

Dark Field Electron Microscope and Electron Diffraction Studies on Langmuir-Blodgett Films of a TCNQ Derivative

Mutsuo MATSUMOTO* and Natsu UYEDA**

Received September 26, 1988

The fine structure and crystalline state of LB films of 2-octadecyl-7,7',8,8'-tetracyanoquinodimethane (TCNQ-R18) were studied by dark field electron microscopy and electron diffraction. The LB films prepared at consecutive stages of surface pressure were found to change the structure, successively, to the formation of microparticles and microaggregates, small island films with vacant areas, growth of island films and sporadic overlapping of grown island films due to the collapse on film compression. Electron diffractions taken at the same time indicated that all the LB films except for microparticles and microaggregates assume fiber structure, including three-dimensional crystal rather than two-dimensional one. This result was also true for all kinds of solvent and subphase used here to spread TCNQ-R18 molecules.

KEY WORDS: TCNQ derivative/ LB film/ Dark field electron micrograph/ Electron diffraction

INTRODUCTION

The thin films of organic semiconductors such as 7,7',8,8'-tetracyanoquinodimethane (TCNQ) derivatives, capable of forming the charge transfer complex, have been focussed for practical applications to the molecular electro-devices and chemical sensors. The molecular orientation and structure of the thin film have to be artificially regulated to meet the purpose. The vacuum sublimation and Langmuir-Blodgett (LB) methods are two possible ways to assemble the thin film in such regulation. The studies on the applications of thin films of TCNQ derivatives by the vacuum sublimation method are rare so far, but thin crystal film grown epitaxially can be made with the orientation of molecular plane nearly parallel to the substrate surface by the direct interaction of TCNQ molecules with the substrate surface¹⁻³. Most studies, both fundamentals and for applicabilities, on the derivatives, have been carried out, on the other hand, by applying the LB method⁴⁻¹⁰. This is due to that the molecular orientation as well as the final film structure of amphiphilic TCNQ derivatives is usually considered to be easily controlled on subphases as the two-dimensional, homogeneous monolayer and subsequently transferred to other substrate surfaces holding the structural state thus defined. The molecular orientation and structure of LB film on TCNQ derivatives have been mainly studied by spectroscopy, but the direct inspection of

* 松本陸朗: Laboratory of Surface Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

** 植田 夏: Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

the film structure is rare. In the present work, the structure and crystalline state of LB film of a TCNQ derivative are studied by applying the dark field imaging mode of electron microscope and electron diffraction which were found effective to investigate the LB film such as stearic acid¹¹⁾.

EXPERIMENTAL

Materials

2-octadecy-7,7',8,8'-tetracyanoquinodimethane (TCNQ-R18) which was the commercially available purest reagent was used to spread on subphases as the surface film. The spreading solvents for TCNQ-R18 were benzene, acetonitrile and xylene which were of commercially analytical grade. Water and glycerin used for the subphase were doubly distilled in Pyrex glass vessels.

Preparation and electron microscope observation of LB films

The LB film of TCNQ-R18 molecules was prepared by the print out procedure. A specimen grid covered with carbon supporting film attached to the end tip of a fine glass rod in air was held in parallel to TCNQ-R18 surface film spread on water or glycerin surface, being moved down slowly to get just in touch with the surface film and then withdrawn by a motor drive apparatus. It is reasonably considered that the portion of the surface film touched by the carbon film is fully transferred to the grid without any dropping. This is because the surface film is sandwiched between the supporting film and the small water droplet which accompanies the grid as the hydrophilic side of the film is facing the subphase. The droplet was then taken out by a filter paper, thus leaving the single layer film of TCNQ-R18 on the supporting film. Transfer ratios of TCNQ-R18 surface film, separately measured using slide glass covered with a similar carbon film deposited by vacuum sublimation, were unity with an error of 2%.

The observation of fine structure of LB film was carried out by adapting the dark field imaging mode based on blocking the main electron beam by shifting the objective aperture and by passing the electron beam scattered mainly from the LB film. In this observation the LB film appeared as bright images in a dark background. The minimum dose system equipped to JEM-200CX electron microscope was applied to minimize the radiation damage to the LB film. The direct magnification to record the image was set to be $\times 2800$ at the maximum.

