

# Infrared and Ultraviolet–Visible Spectroscopic Studies on Premelting Behavior of One- and Eleven-Layer Langmuir–Blodgett Films of 2-Dodecyl-, 2-Pentadecyl-, and 2-Octadecyl-7,7,8,8-tetracyanoquinodimethane

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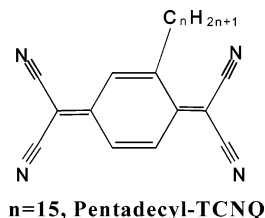
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Premelting behavior of one- and eleven-layer Langmuir–Blodgett (LB) films of 2-dodecyl-, 2-pentadecyl-, and 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (dodecyl-TCNQ, pentadecyl-TCNQ, and octadecyl-TCNQ) has been investigated by infrared (IR) and ultraviolet–visible (UV–vis) spectroscopies. It has been suggested from the temperature-dependent variations in the CH<sub>2</sub> scissoring band region of the one-layer LB film of pentadecyl-TCNQ that the packing of the alkyl chains is changed to the hexagonal state from the highly packed state around 60 °C. A CH<sub>2</sub> symmetric stretching band near 2850 cm<sup>−1</sup> of the pentadecyl-TCNQ LB film shows an apparent shift with temperature, indicating that the alkyl chain undergoes premelting phase transitions near 60 and 90 °C. It seems likely that the thermal movement by the alkyl chains in the hexagonal state plays the role of the trigger for the melting phenomenon. The IR and UV–vis studies of the premelting behavior of the pentadecyl-TCNQ LB film suggest that there are one intermediate state between 60 and 90 °C and another intermediate state between 90 and 120 °C. The comparison among the temperature-dependent profiles of the peak maximum position of the CH<sub>2</sub> symmetric stretching band of one-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ suggests that all the one-layer LB films have two intermediate states between the solid and liquid states and that the longer alkyl chain assumes the more ordered conformation due to van der Waals attraction force among the alkyl chains. The eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ show the temperature-dependent profiles different from those of the one-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ. The temperatures for the formation of the second intermediate state of the eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ are lower than those of the corresponding one-layer LB films, probably because of the layer–layer interaction in the eleven-layer LB films.

## Introduction

The investigations of thermal behavior of Langmuir–Blodgett (LB) films are of great importance from the viewpoints of both basic research and practical applications because of the following reasons.<sup>1–21</sup> First, the LB films may demonstrate specific thermal behavior different from that of bulk materials. For example, it was reported that the mechanism of the annealing process for some LB films deviates from the accepted mechanism for most materials.<sup>1</sup> Second, the studies on thermal behavior may yield significant ramifications for the service life of microelectronic devices based upon the LB films. Third, the temperature-dependent structural variations in LB films may be simplified models for those in biological membranes. The thermal behavior of LB films have been investigated extensively;<sup>1–21</sup> however, detailed studies on the premelting behavior are limited,<sup>11,13,14</sup> particularly for LB films with a chromophore.

We have studied the thermal behavior of LB films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ),<sup>10,12–14</sup> mixed-



**Figure 1.** Structural formula of 2-alkyl-7,7,8,8-tetracyanoquinodimethane.

stack charge transfer (CT) complex films of octadecyl-TCNQ doped with 3,3',5,5'-tetramethylbenzidine (TMB),<sup>15,16</sup> and those of octadecyl-TCNQ doped with 5,10-dimethyl-5,10-dihydro-phenazine.<sup>17–19</sup> Figure 1 shows the molecular structure of alkyl-TCNQ. For the LB films of alkyl-TCNQ, we have employed ultraviolet–visible (UV–vis) and IR spectroscopies and atomic force microscopy (AFM) to explore the order–disorder phase transition and annealing effects from both the structural and topological points of view.<sup>10,12–14</sup> We have found that a number of thermally induced phenomena of the LB films of alkyl-TCNQ depend on the number of layers.<sup>10,12–14</sup> For example, the domains in the one-layer films decompose progressively with temperature even just above room temperature while those in

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the multilayer films are stable until 80 °C and undergo a rather abrupt collapse between 80 and 90 °C.<sup>13</sup> Although the domain structure of the one-layer films shows a gradual temperature change, the molecular orientation and structure in the domains experience a clear order–disorder transition. The order–disorder transition temperature increases and approaches the bulk melting point with the number of layers. Moreover, the thermal behavior of an eleven-layer LB film of octadecyl-TCNQ has been compared with that of the corresponding films of dodecyl-TCNQ and pentadecyl-TCNQ to investigate the effect of the length of the alkyl chain on the order–disorder transitions.<sup>10</sup>

The purpose of the present study is to provide further insight into the thermal behavior of one- and eleven-layer LB films of dodecyl-TCNQ, pentadecyl-TCNQ, and octadecyl-TCNQ. In this study special emphasis has been placed on the premelting behavior of the films. To investigate the premelting behavior, we have undertaken a strategy. The strategy is to measure temperature-dependent changes in UV–vis and IR spectra of one- and eleven-layer LB films of the three kinds of TCNQ more precisely and analyze them in more detail. We have devised a new temperature cell for the spectral measurements which enables us to measure the temperature-dependent spectral changes more precisely. By means of this strategy, we have found that the one-layer LB film of pentadecyl-TCNQ undergoes premelting transitions near 60 and 90 °C and that there may be two intermediate states, between 60 and 90 °C and between 90 and 120 °C.

