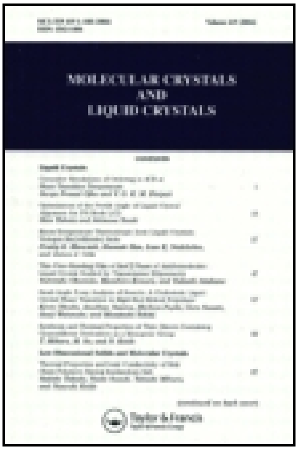

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Novel Conducting LB Films

A. Ruaudel-teixier [a] , M. Vandevyver [a] & A. Barraud [a]
[a] Commissariat à Ĭ Energie Atomique, DPC/SCM, CEN. SACLAY, 91191, GIF SUR YVETTE CEDEX, France

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NOVEL CONDUCTING LB FILMS.

A. RUAUDEL-TEIXIER, M. VANDEVYVER, A. BARRAUD
Commissariat à l'Energie Atomique, DPC/SCM, CEN.SACLAY,
91191 GIF SUR YVETTE CEDEX, France.

Abstract A layered anisotropic conducting structure is described. The LB technique is used for an amphiphilic TCNQ salt.

During the past two decades, organic chemists and solid-state physicists have been keenly interested in 1D organic conductors. In fact highly organised organic molecules exhibiting electronic conductivity now exist. These properties were formely only known amongst inorganic elements. In another connection the intercalated compounds have already opened the way of layered alternating structures of organic sequences followed by inorganic ones (ex. dichalcogenides and amines or cobaltocens). However in these structures it is the inorganic plane which is the conductor. The L.B. technique offers the possibility of organising organic molecules into close-packed multilayers by an already well established method (1). These molecules have to be amphiphilic i.e. hydrophobic (long aliphatic chains of at least 18 carbons) and hydrophilic. This hydrophilic moeity is chosen so as to confer specific physical properties to the LB film. The inert hydrophobic chains play the role of an organising matrix due to the lateral Van der Waals interactions, thus inducing order in the polar heads. A logical approach then, was to try to adapt this technique to order suitable conducting organic compounds which precisely require long range packing.

To obtain conducting polymers in the form of LB films of the

$(CH)_x$ or $(C_6H_4)_x$ type did not seem attractive for a first attempt because of the difficult synthesis within multilayers. Therefore a more facile approach was to work with TCNQ complexes in order to prove the feasability of the concept of a conducting layered system. As one of the simplest examples, we chose the pyridinium-TCNQ system and rendered it amphiphilic in the form of the N-docosylpyridinium-TCNQ complex : the close packed aliphatic chains order the pyridinium rings (cations) which in turn induce the staking of the TCNQ (anions). As in the intercalated compounds a layered structure is obtained : the polar planes are the active areas and are kept apart by insulating aliphatic regions.

EXPERIMENTAL

A certain number of amphiphilic conductors were synthetised as powders by classical methods (2). However it was found tricky to build up LB films with these molecular complexes. It appeared more elegant to realise their synthesis into the LB film using the high reactivity of the polar planes (3).

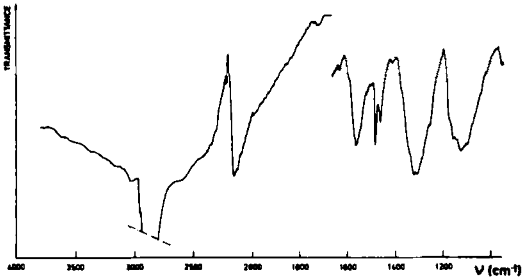
i) Preparation of an insulating LB film.

The N docosylpyridinium-TCNQ was built up from a fresh $CHCl_3$ 10^{-3}M solution of the (1-1) complex on a CaF_2 substrate. The transfer pressure was 35 mN/m and the area per molecule was 20 ± 4 Å^2. The IR spectrum of a 15 layer sample is identical to the spectrum of the blue powder (KBr disc) of the 1-1 complex synthetized,analysed and titrated. It is the spectrum of an insulator, the absorption bands of which are enhanced by the appearance of permanent dipoles on specific bonds of TCNQ ($\nu_{C\equiv N}$ 2170 cm^{-1} $\nu_{C=C}$ 1580 and 1508 cm^{-1} $\delta_{C-C\equiv N}$ 1357 and 1180 cm^{-1}). The UV-visible spectrum exhibits a CT band at 1050 nm (1.3 ev) and the assigned bands of TCNQ$^-$ in the solid state ring.

ii) Synthesis of the conductor "in situ".

This complex requires partial oxidation of TCNQ$^-$ to be rendered conductive. This was performed by diffusing iodine vapours.

a) mild conditions : the sample is immersed for a few minutes in iodine vapours highly diluted in a stream of dry N_2. The blue colour fades and the sample develops a uniform purple coloration whilst kept in a moist atmosphere (1 to 2 h). After this treatment the IR spectrum exhibits the characteristics of an organic conductor : a broad CT band between 4000-1600 cm^{-1} arising from the optical promotion of an excess charge to a neighbouring. The unoccupied site absorption bands of the previous insulator broaden and are red shifted -($\nu_{C\equiv N}\rightarrow 2140\ cm^{-1}$ $\nu_{C=C}\rightarrow 1560\ cm^{-1}$ $\delta_{C-N}\rightarrow 1310$ and $1120\ cm^{-1}$.



The UV visible spectrum also exhibits drastic modifications : the specific bands of the $TCNQ^-$ vanish and a broad absorption stretches along the whole range of wavelengths (sh.510 nm and 390 nm). The ionic species I_3^- is seen at 290 nm and that of the pyridium at 260 nm. The Raman Resonance spectrum exhibits the I_3^- band at 110 cm^{-1}.

b) severe conditions : the sample is immersed in iodine vapours alone for a few seconds. The blue sample becomes yellow and all the spectra exhibit only $TCNQ_o$ absorptions and a higher content of I_3^-. Kept in a moist atmosphere the sample develops much more slowly (24 to 48 h) its purple colour. The spectra are then identical to those obtained under the mild conditions.

iii) Physical measurements :

Conductivity $\sigma = 10^{-1}\Omega^{-1}.cm^{-1}$

Activation energy E_A 0.15 ev in agreement with the infrared data.

The samples are stable under normal atmosphere condition and do not age.

Discussion : The above results confirm that TCNQ$^-$ is oxidised in the solid state by iodine which enters the network as the I_3^- reduced species.

Iodine is absorbed until all the TCNQ$^-$ molecules are oxidised and the produced I_3^- is trapped in the channels of the structure. The excess iodine vapours desorb. On standing a partial oxydation of L_3^- ions and a partial reduction of TCNQ$_o$ to TCNQ$^-$ occur. This back reaction seems to be due to the action of water ($I_3^- + H_2O \rightarrow IO_nH$). Thus the iodine quantity uptaken is controlled by the formation of the conducting species. We are dealing here with a stoechiometric chemical reaction of the redox type limited by the formation of a stable equilibrium. However a thorough explanation of this control is needed and is under investigations.

CONCLUSION

The work presented here is a preliminary study of anisotropic layered conductors. Electric measurements are in progress and X-ray diffraction studies have revealed interesting phase transitions between the insulating and conducting structures (5).

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