

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. 2. Morphology and Annealing Effects Investigated by Atomic Force Microscopy and Ultraviolet–Visible–Near-Infrared, and Infrared Spectroscopies

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Morphology and annealing effects of mixed-stack charge transfer (CT) complex 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 atomic force microscopy (AFM) and ultraviolet–visible–near-infrared (UV–vis–NIR) and infrared (IR) spectroscopies. The AFM measurements scanned at room temperature show that the 11-layer CT film consists of layered platelet microcrystal domains with a layer distance of 3.3 nm, which is in good agreement with the distance obtained by an X-ray diffraction experiment. It is likely that each layer in the CT film has a bimolecular layer structure as in the case of Langmuir–Blodgett (LB) films of neutral octadecyl-TCNQ. A two-dimensionally resolved molecular arrangement of octadecyl-TCNQ and (Me)₂P is observed inside the domains by a high-resolution AFM image. The inter- and intrastack periods, which are across and along the CT stacks, are 0.96 and 0.83 nm, respectively, with an intersect angle of 59°. A cyclic thermal treatment on the CT film up to 70 °C, which is below the dedope temperature, does not change its morphology, i.e., the molecular arrangement and layered structure in the microcrystal domains are nearly unchanged. However, when the CT film is heated above the dedope temperature, the layered structure vanishes completely and the molecular arrangement becomes similar to that in the LB film of neutral octadecyl-TCNQ. The UV–vis–NIR and IR spectra of the annealed CT films confirm the results obtained by AFM.

Introduction

The preceding paper reported the structure and molecular orientation 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) studied by ultraviolet–visible–near-infrared (UV–vis–NIR) and infrared (IR) spectroscopies and X-ray diffraction.¹ The X-ray diffraction measurement revealed that the CT films consist of a highly ordered multilayered structure with a well-oriented arrangement of donor (D) and acceptor (A) molecules. It was suggested by the IR transmission and reflectance absorption spectra that the D and A chromophoric planes are preferentially perpendicular to the substrate surface with their long axes being almost normal to the surface. The degree of charge transfer (ρ) in the films was estimated to be 0.5 by the ν_{1u} C≡N stretching mode of the TCNQ chromophore. It can be expected that the neutral (N)–ionic (I) phase transition likely occurs in this kind of mixed-stack CT film with the two-dimensional feature.

As the second part of a comprehensive structural characterization for the mixed-stack CT films of octadecyl-TCNQ doped by (Me)₂P, this paper deals with atomic force microscopic (AFM) and UV–vis–NIR and IR spectroscopic studies on their

morphology and annealing effects. The following points will be discussed with particular emphasis: (1) morphological characteristics of the CT complex films studied by the AFM technique; (2) the dependence of morphology on the number of layers; (3) the annealing effects and thermal stability of the CT films explored from the morphological and structural aspects.

As for the N–I phase transition of mixed-stack CT complexes, it is believed that the distance between D and A molecules is shortened by lowering the temperature or applying pressure.^{10,11,15} Thus, the CT complexes surmount the neutral–ionic boundary and transit from the neutral phase to the ionic one because of the enhanced electrostatic Coulomb interaction between D and A. It makes one pair of D and A form a dimer according to the dimeric model.¹¹ Therefore, direct observation of the morphology and molecular arrangement of the mixed-stack CT films by AFM plays an important role in exploring the mechanism of the N–I phase transition. On the other hand, the study on the annealing effect of the mixed-stack CT films aids us in investigating the thermal stability and in revealing the thermally induced decomposition nature of the CT complex.

Experimental Section

The detailed procedure for the preparation of mixed-stack CT films of octadecyl-TCNQ and (Me)₂P was described in preceding papers.^{1,2} In the AFM experiments, a NanoScopeIII (Digital Instruments) was used to investigate the morphology of the CT complex films that had been built up onto silicon substrates (*n*-Si(100) surface) in order to achieve a high resolution. We used a silicon nitride tip on a cantilever with a

