J-aggregate Formation in Single-Layer Amphiphilic Spiropyran Langmuir–Blodgett Films

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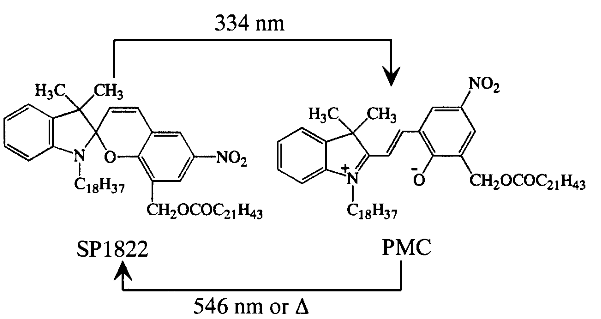
J-aggregate formation was observed in single-layer Langmuir–Blodgett films of an amphiphilic spiropyran when they were irradiated with UV light at room temperature. We have revealed that tree-like structures with many branches are formed, accompanying the J-aggregate formation, which consist of a number of crystalline J-aggregates.

It is well known that a variety of dyes, such as cyanine and merocyanine, form J-aggregates in solution, thin films, and Langmuir–Blodgett (LB) films.[1,2] The J-aggregates exhibit unique properties, such as photoluminescence, liquid crystal properties,[3] and optical nonlinearities.[4,5] Furthermore, their sharp absorption bands enable us to envisage the possibility of recording and storage of optical information.[6] Recently, the morphology of the J-aggregates has been investigated by utilizing scanning probe microscope (SPM) techniques, such as atomic force microscopy (AFM)[7,8] and near-field scanning optical microscopy (SNOM).[9] We have also demonstrated that three-dimensional structures appear, accompanied with J-aggregate formation, by *cis–trans* photoisomerization of azobenzene in the LB films mixed with cyanine[10,11] and with spiropyran.[12] In this letter, we report J-aggregate formation in single-layer LB films of SP1822 (1',3'-dihydro-3',3'-dimethyl-6-nitro-1'-octadecyl-8-(docosanoyloxymethyl)spiro[2*H*-1-benzopyran-2,2'-(2*H*)-indole]) without a matrix on irradiation with UV light at room temperature (23 °C).



Scheme 1. The chemical structure of SP1822 used in this study and the photochromic reaction.

SP1822 (Nippon Kankoh-Shikiso Kenkyusho Co., Ltd.) was used as received, without any further purification (Scheme 1). A Lauda Film Balance was used for the monolayer formation and the deposition. A chloroform solution of SP1822 (1×10^{-4} M) was spread onto pure water at 30 °C, and the monolayer was transferred at 10 mN m^{-1} onto solid substrates by the vertical dipping method.

Figure 1 shows the UV–visible spectral change of single-layer SP1822 LB films on irradiation with monochromatic UV light (334 nm) at 23 °C. On irradiation with UV light, a broad absorption is observed around 560 nm, which is assigned to open colored photomerocyanine (PMC) in the monomeric form (Scheme 1).[13] On prolonged irradiation, the absorption band shifts to 620 nm. In addition, the spectral profile, which featured broad structures, changes into a sharper format, accompanied by an increase in intensity, due to J-aggregate formation of the PMC. In the inset of Figure 1, the intensity of the J-band at 620 nm is plotted as a function of irradiation time. The J-band absorbance became constant when UV light was applied for more than a few hundred minutes. A similar J-aggregate formation has been reported in a 6-layer LB film of SP1822 mixed with octadecane when irradiated with UV light, though not at room temperature but at a temperature of more than 35 °C.[13]

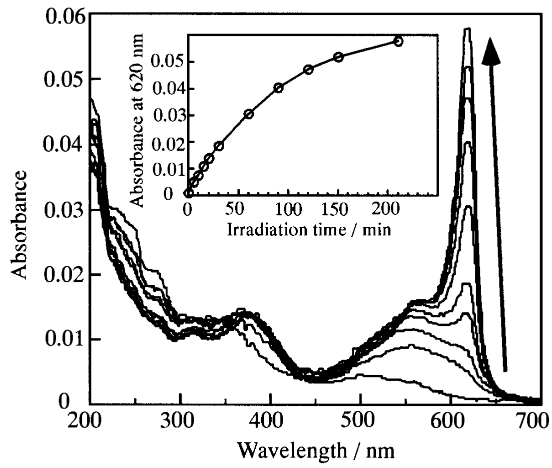


Figure 1. UV-visible spectral changes of single-layer SP1822 LB films on irradiation with UV light (334 nm). The inset represents the change in absorption at 620 nm as a function of irradiation time.

To clarify the J-aggregate formation in the single-layer SP1822 LB film at room temperature, the morphology before and after irradiation was investigated by measurement with a non-contact mode AFM. The AFM images before irradiation (Figure 2(a)) show many large circular domains with a diameter of 10–20 μm and a height of 4–5 nm. Considering that the molecular length estimated from the CPK model is 2.5 nm, the circular domains probably consist of bilayers. Furthermore, irregularly shaped structures are observed in the center of most of the domains.

