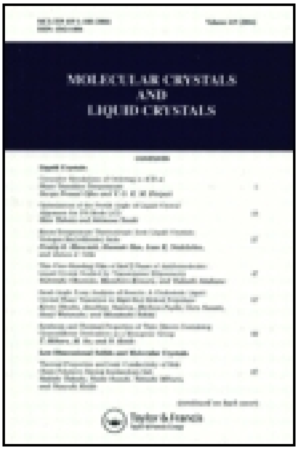

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CONDUCTING MONOLAYERS AND LANGMUIR-BLODGETT FILMS BASED ON BEDO-TTF AND DECYL-TCNQ COMPLEX

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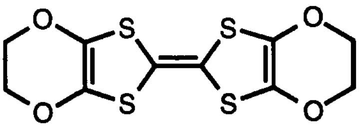
Abstract The Langmuir-Blodgett (LB) films based on BEDOTTF-C_{10}TCNQ (bisethylenedioxytetrathiafulvalene-decyltetracyanoquinodimethane) complex have an essentially metallic nature. Physical properties of the LB films are briefly summarised in addition to those of the monolayers at the air-water interface.

INTRODUCTION

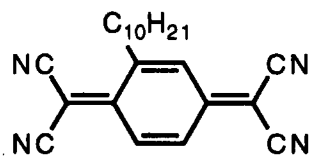
Langmuir-Blodgett (LB) technique is one of the most powerful tools for the control over molecular orientation and organisation.[1,2] With this approach, it is possible to fabricate organic materials into tailored molecular assemblies where the thickness of the film is controlled at the molecular level.

The LB films with metallic conductivity may be one of the most attractive target to be realised. The interest of this material is twofold. On a fundamental level, the electrical and magnetic properties of the organic conductor in two-dimension (in the form of ultra-thin film), which may be quite different from those of bulk crystals, should be revealed. More practically, these films may be indispensable parts for constructing future electronic devices. The first LB film of molecular conductor was reported in 1984.[3] Since then a number of conducting LB films have been so far reported, which are based on anion-radical salts, cation-radical salts, charge transfer complexes and transition metal complexes.[4,5] The LB films of conducting polymers have been also extensively studied.[6] No LB film until now have shown a macroscopically metallic conductivity (i.e. metallic temperature dependence in dc conductivity) down to low temperature (e.g. liquid helium temperature). Nevertheless, it has been indicated that several LB films have essentially metallic properties.[5]

We have already reported the LB films composed of BEDO-TTF (bisethylenedioxytetrathiafulvalene) complex of C_{10}TCNQ (2-decyltetracyanoquinodimethane). The physical properties of the film were examined by optical and electrical measurements[7,8] including the conductivity measurements under high pressure.[9] The metallic nature of the film was confirmed by thermoelectric power[7] and ESR[10,11] measurements. The temperature dependence of the Hall effect was measured for the first time on LB films.[12] The high conductivity of the film enabled us to observe the electronic conduction of the monolayer on pure water.[13,14] In this paper, we will give a brief summary of the physical properties of the monolayers and the LB films of BEDOTTF-C_{10}TCNQ complex.



BEDO-TTF



C_{10}TCNQ

PREPARATION OF LB FILMS

The charge transfer complex was obtained as black solid with a stoichiometry of BEDO-TTF: C_{10}TCNQ :H_2O = 10:4:1. The conductivity measured on a powder compacted sample was 3.5 S/cm. Although this compound gave a monolayer at the air-water interface, the quality of the LB films obtained from these monolayers was relatively poor. By mixing with 1:1 with arachidic acid (the mixing ratio is based on the molar ratio of C_{10}TCNQ in the complex and arachidic acid), a stable monolayer was formed at the air-water interface, which was deposited on solid substrates to form conducting LB films. The conductivity of the film strongly depended on the film forming conditions. However, the LB films fabricated by the horizontal lifting method showed a high conductivity (10 S/cm), which were the subject of physical measurements.

PHYSICAL PROPERTIES OF THE LB FILM

IR spectra

The IR spectra were measured on 42-layered LB film deposited on CaF_2 substrate. A broad band due to the conduction electron appeared in the whole measuring range, which is consistent with the high conductivity of the film. The spectrum was somewhat complicated because the film was composed of three components, BEDO-TTF and C_{10}TCNQ, which form a charge transfer complex, and arachidic acid as a matrix. However, there are relatively strong bands appeared below 1100 cm^{-1} which are attributed to Ag and B_{2u} modes of BEDO-TTF.[15] The CN stretching mode of the TCNQ moiety was observed at around 2200 cm^{-1}.

