

Molecular Orientation of Langmuir-Blodgett Films of AlkylDCNQI-Cu and AlkylTCNQ-Cu Complexes

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LB films of organic-inorganic charge-transfer systems, Cu-complexes of 2-methyl-5-octadecylDCNQI ($C_{18}Me$ -DCNQI) and 2-alkylTCNQ (C_n TCNQ with $n = 12, 15$ and 18), were successfully fabricated by utilizing the air-water interface as a reaction field for the reduction of the acceptor moieties. The charge transfer degrees of the $C_{18}Me$ DCNQI and C_n TCNQ in the LB films were estimated at -1 , respectively, from the changes in their IR absorption spectra upon the reduction. The molecular orientation in the films were discussed on the basis of polarized IR spectroscopy. It is suggested that the molecular orientation in the present LB films is largely affected by the coordinate bonds between the Cu cations and the cyanic groups.

Key words: Langmuir-Blodgett films, molecular orientation, charge-transfer complex, FT-IR

1. INTRODUCTION

N,N' -dicyanoquinonediimine (DCNQI) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are organic electron acceptors generating crystalline charge-transfer (CT) complexes with fascinating electronic functions.^{1,2} We intended to introduce CT complexes of these acceptors with transition metals to ultrathin-film systems. For such purpose, the Langmuir-Blodgett (LB) technique³ is one of the most appropriate methods to fabricate films, because with this technique the interaction between the substrate and the organic molecules can be weaker than that between the molecules themselves. In other words, with the LB technique, the molecular arrangements in the fabricated films are determined mainly by the intermolecular interaction. Another advantage of this technique is that we can utilize the air-water interface, which is highly active and highly anisotropic, as a reaction field.

Therefore, we tried to fabricate LB films of Cu-complexes of 2-methyl-5-octadecylDCNQI ($C_{18}Me$ -DCNQI)^{4,5} and 2-alkylTCNQ (C_n TCNQ with $n = 12, 15$ and 18).^{6,7} The chemical structures of these alkylated acceptors are shown in Fig.1. The Cu-complexes could be obtained by spreading the alkylated acceptors mixed with copper iodide and transferred onto solid substrates by the horizontal lifting method. The obtained complex films, as well as the LB films of the neutral $C_{18}Me$ DCNQI and C_n TCNQ, were characterized by

optical measurements. The molecular orientations of the $C_{18}Me$ DCNQI-Cu and C_n TCNQ-Cu films are different from each other, while those of the pure $C_{18}Me$ DCNQI and pure C_n TCNQ films are similar to each other. Noting that DCNQI contains two cyanic groups, while TCNQ contains four, we can conclude that the coordinate bonds between the Cu cations and the cyanic groups strongly affect the molecular arrangements.

2. EXPERIMENTAL

$C_{18}Me$ DCNQI was synthesized by condensation of 2-methyl-5-octadecyl-1,4-benzoquinone and bis(trimethylsilyl)carbodiimide in the presence of $TiCl_4$.⁸ C_n TCNQ and CuI were purchased from The Japanese Research Institute for Photosensitizing Dyes, Co. and Wako Pure Chemical Industries, Ltd., respectively, and used without further purification. Pure water with a

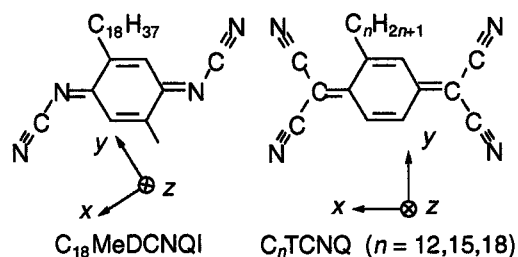


Fig.1 Chemical structures of $C_{18}Me$ DCNQI and C_n TCNQ. Definitions of the axes of the molecular plane are also displayed for each acceptor moiety.

resistively greater than $1.8 \times 10^7 \Omega \text{cm}$ was prepared by using a Millipore Milli-Q system.