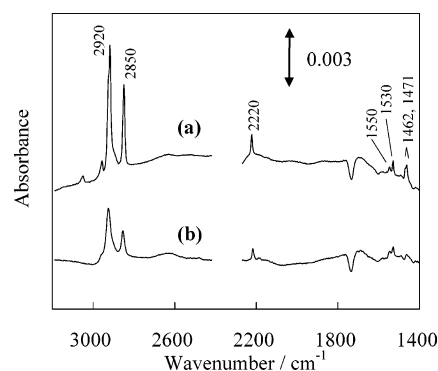
In this paper, we mainly report the result for the one-layer LB film of pentadecyl-TCNQ, but in the last part of this paper we describe the corresponding results for the one-layer LB films of dodecyl- and octadecyl-TCNQ and for the eleven-layer LB films of the three kinds of alkyl-TCNQ to discuss the dependences of the premelting behavior on the length of the alkyl chain and the number of LB layers.

## Experimental Section

**Sample Preparation.** Dodecyl-, pentadecyl-, and octadecyl-TCNQ were purchased from Kankoh-Shikiso Institute, Hayashibara Biochemical Laboratories, Inc., and used without further purification. Thin layer chromatographic examinations revealed that they did not contain any other colored components. Water was prepared by passing city water through activated charcoal and reverse osmosis filters and then distillation. Finally, it was purified by a Ultrapure Water System Model CPW-101 (Advantec, Tokyo). The resistance of the finally prepared water was larger than 18.1 MΩ cm.

LB films of alkyl-TCNQ were fabricated by use of a Kyowa Kaimen Kagaku HBM-AP Langmuir trough with a Whilhelmy balance. Many drops of alkyl-TCNQ in chloroform ( $1.0 \times 10^{-3}$  M) were placed onto an aqueous subphase of water. After evaporation of the solvent, the monolayers were compressed at a constant rate of 20 cm<sup>2</sup>/min up to the surface pressure of 10 mN m<sup>-1</sup> (293 K). The  $\pi$ -A isotherm showed that the monolayers were solid condensed films at surface pressure of 10 mN m<sup>-1</sup>. At this surface pressure, the spread Langmuir film at air/water interface was transferred onto a CaF<sub>2</sub> substrate (for UV–vis and IR measurements) by the vertical dipping method. The transfer ratio was found to be nearly unity throughout the experiments. The CaF<sub>2</sub> substrates were cleaned by ultrasonification in acetone, chloroform, and acetone, then in distilled water, and then by a homemade UV–ozone cleaner.

**Spectroscopy.** UV–vis spectra of the LB films were obtained by means of a Shimadzu UV–visible 3101 spectrophotometer. IR spectra were measured at a 4 cm<sup>-1</sup> resolution with a Nicolet



**Figure 2.** IR transmission spectra of a one-layer LB film of pentadecyl-TCNQ at (a) 30 and (b) 120 °C (offset is arbitrarily adjusted).

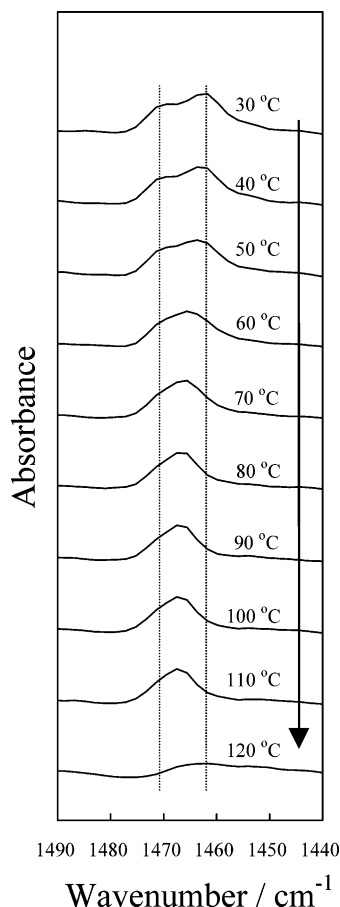
Magna-IR Spectrometer 550 with an MCT detector. To generate the spectra with a high signal-to-noise ratio, 256 interferograms were coadded. To measure temperature-dependent UV–vis and IR spectra, the CaF<sub>2</sub> substrates on which the LB films had been deposited were inserted into a sample holder with a thermocouple and a metal heater. Temperature control was achieved by using an Omron EST temperature controller. The system used in the present study was much better, especially in the point of temperature stability above 100 °C, than the previous one employed in our research group. Moreover, calibration lines for the temperature measurements were developed to measure temperature more accurately at the point where the UV–vis or IR beam passed. Reproducibility of the temperature measurements was better than  $\pm 1$  °C above 70 °C. Thus, it has become possible to obtain more reliable temperature-dependent spectral data than before. The UV–vis and IR spectra of the one- and eleven-layer films of dodecyl-, pentadecyl-, and octadecyl-TCNQ were measured at an increment of 10 °C from 30 to 70 °C, and at an increment of 2 °C above 70 °C.

