Molecular Orientation and Aggregation in Mixed Langmuir−Blodgett Films of 5-(4-*N*-Octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin and Stearic Acid Studied by Ultraviolet−Visible, Fluorescence, and Infrared Spectroscopies

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Molecular aggregation and orientation in mixed Langmuir−Blodgett (LB) films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a) and stearic acid have been investigated by means of ultraviolet−visible (UV−vis), fluorescence, and infrared (IR) spectroscopies. It has been found that for the multilayer mixed LB films deposited onto glass and gold-evaporated glass substrates, the formation of porphyrin aggregates is facilitated by adding stearic acid, evidenced by a 3−6 nm red shift of the Soret band in the UV−vis spectra and a 5 nm red shift of the $Q(x)(0,0)$ band in the fluorescence emission spectra, compared to the corresponding LB films of porphyrin 338a. This result and that for the one-layer mixed films suggest that fatty acid molecules impose their effect on promoting the porphyrin aggregation in the mixed films via interlayer interactions. Comparison of IR spectra between the mixed films and those of porphyrin 338a leads to the conclusion that the alkyl chains of porphyrin 338a molecules in the mixed LB films become ordered and closely packed and more perpendicular to the substrate surface compared to those in the LB films of porphyrin 338a. The comparison of ratio of intensities of CH_2 antisymmetric and C═N (pyridyl group) stretching bands in the IR spectra between mixed LB films and the LB films of porphyrin 338a also supports this conclusion.

Introduction

Mixed Langmuir−Blodgett (LB) films consisting of functional dyes and diluents, such as fatty acids and lipids are of current interest for two major reasons:[1−16] (1) They provide a way to make LB films for materials which cannot form stable LB films by themselves. (2) Changing the ratio of each component in mixed LB films, one may be able to control the molecular aggregation, orientation, and structure and properties of LB films. Among various kinds of mixed LB films, those of porphyrin derivatives and diluent molecules have been attracting much attention.[5−16] Vandevyver et al.[5] investigated mixed LB films of 5,10,15,20-tetrakis(*p*-alkoxyphenyl)porphyrin and behenic acid by means of ultraviolet−visible (UV−vis) linear dichroism, infrared (IR) linear dichroism, and electron paramagnetic resonance (EPR) techniques and estimated the orientation of the porphyrin macrocycle. According to them, the porphyrin molecules are squeezed out from the layer of behenic acid. Azumi et al.[6−9] found that control of the molecular orientation in mixed LB films of *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphinatocopper and cadmium icosanate can be achieved by adding a small amount of the trigger molecule, *n*-hexatriacntane. Their observations have opened a way to modulate the molecular orientation in the LB films without chemical modification of molecular structure of constituents.[6] By UV−vis,

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steady-state, and time-resolved fluorescence spectroscopies, Gust et al.[10] studied systematically the aggregation properties of mixed LB films of 5-(4-acetamidophenyl)-10,15,20-tri-*p*-tolylporphyrin and several kinds of diluents such as fatty acids and lipids. They demonstrated that by choosing a suitable lipid diluent, it is possible to prepare the LB films where the porphyrin molecules exist only as monomeric species. Yoneyama, one of the present authors, and his colleagues[17] investigated a series of mixed Langmuir films of pyridiniumylporphyrins substituted with one long aliphatic chain structurally similar to the title compound and fatty acid at the air−water interface. It was found that the porphyrin planes assume a nearly flat orientation with respect to the water surface irrespective to the diluents.

In previous papers, we reported spectroscopic studies on molecular aggregation, orientation, and energy transfer in LB films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a, Figure 1 A).[18,19] The following conclusions could be reached by our studies: (1) In the LB films of porphyrin 338a, porphyrin macrocycles arrange themselves nearly parallel to the substrate surface, irrespective of the number of layers. (2) The porphyrin 338a molecules form different kinds of aggregates in the LB films deposited on glass and gold-evaporated glass substrates, respectively. (3) Effective energy transfer takes place in the LB films of porphyrin 338a. For the porphyrin LB films on the glass substrates, energy transfer through interlayer interaction dominates, while for those on the gold-evaporated glass substrates, efficient energy transfer from porphyrin 338a molecules to the gold surface, as well as interlayer energy transfer in the neighboring monolayers, occurs.

