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Self-Organization of Amphiphilic Porphyrins at the Air-Water Interface

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The Langmuir-Blodgett film forming properties of a series of pyridyl(hexadecyloxy)phenylporphyrins have been examined. Good monolayers of these compounds have been prepared in most cases without the use of matrix molecules and the monolayers are readily transferable to glassy slides. The small mean molecular areas, as obtained from the surface-pressure-area isotherms, indicate a tilted orientation of the porphyrin rings with respect to the water surface. It was found by means of UV-vis absorption spectroscopy at the air-water interface and by Brewster angle microscopy that intermolecular interaction between porphyrin rings mutually directs the organization at submonolayer coverage. Upon compression, the self-assembled domains come into close contact without reorganization of the layer structure. It was also demonstrated that porphyrins with three and four aliphatic side chains self-assembled into a highly ordered arrangement in contrast to the porphyrins with one and two alkyl chains.

Introduction

Nature has developed a fascinating device to make use of sunlight in order to run the photosynthetic process in which carbon dioxide is eventually reduced to carbohydrates and oxygen. The photosynthetic unit, assembled in a membrane matrix, comprises antenna pigments for light energy harvesting and a reaction center where this energy is used to initiate a series of consecutive electron transfer steps producing a transmembrane potential.

The active components in the solar energy conversion process in the photosynthetic unit are mostly ordered assemblies in which porphyrins (chlorophylls) play a major role.

Over the past decade, a large number of molecules have been designed to mimic some aspects of the photosynthetic machinery.¹⁻⁴ It has been found to be of great importance to control the molecular arrangement in terms of distance, orientation, and redox potential. One of the most appropriate methods of achieving this is the Langmuir-Blodgett technique, by which the spatial arrangement of the various moieties across the film can be constructed readily at atomic distances, although it imposes some restrictions on the materials that can be used.

Organized monolayers of porphyrins⁵⁻¹⁶ and phthalocyanines¹⁶⁻²¹ have received a lot of attention. A great deal of effort has been made to control the orientation of these molecules in a Langmuir-Blodgett film, by making structural modifications in order to create highly ordered structures which offer the possibility for practical applications in photoelectric devices.

In this paper we present a study of a series of amphiphilic meso-substituted free base porphyrins, containing polar pyridyl groups as the hydrophilic part and (hexadecyloxy)phenyl groups as the hydrophobic part of the molecule. In order to enhance the electrostatic interaction of the headgroups with the water surface and to improve the spreading of the molecules, methylation of the pyridyl groups is carried out, thus creating a positively charged methylpyridinium group.

The monolayer formation of these compounds together with the spectral characteristics of the monolayers at the air-water interface and on solid supports are investigated.

Experimental Section

Chart 1 shows the structures of the compounds 1, 2-cis, 2-trans, 3, 3pyr+ and 4. Synthetic details will be published elsewhere.²²

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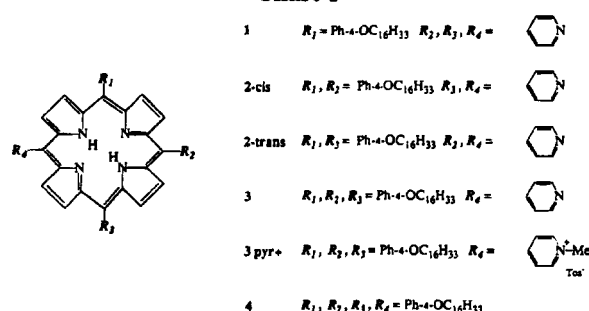
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Table 1. Mean Molecular Area, Compressibility (α), Transfer Properties, and Absorption Characteristics of the Amphiphilic Porphyrins^a

compound	mean molecular area ($\text{\AA}^2/\text{molecule}$) ^b	α (nM/m^{-2}) ^c	type of transfer	transfer ratio		maximum Soret absorption band (nm)	
				downstroke	upstroke	solution	air/water
1	60	0.0043	Z	<0.2	>0.6	420	445
2-cis	88	0.0084	Y	0.7-0.9	1.0	420	432
2-trans	<i>d</i>	<i>d</i>					
3	115	0.017	Y	>0.8	1.0	420	398/440
3pyr+	136	0.026	Y	0.4-0.8	>0.9	422	433
	112	0.014					
4	50	0.015				420	398/440

^a The maxima of the absorptions at the air-water interface were recorded after equilibration of the monolayer. ^b The mean molecular areas were obtained by taking the tangent of the isotherms at the pressure of monolayer transfer and extrapolating this to zero pressure. The pressures for monolayer transfer were 20 mN/m for 1, 2-cis, and 3pyr+ respectively, while for 3 a pressure of 10 mN/m was taken. In the case of 3pyr+ we have defined two areas, one before and one after the phase transition (8 and 20 mN/m, respectively). ^c As calculated via eq 1. ^d The mean molecular area and compressibility for 2-trans were found to be highly irreproducible and is therefore omitted in this table.

