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## Study of ultra thin films based on the charge-transfer salts aimed for the onset of the superconductivity

Mitsuru IZUMI and Hitoshi OHNUKI

*Laboratory of Applied Physics, Tokyo University of Mercantile Marine,  
Etchu-jima, Koto-ku 135, Tokyo, JAPAN  
e-mail: izumi@zairyo.phys.tosho-u.ac.jp ; Fax: +81-3-5245-7462*

### Abstract

In the basic research of Langmuir-Blodgett (LB) films, most of the difficulties to deduce the inherent structural and physical properties come from the existence of many small regions with differing orientation as two dimensional (2D) domain plates in each monolayer. To overcome such difficulties we emphasize a strategy of studying the single crystal and the LB films which have the identical molecular organization. As an example, we show a series of comparative studies on a stable conducting LB films of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> and its single crystal. The success of growth of the single crystals leads to a proposal of possible 3D model of molecular organization and clarification of the electronic states responsible for the conductivity.

### Résumé

Dans la recherche de base des couches Langmuir-Blodgett, la plupart des difficultés pour déduire les propriétés inhérentes structurelles et physiques viennent de l'existence de beaucoup de petites régions avec être différent orientation comme des plaques domaine bidimensionnels (2D) dans chaque monocouche. Pour vaincre telles difficultés, nous accentuons une stratégie d'études le monocristal et les couches Langmuir-Blodgett qui vont l'organisation identique moléculaire. Comme un exemple, nous montrons une série d'études comparatives sur les couches Langmuir-Blodgett de la conduite stable filme de [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> et son monocristal. Le succès d'augmentation des monocristaux mène à une proposition de possible 3D modèle d'organisation moléculaire et éclaircissement des états électroniques responsable pour la conductivité.

### Footnote

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## 1. Introduction

In thin organized molecular films such as multilayered ultra-thin films, the molecular assemblies with the well-defined structure are essential for the realization of the potential applications [1]. The term "Langmuir-Blodgett (LB) Films" is used to denote monolayer and multilayers deposited from the liquid-gas interface onto a solid substrate with ordered structure. It is a historical trend to try to fabricate highly conducting LB films based on charge-transfer (CT) complex or CT salt by using electroactive donor and/or acceptor molecules among fruitful functional molecules from the viewpoint of molecular electronics[2]. Most of the studies following the above trend have been encouraged by the rapid progress in the study of single crystals of CT compounds based on a donor molecule TTF (tetrathiafulvalene, Fig. 1-1) or an acceptor molecule TCNQ (tetracyanoquinodimethane) and their derivatives [2]. The LB technique allows one to produce films of a precisely determined number of layers in principle, which ordinary crystallization methods do not and LB films is much easier to incorporate into practical device structure [1]. On the other hand, as the disadvantage of LB method we note that proper long-range order in the film plane has not yet been achieved and it prevents to clarify physical properties [3]. In spite of the importance to the in-plane molecular packing structure responsible for conductivity as described later, the existence of many small regions with differing orientation in each monolayer makes difficulties in the study of intrinsic structural and physical properties in the study on conducting LB films. Although x-ray crucial ones to obtain the informations on the molecular organization and electronic transport properties in the case of the crystals, these experimental techniques are strongly influenced by the effect of the existence of the above mentioned domains in the case of LB films. Hence, the results of such experiments show the averaged properties of randomly distributed domains. Therefore, it is impossible to obtain the inherent physical properties on a single domain that should be essential to conductivity. In this paper, we show that one of the strategies to deduce the inherent information on structural and physical properties from the LB films is to study comparatively on the single crystal which is composed of the same molecules and assembly with that of the LB films. Such approach would provide the mechanism to realize higher conductivity and show the ways improve the conductivity. As an example of the study following the present strategy, we exhibit what is going on the comparative study on conducting LB films of cation radical salt based on EDT-TTF(SC<sub>18</sub>)<sub>2</sub> ((ethylenedithio)-bis(octadecylthio)tetrathiafulvalene Fig. 1-4 ) and its single crystal.

In the present organization, firstly we give a brief summary of the progress in the study of organic CT crystals, which has given rise to the motivation of the study of conducting LB films (Sec. 2). Secondly, we deal with the electronic state to obtain conducting organic CT molecular assembly and the difficulties to achieve a well-defined electronic transport in LB films (Sec. 3). Subsequently, in Sec. 4 we describe a basic strategy as the comparative study. In Sec. 5, we exhibit a general preview on the conducting LB films of cation radical salt [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> which we have applied the present strategy. In Sec. 6, we report that the success in the crystal growth leads to a proposal of the model of molecular assembly and precise clarification of inherent physical properties.

