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

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The molecular orientation and aggregation behavior of 5-(4-*N*-octadecyl-pyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a) in mono- and multilayer Langmuir−Blodgett (LB) films have been investigated by employing ultraviolet−visible (UV−vis) and infrared (IR) spectroscopies. It has been found that the porphyrin planes assume a nearly flat orientation with respect to the surface of the solid substrates in the LB films, irrespective of the number of layers. This orientation remains unaltered even after aging of the LB films for 1 month or heating up to 150 °C, indicating high chemical and thermal stabilities of molecular arrangement in the porphyrin LB films. On the other hand, the porphyrin cores are distorted to some extent, and the attached long hydrocarbon chains are loosely packed in the LB films, as deduced from a comparison of the IR spectra of the LB and cast films with that of the solution. The porphyrin molecules form head-to-tail type (J-type) aggregates in the mono- and multilayer LB films, evidenced by significant red shift of the Soret bands in the UV−vis spectra of the LB films, compared to solution. The comparative and complementary investigations by the UV−vis and IR techniques also suggest that the structural features of the porphyrin mono- and multilayer LB films on CaF_2 plate are similar to each other.

Introduction

In recent years, Langmuir−Blodgett (LB) films of functional organic compounds have been attracting much attention because the LB technique prepares organic assemblies with planned structure and properties at the molecular level.[1−3] Apart from various investigations being carried out on LB films of different functional compounds of theoretical and practical significance, considerable effort is being directed toward fabrication and characterization of porphyrin LB films for two main reasons.[4−10] First, many porphyrin LB films have shown notable promise as efficient molecular photovoltaic devices.[5,6,10] For example, the short-circuit photocurrent from the LB films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin derivatives has achieved a value on the order of 10^{-7} A/cm^2 for 100 μW/cm^2 illumination, 2 orders of magnitude higher than that obtained from typical LB films containing other organic dyes with long aliphatic chains.[5] The second reason, which has spurred the study of porphyrin LB films, is that the porphyrin moiety plays crucial roles in biochemical processes, such as oxygen transport, energy transfer, and photosynthetic catalysis.[11a] Such functions can only be performed by well-organized molecular assembly in the biosystems, and LB technique is a useful tool that can be employed to create highly-ordered organic assemblies which mimic biological systems. For proper understanding of the structure−function relationship and interesting physical properties of the porphyrin LB films, structural details must be investigated extensively for the films. However, in contrast to the active investigations of the functions of porphyrin LB films, the structural characterization has fallen behind the studies of the physical properties. Most of the studies of the porphyrin LB films thus far carried out were based on one or two analytical techniques, and thus the information obtained is rather scattered. Therefore, we have aimed at a better understanding of the structural characteristics

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of the porphyrin LB films such as molecular orientation, aggregation, morphology and thermal behavior, etc., by using UV−vis, fluorescence, and Fourier-transform infrared (FTIR) spectroscopies and atomic force microscopy (AFM). Yoneyama et al.[5,12] have studied the molecular orientation and aggregation properties of the monolayers of the porphyrin 338a family at the water−air interface, as well as the photovoltaic properties of the LB films of these porphyrin molecules. Here we shall be focusing on structural characterization of the LB films of these porphyrin derivatives on solid substrates, which may lay a foundation for a proper understanding of their physical properties and a further search for applications in devices.

As a first part of systematic studies on structural characterization of porphyrin LB films, we present here UV−vis and IR studies on the molecular orientation and aggregation in mono- and multilayer LB films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a) on solid substrates. Among many factors that influence the functional properties of LB films are the molecular orientation and aggregation. Bardwell et al.[10] explored the photovoltaic properties of porphyrin multilayer sandwich cells and found that the molecular orientation and aggregation have important effects on photocurrent from the porphyrin LB films. The aggregation behavior of porphyrins in various states, such as in solutions and LB films etc is an active area of research[11−14] for deeper understanding of the biofunctions of porphyrins and aggregation dependent photophysical properties of porphyrin LB films.[15,16]

From our studies, we have found that in the mono- and multilayer LB films, porphyrin 338a forms aggregates which show a red shift of the Soret band compared to that of the monomeric species. Porphyrin macrocycles lie nearly flat to the surface of the solid substrate in the LB films deposited on CaF_2 and glass plates, and this parallel orientation remains almost unchanged upon heating to 150 °C. The porphyrin macrocycles exhibit distortion in the LB films on a solid substrate, and the long hydrocarbon chains pack in a disorderly manner, including adopting gauche conformations.

