

Protoporphyrin IX Zinc(II) Organization at the Air/Water Interface and Its Langmuir–Blodgett Films

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Protoporphyrin IX zinc(II) (ZnPP) and its mixtures with *N*-hexadecylethylenediamine, hexadecyltrimethylammonium bromide, and didodecyltrimethylammonium bromide in a molar ratio of 1:2 were used to investigate the Langmuir monolayer and Langmuir–Blodgett (LB) film behaviors. The well-defined Langmuir monolayers were formed at the air/water interface for ZnPP alone and its hybrids with surfactants. While the ultraviolet–visible spectrum of ZnPP alone indicated the formation of an H-aggregate in the LB film from the blue shift of the Soret band, the introduction of surfactants into the ZnPP LB film reduced the π – π interaction between ZnPP macrocycles. Linear dichroism revealed that the average orientation angle of the protoporphyrin macrocycle against the substrate surface was in the range of 39.5–44.5° in a ZnPP LB film and three ZnPP/surfactant LB films. Fourier transform infrared spectra of the LB films suggested that the alkyl chains of the surfactants take a disordered gauche conformation and porphyrin carboxylic acids partly converted to carboxylates with the introduction of surfactants. The atomic force microscopic results further confirmed the formation of homogeneous LB monolayers. These results demonstrate that there is preferable mutual miscibility in ZnPP/surfactant hybrids, and no isolated phase or domain formed by the surfactants exists in the hybrid LB films.

1. Introduction

In recent years, much work has been concentrated on the construction of organized aggregates from porphyrin and its derivatives due to their crucial roles in making functional materials, and also as a model for some biochemical processes.^{1–14} Several types of systems such as micelles,^{7,10} vesicles,^{2,4} Langmuir–Blodgett (LB) films,^{3,5,9,11} self-assembled monolayers (SAMs),^{12–14} and layer-by-layer deposition films⁸ have been developed to construct ordered aggregates of porphyrin. Among them, the fabrication of mono- or multilayers from natural porphyrins, such as proto- and hematoporphyrin derivatives, has become a topic of increasing interest for their biological and chemical importance.^{15–18} The self-as-

sembled monolayers formed by chemical binding of the porphyrin functional groups to the substrate^{15,16} or by axial coordination of the porphyrin central metal onto a ligand covalently bound to the substrate^{17,18} have been reported.

In a previous paper,¹⁹ T.I. reported a stable monolayer derived from self-assembly of protoporphyrin IX zinc(II) (ZnPP), a natural porphyrin with two carboxyl groups, onto a Au surface by the adsorption from a ZnPP solution. It was shown that the porphyrin is chemically bound to the Au surface via one of the two COOH groups. The other one remains unbound to the surface but forms a hydrogen bond with the COOH group of an adjacent porphyrin molecule. This is the first report on SAMs formed directly from natural porphyrins onto a solid surface, different from the monolayers formed from chemically modified porphyrins on the substrate surface.

In the present study, we focus on the construction of ordered molecular assemblies of ZnPP using the LB approach, which is one of the most useful techniques for the fabrication of functional ultrathin films with a controlled thickness and an ordered structure.²⁰ The Langmuir-monolayer-forming properties and LB films of ZnPP alone and its hybrids with surfactants, *N*-hexadecylethylenediamine (hexd-en), hexadecyltrimethylammonium bromide (C₁₆TAB), and didodecyltrimethylammonium bromide (2C₁₂DAB), were investigated by surface pressure–molecular area (π –*A*) isotherm examination, ultraviolet–visible (UV–vis) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and atomic force microscopy (AFM). The influences of added surfactants on the monolayer organization and on the interactions between porphyrin macrocycles are discussed.

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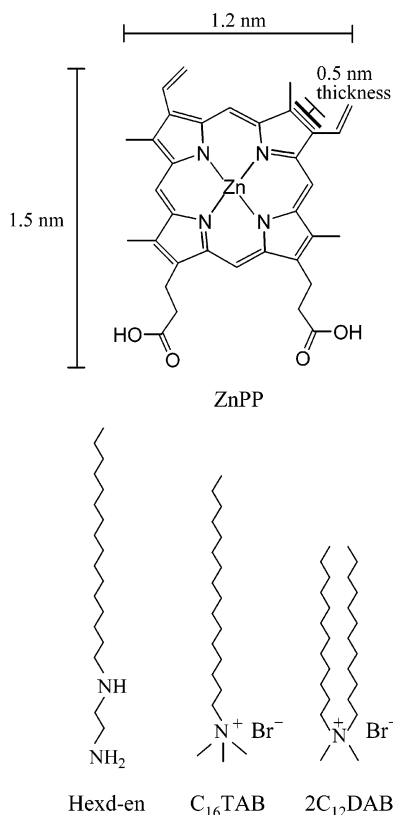


Figure 1. Schematic drawing of the chemical structures of ZnPP, hexd-en, C_{16} TAB, and $2C_{12}$ DAB.

