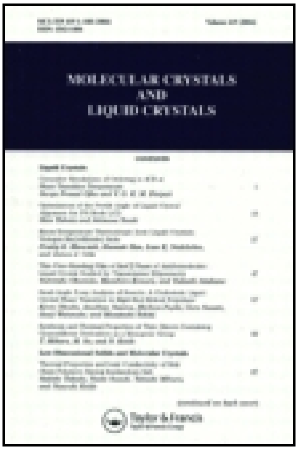

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Orientation of Merocyanine Dye in Mixed Langmuir-Blodgett Films Investigated by Visible Absorption Spectroscopy

Yoshiaki Hirano [a] [b] , Masaharu A. Ohkubo [a] , Yoshikazu Tokuoka [a] , Norimichi Kawashima [a] & Yukihiro Ozaki [b]

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

[b] Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Japan

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Orientation of Merocyanine Dye in Mixed Langmuir-Blodgett Films Investigated by Visible Absorption Spectroscopy

Yoshiaki Hirano
Department of Biomedical Engineering, Faculty of Engineering, Toin University of Yokohama, Aoba-ku, Yokohama, Japan and Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Japan

Masaharu A. Ohkubo
Yoshikazu Tokuoka
Norimichi Kawashima
Department of Biomedical Engineering, Faculty of Engineering, Toin University of Yokohama, Aoba-ku, Yokohama, Japan

Yukihiro Ozaki
Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Japan

We have investigated the out-of-plane and the in-plane orientations of the transition dipole moments of merocyanine dye (MS) with various aggregation states including J- and H-aggregates in the mixed LB films by means of visible absorption spectroscopy. The results of the MS orientation estimated using the simple geometrical model suggest that the MS transition dipole moments lie in the film plane in all the aggregation states, and that the relationships between the dichroic behaviors observed and the in-plane order parameters obtained from the model are well recognized in the individual red-shifted and the blue-shifted aggregates.

Keywords: H-aggregate; J-aggregate; Langmuir-Blodgett (LB) films; merocyanine dye; simple geometrical model; visible absorption spectroscopy

Address correspondence to Yoshiaki Hirano, Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, 669-1337, Japan. E-mail: baw91933@ksc.kwansei.ac.jp

INTRODUCTION

Organized molecular films containing dyes have attracted much attention because of potential applications to various molecular devices such as photovoltaic cells, optical memory media and optical waveguides [1–4]. While the dyes are well-known to form a variety of aggregation states, thin films with the dye aggregation states, which are called H-aggregates, have been found to be useful in developing and improving the devices [2–4]. Therefore, studies on the formation mechanism of the H-aggregates are of great interest not only for practical application but also for basic research of assembled organic molecules.

We have engaged in the research subject of the formation mechanism of the blue-shifted aggregates including H-aggregates using Langmuir-Blodgett (LB) films of merocyanine dye (MS shown in Fig. 1) with various aggregation states including red-shifted J- and blue-shifted H-aggregates [5,6]. In the course of the studies, we have explored the structural factors governing the dye aggregation states by characterizing the MS structures of the red-shifted and the blue-shifted aggregates aiming at the clarification of the formation mechanism of the blue-shifted aggregates including the H-aggregates [5,6]. In the studies of the structural characterizations [5,6], without the experimental evidence, we have so far assumed that the MS transition dipole moments lie in the film plane in all the aggregation states. Therefore, the validity of the assumption of the MS orientation should be demonstrated experimentally.

In the present study, we report the results of the investigation of out-of-plane and in-plane orientations of the MS transition dipole moments in various aggregation states including J- and H-aggregates in the MS-containing LB films by means of visible absorption spectroscopy.

EXPERIMENTAL

Merocyanine dye (MS), arachidic acid (C_{20}), *n*-octadecane (AL_{18}) were used as the film-forming materials. MS, C_{20}, and AL_{18} were dissolved

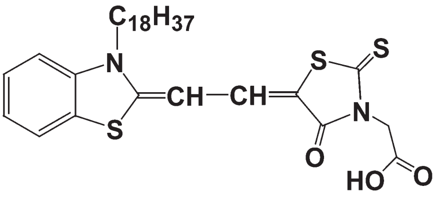

FIGURE 1 Chemical structure of the merocyanine dye (MS).

in freshly distilled chloroform with the molar mixing ratios of [MS]:$[C_{20}]$:$[AL_{18}] = 1{:}2{:}x$ ($x = 0$–5). The MS concentration was of the order of 10^{-4} M. The solutions were spread on the air–water interface to form the binary and the ternary monolayers after solvent evaporation. The aqueous subphase and the deposition conditions were the same as those reported previously [5,6]. CaF_2 substrates precoated with five monolayers of cadmium arachidate (CdC_{20}) were used. Two-layered LB films deposited on both sides of the precoated substrates were used as samples. All the LB films were of Y-type with a transfer ratio of around unity. Visible absorption spectrum measurements were carried out at room temperature using a JASCO UV/visible V-550 spectrometer.

