

# Control of Aggregate Formation in Langmuir-Blodgett Films of Merocyanine Dye - Arachidic Acid - *n*-Octadecane Ternary System

Yoshiaki Hirano<sup>a</sup>, Takuya M. Okada<sup>a</sup>, Yasuhiro F. Miura<sup>a</sup>, Michio Sugi<sup>a</sup>  
and Toshio Ishii<sup>b</sup>

<sup>a</sup> Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama, 225-8502, Japan  
Fax: +81-45-972-5972, e-mail: yohirano@cc.toin.ac.jp

<sup>b</sup> Tsurumi University, 2-1-3 Tsurumi, Tsurumi-ku, Yokohama, 230-8501, Japan  
Fax: +81-45-573-9599

We have studied the blue-shifted H- and the red-shifted J-bands formed in the mixed Langmuir-Blodgett (LB) films of the merocyanine dye (MS) - arachidic acid (C20) - *n*-octadecane (AL18) ternary system with the molar mixing ratio [MS]:[C20]:[AL18]=1:2:0.5. The aggregation number *N* and the structural parameters of the J- and the H-aggregates are examined by using the point dipole model. The separation *d* between two adjacent point dipole vectors is estimated to be  $d \approx 3.50 \times 10^{-10}$  m where the minimum of the potential energy *J* is in good agreement with the energy shift  $-3.20 \times 10^{-20}$  J/molecule of the J-band at 590 nm. For the J-aggregate of MS, we estimate the minimum aggregation number  $N_{\min.} = 40$  and the slip angle  $\alpha \approx 40^\circ$ . If we assume the same  $N_{\min.}$ -value for the H-aggregate, we obtain  $\alpha \approx 60^\circ$ . The  $N_{\min.}$ -value is in good agreement with the estimates in the earlier works, while the  $\alpha$ -value for the J-aggregate is appreciably larger than the earlier estimates, reconfirming the validity of the application of the extended dipole model.

Keywords: merocyanine dye, Langmuir-Blodgett films, blue-shifted band, H-aggregate, point dipole model

## 1. INTRODUCTION

The Langmuir-Blodgett (LB) technique is useful for arranging various kinds of functional molecules, and dye aggregates in the LB system have been the subject of keen interest because of their potentiality for organic solar cells and optical memory media.<sup>1,2)</sup>

It is well known that the LB films of the merocyanine dye (MS)-arachidic acid (C20) binary system are blue in color due to the sharp absorption peak at around 590 nm, which is red-shifted from the absorption maximum of the monomer band (540 nm), when they are prepared under the conventional subphase condition containing  $\text{Cd}^{2+}$ .<sup>3-8)</sup> The red-shifted band is called J-band and originates from the specific alignment of the MS molecules, i.e., the J-aggregate. Its sharp absorption is due to the excitons delocalized over the aggregate.<sup>3-8)</sup>

We have found a blue-shifted band at around 505 nm in the mixed LB films of the MS-C20-*n*-octadecane (AL18) ternary system.<sup>9-12)</sup> The blue-shifted band is identified as an H-aggregate referring to the energy shift, the spectral shape and the in-plane anisotropy of the band. In this paper, we discuss the aggregation number and the configuration of MS in the J- and the H-aggregates using the point dipole model.<sup>13)</sup>

## 2. EXPERIMENTAL

The surface-active merocyanine dye (MS), arachidic acid (C20) and *n*-octadecane (AL18) were used in this study. MS, C20 and AL18 were dissolved in the freshly-distilled chloroform with the molar mixing ratios [MS]:[C20]:[AL18]=1:2:*x* (*x*=0, 0.5). The concentration of MS was of the order of  $10^{-4}$  M. The LB films were prepared by the standard vertical dipping method. The aqueous subphase and the deposition condition were the same as reported previously.<sup>9-12)</sup> A glass substrate precoated with five monolayers of cadmium arachidate (CdC20) was used. All the LB films were of Y-type with a transfer ratio close to unity.

