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LANGMUIR-BLODGETT CONDUCTING FILM AND ITS PRECURSOR.

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Abstract Recently, Ruaudel and al.¹ demonstrated that reasonably low resistivity organic conductors could be obtained after an "in situ" chemical reaction in a Langmuir-Blodgett film. In the present paper, we summarize the results and point out some questions arising from this work.

I. INTRODUCTION.

The Langmuir-Blodgett (LB) method is known to provide solid, ultrathin, periodic lamellar arrangements of especially designed amphiphilic molecules. These molecules are made of an hydrophilic group at one end of which is attached one or several hydrophobic long aliphatic chains (more than sixteen carbon atoms). Using this method, Ruaudel obtained a conducting LB film in two steps : transfer onto a solid substrate of a precursor molecule which is a charge transfer complex (namely : N-docosyl pyridinium tetracyanoquinodimethane salt) followed by a partial oxidation "in situ" by iodine vapor. The present paper summarizes new results obtained in this field.

II. EXPERIMENTAL METHOD.

The synthesis of the complex is given elsewhere ² together with details on the cleaning and precoating procedure of the substrate, the deposition conditions etc...³. We must point out that, in the charge transfer complex (CTC) used in this experiment, no aliphatic chain is attached to TCNQ⁻. N-docosyl pyridinium halogenide can form stable films on the water surface. In our particular situation, the trick lies in making use of the Coulombic interaction between the two parts of the complex : the positive amphiphilic pyridinium drags the negative TCNQ⁻ along from the water surface onto the solid substrate. In addition, TCNQ⁻ keeps a sufficient degree of freedom to stack in its own crystalline form.

III. PRECURSOR FILM.

As a first result, the precursor film is a very well organized medium as shown by ESR as well as from spectroscopic measurements.

III.a) ESR Results.

An ESR investigation of the powder of the CTC used to make spreading solutions shows a non symmetrical narrow line at $g = 2$ together with a thermally activated triplet signal arising from TCNQ⁻ dimers ³. The latter fits the Hamiltonian :

$$H = g\mu_B \vec{S} \cdot \vec{B} + D [S_z^2 - 1/3 S^2] + E [S_x^2 - S_y^2]$$

with $D = 1.37 \cdot 10^{-2} \text{ cm}^{-1}$ and $E = 2.2 \cdot 10^{-3} \text{ cm}^{-1}$.

The triplet activation energy is found to be $J = 0.14$ eV. These two signals are again present in the ESR spectra of the film but, i), they depend strongly on the orientation of the film in the magnetic field and ii), the triplet parameters are different from those in the powder. In fig. 1 is shown the dependence of the triplet spectrum with the angle θ between the normal to the substrate and the magnetic field. The θ dependence of these spectra shows that TCNQ^- dimers are organized in the film.

FIGURE 1 (left) Angular variation of the ESR triplet signal. The $g=2$ line has been suppressed.

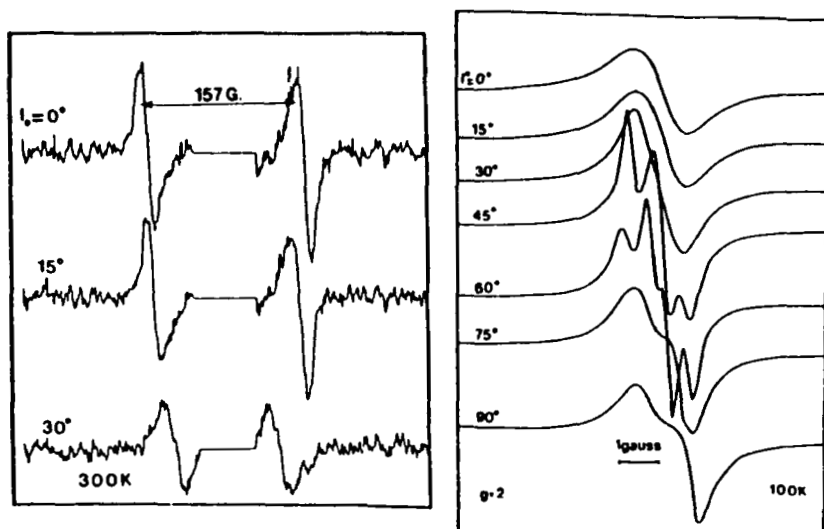


FIGURE 2 (right) Low temperature angular dependence of the $g=2$ line.

