Electronic, Structural, and Spectroscopic Properties of Langmuir–Blodgett Films of (*O*-Hexadecylthiocarboxy)tetrathiafulvalene (HDTTTF)

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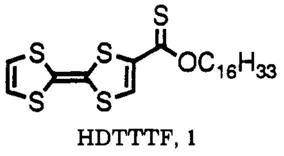
The title compound forms Langmuir–Blodgett (LB) films which, after doping with iodine, are among the most highly conducting LB films reported for a charge-transfer salt (the in-plane value of the room-temperature conductivity is $\sigma_{rt} = 1.0 \pm 0.2$ S cm^{-1}; thermal activation energy, $E_a = 0.09$ eV). The electronic, structural, and spectroscopic properties of these films are discussed. Low-angle X-ray diffraction reveals that, as deposited, the layers are organized in head-to-head and tail-to-tail configuration (i.e., Y-type deposition). On doping with iodine, the X-ray *d* spacing decreases significantly, implying interdigitation of the molecules. Infrared spectroscopy confirms the formation of a charge-transfer band for the iodine-doped multilayers and reflection/absorption infrared spectra (RAIRS) and attenuated total reflection (ATR) spectra imply that the TTF ring and the side chain are both aligned at a high angle to the substrate surface. Experiments using X-ray photoelectron spectroscopy and UV–visible absorption spectroscopy are consistent with the conducting properties of these films being due to the formation of a mixed-valence charge-transfer complex of formula HDTTTF$^{+\cdot}(I_3^-)_x$, where $x < 1$.

Introduction

There is now a sustained interest in the characterization of low-dimensional organic conductors formed by charge-transfer salts.[1] A new direction for research in this field is emerging with the application of the Langmuir–Blodgett (LB) deposition technique to organize the constituent donor and acceptor molecules at the molecular level.[2] Initial work concentrated on LB films formed by salts of the acceptor tetracyano-*p*-quinodimethane (TCNQ); in these materials a long hydrophobic chain was attached either to the TCNQ molecule[3] or to its counterion, e.g., a pyridinium cation,[4] sulfonium cation,[5] or tetrathiafulvalene (TTF) derivative radical cation.[6] More recently the focus of attention has moved to amphiphilic donor molecules that form LB films. Lateral room-temperature conductivity values of 10^{-3}–10^{-1} S cm^{-1} have been reported for films of several derivatives of bis(ethylenedithiolato)tetrathiafulvalene (BEDT-TTF),[7] tetrathiotetracene (TTT),[8] and TTF[9] that are either doped with iodine or complexed with TCNQ or TCNQF$_4$.

In the present paper we discuss the characterization of LB films of the title TTF thioester derivative (1, HDTTTF). We have used the techniques of variable-temperature conductivity, UV-visible absorption spectroscopy, attenuated total reflection (ATR) and reflection/absorption infrared spectroscopy (RAIRS), low-angle X-ray diffraction, and X-ray photoelectron spectroscopy (XPS) to investigate the molecular arrangements of the multilayer samples. Notably, doped films of thioester 1 display the highest in-plane conductivity reported to date for an amphiphilic TTF derivative.[10]



HDTTTF, 1

Experimental Section

Synthesis. The synthetic procedure for the formation of TTF

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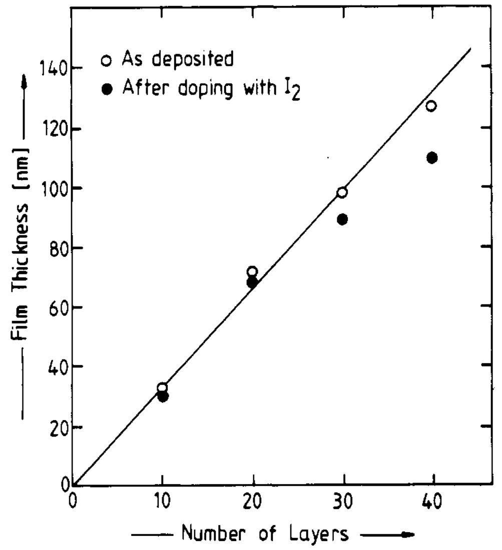

Figure 1. Ellipsometric data for LB layers of HDTTTF (1).