The polarizing absorption spectra  $A_{\parallel}$  and  $A_{\perp}$  of the mixed LB films were measured using a normal

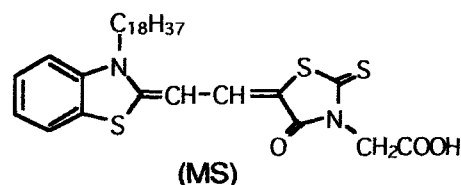


Fig. 1 Chemical structure of the merocyanine dye (MS).

incident of linearly polarized light with the electric vector parallel and perpendicular to the dipping direction, respectively. Twenty-layered LB films deposited on both sides of the substrates were used as the samples. The measurements were carried out immediately after the sample preparation unless

otherwise stated.

### 3. RESULTS AND DISCUSSION

Figures 2 (a) and (b) show the absorption spectra of the MS-C20 binary and the MS-C20-AL18 ternary systems ([MS]:[C20]:[AL18]=1:2:*x*), where *x*=0 and *x*=0.5, respectively. The solid and the dashed lines refer to the absorption spectra  $A_{\parallel}$  and  $A_{\perp}$ , respectively. In Fig. 2 (a), the absorption maximum located at around 590 nm is 0.20 eV red-shifted from that of the MS monomer band (540 nm). The J-band shows the in-plane anisotropy with the dichroic ratio  $R > 1$ , where  $R$  is defined as  $R = A_{\parallel} / A_{\perp}$ . These features are consistent with those of J-band reported in the earlier works.<sup>3-8</sup> On the other hand, in Fig. 2 (b), the pronounced blue-shifted band at around 505 nm is seen, together with the red-shifted component. The 505-nm band is 0.15 eV blue-shifted from the MS

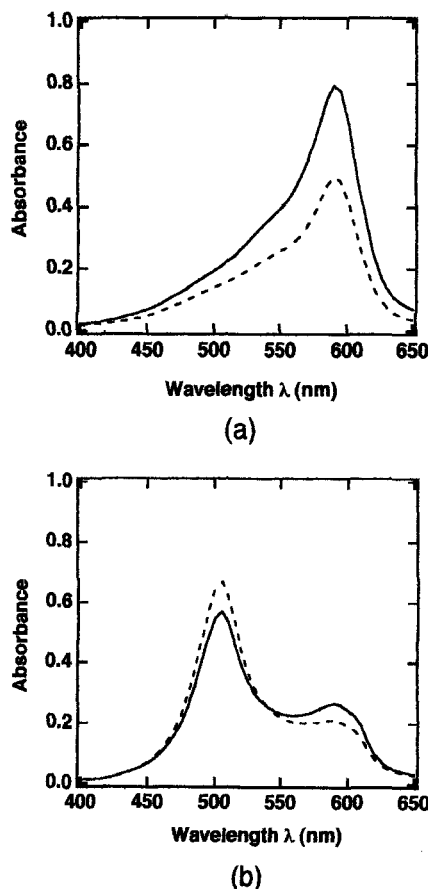


Fig. 2 The absorption spectra of the mixed LB films of the MS-C20 binary and the MS-C20-AL18 ternary systems. The molar mixing ratio [MS]:[C20]:[AL18]=1:2:*x*, where (a) *x*=0 and (b) *x*=0.5. The solid and the dashed lines refer to the absorption spectra  $A_{\parallel}$  and  $A_{\perp}$  per  $2 \times 20$  monolayers, respectively.

monomer band. The red-shifted band at 590 nm and the blue-shifted band at 505 nm show the opposite in-plane anisotropies to each other with  $R > 1$  and  $R < 1$ ,

respectively.

The formation of the blue-shifted and the red-shifted bands and the observed dichroic behavior of each band in Fig. 2 can be interpreted as follows.