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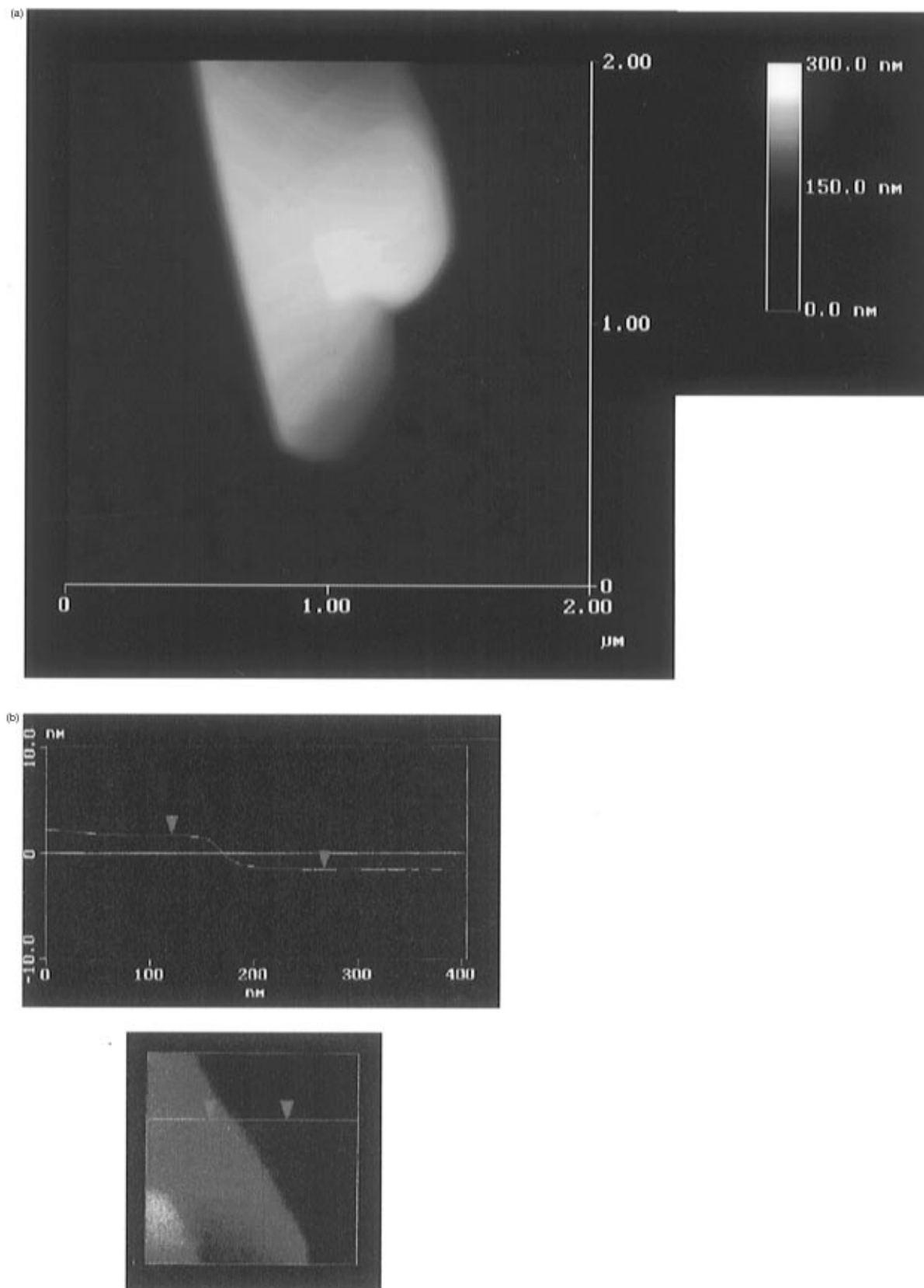


Figure 1. (a) AFM image of an 11-layer mixed-stack CT film of octadecyl-TCNQ doped by $(\text{Me})_2\text{P}$ scanned at room temperature with a scan area of $2 \times 2 \mu\text{m}^2$. (b) AFM cross-sectional profile scanned across the microcrystal domain shown in part a. The step of 3.3 nm is attributed to the layered structure inside the domain.

spring constant of 0.06 N/m. Only tips giving atomic resolution on mica were selected. The instrumentation adopted for measuring the UV-vis-NIR and IR spectra was the same as that described in the preceding paper.¹

Cyclic thermal treatment experiments of the CT complex films were carried out as follows. The films were heated to a

certain temperature by an increment of $1^\circ\text{C}/\text{min}$ and then left as they were to cool to room temperature.

Results

Atomic Force Microscopy. *Morphology of Mixed-Stack CT Films at Room Temperature.* Figure 1a shows the AFM image

