Semiconducting Langmuir–Blodgett films of ethylenedithiotetrathiafulvalene (EDT–TTF) derivatives bearing charged and uncharged aromatic substituents

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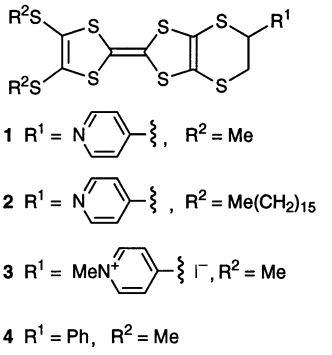
Ethylenedithiotetrathiafulvalene (EDT–TTF) derivatives **1**–**4** functionalised with a single aromatic ring have been synthesised and their Langmuir–Blodgett (LB) films have been assembled utilising only 25% molar ratio of fatty acid. For compounds **1**, **3** and **4**, predominantly Y-type deposition onto solid supports was observed with a transfer ratio close to unity. After doping with iodine vapour, the maximum in-plane conductivity values obtained were $\sigma_{rt} = 10^{-3}$ S cm^{-1} for **1** and **3**, and 10^{-5} S cm^{-1} for **4**. LB deposition of **2** was not uniform and the conductivity value after doping was low. UV–VIS spectra of the LB films reveal the appearance of a charge-transfer (CT) band at $\lambda_{max} = ca.$ 900 nm for **1** and **4** after iodine doping. A solution of compound **3** exhibited a weak absorption band at *ca.* 665 nm which is assigned to an intramolecular CT band; the intensity of this band increases on exposure of the solution to light. This band is not observed in LB films of **3**, neither as-deposited nor after doping. Molecular orbital calculations indicate that in the minimum energy conformation of **3**, the pyridinium moiety is practically orthogonal to the TTF unit and this conformation may be obtained in solution, enabling charge-transfer to occur. A more linear conformation of **3** in the LB films may prevent intramolecular charge-transfer from occurring. Monolayers of **1**, **3** and **4** were characterised by cyclic voltammetry which revealed two redox steps consistent with the formation of the EDT–TTF cation radical and dication, respectively.

Within the field of molecular conductors,[1] bis(ethylenedithio)-tetrathiafulvalene (BEDT–TTF) derivatives command a central position as many of their crystalline cation–radical salts are metals or superconductors.[2] Amphiphilic analogues which form Langmuir–Blodgett (LB) films have been studied by a number of groups[3–19] and some multilayer LB films display conductivity values as high as 1 S cm^{-1} after doping with iodine vapour.[18] Amphiphilic derivatives of the closely related donor ethylenedithiotetrathiafulvalene (EDT–TTF) substituted with one hydrophobic $CH_2OC(O)C_{17}H_{35}$ chain were recently shown to form semiconducting LB films.[20]



In the present work, we report the study of LB films of three novel non-amphiphilic derivatives of EDT–TTF, compounds **1**, **3** and **4**, and the amphiphilic derivative **2**. All of these molecules contain a single aromatic substituent, which could serve as the 'traditional' hydrophobic tail in the case of compounds **1** and **4**, or as a hydrophilic head group in the case of compound **3**. Compounds **1** and **3** have been discussed recently by us in a preliminary communication.[21] Prior to this work, the only non-amphiphilic TTF derivative that was reported to form LB films was tetrakis(benzylthio)–TTF [$(PhCH_2S)_4TTF$]. This compound did not produce a stable monolayer at the air–water interface unless at least a 50% molar ratio of a fatty acid was added.[22] Subsequently a non-amphiphilic bis(EDT–TTF) derivative was shown to make a semiconducting LB film after iodine doping, without added fatty acid.[23] Unsubstituted BEDT–TTF, which is non-amphiphilic, forms conducting aggregates if mixed with 50% C_{60} or stearic acid.[24] Furthermore, it is noteworthy, that compound **3** contains both donor (TTF) and acceptor (pyridinium) moieties covalently linked *via* a non-conjugated spacer: as both these moieties should be almost orthogonal (see Fig. 6) no substantial intramolecular donor–acceptor (DSA) electronic interaction would be expected. Compound **3** is analogous to the amphiphilic D-σ-A and D-π-A systems, based on TCNQ and aromatic donors, studied by Metzger and co-workers,[25,26] and Ashwell and co-workers,[27–29] respectively. This compound may, therefore, be relevant to studies on molecular rectification and/or second-order nonlinear optics.

Experimental

Syntheses

Compounds **1**–**4** were obtained as racemic mixtures. *J* Values in Hz.