**Spectral Analysis.** A Grams/386 software (Galactic Industries Corp.) was used to analyze the spectral data. A four-point spline algorithm was used to calculate more accurate peak maximum positions in the IR spectra, where the interpolated cubic polynomial functions were derived from the closest four adjacent actual data points.

## Results

**Thermal Behavior of a One-Layer LB Film of Pentadecyl-TCNQ Studied by IR Spectroscopy.** Figure 2 shows IR transmission spectra of a one-layer LB film of pentadecyl-TCNQ measured at 30 and 120 °C. IR band assignments for both the TCNQ chromophore and alkyl chain have been well established.<sup>10,13,22,23</sup> The assignments for key bands at 30 °C (Figure 2a) are as follows: 2920 cm<sup>-1</sup>, CH<sub>2</sub> antisymmetric stretching; 2850 cm<sup>-1</sup>, CH<sub>2</sub> symmetric stretching; 2220 cm<sup>-1</sup>, C≡N stretching; 1550 and 1530 cm<sup>-1</sup>, C=C stretching; 1471 and 1462 cm<sup>-1</sup>, a doublet due to the CH<sub>2</sub> scissoring vibrations.

Figure 3 shows temperature-dependent IR spectra from 30 to 120 °C at an increment of 10 °C in the region from 1490 to 1440 cm<sup>-1</sup>. In Figure 3, two bands near 1465 cm<sup>-1</sup> at 30 °C are assigned to the CH<sub>2</sub> scissoring modes. In our previous paper, we reported that the CH<sub>2</sub> scissoring band of the LB films of pentadecyl-TCNQ does not split into two bands.<sup>23</sup> Probably spectral quality was not good enough to observe the splitting. By use of a CH<sub>2</sub> scissoring band one can investigate the packing of alkyl chains. It is well-known that the splitting of the scissoring band is characteristic of *n*-paraffins with a packing where the hydrocarbon chains are packed nearly perpendicularly.<sup>24,25</sup> In contrast, the CH<sub>2</sub> scissoring band appears as a

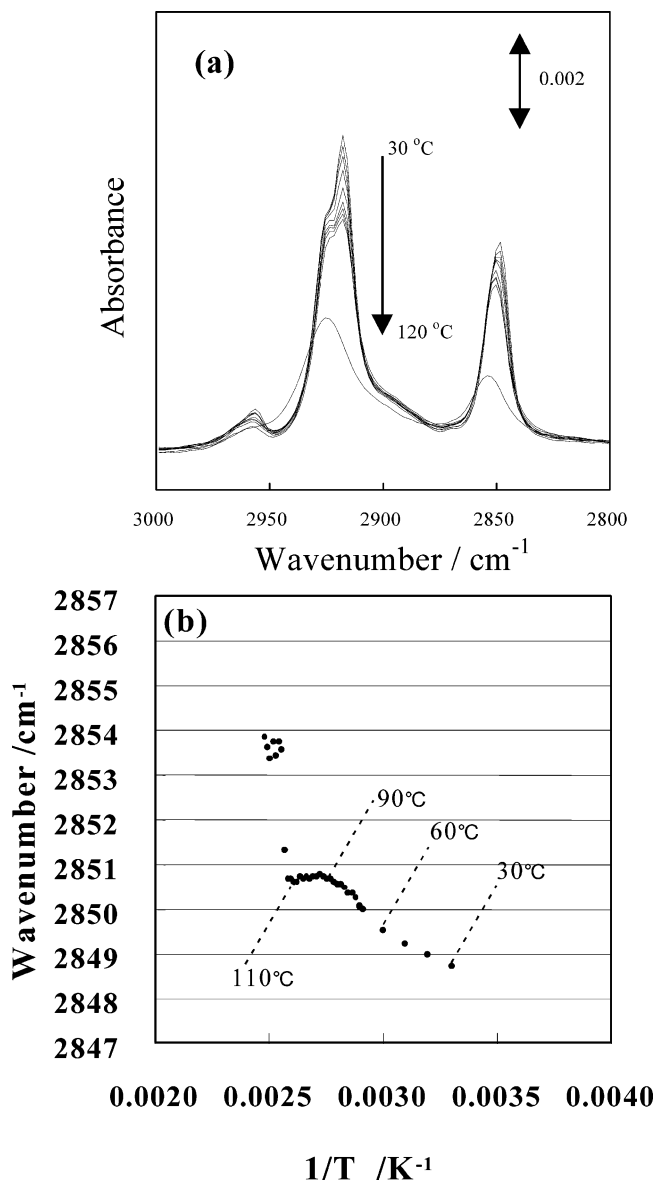


**Figure 3.** Temperature-dependent IR spectra in the region from 1490 to 1440  $\text{cm}^{-1}$  of a one-layer LB film of pentadecyl-TCNQ from 30 to 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$  (offset is arbitrarily adjusted).

singlet band when the *n*-paraffins are in a hexagonal or pseudohexagonal packing, or in a packing where the hydrocarbon chains are packed in parallel.

