

Structural Characterization of Mixed-Stack Charge Transfer Films of 2-Octadecyl-7,7,8,8-tetracyanoquinodimethane and 5,10-Dimethyl-5,10-dihydrophenazine Prepared by the Langmuir–Blodgett Technique and Donor Doping. 1. Molecular Orientation and Structure Investigated by Ultraviolet–Visible–Near-Infrared and Infrared Spectroscopies and X-ray Diffraction

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Molecular orientation and structure in mixed-stack charge transfer (CT) films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) doped by 5,10-dimethyl-5,10-dihydrophenazine ((Me)₂P) have been investigated by using ultraviolet–visible–near-infrared (UV–vis–NIR) and infrared (IR) spectroscopies and X-ray diffraction. The degree of charge transfer (ρ) was determined to be 0.5 by a shift of a b_{1u} C≡N stretching band of the TCNQ chromophore, suggesting that the complex is close to the neutral–ionic boundary. An X-ray diffraction pattern indicates that the CT films consist of a highly ordered multilayered structure in which donor ((Me)₂P) and acceptor (octadecyl-TCNQ) molecules are periodically arranged. The d value was calculated to be 3.3 nm, implying that each layer of the CT films comprises bimolecular layers. Comparison of IR intensities of b_{1u} , b_{2u} , and a_g C≡N stretching bands of the acceptor (A) and a totally symmetric band at 1255 cm^{−1} of the donor (D) between the transmission and reflectance absorption (RA) IR spectra indicates that the chromophores of D and A are almost perpendicular to the substrate surface with their long molecular axes being nearly parallel to the surface normal in the one-layer mixed-stack CT films. The hydrocarbon chain of octadecyl-TCNQ was evaluated to lie on the substrate. In the multilayer CT films the D and A chromophoric planes seem to be slightly tilted with respect to the substrate surface.

Introduction

Organic donor–acceptor charge transfer (CT) complexes have been recognized to be of particular importance from the standpoint of material research since the discovery that the segregated-stack CT complexes show metal electrical conductivity and even superconductivity.¹ Interest in the mixed-stack CT complexes, forming another class of donor–acceptor CT complexes, was awakened by a neutral-to-ionic phase transition induced by pressure or temperature.^{2–4} The mixed-stack CT complexes have been studied extensively because they show a variety of physical properties, such as nonlinear electrical and optical properties, and an anomalous dielectric response.^{2–21} The mixed-stack CT complexes, with the CT transition moments along the one-dimensional columns of donor (D) and acceptor (A) molecules, are further divided into quasi-neutral (N) and quasi-ionic (I) states by the magnitude of a partial electron transfer (ρ) from the D to A molecules. When ρ is less than or greater than the value of the neutral–ionic (N–I) boundary, a CT complex is in the quasi-neutral or quasi-ionic state, respectively.^{3,12,17}

The mechanism of the N–I phase transition phenomenon in the mixed-stack CT complexes, as well as the nonlinear electrical conduction and anomalous dielectric response, has not been fully understood, although a few models have been

proposed to explain them.^{5,10–13,15} One of the major difficulties comes from the fact that the attractive and repulsive Coulomb interactions between the D and A moieties become much complicated in a three-dimensional CT complex crystal.⁵ The thermally-induced N–I phase transition does not occur at a critical temperature but takes place in a certain temperature range.⁵

An effective method to overcome this difficulty is to prepare a two-dimensional mixed-stack CT complex film because of the simplified Coulomb interactions between D and A. It can be expected that the N–I phase transition takes place discontinuously at a certain critical temperature (first order).⁵ Furthermore, the nonlinear electrical conduction would be improved in the two-dimensional mixed-stack CT complexes. The authors have been employing the Langmuir–Blodgett (LB) and donor doping techniques to prepare two-dimensional mixed-stack CT films.^{21–26} In our previous studies we investigated the structure, morphology, and function of the mixed-stack CT films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) doped with 3,3',5,5'-tetramethylbenzidine (TMB) in a liquid phase.^{21–23} It was found that the nonlinear electrical conduction was successfully detected but the N–I phase transition did not take place at low temperature.^{21–23} Therefore, selecting a more suitable donor to dope the LB films of octadecyl-TCNQ is necessary for improving the CT film crystallinity and making the ρ value locate closer to the N–I phase boundary. In this experiment, 5,10-dimethyl-5,10-dihydrophenazine ((Me)₂P) has been selected as a donor for doping the LB films of octadecyl-TCNQ.

