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Highly-Conducting Langmuir-Blodgett Films of an Amphiphilic Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Derivative: BEDT-TTF-$C_{18}H_{37}$

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Langmuir-Blodgett films of (octadecylethylenedithio)(ethylenedithio)tetrathiafulvalene (1, BEDT-TTF-$C_{18}H_{37}$), mixed with 10-20% tricosanoic or stearic acid, have room-temperature conductivity values as high as $\sigma_{rt} = 10^{-1}$ S cm^{-1} as-deposited, and $\sigma_{rt} = 1.0$ S cm^{-1} after iodine doping. Moreover, these values are stable upon storage of the films for up to 4 weeks in air. The LB films have been characterized by UV-visible and IR spectroscopy and by cyclic voltammetry.

Introduction

There is considerable current interest in using the Langmuir-Blodgett (LB) technique to organize amphiphilic tetrathiafulvalene (TTF) and BEDT-TTF derivatives with the aim of obtaining highly conducting ultrathin films.[1-12] Room-temperature conductivity values within the range $\sigma_{rt} = 10^{-2}$-1.0 S cm^{-1} have been reported for LB films of several TTF derivatives after doping with iodine. It is well-known that bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) yields cation radical salts which, as single crystals, are conducting or superconducting.[13] There is, therefore, keen interest in studying the behavior of new derivatives of BEDT-TTF in the form of LB films. Compound 1, in which the hydrophobic chain facilitates monolayer film formation, had been briefly studied previously as a 1:1 mixture with a fatty acid,[10] and the conductivity value for LB films of the mixture after doping with ICl vapor was $\sigma_{rt} = 10^{-3}$ S cm^{-1}. Doping with I_2 vapor was reported to lead to insulating films[10] possibly due to the large proportion of fatty acid present. In this paper we report our work on (octadecylethylenedithio)(ethylenedithio)tetrathiafulvalene (ODEDT-EDT-TTF, 1).

Experimental Section

Synthesis of Compound 1. Our initial attempts to obtain long-chain substituted BEDT-TTF derivatives by alkylation of 1,3-dithiole-2-thione-4,5-dithiolate (or its zincate complex salt) led to the formation of compound 3 in only 4-6% yield, contaminated with unidentified impurities. The resultant BEDT-TTF derivative was also contaminated with unwanted byproducts, which we were unable to separate. The sample of compound 1 prepared by this method melted in the range 91-94 °C, despite repeated column chromatography. From our experience the purity of a TTF amphiphile is crucial for gaining reproducible results in LB film studies. We therefore elaborated the methodology used previously for the synthesis of the C_{16} analogue[14] to prepare a pure sample of 1 according to Scheme 1.

Compound 1 was prepared, as a racemic mixture which we were unable to resolve, by the following method: refluxing a suspension of polymeric 1,3-dithiole-2,4,5-trithione (**2**,[15] 1.3 mol equiv) and eicosene (1.0 equiv) in toluene led to thione **3** [82-85% yield, yellow crystals, mp 79.5-80 °C (from ethanol)]. Reaction of **3** with mercuric acetate in dichloromethane[16] gave ketone **4** [95% yield, off-white crystals, mp 52-53 °C (from ethanol)]. The coupling of ketones **4** (1.0 equiv) and **5**[17] (1.4 equiv) was achieved in refluxing toluene in the presence of freshly distilled triethyl phosphite (2 h, under argon).[18] Workup involved cooling the reaction mixture and adding ethanol to precipitate a mixture of compound **1** and the corresponding self-coupled products [*viz.* BEDT-TTF and BEDT-TTF($C_{18}H_{37}$)$_2$ (combined

