

Light-Induced J-aggregation in Langmuir and Langmuir-Blodgett Films

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Light-induced J-aggregation in Langmuir and Langmuir-Blodgett (LB) films of an amphiphilic spiropyran (SP) and SP/n-alkane is reviewed. The isotherm of SP depends strongly on the subphase temperature. Light-induced J-aggregation occurs in the Langmuir film of SP only in the presence of circular trilayer domains. Large morphological changes are evident when J-aggregation is induced in the Langmuir and LB films of SP. The structures of the Langmuir films of SP/n-alkane are almost the same as those of SP when the subphase temperature is above the melting point of n-alkane/SP. In that case, light-induced J-aggregation proceeds. On the other hand, J-aggregation is suppressed when the temperature is below the melting point.

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

1. INTRODUCTION

Langmuir and Langmuir-Blodgett (LB) films have attracted considerable attention from the viewpoint of the applications to various functionalized materials such as molecular electronics, switches, sensors and memories. Prominent characteristics of the LB films are the structures defined at the molecular level, structures with reduced dimensionality, thickness controllable at the molecular level, and ease with which to fabricate superstructures.

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. Further, photoreactions will depend strongly on the film structures and molecular packing. The ordered structures will enable us to detect subtle changes, if any, in the structures, accompanied by the photoreactions using scanning probe microscopies. For example, reversible morphological changes of LB films are accompanied by photoisomerization of azobenzene.¹ Large morphological changes of LB films occur with light-induced J-aggregation and triggered J-aggregation of dyes.²⁻⁶

J-aggregates of dyes have been investigated extensively from the viewpoint of applications to spectral sensitization, optical storage and nonlinear optics. When chromophores form J-aggregates and excitonic state is delocalized, the absorption band is red-shifted and very narrow with a small Stokes shift compared to the case of a monomeric state. Light-induced J-aggregation and triggered J-aggregation of dye molecules in Langmuir and LB films is particularly important because the optical properties of selected areas of the films can be modified by photoirradiation through photomasks.⁷

Light-induced J-aggregation has been reported in multilayer LB films of an amphiphilic spiropyran, 1',3'-dihydro-3',3'-dimethyl-6-nitro-1'-octadecyl-8-(doosanoyloxymethyl)spiro[2H-1-benzopyran-2,2'-(2H)-

dole] (SP in Figure 1) mixed with a matrix.⁸ When these film are irradiated with UV light at high temperatures, J-aggregates of the corresponding merocyanine (MC in Figure 1) are formed. Room-temperature UV irradiation gives rise only to the isomerization of SP into MC without the formation of the J-aggregates of MC.

In this review, light-induced J-aggregation in the Langmuir and LB films of SP is first discussed. Then SP/n-alkane systems are described by comparing with the results reported in the literature.

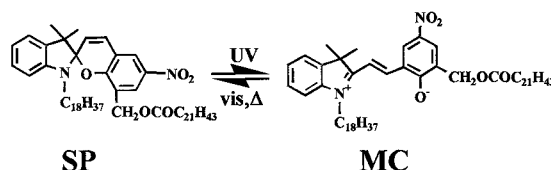


Figure 1. Structure of SP and photoisomerization to MC.

2. LIGHT-INDUCED J-AGGREGATION IN LANGMUIR FILMS OF SPIROPYRAN

2.1 Phases of the Langmuir films of SP

The Langmuir films of SP in the temperature range of 7-40°C are divided into three regimes on the basis of the isotherms and Brewster angle microscopy (BAM) observations: a low-temperature regime at 7-13°C, a medium-temperature regime at 23-30°C, and a high-temperature regime at 40°C.

In the low-temperature regime, the isotherm is of condensed type. The slope is steep and the surface pressure rises at 0.4-0.5 nm². The compression of the molecules induces a gradual fusion of the domains, resulting in a continuous trilayer film around the onset of the surface pressure.

In the medium-temperature regime, the surface pressure rises at larger area per molecule than in the low-temperature regime and the isotherm is expanded at low surface pressures. A phase transition occurs at ca. 5

mN m⁻¹. The higher surface pressure regions of the isotherms are almost the same as those in the low-temperature regime. After the spreading of SP followed by solvent evaporation, the film is continuous with a small number of bright spots. These bright spots grow and increase in number during compression. The size and the number of the structures increase rapidly near the phase transition point. It is suggested that “embryos” are formed during the evaporation of the solvent. With increasing size of the “embryos” during compression, more and more “embryos” become detectable with BAM. After the phase transition, the film is comprised of bright structures that have grown into circular domains. These circular domains have trilayer structures. The “embryos” serve as the nucleation sites of the circular domains.