4,5-Bis(methylthio)-4′,5′-(4-pyridylethylenedithio)tetrathiafulvalene.[†] Compound **1** was prepared by cross-coupling of 4,5-bis(methylthio)-1,3-dithiole-2-thione[30] (3 equiv.) and 4,5-(4-pyridyl)ethylenedithio-1,3-dithiole-2-one (1 equiv.) (see

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[†] IUPAC name: 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5,6-dihydro-5-(4-pyridyl)-1,3-dithiolo[4,5-*b*][1,4]-dithiine. Related compounds **2**–**4** can be named similarly.

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below), in neat trimethyl phosphite at reflux under nitrogen. After chromatographic separation from self-coupled products, compound **1** was isolated as yellow crystals in 22% yield, mp 158–159 °C (from acetonitrile). $\delta_H(CDCl_3)$ 2.42 (s, 6H), 3.41 (d, *J* 5.4, 2H), 4.72 (t, *J* 5.4, 1H), 8.29 (d, *J* 5.7, 2H), 8.61 (d, *J* 5.7, 2H). Calc. $C_{15}H_{13}NS_8$: C, 38.85; H, 2.83%. Found: C, 39.02; H, 2.72%.

4,5-(4-Pyridylethylenedithio)-1,3-dithiole-2-thione. This was prepared according to a modified literature procedure[31] using 4-vinylpyridine as the alkene, and was obtained as yellow crystals in 60% yield, mp 125–126 °C (from acetonitrile). Calc. $C_{10}H_7NS_5$: C, 39.84; H, 2.34%. Found: C, 40.57; H, 2.41%.

4,5-(4-Pyridylethylenedithio)-1,3-dithiole-2-one. This was synthesised by reaction of its respective 2-thione derivative with mercury(II) acetate, in chloroform–acetic acid under reflux, according to the known procedure[31] and isolated as yellow crystals in 68% yield, mp 129–130 °C. Calc. $C_{10}H_7NOS_4$: C, 42.08; H, 2.47%. Found: C, 41.86; H, 2.17%.

4,5-Bis(hexadecylthio)-4′,5′-(4-pyridylethylene)dithiotetrathiafulvalene 2. Compound **2** was prepared from 4,5-bis(hexadecylthio)-1,3-dithiole-2-thione[30,32] by an analogous procedure used for the synthesis of derivative **1** and isolated as a red solid in 28% yield, mp 58–59 °C. Calc. $C_{45}H_{73}NS_8$: C, 61.10; H, 8.32%. Found: C, 61.36; H, 8.41%.

4,5-Bis(methylthio)-4′,5′-(4-methylpyridinioethylenedithio)-tetrathiafulvalene iodide 3. Compound **3** was formed by refluxing compound **1** with methyl iodide (excess) in acetone in the dark for 0.5 h, and isolated in 96% yield as red crystals, mp 160–170 °C (slow decomposition). Calc. $C_{16}H_{16}INS_8$: C, 31.73; H, 2.66%. Found: C, 32.00; H, 2.48%.

4,5-Bis(methylthio)-4′,5′-(4-phenylethylenedithio)tetrathiafulvalene 4. Compound **4** was synthesised according to the general procedure[33] starting from 4,5-(phenylethylenedithio)-1,3-dithiole-2-thione and 4,5-bis(methylthio)-1,3-dithiole-2-thione, and isolated in 60% yield as orange crystals, mp 109.7–110.2 °C. Calc. $C_{16}H_{14}S_8$: C, 41.52; H, 3.05%. Found: C, 41.39; H, 3.12%. $\delta_H(CDCl_3)$ 2.44 (s, 6H), 3.32 (dd, ABX, J_{ax} 3.6, J_{ab} 12, 1H), 3.42 (dd, ABX, J_{bx} 8, J_{ab} 12, 1H), 4.62 (dd, ABX, J_{ax} 3.6, J_{bx} 8, 1H), 7.31 (s, 5H); *m/z* (CI) 464.2 (M^+).

4,5-(Phenylethylenedithio)-1,3-dithiole-2-thione. This was prepared as follows. A mixture of oligomeric 1,3-dithiole-2,4,5-trithione[34] (0.59 g, 3 mmol) and styrene (0.31 g, 3 mmol) in toluene (30 ml) was refluxed for 40 min, evaporated, and the residue was recrystallised from acetonitrile with addition of activated carbon to yield the product as shiny yellow crystals (0.51g, 60%), mp 77–78 °C. $\delta_H(CDCl_3)$ 3.40 (dd, ABX, J_{ax} 3.0, J_{ab} 13.2, 1H), 3.60 (dd, ABX, J_{bx} 9.6, J_{ab} 13.2, 1H), 4.7 (dd, ABX, J_{ax} 3.0, J_{bx} 9.6, 1H), 7.36 (s, 5H). Calc. $C_{11}H_8S_5$: C, 43.97; H, 2.68%. Found: C, 44.18; H, 2.59%.