The purpose of the present study is to explore alterations in molecular orientation and aggregation induced by incorporating stearic acid into LB films of porphyrin 338a. UV−vis, fluorescence, and IR transmission and reflection−absorption (RA) spectroscopies have been employed to compare the structural features between the LB films of porphyrin 338a and the mixed ones. The direct interaction between porphyrin 338a and stearic acid has been verified by the following observations: (1) stearic acid facilitates the porphyrin aggregation, evidenced by a red shift of the Soret band in the UV−vis spectra and that of the $Q(x)(0,0)$ band in the fluorescence spectra, compared to the LB films of porphyrin 338a alone, and (2) alteration in the orientation of the alkyl chain of porphyrin 338a occurs in the mixed LB films. The present investigation may provide useful information for control of the molecular orientation and aggregation in the mixed LB films of porphyrins.

Experimental Section

Sample Preparation. The porphyrin sample investigated was the same as that described in our previous papers.[18,19] To observe bands due to methylene stretching modes of the alkyl chains of porphyrin 338a and stearic acid separately in the IR spectra, deuterated stearic acid was used to prepare the mixed LB films. It was purchased from Cambridge Isotope Laboratories (D 98%) and used without further purification. Porphyrin 338a and deuterated stearic acid were dissolved in spectrograde chloroform (1.0 mM). After the sample was mixed, the solution was spread onto a pure water subphase at 20 °C. After evaporation of the solvent, the mixed monolayer film was compressed at a speed of 20 cm^2/min up to a surface pressure of 20 mN m^{-1} and then transferred by conventional vertical dipping method onto glass, CaF_2, and gold-evaporated glass substrates. The average transfer ratio was about 1.10 ± 0.10. The transfer ratio for downward deposition was about 80% of that for the upward deposition. The mixed LB films of porphyrin 338a and stearic acid with a 1:1 molar ratio were prepared to avoid phase separation in the mixed LB films;[17] in the mixed monolayers in which the molar ratio of the acid is larger than that of the porphyrin, the excess amount of the acid tends to form crystalline domains even in expanded states (~0 mN m^{-1}).

Spectroscopy. Instrumentation and methods for measuring UV−vis (including polarized UV−vis), fluorescence, and IR transmission spectra were the same as those described in our previous papers.[18,19] The IR RA spectra were obtained at a 4 cm^{-1} resolution with a Nicolet Magna 550 FTIR spectrometer with a MCT detector, and a JEOL IR-RSC 110 reflection attachment at the incident angle of 80°, together with a JEOL IR-OPT02 polarizer.

Results and Discussion

Formation of Porphyrin 338a−Stearic Acid Mixed Monolayer at the Air−Water Interface. Figure 1 shows a $\pi-A$ isotherm of mixed monolayer of porphyrin 338a and stearic acid (molar ratio 1:1) (a), together with that of porphyrin 338a alone (b) on pure water subphase. It can be seen from the $\pi-A$ isotherm (a) that the mixture of porphyrin 338a and stearic acid can form a stable solid condensed monolayer at the air−water interface. Two characteristic features for the $\pi-A$ isotherm of the porphyrin−fatty acid mixed monolayer compared with that of porphyrin 338a monolayer are observed. A plateau appears at about 36 mN m^{-1} in the former, 9 mN m^{-1} lower than in the latter (about 45 mN m^{-1}),[18] indicative of a structural alteration in the porphyrin 338a molecules upon mixing porphyrin 338a with the fatty acid molecule. Above 36 mN m^{-1} the porphyrin 338a molecules may be squeezed out from the stearic acid monolayer on the water subphase.[17b] The second feature is that the area per porphyrin molecule is estimated to be 160 $Å^2$ by extrapolating the steeply rising part of the curve to zero pressure. This value is smaller than the planar area of the porphyrin ring, for which a value of about 200$Å^2$ was estimated,[20] but larger than that of the porphyrin 338a monolayer (about 140$Å^2$).[18] Considering a very small area occupied by a stearic acid molecule (about 20$Å^2$), the area of 160$Å^2$ indicates that porphyrin molecular packing dominates the monolayer structure in the mixed monolayers. In other words, the porphyrin molecular orientation should not change significantly. Otherwise, a much larger or smaller area would be occupied by a porphyrin 338a molecule in the mixed monolayer. It should be noted, however, that the slight increase in the area per porphyrin molecule for the mixed Langmuir film indicates partial phase separation, which we will discuss later on the basis of infrared spectra.

