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Control of J-aggregates in the Merocyanine-containing LB Films by Hydrothermal Treatments

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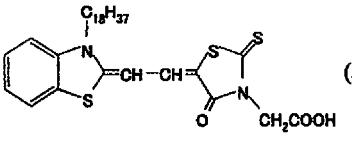
Effects of hydrothermal treatments (HTT) have been investigated on the merocyanine (MS) - Cd arachidate mixed Langmuir-Blodgett (LB) films. The as-deposited J-band is reorganized by HTT under the 100%-humidity condition in the range 30~90°C, forming a new phase with spectra sharper than those before HTT. The spectra after HTT can be deconvoluted into Bands I and II, Gaussian-type centered at 515 nm and 555 nm, respectively, and Band III, the remainder identifiable with the J-band with its peak at 590~600 nm. The relative fraction of oscillator strength of Band II is insensitive to both time t_H and temperature T_H of HTT. The Band-III and Band-I fractions are approximated by exponential saturation and decay functions of t_H when T_H=const, and by sigmoid and inverse-sigmoid functions of T_H when t_H=const, respectively. These suggest that the reorganization process is described as a first-order reaction between Band-I and Band-III components.

Key words: Langmuir-Blodgett films, Merocyanine chromophores, Control of J-aggregate, Formation of superstructures, Hydrothermal treatments

1. INTRODUCTION



(a) MS

$CH_3(CH_2)_{18}COOH$ (b) C_{20}

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

A surface-active merocyanine MS shown in Fig. 1 (a) is well known to form stable monolayers at the air-water interface when it is mixed with arachidic acid (Fig. 1 (b)) [1]. The MS-C_{20} mixed monolayers formed on an aqueous subphase containing Cd^{2+} ions are easily deposited to form Langmuir-Blodgett (LB) films, which are blue in color in the as-deposited state due to a J-band with its peak located around 590 nm [2]. The J-band is characterized by remarkable redshift up to several tens of nanometers and an intense fluorescence with zero or small Stokes shift as a consequence of a specific low-dimensional, dipole-coupled array that is often referred to as the J-aggregate [3].

The dissociation-restoration processes of the J-band are interesting in relation to optical memory media such as CD-Rs because of the large amounts of shift caused by them. Indeed, there are many reports on the color-phase transition of the present MS-C_{20} mixed LB system induced by various secondary treatments including acid and basic treatments (ATs and BTs, respectively) in both gas- and liquid-phases, and heat treatment (HTs) in gas phase [2, 4]. AT dissociates the J-band, BT restores it, and HT dissociates it at higher temperatures (90°C, typically) [2] but reorganizes it at lower temperatures ("mild" HT at 60°C~70°C) to form a new phase with spectra further red-shifted and sharper in shape than those before the treatment [5, 6].

Recently, we have found that the reorganization of J-band is induced in a similar manner for a wider range of temperature, 30°C~90°C, by hydrothermal treatments (HTTs) under 100% relative humidity [7, 8].

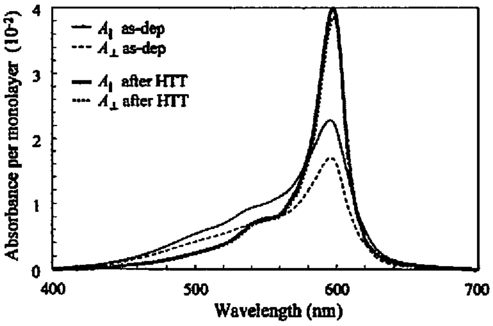


Fig. 2 Typical absorption spectra of a 10-layered MS-C_{20} LB film before and after 65°C-HTT for t_H=60 min.

In the present paper, we will describe the HTT-induced reorganization process of the J-band as a function of the heating temperature T_H and the heating time t_H under the condition of 100% relative humidity in order to examine the feasibility of HTT as a tool for controlling the in-plane molecular organization in LB films.

