First *in situ* Monolayer Conductivity Measurements on Water: Bis(ethylenedioxy)tetrathiafulvalene and 2-Decyl-7,7,8,8-tetracyanoquinodimethane Systems

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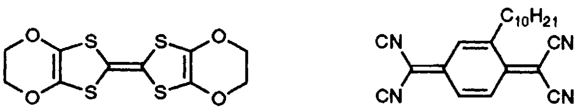
The first *in situ* electrical conductivity measurement of monolayers on water during compression on a Langmuir–Blodgett trough are reported for bis(ethylenedioxy)tetrathiafulvalene and 2-decyl-7,7,8,8-tetracyanoquinodimethane systems, the conductivity of the monolayers being *ca.* 0.6 S cm^{-1}.

The Langmuir–Blodgett (LB) technique has been attracting considerable attention because it gives very thin films of ordered structures with controlled thicknesses at the molecular level.[1] Functionalised LB films based on donors and acceptors have been investigated from the viewpoint of constructing molecular devices.[2,3] Conductive LB films based on intrinsic conductors are of special interest since high conductivities are obtained without any doping.[4–15] This class of compounds provides a possibility of examining film properties such as conductivity and structure starting from isolated molecules or molecular arrays which are compressed together to form monolayers at the air-liquid interface followed by transfer to solid substrates as LB films. Conductivity measurements of a monolayer on an insulating glycerine subphase have been reported[4–6,8,10,11] while conductivity measurements on water have not been done.[8] The monolayer on water, not on glycerine, is directly connected with the resulting LB film since the LB deposition is possible only for a monolayer on water not on glycerine. Here, we report the first *in situ* conductivity measurements of monolayers at the air–water interface and compare the results with those of the LB films on solid substrates.

Powdered charge-transfer complex bis(ethylenedioxy)tetrathiafulvalene **1** (BO, donor) and 2-decyl-7,7,8,8-tetracyanoquinodimethane **2** ($C_{10}TCNQ$, acceptor) (BO–$C_{10}TCNQ$, the stoichiometry is BO : $C_{10}TCNQ$: H_2O=2.5 : 1 : 0.25) or a mixture of the complex with icosanoic acid (C20) at a ratio of 1 : 1 with respect to **2** and C20 was spread on water at 290 K from an acetonitrile : benzene 1 : 1 mixed solution. The LB film of the complex with C20 has been characterised at ambient pressure, the conductivity being as high as 10 S cm^{-1} at room temp. for a 20-layer sample.[15]

Monolayer experiments were done on a Lauda film balance with a compression speed of 2 cm min^{-1}. Monolayer conductivity measurements in the lateral direction were performed with platinum electrodes both in a two-probe (10 kHz, V_{pp} = 5 V) and in a four-probe method (DC, 10 μA). The two-probe measurements were done as reported previously.[6] No pronounced effect of either voltage or frequency over scatter between the measurements was seen. The data (Figs. 1–3) were taken using the two-probe method with the platinum electrodes perpendicular to the moving barrier. Since the measured conductance included both frequency dependent water and frequency independent monolayer contributions, we subtracted the conductance of water (which corresponds to 0.5 S cm^{-1} at 10 kHz if reduced to a monolayer



1 **2**

Fig. 1 Chemical structures of BO **1** and $C_{10}TCNQ$ **2**

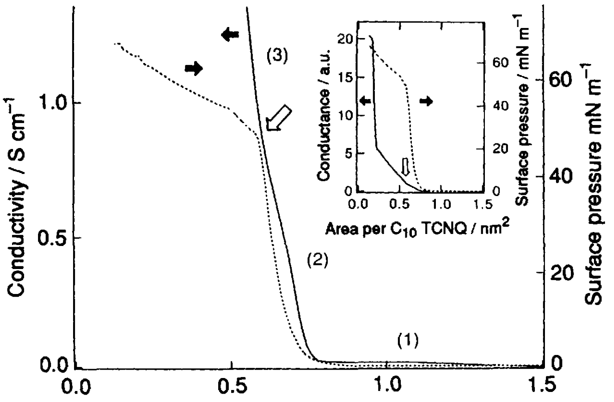


Fig. 2 The σ-A (conductivity area: solid lines) and π-A (surface pressure area: dotted lines) isotherms of BO–$C_{10}TCNQ$ with C20. The numbers in parentheses show the three regions mentioned in the text. The empty arrow indicates an inflection point in the σ-A isotherm, which roughly coincides with the collapse point in the π-A isotherm. The ordinate of the σ-A isotherm is changed in the inset.

