Rectifying Characteristics of Mg|($C_{16}H_{33}$-Q3CNQ LB Film)|Pt Structures

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The Mg|(LB monolayer)|Pt structures of *Z*-β-(1-hexadecyl-4-quinolinium)-α-cyano-4-styryldicyanomethanide ($C_{16}H_{33}$–Q3CNQ) show asymmetric current–voltage characteristics; the behaviour is attributed to the organic monolayer although whether it is due to the presence of the permanent dipole moment or molecular rectification is unclear.

Aviram and Ratner[1] postulated that oriented films of the bicyclo[2.2.2]octane bridged donor–acceptor molecule, TTF-σ-TCNQ, would show rectifying characteristics because the energy barrier to TTF$^+$-σ-TCNQ$^-$ is low relative to TTF$^-$-σ-TCNQ$^+$. The difference between the ionisation energy of the donor part, TTF (tetrathiafulvalene), and electron affinity of the acceptor part, TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), is 4.0 eV (*cf.* 9.6 eV when the roles are reversed).[2] The molecule was never synthesised but suitable urethane bridged *D*-σ-*A* materials (*e.g.* *A*, 5-bromo-TCNQ;

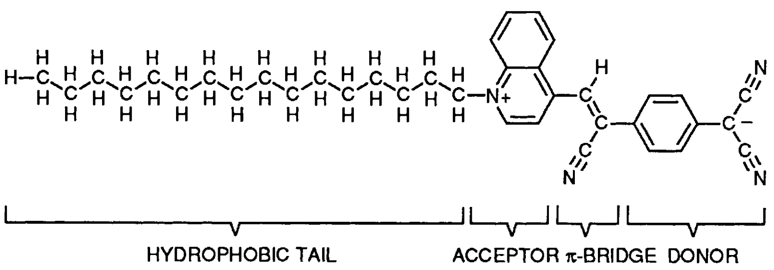

Fig. 1 Molecular structure of $C_{16}H_{33}$–Q3CNQ. The molecule is probably non-planar with rotations about the single bonds linking the acceptor and donor parts to the –CH=C(CN)– bridge. The pyridinium analogue, *Z*-β-(1-methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide,[6] has dihedral angles of 36.1 and 5.0° between the plane of the bridge and the planes through the acceptor (D^+) and donor (A^-) respectively

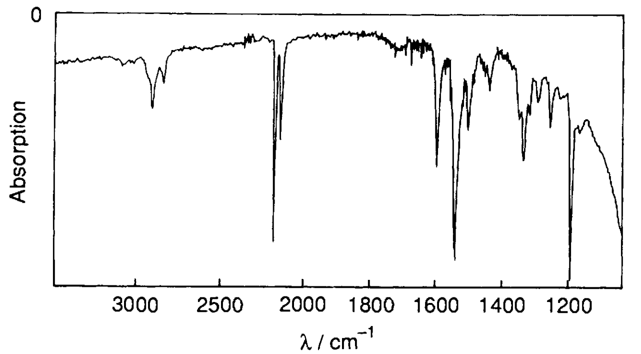

Fig. 2 Infrared spectrum of a 50 layer LB film of $C_{16}H_{33}$–Q3CNQ on a calcium fluoride substrate. The curvature on the right-hand side corresponds to absorption by the substrate

D, TTF, pyrene, *N*,*N*-dialkylaniline) have been reported by Metzger and co-workers.[2,3] Metzger[4] has reviewed the molecular and device requirements and recently a report has appeared of asymmetric *I–V* characteristics with such a σ-bridged system.[5] In this work we report the first example of asymmetric *I–V* characteristics for a metal|(LB monolayer)| metal structure based upon a π-bridged donor–acceptor molecule (Fig. 1).

The $C_{16}H_{33}$–Q3CNQ[6] was synthesised by refluxing an ethanolic solution of 1-hexadecyl-4-methylquinolinium bromide with either Li^+TCNQ^- for six weeks or neutral TCNQ and *N*-methylpiperidine† for one week. Recrystallisation from acetonitrile gave fine green needles. The structure may be depicted as either neutral or zwitterionic but, based upon the infra-red data in the C≡N stretching region (a doublet at 2180 and 2140 cm^{-1}, Fig. 2), the latter is more likely. The higher frequency band is particularly sensitive to charge density and may be compared with a corresponding value of 2185 cm^{-1} for $TCNQ^-$ (*cf.* 2235 cm^{-1} for neutral TCNQ). Also, for the related pyridinium analogue, *Z*-β-(1-methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide, the X-ray crystal structure and INDO calculated charge distribution have unambiguously confirmed a zwitterionic ground state.[7]

Solutions of $C_{16}H_{33}$–Q3CNQ (2.5×10^{-5} mol dm^{-3}) in Aristar grade dichloromethane were spread on the pure water subphase (18 MΩ cm) of a Langmuir–Blodgett (LB) trough and compressed to a surface pressure of 25 mN m^{-1}. Films were transferred to both hydrophilically treated calcium fluoride slides and platinum coated, flame polished, glass substrates at 0.15 mm s^{-1}. The structures produced are *Z*-type, the non-centrosymmetric arrangement being confirmed by second-harmonic generation (SHG) studies in which an SH intensity is observed that increases quadratically with the number of LB layers.[8]

Mg|($C_{16}H_{33}$–Q3CNQ LB film)|Pt structures were formed using the procedure of Geddes *et al.*[5,9] Magnesium top electrodes were deposited by evaporation and, without breaking the vacuum, coated with silver; electrical contact to the silver pads was made using a Ga/In eutectic and gold wire. The results of our electrical characterisation of mono- and multi-layer LB films are shown in Fig. 3. The high resistances indicate that there are no filamentary metallic pathways through the films. Also, in contrast to reference Mg|(LB film)|Pt structures of ω-tricosenoic acid, which show symmetrical *I–V* characteristics, those of $C_{16}H_{33}$–Q3CNQ are asymmetric and this we attribute to the presence of non-centrosymmetric layers.