In the high-temperature regime at 40 °C, the isotherm is almost the same as that at 30 °C except for the absence of a steep rise after the phase transition. BAM images of the Langmuir films are similar to those in the medium-temperature regime below the phase transition. However, the “nucleation sites” that are formed around the phase transition do not lead to the formation of circular trilayer domains. Only the reflection from the “nucleation sites” becomes more intense. Further compression also fails to develop circular trilayer domains. The reason of the absence of circular trilayer domains may be due to the fact that this temperature is higher than the melting point of SP in the bulk.

On the basis of the above results, the phases of the Langmuir film of SP are determined. There are many phases such as “continuous trilayer”, “monolayer with grains”, “monolayer with circular trilayer domains”, “multilayer with circular trilayer domains”, and “collapsed film” under the experimental conditions studied.

These results indicate that the molecular area is not the only decisive parameter in the determination of the structure of the Langmuir film. By measuring simply the surface pressure-area isotherms of SP without BAM observations, one might assume that the structure of the condensed phase of the Langmuir film should be the same in the low-temperature and medium-temperature regimes. Similarly, the structures of the Langmuir films up to the end of the plateau region in the medium-temperature and high-temperature regimes might be assumed to be the same. These assumptions are denied by the present results.⁵

2.2 Photoreactions of the Langmuir films of SP

Photoreactions of SP in the Langmuir films are monitored by measuring UV/vis reflection spectra of the Langmuir films during UV illumination. The photoreaction of SP depends strongly on the phase in the Langmuir film. The region of the occurrence of light-induced J-aggregation roughly coincides with the region where “circular trilayer domains” are present.

The occurrence of light-induced J-aggregation of MC should depend on the presence of the nucleation sites, the concentration of MC and the mobility of MC under isothermal conditions. The absence of J-aggregation in the low-temperature regime should be ascribed to the insufficient mobility of MC. On the other hand, the J-aggregation does not proceed in the Langmuir film of

SP in the high-temperature regime, which should be related with the fact that SP is melted in this regime.

Structural changes of the Langmuir film with UV illumination are monitored using BAM. When the Langmuir film located in the phase of “continuous trilayer” is illuminated with UV illumination, only the isomerization of SP into MC proceeds without the formation of J-aggregates of MC. The film is homogeneous before and even after UV illumination. The reflection from the whole part of the film increases with UV illumination.

The Langmuir film in the phase of “monolayer with circular trilayer domains” is illuminated with UV light. This phase is characterized by the occurrence of the light-induced J-aggregation of MC. Before UV illumination, trilayer domains with grains are evident. With UV illumination, these grains become brighter and increase in size within the circular trilayer domains. These bright structures should consist of J-aggregates of MC.⁵

3. LIGHT-INDUCED J-AGGREGATION IN LB FILMS OF SPIROPYRAN

3.1 Structures of the LB films of SP

The transfer of the Langmuir film of SP onto solid substrates is difficult under usual conditions. However, the transfer of the Langmuir film of SP is successful when the subphase temperature is 30°C. The transfer ratio is significantly smaller than unity at lower temperatures. The AFM image of a single-layer LB film of SP shows that the films consist of circular trilayer domains with a diameter of 10 to 20 μm and a height of 4 to 5 nm. These domains are separately positioned on the solid substrate. The monolayer region that exists between the trilayer domains in the Langmuir films should fail to be transferred onto the solid substrates.

Three-dimensional structures are evident in most of the domains. These structures should be the same ones that are observed in the trilayer domains in the Langmuir films using BAM. 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. These embryos that are undetectable in the initial stage of compression grow with compression and become detectable with BAM around the phase transition point.⁴

3.2 Photoreactions of the LB films

The photoreaction of a single-layer LB film of SP is examined. When the film is illuminated at 23°C, J-aggregation of MC proceeds. This is evident by the development of an absorption band at ca. 620 nm with a linewidth of 12 nm. The linewidth is small compared to that of the J-aggregates in the Langmuir films while the peak position is almost the same. Assuming the presence of various 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.

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. The

three-dimensional structures should serve as nucleation sites for the J-aggregates of MC.

Strong emission is evident due to the J-aggregates of MC in the fluorescence microscopic images of the LB films after UV illumination for 2 h. Polarizing microscopic observations reveal Maltese crosses in the domains, showing that the molecules are aligned radially starting from the nucleation sites. Each dendritic structure consists of a number of small crystallites of J-aggregates.⁴

When a single-layer LB film of SP is illuminated with UV light at 7°C, only the photoisomerization of SP to MC proceeds. The mobility of the molecules that depends on the illumination 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 a matrix on illumination at high temperatures because of the differences in the fabrication conditions such as the layer number and the concentration of the spreading solution.⁸ 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 will result in the melting of the films.

