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A Novel Highly Conducting Tetracyanoquinodimethane (TCNQ) Langmuir–Blodgett Film

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A novel dimethyl octadecyl sulphonium–tetracyanoquinodimethane (TCNQ) salt forms Langmuir–Blodgett films, which show a high degree of organization and which, after exposure to iodine vapour, give highly conducting films.

Langmuir–Blodgett (L.B.) films have attracted much interest in recent years, and a number of studies of L.B. films prepared from tetracyanoquinodimethane (TCNQ) and pyridinium salts have been reported.[1—4] We report here a new L.B. conducting material, produced by treating with iodine vapour a thin layer of the semi-amphiphilic salt $C_{18}H_{37}S^+Me_2$–$TCNQ^-$ (**1**). The latter was synthesized by metathesis between LiTCNQ and dimethyl octadecyl sulphonium iodide. A 2×10^{-4} M solution of (**1**) in $CHCl_3$ spread at the air–water interface of a Langmuir trough provides a monomolecular layer after evaporation of the solvent. The monolayer is then slowly compressed by use of a mobile barrier monitored by a Wilhelmy balance, which measures the surface pressure π. The monolayer is stable up to $\pi = 8$ mN m^{-1}. At this step, the molecular area of (**1**) is found to be about 50 Å^2 per molecule. For higher surface pressure the π (A) compression isotherm exhibits a plateau which is presumably connected to the formation of crystallites at the air–water interface itself.[1] When equilibrium is reached, the transfer onto a solid substrate by the Langmuir–Blodgett method can be achieved at a surface pressure as high as 25 mN m^{-1} without any observed collapse. The transfer rate is poor, but can be improved considerably by mixing (**1**) with octadecanol (molar ratio 1/1) in the spreading solution. In both preparations, the properties of the resulting solid films are the same. (i) As far as the TCNQ species is concerned, the u.v.–visible spectrum is nearly identical with the one obtained from $C_{22}H_{45}$-pyridinium$^+TCNQ^-$.[2] This clearly shows that all the TCNQ molecules are dimerized species $(TCNQ^-)_2$. (ii) The i.r. diagnostic region (1000—1700 cm^{-1}) of the solid film deposited onto an i.r.-transparent CaF_2 substrate is shown in Figure 1 (a and b) for two different configurations of the classical linear dichroism method,[5] namely $i = 0°$ (Figure 1a) and $i = 60°$ (Figure 1b), where i is the incident angle, the light being polarized with the electric vector in the incident plane (transverse magnetic waves). The sharp peak at 1510 cm^{-1} is attributed to the b_{1u} ν_{20} mode of the $TCNQ^-$ species[2] in the dimeric state. Its dichroic ratio: $\beta(i) = \alpha(i)/\alpha(o)$ where α is the amplitude of the absorption is 0.64 for $i = 60°$. This corresponds to a dipole moment exactly parallel to the substrate. Hence we conclude that the long axes of the $TCNQ^-$ anions are also parallel to the substrate. The 1365 cm^{-1} peak is complex $(a_g\ \nu_4 + b_{2u})^2$ and is not considered at this stage of the discussion. On the other hand, the sharp peaks at 1590 and 1184 cm^{-1} are assigned respectively to the a_g ν_3 and a_g ν_5 i.r.-activated transitions with dipole moments[2] both parallel to the direction of the charge-transfer interaction. For these two peaks, the dichroic ratio is close to ten and the maximum calculated tilt angle ϕ is about 15°. A scheme for the molecular arrangement is suggested in Figure 1c. (iii) The e.s.r. spectra show a triplet signal, arising from $(TCNQ^-)_2$ dimers, which is strongly dependent on the value of the angle between the normal to the support and the

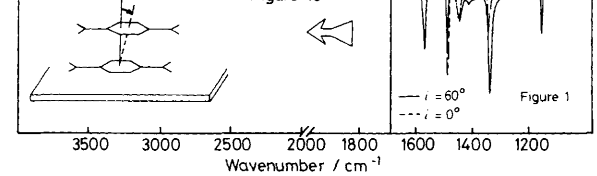

Figure 1. (a and b): i.r. linear dichroism spectra of films built up from (**1**), in the diagnostic region (1000—1700 cm^{-1}), recorded for the two different configurations $i = 0°$ and $i = 60°$. (c): A suggested scheme of the $(TCNQ^-)_2$ dimer arrangement in the polar planes of the films.
Figure 2. Typical i.r. absorption spectrum (4000—1000 cm^{-1}) of conducting films, obtained after treatment with iodine.

permanent magnetic field. A quantitative analysis of this behaviour will be reported elsewhere. (iv) As expected, the film is electrically nonconducting.

When oxidized by iodine vapour according to the process described in ref. 6, the film immediately becomes brown–purple in colour and the material incorporating iodine becomes an electrical conductor. This property is consistent with its i.r. absorption spectrum (Figure 2). The main feature of this spectrum is a broad charge-transfer absorption band centred near 2000 cm^{-1}, together with an obvious antiresonance dip in the $C\equiv N$ stretching region (2200 cm^{-1}) and two broad bands with maxima at 1260 and 1050 cm^{-1}. These latter bands originate from a_g activated i.r. modes and are considerably broadened and red-shifted as compared with the corresponding bands of the 'undoped' sample (1365 and 1184 cm^{-1}). As expected, all the dipole moments are polarized almost parallel to the substrate. A correlation between D.C. conductivity and the energy of the maximum of the charge-transfer absorption band has been suggested by Jacobsen.[3]

The behaviour of our films presents a striking analogy with dibenzo-TTF–dichloro-TCNQ (TTF = tetrathiafulvalene), for which the maximum of charge transfer absorption is situated at 2100 cm^{-1} and the D.C. conductivity at room temperature is 40 Ω^{-1} cm^{-1}. This high conductivity value is also consistent with results obtained for other ternary TCNQ salts with sulphonium cations, namely Me_2EtS^+ and Me_3S^+, the conductivities of which have been found to be 20—50 Ω^{-1} cm^{-1} at room temperature.[7] Preliminary D.C. measurements show a strong dispersion in the conductivity, and its value is often at least ten times lower than the value estimated from optical measurements. This behaviour is attributed to the polycrystalline nature of the films.

This synthetic method leads to the best conducting films so far reported.[4,6,8]

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