LB Film formation and characterisation

Tricosanoic acid [TA, $Me(CH_2)_{21}CO_2H$] (Sigma, 99%) was used as received. The Durham LB troughs were housed in a class 10 000 microelectronics clean room and have been described previously.[35] Compounds **1–4** were spread on the surface of ultrapure water (obtained by reverse osmosis, deionisation and ultraviolet sterilisation) from CH_2Cl_2 or tetrahydrofuran (THF) solutions ($0.5\ g\ l^{-1}$) or acetone–CH_2Cl_2 mixtures (3:2 or 2:3, v/v). The surface pressure *versus* molecular area isotherms were measured at 20 ± 2 °C; pH = 5.8 ± 0.2, and compression rate *ca.* $4\times10^{-3}\ nm^2\ molecule^{-1}\ s^{-1}$. A mixture of **1**, **3** and **4** with TA was also used. The optimal mixture was made from a THF solution of compounds **1**, **3** and **4**, and a chloroform solution of TA to obtain *ca.* 25% molar of TA. The optimal dipping pressure for this mixture was found to be 35–40 $mN\ m^{-1}$.

LB films were deposited onto glass slides, quartz windows, single crystal silicon, conducting indium tin oxide (ITO, sheet resistance 300 ohms per square, from Balzers) glass slides 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 deposited on the upstroke with the slide immersed in the subphase before compression of the monolayer. To improve the hydrophilic properties of ITO, the slides were treated with saturated $Na_2Cr_2O_7$–concentrated H_2SO_4 solution for *ca.* 10 s and carefully washed with ultrapure water.[36] Substrates with areas of between 20 and 30 cm^2 were used for LB transfer. After LB film deposition, these were carefully cut with a diamond tipped stylus to form several electrodes with contact areas between 0.1 and 0.5 cm^2.

Doping of the LB films was carried out by exposure to iodine vapour for a given time in a sealed vessel. UV–VIS absorption measurements were performed using a Perkin-Elmer Lambda 19 spectrophotometer for films deposited on glass slides and quartz windows. The film thickness was measured using both a surface profiling Tencor Instruments Alpha-Step 200 (stylus force = 11 ± 1 mg) and a Rudolf Research Auto EL IV ellipsometer (operating wavelength = 633 nm). LB films were deposited onto single crystal silicon for these experiments. For the Alpha-Step measurements, a layer of aluminium (thickness *ca.* 200 nm) was evaporated over the step between the organic layer and the uncoated substrate and between two organic layers of different thicknesses. DC conductivity measurements were made in air by a standard two-contact method using silver paste contacts. The conductivity was calculated on the basis of the measured single layer thickness of *ca.* 5 nm. Current–voltage characteristics were ohmic, and by varying the distance between the electrodes, it was established that the contact resistance was negligible. Single crystal DC conductivity was measured by a four-probe method. Cyclic voltammetry was performed using a EG&G PARC, model 273 potentiostat with an Advanced Bryans XY recorder. Pt mesh served as the counter electrode. All potentials were measured *versus* a Ag/AgCl reference electrode and were tested, if necessary, with a ferrocene/ferrocinium couple as internal reference. Cyclic voltammetry in solution was performed in 0.2 M Bu_4NPF_6/CH_2Cl_2 solution on a Pt disk [0.13 or 0.5 mm diameter (both homemade) or 1.6 mm diameter (Bioanalytical System Inc.)] working electrode, employing IR compensation. $LiClO_4$ (Fluka, microselect), Bu_4NPF_6 (Fluka, electrochemical grade), KCl (Fluka, microselect), $HClO_4$ (Aldrich, ACS reagent), CH_2Cl_2 (Aldrich, HPLC, distilled from P_2O_5) and ultrapure water were used for the preparation of electrolyte solutions. The Pockels electrooptic effect was measured to test for second-order optical nonlinearity (by monitoring reflectivity) in monolayers deposited on Ag-coated glass using the technique of surface plasmon resonance at a wavelength of 633 nm.[37]

Results and Discussion

Synthesis of EDT–TTF derivatives

The synthesis of the EDT–TTF systems **1**, **2** and **4** was accomplished by standard cross-coupling[23] of the two 1,3-dithiol-2-one (or 1,3-dithole-2-thione) half-units in the presence of trimethyl phosphite. *N*-Methylation of compound **1** was readily accomplished with methyl iodide in refluxing acetone to form compound **3**. However, attempted methylation of analogue **2** was not a clean reaction, possibly due to the influence of the two long alkyl chains: more forcing conditions were required for reaction to occur, and a complicated mixture of decomposition products was obtained, possibly arising from radical reactions. We did not pursue this alkylation further, as the focus of this study was the LB films of derivatives *without* long alkyl chains.