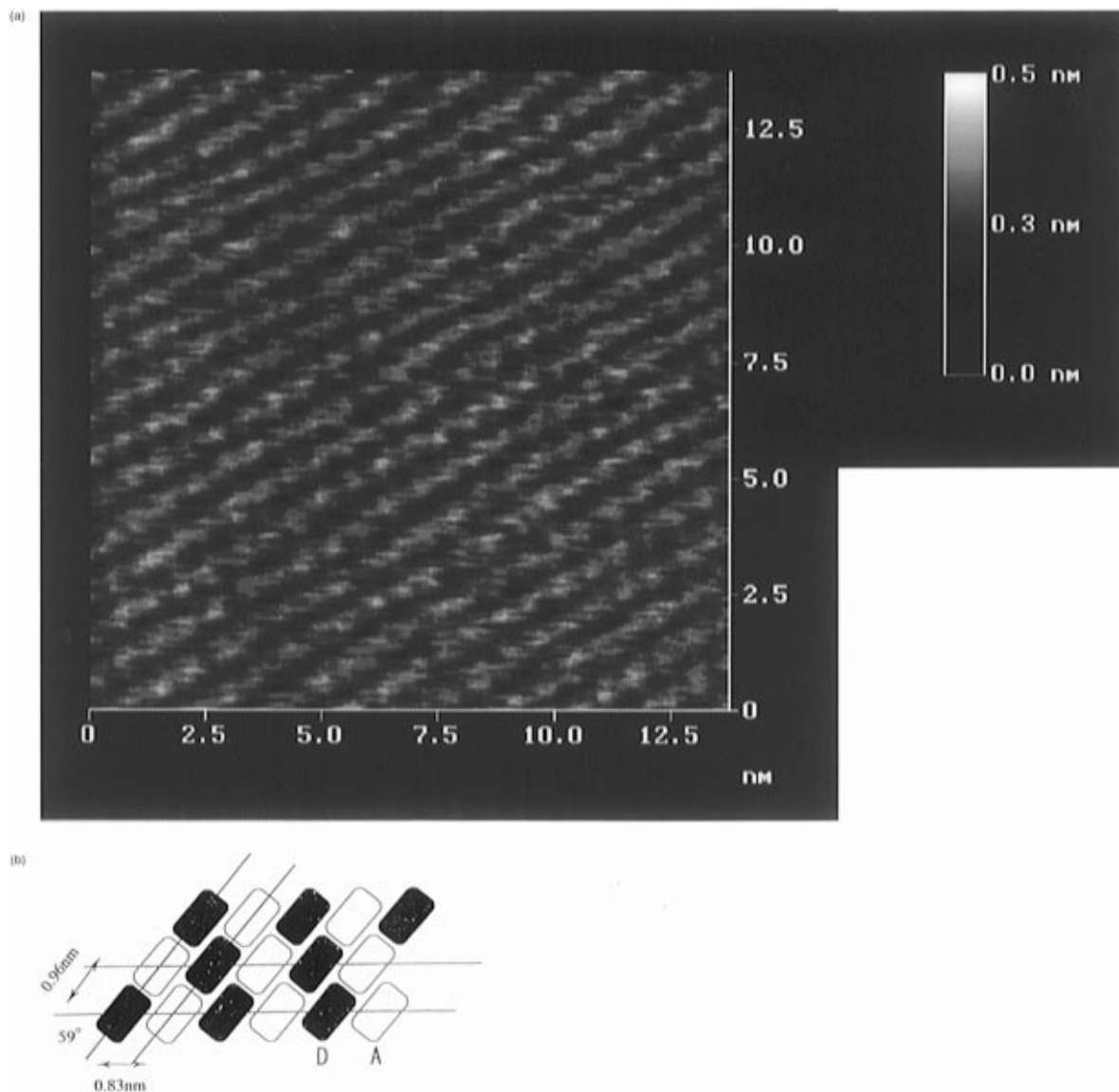


Figure 2. (a) A high-resolution AFM image scanned on the surface of the platelet microcrystal domain in Figure 1a. (b) Molecular arrangement of acceptor (octadecyl-TCNQ) and donor ((Me)₂P) inside the platelet microcrystal domains of the CT films.

of an 11-layer mixed-stack CT film of octadecyl-TCNQ and (Me)₂P scanned at room temperature with a scan area of $2 \times 2 \mu\text{m}^2$. It can be seen from the image that the CT film consists of platelet microcrystal domains of a few micrometers in size in which a multilayered structure with many steps is observed. The layered structure can be explored by an analysis of the cross-sectional profile shown in Figure 1b. It reveals that the layered platelet microcrystal domains have a step of 3.3 nm thickness. This is in good agreement with the d value measured by the X-ray diffraction method.¹ Therefore, it seems that the X-ray diffraction peaks originate from the multilayered structure inside the domains. Each layer in the domains apparently consists of bimolecular layers of octadecyl-TCNQ and (Me)₂P because the layer thickness of 3.3 nm is larger than the molecular length (3.0 nm) of octadecyl-TCNQ.³ The bimolecular layer structure also supports that the CT film is in a mixed-stack pattern.

Figure 2a depicts a highly resolved AFM image ($13 \times 13 \text{ nm}^2$) scanned on the surface of the platelet microcrystal domain in the 11-layer mixed-stack CT film (Figure 1a). A highly ordered periodic molecular arrangement of D and A can be observed in the image. The parallel ridges are considered to be due to the stacks of D and A in the mixed-stack CT film. The interstack period across the parallel ridges was calculated to be 0.96 nm, while the intrastack period along the CT stacks

was found to be 0.83 nm. The angle between the inter- and intrastack axes was measured to be 59° . These three parameters of molecular arrangement are described as (0.96 nm \times 0.83 nm, angle 59°) hereafter. Figure 2b illustrates a schematic model for the molecular arrangement of D and A in the CT film. The above AFM images provide morphological evidence for the result obtained by the X-ray measurement, i.e., the mixed-stack CT films have the well-ordered layered structure in which the highly crystalline structure exists.¹ A similar morphological study was carried out by Nichogi et al.² for the mixed-stack CT complex films of octadecyl-TCNQ doped by (Me)₂P. They deposited the LB films of octadecyl-TCNQ onto mica instead of silicon and doped them under vacuum. The present result is in good agreement with their's, indicating that the morphological features of CT films exhibit no significant substrate dependence and are not affected by oxygen in the air during the doping process.

