

Thermal Stability of the Hydrothermally-induced J-band in Merocyanine-containing LB Films

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We have examined the thermal stability of the reorganized J-band induced by the hydrothermal treatment under 100% humidity (HTT) in merocyanine-arachidic acid (MS- C_{20}) mixed Langmuir-Blodgett (LB) films. The reorganized J-band is found to be more stable than the as-deposited J-band: the former remains almost unchanged after DHT at 70°C for 75 min in total, and retains ~86% of the initial height after dry-heat treatment (DHT) at 90°C for 270 min in total, while the latter loses ~70% of the initial height after DHT at 90°C for 40 min in total. The reorganized J-band is dissociated by DHT at 110°C for 150 min, resulting in a spectrum considerably different from those observed after DHT at $t_H \leq 90^\circ\text{C}$. The observed thermal behavior is suggested to be closely related to that of the LB lamellar structure in CdC_{20} LB films stabilized by Cd^{2+} ions.

Key words: Langmuir-Blodgett films, Merocyanine dye, Thermal stability, Hydrothermal treatments, Dry-thermal treatments

1. INTRODUCTION

Langmuir-Blodgett (LB) technique is a useful method to fabricate multilayered structures of molecular dimensions. The technique is based on the preparation of monolayers at the air-water interface followed by the transfer of them one after another onto a solid substrate by dipping and raising it traversing the interface [1]. A product, often referred to as LB film, is associated with a one-dimensional (1D) sequence of monolayers in accordance with a given plan. A variety of 1D sequences are realized when two or more monolayer species are available [2]. Indeed, there are many film-forming molecules that are made compatible with the LB technique by introducing one or two long alkyl substituents aiming to utilize the advantage of designing 1D sequences [2, 3].

Among those film-forming molecules, a surface-active merocyanine MS shown in Fig. 1 (a) is known to form stable monolayers at the surface of Cd_{2+} -containing water when it is mixed with arachidic acid (Fig. 1 (b)). Thus prepared monolayers are easily deposited to form Langmuir-Blodgett (LB) films, which are blue in color associated with a J-band with its peak located at 590~595 nm [3-6]. Here, the J-band originates from a specific dipole-coupled array often referred to as the J-aggregate, resulting in a prominent redshift up to several tens of nanometers, and an intense fluorescence with zero or small Stokes shift [7].

There are many reports on the dissociation-restoration processes in the MS- C_{20} mixed LB films induced by various secondary treatments, since the associated color-phase transitions are of interest from the viewpoint of fabricating prototypes of optical memory media. It has been reported that the J-band is dissociated by acid treatments (ATs) and dry-heat treatments (DHTs), and restored by basic treatments (BTs) [5, 6]. Further, we have recently shown that the J-band is reorganized by hydrothermal treatments (HTTs) under condition of 100% humidity at a temperature range of 30 ~90°C to form a new phase of J-aggregate with spectra further redshifted and sharper in shape than that in the as-deposited state [8-16]. The photomicroscopic image, initially anisotropic and featureless, is changed by the application of HTT into isotropic and filled with round-shaped superstructures as large as up to ca. 0.1

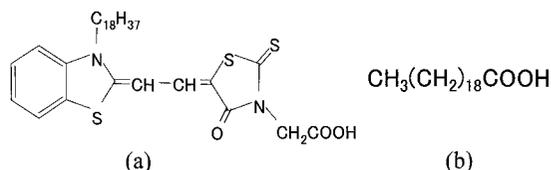


Fig. 1 Chemical formulas of the film-forming materials: (a) merocyanine (MS), and (b) arachidic acid (C_{20}).

mm in diameter [12, 14-16]. The growth of HTT-induced domains has a delay compared to that of the peak height of the reorganized J-band, indicating that it is a phenomenon occurring subsequent to the J-band reorganization process rather than being an aspect of the process [14, 16].

On a course towards practical devices, it is important for the materials to have a sufficient thermal stability. In this respect, the practical devices should withstand temperatures at least up to ~80°C, e.g., allowing for the operations under the direct rays of the sun.

We have been studying the thermal stability of the HTT-induced J-band. It has been found that the HTT-induced J-band is far more stable against heat than the as-deposited J-band. The preliminary results will be shown in the present paper. In the following text, the HTT and DHT processes will be referred to as $\text{HTT}(T_H, t_H)$, and $\text{DHT}(T_H, t_H)$, respectively, when it is convenient to explicitly give the heating temperature T_H and the heating time t_H .