Monolayer behaviour at the air–water interface and LB film transfer

Compound **1** spread on a water surface from dichloromethane or tetrahydrofuran (THF) solution exhibited an isotherm of surface pressure *versus* molecular area consisting of two condensed regions [Fig. 1(*a*)]. The extrapolated limiting molecular areas for the first and second region were *ca.* 0.30 and 0.14 nm^2, respectively. It is notable that the molecular area in the first condensed region is nearly double that in the second region, which may suggest formation of a bilayer, or molecular reorganisation may occur in the latter region. Fig. 1 also shows the change in the isotherm with time, in the expanded state. The final curve [Fig. 1(*c*)], obtained 2 h after spreading, was steep with a limiting molecular area of *ca.* 0.22 nm^2. A striking feature of the isotherms in Fig. 1 is their intersection through one 'isosbestic' point, a feature which has not, to our knowledge, been reported before for monolayers. The shape of the isotherms depended upon the quantity of material spread on the surface; the limiting molecular area decreased with increasing amount of material, which is indicative of aggregation [Fig. 1(*d*)]. The films of compound **1** were transferred onto glass slides predominantly by Z-type deposition, with a transfer ratio of 0.7 ± 0.1. The LB films were not uniform; they tended to cover only a narrow band near the upper edge of the substrate.

The LB behaviour of many poor amphiphiles can be improved by the addition of fatty acid. For LB films of **1**, TA was used, and with only 25% molar of TA (the experimentally determined minimum amount required to produce a stable film) spread from THF solution, it was possible to observe a condensed isotherm with a limiting average molecular area of *ca.* 0.40 nm^2. The compressed monolayer was stable under these conditions.

Amphiphilic analogue **2** showed an isotherm of surface pressure *versus* molecular area consisting of two condensed regions (Table 1). As this compound did not show good deposition characteristics and the LB film conductivity was low (Table 2) we did not study it any further. In contrast to **1**, compound **3** tended to aggregate on the water surface when spread without TA, affording a small molecular area (Table 1). However, using the same conditions as for **1**, with added fatty acid, a stable floating monolayer with a limiting average molecular area of 0.23 nm^2 was obtained. Compound **3** was also spread from acetone–CH_2Cl_2 mixture (3:2 or 2:3, v/v). Both pure compound **3** and its mixture with 25% of TA showed condensed isotherms (Table 1) with extrapolated average molecular areas of *ca.* 0.15 and 0.20 nm^2, respectively. In contrast to compounds **1** and **3**, compound **4** spread either from CH_2Cl_2 or THF (with addition of 25% of TA) exhibited small molecular areas (Table 1) probably indicating multilayer formation on the subphase surface.

The transfer of compounds **1**, **3** and **4** (mixed with 25% TA) on to solid substrates was achieved by controlling the Langmuir film at 35–40 mNm^{-1}. Predominantly Y-type deposition was observed with a transfer ratio of 1 ± 0.05. The reproducibility of LB transfer is shown for compound **1** in Fig. 2. A linear plot of the optical density of the absorption band at 400 nm *versus* the number of layers was observed. Film thickness determination by ellipsometry and Alpha-Step

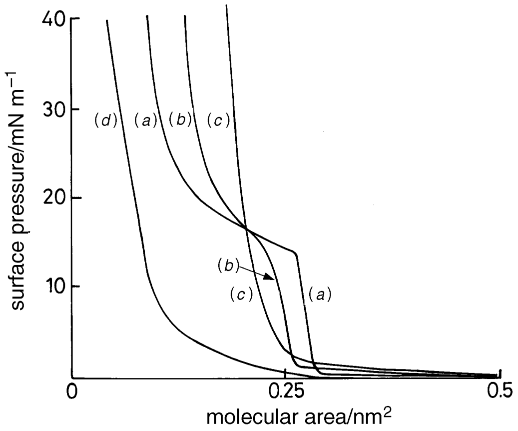

Fig. 1 Surface pressure *versus* area per molecule isotherm for compound **1** measured after leaving the film on the subphase surface for different lengths of time in its uncompressed state (0.12 mg from CH_2Cl_2 solution): (*a*) 10 min after spreading, (*b*) 1 h after spreading, (*c*) 2 h after spreading and (*d*) 0.24 mg from CH_2Cl_2 solution, 10 min after spreading

Table 2 In-plane DC, room temp. conductivity of LB films of compounds **1–4**

compound	1	2	3	4
as deposited/S cm^{-1}	10^{-6}	10^{-8}	10^{-6}	10^{-6}
after I_2 doping/S cm^{-1}	10^{-3}	10^{-6}	10^{-3}	10^{-5}

