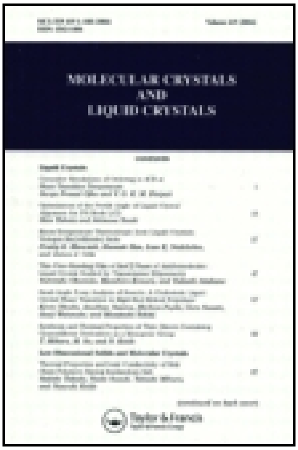

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Formation of Metal-free J-aggregates in Merocyanine/Spiropyran Mixed Langmuir-Blodgett Film

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In order to fabricate metal-free J-aggregate, merocyanine(MD)/spiropyran(SP) mixed LB film was transferred on a glass plate from a pure aqueous solution. Upon UV-light illumination, SP molecules isomerized from SP-form to photomerocyanine (PMC)-form and PMC-form molecules formed J-aggregate with self-assembly. Subsequent vapor-treatment of dimethylamine (DMA) aqueous solution after UV-light illumination induced J-aggregate formation of MD molecules. Metal-free J-aggregate of MD dye was formed by the stepwise treatment of UV illumination and the DMA vapor treatment. The formation mechanism of J-aggregate was discussed.

Keywords: J-aggregates; Langmuir-Blodgett films; merocyanine dyes; spiropyran

INTRODUCTION

Several organic dyes such as cyanine, merocyanine, squarylium and others have the potential ability of J-aggregate formation. J-aggregate

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has been attracted wide attention because of its high photo-quantum absorption efficiency and fast optical nonlinearity. Recent development in the research on J-aggregates derives from the expectations that J-aggregate will be used as materials for optical storage and ultrafast optical switching. Merocyanine (MD) dye is one of the most widely investigated materials on J-aggregate formation. In general, MD J-aggregates are formed from aqueous solution included divalent metal ions such as Cd^{2+}, Ca^{2+} and so on by Langmuir-Blodgett (LB) method [1–4]. MD J-aggregate containing Cd^{2+} is most stable, but cadmium compounds are known as one of most serious environmental pollutant materials. Now a day, novel process of the metal-free J-aggregate formation is desired from a view point of reduction of the impact on the environment. In a previous paper, we have reported that MD dyes in the amorphous film prepared by vapor deposition form J-aggregate with vapor-treatment of dimethylamine (DMA) aqueous solution [5]. Recently, metal-free J-aggregate formation in the LB film has been reported using spiropyran (SP) derivatives [6,7]. This suggests that SP J-aggregate could induce the aggregate formation of MD molecules if SP and MD molecules coexist in the film.

In this study, MD/SP mixed LB film is fabricated and investigated J-aggregate formation of MD without metal ions.

EXPERIMENTAL

Merocyanine dye and spiropyran derivative used here were 3-carboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone and 1-octadecyl-3,3-dimethyl-6-nitro-8-[docosanoyloxymethyl]-spiro[2H-1-benzopyran-2,2-indoline]. The molecular structures are shown in Figure 1. These samples were purchased from Hayashibara Biochemical Labs. INC. Glass plates used as a substrate for preparation of the LB films were cleaned ultrasonically in water with detergent for 15 minutes, in distilled water for 15 minutes, and in acetone for 15 minutes and were hydrophobized by 1,1,1,3,3,3-hexamethyldisilazane. The LB films were prepared on air-water interface of a LB trough (Kyowa Kaimen Kagaku Co. Lt.). A chloroform solution of either SP or MD mixed with arachidic acid (AA) and of SP/MD/AA (molar ratio = 1/1 and 1/1/1, respectively) was spread on a distilled water kept at 5°C. The molecules were compressed with a moving barrier at the speed of $119\,cm^2 min^{-1}$. Layers were transferred at a surface pressure of 25 mN/m onto glass plates by vertical dipping method. The LB films were exposed to a vapor of 10 v/v% dimethylamine (DMA) aqueous solution in a petri dish for 10 min.