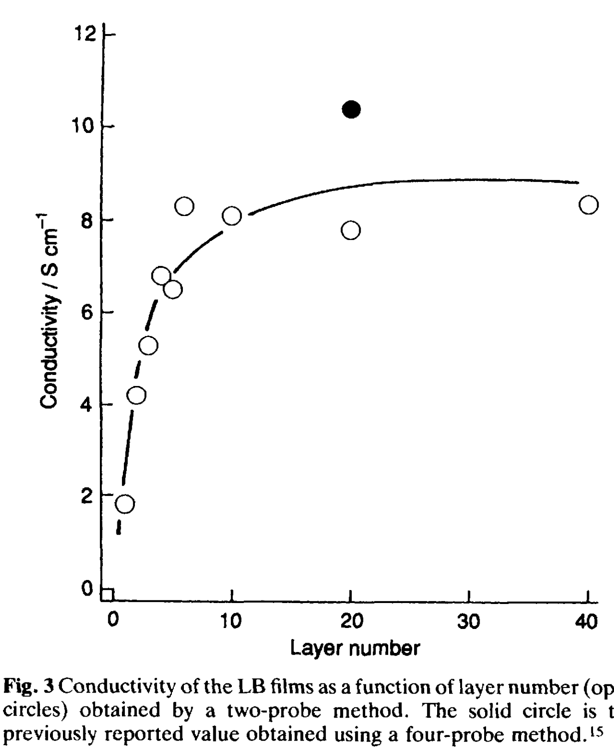


Fig. 3 Conductivity of the LB films as a function of layer number (open circles) obtained by a two-probe method. The solid circle is the previously reported value obtained using a four-probe method.[15]

conductivity) from the results. The thickness of the monolayer was assumed to be 2.5 nm.[15]

The lateral conductivity, as a function of layer number of an LB film transferred at 20 mN m^{-1} using a horizontal lifting method onto a glass plate hydrophobised with 1,1,1,3,3,3-hexamethyldisilazane and coated with gold electrodes, was obtained by a DC two-probe method.

Fig. 2 shows the σ-A (conductivity area) and π-A (surface pressure area) isotherms of the mixed monolayer of BO–C_{10}TCNQ and C20. The isotherms can be divided three ways: i, area compression without any significant increases in surface pressure and conductivity, ii, monolayer formation accompanied by increases in surface pressure and conductivity, and iii, multilayer formation after the collapse point in the π-A isotherm giving rise to an increase in conductance. The empty arrow indicates an inflection point in the σ-A isotherm, which roughly coincides with the collapse point in the π-A isotherm.

The conductivity of the monolayer on water is *ca.* 0.6 S cm^{-1} at 20 mN m^{-1} (*ca.* 0.8 S cm^{-1} at 40 mN m^{-1}). The value of the conductivity is relatively stable and does not change for at least 20 min when measured at a fixed area in the monolayer region. The conductivity is somewhat higher when C20 is not mixed. When the film with C20 is compressed into the monolayer region (<45 mN m^{-1}) and expanded again, the conductivity does not go back to the initial value while the surface pressure goes back to zero. These phenomena may be related to the self-assembly nature of the complex and the structural relaxation of the film.

The lateral conductivity of the LB film is shown in Fig. 3 as a function of layer number. The previously reported value is shown as a solid circle.[15] The conductivity increases with layer number and becomes constant (*ca.* 8 S cm^{-1}) above five layers. The smaller values compared with the previous one (solid circle), which could be due to contact resistance: a four-probe method was used previously. The conductivity of the one-layer LB film is close to that of the monolayer at the air–water interface: slightly lower than the value for the 20-layer LB film. The value of conductivity of the one-layer LB film was unstable and decreased within several minutes in air in contrast to the monolayer at the air–water interface. These results suggest the importance of the substrate–subphase–molecule interaction in monolayer assemblies, which may also cause the layer–number dependent conductivity. Another explanation for the layer–number dependence is based on 2D (two-dimensional)-3D percolation conductivity change as a function of layer number, which has been reported for polyhexylthiophene based LB films, where the conductivity changes by three orders of magnitude.[16]

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