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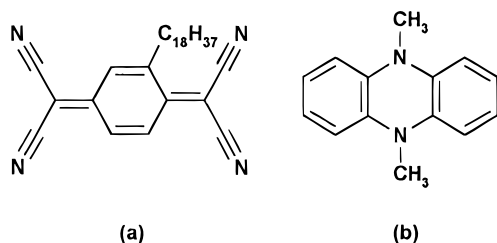


Figure 1. Structure of (a) 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) and (b) 5,10-dimethyl-5,10-dihydrophenazine ((Me)₂P).

The purpose of the present and two succeeding papers^{25,26} is to provide new insights into the structure, morphology, and thermal behavior of the mixed-stack CT films of octadecyl-TCNQ doped by (Me)₂P. The present paper discusses the molecular orientation and structure in the CT films on the basis of ultraviolet–visible–near-infrared (UV–vis–NIR), X-ray diffraction, and infrared (IR) transmission and reflection–absorption (RA) measurements. The second paper²⁵ delineates morphological features of the CT complex films investigated by atomic force microscopy (AFM). It also deals with annealing effects on the CT films studied by AFM and spectroscopic techniques. The third paper²⁶ investigates the thermal behavior of the CT films based upon temperature-dependent changes in UV–vis–NIR and IR spectra as well as in the X-ray diffraction pattern. Particular emphasis is on the comparison of the structure among the LB films of octadecyl-TCNQ and two kinds of CT films of octadecyl-TCNQ doped by TMB and (Me)₂P.

Experimental Section

Sample Preparation. Octadecyl-TCNQ (Figure 1a) was purchased from the Japanese Research Institute for Photosensitizing Dyes Co., Ltd. and used without further purification. A thin-layer chromatographic examination revealed that it did not contain any other colored components. (Me)₂P (Figure 1b) was synthesized from phenazine and used after repeated recrystallization from ethanol.²⁴

The Y-type LB films (except for the one-layer films) of octadecyl-TCNQ were fabricated by use of a Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance. A detailed procedure for the fabrication of LB films of octadecyl-TCNQ was described previously.²⁷ The transfer ratio was found to be nearly unity (0.95 ± 0.05) throughout the experiments. The built-up LB films of octadecyl-TCNQ were doped by (Me)₂P at 75 °C in a Pyrex tube without being vacuumed. It took several hours to ensure their complete charge conversion. The yellow color of the LB films of octadecyl-TCNQ changed to dark-blue after the doping.

Spectroscopy. UV–vis–NIR spectra of the mixed-stack CT films were measured with a Shimadzu UV–vis–NIR 3101 PC spectrophotometer. The low-angle X-ray diffraction measurement was carried out with a Rigaku Rad-rb system (Cu K α ₁, 40 kV, 50 mA). The IR spectra were obtained at a 4 cm^{−1} resolution with a Nicolet Magna-IR Model 550 spectrometer with a MCT detector. To yield the spectra of a high signal-to-noise ratio, 500–1000 interferograms were coadded.

Results

Ultraviolet–Visible–Near-Infrared Spectroscopy. Figure 2 shows a UV–vis–NIR absorption spectrum of a seven-layer film of the mixed-stack CT complex of octadecyl-TCNQ and (Me)₂P deposited on a CaF₂ plate. Of note is a broad absorption band centered at 1730 nm assigned to a CT excitation between octadecyl-TCNQ and (Me)₂P molecules.¹⁶ It arises from the charge transfer from the highest occupied molecular orbital of

