Semiconducting Langmuir–Blodgett Films of Non-amphiphilic Ethylenedithio–Tetrathiafulvalene Derivatives Bearing Pyridine and Pyridinium Substituents

Leonid M. Goldenberg,[a,b,c] James Y. Becker,*[d] O. Paz-Tal Levi,[d] Vladimir Yu. Khodorkovsky,*[d] Martin R. Bryce*[b] and Michael C. Petty*[c]

[a] *Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, 142432 Moscow region, Russia*
[b] *Department of Chemistry, University of Durham, Durham, UK DH1 3LE*
[c] *School of Engineering, University of Durham, Durham, UK DH1 3LE*
[d] *Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84120, Israel*

Compounds **1** and **2** form stable Langmuir–Blodgett films which after iodine doping are semiconducting (σ_{rt} = 10^{-3} S cm^{-1}), demonstrating that the attachment of long alkyl chains is not a prerequisite for the formation of conducting LB films of tetrathiafulvalene (TTF)-based charge-transfer complexes.

The Langmuir–Blodgett (LB) technique has become a powerful tool for producing multilayer films with semiconducting properties.[1] The vast majority of components for conductive LB films are amphiphilic compounds, all based on molecules that were already known to form conducting crystals. Amphiphilic analogues of bis(ethylenedithio)tetrathiafulvalene (ET) have been among the most studied derivatives for conducting LB films, and they show in-plane room temperature dc conductivity values of up to 1 S cm^{-1} after doping with iodine vapour.[2–12] This value was found recently for iodine-doped films of $C_{18}H_{37}$-ET.[12]

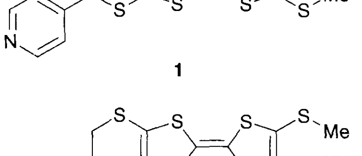
Here we report that two novel non-amphiphilic molecules, 4,5-dimethylthio-4′,5′-(4-pyridyl)ethylenedithio-TTF **1** and its *N*-methyl alkylated pyridinium iodide salt **2**, both form semiconducting LB films. In the former compound either the pyridyl or the TTF group could be the hydrophobic moiety acting as a substitute for the 'traditional' long-chain alkyl tail, whereas in the latter derivative, the pyridinium group is clearly the hydrophilic moiety and the TTF-based part replaces the alkyl tail. To the best of our knowledge, the only known example of a non-amphiphilic TTF-based LB film is provided by $(PhCH_2S)_4TTF$, which does not form a stable monolayer at the air–water interface, unless at least 50% mole ratio of a fatty acid is added.[13] Furthermore, it is noteworthy that compound **2** contains both donor and acceptor units linked together *via* a non-conjugated spacer; analogous (although amphiphilic) D–σ–A and D–π–A systems, based on TCNQ and aromatic donors, have been studied by Metzger and coworkers,[14] and Ashwell and coworkers,[15] respectively.

Compound **1**† was formed in 22% yield by cross-coupling between 4,5-di(thiomethyl)-1,3-dithiole-2-thione[12] and 4,5-(4-pyridyl)ethylenedithio-1,3-dithiole-2-one,[16] in the presence of trimethyl phosphite. Compound **2**† was formed by refluxing **1** with MeI in acetone for 0.5 h.

In a typical experiment, compound **1** was spread on the water surface of a Langmuir–Blodgett trough from CH_2Cl_2 or THF solution (0.5 g l^{-1}), forming an isotherm of surface pressure *vs.* area per molecule consisting of two condensed regions [Fig. 1(*a*)]. The limiting molecular area for the first and second regions were *ca.* 0.30 and 0.14 nm^2, respectively. The nearly double molecule area in the first condensed region relative to the second suggests the 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 isotherm obtained 2 h after spreading [Fig. 1(*c*)] was steep with a limiting molecular area of *ca.* 0.22 nm^2. It is noteworthy that the isotherms in Fig. 1 intersect through one 'isosbestic' point, a feature which has not, to our knowledge, been reported before for monolayers. The films of compound **1** which were transferred onto a glass slide at 40 mN m^{-1} were predominantly of Z-type deposition, with a transfer ratio of 0.7 ± 0.1. Also, they were not uniform, tending to cover only a narrow band near the upper edge of the substrate.

It is well known that the addition of fatty acid improves the LB behaviour of ill-behaved amphiphilic materials. Therefore, to improve the quality of LB films of **1**, tricosanoic acid $[Me(CH_2)_{21}CO_2H]$ was mixed with **1** in a 1 : 3 molar ratio. Using this mixture a steep isotherm was observed with one compression region and a limiting molecular area of *ca.* 0.40 nm^2 [Fig. 2(*a*)]. The compressed monolayer was stable under these conditions.

