Transactions of the Materials Research Society of Japan 33[1] 95-98 (2008)

Restoration of J-band by Hydrothermal Treatments in Dry-heat-treated Merocyanine LB Films

Yuki Koyano, Yuichi Sugano, Hiroko Moshino, Yasuhiro F. Miura and Michio Sugi
Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama 225-8502, Japan
Fax: 81-45-972-5972, e-mail: sugi@cc.toin.ac.jp

We report the restoration of J-band in the merocyanine (MS)-containing LB films induced by the repeated application of heat treatments; a dry-heat treatment (DHT) followed by hydrothermal treatments under 100% humidity (HTTs) (i.e., DHT→*N*×HTT) together with the dissociation of the as-deposited J-band induced by DHTs. The law of additivity is found to roughly hold among the total heating in the *N*×DHT process, during which a fraction of MS molecules is subjected to degradation. In the process of DHT→*N*×HTT, the J-band component, once totally dissociated by DHT, is restored by *N*×HTT. The occurrence and growth of the restored J-band, and the change in film texture are found to be identifiable with those seen in the second-stage when HTT is directly applied to the as-deposited film. It is shown that HTT is feasible as another means to restore the J-band in the DHT-induced red films with lesser risk of degradation than the so far known basic treatments (ATs) in vapor and liquid phases that may be associated with unfavorable chemical reactions.

Key words: Langmuir-Blodgett films, Merocyanine chromophores, Hydrothermal treatments, Dry-thermal treatments, Dissociation and restoration of J-band

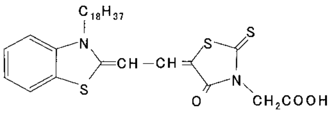
1. INTRODUCTION

As a tool to fabricate ordered molecular assemblies, the Langmuir-Blodgett (LB) technique has been attracting a continued attention. The technique is based on the manipulation 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]. The products, i.e., LB films, are characterized by their designable sequences of monolayers in the direction of surface normal.

A meorcyanine dye MS shown in Fig. 1 (a) is one of the well-known film-forming materials for constructing photoactive LB films. MS forms stable monolayers at the air-water interface when it is mixed with arachidic acid (Fig. 1 (b)) and spread on an aqueous subphase containing Cd^{2+} ion [2-4]. The MS-C_{20} mixed monolayers are easily deposited to form 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. Here, 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 known as the J-aggregate [5].

The aggregation state of MS in the mixed LB films is known to be controlled by various secondary treatments. There are many reports on this subject, since the associated color-phase transitions are of interest from the viewpoint of developing optical memory media. Acid treatments (ATs) and dry-heat treatments (DHTs) dissociate the as deposited J-band with the film color changing from blue to red. Basic treatments (BTs), when applied to the red films after AT or DHT, the J-band is restored and the color returns to be blue [3, 4].

Hydrothermal treatments under 100% humidity (HTTs) first dissociate the original J-aggregate and then reorganize the chromophore alignment to form a new phase of J-aggregate which is deep blue in color with the spectra further redshifted and sharper in shape than those before the treatment [6-14]. In the HTT process, round-shaped superstructures, up to ~0.1 mm or even larger in diameter, are observed under microscope [10-13]. Further, these superstructures are estimated to be one monolayer thick. X-ray diffraction measurements have revealed that AT introduces disorders in the Cd^{2+} ion lattice which is originally located at each hydrophilic interface between the adjacent monolayers in the LB films, and that DHT and HTT, in contrast, enhance the degree of ordering of the Cd^{2+} ion lattice [4, 10, 14].



$CH_3(CH_2)_{18}COOH$

(a) (b)

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

We have been examining the effect of HTT and DHT processes when they are successively applied on the same samples. It has been found that the law of additivity of heating time t_H approximately hold for both HTT and DHT when the heating temperature T_H is kept constant, and that HTT applied after DHT is effective for the new phase of J-band to grow associated with the superstructures as is the case with HTT directly applied on the as-deposited films. The results are shown in the present paper. A successive application, DHT and then HTT, e.g., is hereafter referred to as DHT(T_H, t_H) →HTT(T_H, t_H).

