Light-Induced J-Aggregation of Merocyanine in Langmuir and Langmuir−Blodgett Films

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The structures and photoreactions of the Langmuir and LB films of an amphiphilic spiropyran, 1′,3′-dihydro-3′,3′-dimethyl-6-nitro-1′-octadecyl-8-(docosanoyloxymethyl)spiro[2H-1-benzopyran-2,2′-(2H)-indole] (SP) are investigated. A chloroform solution of SP at a concentration of 0.1 mM is spread on the water surface. When the Langmuir film of SP is compressed on a subphase at 30 °C and a phase transition takes place, the monolayer changes into a mosaic structure where bilayer domains are buried in the monolayer. When the Langmuir films are illuminated with UV light, SP is isomerized to merocyanine (MC). J-aggregates of MC are formed at high temperatures and at high surface pressures where the bilayer domains are formed. The Langmuir films of SP are transferred as LB films onto solid substrates at 30 °C. The LB films consist of the bilayer domains with a diameter of 10 to 20 μm and a height of 4 to 5 nm. Three-dimensional structures are present in almost all the bilayer domains. Room-temperature illumination of the LB films with UV light produces the J-aggregation of MC with the development of dendritic structures starting from the three-dimensional structures in the domains. These dendrites consist of the J-aggregates. Molecules are aligned radially in the dendrites. When the LB film is illuminated at 7 °C, the J-aggregation of MC does not proceed. All these results indicate that the criteria of the J-aggregation of MC in the Langmuir and LB films are the presence of the bilayer domains and the nucleation sites with the mobility of the molecules large enough for the morphological change necessary for the J-aggregation.

Introduction

J-aggregates of dye molecules have been extensively investigated under various conditions[1−6] from the viewpoint of the application to the spectral sensitization,[7] optical storage,[8,9] and nonlinear optics.[10−12] J-aggregates in Langmuir and Langmuir−Blodgett (LB) films are of considerable interest because the films have well-defined structures with low-dimensional nature.[4,8,9,12−27] When chromophores form J-aggregates and the delocalized excitonic state is formed, the absorption band is red-shifted and very narrow with a small Stokes shift compared to the case in which chromophores are in a monomeric state.

Light-induced J-aggregation[9,18,21−24] and triggered J-aggregation[25−27] of dye molecules is particularly important because modification of the optical properties of selected areas will be possible. The J-aggregates of merocyanine (abbreviated as MC and shown in Figure 1) are formed when multilayer LB films of an amphiphilic spiropyran, 1′,3′-dihydro-3′,3′-dimethyl-6-nitro-1′-octadecyl-8-(docosanoyloxymethyl)spiro[2H-1-benzopyran-2,2′-(2H)-indole] (abbreviated as SP and shown in Figure 1) mixed with matrix molecules are illuminated with UV light at high temperatures, e.g., above 35 °C for the mixed LB films of SP and octadecane and 40 °C for the mixed LB films of SP and stearic acid.[9] UV illumination at room temperature causes
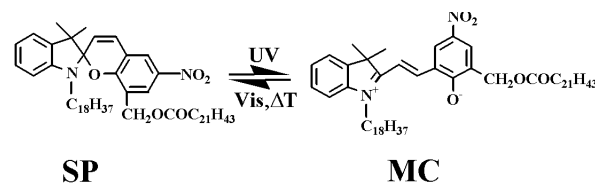

Figure 1. Structure of SP and photoisomerization to MC.

only the isomerization of SP into MC without the formation of the J-aggregates of MC.

