Table IV. Intensity/mg (Arbitrary Units) of EPR Signal for Solids Obtained, at Different Pressures, from GeH_4/CH_4 3:1 Mixtures as a Function of Annealing Temperature

$GeH_4 + CH_4$ total press., kPa	525 K		675 K		875 K	
	$g = 2.0025$	$g = 2.018$	$g = 2.0025$	$g = 2.018$	$g = 2.0025$	$g = 2.018$
46.7	2.06×10^{-4}	3.21×10^{-3}	9.93×10^{-3}	1.63×10^{-2}	6.68×10^{-3}	‖
66.7	5.36×10^{-4}	7.02×10^{-3}	3.32×10^{-3}	7.46×10^{-2}	6.05×10^{-5}	‖

the intensity of the signal first increases to a maximum in the 670–920 K range, according to the authors,[30,32–34] and then decreases. In any case, its attribution to carbon atoms impurities seems to be widely accepted.[32,33,35,36] In a previous study on the solid obtained by radiolysis of pure GeH_4,[34] in the absence of any reasonable source of carbon, the signal at $g = 2.0025$ was attributed to free electrons. Certainly for the material here examined the contribution of carbon atoms to the signal is obviously of major importance.

In our material the signal of Ge dangling bonds also appears. The magnitude and the annealing behavior of both signals are nearly comparable, suggesting that both C and Ge dangling bonds evolve in a similar way vs temperature, in spite of the different M–H bond energies.

In Table IV is evidenced that the dangling bonds in the system (the values are chosen as significative samples but are the same in any experimental condition here used) reach a maximum at about 675 K, i.e., between the first and the second phase transition.

Conclusions

Irradiation of the GeH_4/CH_4 mixtures originates materials with a low carbon content, even when the methane concentration is high.

The solid compounds obtained by irradiation of the GeH_4/CH_4 mixtures at room temperature are generally formed as powder, and, therefore, they do not show any straight application.

However, the study of these materials is important as it permits us to understand the mechanism of formation of alloys in deposition processes. Moreover, the results obtained can be helpful in planning thin-film alloys, which theoretical considerations[6] and some recent experiments indicate to have interesting photovoltaic properties. Preliminary X-ray radiolysis experiments ran at 443 K led to a solid thin homogeneous film.

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Registry No. GeH_4, 7782-65-2; CH_4, 74-82-8.

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Semiconducting Langmuir–Blodgett Films of New Long-Chain Tetrathiafulvalene Derivatives

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Four new tetrathiafulvalene (TTF) derivatives, viz. octadecylthio-TTF (**4**), octadecylseleno-TTF (**5**), octadecyltelluro-TTF (**6**), and 16-(thiotrimethyltetrathiafulvalenyl)hexadecanoic acid (**7**) form Langmuir–Blodgett films which are semiconducting ($\sigma_{rt} = 10^{-3}$–10^{-4} S cm^{-1}) after iodine doping. These layers have been characterized by UV/visible and IR spectroscopy in the undoped and doped states.

Introduction

There is current interest in the use of Langmuir-Blodgett (LB) technique to organize electron donor and acceptor molecules at the molecular level with the aim of producing conducting charge-transfer complexes in the form of ultrathin films.[1–8] In this context, amphiphilic tetrathiafulvalene (TTF) derivatives are at the forefront

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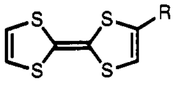
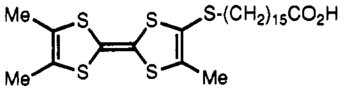
of attention.[9-17] Iodine-doped LB films of compounds **1**,[9,13] and **2**,[14,17] in which the donor is present in a mixed valence state, have maximum conductivity values, $\sigma_{rt} = 10^{-2}$ and 1.0 S cm^{-1}, respectively, while LB films formed by a 1:1 complex of compound **3** and TCNQ have a conductivity value of $\sigma_{rt} = 10^{-3}$ S cm^{-1} without doping.[11]