Analogous behaviour has been reported by Geddes *et al.*[5] for the σ-bridged material DDOP–C–TCNQ,‡ the synthesis of which has been reported by Metzger[10] as part of the molecular rectifier programme at the University of Alabama. The maximum field to which these molecules may be taken is *ca.* 8 V/monolayer compared with *ca.* 2 V/monolayer for the π-bridged zwitterion reported in this work. Also, unlike the curves in Fig. 3, which show little hysteresis, the *I–V* characteristics of DDOP–C–TCNQ are highly hysteretic. These differences may arise from the dissimilar molecular structures, the donor and acceptor groups being linked by a rigid –CH=C(CN)– bridge in $C_{16}H_{33}$–Q3CNQ and a flexible –NH–(C=O)–O–$CH_2CH_2CH_2$–O– bridge in DDOP–C–TCNQ.

It is possible to conjecture that the asymmetric *I–V* curves of $C_{16}H_{33}$–Q3CNQ are interpretable in terms of the Aviram and Ratner[1] model, in which case the steps under forward electrical bias would be (i) resonant (elastic) electron tunnelling from the Mg anode to the quinolinium cation (D+) and from the phenyldicyanomethanide anion (A−) to the Pt cathode; (ii) reversion to the zwitterionic form *via* intramolecular inelastic tunnelling.

$$\mathrm{Mg}|D^+\text{–}\pi\text{–}A^-|\mathrm{Pt} \rightarrow \mathrm{Mg}|D^\circ\text{–}\pi\text{–}A^\circ|\mathrm{Pt} \rightarrow \mathrm{Mg}|D^+\text{–}\pi\text{–}A^-|\mathrm{Pt}$$

Under reverse electrical bias this mechanism would lead, with a high energy barrier, to D^{2+}–π–A^{2-} and not to the reverse polarity zwitterion as is the case for TTF–σ–TCNQ.[1]

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† Piperidine may be used in place of *N*-methylpiperidine. The reaction is faster (*ca.* 24 h) but competitive substitution reactions occur between piperidine and neutral TCNQ.

‡ 2-Bromo-5-(2′-ethoxy)-2,2′-(2,5-cyclohexadiene-1,4-diylidene)-bispropanedinitrile ester of 2-*N*-(4-dodecyloxy)phenylcarbamic acid.

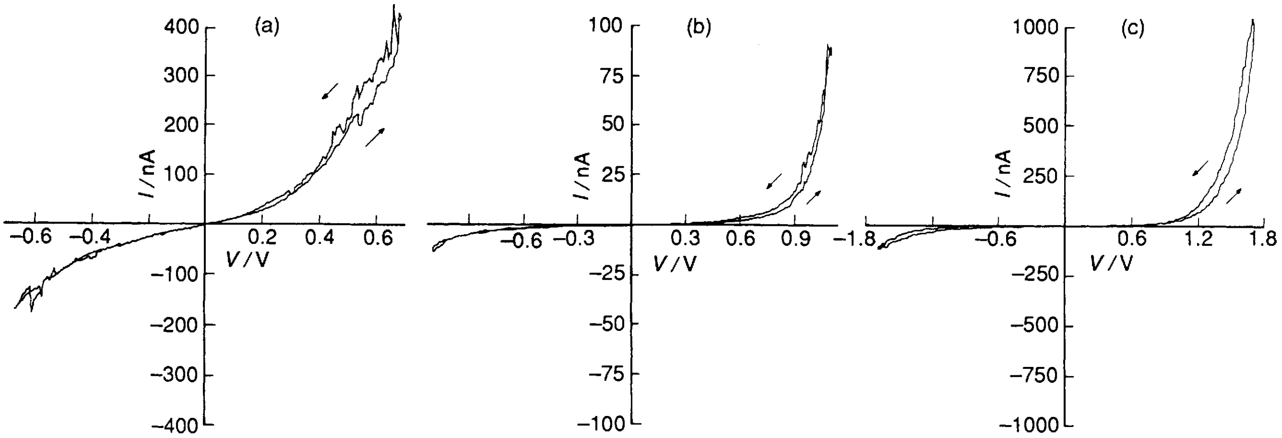

Fig. 3 *I*–*V* plots for Mg|($C_{16}H_{33}$–Q3CNQ LB film)|Pt structures with (*a*) one, (*b*) three and (*c*) four LB layers. In these structures the hydrophobic chain is adjacent to the Mg electrode

However, in view of the fact that there are permanent dipoles in this *Z*-type film, a simpler interpretation would be that the internal dipole field is creating the asymmetry. The existence of asymmetric metal layers, one of which, magnesium, may certainly interact strongly with the head groups of the molecules also adds the possibility of Schottky contact behaviour.

At the present time it is unclear as to what physical processes are dominant in these structures. However, we have shown convincingly that metal|(LB film)|metal structures may be fabricated of π-bridged molecules with no filamentary metallic pathways and showing strongly asymmetric but somewhat noisy *I*–*V* characteristics. This, together with the work of Geddes *et al.*[5] on the σ-bridged molecules, paves the way for a novel series of experiments in molecular electronics.

We are grateful to the SERC for support and for providing studentships to A. S. M. and M. S.

Received, 4th April 1990; Com. 0/01511C

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