We have found that the photoreactions of the LB films of pure SP depend strongly on the concentration of the spreading solution. When the concentration of the spreading solution is 1 mM, room-temperature illumination with UV light gives rise to the isomerization of SP into MC only.[23,24] On the other hand, using the spreading solution at a concentration of 0.1 mM, UV illumination of the LB films of SP at room temperature causes the isomerization of SP into MC, followed by the formation of the J-aggregates of MC.[21] These different behaviors are due probably to the presence or absence of irregularly shaped structures that should serve as nucleation sites for the development of the J-aggregates of MC. However, hardly any information has been given on these irregularly shaped structures. We have also found that the photoisomerization of azobenzene helps the formation of the J-aggregates of MC in the mixed LB films at room temperature.[27]

The formation of the J-aggregates in LB films can be compared to the formation of crystals because dendritic and/or crystalline structures develop with the J-aggregation in many

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cases.[21-23,25-27] Two factors should be considered: nucleation and growth. Nucleation of J-aggregates in the LB films will be related to the defects that are present before the illumination or are formed by the illumination. Growth will be relevant to various factors such as concentration, orientation, and mobility of the molecules that form J-aggregates.

In this paper, we will report on the structures and photoreactions of the Langmuir and LB films of SP. The structures and photoreactions of the Langmuir films are investigated using surface pressure measurements, Brewster Angle Microscope (BAM), and the measurements of reflection spectra. The results indicate that the structures and photoreactions of the Langmuir films depend strongly on the subphase temperature. The structures and photoreactions of the LB films are examined using atomic force microscope (AFM), fluorescence and polarizing microscopes, and the measurements of the absorption spectra at varying temperatures. We will demonstrate that the structure of the film, the nucleation, and the mobility of the molecules play important roles in the J-aggregation of MC.

Experimental Section

Chemicals. Amphiphilic spiropyran SP was purchased from Hayashibara Biochemical Laboratories, Inc., and used as received. Chloroform and toluene were of spectroscopic grade and obtained from Dojindo.

Monolayer Measurements. All the monolayer measurements were done using a NIMA 632D1D2 trough equipped with two moving barriers. The advantage of this trough is that the Langmuir films can be compressed to a very small area, which is important for this study. Chloroform was used as a spreading solvent unless otherwise stated. Solution of SP at a concentration of 1.0×10^{-4} M was spread on an aqueous subphase purified by passing through a milli-Q filter. The molecules were compressed at a speed of 6.6×10^{-2} nm^2 molecule^{-1} min^{-1} after 5 min of evaporation time. The number of the SP molecules spread and the compression speed were kept constant for all the measurements because the surface pressure−area isotherms were sensitive to these factors. The Langmuir film was transferred using the vertical dipping method at a withdrawal speed of 4 mm min^{-1} onto quartz plates for spectroscopic measurements and polarizing and fluorescence microscopic observations, and onto freshly cleaved mica for AFM observations.

Characterization. Reflection spectra of the Langmuir films were measured using an IMUC 700 spectrophotometer (Otsuka Electronics). BAM equipped with a CCD camera and a video recorder was homemade. He−Ne laser at 632.8 nm was used as the monitoring light. UV illumination of the Langmuir films was done at oblique incidence through an optical fiber using a 500-W high-pressure mercury lamp with monochromated radiation at 365 nm. UV/vis absorption spectra were recorded on a Cary 500 Scan (Varian) spectrophotometer. UV illumination of the LB films was carried out at normal incidence using a 500-W high-pressure mercury lamp with monochromated radiation at 365 nm. AFM observations were made using a Seiko SPA300 microscope in a noncontact mode using a silicon tip with a resonant frequency of 28 kHz and a spring constant of 1.9 N m^{-1} unless otherwise stated. In situ AFM observations were performed by illuminating the sample through an optical fiber at oblique incidence. Fluorescence microscopic images were obtained using an Olympus IMT-2 microscope. The samples were excited with green light and the emission at a wavelength more than 590 nm was passed through an Olympus DP12 CCD camera. Polarizing microscopic observations were
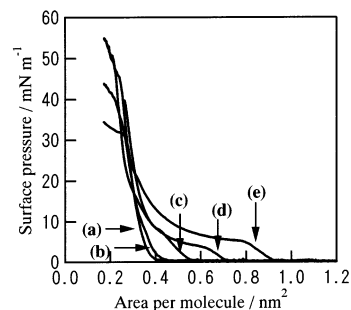

