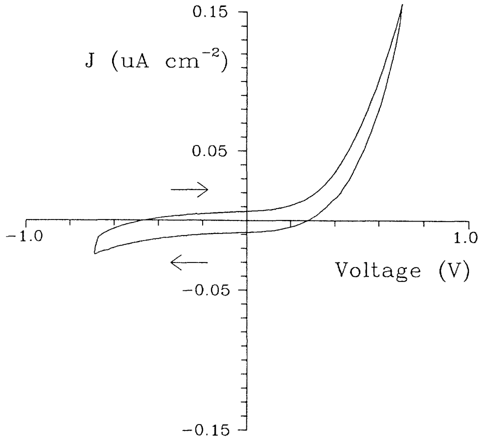

FIG. 3. Current density–voltage curve from a Ag/7 monolayers of $C_{16}H_{33}$-$\gamma$Q3CNQ/Mg junction. The voltage sweep rate is set at 44 mV s$^{-1}$.

substrate). A two-week dessication period was found to be essential for the removal of residual water before the thermal deposition of the top electrode. Magnesium has once again been used as the top electrode material since it minimizes damage to the organic film during electrode deposition [4]. Filled figure-8-shaped magnesium electrodes, of area 0.78 mm$^2$, were deposited at an apparent rate of ~0.5 nm s$^{-1}$ to an apparent thickness of 200 nm. Because of the unpredictable nature of magnesium deposition, these numbers only represent upper limits for film deposition [11]. Following this, two circular silver pads were deposited onto the center of the annular limbs of each magnesium pad without breaking the vacuum. After removal from the vacuum, two electrical contacts were made to the base electrode using silver paste and two contacts to each magnesium/silver electrode established using GaIn eutectic droplets placed on each silver pad and into which fine gold wires were lowered. The four contacts made to each junction permitted continuity checks to ascertain that good electrical contact was made to both the base and magnesium electrodes. A schematic of the sample geometry is shown in Fig. 2. A triangular voltage signal of chosen period and voltage sweep rate was applied to the M/LB/M junction and the current passed was measured using an electrometer. Applied voltages are typically less than 2 V, which corresponds to maximum electric field strengths in the order of 10$^8$ V m$^{-1}$ within the organic film.

Rectifierlike characteristics have been observed in all junctions of the type M/$C_{16}H_{33}$-$\gamma$Q3CNQ/M, lower thickness junctions (including monomolecular junctions) having been described in a previous publication [4]. However, these data are confused by the competition of other conduction processes and high noise levels. The use of thicker (> 5 monolayer) junctions avoids these problems. Figure 3 shows one complete $J/V$ cycle measured from 7 monolayers of $C_{16}H_{33}$-$\gamma$Q3CNQ. Not all of the cycle shown is suitable for further analysis due to capacitive charging currents which flow after reversal of the voltage sweep and which contribute significantly to the current when sweeping away from the voltage extrema. To avoid artifacts from these transient effects only those regions of the curve taken from zero and moving to an extremal applied voltage were used for analysis. These gave the following relationships. The highly enhanced forward bias behavior was found to conform closely to $J-J_0=aV^3+bV$ and is, as yet, unexplained. Reverse bias behavior followed $\ln(I-I_0)\propto V$, which suggests a Poole-type conduction with Poole center separation roughly corresponding to a single molecular length. The experimental data fitted the above relationships extremely well across the whole range of applied bias and gave unambiguous determinations of the different dependences. In Fig. 3 the reverse bias has not been increased sufficiently to observe a strongly nonlinear response. However, when this is done the curve retains the $\ln(I-I_0)\propto V$ dependence and clearly illustrates that the conduction asymmetry cannot be accounted for by a simple shift along the voltage axis which might be proposed due to using electrode metals of differing work functions. A range of voltage sweep rates was studied to discover if this influenced the results. It was found that at a 4 times faster sweep rate the capacitance loop significantly distorts all the data. However, for the sweep rate reduced by factors of 2 and 4 the influence of the capacitance loop is proportionately reduced; the dependences of the $J/V$ trace from 0 V to extrema are invariant. Thus we may safely conclude that the above $J/V$ dependences represent steady-state measurements.

Having characterized the $J/V$ relationships for these junctions, we now have to establish whether they are molecular in origin. First, the $C_{16}H_{33}$-$\gamma$Q3CNQ film

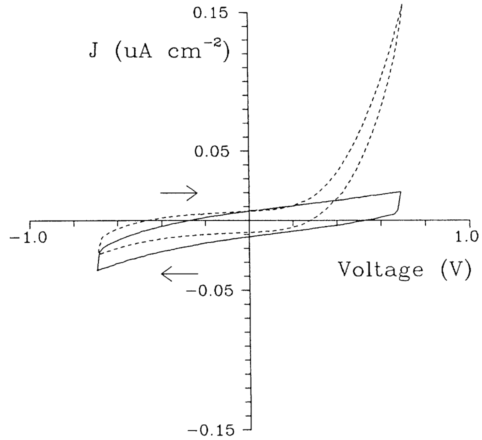

FIG. 4. Current density–voltage curve from a Ag/7 monolayers of "bleached" $C_{16}H_{33}$-$\gamma$Q3CNQ/Mg junction. The dashed line represents the corresponding "unbleached" $J/V$ curve (Fig. 3). The voltage sweep rate is set at 44 mV $s^{-1}$.