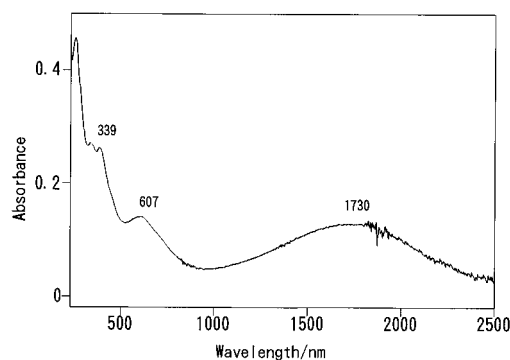


Figure 2. UV–vis–NIR absorption spectrum of a seven-layer film of the mixed-stack charge transfer complex of octadecyl-TCNQ doped by (Me)₂P.

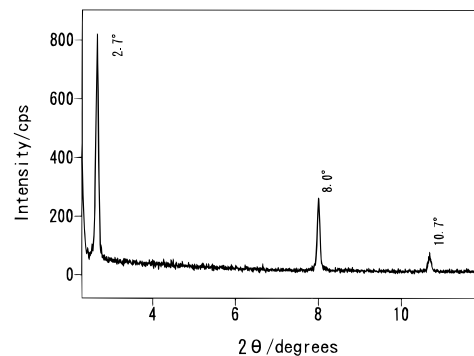


Figure 3. X-ray diffraction pattern of an 11-layer film of the mixed-stack charge transfer complex of octadecyl-TCNQ doped with (Me)₂P.

(Me)₂P to the lowest unoccupied molecular orbital of octadecyl-TCNQ. The observation of the band confirms that the CT complex film consisting of octadecyl-TCNQ and (Me)₂P is formed by the doping. Two bands at 339 and 607 nm can be attributed to localized electronic transitions of the two molecular moieties (the intramolecular excitations of octadecyl-TCNQ and (Me)₂P, respectively) based on the comparison with electronic absorption spectra of neutral and ionized TCNQ and (Me)₂P.

Judging from the fact that the mixed-stack CT complexes with TCNQ derivatives usually give the CT band in the NIR region while the segregated-stack ones show a broad CT band in the IR region,^{16,21–23,28} the CT film of octadecyl-TCNQ doped by (Me)₂P is considered to be in a mixed-stack form. The overlap of molecular orbitals between D and A is larger in the mixed-stack complexes than that in the segregated-stack ones so that the CT band appears in a higher energy region in the former than in the latter.²¹ In addition, it is noted that the UV–vis–NIR spectrum of the CT film of octadecyl-TCNQ and (Me)₂P is similar to that of the oriented polycrystalline film of TCNQ and (Me)₂P, which takes a mixed-stack type.¹⁶ The slight difference in the CT excitation energy between the CT film of octadecyl-TCNQ and (Me)₂P (1730 nm) and the polycrystalline film of TCNQ and (Me)₂P (1818 nm) may be attributable to the differences in the electron affinity of acceptors and/or the molecular arrangement and orientation of D and A. The electron affinity of octadecyl-TCNQ (0.29 V vs SCE) is smaller than that of TCNQ (0.33 V vs SCE).²¹

X-ray Diffraction Pattern. Figure 3 shows the X-ray diffraction pattern of an 11-layer mixed-stack CT film of octadecyl-TCNQ doped with (Me)₂P prepared on a CaF₂ substrate. Peaks at $2\theta = 2.7^\circ$, 8.0° , and 10.7° are assigned to the first-, third-, and fourth-order diffractions. Since the structural requirements for observing several orders of X-ray diffractions are rather stringent, even a few interruptions in the layer structure may cause serious loss of phase coherence and

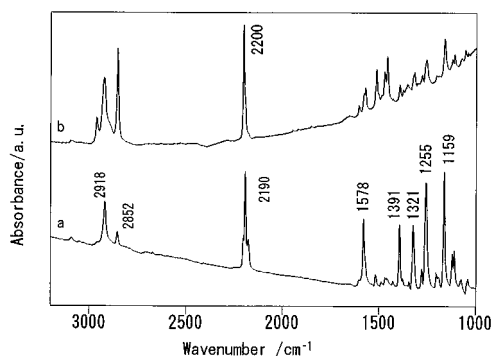


Figure 4. Infrared transmission (a) and reflection-absorption (b) spectra of one-layer films of the mixed-stack charge transfer complex of octadecyl-TCNQ doped with $(\text{Me})_2\text{P}$ prepared on CaF_2 and Au-evaporated glass substrates, respectively.