In contrast to the 11-layer CT film, a 1-layer CT film has rather small microcrystal domains of several tens of nanometers as shown in Figure 3. It seems that the first layer interacts strongly with the substrate, preventing the formation of large microcrystal domains during the doping process. It may be concluded that the first layer and upper layers show significant differences not only in the molecular orientation but also in the morphology. We reported in the first paper that the D and A

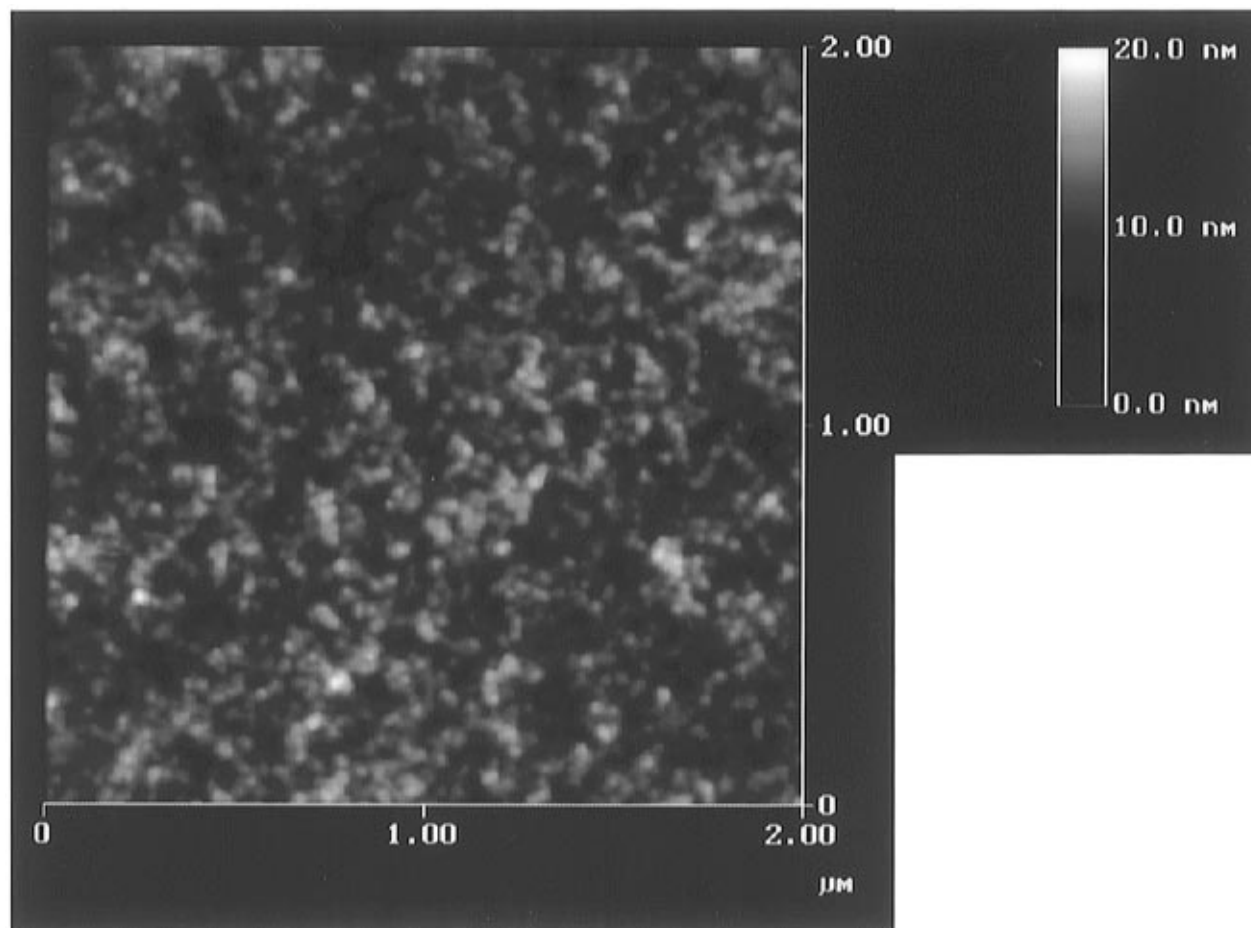


Figure 3. AFM image of a 1-layer mixed-stack CT film of octadecyl-TCNQ doped by (Me)₂P scanned at room temperature with a scan area of $2 \times 2 \mu\text{m}^2$.

chromophoric planes are almost perpendicular to the substrate surface in the 1-layer CT films but they are slightly tilted from the surface normal in the multilayer CT films.¹

Annealing Effects on Morphology and Structure of Mixed-Stack CT Films. Thermal behavior of mixed-stack CT films of octadecyl-TCNQ doped by (Me)₂P was investigated by UV-vis-NIR and IR spectroscopies and X-ray diffraction (see the succeeding paper). According to the study, the donor molecules ((Me)₂P) dedope from the mixed-stack CT films in the temperature range 80–90 °C.⁴ The annealing effects of the CT films were studied for the following two kinds of cyclic thermal treatments. The first one was that the CT films were heated to 70 °C, which is below the dedope temperature, and then were cooled to room temperature. In the second one the temperature of the films was elevated to 90 °C.