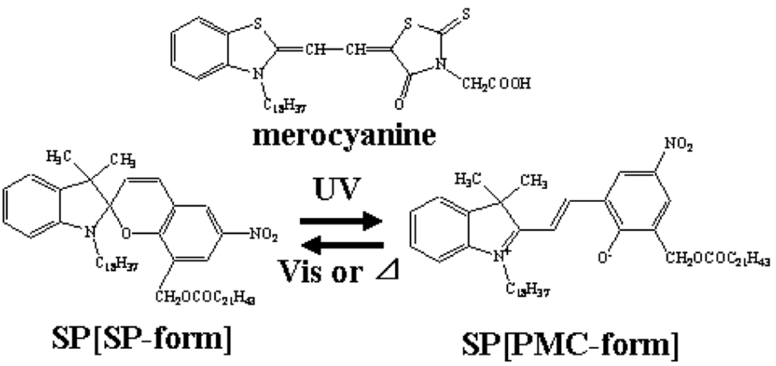

FIGURE 1 Molecular structure of MD (a) and photochromism of SP derivatives (b).

The optical properties and structures of the films were investigated by visible absorption and photoluminescence spectroscopy and atomic force microscopy (AFM).

RESULTS AND DISCUSSION

The SP LB film has no absorption peaks in the visible wavelength range, as shown in Figure 2(a). Upon UV light (365 nm) illumination

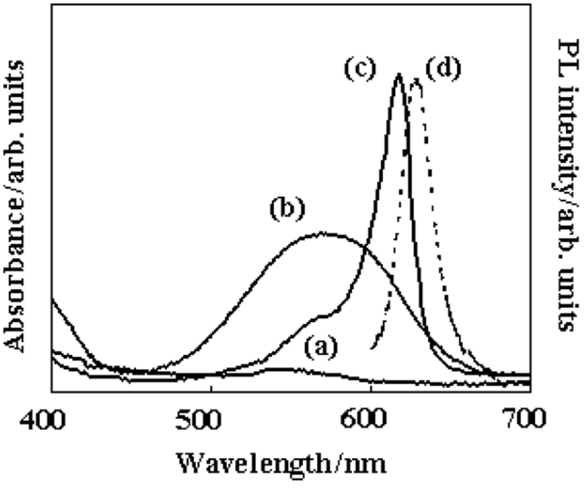

FIGURE 2 Absorption (solid lines) and PL (dotted line) spectra of the LB film of SP before (a) and after UV illumination at room temperature (b) and 40°C (c, d).

at room temperature, the broad absorption band appeared in the wavelength range of 450–650 nm (Fig. 2(b)). This band is assigned to photomerocyanine (PMC)-form of SP molecule. It is clear that only photoisomerization from SP-form to PMC-form was occurred under this illumination condition. When the SP LB film was exposed to UV light at ambient temperature of 40°C, on the other hand, the red-shifted sharp absorption peak with full width at half maximum (FWHM) of 26 nm appeared at 618 nm (Fig. 2(c)). In the fluorescence spectrum of the film, a single emission peak corresponding to J-band was observed at 624 nm (Fig. 2(d)). The Stokes shift between the absorption peak and the emission peak was 6 nm. Consequently, SP molecules isomerize from SP-form to PMC-form by UV illumination and PMC-form molecules form J-aggregate by self-assembly. It is found that J-aggregate formation of SP heavily depends on the condition of UV illumination.

MD LB film was transferred on the SP LB film. MD/SP double layer shows the broad absorption band in the wavelength region of 400–600 nm, as shown in Figure 3(a). This band is assigned to absorption band of MD molecules. When MD/SP double layer was irradiated by UV light at 40°C, the red-shifted absorption peak appeared at 618 nm attributed to J-aggregates of PMC-form molecules. After exposure to DMA vapor, the absorption intensity around 580 nm

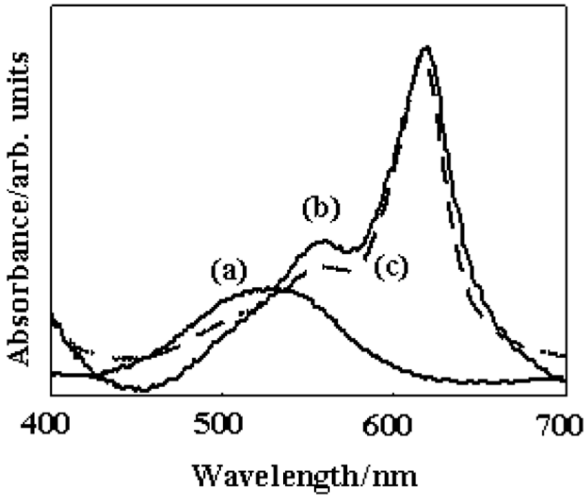

FIGURE 3 Absorption spectra of MD/SP double layer LB film; as-deposited film (a) and after UV illumination at 40°C (b), and after subsequent vapor-treatment of dimethylamine aqueous solution (c).

