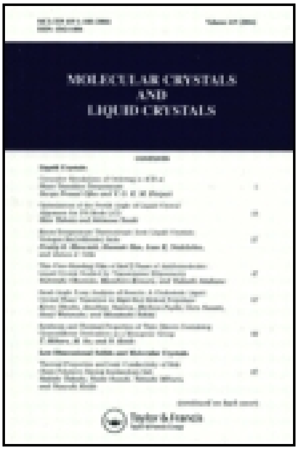

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Light-Induced Structural Change of Langmuir-Blodgett Films

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Light-Induced Structural Change of Langmuir-Blodgett Films

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J-aggregation of cyanine molecules was induced in two types of mixed LB films by the photoisomerization of azobenzene coexisting in the same LB films. Drastic morphological changes involving the formation of three-dimensional cone-shaped structures protruding from the film surfaces were observed accompanied with the J-aggregation. This means that the two-dimensional LB film structures exerted substantial modification by the photoisomerization.

Keywords: LB films; photoisomerization; J-aggregate; azobenzene; cyanine

INTRODUCTION

Langmuir-Blodgett (LB) films have attracted considerable interest from the viewpoint of constructing functionalized materials with well-defined structures. In particular, photoisomerization in LB films have been studied to investigate how the two-dimensional molecular arrangement in the films affect the photoisomerization[1]. All the research has been done under the assumption that the two-dimensional film structures of the LB films will keep unchanged during the photoisomerization processes[2,3]. In this paper, we will demonstrate that the two-dimensional LB film structures exert drastic changes during or after the photoisomerization processes[4].

EXPERIMENTAL

Molecules used in this study are shown in Fig. 1. The monolayers were transferred at 25 mN m^{-1} using a horizontal lifting method on hydrophobized quartz plates for absorption spectroscopic measurements on a Shimadzu UV-265FS spectrophotometer. Photoisomerization of APT in the LB films was monitored by the alternate UV (365 nm) and visible (436 nm) light irradiation. For AFM observations, single-layer LB films were transferred onto mica using a vertical dipping method. The AFM images were taken on a Seiko SPA 300 with an SPI 3700 probe station using noncontact mode at 27 kHz..

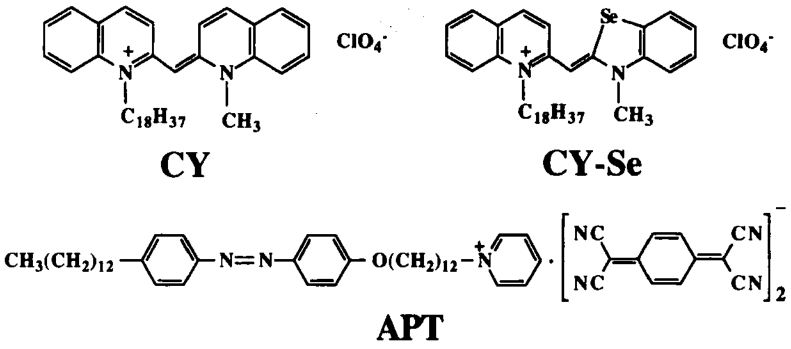

FIGURE 1 Chemical structures of the molecules used in this study.

RESULTS AND DISCUSSION

Spectral Change of CY/APT and CY-Se/APT LB Films

The absorption spectrum of the LB film of CY showed an absorption band due to J-aggregate of CY while absorption bands of a monomer and a dimer appeared in the solution spectrum. Similar features were observed for CY-Se.

This indicates that CY and CY-Se tend to form J-aggregate in a closely packed state of the LB film when the concentration is sufficiently high.

Figure 2A shows a change in the absorption spectrum of a CY/APT 1:1 mixed LB film on alternate illumination with UV and visible light. In the spectrum before illumination, absorption bands due to a monomer, a dimer, and J-aggregate are seen. APT molecules photoisomerized reversibly on the alternate illumination (data not shown). The striking feature is that the J-band becomes more pronounced with increasing number of alternate illumination. The development of the J-band became saturated when a sufficient number of film illumination was done. The results indicate that J-aggregation of CY was induced by the photoisomerization of APT since J-aggregation did not occur when an inert matrix such as octadecanol was used instead of APT.