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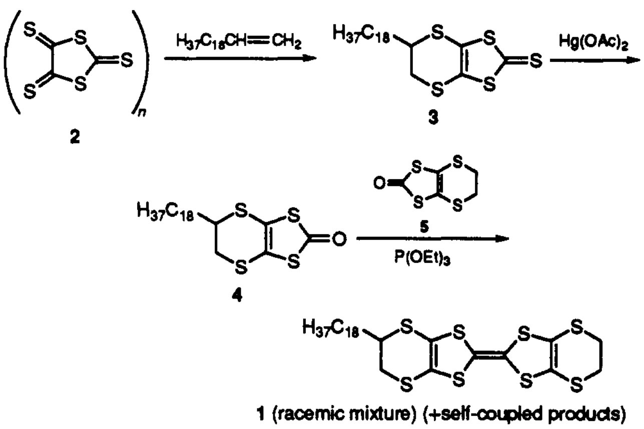
Scheme 1



yield for the three products 82%)]. The product mixture was then dissolved in toluene and filtered to remove some undissolved BEDT–TTF 1, and the filtrate evaporated. Doubly repeated column chromatography [silica gel, eluent carbon disulfide: hexane (1:1 v/v)] afforded pure compound 1 as orange platelets, mp 95.5–96 °C, in 16% yield. Elemental analysis obtained: C, 52.89; H, 6.92; S, 40.17%. Calculated for $C_{28}H_{44}S_8$: C, 52.78; H, 6.96; S, 40.26%.

LB Film Formation and Characterization. Monolayer formation was achieved by spreading a solution of compound 1 in either chloroform (1 g L^{-1}) or benzene (0.5 g L^{-1}) on the surface of a Langmuir–Blodgett trough. Solutions of pure compound 1 and mixtures comprising 10% or 20% tricosanoic acid or stearic acid were used. The optimal dipping pressure was found to be 15 mN m^{-1}.

Samples were deposited onto glass slides, evaporated gold glass slides, zinc selenide crystals, or conducting indium tin oxide (ITO) glass slides. The dipping speed was 2.5 mm min^{-1} for the first cycle and 10 mm min^{-1} for subsequent cycles. Doping of the LB films was carried out by exposure to iodine vapor for 5 min in a sealed vessel.

UV–visible absorption measurements were performed with a Perkin-Elmer Lambda 19 spectrophotometer. Infrared spectra were recorded by reflection–absorption spectroscopy (RAIRS) and attenuated total reflection (ATR) for LB films deposited on Au-covered glass and ZnSe, respectively, using a Mattson-Sirius 100 spectrometer. Dc conductivity was measured in air by standard two-contact methods using silver dag contacts; by varying the distance between the electrodes, it was established that the contact resistance was negligible. Ac conductivity was measured in air with a Hewlett-Packard 4192A LF impedance analyzer. Cyclic voltammetry was performed using a PAR-273 potentiostat and an Advanced Bryans *XY* recorder. All potentials were recorded versus a Ag/AgCl electrode and were tested, if necessary, with the ferrocene/ferrocenium redox couple. Potassium chloride, lithium perchlorate (Fluka microselect), and ultrapure water were used for preparation of electrolyte solutions. Further details of the procedures used in the electrochemical studies are provided in ref 32.

Results and Discussion

LB Film Formation. For the first dipping cycle, deposition of compound 1, with or without added fatty acid, occurred only on the upstroke; in subsequent cycles the transfer ratio on the upstroke was close to unity. For Y-type films, on the downstroke the transfer ratio for the pure material was <0.1, which was increased to 0.6 by addition of 10–20% tricosanoic acid. A typical molecular area versus surface pressure isotherm for a mixture of compound 1 and 10% tricosanoic acid is shown in Figure 1; the compression rate was ca. 10^{-3} nm^2 molecules s^{-1} and the temperature was 18 ± 2 °C. The average area per molecule at a surface pressure of 15 mN m^{-1} was 0.22 nm^2. The compressed monolayers were quite stable; a monolayer at this pressure decreased its surface area by only ca. 10% after 15 h. The isotherms for samples mixed with 10% and 20% tricosanoic acid were superimposable. The collapse point for the monolayer was found, as usual, to depend upon the compression conditions. Most of the multilayers were assembled by Y-type deposition. However, Z-type films were built up using a specifically designed LB trough in which the monolayer area was expanded during each downstroke of the substrate.