X-ray intensity. Therefore, in low-angle X-ray diffraction experiments, more than one diffraction peak are seldom observed for low-ordered LB films.²⁹ In the present experiment, the appearance of higher order diffraction peaks, sharpness of the peaks, alternatively strong and weak intensities for the odd- and even-number peaks, and strong intensity of the first-order diffraction reveal the highly ordered and oriented arrangement of D and A in the mixed-stack CT film. The ordered structure is further verified by AFM images of the mixed-stack CT films in the succeeding paper.²⁵ A layer spacing (the d distance) for the film was calculated to be 3.3 nm according to the Bragg equation. The molecular length of octadecyl-TCNQ is about 3.0 nm so that each layer in the mixed-stack CT film should consist of bimolecular layers of alternating stacks of D and A.³⁰ This supports the above conclusion that the CT complex film of octadecyl-TCNQ and $(\text{Me})_2\text{P}$ assumes a mixed-stack type.

Infrared Spectroscopy. Parts a and b of Figure 4 show the IR transmission and RA spectra of one-layer CT films of octadecyl-TCNQ and $(\text{Me})_2\text{P}$ deposited on CaF_2 and Au-evaporated glass substrates, respectively. The spectra are somewhat complicated because the films are composed of the two components, octadecyl-TCNQ and $(\text{Me})_2\text{P}$. IR bands of octadecyl-TCNQ and $(\text{Me})_2\text{P}$ in the CT films are shifted compared with those of the neutral species because the charge transfer takes place. The band frequencies of the CT films are in good agreement with those of a TCNQ- $(\text{Me})_2\text{P}$ polycrystalline film except for the bands due to the hydrocarbon chain.¹⁶ A band at 2190 cm^{-1} with two shoulders in the transmission spectrum originates from the $\text{C}\equiv\text{N}$ groups of the TCNQ chromophore (Figure 4a). Bands at 1159, 1255, and 1321 cm^{-1} are due to the totally symmetric vibrational modes of $(\text{Me})_2\text{P}$.¹⁶

Molecular Orientation. Evaluation of the molecular orientation of D and A molecules in the mixed-stack CT films is of importance, since it is directly related to the charge transfer process. One of the authors (Nichogi) estimated the orientation of the CT transition moment between D and A in the CT films of octadecyl-TCNQ and $(\text{Me})_2\text{P}$ by use of polarized electronic spectroscopy.²⁴ The result suggested that the CT stack is preferentially orientated along the substrate surface. In the present study, further insight and a more accurate evaluation of the molecular orientation are provided by comparing IR transmission and RA spectra of the CT films.

Parts a and b of Figure 5 present an enlargement of the $\text{C}\equiv\text{N}$ stretching band region of parts a and b of Figure 4, respectively. The three bands at 2200, 2190, and 2175 cm^{-1} , which have their transition moments in different directions, are assigned to b_{1u} (direction of the long molecular axis), a_g (vibronic feature, out-of-plane transitions along the CT stack), and b_{2u} (short molecular axis) modes, respectively.¹⁶ The a_g (2190 cm^{-1})

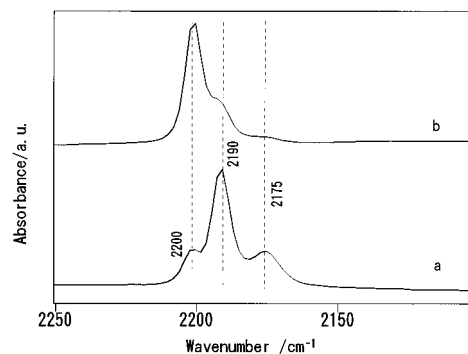


Figure 5. Parts a and b showing the enlargement of the $\text{C}\equiv\text{N}$ stretching band region of the spectra in parts a and b of Figure 4, respectively.