derivative 1 from monolithiated TTF has been described previously.[11]

LB Film Formation. Compound 1. A solution of compound 1 in chloroform (2.0×10^{-3} M) was used for spreading the molecules onto the surface of ultrapure water (obtained by reverse osmosis, deionization, and ultraviolet sterilization). The pressure versus area isotherm has been given previously.[10] Multilayers were deposited in Y-type manner onto zinc selenide, calcium fluoride, or silver-coated glass slides at a dipping pressure of 30 mN m^{-1} and a dipping speed of 1.0 cm min^{-1}. Films of up to 100 monolayers could be deposited. For compound 1 the deposition ratio on the upstroke was 1.0 ± 0.1; for the downstroke the initial deposition was considerably less (ca. 0.7) but improved toward unity as further layers were deposited.

Doping was achieved by exposing the LB films to either iodine or bromine vapor for 2 min in a sealed container.

Characterization. IR spectra were recorded using a Mattson-Sirius 100 Fourier transform spectrometer; θ_{inc} for RAIRS spectra was 86 ± 2°. UV-visible absorption measurements were performed with a Cary 2300 spectrophotometer. XPS measurements were made using a Kratos ES 300 XPS spectrometer using Mg Kα X-rays and a Kratos DS 300 data system. A Rudolf Research Auto EL IV ellipsometer was used to measure the LB thickness. Low-angle X-ray diffraction studies were carried out at the Institute of Crystallography in Moscow: the position-sensitive X-ray diffractometer was purpose built and used Ni-filtered Cu Kα radiation; the X-ray beam was collimated by a three-slit collimator.

Conductivity studies were undertaken using a two-probe technique. The electrical contacts to the film were made using air-drying silver paste. Room-temperature measurements were made in a screened sample chamber, evacuated to a pressure of approximately 10^{-2} mbar using a rotary pump. Measurements over the temperature range 100–300 K were made in helium, in an Oxford Instruments exchange gas cryostat. The voltage source in these experiments was a Time Electronics voltage calibrator and the current was monitored using a Keithley picoammeter.

Results and Discussion

Film Thickness Determination. Figure 1 shows how the film thickness, measured by ellipsometry at a wavelength of 633 nm, varies with the number of LB layers; data are presented for both before and (a few hours) after doping with iodine vapour. Before doping, the average thickness per layer was 3.25 nm. However, after exposure to iodine vapor, the thickness appears to have decreased slightly, to a value of approximately 2.75 nm/monolayer for the 40-layer film. Low-angle X-ray diffraction results are presented in Figure 2; the three sets of data have been obtained for an as-deposited film (31 layers), the film 1 min after iodine doping, and the same film 2 h later. The *d* spacing for the undoped film is calculated to be 5.85 nm, giving the thickness per layer (assuming head-to-head and tail-to-tail packing of the molecules) as 2.93 nm. This value is decreased slightly 1 min after doping; 2 h later the *d* spacing has decreased to 4.0 nm, corresponding to a monolayer thickness of 2.0 nm. Some additional Bragg peaks, for the as-deposited film and for the film measured immediately after doping, were also apparent in our X-ray data; the most pronounced are indicated by arrows in Figure 2. These corresponded to an additional phase (estimated as 3% of the sample volume) with a *d* spacing of 7.3 nm.

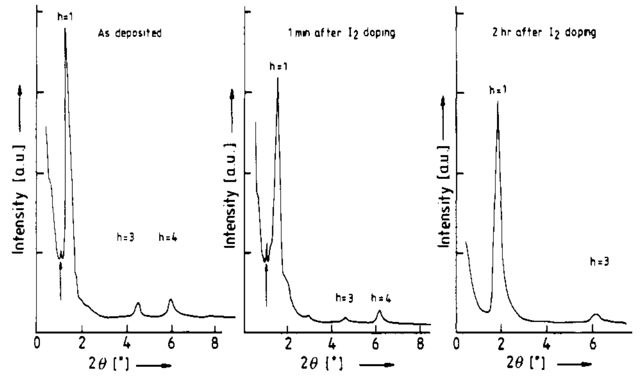

Figure 2. Low-angle X-ray diffraction data for 40 LB layers of HDTTTF (1) deposited onto glass, λ = 0.154 nm.