A notable feature for the  $\text{CH}_2$  scissoring band of the one-layer LB film of pentadecyl-TCNQ is that the two components come close at 1465  $\text{cm}^{-1}$  at 60  $^{\circ}\text{C}$  (Figure 3). However, the band near 1465  $\text{cm}^{-1}$  is not completely symmetrical even above 60  $^{\circ}\text{C}$ . This indicates that there are at least two components for the scissoring mode. We will discuss later the two components due to the scissoring mode of the alkyl chain in the one-layer LB film of pentadecyl-TCNQ.

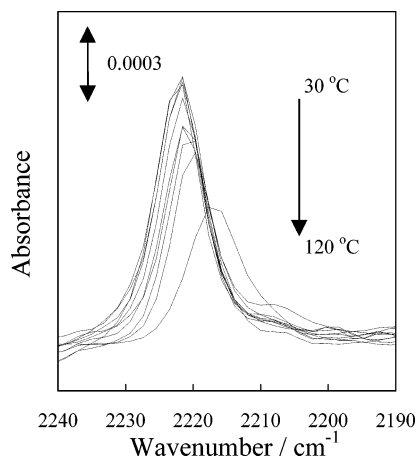
Figure 4a presents temperature-dependent IR spectra from 30 to 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$  in the region from 3000 to 2800  $\text{cm}^{-1}$ . In our experimental system the direction of the electronic vector of the incident IR light is parallel to a transparent substrate surface. In molecular vibrations of a highly oriented organic thin film on the substrate, only the component of a transition moment parallel to the substrate surface must be observed selectively. The direction of the long axis of the trans-zigzag skeleton plane and the direction of  $\text{CH}_2$  symmetric (or antisymmetric) stretching vibration are perpendicular to each other. Thus, the bands due to  $\text{CH}_2$  symmetric and antisymmetric stretching vibrations in the alkyl chain of pentadecyl-TCNQ provide the maximum intensities when the long axis of the trans-zigzag skeleton plane orients perpendicular to the substrate surface. The bands due to  $\text{CH}_2$  symmetric and antisymmetric vibrations in Figure 4a show the gradual intensity decreases from 30 to 110  $^{\circ}\text{C}$ . This observation is mainly because, by heating, the number of the gauche forms in the alkyl chain increases and their absorption intensity projected on the substrate



**Figure 4.** (a) Temperature-dependent IR spectra in the region from 3000 to 2800  $\text{cm}^{-1}$  of a one-layer LB film of pentadecyl-TCNQ from 30 to 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$ . (b) Peak maximum position of the  $\text{CH}_2$  symmetric stretching band versus inverse temperature.

decreases. Of note is that these two bands exhibit sudden intensity decreases between 110 and 120  $^{\circ}\text{C}$  where the melting of the film happens. This suggests that at 120  $^{\circ}\text{C}$  the alkyl chain is in the isotropic state with many gauche forms.

Figure 4b plots a peak maximum position of the  $\text{CH}_2$  symmetric stretching band as a function of inverse temperature. It is well-known that the frequencies of  $\text{CH}_2$  antisymmetric and symmetric stretching bands of an alkyl chain are sensitive to the conformation of the chain.<sup>26,27</sup> In general, the low frequencies (around 2918 and 2848  $\text{cm}^{-1}$ ) of these bands are characteristic of the highly ordered trans-zigzag alkyl chain, while the alkyl chain with some gauche forms provides the corresponding bands at the higher frequencies (up to around 2926 and 2856  $\text{cm}^{-1}$ ) depending on the number of the gauche forms. We mainly use the band near 2850  $\text{cm}^{-1}$  due to the  $\text{CH}_2$  symmetric stretching mode as a monitor for temperature-dependent structural changes of the chain since there is no interference from other bands in this region. The  $\text{CH}_2$  antisymmetric stretching band also provides the same information as its symmetric stretching band; however, for the  $\text{CH}_2$  antisymmetric stretching