Chart 1



Surface-pressure vs area (π -A) isotherms were recorded on a Lauda Filmwaage FW2, which was thermostated at 20 °C and placed in a laminar flow cabinet. Ultrapure water for the subphase was obtained by filtration through a SERALPUR PRO 90C system. The monolayers were formed by spreading the porphyrins from chloroform solutions (10^{-4} - 10^{-3} M) onto a pure water subphase (pH = 5.5 after equilibration with surroundings) by use of a microsyringe. After spreading, the monolayer was allowed to equilibrate for at least 15 min before compression was started. The compression and expansion rates were 3 cm²/min. Monolayer films were transferred to glass substrates by vertical dipping. The dipping/withdrawal rate was 3 mm/min. The substrates were cleaned in a DECON-soap solution by sonification for 15 min. After extensively rinsing with pure water and acetone, the substrates were dried by purging with a stream of N₂.

The electronic absorptions in solution and on glass substrates were recorded with a VARIAN/CARY 1 spectrophotometer. The absorption spectra of monolayers were measured at the air-water interface with a quartz fiber optic probe (Spectrofiop 8452, Photonetics) connected to a HP 8452 diode array spectrophotometer. The spectrum was taken by light passing through the monolayer, reflecting the light beam via a concave-shaped mirror placed just below the water surface through the monolayer again into the fiber.

The Brewster angle microscope experiments were carried out with a BAM1, manufactured by Nano Film Technology, Göttingen. The setup of the BAM has been extensively described in literature.²³

Results and Discussion

Monolayer Formation. Figure 1 shows the π -A isotherms of compounds 1-4 on pure water.²⁴ By extrapolating the tangent on the isotherms at a fixed point to zero pressure, the mean molecular areas of the porphyrins are obtained. These values are compiled in Table 1.

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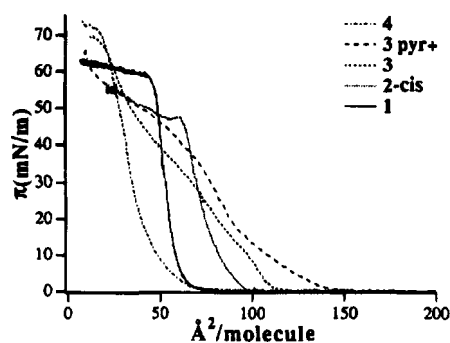


Figure 1. Surface pressure-area (π -A) isotherms of amphiphilic porphyrins 1, 2-cis, 3, 3pyr+, and 4 on pure water at 20 °C.

Based on space filling CPK models of tetraphenylporphyrins, the molecular area of the porphyrin core is estimated to be $15 \text{ \AA} \times 15 \text{ \AA} = 225 \text{ \AA}^2$. As can be seen from Figure 1 and Table 1, the molecular area increases smoothly as the number of alkyl chains increases from one to three, but it was surprising to find that the measured areas are all significantly smaller than the planar area of the porphyrin ring. This means that the porphyrin cores are tilted with respect to the water surface. The larger mean molecular area observed for the ionized triple-chained porphyrin 3pyr+, as compared to 3, is attributed to the electrostatic repulsion between the positively charged headgroups. In contrast to the other systems, the four-chained porphyrin, 4, shows a rather exceptional behavior. The mean molecular area is very small (50 \AA^2) and should thus correspond to an almost perpendicular orientation on the water surface.