Figure 2. Surface pressure−area isotherms of SP (a) at 7 °C, (b) at 13 °C, (c) at 18 °C, (d) at 23 °C and (e) at 30 °C.
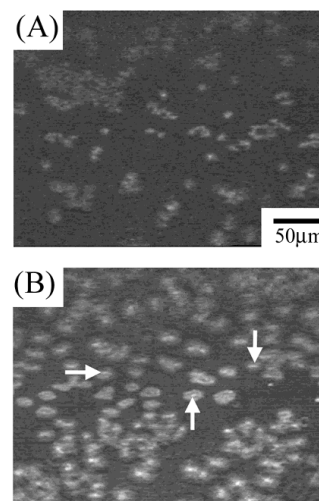

Figure 3. BAM images of the Langmuir films of SP at different surface pressures and different subphase temperatures. (A): at 6 mN m^{-1} at 30 °C, and (B): at 9 mN m^{-1} at 30 °C. Arrows in B indicate some of the brighter regions in the multilayer domains.

performed using a Nikon S-Ke microscope equipped with an Olympus DP12 CCD camera. Photoreaction of the LB film at 7 °C was investigated by keeping the sample at the temperature on a Metter FP82 hot stage equipped with a Metter FP80 temperature controller and a flowing system of evaporating nitrogen gas. The UV illumination was done at normal incidence through an optical fiber.

Results and Discussion

Structure of the Langmuir Film. Figure 2 shows surface pressure−area isotherms of SP on a water surface at varying temperatures. At low temperatures, the isotherms are of condensed type. At higher temperatures, the isotherms become more expanded and a deflection point appears that can be ascribed to phase transition. We used BAM to investigate the structural change of the Langmuir films during compression at varying temperatures (Figure 3). At 30 °C, SP existed as oily domains just after spreading. A continuous film was formed before the compression. Around the phase transition, multilayer domains start to form. The number and the size of the domains increase with compression. This phase transition is characterized as the transition where part of the monolayer is converted to multilayer domains. It is evident that many of the multilayer domains have brighter regions inside. We assume that most of the multilayer domains have brighter regions of this kind and that some of the brighter regions are invisible because of the low resolution of BAM. It is to be noted that the brighter regions in the multilayer domains were formed around the phase transition point.
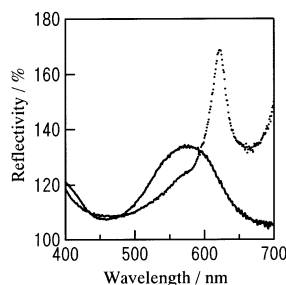
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Figure 4. Reflection spectra of the Langmuir films of SP at 10 mN m^{-1} at photostationary states with UV irradiation. The solid line and the dotted line are the spectra measured at 7 °C and at 30 °C, respectively.

When the film was compressed to more than 20 mN m^{-1}, the reflection from the inter-domain regions became larger until the inter-domain regions were brighter than the domains. The reflection from the domains did not change significantly. This shows that the monolayer (inter-domain) regions started to be collapsed around 20 mN m^{-1} and that the thickness of these regions became larger than that of the domains with compression.

On the other hand, distinct domains were formed on the water subphase at 7 °C. With compression, these domains merged and a continuous film was formed around the onset point of the surface pressure. Isobar measurements were made to investigate whether these domains were monolayers or multilayers. The Langmuir film was formed at 3 mN m^{-1} at 7 °C and the subphase temperature was raised slowly. Around 18 °C, less bright regions appeared inside the continuous film and the molecular area started to increase. These less bright regions spread more with increasing subphase temperature, until the whole film consisted of these less bright regions. The continuous film formed at 7 °C should be most probably bilayers. This is consistent with the small area for the onset of the surface pressure at 7 °C. These results indicate that the structure of the Langmuir films depends strongly on the subphase temperature. This suggests that the arrangement and orientation of the molecules in the Langmuir films also varies with temperature.