There are two limiting types of the dye aggregates recognized as to the orientation of the transition dipole moments and the spectral characteristics. The J-aggregate with the head-to-tail alignment of the transition dipole moments is characterized by the red-shifted absorption.<sup>14,15</sup> The second type is the H-aggregate characterized by the side-by-side alignment of the transition dipole moments, showing a blue-shifted absorption from the monomer transition.<sup>16</sup> It is noted that a sharp and narrow absorption is observed due to the motional narrowing effect in the electronic transition of the large aggregate.

The dichroic behavior is interpreted referring to the flow orientation model by Minari et al.<sup>8</sup> During the vertical-dipping process using a conventional LB trough, the long axis of the one-dimensionally-developed aggregate tends to preferentially align to the dipping direction of the substrate. The orientation of the aggregates, elongated in shape, is governed by the velocity gradient and the rotatory Brownian motion at the air-water interface during the deposition process. When the long axis of the one-dimensionally-developed aggregates grows longer, the relative contribution of the rotatory Brownian motion of the aggregate at the air-water interface decreases. Therefore, the tendency to align parallel to the dipping direction of the substrate is more prominent for the longer aggregates.

The red-shifted and the blue-shifted bands shown in Fig. 2 is consistent with the above prediction that the red-shifted J-band and the blue-shifted H-band will show  $R > 1$  and  $R < 1$ , respectively, if the both dye aggregates are elongated. Therefore, the 590-nm and the 505-nm bands are assigned to the J-band and the H-band, respectively.

We carried out the numerical calculation using the point dipole model by McRae and Kasha<sup>13</sup> to estimate the aggregation number  $N$  and the values of the structural parameters of the J- and the H-aggregates. In the model, the transition dipole moment  $\mu$  of MS is replaced by the classical point dipole of the same magnitude, as shown in Fig. 3 (a). The interaction integral  $J_{ij}$  between two point dipoles is approximated as,

$$J_{ij} = \frac{\mu^2}{4\pi\epsilon_0\epsilon_r r^3} (1 - 3\cos^2\alpha) \quad (1)$$

where  $\mu$ ,  $\epsilon_r$  and  $\alpha$  are the transition moment of the dye chromophore, the relative dielectric constant of the system and the slip angle between the direction connecting the centers of the adjacent point dipoles and that of the point dipole vector, respectively. We employ the value  $\epsilon_r=2.5$  of the hydrocarbons as the relative dielectric constant of the system. It is noted that the transition dipole moment of MS is parallel to

the long axis of the dye chromophore. As is shown in Fig. 3 (b), we assume a two-dimensional arrangement of the point dipoles, in which the point dipole vectors are aligned parallel to one another in

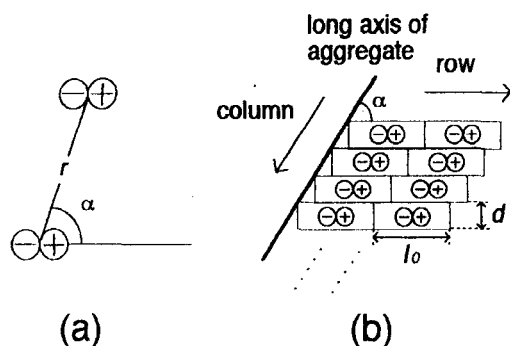


Fig. 3 (a) The configuration of the two point dipole vectors for the calculation of  $J_{ij}$ . (b) Schematic representation of the two-dimensional arrangement of the dye molecules for the aggregate.  $\alpha$ ,  $d$  and  $l_0$  are the slip angle between the long axis of the aggregate and that of the point dipole vector, the separation between two adjacent point dipole vectors and the length of the long axis of the dye chromophore, respectively.

the film plane. The excitation energy  $\Delta E'$  of an  $N$ -mer aggregate is represented by the excitation energy of the monomer transition  $\Delta E$  and the interaction integral  $J_{ij}$  as

$$\begin{aligned} \Delta E' &= \Delta E + J \\ &= \Delta E + 2 \times \frac{1}{2} \times \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N J_{ij} \quad (i \neq j) \end{aligned} \quad (2)$$