Furthermore, all the monolayers exhibit high collapse pressures, suggesting that the porphyrins form stable monolayers on the air-water interface. A better criterion, however, for testing the monolayer stability at higher pressures is by performing stability experiments, at which the development of the area with time is followed after adjusting a fixed pressure. It was found that above certain pressures, depending on the compound, a slowly deas-

(24) Essentially the same isotherms are obtained at lower pH (=2.5) for the pyridyl systems. The pK_a value of pyridin is about 5.5 in bulk solution but it was already shown that the apparent pK_a value of acids near interfaces can be several units lower/greater, depending on the charge type of the acid (see Clint J. H. in *Surfactant Aggregation*; Blackie: Glasgow and London (published in the USA by Chapman and Hall, New York), 1992. In the case of the pyridyl group it is thus expected that at the pH of the subphase the species is nearly neutral while at a pH of 2.5 the pyridyl units are protonated to some extent. However, this does not result in substantial changes in the phase behavior of the amphiphiles.

ing area was observed, indicating some kind of collapse on longer time scales. For 1, 2-*cis*, and 3pyr⁺ large stabilities of the films were found up to 30 mN/m, while 2-*trans*, 3, and 4 show collapse of the monolayer above 10 mN/m.

Also large hystereses were observed at high pressures in compression/expansion cycles with substantial shifts to smaller areas in subsequent runs. Assuming the formation of molecular aggregates, the hysteresis suggests that these aggregates, once formed, do not dissociate when the layer is expanded.

Closer inspection of Figure 1 reveals that the rigidity of the films becomes less pronounced as the number of hydrocarbon chains increases. This is clearly observed in the decreasing slope of the isotherms from 1 to 3 and is commonly expressed by the compressibility, α , which is defined as follows

$$\alpha = A^{-1}(\delta A/\delta \pi)_T \quad (1)$$

where A is the molecular area, π the surface pressure, and T the subphase temperature. The compressibilities are also included in Table 1. Thus, 1 shows more solid-like behavior, while the LB-films of 2, 3, and 3pyr⁺ become more fluid.

It became evident from the mean molecular areas that these porphyrins are tilted with respect to the water surface by a certain angle. The organization of the porphyrin macrocycles is thus largely determined by the balance between π - π interaction energy, the interaction of the hydrophilic headgroups with the aqueous surface, and the sterical repulsion between the hydrocarbon chains.

The extraction of structural information about monolayers from isotherm data is, however, rather error prone as was recently discussed by Chou et al.¹⁵ They found a substantial increase of the mean molecular area from 90 Å² for a single chained porphyrin to 230 Å² for a four-chained porphyrin. In a model in which it is assumed that aggregated molecules form a linear chain of molecules without any overlap of the porphyrin planes, the explanation would be a change from a near vertical orientation to an almost flat orientation on the water surface. However, by means of linear dichroic absorption measurements, it was found that the number of alkyl chains attached to the porphyrin has no effect on the spectroscopically measured tilt angle. The number of alkyl chains determines the packing density of molecules in the LB films, resulting in an increase of the intermolecular distance and consequently the mean molecular area.

Generally, these findings are in agreement with our results of the systems 1-3 and 3pyr⁺, although the increase of the mean molecular area is less pronounced. Furthermore, the increase of the mean molecular area is accompanied by an increase of the compressibility of the LB film. This can be explained that in the case of one alkyl substituent, porphyrin-porphyrin stacking permits close packing of the rings, while increasing the number of alkyl chains a more loose packing of the rings occur.

In contrast to the other porphyrins, the four chained porphyrin 4 does not follow this trend at all. This behavior is not easily explained, but we believe that the low hydrophilicity of this porphyrin results in a weak interaction of these molecules with the aqueous subphase, so that the organization of this molecule at the air-water interface is mainly determined by intermolecular forces like in discotic liquid crystals. This is further supported by the low stability of the LB films. This is in contrast with the porphyrins 1-3 and 3pyr⁺ which contain polar pyridyl groups so that organization is determined by intermolecular forces and attractive forces of the am-

phiphile with the aqueous surface, which makes comparison between these compounds and 4 rather futile.

Deposition Behavior. Monolayers of compounds 1-3 and 3pyr⁺ were transferred to hydrophilic glass substrates at surface pressures not exceeding 20 mN/m, since we have found that at higher pressures slow collapse of the layers occurs. The transfer properties of the porphyrins are compiled in Table 1.

Porphyrins 2-*cis* and 3 were found to deposit in the Y-mode up to 20 layers with remarkable high transfer ratios between 0.8 and 1.0.