A Lauda Filmwaage trough was used for the LB technique. To obtain pure films, toluene solutions (10^{-3} M) of $C_{18}\text{MeDCNQI}$ and $C_n\text{TCNQ}$ were spread on the pure-water surface. An acetonitrile solution of CuI (2×10^{-2} M) was added to the solutions of the alkylated acceptors and then the mixed solutions were spread on the pure water subphase to fabricate complex films. The molar mixing ratio of alkylated acceptors and CuI was 1:5–1:10. The obtained Langmuir films were compressed to the surface pressure of 25 mN/m.

Plates of CaF_2 were used as solid substrates of LB samples for optical measurements and glass plates for X-ray diffraction (XRD) measurements, after precoating of three monolayers of cadmium arachidate. The Langmuir films of pure $C_n\text{TCNQ}$ were transferred by the conventional vertical dipping method, while the other films were transferred by the horizontal lifting method. FT-IR and UV-visible-near infrared (NIR) absorption spectra of the obtained LB films were recorded with Perkin-Elmer System-2000 and Lambda-900 spectrometers, respectively. XRD patterns were taken by a Rigaku rad- γC ($\text{Cu-K}\alpha_1$, 50 kV, 200 mA) with a graphite monochromator at NSG Techno-Research Co. Ltd.

3. RESULTS AND DISCUSSION

3.1 Charge transfer state

Pure LB films of $C_{18}\text{MeDCNQI}$ and $C_n\text{TCNQ}$, respectively, exhibit distinct electronic absorption bands in the 300–400 nm region (Fig.2 (a) and (c)). These bands are assignable to the $\pi\text{-}\pi^*$ transition of the neutral acceptor moieties.^{9,10} The absorption spectra of the

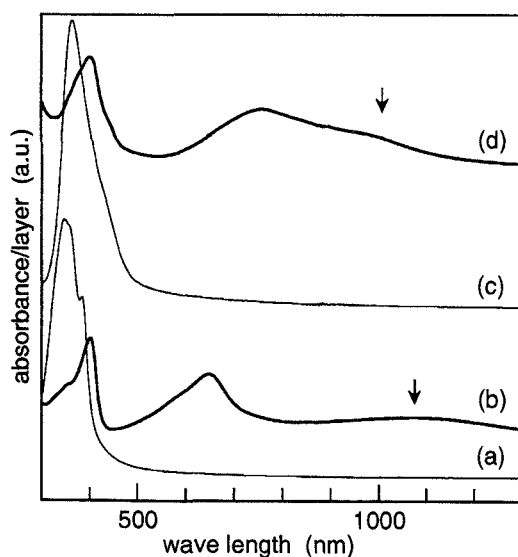


Fig.2 UV-Vis-NIR absorption spectra observed for LB films of (a) pure $C_{18}\text{MeDCNQI}$, (b) $C_{18}\text{MeDCNQI-CuI}$ mixture, (c) pure $C_{15}\text{TCNQ}$ and (d) $C_{15}\text{TCNQ-CuI}$ mixture. The angle of incidence is 0° .

$C_{18}\text{MeDCNQI-CuI}$ and $C_n\text{TCNQ-CuI}$ mixed solutions (data not shown) showed that the alkylated acceptors remain neutral in these solutions.

On spreading the mixed solutions on the pure water surface, however, the absorption spectra of the materials change drastically (data not shown). This fact reflects that chemical reactions take place at the air-water interface. The absorption spectra of the mixed LB films (Fig.2 (b) and (d)) are essentially identical with those of Langmuir films, indicating that the products of the chemical reactions can be transferred onto solid substrates.

The absorption bands around 400 and 650 nm seen in curve (b) in Fig.2 are assignable to anionic DCNQI moieties⁹ and those around 400 and 750 nm in curve (d) to anionic TCNQ moieties.¹⁰ Besides, the bands around 1050 (in curve (b)) and 1000 nm (in curve (d)) can be assigned to CT bands. Therefore, all the observed electronic bands indicate that the acceptor moieties are reduced at the air-water interface. In this case, the copper cations must be included into the films as the counter cation of the anionic acceptor moieties.