2. Experimental Section

2.1. Materials. ZnPP was purchased from Aldrich Chemical Co., C_{16} TAB ($CH_3(CH_2)_{15}N(CH_3)_3 \cdot Br$) and $2C_{12}$ DAB ($[CH_3(CH_2)_{11}N(CH_3)_2 \cdot Br]$) were products from Tokyo Chemical Industries Co., Ltd. Hexd-en ($CH_3(CH_2)_{15}NHCH_2CH_2NH_2$) used in this study is the same as that reported previously.²¹ The chemical structures for ZnPP and the surfactants are illustrated in Figure 1. Dimethylformamide (DMF) and chloroform (Analytical grade) were purchased from Wako Pure Chemical Industries, Ltd. All reagents were used as received without further purification. Ultrapure water ($18.3 \text{ M}\Omega$) for the subphase was prepared using a Milli-Q filtration unit from the Millipore Corp.

2.2. Surface Pressure–Molecular Area Isotherm and LB Film Deposition. Surface pressure measurement and LB film preparation were carried out at $25 \pm 0.5 \text{ }^\circ\text{C}$ on an LB film deposition apparatus (Nippon Laser & Electronics Laboratory). ZnPP and its hybrids with surfactants (hexd-en, C_{16} TAB, and $2C_{12}$ DAB) in a molar ratio of 1:2 were dissolved in chloroform/DMF (4:1 v/v). The concentrations of ZnPP in these four systems are $5.75 \times 10^{-5} \text{ M}$. Monolayers were obtained by spreading an appropriate volume ($0.1\text{--}0.2 \text{ cm}^3$) of the above solutions onto a pure water subphase. After 15 min was allowed for the solvent to evaporate, the surface area of $5 \times 35 \text{ cm}^2$ was compressed at a constant rate of 10 mm/min .

For the LB film fabrication, following the immersion of the substrate in the subphase, the monolayer was spread onto the subphase surface. After the 15–20 min equilibration period, the monolayer was compressed to the given pressure (25 mN/m for the ZnPP monolayer and 30 mN/m for the mixed ZnPP/surfactant ones) and 20 min was spent to establish equilibrium of the monolayer. The monolayer was then transferred onto a cleaned CaF_2 plate (for UV–vis and FT-IR spectroscopy) or a freshly cleaved mica substrate (for AFM) by the vertical transfer method at a speed of 2 mm/min . The multilayer LB films were prepared by successive upstroke and downstroke accumulation. All the LB films were dried overnight in vacuo before characterization.

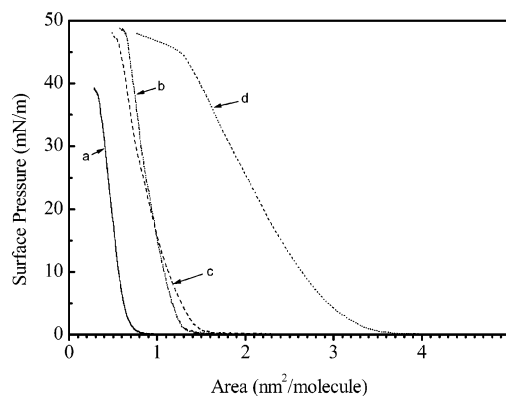


Figure 2. π - A isotherms of ZnPP and its mixtures with surfactants in a molar ratio of 1:2 on a water subphase: (a) ZnPP, (b) ZnPP/hexd-en, (c) ZnPP/ C_{16} TAB, (d) ZnPP/ $2C_{12}$ DAB. The molecular area is based on the amount of ZnPP.

