

Preparation of New Conducting Langmuir–Blodgett Films based on an Ethylenedithiodioctadecylthiotetrathiafulvalene Charge Transfer Complex

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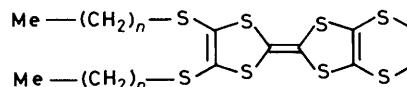
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A novel charge transfer complex of the ethylenedithiodioctadecylthiotetrathiafulvalene donor with tetrafluoro-tetracyanoquinodimethane (TCNQF₄) gives rise to conducting Langmuir–Blodgett films, after *in situ* iodine vapour treatment.

A great deal of interest has centred recently on conducting Langmuir–Blodgett (LB) films.^{1–10} To date, these films have been formed from semi-amphiphilic† tetracyanoquinodimethane (TCNQ) radical anion salts.^{1–4,9,10} The only example of conducting LB films involving a charge transfer (CT) complex has been reported by Nakamura *et al.*⁶ and Kawabata *et al.*,⁷ who have used the octadecylTCNQ–tetramethyltetrathiafulvalene (TMTTF) CT complex. Here we report an investigation into possibilities offered in the field of conducting LB films, by grafting aliphatic chains on a tetrathiafulvalene (TTF) derivative, as suggested by Saito.^{11a} We have synthesized the two ethylenedithiodialkylthioTTF molecules (1) and (2), shown in Figure 1.

We obtained (1) and (2) by cross-coupling the appropriate ketones with triethylphosphite, modifying a reported

synthetic method.^{11b} The asymmetrical TTF derivative was then isolated by chromatography on silica (eluant: n-hexane–CH₂Cl₂ in a concentration ratio 6:4). (1:1) complexes of (1) and (2) with tetrafluorotetracyanoquinodimethane (TCNQF₄) were obtained by mixing equimolar solutions of corresponding donor and acceptor in CH₂Cl₂. Details of the experimental set-up used for building LB films have been given previously, together with the cleaning procedure of the substrates.¹² The subphase used was pure Millipore grade water obtained by reverse osmosis and deionisation. As



(1) $n = 11$

(2) $n = 17$

Figure 1

† We define a semi-amphiphilic salt as one in which only the cation or the anion is amphiphilic.

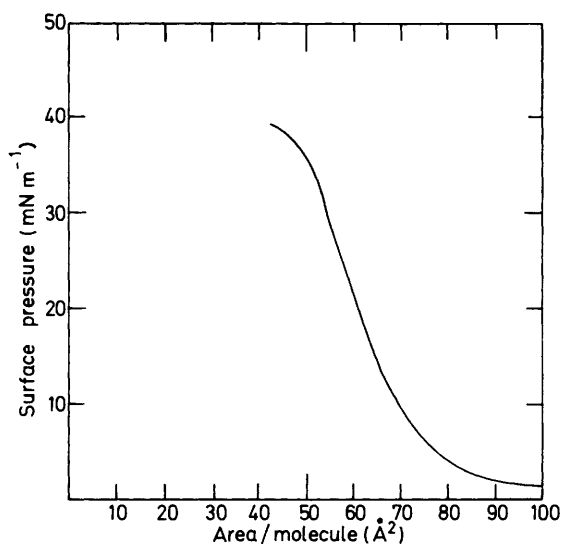


Figure 2. Typical compression isotherm (surface pressure π vs. area A per molecular complex) recorded at 21 °C in quasi-steady state conditions.

expected, (1) and (2), which are both neutral and non-amphiphilic compounds, yield completely unstable monolayers at any surface pressure. In the same way, floating films obtained from the CT complex of (1) with TCNQF₄ exhibit a poor stability for pressures beyond 20 mN m⁻¹ and are not suitable to build up true LB multilayers. This finding is not consistent with the results reported by Saito¹¹ on a similar CT complex (for which $n = 6$ instead of 11 in the present experiment). In contrast, the CT complex of (2) with TCNQF₄ forms floating films which are very stable, even for several hours, up to a surface pressure of about 38 mN m⁻¹ (collapse pressure). The typical surface pressure–area per molecule (π – A) isotherm, recorded under steady state conditions (Figure 2), does not show any plateau which could be related to a 2D \rightarrow 3D phase transition.^{13,14} Moreover, the area occupied by one molecular complex ($A = 53 \text{ \AA}^2$ for $\pi = 35 \text{ mN m}^{-1}$) is quite compatible with two alkyl chains per complex. The transfer onto a solid substrate is achieved at a constant surface pressure of 35 mN m⁻¹, with a constant transfer efficiency of *ca.* 0.8. In this way, hundred-layer-thick films, exhibiting only a small number of optically diffusing defects, can be obtained.