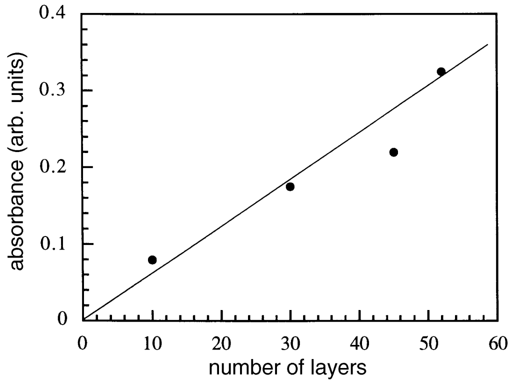

Fig. 2 Plot of optical density of the adsorbance band at 400 nm *versus* number of layers for as-deposited LB films of compound **1** with 25% of TA (predominantly Y-type deposition)

Table 1 Extrapolated average molecular areas (nm^2)[a] for compounds **1–4**, pure and mixed with 25 mol% TA

	compound **1**	compound **2**	compound **3**	compound **4**
pure compound from CH_2Cl_2	0.14, 0.30[b]	0.25, 0.50		
from CH_2Cl_2 with 25% TA				0.09
pure compound from THF	0.10, 0.20		0.05	
from THF with 25% TA	0.40		0.23	0.10
pure compound from acetone–CH_2Cl_2 (2:3, v/v)			0.15	
from acetone–CH_2Cl_2 (2:3, v/v) with 25% TA			0.20	

[a] In the case of films mixed with TA, the area given is that of the active compound + TA (*i.e.* average area). [b] for the change of isotherm with time see Fig. 1.

measurements (Fig. 3) also confirmed reproducible deposition. However, the single layer thickness of *ca.* 5 nm obtained from this plot (Fig. 3) is greater than would be expected: an estimation of the length of molecule **1** by HYPERCHEM gave a value of 1.35–1.5 nm, depending on the conformation, whereas the length of TA is *ca.* 3 nm. This indicates that the floating film is probably more than one molecule in thickness.

The transfer of monolayers of compound **2** onto glass was achieved by controlling the floating film at 25–30 mNm^{-1}. However, as noted above, deposition was not uniform and the conductivity value was low (Table 2). We suggest, therefore, that within this family of materials the presence of two alkyl chains inhibits the formation of conducting films.

LB Film characterisation

Conductivity measurements. Lateral conductivity was measured for films freshly deposited and after doping with iodine vapour, and the values obtained are presented in Table 2. The conductivity of the LB films of compounds **1** and **3** increased upon doping and remained stable within the range $\sigma_{rt} = 10^{-3}$–10^{-4} S cm^{-1} for at least one month after doping. DC conductivity for compound **3** was also measured on single crystals and showed values of 1×10^{-8} S cm^{-1} in the dark and 5×10^{-8} S cm^{-1} in the light. It has been observed that compound **3** is photochemically unstable (see the discussion below). Therefore, we tested the influence of this photochemical reaction on the formation and properties of LB films of **3**. Compound **3** was synthesised in the dark and then all manipulations for LB transfer were undertaken in the dark. For comparison, either the compressed monolayer on the air–water interface, or the LB film deposited on a glass slide, or the LB film after iodine doping, were illuminated with visible light for 10 h. Illumination of the spreading solution with visible light for 10 h caused the solution of compound **3** in THF to turn from red–brown to brown; however, this process did not significantly change the limiting molecular area. We have built up LB films using this illuminated solution. The most significant changes in conductivity (a reduction of up to two orders of magnitude) were found for doped films built-up from an illuminated monolayer, or using the illuminated spreading solution. The influence of light on films that had been deposited in the dark was not found to be significant (for either as-deposited or doped layers).

UV–VIS Spectroscopy. Doping of the LB films with iodine vapour was monitored by visible spectroscopy, which showed the appearance of a charge-transfer (CT) band at *ca.* 900 nm for compounds **1** and **4** [Figs. 4(*a*) and 4(*c*), respectively]. This band remained after storing the films for several hours in air for compound **1** [Fig. 4(*a*), curve (iii)]. The intensity of the CT band decreased in air for compound **4** [Fig. 4(*c*), curve (iii)]. These spectra are qualitatively similar to those of LB films amphiphilic TTF,[19] EDT–TTF[20] and BEDT–TTF[18] derivatives studied previously. Surprisingly, a similar band could not be clearly detected for the LB films of compound **3** [Fig. 4(*b*)] nor was it visible in a doped, cast film of **3** on glass with a thickness corresponding to 15–20 layers of LB film.

