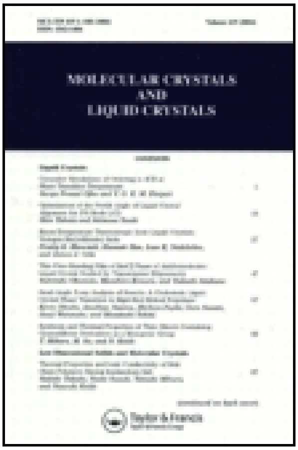

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Modification of optical characteristics in langmuir-blodgett films of merocyanine dye by reduced pressure treatment

Yoshiaki Hirano [a], Takurou Murakami [a], Yuhki Nakamura [a], Yoshinori Fukushima [a], Yoshikazu Tokuoka [a] & Norimichi Kawashima [a]

[a] Department of Biomedical Engineering, Toin University of Yokohama, Aoba-ku, Yokohama, Japan

Version of record first published: 18 Oct 2010

To cite this article: Yoshiaki Hirano, Takurou Murakami, Yuhki Nakamura, Yoshinori Fukushima, Yoshikazu Tokuoka & Norimichi Kawashima (2004): Modification of optical characteristics in langmuir-blodgett films of merocyanine dye by reduced pressure treatment, Molecular Crystals and Liquid Crystals, 425:1, 265-271

To link to this article: http://dx.doi.org/10.1080/15421400490506919

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 265/[543]–271/[549], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506919

MODIFICATION OF OPTICAL CHARACTERISTICS IN LANGMUIR-BLODGETT FILMS OF MEROCYANINE DYE BY REDUCED PRESSURE TREATMENT

Yoshiaki Hirano, Takurou N. Murakami, Yuhki K. Nakamura,
Yoshinori Fukushima, Yoshikazu Tokuoka, and
Norimichi Kawashima
Department of Biomedical Engineering, Faculty of Engineering,
Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku,
Yokohama, 225-8502, Japan

We have modified the optical characteristics of various aggregation states including J- and H-aggregates in Langmuir-Blodgett (LB) films of merocyanine dye (MS) by reduced pressure treatment. The J-band peaks at 590 nm almost remain unchanged after the treatment. On the other hand, the peaks of blue-shifted bands involving the H-band at 505 nm drastically diminish, resulting in the formation of the broad bands having the absorption maximum at 530-540 nm with the bands showing in-plane isotropy. The results indicate the dissociation of the MS aggregates. Therefore, the MS blue-shifted aggregates were found to dissociate easily by the reduced pressure treatment.

Keywords: blue-shifted band; H-aggregate; Langmuir-Blodgett (LB) films; merocyanine dye; reduced pressure treatment

INTRODUCTION

A great deal of attention has been paid towards potential applications of organized molecular films to various molecular devices such as photovoltaic cells, optical memory media and optical waveguides with a lower refractive index [1]. Recently, organic thin films with aggregation states of functional molecules, which are called H-aggregates, have been found to be useful in developing and improving these devices [2–4]. Therefore, studies

---

Received 1 October 2003; accepted 3 February 2004.

Address correspondence to Yoshiaki Hirano, 1614 Kurogane-cho, Aoba-ku, Yokohama, 225-8502, Japan. Tel.: +81-45-972-5881, Fax: +81-45-972-5972, E-mail: yohirano@ce.toin.ac.jp.

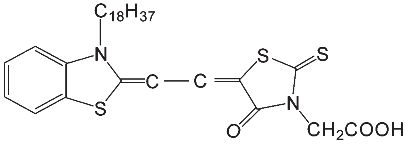

FIGURE 1 Chemical structure of merocyanine dye (MS).

in relation to the H-aggregation are expected to be of great interest not only in practical use but also in basic research of assembled organic molecules.

We have engaged in the research subject using Langmuir-Blodgett (LB) films of merocyanine dye (MS, shown in Fig. 1) as a prototype, since various aggregation states including red-shifted J- and blue-shifted H-aggregates can be easily tuned in the ultra-thin films based on MS [5–7]. In the course of the study, we have so far explored a key for the blue-shifted aggregation by characterizing the structures of the red-shifted and the blue-shifted aggregates [5–7].