For the undoped film, the monolayer thickness revealed by both the X-ray and ellipsometric experiments are similar. The value obtained from the X-ray experiment is probably the most accurate. This is also consistent with that expected from the length of the HDTTTF molecule (calculated to be ca. 3.4 nm from a space-filling molecular model) and suggests that, in the case of the as-deposited film, both the long axis of the TTF moiety and the hydrocarbon chain are aligned at ca. 60° to the substrate surface. Immediately after the iodine treatment, this structure is preserved. However, the X-ray measurements reveal that some molecular rearrangement subsequently occurs, with a resulting reduction in the *d* spacing. We have previously reported a similar situation for LB layers of hexadecanoyl-TTF[9d] and have suggested that, upon doping, the molecules became interdigitated and/or tilted. It should be noted that the same degree of film thickness change is not observed in the ellipsometric experiment, implying that the doped film probably contains a significant proportion of voids.

Infrared Spectroscopy. The IR spectra for 20 layers of compound 1 (as deposited) have been obtained as attenuated total reflection (ATR), transmission (TA), and reflection/absorption (RAIRS) spectra (Figure 3). (RAIRS spectra couple only transition dipoles perpendicular to the substrate.) The prominent IR bands in the transmission spectrum have been assigned as follows, by analogy with data reported previously for TTF[12] and hexadecanoyl-TTF:[9e] 3057 ν (C–H) of TTF, 2955 $\nu_{as}(CH_3)$, 2920 $\nu_{as}(CH_2)$ 2855 $\nu_s(CH_2)$, 1524 and 1505 [central and cyclic ν(C=C), respectively, of the TTF ring], 1472 $\delta(CH_2)$, 1242 ν(C=S),

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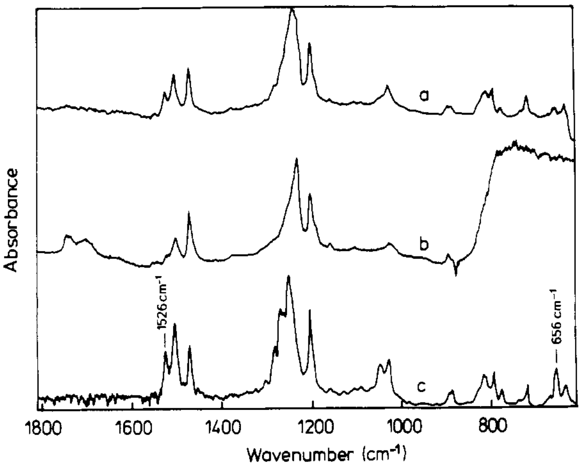

Figure 3. IR spectra of LB films (20 layers) of compound 1 as deposited: (a) attenuated total reflection (ATR); (b) transmission; (c) reflection/absorption (RAIRS), 1800–600-cm^{-1} region.

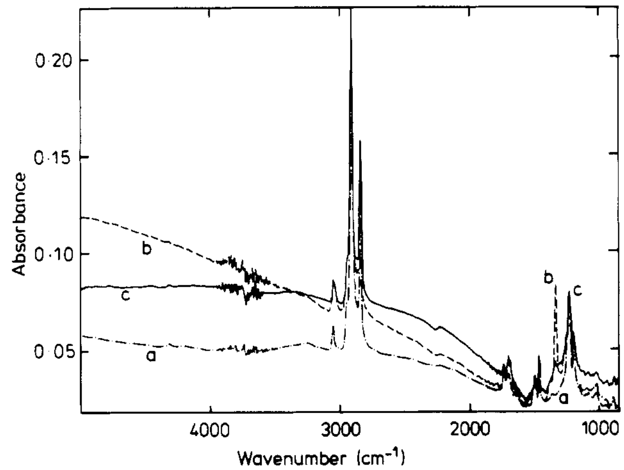

Figure 4. Transmission IR spectra of LB films of HDTTTF (1) (96 layers): (a) before doping; (b) 5 min after doping; (c) 2 h after doping.