However, we found a Z-type deposition for porphyrin 1, which is quite unusual for amphiphiles with alkyl chains of this length. The LB film of this compound displays a very solid-like character (low α , see Table 1), so that it is not surprising that monolayer deposition is not quantitative in the upward stroke (0.7). Consequently, the alkyl chains possess a certain degree of conformational freedom, which makes the effective length of the hydrocarbon chains much smaller. The polar oxygen of the hexadecyloxyphenyl unit is therefore less buried, which offers the possibility of a head-to-tail interaction, resulting in the so called polar deposition.²⁵

In 2-*cis*, 3, and 3pyr⁺ the transfer ratio in the upward stroke is about 0.9-1. This results in a closer packing of the alkyl chains and a good shielding of the ether oxygens, favoring tail-to-tail interactions (Y-type deposition).

A remarkable deposition behavior was found for 2-*trans* and 4 in which transfer in the upward stroke was followed by a peel-off in the downward stroke, suggesting that we are not dealing with monolayers but with clusters of islands/multilayers. This was further supported by the inhomogeneous coverage of porphyrins on the substrates, which was clearly observed by visual inspection.

Electronic Absorption Spectra in Solution and at the Air-Water Interface. The absorption spectra of dilute solutions (10⁻⁶-10⁻⁵ M) of compounds 1-4 in chloroform consist of a strong Soret absorption band centered at 420 nm together with four additional Q-bands between 500 and 650 nm. The absorption of the methylated compound 3pyr⁺ differs somewhat from the other systems in that the Soret band is broadened and shifted to ca. 425 nm, which can be explained in that 3pyr⁺ forms aggregates in chloroform at these very low concentrations. This is further confirmed after measuring an absorption spectrum in dilute ethanol solution. The Soret band is much more narrow as compared to chloroform and is blue shifted to 422 nm.

The electronic spectra of the monolayers at the air-water interface were recorded as a function of time immediately after spreading the chloroform solution in the Soret-band region. It should be noted that in the spreading solutions, the porphyrins exist as monomers, since the absorption spectra at these concentrations do not change as compared to the dilute solutions. The absorption maxima of the Soret-absorption band in solution and of the monolayers are presented in Table 1. The positions of the Q-bands were difficult to determine at the air-water interface, due to a low signal-noise ratio for low absorption values and are therefore not included in Table 1.

The absorption spectra of 1 and 3 developed as a function of time, as is nicely demonstrated in Figures 2 and 3, respectively.

For 1, the peak intensity around 425 nm decreases in a few minutes, while a broad absorption band at 445 nm

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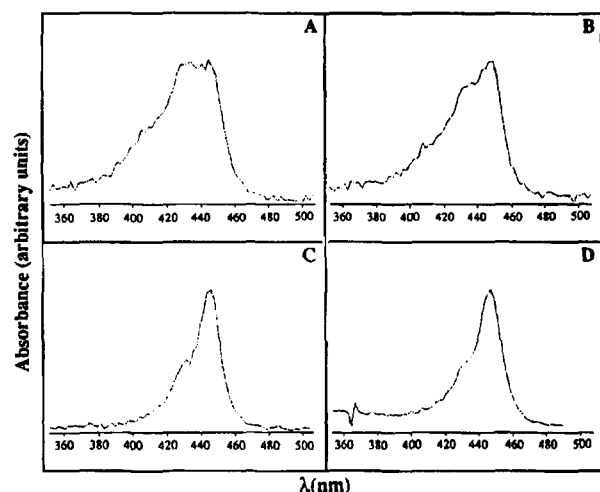


Figure 2. Development of absorption spectra with time and compression for 1. The spectra were measured (A) immediately after spreading the solution, $\pi = 0$ mN/m, (B) after 1 min, $\pi = 0$ mN/m, (C) at equilibrium, $\pi = 0$ mN/m, and (D) at $\pi = 28$ mN/m.

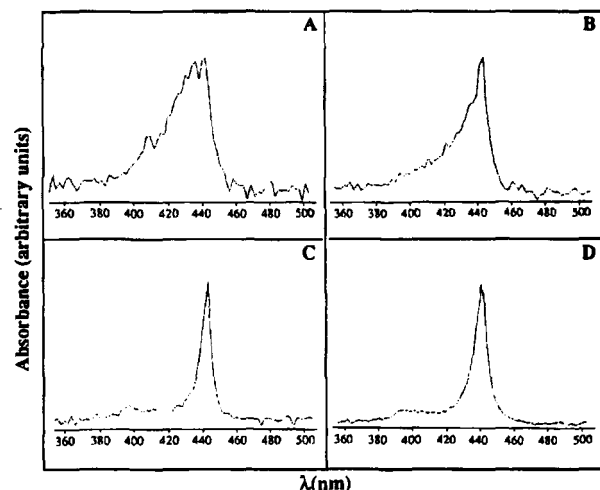


Figure 3. Development of absorption spectra with time and compression for 3. The spectra were measured (A) immediately after spreading the solution, $\pi = 0$ mN/m, (B) after 5 min, $\pi = 0$ mN/m, (C) at equilibrium, $\pi = 0$ mN/m, and (D) at $\pi = 30$ mN/m.