2. EXPERIMENTAL

MS and C_{20} were purchased from Hayashibara Biochemical Lab. Inc. and Fluka AG, respectively. They were dissolved without further purification in optical-grade chloroform from Tokyo Kasei with a molar mixing ratio of [MS] : [C_{20}]=1 : 2. A Cd^{2+} -containing subphase was used for the preparation of monolayers, which were compressed under a surface pressure of 25 mN/m and deposited onto one side of each substrate using the conventional vertical dipping technique as previously described [3-6]. The substrates, each 1/4 of an ordinary slide glass (13 mm×38 mm and 1 mm thick), were put in an ethanol solution of *pro analysi* grade KOH for 4~6 hours, and then rinsed with

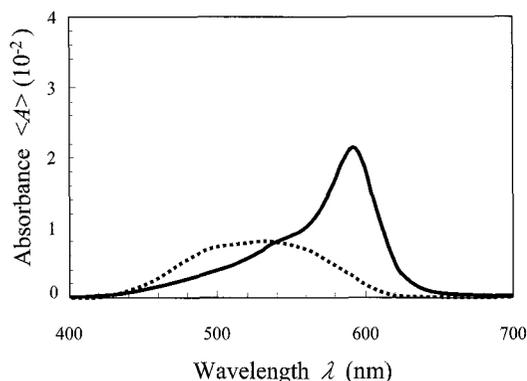


Fig. 2 Absorbance spectra $\langle A \rangle = (A_{\parallel} + A_{\perp})/2$ per monolayer of a film in the as-deposited state and after DHT(90°C, 60 min) are shown by the solid and dotted lines, respectively.

pure water in an ultrasonic bath. After the substrates were dried at 50°C, they were stacked face to face to form substrate pairs for one-side deposition of monolayers. Five monolayers of C₂₀ were first deposited onto the substrate pairs to make their surface hydrophobic, and then ten monolayers of MS-C₂₀ were successively deposited. The so prepared films were of Y-type with a deposition ratio of approximately unity. The substrate pairs were separated and stored in a silica gel desiccator to remove the remaining water content. An aluminum tube (ca. 20 mm in diameter and 150 mm long) with a screw lid at one end was employed for both DHT and HTT. A small amount of pure water (2 cm³ or less) was introduced into the tube to satisfy the condition of 100% humidity for HTT as described in previous papers [8-16]. A spacer was then put at the bottom to avoid direct contact between the sample and the water. After the LB sample was enclosed, the tube was heated for given temperature T_H and time t_H using either a water bath (for $T_H \leq 90^\circ\text{C}$) or an isothermal box (for $T_H > 90^\circ\text{C}$), and then pulled off to cool down to room temperature. UV-visible absorption spectra A_{\parallel} and A_{\perp} were measured using a Shimadzu UV-2100 spectrophotometer. Here, A_{\parallel} and A_{\perp} denote the absorbances for linearly polarized light incidents with the electric vector parallel and perpendicular to the direction of dipping and raising, respectively. The microscopic images were recorded using an Olympus BH-2 photomicroscope with a charge-coupled device (CCD) camera.

3. RESULTS AND DISCUSSION

3.1 Absorbance spectra

3.1.1 Changes induced by DHT

Typical absorbance spectra $\langle A \rangle = (A_{\parallel} + A_{\perp})/2$ per monolayer before and after DHT are shown in Fig. 2. The A_{\parallel} and A_{\perp} components of the as-deposited spectrum are associated with in-plane anisotropy with the dichroic ratio $R = A_{\parallel}/A_{\perp}$ usually falling within a range of 1.2–2.5, depending on the deposition condition [8-12]. Three components are recognized as reported in previous papers [10, 13, 16]: two shoulders at $\lambda \sim 490$ nm and 540 nm, respectively, and the J-band at $\lambda \sim 490$ nm. When DHT(90°C, 60 min) is applied, drastic changes appear in