In the present study, a simple geometrical model [7] where only refraction due to an organic thin film is taken into account was applied for determining the orientation of the MS transition dipole moments. Figure 2(a) shows the configuration of the experiment of visible absorption spectroscopy with the linearly polarized light. β' and β are the incident and the refractive angles, respectively. α denotes the angle between the X-axis and the electric vector of the light, where $\alpha = 0^\circ$ and 90° correspond to *s*- and *p*-polarizations, respectively. The peak intensity A(α, β') of the absorption due to the transition dipole moment m can be expressed as

$$A(\alpha, \beta') \propto \frac{1}{\cos\beta}\langle(\sin\theta\cos\phi\cos\alpha + \sin\theta\sin\phi\cos\beta\sin\alpha + \cos\theta\sin\beta\sin\alpha)^2\rangle \qquad (1)$$

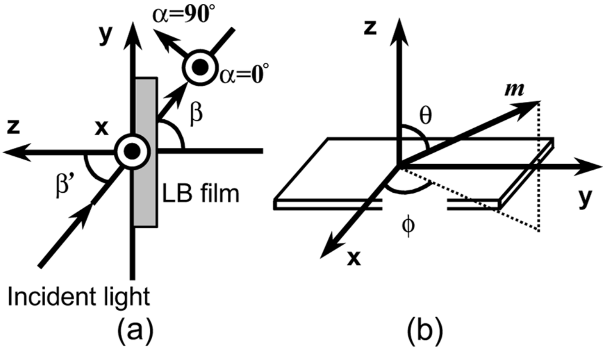

FIGURE 2 (a) The configuration of the experiment of visible absorption spectroscopy with the linearly polarized light. β' and β are the incident and the refractive angles, respectively. α denotes the angle between the X-axis and the electric vector of light. (b) θ and ϕ of polar angles defining the direction of the transition dipole moment m.

where θ and ϕ refer to the polar angles defining the direction of m in Figure 2(b). The angular bracket $\langle\ \rangle$ denotes the statistical average over θ and ϕ. The term of $1/\cos\beta$ represents the difference in the optical path length. Based on Eq. (1), following two parameters concerning the molecular orientation can be obtained as

$$\langle \sin^2\theta \sin^2\phi \rangle = \left[\frac{A(0^\circ,0^\circ)}{A(90^\circ,0^\circ)} \left(1 + \frac{A(90^\circ,\beta')}{A(0^\circ,\beta')\sin^2\beta} \right) - \cot^2\beta + 1 \right]^{-1} \tag{2}$$

and

$$\langle \sin^2\theta \rangle = \langle \sin^2\theta \sin^2\phi \rangle \left(\frac{A(0^\circ,0^\circ)}{A(90^\circ,0^\circ)} + 1 \right) \tag{3}$$

where $\cos\beta = \mathrm{A}(0^\circ, 0^\circ)/\mathrm{A}(0^\circ, \beta')$. Equation (3) is the parameter representing the out-of-plane orientation of m. The parameter showing the in-plane orientation of the projection of m using Eqs. (2) and (3) can be written as

$$p = \frac{\langle \sin^2\theta \sin^2\phi \rangle}{\langle \sin^2\theta \rangle} \tag{4}$$

RESULTS AND DISCUSSION

Figure 3 shows polarized visible absorption spectra of the mixed 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 thick and the thin lines refer to the spectra of A(90°, 0°) and A(0°, 0°), respectively. For $x = 0$, the mixed LB film of the MS-C_{20} binary system exhibits a sharp absorption band at 589.5 nm, which is red-shifted by about 50 nm from that of the MS monomer band at around 540 nm. The absorption maximum at 589.5 nm shows the optical anisotropy with the dichroic ratio $\mathrm{R} > 1$, where R is defined as A(90°, 0°)/A(0°, 0°). The red-shifted band with $\mathrm{R} > 1$ at 589.5 nm is ascribed to J-aggregation elongated in shape, which is associated with the MS chromophore alignments of head-to-tail type in the aggregates [8–11]. For $x = 1.0$, on the other hand, the blue-shifted band with $\mathrm{R} < 1$ is observed at 504.0 nm. The blue-shifted band is assigned to H-band accompanied by MS chromophore alignments of side-by-side type based on the remarkable shift to higher energy sides, the sharpness and the in-plane anisotropy of the band [6].