The difference in the IR absorption of the pure and mixed LB films reflects the reduction of the acceptor moieties in the latter, too. The $\text{C}\equiv\text{N}$ stretching modes, which are seen at 2170 and 2220 cm^{-1} for the pure $C_{18}\text{MeDCNQI}$ and $C_n\text{TCNQ}$ films, respectively, shift to 2150 and 2200 cm^{-1} in the corresponding CuI -mixed films (Fig.3). These red shifts are consequences of the softening of the $\text{C}\equiv\text{N}$ bonds and therefore indications of the reduction of the acceptor moieties.

The reduction of the acceptor moieties soften the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds, too, and cause red shifts of the vibronic bands in the fingerprint region. The charges on the acceptor moieties can be estimated by comparing the observed magnitudes of the red shifts with those reported in the literature¹¹⁻¹³ for alkali-metal salts of the acceptors. Polarized IR absorption spectra were taken with the angle of incidence being 45° in order to assign the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching bands in the LB films by referring the literature.¹¹⁻¹⁴

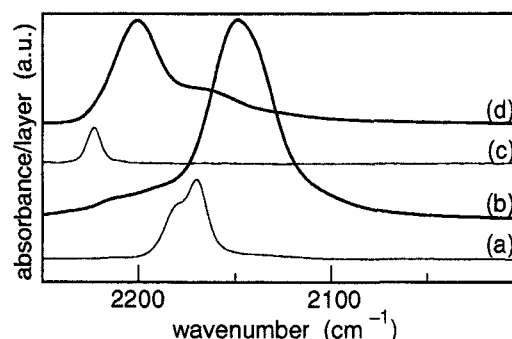


Fig.3 IR absorption spectra in the $\text{C}\equiv\text{N}$ stretching region observed for LB films of (a) pure $C_{18}\text{MeDCNQI}$, (b) $C_{18}\text{MeDCNQI-CuI}$ mixture, (c) pure $C_{15}\text{TCNQ}$ and (d) $C_{15}\text{TCNQ-CuI}$ mixture. The angle of incidence is 0° .

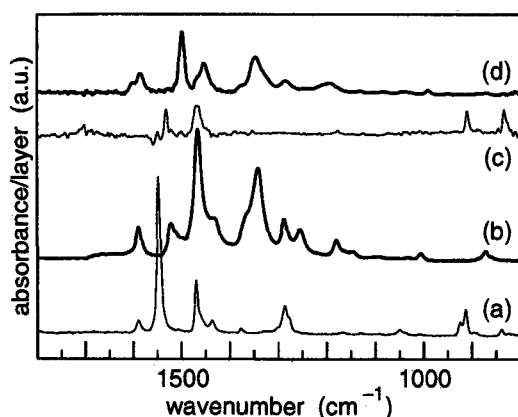


Fig.4 IR absorption spectra in the 1800-800 cm^{-1} region observed for LB films of (a) pure $\text{C}_{18}\text{MeDCNQI}$, (b) $\text{C}_{18}\text{MeDCNQI}$ -CuI mixture, (c) pure C_{15}TCNQ and (d) C_{15}TCNQ -CuI mixture. The angle of incidence is 0° .

In the $\text{C}_{18}\text{MeDCNQI}$ case, the C=C and C=N stretching bands that are observed at 1589 and 1547 cm^{-1} (Fig.4), respectively, for pure films, are observed at 1521 and 1465 cm^{-1} , respectively, for CuI-mixed films. From these shifts, the charge on the DCNQI moiety in the mixed films is estimated at -1 . In the C_nTCNQ case, the two C=C stretching bands that are observed at 1547 and 1530 cm^{-1} , respectively, for pure films, are observed at 1497 and 1504 cm^{-1} (shoulder), respectively, for CuI-mixed films. From these shifts, the charge on the TCNQ moiety in the mixed films is estimated at -1 , too.