The transition dipole moment of  $\mu = 8.256 \times (3.33 \times 10^{-30}) \text{ C} \cdot \text{m}$  given in ref. 7 was used for MS in eq. (1). In Fig. 3 (b), the area of the MS chromophore ( $=d \times l_0$ ) is identified with the occupied area per molecule ( $=56 \text{ \AA}^2/\text{molecule}$ ) of MS at 25 mN/m estimated from the surface pressure ( $\pi$ )-area (A) isotherm measurement.<sup>11,12)</sup>

Figure 4 shows the equi-potential lines for  $J$  in the slip angle ( $\alpha$ )-separation ( $d$ ) plane with the aggregation number  $N=40$  in one single row, where  $J$  for  $N=40$  is found to be 95% or more of that for  $N \rightarrow \infty$ . The solid and dashed curves refer to the energy shifts  $-3.20 \times 10^{-20} \text{ J/molecule}$  and  $+2.60 \times 10^{-20} \text{ J/molecule}$ , corresponding to the absorption maximum of the J-band at around 590 nm and the H-band at around 505 nm, respectively. The line for  $J=0$  is located at around  $\alpha \cong 55^\circ$  in accordance with eq. (1). Around  $d \cong 3.5 \times 10^{-10} \text{ m}$ , the minimum  $J$  is in good agreement with the energy shift  $-3.20 \times 10^{-20} \text{ J/molecule}$ . The result suggests that  $d \cong 3.5 \times 10^{-10} \text{ m}$ , which leads to  $l_0 \cong 1.60 \times 10^{-9} \text{ m}$  allowing for the occupied area of the MS chromophore.

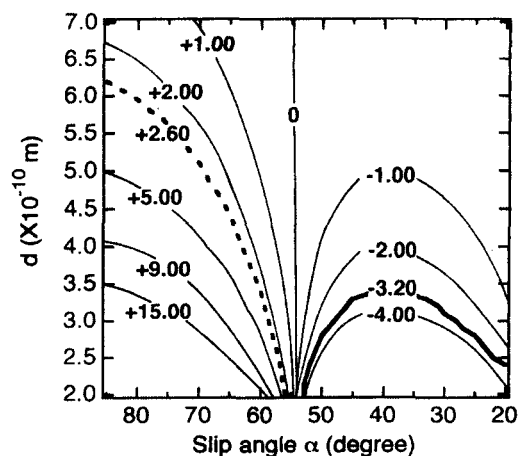


Fig. 4 The equi-potential lines for the potential energy  $J$  in the slip angle ( $\alpha$ )-separation ( $d$ ) plane with the aggregation number  $N=40$  in one single row. The numerical figure added to each line denotes  $J/(10^{-20} \text{ J/molecule})$ . The solid and the dashed lines refer to the energy shifts  $-3.20 \times 10^{-20} \text{ J/molecule}$  and  $+2.60 \times 10^{-20} \text{ J/molecule}$  for the J- and the H-aggregates, respectively.