1; R = C(O)-$C_{15}H_{31}$
2; R = C(S)-O-$C_{16}H_{33}$
3; R = CH(OH)-$C_{17}H_{35}$
4; R = S-$C_{18}H_{37}$
5; R = Se-$C_{18}H_{37}$
6; R = Te-$C_{18}H_{37}$



7

We now describe the formation and characterization of LB films of a range of new amphiphilic TTF derivatives **4–7** which bear one long side chain, attached to the TTF ring via a chalcogen atom. The side chain of compounds **4–6** is hydrophobic and so the TTF ring is the hydrophilic part of these molecules. In contrast, the side chain of compound **7** carries a terminal, hydrophilic, carboxylic acid group.

Experimental Section

Synthesis and Solution Electrochemistry. The syntheses of compounds **4–6**,[16] which were prepared in Durham, and compound **7**,[18] which was prepared in Copenhagen, are described elsewhere. Compound **4**: analysis found C, 59.3; H, 8.2; $C_{24}H_{40}S_5$ requires C, 59.0; H, 8.2%. Compound **5**: analysis found C, 53.5; H, 7.7; S, 30.1; $C_{24}H_{40}S_4Se$ requires C, 53.8; H, 7.5; S, 29.3%. Compound **6**: analysis found C, 49.4; H, 6.7; $C_{24}H_{40}S_4Te$ requires C, 49.3; H, 6.9%. Compound **7**: analysis found C, 56.7; H, 7.4; S, 29.6; $C_{25}H_{40}S_5O_2$ requires C, 56.4; H, 7.5; S, 30.1%. A complex of compound **7** and tetracyano-*p*-quinodimethane (TCNQ) was prepared by mixing the two components in dichloromethane solution. A purple complex of 1:1 stoichiometry was isolated in 90% yield. Analysis found: C, 60.4; H, 6.1; N, 7.6; $C_{37}H_{44}N_4O_2S_5$ requires C, 60.3; H, 6.0; N, 7.6%. ν_{max} (KBr) 2193 (C≡N) cm^{-1}. The complex has a two probe, compressed pellet conductivity value, $\sigma_{rt} = 10^{-10}$ S cm^{-1}. Cyclic voltammetric data for TTF derivatives **4–7** were recorded versus Ag/AgCl, Pt button electrode, 20 °C, scan rate 100 mV s^{-1}; 5×10^{-5} mol dm^{-3} compound, 0.1 mol dm^{-3} $Bu_4N^+ClO_4^-$ in acetonitrile using a BAS 100 electrochemical analyzer.

Table I. Solution Redox Potential for Compounds 4–7: Area/Molecule at 30 mN m^{-1} Pressure and Conductivity Data for LB Films of Compounds 4–7

				conductivity σ_{rt}, S cm^{-1}	
compd	$E_1^{1/2}$, V	$E_2^{1/2}$,[a] V	area/ molecule, nm^2	before doping	18 h after I_2 doping
4	0.50	0.88	0.16	1×10^{-5}	8×10^{-2}
5	0.49	0.90	0.17	3×10^{-6}	6×10^{-3}
6	0.46	0.89	0.14	1×10^{-6}	1×10^{-3}
7	0.50	0.89	0.30	2×10^{-6}	8×10^{-3}

[a] Cf. values of $E_1^{1/2}$ and $E_2^{1/2}$ obtained under identical conditions for the following compounds: TTF, 0.34, 0.78; compound **1**, 0.52, 0.90; compound **2**, 0.49, 0.86; compound **3**, 0.41, 0.76 V.

