A Comparative Study of Hydrothermal and Dry-heat Treatments in the Merocyanine-containing LB Films

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Hydrothermal and dry-heat treatments (HTT and DHT, respectively) in the morocyanine-containing LB films are studied in relation to the "mild" heat treatment, which leads to two different consequences in the spectral change. Close resemblance is found between the HTT-type and the HTT spectra associated with a sharp J-band peak, and also between DHT-type spectra and the DHT ones with a broad band. It is suggested that the underlying processes of the HTT-type and the DHT-type are essentially identical with those of the HTT and the DHT, respectively. The season-dependent occurrence of the both types after the "mild" HT suggests that the humid and cool weather leads to the high yield of the HTT-type spectra. The water remaining on the sample is presumably assumed to act as a humidifier to supply the sufficient amount of water for inducing the HTT-type spectral changes.

Key words: Langmuir-Blodgett films, Merocyanine chromophores, Formation of supestructures, Hydrothermal treatments, Dry-thermal treatments

1. INTRODUCTION

As is well known, a surface-active merocyanine MS shown in Fig. 1 (a) forms stable monolayers at the air-water interface when it is mixed with arachidic acid (Fig. 1 (b)) and spread using an aqueous subphase containing Cd^{2+} ion [1-4]. Thus prepared mixed monolayers 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 at 590-595 nm. 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 dipole-coupled array that is often referred to as the J-aggregate.

There are many reports on the dissociation-restoration processes in the MS-C₂₀ mixed LB films induced by various secondary treatments, since the associated color-phase transitions are of interest from the viewpoint of developing optical memory media. It has been reported that acid treatments (AT) dissociate the J-band, basic treatments (BT) restore it, and heat treatments (HT) dissociate it at higher temperatures (90°C, typically) [3,4], but reorganize it at lower temperatures ("mild" HT at 60°C~70°C) to form a new phase of J-aggregate with spectra further redshifted and sharper in shape than those before the treatment [5-7].

Recently, we have shown that hydrothermal treatments (HTT) under 100% relative humidity induce a new phase closely similar to that caused by "mild" HT for a wider temperature range of $30 \sim 90^{\circ}$ C [8,9]. After HTT, the photomicroscopic image, initially anisotropic and featureless, is found to be changed into isotropic and filled with round-shaped superstructures as large as up to ca. 0.1 mm in diameter [9]. It has been strongly suggested a crucial role of the water content in HTT to facilitate the reorganization of the J-band into the new phase by its lubricating and/or hydrating effects to soften the film structure [8,9].

The present paper aims to examine the mutual relations of HTT, HT and "mild" HT for a better understanding of the color-phase transitions in the MS- C_{20} mixed LB system. In the following, the conventional HT to dissociate the J-aggregate is referred



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

to as the dry-heat treatment (DHT).

2. EXPERIMENTAL

MS and C₂₀ 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 [6]. The monolayers were prepared on a Cd2+-containing subphase and successively deposited onto one side of a substrate using the conventional vertical dipping technique as described in the previous papers [3-6]. The substrates, each 1/4 of an ordinary slide glass (13 mm×38 mm and 1 mm thick), were soaked in an ethanol solution of pro analysi grade KOH for 4-6 hours, and then rinsed with pure water in an ultrasonic bath. Thus cleaned substrates were used for the monolayer deposition in two different manners: (1) immediately after rinsing - the wet-substrate case - [6], and (2) after removing the remaining water content - the dry-substrate case - [3,4,8,9]. In the dry case, the substrates were kept at room temperature overnight in a silica gel desiccator or heated in a dryer at 85°C for 4~6 hours. Five monolayers of Cd salt of pure C₂₀ were deposited onto the substrates to make the surfaces hydrophobic. Ten monolayers of the MS-C₂₀ mixture were then successively deposited. An aluminum tube (ca. 20 mm in diameter and 150 mm long) with a screw top at one end was used for heating. For HTT, a small amount of pure water (2 cm² or less) was introduced into the tube to realize the condition of 100% relative humidity as described in the previous papers [8,9].

After the LB sample was enclosed, the tube was immersed for a given heating time in a water bath kept at a constant temperature and then pulled off from the bath to cool down to room temperature. UV-visible absorption spectra A_{\parallel} and A_{\perp} were measured using a Shimadzu UV-2100 spectrophotometer, where A_{\parallel} and A_{\perp} refer to absorbances taken using linearly polarized light incidents with the electric vector parallel and perpendicular to the direction of dipping and raising, respectively. The microscopic images were taken using an Olympus BH-2 photomicroscope with a CCD camera.

3. RESULTS AND DISCUSSION

3.1 Comparison between HTT and DHT

Figures 2 (a) and (b) shows typical absorbance spectra $\langle A \rangle = (A_{\parallel} + A_{\perp})/2$ per monolayer after HTT and after DHT at two different heating temperatures $T_{\rm H} = 65^{\circ}$ C and 90°C, respectively. The as-deposited spectra are associated with in-plane anisotropy with the dichroic ratio $R = A_{\parallel}/A_{\perp} > 1$ (usually within a range of R = 1.2 - 2.5, depending on the deposition condition). In each figure, a typical as-deposited $\langle A \rangle$ is also shown. The reorganized J-band is fully developed after 65°C-HTT for 15 min as seen in Fig. 2 (a). In the case of DHT, in contrast, the J-band component decreases, while other components at shorter wavelengths appreciably increase.