and 1204 cm^{-1} [ν(C–O–C)]. From a comparison of the ATR, TA, and RAIRS spectra of LB films of 1 it can be seen that, relative to the absorptions in the lower frequency region, the $\nu(CH_2)$ vibrations are the strongest in the transmission spectrum and they become progressively weaker in ATR and RAIRS spectra. This implies that the chains are aligned at a high angle to the substrate surface. More conclusive evidence for this molecular orientation is provided by examination of the absorption due to the central C═C bond of the TTF framework. This band at 1526 cm^{-1} is significantly stronger in RAIRS than in ATR (cf. Figure 3a,c). By assuming the transition dipole moment of the ν(C–O–C) mode is along the chain orientation and that of $\nu_{as}(CH_2)$ is perpendicular to the chain, the orientation of the chain can be estimated using the method reported previously[15] to be 53 ± 5° to the substrate surface. These calculations do not provide information on the orientation of the TTF moiety. There is, therefore, agreement within experimental error, of the IR data with the X-ray and ellipsometric results reported above.

The transmission IR spectra obtained before and after doping the film of thioester-TTF compound 1 with iodine are shown in Figure 4 and 5. A number of changes become apparent immediately after the doping process. A striking feature is the appearance of a charge-transfer absorption band extending from ca. 1600 to beyond 4000 cm^{-1} (Figure 4). A similar band has been reported previously for iodine-doped LB layers of pyridinium-TCNQ complexes and other TTF systems.[9c,d] Before doping, compound 1 exhibits a strong absorption at ca. 1250 cm^{-1} (Figure 5a) which is assigned to the C═S group, probably in combination with the C–H in-plane bending mode of the TTF ring (which occurs at 1255 cm^{-1} for TTF[12b]). This band shifts immediately upon doping to ca. 1270 cm^{-1} which is consistent with oxidation having occurred at the TTF ring to yield the radical cation species 1. After 5 min the reemergence of the 1250-cm^{-1} band is apparent (Figure 5b). Furthermore, a new intense band centered at 1346 cm^{-1} appears upon doping (Figure 5b) which is explained by the strong coupling of electrons to the vibrational modes (vibronic coupling) of compound 1 allowing a previously inactive IR band to become active.[12a] This band at 1346 cm^{-1} is stronger in ATR than in RAIRS, indicating that the TTF planes are at a high angle to the substrate surface. The spectrum taken 2 h after doping is again quite different. There is a considerable reduction in intensity of both the conduction band and the charge-transfer band; 50 h after doping the conduction band has disappeared and the intensity of the charge-transfer band is further reduced.

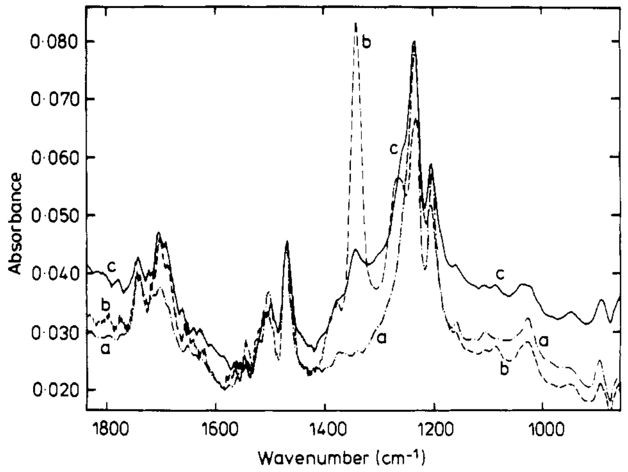

Figure 5. As in Figure 4, expansion of the 1800–900-cm^{-1} region.

An interesting feature of these spectra of compound 1 concerns the effect of doping on the $\delta(CH_2)$ band of the hydrocarbon chain, which is observed at 1472 cm^{-1}. Doping the LB films with iodine or bromine resulted in no observable change in this region of the spectrum. This suggests that the ordering and orientation of the hydrocarbon chains of thioester (compound 1) are not significantly altered by the doping process. This contrasts with the results of similar experiments on the acyl analogue (hexadecanoyl-TTF) which indicate that a change in the packing of the (C_2H_4) subunits in the alkyl chain occurs upon iodination.[9e] Thus the IR data seem to support the view that the observed decrease in *d* spacing upon doping is the result of an interdigitation rather than a tilting of the HDTTTF molecule.

