

Structure and electrical conductivity of Langmuir films: tetracyanoquinodimethane + N-octadecylpyridine

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(Submitted 8 October 1988)

Pis'ma Zh. Eksp. Teor. Fiz. **48**, No. 10, 532–535 (25 November 1988)

A study has been made of the structure of conducting Langmuir-Blodgett films of organic complexes of tetracyanoquinodimethane + N-octadecylpyridine in the original state and after doping with iodine. The films ranged in thickness from 300–600 Å. The doping changes the structure of the films only insignificantly, while the electrical conductivity falls from 10^{-3} S/cm in the original films to 2×10^{-8} S/cm.

The Langmuir-Blodgett method makes it possible to create a monolayer of amphiphilic molecules on the surface of water and to then transfer it to a substrate. It thus becomes possible to carry out a controllable layer-by-layer crystallization. The "ultrathin" Langmuir-Blodgett films which have been produced can contain precisely one, two, three, four, etc., layers of molecules.^{1,2} Langmuir-Blodgett films of insulators, semiconductors, and (just recently) conductors have been synthesized. The first conducting films to be synthesized (in 1985; Ref. 3) were films of complexes of tetracyanoquinodimethane + N-dococylpyridine (TCQM + N-pyr C₂₂H₄₅). The conductivity in these films arose after saturation in iodine vapor. The appearance of a conductivity was accompanied by a decrease in the repetition period in the packing of the layers and by a change in the orientation of the TCQM molecules, from parallel to perpendicular to the film.⁴ These results have sparked a discussion of possible mechanisms for the conductivity in these films which involve both an oxidation of TCQM and a change in their relative arrangement in the layers.^{5,6}

In 1987, Langmuir-Blodgett films of TCQM + N-octadecylpyridine (TCQM + N-pyr C₁₈H₃₇) were synthesized at the Molecular Electronics Center at the University of Durham (England). These films turned out to be conducting without doping with iodine.⁵ We studied the structure of these films under the assumption that the conductivity might be caused by the particular type of ordering of the TCQM molecules.

To synthesize the films, we used TCQM + N-pyr C₁₈H₃₇ and TCQM + N-pyr C₂₂H₄₅ complexes synthesized at the University of Durham. These complexes were dissolved in chloroform. The resulting solution was deposited drop by drop on the surface of doubly distilled, deionized water. Multiple layers were deposited by the Langmuir-Blodgett method on glass substrates at a surface pressure of 48 mN/m. The deposition was of type Y; i.e., the molecules in the film were presumably organized in bilayers. We studied two lots of samples, differing in the length of the hydrocarbon chain and containing from 19 to 41 monomolecular layers.

For the x-ray structural analysis we used a small-angle diffractometer with an AMUR-K position-sensitive detector; the angular resolution of the detector was 0.02°.

We used $\text{CuK}\alpha$ radiation. The diffraction patterns were recorded by the rocking method,² displayed on a crt monitor, plotted, and analyzed.

For the same samples we measured the electrical conductivity in the lateral direction. These measurements, both dc and ac, were carried out in a two-electrode arrangement. Contacts were deposited on the films with conducting silver paint, which penetrated into the films. These contacts were 1–2 mm apart. Leads were cemented to the contacts. For these measurements we used an E6-13A teraohmmeter and an E8-2 capacitance bridge with a GZ-36A external generator and an F-852 null indicator. For the dc measurements, we applied voltages of 10 and 100 V to the contacts over the temperature interval 278–341 K.

Figure 1 shows curves of the small-angle x-ray scattering from a Langmuir-Blodgett film of TCQM + N-pyr $\text{C}_{18}\text{H}_{37}$ containing 31 monolayers. Three diffraction orders were detected, corresponding to a multilamellar packing of the molecules with a repetition period $D = 33.4 \pm 0.2 \text{ \AA}$ and an order parameter $R_c = 400 \text{ \AA}$ in the packing of the layers (a correlation radius). For the Langmuir-Blodgett films of TCQM + N-pyr $\text{C}_{22}\text{H}_{45}$ we also detected three reflections, finding $D = 37.2 \pm 0.2 \text{ \AA}$ and $R_c = 370 \text{ \AA}$.