As shown in Fig. 2 (b), the DHT-induced dissociation process nearly saturates at $T_{\rm H}$ =90°C for $t_{\rm H}$ =30 min resulting in a broad, bell-shaped spectrum with a weak shoulder plausibly assignable to the remaining J-band component [7]. The spectral shape after 90°C-HTT closely resembles that after 65°C-HTT with their sharpened and further redshifted J-band compared to the as-deposited J-band, although the both spectra are quantitatively different from each other as to the peak height and the shift amount. In this respect, the reorganization and the dissociation of J-band will be referred to as HTT-type and DHT-type, respectively, in the following.

3.2 Different types of spectra induced by "mild" HTT

The HTT-type changes in spectrum have so far been observed when the heat treatments are applied to the wet-substrate samples in the temperature range of $T_{\rm H}$ =60~70°C as reported previously [5,6]. Although, these conditions are prerequisites for the "mild" HT as they are, the same treatments result in either of the two alternatives in spectral changes, i.e., the HTT-type and the DHT-type.

Figure 3 (a) shows a typical HTT-type spectrum induced by a "mild" HT at $T_{\rm H}$ =70°C for $t_{\rm H}$ =15 min. The corresponding HTT-induced spectrum is also given in the figure. Both spectra closely resemble each other, where the higher peak height of the HTT-induced J-band is plausibly regarded as representing the more advanced stage of the reorganization process. In addition, the location of crossover point between the HTT and HTT-type spectra is identifiable with that of the isosbestic point at ~567 nm recognized among the HTT-induced spectra at $T_{\rm H}$ =65°C for different $t_{\rm H}$



Fig. 2 Typical absorbance spectra $\langle A \rangle = (A_{\parallel} + A_{\perp})/2$ per monolayer in the as-deposited state, after HTT and after DHT, shown by the thin solid, thick solid and dotted lines, respectively: (a) HTT and DHT at $T_{\rm H}=65^{\circ}$ C for $t_{\rm H}=30$ min, (b) HTT at $T_{\rm H}=90^{\circ}$ C for $t_{\rm H}=15$ min and DHT at $T_{\rm H}=90^{\circ}$ C for $t_{\rm H}=30$ min. Typical spectra in the as-deposited state are also given for comparison.



Fig. 3 Typical absorbance spectra $\langle A \rangle$ after "mild" HT at 70°C for 15 min: (a) An HTT-type spectrum, and (b) a DHT-type spectrum. The corresponding HTT and DHT spectra are added in (a) and (b) by the thin solid lines with arrows indicating the isosbestic points recognized, respectively.



Fig. 4 Round-shaped domains observed when the HTTtype spectrum is induced by "mild" HT at 70°C for 15 min (an image from the same sample as in Fig. 3).

reported in the previous paper [8]. It is therefore plausibly assumed that the HTT-type reorganization process induced by the "mild" HT is essentially identical with the HTT-induced process.

Figure 3 (b) exemplifies the other alternative in spectral changes, i.e., a typical DHT-type spectrum induced by a "mild" HT at $T_{\rm H}$ =70°C for $t_{\rm H}$ =15 min together with the corresponding DHT-induced spectrum. Both spectra closely resemble each other, where the lower peak height of the remaining J-band after "mild" HT is plausibly interpreted as representing the more advanced stage of the dissociation process. Here, it is noted that the crossover point between the both spectra is located approximately at the same wavelength as the isosbestic point at ~536 nm recognized for the 90°C-BHT case [3]. The DHT-type dissociation process is therefore plausibly assumed to be identical with the DHT-induced process.

3.3 Co-occurrence of the spectral and structural changes

The reorganization of J-band induced by HTT is accompanied by a global change in molecular arrangements, which is observed after HTT by means of photomicroscopy as the round-shaped domains as large as up to ~100 μ m [9]. In this respect, it is found that the similar domains appear in the image when the "mild" HT results in an HTT-type spectrum as shown in Fig. 4. The co-occurrence of the spectral and structural changes is another evidence in favor of the assumption that the HTT-type and the HTT-induced processes are identical with each other, since one cannot miss the apparent similarity of the present image for the HTTtype case and those for the HTT case reported so far [9].

It is noted that we have not yet recognized the round-shaped domains formed after DHT: the image is featureless in contrast to the HTT case, associated with a vague local inhomogeneity in the brightness, which is anisotropic in the initial stage and tends to be isotropic as the process proceeds. An image after "mild" HT closely resembled the corresponding DHT case when the treatment resulted in a DHT-type spectrum. These observations support the assumption that the DHT-type



Fig. 5 Season-dependent yields of the HTT-type and the DHT-type spectra induced by "mild" HT (based on the data from 205 samples prepared during April 2004 – March 2006).

and the DHT processes are essentially identical with each other.

