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Further Evidence for Molecular Rectification in M|LB|M Junctions

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Abstract A zwitterionic molecule has been incorporated as a Langmuir-Blodgett (LB) film between two electrodes. Current-voltage curves are presented which exhibit rectifier-like behaviour. By placing passive organic layers between the zwitterionic LB film and each electrode we show that Schottky contact and similar interfacial effects are not important and, therefore, that the rectifier-like behaviour is unequivocally associated with the zwitterionic molecular structure.

INTRODUCTION

Many attempts have been made over the last two decades to successfully synthesize and incorporate novel molecules into a metal|organic layer|metal (M|LB|M) junction and to demonstrate that such a structure would possess current voltage characteristics analogous to a p-n junction. Recently, Geddes[1] presented such data and continuing from this we published similar results[2] obtained from as little as a monolayer of the zwitterionic material $C_{16}H_{33}$-γQ3CNQ[3] (Figure 1) between platinum and magnesium electrodes. Although the data was extremely promising we could not claim this as proof positive for molecular rectification because interfacial effects such as Schottky contacts could constitute an alternative explanation for the observations[4,5]. In subsequent experiments we have interposed, between the zwitterionic film and the metallic electrodes, passive organic LB films which are designed to prevent the formation of Schottky type effects.

EXPERIMENTAL

Following the method first developed by Geddes[6] and which has subsequently been refined (Figure 2), metal | Langmuir-Blodgett multilayer | metal junctions were fabricated using a planar geometry. For details on sample fabrication the reader is directed to reference 7. A triangular voltage signal of chosen period and voltage sweep rate was applied across the M|LB|M junction and the current 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 Vm^{-1} within the organic film. Current-voltage data recorded from junctions of the type $Ag|C_{16}H_{33}$-γQ3CNQ|Mg|Ag (Figure 3) were analysed to ascertain the functional dependences of the various parts of the curve. It was found that the region of the I/V data moving from zero to maximum positive (this is defined as a the base electrode positive) applied field followed a $I\text{-}Io=AV^3+BV$ dependence very closely. The corresponding reverse bias region i.e. moving from zero to maximum applied negative field, conformed to a dependence of $\ln(I\text{-}I_o) \propto V$. While this reverse bias behaviour might be considered evidence for a Schottky contact, quantitative analysis reveals that the curve cannot be reproduced using this model. Instead a Poole type conduction was found to give excellent agreement with the inter-Poole centre separation being roughly that of a monomolecular length. Having observed that this simple M|LB|M junction possessed the features which had been predicted we next had to unequivocally demonstrate that these features were a manifestation of the molecular structure rather than of the sample fabrication.

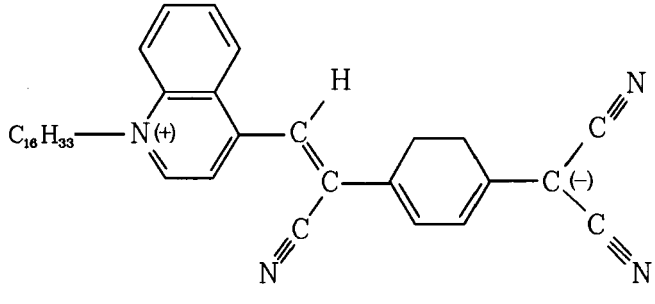

FIGURE 1 Molecular structure of $C_{16}H_{33}$-γQ3CNQ.

Firstly, another type of junction was made using an altered form of $C_{16}H_{33}$-γQ3CNQ. While as a Langmuir film on the subphase a small amount of metallic contamination was introduced to the water producing a "bleached" form of the molecule. Instead of being a deep blue colour like the unaltered film, this bleached film was almost colourless; a change attributed to the suppression of the charge transfer within the molecular headgroup. Junctions fabricated using these films exhibited I/V curves of the type shown in Figure 4. Forward bias no longer produces enhanced forward currents and analysis reveals that the dependence is $\ln(I\text{-}I_o) \propto V^{\frac{1}{4}}$ reminiscent of fatty acid M|LB|M junctions. The reverse bias behaviour remains very similar in character to that of the unaltered film junctions with the $\ln(I\text{-}I_o) \propto V$ again suggesting Poole conduction. It is noteworthy that the capacitance and DC conductance of the bleached and unbleached film junctions are of similar values which implies that the films are of similar thickness and DC permittivity. This suggests that the bleaching process has neither radically altered the molecular dimensions nor has it significantly changed the LB deposition conditions. This experiment links the presence of the enhanced forward bias conduction with the molecular charge transfer resonance, but the importance of contact effects is yet to be resolved.

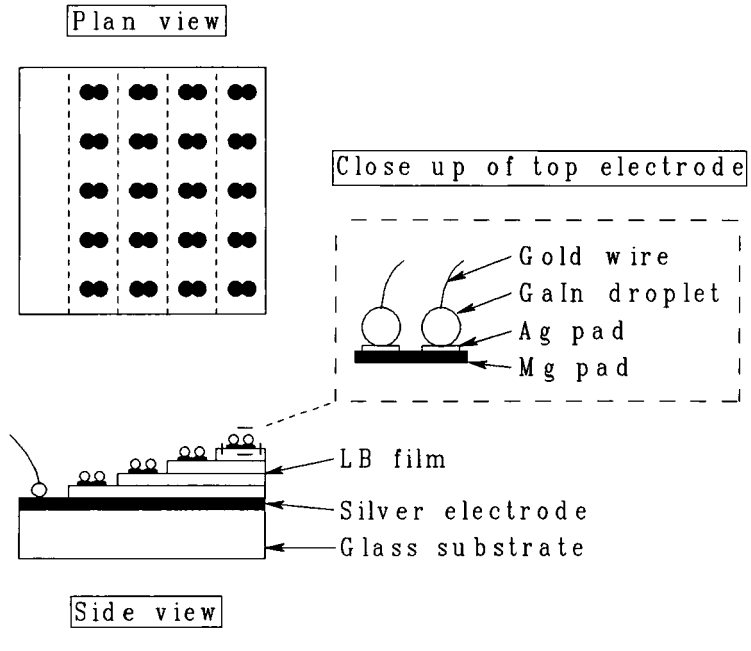

FIGURE 2 Schematic diagram of sample construction.