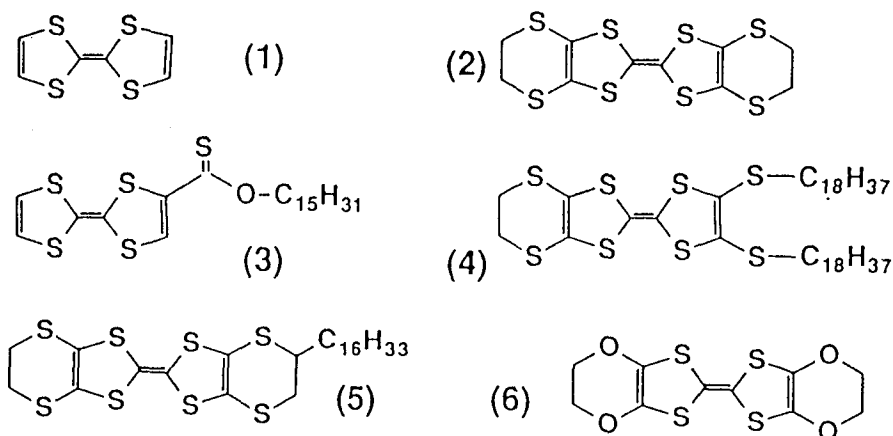


Fig. 1 TTF and its derivatives with long alkyl chain which provides highly conducting Langmuir-Blodgett films. TTF (1), BEDT-TTF (2), HDT-TTF (3) [16], EDT-TTF(SC<sub>18</sub>)<sub>2</sub> (4), C<sub>16</sub>-BEDT-TTF (5) [17] and BEDO-TTF(BO) (6) [18].

## 2. Historical background

Since the discovery of metallic conductivity peak in the crystal of CT complex, TTF-TCNQ in 1973 [4], the research field of crystals of organic low-dimensional conductor has been drastically extended via the synthesis of a number of superconducting CT salts with the critical temperature up to 12.8 K in BEDT-TTFCu[N(CN)<sub>2</sub>]Cl [5]. Thanks to the low ionization potentials of the constituent donor molecules and the high electron affinities of the acceptor molecules, the several classes of binary materials assigned as CT complex or CT salt (ion-radical salt) have been studied as the ionic or mixed valence molecular species in the ground state. In these materials, a CT donor-acceptor intermolecular interaction after Mulliken [6] is essential to the appearance of the electrical conductivity, where its magnitude and the difference in the orbital energies of adjacent molecules are important [7]. Crystals formed by both open-shell molecular ions and closed-shell counter-ions exhibit numerous fruitful physical properties. Cation-radical salts of 2-1 stoichiometry (we note it as D<sub>2</sub>X, where D is a donor TTF derivatives and X is an anion, respectively) issued from the TTF (Fig. 1- 1) backbones present a series of organic conductors with a variety of ground states [8-9]. They are characterized by segregated stacks of TTF-type molecules with a regular packing of dimers, where mixed valence dimers D<sub>2</sub><sup>+</sup> are formed with molecules mostly associated with a monovalent diamagnetic anion X<sup>-</sup>. In that case, carriers are able to move by hopping from dimer to dimer, which conducts to metallic or semiconducting electronic properties. In physical interpretation of such electronic system, during the last two decades, an extended Hubbard electronic and spin Hamiltonian have described well those physical properties in most of quasi-one dimensional (1D) organic conductors and during the last decade one finally achieved Fermi surface formed by two dimensional (2D) molecular overlap in the electronic system, which has provided stable metallic conductors and/or superconductors. Among the TTF derivatives, many compounds based on the donor BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene, ET : Fig. 1-2) molecule have been synthesized [10]. In this system, it is shown that the anion size and anion -CH<sub>2</sub> hydrogen interactions are critical factors that control the packing of the ET donor molecule and determine the

transport properties [11]. It can be easily seen that a series of quite fruitful electronic and magnetic properties originate from different packing schemes of donor in cation-radical salts of ET molecule [12]. The discovery of the superconductivity of CT systems seems to have been accepted with great technological relevance.

To submit such interesting donor-type TTF derivatives to the fabrication of the multilayered thin films by LB techniques, it is necessary to obtain the stable monolayer on the water surface [2,13]. In contrast to the case of organic crystals, donor-type TTF molecules generally oblige to have long aliphatic chains to constitute a stable packed molecular assembly on the water surface, since the molecule should be amphiphilic. Therefore, if we use the same TTF-type donor molecule and anion to fabricate LB films as used in the CT crystal, the obtained molecular assembly is not generally identical in both LB films and crystals. Historically, Saclay group [14] in France succeeded to build conducting LB films of charge-transfer complex based on an acceptor-type TCNQ for the first time and subsequently the fabrication of LB films of TTF/TCNQ has been done by Nakamura et al [15]. Figure 1 exhibits several TTF-family molecules which have given highly electrical conductivity in the form of LB films. As summarized by Roberts [1], mostly ohmic behavior is observed with room temperature dc conductivities in the range  $10^{-4}$  -  $10^2$  S/m. The conductivities are thermally activated as in doped inorganic semiconductors. However, higher conductivities than those above are inferred from optical conductivities, which has been interpreted that "grain boundaries" in the film plane may well be limiting the dc values [1].