3.2 Molecular orientation

To discuss the molecular orientation, we at first define the coordinate axes. For the acceptor moieties, x , y and z of the molecular planes are defined as displayed in Fig.1, because the shape of DCNQ and TCNQ molecular planes can be approximated by a lozenge and a rectangle, respectively. The orientation of the alkyl chain is not uniquely determined by the orientation of the acceptor moieties because of the rotation around the C-C bond connecting these two parts. Therefore, to discuss the orientation of the alkyl chain, its axes should also be introduced. Assuming the all-*trans* conformation of the chains, as the lowest order approximation, the direction of the CH_2 symmetric and antisymmetric modes are denoted as u and v , although the frequencies of these bands observed for CuI-mixed films suggest the presence of the *gauche* conformations to a certain extent. As for the laboratory system, the normal axis of the substrate surface is defined as Z and X is chosen so that the ZX plane includes y .

On one hand, quantitative analyses of the anisotropy in the peak intensities of the IR spectra gives the average of the squared direction cosines of a molecular axis (k) with respect to Z , denoted as $\langle I_k^2 \rangle$.¹⁵ It should be noted that the two parameters, $\langle I_u^2 \rangle$ and $\langle I_v^2 \rangle$, corresponds to only one degree of freedom: the rotation angle

around the C-C bond, φ , as described above. Therefore, the least squares method is employed to determine φ from $\langle I_u^2 \rangle$ and $\langle I_v^2 \rangle$.¹⁶ On the other hand, the XRD patterns of the films provide the thickness of the unit layers. Combining these experimentally obtained parameters, schematic structural models can be drawn.

For the $\text{C}_{18}\text{MeDCNQI}$ case, $\langle I_x^2 \rangle \approx 0.06$ and $\langle I_y^2 \rangle \approx 0.78$ were obtained for the pure films from the anisotropy in the 2170 (C=N) and 1377 cm^{-1} (C-C) bands, respectively, and $\langle I_u^2 \rangle \approx 0.21$ and $\langle I_v^2 \rangle \approx 0.18$ were obtained from the anisotropy in the 2849 and 2917 cm^{-1} bands, respectively. For the CuI-mixed films, $\langle I_x^2 \rangle \approx 0.10$ and $\langle I_y^2 \rangle \approx 0.14$ were obtained from the anisotropy in the 2149 (C=N) and 1180 cm^{-1} (C-C) bands, respectively, and $\langle I_u^2 \rangle \approx 0.30$ and $\langle I_v^2 \rangle \approx 0.30$ were obtained from the anisotropy in the 2851 and 2921 cm^{-1} bands, respectively. The thicknesses of the unit layers in the pure and CuI-mixed (1:5) films were estimated at 3.7 and 2.1 nm, respectively. Schematic models of possible layer structures of these films, which are displayed in Fig.5 (a) and (b), respectively, are drawn based on these parameters.

For the C_{15}TCNQ case, $\langle I_y^2 \rangle \approx 0.1$ and $\langle I_z^2 \rangle \approx 0.4$ were obtained for the pure films from the anisotropy in the 1530 and 908 cm^{-1} bands (b_{2u} modes), and 833 cm^{-1} band (b_{3u} mode), respectively, and $\langle I_u^2 \rangle \approx 0.10$ and $\langle I_v^2 \rangle \approx 0.14$ were obtained from the anisotropy in the 2849 and 2917 cm^{-1} bands, respectively. For the CuI-mixed films, $\langle I_x^2 \rangle \approx 0.16$ and $\langle I_y^2 \rangle \approx 0.63$ were obtained from the anisotropy in the 1497 (b_{1u} mode) and 1284 cm^{-1} (b_{2u} mode) bands, respectively, and $\langle I_u^2 \rangle \approx 0.41$ and $\langle I_v^2 \rangle \approx 0.42$ were obtained from the anisotropy in the 2853 and 2924 cm^{-1} bands, respectively. The thicknesses of the unit layers in the pure and CuI-mixed (1:10) films were estimated at 3.3 and 1.8 nm, respectively. Schematic models of possible layer structures of the pure and mixed films, which are displayed in Fig.5 (c) and (d), respectively, are drawn based on these parameters.