UV–Visible Spectroscopy. The UV–vis solution spectrum of compound 1 exhibits two strong absorption maxima at λ_{max} (CH_2Cl_2) 309 and 315 nm (molar extinction coefficients $\epsilon = 6 \times 10^3$ dm^3 mol^{-1} cm^{-1}) together with a broad, weaker band at λ_{max} 539 nm ($\epsilon = 2.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The bands near 300 nm can be assigned to the lowest π–π* intramolecular transitions of the highly conjugated π-system of the molecules, while the longer wavelength band may be attributed to the orbitally- or symmetry-forbidden n–π* transitions of compound 1.

Figure 6 shows the UV–visible-near-IR spectra for LB films of compound 1. For the as-deposited films absorption bands occur at λ_{max} 225, 305, 350 (shoulder), and 600 nm. This spectrum (Figure 6a) is, therefore, qualitatively sim-

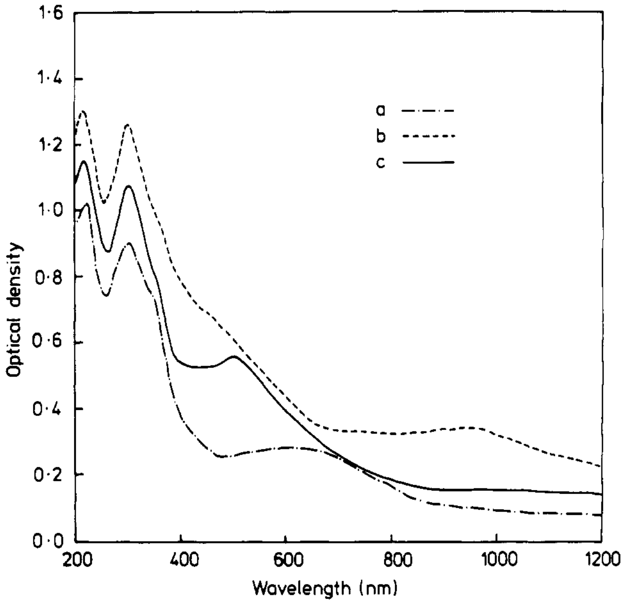

Figure 6. UV visible spectra of LB films of compound 1 (96 layers): (a) before doping; (b) 5 min after doping; (c) 4 h after doping.

ilar to the solution spectrum (see above) except that no structure is seen in the UV absorption band and there is weak absorption at ca. 800 nm, i.e., beyond the absorption range of neutral TTF,[13] possibly implying the presence of a small amount of $TTF^{•+}$ in the film. Iodination has a marked effect on the absorption spectrum of the LB film. Spectrum 6b, recorded immediately after doping, shows absorption bands at λ_{max} 215, 300, 500 (shoulder), and 950 nm. The last absorption is due to the conductivity band (cf. Figure 4b), and the other absorptions are assigned to intramolecular (LE) transitions of the conjugated π-molecular system of the $HDTTTF^{•+}$ radical cation. Four hours after doping (Figure 6c) the spectrum of the films was strikingly different: the intensity of the CT band was considerably reduced and a peak, rather than a shoulder, was present at 500 nm. The optical density of the bands at 225, 305, and 605 nm (Figure 6a) scale approximately linearly with the number of layers in the LB assembly which is indicative of reproducible monolayer deposition (data obtained for 10, 21, 31, and 39 layers). A similar linear relationship between optical density and number of layers is observed for the bands at 215 and 300 nm (Figure 6b) data for the same number of layers); thus we conclude that the doping is uniform throughout the 39 layers.

Similar initial changes to the UV spectrum were observed on doping films of compound 1 with bromine, but in contrast to iodine-doped films, there was no further change with time.

X-ray Photoelectron Spectroscopy. Experiments on HDTTTF (1) have been performed on powdered samples and LB films (nine layers) before and after doping. Examination of the $S(2p_{3/2},2p_{1/2})$ XP spectra of a powdered sample reveals two distinct sulfur environments (Figure 7a) at ca. 164 and 162 eV with the expected intensity ratios of 4:1, arising from the four heterocyclic sulfur atoms and the one thioester sulfur atom, respectively, of compound 1. The as-deposited LB films of 1 exhibit a marked change in the $S(2p_{3/2},2p_{1/2})$ peak shape (Figure 7b): the thioester component is now overlapped by the more intense signal from the four heterocyclic sulfur atoms. This indicates that the two types of sulfur environment are more similar in chemical character in the LB film than in the powder. The LB film was not totally free of pinholes since some silicon was also detected from the glass substrate.