decreased and J-band peak sharpened, resulting narrowing of FWHM: from 59 nm to 37 nm. In comparison with adsorption spectrum of SP J-aggregates in LB film (Fig. 2(c)), FWHM was wide. J-aggregation formation of SP molecules seems to be prevented by interaction with MD molecules in upper layers. Generally, J-band of MD J-aggregate is characterized by narrow peak around at 620 nm. It is noteworthy that the intensity of the J-band does not change. Therefore, J-aggregate formation of MD molecules dose not occur by DMA vapor treatment. In the case of MD/ PMC J-aggregate double layer, similar situation was observed.

Figure 4 shows the spectral change of MD/SP mixed LB film. As-deposited film indicates the similar spectrum to as-deposited MD/SP double layer shown in Figure 3(a). Upon UV-light illumination, J-band peak of PMC-form J-aggregate appeared (Fig. 4(b)). However, broad shoulder also observes. This indicates that J-aggregate formation of SP molecules occurs by photochemical isomerization and spontaneous self-assembly even in coexisted MD/SP film. When MD/SP mixed LB film was exposed to DMA vapor after UV illumination, absorption intensity of shoulder peak decreased and that of J-band increased, as shown in Figure 4(c). This result indicates that MD molecules formed J-aggregates with narrow FWHM (29 nm) by subsequent DMA vapor treatment.

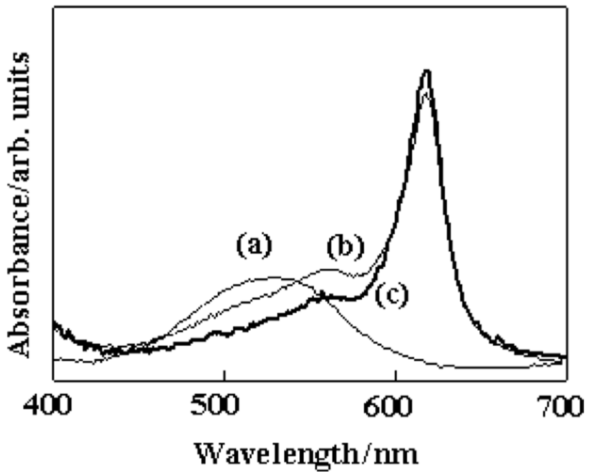

FIGURE 4 Absorption spectra of MD/SP mixed LB film; as-deposited film (a) and after UV illumination at 40°C (b), and after subsequent vapor-treatment of dimethylamine aqueous solution (c).

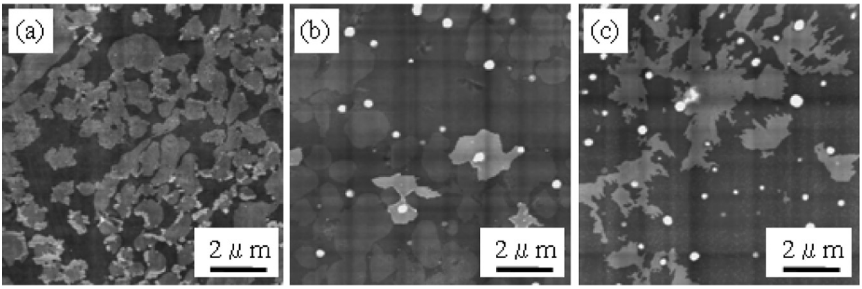

FIGURE 5 AFM images of MD/SP mixed LB film: as-deposited film (a), after UV illuminatin at 40°C (b), after subsequent vapor-treatment of dimethylamine aqueous solution (c).

Figure 5 shows AFM image of MD/SP mixed LB film. There are two regions; bright and dark regions. Structure of LB film of individual MD and/or SP dyes has been investigated in detail [1,2]. As a result of reference to reported structure, it is found that bright and dark regions are composed of arachidic acid molecules and monomeric dye molecules which mean dye molecules taking no regular structure such as J-aggregate. Upon UV-light illumination, many small dots and brighter domains appeared. These are identified as J-aggregate of PMC-form molecules. After exposure to DMA aqueous vapor, new layers grew from the edge of J-aggregate consisted of PMC-form. These layers seem to be J-aggregate of MD molecules. Consequently, it is concluded that PMC-form J-aggregate plays a role of nuclei for J-aggregate formation of MD molecules.