2.3. Instruments. UV–vis transmission spectra were recorded at room temperature on a Shimadzu UV-2200 spectrophotometer. The reference used was a blank CaF_2 plate. For linear dichroism measurements, a UV dichroic polarizer was placed between the incident beam and the sample. The light with the polarization directions parallel and vertical to the dipping direction is denoted as s-polarized and p-polarized light, respectively.

FT-IR spectra were recorded at room temperature on a Bio-Rad FTS 575C FT-IR spectrometer equipped with a cryogenic mercury cadmium telluride (MCT) detector. The spectra were collected with 512 scans at 4 cm^{-1} resolution. Ultimate spectra were obtained by subtracting the spectra of the blank CaF_2 from those of the substrates with LB films.

AFM observations were performed at room temperature in the tapping mode on an AFM Nanoscope III (Digital Instruments, Inc.). A crystalline silicon tip on a cantilever was used. The surface roughness of the LB films was obtained by sectional analysis.

3. Results and Discussion

3.1. Monolayer Formation at the Air/Water Interface and Monolayer Transfer onto Substrates. Figure 2 shows the π - A isotherms of ZnPP and its mixtures with hexd-en, C_{16} TAB, and $2C_{12}$ DAB in a molar ratio of 1:2. The concentrations of ZnPP in all spreading solutions were the same, and the occupied molecular areas were calculated on the basis of the amount of ZnPP. The occupied molecular areas (A_{obs}) obtained by extrapolating the linear parts of the π - A isotherms to zero pressure are listed in Table 1. The occupied area of a monolayer of ZnPP alone (0.64 nm^2) is smaller than the molecular area of the porphyrin macrocycle lying flat on water (1.45 nm^2).²² Such a small area per molecule should be due to the molecule aggregation at the air/water interface.

Generally, there is substantial attractive π - π interaction between porphyrin macrocycles which is strong enough to cause significant aggregation. Chou et al.²³ have proposed an orientation model to elucidate the organized structures of porphyrin monolayers in which tilted porphyrin–porphyrin overlap occurred in the absence of steric constraint from aliphatic chains. In the present study, since ZnPP contains hydrophilic carboxylic acid moieties, the small occupied ZnPP molecular area may be due to the spontaneous formation of aggregates with carboxylic acid moieties facing the water subphase, when the solutions were spread and the solvent was evaporated; after compression, the ZnPP aggregates were closely packed by the strong π - π stacking interaction. The

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Table 1. Characteristics of Langmuir Monolayers and LB Films

composition (molar ratio)	A_{obsd} (nm ²)	A_{calcd} (nm ²)	transfer pressure (mN/m)	transfer ratio		λ_{max} (nm)	half-width of the Soret band (nm)	ratio of As to Ap at Soret maxima ^a	orientation angle of the ZnPP ring (deg)
				upstroke	downstroke				
ZnPP in solution ^b						419.0	10.0		
ZnPP	0.64		25	1.1 ± 0.1	no transfer	412.0	39.0	1.327 (1.000)	39.5
ZnPP/hexd-en (1:2)	1.10	1.04	30	1.4 ± 0.1	0.8 ± 0.1	420.5	30.5	1.281 (0.988)	40.9
ZnPP/C ₁₆ TAB (1:2)	1.10	1.04	30	1.1 ± 0.1	0.8 ± 0.1	417.5	40.0	1.277 (0.980)	41.4
ZnPP/2C ₁₂ DAB (1:2)	2.90	1.44	30	1.7 ± 0.1	no transfer	419.5	38.0	1.177 (0.964)	44.5

^a Incidence angles were 45° and 0° (the values in parentheses). ^b The UV spectral result of ZnPP in solution has been shown here to allow a comparison with LB films.

occupied area is comparable to the calculated value (0.60 nm²) for the porphyrin with carboxylic acids facing the water surface. A similar arrangement of ZnPP was also obtained by adsorption from a ZnPP solution on a hydrophilic solid substrate.²⁴