For $x = 2.0$ and 3.0, the blue-shifted bands are located at 527.5 and 522.0 nm, respectively. These bands are the overlapped spectra of the two species; one contains the blue-shifted band at around 520 nm and

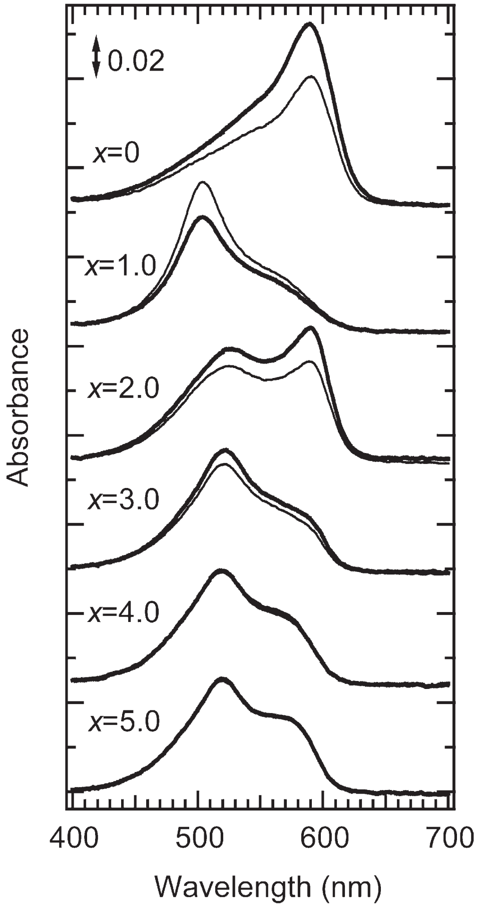

FIGURE 3 The polarized visible absorption spectra of the mixed LB films of the MS-C_{20} binary and the MS-C_{20}-AL_{18} ternary systems with the molar mixing ratios of [MS]:[C_{20}]:[AL_{18}] $= 1{:}2{:}x$ ($x = 0$–5). The thick and the thin lines refer to A(90°, 0°) and A(0°, 0°), respectively.

the other shows red-shifted band at around 590 or 580 nm with $R > 1$ (data not shown) [6]. The bands at around 520 nm are somewhat less blue-shifted and broader in shape than the H-band. Therefore, the blue-shifted bands at around 520 nm with $R > 1$ are caused by oligomers with side-by-side alignments of the MS chromophores [6]. In addition, the red-shifted bands with $R > 1$ at 590 and 580 nm are caused by J-aggregation and oligomeric aggregation with head-to-tail alignments of the chromophores [6].

Furthermore, for $x = 4.0$ and 5.0, the blue-shifted peaks at 521.0 nm and 519.0 nm are observed with the red-shifted shoulder at 580–590 nm, showing $R = 1$ over the visible range. The spectra with $R = 1$ are the result from the convolution of the blue-shifted band at 520 nm and the red-shifted band at 580 nm (data not shown). 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 smaller energy shift, the broadening shape and the in-plane isotropy of the bands in comparison with those for $x = 0$–3.0 [6]. Main features of these spectra in Figure 3 are well consistent with those reported in our previous studies. Among the changes in the MS aggregation states from $x = 0$–5.0, we are not sure why the red-shifted J-band component at 590 nm appears again in the case of $x = 2.0$.

The out-of-plane and the in-plane orientations of the MS transition dipole moments in these bands have been examined using Eqs. (1)–(4) from the simple geometrical model, where the individual parameters of the red-shifted component in the ternary systems for $x = 3.0$–5.0 have been estimated assuming the absorption position at 580 nm. As shown in Table 1, $\langle \sin^2\theta \rangle$ values in all the molar mixing ratios are in the range from 0.950 to 1.00, indicating that the MS transition dipole moments of the red-shifted and the blue-shifted components lie in the film plane.

Furthermore, the p-values of the J- and the H-bands for $x = 0$ and 1.0 are 0.585 and 0.429, respectively. These results suggest that the MS transition dipole moments of the J-bands are oriented towards

TABLE 1 The Parameters Concerning the Molecular Orientation

AL_{18} content x^a	Absorption peak (nm)	$\langle \sin^2\theta \rangle$	$\langle \sin^2\theta \sin^2\phi \rangle$	p
0	589.5	0.976	0.571	0.585
1.0	504.0	0.972	0.417	0.429
2.0	527.5	0.995	0.535	0.538
	590.5	0.994	0.565	0.568
3.0	522.0	0.951	0.503	0.529
	580.0^b	0.994^b	0.510^b	0.527^b
4.0	521.0	0.981	0.493	0.503
	580.0^b	0.980^b	0.485^b	0.495^b
5.0	519.0	0.986	0.488	0.495
	580.0^b	0.976^b	0.483^b	0.495^b

[a] The molar mixing ratio is $[MS]:[C_{20}]:[AL_{18}] = 1:2:x$.

[b] $\langle \sin^2\theta \rangle$-, $\langle \sin^2\theta \sin^2\phi \rangle$-, and p-values have been estimated assuming the absorption position at 580 nm.

the Y-axis rather than the X-axis, and that those of the H-bands are towards the X-axis. With the increase of AL_{18} content, the *p*-values approach to 0.5, indicating the in-plane isotropy. Therefore, it is suggested that the MS transition dipole moments lie in the film plane in all the red-shifted and the blue-shifted aggregates, and that the relationships between the results of the dichroic behaviors in Figure 3 and the estimates of the *p*-values from the simple geometrical model are well seen in the individual aggregation states. Thus, a series of the experimental results in this paper support the validity of our assumption of the MS in-plane orientation in the individual aggregates.

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