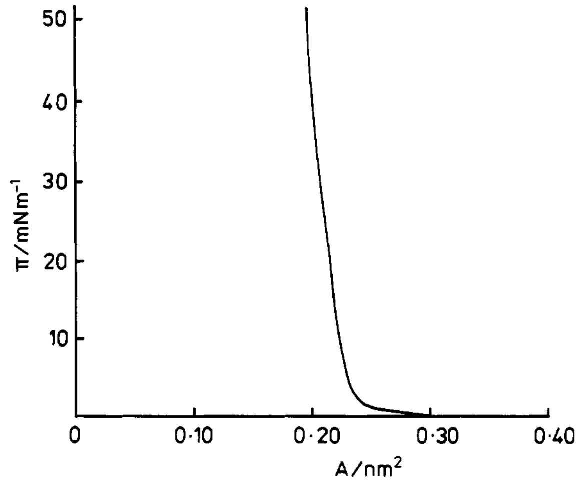


Figure 1. Surface pressure versus area per molecule isotherm for compound 1 mixed with 10% tricosanoic acid (from dichloromethane solution; temperature 18 ± 2 °C; compression rate ca. 10^{-3} nm^2 molecules s^{-1}).

Conductivity Studies. The room-temperature conductivity values, σ_{rt}, for as-deposited LB films of compound 1 depended upon the mode of deposition and the number of layers. For Y-type films, σ_{rt} was generally in the range 10^{-2}–10^{-3} S cm^{-1}, and for some samples this value *increased* to 10^{-1} S cm^{-1} upon storage of the films in air for 10 days. LB films constructed by Z-type deposition had a significantly lower conductivity value, σ_{rt} = 10^{-4}–10^{-5} S cm^{-1}, that tended to decrease upon storage of the films in air. The conductivity of a monolayer film of compound 1 (TTF head group adjacent to the substrate) was ca. 10^{-6} S cm^{-1}, and these films were, therefore, not investigated further. A monolayer thickness of 3.5 nm was assumed in all conductivity calculations, by analogy with previous work on related systems.[5,6]

Such high conductivity values for as-deposited multilayers of a π-donor system are most unusual and an explanation has not been found, although a similar value was reported previously by us for LB films of (*O*-hexadecanoylthiocarboxy)tetrathiafulvalene.[6] The ac conductivity value for as-deposited films of compound 1 was the same as the dc conductivity and did not vary with frequency over the range 50 Hz–10 MHz. This result excludes the possibility of ionic conduction processes in the as-deposited films.

The presence of at least a small percentage of oxidized BEDT–TTF units within the LB film is implied by this high conductivity value. We considered the possibility that doping of the films had occurred inadvertently due to an unknown oxidant in the chloroform spreading solution, perhaps trace amounts of HCl yielding a chloride salt or alternatively a photochemical reaction could occur between donor 1 and $CHCl_3$, yielding $1^{\bullet+}Cl^-$ and $^{\bullet}CHCl_2$. However, no data could be obtained to support this: the isotherms of pure compound 1 spread from benzene solution were identical with those from chloroform solution; also, the conductivity values and UV–visible spectra (see below) of the as-deposited films are indistinguishable from the data obtained from films of the same thickness assembled from chloroform solution. It is conceivable that in both chloroform and benzene solution, molecular oxygen serves as the acceptor to generate the anion radical of O_2 and $1^{\bullet+}$. However, there is no evidence for the presence of oxidized BEDT–TTF molecules in the spectra of the as-deposited films (see below). A few neutral (undoped) TTF derivatives are known to be organic semiconductors (typically $\sigma_{rt} = 10^{-3}$–10^{-5} Scm^{-1}) as single crystals, or thin films prepared by sublimation, due to especially strong intermolecular interactions, arising from short sulfur–sulfur contacts and π–π stacking effects,[19] and it is possible that similar intermolecular interactions operate within the LB film structure of compound 1. Compressed pellet samples of compound 1 are insulating, $\sigma_{rt} = 10^{-12}$ S cm^{-1} (two-probe measurement).

Monolayer films of compound 1 could not be doped (UV spectroscopic evidence) and consequently the conductivity did not change. Iodine doping of multilayers (>4 layers) formed by both Y-type and Z-type deposition reproducibly result in an increase in conductivity of 1–2 orders of magnitude, to a value of 10^{-1} S cm^{-1}. Upon storage in air, the conductivity of the doped multilayer films was stable for up to 4 weeks, and even *increased* for some samples, to reach a maximum value of 1.0 S cm^{-1}. After 4 weeks, a gradual drop in conductivity was observed. This stability of the conducting state represents an important advance in the characterization of conducting LB films of fulvalene-based donors, especially if the materials are to find application in devices.[20] Previous work has shown that conductivity values of LB films of several TTF derivatives decrease by several orders of magnitude within a few days of doping.[5,6] We note that these high conductivity values for LB films of compound 1, mixed with 10–20% fatty acid, are in marked contrast to a previous report by other workers who obtained insulating films of the same compound, mixed with 50% fatty acid, after doping with iodine.[10] In our hands LB films of compound 1 mixed with 50% tricosanoic acid also resulted in insulating LB films.