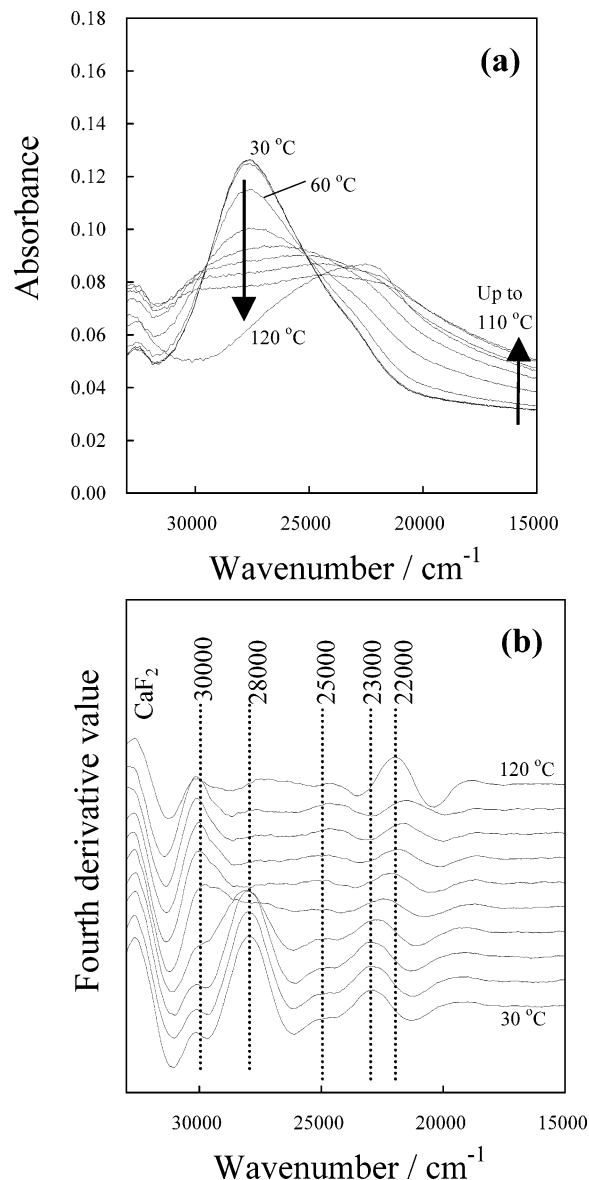
**Figure 5.** Temperature-dependent IR spectra in the region from 2250 to 2190  $\text{cm}^{-1}$  of a one-layer LB film of pentadecyl-TCNQ from 30 to 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$ .

band we cannot neglect completely interference from the other overlapping components. It is clearly seen in Figure 4b that there are some points of inflection particularly at 60 and 90  $^{\circ}\text{C}$  before the melting phenomenon of the one-layer LB film of pentadecyl-TCNQ. This suggests that the mobility of the alkyl chain has intermediate states between those in the ordered and disordered states in the one-layer LB film of pentadecyl-TCNQ.

Figure 5 shows temperature-dependent IR spectra from 30 to 120  $^{\circ}\text{C}$  in the region of 2190–2250  $\text{cm}^{-1}$ . The band near 2220  $\text{cm}^{-1}$  is due to the  $\text{C}\equiv\text{N}$  stretching mode. The band exhibits a gradual downward shift by 5  $\text{cm}^{-1}$  with temperature. The most significant spectral change is observed in the order–disorder transition between the spectra measured at 110 and 120  $^{\circ}\text{C}$ . As will be mentioned below, the temperature-dependent UV–vis spectra of the one-layer LB film of pentadecyl-TCNQ suggest that there are some aggregation states of the TCNQ chromophore planes and that the ratio among these aggregation forms of the TCNQ chromophore planes changes with temperature before the order–disorder transition. Probably, this effect is reflected in the gradual downward shift of the  $\text{C}\equiv\text{N}$  stretching band.

**Thermal Behavior of a One-Layer LB Film of Pentadecyl-TCNQ Studied by UV–Vis Spectra.** Figure 6a shows the temperature-dependent UV–vis spectra of the one-layer LB film of pentadecyl-TCNQ between 30 and 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$ . A broad feature in the 30 000–20 000  $\text{cm}^{-1}$  region is attributed to a  $\pi\rightarrow\pi^*$  transition of TCNQ chromophore. A UV–vis spectrum of pentadecyl-TCNQ in a chloroform solution shows an absorption band at 25 000  $\text{cm}^{-1}$  due to the monomeric form of the chromophore. The major band at 28 000  $\text{cm}^{-1}$  is due to the stacked form in the column structure consisting of the TCNQ chromophore planes.<sup>12</sup> A shoulder near 23 000  $\text{cm}^{-1}$  in the spectra in Figure 6a is located at the lower wavenumber by about 2000  $\text{cm}^{-1}$  compared to the position of the monomer band, and then it may be assigned to a  $\pi\rightarrow\pi^*$  transition of another aggregation form. Note that the band due to another aggregation form near 23 000  $\text{cm}^{-1}$  increases its height gradually with temperature from 60  $^{\circ}\text{C}$ .

Figure 6b depicts the fourth derivative of the UV–vis spectra shown in Figure 6a. Fourth-derivative spectra are powerful in identifying band positions and monitoring subtle spectral changes. It can be seen from Figure 6b that there are at least five components at 30 000, 28 000, 25 000, 23 000, and 22 000  $\text{cm}^{-1}$  assignable to the  $\pi\rightarrow\pi^*$  transition of TCNQ chromophore in various states. The band at 28 000  $\text{cm}^{-1}$  due to the stacked



**Figure 6.** (a) Temperature-dependent UV–vis spectra of a one-layer LB film of pentadecyl-TCNQ from 30 to 120  $^{\circ}\text{C}$  at an increment of 10  $^{\circ}\text{C}$ . (b) The fourth derivative of the spectra in (a).