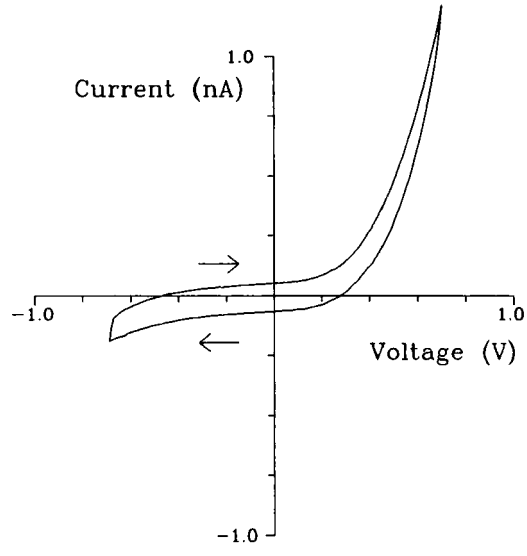

FIGURE 3 Current-voltage curve from Ag | seven monolayers of $C_{16}H_{33}$-γQ3CNQ | Mg junction. Voltage sweep rate set at 44 mV s^{-1}.

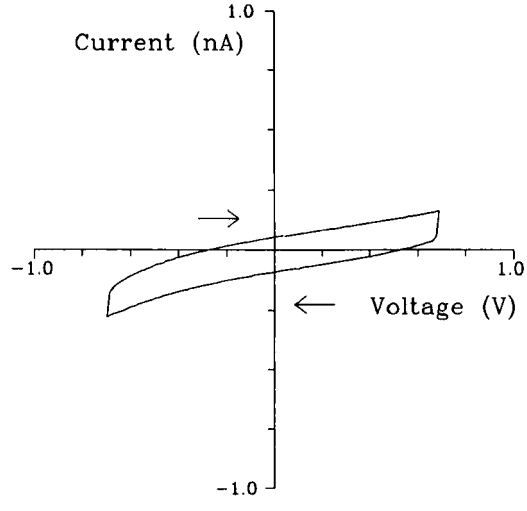

FIGURE 4 Current-voltage curve from Ag | seven monolayers of $C_{16}H_{33}$-γQ3CNQ | Mg junction in which the LB film was bleached. Voltage sweep rate set at 44 mV s^{-1}.

Secondly, and more importantly, ω-tricosenoic acid LB spacer layers were incorporated into junction construction so that the zwitterionic LB film was separated from both of the electrodes. In the data shown in Figure 5 the two passive layers were of bilayer thickness and the $C_{16}H_{33}$-γQ3CNQ film of trilayer thickness. Clearly, the enhanced forward bias conduction persists and again follows $I\text{-}Io=AV^3+BV$. Reverse bias behaviour similarly still conforms to $\ln(I\text{-}I_o) \propto V$. The maximum current under forward bias has been proportionately reduced because there are less active layers within the junction. Thus it has been shown that the interesting electrical behaviour of the unbleached $C_{16}H_{33}$-γQ3CNQ junctions does not arise from molecular associations with the electrode materials.

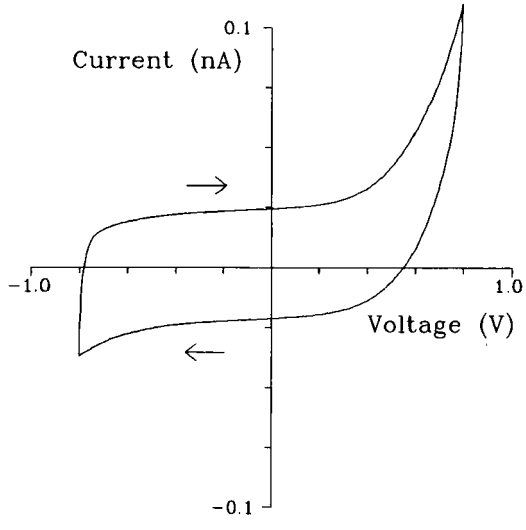

FIGURE 5 I/V curve from a Ag|22TA|$C_{16}H_{33}$-γQ3CNQ|22TA|Mg junction with bilayers of ω-tricosenoic acid and 3 monolayers of $C_{16}H_{33}$-γQ3CNQ. Voltage sweep rate set at 22 mV s^{-1}.

CONCLUSIONS

It has been demonstrated that electrode effects do not cause the rectifying behaviour of the M|$C_{16}H_{33}$-γQ3CNQ|M junctions and that the I/V asymmetry is caused by the chromophore of the $C_{16}H_{33}$-γQ3CNQ molecular headgroup. It is concluded, therefore, that the rectifier-like 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 dependence recorded for these structures, although a simple perturbation expansion of non-linear conduction would be expected to have a V^3 term as its first non-linear term.

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