### 3 . What controls the electronic properties in LB films?

In the following, we will focus on the conducting LB films of 2-1 cation radical salts based on long chain alkyl TTF derivatives. Several key factors have been proposed to obtain a well-defined conducting LB films [2,13]. We can summarize them as: (1) stability and transferability of monomolecular layer on the water surface, (2) stability of multilayered films after the deposition, (3) achievement of the dimer with mixed-valence state as cation-radical salts which is also essential in the case of crystals. However, we think that the above mentioned points are not sufficient and the following important point should compensate : (4) formation of 2D in-plane molecular packing to achieve sufficient values of transfer integrals intra- and/or interdimer. The last point (4) is quite important for higher conductivity, since the development of 2D lateral overlap of the molecular orbital gives a metallic state and dominates electronic properties. That is, the origin of electronic properties is attributed to the dimer packing arrangement in the film plane. As described in the preceding section, we can easily see in the case of crystals that a series of quite fruitful electronic and magnetic properties originate from 2D different packing schemes of donor in cation-radical salts of ET molecule [12].

Let's us consider more detailed electronic state in dimers to provide electrical conductivity. Supposing the mixed valence isolated dimer as  $D_2^+$  or  $D^+D^0$ , the electronic state has two energy levels separated by an energy gap with  $2t$  between bonding and antibonding orbitals from HOMO, where  $t$  is the electron transfer interaction (transfer integral) between two equivalent monomers as

shown in Fig. 2 [19]. If relatively strong dimerization exists, the interdimer overlap integral  $t'$  can be defined. With increasing  $t'$ , half-filled upper band becomes broad as shown in Fig. 2(b) and subsequently in Fig. 2(c). Consequently, as a function of  $2t-t'$  in the electronic structure we shall obtain the electronic properties responsible for metallic conductivity. In the case of LB films based on CT salt, in principle, the electrical conductivity should be realized by following the same mechanism as described above. However, it is reminded as described in Sec. 2 that donor molecules are generally obliged to have long aliphatic chains to constitute a stable amphiphilic structure on the water surface. To prepare a conducting LB films of CT salts, several methods have been developed. In the first way, one obtained LB films of donor molecules with long alkyl chain and final conducting LB films as  $D_2X$  were fabricated after the oxidation process under the exposure to halogen gas. In the second way, one could reach an idea of autodoping (homodoping strategy) by mixing, for example,  $D^0$  and  $D^{+1}$  molecules (but not realized for TTF derivatives) [20]. Many interesting TTF type donor molecules with long alkyl chains do not have desirable amphiphilic character but rather hydrophobic. In this situation, mixed LB films of the interesting cation-radical salt with fatty acid appeared and it has sometimes given better electrical conductivity [21]. Among

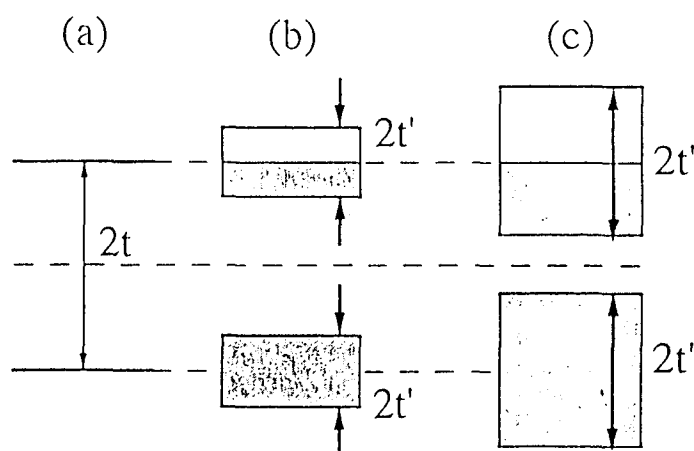


Fig. 2 Schematic energy spectra for (a) isolated donor dimer, (b) chain of quasi-isolated donor dimers ( $t' \ll t$ ), and (c) chain of strongly interacting donor dimers ( $t' \ll t$ ).

conducting LB films based on such CT salts, most of them are semiconductors even with the existence of the mixed valence state dimer and quite a few ones exhibit metallic electrical conduction [1,22]. Then, how can we obtain the reason why they exhibit semiconducting properties? Is it only due to the existence of "grain boundaries"? Is it intrinsically semiconductor or metal? How can we achieve any information to improve the electrical conductivity? The first step to further breakthrough is to clarify the structure of the molecular organization in the segregated layer stacks which remain not to be clarified well in most of the conducting LB films. In particular, packing structure of donor molecules in the film plane is suffered by the lateral packing scheme of long alkyl chains. Therefore, we easily imagine that both of them are deeply correlated to the control of both  $t$  and  $t'$  values cited above. Possibly, the electronic state of the molecular condensates such as LB films shall be

attributed to the packed structure determined by a competition between the charge-transfer interaction between donor-counter ion molecules and intermolecular interaction in long alkyl chains. Thanks to the knowledge of the in-plane structure of molecular assembly, we shall be able to interpret the physical properties and reconsider the molecular conformation to improve the conductivity.