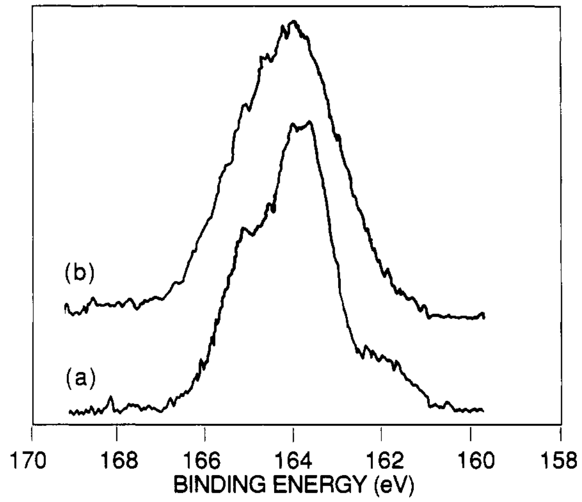

Figure 7. $S(2p_{3/2},2p_{1/2})$ XPS region of (a) powder HDTTTF (1) and (b) HDTTTF LB film.

Upon iodine doping of both the powder and the LB film there is a shift in the overall peak shape toward higher binding energies which is consistent with oxidation of the TTF system having occurred upon doping. It is noteworthy that all the sulfur atoms in these samples are present as divalent sulfur with no evidence for the presence of any sulfoxide group.

The $I(3d_{5/2})$ XPS spectrum of the LB layers immediately after doping was examined. The ratio of C:O:S:I was found to be 6.50:0.95:1.00:0.05, which implies the presence of one iodine atom for every four HDTTTF molecules. Most of the iodine (ca. 74%) is present as I^- (binding energy of 618.9 eV) with a shoulder at 620.6 eV which is indicative of covalently bonded iodine (presumably in the form of I_3^-). Thus, there is approximately one I^- species per six TTF units. However, these values are almost certainly underestimates of the levels of iodine dopant in the films as it is unavoidable that some iodine had been lost in the vacuum system before the measurement could be completed.

Conductivity Studies. The lateral dc conductivity of the as-deposited LB films of HDTTTF (10–30 layers) is $\sigma_{rt} = 4 \times 10^{-2}$ S cm^{-1} (cf. $\sigma_{rt} = 10^{-15}$ S cm^{-1} for compressed pellets of HDTTTF). By varying the distance between the electrodes, it was established that the effect of contact resistance was negligible. No anisotropy of conductivity was found in the film plane. Such a high conductivity value for an LB assembly of neutral molecules is unprecedented. An ionic conduction process may be responsible; however, it is more likely that a small amount of adventitious doping, by an unidentified oxidant, could have occurred during the LB deposition procedure and that electronic conductivity was being measured. It is extremely unlikely that the oxidizing agent is derived from the solvent chloroform used for monolayer spreading, as use of this solvent has not resulted in high conductivities for the as-deposited films of similar amphiphilic charge-transfer materials.[9] It should be emphasized that IR and X-ray photoelectron spectroscopy of the as-deposited films provide no evidence for any oxidation of the TTF system 1 having occurred at this stage, although the UV spectra,

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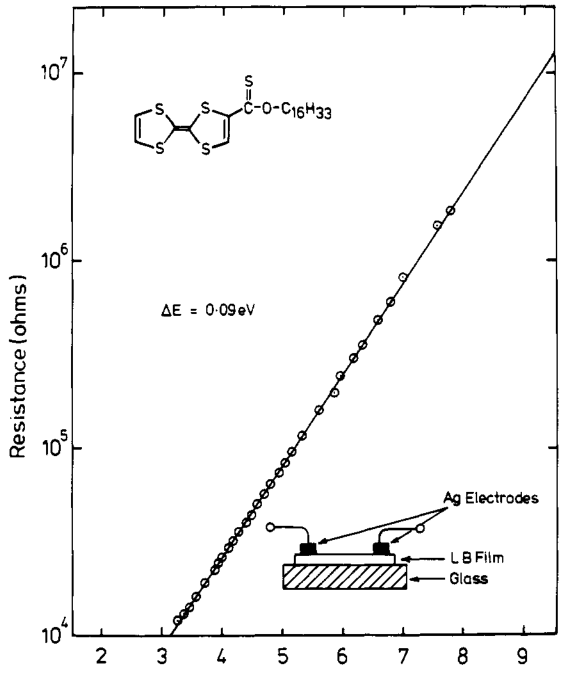

