

Effect of Fabrication Conditions on the Structures and Photoreactions of Langmuir-Blodgett Films of Amphiphilic Spiropyran

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We studied the effect of fabrication conditions on the structures and photoreactions of Langmuir and Langmuir-Blodgett (LB) films of an amphiphilic derivative of spiropyran (SP1822). Pure LB films of SP1822 and mixed LB films of SP1822 and arachidic acid (C20) fabricated at high fabrication temperatures consisted of circular domains with a constant height of 4 nm. UV illumination gave rise to the formation of J-aggregates, accompanied by the development of structures extending radially from the nuclei in the domains. Pure LB films of SP1822 fabricated at low temperatures were comprised of 4-nm-high domains with a considerable amount of voids. On UV illumination, J-aggregation proceeded accompanied with morphological changes. In the mixed LB films of SP1822 and C20 fabricated at low temperatures, the presence of C20 molecules suppressed the diffusion of dye molecules in the films, thereby inhibiting the J-aggregation.

Key words: spiropyran, merocyanine, LB film, J-aggregate, isomerization

1. INTRODUCTION

The Langmuir-Blodgett (LB) technique has been used to fabricate organic ultrathin films with well-defined structures. LB films have been expected to be applied to molecular devices, switches, and memories [1].

Spiropyran (SP) is a representative photochromic molecule. UV illumination of SP causes the photoisomerization of SP into merocyanine (MC), followed by the formation of J-aggregates of MC under appropriate conditions. J-aggregates of dye molecules have been investigated extensively from the viewpoint of the applications to the spectral sensitization, optical storage, and optical switching [2]. J-aggregates in Langmuir and LB films are particularly interesting because of the low-dimensional structures of the films [3-18]. The absorption bands of J-aggregates are red-shifted and very narrow compared to the monomer bands.

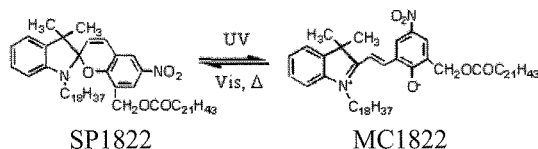


Fig. 1 Structure and photoisomerization of SP1822

Light-induced J-aggregation of SP in LB films was first reported by Ando et al [3]. They fabricated multilayer mixed LB films of SP and octadecane. When the films were irradiated with UV light at room

temperature, isomerization of SP to MC proceeded. UV irradiation of the films at temperatures higher than 35°C gave rise to isomerization followed by J-aggregation of MC. Unuma and Miyata fabricated multilayer mixed LB films of SP and stearic acid [4]. They also observed photoisomerization only on UV irradiation of the films at room temperature and J-aggregation on UV irradiation at temperatures higher than 40°C. The matrix molecules were mixed because the fabrication of pure LB films of SP was difficult.

We have found that the LB transfer of SP1822 is easy at 30°C and that the UV irradiation of the LB film at room temperature induces J-aggregation [10]. AFM observation of a single-layer LB film of SP1822 reveals that the film consists of circular trilayer domains and that J-aggregation of MC1822 is accompanied by large morphological changes of the LB film. The J-aggregates of MC1822 have dendritic structures and grow radially from the nuclei in the domain. On the other hand, when the fabrication temperature was low, the transfer ratio was small and J-aggregation did not proceed [10].

In this study, we report the effect of the fabrication temperature on the structures and photoreactions of the LB films of SP1822. The photoreactions of the LB films of SP1822 were monitored using absorption spectroscopy. The structures of the films were investigated using AFM.