Structural information was obtained from X-ray diffraction experiments. The typical low angle reflection pattern exhibits a series of peaks indexed as 001 reflections, up to the fourth order. This result indicates a reasonably well-ordered lamellar structure with an interplanar spacing of $52 \pm 1.5 \text{ \AA}$. The u.v.–visible spectrum of the film (Figure 3a) exhibits three major electronic bands located at 380, 730, and 1400 nm, together with three smaller peaks at 270, 485, and 870 nm. Comparison of u.v.–visible spectra of several CT complexes of (2) with different acceptors leads us to the conclusion that these latter three peaks belong to the cation. On the other hand, the 1400 nm broad band is believed to originate from a charge transfer interaction between TCNQF₄⁻ anions, whereas the 380 and 730 nm bands are attributed to intramolecular electronic transitions within TCNQF₄⁻ anions.¹⁵ Accurate information can also be gained from the inspection of the i.r. spectrum. The diagnostic regions (2300–2000, 1650–850 cm⁻¹) are shown in Figure 4. Following Meneghetti *et al.*,¹⁶ we can readily analyse the main features of the i.r. spectrum. Firstly, the observed frequencies are typical of the TCNQF₄^{•-} radical anion, without any evidence of neutral species

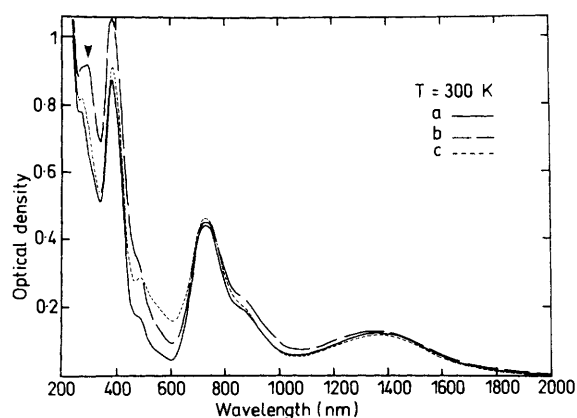


Figure 3. U.v.–visible absorption spectrum of built-up LB films of the semi-amphiphilic complex (recorded at 300 K in the 200–2000 nm range): (a) in the precursor insulating state (before iodination); (b) after the first step of treatment (exposure to iodine vapour); (c) in the conducting state (after exposure to iodine vapour and moderate heating at about 40 °C).

TCNQF₄⁰. Secondly, no a_g i.r. activated mode of vibronic origin (due to electron-molecular vibration coupling) can be detected at room temperature, hence providing a strong argument against the presence of (TCNQF₄^{•-})₂ dimers at 300 K in the LB assembly.^{16,17} Moreover, the i.r. linear dichroism method^{13,18} has enabled us to determine the average orientation of the short molecular axis of TCNQF₄^{•-} anions, which is found to lie exactly parallel to the substrate. However, the dichroic behaviour of the i.r. spectrum has yielded neither the average orientation of the long axis of this species nor that of the cation as yet. Finally, the e.s.r. spectrum exhibits a single symmetrical line in the $g = 2$ region, of width $\Delta H_{1/2} = 11.5 \text{ G}$, without any evidence of a triplet signal, arising from dimeric species.¹³ As expected, these films exhibit an insulating behaviour, due to total charge transfer between the alkylTTF derivative and TCNQF₄, which is known as a strong electron acceptor.^{15,16}

Upon iodine vapour treatment, the u.v.–visible spectrum of the films exhibits two successive changes: i, in a first step, a new band assigned to the isolated I₃⁻ species¹⁹ appears at 296 nm, while the band located at 380 nm increases markedly (Figure 3b). At this stage the films remain insulating. ii, After moderate heating at *ca.* 40 °C for a few minutes, the 296 nm band vanishes, while the 380 nm band decreases to its initial intensity. In the same time, a broad absorption peak rises between 500 and 600 nm (Figure 3c). Correlatively, in-plane direct current (d.c.) conductivity jumps to *ca.* $5 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at room temperature (assuming the conducting phase thickness to be 10 Å per bilayer²⁰).