2. EXPERIMENTAL

MS and C_{20} were purchased from Hayashibara Biochemical Lab. Inc. and Fluka AG, respectively. They were dissolved in optical-grade chloroform from Tokyo Kasei with a molar mixing ratio of [MS] : [C_{20}]=1 : 2 [10]. 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 described in the previous papers [2-13]. 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 pure water in an ultrasonic bath. After dried at 50°C, each substrate

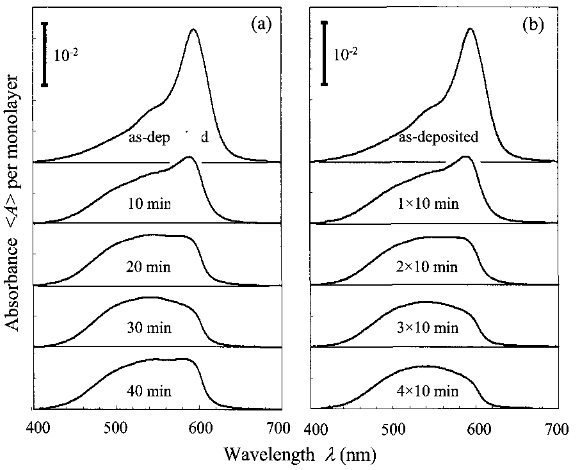


Fig. 2 Absorbance spectra $\langle A \rangle$ per monolayer: (a) after DHT(90°C, t_H) with t_H=10, 20, 30 and 40 min applied to samples belonging to the same batch, and (b) after N×DHT(50°C, 10 min) with N=1, 2, 3 and 4 successively applied to the same sample. The spectrum in the as-deposited state is also shown at the top of each figure.

was covered with five monolayers of C_{20} to make its surface hydrophobic, and then ten monolayers of MS-C_{20} were deposited. The films were of Y-type with a deposition ratio of ~1. The samples were stored in a desiccator to remove the remaining water. For both HTT and DHT, an aluminum tube (ca. 20 mm in diameter and 150 mm long) with a screw lid was employed. For HTT, small amount of pure water (2 cm^3 or less) was introduced into the tube as described previously [9]. A spacer was then put at the bottom to separate the sample from the water. After the sample was enclosed, the tube was settled for a given heating time in a water bath controlled at a constant temperature and then water-cooled down to room temperature. Absorption spectra $\langle A \rangle=(A_{\parallel}+A_{\perp})/2$ were obtained using a Shimadzu UV-2100 spectrophotometer. Here, $A_{\parallel}$ and $A_{\perp}$ denote absorbances for normal 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 Characterization of the DHT process

3.1.1 Law of additivity of t_H in the spectral change

Figure 2 (a) shows the UV-visible absorbance spectra $\langle A \rangle=(A_{\parallel}+A_{\perp})/2$ in the as-deposited state, and after DHT(90°C, t_H) with t_H=10, 20, 30 and 40 min applied to samples belonging to the same batch. The case of repeated application of DHT is referred to in Fig. 2 (b), in which N×DHT(50°C, 10 min) with N=1, 2, 3 and 4 are successively applied to the same sample. Figures 3 (a) and (b) show the difference spectra defined as $\Delta\langle A \rangle=\langle A \rangle-\langle A \rangle_{\text{as-deposited}}$ obtained using the data shown in Figs. 2 (a) and (b), respectively. In both $\langle A \rangle$ and $\Delta\langle A \rangle$ representations, the two sets of spectra closely resemble to each other. Therefore, the law of additivity holds between t_H and Σt_H in the spectral change. The band components on the right- and left-hand sides of an isosbestic point at~540 nm show a tendency to decrease and increase, respectively, as the process proceeds.

