Langmuir–Blodgett films of a tetrathiafulvalene derivative substituted with an azobenzene group

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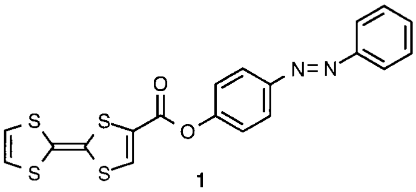
The new tetrathiafulvalene derivative **1**, functionalised with an azobenzene substituent, has been synthesised. Cyclic voltammetric and spectroelectrochemical studies in solution demonstrate the reversible formation of the radical cation of **1**. UV–VIS spectroscopy suggests that there is a weak interaction between the TTF and azobenzene moieties in compound **1**, and demonstrates that *trans–cis* isomerisation occurs upon photolysis of the azobenzene substituent. Semi-conducting LB films of **1** have been assembled without the need for added fatty acid: room temperature conductivity values of the films before and after doping with iodine vapour were $\sigma_{rt} = 10^{-3}$–10^{-5} S cm^{-1} and 2×10^{-2}–10^{-3} S cm^{-1}, respectively. No change in the conductivity of the LB films was observed under irradiation.

Tetrathiafulvalene (TTF) derivatives have attracted considerable interest in recent years as a number of their crystalline cation-radical salts are molecular metals and superconductors.[1–5] In order to achieve high conductivity in thin films,[6] several amphiphilic analogues of TTF have been prepared and their Langmuir–Blodgett (LB) films built up. These generally exhibit in-plane direct current (dc) room temperature conductivity values in the range $\sigma_{rt} = 10^{-3}$–10^{-1} S cm^{-1} after formation of a mixed valence state by doping with iodine vapour,[7,8] although higher conductivities, $\sigma_{rt} =$ *ca.* 1 S cm^{-1}, have been achieved with a few derivatives.[9,10]

In the present work we report on the properties of compound **1** in solution and in LB films. This compound is a novel non-amphiphilic derivative of TTF.



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Based upon experimental and theoretical data for related TTF–C(O)R derivatives (R = OBu and NMe$_2$)[11] the electron-withdrawing ester group attached to the TTF ring in compound **1** should increase the polar nature of the TTF ring system, which presumably serves as the hydrophilic portion of the molecule, while the aromatic rings replace the 'traditional' hydrophobic alkyl chain(s). This present study is timely in the light of current interest in the formation of LB films of charge-transfer materials which do not possess long alkyl chains. In this context, we have recently reported the formation of conductive LB films of three derivatives of ethylenedithio-TTF (EDT-TTF) bearing aromatic substituents (phenyl, pyridyl and pyridinium); for these compounds 25 mol% of fatty acid was needed to stabilise monolayer formation.[12,13] Other examples of non-amphiphilic TTF materials which form LB films are (PhCH$_2$S)$_4$TTF, which did not form a stable monolayer at the air–water interface unless at least 50% mole ratio of a fatty acid was added,[14] and a bis(EDT-TTF) derivative, which did not require the addition of any fatty acid.[15]

The azobenzene group was incorporated into compound **1** because azo derivatives are known to undergo photochemical *cis–trans* isomerisation in LB films and this reaction can be monitored electrochemically.[16–19] Moreover, for pyridinium–TCNQ LB films, where the pyridinium moiety was substituted with an azobenzene derivative, Matsumoto *et al.*[18] reported a 30% conductivity change upon photochemical isomerisation of the azo group in the LB film. A polypyrrole copolymer film, where polypyrrole was substituted with an azobenzene group, is reported to change its conductivity by up to 50% under illumination; however, the authors of this work concluded that the conductivity change was not triggered by isomerisation of the azo group.[20]