Figure 5 shows the potential energy  $J$  plotted against the slip angle  $\alpha$ , where  $d=3.50 \times 10^{-10} \text{ m}$  and  $l_0=1.60 \times 10^{-9} \text{ m}$ , respectively. The curves refer to the various values of the aggregation number  $N$  in one single row: (a)  $N=2$ , (b)  $N=4$ , (c)  $N=6$ , (d)  $N=8$ , (e)  $N=10$ , (f)  $N=20$ , (g)  $N=40$ , (h)  $N=60$ , (i)  $N=80$  and (j)  $N=100$ . The solid and the dashed lines refer to the energy shifts  $-3.20 \times 10^{-20} \text{ J/molecule}$  and  $+2.60 \times 10^{-20} \text{ J/molecule}$ , respectively. Each curve of  $J$  shows the minimum value around  $\alpha \cong 40^\circ$ . The potential energy  $J$  shows the sublinear dependence on  $N$ , converging to a constant value as  $N \rightarrow \infty$ . In the interaction of  $J$  for  $N \geq 40$ ,  $J$  around  $\alpha \cong 40^\circ$  is in good agreement with the energy shift  $-3.20 \times 10^{-20} \text{ J/molecule}$  to the absorption maximum of the J-band at around 590 nm. Consequently, the minimum aggregation number  $N_{\text{min}}$  is estimated as  $N_{\text{min}}=40$  for the J-aggregate. We obtain  $\alpha \cong 60^\circ$  for the H-aggregate, assuming the same  $N_{\text{min}}$ -value.

The estimated aggregation number  $N_{\text{min}}$  is compatible with  $N \sim 10^2$  which is estimated from the analysis of the line shape of ESR measurement by Kuroda *et al.*<sup>4)</sup> The  $N_{\text{min}}$  obtained above is also consistent with  $N \sim 10^2$  deduced from the flow orientation model by Minari *et al.*<sup>8)</sup> The estimated slip angle  $\alpha \cong 40^\circ$  for the J-aggregate is, however, appreciably larger than the value  $\alpha \cong 30^\circ$  deduced from the extended dipole model by Nakahara *et al.*<sup>7)</sup> the value  $\alpha \cong 25 \sim 30^\circ$  determined from the analysis of the line shape of ESR by Kuroda *et al.*<sup>4)</sup> and the value  $\alpha = 33.5^\circ$  derived from the flow orientation model by Minari *et al.*<sup>8)</sup>

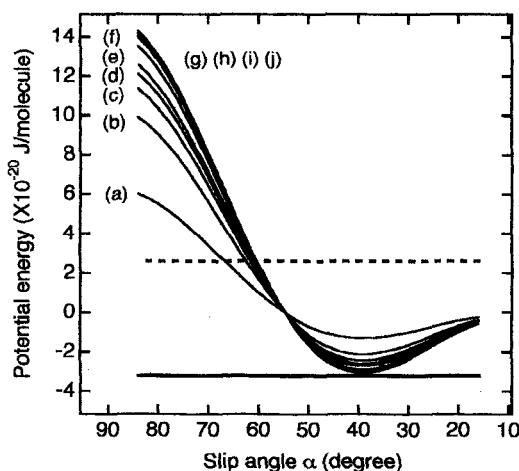


Fig. 5 The potential energy  $J$  is plotted against the slip angle  $\alpha$  between the long axis of the aggregate and the adjacent point dipoles, where  $d=3.50 \times 10^{-10}$  m and  $l_0=1.60 \times 10^{-9}$ . The curves refer to the different values of the aggregation number  $N$  in one single row: (a)  $N=2$ , (b)  $N=4$ , (c)  $N=6$ , (d)  $N=8$ , (e)  $N=10$ , (f)  $N=20$ , (g)  $N=40$ , (h)  $N=60$ , (i)  $N=80$  and (j)  $N=100$ . The solid and the dashed lines refer to the energy shifts  $-3.20 \times 10^{-20}$  J/molecule and  $+2.60 \times 10^{-20}$  J/molecule, respectively.

Therefore, the present slip angle  $\alpha$  in the J-aggregate, and that in the H-aggregate as well, should be reexamined using the extended dipole model by Kuhn and his collaborators.<sup>17)</sup>

#### 4. CONCLUDING REMARKS

We have studied the blue-shifted H- and the red-shifted J-bands formed in the ternary LB system with the molar mixing ratio [MS]:[C20]:[AL18]=1:2:0.5.

