Highly-conducting Langmuir-Blodgett Films Based on Ni(dmit)$_2$ Anions†

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Langmuir–Blodgett (LB) films of the complex bis-(*N*-octadecylpyridinium)–[Ni(dmit)$_2$] **1** are highly conducting, σ_{max} = 0.8 S cm^{-1} after iodine doping, and have been characterised, in the as-deposited and doped states, by IR and X-ray photoelectron spectroscopy; LB films of complex **1** alternated with *O*-hexadecylthiocarboxytetrathiafulvalene **2** are conducting, σ_{max} = 0.1 S cm^{-1} after iodine doping.

Extensive interest is currently focused on using the Langmuir–Blodgett (LB) technique to produce highly-conducting ultrathin films of charge-transfer complexes.[1] Most of the materials studied are amphiphilic systems based on TCNQ,[2] TTF[3] or related π-donors.[4] Single crystal studies have established that metal(dmit)$_2$ anions (metal = Ni, Pt or Pd) form organic metals and superconductors when complexed with TTF,[5] tetraalkylammonium cations[6] or alkali metal cations,[7] and Japanese workers have obtained conductive thin films of tetraalkylammonium metal(dmit)$_2$ complexes (metal = Ni or Au) by attaching hydrophobic chains to the cation.[8]

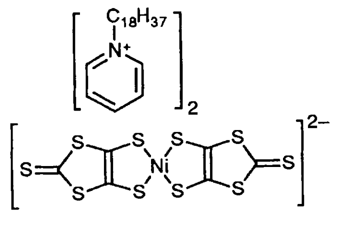
In this communication we discuss the preparation and characterisation of LB films of a new Ni(dmit)$_2$ charge-transfer complex, *viz.* (*N*-octadecylpyridinium)$_2$–Ni(dmit)$_2$ **1**. We also report the formation of the first LB films that incorporate both TTF and Ni(dmit)$_2$ derivatives, *viz. O*-hexadecylthiocarboxy-TTF **2**[3c] and complex **1**.

Complex **1**‡ was prepared from *N*-octadecylpyridinium iodide, following the procedure of Steimecke *et al.*[9] A solution of complex **1** in chloroform (1.0 × 10^{-3} mol dm^{-3}) was used for spreading the molecules onto the surface of ultrapure water. A pressure *vs.* area curve (at 20 ± 2°C) is shown in Fig. 1. Y-type deposition of monolayers of complex **1** has been achieved onto hydrophilic glass substrates at a dipping pressure of 25–30 mN m^{-1} and a maximum dipping speed of 1.0 cm min^{-1}. Films of up to 60 monolayers could readily be deposited. The deposition ratio on the up-stroke was found to be 1.0 ± 0.05; for the down-stroke the deposition ratio was 0.7 ± 0.1.

Transmission IR spectra of a powdered sample of complex **1** show absorption bands at 1437 (C=C), 1051 and 1024 (both C=S) cm^{-1}, which are clearly diagnostic of the [Ni(dmit)$_2$]$^{2-}$ oxidation state.[9] For the as-deposited LB films of complex **1**, these absorptions are replaced by bands at 1348 (C=C) and 1069 (C=S) cm^{-1}, which are consistent with one-electron oxidation having occurred to yield [Ni(dmit)$_2$]$^-$ (Fig. 2*a*). The IR spectrum of the films changed markedly upon doping; immediately after exposure to iodine vapour for 2 min in a sealed container the band at 1348 cm^{-1} disappears, the 1069 cm^{-1} band broadens and a new broad C=C absorption band is present at 1260 cm^{-1} (Fig. 2*b*). This band was originally assigned to the Ni^{4+} oxidation state,[9] *i.e.* [Ni(dmit)$_2$]^0, but it may arise from a mixed valence species.[6a]

X-Ray photoelectron spectroscopy (XPS) provides detailed information about the oxidation processes involved. The Ni(2p$_{3/2}$) binding energies for the powdered sample, undoped film and doped film are 854.4, 854.5 and 854.7 eV, respectively. Compared to the powder, both undoped and doped LB films have a shake-up peak associated with the Ni(2p$_{3/2}$) region. Both nickel features shift to slightly higher binding energies on doping the LB film with iodine. Clear evidence that oxidation occurs in the nickel vicinity is obtained by the examination of the S(2p) XPS spectra. In the case of the powdered sample, the S(2p) region can be fitted to the theoretical 4 : 4 : 2 peak ratios. On forming the LB film, there is the appearance of a new feature at 164.5 eV; this is at the expense of the peak associated with the four sulphur atoms around the nickel centre in the powder form and this new peak becomes more prominent on exposure to iodine vapour. Ionic (618.6 eV, 77%) and covalent (620.9 eV, 23%) iodine species were found to yield the best peak fit for the I(3d$_{5/2}$) spectrum.