The vibration bands of BEDO-TTF and C_{10}TCNQ are shifted compared with those of the neutral molecules when the charge transfer takes place. The positions of the specific bands reflect the degree of the charge transfer. The amount of charge on the TCNQ molecule has been estimated from the shift of the CN stretching mode.[16] We have prepared potassium salt of C_{10}TCNQ, in which the TCNQ moiety should be an anion radical state. The CN stretching band of the C_{10}TCNQ of BEDO-TTF complex appeared almost the same position as that of the potassium salt, indicating that the charge transferred onto the C_{10}TCNQ part of the complex is close to unity.

The charge transfer ratio can be also estimated by the shift of the vibration bands of BEDO-TTF. Recently, Moldenhauer *et al.* reported that the frequencies of the vibration bands concerning C-O bonds of BEDO-TTF are directly related to the average charge on the donor molecules.[17] They used four vibrational bands in the wavenumber region of 1100-800 cm^{-1}, two B_{2u} modes and two A_g modes, the frequencies of which decreased with an increase in the transferred charge. The relationship between the frequency and the degree of charge transfer was not linear. However, two salts with the same charge of +0.5 on BEDO-TTF (BEDO-$TTF_2ReO_4H_2O$ and BEDO-TTF_2Cl) showed the identical shifts, indicating the validity of the estimation.[17]

The two $A_g$bands showed anti-resonant behaviours in the spectra of BEDOTTF-C_{10}TCNQ complexes due to the EMV (electron-molecular vibration) coupling, with the peak frequency being ambiguous due to the broadening of the bands. On the other hand, B_{2u} bands had symmetrical shapes, and we adopted these two bands for the estimation of the degree of the transferred charge. The bands appeared at 1080 and 958 cm^{-1} for the BEDOTTF-C_{10}TCNQ complex in KBr pellet and 1079 and 957 cm^{-1} for the LB film. The difference of 1 cm^{-1} could be an experimental error. The frequency shifts were 3 and 5 cm^{-1} in the case of LB film, which are between the values of 0 and 3 cm^{-1} for BEDO-$TTF_3Cu_2(NCS)_3$ (average charge per BEDO-TTF is +0.33) and 4 and 8 cm^{-1} for BEDO-$TTF_{2.4}I_3$ (average charge per BEDO-TTF is +0.42). The results are in good agreement with the average charge per BEDO-TTF of +0.4 calculated by assuming the charge of -1 for C_{10}TCNQ, taking into account the composition of the complex (BEDO-TTF:C_{10}TCNQ = 10:4). In the complex, the C_{10}TCNQ part is in fully charge transferred state acting as a counter anion, and only BEDO-TTF part is in partially charge transferred state and governs the conductivity.

Conductivity measurements

The conductivity of the film increased with the decrease in temperature down to 250 K, although it decreased with the decrease in temperature below that temperature. We can fit the conductivity behaviour in whole measuring range by a formula of common semiconductor taking into account the mobility change.