Experimental Section

Sample Preparation. The structure of the LB film forming material, 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a), is shown in Figure 1. The sample was dissolved in spectrograde chloroform (concentration 1.0 mM) and spread onto a pure water subphase at 20 °C. After the evaporation of the solvent, the monolayer film was compressed at a speed of 20 cm^2/min up to the surface pressure of 20 mN m^{-1} and then transferred by typical vertical dipping technique onto CaF_2 and glass plates for IR and/or UV−vis transmission measurements. The glass and CaF_2 plates had been treated under ultrasonification in a hot 50% aqueous solution of DCN 90 of Decon Laboratories, Ltd. (an alkaline surfactant) and then in distilled water. The transfer ratios from water subphase to solid support were usually about 1.20 ± 0.10, and the transfer ratio for downstroke deposition was about 70% of that for the upstroke during the deposition of multilayer LB films.

Instrumentation. A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance was employed for the measurement of the surface pressure-area isotherm of the LB films on the water subphase as well as for fabrication of LB films. The UV−vis spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. For the polarized UV−vis spectral measurements, a dichroic sheet polarizer (MELLES GRIOT) was placed in front of the LB films. The light with the polarization direction perpendicular (parallel to the dipping direction) and parallel (vertical to the dipping direction) to the incidence plane is denoted as s-polarized and p-polarized light (see inset in Figure 4), respectively.

The IR spectra were measured with a Nicolet Magna 550 FTIR spectrometer equipped with an MCT detector. All spectral data were collected at a spectral resolution of 4 cm^{-1}, and generally, several hundreds of scans were coadded for the spectral measurement. The procedure for heating the LB films on CaF_2 plate was similar to that reported earlier.[17]

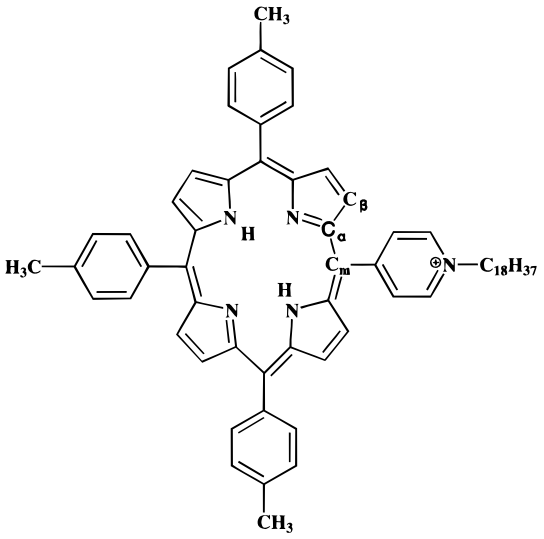

Figure 1. Structure of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (abbreviated as porphyrin 338a).

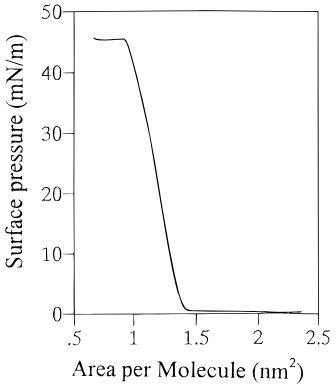

Figure 2. Surface pressure−area per molecule isotherm of a Langmuir film of porphyrin 338a on water subphase measured at 20.0 °C.

Results and Discussion

Fabrication of LB Films. Figure 2 shows the $\pi-A$ isotherm of the porphyrin Langmuir film on the water subphase, from which an area of about 140 $Å^2$ per molecule is calculated. It is strikingly smaller than the area estimated for the porphyrin ring of about 200 $Å^2$.[18] The deviation may arise from two main reasons: either a remarkable tilting of the porphyrin plane with respect to the surface of water subphase and/or a strong overlapping of the porphyrin planes on the surface of subphase due to strong interactions between porphyrin molecules in the