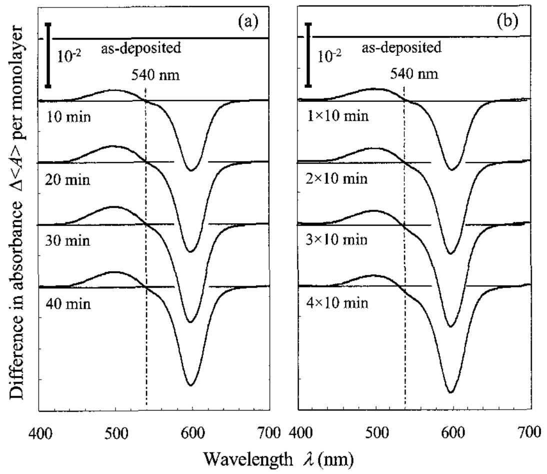


Fig. 3 Difference spectra $\Delta\langle A \rangle=\langle A \rangle-\langle A \rangle_{\text{as-deposited}}$ obtained using the data shown in Fig. 2: (a) after DHT(90°C, t_H) with t_H=10, 20, 30 and 40 min applied to samples belonging to the same batch, and (b) after N×DHT(50°C,10 min) with N=1, 2, 3 and 4 successively applied to the same sample. A flat line at the top of each figure refers to the as-deposited $\Delta\langle A \rangle$=0. .

It should be noted that apparent deviations from the law of additivity were observed for $t_H \leq 10$ min in the previous study [3]. This may result from the difference between the present and the previous heating systems in attaining the equilibrium. Here, the present system with a water bath is expected to have the shorter response time than the previously used test chamber controlling the temperature of the air contained in it.

3.1.2 Correspondence to the three-component model

In previous papers [8, 11, 14], it has been indicated that the spectra are deconvoluted into three components, Bands I, II and III centered at 485-515, 525-555 and 590-600 nm, respectively, and that these three, Bands I, II and III are presumably assigned to be the blue shifted dimer, monomer and redshifted J-bands, respectively. The dissociation of the as-deposited J-band in the DHT process is expressed as [Band III (as-deposited)]→ [Band I], while the Band-II component remains almost constant throughout the process [11, 14].

In each $\Delta\langle A \rangle$ spectrum shown in Figs. 3 (a) and (b), a single peak and a single valley are seen at right and left of the intersection with the horizontal axis at ~540 nm, respectively [3]. The results are consistent with the previous analysis based on the three-component model, indicating the approximate invariance of the Band II component in the DHT process.

3.1.3 Degradation of MS molecules during DHT

The relative oscillator strength $\int \Delta\langle A \rangle d\nu$ is plotted against t_H and Σt_H in Figs. 4 (a) and (b), respectively, for the corresponding peak and valley at left and right of the difference spectra $\Delta\langle A \rangle$ in Fig. 3, where ν denotes $1/\lambda$. Here, the pair of the upper and lower curves in each figure should hold symmetry with respect to the

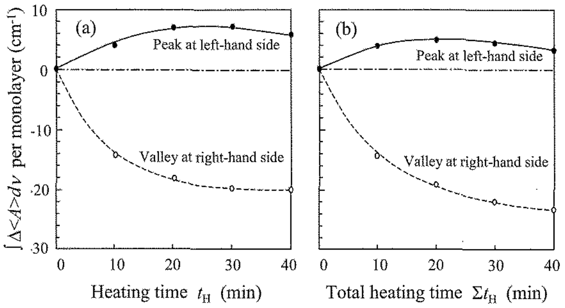


Fig. 4 $\int \Delta\langle A\rangle d\nu$ plotted against t_H (a) and Σt_H (b) for the peak and the valley at left-hand and right-hand sides of the difference spectra $\Delta\langle A\rangle=\langle A\rangle-\langle A\rangle_{\text{as-deposited}}$ obtained using the data shown in Figs. 3 (a) and (b), respectively, where $\nu=1/\lambda$ is the wavenumber.