Experimental

Synthesis

Compound **1** was synthesised as follows. Equimolar quantities of 4-phenylazophenol (Aldrich) and triethylamine were dissolved in dichloromethane. After 10 min, a solution of tetrathiafulvalenecarbonyl chloride [TTF–C(O)Cl] (prepared from tetrathiafulvalene carboxylic acid,[21] by a modification of the literature procedure)[22] in dichloromethane was syringed into the solution, and the mixture was stirred at room temp. for 12 h. The mixture was then acidified with 2 M aqueous HCl; the organic layer was separated, washed with water and dried (MgSO$_4$). The solvent was evaporated *in vacuo* and the residue was chromatographed on a neutral alumina column (eluent dichloromethane) to afford compound **1** as a purple solid in 51% yield, mp 148 °C (Found: C, 52.9; H, 3.0; N, 6.2. $C_{19}H_{12}N_2O_2S_4$ requires: C, 53.2; H, 2.8; N, 6.5%); *m/z* (DCI) 429 (M$^+$ + 1); δ_H (200 MHz, CDCl$_3$) 7.99 (2H, dd), 7.92 (2H, dd), 7.63 (1H, s), 7.52 (3H, m), 7.33 (2H, dd) and 6.37 (2H, s).

Characterisation

Cyclic voltammetry (CV) was performed using an EG&G PARC model 273 potentiostat with an Advanced Bryans XY recorder. Pt mesh served as the counter electrode, a saturated calomel electrode (SCE) served as the reference electrode in

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$HClO_4$ solution, and Ag wire as the quasi-reference electrode in acetonitrile solution. Potentials for solution CV were corrected to Ag/AgCl with the ferrocene/ferrocenium couple as the internal reference (+0.35 V *vs.* Ag/AgCl). CV in solution was performed in 0.2 M Bu_4NPF_6–acetonitrile on a Pt disk working electrode (1.6 mm diameter, Bioanalytical System Inc.) employing IR compensation. Bu_4NPF_6 (Fluka, electrochemical grade), $HClO_4$ (Aldrich, ACS reagent), acetonitrile (Aldrich, HPLC) and ultrapure water were used for preparation of the electrolyte solutions.

Spectroelectrochemistry was undertaken using a Perkin-Elmer Lamda 19 spectrometer with a Ministat (Thomson Electrochem. Ltd, Newcastle upon Tyne, UK) using a 0.2 M Bu_4NPF_6–acetonitrile solution of compound **1**. The spectroelectrochemical cell was based on a 1 cm thick cuvette; Pt wire was used as the counter electrode, while Ag wire (with a potential approximately equal to that of Ag/AgCl in this solution) served as a quasi-reference. Thin layer electrodes were constructed from indium tin oxide (ITO, sheet resistance 30 Ω per square, from Balzers) and glass with a *ca.* 100 μm thick PTFE spacer.

The Durham LB troughs were housed in a class 10 000 microelectronics clean room and have been described previously.[23] Compound **1** was spread on the surface of ultrapure water (obtained by reverse osmosis, deionisation and ultraviolet sterilisation) from CH_2Cl_2 solutions ($0.1\ g\ l^{-1}$). The surface pressure *versus* molecular area isotherm was measured at $20 \pm 2\,°C$, $pH = 5.8 \pm 0.2$ and a compression rate *ca.* $4 \times 10^{-3}\ nm^2\ molecule^{-1}\ s^{-1}$. The optimal dipping pressure was found to be $35\ mN\ m^{-1}$. LB films were deposited onto glass slides, quartz, conducting ITO glass slides (sheet resistance 300 Ω per square, from Balzers) and Au- and Ag-coated glass slides by the conventional vertical dipping technique. Unless specified otherwise, a dipping speed of $10\ mm\ min^{-1}$ was employed and the first monolayer was dipped on the upstroke when the slide was immersed in the subphase before compression of the monolayer. To improve the hydrophilic properties of ITO, the slides were pretreated with saturated $Na_2Cr_2O_7$–concentrated H_2SO_4 solution for approximately 10 s and carefully washed with ultrapure water.[24] Substrates with areas between 20 and 30 cm^2 were used for LB film transfer. After LB film deposition, the slides were cut carefully with a diamond tipped stylus to form several electrodes with contact areas between 0.1 and 0.5 cm^2. Au electrodes with a gap of *ca.* 30 μm and interdigitated Au electrodes with a gap of 20 μm were used for electrochemical doping of the LB films. These electrodes were produced as previously described.[25] Electrochemical doping during LB film transfer was achieved on a KI subphase (0.1 M) with a current of 6 μA, using a similar procedure to that described earlier.[25] Chemical doping of the LB films was carried out by exposure to iodine vapour for a given time in a sealed vessel.