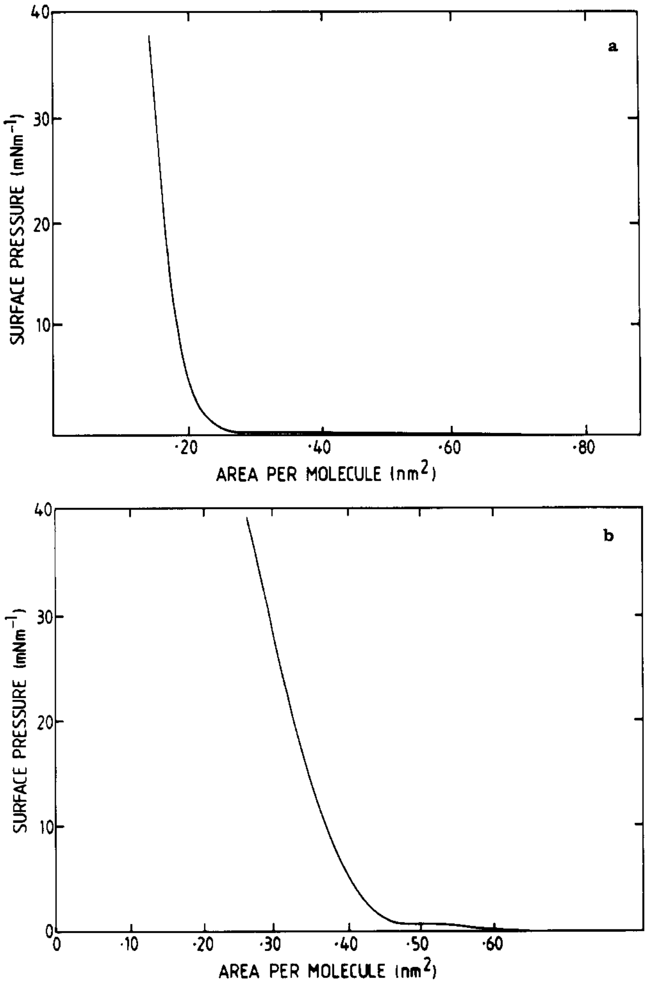


Figure 1. Surface pressure versus area per molecule isotherms for compounds **4** (a) and **7** (b) (temperature 20 °C; compression rate 5.0 cm^2 min^{-1}).

LB Film Formation. A fresh ca. 2×10^{-3} M solution of the compounds in chloroform was spread onto an ultrapure water surface at 20 °C. After evaporation of the solvent, the film was compressed at a rate of 2×10^{-3} nm^2 molecule^{-1} s^{-1} while the surface pressure versus area was monitored. Y-type deposition of compound **4–7** has been achieved onto hydrophobic or hydrophilic glass substrates. In all cases the dipping pressure was 30 mN m^{-1} and the maximum dipping speed was ca. 1 cm min^{-1}. Film quality was significantly increased when 15% stearic acid was added to the solution of compounds **4–7**. The deposition ratio for the mixtures was ca. 0.9–0.95, (cf 0.7–0.75 for pure materials **4–7**). Doping was achieved by exposing the LB films to iodine vapor in a sealed container for 2 min.

Characterization of the LB Films. Infrared and UV/visible near-IR absorption measurements on the LB films deposited on CaF_2 crystal were recorded using Mattson Sirius 100 Fourier transform and Cary 2300 spectrophotometers, respectively. Direct current lateral conductivity data for different numbers of layers on glass substrates were obtained using standard two-probe

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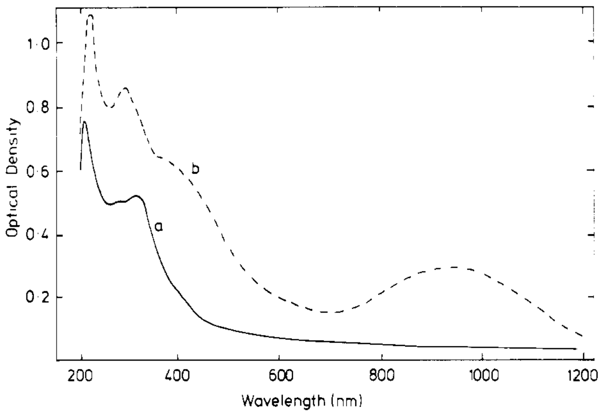

Figure 2. UV visible near-IR absorption spectra of LB films of compound 4 (36 layers): a, as deposited; b, 1 h after iodine doping.

techniques. Electrodes were attached to the film by the use of air-drying silver paste.