Let us examine possible types of packing of the molecules in these films. The lengths of the molecules without the TCQM are 28.5 and 33.5 \AA , respectively; the dimensions of the TCQM molecule in the plane of the ring are about $7 \times 4 \text{ \AA}$. A

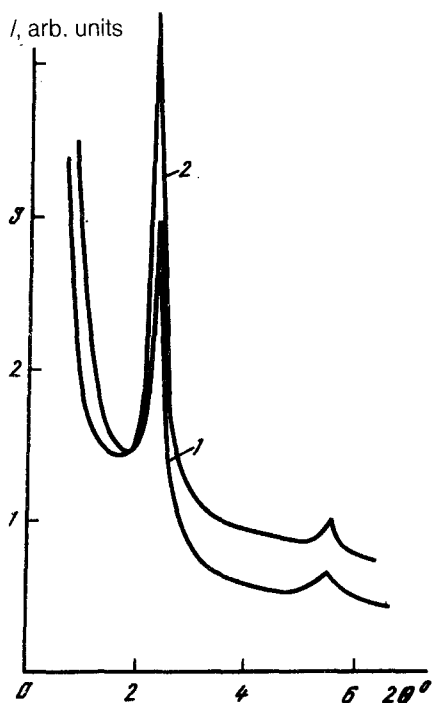


FIG. 1. Intensity of the small-angle x-ray scattering, $I(2\theta)$, from Langmuir-Blodgett films of TCQM + N-pyr $\text{C}_{18}\text{H}_{37}$. 1—In the undoped state; 2—after doping.

comparison of the dimensions of the complex with the repetition periods suggests that the molecules are packed in bilayers and that there is a mutual penetration of the hydrocarbon chains of adjacent rows of molecules between each other. The inclination of the molecules with respect to the normal to the surface of the film should then be 30° . The values of D for the two films agree: The difference in the values of D is 3.8 \AA , which corresponds to an elongation of $(33.5-28.5)\cos 30^\circ$ of the hydrocarbon chain, when the inclination of the molecules is taken into account.

Because of an insufficient order in the packing of the layers and thus the small number of Bragg reflections detected, we were not able to carry out a Fourier synthesis of electron density profiles for the undoped Langmuir-Blodgett films.

Figure 2 shows the temperature dependence of the dc electrical conductivity of a TCQM + N-pyr $C_{18}H_{37}$ film. In the interval 278–308 K the activation energy during the heating of the sample is $0.20 \pm 0.01 \text{ eV}$, while during cooling it is $0.22 \pm 0.1 \text{ eV}$. The film begins to melt at 325 K, the layered structure is destroyed (according to the data of the x-ray analysis), and the electrical conductivity decreases sharply and irreversibly by five orders of magnitude. The conductivity of the film at room temperature was $1 \times 10^{-3} \text{ S/cm}$. For making a comparison with the conductivity of 0.02 S/cm which was reported in Ref. 5, we should assign this figure not to the total thickness of the film but only to the conducting regions: the layers of TCQM molecules ($\sim 7 \text{ \AA}$). Furthermore, we should ignore the nonconducting part of a bilayer, which contains hydrocarbon chains with a crystalline packing. We then find the value 0.005 S/cm ,

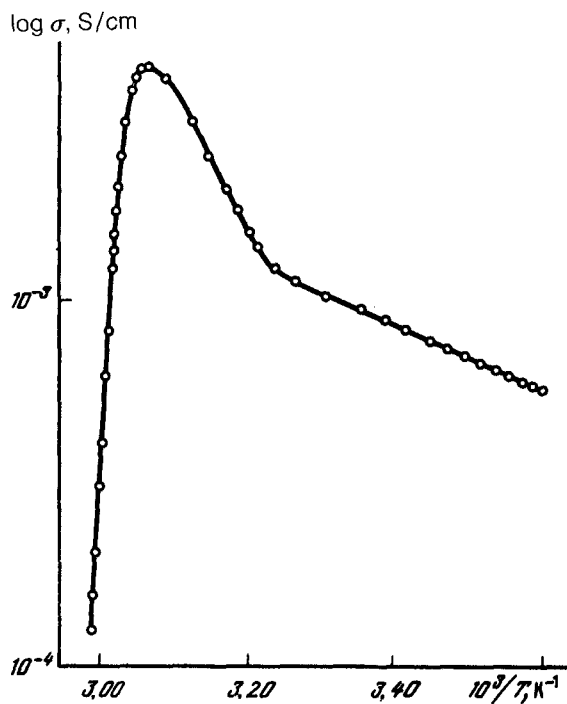


FIG. 2. Temperature dependence of the dc electrical conductivity of a film of TCQM + N-pyr $C_{18}H_{37}$. The thickness of the film was 41 monolayers.