For the C_{12}TCNQ and C_{18}TCNQ cases, we can say that the estimated molecular orientation is similar to the C_{15}TCNQ case, although insignificant differences in the orientation parameters are detected.^{6,7}

Comparing the pure $\text{C}_{18}\text{MeDCNQI}$ and C_nTCNQ LB films, the similarity of the suggested molecular orientation between these systems is clearly noted. This may imply the similarity of the amphiphilic properties between these molecules. However, largely different molecular orientation is suggested for their CuI-mixed LB films. On the contrary, no significant effect of the alkyl-chain length, n , on the molecular arrangements was detected for both pure and CuI-mixed LB films of C_nTCNQ . As for the CuI-mixed films, therefore, the

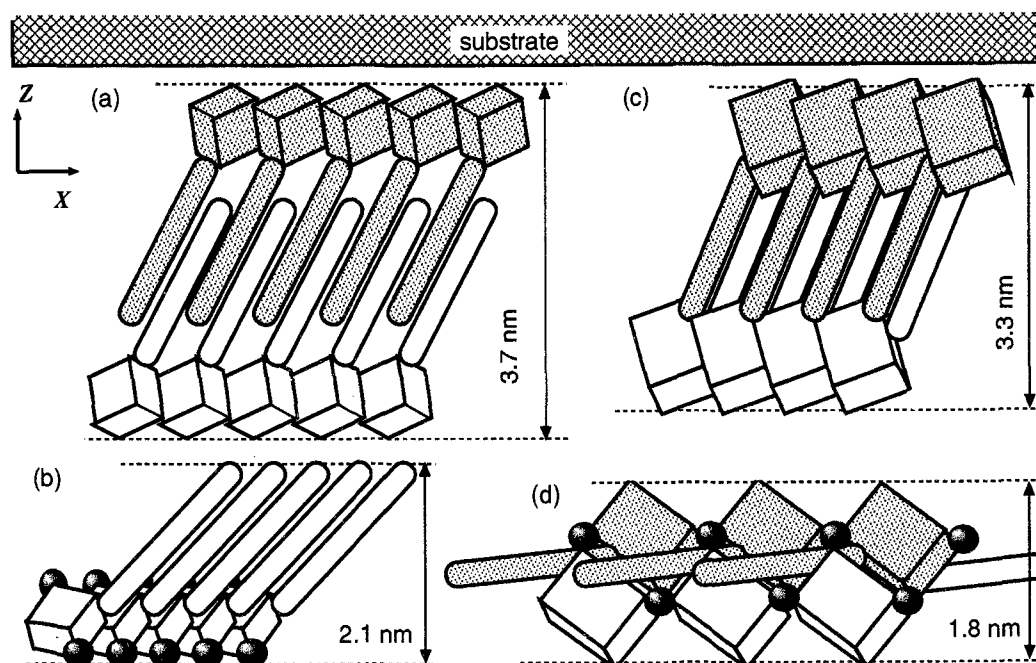


Fig.5 Possible structures suggested for LB films of (a) pure $C_{18}MeDCNQI$, (b) $C_{18}MeDCNQI-CuI$ mixture, (c) pure $C_{15}TCNQ$ and (d) $C_{15}TCNQ-CuI$ mixture. The paper plane includes the short (y) axis of the molecular plane of each acceptor moiety, as well as the normal axis (Z) of the solid substrate, but not the long axes of the molecular planes of the acceptor moieties and those of alkyl chains. In (b) and (d), Cu ions are represented by balls.

difference in the number of cyanic groups, which make coordinate bonds to Cu ions, born by DCNQI and TCNQ must be the dominant factor controlling the molecular orientation.

4. CONCLUDING REMARKS

LB films of Cu-complexes of $C_{18}MeDCNQI$ and C_nTCNQ could be obtained by utilizing the air-water interface as a reaction field for CuI-mixtures of these alkylated acceptors, whereas no chemical reaction was detected in the solutions of those mixtures. Analyses of the polarized IR absorption spectra showed that the molecular orientation of the $C_{18}MeDCNQI-Cu$ films and that of the $C_nTCNQ-Cu$ films are different from each other, while those of the pure $C_{18}MeDCNQI$ and the pure C_nTCNQ films are similar to each other. This fact suggests that the molecular orientation in the LB films of these transition metal-organic acceptor complexes are mainly determined by the coordinate bonds between the metal cations and the cyanic groups.

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