UV–Vis Spectroscopy. UV–visible spectra were obtained for multilayer films of a mixture of compound 1 and 20% fatty acid. For LB films of >20 layers thickness, formed by Y-type deposition, the optical density of the absorption band at λ_{max} = 380 nm scaled linearly with the number of layers, indicative of reproducible monolayer deposition (Figure 2, inset). However, the LB films had a patchy appearance and IR spectroscopic studies revealed that they were not well ordered (see below).

Figure 2 shows the UV–vis spectra for 7-layer LB films of compound 1 mixed with 20% tricosanoic acid. Curve a was obtained before doping; curve b was measured immediately after doping with iodine vapour; and curve c was measured after several hours storage in vacuo. For the undoped sample, shoulders are seen at ca. 390 and 500 nm. Curve b shows that iodination has a marked effect on the absorption spectrum of the LB film. The optical density increases and a broad absorption band appears in the 800–1300-nm region of the spectrum, probably corresponding to the BEDT–TTF–C_{18} cation radical species. Similar UV–visible spectra have been reported previously by ourselves[3,5,6] and other workers[7] for LB films of related materials.

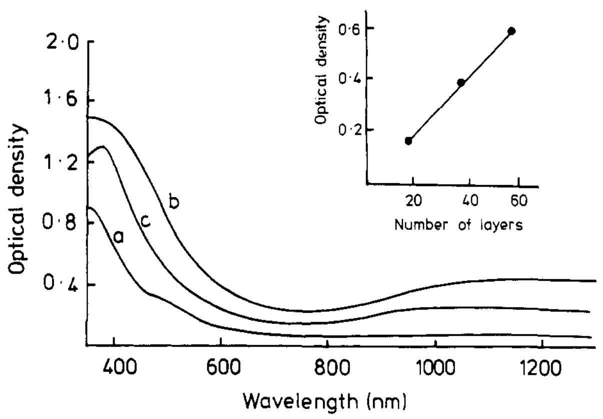


Figure 2. UV–visible spectra of LB films of compound 1 mixed with 20% tricosanoic acid (seven layers, Y-type deposition): a, as deposited; b, immediately after iodine doping; c, several hours after storage of doped film in vacuum. Inset shows the optical density of the adsorption band at λ 380 nm versus number of layers for the as deposited films.