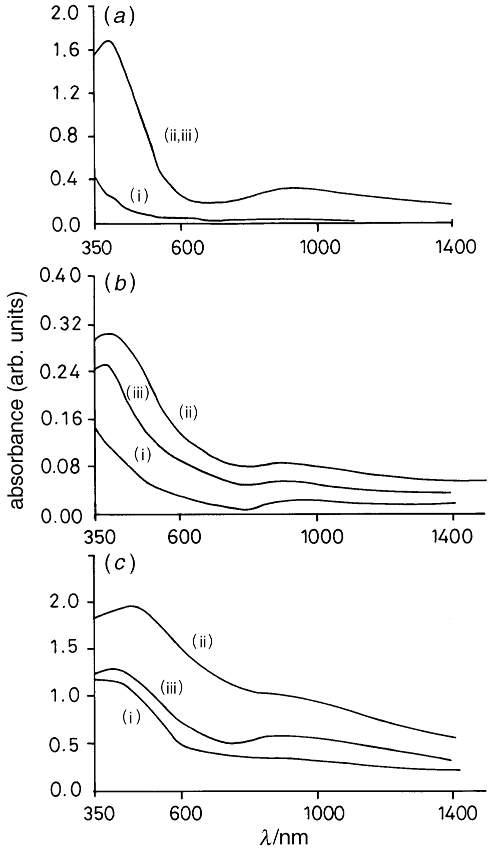

Fig. 4 UV–VIS Spectra of LB films of (*a*) compound **1** (42 layers), (*b*) compound **3** (22 layers) and (*c*) compound **4** (38 layers) mixed with 25% of TA: (i) as-deposited; (ii) immediately after iodine doping; (iii) 1 h after doping

It is known that the pyridinium cation is an extremely strong acceptor with an electron affinity of *ca.* 5 eV[38] and that tetrathiafulvalene (TTF) interacts with acceptors which possess an electron affinity higher than 2.5 eV.[39] We have performed AM1 geometry optimisation by HYPERCHEM software for compound **3**. The molecular conformation obtained by calculation is shown in Plate 1. The results suggest that the

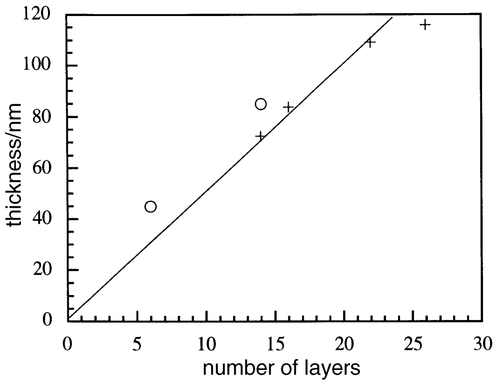

Fig. 3 Plot of film thickness obtained by ellipsometry (+) and Alpha-Step (○) for LB films of compound **1** mixed with 25% of TA *versus* number of layers

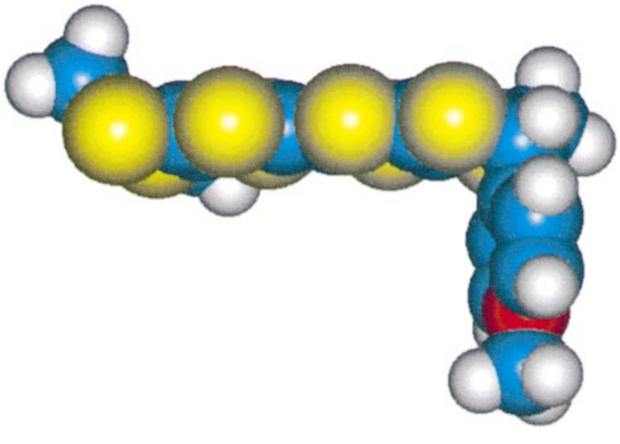

Plate 1 Geometry optimisation for compound **3** obtained by MNDO (AM1) methods using HYPERCHEM programs (blue = carbon, yellow = sulfur, red = nitrogen, white = hydrogen)