The dc conductivity data were obtained in air by a standard two-contact method using silver paste contacts. By varying the distance between the electrodes, it was established that the contact resistance was negligible. The conductivity values were calculated using a monolayer thickness of 1.5 nm (estimated from molecular modelling). The capacitance was measured by a Boonton Electronics model 72BD capacitance meter. The conductivity normal to the film surface was measured by using evaporated Au top contact dots (diameter 0.1 cm, slowly evaporated at rate of about 0.5–1.0 $nm\ min^{-1}$) for films deposited on Au-coated glass slides. The Pockels electro-optic effect was measured for monolayers deposited on Ag-coated glass using the technique of surface plasmon resonance at a wavelength of 633 nm.[26] Optical absorption spectra of solutions were obtained using a Hitachi U-3000 spectrometer, and of LB films using a Perkin-Elmer Lamda 19 spectrophotometer. A mercury lamp with a 314 nm interference filter was used for photolysis in solution. Solutions of **1** or azobenzene (Aldrich) in acetonitrile (*ca.* 10^{-5} M) (Aldrich, spectrometric grade) were contained in 10 mm cells and studied at 18 °C. A xenon lamp (1 kW) with a glass bandpass filter centred at 350 nm was used for photolysis of the LB films.

Results and Discussion

Solution studies

The cyclic voltammetry of compound **1** in acetonitrile solution revealed two, reversible, one-electron waves, which are typical of TTF esters,[11] at $E^{1/2} = +0.40$ and $+0.75$ V, *vs.* Ag/AgCl. These redox potentials are raised slightly relative to TTF under the same conditions ($E^{1/2} = 0.34$ and 0.71 V) by conjugation of the TTF system and the electron-withdrawing carbonyl group.[11] No reduction peak was observed between 0 and −1.8 V in the cyclic voltammetric measurements where reduction of an azo group would be expected;[16,17] this is consistent with a *trans*-azo group, which usually gives a very broad, ill-defined reduction wave, whereas the *cis*-isomer gives a clearly observable peak.[16] We have measured the spectroelectrochemistry of compound **1** in acetonitrile solution (Fig. 1). The appearance of a new absorption peak at λ_{max} 430 nm along with a shoulder at λ_{max} 580 nm, when the spectrum was obtained at +1.2 V, are consistent with the generation of the cation radical of compound **1**.[27] (We note that the potentials are shifted considerably with respect to the CV data reported above, due to uncompensated resistance in the thin-layer spectroelectrochemical cell.) These spectroscopic changes were reversible and the spectrum of compound **1** reverted to that of the neutral species measured initially when the potential was returned to 0 V.

The optical absorption spectrum of compound **1** in acetonitrile [Fig. 2(*a*)] is similar but not identical to a linear combination of the absorption spectra of TTF[28] and *trans*-azobenzene Fig. 2(*d*) (inset). This suggests that there is some interaction between the TTF and azobenzene groups, but the small differences in comparison with those between azobenzene and its disubstituted donor–acceptor derivatives[29] indicates that this interaction is relatively weak. The differences between the spectra of compound **1** shown in Fig. 1 (0 V) and Fig. 2(*a*) are due to absorption by the ITO thin layer electrode in the former case.