mode gives a strong absorption in the transmission spectrum, while it appears only as a shoulder in the RA spectrum. According to the selection rule of RA spectroscopy,^{31,32} it can be concluded that the transition moment of the a_g mode is preferentially parallel to the substrate surface. Therefore, it seems that the plane of TCNQ chromophore is almost perpendicular to the substrate. In contrast to the a_g mode, the b_{1u} mode appears weakly and strongly in the transmission and RA spectra, respectively, indicating that the long axis of the TCNQ chromophore is nearly perpendicular to the substrate. Accordingly, the short axis of TCNQ should be parallel to the surface. A comparison of the intensities of the b_{2u} mode between the transmission and RA spectra also suggests that the short axis lies on the substrate.

A similar analysis can be applied to the estimation of the orientation of $(\text{Me})_2\text{P}$. For instance, the band at 1255 cm^{-1} , which is assigned to a totally symmetric mode of $(\text{Me})_2\text{P}$, has a vibrational direction parallel to the CT transition moment.¹⁶ It absorbs strongly in the transmission spectrum and weakly in the RA one, indicating that the $(\text{Me})_2\text{P}$ plane is oriented nearly perpendicular to the substrate as in the case of the plane of octadecyl-TCNQ. Since the mixed-stack CT films require an alternating arrangement of D and A along the CT stack and a strong effect of charge transfer between D and A, the D and A should be packed in a face-to-face pattern.

Bands at 2918 and 2852 cm^{-1} are due to antisymmetric and symmetric CH_2 stretching modes of the hydrocarbon chain, which are often used to estimate its orientation.³³ Relations between the molecular orientation of the hydrocarbon chain and the intensities of the two CH_2 bands in the IR transmission and RA spectra were described in detail previously.³³ The integrated intensity ratio of the two bands (I_{2852}/I_{2918}) is a useful parameter for investigating the orientation of the hydrocarbon chain. The ratio of 0.59 is used as a standard indicator in this paper. It was calculated from an IR transmission spectrum of octadecyl-TCNQ in the solid state.³³ Both bands at 2918 and 2852 cm^{-1} , particularly the latter, show stronger intensities in the RA spectrum than in the transmission spectrum (Figure 4). It is also noted that the CH_2 symmetric stretching band is stronger than the antisymmetric one in the RA spectrum. The intensity ratios of the two bands are calculated to be 0.20 and 0.97 for the transmission and RA spectra, respectively, in the one-layer CT films. These data lead us to conclude that the molecular axis of the hydrocarbon chain is preferentially parallel to the substrate surface with the plane of the hydrocarbon chain nearly perpendicular to it.

Dependence of the Molecular Orientation on the Number of Layers. It is of essential importance to compare the molecular orientation in the one-layer mixed-stack CT film with that in the multilayer one. Parts a and b of Figure 6 compare IR transmission and RA spectra of the seven-layer mixed-stack

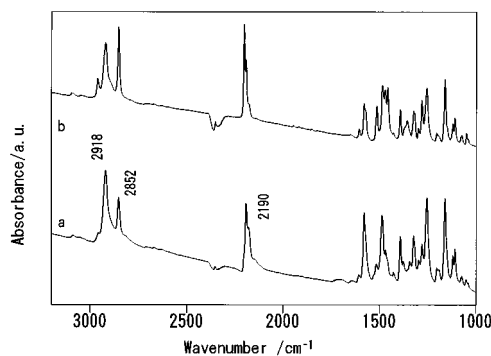


Figure 6. Infrared transmission (a) and reflection-absorption (b) spectra of seven-layer films of the mixed-stack charge transfer complex of octadecyl-TCNQ doped with (Me)₂P prepared on CaF₂ and Au-evaporated glass substrates, respectively.