RESULTS AND DISCUSSION

To spread TCNQ-R18 molecules on water or glycerin surface the molecules were dissolved in benzene, acetonitrile-benzene mixture (molar ratio 1:1) and xylene as electron donating solvents. Yellowish TCNQ-R18 molecules in benzene and mixed solvent changed into orange in xylene being a stronger electron donor. This phenomenon was expected to exhibit a possible formation of TCNQ-R18 charge transfer complex with xylene.

Figure 1 shows the surface pressure (π)-area (A) curves for surface films of TCNQ-R18 spread from three solvent systems mentioned above on water surface

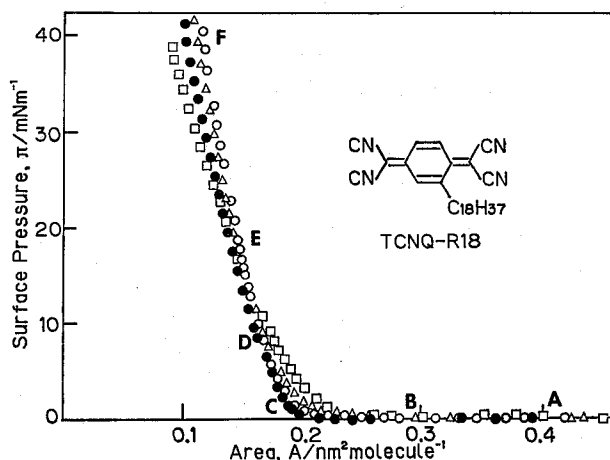


Fig. 1. Effect of spreading solvents and subphases on surface pressure (π)-area (A) isotherms of TCNQ-R18.

●, benzene; ○, acetonitrile-benzene mixture (1:1);
 △, xylene as spreading solvents on water surface; □,
 acetonitrile-benzene mixture (1:1) on glycerin surface.

and from the mixed solvent on glycerin. In all the curves the surface pressure steeply increased with the decrease in area as a possible example of less compressible surface film. It is worth to note that all curves indicated almost similar behavior being independent of the nature of solvent and subphase. This suggests that TCNQ-R18 molecules interact with water or glycerin molecules both in a similar manner without forming irreversible charge transfer complexes with solvent molecules in spite of the change in color of the original solution.

Moreover, the limiting areas obtained from the curves were approximately 0.20 and 0.21 nm² for water and glycerin subphases, respectively. These values were entirely smaller compared to the cross-sectional areas, 0.84, 0.38 and 0.65 nm², when the plane of TCNQ-R18 molecule was oriented parallel and normal to the subphase surface. This result suggests that TCNQ-R18 molecules do not form a two-dimensionally homogeneous surface film but a three-dimensionally heterogeneous film is formed.

To inspect the dependence of surface pressure on the fine structure and crystalline state of surface films on water and glycerin surfaces, the surface films were transferred to the carbon supporting film at six consecutive stages of the compression. The sampling points were denoted by the capital alphabet in Fig. 1. Figure 2 is the dark field electron micrographs for LB films of TCNQ-R18 surface film prepared on water surface from benzene solution. In Fig. 2A where the surface pressure $\pi=0$ mN·m⁻¹ and area $A=0.50$ nm², the LB film was found to consist of finely dispersed microparticles and partial microaggregates. In Fig. 2B, $\pi=0$ mN·m⁻¹ and $A=0.27$ nm², the formation of irregular island films with vacant area ranging from 0.1 to 0.4 μ m appeared in addition to the microaggregates. The growth and abundance of island films were observed as the increase in the surface pressure ($\pi=1$ mN·m⁻¹ and $A=0.20$ nm²), while the microaggregates disappeared as

shown in Fig. 2C. A similar trend was also observed in Fig. 2D where $\pi=8$ $\text{mN}\cdot\text{m}^{-1}$ and $A=0.17\text{ nm}^2$ on film compression. In Fig. 2E where $\pi=18\text{ mN}\cdot\text{m}^{-1}$ and $A=0.14\text{ nm}^2$ the island films which had grown markedly started to collapse everywhere, resulting in the mutual overlap. These collapsed films could densely cover the carbon supporting film at such a high surface pressure as $\pi=43\text{ mN}\cdot\text{m}^{-1}$ and a small area as $A=0.09\text{ nm}^2$ (Fig. 2F).