Interpretation of the XPS spectra is not as straightforward as it might initially appear, owing to the significant degree of covalent character in the Ni–S bond. Previous XPS studies on a nickel dithiene compound [Ni(S$_2$C$_2$Ph$_2$)$_2$]^z, where z is 0, −1, or −2, indicate that the negative charge in these anions is delocalised on the ligands and resides mainly on the sulphur (evenly distributed over the four equivalent sulphur atoms),



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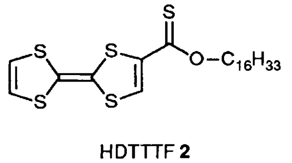

HDTTTF **2**

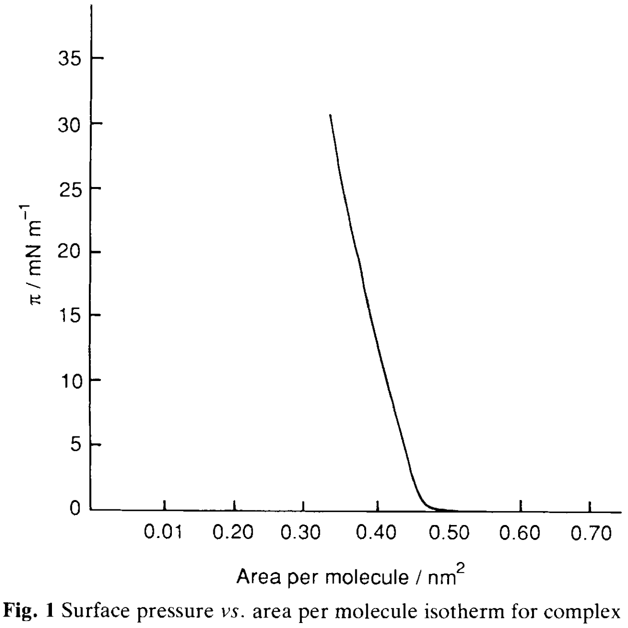

Fig. 1 Surface pressure *vs.* area per molecule isotherm for complex **1**

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† H$_2$dmit = bis-(4,5-dimercapto-1,3-dithiole-2-thione); TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane; TTF = tetrathiafulvalene.

‡ Complex **1**, a black powder, mp 91°C [Found C, 54.5; H, 7.2; S, 29.3; Ni, 5.8. $C_{52}H_{84}N_2NiS_{10}$ (*i.e.* a 2 : 1 complex) requires C, 56.0; H, 7.5; S, 28.7; Ni 5.3%].

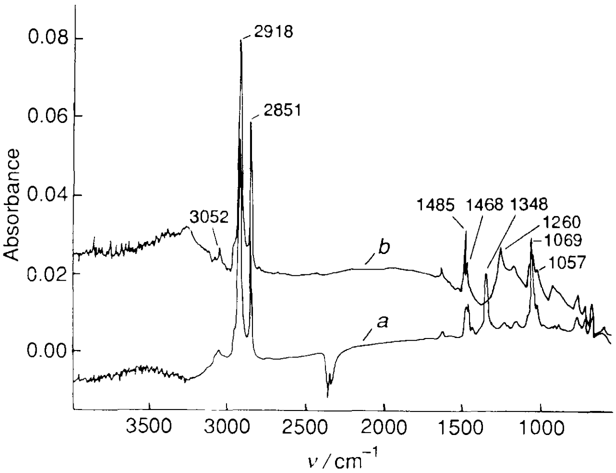

Fig. 2. Transmission IR spectra of LB films of complex **1** (44 layers) (*a*) before doping, (*b*) after iodine doping

whereas the charge on the metal remains essentially constant.[10] Paramagnetic nickel complexes have been shown to exhibit intense shake-up satellites on the higher energy side of the primary peaks in the Ni(2p) photoelectron region, whereas no shake-up satellites occur for diamagnetic nickel complexes. For the powder of complex **1**, there is an absence of a Ni($2p_{3/2}$) shake-up satellite; this is consistent with the diamagnetic square-planar structure of the nickel compound. However, on oxidation the appearance of a shake-up satellite in the Ni($2p_{3/2}$) region implies that the nickel centre has become paramagnetic. Possible cause of this transformation could be attributed to $\mathrm{Ni^{II}} \rightarrow \mathrm{Ni^{III}}$ or Ni(square-planar) → Ni (tetrahedral) or Ni· · · Ni interactions.

The lateral DC conductivity at room temperature of the as-deposited films of complex **1** is $\sigma = 6 \times 10^{-6}$ S cm^{-1} (two-probe measurement). Following iodine doping the conductivity increased with time reaching a maximum after 5 h in the range 0.2–0.8 S cm^{-1}. Conductivity data have been obtained over the temperature range 300–100 K and there is evidence of space charge injection in both the undoped and doped films. These data will be presented in detail elsewhere.

We have recently reported the fabrication of alternate layer LB films of long-chain TTF and TCNQ derivatives using a specially-designed LB trough; these layers were semi-conducting in the as-deposited state.[11] We now report that this technique can be successfully applied to the formation of alternate layers of the Ni(dmit)$_2$ complex **1** and HDTTTF **2**. Complex **1** and HDTTTF **2** were dissolved (separately) in chloroform (1.0×10^{-3} and 2.0×10^{-3} mol dm^{-3} solutions, respectively) before being spread onto the two areas of the alternate-layer trough. Alternate layers of complex **1** and compound **2** were assembled on hydrophilic glass. The lateral DC conductivity at room temperature of an as-deposited 19 layer sample (10 layers of complex **1** and 9 layers of HDTTF) is $\sigma = 1 \times 10^{-6}$ S cm^{-1}; after iodine doping the conductivity increases to a maximum value of 0.1 S cm^{-1}. A full investigation into the structure and properties of these films is currently underway.

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