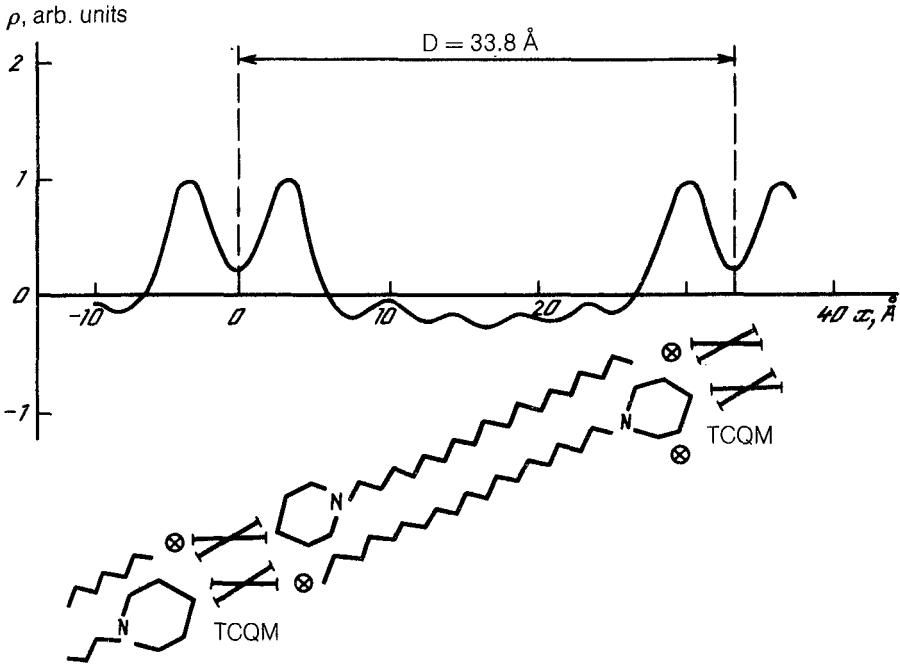


FIG. 3. Electron density profile $\rho(x)$ of a doped Langmuir-Blodgett film of TCQM + N-pyr $C_{18}H_{37}$; arrangement of molecules in a bilayer. The crosses are iodine ions.

which is smaller than the value reported in Ref. 5 by a factor of four.

The same samples were then placed in a weighing bottle with saturated iodine vapor. In 1–2 s, the initially blue films turned red, and then orange. The films became “nonconducting”; their resistance increased by a factor of 10^5 . From these samples we obtained x-ray scattering patterns (Fig. 1) which demonstrate an improvement in the layered ordering in the doped films: We detected seven reflections. The repetition period of the films of TCQM + N-pyr $C_{18}H_{37}$ became $D = 33.8 \pm 0.2 \text{ \AA}$ with $R_C = 800 \text{ \AA}$, while for the TCQM + N-pyr $C_{22}H_{45}$ films we found $D = 38.0 \pm 0.2 \text{ \AA}$ and $R_C = 700 \text{ \AA}$. Working from the intensities of the reflections by the method of Ref. 2, we calculated the electron density profile across the films (Fig. 3). The density maximum near the “heads” of the molecules is split in two, indicating that there are two rows of “heads” which are the positions of iodine ions. The Patterson function has a peak at 7 \AA , which correlates with the density resolution on the profile. Shown below the profile is the probable arrangement of molecules in the doped Langmuir-Blodgett films. The resolution achieved on this profile indicates that the TCQM molecules are oriented approximately perpendicular to the layer, and it demonstrates a mutual penetration of the hydrocarbon “tails” of the molecules in neighboring monolayers. The approximately equal repetition periods for the undoped Langmuir-Blodgett films suggest that the packing of these molecules is the same.

We did not control the initial degree of oxidation of the TCQM, which was

governed by the particular method used to synthesize the films, in this study, but this study has shown that the TCQM molecules occupy ordered rows in Langmuir-Blodgett films and form 25, as it were, elementary crystalline formations. Interestingly, in Refs. 4, 6, and 7, where TCQM-containing Langmuir-Blodgett films acquired a conductivity only after doping with iodine, this process was accompanied by a rotation of the TCQM molecules from a position horizontal with respect to the plane of the film to a vertical position. In our case, on the other hand, the rows of molecules are vertical even in the original state, without iodine doping. This is an important point.

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Translated by Dave Parsons