$$\sigma = AT^{-\alpha}\exp\left(-\frac{\Delta E}{kT}\right) \tag{1}$$

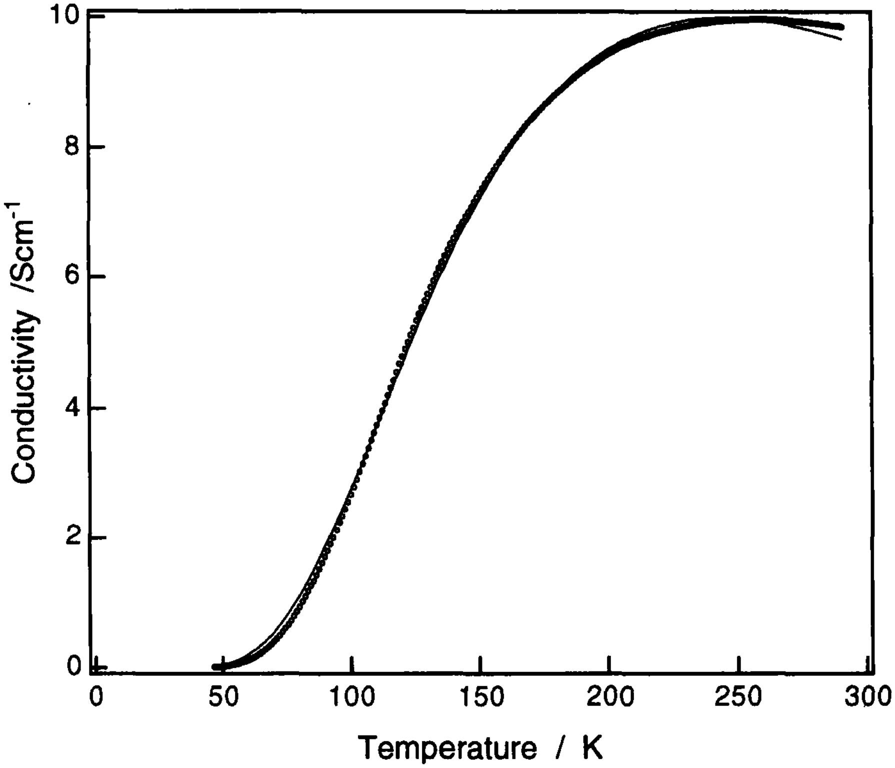


FIGURE 1. The temperature dependence of the conductivity of a 20-layer LB film. The solid curve is a theoretical fit with $\alpha = 2.34$ and $\Delta E = 570$ K.

Due to the strong intermolecular interactions, film had a glanular structure as in the case of the majority of LB films. The domain size was at about 0.1 μm, which was revealed by AFM. The conductivity behaviour of the film is strongly affected by this domain structure.

The conductivity between domains should be much smaller than that within domains. In this case, the total conductivity of the film is expressed by,

$$\sigma \approx \frac{1}{\gamma}\sigma_{boundary} \qquad (2)$$

where, γ and $\sigma_{boundary}$ are the area fraction and the conductivity of the domain boundary, respectively. Consequently, the intrinsic conductivity within domains can not be observed by dc measurements. On the other hand, the thermoelectric power of the film is mainly governed by that of domains as,

$$S \approx (1-\gamma)S_{domain} + \gamma S_{boundary} \qquad (3)$$

where, S_{domain} and $S_{boundary}$ are the thermoelectric power of domain and domain boundary, respectively.[7]

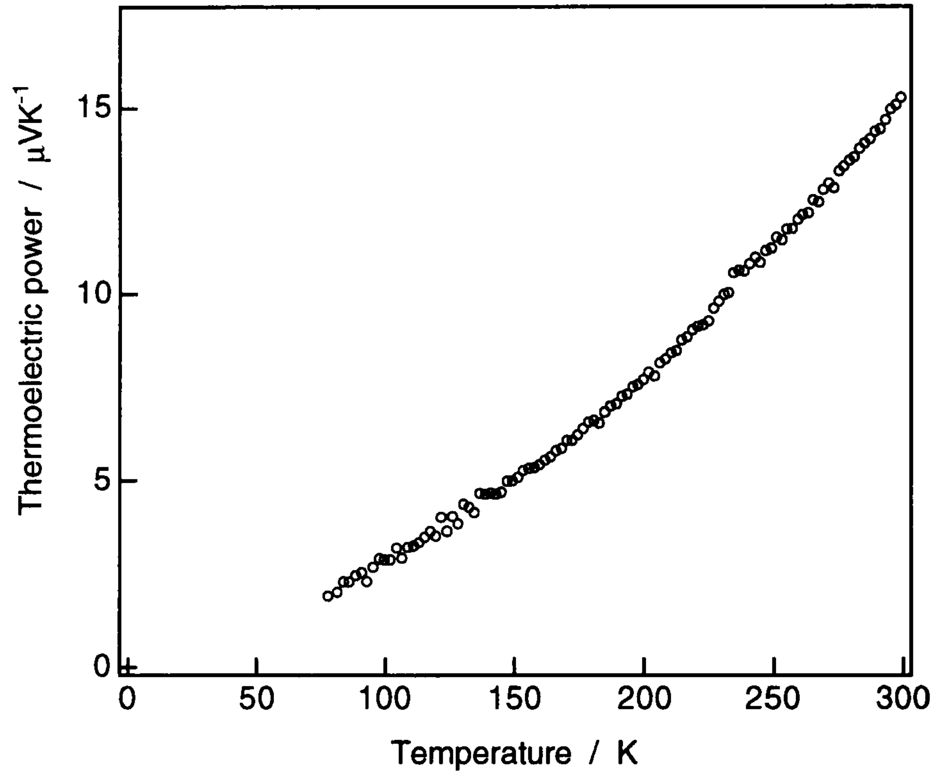


FIGURE 2. The temperature dependence of the thermoelectric power of an LB film.