remains. Porphyrin 3 shows a broad absorption directly recorded after spreading and in a few minutes the shoulder around 425 nm decreased and a very narrow strong absorption band at 440 nm and an absorption of low intensity at the blue side appears. We tentatively assign the initial absorption band at 425 nm to the monomeric form. The small red shift (+5 nm) relative to chloroform solution can be explained by a change of an apolar to a polar environment. After about 5 min the monolayers have reached an equilibrium situation.

The spectra were also monitored during the compression of the monolayers and no changes were observed. This supports the view that at submonolayer coverage the molecules form islands of self-oriented domains and are thus not uniformly distributed on the entire water surface. This was further confirmed by the observation that at submonolayer coverage the islands are very dynamic on the water surface and thus sometimes no absorption peak intensity could be detected. After compression, the

domains of stacked porphyrins come into close contact which does not result in any reorganization of the layer.

The spectra of 2, 3pyr⁺, and 4 were constant from the initial measurement, but they were clearly different from those in solution. For these systems, self-organization already occurred on a very fast time scale.

The splitting and broadening of the absorption spectra of aggregated species in LB-films, relative to the monomeric spectra in solution, are mostly interpreted by application of the exciton model developed by Kasha.²⁶ This theory predicts that splitting of absorption bands in weakly coupled electronic systems is caused by interaction of localized transition dipole moments. The coupling splits the absorption band in a high-energy component (E^+) and a low-energy component (E^-).

For an aggregate, the resulting transition energy (E^\pm) is related to its energy of the monomer, E^0 , by

$$E^\pm = E^0 + D \pm V \quad (2)$$

in which D is a dispersion energy term and reflects the change in environment from monomer to multimer, while V is the exciton splitting energy. For a cofacial array of N chromophoric units this term is related to the magnitude of the transition moment (M) and the geometry of the aggregate as given by eq 3

$$V \approx 2 \left\langle \left(\frac{N-1}{N} \right) \frac{M^2}{R^3} (1 - 3 \cos^2 \alpha) \right\rangle \quad (3)$$

In eq 3, R is the center-to-center distance of two chromophores in the aggregate and α is the angle between the center-to-center vector and the transition moment. The observed exciton splitting energy V doubles going from a dimer ($N = 2$) to extended aggregates ($N = \infty$). One of the two resulting transitions is usually forbidden which result in only one absorption band. However, in porphyrins the excited state is 2-fold degenerated, with one transition moment aligned along the x -axis and the other along the y -axis. So, one can explain the splitting patterns in terms of displacements along the x - and y -axes, in which a cofacial arrangement of transition moments results in a red-shifted absorption band while a coplanar arrangement results in a blue shift.

If this model is qualitatively used for our systems, we propose that each molecule in the LB-film experiences the same degree of coupling irrespective of the surface pressure, due to the fact that no changes in the absorption spectra were found after compression of the equilibrated monolayer. Similar results have also been reported for other porphyrin and phthalocyanine LB films.^{15,21}

Furthermore, the observed red-shift of the Soret band for all porphyrin systems indicates that we are dealing with typical J or edge-to-edge type of aggregates, which means that there is an interaction between transition dipoles which are largely displaced along one axis and have an angle α smaller than 54.7° . The broadening of the bands is mainly caused by the inhomogeneity associated with the irregular orientation of neighboring molecules. Thus, as the degree of order in the film increases, the peaks become narrower.