The 11-layer CT film after the thermal treatment up to 70 °C gives a morphological feature similar to that before the thermal treatment. The layered structure in the domains and the molecular arrangement (0.96 nm \times 0.83 nm, angle 59°) of D and A molecules are unchanged by the annealing up to 70 °C. These observations verify that the CT films are thermally stable if the temperature is kept below 70 °C. An analogous result can be obtained from an AFM image for the 1-layer CT film annealed from 70 °C.

The cyclic thermal treatment of the 11-layer CT film up to 90 °C brings about interesting morphological changes. Figure 4a shows an AFM image ($2 \times 2 \mu\text{m}^2$) of the 11-layer CT film after annealing from 90 °C. The annealed CT film still consists of platelet microcrystal domains, but the layered structure inside the domains disappears completely. This is supported by the vanishing of the X-ray diffraction peaks of the 11-layer CT film as will be shown in the succeeding paper.⁴ Furthermore, the

molecular arrangement is changed substantially after annealing over the dedope temperature. Figure 4b depicts a high-resolution AFM image scanned on the surface of the domain shown in Figure 4a. The two-dimensionally resolved molecular arrangement (0.96 nm \times 0.83 nm, angle 59°) inside the domain changes into a one-dimensionally resolved pattern with a period of 0.85 nm across the parallel ridges. The latter is almost identical with that of LB films of octadecyl-TCNQ.^{3,5} This morphological change indicates that (Me)₂P molecules dedope from the CT films, resulting in a restoration of octadecyl-TCNQ molecules from the CT state to the neutral one.

An AFM image of the 1-layer mixed-stack CT film annealed from 90 °C is shown in Figure 5. The annealed film is composed of small size microcrystal domains and some amorphous spots on them. The morphology of the small size microcrystal domains resembles that of the 1-layer CT film before heating, but the CT bands in the UV-vis-NIR and IR spectra of the annealed film disappear completely. This suggests that the annealed 1-layer CT film contains only the neutral octadecyl-TCNQ moiety. On the other hand, the amorphous spots may be formed during the dedoping process of (Me)₂P by thermal disturbance.

UV-Visible-NIR Spectra. Figure 6 shows the annealing effects on a UV-vis-NIR spectrum of the 11-layer CT complex film of octadecyl-TCNQ doped by (Me)₂P. Spectrum a was measured at room temperature before heating the film, while spectra b and c were obtained at room temperature after annealing from 70 and 90 °C, respectively.⁴ As discussed in the preceding paper,¹ a broad absorption band appearing at 1730 nm confirms the formation of the CT complex between octadecyl-TCNQ and (Me)₂P. The spectrum of the CT film annealed from 70 °C retains the original spectroscopic features