Another set of observations of dark field electron micrographs and diffractions was also performed as to the surface films prepared from the different solvents on

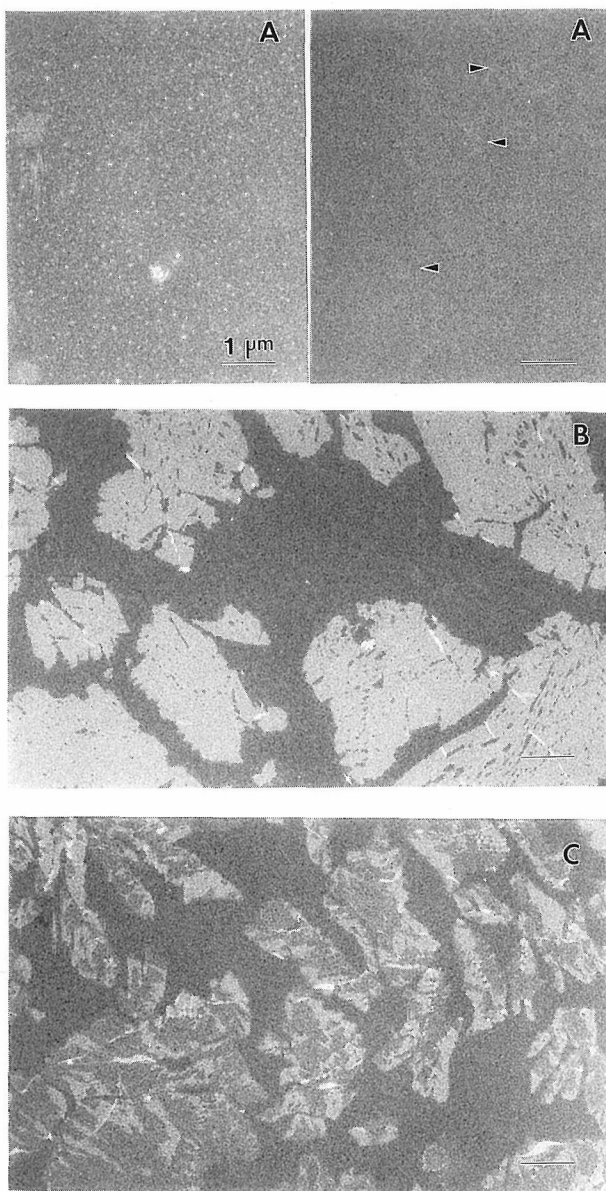


Fig. 2

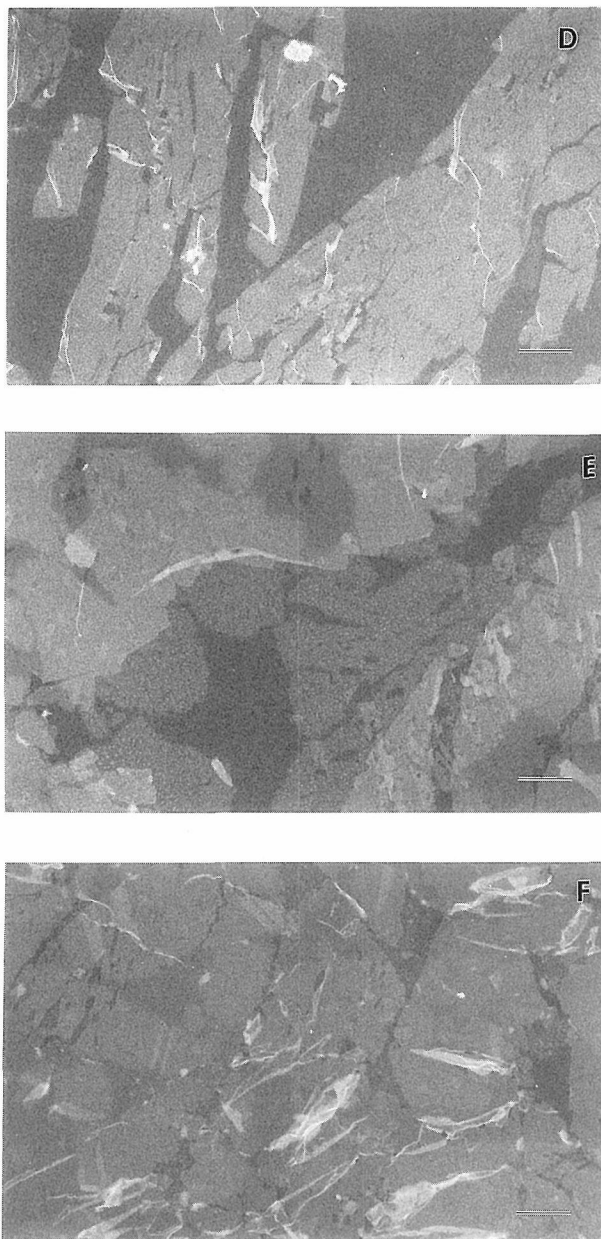


Fig. 2. Dark field electron micrographs of TCNQ-R18 LB films of which the surface film was prepared from benzene as the spreading solvent on water surface. A, $\pi=0 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.50 \text{ nm}^2$; B, $\pi=0 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.27 \text{ nm}^2$; C, $\pi=1 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.20 \text{ nm}^2$; D, $\pi=8 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.17 \text{ nm}^2$; E, $\pi=18 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.14 \text{ nm}^2$; F, $\pi=43 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.09 \text{ nm}^2$. Bright textures found in the island film were due to the scattered contrast, being independent of the fine structure of LB film.

water and glycerin surfaces. All the results obtained were found to be almost identical to those in Fig. 2, except for the feature of wide needle-like island film with no vacant areas as formed on a glycerin surface.

The selected area electron diffraction patterns were also recorded to investigate the crystallinity of the LB film, including every specimen transferred during the compression. At very early stage such as that for Fig. 2A, no clear patterns were obtained excepting a diffuse ring pattern mostly due to the carbon supporting film. Once the solid islands and discrete films were formed as shown in Fig. 2B-2F, strong Debye-Scherrer rings appeared with the vertical incidence of the electron

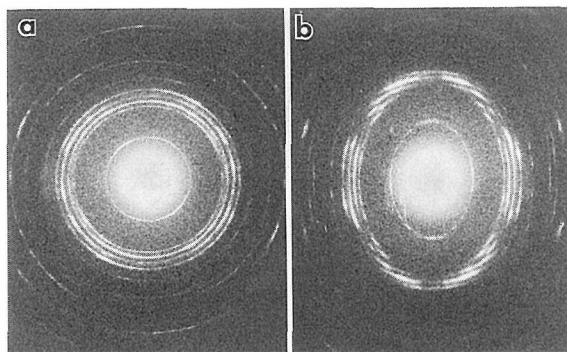