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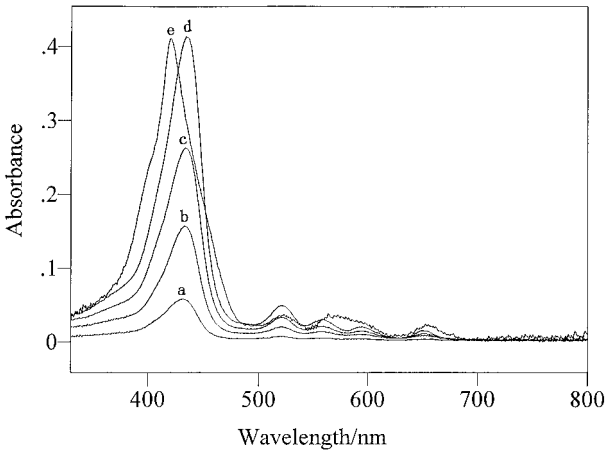

Figure 3. UV−vis spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer LB films of porphyrin 338a on CaF_2 plates. For comparison purpose, a UV−vis spectrum of porphyrin 338a in chloroform solution is also plotted (e).

monolayer films. By using a porphyrin molecule similar to ours (the only difference is the number of carbon atoms of the hydrocarbon chain; the porphyrin molecule which we have investigated has 18 carbon atoms while that which they employed has 14 carbon atoms.), Adachi et al.[12] from polarized UV−vis studies have suggested that the deviation of area per molecule obtained by the $\pi-A$ isotherm from that calculated was largely due to the overlapping of the porphyrin planes on aqueous subphase, rather than due to considerable tilting of the porphyrin plane to the substrate surface. What we would like to know is whether the molecular orientation is altered or not during the transfer of the porphyrin monolayers from the aqueous subphase onto the solid substrates, because this is closely connected with the functions and physical properties of the LB films deposited onto solid supports, such as conductivity of porphyrin LB films.[5,10]

The transfer ratio obtained in our experiment was slightly larger than unity, suggesting that during the transfer of the monolayers from the water subphase to solid substrate, the porphyrin molecules had undergone some rearrangement. This rearrangement, however, hardly changed the nearly flat orientation of the porphyrin molecules in the LB films, as will be discussed later in this paper. The linear relationship between the number of layers and the absorbance of the Soret band in the UV−vis spectra indicates that the porphyrin monolayers were successfully deposited onto glass and CaF_2 substrates.

Aggregation Behavior of Porphyrin Molecules in LB Films. Figure 3 shows the UV−vis spectra of porphyrin LB films with one, three, five, and nine layers on CaF_2 plates. For comparison purposes, the UV−vis spectrum of porphyrin 338a in a chloroform solution (the spreading solution) is also presented in Figure 3. The Soret maxima of the UV−vis spectra of the LB films and the spreading solution are listed in Table 1. Porphyrin 338a, like other ordinary metal-free porphyrins, shows a strong Soret band (or B band), and four weaker Q bands in the UV−vis region. These bands arise from the $\pi-\pi^*$ transition of the macrocycle.[11] We have observed a red shift of more than 10 nm of the Soret bands for the LB films on CaF_2 plates (ca. 434 nm) compared to the spreading solution (421 nm). Similar shifts of the Soret band were observed for the LB films of the relatively rigid indium complex of this porphyrin (444 nm) compared to that in the chloroform solution (432 nm), suggesting that the core deformation of the free base porphyrin does not make a significant contribution to the red shift of the Soret band in the LB films. Moreover, the UV−vis spectra of porphyrin 338a in several polar and nonpolar solvents show much smaller bathochromic shifts than in the LB films. Thus, the red shift of the Soret band observed for the LB films of porphyrin 338a may arise primarily from excitonic interactions between the chromophores and aggregation in the film environment.[1,19] A quite distinct emission behavior of porphyrin 338a in LB films compared with that in the solution[20] further substantiates our contention of formation of J-type aggregates in the LB films. It is interesting to note that the UV−vis spectra of porphyrin LB films did not show significant layer dependence, apart from intensities, suggesting similarity in the structure of the aggregates formed in the porphyrin mono- and multilayer LB films. We also found that the Soret bands of the LB films on CaF_2 and glass plates are quite consistent with those of the monolayer films on water subphase,[5c] indicating that the nature of porphyrin aggregates formed on the water surface upon compression did not change significantly during the transfer from the water subphase to solid substrates.