The occupied ZnPP molecular areas in the mixtures with surfactants depend on the composition of the spreading solutions. The areas of vertically orientated hexd-en and C₁₆TAB are about 0.20 nm², and that of 2C₁₂-DAB must be 0.40 nm² because of the double chains. For a completely immiscible or ideally mixed monolayer, the molecular area of the hybrid monolayer should follow the additivity rule,^{25–27} and we can obtain the total molecular area of the ZnPP/surfactant (1:2) hybrid by using the equation $A_{\text{calcd}} = A_{\text{ZnPP}} + 2A_{\text{surfactant}}$. The calculated total molecular areas of these mixed systems (A_{calcd}) are also listed in Table 1. It could be found that the observed values of ZnPP/hexd-en and ZnPP/C₁₆TAB hybrids are only slightly larger than or almost comparable to the calculated ones in the same molar ratios. For these cases, ZnPP and the surfactants must keep their original orientations at the air/water interface, in which only hydrophilic moieties of porphyrin and the surfactant contact the water subphase. On the other hand, the observed molecular area for the ZnPP/2C₁₂DAB hybrid is much larger than the calculated one. This result indicates that the complexation of ZnPP with surfactants occurs at the air/water interface and greatly influences the organization of porphyrin molecules. In this case, a flat orientation of the porphyrin molecules with respect to the water surface and the expansion of surfactant alkyl chains are expected, since the observed area is still larger than the calculated value for a hybrid with a flat-lying porphyrin molecule (2.25 nm²).

The transfer ratio obtained in the present work (Table 1) depends on the systems. For ZnPP alone and the ZnPP/2C₁₂DAB hybrid, the monolayers can be transferred onto solid substrates only in the upstroke mode, and Z-type LB films were obtained. On the other hand, for ZnPP/hexd-en and ZnPP/C₁₆TAB hybrids, the monolayers were transferred in both upstroke and downstroke modes, and Y-type LB films were fabricated. As seen in Table 1, the transfer ratios were larger than unity in the upstroke mode and smaller than unity in the downstroke mode, suggesting that, during the transfer of the monolayers from the water subphase onto the solid substrate, the porphyrin molecules had undergone some rearrangement. This rearrangement changed the orientation of the

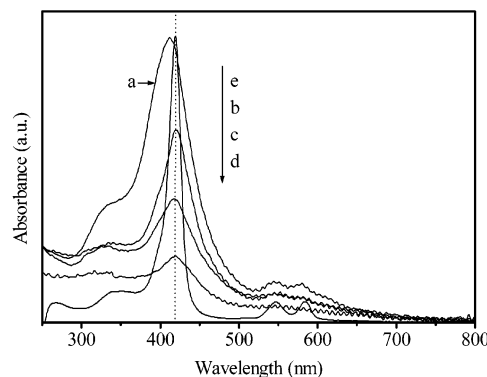


Figure 3. UV-vis spectra of LB films and ZnPP in solution: (a) 5-layer ZnPP, (b) 9-layer ZnPP/hexd-en, (c) 9-layer ZnPP/C₁₆TAB, and (d) 21-layer ZnPP/2C₁₂DAB LB films, (e) ZnPP in a chloroform/DMF (4:1 v/v) solution with a concentration of 5.75×10^{-5} M.

porphyrin molecules in the LB films, as will be discussed later in this paper.

3.2. UV-Vis Spectra and Orientation of Porphyrin in the LB Films. It is well-known that UV-vis spectra of the chromophores are used to investigate the aggregation and orientation of the porphyrin macrocycles.^{9,17–19,26,28} Figure 3 compares UV-vis spectra of LB multilayer films and ZnPP in a chloroform/DMF (4:1 by volume) solution. The ZnPP molecules in the solution exhibit three bands at 419, 547, and 584 nm, assignable to the Soret band and two Q-bands, respectively.^{18,19,29} For the ZnPP LB film, the Soret band of ZnPP is broader and blue-shifted to 412 nm. This is different from the chemisorption of ZnPP on a Au substrate,^{18,19} in which a small red shift of the Soret band was observed. According to the excitonic coupling theory of the electronic transitions in the porphyrin π system,³⁰ the blue shift of the Soret band is consistent with a parallel stacking of the macrocycles. This result indicates that the ZnPP molecules form an H-aggregate in the LB film. On the other hand, the Soret bands for the LB films of ZnPP/surfactant hybrids show no distinct shift but become broad in comparison with that for the solution. Therefore, for these three systems, there is no direct evidence for the formation of the ZnPP aggregate through π - π interaction, as such aggregation may shift the Soret band significantly. The monolayers of ZnPP/surfactant hybrids were prepared by the cospreading method. The ZnPP/surfactant complex through electrostatic interaction should be formed even in the spreading solution and was kept after spreading