Photoreactions of the Langmuir Films. We investigated the photoreactions of the Langmuir films to examine if the changes in the structure and the temperature of the Langmuir films affect the photoreactions. Figure 4 shows the reflection spectra of the Langmuir films of SP after UV irradiation. We selected two different temperatures at the same surface pressure. At 7 °C photoisomerization of SP to MC was observed, while J-aggregates of MC were formed at 30 °C with an absorption band at ca. 620 nm. The peak position coincides with the ones reported in the literature.[9,26] Considering that these films have almost the same molecular density, the photoreactions of the Langmuir films depend strongly on the subphase temperature. The line width of the J-band is ca. 25 nm. The Langmuir films were irradiated at different temperatures and at different surface pressures. It was found that J-aggregation was favored at high temperatures and at high surface pressures. This region almost coincided with the one where multilayer domains are formed in the Langmuir films. These results suggest that the J-aggregation of MC proceeds in the multilayer domains and not in the monolayer region. However, we should also consider the effect of the subphase temperature on which the mobility of molecules depends.

BAM was used to monitor the structural change of the Langmuir films during the photoreactions (Figure 5). When the film was illuminated with UV light at 30 °C at 10 mN m^{-1}, the
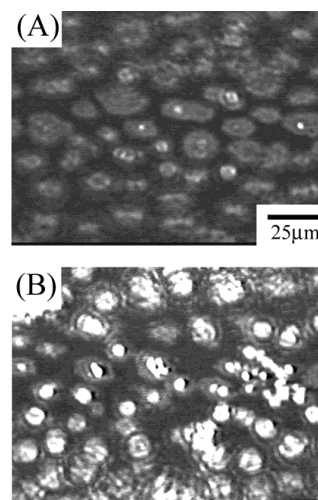

Figure 5. Change in the BAM image of the Langmuir film of SP at 10 mN m^{-1} at 30 °C with UV illumination for (A): 5 min, and (B): 10 min.

reflection from the brighter regions in the domains started to increase and the size of the brighter regions increased. This should be due to the J-aggregates of MC that started to develop from the brighter regions in the domains. Such a change was not observed in the monolayer regions. The whole domains also became brighter with the UV illumination but to a much lesser extent. This is ascribed to isomerization of SP to MC. When the film was illuminated with UV light at 7 °C at 10 mN m^{-1}, the reflection from the whole Langmuir film increased due to isomerization of SP to MC. Prolonged illumination for 2 h did not cause any significant change in the results of BAM observations. This is consistent with the spectral change of the Langmuir film where the J-aggregation of MC did not proceed under these conditions.

Structure of the LB Films. The transfer of the Langmuir film of SP was successful when the subphase temperature was 30 °C. The transfer ratio was significantly smaller than unity at lower temperatures. The AFM image of a single-layer LB film of SP shows that the films consist of multilayer domains with a diameter of 10 to 20 μm and a height of 4 to 5 nm (Figure 6A). When we scanned the film surface using AFM in the contact mode with a larger stylus force than in the usual observations, we could remove the domains with the inter-domain region intact. This shows that the LB film consists of bilayer domains that are separately positioned on the solid substrate. The multilayer domains observed in the BAM images of the Langmuir films have similar size and should have a bilayer structure. The monolayer region that exists between the bilayer domains in the Langmuir films should fail to be transferred onto the solid substrates considering that the Langmuir monolayer films that form at low surface pressures at 30 °C were not readily transferred on the substrates. The possibility that the monolayer region is converted into the bilayer domains during the transfer seems less probable.