Photolysis of **1** in acetonitrile resulted in changes in the absorption spectrum [Fig. 2(*b*,*c*)] which were similar to those observed on photolysis of *trans*-azobenzene [Fig. 2(*e*,*f*,*g*)]. Photolysis of *trans*-azobenzene is known to result in *trans*–*cis* photoisomerisation,[30] and the changes in the spectra are characteristic of this process. These changes were observed to persist for at least 1 h in the dark, indicating that *cis*-**1**, like

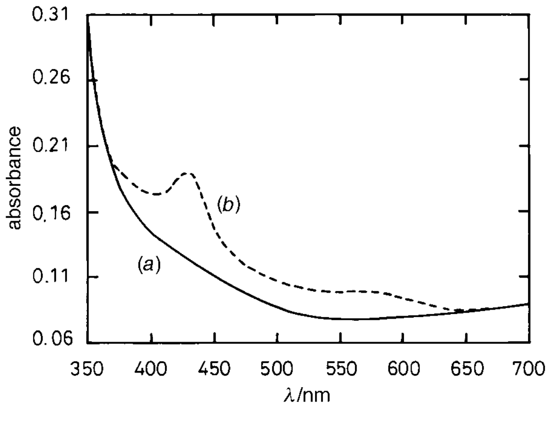

Fig. 1 Optical absorption spectra of compound **1** in 0.2 M Bu_4NPF_6–acetonitrile solution using a thin layer electrode: measurements at (*a*) 0 and (*b*) +1.2 V *vs.* Ag wire

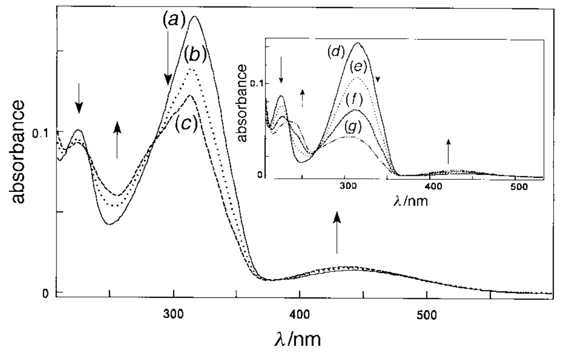

Fig. 2 Optical absorption spectra of compound **1** and azobenzene (inset) in acetonitrile solution. Spectra of **1** obtained: (*a*) before photolysis, (*b*) 3 and (*c*) 8 min after photolysis at 314 nm. Spectra of *trans*-azobenzene obtained: (*d*) before photolysis, (*e*) 1.5, (*f*) 4 and (*g*) 10 min after photolysis at 314 nm.

cis-azobenzene,[30] is relatively stable to thermal *cis–trans* isomerisation. Prolonged photolysis (> 10 min) of the azobenzene solution resulted in no further changes in the spectrum, indicating that Fig. 2(*g*) is the spectrum of the photostationary state mixture. In contrast, prolonged photolysis of **1** resulted in further changes in the spectrum for which the earlier isosbestic points were not maintained, indicating that additional photochemical pathways are available to **1**.

Monolayer behaviour of 1 on the air–water interface and LB film transfer

The condensed pressure *vs.* area isotherm for compound **1** is shown in Fig. 3. This was reproducible and stable at the deposition pressure and was not affected by the time that the monolayer remained on the subphase before compression.[31] There was no evidence of collapse during compression of the monolayer up to the highest pressure measured (40 mN m^{-1}). The extrapolated limiting area (to zero pressure) is 0.21 nm^2 molecule^{-1}, which is slightly less than that expected for the cross-sectional area of the molecule obtained from molecular modelling studies with geometry optimisation using Chem3D for Macintosh. We have observed this previously in isotherms of TTF derivatives,[32] and we suspect that this is simply due to a very slight solubility of the compound in the subphase. A schematic representation of a possible close-packing arrangement of molecules of **1** in the LB film structure is shown in Fig. 4. LB films of compound **1** were built up by predominantly Z-type deposition with a transfer ratio on the upstroke of 0.9 ± 0.1.