Results and Discussion

Solution Electrochemistry. The electron-donor ability of the new TTF derivatives 4–7 has been studied by cyclic voltammetry which reveals the presence of two, reversible, one-electron oxidation waves for each of the donors (Table I). The higher oxidation potential of compounds 4–7, relative to TTF, shows that the donor ability is slightly reduced by attachment of the chalcogen atom to the ring system. A similar increase in oxidation potential was observed with compounds 1[9] and 2.[14]

Isotherms. Figure 1 shows the surface pressure, π, versus area per molecule isotherm for compound 4 (Figure 1a) and compound 7 (Figure 1b). Data for compounds 4–7 are presented in Table I. The area per molecule in the condensed phase, assuming monolayer coverage, for compounds 4–6 is significantly lower than that expected for the cross-sectional area of the molecules (estimated using conventional space-filling models and X-ray crystal structure data for TTF derivatives), whereas for 7 the area is closer to the expected value (ca. 30 Å). This may be due to a slight solubility of the compounds in the subphase or the presence of small amounts of impurities in the samples. (Samples 4–7 were pure as judged by elemental combustion analysis: see Experimental Section). These isotherms suggest that molecules 4–7 are arranged with the side chains near normal to the subphase plane. For compounds 4–6 it is likely that the relatively hydrophilic TTF ring is in contact with the water surface, by analogy with compounds 1 and 2.[13,14,17] While in contrast to this orientation, compound 7 is probably inverted, with the polar carboxylic acid group on the water surface.

Conductivity Studies. Room-temperature conductivity data for LB films of compounds 4–7 are given in Table I. A monolayer thickness of 3.5 nm was assumed in all conductivity calculations. The conductivity of the as-deposited films was typically 10^{-5}–10^{-6} S cm^{-1}. The maximum conductivity of the doped films, measured 18 h after exposure of the LB films to iodine vapor for 2 min, was 10^{-3}–10^{-4} S cm^{-1}.

Ultraviolet Spectroscopy. Spectra were obtained from solution and from LB films of compounds 4, 5, and 7. Spectra for sulfide and selenide derivatives 4 and 5 were identical in all cases. The solution spectra of compounds 4 and 5 in acetonitrile showed absorptions at 235, 320, and 375 nm. Figure 2 shows the UV/vis/near IR spectra for LB films of TTF derivative 4. Curve a was obtained for 36 layers deposited onto glass; curve b was measured for the same thickness sample 1 h after doping with iodine vapor (this spectrum was unchanged after 25 h).

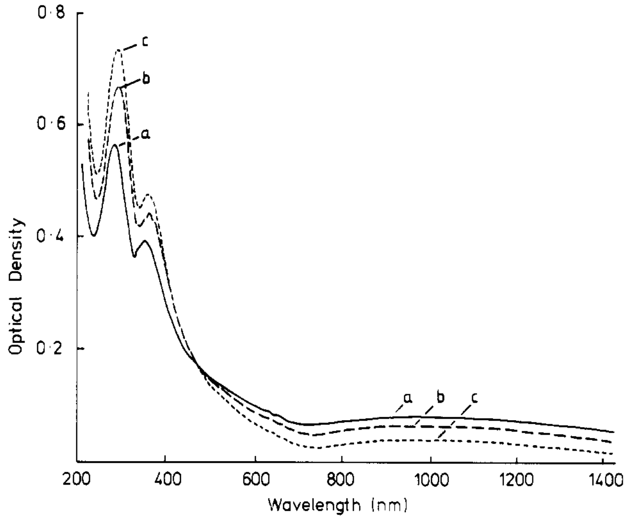

Figure 3. UV visible near-IR absorption spectra of LB films of compound 7 (30 layers): a, 5 min after iodine doping; b, 2 h after doping; c, 18 h after doping.