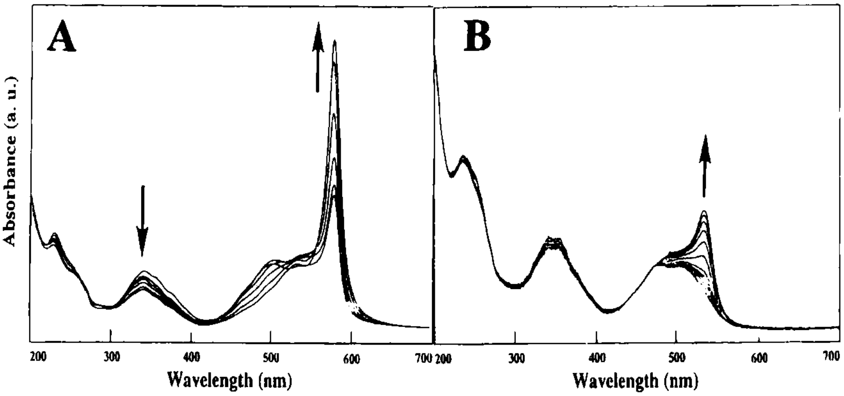

FIGURE 2 (A): Change in absorption spectrum of a CY/APT 1:1 mixed LB film on alternate illumination of UV and visible light. Spectra after every three cycles of film illumination are shown. (B): Change in absorption spectrum of a CY-Se/APT 3:1 mixed LB film measured every hour after three cycles of alternate illumination of UV and visible light.

Figure 2B shows a change in the absorption spectrum of a CY-Se/APT 3:1 mixed LB film measured every hour after three cycles of alternate illumination with UV and visible light. In the spectrum before illumination, absorption bands due to a monomer and a dimer are seen while J-band is missing. Photoisomerization of APT occurred reversibly on the alternate illumination though no development of J-band was observed during the illumination.

However, the J-aggregation proceeded while the film was stored in the dark after the illumination. The development of the J-band became saturated in ca. 12 hours. The alternate illumination is crucial to the development of the J-band since no J-band emerged without the illumination.

Morphological Change of CY/APT and CY-Se/APT LB Films

The J-aggregation process of CY induced by the photoisomerization of APT in the CY/APT mixed LB films was investigated using AFM. Before illumination, the surface undulation of the mixed LB film is a few nanometers.

Figure 3 shows the AFM image of the mixed LB film after three cycles of alternate illumination. The prominent feature is the development of a number of three-dimensional structures. The height of these cones is ca. 10 nm, and the diameter of the base is ca. 100 nm. We claim that the photoisomerization of APT has induced the development of these cones. Most probably, these cones consist of CY molecules since the morphology of a pure LB film of APT did not change significantly by the photoisomerization of APT.

In the saturated state of J-aggregation after sufficient numbers of alternate illumination, the cones are larger than those in Fig. 3: the height of the largest cones is ca. 30 nm and the diameter of the base is ca. 200 nm. The increase in size of the cones with the development of the J-band supports the assumption that these cones are associated with the J-aggregate of CY.

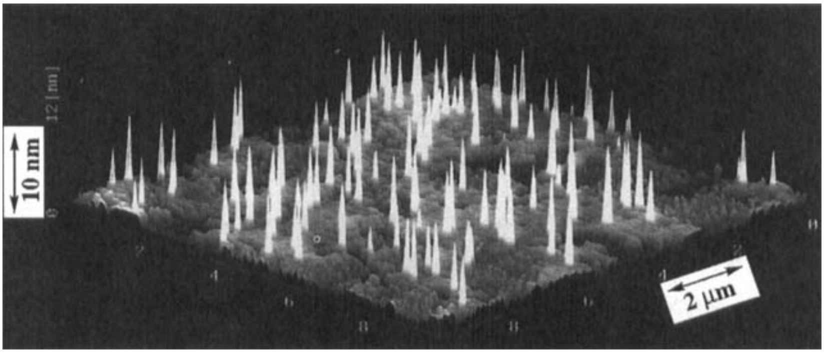

FIGURE 3 AFM image of a CY/APT 1:1 mixed LB film after three cycles of alternate illumination with UV and visible light.