The temperature dependent thermoelectric power measurement clearly indicated a metallic nature of the domains (Fig. 2). The thermoelectric power was positive and in the range of 15 μV/K at room temperature and showed a nearly metallic temperature dependence. Positive thermoelectric power is in good agreement with the fact that the conduction is dominated by BEDO-TTF part expected from the results of IR measurements.

The metallic nature of the film was also confirmed by the ESR measurements by Ikegami *et al.*[10,11] The ESR signal of the film was composed of two species and the major component showed the Pauli paramagnetic susceptibility due to the conduction electron on the BEDOTTF stacks. The temperature dependent Hall effect[12] and the conductivity at high pressure were also measured.[13]

PHYSICAL PROPERTIES OF MONOLAYERS AT THE AIR-WATER INTERFACE

Conductivity-area isotherms

The high conductivity of the complex enabled us to measure the conductivity of the monolayer at the air-water interface. We used dc or ac 2-probe method for the measurements. The details of the experimental setup was reported elsewhere.[14]

Typical conductivity-area (σ-A) isotherms measured by ac and dc together with a surface pressure-area (π–A) isotherm are shown in Fig. 3 for the monolayer of BEDOTTF-C_{10}TCNQ complex mixed with arachidic acid at a molar fraction of 0.5, the same ratio as that for the preparation of the LB films described above. As we used the plane parallel electrodes, we can define the conductivity of the monolayer simply as,

$$\sigma = \frac{1}{R}\frac{W}{Ld} \tag{4}$$

where, R, W and L are the measured resistance, the interfacial electrode spacing and the width of the electrodes, respectively. We assume that the thickness of the monolayer (d) as 25 Å. Here, we neglect the enhanced conductance (ΔG) of the interfacial water resulting from the formation of the monolayer[18,19] which will be discussed later. In ac measurements, the conductivity almost corresponds to the surface pressure. On the other hand, the high dc conductivity was observed only at higher pressure region. The difference between dc and ac measurements may be due to the domain structure of the monolayer.

The monolayer should be composed of conducting domains (see next section) which gather as the surface area is reduced. The space between the conducting domains may act as a kind of two-dimensional capacitor. This two-dimensional capacitor array should be highly conducting at high frequency in ac measurements and should interrupt the conduction in dc measurements. As a result, the conductivities measured by ac are much higher than those measured by dc in the region where the surface pressure increases steadily and the monolayer becomes condensed. The dc measurement is much more sensitive to the nature of the domain boundaries compared to ac measurements, because the direct interactions between the domains are essential to form conduction paths for dc current.