The Soret bands of 1, 2-cis, and 3pyr⁺ display a broadening and a red-shifted component, indicating an inhomogeneous LB film of porphyrin J-aggregates. In these spectra, the other component originating from interaction of transition dipoles aligned along the other

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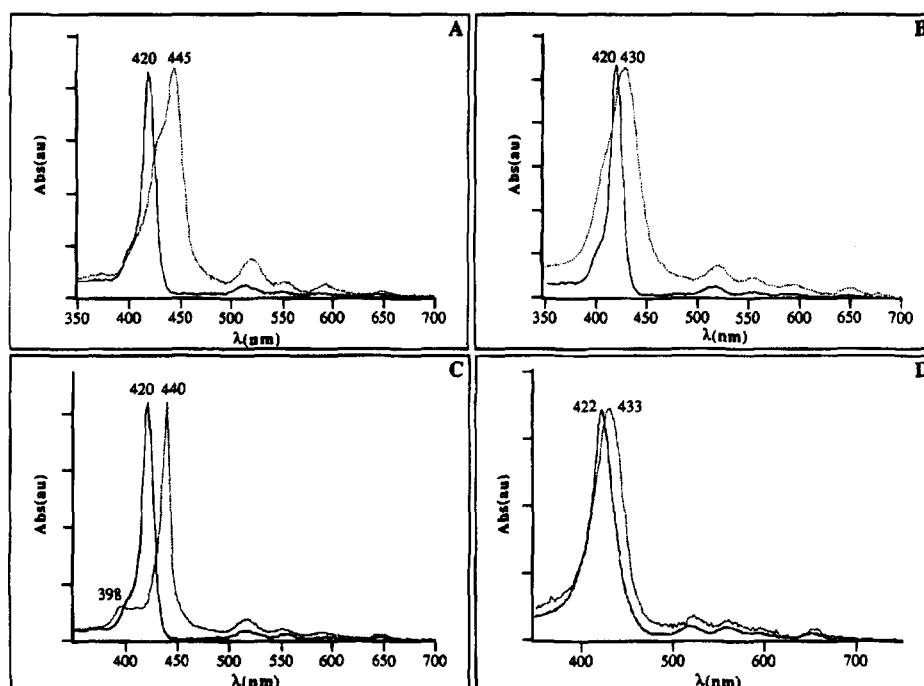


Figure 4. UV-vis absorption spectra in dilute solution (solid line) and of LB multilayers on glass substrates (dotted line) for (A) 1, (B) 2, (C) 3, and (D) 3pyr+. The spectra were recorded in chloroform for 1-3 and in ethanol for 3pyr+. The monolayers were transferred at 20 mN/m for 1, 2, and 3pyr+, while 3 was deposited at 10 mN/m.

axis could not be resolved. If it is a low intensity band, it can be completely obscured by the broad red-shifted component and a second possibility is that the angle α is about 54° , which does not result in a spectral shift.

On the contrary, totally different spectra were recorded for 3 and 4. Both compounds show essentially the same features. The Soret band absorption is now split up into two components, one narrow band of high intensity at 440 nm and one band of low intensity around 400 nm (see Figure 3). An identical splitting pattern was observed by van Esch²⁷ in which aggregates of 4 were incorporated in bilayers and Schick⁹ for a derivative of 4, e.g. tetrakis-(4-(1-octyloxy)phenyl)porphyrin. The spectral data were quantitatively interpreted using the exciton model²⁶ and a highly ordered stack-of-cards arrangement was proposed, in which the members of the aggregates are separated by $\sim 4-5$ Å, slipped by $\sim 47^\circ$ with respect to one another, and tilted (in a domain-fixed axis system) by $\sim 40^\circ$. The similarities in the spectral data indicate that *meso*-tetraarylporphyrins tend to assemble into similar aggregate structures, although this was not earlier observed for tetraarylporphyrins containing pyridyl groups. It is not clear yet what the structural factors are which determine the formation of such highly ordered films. Surprisingly, in spite of the high degree of order in the film itself, the molecules do not form very stable monolayers on the water surface, which can be due to a less favored interaction of the porphyrins with water as compared with the $\pi-\pi$ interaction energy.

In the former section we have stated that an increase of the intermolecular distance probably occurs by increasing the number of hydrocarbon chains at the periphery of the porphyrin ring. Consequently, in the framework of the exciton theory (e.g. eqs 2 and 3), this must then result in a smaller red-shift of the Soret band, since the degree

of exciton coupling depends on the magnitude of the transition dipole moment and the distance between them. In the film of 1, in which the molecules are very closely packed, the observed red-shift, relative to solution, is +24 nm, while for 2 and 3pyr+ red shifts of +10 and +11 nm were found, respectively. The monomeric spectrum in solution is in fact not a good reference, since the change of environment results probably also in a small red-shift (e.g. the dispersion energy D). These observations correlate well with the findings of Chou¹⁵ but cannot be applied for 3, for which the red-shifted component was found to be at 440 nm (+20 nm).