pyridinium moiety is practically orthogonal to the TTF unit and, therefore, the substituent should not influence the oxidation potential that is observed by solution electrochemistry (discussed below). In solution, simple pyridinium salts do not react with TTF because of strong solvation effects. Therefore, when equimolar amounts of *N*-methylpyridinium iodide and TTF were mixed in acetone solution, a CT band was not observed in the visible spectrum. However the situation is different with compound **3**, where the pyridinium moiety is covalently linked to the TTF unit, which, due to the close proximity of the electroactive groups, makes charge transfer possible.‡ Indeed, a solution of derivative **3** in dry acetone, freshly prepared in the dark, exhibited a weak absorption at *ca.* 665 nm (Fig. 5), the extinction coefficient of which was independent of concentration (within experimental error). This band can, therefore, be attributed to an intramolecular charge transfer band. This solution is quite stable in the absence of light, but even the weak spectrophotometer beam during scanning between 800 and 350 nm triggered the electron transfer from the electron donating moiety (TTF) to the electron accepting moiety (*N*-methylpyridinium) as evidenced by the appearance of the strong band at *ca.* 675 nm, which is the characteristic signature of the TTF cation radical[40] (Fig. 5). Formally, this process should afford a molecule consisting of the cation radical located on the TTF moiety, and the unstable *N*-methylpyridinium radical moiety. When a solution which had been prepared in the dark and used for recording the UV–VIS spectra was stored in the dark, the band at 675 nm reached its maximum extinction coefficient after 8–10 h (the solution gave a strong, poorly resolved EPR signal at this stage) and this absorption band almost completely disappeared within 2 d. This process proceeds considerably faster in light or in more polar solvents (*e.g.* Me_2SO, or in the presence of water). The solution, after disappearence of the 675 nm band, contained a complex mixture of unidentified products (TLC evidence) presumably resulting from further reactions of the *N*-methylpyridinium radical. Therefore, we prepared a solution of compound **3** in acetone, observed the charge-transfer band in the solution spectrum and then built up LB films using a mixture of this solution plus TA in CH_2Cl_2. As above, we did not observe a CT band in these films either as-deposited or after iodine doping. The limiting molecular areas observed for compound **3** (Table 1) are close to the cross-section of an alkyl chain and indicate a very compact structure. It is possible that the molecules of compound **3** in a Langmuir layer adopt a linear conformation to maximise intermolecular packing forces.

The calculated energy of the HOMO for compound **3**, located predominantly on the TTF moiety and the four attached sulfur atoms, is -8.99 eV. This value is considerably higher then the experimental ionisation potential of TTF (6.70–6.92 eV)[41] but all MNDO-type methods, according to our experience, underestimate the donating ability of sulfur-containing heterocycles. The calculated energy of the LUMO of **3**, located mostly on the pyridinium moiety (and to a lesser extent on both sulfur atoms of the ethylenedithio group) is -5.33 eV, in good agreement with the reported data.[38] Before intramolecular electron transfer occurs, the oscillator strength of the long wave transition (which is essentially a charge-transfer D–A interaction) is close (but not equal) to zero, owing to the symmetry mismatch. This point is also supported by calculations. After the electron transfer has occurred, the strong absorption typical of a TTF radical cation should be observed. The triggering process for the electron transfer is not clear at present and requires further investigation. It should be noted that the isolation of a system comprising both donor and acceptor moieties with the ionisation potential of the donor (*ca.* 6.8 eV) higher than the electron affinity of the acceptor (*ca.* 5.4 eV) is unprecedented to the best of our knowledge.

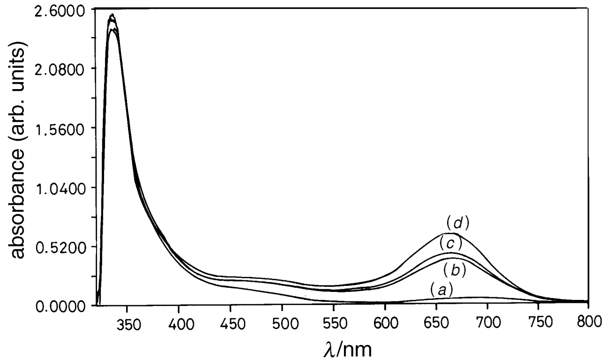

Fig. 5 Visible spectra for compound **3** in acetone (0.08 g l^{-1}): (*a*) freshly prepared solution, and consecutive runs after (*b*) 1, (*c*) 2 and (*d*) 3 h, respectively

The calculated minimum energy conformation of **3** should be attained in the gas phase or solution where the molecules are free to adopt their optimum conformation, but this may not be the case in the LB films where they are forced to adopt a more linear conformation. In a linear conformation of compound **3**, the positive charge on the pyridinium cation will be at a greater distance from the conjugated TTF system, which could prevent charge transfer in the LB films. It is not completely clear whether the absence of the absorption at 675 in the spectra of LB films of derivative **3** is the result of: (i) the decomposition of the product of electron transfer; (ii) the fact that electron transfer cannot occur in an LB film due to the specific packing of the molecules, or (iii) the effective solvation of the pyridinium moiety.