Fig. 2 shows the angular dependence of the $g = 2$ line at low temperature and again denotes a high degree of organization of this species. Integration of this ESR

signal provides an overall bandwidth which is clearly dependent on both temperature and angle i_0 . In all cases the spin resonance line width $\Delta H_{1/2}$ is minimum around $i_0 = 50^\circ$ and changes very little with temperature between 300 and 180 K. However it increases linearly with decreasing temperature at lower temperature. Finally, double integration of the ESR signal demonstrated that the spin susceptibility is roughly proportional to T^{-1} . This clearly corresponds to isolated paramagnetic species generally considered as "impurities".

III.b) Optical spectra.

A typical UV-visible spectrum ³ of a CTC LB film is shown in fig. 3. Beside a sharp peak arising from the pyridinium⁺ ion at 260 nm, two strong bands of TCNQ⁻ in the solid phase appear at 380 and 675 nm. Linear dichroism experiments show that within experimental error the dipole transition moment of the 675 nm band is parallel to the substrate. In the same manner IR linear dichroism experiments were performed over the range 1800 to 1100 cm^{-1} . The samples are highly dichroic as shown in fig. 4. Spectrum 1 was obtained at normal incidence ($i = 0$) ; spectrum 2 was recorded with linearly polarized light, electric field in the incident plane, at an incident angle $i = 60^\circ$. For the four major peaks (1580, 1505, 1350, 1180 cm^{-1}), the dichroism ratio $A = \text{Abs}_{i=60} / \text{Abs}_{i=0}$ was found to be 1.84, 0.74, 1.23 and 1.70 respectively. Clearly, the 1580, 1350 and 1180 cm^{-1} transitions are polarized somewhat out of the film plane and the 1505 cm^{-1} line lies almost in the plane. We can go further and obtain the average tilt angle, φ , between the transition dipole moment and the normal to the substrate. Using the

procedure given in ref. 4 for a non degenerate transition we derived : $\varphi = 36^\circ, 65^\circ, 45^\circ, 37^\circ$ for the 1580, 1505, 1350 and 1180 cm^{-1} peaks respectively. The spectral region of the $\text{C}\equiv\text{N}$ bonds, around 2180 cm^{-1} , also shows dichroic behaviour but it will not be discussed in this paper.

FIGURE 3 (left) UV-Vis. spectrum of insulator film.

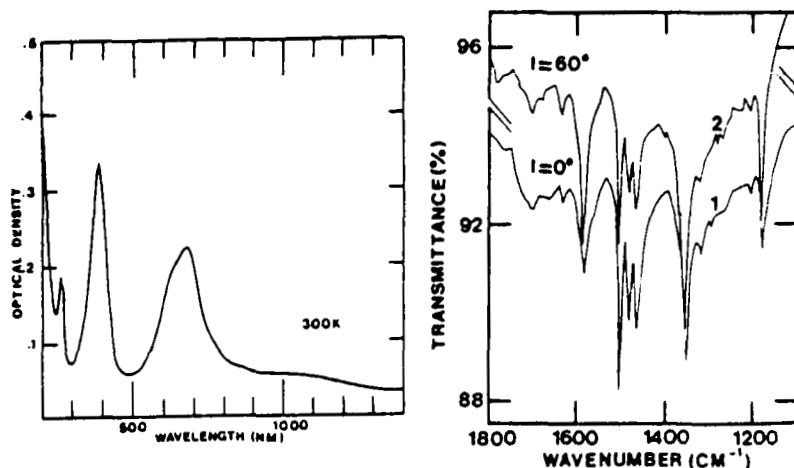


FIGURE 4 (right) IR spectra in the 1800-1100 cm^{-1} region.

IV. CONDUCTING FILMS.

Conducting films are obtained in the following way : the sample is exposed to iodine vapor. Then keeping it at ambient conditions for a few hours after iodine exposure brings an important molecular rearrangement ¹⁻² leading to a conductivity of about $10^{-1} \Omega^{-1} \text{cm}^{-1}$.

IV.a) ESR Results.

As expected the triplet signal arising from TCNQ⁻ dimers disappears. In contrast, the signal at $g = 2$ is still present and still anisotropic but less structured than that of the precursor. Rotating the sample in the magnetic field results in a peak whose width passes through a minimum (fig. 5) at an angle θ_0 close to the magic angle (54°).