Fig. 3. Electron diffractions of TCNQ-R18 LB films. a, electron diffraction of TCNQ-R18 LB film at normal beam incidence ($\pi=1 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.20 \text{ nm}^2$); b, electron diffraction by tilting the TCNQ-R18 LB film at the angle 45° ($\pi=18 \text{ mN}\cdot\text{m}^{-1}$ and $A=0.14 \text{ nm}^2$).

beam as reproduced in Fig. 3a for example. The systematic analysis indicated that the film consists of small crystallites which assume a fiber structure with chain axis normal to the film. It was also indicated that the arrangement of TCNQ moieties, when projected to the plane of the film as shown in Fig. 4A, is quite identical to that in an epitaxial thin film of pure TCNQ vacuum-deposited on the surface of alkali halides¹²⁾. When the film was tilted by 45° to the incident beam, an oblique textured pattern was recorded as reproduced in Fig. 3b. Although the appearance of the rings is just the same as that in Fig. 3a, they are elliptically elongated along the meridian, being divided into discrete arcs. This effect strongly indicated that the film mainly consists of small three-dimensional crystallites in a preferred orientation with the fiber axis normal to the film surface. The periodicity along this b-axis was also estimated from the pattern to be about 3.53 nm, reflecting the effect of long hydrocarbon chains extending along the depth direction of the film.

In Table 1 the lattice constants for TCNQ-R18 LB film which were deduced from the above diffraction data were listed with those for the vacuum sublimation film on an alkali halide substrate and the single crystal of TCNQ^{1,12)} as reference. All values fairly agreed well with each other except for the length of b axis of LB film, which is certainly due to alkyl chain of 18 carbon atoms. Figure 4 is the possible two- and three-dimensional structures of TCNQ-R18 LB film based

Table 1

Axis & angle	Vacuum sublimation film/nm (TCNQ)	LB film/nm (TCNQ-R18)	Single crystal/nm (TCNQ)
a	0.93	0.93	0.89
b	—	3.53	0.71
c	1.58	1.61	1.64
β	100°	97°	99°