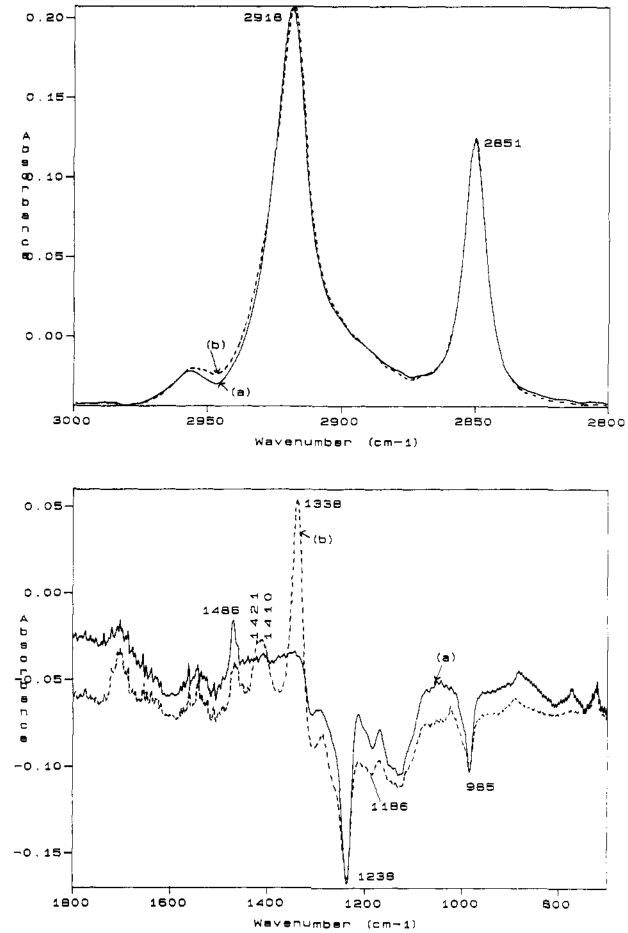


Figure 3. ATR IR spectra of undoped (spectrum a) and iodine-doped (spectrum b) LB films of compound 1 mixed with 20% tricosanoic acid (19 layers, Y-type deposition): (top) 3000–2800-cm^{-1} region; (bottom) 1800–700-cm^{-1} region.

IR Spectroscopy. The IR spectra of Y-type LB films of compound 1 mixed with 20% tricosanoic acid are shown in Figures 3 and 4. The C=C vibrations of the TTF unit are all weak and they appear only in the ATR spectra as a broad band centred at ca. 1520 cm^{-1} (Figure 3, bottom). (This absorption is shifted to low frequency, compared

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with an isolated C=C group, by the presence of attached sulfur atoms.)[21]

Indicators of chain tilt, such as the C=O group (of the fatty acid) and C–H vibrations, suggest that the chains are not oriented perpendicular to the substrate. The C–H and C=O vibrations were examined by ATR and grazing incidence methods, and they show little variation when using the two techniques. From this we conclude that either the chains of the fatty acid and compound 1 in the LB films are tilted at an angle close to 45° or a random distribution of orientations is adopted. Were the chains to be oriented at an angle close to the substrate normal, dichroism would be expected, with the CH_3 stretching bands being enhanced in the grazing incidence spectra (due to the dipoles being perpendicular to the substrate plane). The carbonyl band of the fatty acid chains appears in the same position in both the RAIRS and ATR spectra at 1709 cm^{-1}. Disorder in the C_{18} side chain of compound 1, can be readily explained due to the conformational flexibility of the ethylenedithio bridges of the BEDT-TTF molecule.

Upon doping the LB films of compound 1, marked changes are seen in the infrared spectra: two new bands appear at 1423 and 1342 cm^{-1} in the RAIRS spectra and the intensity of the 1467-cm^{-1} band (CH_2 scissoring vibration) is reduced (Figure 4). These new bands are interpreted as being vibronic in character, i.e., they arise from the interaction of electrons with vibrational modes of the ring system of molecule 1. Similar bands have been noted for TTF and other charge-transfer materials,[4,6,22–25] although it is notable that the strong vibronic mode of conducting LB films of a similar ethylenedithio–TTF derivative[25] occurs at ca. 1200 cm^{-1}. Interestingly, whereas only one vibronic band is observed for doped LB films of TTF derivatives, two bands are seen for compound 1. This is consistent with data for crystalline samples of BEDT–TTF salts.[25,26] It is also noteworthy that in previous work on TTF LB films, doping has had little effect on the alkyl chains,[4,6] whereas in the current study the marked reduction in intensity of the 1467-cm^{-1} band and of the ν-(CH_2) bands near 3000 cm^{-1} (Figure 4) indicates that rearrangement of the alkyl chains occurs upon doping.

Another interesting feature of the IR spectra of compound 1 is the appearance of peaks having negative absorbance values. These can be seen at 1238 and 985 cm^{-1} in the ATR spectra of both the doped and undoped forms of the material (Figure 3). They are caused by large changes of the refractive index at the organic semiconductor interface over the frequency range around the absorption maxima. Their appearance is dependent on a number of factors, but it has been observed that they are characteristic of very strong bands in conjugated or conducting materials.[27,28] We are able to assign the 1238-cm^{-1} band to CH_2 wagging vibrations of the chain of compound 1, but the assignment of the other band with negative absorption is less clear.