Molecular Aggregation. Figures 2 and 3 display UV−vis spectra of one-, three-, five-, and nine-layer mixed LB films of porphyrin 338a and stearic acid at a ratio of 1:1 deposited on glass and gold-evaporated glass substrates, respectively. Compared to that of chloroform solution (421 nm), the Soret bands for one-, three-, five-, and nine-layer mixed LB films of porphyrin 338a and stearic acid on glass substrates show red shifts 11, 15.5, 18.5, and 20 nm, respectively. Of note in Figures 2 and 3 is that, for the multilayer mixed LB films deposited on both glass and gold-evaporated glass plates, the Soret bands show a red shift by more than 3 nm (6 nm for the nine-layer mixed

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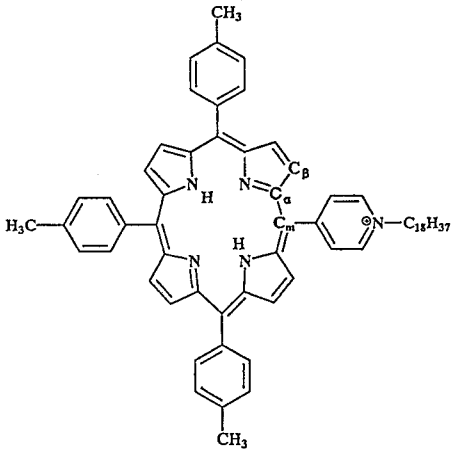
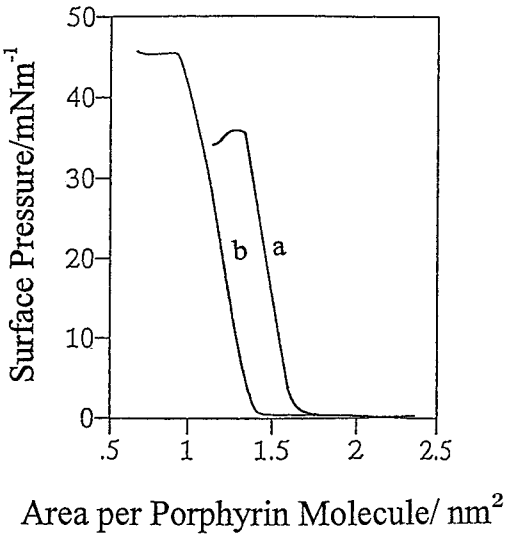


(A)



(B)

Figure 1. (A) Structure of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a). (B) (a) Surface pressure−area isotherm of a mixed monolayer consisting of porphyrin 338a and stearic acid at an air−water interface at 20 °C. (b) Surface pressure−area isotherm of a porphyrin 338a monolayer at an air−water interface at 20 °C.

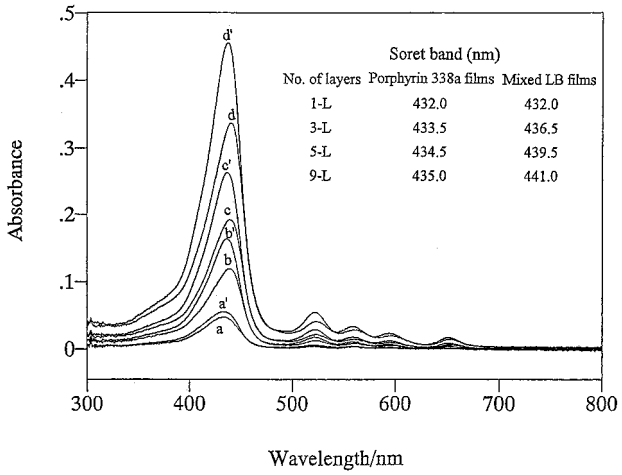


Figure 2. UV−vis transmission spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and stearic acid at a molar ratio of 1:1 deposited on glass substrates. UV−vis spectra of the corresponding LB films of porphyrin 338a on glass substrates are also plotted as (a′), (b′), (c′), and (d′), respectively.

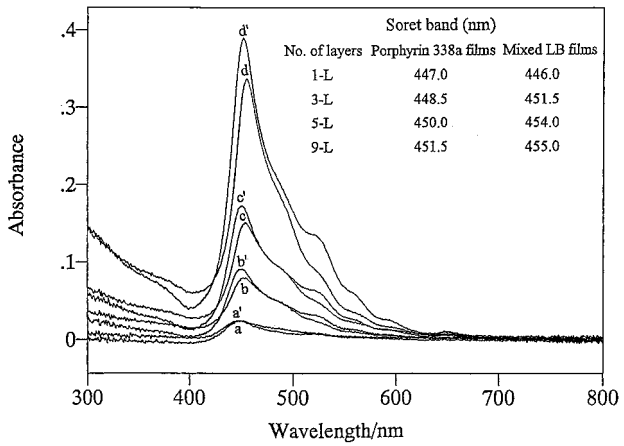


Figure 3. UV−vis RA spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and stearic acid at a molar ratio of 1:1 deposited on gold-evaporated glass substrates. UV−vis spectra of the corresponding LB films of porphyrin 338a on gold-evaporated glass substrates are also plotted as (a′), (b′), (c′), and (d′), respectively.

