

## Electroactive Langmuir–Blodgett Films of *O*-Hexadecylthiocarboxytetrathiafulvalene (HDTTTF)

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The title compound forms stable, high-quality Langmuir–Blodgett films which are highly conducting after iodine doping ( $\sigma_{\max}$   $1.0 \pm 0.2$  S cm<sup>-1</sup>); the films have been characterised, in the as-deposited and doped states, by variable temperature conductivity experiments, UV/VIS, IR, and photoelectron spectroscopy, and by low-angle X-ray diffraction.

There is considerable current interest in applying the Langmuir–Blodgett (LB) technique to organise electron donor and acceptor molecules at the molecular level with the aim of producing highly conducting ultra-thin films.<sup>1</sup> In this context tetrathiafulvalene (TTF) derivatives are at the forefront of attention,<sup>2</sup> and we have recently described electroactive LB films of hexadecanoyl-TTF with maximum room-temperature conductivity values,  $\sigma_{\text{rt}} = 10^{-2}$  S cm<sup>-1</sup>, after iodine doping.<sup>2a,b,h,i</sup> In this communication we discuss the preparation and characterisation of LB films of the title compound, HDTTTF (**1**), which displays the highest in-plane conductivity reported to date for an amphiphilic TTF derivative.

Compound (**1**) was prepared directly from TTF,<sup>3</sup> and cyclic voltammetry of HDTTTF (**1**) reveals the presence of two, reversible, one-electron oxidation waves at  $E_p = +0.49$  and  $+0.86$  V (platinum electrode vs. Ag/AgCl in dichloromethane). The higher oxidation potential of HDTTTF (**1**) relative to TTF ( $E_p = +0.34$  and  $+0.78$  V) shows that the donor ability of the system is slightly reduced by attachment of the thioester chain, in agreement with the electrochemical data for acyl-substituted analogues.<sup>2a,4</sup>

A solution of compound (**1**) in chloroform ( $2.0 \times 10^{-3}$  M)

was used for spreading the molecules onto the surface of ultrapure water. A pressure vs. area curve (at  $18 \pm 2$  °C) reveals a condensed area per molecule of *ca.* 0.15 nm<sup>2</sup> (Figure 1). This is significantly less than that expected for the cross-sectional area of the molecule (assumed to be standing upright on the water surface) from a space-filling model and is even less than the cross-sectional area of a hydrocarbon chain (0.19–0.20 nm<sup>2</sup>). We suspect that this is simply due to a (very) slight solubility of the compound in the subphase. An alternative explanation is that the floating layer is more than one molecule in thickness; however, ellipsometric measurements on built-up films reveal that each transferred layer is *ca.* 3 nm thick, *i.e.*, that expected for a monomolecular layer. Y-type deposition of monolayers of (**1**) has been achieved onto hydrophobic glass substrates at a dipping pressure of 30 mN m<sup>-1</sup> and a dipping speed of 1.0 cm min<sup>-1</sup>. Films of up to 100 monolayers could readily be deposited. The deposition ratio on the up-stroke was found to be  $1.0 \pm 0.1$ ; for the down-stroke the initial deposition was significantly less (*ca.* 0.7) but improved towards unity as further layers were deposited.

Low-angle, X-ray diffraction experiments reveal that before

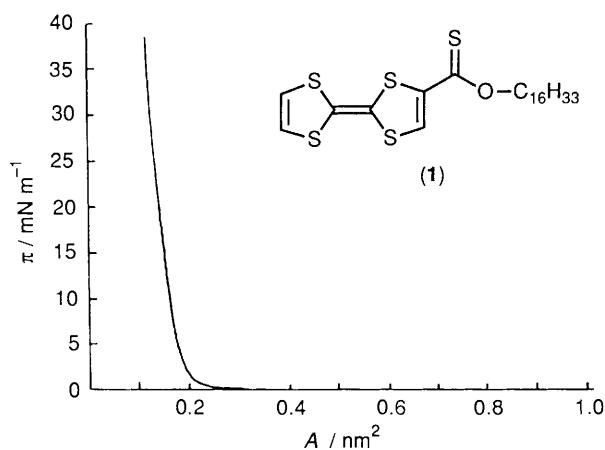


Figure 1. Surface pressure ( $\pi$ ) vs. area per molecule ( $A$ ) isotherm for HDTTTF (1).

doping, films of HDTTTF (1) consist of a single phase possessing a  $d$ -spacing of 5.9 nm; this value corresponds to  $ca.$  twice the length of HDTTTF, consistent with the observed Y-type deposition. Measurements after iodine doping show that the  $d$ -spacing is reduced to 4.0 nm, implying that the molecules become interdigitated or tilted (or both).<sup>2i</sup>

The UV/VIS solution spectrum of HDTTTF (1) exhibits absorption maxima at  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 309, 315, and 539 nm. For the as-deposited LB films, absorption bands occur at  $\lambda_{\text{max}}$  225, 305, 350 (shoulder), and 600 nm. The last band is assigned to the  $n-\pi^*$  transition, while the remaining bands are due to  $\pi-\pi^*$  transitions of the TTF ring. The absorbance of these bands varies linearly with the number of layers which is indicative of reproducible monolayer deposition (data obtained for 10, 21, 31, and 39 layers). The UV/VIS spectra of the films changed markedly upon iodine doping. Immediately after exposure to iodine vapour for 2 min in a sealed container, absorption bands at  $\lambda_{\text{max}}$  215, 300, 500 (shoulder), and 950 nm are observed. The last absorption is due to the charge-transfer (CT) band, and the other absorptions are assigned to intramolecular (LE) transitions of the conjugated  $\pi$ -system of the HDTTTF<sup>+</sup> radical cation. Two hours after doping, the spectrum of the films was significantly different: the CT band was then considerably weaker in intensity and a peak, rather than a shoulder, was visible at 500 nm.