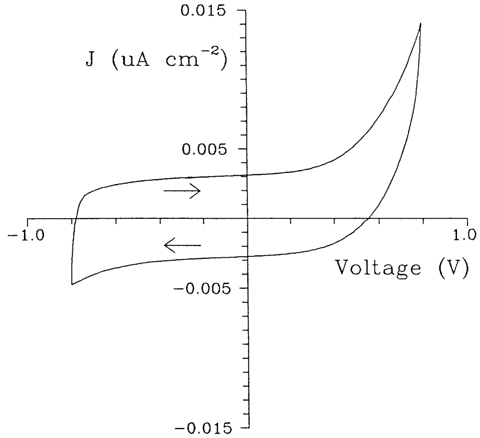

FIG. 5. Current density–voltage curve from a Ag/22TA/$C_{16}H_{33}$-$\gamma$Q3CNQ/22TA/Mg junction with bilayers of $\omega$-tricosenoic acid and 3 monolayers of $C_{16}H_{33}$-$\gamma$Q3CNQ. The voltage sweep rate is set at 22 mV $s^{-1}$.

may be "bleached" while on the subphase by addition of low levels of metallic ions into the water. This process changes the color of the spread film from the normal deep blue to an almost colorless state. Junctions have been fabricated using these altered films in which the charge transfer has been suppressed. In Fig. 4 a bleached-film $J/V$ curve is shown with the data from Fig. 3 superimposed to illustrate the similarity of the current density intercepts and zero applied bias slopes. These indicate that the capacitances and linear conductances of the junctions are much the same, and therefore so are the organic film thicknesses. The enhanced forward bias current is, however, absent, suggesting that the rectification and molecular charge transfer are intimately related [12].

Second, and more importantly, structures of the type

$$\mathrm{Ag/22TA/C_{16}H_{33}\text{-}\gamma Q3CNQ/22TA/Mg/Ag}$$

have been fabricated and studied, where 22TA represents an interposed $\omega$-tricosenoic acid LB film. This geometry excludes intimate contact of the $C_{16}H_{33}$-$\gamma$Q3CNQ with the electrodes and thus prevents the formation of Schottky contacts or other chemical associations. A typical $J/V$ curve for a bilayer $\omega$-tricosenoic acid/trilayer of $C_{16}H_{33}$-$\gamma$Q3CNQ film/bilayer $\omega$-tricosenoic acid film is presented in Fig. 5. The capacitance of the junction compares favorably with other junctions of similar thickness as does the low bias resistance. Primarily, though, our interest is with the enhanced forward bias conduction which still prevails, although, due to the reduction in the proportion of active layers in the structure, the maximum current is significantly reduced. Data for the forward bias curve again fit $J-J_0=aV^3+bV$ while the reverse bias conforms once more to $\ln(I-I_0)\propto V$. These dependences are the same as observed for single-component unbleached $C_{16}H_{33}$-$\gamma$Q3CNQ junctions and dominate over contributions from the $\omega$-tricosenoic acid spacer layers which would be expected to follow either $\ln(J)\propto V^{1/4}$ or $\ln(J)\propto V^{1/2}$ as previously measured for pure $\omega$-tricosenoic acid junctions [10]. Thus we have, first, bleached the active molecule and removed the rectifying characteristics, showing they are associated with the active molecule, and now, and more importantly, we have separated the active moieties from the metal electrodes and still record the same type of rectifying behavior. This is definitive evidence for molecular rectification, attributable to the active *zwitterionic* species.

It has been demonstrated that electrode effects do not cause the rectifying behavior of the M/$C_{16}H_{33}$-$\gamma$Q3CNQ/M junctions and that the $J/V$ asymmetry is caused by the chromophore of the $C_{16}H_{33}$-$\gamma$Q3CNQ molecular headgroup. It is concluded, therefore, that the rectifierlike characteristic is unequivocally associated with the molecular structure. In particular, it is associated with the presence of a spatial asymmetry due to the $Z$-type deposition of the *zwitterionic* Langmuir-Blodgett film. Currently, there is available no satisfactory theory to explain the $V^3$ forward current density dependence recorded for these structures, although a simple perturbation expansion of nonlinear conduction would be expected to have a $V^3$ term as its first nonlinear term.

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