LB films on the glass plate) compared to the LB films of porphyrin 338a alone. For the monolayer LB films, on the other hand, the Soret bands do not show a significant shift between the mixed and pure porphyrin LB films irrespective of the substrates used. The red shifts observed for the multilayer mixed LB films may be explained in terms of facilitation of porphyrin aggregation induced by incorporating stearic acid into the LB films of porphyrin 338a. There are two possibilities for the enhancement of porphyrin chromophore−chromophore interaction by mixing porphyrin 338a and stearic acid. One is the formation of some kind of complex between the cationic porphyrin and stearic acid molecules.[13] The other possibility is that the addition of the long-chain fatty acid alters the structure of the porphyrin aggregates due to an interdigitate effect of the long alkyl chains between adjacent layers in the multilayer mixed LB films. Considering that there is no appreciable change in the UV−vis and fluorescence emission spectra between the one-layer LB film of porphyrin 338a and one-layer mixed LB film of porphyrin 338a and stearic acid, we can rule out the first possibility. It is reasonable to think that for the multilayer mixed LB films, interlayer interaction plays an important role. Later, we will show how incorporation of the fatty acid influences the orientation of alkyl chain attached to porphyrin 338a macrocycle based upon the IR transmission and RA spectra.

As in the case of the LB films of porphyrin 338a, the UV−vis spectra of the mixed films on the gold-evaporated glass substrates show a shoulder at about 480 nm, indicating the coexistence of two kinds of aggregates with the red-shifted Soret bands in the mixed LB films of porphyrin 338a and stearic acid.[19] The observed aggregates with the Soret band at about 480 nm may have geometry different from those with the Soret band at 450 nm. Further studies are needed to clarify the two different types of the porphyrin aggregates formed in the LB films on the gold-evaporated glass substrates.

In agreement with the red shift of the Soret bands in the UV−vis spectra, the $Q(x)(0,0)$ bands in fluorescence spectra of the three-, five-, and nine-layer mixed LB films

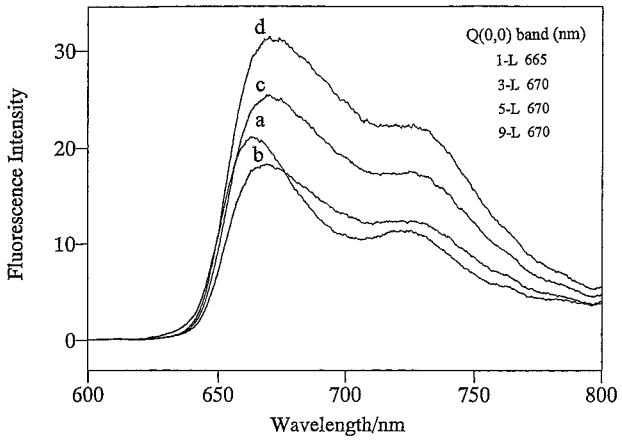


Figure 4. Fluorescence emission spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and stearic acid deposited on glass substrates excited at 435 nm.

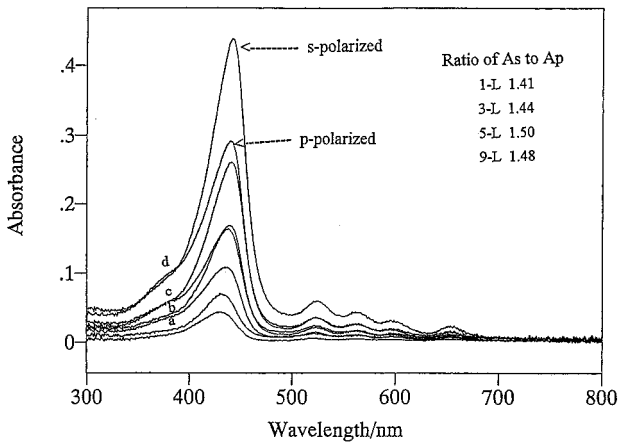


Figure 5. Polarized UV−vis spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and stearic acid at a molar ratio of 1:1 deposited on glass substrates. The incidence angle is 45°.