Inspection of the i.r. spectrum of the iodine doped conducting LB films (Figure 5) strongly suggests that the TCNQF₄^{•-} species are not involved in the conduction mechanism: if they were, their characteristic bands should be strongly modified upon iodination. Figures 4 and 5 do not show any detectable variation of the narrow characteristic bands of TCNQF₄⁻, either in energy, amplitude or shape. Thus, TCNQF₄^{•+} moieties apparently remain in a fully ionic state during the iodine treatment, which prevents them from participating to the conduction process.

Investigation of the temperature dependence of the d.c. conductivity (between 292 and 85 K) points out an activation energy lower than 150 meV; such a low value rules out an ionic conduction mechanism *via* iodine. Similarly, an electronic mechanism for conduction in the iodine array would not give

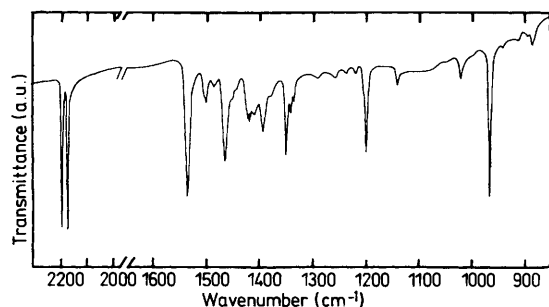


Figure 4. I.r. absorption spectrum of built-up LB films of the semi-amphiphilic complex in the diagnostic regions (2300–2000 and 1650–850 cm^{-1}), recorded at 300 K.

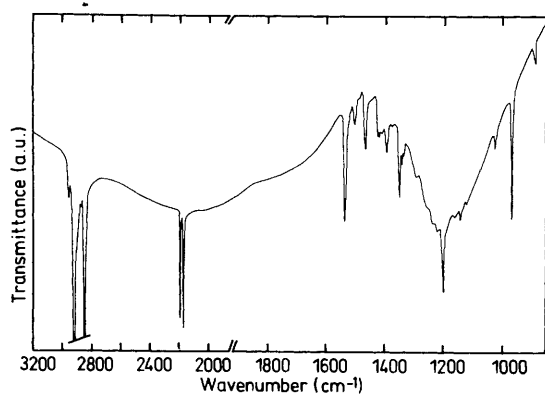


Figure 5. I.r. absorption spectrum of the iodine doped conducting LB films in the range 3200–850 cm^{-1} , recorded at 300 K.

rise to the large broad bands observed in the 3000–1000 cm^{-1} range (Figure 5), which are obviously related to charge transfer interactions arising from a mixed-valence state, as classically observed in similar, organic, conducting, CT complexes or salts.^{21–23} Finally, the I_3^- ions, which do exist in the first step of iodine treatment, do not give rise to conduction, indicating that I_3^- , physically held in the LB matrix, is unable to conduct by itself. All these results lead to the conclusion that the TTF derivative moieties are responsible for conduction mechanism.

E.s.r. measurements show a noticeable decrease of the magnetic spin susceptibility (by 5 to 10%) upon iodine treatment, which reflects the conversion of a small amount of paramagnetic radical monocation into diamagnetic (neutral or doubly charged) species. However, voltammetric experiments performed in CH_2Cl_2 solution show that the second redox potential step for (2) takes place at 0.94 V vs. s.c.e. (s.c.e. = standard calomel electrode), whereas the first redox step for iodine is below 0.6 V vs. s.c.e. This result is a strong argument against the formation of the dication during the reaction of the films with iodine, and hence against a mixed-valence state involving the dication. On the other hand, reduction of the monocation by I_3^- into the neutral species during the second step of iodination (moderate heating), which is in accordance with the decrease of I_3^- , is more likely to take place, leading to a conducting compound.

The effect of iodine vanishes very slowly in ambient atmosphere (over a few days) and more quickly *in vacuo*,

giving the insulating precursor film. However, when kept in a closed tube, the conducting films remain quite stable for ca. one month.