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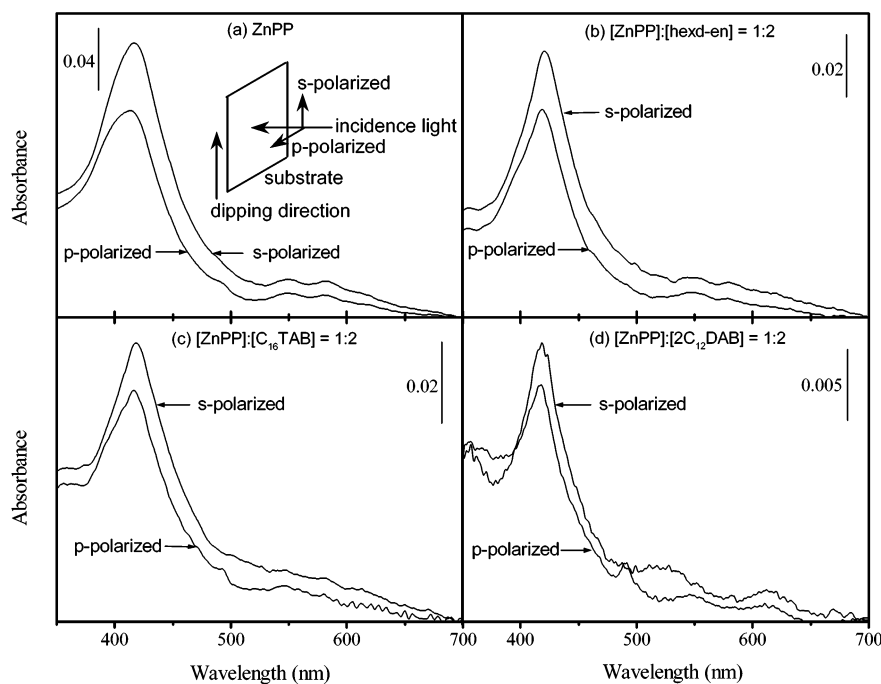


Figure 4. Polarized UV-vis spectra with an incidence angle of 45° of LB films. The notations of (a)–(d) are the same as in Figure 3. The inset in (a) indicates the geometrical definitions.

onto the water subphase, which was confirmed by the infrared spectra discussed below. The complex formation of ZnPP with surfactants seems to have broken the π - π interaction between ZnPP macrocycles at the air/water interface.

Polarized UV-vis spectroscopy is a convenient and useful tool in evaluating the molecular orientation of the chromophore in a thin solid film. To estimate the orientation of ZnPP molecules in the LB films, we measured polarized UV-vis spectra with incident angles of 0° and 45° . Figure 4 shows the polarized spectra of the LB films at an incidence angle of 45° . The tilted angles between the porphyrin macrocycle and the substrate surface were calculated from the intensity ratios of s-polarized (A_s) to p-polarized (A_p) bands of the Soret band at 45° and 0° ,³¹ and the results are listed in Table 1 together with the intensity ratios. Considering the uncertainty of $\pm 5^\circ$ that comes from using the polarized UV-vis method, we found little difference in the orientation of the porphyrin macrocycles. However, we have revealed that the occupied molecular areas per ZnPP unit in these four systems are quite different, from 0.64 to 2.90 nm² (see Table 1). These results should be due to the rearrangement of porphyrins during transfer of monolayers onto solid substrates. This fact indicates that structural information about LB films is not necessarily inferred from the isotherm data.

3.3. FT-IR Spectra and Arrangement of Surfactants in the LB films. Figure 5 shows transmission IR spectra of the ZnPP and hybrid LB multilayer films. For a ZnPP LB film, two broader bands at 2925 and 2859 cm⁻¹, assignable to the CH₂ antisymmetric and symmetric stretching vibration modes of the short alkyl chain, respectively, were observed. The CH₂ scissoring modes give rise to medium-intensity peaks near 1451 and 1383 cm⁻¹.^{19,32} The band at 1727 cm⁻¹ is ascribable to the hydrogen-bonded C=O stretching vibration mode of the