Complementary changes are observed in the transmission IR spectra of HDTTTF films upon iodine doping (Figure 2a–c). Before doping, the C=S band is present at 1250  $\text{cm}^{-1}$  (Figure 2a); this band shifts immediately upon doping to higher wavenumber, which is consistent with oxidation having occurred, *i.e.* HDTTTF<sup>0</sup>  $\rightarrow$  HDTTTF<sup>+</sup>. Furthermore, a new, sharp band appears at 1350  $\text{cm}^{-1}$  in Figure 2b, which is explained by the strong coupling of electrons to the vibrational modes of molecule (1) allowing previously inactive IR bands to become active.<sup>5</sup> A strong, broad CT band also appears at  $\nu_{\text{max}}$  5000  $\text{cm}^{-1}$ . Two hours after doping, the CT band shifted markedly to  $\nu_{\text{max}}$  2500  $\text{cm}^{-1}$ , the 1350  $\text{cm}^{-1}$  band was considerably weaker, and the C=S band exhibited shoulders (Figure 2c).

The lateral DC conductivity of the as-deposited films of HDTTTF is  $\sigma_{\text{rt}} = 4 \times 10^{-2} \text{ S cm}^{-1}$ . This is a remarkably high value for an undoped film (*cf.*  $\sigma_{\text{rt}} = 10^{-15} \text{ S cm}^{-1}$  for compressed pellets of HDTTTF) and we cannot exclude a contribution from ionic conductivity. Immediately after exposing the LB films of compound (1) to iodine vapour for 1

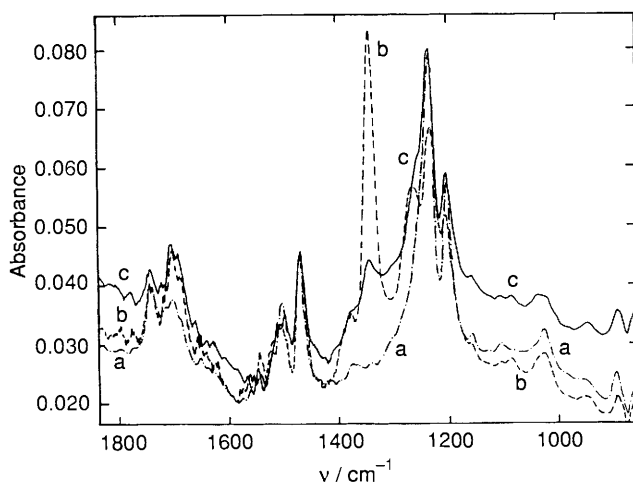
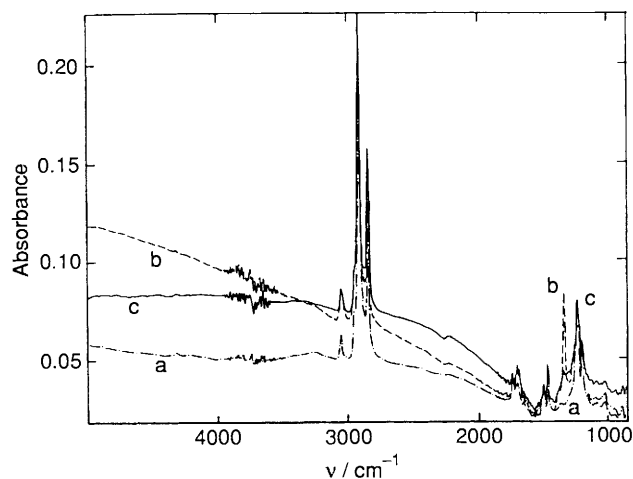


Figure 2. Transmission IR spectra of LB films of compound (1) (96 layers), including an expansion of the 1800–900  $\text{cm}^{-1}$  region; (a) before doping, (b) 5 min after doping, (c) 2 h after doping.

min, the conductivity value dropped to  $\sigma_{\text{rt}} = 10^{-4} \text{ S cm}^{-1}$ . Then, following this doping procedure, the conductivity increased with time reaching a maximum value after 2 h of  $\sigma_{\text{rt}} = 1.0 \pm 0.2 \text{ S cm}^{-1}$ . After 24 h the value was  $\sigma_{\text{rt}} = 0.3 \text{ S cm}^{-1}$  which remained approximately constant after storage of the films in air for several weeks. The activation energy measured between 300 and 100 K, 2–4 h after doping, was  $E_a = 0.09 \text{ eV}$ , suggesting an electronic, rather than an ionic, conduction process. Combining these conductivity and spectroscopic data, we suggest that immediately upon doping an unstable, highly oxidised, system is formed which decomposes with time giving rise to a stable mixed-valence system HDTTTF<sup>x+</sup> I<sub>3</sub><sup>-</sup> [or HDTTTF<sup>x+</sup> (I<sub>3</sub><sup>-</sup>)<sub>x</sub>], where  $x < 1$ , which is highly conducting.

X-Ray photoelectron (XP) spectroscopy also provides evidence that a charge-transfer salt is formed upon iodination of films of compound (1). All the sulphur in the undoped and doped films is present as divalent sulphur, consistent with formula (1). The S<sub>2p</sub> XP feature at 164.2 eV in the undoped films shifts to higher energy, 164.4 eV, in the doped films, which is consistent with oxidation occurring in the TTF system. Data obtained immediately after doping are consistent with the presence of one I<sup>-</sup> species for every six TTF units. However, this is almost certain to be an underestimate of the

dopant level as it is inevitable that some iodine had been lost in the vacuum system before the measurement could be completed.

We thank SERC for financial support.

Received, 19th March 1990; Com. 0/01186J

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