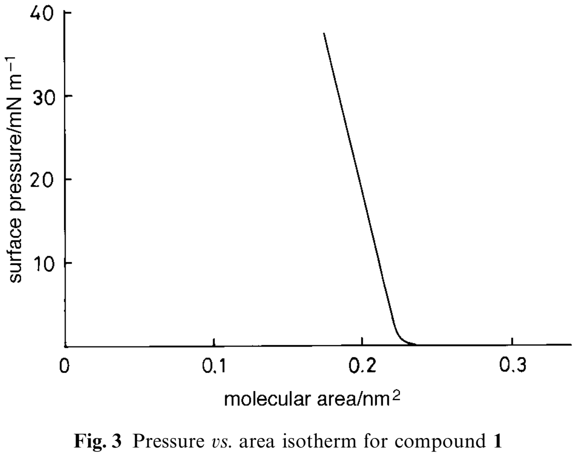

Fig. 3 Pressure *vs.* area isotherm for compound **1**

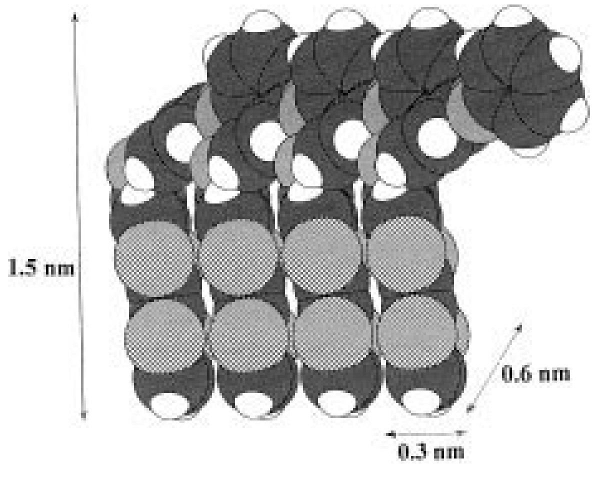

Fig. 4 A model of an LB monolayer of compound **1**; molecular geometry optimisation obtained using Chem3D for Macintosh

LB film characterisation

The in-plane dc conductivities for as-deposited LB films of compound **1** were in the range $\sigma_{\rm rt}=10^{-3}$–10^{-5} S cm^{-1}. After doping with iodine vapour, the room temperature conductivity value of each sample rose by *ca.* one order of magnitude to values of $\sigma_{\rm rt}=2\times10^{-2}$–$10^{-3}$ S cm^{-1}. For LB films with a top Au contact, ohmic current–voltage characteristics were observed. Normal to the film surface, conductivity values of $\sigma_{\rm rt}=10^{-6}$ and 5×10^{-5} S cm^{-1} were measured for a 25-layer LB film, before and after iodine doping, respectively. The capacitance of the same device was found to be 550 ± 27 and 627 ± 56 pF, for the as-deposited and doped films, respectively, which correspond to permittivity values, $\varepsilon_{\rm r}=2.9$ and 3.3 (using a film thickness of 1.5 nm per monolayer obtained from molecular modelling studies).

It is well known that azo compounds undergo *trans–cis*-isomerisation under illumination, even as thin films, and that this can lead to a change in conductivity.[16–19] However, illumination of a 15 layer LB film of **1** using either visible light, a wide-range UV source, a sodium lamp or monochromatic light at 320 nm, did not result in any detectable change in the value of the lateral conductivity. This result suggests that for LB films of **1** either: (*a*) *trans–cis*-isomerisation does not proceed due to steric hindrance in a compact LB film structure, or (b) the isomerisation proceeds but this structural change does not influence the conductivity of the film. Fig. 4 shows a geometry optimisation of an LB monolayer of **1** which indicates that the molecules are bent to afford the experimentally observed molecular area of 0.21 nm^2. This tightly packed structure could imply that the first explanation is more plausible. We note that the LB films studied by Matsumoto *et al.*[18] were assembled at a lower surface pressure than we used in the present work, and by using the horizontal touching technique. Both these experimental conditions may result in a less dense film structure which would allow isomerisation to proceed. However, the optical absorption spectra of LB films of compound **1** (Fig. 5) suggest that some *trans–cis*-isomerisation does occur upon photolysis: after 10 min irradiation there was a slight decrease in the intensity of the absorption peaks at 320 and 235 nm, and a slight increase in the absorption in the range 420–550 nm. These data are qualitatively similar to those of the solution spectra shown in Fig. 2, and, therefore, we favour explanation (*b*) above.