Electronic Absorption and Fluorescence of Transferred LB Films. Figure 4 shows the absorption spectra of the compounds 1-3 in dilute chloroform and 3pyr+ in dilute ethanol solution, for reasons mentioned in the former section, and of the transferred LB multilayers. The films were deposited at 20 mN/m for each of the porphyrins, except porphyrin 3 which was deposited at 10 mN/m, due to the instability of the layer at higher pressures. The spectra of the LB multilayers are essentially the same as those of the monolayers at the air-water interface, indicating that the organization of porphyrins during and after the transfer is maintained.

After closer inspection of Figure 4, the Q-bands of the aggregates show only minor shifts and no splittings relative to solution (see also Table 2).

This is in qualitative agreement with the exciton theory, since the coupling between porphyrins is proportional to the oscillator strength of the transitions (see eq 3). The oscillator strength of the Soret band is much higher than those of the Q-bands, so one can thus calculate via eq 2 that exciton displacement of the Q-bands is at least 20 times smaller than that of the Soret band. Small wavelength shifts must then be governed by the energy dispersion parameter D .

The fluorescence spectra of transferred monolayers show two bands around 660 and 725 nm with an intensity ratio

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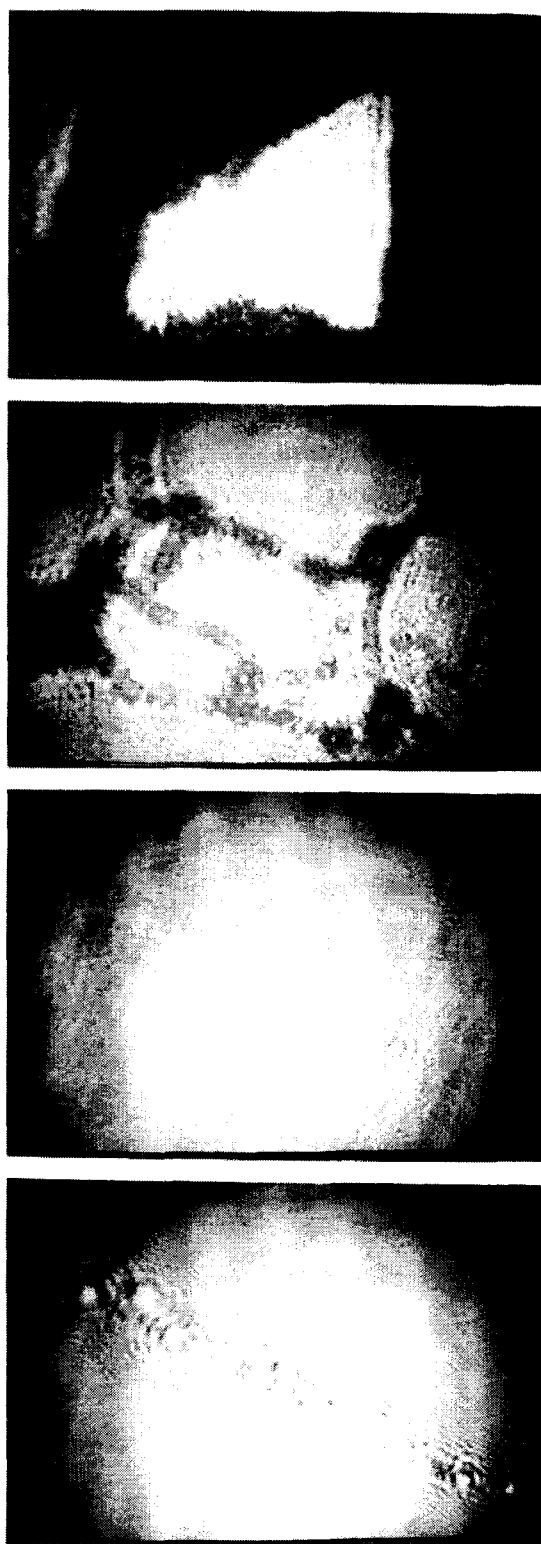


Figure 5. Visualized domain images as observed with Brewster angle microscopy of porphyrin 1 at 20 °C (a, top) after equilibration, $\pi = 0$ mN/m, (b) during compression, $\pi = 0$ mN/m, (c) $\pi = 10\text{--}40$ mN/m, and (d, bottom) collapse of the monolayer. The diameter of the spot is 0.68 mm.

of about 2.25 and no substantial shifts of the emission wavelengths were observed relative to solution (Table 2),

although in some cases the bands are somewhat broadened indicating that we are dealing with aggregates.