Table 1. Soret Band Maxima and Ratios of the s-Polarized (As) to p-Polarized (Ap) Absorbances of the Soret Bands in the UV−Vis Spectra of one-, three-, five-, and nine-Layer LB Films of Porphyrin 338a on CaF_2 Plates[a]

no. of layers	Soret maxium (nm)	ratio of As to Ap at Soret maxima
1	432.0	0.069/0.047 = 1.47 (0.040/0.026 = 1.53)
3	433.5	0.198/0.133 = 1.49
5	434.5	0.335/0.241 = 1.39
9	435.0	0.510/0.368 = 1.39 (0.426/0.307 = 1.39)

[a] Data in parentheses were measured after heating the LB films up to 150 °C for 10 min and then letting them to cool down to 25 °C.

Molecular Orientation: (a) Polarized UV−Visible Spectra. Polarized UV−vis spectroscopy has often been used to study the chromophore orientation of organic dyes in LB films.[4,9,21,22] For porphyrin molecules, the two transition dipoles lie in the molecular plane at an angle of 90° along the axis through the pyrrole nitrogens at opposite positions. The polarization direction of the $\pi-\pi^*$ Soret band is parallel to the molecular plane. In order to explore the in- and out-of-plane anisotropies of LB films, we measured polarized UV−vis spectra of one-, three-, five- and nine-layer LB films of porphyrin 338a on glass and CaF_2 plates at incidence angles of 0 and 45°. For the incidence angle of 0°, no anisotropy was observed for the mono- and multilayer LB films either on the CaF_2 or glass plates. As shown in Figure 4, for the incidence angle of 45°, the position of the Soret band alters slightly (within a range of 3 nm), but the absorbance of the Soret bands decreases considerably in all of the mono- and multilayer LB films deposited on CaF_2 and glass plates, upon changing the polarization direction of light from s-polarized (parallel to the dipping direction) to p-polarized (perpendicular to the dipping direction). The ratio of the absorbances of the Soret band observed with s- (A_s) and p- (A_p) polarized light was calculated for the LB films on the CaF_2 plates. Table 1 shows the results for the films on the CaF_2 plate. Similar A_s to A_p ratios were also

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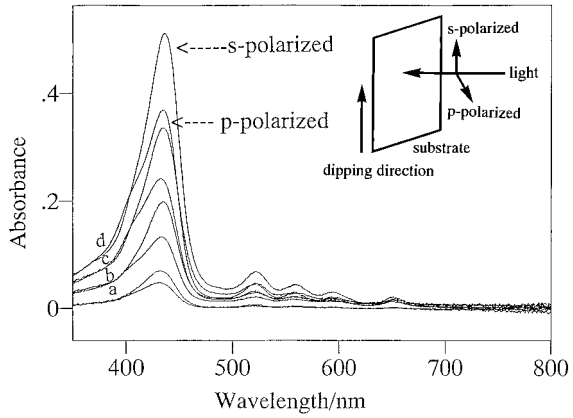

Figure 4. Polarized UV−vis spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer LB films of porphyrin 338a on CaF_2 plates. Incidence angle: 45°. The inset in this figure indicates the geometrical definitions.

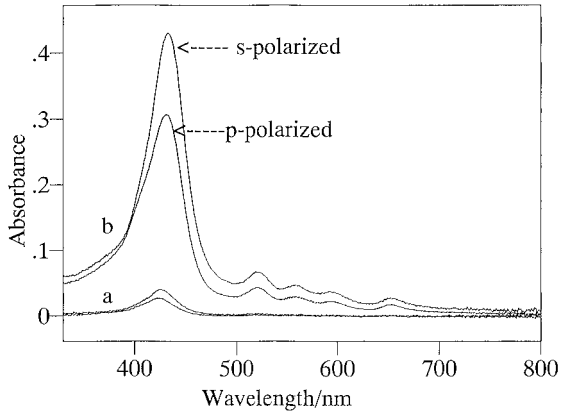

Figure 5. Polarized UV−vis spectra of (a) one- and (b) nine-layer LB films of porphyrin 338a on CaF_2 plates before and after heating to 150 °C. Incidence angle 45°.

obtained for LB films on glass plate (data not shown). The A_s to A_p ratio for the one-, three-, five- and nine-layer LB films on the CaF_2 or glass plate is 1.5 ± 0.1, in good agreement with that obtained for a Langmuir film of the same porphyrin sample on the water subphase by Yoneyama and his colleagues.[12,23] According to the theory developed by Orrit et al.,[21] this A_s to A_p ratio of 1.5 ± 0.1 for the porphyrin LB films corresponds to the nearly flat orientation of porphyrin macrocycle to the substrate surface. This leads us to conclude that the molecular rearrangement in the LB films during the transfer from aqueous subphase onto solid substrates is mainly due to larger overlapping of the porphyrin planes rather than greater tilting of porphyrin rings in the LB films on solid substrates such as CaF_2 and glass plates.