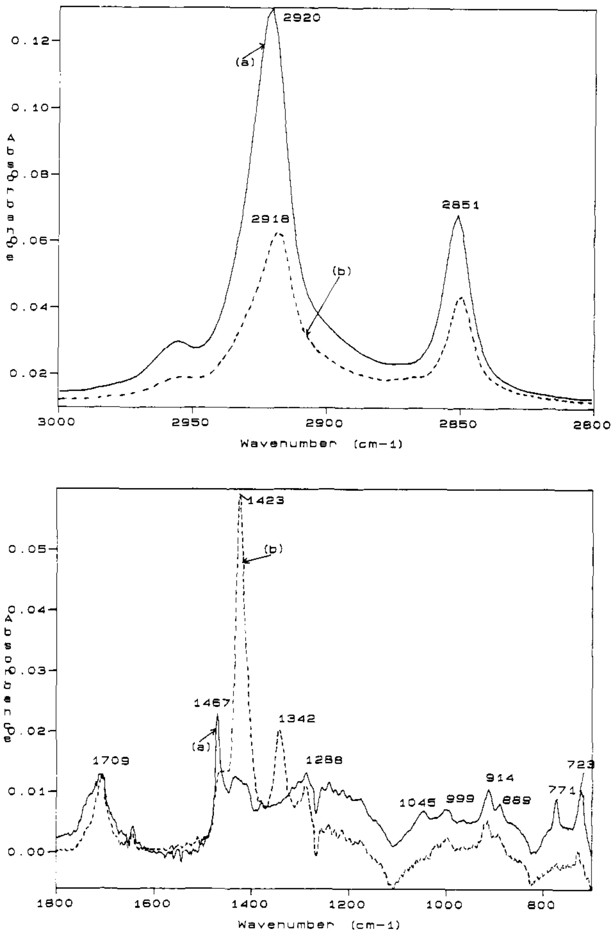

Figure 4. RAIRS spectra of undoped (spectrum a) and iodine-doped (spectrum b) LB films of compound 1 mixed with 20% tricosanoic acid (31 layers, Y-type deposition): (top) 3000–2800-cm^{-1} region; (bottom) 1800–700-cm^{-1} region.

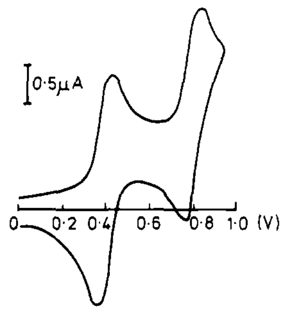

Figure 5. Cyclic voltammogram of compound 1 in dichloromethane solution, 0.1 M $Bu_4N^+PF_6^-$, Pt disk electrode (1.6 mm diameter) versus Ag/AgCl, scan rate 100 mV s^{-1}.

Electrochemistry. We have studied the electrochemistry of compound 1, in solution and in LB film form by cyclic voltammetry. Compound 1 undergoes two, reversible, one-electron oxidations in dichloromethane solution at $E^{1/2}$ = 0.42 and 0.90 V (Figure 5). These data are similar to those reported for the parent unsubstituted BEDT–TTF.[29]

There are very few reports on electrochemical studies on LB films of charge-transfer materials.[30–32] The elec-

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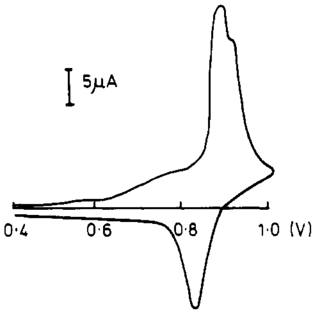

Figure 6. Cyclic voltammogram of a five-layer LB film of a mixture compound 1 and 20% stearic acid on indium tin oxide glass, saturated aqueous KCl solution, scan rate 50 mV s^{-1}.