#### 4. Basic strategy to study physical and structural properties of conducting LB films

As described before, the existence of the ensemble of 2D domains in each mono-molecular layer gives a limited information on structural and physical properties and makes difficulties to deduce intrinsic properties. When we consider that the starting point of material research is to get the knowledge of precise structure of the material, one of the strategies to deduce the inherent structural and physical properties is to study comparatively on the single crystal which is composed of the same molecules and assembly with that of the LB film. Single crystal X-ray diffraction will exhibit the precise crystal structure and compensate deficient structural parameters in the case of X-ray diffraction on the LB films. There, we will be able to get precise packing structure of donor TTF-type molecules which is crucial information to take account of the conducting properties. In the next step, one would study the inherent physical properties induced from the determined structure. For example, polarized infrared-absorbance spectroscopy will give the anisotropy of the overlap integral of donor-molecular orbitals by the analysis of the charge-transfer absorption band. This result may provide the quantitative estimation of intra- and interdimer transfer integral. By measuring the electrical conductivity in single crystals we shall overcome the effect of the domains on the electrical conduction in the case of LB films and deduce the precise properties of the conductivity. In contrast to the case in the LB films, we will be able to clarify any in-plane anisotropy in conductivity, dielectric constant, magnetic susceptibility by the experiments on single crystals. As the candidate following the present strategy, we focused on the conducting LB film of cation radical salt based on EDT-TTF(SC<sub>18</sub>)<sub>2</sub> ((ethylenedithio)-bis(octadecylthio)tetrathiafulvalene Fig. 1-4). Properties of the LB film formed by the mixture with behenic acid have been extensively studied [21,23,24]. As it becomes a stable semiconducting film after the oxidation process with iodine vapor and shows dc conductivity up to ~1 S/cm. Moreover, its semiconducting property has been submitted to the test for the FET device [25]. To understand the mechanism of the electronic transport, firstly one have to clarify whether the observed semiconducting properties are originated from the effect of "grain boundaries" or intrinsic properties. Secondly, we have to understand what kind of structural assembly of EDT-TTF brings about the electronic states (t or t') responsible for the conductivity.

#### 5. General description of conducting LB films of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub>

Mixed LB films of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> and behenic acid has been investigated intensively due to stability of the conducting state [21,23,24]. The technique to fabricate LB films is a vertical dipping-type classical method as described in earlier paper [26]. After the Y-type deposition of the 1:1 mixed LB films of EDT-TTF(SC<sub>18</sub>)<sub>2</sub> and behenic acid, the oxidation process by iodine vapor is

performed and finally we obtain purple colored conducting LB films by annealing process at  $50^{\circ}\text{C}$  for 2 hours. Such annealing process is necessary to achieve a stable film, since the iodine deintercalation process to the neutral phase occurs after the doping process at room temperature without annealing. This is easily detected by X-ray diffraction. Figure 3 exhibits the X-ray diffraction profiles from LB films oxidized by iodine vapor. Each profiles was observed at 0 hours (a), 24 hours (b), 72 hours (c), 5 days (d), 3 weeks (e) and 6 weeks (f) after the oxidation without annealing process. In Fig. 3 four stable diffraction peaks (\*) are assigned as those from behenic acid clusters. It is clearly observed that both the angles and the intensity of diffraction peaks with  $55 \text{ \AA}$  periodicity from EDT-TTF(SC<sub>18</sub>)<sub>2</sub> (a) are modified to those with  $45 \text{ \AA}$  periodicity from [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> as in (b), (c), (d) and (e) due to the iodine intercalation. However, after 6 weeks, the similar profile with (a) can be seen in (f) as the result of the deintercalation process of iodine. Figure 4 shows the x-ray diffraction profile of the stabilized LB films after the annealing process. The obtained stacking periodicity is  $45 \text{ \AA}$  from the stabilized [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> [21]. The maximum conductivity reached 1 S/cm in the film plane for the 50 layered films (25 bilayers