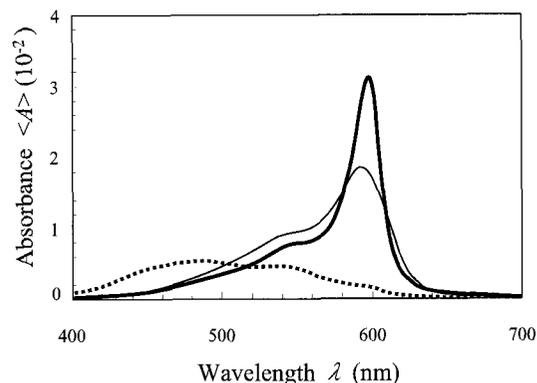


Fig. 3 Absorbance spectra $\langle A \rangle$ of an LB film in the as-deposited state, after HTT(60°C, 40 min) and after HTT(60°C, 40 min)→DHT(110°C, 150 min) shown by the thin solid, thick solid and dotted lines, respectively.

the spectrum. The original J-band is almost completely dissociated, with the band component at $\lambda \sim 490$ nm appreciably increasing. The film, originally blue in color, turns red as a consequence. It has been previously reported that the in-plane anisotropy tends to decrease as the DHT process proceeds, with R decreasing down to approximately unity in the present case [10-16].

3.1.2 Changes induced by HTT

Figure 3 shows the $\langle A \rangle$ spectra successively taken on the same sample, where the thin solid, thick solid and dotted lines refer to the as deposited state, after HTT(60°C, 40 min) and after HTT(60°C, 40 min)→DHT(110°C, 270 min), respectively. The reorganized J-band, higher in height and narrower in width than the original one, is clearly observed after HTT, while the band component at $\lambda \sim 490$ nm is appreciably decreased. This new peak is further redshifted to $\lambda \sim 600$ nm, and the film color turns from blue to deep blue as a consequence, as the process proceeds.

As reported in previous papers, the present HTT(60°C, 40 min) case represents the saturation phase of the J-band reorganization in the second stage of the HTT process [13, 16]. In this respect, it has been found that the kinetics of the J-band growth at a given T_H can be described by a simple exponential saturation function as $a - b \exp(-kt_H)$ involving three parameters, where k is the sum of the forward and reverse rate constants of activation type, k_f and k_r , respectively [13, 16].

3.1.3 Changes induced by HTT→DHT

The HTT-induced J-band is dissociated by applying DHT(110°C, 270 min) as seen in Fig. 3. Although the film color turns from deep blue to red after DHT in this case, the spectral shape is considerably different from that for the case of DHT(90°C, 60 min) directly applied to an as-deposited film as seen in Fig. 2. The spectrum is in this case associated with another band component at $\lambda \sim 450$ nm, whose width is large enough for its foot to extend towards the region of $\lambda < 400$ nm. This, together with the relatively low level of $\langle A \rangle$, suggests that a certain fraction of MS molecules is subjected to degradation.

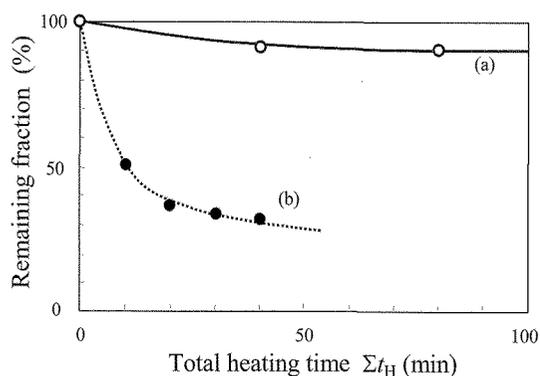


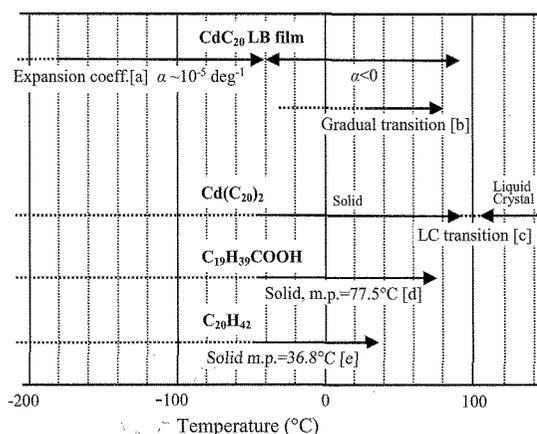
Fig. 4 Remaining fraction $\langle A \rangle / \langle A \rangle_{\text{initial}}$ at 599 nm after HTT(60°C, 40 min) \rightarrow $N \times$ DHT(90°C, 40 min) (a), and at 592 nm after $N \times$ DHT(90°C, 10 min), respectively.