2. EXPERIMENTAL SECTION

All the monolayer experiments were done using a NIMA 632D1D2 trough. Chloroform was used as a spreading solvent. The concentration of SP1822 was 0.1mM, and the molar ratio of SP1822 to C20 was 1 to 2. The solution was spread on an aqueous subphase purified using a Barnstead NANOpure Diamond ($> 18 \text{ M}\Omega \text{ cm}$). The molecules were compressed at a speed of $3.3 \times 10^{-2} \text{ nm}^2 (\text{SP molecule})^{-1} \text{ min}^{-1}$ after 5 min of evaporation time. Single-layer LB films were fabricated using the vertical dipping method at a withdrawal speed of 4 mm min^{-1} onto quartz plates for spectroscopic measurements and onto mica for AFM observations. Transfer pressure was 15 mN m^{-1} . In a previous paper we reported that the transfer ratio was unity at 30°C and very small at 7°C [10]. In this study, the transfer ratio was ca. 0.7 at 7°C . The moderate transfer ratio observed in this study suggests that the LB transfer should be affected largely by a subtle change in the fabrication conditions. UV/vis absorption spectra of LB films were recorded on a JASCO V-560 spectrophotometer. UV illumination of the LB films were performed using $340 \pm 25 \text{ nm}$ light from a Xenon lamp for the measurements of UV/vis spectra and ex situ AFM observations and using 334.2 nm light from a high pressure Hg lamp for in situ AFM observations. In situ and ex situ AFM observations were carried out using a Seiko SPA300 microscope in a non-contact mode using a silicon cantilever with a resonant frequency of 26 kHz and a spring constant of 1.4 Nm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Surface pressure-area isotherms

Figure 2 shows surface pressure-area isotherms of pure SP1822 (A) and a mixture of SP1822 and C20 (B) in the subphase temperature range of $7\text{--}30^\circ\text{C}$. The abscissa shows area per SP1822 molecule. Both of the isotherms depend strongly on the subphase temperature. The isotherms of SP1822 are divided into two regimes: a low-temperature regime at $7\text{--}13^\circ\text{C}$ and a high-temperature regime at $23\text{--}30^\circ\text{C}$. At 17°C the isotherm shows an intermediate behavior. In the low-temperature regime, the surface pressure rises sharply at small area. In the high-temperature regime, the surface pressure rises at larger area and a phase transition occurs at $7\text{--}8 \text{ mN m}^{-1}$. The onset point of the surface pressure in the Langmuir film of pure SP1822 is ca. 0.45 nm^2 in the low-temperature regime and ca. 1 nm^2 in the high-temperature regime. On the other hand, the surface pressure of the mixture rises at ca. 1 nm^2 in the low-temperature regime and at ca. 1.8 nm^2 in the high-temperature regime. C20 is amphiphilic and should occupy some area in the film. Considering that the cross section of C20 is $0.2\text{--}0.25 \text{ nm}^2$, effective area occupied by one SP molecule at the onset point in the mixed film

should be $0.5\text{--}0.6 \text{ nm}^2$ in the low-temperature regime and $1.3\text{--}1.4 \text{ nm}^2$ in the high-temperature regime. These results suggest that the mixing of C20 molecules changes the structure of SP1822 films.

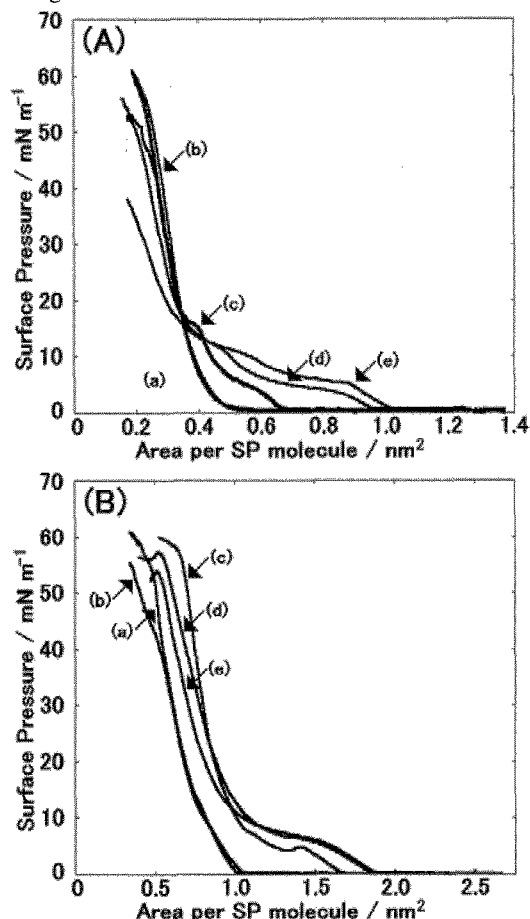


Fig. 2 Surface pressure-area isotherms of SP1822 (A) and a mixture of SP1822 and C20 at a molar ratio of 1 to 2 (B) at subphase temperatures of (a) 7°C , (b) 13°C , (c) 17°C , (d) 23°C , (e) 30°C .