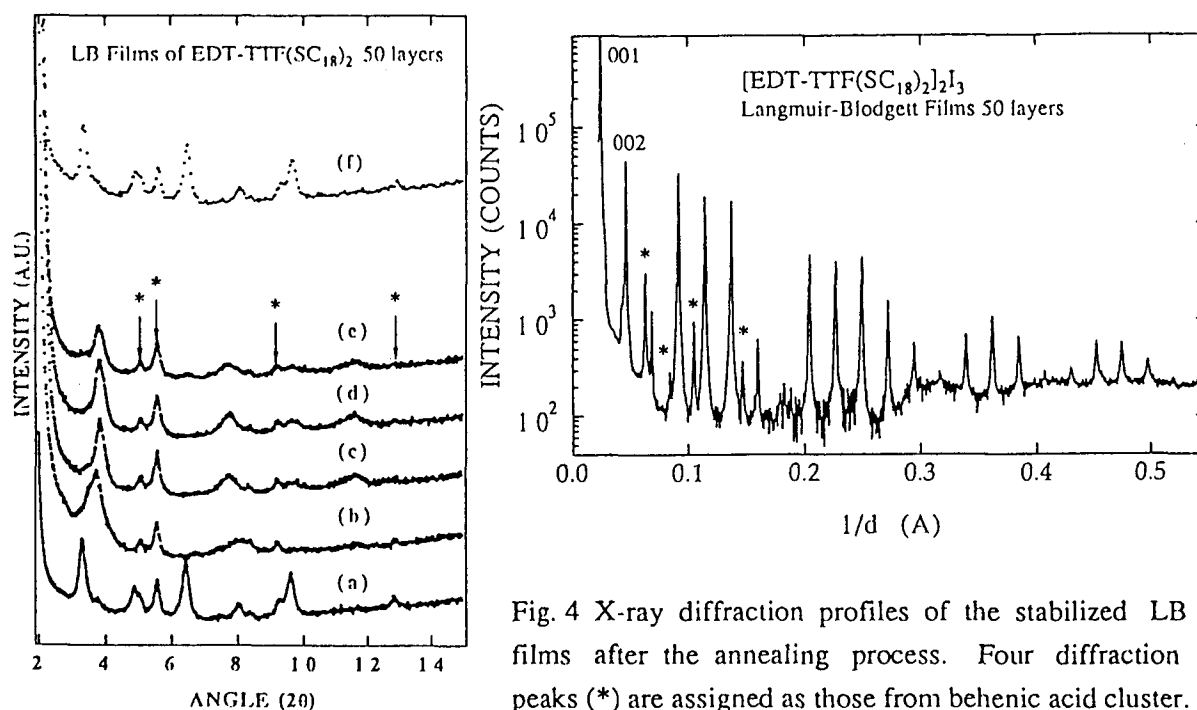


Fig. 4 X-ray diffraction profiles of the stabilized LB films after the annealing process. Four diffraction peaks (\*) are assigned as those from behenic acid cluster.

Fig. 3 X-ray diffraction profiles of LB films as a function of time after the iodine oxidation at room temperature : (a) 0 h, (b) 24 h, (c) 72 h, (d) 5 days, (e) 3 weeks, (f) 6 weeks after the oxidation. Sample was placed in the atmosphere. CuK $\alpha$  line was used. The diffraction peaks (\*) are assigned as those from behenic acid cluster.

followed by the definition of Y-type films). By the plot of room temperature conductivity vs. number of layers or mixed ratio, it has been concluded that the conduction follows more or less a 3D percolation model and the conductivity 1 S/cm of films with 1:1 mixed ratio has been assigned as



one at percolation limit [21].

In the study of organic superconductors, the great interest to the infrared absorbance has been given due to the proposed mechanism of superconductivity mediated the electron-molecular vibration (e-mv) coupling by Yamaji [27]. One can deduce the e-mv coupling constants from the optical spectra of these compounds [7]. In the mixed LB films of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> and behenic acid, the vibronic mode based on the e-mv coupling was observed associated with the charge-transfer absorption as shown in Fig. 10 of ref. 21 (Torrance's "A" band [28]). From the absorption profile, Dourthe et al. [21] have analyzed by using the optical dielectric function of charge-transfer excitation associated with the e-mv coupling under the assumption of the existence of the ensemble of single charged isolated dimers in the first approximation with a Drude-Lorentz model (in presence of a narrow continuum). The above mentioned progress has not yet reached the goal to clarify the origin of the electrical conductivity. The definitive reason for this is that we have not yet clarified the packed structure composed of the donor molecules in the film plane, which shall be submitted to some comparison with the FT-IR data.

Thus, as in most works on conducting LB films, the research for individual materials is obliged to stop at the equivalent stage on which they stay at the point of success of the determination of the molecular orientation. As described in the preceding sections it is more important to get the exact information on the molecular organization in the film plane. To obtain any advancement, it is clear to need the information on not only orientation correlation but also spatial correlation, in other words, the column structure and/or the packing of TTF dimers in the film plane. In summary, when one would try to definitively clarify the mechanism of the electrical conductivity, the following tasks always remain. Firstly, one have to study molecular organization of EDT-TTF in the film plane which gives us the opportunity to estimate  $t$  and  $t'$  and intrinsic mechanism of electrical conduction.