Three-dimensional structures of a typical height of several tens of nanometers are evident in most of the domains. These structures should be the same ones that were observed in the bilayer domains in the Langmuir films using BAM. Dark images without any significant structures were observed using fluorescence microscopy, indicating that the domains and the three-dimensional structures in the domains are indistinguishable from the solid substrates with respect to the emission. Fluorescence microscopic observations also yielded dark images, indicating that the molecular arrangement in the domains and the three-
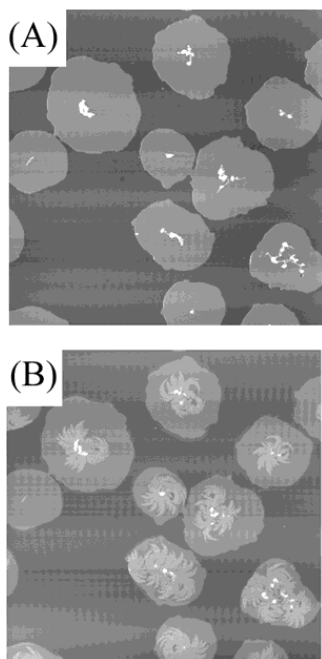
Figure 6. Change in the AFM image of the LB film of SP transferred at 10 mN m^{-1} at 30 °C with UV illumination. (A): before illumination, (B): after UV illumination for 240 min. The size of the images is 70 μm × 70μm.

Figure 7. Change in the absorption spectrum of the LB films of SP with UV illumination at 23 °C.

dimensional structures was not like that in single crystals or in liquid crystals. These three-dimensional structures are formed in the Langmuir films around the phase transition point as shown in the BAM observations. When the concentration of the spreading solution was 10 times higher (1.0 × 10^{-3} M), these three-dimensional structures were not observed.[23,24] When the spreading solvent was toluene and the concentration of the spreading solution was 1.0 × 10^{-4} M, similar three-dimensional structures were observed in the domains. These results suggest that the mechanism of the formation of these three-dimensional structures will be different from the usual crystallization process because these structures are formed when the concentration of the spreading solution is low. The fact that changing the solvent did not cause any significant change suggests that these structures are not influenced by the impurities in the spreading solvent as reported for the Langmuir films of DPPC.[28] All the above results strongly suggest that these structures should be some kind of assemblies of SP. The embryos of these structures should be formed during the evaporation of the organic solvent after the spreading of SP on the water surface. The formation of these embryos depended strongly on the concentration of the spreading solution, suggesting that dynamic processes played important roles in the nucleation process. These embryos that are invisible in the initial regime of compression grow with compression and become visible using BAM around the phase transition point.

Photoreactions of the LB Films. The photoreaction of a single-layer LB film of SP was examined. When the film was illuminated at 23 °C, the J-aggregation of MC proceeded, which was clearly seen by the development of an absorption band at ca. 620 nm with a line width of 12 nm (Figure 7). The line width is small compared to that of the J-aggregates in the Langmuir films while the peak position is almost the same. Similar phenomena were reported for the Langmuir films of a different merocyanine (spiropyran) derivative.[18] If we assume that there are different types of J-aggregates in the Langmuir and the LB films in terms of excitonic delocalization, the
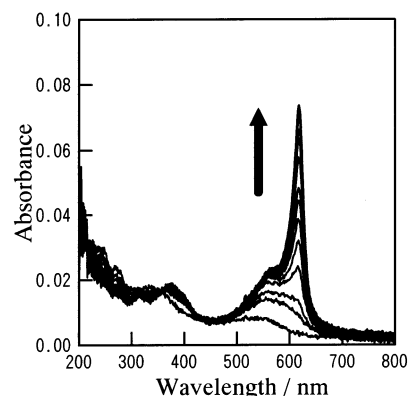
distribution in the Langmuir films should be much larger than that in the LB films.