3.2 UV/vis absorption spectra

Figure 3 shows changes in UV/vis absorption spectra of the LB films of pure SP1822 and mixed LB films of SP1822 and C20 fabricated at 30 and 7°C . The broad band centered at ca. 550 nm is assigned to MC1822. In the initial stages of UV irradiation, the absorption of MC1822 increases in all the films, showing the isomerization of SP1822 into MC1822. UV irradiation of the pure LB films fabricated at both temperatures gives rise to red-shifted and narrow absorption bands at ca. 617 nm , indicating the formation of J-aggregates. The intensity of the J-band of a mixed LB film fabricated at 30°C was smaller than that of a pure LB film fabricated at the same temperature, due probably to the difference between the concentrations of SP1822 in the two films.

Light-induced J-aggregation proceeds in a mixed LB film fabricated 30°C (Fig. 3C) whereas UV irradiation of

a mixed LB film fabricated at 7°C gives rise to isomerization only (Fig. 3D). These results indicate that the presence of C20 molecules in the mixed LB films fabricated at low temperatures suppresses the formation of J-aggregates.

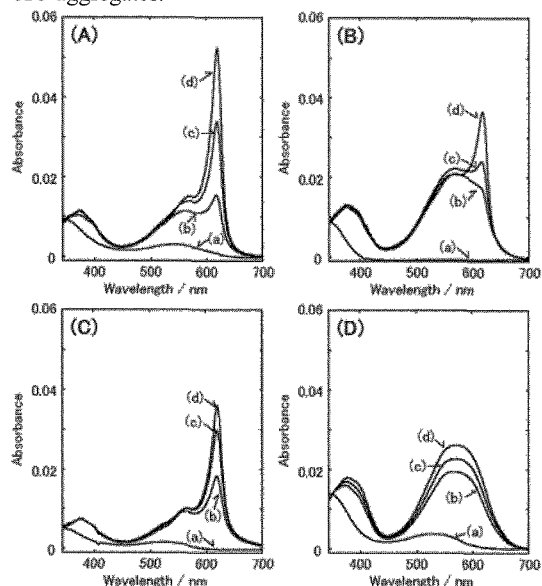


Fig. 3 Change in UV/vis absorption spectrum with UV irradiation at room temperature. (A): pure LB film of SP1822 fabricated at 30°C, (B): pure LB film of SP1822 fabricated at 7°C, (C): mixed LB film of SP1822 and C20 fabricated at 30°C and (D): mixed LB film of SP1822 and C20 fabricated at 7°C (D). UV irradiation times are (a): 0 min, (b): 5 min, (c): 10 min, (d): 30 min.

3.3 AFM observations

Figure 4 shows in situ AFM images of a pure LB film fabricated at 30°C before and after UV irradiation. Before irradiation, the film consists of circular domains with a constant height of ca. 4 nm and with higher structures in the centers of the domains. UV illumination causes a large morphological change. Dendritic structures that are higher than the domain surface by ca. 4 nm develop radially from the higher structures in the centers of the domains. These structures should consist of J-aggregates and are surrounded by grooves [10]. These results indicate that during the J-aggregation MC1822 molecules diffuse on the domains and form dendritic structures, leaving voids around them.

In situ AFM images of a pure LB film fabricated at 7°C before and after UV irradiation are shown in Fig. 5. Before irradiation, continuous domains with a constant height of ca. 4 nm form with a large amount of voids. UV irradiation gives rise to a morphological change very different from that in a pure LB film fabricated at 30°C. In this film, the amount of voids increases with UV irradiation. These results show that the morphological changes during the J-aggregation depend strongly on the fabrication temperature of pure LB films of SP1822.