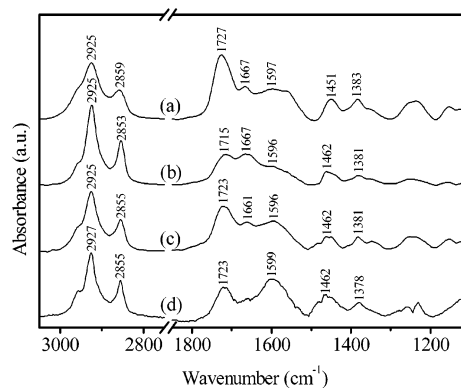


Figure 5. FT-IR spectra of LB films: (a) 5-layer ZnPP, (b) 21-layer ZnPP/hexd-en, (c) 21-layer ZnPP/C₁₆TAB, (d) 21-layer ZnPP/2C₁₂DAB.

carboxyl group,^{18,33,34} since it shifted to the lower-frequency region in comparison with the free state of the carboxyl group (about 1745 cm⁻¹),¹¹ which is different from the IR result of ZnPP powder at 1708 cm⁻¹ by forming a ring dimer structure.¹⁹ The bands around 1667 and 1597 cm⁻¹ are due to the modes of the skeleton of the porphyrin molecule.^{18,32,35}

For the LB films transferred from mixed ZnPP/surfactant monolayers, the chain conformation estimated from the high-frequency region can be used as a probe to detect the packed density of the alkyl chains.^{36,37} Higher wavenumbers near 2925 and 2854 cm⁻¹ of the antisymmetric and symmetric CH₂ stretching vibrations for ZnPP/hexd-en, ZnPP/C₁₆TAB, and ZnPP/2C₁₂DAB hybrids suggest a disordered gauche conformation, different from

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surfactant LB films with a highly ordered all-trans conformation,^{38,39} indicating that no isolated phase formed by the surfactants exists in the LB films. Therefore, the LB films of the hybrids cannot be interpreted by a mere juxtaposition of ZnPP domains and surfactant domains inside the LB films. This conclusion was further confirmed by the AFM observation as discussed below.

The band at 1727 cm^{-1} is weakened in intensity and shifted to lower wavenumbers, and simultaneously, the band near 1596 cm^{-1} increases in intensity. The band near 1596 cm^{-1} is due to the COO^- antisymmetric stretching mode^{40,41} (overlapped with the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations of the porphyrin macrocycle and the $\text{C}=\text{C}$ stretching vibration of the vinyl substituent³⁵). The COO^- symmetric stretching mode (around 1380 cm^{-1})⁴¹ overlaps the CH_2 scissoring absorption of ZnPP.³² The band at 1462 cm^{-1} is assigned to the CH_2 scissoring band of the long alkyl chains of the surfactants.^{38,39} These results indicate the change of COOH to COO^- ,^{40,41} suggesting that there is interaction between ZnPP carboxylate groups and surfactant hydrophilic groups. While for the chemisorption of ZnPP onto a Au substrate, only a symmetric COO^- stretching band at 1412 cm^{-1} was observed due to the surface selection rules of SEIRAS.¹⁹

3.4. AFM and Miscibility of Porphyrin and Surfactant in the LB Films. The AFM technique was used to investigate the miscibility and phase separation of the component molecules in the mixed LB films.^{42–44} Generally, two scenarios are possible when two kinds of molecules are mixed. One is that two-component hybrids form the homogeneous monolayer with preferable mutual miscibility. The other is that two molecules are completely immiscible and form the isolated phases or domains which can be directly visualized by AFM. Figure 6 shows AFM images of the LB films deposited from ZnPP, hexd-en, and ZnPP/hexd-en, ZnPP/ C_{16}TAB , and ZnPP/ $2\text{C}_{12}\text{DAB}$ hybrid monolayers. All the LB monolayer films on the mica surfaces are uniform and smooth, indicating that, for these systems, homogeneous monolayers are formed at the air/water interface. This result is consistent with that from the UV–vis and IR measurements; that is, the introduction of surfactants can break the π – π interaction between porphyrin macrocycles and form monolayers with mutual miscibility.

3.5. Models of Molecular Organization in the Langmuir and LB Films. On the basis of the above presented results, schematic models of molecular organization in Langmuir and LB films are depicted in Figure 7. For ZnPP Langmuir and LB films, it can be supposed that the ZnPP molecules are stacked to form H-aggregates in which the overlap occurs between adjacent porphyrin rings and there is a substantial attractive π – π interaction between porphyrin macrocycles. Porphyrins maintain a tilt angle of ca. 39.5° of the macrocycles with respect to the substrate in the LB film.