form of the TCNQ chromophore planes shows a sudden decrease in intensity around 60  $^{\circ}\text{C}$  (Figure 6). Concomitant with the intensity decrease in the band at 28 000  $\text{cm}^{-1}$ , the intensity of the band at 30 000  $\text{cm}^{-1}$  increases and remains until melting. This component is located at a higher energy position than that due to the stacked form at 28 000  $\text{cm}^{-1}$ . When the angle between the direction of the transition moment of the chromophore and the direction in which the chromophore planes stack is larger than the critical angle ( $55^{\circ}$ ), one can observe the higher energy position of the absorption band relative to the position of the absorption band due to the monomeric form of the chromophore.<sup>28</sup> Moreover, when an aggregation has the larger number of stacking chromophores, its absorption band shifts to the higher energy position.<sup>28</sup> Thus, the component at 30 000  $\text{cm}^{-1}$  may arise from a more ordered stacked form of the TCNQ chromophores. Another important observation in the temperature-dependent UV–vis spectral changes is an abrupt appearance of the band at 22 000  $\text{cm}^{-1}$  in concert with the rapid decrease in the band at 30 000  $\text{cm}^{-1}$ . This indicates that the higher stacked species abruptly change into another aggregation form near the order–disorder transition.



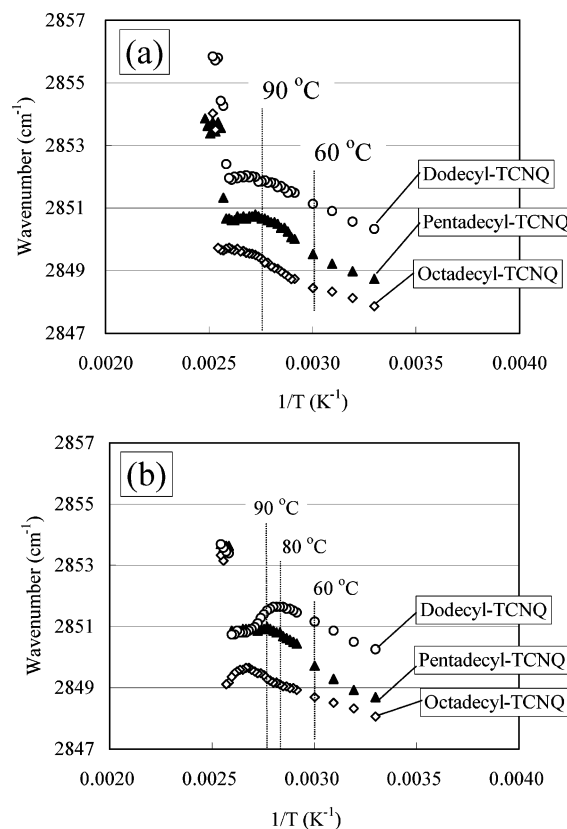
As already reported in our previous paper,<sup>13</sup> the baseline near 15 000  $\text{cm}^{-1}$  shows an upward shift from 60 to 100 °C. The baseline shift implies topological changes in the domains, whose size is comparable to the wavelength of the UV–vis light. The baseline decreases above 110 °C, showing that topological changes occur in the film.

## Discussion

**Thermally Induced Changes in the Alkyl Chain Packing and Its Arrangement.** We previously reported the splitting of the  $\text{CH}_2$  scissoring band for LB films of octadecyl- and dodecyl-TCNQ.<sup>10,22,23</sup> The splitting was ascribed to the orthorhombic subcell packing of the alkyl chains. However, we have found that this conclusion is not reasonable. In the orthorhombic subcell packing, the trans-zigzag planes formed by the alkyl chains are packed nearly perpendicular to one another. TCNQ chromophores form parallel column-like aggregation lines easily because they have strong aggregation ability.<sup>29–31</sup> Thus, it seems very unlikely that the alkyl chains are packed nearly perpendicular to one another. Moreover, our recent X-ray crystallographic study of dodecyl-TCNQ revealed that the alkyl chains are packed parallel to one another.<sup>31</sup> This may be very important information for understanding the packing of the alkyl chains in the one-layer LB film of pentadecyl-TCNQ. Other important information came from an AFM study on a LB film of alkyl-TCNQ by Nichogi et al.<sup>32,33</sup> They observed in an AFM image of the LB film that, as in the case of the crystal of dodecyl-TCNQ, the TCNQ chromophores are packed parallel to one another.

It should be noted that, even for the hexagonal state of the alkyl chains appearing above 60 °C, there are at least two components in the scissoring band region. It was found from the X-ray crystallographic study of dodecyl-TCNQ that the interdigitated alkyl chains exist in the crystal structure. A key factor to interpreting the splitting of the  $\text{CH}_2$  scissoring band may be the interdigitated alkyl chains. Probably the one-layer LB film of pentadecyl-TCNQ has a bimolecular structure as in the case of LB films of octadecyl-TCNQ.<sup>13</sup> Therefore, the alkyl chain may be divided into two parts, i.e., the interdigitated and noninterdigitated parts in the LB film of pentadecyl-TCNQ. In the former the interaction due to van der Waals is strong, while in the latter the alkyl chains have much wider space. Thus, we infer that the two components of the scissoring band arise from the interdigitated and noninterdigitated parts. Moreover, the conjugated system of the TCNQ chromophore may have a significant influence on the vibrations of the  $\text{CH}_2$  groups close to the quinone ring.