Electrochemistry. The electrochemistry of these materials in solution and in LB films has been studied by cyclic voltammetry, and the data are collated in Table 3. All the compounds displayed essentially the same redox properties in solution, *viz.* two reversible single-electron oxidation waves at potentials typical of the EDT–TTF ring system,[20] which indicates that the aromatic substituents, even in the case of pyridinium compound **3** (in agreement with MNDO calculations), do not interact with the EDT–TTF redox system. Monolayer LB films were characterised by CV when deposited onto ITO glass electrodes (Fig. 6). Two redox steps have been observed for the monolayer films of compounds **1**, **3** and **4** (in each case mixed with TA). However, the redox peaks for compound **3** were very broad and ill-developed [Fig. 6(*b*)]. Changing the electrolyte (KCl or $HClO_4$) did not improve the CV response, and Fig. 6(*b*) presents the best response obtained. The peak currents decreased in subsequent scans as shown in Fig. 6.

Table 3 Redox potentials for compounds **1–4** (*versus* Ag/AgCl, V)

	compound **1**	compound **2**	compound **3**	compound **4**
solution	0.45; 0.8	0.44; 0.82	0.45; 0.8	0.45; 0.8
LB monolayer (mixed with TA)	0.45; 0.55		0.55; 0.8	0.4; 0.7

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‡*Note added at proof*: After submission of our manuscript, other workers reported the synthesis of covalently linked TTF–bipyridinium derivatives which display intramolecular charge-transfer in solution (K. B. Simonsen, K. Zong, R. D. Rogers, M. P. Cava and J. Becher, *J. Org. Chem.*, 1997, **62**, 679).

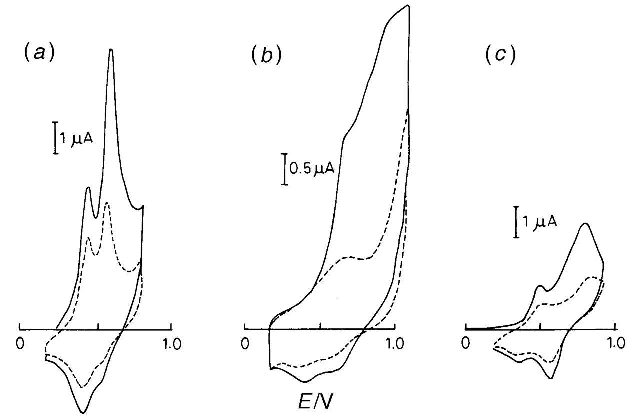

Fig. 6 Cyclic voltammograms of LB monolayers of a mixture compounds **1**, **3** and **4** with 25% of TA on an ITO electrode, 0.4 M $LiClO_4$ solution, *versus* Ag/AgCl: (*a*) compound **1**, scan rate 100 mV s^{-1}; (*b*) compound **3**, scan rate 200 mV s^{-1}, (*c*) compound **4**, scan rate 50 mV s^{-1}. Solid line, first cycle; dashed line, second cycle.

Table 4 Pockels effect measurements

compound	thickness/ nm	$\chi^{(2)}(-\omega;\omega,0)$/ pm V^{-1a}	*r*/pm V^{-1b}
1 (with TA)	1.2	3.4	1.0
3 (with TA)	4.3	0.49	0.16

$^a\chi^{(2)}$ is the second-order nonlinear susceptibility.
$^b r$ is the electrooptic coefficient[37].

Nonlinear optical measurements. The Pockels electrooptic effect was measured for monolayers of compounds **1** and **3** (both mixed with TA). The surface plasmon resonance (SPR) method also allowed estimates 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 4. In each case the nonlinear optical *r* coefficient is relatively small.[37,42] This is most likely due to poor alignment of the molecules, 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 length of the molecule (see earlier discussion) and suggests that the film is one molecule in thickness. This result is different from that obtained from ellipsometry and the Alpha-Step (*ca.* 5 nm). However, these experiments were both undertaken with thicker films (Fig. 3). It is also quite likely that the structure of a monolayer film depsosited on Ag-coated glass (used for the SPR work) differs from that on silicon.

Conclusions

This work has demonstrated that semi-conducting LB films can be formed from non-amphiphilic TTF-derived compounds that contain an aromatic ring substituent, utilising only 25% molar ratio of fatty acid. The LB films have been characterised by UV–VIS spectroscopy, conductivity measurements and cyclic voltammetry. In spite of differences in the electronic properties of compounds **1** and **3** (the former is neutral, the latter is ionic) their corresponding LB films show similar conductivities, those of **1** being more stable. This work paves the way for the study of conducting LB films of a wide range of neutral and ionic electron donor molecules, where it may not be necessary to attach the traditional long alkyl chains that render the systems amphiphilic.

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