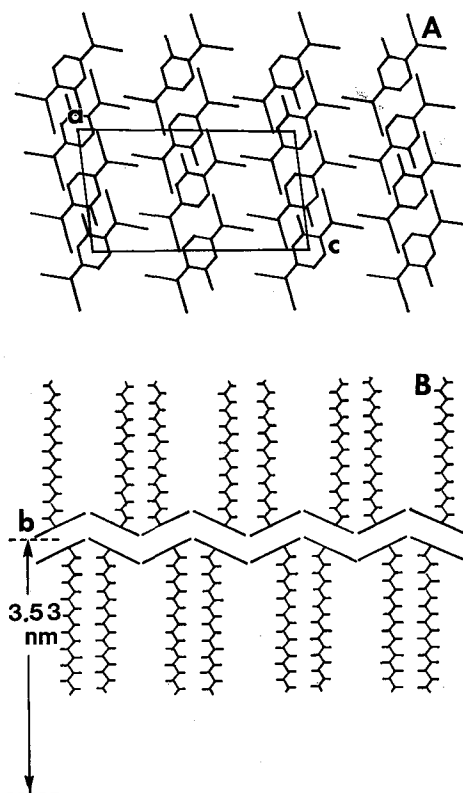


Fig. 4. Two- (A) and three-dimensional (B) structures of TCNQ-R18 LB film deduced from the lattice constant.

on the lattice constants. It can be deduced that TCNQ-R18 molecules form three-dimensional crystal in which the molecular planes of TCNQ moiety are stacked with each other in a zigzag array due to π electron interaction while the alkyl chains are oriented normal to the film plane due to van der Waals cohesion.

In conclusion, the introduction of substituent such as long alkyl chain on TCNQ derivative is not effective to control the surface film two-dimensionally on water or glycerin surface by monolayer technique because of the dominant association among the molecular planes. To make the film regulation possible on water, an advanced molecular design necessitates the introduction of hydrophilic group

to TCNQ molecule and superiority of the amphiphilic polymerization over the self-association among TCNQ molecular planes.

ACKNOWLEDGEMENT

The authors wish to express their gratitudes to Mr. Takahiro Nishida for his valuable co-operations on the present experiment.

REFERENCES

- (1) N. Uyeda, Y. Murata, T. Kobayashi and E. Suito, *J. Cryst. Growth*, **26**, 267 (1974).
- (2) N. Uyeda, T. Kobayashi, K. Ishizuka and Y. Fujiyoshi, *Nature*, **285**, 95 (1980).
- (3) N. Uyeda, T. Kobayashi, K. Ishizuka, Y. Fujiyoshi, H. Inokuchi and G. Saito, *Mol. Cryst. Liq. Cryst.*, **125**, 103 (1985).
- (4) T. Nakamura, M. Tanaka, Mutsuyoshi Matsumoto, T. Sekiguchi, E. Manda, Y. Kawabata and G. Saito, *Chem. Lett.*, 323 (1986).
- (5) T. Nakamura, Mutsuyoshi Matsumoto, F. Takei, M. Tanaka, T. Sekiguchi, E. Manda and Y. Kawabata, *Chem. Lett.*, 709 (1986).
- (6) A. Ruaudal-Teixier, M. Vandevyver and A. Barraud, *Mol. Cryst. Liq. Cryst.*, **120**, 319 (1985).
- (7) G.G. Roberts, B. Holcroft, A. Barraud and J. Richard, *Thin Solid Films*, **160**, 53 (1988).
- (8) Mutsuyoshi Matsumoto, T. Nakamura, E. Manda, Y. Kawabata, K. Ikegami, S. Kuroda, M. Sugi and G. Saito, *Thin Solid Films*, **160**, 61 (1988).
- (9) A. Barraud, P. Lesieur, J. Richard, A. Ruaudal-Teixier, M. Vandevyver, M. Leguan and R.M. Lequan, *Thin Solid Films*, **160**, 81 (1988).
- (10) K. Ikegami, S. Kuroda, M. Saito, K. Saito, M. Sugi, T. Nakamura, Mutsuyoshi Matsumoto and Y. Kawabata, *Thin Solid Films*, **160**, 139 (1988).
- (11) N. Uyeda, T. Takenaka, K. Aoyama, M. Matsumoto and Y. Fujiyoshi, *Nature*, **327**, 319 (1987).
- (12) R.E. Long, R.A. Spaks and K.N. Trueblood, *Acta Cryst.*, **18**, 932 (1965).