**Thermal Effects on the Aggregation of the TCNQ Chromophore.** Thermal effects on the aggregation of the TCNQ chromophore can be explored by analyzing the temperature-dependent changes in the  $\text{C}\equiv\text{N}$  stretching band (Figure 3) and in the absorption bands due to the  $\pi\rightarrow\pi^*$  transition (Figure 6). As described under Results, the temperature-dependent UV–vis spectra suggest the existence of four kinds of aggregation as well as the monomeric form in the one-layer LB film of pentadecyl-TCNQ: (1) the highly ordered stacked form; (2) the stacked form; (3) the monomeric form, (4) and (5) two other kinds of aggregation forms. The temperature-dependent variations in the aggregation of the TCNQ chromophore in the one-layer LB film of pentadecyl-TCNQ may be summarized as follows: at 30 °C the TCNQ chromophore assumes the stacked form as the major component as well as the monomeric species, and one aggregation form exists as a minor component. Around 60 °C, the change in the subcell packing of the alkyl chains



**Figure 7.** Peak maximum positions of  $\text{CH}_2$  symmetric stretching band versus inverse temperature for (a) one-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ, and (b) eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ.

causes conversion from the stacked form to the highly ordered stacked form. Some extent of the TCNQ chromophores may be kept in the highly ordered stacked form until the melting point. With temperature, the chromophores due to another aggregation form increase gradually. Upon melting, most of the chromophores are changed into another aggregation form near the order–disorder transition. The thermal motion of the alkyl chains may play a key role in converting the highly ordered stacked form to another aggregation form.

## Dependence of Thermal Behavior on the Alkyl Chain Length and the Number of Layers of Alkyl-TCNQ LB Films.

As shown in Figure 4b, the temperature-dependent plot of the peak maximum position of the  $\text{CH}_2$  symmetric stretching band is a useful indicator for exploring the premelting behavior of alkyl chains of LB films of alkyl-TCNQ. By using corresponding plots, one can discuss dependence of the thermal behavior on the alkyl chain length and the number of layers of the alkyl-TCNQ LB films.

Figure 7a shows temperature-dependent plots of the peak maximum positions due to the  $\text{CH}_2$  symmetric stretching band of one-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ. The three kinds of LB films show similar temperature profiles except for the peak maximum positions. The differences in the peak maximum positions can be explained by the difference in the alkyl chain length. The longer the alkyl chain, the greater stability to keep trans-zigzag conformation of the alkyl chain due to van der Waals attraction force among alkyl chains. This leads to the downward shifts of the plots. The plots in Figure 7a reveal that the three kinds of alkyl-TCNQ LB films have intermediate states between the solid and liquid states. The first intermediate states appear around 60 °C for the three kinds of LB films, and the second intermediates are formed from 94,

**TABLE 1: Temperatures for Formation of Second Intermediate States ( $T_i$ ) and Film Melting ( $T_m$ ) of One- and Eleven-layer LB Films of Dodecyl-, Pentadecyl-, and Octadecyl-TCNQ**

	one-layer		eleven-layer	
	$T_i$	$T_m$	$T_i$	$T_m$
dodecyl-TCNQ	94	116	80	114
pentadecyl-TCNQ	94	118	88	114
octadecyl-TCNQ	108	122	100	118

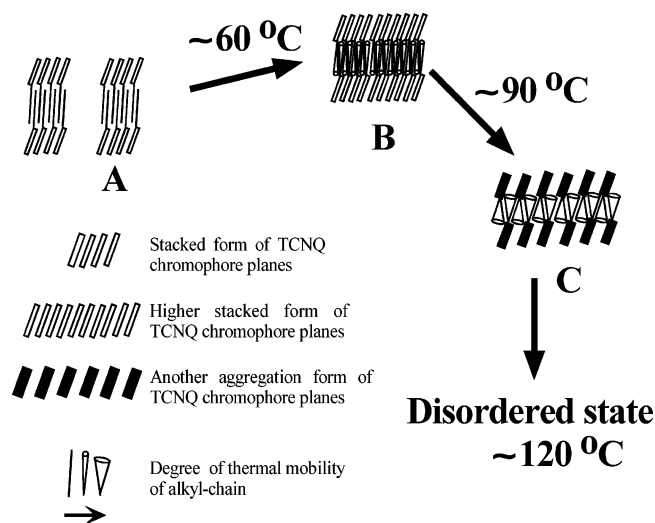
94, and 108 °C for dodecyl-, pentadecyl-, and octadecyl-TCNQ LB films, respectively.