In addition, the analysis of linear dichroism spectra of the conducting films clearly shows that the short molecular axis of the TCNQF_4^+ species remains parallel to the substrate. This property strongly suggests that iodine treatment induces only minor changes in the molecular arrangement of the TCNQF_4^+ species. This statement is fairly consistent with X-ray diffraction measurements performed after iodine treatment, which indicate that the lamellar structure is retained with nearly the same interplanar distance ($49.5 \pm 0.5 \text{ \AA}$). Obviously, the chemical treatment has not induced a molecular reorganisation similar to that observed in LB films of semi-amphiphilic TCNQ salts.^{2,10,13,14}

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References

- 1 A. Ruau-del-Teixier, M. Vandevyver, and A. Barraud, *Mol. Cryst. Liq. Cryst.*, 1985, **120**, 319.
- 2 A. Ruau-del-Teixier, A. Barraud, M. Vandevyver, B. Belbeoch, and M. Roullay, *J. Chem. Phys.*, 1985, **82**, 711.
- 3 M. Vandevyver, A. Barraud, P. Lesieur, J. Richard, and A. Ruau-del-Teixier, *J. Chem. Phys.*, 1986, **83**, 599.
- 4 M. Vandevyver, P. Lesieur, J. Richard, A. Ruau-del-Teixier, and A. Barraud, *Mol. Cryst. Liq. Cryst.*, 1986, **134**, 337.
- 5 T. Nakamura, M. Matsumoto, F. Takei, M. Tanaka, T. Sekiguchi, E. Manda, and Y. Kawabata, *Chem. Lett.*, 1986, 709.
- 6 T. Nakamura, F. Takei, M. Tanaka, M. Matsumoto, T. Sekiguchi, Y. Kawabata, and G. Saito, *Chem. Lett.*, 1986, 323.
- 7 Y. Kawabata, T. Nakamura, M. Matsumoto, M. Tanaka, T. Sekiguchi, H. Komizu, E. Manda, and G. Saito, *Synth. Met.*, 1987, **19**, 663.
- 8 M. Matsumoto, T. Nakamura, F. Takei, T. Sekiguchi, M. Mizuno, E. Manda, and Y. Kawabata, *Synth. Met.*, 1987, **19**, 675.
- 9 A. Barraud, M. Lequan, R. M. Lequan, P. Lesieur, J. Richard, A. Ruau-del-Teixier, and M. Vandevyver, *J. Chem. Soc., Chem. Commun.*, 1987, 797.
- 10 M. Vandevyver, J. Richard, A. Barraud, A. Ruau-del-Teixier, M. Lequan, and R. M. Lequan, *J. Chem. Phys.*, 1987, **87**, 6754.
- 11 (a) G. Saito, *Pure Appl. Chem.*, 1987, **59**, 999; (b) P. W. G. Saito, K. Imaeda, Z. Shi, T. Mori, T. Enoki, and H. Inokuchi, *Chem. Lett.*, 1986, 441.
- 12 A. Barraud, P. Lesieur, J. Richard, A. Ruau-del-Teixier, and M. Vandevyver, *Thin Solid Films*, 1985, **133**, 125.
- 13 J. Richard, M. Vandevyver, P. Lesieur, A. Ruau-del-Teixier, A. Barraud, R. Bozio, and C. Pecile, *J. Chem. Phys.*, 1987, **86**, 2428.
- 14 J. Richard, Thèse de Doctorat Université Paris VI, 1987.
- 15 J. B. Torrance, J. J. Mayerle, K. Bechgaard, B. D. Silvermann, and Y. Tomkiewicz, *Phys. Rev. B*, 1980, **22**, 4960.
- 16 M. Meneghetti and C. Pecile, *J. Chem. Phys.*, 1986, **84**, 4149.
- 17 J. B. Torrance, Y. Tomkiewicz, R. Bozio, C. Pecile, C. R. Wolfe, and K. Bechgaard, *Phys. Rev. B*, 1982, **26**, 2267.
- 18 M. Vandevyver, A. Barraud, A. Ruau-del-Teixier, P. Maillard, and C. Gianotti, *J. Colloid Interface Sci.*, 1982, **85**, 571.
- 19 T. J. Marks and D. W. Kalina, in 'Extended Linear Chain Compounds 1,' ed. J. S. Miller, Plenum, New York, 1983, 222.
- 20 J. Richard, M. Vandevyver, A. Barraud, and K. Holczer, *J. Phys. D: Appl. Phys.*, 1986, **19**, 2421.
- 21 J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, 1975, **17**, 1369.
- 22 M. Meneghetti, R. Bozio, and C. Pecile, *J. Physique*, 1986, **47**, 1377.
- 23 C. Carrigou-Lagrange, R. Laversanne, and P. Delhaes, *Nouv. J. Chim.*, 1985, **9**, 379.