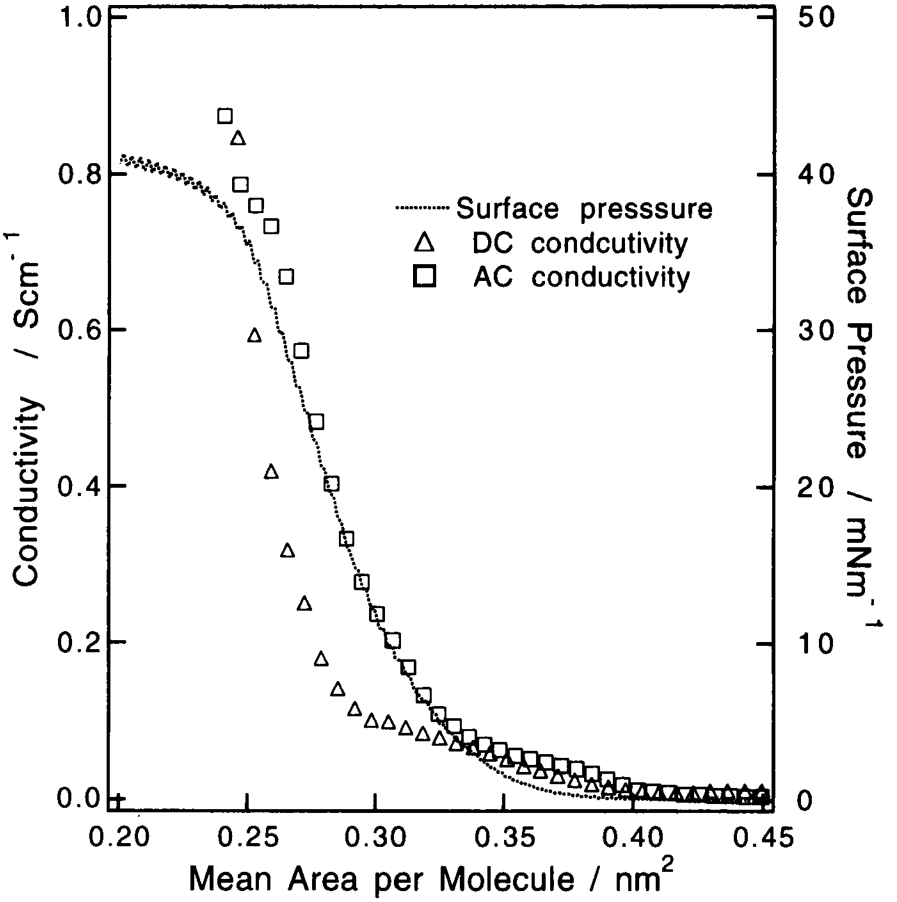


FIGURE 3. The dc and ac (at 10 kHz) conductivity as a function of surface area (σ-A isotherms) together with the π-A isotherm of the mixed monolayer of BEDOTTF-C_{10}TCNQ and arachidic acid at the molar fraction of 0.5.

At lower pressures, the σ-A isotherms showed almost the same behaviour in both dc and ac measurements: the conductivity increases nearly linearly with the decrease in area up to around 0.1 S/cm where the conductivity starts to increase rapidly. The conductivity of 0.1 S/cm corresponds to the value calculated from the ΔG for arachidic acid at the condensed phase measured separately. Therefore, we can tentatively conclude that the increase in the conductivity at lower pressure region is due to the enhanced conductance of the interfacial water.

π-A isotherms at different molar fraction

Figure 4 shows the π-A isotherms at different molar fraction. We are using the molar fraction of the complex in the mixed monolayer based on the molar ratio of C_{10}TCNQ and arachidic acid as mentioned before. For example, the monolayer of the molar fraction of 0.5 is composed of one C_{10}TCNQ, 2.5 BEDO-TTF and one arachidic acid.

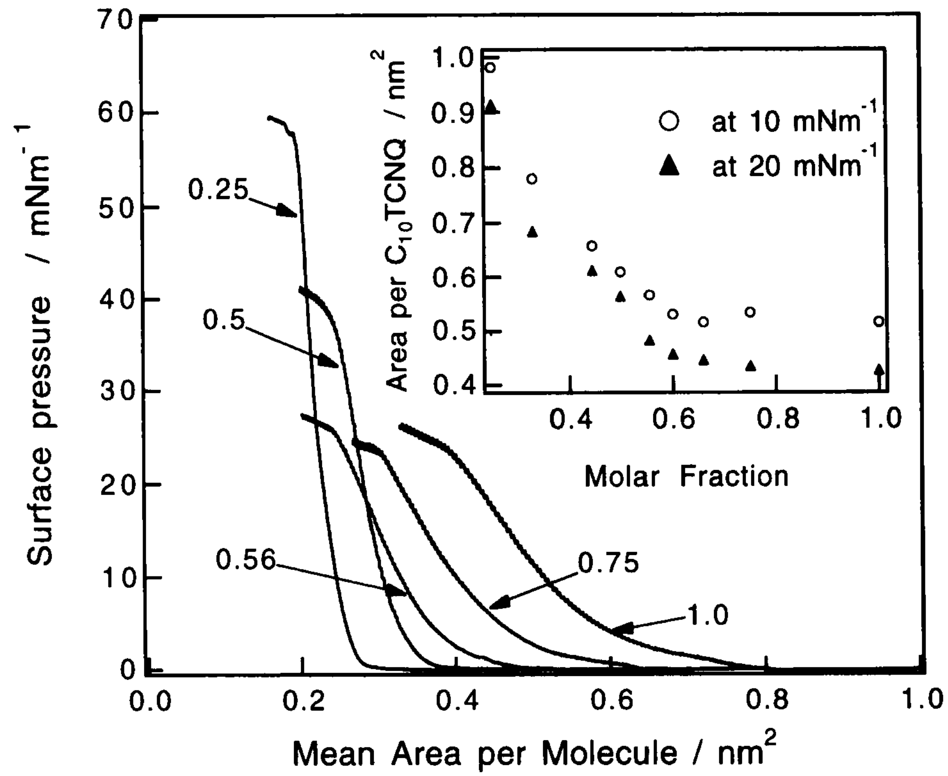


FIGURE 4. π-A isotherms of the mixed monolayers of BEDOTTF-C_{10}TCNQ and arachidic acid at different molar fraction of the complex. Inset, the area which one CT complex exists on average at the air-water interface versus molar fraction