Here, we attempt to modify the MS aggregation states from blue-shifted aggregate to monomer or dimer by second treatments, since the mechanism of the blue-shifted aggregation may be clarified by the comparison of their structural characterizations. In the second treatments of the MS-containing LB films, the red-shifted J-aggregate has been so far reported to dissociate by heat or acid treatment [8]. However, no attempt to modify the MS aggregation states employing reduced pressure, as parameters of external environments, has come to our knowledge.

In the present study, we report preliminary results on the modification by the reduced pressure treatment of the optical characteristics of various aggregation states including J- and H-aggregates in the MS-containing LB films.

EXPERIMENTAL

Surface-active merocyanine dye (MS), arachidic acid (C_{20}) and n-octadecane (AL_n; $CH_3(CH_2)_{n-2}CH_3$, n = 18) were used as film-forming materials. MS, C_{20} and AL_{18} were dissolved in freshly-distilled chloroform with molar mixing ratios $[MS]:[C_{20}]:[AL_{18}] = 1:2:x$ ($0 \leqq x \leqq 5.0$). The MS concentration was of the order of 10^{-4} M. Solutions were spread on the air-water interface to form mixed monolayers after solvent evaporation. Aqueous subphase containing Cd^{2+} and deposition conditions were the same as given in the previous papers [5–7]. A glass substrate precoated with five monolayers of cadmium arachidate (CdC_{20}) was used. Ten-layered mixed LB films deposited on both sides of the precoated substrates were used as samples. These mixed LB films were treated at 10^{-4} Pa and room temperature for 5 min. Polarizing visible spectra $A_{||}$ and $A_{\perp}$ of the mixed LB films were measured using a linearly polarized light with the electric vector parallel and perpendicular to the dipping direction, respectively, before and after the second treatments. The data were taken around the center of the substrate.

RESULTS AND DISCUSSION

Figures 2(a)–(f) show typical polarizing visible spectra of as-deposited LB films of the MS-C_{20} binary and the MS-C_{20}-AL_{18} ternary systems ([MS]:[C_{20}]:[AL_{18}] = 1:2:x), where $x = 0$, 1.0, 2.0, 3.0, 4.0 and 5.0. The solid and the dotted lines refer to the spectra $A_{||}$and $A_{\perp}$, respectively. In Figure 2(a), the mixed LB films of the MS-C_{20} binary system exhibit a sharp

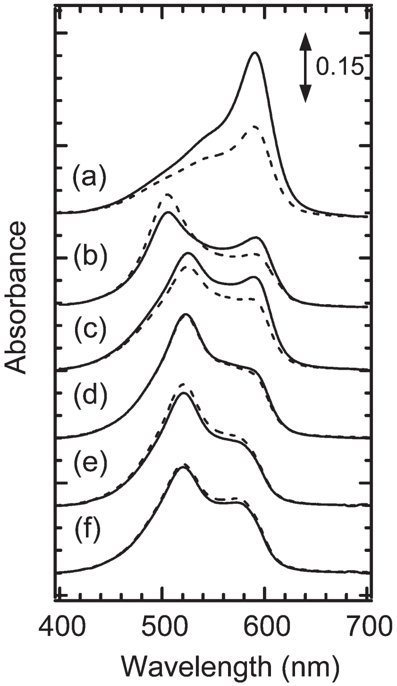

FIGURE 2 Polarizing visible spectra of as-deposited LB films of the MS-C_{20} binary and the MS-C_{20}-AL_{18} ternary systems. The molar mixing ratio of [MS]:[C_{20}]:[AL_{18}] = 1:2:x, where x = (a) 0, (b) 1.0, (c) 2.0, (d) 3.0 (e) 4.0 and (f) 5.0. The solid and the dotted lines refer to the spectra $A_{||}$ and $A_{\perp}$, respectively.

absorption band at 590 nm, which is red-shifted from that of the MS monomer band at around 540 nm [8,9]. The absorption maximum at 590 nm shows the optical anisotropy with dichroic ratio $R > 1$, where R is defined as $R = A_{\parallel}/A_{\perp}$. The red-shifted band with $R > 1$ at 590 nm is ascribed to J-aggregation elongated in shape, which is associated with MS chromophore alignments of head-to-tail type in the aggregates [5–11].