on glass substrates show a significant red shift by about 5 nm (from 665 to 670 nm) (Figure 4). This observation also reveals the enhancement of porphyrin aggregation in the multilayer mixed LB films on the glass substrates. In contrast, the emission spectra of the monolayer mixed LB films show no obvious change between the mixed and pure porphyrin LB films, consistent with the absorption spectra. It is noted that the three-layer mixed LB film shows weaker fluorescence than the one-layer LB film, due to energy transfer through interlayer interactions, as observed for LB films of porphyrin 338a.[19] As for the fluorescence emission spectra of the mixed LB films on the gold-evaporated glass plates, it is difficult to compare between the one-layer and multilayer films due to very weak fluorescence detected for the one-layer film (data not shown). This can be explained in terms of effective energy transfer from porphyrin 338a molecules to the gold surface which quenches the excited energy of porphyrin molecules.[19] The energy transfer in the porphyrin−stearic acid mixed LB films will be reported soon in a separate paper.

The observations in the UV−vis and fluorescence emission spectra suggest that the addition of stearic acid to the porphyrin 338a LB films influences the structure of aggregates more strongly for the multilayer mixed films than for the one-layer mixed films. It was reported by Gust and co-workers[10] that a one-layer mixed LB film of 5-(4-acetamidophenyl)-10,15,20-tri-*p*-tolylporphyrin and arachidic acid at a molar ratio of 1:50 exhibits only a slight blue-shift in the Soret band compared to the porphyrin LB films without the fatty acid. They did not perform further experiment on the multilayer mixed LB films. Apparently, the fatty acid should not be treated simply as a diluent under our experiment conditions; head (the carboxylic group of stearic acid)−head (porphyrin macrocycle) and tail (the alkyl chain of stearic acid)−tail (the alkyl chain of porphyrin 338a) interactions and an alteration in the orientation of the alkyl chain of porphyrin 338a will be discussed later in more detail based upon the results of IR spectra.

Molecular Orientation. To obtain information about the orientation of the porphyrin macrocycle in the mixed LB films, we measured polarized UV−vis spectra of one-, three-, five-, and nine-layer mixed films on the glass substrates at incidence angles of 0 and 45°. Figure 5 shows the results for the incidence angle of 45°. No in-plane anisotrope was observed for all the mixed LB films, as in the case of LB films of porphyrin 338a.[18] However, it can be seen from Figure 5 that the ratio of absorbance in the s-polarized direction to that in the p-polarized direction is in the range of 1.4 to 1.5 for all the mixed films examined, similar to that observed for the LB films of porphyrin 338a. This suggests that the porphyrin plane in the mixed films is still nearly parallel to the substrate surface. In other words, the incorporation of the fatty acid did not bring a significant change in the orientation of porphyrin ring. Comparison of the area per porphyrin 338a molecule between the porphyrin 338a monolayer (140 Å^2/porphyrin 338a molecule) and the porphyrin 338a−stearic acid mixed monolayer (160 Å^2/porphyrin 338a molecule) at the air−water interface indirectly supports this conclusion.

Comparison of band intensities between IR transmission and RA spectra can provide important information about the molecular orientation in LB films.[21−24] In our previous paper,[18] we pointed out insufficiency of this method due to different porphyrin molecular arrangement in the LB films deposited onto the glass and gold-evaporated glass substrates. However, we may be able to monitor changes in the molecular orientation of the alkyl chain of porphyrin 338a upon mixing with stearic acid by use of the IR transmission and RA spectra.[21−24] Figures 6 and 7 display IR transmission and RA spectra of one-, three-, five-, and nine-layer mixed LB films on CaF_2 and gold-evaporated glass plates, respectively. CH_2 antisymmetric and symmetric stretching bands of the alkyl chain of porphyrin 338a appear at 2921 and 2851 cm^{-1} in the transmission spectra of the multilayer mixed LB films, respectively. They shift slightly (1 to 2 cm^{-1}) downward compared to those in the LB films of porphyrin 338a.[18] The shifts are small but reproducible. The frequencies of the CH_2 stretching bands are very sensitive to the conformation of the hydrocarbon chain;[25,26] the low frequencies (2920 and 2850 cm^{-1}) of the bands are characteristic of the highly ordered (trans-zigzag) alkyl tail, while their upward shifts are indicative of the increase in conformational disorder, i.e., gauche conformation, in the hydrocarbon chain. The observed frequencies of 2921 and 2851 cm^{-1} suggest that