In situ AFM images before and after the UV illumination are shown in Figure 6. When the J-aggregates of MC are formed, dendritic structures develop from the three-dimensional structures on the domains. These dendritic structures are assigned to the J-aggregates of MC. Similar structures were ascribed to the J-aggregates of MC in the mixed LB films of MC and an azobenzene derivative.[27] When the LB film was fabricated from the spreading solution at a concentration of 1.0 × 10^{-3} M, no J-aggregation was detected by the absorption spectroscopy and no morphological change was observed by room-temperature illumination. These results indicate that the three-dimensional structures should serve as nucleation sites for the J-aggregates of MC and strongly suggest that the J-aggregation of MC should not proceed without the nucleation sites as long as single-layer LB films are illuminated with UV light at room temperature. We have reported that the J-aggregates of MC are formed in the mixed LB films of SP and an azobenzene derivative by the alternate illumination with UV and visible light.[27] The present results suggest that one of the roles played by the azobenzene is to create nucleation sites using photoisomerization of azobenzene. When the Langmuir film at 10 mN m^{-1} at 30 °C was illuminated with UV light for 2 h and was transferred on a solid substrate as LB film, dendritic structures were also observed that started from the three-dimensional structures though the domains had irregular shapes due probably to the incomplete transfer of the Langmuir films after J-aggregation. These results together with the BAM observations that the J-aggregates developed from the nucleation sites in the Langmuir film indicate that the J-aggregation in the Langmuir film gives rise to morphological changes that are similar to those of the LB films.

Figure 8 shows the fluorescence and polarizing microscopic images of the LB films after UV illumination for 2 h. Strong emission is evident due to the J-aggregates of MC in Figure 8A. By changing the contrast, the whole domains were visible, indicating the presence of MC in the domains. Polarizing microscopic observations reveal the Maltese crosses for the domains although in many cases a few crosses are seen in individual domains. This shows that the molecules are aligned radially starting from the nucleation sites. These results indicate that each dendritic structure consists of a number of small crystallites of J-aggregates.

When a single-layer LB film of SP was illuminated with UV light at 7 °C, only the photoisomerization of SP to MC was observed. Because this LB film was fabricated under the same conditions with the above LB films, the LB film should have
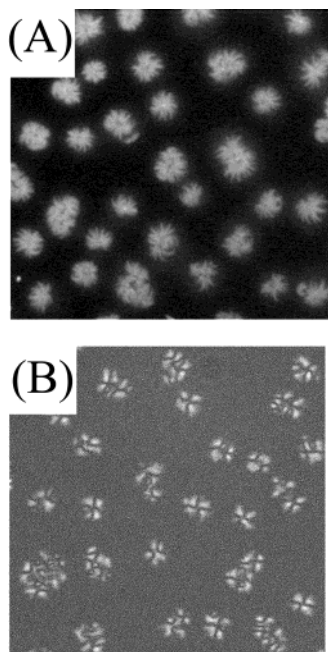
Figure 8. Fluorescence (A) and polarizing (B) microscopic images of the LB film of SP after UV illumination for 2 h. The size of the images is 100 μm $\times$ 100μm.

essentially the same structure with the above in terms of the domain formation and the nucleation sites in the domains. These results indicate that the mobility of the molecules that depends on the illumination temperature and not on the fabrication temperature plays an important role in the J-aggregation of MC. This is consistent with the large morphological change accompanied by the J-aggregation because diffusion of the molecules is involved in the J-aggregation. The present results cannot be compared directly with the previously reported J-aggregation of MC in multilayer LB films mixed with matrix on illumination at high temperatures[9] because of the differences in the fabrication conditions such as the layer number and the concentration of the spreading solution. These factors will significantly influence the structures of the LB films especially in terms of the nucleation sites. Furthermore, the rising of the temperature of the LB films up to 35 °C or 40 °C may considerably change the structures of the films, whereas the lowering of the temperature of the LB films down to 7 °C will not change the structures of the films significantly. In that sense, the structure of a single-layer LB film of SP without the three-dimensional structures in the domains should be considerably changed with possible formation of nucleation sites by heating at 50 °C, which should facilitate the J-aggregation of MC when the film is illuminated at this high temperature.[23]

Conclusions

We have investigated the structures and photoreactions of the Langmuir and LB films of SP. The J-aggregation of MC proceeds in the Langmuir films when bilayer domains are present at high temperatures. UV illumination of the LB films gives rise to the development of the J-aggregates of MC when the nucleation sites are present in the domains and the mobility of the molecules is sufficiently large. All these results indicate that the criteria of the J-aggregation of MC in the Langmuir and LB films are the presence of the bilayer domains and the

nucleation sites with the mobility of the molecules large enough for the morphological change necessary for the J-aggregation.

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