3.1.4 Thermal stability of the J-bands

Fig. 4 shows the remaining fraction $\langle A \rangle / \langle A \rangle_{\text{initial}}$ relative to the initial J-band peak height plotted against the total heating time Σt_H , where the sets of data (a) and (b) refer to the cases of HTT(60°C, 40 min) \rightarrow $N \times$ DHT(90°C, 40 min) and $N \times$ DHT(90°C, 10 min), respectively. Here, the sets (a) and (b) are regarded as representing the dissociation processes of the as-deposited and reorganized J-bands, respectively. It is therefore shown that the reorganized J-band has a much higher thermal stability than the original J-band. In this respect, we have found that the reorganized J-band peak retains $\sim 86\%$ of the initial peak height after $3 \times$ DHT(90°C, 90 min) with $\Sigma t_H = 270$ min, and that the $\langle A \rangle$ spectrum remains approximately unchanged for HTT(70°C, 15 min) \rightarrow $N \times$ DHT(70°C, 15 min) with $N = 1-5$.

The DHT-induced dissociation process of the as-deposited J-band proceeds much faster: the peak height decreases down to $\sim 30\%$ of the initial height after $4 \times$ DHT(90°C, 10 min) with $\Sigma t_H = 40$ min as seen in the

Table I Thermal behavior of the CdC₂₀ LB film and the related materials.



[a] T. Fukui et al.: *Phys. Rev.* **B22**, 4898 (1980).

[b] C. Naselli et al.: *Thin Solid Films* **134**, 173 (1985).

[c] P. A. Spegt and A. E. Skoulios: *Acta Cryst.* **16**, 301 (1963).

[d] "Rikagaku Jiten, 3rd ed.", Iwanami Shoten (1971) p. 39.

[e] "Rikagaku Jiten, 4th ed.", Iwanami Shoten (1987) p. 69.

curve (b) of Fig. 4. The as-deposited J-band is so far recognized to dissociate at temperatures as low as down to $T_H = 65^\circ\text{C}$, and it can be described at a given T_H by an exponential decay function $a' + b' \exp(-k' t_H)$ with an activation-type rate constant k' [16-18]. As to the reorganized J-band, the dissociation process can be of the same functional form, although it is difficult to say anything decisive since the process is observable in a relatively narrow temperature range.

3.2 Thermal stability of LB lamellar structure

3.2.1 CdC₂₀ LB film as a lamellar structure

The CdC₂₀ LB film can be regarded as a prototype of lamellar structure composed of bilayer unit cells, each consisting of a pair of CH₁₉COO⁻ ion slabs sandwiching a Cd²⁺ ion lattice. In each slab, the CH₁₉COO⁻ ions stand upright with their -COO⁻ groups anchored at the lattice plane. Table I shows the thermal behavior of the CdC₂₀ LB film and the related materials. It has been reported that the thermal expansion coefficient of CdC₂₀ LB films is $\alpha \sim 10^{-5} \text{ K}^{-1}$ up around -40°C , then turns to be $\alpha < 0$ which is characteristic of the rubberlike elasticity indicating that the fraction of gauche conformation increases with temperature in the CH₁₉ moiety [19, 20]. T. Fukui et al. have examined the change in X-ray diffraction intensity induced by DHT [21]. It has been reported that the (0, 0, 3) peak after DHT(T_H , 15 min) remains unchanged for $T_H \leq 100^\circ\text{C}$, retains $\sim 60\%$ of the initial intensity at $T_H = 110^\circ\text{C}$, decreases down to 26% at $T_H = 115^\circ\text{C}$, but falls down to $\sim 1.4\%$ at $T_H = 150^\circ\text{C}$. It should be noted that the same process is referred to by C. Naselli et al. as a "gradual transition" [22].

3.2.2 Related materials

It is worthwhile to refer to the related materials for the better understanding of the present LB system. According to P. A. Spegt and E. A. Skoulios, the Cd(C₂₀)₂ lamellar crystal is composed of bilayer unit cells closely similar to those of the LB films, and it is subjected to a solid-liquid crystal (LC) transition in a temperature range 90–100°C [23]. The C₁₉H₃₉COOH crystal is also composed of bilayer unit cells which are stabilized by the hydrogen-bonded ring dimers formed between each hydrophilic interface, and the melting point is m.p. = 77.5°C. The n-C₂₀H₄₂ crystal is one of the typical van der Waals solids which are condensed by the dispersive forces, and the melting point is as low as m.p. = 36.8°C. These suggest that the ionic bonds between Cd²⁺ and -COO⁻ play the dominant role in realizing the highest thermal stability of the LB films among the related materials.