Figure 7b presents temperature-dependent plots of the peak maximum positions of the  $\text{CH}_2$  symmetric stretching band of eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ. The profiles of the three kinds of LB films in Figure 7b are very similar to those in Figure 7a below 80 °C; however, the profiles of the eleven-layer LB films of dodecyl- and octadecyl-TCNQ show remarkable downward shifts above 80 and 100 °C, respectively. On the other hand, above 80 °C, the profile of the eleven-layer LB films of pentadecyl-TCNQ is similar to the profile of the one-layer LB films of pentadecyl-TCNQ. These facts are probably because only pentadecyl-TCNQ has an alkyl chain with an odd number of carbon atoms while dodecyl- and octadecyl-TCNQ have those with an even number of carbon atoms and the nature of layer–layer interaction is different between the LB film of pentadecyl-TCNQ and those of dodecyl- and octadecyl-TCNQ; the terminal  $\text{CH}_3$  groups of the alkyl chains with odd and even numbers of carbon atoms orient in opposite directions.

Table 1 summarizes temperatures for the formation of the second intermediate state ( $T_i$ ) and film melting ( $T_m$ ) of the one- and eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ. In Table 1 we do not show the temperatures when the first intermediate states appear because it is rather difficult to determine the precise temperatures. The  $T_i$  values of the eleven-layer LB films of the three kinds of alkyl-TCNQ are lower than those of the corresponding one-layer LB films. This indicates that the intermediate states in the eleven-layer LB films are more stable than those in their one-layer LB films. In the intermediate states the TCNQ chromophore planes of the eleven-layer LB films of three kinds of alkyl-TCNQ can form aggregates. The aggregates may lead the layer–layer interaction which results in the more stable molecular assembly.

Of particular note for the second intermediate states is that the  $\text{CH}_2$  stretching band shows a downward shift with temperature. However, it is very unlikely that the number of trans conformations increases while that of the gauche conformations decreases as temperature increases. Thus, it seems that the downward shift is caused by a different factor from the conformation effect.

We recently applied the global phase angle description derived from generalized two-dimensional correlation spectroscopy (global two-dimensional phase map) to the infrared spectra of the eleven-layer LB film of dodecyl-TCNQ, in order to study the second intermediate state between the solid and melting states from 80 to 120 °C,<sup>34</sup> although we could not apply this method to the infrared spectra of the one-layer LB film because their signal-to-noise ratio was not sufficient for the analysis. The global two-dimensional phase map calculated from IR spectra from 30 to 80 °C of the LB film revealed that the thermally induced intensity changes in the  $\text{CH}_3$  asymmetric stretching bands at 2954.5 and 2964.1  $\text{cm}^{-1}$  show higher phase angles with respect to that at 2844.5  $\text{cm}^{-1}$  due to the  $\text{CH}_2$  symmetric stretching band. This result indicates that the active



**Figure 8.** Possible model for premelting behavior of the one-layer LB film of pentadecyl-TCNQ. A, highly stacked form; B and C, two kinds of intermediate states.

thermal movement of the alkyl chain loses the trans-zigzag skeleton plane in the intermediate state after 80 °C between the solid and melting states. Therefore, it seems that in the second intermediate state of the eleven-layer LB film of dodecyl-TCNQ the alkyl chains lose their order partly, although as a molecular assembly the LB film keeps its order. It may be concluded that from 30 to 80 °C the TCNQ chromophores of the LB film assume the highly stacked form but from 80 to 120 °C they cannot keep the stacked form because of the very high mobility of alkyl chains and the stacked form is converted to another form that has the high mobility of the alkyl chains and at the same time retains the order of the whole molecular assembly.

Figure 8 illustrates a possible model that is based on the results and discussion in this study. The figure shows the mobility of the alkyl chains and the aggregations of TCNQ chromophores. We infer that the two kinds of intermediate states exist in the LB films investigated irrespective of the length of alkyl chain and the number of layers.

## Conclusion

The present study has aimed at investigating the premelting behavior of the one- and eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ by using UV–vis and IR spectroscopies. Conclusions reached from the temperature-dependent measurements of IR and UV–vis spectra are summarized as follows:

(i) The peak maximum position of the  $\text{CH}_2$  symmetric stretching band of the one- and eleven-layer LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ shows some points of inflection as a function of inverse temperature, indicating the existence of two intermediate states between the solid and liquid states.

(ii) The thermal behavior of the  $\text{CH}_2$  scissoring band of pentadecyl-TCNQ suggests that the alkyl chain attached to the TCNQ chromophore plane is divided into two parts, the interdigitated part and noninterdigitated part, and that each part yields the  $\text{CH}_2$  scissoring band at slightly different positions. In the interdigitated part, the alkyl chain has interaction with the surrounding chains by van der Waals attraction, while in the noninterdigitated part, the alkyl chain has little interaction with the surrounding alkyl chains and it has some influence

from the conjugated system of the quinone ring of TCNQ chromophore.

(iii) It is suggested from the UV–vis and IR measurements that the stacked form of the TCNQ chromophore plane is stimulated by the thermal movement due to the hexagonal state in the alkyl chains. The fourth derivative of the temperature-dependent UV–vis spectra of the one-layer LB film of pentadecyl-TCNQ suggests the existence of four kinds of aggregations as well as the monomeric form.

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