The behaviour is different to each other below and above the molar fraction around 0.5. With the molar fraction above 0.56, the π-A isotherms resembles to each other. On the other hand, the shape of the isotherm changed gradually with the molar fraction below 0.5. To clarify the difference in the π-A isotherms, we plotted the area which one CT complex exists on average at the air-water interface versus molar fraction (Fig. 4, inset). The area almost unchanged above the molar fraction of 0.6. In other words, the area which one CT complex can be found on the surface seems to be indifferent to the amount of the arachidic acid in this region. These results suggest that the π-A isotherm is governed by BEDOTTF-C_{10}TCNQ and that arachidic acid molecules do not occupy the surface area at the higher molar fraction region above around 0.6.

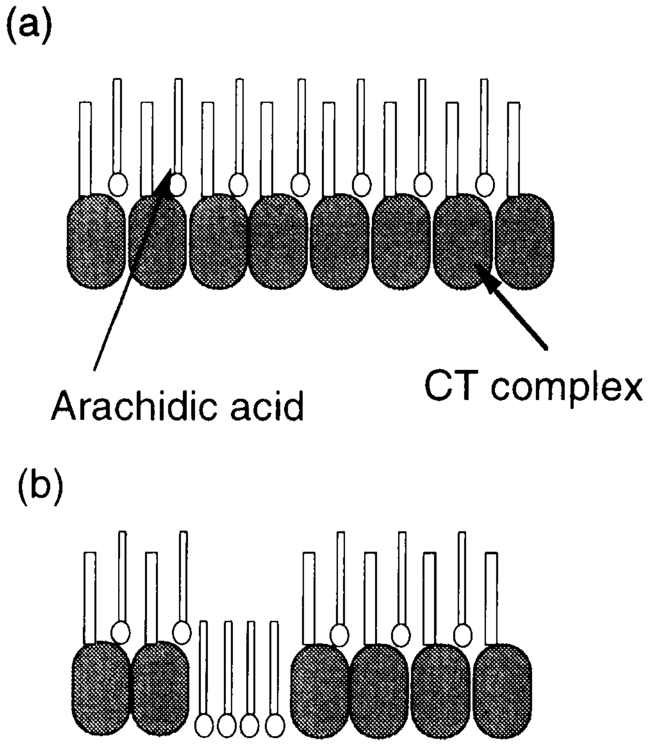


FIGURE 5. Schematic view of possible structures of the mixed monolayers at the air-water interface. (a) BEDOTTF-C_{10}TCNQ and arachidic acid form a kind of 'supermonomolecular'[20] layer with the higher molar fraction of the complex. (b) A part of arachidic acid become phase-separated with lower molar fraction of the complex.

One possible model for explaining these experimental results is as follows. The monolayer at the air-water interface should have a domain structure and the surface area of BEDOTTF-C_{10}TCNQ should be determined not by the alkyl chains but by the charge transfer complex part (BEDO-TTF and TCNQ part) due to the strong intermolecular interactions in the complex. As the cross-sectional area of the alkyl chain is smaller than that of the charge transfer complex part, there should be spaces between the alkyl chains of C_{10}TCNQ. Consequently, arachidic acid molecules can fill the spaces between the alkyl chains of C_{10}TCNQ in the domains of BEDOTTF-C_{10}TCNQ to form a kind of 'supermonomolecular' structure,[20] showing no surface area at higher molar fraction region (Fig. 5 (a)).

At lower molar fraction region below around 0.6, the area per C_{10}TCNQ increases with the decrease in molar fraction, suggesting that arachidic acid molecules occupy certain area at the air-water interface. Considering limited amount of the spaces acting as a host for arachidic acid molecules in the BEDOTTF-C_{10}TCNQ domains, arachidic acid molecules may be partly phase-separated in this region and exist between the conducting domains (Fig. 5.(b)). As a result, π-A isotherms become gradually taking on a character of that of arachidic acid with the decrease in molar fraction (with the increase in the amount of phase-separated arachidic acid).