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 to 50°C,⁹ which should facilitate the J-aggregation of MC when the film is illuminated at that high temperature.

4. LIGHT-INDUCED J-AGGREGATION IN SPIROPYRAN/n-ALKANE SYSTEMS

4.1 Structures of the Langmuir films of SP and SP/n-alkane.

Mixing octadecane (HC18) with SP causes large changes to the surface pressure-area isotherms. The isotherms of SP/HC18 (mixing ratio of 1/2) can be divided into a low-temperature regime and a high-temperature regime. In the low temperature regime from 7 to 23 °C, the isotherms are similar to each other and are of condensed type. The surface pressure rises steeply at ca. 0.6-0.7 nm² (SP molecule)⁻¹. No phase transition point appears in this temperature regime.

The isotherms have common features in the high-temperature regime from 30 to 40 °C and are almost the same as those of the isotherms of pure SP.

Above results should be related to the physical properties of HC18 mixed in the Langmuir films. DSC thermograms show that the melting point of HC18/SP in the bulk is 27-31 °C, which is similar to that of HC18 bulk of 28 °C. The high-temperature regime coincides with the temperature region above the melting point of HC18/SP. This strongly suggests that SP is melted in the Langmuir films. On the other hand, the isotherms of SP/HC18 are very different from those of pure SP in the low-temperature regime. The fact that the surface pressure rises more steeply at larger area for SP/HC18 than for pure SP shows that the structures of the Langmuir films of SP/HC18 should be different from

continuous trilayers observed for the Langmuir film of pure SP. The most plausible structural model is the one in which HC18 molecules are incorporated in the hydrophobic part of SP monolayer and packed with the alkyl chains of SP. The structures of the Langmuir films of SP are affected to a large extent by the addition of n-alkane below the melting point of n-alkane/SP.

4.2 Photoreaction of the Langmuir film of SP/n-alkane

The photoreaction of the Langmuir film of SP/n-alkane is examined to reveal the effect of n-alkane on the light-induced J-aggregation.

The UV/vis reflection spectra of the Langmuir film of SP/nonadecane (HC19) below the melting point of HC19/SP show the isomerization of SP to MC without the J-aggregate formation. Light-induced J-aggregation proceeds in the Langmuir film of pure SP at the same surface pressure and temperature. SP and HC19 are not phase-separated in the Langmuir film, which supports the structural model proposed on the basis of the isotherms. On the other hand, the reflection spectrum of the Langmuir film of SP/deuterated nonadecane (DC19) above the melting point of DC19/SP reveals the absorption band due to J-aggregate of MC. The added n-alkane has a large effect on the photoreaction of SP in the Langmuir film below the melting point of the n-alkane/SP whereas the photoreaction of SP is not influenced significantly above the melting point of the n-alkane/SP.

The photoreactions of the Langmuir films of SP/n-alkane are studied with variations in the n-alkane species and the subphase temperature. When n-alkane is longer, in other words, when the melting points of n-alkane and n-alkane/SP are higher, the starting temperature of J-aggregation of MC is higher. When SP is mixed with tetracosane (HC24), no light-induced J-aggregation proceeds below 40 °C.

Considering that the starting temperature of light-induced J-aggregation in the Langmuir film of pure SP is lower than the melting point of any n-alkane/SP used in this study, light-induced J-aggregation is hindered by the presence of n-alkane below the melting point of n-alkane/SP. When n-alkane is in a solid phase, n-alkane should be packed with the alkyl chains of SP as in the aforementioned structural model. SP can be photoisomerized to MC. However, light-induced J-aggregation of MC is hindered because the structure of the Langmuir film is not appropriate for the J-aggregation. On the other hand, when n-alkane is melted, the interaction between n-alkane and the alkyl chains of SP should be smaller than that in the solid state. SP can be photoisomerized to MC, followed by the spontaneous formation of the J-aggregates of MC because J-aggregation proceeds in the Langmuir film of pure SP at the same surface pressures and temperatures.

4.3 Structural change in the Langmuir film of SP/n-alkane with photoreaction

External IR reflection spectroscopy is used to monitor structural changes accompanied by photoreactions of the Langmuir films of SP/n-alkane. Deuterated n-alkanes are used for this purpose.