For the undoped sample 4, absorptions are present at 218, 285, and 316 nm (curve a) which can be assigned to intramolecular π–π^* transitions of the TTF unit.[19] Curve b in Figure 2 shows that oxidation with iodine has a marked effect on the absorption spectrum of the LB film. Absorption bands at 225, 290, 375 (shoulder), and 985 nm are now observed, and there is a marked increase in intensity of the absorption bands relative to the undoped sample. The new bands at 375 and 985 nm (curve b) can be assigned to π–π^* intramolecular electronic transitions of the TTF radical cations and charge-transfer absorptions, respectively, which are produced upon doping.[19] The optical density of the 285/290 nm absorption band of the undoped and doped films scales approximately linearly with the number of layers in the LB assembly (data obtained for 20, 30, and 40 layers), which is indicative of reproducible monolayer deposition.

LB films of compound 7 (30 layers) show absorptions before doping at 290 (shoulder) and 400 (broad shoulder) nm. Figure 3 presents data obtained for the same sample 7 at 5 min, 2 h and 18 h after iodine doping: curves a, b, and c, respectively. These spectra are qualitatively very similar to those of the doped sample 4 (Figure 2). Bands are observed at 285 and 360 nm along with a very broad band at 900 nm. It is noteworthy that the intensity of all the bands for the doped sample 7 decreases with time, and, in contrast to sample 4, the absorption at 900 nm has disappeared after 18 h.

Polarized UV spectra of LB films of compound 7 after iodine doping are shown in Figure 4. The charge-transfer band decreases in intensity with increasing angle of incidence of linearly polarized light, while the π–π^* transitions of the TTF system increase in intensity. This provides evidence that the TTF system in the doped films is aligned at a high angle to the substrate surface.

Infrared Spectroscopy. The transmission IR spectra for LB films of compounds 4 and 7, deposited on calcium fluoride substrate, have been obtained before and after doping. Figure 5 shows the spectra for 36 layers of compound 4 before doping (Figure 5a), 5 min after iodine doping (Figure 5b) and 26 h after iodine doping (Figure 5c). Most of the features observed in Figure 5a are asso-

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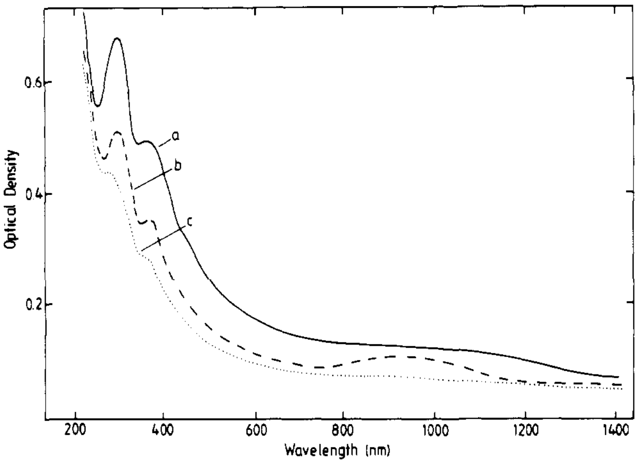

Figure 4. Polarized UV/visible/near-IR absorption spectra of LB films of compound 7 (42 layers) 2 h after iodine doping at different angles of incidence parallel to the plane of the substrate: a, angle = 0°; b, angle = 30°; c, angle = 45°.

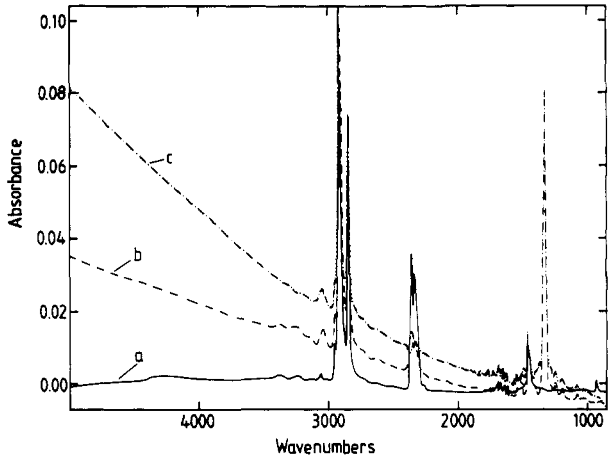

Figure 5. IR transmission spectra for LB films of compound 4 (36 layers): a, as deposited; b, 5 min after iodine doping; c, 26 h after iodine doping.