The aggregation number  $N$  and the structural parameters of the J- and the H-aggregates have been examined by using the point dipole model. The separation  $d$  between two adjacent point dipole vectors, which has been assumed referring to analogous crystalline materials so far, is estimated to be  $d \approx 3.50 \times 10^{-10}$  m where the minimum  $J$  is in good agreement with the energy shift  $-3.20 \times 10^{-20}$  J/molecule of the J-band at 590 nm. The estimate of  $d$  leads to the length of the long axis of the MS chromophore  $l_0 \approx 1.60 \times 10^{-9}$  m allowing for the occupied area of MS.

For the J-aggregate of MS, the minimum aggregation number  $N_{\min.}$  and the slip angle  $\alpha$  are estimated to be  $N_{\min.}=40$  and  $\alpha \approx 40^\circ$ , respectively. The value of  $N_{\min.}$  is consistent with that of  $N \sim 10^2$  estimated from the analysis of the line shape of ESR measurement by Kuroda *et al.* and from the flow orientation model by Minari *et al.* If we assume the same  $N_{\min.}=40$  for the H-aggregate, we obtain  $\alpha \approx 60^\circ$ . However, the estimate of  $\alpha$  of the J-

aggregate is appreciably larger than that obtained from the extended dipole model by Nakahara *et al.*, the analysis of the line shape of ESR by Kuroda *et al.* and the flow orientation model by Minari *et al.* Further studies are now in progress for estimating  $N$  and  $\alpha$  in the J- and the H-aggregates using the extended dipole model.

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#### 6. REFERENCES

- 1) H. Kuhn, *Thin Solid Films* 178, 1 (1989).
- 2) M. Sugi, *J. Mol. Electron.* 2, 3 (1985).
- 3) M. Sugi, T. Fukui, S. Iizima and K. Iriyama, *Mol. Cryst. & Liq. Cryst.* 62, 165 (1980).
- 4) S. Kuroda, K. Ikegami, K. Saito, M. Saito and M. Sugi, *J. Phys. Soc. Jpn.* 56, 3319 (1987).
- 5) M. Sugi, M. Saito, T. Fukui and S. Iizima, *Thin Solid Films* 129, 15 (1985).
- 6) H. Nakahara and D. Möbius, *J. Colloid & Interface Sci.* 114, 363 (1986).
- 7) H. Nakahara, K. Fukuda, D. Möbius and H. Kuhn, *J. Phys. Chem.* 90, 6144 (1986).
- 8) N. Minari, K. Ikegami, S. Kuroda, K. Saito, M. Saito and M. Sugi, *J. Phys. Soc. Jpn.* 58, 222 (1989).
- 9) Y. Hirano, H. Sano, J. Shimada, H. Chiba, J. Kawata, Y. F. Miura, M. Sugi and T. Ishii, *Mol. Cryst. & Liq. Cryst.* 294, 161 (1997).
- 10) Y. Hirano, J. Kawata, Y. F. Miura, M. Sugi and T. Ishii, *Thin Solid Films* 327-329, 345 (1998).
- 11) Y. Hirano, K. N. Kamata, J. Kawata, Y. F. Miura, M. Sugi and T. Ishii, *Mol. Cryst. & Liq. Cryst.* 322, 111 (1998).
- 12) Y. Hirano, K. N. Kamata, Y. S. Inadzuki, J. Kawata, Y. F. Miura, M. Sugi and T. Ishii, *Jpn. J. Appl. Phys.* 38, 6024 (1999).
- 13) E.D. McRae and M. Kasha, *J. Chem. Phys.* 28, 721 (1958).
- 14) E. E. Jelley, *Nature* 138, 1009 (1936).
- 15) G. Scheibe, *Angew. Chem.* 49, 563 (1936).
- 16) See, for example, E.S. Emerson, M.A. Conlin, A.E. Rosenoff, K.S. Norland, H. Rodriguez, D. Chin and G.R. Bird, *J. Phys. Chem.* 71, 2396 (1967).
- 17) V. Czikkely, H.D. Försterling and H. Kuhn, *Chem. Phys. Lett.* 6, 207 (1970).

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