In the IR external reflection spectra of the Langmuir film of SP/deuterated tetracosane (DC24) at 23 °C

(below the melting point of DC24/SP), the bands assigned to CH₂ asymmetric and CH₂ symmetric stretching vibrations of the alkyl chains of SP and those assigned to CD₂ asymmetric and CD₂ symmetric stretching vibrations of the alkyl chain of DC24 are evident. The band intensities change by the UV irradiation, suggesting that the orientation of the alkyl chains of SP and DC24 change during photoisomerization of SP to MC.

On the other hand, the IR external reflection spectra of the Langmuir film of SP/DC19 at 30 °C (above the melting point of DC19/SP) show that the bands of CD₂ stretching vibrations disappear by the UV irradiation. Under these conditions, DC19 is melted in the film and is eliminated from the Langmuir film through the emulsification into the subphase and/or evaporation, because the local temperature of the Langmuir film should be higher than the subphase temperature during the UV irradiation.

The effect of the phase of n-alkane/SP on the morphology of the Langmuir film is studied using BAM. In the Langmuir film of SP/HC18 at 10 mN m⁻¹ at 30 °C, which is around the melting point of HC18/SP, SP forms trilayer domains. Bright regions grow on the circular domains with UV irradiation during the light-induced J-aggregation as in the case of the Langmuir film of pure SP. In the Langmuir film of SP/HC24 at 10 mN m⁻¹ at 23 °C, which is lower than the melting point of SP/HC24, SP forms a continuous film without any trilayer domains. The reflection of the whole part of the film increases when SP isomerizes to MC on UV irradiation. It is to be noted that the Langmuir film of pure SP at the same surface pressure and temperature contains circular trilayer domains with nucleation sites, around which MC molecules are gathered to form J-aggregate with UV irradiation.

When the subphase temperature is higher than the melting point of n-alkane/SP, the interaction between n-alkane and the alkyl chains of the dye should be weak. Light-induced J-aggregation proceeds as in the Langmuir film of pure SP. On the other hand, when the temperature is lower than the melting point of n-alkane/SP, light-induced J-aggregation is inhibited at the temperatures and surface pressures at which J-aggregation proceeds in the Langmuir films of pure SP.

4.4 Photoreaction of the LB films of SP/n-alkane

The photoreactions of the LB films of SP/n-alkane are investigated to reveal the effect of n-alkane on the light-induced J-aggregation. In the absorption spectrum of the LB film of SP/DC19 transferred at 10 mN m⁻¹ at 30 °C, J-aggregation proceeds as in the LB films of pure SP. On the other hand, only the photoisomerization of SP to MC proceeds by UV irradiation at room temperature of the LB film of SP/HC24 transferred at 10 mN m⁻¹ at 30 °C. This shows that the light-induced J-aggregation of MC is hindered by the presence of HC24 in the LB film.

Structural changes of the LB films of SP/n-alkane on UV irradiation are investigated using IR spectroscopy. The LB film is fabricated at 20 mN m⁻¹ at 23 °C. The structure of the hydrophobic region of the LB film is not affected significantly by the UV irradiation when SP

photoisomerizes to MC without J-aggregation below the melting point of n-alkane/SP.

On the other hand, when the LB film is fabricated above the melting point of n-alkane/SP, the absorption bands of CD₂ stretching vibrations are hardly seen in the spectrum of the LB film even before UV irradiation. N-alkane is not incorporated in the LB film when the temperature is much higher than the melting point of n-alkane/SP.

Structural changes of the LB film with UV irradiation are studied using AFM. The morphology of the LB film of SP/HC18 fabricated at 20 mN m⁻¹ at 30 °C is essentially the same as that of pure SP. Further, morphological changes with UV irradiation are also very similar to those of pure SP. This is consistent with the finding that n-alkane is not incorporated in this LB film.

On the other hand, the LB film of SP/HC24 fabricated at 20 mN m⁻¹ at 23 °C forms a continuous film. Considering that the transfer of the Langmuir film of pure SP onto solid substrates is difficult at the same surface pressure and temperature, the addition of HC24 facilitates the fabrication of the LB film, suggesting a large structural change of the Langmuir film due to the addition of HC24. No significant structural change of the film with the UV irradiation is observed.⁶

5. CONCLUSION

Light-induced J-aggregation that occurs in Langmuir and LB films of SP and SP/n-alkane has been described. Photoresponsivity depends strongly on the structures of molecular assemblies of SP in the films. Furthermore, light-induced J-aggregation under isothermal conditions is accompanied by large morphological changes, which is absent in the case of light-induced J-aggregation under isobaric conditions.⁷ These results indicate that further research is required to elucidate the light-induced J-aggregation.

6. REFERENCES

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