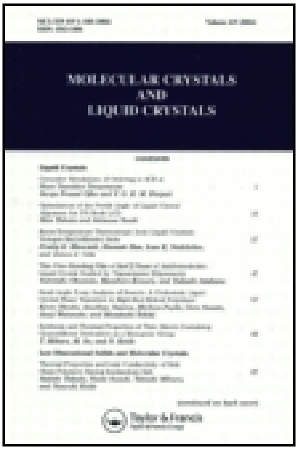

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Studies on Control of Molecular Re-Arrangement in Langmuir-Blodgett Films of 2-Pentadecyl-7,7,8,8-Tetracyanoquinodimethane by Infrared and Ultraviolet-Visible Spectroscopy

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Studies on Control of Molecular Re-Arrangement in Langmuir-Blodgett Films of 2-Pentadecyl-7,7,8,8-Tetracyanoquinodimethane by Infrared and Ultraviolet-Visible Spectroscopy

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Ultraviolet-visible and FT-IR spectroscopy have been applied to monitor molecular re-arrangement in Langmuir-Blodgett (LB) films of 2-pentadecyl-7,7,8,8-tetracyanoquinodimethane (C_{15}TCNQ) prepared under the surface pressure of 5 and 2 mN/m and in those of C_{15}TCNQ deposited on LB films of deuterated stearic acid (SA-d_{35}). It was found that the molecular re-arrangement can be controlled both by adjusting the packing density of C_{15}TCNQ and by changing the nature of the substrate surface.

Keywords: LB films; IR spectroscopy; molecular orientation; TCNQ

INTRODUCTION

We have been studying the molecular orientation and structure in LB and evaporated films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (C_nTCNQ)(1-2). Recently, we found that the molecular orientation and structure of C_{15}TCNQ in LB films change with time after the film deposition on a substrate(3). The purpose of the present study is to provide further insight into the molecular re-arrangement in the LB films of C_{15}TCNQ. For this purpose, we prepared the LB films of C_{15}TCNQ under the surface pressure of 5 and 2 mN/m and also its LB films on two-layer LB films of SA-d_{35}.

EXPERIMENTAL

C_{15}TCNQ and SA-d_{35} were obtained from the Japanese Research Institute for Photo-sensitizing Dyes Co., Ltd. and from Cambridge Isotope Laboratories (D98%), respectively, and used without further purification. LB films of C_{15}TCNQ and those of SA-d_{35} were fabricated by using a Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance. FT-IR spectra were obtained at a 4 cm^{-1} resolution with a Nicolet Magna IR™ Spectrometer 550 with a MCT detector. UV-Visible spectra were measured on a Shimadzu UV-visible 3101 spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows time-dependent changes in IR transmission spectra (CH stretching band region) of a one-layer LB film of C_{15}TCNQ after the film deposition on a CaF_2 plate at 5 mN/m. It is noted that the intensity of a CH_2 antisymmetric stretching band (2918 cm^{-1}, ν_{as}) decreases while that of a CH_2 symmetric stretching band (2850cm^{-1}, ν_s) increases a little with time. This result indicates that the orientation and structure of the hydrocarbon chain in the C_{15}TCNQ LB film are time-dependent (3). The absorbance of the band (365nm) due to a π-π^* transition of the TCNQ chromophore in UV-visible spectra of a one-layer LB film of C_{15}TCNQ decreases with an isobestic point at 425 nm as a function of time, suggesting that the stacking of the chromophore alters with time.

Of particular note in Fig.1 is that a feature near 2920 cm^{-1} splits into two bands and the shoulder band (2926 cm^{-1}) becomes clearly discernible with time. In order to assign the origin of the split, principal component analysis (PCA) was applied to the time-dependent IR spectra(4). The loading plot of PCA suggests that two conformers of the hydrocarbon chain coexist in the

LB films; one is a highly ordered form (trans-zigzag) with the CH_2 stretching bands at 2918 and 2850 cm^{-1}, while the other is a disordered form (conformer with several gauche conformations) with those at 2926 and 2856 cm^{-1} (4).