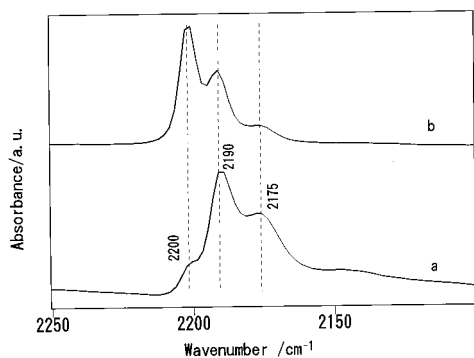


Figure 7. Parts a and b showing the enlargement of the C≡N stretching band region of the spectra in parts a and b of Figure 6, respectively.

CT films, respectively. The relative intensities of both the antisymmetric and symmetric CH₂ stretching bands at 2918 and 2852 cm⁻¹ in the transmission spectrum become stronger in the seven-layer CT film than in the one-layer CT film (Figures 4a and 6a). The values of the ratio I_{2852}/I_{2918} for the seven-layer CT films are 0.23 and 0.78 for the transmission and RA spectra, respectively. This indicates that the hydrocarbon chain is slightly tilted toward the substrate in the multilayer CT films. Enlargement of the C≡N stretching region of parts a and b of Figure 6 is shown in parts a and b of Figure 7, respectively. The relatively strong absorption can be found for the a_g mode in the RA spectrum, implying that the CT stacks become tilted a little in the multilayer CT films.

Degree of Charge Transfer. Determination of the degree of charge transfer (ρ) in the mixed-stack CT films is another major task in the present study because of the interest in the N-I phase transition phenomenon. IR spectroscopy offers a useful method for determining the ρ value. Two prerequisites must be fulfilled: (1) a detailed vibrational analysis for at least one molecular component (D or A) in its neutral and fully ionized states; (2) understanding how the vibrational spectra are influenced by the electron-molecular vibration (e-mv) interaction (vibronic interaction). The ρ value can be estimated from the vibrational frequencies not affected by the e-mv interaction.¹⁶

The b_{1u} stretching mode at 2200 cm⁻¹ is suitable for determining the ρ value because it shows the largest frequency shift in the mixed-stack CT films and is not perturbed by the e-mv interaction.¹⁶ The value of ρ was calculated to be 0.5 by a linear interpolation between the corresponding frequencies of the neutral and fully ionized species of octadecyl-TCNQ. (As a reference, neutral octadecyl-TCNQ and the fully charge-transferred octadecyl-TCNQ anion (K⁺-octadecyl-TCNQ⁻) powder were used. The peak positions of the C≡N stretching

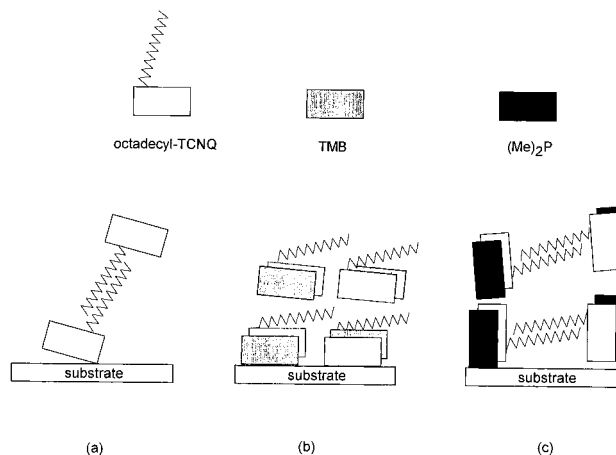


Figure 8. Schematic models for the molecular orientation and stacking pattern of D and A molecules: (a) the LB films of octadecyl-TCNQ; (b and c) the mixed-stack CT films of octadecyl-TCNQ doped by TMB and (Me)₂P, respectively.

band of octadecyl-TCNQ and octadecyl-TCNQ⁻ are 2222 and 2184 cm⁻¹, respectively.²¹ The result reveals the formation of the CT complex film where the partial charge transfer occurs. It is also noted that no band assignable to the neutral species is detected in the spectra. This suggests that CT formation proceeds completely in the film.

Discussion

Dependence of the Structure and Molecular Orientation of Mixed-Stack CT Films on the Different Donors.