In Figure 2(b), on the other hand, the observed spectrum is the superposition of the blue-shifted band with $R < 1$ at 505 nm and the red-shifted J-band $R > 1$ at 590 nm. The blue-shifted band is assigned to H-band accompanied by MS chromophore alignments of side-by-side type, based on the energy shift, the sharpness and the in-plane anisotropy of the band [6]. In Figure 2(c), the blue-shifted and the red-shifted bands are located at 525 nm and 590 nm, respectively. The overlapped spectra can be deconvoluted into the blue-shifted band at 520 nm and the red-shifted J-band at 590 nm, with their bands showing $R > 1$ as well [6]. (data not shown). The 520-nm band deconvoluted is somewhat less blue-shifted and broader in shape than the H-band. Therefore, the blue-shifted band at 520 nm is caused by oligomer with side-by-side alignments of chromophores, of which less blue-shift has been interpreted to be probably due to a decrease in the aggregation number as compared with that of the H-aggregates at 505 nm [6].

Furthermore, the blue-shifted peak at 520 nm and the red-shifted shoulder at 580-590 nm are seen in Figures 2(d), (e) and (f). The observed spectra can be divided into the blue-shifted band at 520 nm and the red-shifted band at 580 nm, showing $R = 1$ for both bands [6]. (data not shown). Consequently, the blue-shifted band at 520 nm and the red-shifted band at 580 nm are attributed to relatively small aggregates with chromophore alignments of side-by-side and head-to-tail types, respectively, on the basis of the small energy shift, the broadening and the in-plane isotropy of the bands in comparison with those in Figures 2(a)–(c) [6]. Main features of these spectra in Figure 2 coincide well with those reported in our previous works [6].

All the mixed LB films in Figure 2 were treated by reduced pressure in order to dissociate the blue-shifted aggregates including the H-aggregate. Figures 3(a)–(f) represent polarizing visible spectra of the cases ($[MS]:[C_{20}]:[AL_{18}] = 1:2:x$) after the reduced pressure treatment, where $x = 0$, 1.0, 2.0, 3.0, 4.0 and 5.0. The solid and the dotted lines refer to $A_{\parallel}$ and $A_{\perp}$, respectively. In Figure 3(a), the peak intensity of the J-band decreases by about 10% and the absorption from 450 to 560 nm slightly increases. The result suggests the dissociation of the J-aggregates in the outermost layer of the LB films deposited.

In Figures 3(b) and (c), on the other hand, the 505-nm and the 520-nm bands drastically diminish, and the absorption increases in the range from

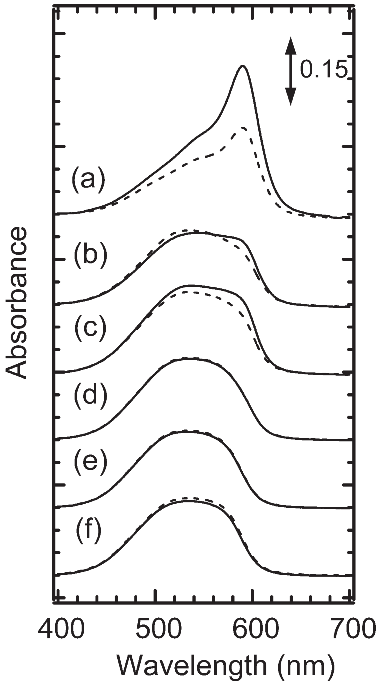

FIGURE 3 Polarizing visible spectra of mixed LB films of the MS-C_{20} binary and the MS-C_{20}-AL_{18} ternary systems after reduced pressure treatment. The molar mixing ratio of [MS]:[C_{20}]:[AL_{18}] = 1:2:x, where x = (a) 0, (b) 1.0, (c) 2.0, (d) 3.0 (e) 4.0 and (f) 5.0. The solid and the dotted lines refer to the spectra $A_{\|}$ and $A_{\perp}$, respectively.

530 to 560 nm. In addition, the spectra become appreciably broad in shape and R approaches unity. It is also noted that the red-shifted shoulders with $R > 1$ are observed, indicating that the J-band component still remains after the treatment.