In order to gain information about aging and annealing effects on the molecular orientation in the LB films, we measured the polarized UV−vis spectra of the one-, three-, five-, and nine-layer LB films of porphyrin 338a on glass slides which were kept under dark for 1 month and those of the one- and nine-layer LB films before and after heating up to 150 °C for 10 min, respectively. The polarized UV−vis spectra (not shown) demonstrate that the aging of the LB films for 1 month did not bring a noticeable change in the molecular orientation, though the absorbances of the mono- and multilayer films decreased slightly (absorbance losses for the three-, five-, and nine-layer LB films were about 10%, and for the monolayer, about 2%). Regarding thermal-dependent orientational changes in the LB films for the monolayer and multilayer LB films, we obtained A_s to A_p ratios of 1.5 ± 0.1 for the out-of-plane anisotropies (Figure 5 and Table 1), respectively, demonstrating that the nearly flat orientation of porphyrin plane with respect to the surface of solid substrate remained unaltered even after heating up to 150 °C for 10 min. This indicates that the thermal stability of porphyrin LB films is high compared with LB films containing other functional organic pigments such as tetracyanoquinodimethane (TCNQ) and azodyes.[24−26] The reduction of the optical absorbances following heating cycles may be due to the reduction of the molecular density, a very common phenomenon for solid substances. The differential scanning calorimetry measurement of the porphyrin bulk material from 30 to 200 °C showed no abrupt change, indicating that porphyrin 338a does not undergo any significant decomposition, evaporation, and melting during the heating.

It is of particular interest to notice that a small peak having $A_s/A_p < 1$ appears near 400 nm only in the p-polarized spectra of the LB films with different layers at an incidence angle of 45° (Figure 4). This band may originate from the minor associated species of the porphyrin molecules with the transition moment nearly perpendicular to the substrate plane. This phenomenon is quite similar to that observed for azodye LB films by Orrit et al.[21] To understand this effect further, we compared the spectra measured with the s- and p-polarized light at an incidence angle of 45° before and after heating films to 150 °C. We have found that the small peak at 400 nm was weakened slightly after heating, though still recognizable, in the p-polarized UV−vis spectra, indicating partial conversion of vertically oriented porphyrins to parallel oriented ones on heating. Nearly similar fluorescence characteristics of the LB films before and after heating up to 150 °C further substantiate that the aggregation state of the porphyrin molecules in LB films remains unaltered after heating. A detailed study on the aggregation behavior of porphyrins in LB films on different substrates by using fluorescence spectroscopy will be reported elsewhere.[20]

On the basis of the discussion about the molecular aggregation and orientation in the porphyrin LB films, we deduce that the porphyrin macrocycles arrange themselves nearly parallel to the plane of the glass and CaF_2 plates, irrespective of the number of layers. The possible model of porphyrin molecular arrangement in the LB films is similar to that proposed by Yoneyama et al.[23] The head-to-tail model is consistent with one of the three possible models of porphyrin aggregates proposed by Schenning et al.[27] According to their models, the three tpyes of the aggregates differ in the angles between the center to center vector and the two transition moments α_1 and α_2: face-to-face type aggregates ($\alpha_1 = \alpha_2 = \pi/2$) which may show a blue shift of the Soret band to that of the monomeric state; edge-to-edge type ($\alpha_1 = 0$, $\alpha_2 = \pi/2$) in which the Soret band may split; head-to-tail aggregates ($\alpha_1 = \alpha_2 = \pi/4$) which should show a red shift of the Soret band. The red-shifted Soret band in the LB films in our case suggests head-to-tail aggregation (also called J-aggregation) of porphyrin molecules. The J-aggregation

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Table 2. Peak Positions and Their Assignment in the IR Transmission Spectra of the LB and Cast Films and a Chloroform Solution of Porphyrin 338a