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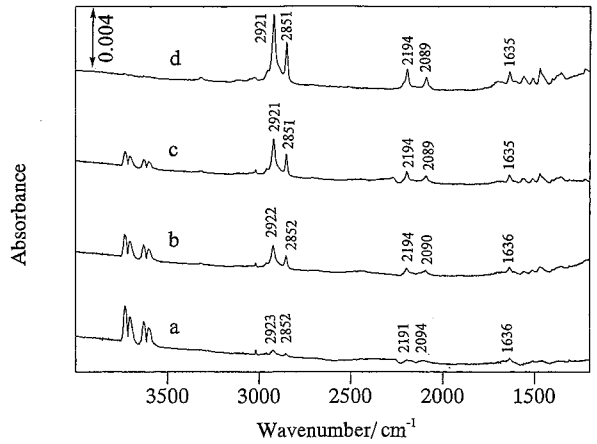

Figure 6. IR transmission spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and deuterated stearic acid on CaF_2 plates.

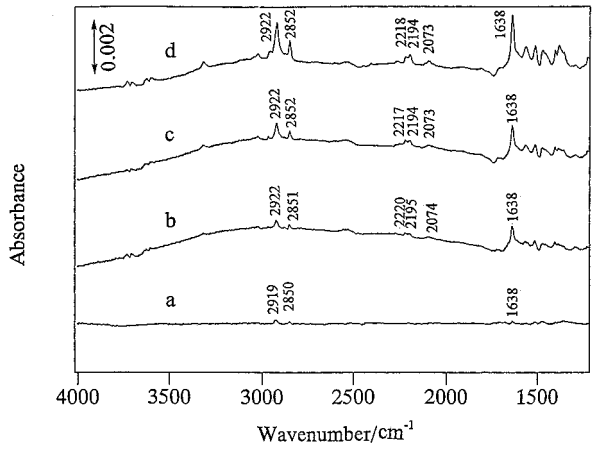

Figure 7. IR RA spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer mixed LB films of porphyrin 338a and deuterated stearic acid on gold-evaporated glass plates.

the alkyl chain of porphyrin 338a in the films contains only a few gauche conformers. This indicates that adding stearic acid improves the packing order of the alkyl chains of the porphyrin molecules in the mixed LB films.

To evaluate the orientational changes in the pyridyl group and aliphatic chain of the porphyrin 338a molecules, the IR transmission and RA spectra of nine-layer mixed and pure porphyrin LB films are compared in Figures 8 and 9, respectively. The ratio of absorbance of the CH_2 antisymmetyric and symmetric stretching bands in the transmission and RA spectra of the nine-layer mixed LB films is calculated to be 2.7 and 3.1, respectively (Figure 8). These values are much larger than those for the LB films of porphyrin 338a (1.2 and 1.3) (Figure 9). These observations indicate that the alkyl chain attached to the porphyrin macrocycle tends to become more perpendicular to the substrate surface in the mixed films. Similar results are obtained for the three- and five-layer mixed LB films (see Table 1). Comparison of the ratio of the intensities of CH_2 antisymmetric and C=N stretching bands in the IR spectra between the mixed LB films and the corresponding films of porphyrin 338a also provides useful information on alteration in the orientation of the alkyl chains induced by mixing of porphyrin 338a with stearic acid. As listed in Table 2, for the mixed films, with increase in the number of the layers, the ratio increases steeply (from 3.5 to 6.3 and 0.4 to 0.9 for the three- and nine-layer mixed LB films on CaF_2 and gold-evaporated glass substrates, respectively). On the other hand, in the case

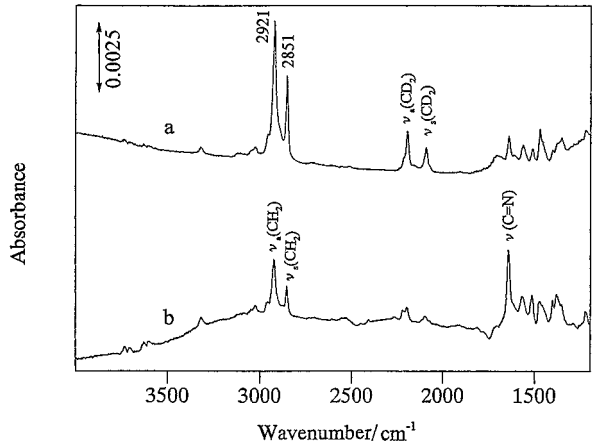

Figure 8. IR transmission (a) and RA (b) spectra of nine-layer mixed LB films of porphyrin 338a and deuterated stearic acid at a molar ratio of 1:1 deposited on CaF_2 and gold-evaporated glass substrates, respectively.

