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# J-aggregate formation of dyes in Langmuir–Blodgett films

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## Abstract

J-aggregate formation of dyes in the Langmuir–Blodgett (LB) films was examined. UV illumination of a single-layer LB film of an amphiphilic spiropyran caused the photoisomerization of spiropyran into merocyanine, followed by the formation of J-aggregates of merocyanine. A large morphological change accompanied the J-aggregation. Alternate illumination of mixed LB films of dyes and azobenzene triggered the formation of J-aggregates of dyes in the films irrespective of whether the dyes were photochromic or not. The J-aggregation of this type was also accompanied by large morphological changes.

*Keywords:* LB films; J-aggregate; Cyanine; Merocyanine; Azobenzene

## 1. Introduction

Langmuir–Blodgett (LB) films are formed by transferring spread films at the air–water interface onto solid substrates. LB films have well-defined structures with reduced dimensionality. Researches have been conducted not only for the basic understanding of the film-forming processes, the film structures and physical properties of the films but also for the formation of nanostructured materials that have potential applications to molecular devices and other functionalized materials [1–6]. The incorporation of photoactive moieties in the films is particularly important since the photoreactions provide mechanisms for the modification of the structures and physical properties of the LB films, acting as triggers to control the functions of the films. Photoreactions will depend strongly on the film structures and molecular packing. The well-defined structures and the reduced dimensionality of the LB films give special features to the photoreactions in LB films. Further, the ordered structures will enable us to detect a subtle change in the structures, if any, accompanied by the photoreactions.

Molecular aggregates have been attracting considerable attention due to their relevance to the light-harvesting and primary charge separation steps in photosynthesis. In particular, J-aggregate formation of dye molecules has been investigated under various conditions [5–26]. Interest in J-aggregates stems originally from the spectral sensitization. Recent development in the research on J-aggregates derives from the expectations that J-aggregates will be used as materials for optical storage and ultrafast optical switching.

The formation of J-aggregates can be compared to the formation of single crystals. Two factors should be considered: nucleation and growth. Nucleation of J-aggregates in the photochromic 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. The J-aggregate formation can be monitored easily by the spectroscopic measurements. When chromophores form J-aggregates and 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.

In this paper light-induced J-aggregation and triggered J-aggregation of dyes in the LB films are discussed with a special emphasis on the structural changes of the LB films accompanied by the photoreactions.

## 2. Light-induced J-aggregation of merocyanine

Light-induced J-aggregation of dye molecules is particularly important because modification of the optical properties of selected areas is possible [12,14,27–30]. J-aggregate formation of MC (see Fig. 1 for the chemical structure) was investigated using matrix molecules because the transfer of

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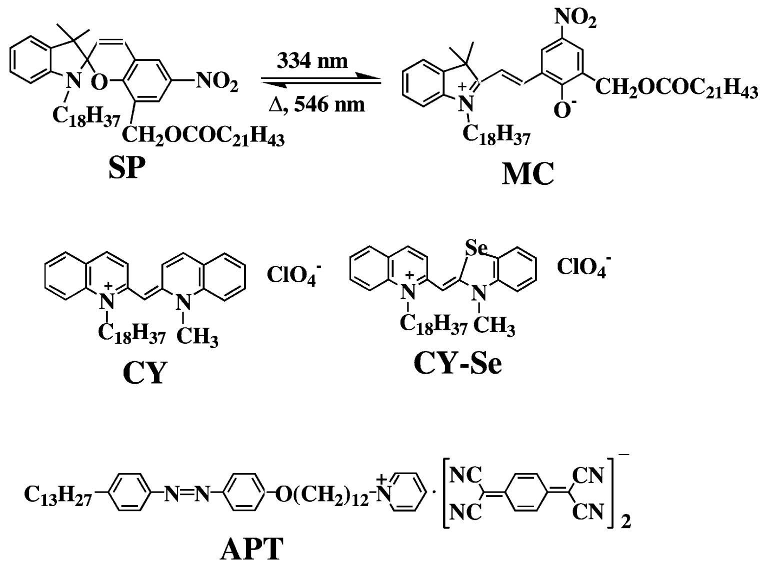

Fig. 1. Molecules used in this study.

the spread films of MC alone to solid substrates was not easy at room temperature [12,14]. The LB films of MC were formed in a two-step process. First, mixed solution of SP and matrix was spread on the water surface, followed by compression of the films and transfer of the compressed films on the solid substrates. Then the LB films were illuminated with UV light to convert SP into MC. The illumination at room temperature gave rise to photoisomerization of SP into MC. However, when the films were illuminated at higher temperatures, e.g., above 35 °C for the mixed LB films of SP and octadecane [12] and 40 °C for the mixed LB films of SP and stearic acid [14], J-aggregates of MC were formed.