#### 6. An introduction to the comparative study on structural and electronic properties in both LB films and crystals of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub>

Single crystals were obtained by electrochemical crystallization and the detailed description was given in ref. 24. X-ray diffraction study exhibited that the crystal symmetry is orthorhombic,  $a=10.5 \text{ \AA}$ ,  $b=5.4 \text{ \AA}$  and  $c=45 \text{ \AA}$  [24]. Even by using both rotating anode X-ray source and imaging plate, it is difficult to collect enough number of intensified diffraction spots. Thus, the determination of the crystal structure by the conventional crystal structure analysis has not been succeeded. The length of the c-axis of the crystal coincides with that of the stacking periodicity in the LB films. The intensity distribution of the present diffraction series in crystals and LB films is similar each other, which suggests that linear electron density distribution along the c axis (the direction of the layer stacking in LB films) is identical in both LB films and crystals. Then, the emphasis is placed on bilayer packing arrangement in the film plane. From the viewpoint of the lateral packing of alkyl chains, the subcell type of alkyl chains which forms the orthorhombic one is O type [29]. Taking into account of the space filling of the alkyl chain and assuming the O[±3,0] subcell structure, the cell dimensions are calculated to be  $a=10.62 \text{ \AA}$  and  $b=4.96 \text{ \AA}$  which reproduce

well the observed dimension of a-b plane. Under the substantial coincidence of inclination angle of alkyl chain of LB films and crystals with the result of FT-IR on LB films [21], molecular assembly of in-plane structure was proposed. Subsequently, a full unit cell structural model including bilayer and occupation of triiodide has been reported as shown in Fig. 5 [24], which exhibits a possible model of the molecular organization of the observed orthorhombic cell. In this model, the interdigitation between upper and lower layer of EDT-TTFS<sub>2</sub> parts takes in place the bilayered Y-type structure, which leads to the appearance of shorter intermolecular distance between adjacent EDT-TTF parts and brings about an enhancement of overlapping integral along the b axis. It may be worthwhile to note that the presently proposed herringbone packing of EDT-TTF skeleton head parts resembles the crystal structure of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> which is one of the typical packing structure for ET molecules [30].

The dc electrical conductivity along the b axis is 1.1 S/cm (T=300K). It is in good agreement with 1.0 S/cm in LB films. In single crystal, both dc and microwave conductivity under 50 GHz as a function of temperature exhibit semiconducting behavior below room temperature [24,31], which confirms that the observed semiconducting characteristics in LB films shows the intrinsic properties of cation-radical salt [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub>. Thus, the obtained result suggests that the LB films is not a semiconductor originated from the existence of possible "grain boundaries" but an intrinsic semiconductor. Metal-Insulator transition was observed at 310 K as shown in Fig. 6, which

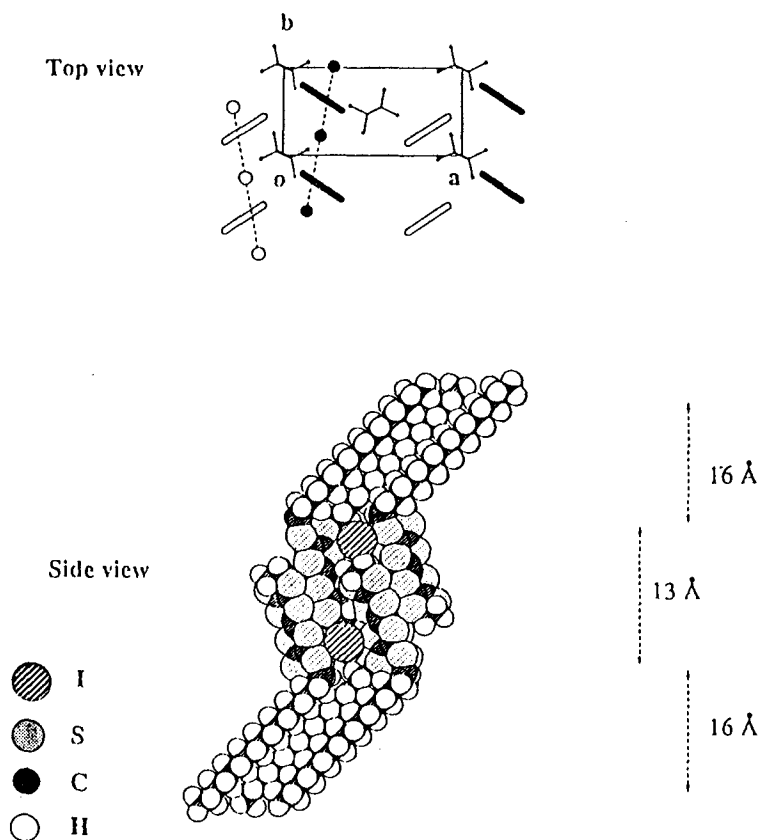


Fig. 5 Structural model proposed based on X-ray diffraction and XANES study.