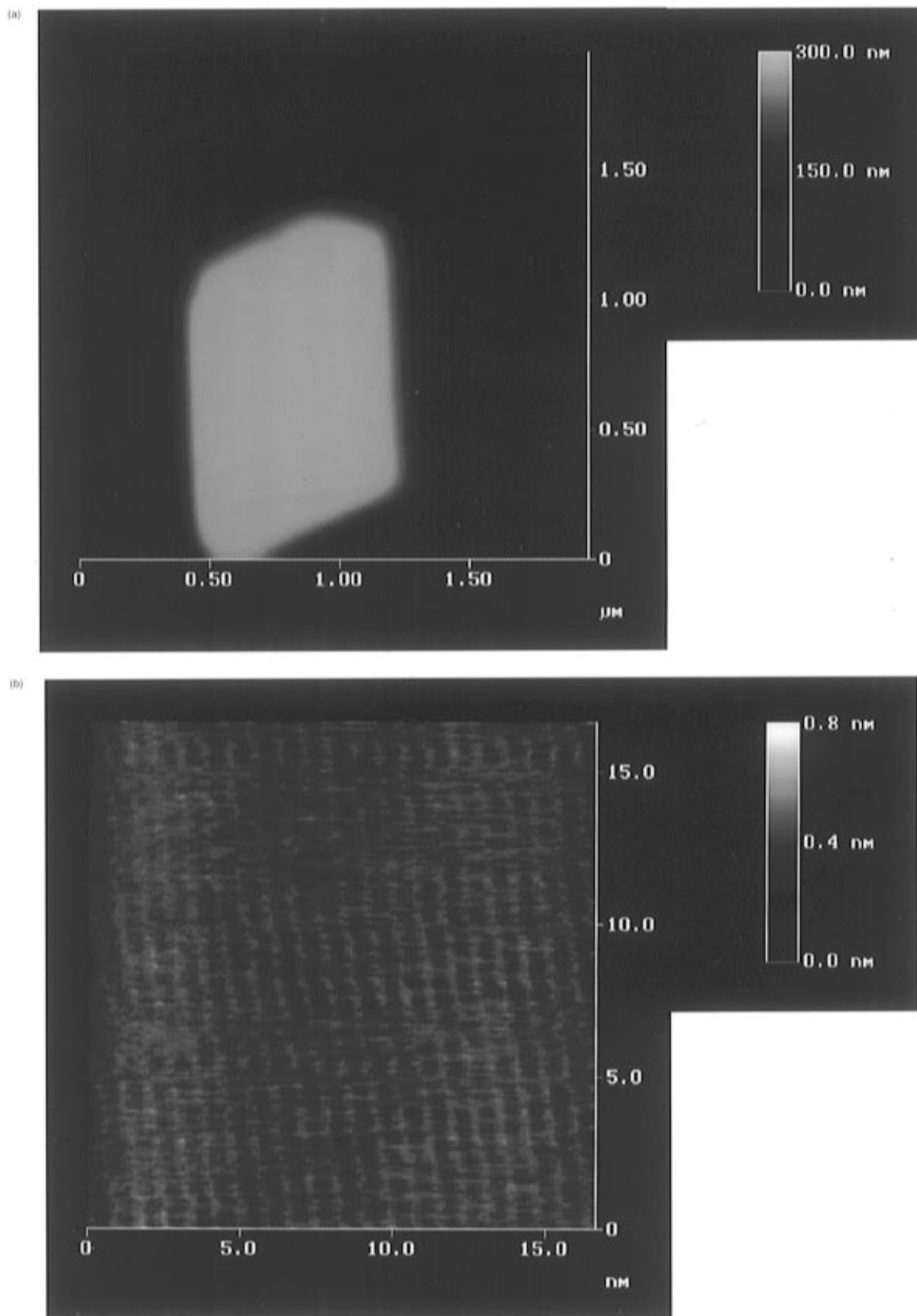


Figure 4. (a) AFM image of an 11-layer mixed-stack CT film of octadecyl-TCNQ doped by (Me)₂P annealed from 90 °C with a scan area of $2 \times 2 \mu\text{m}^2$. (b) A high-resolution AFM image scanned on the surface of the domain shown in part a.

of the CT complex film, although the band intensities decrease to some extent. This is consistent with the result of the AFM measurement described above. The UV-vis-NIR spectrum of the CT film annealed from 90 °C is very close to that of an annealed LB film of octadecyl-TCNQ.⁵ The characteristic CT band (1730 nm), along with the localized excitations of two moieties at 339 and 607 nm of D and A, respectively, vanishes, and instead, a new band at 360 nm appears that can be attributed

to a $\pi-\pi^*$ transition of the chromophore of octadecyl-TCNQ in a neutral state.⁶

IR Spectra. Figure 7a presents an IR transmission spectrum of the 11-layer CT complex film measured at room temperature, while parts b and c of Figure 7 show the spectra of the same film after cyclic thermal treatment up to 70 and 90 °C, respectively. Bands at 2917 and 2852 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the