		LB films				
cast film	chloroform solution	1-layer	3-layer	5-layer	9-layer	tentative assignment for major peaks
3317	3320		3316	3318	3318	ν(N−H(pyrrole))
3100						$\nu(C_\beta-H)$
3024			3024	3025	3024	ν(C−H(phenyl, pyridyl))
2922	2928	2924	2923	2923	2923	$\nu(CH_2)_{antisym}$(alkyl chain)
2852	2854	2852	2852	2853	2852	$\nu(CH_2)_{sym}$ (alkyl chain)
1637	1634	1635	1635	1635	1634	ν(C=N(pyridyl))
1562	1559			1564	1565	$\nu(C=C)$; $\nu(C_\alpha C_\beta)$; $\nu(C_\beta C_\beta)$
1510	1507	1508	1510	1510	1511	ν(C=C (phenyl,pyridyl)); $\nu(C_\alpha C_m)$
1474						δ CH_2 scissoring(alkyl)
1466		1466	1466	1467	1466	$\nu(C_\beta C_\beta)$; $\nu(C_\alpha C_\beta)$
1455						
1351	1361	1350	1353	1350	1350	$\nu(C_\alpha N$(pyrrole)); $\nu(C_\alpha C_\beta)$
1182	1183	1182	1181	1182	1182	$\delta(C-H)_{bending}$
1023		1024		1024	1024	$\nu(C_\beta H)$
995	995	996	996	996	995	
981	982		984	982	982	$C-H_{rock}$(pyrrole)
967	968	968	968	968	967	

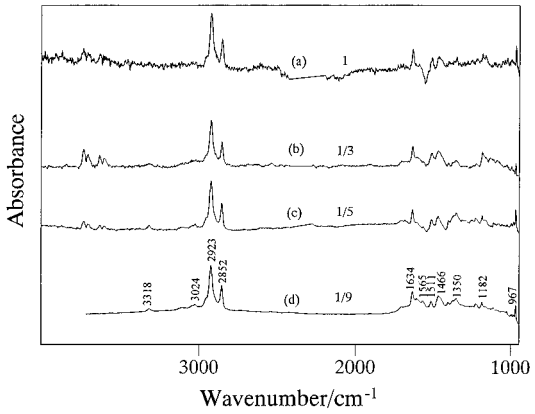

Figure 6. IR transmission spectra of (a) one-, (b) three-, (c) five-, and (d) nine-layer LB films of porphyrin 338a on CaF_2 plates. To facilitate comparison of the four spectra, each spectrum was divided by the film thickness.

may be energetically favorable due to the severe steric hindrance imposed by the long alkyl chain of the porphyrin macrocycle.

Owing to nearly parallel orientation of the porphyrin plane to the solid surface, a larger space is available for the long aliphatic chains of the porphyrin molecules to move freely, resulting in a loose packing of the aliphatic chains in the LB films. We have investigated the conformational order of alkyl chains of porphyrin 338a in LB films on a CaF_2 plate by IR spectroscopy.

(b) IR Spectra. Figure 6 shows the IR transmission spectra of one-, three-, five-, and nine-layer LB films of porphyrin 338a on CaF_2 plates. In order to discuss molecular structure in the LB films, it is necessary to assign the major peaks in the IR spectra. Assignments for the major peaks in the transmission IR spectra of the LB and cast films of porphyrin 338a and the chloroform solution are given in Table 2.[1,28−30] Referring to the spectra shown in Figure 6 and the band positions presented in Table 2, one finds that the transmission spectra of LB films with various layers are quite similar to each other except for band intensities, which show an almost linear relation with the number of layers. This suggests that there is no substantial layer-dependent structural alteration in the porphyrin LB films, and this result is consistent with that reached by UV−vis spectra discussed above.

Comparison of the IR transmission and reflection−absorption (RA) spectra of LB films is frequently employed to evaluate the molecular orientation in LB films.[31−35] In the case of molecules like long chain fatty acids, such qualitative or quantitative estimation of the molecular orientation may be valid, with the inherent assumption that the molecules assume identical orientation and maintain a similar aggregation state in the LB films deposited onto a transparent substrate like CaF_2 and onto an opaque substrate like gold or silver. For strongly absorbing chromorphores, great care should be taken when discussing molecular orientation by comparing IR transmission and RA spectra, as the molecular aggregation and orientation may vary significantly due to different interactions between the film forming molecules and substrates. We have considered it improper to compare the RA and transmission spectra of porphyrin LB films deposited onto gold and CaF_2 plates for the evaluation of orientations of the porphyrin ring and alkyl chain in LB films, because porphyrin molecules form different kind of aggregates in the LB films on gold and CaF_2 plates, as evidenced by marked changes in the profiles of the UV−vis spectra and emission properties.[20]