2. EXPERIMENTAL

MS and C_{20} were purchased from Hayashibara Biochemical Lab. Inc. and Fluka AG, respectively, and used without further purification. They were dissolved in optical-grade chloroform from Tokyo Kasei with a molar mixing ratio of [MS] : [C_{20}]=1 : 2. The monolayers were prepared on a Cd^{2+}-containing subphase and successively deposited onto one side of a substrate using the conventional vertical dipping technique as described in the previous papers [2, 5, 6]. The substrates, each 1/4 of an ordinary slide glass, were hydrophobized by coating with five monolayers of C_{20}. Ten monolayers of MS-C_{20} mixture were then successively deposited onto the substrate. Thus prepared LB films were of Y-type with a deposition ratio of approximately unity for

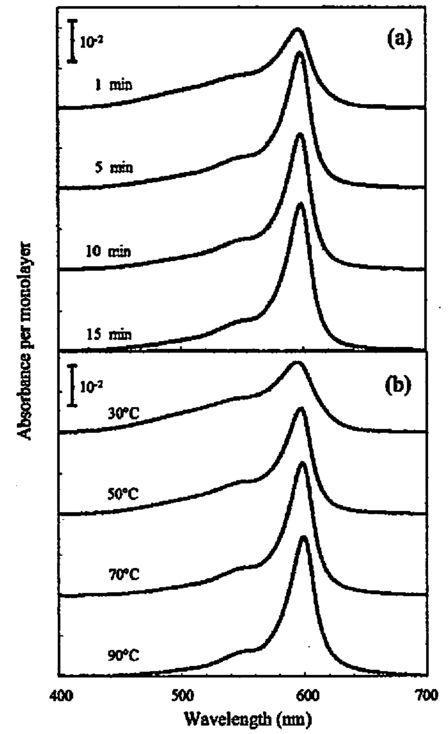


Fig. 3 Absorption spectra $<A>=(A_{\|}+A_{\perp})/2$ of 10-layred LB films after 65°C-HTT for 1, 5, 10 and 15 min (a), and after 15-min HTT at 30, 50, 70 and 90°C (b).

both upward and downward strokes. An aluminum tube (ca. 20 mm in diameter and 150 mm long) with a screw top at one end was used for HTT [7]. A small amount of pure water (2 cm^2 or less) was first introduced into the tube to realize the condition of 100% humidity, a spacer was then settled at the bottom in order to prevent the direct contact between the water and the sample that was finally placed in the tube. The tube was immersed for a given heating time in a water bath kept at a constant temperature and then cooled down to room temperature. The absorption spectra $A_{\|}$ and $A_{\perp}$ were measured using a Shimadzu UV-2100 spectrophotometer, where $\|$ and $\perp$ refer to the linearly polarized light incidents with the electric vector parallel and perpendicular to the dipping direction in the deposition process, respectively.

3. RESULTS AND DISCUSSION

3.1 Changes in absorption spectra induced by HTT

3.1.1 Spectral shape

Figure 2 exemplifies typical absorption spectra of an MS-C_{20} LB film in the as-deposited state and after HTT. The as-deposited spectra $A_{\|}$ and $A_{\perp}$ are anisotropic with a dichroic ratio $R=A_{\|}/A_{\perp}>1$ (R=1.33 in this case), each associated with a J-band centered at ca. 590 nm. After HTT at T_H=65°C for t_H=60 min, the reorganized phase of J-band is fully developed with the $A_{\|}$ and $A_{\perp}$ spectra being identical with each other as seen in the figure.

Figure 3 (a) shows the t_H-dependent spectral change induced by 65°C-HTT measured employing samples belonging one single batch, where each spectrum refers to the average absorbance $<A>=(A_{\|}+A_{\perp})/2$ to exclude apparent contributions from the varying in-plane anisotropy. The T_H-dependence of $<A>$ is given in Fig. 3 (b) for a constant heating time t_H=15 min measured on another batch. It is indicated that the reorganization rate is an increasing function of both t_H and T_H, since the peak height increases towards the bottom in both Fig. 3 (a) and (b).

3.1.2 Half-widths at half-maximum

We adopt the half-widths at the low and high-energy sides, HWHM/L and HWHM/H, respectively, as in a preliminary report allowing for the overlapping with other band components located at the high-energy side. In Fig. 4 (a), the half-widths for T_H=65°C are plotted against t_H in a semilogarithmic scale. Both HWHM/L and HWHM/H rapidly decrease with t_H, and the former is always smaller than the latter, settling down to levels, ~3×10^2 and ~5×10^2 cm^{-1}, respectively, within the first 5 min. These are consistent with the data for T_H=60°C reported previously [7]. Figure 4 (b) shows the T_H-dependence of the half-widths for t_H=15 min. Both HWHM/L and HWHM/H monotonically decrease with T_H, tending to ~3×10^2 and ~5×10^2 cm^{-1}, respectively, with increasing T_H. The behavior of HWHM/H in the present case presents a contrast to that for 60-min HTT reported previously [7], where HWHM/H remains in a range of 1×10^3~2×10^3 cm^{-1} up to T_H =45°C. The difference suggests that 15-min HTT is insufficient for the reorganization to saturate at the lower temperatures.