ciated with the thioalkyl chain of compound 4. (The band at 2350 cm^{-1} is due to atmospheric carbon dioxide absorption.) The strong bands at 2918 and 2852 cm^{-1} are easily assigned to asymmetric and symmetric CH_2 stretching vibrations, respectively. The small absorption at 2958 cm^{-1} is associated with terminal CH_3 stretching vibrations, and the band at 1472 cm^{-1} is the CH_2 scissoring vibration.

The spectra obtained after doping the film of compound 4 in iodine vapor show two striking new features: a charge-transfer band extends from ca. 1800 to beyond 5000 cm^{-1} and an intense absorption has appeared at 1333 cm^{-1}. This last peak can be explained by the coupling of conduction electrons to the vibrational modes of compound 4, which allows previously inactive IR bands to become active.[20] Similar data have been obtained previously for LB films of related charge-transfer materials.[3,4,13]

Infrared spectra for 38 layers LB films of compound 7 are shown in Figure 6. The spectra obtained before doping

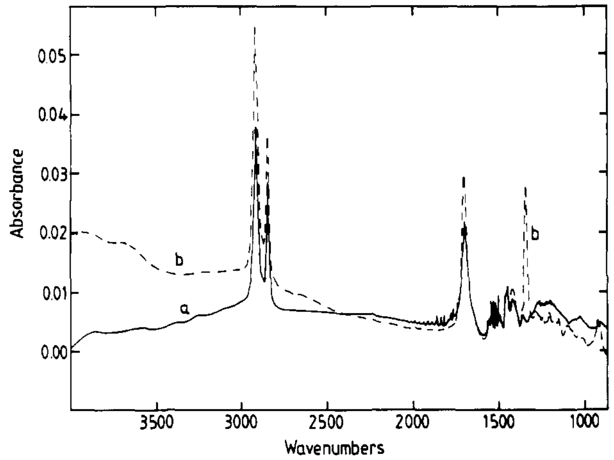

Figure 6. IR transmission spectra for LB films of compound 7 (38 layers): a, as deposited; b, 72 h after iodine doping.

(Figure 6a) and 72 h after doping with iodine (Figure 6b) are qualitatively similar to those obtained for compound 4 discussed above. The carbonyl group of compound 7 accounts for the absorption at 1703 cm^{-1} (Figure 6a) which shifts slightly to 1707 cm^{-1} in the doped sample (Figure 6b). The vibronic coupling band in the doped films is observed at 1346 cm^{-1}, and the intensity of this band increases with time for ca. 0.5 h after doping. This is in contrast to films of compound 4 for which the intensity of the vibronic coupling band is unchanged between 5 min and 26 h after doping (Figure 5). This implies that iodine oxidation occurs more slowly for compound 7 than for compound 4.

Compound 7 forms a 1:1 complex with TCNQ. Unfortunately, attempts to form LB films of the complex were unsuccessful: the films which formed on glass slides were composed solely of the donor 7 (IR evidence).

Conclusion

This work has extended the range of electron donors that form LB films which are conducting upon oxidation. It is noteworthy that the TTF derivatives 4–7 described herein form films of lower conductivity than derivatives 1 and 2 that we have studied recently,[9,13,14,17] although the side chains are of similar length and the solution redox properties of the systems are comparable. We conclude, therefore, that the carbonyl and thioester groups adjacent to the TTF ring of compounds 1 and 2, respectively, play a significant role in ordering the monolayers of these materials at the air–water interface and in establishing order within the LB multilayers. This may be a consequence of the increased polarity of the TTF ring resulting from π-conjugation with the C=O or C=S: to shed light on this, further experiments are in progress using TTF derivatives carrying various functional groups in the side chain.

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Registry No. 4, 128881-69-6; 5, 128881-70-9; 6, 128881-71-0; 7, 136058-14-5; I_2, 7553-56-2.

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