We also attempted to increase the conductivity values of LB films of compound **1** by electrochemical oxidation either during or after LB film deposition.[33] However, neither of these methods affected the conductivity of the films, and a low transfer ratio was observed in the former experiments. This

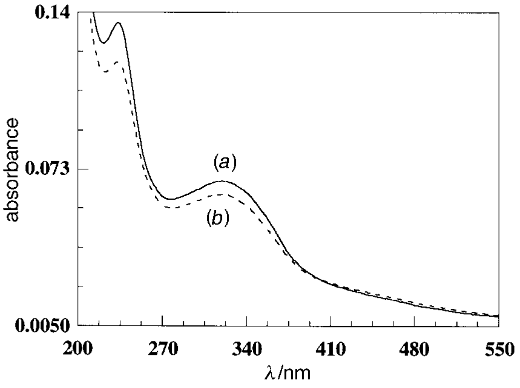

Fig. 5 Optical absorption spectra for a six-layer LB film of compound **1** on quartz: (*a*) before photolysis and (*b*) after photolysis for 10 min

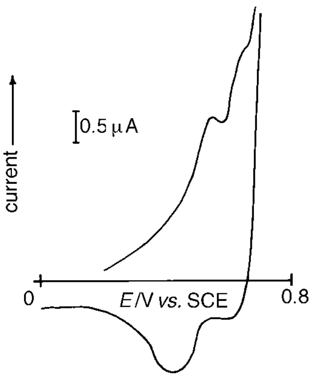

Fig. 6 Cyclic voltammogram for a five-layer LB film of compound **1** deposited on an ITO electrode, 0.2 M $HClO_4$, scan rate 50 mV s^{-1}

Table 1 Pockels effect measurements

compound	thickness/nm	$\chi^{(2)}(-\omega;\omega,0)$/pm V^{-1}	r/pm V^{-1}
1	1.2	5.0	1.6

may be explained by two factors: (*a*) hindered anion diffusion within the multilayer assembly, which is quite compact as judged by the molecular area obtained from the isotherm; (*b*) instability of the films upon application of an electrochemical potential. The cyclic voltammetric response of LB films of **1** was measured and the best response was obtained for a five-layer film (Fig. 6). However, the electroactivity disappeared after a few cycles, which is consistent with film desorption. We consider, therefore, that (*a*) explains the results of attempted post-deposition electrochemical oxidation, and (*b*) affects the electrochemical doping during film deposition.

The Pockels electro-optic effect was measured for monolayers of compound **1**. The surface plasmon resonance method also allowed an estimate of the film thickness to be made by assuming a value of the permittivity ($\varepsilon_r = 2.5$ was used in this case). The results are given in Table 1. In each case the nonlinear optical r coefficient is relatively small. This is likely to be due to poor alignment of the molecules of **1**, as the chromophores themselves should have large values of hyperpolarisability. The thickness obtained for a monolayer of **1** (1.2 nm) is consistent with the value for the length of the molecule obtained from molecular modelling studies (1.5 nm, see above) and suggests that the film is one molecule in thickness.

Conclusions

We have synthesised the new TTF derivative **1** and demonstrated that *trans–cis* isomerisation of the azobenzene substituent occurs upon photolysis. Semi-conducting LB films of **1** have been assembled without the need for added fatty acid: presumably, the TTF group (the polarity of which is increased by conjugation with the carbonyl substituent) is hydrophilic, and the azobenzene unit serves as the hydrophobic portion of the molecule, instead of the traditional alkyl chain(s). No change in the conductivity of the LB films was observed under irradiation. Further studies on LB films of non-amphiphilic TTF systems will be reported in due course.

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