3.1.3 Peak location of the reorganized J-band

The peak narrowing of the J-band is associated with the change in the position $\lambda(<A>_{max})$ as shown in Fig. 5 (a). $\lambda(<A>_{max})$ for 65°C-HTT is an increasing function of t_H, shifting from ~592 nm in the as-deposited state towards longer wavelengths in the first 1 min, and then tending to a level of ~598 nm. For 15-min HTT, $\lambda(<A>_{max})$ for 15-min HTT is described as a sublinearly increasing function of T_H up to 90°C at which $\lambda(<A>_{max})$ exceeds 599 nm. These are consistent with the previously reported results for T_H=60°C and t_H=60 min [7]. Here, it is suggested that t_H=15 min is insufficient for the reorganization to saturate at the lower temperatures, in accordance with the remarks from HMHW/H.

3.2 Deconvolution based on a three-component model

3.2.1 Outline of the procedure

As described in a previous paper, the spectrum for each case can be deconvoluted into three bands, Bands I, II and III (J-band), employing the following procedure which consists of four steps [9].

(1) Bands I and II are represented by the Gaussian distributions of the form,

$$A(\nu)=\frac{A_0}{\sqrt{2\pi}\sigma}\exp\left\{-\frac{(\nu-\nu_0)^2}{2\sigma^2}\right\}, \qquad (1)$$

where $\nu=1/\lambda$ is the wavenumber with $\nu_0=1/\lambda_0$ being the peak position, σ denotes the standard deviation, and the scaling factor,

$$A_0 \equiv \int_{-\infty}^{+\infty} A(\nu)d\nu, \qquad (2)$$

is a measure of oscillator strength.

(2) For Band I, λ_0=515 nm is chosen among multiples of

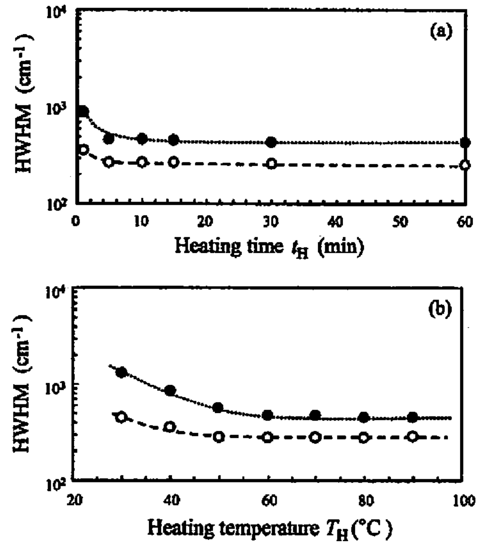


Fig. 4 HWHM/H (●) and HWHM/L (○) after 65°C-HTT plotted against t_H (a), and after 15-min-HTT plotted against T_H (b), each in a semilogarithmic scale.

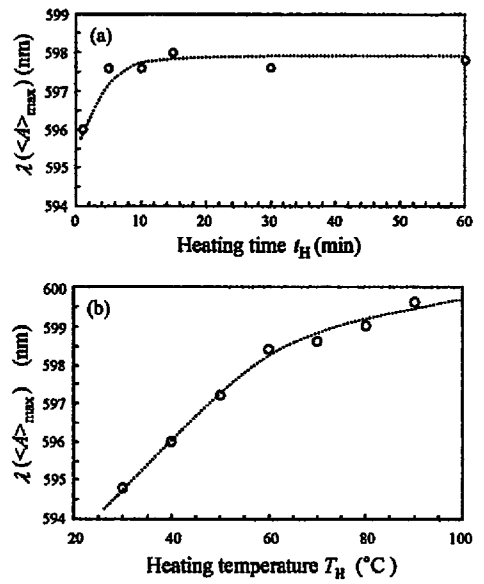


Fig. 5 Peak position $\lambda(\langle A\rangle_{max})$ after 65°C-HTT plotted as a function of t_H (a), and after 15-min-HTT as a function of T_H (b).

5 as giving the best fit to the spectrum in the range of 400~470 nm by adjusting the values of A_0 and σ. Thus estimated A^I for Band I is subtracted from the original spectrum A.