The transfer of the spread film of SP alone became easy when the subphase temperature was 30 °C [27–30]. When the LB film thus prepared was illuminated with UV light at room temperature, SP was isomerized to MC, followed by the formation of J-aggregates of MC. This is in contrast to the fact that the illumination at higher temperatures was necessary for the J-aggregation of MC in the mixed LB films [12,14]. This may be caused by the difference in the experimental conditions of the film fabrication, which may affect the nucleation process of J-aggregation.

The morphological change of the film accompanied by the illumination was monitored using AFM. In situ AFM is particularly suitable for this type of measurements since the local morphological change can be monitored. Before illumination, the film consisted of circular domains with a diameter of 10–20 μm and most of the domains possessed defect regions inside. The UV illumination caused a drastic change in the morphology of the film. Hills and valleys were formed starting from the defect regions in the domains and extending to the rims of the domains until the circular domains were converted to dendritic structures. This morphological change is reminiscent of some crystallization or aggregation phenomenon. In molecular layers, fractal-like structure growth has already been observed in the formation of crystalline domains in phospholipids at the air–water interface [31,32]. The so-called diffusion-limited aggregation model has been used to describe these multibranched shapes [33].

## 3. Triggered J-aggregation of dyes

Photoisomerization of chromophores in proteins is associated with the biological activities of living creatures. Photoisomerization of retinal chromophores in rhodopsins and in bacteriorhodopsins results in nerve impulses and proton pumping across the membrane, respectively [34]. It should be noted that the structural change of the proteins triggered by the photoisomerization is a key process for the biological activities. This gives us examples of information processing utilizing photoisomerization as a trigger. Photoisomerization has been investigated extensively in spread films and LB films [35–55]. The configurational change of the azobenzene has been used to control the electrical conductivity of the films [38–42] and the orientation of liquid crystal molecules lying on the films [43,44]. These examples demonstrate that the photoisomerization in the LB films can be considered as a trigger.

Triggering J-aggregate formation of dye molecules is an interesting subject since that methodology also provides us with a means to modify the optical properties of selected regions. The important point is that this methodology is applicable to the systems where the dye molecules that form J-aggregates are non-photochromic. When azobenzene molecules are mixed at the molecular level with the chromophores that tend to form J-aggregates, the formation of the J-aggregates will be suppressed to some extent in the mixed LB films. Photoisomerization of azobenzene will serve as

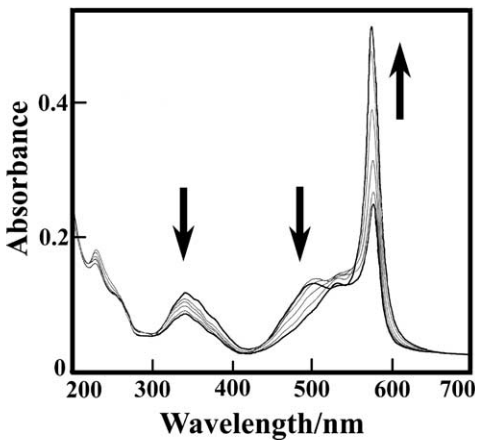

Fig. 2. Change in absorption spectrum of the mixed LB films of CY and APT with alternate UV/visible illumination. The spectra taken after every three cycles of illumination are shown. The spectrum before the illumination and the one after the final illumination are shown in bold.

an external stimulus that triggers the J-aggregate formation of the chromophores.