The introduction of surfactants into monolayers is effective in breaking the π – π interaction between porphyrin macrocycles and forming hybrid monolayers with preferable miscibility. During the transfer of the mono-

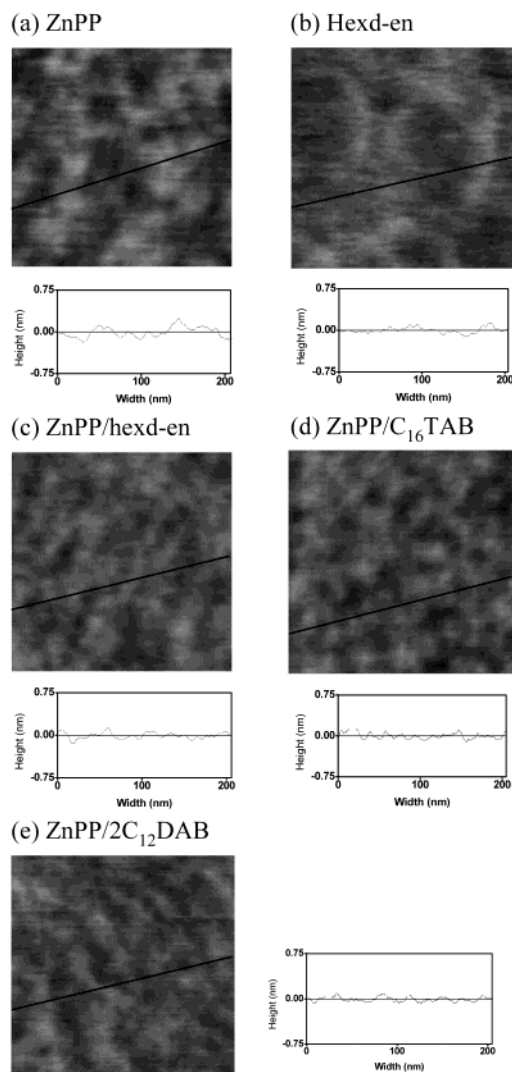


Figure 6. AFM images ($200 \times 200\text{ nm}^2$) and their section analyses of monolayer LB films transferred onto mica: (a) ZnPP, (b) hexd-en, (c) ZnPP/hexd-en, (d) ZnPP/ C_{16}TAB , (e) ZnPP/ $2\text{C}_{12}\text{DAB}$.

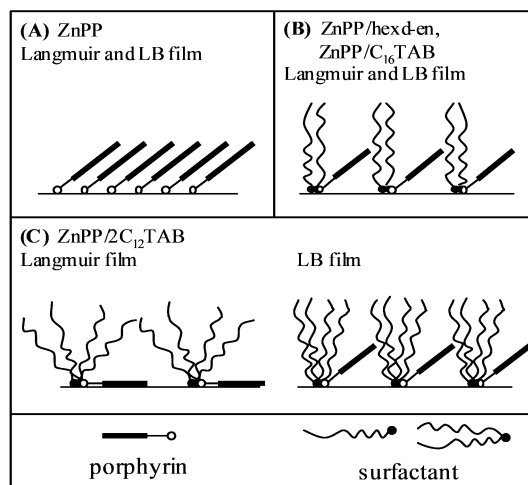


Figure 7. Schematic illustration of possible arrangements of ZnPP and surfactant molecules in Langmuir and LB films: (A) ZnPP, (B) ZnPP/hexd-en and ZnPP/ C_{16}TAB , (C) ZnPP/ $2\text{C}_{12}\text{DAB}$.

layers from the water subphase onto the solid substrate, the molecules had undergone some rearrangements which changed the orientation of the porphyrin molecules in the

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LB films, especially for the ZnPP/2C₁₂DAB hybrid. A flat orientation of the porphyrin molecules with respect to the water surface in the Langmuir monolayer changed to a 44.5°-tilted orientation in the LB film on the substrate.

Conclusions

In the present work, air/water surface behaviors and LB films of ZnPP, a natural porphyrin without any modification, and the ZnPP/surfactant hybrids have been investigated. It was demonstrated that ZnPP and its

hybrids with surfactants form stable monolayers at the air/water interface which can be transferred onto solid substrates. While the ZnPP molecules form an H-aggregate in a one-component LB film, the introduction of surfactants reduces the π - π interaction between porphyrin macrocycles, changes the molecular organization, and forms homogeneous LB films with preferable miscibility.

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