(3) For Band II, λ_0=555 nm is assumed as an appropriate value, and A_0 and σ are estimated in a similar manner as in Step (2), where the spectrum to fit is now $A - A^I$ in the spectral range of 460~520 nm.

(4) The remainder $A - A^I - A^{II}$ corresponds to Band III representing the J-band, i.e., $A^{III} = A - A^I - A^{II}$, if it is larger than $-$(noise level, ~10^{-4}, typically) everywhere. When this criterion is not satisfied, one should then go back to Step (3) to make a compromise by reducing the upper limit of the range for fitting A^{II}.

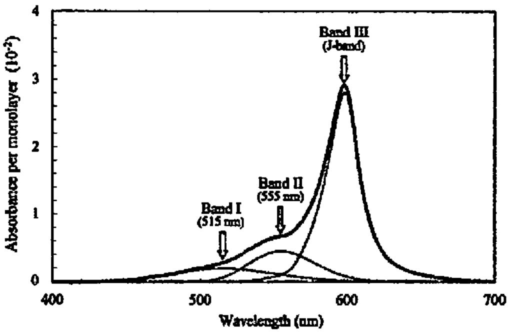


Fig. 6 Typical example of deconvolution. The original spectrum $\langle A\rangle$ after 65°C-HTT for t_H=15 min is shown by the thick line. The thin lines refer to the deconvoluted spectra A^I, A^{II} and A^{III} for Bands I, II and III, respectively.

3.2.2 Relative fractions of oscillator strengths

The relative fraction of oscillator strengths of Bands I, II, and III are given as,

$$f_I = \int A^I(\nu)\, d\nu \,/ \int \langle A(\nu)\rangle d\nu, \qquad (3)$$

$$f_{II} = \int A^{II}(\nu) d\nu \,/ \int \langle A(\nu)\rangle d\nu, \qquad (4)$$

and,

$$f_{III} = \int A^{III}(\nu) d\nu \,/ \int \langle A(\nu)\rangle d\nu, \qquad (5)$$

respectively.

Figure 6 shows a typical example of deconvolution of A after 65°C-HTT for t_H=15 min into Bands I, II and III, the relative fractions of which are f_I =15.9%, f_{II} =19.9% and f_{III}=64.2%, respectively, to the total integral $\int \langle A(\nu)\rangle d\nu$=41.34 cm^{-1}.

3.2.3 Invariance of band-II component

The relative fractions f_I, f_{II} and f_{III} for 65°C-HTT are plotted against the heating time t_H in Fig. 7 (a). The value of f_{II} remains roughly constant, f_{II}=(20.6±0.9)%, for the whole range, while the t_H-dependence of f_I and f_{III} are reminiscent of the exponential decay and saturation, each monotonically decreasing and increasing with t_H.

The growth and decay processes of Band III and Band I (i.e., the reorganized J-band) are therefore assumed to be governed by a first-order reaction as,

$$f_I \xrightleftharpoons[k_r]{k_f} f_{III}, \qquad (6)$$

where the forward and reverse rates k_f and k_r generally depend on T_H. When T_H is held constant, we obtain,

$$f_I(t_H) = (f_I(0) - f_I(\infty))e^{-(k_f+k_r)t_H} + f_I(\infty), \qquad (7)$$

$$f_{II}(t_H) = f_{II} = \text{const}, \qquad (8)$$

and,

$$f_{III}(t_H) = (f_{III}(0) - f_{III}(\infty))e^{-(k_f+k_r)t_H} + f_{III}(\infty), \qquad (9)$$

taking the boundary conditions into account, where $f_I(\infty)/f_{III}(\infty)=k_r/k_f$ and $f_I(t_H) + f_{II} + f_{III}(t_H)=1$.

The lines in Fig. 7 (a) are drawn assuming $f_I(0)$

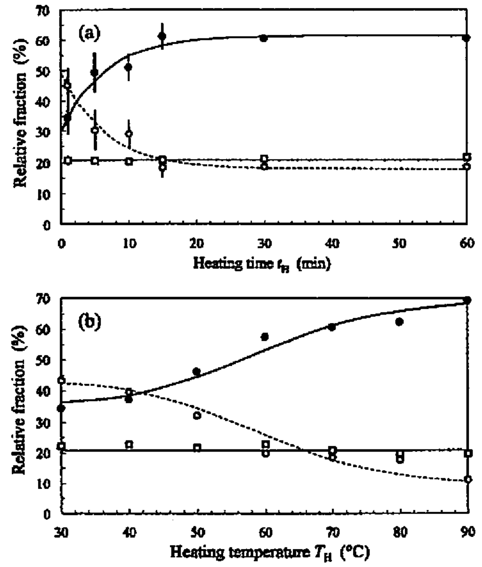


Fig. 7 Relative fractions of oscillator strength of Bands I (○), II (□), and III (●) as a function of t_H after 65°C-HTT (a), and as a function of T_H for 15-min HTT (b).