It is, however, well-known that the wavenumbers of the CH_2 symmetric and antisymmetric modes can be used to monitor the degree of conformational order of the alkyl chain.[31b,34] When the hydrocarbon chain is highly ordered (trans-zigzag conformation), the bands due to CH_2 symmetric and antisymmetric modes appear near 2848 and 2918 cm^{-1}, respectively, while if conformational disorder is induced in the alkyl chain, these bands shift up to 2856 and 2927 cm^{-1}, respectively, depending upon the extent of disordering. In the present case, the CH_2 antisymmetric and symmetric bands appear at ∼2923 and 2853 cm^{-1}, respectively, suggesting the existence of considerable gauche conformations in the hydrocarbon chain in the LB films. A comparison of the IR spectra of porphyrin 338a in chloroform solution and in the LB and cast films in Table 2 provides further information about the structural

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modification of the porphyrin on formation of the LB and cast films. The higher frequencies for the CH_2 antisymmetric (2854 cm^{-1}) and symmetric (2928 cm^{-1}) modes in the chloroform solution compared to the corresponding bands at 2852 and 2923 cm^{-1} in the LB films indicate a higher degree of randomness and a greater extent of gauche conformations of the hydrocarbon chain in solution. However, the structural features of the cast and LB films of porphyrin 338a are similar to each other, indicating that the hydrocarbon chains in both of the films are in a slightly disordered packing state.

In contrast to the orientation of the porphyrin macrocycle, which shows no significant alteration caused by heating, the alkyl chain attached to the porphyrin core tends to become more disordered when heating, as evidenced by the shift in the frequencies of the CH_2 antisymmetric and symmetric stretching bands toward higher wavenumbers in the IR spectra. We will report in more detail on the thermal behavior of porphyrin LB films elsewhere.

Although no systematic correlations have been established for the core size variations and other distortions with marker bands in the IR spectra of free base porphyrins, one may expect similarities in the spectral shifts observed in IR spectra for certain modes as in Raman spectra of porphyrins accompanying various distortions. Prendergast and Spiro[35] have discussed the dependence of skeletal mode frequencies in Raman spectra due to changes in the core size and nonplannar distortions of the porphyrins and found that the $C_\alpha C_m$, $C_\alpha C_\beta$ and $C_\beta C_\beta$ bonds and the $C_\alpha C_m C_\alpha$ (For the C_i-C_j nomenclature, see Figure 1) angles increase while the $C_\alpha N$ bonds contract with the expansion of the porphyrin core. In our case, the skeletal modes at 1559 and 1507 cm^{-1} involving mainly the $C_\alpha C_\beta$ and $C_\alpha C_m$ bonds increase by 3−4 cm^{-1}, while the $C_\alpha N$ stretching mode at 1361 cm^{-1} decreases by about 10 cm^{-1} in the IR spectra of LB films, compared to the respective bands in solution. This trend indicates that the porphyrin core contracts slightly on solidification in the LB films.

Conclusion

By employing UV−vis and IR spectroscopies, we have studied the molecular orientation and aggregation in the LB films of porphyrin 338a. It has been found that the porphyrin rings overlap each other, and lie almost flat to the substrate surface, irrespective of the number of layers in the LB films. The flat orientation of the porphyrin did not alter upon aging for 1 month and after heating up to 150 °C showing that the LB films have excellent chemical and thermal stability superior to those of many other organic dyes. The IR spectra of the porphyrin LB films deposited onto CaF_2 indicate that hydrocarbon chains attached to porphyrin macrocycle are packed loosely and, to some extent, are disordered.

It is also found that aggregation in porphyrin LB films, evidenced by the red shift of the Soret bands in monolayer LB films on solid substrates, such as glass and CaF_2 plates, as well as on the water subphase, occurred similar to that in the spreading solution. The structure of the aggregates formed in the LB films with different layers deposited on the CaF_2 or glass substrates are similar to each other, as indicated by the UV−vis spectra of one-, three-, five-, and nine-layer LB films.

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