APT was used as a photoisomerizing trigger because this molecule photoisomerizes reversibly in the LB films. Mixed LB films of CY/APT, CY-Se/APT or SP/APT were fabricated and then the photoirradiation was carried out [56–59]. The criterion of the selection of CY, CY-Se, and MC (SP) is that these molecules can form J-aggregates in single-component LB films.

First, a non-photochromic dye/azobenzene mixed system was examined. Mixed LB films of CY and APT (molar ratio = 1/1) were fabricated and illuminated alternately with UV and visible light [56]. Change in absorption spectrum of the mixed LB films with illumination is shown in Fig. 2. Before irradiation, an absorption band is seen at ca. 580 nm due to J-aggregates of CY. This band is accompanied by two broad absorption bands ranging from 500 to 550 nm, each assigned to a dimer and a monomer of CY, respectively. The absorption band due to *trans* APT is evident at 340 nm. APT isomerizes almost reversibly in the LB films on alternate irradiation with UV and visible light. The important feature is that the J-band grows with this photoisomerization until it comes to a saturated state after a sufficient number of irradiation cycles.

The morphology of the CY/APT LB films was investigated using AFM. Before irradiation, the surface roughness was a few nanometers, showing that this film was two-dimensional. Photoirradiation changed the morphology of the film drastically. The most striking feature was the development of a number of cone-shaped structures in contrast to the dendrites for the LB films of SP (MC). The height of these structures was ca. 10 nm, and the diameter of the base was ca. 100 nm. The photoisomerization of APT is considered to induce the formation of these three-dimensional structures that should be closely associated with the J-aggregate formation. In this sense, the morphological change observed in the mixed LB films should have a different mechanism compared to the case where a reversible morphological change was observed with photoisomerization of azobenzene [52]. After a sufficient number of alternate irradiation cycles were applied, J-aggregate formation came to a saturated state. In the saturated state, the three-dimensional cone-shaped structures were larger and, for large cones, the height was ca. 30 nm and the diameter of the base ca. 200 nm. This suggests that the cone-shaped structures consisted of J-aggregates of CY.

Photoirradiation should play an important role in the J-aggregate formation since keeping the as-deposited mixed LB film in the dark caused no J-aggregate formation. The presence of APT was critical since no J-aggregate formation of CY was induced by the photoirradiation of mixed LB films when an inert matrix such as octadecanol was used. Hence, the configurational change of APT is considered to serve as a trigger to induce the self-organization of CY, promoting the J-aggregation of CY in the LB films. Light-induced J-aggregation was also observed for the mixed LB films of CY-Se/APT = 3/1 [57,58]. The morphology of the film also changed drastically with the J-aggregation.

The overall picture of light-induced J-aggregation of non-photochromic dye/azobenzene mixed systems is that molecules that are forced to mix with each other in an as-deposited state are driven to self-organize by the stimulus produced by the photoisomerization of APT. The prominent feature of this self-organization process is that CY or CY-Se, which forms three-dimensional structures, does not photoisomerize. The energy necessary for this self-organization should be provided by APT molecules and by thermal processes. The results indicate that the triggered J-aggregate formation of this type is a general process and is not specific to the CY/APT and CY-Se/APT systems. This self-organization method should be applied to other systems as well. Another important point is that the two-dimensional LB film structures exert substantial modification by the photoisomerization. The J-aggregate formation in the present systems is not reversible. This should be due to the fact that the three-dimensional systems are thermodynamically more stable than the two-dimensional systems. Furthermore, it is not assumed that each cone should have a crystalline structure or that a single J-aggregate in terms of electronic interaction should correspond to each cone. It is probable that each cone consists of a number of J-aggregates of the dyes.