$=49.1\%$, $f_I(\infty)=18.0\%$, $f_{II}=20.6\%$, $k_b/k_f= 0.294$, and $k_f+k_r = 2.56\times10^{-3}$ sec^{-1}.

It is indicated that the reorganization of J-band proceeds following the dissociation of the original J-band, since the above estimated k_f+k_r gives the time constant, $\tau_{I\leftrightarrow III}=6.5$ min, given by the above estimated k_f+k_r is appreciably larger compared to $\tau<1$ min for the peak shift shown in Fig. 5 (a). In this respect, the invariance of f_{II} throughout the process allows an assumption that the predominant reaction path in the initial stage is from the as-deposited J-band to Band I. This is supported by the HTT-induced spectral change given as the difference $\Delta(\langle A\rangle)=\langle A(t_H)\rangle-\langle A(0)\rangle$ as shown in Fig. 8. Each curve involves a broad structure corresponding to Band I and a sharp peak with a pair of valleys reflecting the reorganization of J-band. The curve for $t_H=1$ min shows that Band-I component actually increases in the initial stage at the expense of the original J-component.

Figure 7 (b) shows f_I, f_{II} and f_{III} for 15-min HTT as functions of T_H. The f_{II}-value is approximately a constant, $f_{II}=(21.0\pm1.1)\%$, while f_I and f_{III} show inverse-sigmoid and sigmoid dependences on T_H, respectively. These are compatible with the above scheme: $f_{III}(T_H)\approx f_{III}(0)$ towards lower T_H and $f_{III}(T_H)\approx f_{III}(\infty)$ towards higher T_H, forming a sigmoid curve associated with a point of inflexion. Here, k_f and k_b are plausibly assumed as Arrhenius-type functions increasing with T_H, while $f_{III}(0)$ and $f_{III}(\infty)$ should be far less sensitive to T_H. The curves in the figure are tentatively drawn allowing for the above consideration.

4. CONCLUDING REMARKS

We have investigated the effects of HTT on UV-visible spectra of MS – C_{20} mixed LB films. The as-deposited J-band is reorganized by HTT at temperatures ranging from 30°C to 90°C to form a new phase of J-band with spectra sharper than those of the as-deposited J-band.

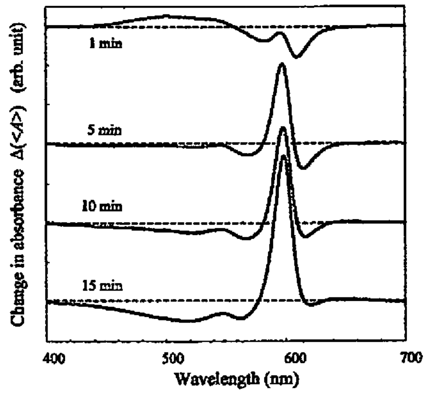


Fig. 8 Change in absorbance spectrum induced by 65°C-HTT, $\Delta(\langle A\rangle)=\langle A(t_H)\rangle-\langle A(0)\rangle$. The zero level for each curve is shown by the dashed line.

The reorganized spectra after HTT can be deconvoluted to three components: Bands I and II of Gaussian-type centered around 515 nm and 555 nm, respectively, and the remainder, Band III with its peak at 590~600 nm, which is identifiable with the J-band.

The relative fraction of oscillator strength of Band II is found to be essentially invariant to both heating time t_H and heating temperature T_H. The Band-III and Band-I fractions are approximated by exponential saturation and decay functions of t_H for T_H=const, and by sigmoid and inverse-sigmoid functions of T_H for t_H=const, respectively. It is suggested that the reorganization process is described as a first-order reaction between Band-I and Band-III components following a quick dissociation of the as-deposited J-band into Band-I component.

The present results may well open up a prospect of HTT as a practical tool to modify the property of LB films. Further study of kinetic features of HTT-induced spectral change is now in progress and the results will be reported elsewhere.

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