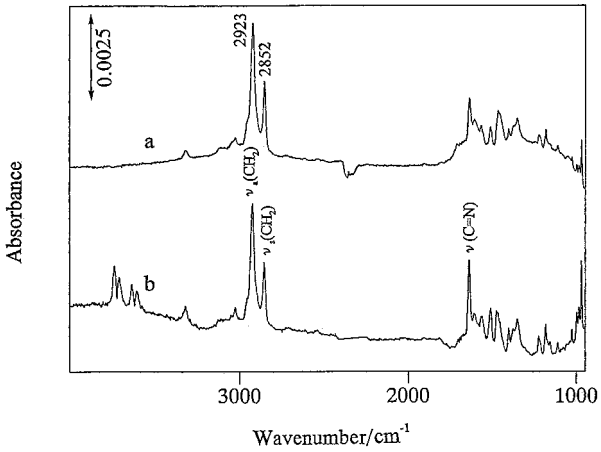

Figure 9. IR transmission (a) and RA (b) spectra of nine-layer LB films of porphyrin 338a deposited onto CaF_2 and gold-evaporated glass plates, respectively.

Table 1. Ratios of the Absorbances of CH_2 (Alkyl Chain Attached to the Porphyrin Ring) and C=N (Pyridyl Group) Stretching Modes in the IR Transmission Spectra to Those in the RA Spectra for Mixed LB Films of Porphyrin 338a and Deuterated Stearic Acid (Data in Parentheses Are for LB Films of Porphyrin 338a)

no. of layers	CH_2 antisymmetric	CH_2 symmetric	C=N
1	2.0		
3	3.5 (1.1)	3.7 (1.3)	0.5 (0.5)
5	2.7 (1.2)	3.1 (1.3)	0.5 (0.5)
9	2.4 (1.0)	3.0 (1.1)	0.4 (0.5)

Table 2. Ratios of Intensities of CH_2 Antisymmetric and C=N (Pyridyl) Stretching Bands in the IR Spectra of Mixed LB Films of Porphyrin 338a and Deuterated Stearic Acid as Well as of LB Films of Porphyrin 338a (in parentheses)

	$I(\nu_a(CH_2))/I(C{=}N)$	
no. of layers	CaF_2	Au
3	3.5 (2.8)	0.4 (1.2)
5	4.6 (3.2)	0.7 (1.3)
9	6.3 (3.6)	0.9 (1.8)

of the LB films of porphyrin 338a, the ratio also rises, but much slowly (from 2.8 to 3.6 and 1.2 to 1.8 for the three- and nine-layer LB films on the CaF_2 and gold-evaporated glass substrates, respectively). In addition, the differences in the ratio between the LB films on the CaF_2 and the gold-evaporated glass substrates are much sharper for

the mixed films than for the LB films of porphyrin 338a. Clearly, the existence of fatty acid alters the molecular orientation of the alkyl chain of porphyrin 338a in the mixed LB films. Taking account of the red shifts observed in the UV−vis and fluorescence emission spectra of these films, it seems reasonable to conclude that the fatty acid influences the porphyrin aggregation by the direct interaction between the alkyl chains of both fatty acid and of porphyrin 338a molecules. Leblanc et al.[12] described the influence of alkyl chains on the porphyrin aggregation but gave no detailed explanation.