Conductivity of the monolayers at different molar fraction

Figure 6 shows the relationships between the surface pressure and the dc conductivity at various molar fraction of BEDOTTF-C_{10}TCNQ complex. The arrows indicate the collapse points. Relatively high conductivities are obtained at high molar fraction of the CT complex. In the inset, the conductivity of the monolayers at the surface pressure value of 20 mNm^{-1} is plotted against the molar fraction of the complex. It seems that a certain transition exists at around the molar fraction of 0.55.

At the molar fraction of 0.25, only low conductivity was observed even at the collapse point; this probably corresponds to the percolation limit of this system. The conductivity at the collapse point increased with the increase in molar fraction. However, there is keen difference in the σ-π behaviour between those above and below the molar fraction of around 0.55. At lower mixing ratios, the conductivity increases only in the pressure region just before the collapse occurs. The conductivity at 20 mN/m is at most 0.5 S/cm. On the other hand, the monolayers with the molar fractions more than 0.6 exhibit the conductivity increasing almost linearly with the increase in pressure.

As discussed above, with the molar fraction of less than 0.6, the arachidic acid molecules should be partly phase-separated and have a certain surface area. The arachidic acid molecules can interrupt the direct contact between the conducting domains. Conduction paths will be created only when the domains contact closely with each other pushing aside the arachidic acid molecules at higher pressures just below the collapse points. At lower pressures the phase-separated arachidic acid may act as an insulating separator between conducting domains to interrupt the conduction, although the effect of this separator on the ac conductivity may be small, which is expected from the measurements for the monolayers at the molar fraction of 0.5. At higher molar-fraction region above 0.6, it is suggested that the arachidic acid molecule in the monolayer occupies almost no surface area and does not exist between the conducting domains. In this situation, the conduction paths will be easily produced by the direct contact between the domains even at lower surface pressures.

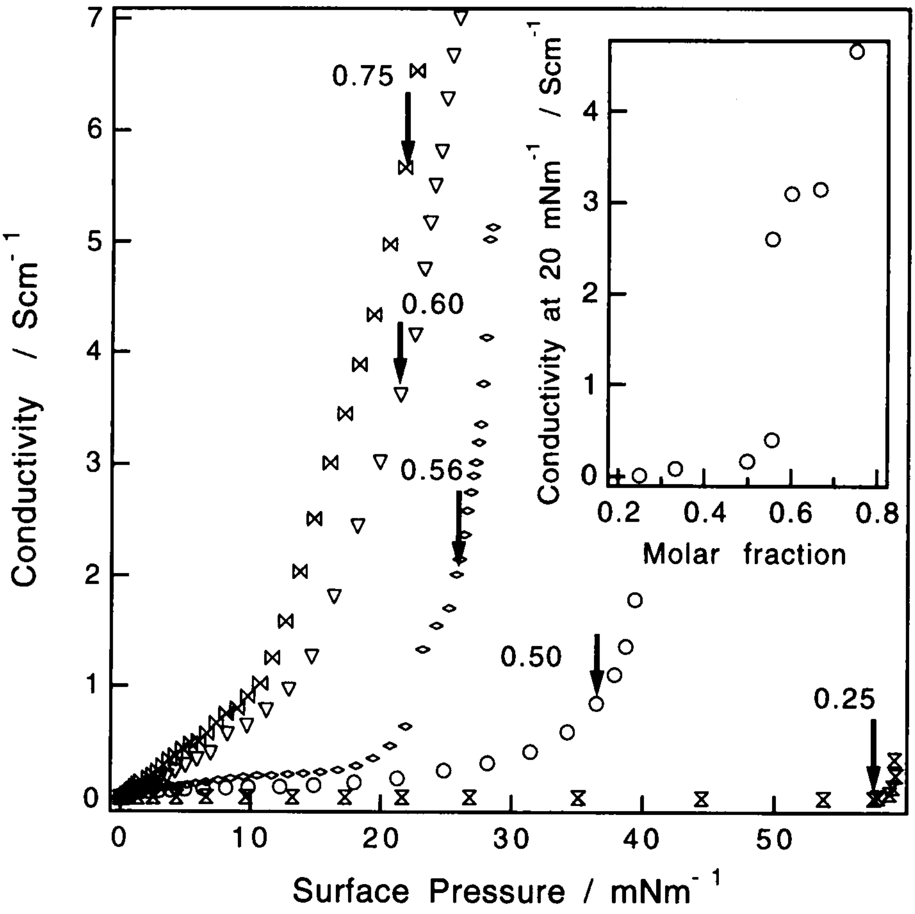


FIGURE 6. The relationships between the monolayer conductivity and the surface pressure at different molar ratios. The collapse points are indicated by arrows. Above this point, we can not determine the 'monolayer conductivity'.