In some of the systems studied, 2-cis, 3, and 3pyr⁺, the monolayers are deposited in the Y-type mode, so that there must be a head-to-head and tail-to-tail interaction in these molecules. Surprisingly, this interaction does not influence the spectral characteristics of the multilayers as compared to the monolayers, as was indicated by the similarity of the absorption spectra. It is therefore concluded that only lateral interactions of the porphyrin macrocycles in the multilayer determine the spectral features of these aggregates.

Brewster Angle Microscopy. The in situ UV-vis absorption measurements at the air-water interface have demonstrated that the porphyrin amphiphiles form self-organized structures immediately after spreading of the solution. In order to provide further evidence for this behavior, we have performed some preliminary and qualitative Brewster angle microscopy (BAM) experiments. This technique allows the visualization of monolayer domains and reveals information about monolayer morphology.

This can also be detected by fluorescence microscopy but BAM has the advantage that it does not need probe molecules, which makes it a powerful tool for monolayer research. The technique is relatively new and developed by Möbius et al.²³ and Meunier.²⁸ In Figure 5 some representative examples are shown for porphyrin 1, while essentially the same results were obtained for the other porphyrin systems.

In Figure 5a, a picture is taken after an equilibration period of at least 15 min at a surface pressure of 0 mN/m. It is clearly demonstrated that at submonolayer coverage the molecules are not uniformly distributed but clustered in domains of different sizes and shapes. During the compression, the domains come together (Figure 5b) and the boundaries of the domains become obscured until, after increase of the surface pressure, a more or less homogeneous image without structure is observed (Figure 5c). The collapse of the monolayer is nicely observed by the appearance of intense lines in the image (Figure 5d), indicating the rigidity of the film in its solid phase.

The BAM experiments support our view that the porphyrins spontaneously organize into domains of different sizes and shapes, which is dependent on the system studied.

Concluding Remarks

Summarizing, we have presented a systematic study of LB films of meso-substituted free base porphyrins in which it was shown that in most cases stable monolayers on the air-water interface could be formed without the use of matrix molecules.

The isotherm data show that the porphyrins studied do have a tilted orientation on the water surface, as was indicated by the small molecular areas.

The UV-vis spectra and BAM-pictures at the air-water interface reveal that the intermolecular interaction between porphyrin rings is strong enough that sufficient preaggregation occurs already at submonolayer coverage. Upon compression, the self-organized domains of stacked porphyrins are driven together and come into close contact, without reorganization of the layer structure.

The monolayers are readily transferable to solid substrates with high transfer ratios, although the transfer ratio decreases as the film becomes more solid (e.g. 1). During transfer, the organization of the porphyrins is maintained, which was confirmed by the identical ab-

Table 2. Peak Maxima (in nm) in Q-Band Region of Transferred Porphyrin Monolayers on Glass (Absorption) and Quartz (Emission) Substrates and in Solution

porphyrin	absorption spectrum		fluorescence spectrum ^a	
	solution ^b	on glass	solution ^b	on quartz
1	514, 550, 589, 645	520, 552, 593, 649	661, 724	not determined
2-cis	517, 553, 591, 647	520, 555, 595, 650	662, 726	662, 726
3	518, 554, 592, 649	518, 552, 592, 648	664, 729	660, 722
3pyr+	520, 563, 592, 654	524, 562, 594, 654	673, 732	672, 732

^a Excitation is at wavelengths corresponding to the Soret-band maxima in the UV-vis absorption spectra. ^b The solvent used for 1, 2-cis, and 3 was chloroform, while ethanol was used for 3pyr+.

sorption spectra of the monolayers at the air-water interface and on the solid substrates.

It was also demonstrated that specific porphyrins (e.g. 3 and 4) self-assembled into a highly ordered arrangement. This exceptional behavior of these two porphyrins as compared to the other systems probably originates from the lower tendency of porphyrins 3 and 4 to interact with the water surface. Therefore, the organization of these porphyrins at the air-water interface mainly occurs by intermolecular forces, like in discotic liquid crystals.

In conclusion, the orientation of amphiphiles with extended π -systems on the water surface is strongly

determined by the balance of intermolecular π -interaction forces and attractive forces between the π -systems and the aqueous surface.

In order to quantitate the orientation angles of the various porphyrins, further research is now in progress by performing polarized absorption spectroscopy and X-ray diffraction measurements.

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