horizontal axis when the total oscillator strength remains unchanged, and the observed downward deviation corresponds to the decrease in the total oscillator strength. It is therefore suggested that MS molecules are subjected to degradation or hypochromic effect besides the main reaction [Band III]→[Band I]. Of these two, degradation is presumably preferred to hypochromic effect since the upper curve for the peak at left-hand side in each figure shows a maximum, indicating that the Band I component turns to decrease as the DHT process proceeds. The larger downward deviation in Fig. 4 (b) than in Fig. 4 (a) indicates the larger degradation rate for the N×DHT case than that for the single DHT case. This suggests the role of the heating and cooling stages involved in each individual DHT process to induce the degradation.

3.2 Characterization of the HTT process

3.2.1 HTT directly applied to the as-deposited samples

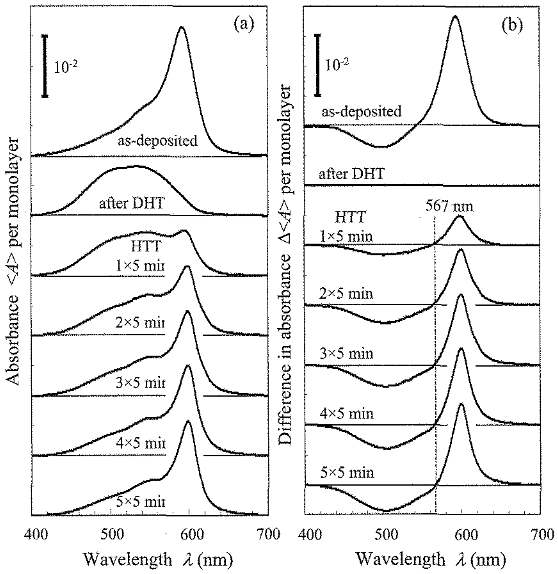


Fig. 5 (a) Absorbance spectra $\langle A\rangle$ for the repeated application DHT(90°C, 60 min)→N×HTT(50°C, 5 min) with N being 1, 2, 3, 4 and 5. (b) Difference spectra $\Delta\langle A\rangle=\langle A\rangle-\langle A\rangle_{\text{after DHT}}$ for the same processes of repeated application. The spectra for the as-deposited and the after-DHT cases are also shown in each figure.

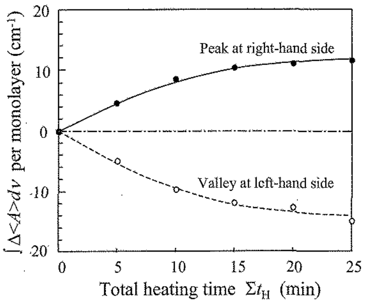


Fig. 6 $\int \Delta\langle A\rangle d\nu$ plotted against Σt_H for the peak and the valley at left-hand and right-hand sides of the difference spectra $\Delta\langle A\rangle=\langle A\rangle-\langle A\rangle_{\text{after DHT}}$ obtained using the data shown in Fig. 5 (b), where $\nu=1/\lambda$ is the wavenumber.

In previous papers [11, 14], we have shown that the HTT process, when directly applied to the as-deposited film, involves two stages: [Band III (as-deposited)] →[Band I] and [Band I]⇄[Band III (reorganized)] in the first and second stages, respectively. The kinetics of the second stage reaction is found to obey a simple first-order law, while the first-stage reaction has not yet been analyzed due to its transient nature with faster reaction rates than those of the DHT process, e.g., the saturation of the first stage with the onset of the second stage is recognized in the spectrum after HTT(65°C, 1 min) [11, 14].

In the case of repeated application of HTT to the as-deposited films, it has been found that the additivity of t_H in spectral change holds for N×HTT(65°C, 5 min) with N being 1, 2, and 3 within the deviation among individual samples belonging to the same batch. The details will be reported elsewhere.

3.2.2 HTT applied after DHT

The as-deposited J-band is dissociated by applying DHT prior to the application of HTT in order to evaluate the second-stage reorganization of the J-band in the HTT process separately from the first-stage dissociation.