Second, a photochromic dye/azobenzene mixed system, mixed LB films of SP and APT, was studied. This system is more complicated than the previous systems since the dye molecules that form J-aggregates can also photoisomerize. The mixed LB films of SP/APT (mixing ratio = 1/1) were fabricated first, and then the films were illuminated with UV light to convert SP to MC [59]. This illumination also photoisomerized *trans* APT into *cis* APT. Then the films were illuminated alternately with visible and UV light. Before illumination, three absorption bands of SP and *trans* APT

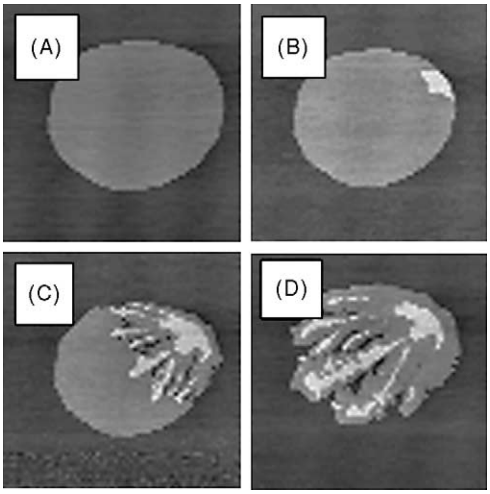

Fig. 3. AFM images of a single-layer SP/APT LB film before and after alternate illumination: (A) before illumination; (B) after the first visible illumination; (C) after the second UV illumination; (D) after the third visible illumination. The images after the first UV illumination (between A and B), after the second visible illumination (between C and D) and after the third UV illumination (between C and D) are not shown. Area: 5 μm × 5 μm.

were observed. After the first illumination with UV light, absorption bands of MC were observed at 380 and 600 nm with a concomitant decrease of the SP absorption bands. The isomerization of *trans* APT to *cis* APT also occurred. The following illumination with visible and UV light alternately caused reversible *cis–trans* isomerization of APT, which was accompanied by a quick increase in the J-band of MC at 618 nm.

The morphological change of the film accompanied by the illumination was monitored using in situ AFM. Fig. 3 shows the AFM image of one of the domains and subsequent changes in the image with alternate illumination for a single-layer SP/APT LB film. The image shows a large circular domain above a homogeneous phase (Fig. 3(A)). Because the height difference between the two main phases is 3.5 ± 1.0 nm, these circular domains should be bilayers. These bilayer domains are found to be SP-rich phases. When this film is illuminated with UV light, the morphology does not change significantly. However, the succeeding alternate illumination produces a roughening effect of the circular domains. Nucleation starts near the edge of the domain is shown in Fig. 3(B). After further illumination, hills and valleys are visible (Fig. 3(C) and (D)). On increased number of alternate irradiation, this roughening increases within the bilayer structure until the affected domain takes fractal-like shape. Considering that similar morphological change accompanied the J-aggregation in single-component LB films of SP by UV illumination, the roughening process should be related to the irreversible J-aggregate formation of MC.

It is important to compare the results of SP/APT LB films with those of the LB films of SP. In the LB films of SP alone, UV illumination gave rise to J-aggregate formation of MC with a morphological change starting from the defect regions that were present in the multilayer domains before the illumination. Alternate illumination of SP/APT LB films with UV and visible light also caused the J-aggregate formation of MC with a sudden appearance of nucleation points on the bilayer domains followed by the growth of dendritic structures from the nucleation points. This suggests that photoisomerization of APT serves to create defects, which work as nucleation points for the development of the J-aggregates of MC.

## 4. Conclusions

Light-induced J-aggregation and triggered J-aggregation of dyes in the LB films provides us with means to control the optical properties of the films. It is to be considered that these types of J-aggregations may accompany structural changes of the films. Light-induced J-aggregation of merocyanine is accompanied with large morphological changes of the films. J-aggregation of dyes can be triggered by the photoisomerization of azobenzene in the mixed LB films of dyes and azobenzene irrespective of whether the dyes are photochromic or not. The triggered J-aggregation is also accompanied by large morphological changes. The results indicate that the photoisomerization of azobenzene can be used as a trigger to control the structures and functions of the LB films. The phenomenon is reminiscent of the isomerization of retinal dyes in the vision systems serving as a trigger to the biological activities.

These results indicate that care should be taken when dealing with photoreactions in LB films because the two-dimensional film structures may be reorganized during the photoreactions. Structural changes of LB films have also been observed during the photoisomerization of azobenzene [51,52] and the photopolymerization of diacetylene [60]. In other words, well-defined structures of LB films render it possible to detect subtle structural changes of the films. This feature is particularly important not only to the understanding of the basic natures of photoreactions but also to the applications of photoreactions in organic materials.

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