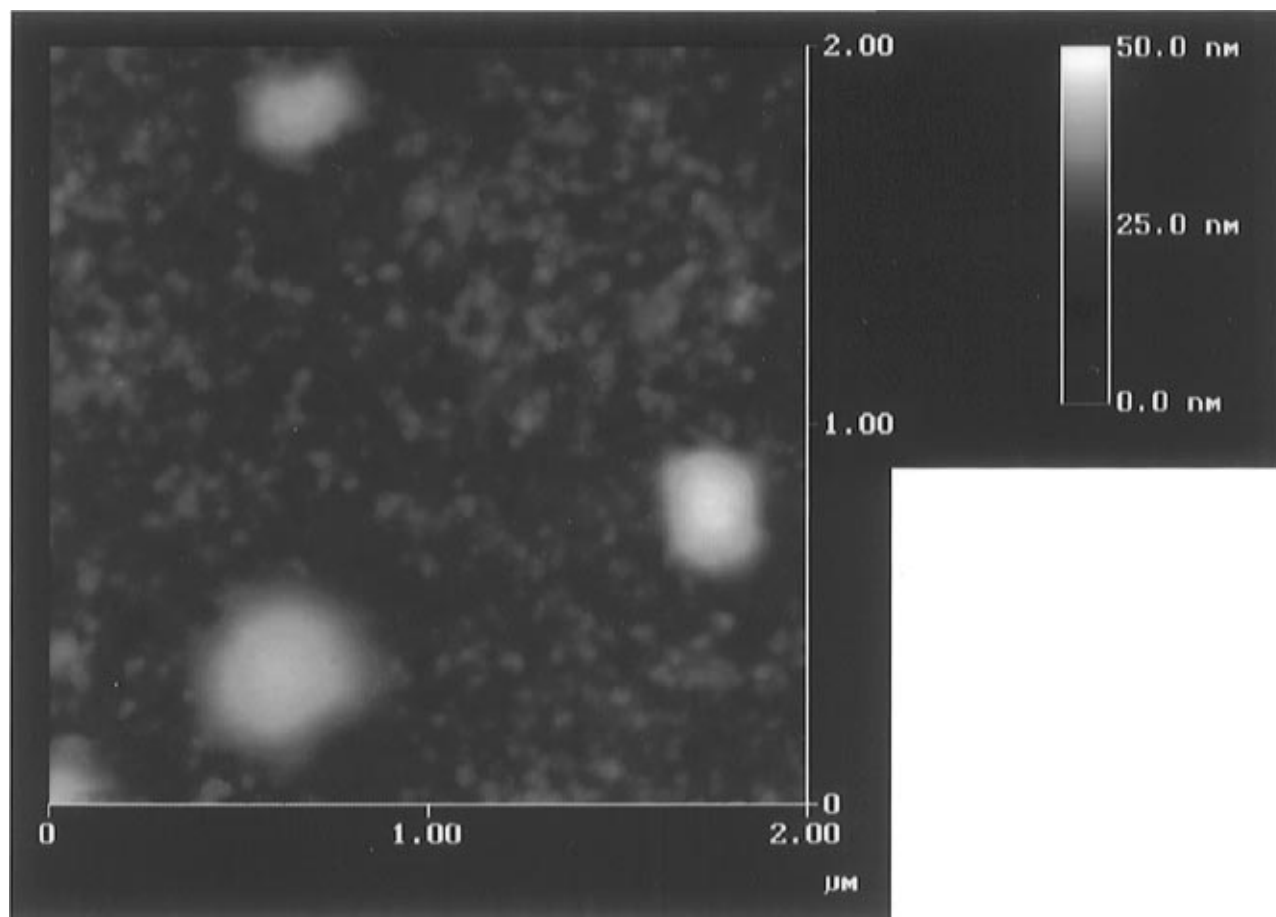


Figure 5. AFM image of a 1-layer CT film of octadecyl-TCNQ doped by $(\text{Me})_2\text{P}$ annealed from 90 °C with a scan area of $2 \times 2 \mu\text{m}^2$.

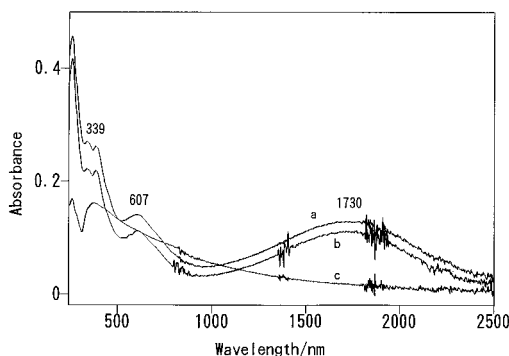


Figure 6. UV-vis-NIR absorption spectra of a 7-layer CT film of octadecyl-TCNQ doped by $(\text{Me})_2\text{P}$ measured at room temperature: (a) before the annealing; (b) after the annealing from 70 °C; (c) after the annealing from 90 °C.

hydrocarbon chain of octadecyl-TCNQ in the CT film, while a band at 2190 cm^{-1} is due to the a_g $\text{C}\equiv\text{N}$ stretching mode of the chromophoric part.¹ Note that the IR spectrum measured after annealing from 70 °C (spectrum b) is very close to the original one (spectrum a), suggesting that the molecular orientation and structure in the film change little by the cyclic thermal treatment up to 70 °C. In contrast, the spectrum of the CT film after annealing from 90 °C is markedly different from the original one; the $\text{C}\equiv\text{N}$ band shifts to 2220 cm^{-1} and the bands at 1578, 1390, and 1253 cm^{-1} due to the CT complex disappear. These are clear pieces of evidence for the dedope of $(\text{Me})_2\text{P}$ from the CT complex. It is also worthy of note that the intensity of the symmetric stretching band of hydrocarbon chains becomes stronger in the annealed CT film from 90 °C. This means that the hydrocarbon chains reorient from a nearly parallel configuration to a tilted one with respect to the substrate surface upon the annealing. The 1- and 3-layer CT films annealed from 70

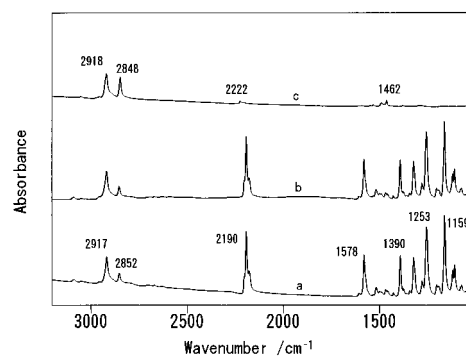


Figure 7. IR transmission spectra of a 7-layer CT film of octadecyl-TCNQ doped by $(\text{Me})_2\text{P}$ measured at room temperature: (a) before the annealing; (b) after the annealing from 70 °C; (c) after the annealing from 90 °C.

or 90 °C exhibit thermal behavior similar to that of the 11-layer CT film with the same treatment.

Discussion

Different Morphological Features of the Two Kinds of Mixed-Stack CT Complex Films. It is of interest to compare the morphological features among the mixed-stack CT films of octadecyl-TCNQ doped by different donors with different ionization potential energies, $(\text{Me})_2\text{P}$, and previously investigated TMB.⁷⁻⁹ It has been illustrated from studies of single crystals of mixed-stack CT complexes that the N-I phase transition phenomenon is closely related to the dimeric distortion of D and A in the CT stacks due to the electron-lattice interaction.¹⁰⁻¹³ For example, the major driving force for the N-I transition in the CT complex of TCNQ and TMB is thought to be the energy gain by the lattice dimerization.¹⁰ Therefore, the investigation

of the morphology and its variation in the mixed-stack CT films is of essential importance for exploring the mechanism of N–I transition phenomenon.