Figure 5 (a) shows the absorbance spectra $\langle A\rangle$ for DHT(90°C, 40 min)→N×HTT(50°C, 5 min) with N being 1, 2, 3 and 4 successively applied to the same sample together with those for the as-deposited and after-DHT cases. The difference spectra $\Delta\langle A\rangle=\langle A\rangle-\langle A\rangle_{\text{after DHT}}$ are also shown in Fig. 5 (b) for the corresponding cases. After DHT(90°C, 60 min), the Band I component increases at the expense of the original J-band [i.e., Band III (as-deposited)], which is almost completely dissociated. Here, it is noted that the $\Delta\langle A\rangle$ spectra at the top of Fig. 5 (b) corresponds to the inversion with respect to the horizontal axis of those shown in Fig. 3, where the subtracter is not $\langle A\rangle_{\text{after DHT}}$ but $\langle A\rangle_{\text{as-deposited}}$. The spectral change in the N×HTT (50°C, 5 min) process closely resembles to that in the second stage of the HTT directly applied to the as-deposited samples. The Band III component increases at the expense of Band I as the process proceeds. The intersection of each curve for $N\geq1$ is identifiable with the isosbestic point λ=567 nm reported previously [9]. This is consistent with the invariance of the Band II component reported in previous papers.

3.2.3 Degradation of MS molecules during N×HTT

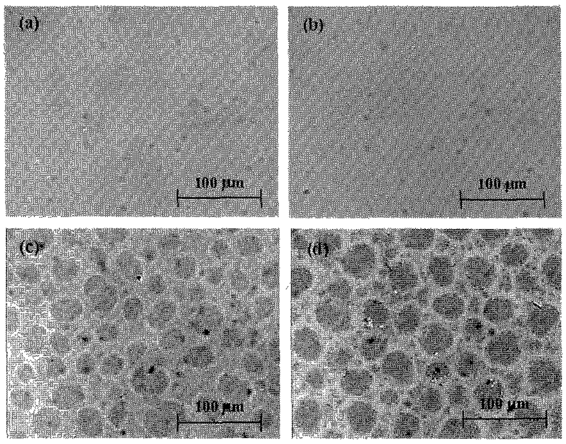


Fig. 7. Photomicrographs of MS-C_{20} mixed LB films: (a) As-deposited state, (b) DHT(90°C, 60 min), (c) DHT (90°C, 60 min)→HTT(50°C, 5 min), and (d) DHT(90°C, 60 min)→5×HTT(50°C, 5 min).

Figure 6 shows $\int\Delta<A>dv$ as a function of Σt_H for the corresponding valley and peak at left and right of the difference spectra $\Delta<A>$ in Fig. 5 (b). The pair of the upper and lower curves is associated with much smaller downward deviation from the symmetry with respect to the horizontal axis than the DHT cases shown in Fig. 3, indicating that the reorganized Band III component is thermally more stable than other three including the as-deposited J-band, and that the degradation of MS molecules mainly proceeds via the Band I state. Here, the hypochromic effect may be discarded as unrealistic in the reorganization of the J-aggregate. The thermal stability of the reorganized J-band is dealt with in a separate paper.

3.3 Change in the film texture

3.3.1 Absence of superstructure after DHT

As reported previously [10-13], the microscopic image is featureless in the as-deposited state and after DHT as shown in Figs. 7 (a) and (b). When observed under polarized light, however, the in-plane anisotropy seen in the as-deposited films tends to decrease as the DHT process proceeds. The observed decrease in the anisotropy reflects the gradual randomization of the choromophore by the thermal agitation, suggesting that the DHT-induced isotropic state is thermodynamically more stable than the as-deposited state.