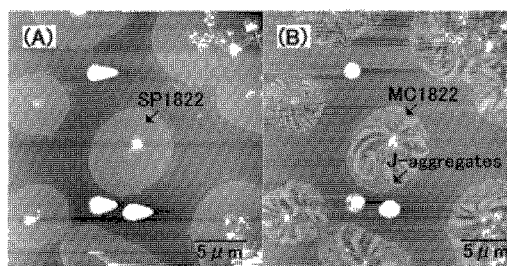


Fig. 4 In situ AFM images of an LB film of SP1822 fabricated at 30°C. (A): before illumination, (B): after UV illumination for 30 min.

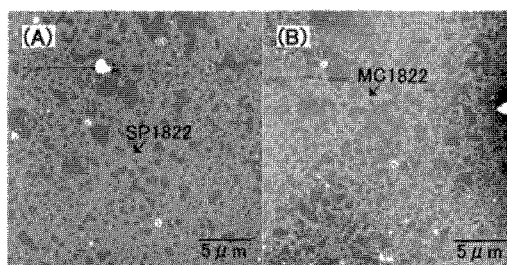


Fig. 5 In situ AFM images of an LB film of SP1822 fabricated at 7°C. (A): before illumination, (B): after UV illumination for 30 min.

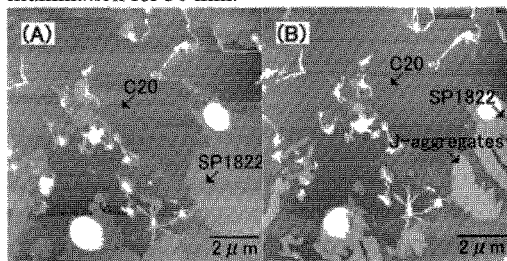


Fig. 6 In situ AFM images of a mixed LB film of SP1822 and C20 fabricated at 30°C. (A): before illumination, (B): after UV illumination for 30 min.

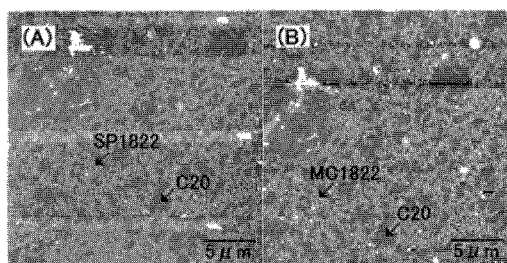


Fig. 7 In situ AFM images of a mixed LB film of SP1822 and C20 fabricated at 7°C. (A): before illumination, (B): after UV illumination for 30 min.

We performed in situ AFM observations of a mixed LB film fabricated at 30°C during the UV irradiation (Fig. 6). The structure of the film is similar to that of a pure LB film fabricated at 30°C in that the LB film has circular domains with a constant height of ca. 4 nm. Differences are that the circular domains are less-defined and that there are structures of undefined shape. UV irradiation causes a morphological change of the domains similar to that of a pure LB film fabricated at the same temperature.

The structures of undefined shape are not subjected to a morphological change during the J-aggregation, suggesting that these structures are a C20-rich phase.

Figure 7 shows in situ AFM images of a mixed LB film fabricated at 7°C before and after UV irradiation. The morphology of this film is similar to that of a pure LB film fabricated at 7°C. Morphological changes do not occur with UV irradiation, which is consistent with the fact that only the isomerization proceeds with UV irradiation. These results suggest that the presence of C20 molecules suppress the diffusion of MC1822 molecules, thereby inhibiting J-aggregation.

4. CONCLUSIONS

This study shows that the structures and the photoreactions of LB films of SP1822 depend strongly on the fabrication temperature. Pure LB films of SP1822 and mixed LB films of SP1822 and C20 consist of circular domains with a constant height of 4 nm at high fabrication temperatures. Light-induced J-aggregation proceeds on UV illumination, accompanied by large morphological changes of the films. Light-induced J-aggregation also occurs in pure LB films of SP1822 fabricated at low temperatures. Morphological changes different from above occurs during the J-aggregation. In mixed LB films of SP1822 and C20 fabricated at low temperatures, the presence of C20 molecules suppresses the diffusion of dye molecules in the films, thereby inhibiting the J-aggregation. Further studies are now in progress to clarify the relationship between the mechanism of light-induced J-aggregation and the structure of the film.

5. REFERENCES

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