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REFERENCES

1. *Langmuir-Blodgett Films*, Edited by G. G. Roberts, Plenum Press, New York (1990)
2. *Introduction to Molecular Electronics*, Edited by M. C. Petty , M. R. Brice and D. Bloor, Edward Arnold, London (1995)
3. A.Ruaudel-Teixier, M. Vandevyver, and A. Barraud, *Mol. Cryst. Liq. Cryst.*, **120**, 319 (1985)
4. M. R. Bryce and M. C. Petty, *Nature,* **374**, 771 (1995).
5. M. Matsumoto, H. Tachibana and T. Nakamura in Organic Conductor - Fundamentals and Applications, Editied by J.-P. Farges, pp759-789, Marcel Dekker, Inc., New York (1994)
6. M. F. Rubner, in Polym. Electron. Photonic Appl., Edited by C. P. Wong, pp601-631, Academic press, Boston, Mass (1993)
7. T. Nakamura, G. Yunome, R. Azumi, M. Tanaka, H. Tachibana, M. Matsumoto, S. Horiuchi, H. Yamochi and G. Saito, *J. Phys. Chem.*, **98**, 1882 (1994)
8. T. Nakamura, G. Yunome, M. Matsumoto, Y. F. Miura, S. Horiuchi, H. Yamochi, G. Saito, H. Isotalo and H. Stubb; *Synthetic Metals*, **71**, 1993 (1995)
9. H. Isotalo, G. Yunome, R. Azumi, M. Matsumoto, T. Nakamura, S. Horiuchi, H. Yamochi and G. Saito, *Synthetic Metals*, **70**, 1229 (1995)
10. K. Ikegami, S. Kuroda, T. Nakamura, G. Yunome, M. Matsumoto, S. Horiuchi, H. Yamochi and G. Saito, *Phys. Rev. B*, **49**, 10806 (1994)
11. K. Ikegami, S. Kuroda, T. Nakamura, R. Azumi, G. Yunome, M. Matsumoto, S. Horiuchi, H. Yamochi and G. Saito, *Synthetic Metals*, **71**, 1909 (1995)
12. M. Takenaga, A. Abdulla, A. Kasai, A. Nakamura, T. Nakamura, M. Matsumoto, S. Horiuchi, H. Yamochi and G. Saito, *Appl. Phys. Lett.*, **64** (1994) 2602.
13. H. Isotalo, G. Yunome, M. Abe, S. Horiuchi, H. Yamochi, G. Saito, H. Tachibana, T. Nakamura and M. Matsumoto, *J. Chem. Soc. Chem. Commun.*, **1994**, 573
14. T. Nakamura, H. Isotalo, T. Akutagawa, H. Tachibana, R. Azumi, M. Matsumoto, S. Horiuchi, H. Yamochi and G. Saito, *Thin Solid Films*, in press.
15. K. I. Pokhodnia, M. E. Kozlov, V. G. Onischenko, D. Schweitzer, J. Moldenhauer and R. Zamboni, *Synth. Met.* **56**, 2364 (1993)
16. J. S. Chappell, A. N.Bloch, W. A.Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981)
17. J.Moldenhauer, K. I. Pokhodnia, D. Schweitzer, I.Heinen and H. J. Keller, *Synth. Met.*, **56**, 2548 (1993)
18. H. Morgan, D. M. Taylor and O. N. Oliveira Jr., *Chem. Phys. Lett.*, **150**, 311 (1988)
19. H. Morgan, D. M. Taylor and O. N. Oliveira Jr., *Thin Solid Films*, **178**, 73 (1989)
20. Y. Kawabata, T. Sekiguchi, M. Tanaka, T. Nakamura, H. Komizu, H. Honda and E. Manda, *J. Am. Chem. Soc.*, **107**, 5270 (1985)