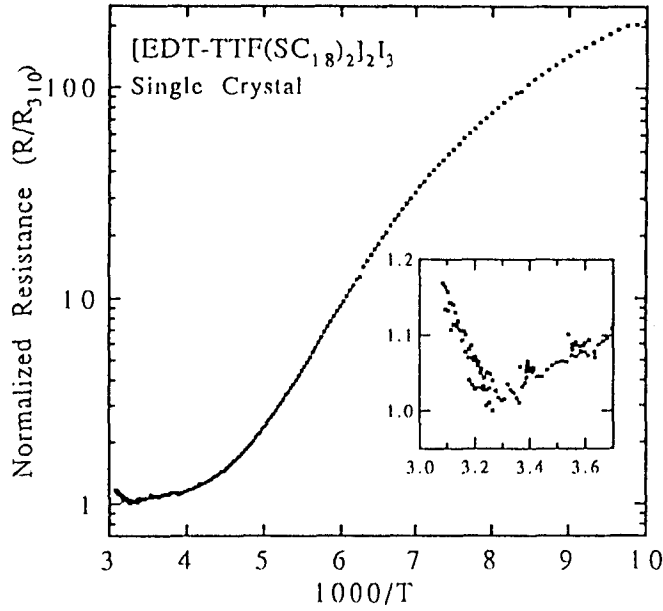


Fig. 6 Temperature dependence of the DC electrical resistance of single crystal of  $[\text{EDT-TTF}(\text{SC}_{18})_2]_2\text{I}_3$ . It clearly exhibits a sign of the onset of a metal-semiconductor transition at 310 K.

suggests the onset of delocalization of molecular-orbital holes of the  $\text{EDT-TTF}(\text{SC}_{18})_2$  above 310 K in the present material. No evidence of the structural phase transition has been given by X-ray diffraction.

Figure 7 shows the absorbance spectra of crystals and LB films in  $800$  to  $6000\text{ cm}^{-1}$  range. As assigned in ref. 21, broad electronic absorption band around  $2200\text{ cm}^{-1}$  and asymmetric resonance peak around  $1230\text{ cm}^{-1}$  are originated from charge-transfer and vibronic excitation based on e-mv coupling, respectively. The former excitation corresponds to dimer charge oscillations and is characteristic of the existence of single charged dimer state. The anti-resonance dip at  $1450\text{ cm}^{-1}$  between the former and latter peaks is observed together with  $\text{CH}_2$  bending absorption peak. There, in the presence of some symmetry breaking, the e-mv interactions induce oscillations of the conduction electron density along the direction of conducting axis at frequencies close to those of the unperturbed totally symmetric intramolecular modes [32]. On the other hand, the charge-transfer excitation energy ( $\hbar\omega_{\text{CT}}$ ) is attributed to the excitation from the bonding state to anti-bonding state in zero-order approximation (see Fig. 2(a)). The dielectric function along the direction joining the molecular entities in the dimer, in the presence of the e-mv coupling, may be written for the assembly of isolated dimers in the following way[7,32]:

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \frac{f_0}{\omega_{\text{CT}}^2(1 - D(\omega)) - \omega^2 - i\omega\Gamma}$$

with

$$f_0 = 2\omega_{\text{CT}} \frac{e^2 d^2}{4} |\langle \beta | n_1 - n_2 | 0 \rangle|^2, \quad n_i = \sum_{\sigma} a_{i\sigma}^{\dagger} a_{i\sigma} \quad \text{and} \quad D(\omega) = \sum_{\alpha} \frac{\lambda_{\alpha} \omega_{\alpha}^2}{\omega_{\alpha}^2 - \omega^2 - i\omega\gamma_{\alpha}},$$

where  $d$  is the intermolecular spacing,  $n_i$  is the electron number operator for molecule  $i=1,2$ .  $D(\omega)$  is the propagator which presents the  $\alpha$  vibronic modes defined by bare frequency  $\omega_\alpha$  and damping constant  $\gamma_\alpha$ . It couples linearly to the electrons with the  $e$ - $m\nu$  coupling constant  $\lambda_\alpha$ . Figure 5 exhibits the result of the model calculation with  $\omega_{CT} = 2t = 1500 \text{ cm}^{-1} = 0.18 \text{ eV}$ ,  $\omega_\alpha = 1480 \text{ cm}^{-1}$ ,  $\lambda_\alpha=0.2$  and  $\Gamma=2000 \text{ cm}^{-1}$ . On the vibronic feature, two central C=C stretching  $a_g$  vibrations locate around  $1400\text{-}1500 \text{ cm}^{-1}$  in ET family molecules [33]. Then it is natural to conclude that this vibration is strongly coupled to electrons. As shown in Fig. 2 a qualitative description of the electronic states of such narrow-band conduction materials gives a variety of the conducting properties. For example, the half-filled upper band is narrow in the case of poor interdimer overlap, the dc conductivity is lower. On the other hand, supposing a slight dimerization, half-filled conduction band has a larger width, hence we may expect higher conductivity. In the strongly dimerized stacks, within the atomic limit one can expect simply two excitations  $2t$  and  $2t'$ . If there exists strongly dimerized stacks it is probable to observe two CT bands around "A" band region associated with the intradimer and interdimer charge excitations as  $(\text{DIMET})_2\text{SbF}_6$  [34].