In comparison to **1**, compound **2** tends to aggregate on the water surface when spread without fatty acid, affording a small molecular area of 0.05 nm^2. However, upon employing the same conditions as for **1** with fatty acid, a stable floating



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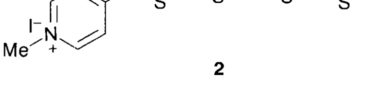

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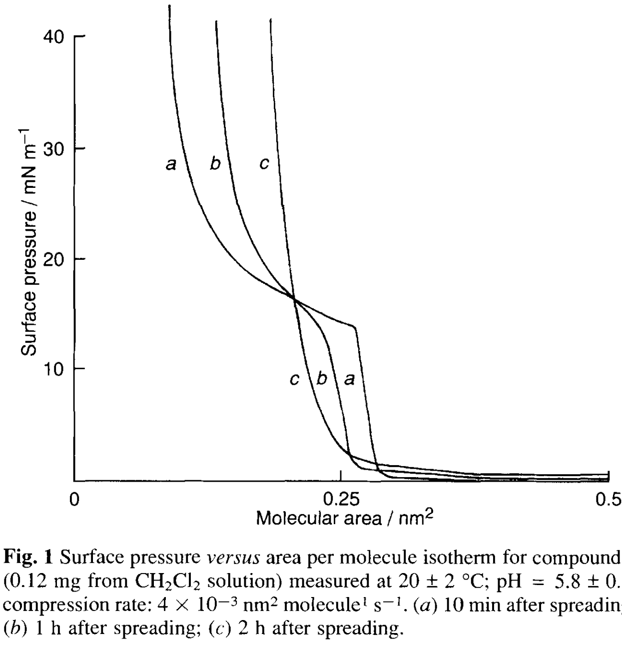

Fig. 1 Surface pressure *versus* area per molecule isotherm for compound **1** (0.12 mg from CH_2Cl_2 solution) measured at 20 ± 2 °C; pH = 5.8 ± 0.2; compression rate: 4 × 10^{-3} nm^2 molecule^{-1} s^{-1}. (*a*) 10 min after spreading; (*b*) 1 h after spreading; (*c*) 2 h after spreading.

monolayer of **2** with a molecular area of 0.23 nm^2 was formed [Fig. 2(*b*)].

The transfer onto a solid substrate of both compounds **1** and **2**, mixed with 25 mol% of tricosanoic acid was achieved by compressing the Langmuir film at 40 mN m^{-1}. Predominantly Y-type deposition could be observed with a transfer ratio close to unity. In-plane conductivity (two-probe) was measured for both freshly deposited films and after doping with iodine vapour, employing silver paste for contacts. Values as high as $\sigma_{\rm rt}$ = 10^{-6}–10^{-5} S cm^{-1} were measured for as-deposited films of both **1** and **2**, whereas doping the samples with iodine vapour resulted in an increase in conductivity up to $\sigma_{\rm rt}$ = 10^{-3} S cm^{-1} for both compounds. The conductivity of the doped LB films remains in the range of $\sigma_{\rm rt}$ = 10^{-3}–10^{-4} S cm^{-1} for several weeks.

The iodine doped LB films were also monitored by visible spectroscopy, showing a charge transfer band at around 900 nm for **1**, which is retained even after storing the film for several hours in air. Surprisingly, a similar band could not be detected for **2**, even for a doped cast film from THF solution, with a thickness corresponding to 15–20 layers of LB film.

In conclusion, this work has demonstrated that semiconducting LB films can be obtained from non-amphiphilic compounds, utilising only 25% molar ratio of a fatty acid. In spite of the differences in the electronic properties of **1** and **2**, their corresponding LB films show similar conductivities, that of **1** being more stable. In addition, only the iodine doped film of **1** shows a characteristic CT band in its visible spectrum.

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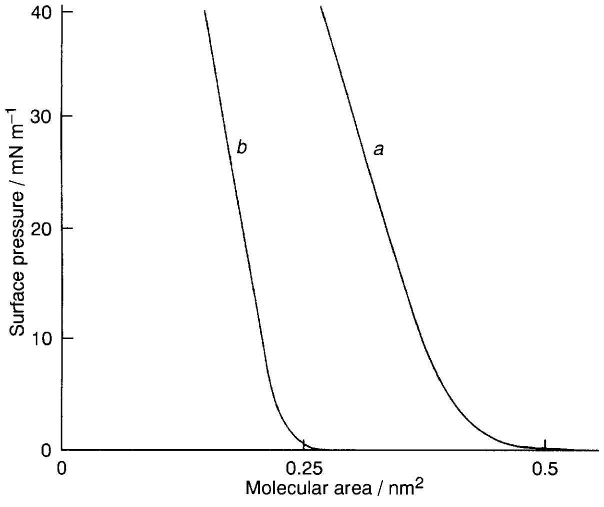

Fig. 2 Surface pressure *versus* area per molecule isotherm for compounds (*a*) **1**, and (*b*) **2**, both from THF (0.5 mg ml^{-1}) with 25% mole of tricosanoic acid (measurement conditions as described in caption of Fig. 1)

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Footnote

† Compound **1**: obtained in 22% yield as yellow crystals from acetonitrile; mp 158–159 °C; ^{1}H NMR (δ, CDCl$_3$): 2.42 (s, 6H), 3.41 (d, 2H), 4.72 (t, 1H), 8.29 (d, 2H), 8.61 9d, 2H). Compound **2**: obtained in 96% yield as red crystals, mp 160–170 °C (slow decomposition). Satisfactory elemental analyses were obtained for both compounds.

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