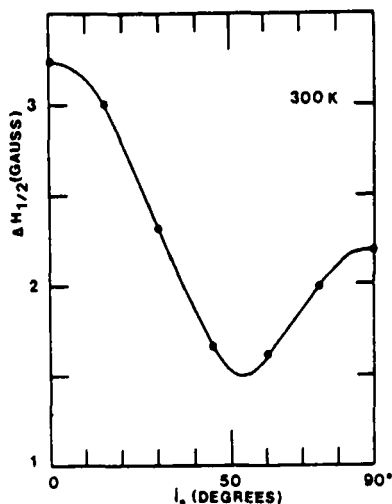


FIGURE 5. Half amplitude linewidth variation with angle θ_0 of the $g=2$ line of a conducting sample.

Down to 180 K the width was found to be temperature independent and then increased linearly with decreasing temperature⁵. In addition the magnetic spin susceptibility was found almost independent of temperature down to 100K. This last feature might be interpreted in terms of a metallic Pauli-like susceptibility but the behaviour of this signal, especially its angular dependence, is very similar to that of the precursor. Hence this $g = 2$ signal can presumably be considered as due to "impurities" or defects and the attribution of the

$g=2$ line to Pauli electrons is highly questionable.

IV.b) Electrical properties.

The very high resistance of these ultrathin samples makes DC electrical measurements particularly difficult. For example, a source impedance in the megohm range and an expected DC signal in the microvolt range make the measurement of the Hall effect quite unrealistic. The DC resistivity was measured between 300 and 120 K using a 616 KEITHLEY electrometer in order to check for the possible occurrence of a conductor to insulator, Piers-like, transition. The room temperature value of the resistivity was confirmed ⁶. Its variation, without any measurable deviation over a range of 3 orders of magnitude, is given by the expression:

$$\rho = \rho_0 e^{\Delta E/kT}, \quad \Delta E = 0.15 \text{ eV.}$$

The high resistance of the sample prevents reliable measurements at lower temperatures. No conductor to insulator transition is observed between 300 and 120 K. This semi-conductor behaviour can result from the possible but not yet established microcrystalline structure of these films. Thus no information can be obtained on the nature of the conduction mechanism.

IV.c) Optical spectra.

As opposed to electrical DC measurements with their inherent difficulties, the absorption spectroscopic method is very easy to perform on these materials due to their large area and their uniform thickness. In addition, it offers the advantage of requiring no electrodes. A typical IR spectrum of a conducting film shows three broad bands near

1150, 1320 and 1560 cm^{-1} together with a very broad one around 3000 cm^{-1} . All these bands are polarized practically in the plane of the support. This behaviour is not surprising if we keep in mind that this band (3000 cm^{-1}) is generally considered as the solid state mixed valence charge transfer excitation and related to high DC conductivity.

V. CONCLUSION.

At present, a reasonably realistic view of the structural properties of this charge transfer precursor and conducting films has been obtained. However the chemistry and the mechanism of the electronic conduction is not yet properly understood. Even the nature of the conductor (metal or narrow gap semi-conductor) is unknown and requires further investigations (electrodeless microwave electrical measurement for instance). However, this new method of LB film fabrication which gives rise to monomolecular layers of charge transfer complexes in which one of the moieties is non amphiphilic, opens the way to a new class of materials with promising properties. The method is quite general and is thought to be applicable to a number of CTC which are expected to give rise to ultrathin conducting films upon "in situ" chemical modification.

REFERENCES

1. A. Ruaudel-Teixier, M. Vandevyver, A. Barraud, Mol. Cryst. Liq. Cryst. **120** 319 (1985).

2. A. Ruaudel-Teixier, A. Barraud, M. Vandevyver, B. Belbeoch, M. Roullia, Journal de Chimie Physique, **82** n° 6 (1985).
3. A. Barraud, P. Lesieur, J. Richard, A. Ruaudel-Teixier, M. Vandevyver, Thin Solid Films. To be published.
4. M. Vandevyver, A. Barraud, A. Ruaudel-Teixier, P. Maillard, C. Gianotti. Journal of Colloid and Interface Science, **85**, 2, 571 (1982).
5. A. Barraud, P. Lesieur, A. Ruaudel-Teixier, M. Vandevyver, Thin Solid Films, to be published.
6. A. Barraud, A. Ruaudel-Teixier, M. Vandevyver, P. Lesieur Nouveau Journal de Chimie **9** n°5 365 (1985).