Figure 8. Activation plot for 40-layer HDTTTF LB film doped with iodine vapor.

discussed above, are less clear on this point.

Exposure of the LB films of HDTTTF (1) to iodine vapor for 1–2 min led to an immediate drop in the conductivity value to $\sigma_{rt} = 10^{-4}$ S cm^{-1}. Subsequently there was a steady rise in the conductivity to reach a maximum value after 2 h of $\sigma_{rt} = 1.0 \pm 0.2$ S cm^{-1}. This represents one of the highest values reported for LB films of a TTF or TCNQ system. Twenty-four hours after doping the conductivity had declined to a value of $\sigma_{rt} = 0.3$ S cm^{-1}, which remained essentially unchanged after storing the doped film in air for several weeks. However, storage for a few months resulted in a decrease in the conductivity value by a factor of 2 or 3.

Variable temperature conductivity data were obtained for the films 2–4 h after doping, and typical semiconducting behavior was observed (Figure 8). Over the temperature range 300–100 K the films exhibited a linear current versus voltage relationship; the activation energy for conductivity is $E_a = 0.09$ eV which is the lowest value that has been reported for LB films of a TTF derivative.[9] (French workers report $E_a = 0.08$ eV for LB films of a CT complex of BEDT-TTF derivative and TCNQF$_4$.[7b])

When LB films of HDTTTF (1) were doped with bromine, the conductivity value dropped to $\sigma_{rt} = 10^{-4}$ S cm^{-1}, as with iodine doping, but the conductivity of the bromine-doped films did not then increase with time. This conductivity behavior upon halogen doping, which is qualitatively similar to that which we have reported previously for LB films of acyl-TTF system (2),[9a,b] is entirely consistent with the spectroscopic data discussed above.

We infer that HDTTTF molecules in the LB films are oxidized fully to ion radical salts of formulae HDTTTF$^{\bullet+}$(I$_3$)$^-$ (I$_3^-$ is in equilibrium with I$_2$ + I$^-$, as revealed by XPS) and HDTTTF$^{\bullet+}$Br$^-$ immediately upon exposure to either iodine or bromine vapor. This iodine-doped salt decomposes over a few hours to give a more-stable partially-oxidized (mixed valence) salt of type HDTTTF$^{\bullet+}$(I$_3^-$)$_x$, where $x < 1$, which gives rise to the high conductivity of the iodine-doped films. In contrast to this behavior, the salt formed upon bromine doping is thermally more stable and does not give rise to a significant amount of a mixed valence complex; thus the conductivity of the bromine-doped films does not increase with time. This hypothesis is based on previous studies on a series of crystalline TTF-halide systems; high conductivity was observed for mixed valence salts, e.g., TTF$^{\bullet+}$(X)$_x^-$ (X = Cl or Br, $x < 1$) whereas stoichiometric salts, e.g., TTF$^{\bullet+}$X$^-$ (X = Cl or Br), were (relatively) insulating.[14]

Conclusions

In this work we have reported the use of a number of techniques to probe the structure of Langmuir–Blodgett layers of a long-chain tetrathiafulvalene compound, which upon doping with iodine are highly conducting. Low-angle X-ray diffraction demonstrates that the molecules reorganize when the film is exposed to iodine, probably taking up a structure in which the HDTTTF molecules are interdigitated. Spectroscopic studies reveal a charge-transfer band in the doped films for which a mixed-valence system, HDTTTF$^+$(I$_3^-$)$_x$, $x < 1$, is considered to be responsible for the conducting properties.

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Registry No. HDTTTF, 128881-62-9; I$_2$, 7553-56-2.

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