Similarly, broad bands with the absorption maximum at 530–540 nm are also observed in Figures 3(d), (e) and (f), showing $R = 1$ over the visible range. In particular, the spectrum features resemble fairly well those treated by heat [8]. Here, it should be noted that no red-shifted shoulder at 580–590 nm is observed unlike the case of the red-shifted J-band at 590 nm.

In the above experimental results, our tentative assignments of the spectra in Figures 3(b) and (c), and Figures 3(d)–(f) are the convolution of the monomer and the red-shifted J-like component, and the monomer, respectively, referring to the dramatic diminution of the peak due to the aggregation, the broadening and the dichroic behavior in the observed bands. Thus, various MS aggregation states in the inner LB films deposited as well as in the outermost films were found to dissociate rapidly with the reduced pressure treatment, except for the J-aggregates at 590 nm.

As seen in Figure 3, the phenomena induced by reduced pressure can be currently interpreted as follows: In previous papers [5–7], we have confirmed the presence and the orientation of AL_{18} molecules which trigger off the blue-shifted aggregation in the mixed LB films of the ternary systems with the surface pressure-area isotherm and the infrared spectroscopy measurements. In all the ternary systems, the AL_{18} molecules tend to fill the MS empty space which can approximately accommodate two straight-chain hydrocarbons, and the long axis of the AL_{18} molecules with the all-trans conformation is almost perpendicular to the film surface. Taking into consideration the structural characterizations of the previous works, the dissociation of the MS aggregation states in Figure 3 is postulated to be possibly ascribed to the removal of the AL_{18} molecules from the mixed LB films of all the ternary systems under reduced pressure, leading to a change in the MS permanent dipole interaction. Further studies for the concrete assignment of the spectra after the treatment and the origin of the phenomena are now in progress.

SUMMARY

We have executed the modification of the optical characteristics of the red-shifted and the blue-shifted aggregates by reduced pressure treatment in the ternary LB systems with the molar mixing ratios of $[MS]:[C_{20}]:[AL_{18}] = 1:2:x$ in the range of $0 \leqq x \leqq 5.0$. The peaks of the red-shifted J-band at 590 nm are almost kept constant after the treatment. On the other hand, the blue-shifted bands at 505 nm and 520 nm, and the red-shifted shoulders at 580–590 nm dramatically diminish, resulting in the formation of the broad bands having the absorption maximum at 530–540 nm with the bands showing the in-plane isotropy over the visible range. The results indicate the dissociation of the MS aggregates. Thus, the MS aggregation states expect for J-aggregates at 590 nm were found to dissociate easily by the reduced pressure treatment.

REFERENCES

[1] Kuhn, H. (1989). *Thin Solid Films*, *178*, 1.
[2] Saito, K. (2001). *J. Phys. Chem. B*, *103*, 4235.
[3] (2001). *Molecular Electronics and Bioelectronics 12*, 143. (in Japanese)
[4] Watanabe, K., Wakamatsu, T., & Saito, K. (2002). *IEICE Technical Report*, *102*, 19. (in Japanese)

[5] Hirano, Y., Kamata, K. N., Inadzuki, Y. S., Kawata, J., Miura, Y. F., Sugi, M., & Ishii, T. (1999). *Jpn. J. Appl. Phys. 38*, 6024.

[6] Hirano, Y., Okada, T. M., Miura, Y. F., Sugi, M., & Ishii, T. (2002). *J. Appl. Phys.*, 88, 5194.

[7] Hirano, Y., Inadzuki, Y. S., Miura, Y. F., Sugi, M., & Ishii, T. (2002). *Trans. Mater. Res. Soc. Jpn.*, *27*, 521.

[8] Sugi, M., Saito, M., Fukui, T., & Iizima, S. (1985). *Thin Solid Films*, *132*, 15.

[9] Ikegami, K., Mingotaud, C., & Lan, M. (1999). *J. Phys. Chem. B*, *103*, 11261.

[10] Sugi, M., Fukui, T., Iizima, S., & Iriyama, K. (1980). *Mol. Cryst.* & *Liq. Cryst.*, *62*, 165.

[11] Kobayashi, T. (1996). *J-Aggregates*, (World Scientific, Singapore).