The J-aggregation process of CY-Se in the CY-Se/APT 3:1 mixed LB films was also investigated using AFM. Figure 4 shows the AFM image of the mixed LB film measured in 12 hours after three cycles of alternate illumination. Three-dimensional cones much larger than those in the CY/APT mixed films are observed. Grooves and ridges are the artifacts created by the flattening procedures of the image due to the large size of the cones. The height of the largest cones is ca. 250 nm and the diameter of the base is ca. 2000 nm. These cones should also be related to the J-aggregation of CY-Se in the LB films. The much larger size of the scanned area compared with the CY/APT system indicates that the number of cones is much smaller in the CY-Se/APT system.

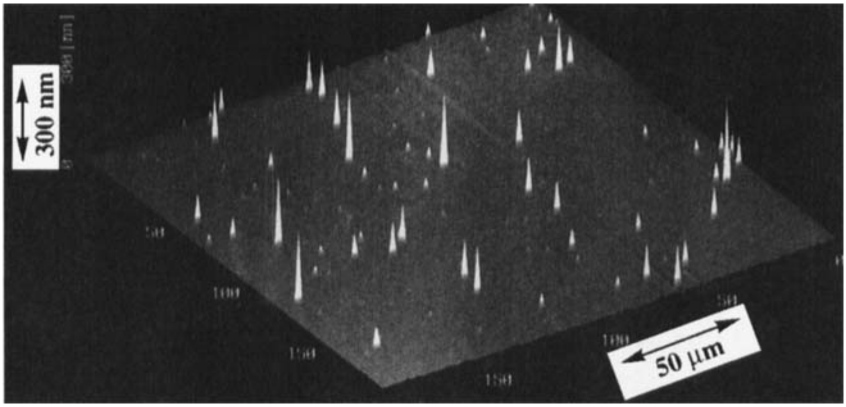

FIGURE 4 AFM image of a CY-Se/APT 3:1 mixed LB film measured in 12 hours after three cycles of alternate illumination with UV and visible light.

Number of Molecules in the Cones in the Mixed LB Films

The number of cyanine molecules in one cone can be obtained by estimating the sizes of the cones and cyanine molecules by assuming that the cones consist solely of cyanine molecules and that the molecules are arranged two-dimensionally in the cones as in typical LB films. The results are summarized in Table I. The sizes of the cones were obtained from the AFM images. The lengths of the molecules were estimated using the CPK models. The cross sections of the molecules were obtained from surface pressure-area isotherms.

The number of molecules in one cone is ca. 10^3 times larger for the CY-Se/APT system compared with the CY/APT system. In the CY/APT system, the J-band grew during the photoisomerization while in the CY-Se/APT system the J-band did not emerge during the photoisomerization and it developed after the illumination. This suggests that time necessary for the J-aggregation is much longer in the CY-Se/APT system. The difference in time for the J-aggregation and that in number of cones may be reflected in the difference in the number of molecules in one cone.

TABLE I Estimation of the number of cyanine molecules in one cone

	CY	CY-Se
Size of the cones		
height	30 nm	250 nm
diameter of the base	200 nm	2000 nm
Size of the molecules		
length	3 nm	3 nm
cross section	0.5 nm^2	0.4 nm^2
Number of molecules in one cone	2×10^5	2×10^8

CONCLUSIONS

This study indicates that the J-aggregation of cyanine molecules is induced by the photoisomerization of azobenzene coexisting in the same LB films. Drastic morphological changes accompanied with the J-aggregation mean that the two-dimensional LB film structures exert substantial modification by the photoisomerization. In this sense, careful investigation should be necessary when dealing with photoisomerization in LB films.

References

[1.] D. G. Whitten, *Angew. Chem. Int. Ed. Engl.*, **18**, 440(1979).
[2.] H. Tachibana and M. Matsumoto, *Adv. Mater.*, **5**, 796(1993).
[3.] H. Tachibana, R. Azumi, M. Tanaka, M. Matsumoto, S. Sako, H. Sakai, M. Abe, and N. Yoshino, *Thin Solid Films*, **284-285**, 73(1996).
[4.] M. Matsumoto, H. Tachibana, F. Sato, and S. Terrettaz, *J. Phys. Chem. B*, **101**, 702(1997).