3.3.2 Round-shaped superstructures induced by HTT

When HTT is applied to the as-deposited films, we have found that the microscopic image, initially anisotropic and featureless, tends to be isotropic and filled round-shaped domains as large as 0.1 mm or more in diameter and one monolayer thick, and that the growth process of the domains has a delay compared to that of the peak height of the reorganized J-band, indicating that it occurs subsequent to the spectral change [10, 12, 14]. The occurrence of the domains in the present case of DHT→N×HTT is essentially identical with that in the previous case starting from the as-deposited state. Figures 7 (c) and (d) show the images for N=1 and 5, respectively. The average sizes $<d>$=31±7 and 35±7 μm for N=1 and 5, respectively, in the present case is comparable to the previously obtained value of 30±10 μm for HTT (50°C, 60 min) [12].

4. CONCLUDING REMARKS

We have reported the reorganization of J-band in the MS-containing LB films induced by the repeated application DHT→N×HTT together with the dissociation of the as-deposited J-band by DHT and N×DHT. The law of additivity is found to roughly hold between t_H and Σt_H in the DHT process, during which the Band I component is subjected to degradation while the Band II remains almost unchanged. In the process of DHT→N×HTT, the Band III component, once totally dissociated by DHT, is reorganized by N×HTT. The occurrence and growth of the reorganized J-band, and the change in the film texture as well, are found to be essentially identical with those seen in the second-stage when HTT is directly applied to the as-deposited film. The present results show that HTT is feasible as another means to restore the J-band in the DHT-induced red films with lesser risk of degradation than the so far known AT that may be associated with unfavorable chemical reactions.

Acknowledgements

The authors would like to thank Mr. S. Mouri, Ms. S. Hasegawa and Mr. J. Miyata for their contributions in the early stages. This work was supported in part by University-Industry Joint Research Project for Private University: matching fund subsidy from MEXT, 2002-2007.

REFERENCES

[1] K. B. Blodgett: *J. Am. Chem. Soc.* **57**, 1007 (1936).
[2] M. Sugi and S. Iizima: *Thin Solid Films* **68**, 199 (1980).
[3] M. Sugi, M. Saito, T. Fukui and S. Iizima: *Thin Solid Films* **129**, 15 (1985).
[4] M. Saito, M. Sugi, K. Ikegami, M. Yoneyama and S. Iizima: *Jpn. J. Appl. Phys.* **25**, L478 (1986).
[5] See, for example, "J-aggregates", Ed. by T. Kobayashi, World Scientific, Singapore (1996).
[6] J. Miyata, S. Morita, Y. F. Miura and M. Sugi: *Jpn. J. Appl. Phys.* **44**, 8110 (2005).
[7] J. Miyata, S. Morita, Y. F. Miura and M. Sugi: *Colloids Surf.* A **284-285**, 509 (2006).
[8] S. Mouri, J. Miyata, S. Morita, Y. F. Miura and M. Sugi: *Trans. Mater. Res. Soc. Jpn.* **31**, 573 (2006).
[9] S. Mouri, S. Morita, Y. F. Miura and M. Sugi: *Jpn. J. Appl. Phys.* **45**, 7925 (2006).
[10] S. Mouri, H. Moshino, S. Hasegawa, Y. F. Miura and M. Sugi: *Jpn. J. Appl. Phys.* **46**, 1650 (2007).
[11] H. Moshino, S. Hasegawa, S. Mouri, Y. F. Miura and M. Sugi: *Trans. Mater. Res. Soc. Jpn.* **32**, 305 (2007).
[12] S. Hasegawa, H. Moshino, S. Mouri, Y. F. Miura and M. Sugi: *Trans. Mater. Res. Soc. Jpn.* **32**, 309 (2007).
[13] M. Sugi, H. Moshino, S. Hasegawa, S. Mouri and Y. F. Miura and M. Sugi: *Trans. Mater. Res. Soc. Jpn.* **32**, 313 (2007).
[14] H. Moshino, S. Hasegawa, S. Mouri, Y. F. Miura, and M. Sugi: *Jpn. J. Appl. Phys.* **47** (2008), in press.

(Received January 9, 2008;Accepted Febrary 15, 2008)