3.2 J-bands, the as-deposited and reorganized

As we have already seen, the reorganized J-band is highly stable up to $T_H = 90^\circ\text{C}$ at which the LB lamellar structure is assumed to be more or less disordered as we have seen in the preceding subsection. The introduced disorder is, however, regarded as reversible in the sense that it is relaxed towards higher order during the cooling process. X-ray diffraction measurements at room temperature have actually shown that the ordering of the Cd²⁺ ion lattice is enhanced for both HTT and DHT processes as reported in previous papers [6, 11]. The as-deposited J-band is, however, dissociated by DHT at

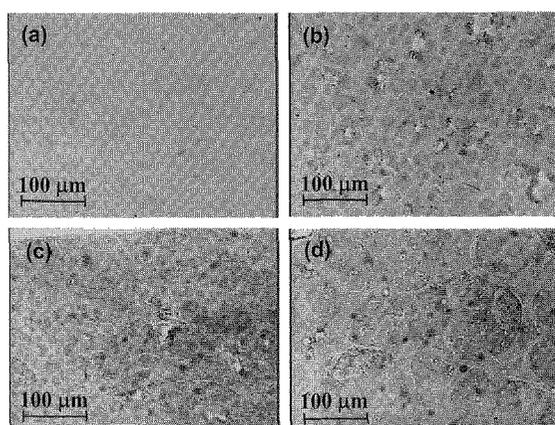


Fig. 5 Photomicrographs of 10-layered MS-C₂₀ mixed LB films for: (a) the as-deposited state, (b) HTT(60°C, 40 min), (c) HTT(60°C, 40 min)→DHT(90°C, 40 min) and (d) HTT(60°C, 40 min)→DHT(110°C, 90 min).

$T_H=90^\circ\text{C}$ in contrast. The as-deposited J-band is therefore assumed to be thermodynamically less stable than the reorganized J-band.

3.3 Photomicroscopic images

Figure 5 shows examples of photomicrographs taken in different conditions. The image of an as-deposited film is shown in Fig. 5 (a). As previously reported, the brightness of the field varies with a π -periodicity when the sample is rotated on the stage as is the case with the in-plane anisotropy $R>1$ observed in the $\langle A \rangle$ spectra, while it is associated with local inhomogeneity [12, 14].

Figure 5 (b) refers to the case of HTT(60°C, 40 min). The image is now filled with round-shaped domains, each brightly rimmed and 15–30 μm in diameter. The in-plane anisotropy is no more observed.

Changes in the domain shape are introduced by HTT(60°C, 40 min)→DHT(90°C, 40 min) as seen in Fig. 5 (c). The shape of the domains is more irregular than that before DHT as seen in Fig. 5 (b), with the size being comparable to that before DHT.

The HTT(60°C, 40 min)→DHT(110°C, 90 min) process is found to lead to diverse variations of the images ranging from disappearance to further growth of the initially observed round-shaped domains. Fig. 5 (d) shows a typical example of the further growth. The size of the domains sometimes exceeds 100 μm as seen in the figure.

4. CONCLUDING REMARKS

We have investigated the thermal stability of the reorganized J-band induced by HTT in the MS-C₂₀ mixed LB films in comparison to that of the as-deposited J-band. The reorganized J-band has been found to be significantly more stable than the as-deposited J-band: e.g., the former remains almost unchanged after 5×DHT(70°C, 15 min) and retains ~86% of the initial height after 3×DHT(90°C, 90 min), while the latter loses ~70% of the initial height after 4×DHT(90°C, 10 min). The reorganized J-band is dissociated by DHT(110°C, 150 min), resulting in a spectrum different in shape from those observed in the DHT processes with $t_H \leq 90^\circ\text{C}$. Referring to the thermal

behavior of CdC₂₀ LB films and the related materials, it is suggested that the observed thermal behavior of the reorganized J-band is closely related to that of the LB lamellar structure stabilized by Cd²⁺ ions.

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