As clearly seen in Figure 2(b), the morphology changes markedly accompanying the J-aggregate formation on irradiation with UV light. Tree-like structures with many branches are observed on the surface of most of the domains. From the cross-section analysis of the height image, the structures accompany the lower regions side by side. The height difference between the highest regions and the lower ones is 8–10 nm, which corresponds to twice that of the circular domains

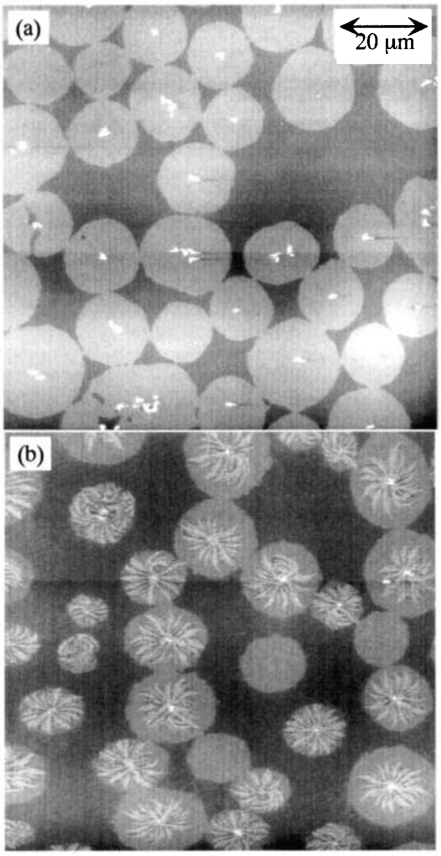


Figure 2. AFM image (100 μm x 100 μm) of single-layer SP1822 LB films (a) before irradiation and (b) after reaching the saturated state of J-aggregate formation on irradiation with UV light.

before irradiation. From these results we conclude that the UV irradiation induces the PMC, leading to J-aggregate formation, thereby resulting in tree-like structures by the migration and diffusion of the J-aggregates.

The tree-like structures were characterized by measurements made using various optical microscopes. Figures 3(a) and (b) show images made by fluorescence and polarized optical microscopes respectively, in single-layer SP1822 LB films after they have reached a saturated state of J-aggregate formation. The sample was illuminated with 546-nm light and emitted wavelengths longer than 590 nm were passed to an intensified CCD camera to capture the fluorescence image. Images from fluorescence microscopy reveal that the LB films fluoresce strongly in the red, the source of which is localized within the tree-like patterned region. Since such an intense fluorescence is observed at nearly the same wavelengths relative to the absorption peak due to the J-aggregates, with minimal Stokes shift, we consider that the tree-like structures observed in the topographic AFM images correspond to the J-aggregates. The images obtained by polarized optical microscopy under crossed polarized light show up as Maltese crosses. Their diameter is the same as those of the tree-like structures observed in the AFM images. It is known that the size of J-aggregates in which excitation can migrate without being trapped by defects is less than a few tens of nm.[9] Thus, the tree-like structures consist of a number of crystalline J-aggregates.

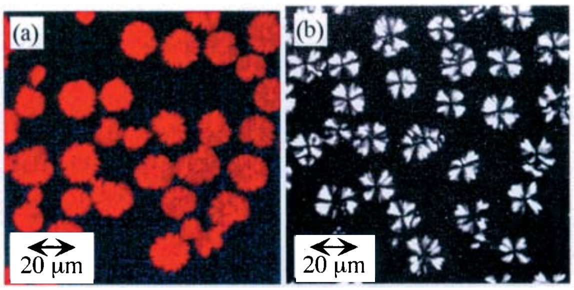


Figure 3. Fluorescence microscopy image (a) and polarized light microscopy image in crossed polarized light (b) of single-layer SP1822 LB films at saturated state of J-aggregate formation.

When following the morphological changes accompanying the J-aggregate formation under irradiation with UV light by in situ AFM measurements, we observe that the tree-like structures begin to spread from the irregularly shaped structures in the center of the circular domains and become larger with J-aggregate formation. Furthermore, when comparing both AFM images before and after irradiation in detail, the morphology of the circular domains without the irregular structures on the surface remain unchanged during irradiation, though the SP1822 molecules isomerize to PMC. In fact, when single-layer LB films were fabricated by using SP1822 solution at a concentration of 1×10^{-3} M, the same circular domains were observed but without the irregularly shaped structures on the surface. Formation of J-aggregates of PMC was not induced on irradiation with UV light at room temperature. From these results, the irregularly shaped structures appear to assist significantly in the initial formation and growth of the J-aggregates, resulting in the initiation the J-aggregate formation at room temperature. This is consistent with the results of the previous study.[12,13] Since none of the irregularly shaped structures have been observed on the surface of the circular domains in mixed SP1822 LB films with the matrix,[12] external stimuli such as heat[13] and morphological change[12] are necessary for the J-aggregate formation of PMC.

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