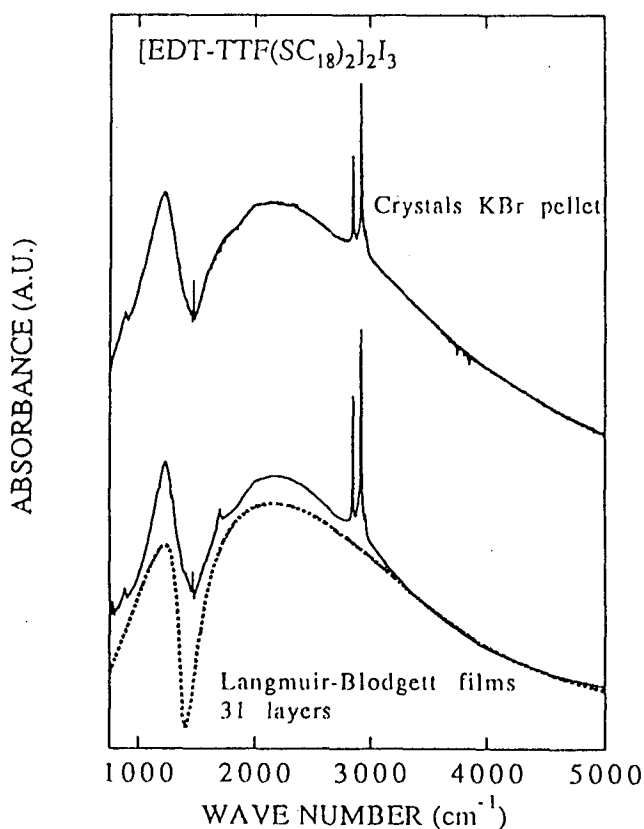


Fig. 7 Infrared absorbance spectra of crystals and LB films of  $[\text{EDT-TTF}(\text{SC}_{18})_2]_2\text{I}_3$ . The broken curve exhibits the calculated absorbance on the basis of the microscopic theory.

As shown in Fig. 7, single broad band CT excitation was observed in the present single crystals and LB films. The charge-transfer excitation energy,  $\omega_{CT}$  is almost identical in both crystal and LB films. These results suggest that the electronic state in crystals is close enough to that in LB films. Its excitation energy value suggests the existence of relatively narrow band width associated probable slightly dimerized stack. The composition and the precise origin of the broad band CT absorption cannot be clarified in the present stage. However, the success of larger single crystals would conduct to the study of the infrared absorption under the polarization configurations.

## 7. Concluding Remarks

There exist two subjects to improve in the basic research of conducting Langmuir-Blodgett (LB) films based on TTF derivative with long alkyl chains. Firstly, it is essential to achieve the knowledge of packing structure of molecular assembly in the film plane, since the crystals of ET salts are composed of 2D arrangement of dimerized molecular units with various polymorphisms and the donor molecular arrangement in the film plane may be different from that in the case of crystals without long alkyl chains. Secondly, we must deduce not only the inherent structural properties as described above but also intrinsic electronic properties to characterize the present LB films. The difficulties to realize both of them come from the existence of many small regions with differing orientation in the film plane. To overcome such difficulties we emphasize a strategy in which one studies comparatively the single crystal and the LB films which have the identical molecular organization. A series of studies on a stable conducting LB films of [EDT-TTF(SC<sub>18</sub>)<sub>2</sub>]<sub>2</sub>I<sub>3</sub> and its single crystal was introduced. The success of the growth of single crystals leads to a proposal of possible 3D model of molecular organization and clarification of the electronic states responsible for the conductivity. From presently proposed 3D model, 2D S-S network seems to be the key to achieve highly conducting LB films. Comparative FT-IR study shows that the electronic system is characterized by the dimerized stack with narrow bandwidth. Therefore, it is stressed that the increase of the interdimer interaction  $t'$  is necessary to realize higher conductivity in the present system. A series of comparative studies on LB films and crystals give us fruitful and intrinsic information about structural and electronic properties.

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## あとがき

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