It has been reported that a number of mixed-stack CT complexes exhibit the N-I phase transition phenomenon.³ Two kinds of donors have been selected by the authors to prepare the low-dimensional mixed-stack CT films. One is TMB; the structure, molecular orientation, thermal behavior, and morphology of the CT films consisting of octadecyl-TCNQ and TMB were reported previously.²¹⁻²³ Another donor is (Me)₂P. It is of interest to compare the structural differences among LB films of octadecyl-TCNQ and the two kinds of mixed-stack CT films. In light of the above and previously reported results,^{21-23,34,35} schematic models for the molecular orientation and stacking pattern of D and/or A molecules in the three kinds of films are drawn in Figure 8.

The previous X-ray diffraction, IR, and AFM studies on the LB films of octadecyl-TCNQ revealed that the films consist of the well-ordered layered microcrystal domains with a layer thickness of 3.6 nm.³⁴ Each layer actually contains bimolecular layers of octadecyl-TCNQ with the hydrocarbon chains penetrating into each other to some extent. The TCNQ chromophore is oriented nearly perpendicular to the substrate surface with the long axis being neither parallel nor perpendicular to the substrate.³⁵ The hydrocarbon chain is tilted with respect to the surface normal (Figure 8a).

Doping of TMB in the liquid phase into the LB films of octadecyl-TCNQ induces marked changes in both the morphology and molecular orientation and structure.²³ Upon doping, the two-dimensional layered domains in the LB films of octadecyl-TCNQ are changed into the one-dimensional needle-like microcrystals in the mixed-stack CT films of octadecyl-TCNQ and TMB. The one-dimensional microcrystals are piled up in the films and give no X-ray diffraction peak, indicating that no layered structure exists. Both the D and A chromophoric planes forming the CT stacks inside the microcrystals are nearly perpendicular to the substrate with the long axes lying on the substrate. The hydrocarbon chains of octadecyl-TCNQ are nearly parallel to the substrate surface (Figure 8b).³⁶

In the case of the mixed-stack CT films of octadecyl-TCNQ and (Me)₂P, the X-ray diffraction measurement indicates that the two-dimensional layered structure of octadecyl-TCNQ molecules is kept even after the doping with (Me)₂P. It is considered that (Me)₂P molecules are incorporated into the LB film of octadecyl-TCNQ during the doping process in the vapor phase, resulting in the formation of CT stacks of D and A in a face-to-face pattern. However, the layer distance (*d*) changes from 3.6 to 3.3 nm, revealing that reorientation takes place during the doping, although the bilayer structure remains. The D and A chromophoric planes are almost perpendicular to the substrate surface as in the case of the mixed-stack CT film of octadecyl-TCNQ and TMB, but the long axes become nearly perpendicular to the surface (Figure 8c). The differences in the structure, molecular orientation, and morphology between the two kinds of CT films may be attributed to the different ionization potential energies of the two donors as well as the doping processes in the different phases.

Conclusions

The two-dimensional mixed-stack CT complex films have been successfully prepared by doping (Me)₂P into the LB films of octadecyl-TCNQ in the vapor phase. The X-ray diffraction pattern verifies that the films have a well-ordered layered structure in which the D and A are highly oriented. A *d* value of 3.3 nm indicates that each layer in the CT films contains bimolecular layers of alternately stacked D and A. The CT degree (ρ) is determined to be 0.5 by the frequency of the ν_{1u} C≡N stretching mode of the TCNQ chromophore. A comparison of the IR transmission and RA spectra of the one-layer mixed-stack CT films delineates the molecular orientation in the films. Both chromophoric planes of D and A and their long molecular axes are preferentially perpendicular to the substrate surface, while the hydrocarbon chains are parallel to it. In the case of the multilayer CT films, the D and A planes are found to be slightly tilted with respect to the surface normal and the hydrocarbon chains are no longer lying on the surface but tilted a little from it. The dependence of the molecular orientation on the number of layers may be attributed to the direct interaction between the first layer and the substrate in the one-layer CT films and to the longitudinal interactions between the sheets of two-dimensional microcrystals in the multilayer CT films.

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