Doping of the two different donors into the LB film of octadecyl-TCNQ makes its morphology change into two different types. According to the previous morphological observation of the LB film of octadecyl-TCNQ by AFM,^{3,5} the film consists of layered platelet microcrystal domains with a step of 3.7 nm, indicating the bimolecular layer structure. Inside the domains a periodic structure of octadecyl-TCNQ molecules with a one-dimensionally resolved period of 0.85 nm can be observed. These were confirmed by the higher orders of diffraction in the low-angle X-ray diffraction measurement.³ When the LB films of octadecyl-TCNQ are doped by TMB, the two-dimensional platelet microcrystal domains change into the one-dimensional needle-like microcrystals formed by the CT stacks of D and A.⁸ In addition, the bimolecular structure becomes the one-molecular layer feature. In contrast, the two-dimensional platelet microcrystal domains, as well as the bimolecular structure, remain unchanged after doping (Me)₂P into the LB films of octadecyl-TCNQ. However, the *d* value of the layer distance becomes shorter from 3.6 to 3.3 nm upon doping. These differences in morphology between the two kinds of mixed-stack CT films may be attributable to the different ionization potential energies of the donors and the different doping process in the liquid (TMB) and vapor ((Me)₂P) phases.

The molecular arrangement in the mixed-stack CT films of octadecyl-TCNQ doped by TMB and that in the films of octadecyl-TCNQ doped by (Me)₂P are largely different from each other. The inter- and intrastack periods and the angle between the two axes in the former⁸ and latter films are 1.2 nm, 0.7 nm, and 102°, and 0.96 nm, 0.83 nm, and 59°, respectively. The difference in the interstack period may be due to the difference in the molecular orientations of D and A in the films. The long axes of D and A in the CT films of octadecyl-TCNQ and TMB are evaluated to be almost parallel to the substrate surface,¹⁴ while they are preferentially perpendicular to the substrate in those of octadecyl-TCNQ and (Me)₂P.¹ It is unlikely that the orientation of hydrocarbon chains also has influence upon the interstack period because they seem to be preferentially parallel to the substrate surface in both kinds of CT films.^{1,14}

Annealing Effects of Mixed-Stack CT Complex Films of Octadecyl-TCNQ and (Me)₂P. A combination of UV–vis–NIR and IR spectroscopies with AFM microscopy enables us to study annealing effects of the mixed-stack CT complex films of octadecyl-TCNQ and (Me)₂P from both structural and morphological aspects. The following observations verify that the CT complex films decompose irreversibly if they are heated over the dedope temperature. (i) In the UV–vis–NIR spectrum of the 11-layer CT film annealed from 90 °C (Figure 6c), only the absorption band due to neutral octadecyl-TCNQ molecules appears. (ii) The IR spectrum of the 11-layer CT film after annealing from 90 °C (Figure 7c) also reveals that the remaining bands are attributable to neutral octadecyl-TCNQ molecules. (iii) The morphological characteristics of the annealed CT films studied by AFM are similar to those of the LB films of octadecyl-TCNQ.^{3,5}

Conclusion

The present paper presents new insight into the morphological features and annealing effects of the mixed-stack CT complex

films of octadecyl-TCNQ doped by (Me)₂P. As for the morphological aspect, AFM measurements have elucidated that the CT films consist of layered platelet microcrystal domains with a step of 3.3 nm. A highly oriented molecular arrangement of D and A has been observed in the high-resolution AFM image. The inter- and intrastack periods are calculated to be 0.96 and 0.83 nm, respectively, with an angle of 59° between the two axes of the inter- and intrastacks. These morphological results give a direct interpretation to the appearance of higher-order peaks in the X-ray diffraction of the mixed-stack CT films. Moreover, doping (Me)₂P into LB films of octadecyl-TCNQ under vacuum² and nonvacuumed conditions gives quite similar morphological and structural characteristics of the CT films. This demonstrates that oxygen did not react with the CT complex during the doping process at 75 °C. It can be concluded from a comparison of the present study with the previous morphological study on the mixed-stack CT films of octadecyl-TCNQ doped by TMB that doping of the LB films with octadecyl-TCNQ by different donors under different conditions allows us to prepare low-dimensional mixed-stack CT films with different morphological features, i.e., the one-dimensional needle-like microcrystal complex of octadecyl-TCNQ and TMB and the two-dimensional platelet microcrystal complex of octadecyl-TCNQ and (Me)₂P.

The AFM study of the annealing effects, on which we put an emphasis, has revealed that almost no change takes place on the two-dimensional layered microcrystal domains and in the molecular arrangement inside the domains, if the CT film is annealed below the dedope temperature. The UV–vis–NIR and IR spectra of the annealed CT films have also verified the above conclusion. In contrast, the donor molecules dedope from the CT complex and the acceptor molecules are restored from the CT state to the neutral one, if the CT film is heated above the dedope temperature. More detailed studies of the thermally induced decomposition mechanism of the mixed-stack CT films will be reported in the succeeding paper.⁴

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