In addition to the alkyl chain attached to the porphyrin 338a macrocycle, it is important to investigate the molecular orientation of the aliphatic chain of deuterated stearic acid because it may be directly related to the orientation of porphyrin 338a molecules in the mixed LB films. Bands at 2194 and 2089 cm^{-1} in the spectrum in Figure 6 are assigned to CD_2 antisymmetric and symmetric stretching modes, while the other two peaks at 2220 and 2080 cm^{-1} are due to the CD_3 modes of deuterated stearic acid, respectively.[27,28] The frequencies of the CD_2 stretching bands are also sensitive to the conformation of the alkyl chain. According to Cameron et al.,[28] they appear at 2194 and 2090 cm^{-1} when the chain assumes trans-zigzag conformation while their upward shifts show the increase in the gauche conformers in the chain. The observation in Figure 6 indicate that the alkyl chains of deuterated stearic acid are highly ordered in the mixed LB films. This observation, together with the increase in area per porphyrin molecule, supports that at least partial phase separation occurs in the mixed LB films. The intensities of the CD_2 antisymmetric and symmetric bands are much stronger in the transmission spectra than in the RA spectra, suggesting that the alkyl chains of deuterated stearic acid are nearly perpendicular to the substrate surface. It is noted that the mixing of porphyrin 338a with deuterated stearic acid does not introduce significant disorder in the conformation of the alkyl chains of the fatty acid. Therefore, a close packing of the alkyl chains of porphyrin 338a and deuterated stearic acid is achieved in the mixed LB films. This fact is in agreement with a more ordered packing of alkyl chains of the porphyrin molecules in the mixed LB films compared to the LB films of porphyrin 338a.

There are several possible models for the structure of the mixed LB films. The system could be purely segregated domains or interdigitated structure of porphyrin 338a and fatty acid molecules. The third model in which porphyrin 338a and stearic acid molecules are partially segregated and partially interdigitated is shown in Figure 10. For comparison, the model for the aggregates in the porphyrin 338a LB films is also depicted.[18] We believe that the third case may be more probable. The improvement of packing order and alteration in orientation of the alkyl chains need close contact between alkyl chains of porphyrin and of the fatty acid molecule. In these models shown in Figure 10, the porphyrin macrocycles assume a nearly flat orientation with respect to the substrate surface and overlapped each other slightly. On the other hand, the aliphatic chains of porphyrin molecules in the mixed LB films tend to become more perpendicular to the substrate surface compared to the LB films of porphyrin 338a. Such orientation may be achieved through the interaction between the alkyl chains from both porphyrin 338a and fatty acid molecules. In the mixed LB films partial phase separation occurs as discussed earlier in this paper. In many other microdomains, on the other hand, the head part of the fatty acid locates close to the positively charged pyridyl group and on the top of the porphyrin plane which has enough space (160 $Å^2$) to accommodate the acid (about 20 $Å^2$). Similar models for the mixed Langmuir monolayer of porphyrin and fatty acid were suggested by Gruniger et al.[13] and Yoneyama et al.[17a] to explain observed the $\pi-A$ curve and UV−vis spectral data. However, they did not discuss in detail the effect of the incorporation of fatty acid on porphyrin aggregation and on the alteration of alkyl chains of porphyrin and fatty acid molecule upon the formation of mixed LB films.

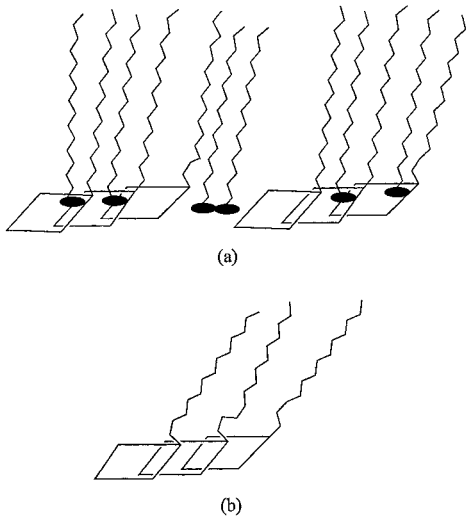

Figure 10. Possible models for (a) a mixed LB film of porphyrin 338a and stearic acid and (b) a LB film of porphyrin 338a. The carboxylic group of stearic acid is illustrated as (●).

Conclusion

The following conclusions may be reached from the present study: (1) In the multilayer mixed LB films of porphyrin 338a and stearic acid, the porphyrin aggregation is facilitated by the existence of fatty acid, evidenced by the observations of the red shift of the Soret band in the UV−vis spectra and that of the $Q(x)(0,0)$ band in the fluorescence emission spectra. In contrast to the multilayer mixed LB films, such an effect is negligible for the one-monolayer LB films. (2) The addition of fatty acid exerts little alteration in the molecular orientation of the porphyrin macrocycles, but it makes the alkyl chains attached to the porphyrin macrocycles become ordered and closely packed, and more perpendicular to the substrate surface, compared to those in the LB films of porphyrin 338a. The alteration in the alkyl chain orientation as well as the direct interaction between alkyl chains of porphyrin 338a and stearic acid molecules result in stronger porphyrin chromophore−chromophore interaction in the mixed multilayer LB films.

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