Figure 6 shows the possible formation mechanism of J-aggregate in MD/SP mixed LB film. As-deposited film is consisted of SP (SP-form) and MD molecules (Fig. 5(a)). By UV-illumination, SP molecules isomerize from SP-form to PMC-form and PMC-form molecules rearrange with spontaneous self-assembly, resulting J-aggregate of PMC-form molecules (Fig. 5(b) and (c)). In this time, UV-illumination dose not affect molecular rearrangement of MD molecules and both domains of J-aggregate of PMC-form and MD monomer coexist discretely in the film, resulting wide FWHM of J-band. By DMA vapor treatment, MD molecule forms MD-DMA complex salt with hydrogen bonding between carboxyl group in thiazolidinone ring and amine group in DMA. MD-DMA complex salt near PMC J-aggregate domain aligns two-dimensionally with PMC J-aggregate as nuclei, resulting J-aggregate formation of MD (Fig. 5(d)). Thus, metal-free J-aggregate is formed. As mentioned above, there are no spectral

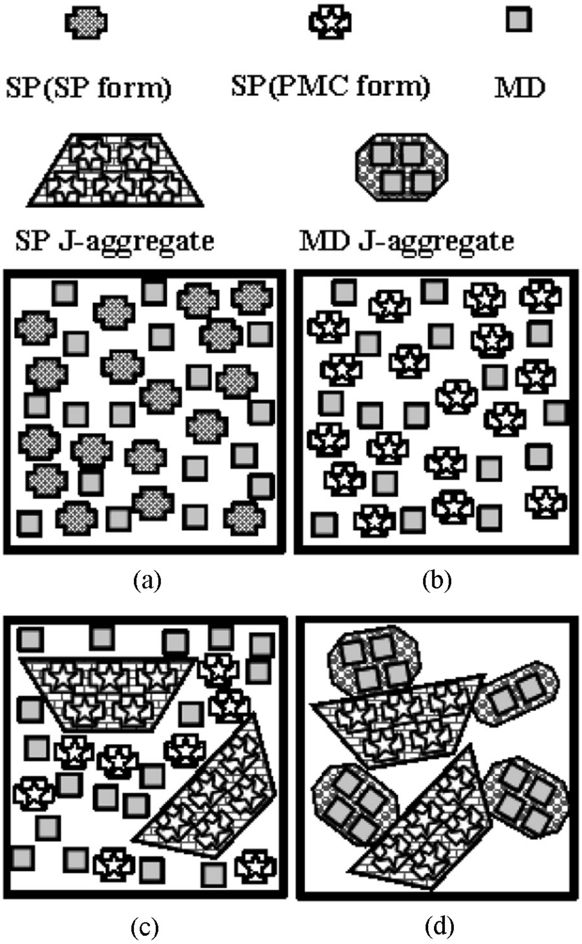

FIGURE 6 Aggregate formation mechanism in MD/SP mixed LB film: as-deposited film (a), after UV illuminatin at room temperature (b) and at 40°C (c), and after subsequent vapor-treatment of dimethylamine aqueous solution (d).

changes of MD/SP and MD/PMC J-aggregate double layers by DMA vapor-treatment. MD molecules stack densely on SP and/or PMC J-aggregate layers. Therefore, hydrated DMA molecules can not penetrate into molecular interface of MD layer. It is concluded that MD/SP mixed layer is very important for metal-free J-aggregate formation of MD molecules.

CONCLUSIONS

MD/SP mixed LB film was fabricated in order to fabricate metal-free J-aggregate. J-aggregate formation was dependent on after-treatment condition. When MD/SP mixed LB film was illuminated with UV light under ambient temperature, only photoisomerization of SP molecules from SP-form to PMC-form occurred. On the other hand, PMC-form J-aggregate was formed by UV illumination at 40°C. Moreover, subsequent vapor-treatment with DMA aqueous solution after UV illumination induced J-aggregate formation of MD molecules. PMC-form J-aggregates co-excited in the film acted as nuclei of J-aggregate formation of MD molecules. UV illumination and subsequent DMA vapor treatment to MD/SP mixed layer were very useful for formation of metal-free J-aggregate of MD molecules.

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