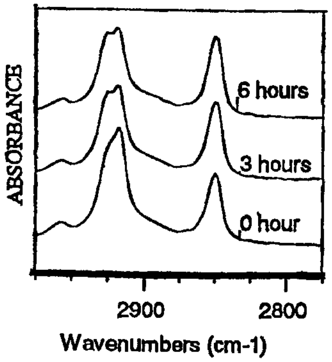

FIGURE 1 Time-dependent IR spectra of a one-layer LB film of C_{15}TCNQ deposited at 5 mN/m

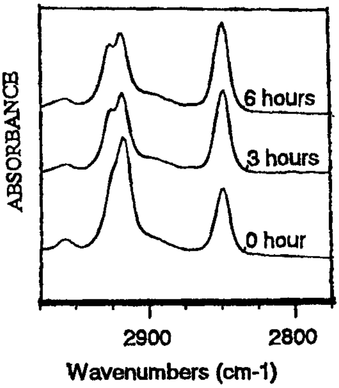

FIGURE 2 Time-dependent IR spectra of a one-layer LB film of C_{15}TCNQ deposited at 2 mN/m

Figure 2 shows time-dependent IR spectra of a one-layer LB film of C_{15}TCNQ deposited on a CaF_2 substrate at 2 mN/m. The intensity ratio of the two bands at 2918 and 2850 cm^{-1} was used to monitor the re-arrangement. By comparing the spectra in Fig.2 with those in Fig.1, it can be seen that the re-arrangement occurs much faster in the LB film prepared at the lower pressure than in the film at the higher pressure. The packing density would become subtle when the LB film is deposited at the low pressure. It seems that the molecules in the higher packing density would exert more strongly hindrance each other than those in the lower packing density. Therefore, the lower the packing density of C_{15}TCNQ in the LB film is, the faster the speed of the re-arrangement is. The above result indicates that the molecular re-arrangement can take place more easily when the molecules have more free space.

The re-arrangement in C_{15}TCNQ multilayers takes place much more slowly than that in the one-layer LB film deposited at the same pressure. We can imagine that the molecular re-arrangement in the inner layers would be more difficult because of the hindrance of adjacent layers.

The interaction between the substrate and C_{15}TCNQ plays an important role in the re-arrangement. A one-layer LB film of C_{15}TCNQ was deposited on a gold-evaporated glass slide at 5 mN/m and it was found that the re-arrangement proceeds very fast(3). In order to study substrate-dependence of the re-arrangement further, a two-layer (up- and down-stroke) LB film of SA-d_{35} was deposited on a CaF_2 substrate at 15mN/m, and then a one-layer C_{15}TCNQ LB film was dipped (up-stroke) on it at 5 mN/m. Figure 3 depicts time-dependent IR spectra of the one-layer LB film of C_{15}TCNQ after the film deposition on the two-layer LB film of SA-d_{35}. The re-arrangement still occurs but its rate is much slower on the LB film of SA-d_{35} than on the CaF_2 plate. Therefore, the order of the re-arrangement rate is as follows; gold-evaporated glass slide > CaF_2 > LB film of deuterated stearic acid. This result suggests that the re-arrangement rate of C_{15}TCNQ in the LB films can be controlled by changing the nature of the substrate surface.

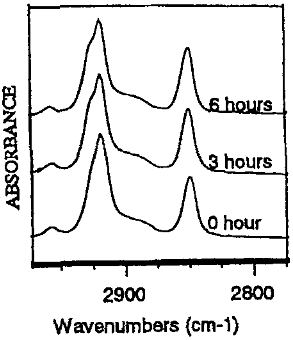

FIGURE 3 Time-dependent IR spectra of a one-layer LB film of C_{15}TCNQ after the film deposition at 5 mN/m on a two-layer LB film of deuterated stearic acid

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