3.4 Season-dependent yield of the two different types

As we have seen, the use of wet substrates is a prerequisite for the "mild" HT, but not the sufficient condition for the HTT-type spectra to take place. Analysis of the spectral data accumulated for two years has revealed that there is a season-dependence of the occurrence of the two alternatives in spectral shape. Figure 5 shows the quarterly plots of the yields η of HTT-type and DHT-type spectra. Each η -value can be correlated with the weather here in Yokohama. As to the occurrence of the HTT-type, e.g., the maximum value of η =89% is attained in the second quarterly including June known as the most humid month in a year. The minimum, η =11%, in October – December may be related with the moderate weather with lower humidity in this season.

The correlation between the weather and the yield leads to an assumption that the water content remaining on the wet substrates plays a significant role for the HTT-type spectra to take place. Here, it should be mentioned that the laboratory ambient in the present experiment is only incompletely regulated: no active means of humidity control is introduced yet while the temperature is kept within a range of 15~25°C throughout the year by employing an air conditioner. The indoor laboratory ambient is therefore more or less correlated with the outdoor weather in the present experiment.

3.5 Possible effect of the remaining water content

We have seen the close resemblance between the HTT and HTT-type spectra and that between the DHT and DHT spectra, and the season-dependent occurrence of the both types induced by the "mild" HT. To examine the possible effect of the water content occasionally remaining on the wet substrates, it is necessary to estimate the relative humidity that may be realized in the aluminum tube used for the heating processes in the present experiment.



Fig. 6 Water content necessary for filling a 50-cm³ vessel with an ambient of 100% relative humidity.

The relative humidity *RH* at a given temperature is defined as,

$$RH^{=} p_{act} / p_{sats} \tag{1}$$

where p_{act} is the actual water vapor pressure, and p_{sat} is the saturated water vapor pressure, which is a function of temperature empirically simulated using Tetens' equation [10] written as,

$$p_{\rm sat} = 6.11 \times 10^{7.5T/(T+237.5)}$$
 (hPa) (2)

where T is the temperature measured in °C. Thus obtained values of p_{sat} are translated into the saturated vapor quantities n_{W} in mol using the equation of state for ideal gas,

$$p_{\rm sat} V = n_{\rm W} R(T+273),$$
 (3)

where V, n_W and $R = 8.31 \text{ J mol}^{-1} \text{ K}$ denote the volume, the water content in mol and the gas constant, respectively. Using Eqs. (1)-(3) together with MW= 18.0 for H₂O, we have estimated the water content m_W necessary for filling a vessel with an ambient of RH=100%, where the inner volume of the tube used in the present experiment is estimated as $V = 50 \text{ cm}^3$ referring to the dimensions given in Sect. 2. The resultant $m_W - T$ curve is a superlinearly increasing function of T as shown in Fig. 6.

Of possible factors regulating the local humidity in the aluminum tube, a highly humid laboratory ambient will be certainly effective for retarding the drying-up of the wet substrates, whose water contents are kept without decrease under 100%-*RH* as a matter of course. The direct contribution to the local humidity is, however, far less effective. The laboratory ambient of 25°C, e.g., may introduce only $m_W=1.15$ mg water into the tube even when RH=100%, whereas nearly an order of magnitude larger value, $m_W=6.48-9.86$ mg, is calculated to be necessary to realize 100%-*RH* in the range $T_H=60-70^\circ$ C where the "mild" HT is carried out. The above estimated m_W -values lead to an average thickness of 5.9-9.0 µm if a substrate of 10.9 cm² is entirely covered with a layer of the remaining water.

Another factor is the oxide layer covering the inner wall of the aluminum tube, since Al_2O_3 is a well-known

desiccant. If we assume the monomolecular adsorption of H₂O with an area of 10 Å² /(molecule), the inner area of the tube S=100 cm² may adsorb H₂O molecules up to 3×10^{-3} mg, which is three orders of magnitude smaller than the above estimated m_W -values required for RH =100% to be realized in the range of T_H =60~70°C. It is therefore indicated that the oxide layer does not play the dominant role in regulating the local humidity.

The above discussion leads to a tentative scheme that the water content on the sample partially remains due to the retarded drying-up until it is enclosed in the tube when the laboratory ambient is sufficiently cold and/or humid, and that the HTT-type changes in spectra take place if the appropriate local humidity is realized by the water content introduced in the tube.

4. CONCLUDING REMARKS

We have described two different consequences in the spectral changes, the HTT-type associated with a sharp J-band peak and the DHT-type with a broad band, caused by the "mild" HT carried out at temperatures $T_{\rm H}$ =60~70°C employing the wet substrates. Close resemblance is found between the HTT-type and the HTT spectra, and also between DHT-type spectra and the DHT ones, suggesting that the underlying processes of the HTT-type and the DHT ones, suggesting that the DHT-type are essentially identical with those of the HTT and the DHT, respectively. The season-dependent occurrence of the both types has suggested that the cool and/or humid weather leads to the high yield of the HTT-type spectra after "mild" HT.

The water remaining on the sample is presumably assumed to act as a humidifier to supply the water content sufficient for inducing the HTT-type spectral changes by its lubricating and/or hydrating effects.

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