trochemistry of a monolayer and multilayers of compound 1 was studied in saturated KCl, saturated $LiClO_4$ and 0.2 M $LiClO_4$ aqueous solutions. In all cases the peak current decreased rapidly, possibly due to instability of the cation radical of compound 1 in aqueous solution or to partial solubility of the oxidized material. The cyclic voltammograms typically showed prepeak and postpeak shoulders which varied with different samples. We tentatively suggest that these additional peaks relate to different domains in the LB film structure (cf. the IR spectroscopic results discussed above which suggest the films are not well-ordered). However, the main redox peaks observed for LB films of compound 1 were highly reproducible for different samples, and they do *not* correspond to the solution electrochemistry. In saturated KCl solution the first oxidation peak occurs at ca. 0.9 V (following a prewave shoulder at ca. 0.8 V), i.e., the first oxidation wave seen at 0.42 V in the solution voltammogram is absent in the LB film. Data for a five-layer LB film are shown in Figure 6. It appears, therefore, that the first oxidation of compound 1 is shifted anodically to coincide with the second oxidation potential. However, it is not clear whether or not under these conditions this is a two-electron wave. The anodic peak half-width was higher than the value expected for a two-electron surface wave (45 mV); a difference of 60–80 mV between the peak potentials was usually observed. However, the cyclic voltammogram of a monolayer LB film in 0.2 M $LiClO_4$ solution suggests that the two oxidation waves do coalesce, as two separate reduction peaks are clearly seen at 0.65 and 0.4 V (Figure 7). Thus we conclude that the dication of compound 1 is formed upon electrochemical oxidation of the LB film. The different electrochemical behavior of solution and LB film samples of compound 1 may be due to increased strength of interaction between the cation radical and dication states in the LB film samples.[33]

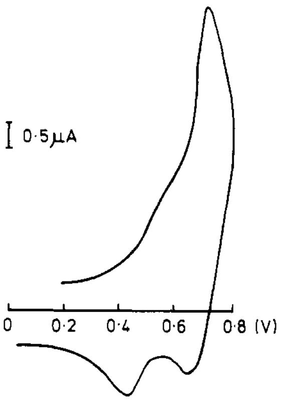

Figure 7. Cyclic voltammogram of a monolayer LB film of a mixture of compound 1 and 20% stearic acid on ITO glass, 0.2 M $LiClO_4$ solution, scan rate 100 mV s^{-1}.

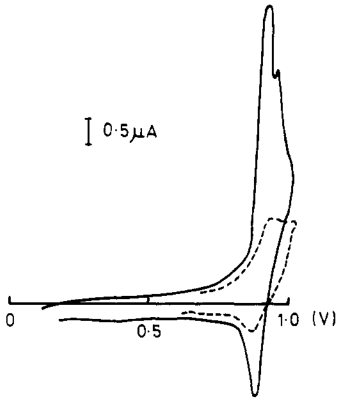

Figure 8. Cyclic voltammograms of a monolayer LB film of a mixture of compound 1 and 20% stearic acid on ITO glass in saturated KCl solution, scan rate 25 mV s^{-1}; initial scan (full line); second scan (dashed line).

Due to the rapid decrease in peak intensity upon recycling, we have not been able to determine the dependence of peak current on scan rate, and therefore we cannot establish whether or not the CV response corresponds to a surface wave.[34] The cyclic voltammograms of a monolayer film (first and second scans) are shown in Figure 8. Estimation of the electroactive coverage from the charge consumed under the anodic peak suggests that the electroactivity of the LB films was not complete. However, the electroactivity of five-layer films was several times higher than that of a single monolayer, so clearly the multilayer structure, and not just the inner monolayer, is electroactive. We suggest that the disorder within the layers (IR evidence) facilitates the transport of ions through the film, and possible nonbonded S- - -S interactions between molecules from different layers facilitate electron transport.

Conclusion

Compound 1 mixed with 10–20% stearic acid forms stable monolayers at the air–water interface which can be transferred onto a variety of substrates. Both Y-type and Z-type multilayers could be built up. The LB films of compound 1 possess high conductivity values in both the as-deposited and iodine-doped states; *the conductivity remained approximately constant for as long as 4 weeks upon storage of the films in air.* This stability represents an important step forward in the study of LB films of charge-transfer systems. The discrepency between these high conductivity values and the insulating LB films of the same compound reported previously by other workers[10] is explained by the large proportion of fatty acid used in the previous study. IR spectroscopy shows the presence of two vibronic bands after oxidation of the LB films with iodine. The films are not well-ordered, and the side-chain

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is tilted relative to the substrate surface. The disorder can be explained by the conformational flexibility of the ethylenedithio bridges of BEDT–TTF system 1. Cyclic voltammetry shows that the oxidation of the LB layers of compound 1 is shifted anodically, compared with solution data, and both redox couples LB films are not stable electrochemically in aqueous media. This work emphasises the key role played by monolayer organisation of charge-transfer materials in determining the conduction properties of the resulting LB films. Further studies on new TTF and BEDT–TTF derivatives can be expected to shed light on structure/property relationships of conducting LB films.

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