

## Langmuir–Blodgett Films of Amphiphilic Push–Pull Porphyrins

Homer Chou, Chin-Ti Chen, Kurt F. Stork, Paul W. Bohn,\* and Kenneth S. Suslick\*

Department of Chemistry and The Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

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A series of nitrophenyl–amidophenyl-substituted porphyrins with  $n$ -C<sub>17</sub>H<sub>35</sub> tails have been synthesized and fully characterized. Good Langmuir–Blodgett films of these materials can be prepared on water and transferred successfully to glass slides. Mean molecular areas for the series were measured and found to increase from 80 to 230 Å<sup>2</sup> as the number of aliphatic chains increased from one to four. As determined by linear dichroic measurements, this change in area does *not* correspond to a change in the orientation of the porphyrin with respect to the surface. In the absence of the steric constraints of multiple aliphatic chains, porphyrin–porphyrin stacking permits close packing of the rings. As the number of aliphatic chains on the porphyrin periphery increases, however, the porphyrin planes must pack more loosely. Thus, the porphyrin macrocycle orientation is determined by interactions between porphyrin rings and between porphyrins and the aqueous (or polar glass) surface. In contrast, the differences in the observed mean molecular area are determined independently by packing constraints imposed by the pendant hydrocarbon chains.

The potential applications of nonlinear optical organic materials for processing electrooptical signals<sup>1</sup> have spurred the investigation of Langmuir–Blodgett (LB) techniques in order to prepare noncentrosymmetric layers of molecules exhibiting large second-order nonlinear hyperpolarizabilities.<sup>2</sup> We have recently synthesized a series of donor–acceptor-substituted, “push–pull” porphyrins<sup>3</sup> which exhibit substantial second-order molecular hyperpolarizabilities,  $\beta$ . In order to determine how these molecular hyperpolarizabilities will translate into  $\chi^{(2)}$  for an ensemble of these molecules, we have synthesized a series of “push–pull” porphyrins with pendant alkyl tails and characterized their formation of LB films. Here we describe the surprising structural properties of LB films of amphiphilic derivatives of these push–pull porphyrins.

A series of nitrophenyl–amidophenyl-substituted porphyrins with  $n$ -C<sub>17</sub>H<sub>35</sub> tails have been synthesized and fully characterized.<sup>4</sup> As shown in Figure 1, good LB films of these materials can be prepared on water.<sup>5</sup> Table 1 gives the mean molecular areas for the series. Based on single-crystal structures or CPK models of simple tetraarylporphyrins, the expected mean molecular areas of LB films would be  $\approx 90$  Å<sup>2</sup> if the porphyrin rings lie vertical to the aqueous surface and  $\approx 225$  Å<sup>2</sup> if the porphyrin ring lie parallel.<sup>6,7</sup> As the number of aliphatic chains increases from one (compound 1 in Figure 1) to four (4), the mean molecular areas increase smoothly from the expected value for a vertical orientation up to that for a horizontal orientation. This would seem to imply that the orientation of the porphyrin rings changes from nearly vertical for a single aliphatic chain to nearly horizontal for four chains. This variable orientation model is shown schematically in Figure 2A. However, linear dichroic determinations of the porphyrin orientation demonstrate that this simple hypothesis is *incorrect*.

To test the variable orientation model, we used UV–visible transmission linear dichroism<sup>8</sup> to characterize directly the porphyrin alignment, both on trough and after transfer to a glass substrate. The intense  $x$ – $y$  degenerate transition responsible for the Soret absorbance of porphyrins ( $\epsilon \approx 10^5$  near 420 nm) provides an excellent spectroscopic probe from which the average orientation of the macrocycles can be deduced.<sup>9</sup> In order to reflect the orientation of the porphyrins accurately, the on-trough linear dichroism measurements were taken at pressures comparable to

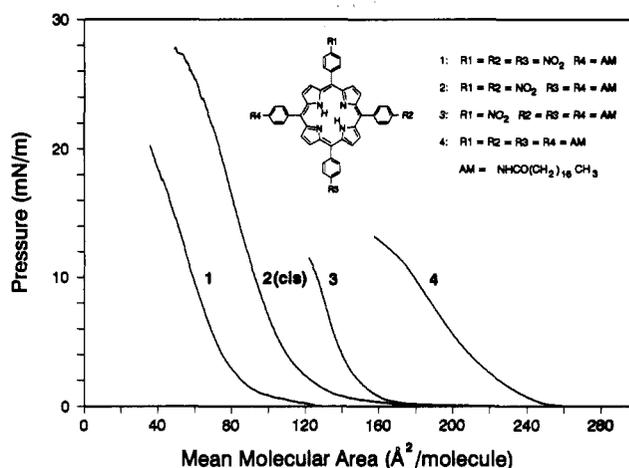


Figure 1. Langmuir–Blodgett isotherms of amphiphilic derivatives of push–pull porphyrins.

TABLE 1: Mean Molecular Areas and Orientation Angles of Amphiphilic Push–Pull Porphyrins<sup>a</sup>

porphyrin	Mma (Å <sup>2</sup> )	$\theta_{\text{slide}}$ (deg)	$\theta_{\text{trough}}$ (deg)
1	80	32	42
2	120	31	42
3	150	33	47
4	230	36	48

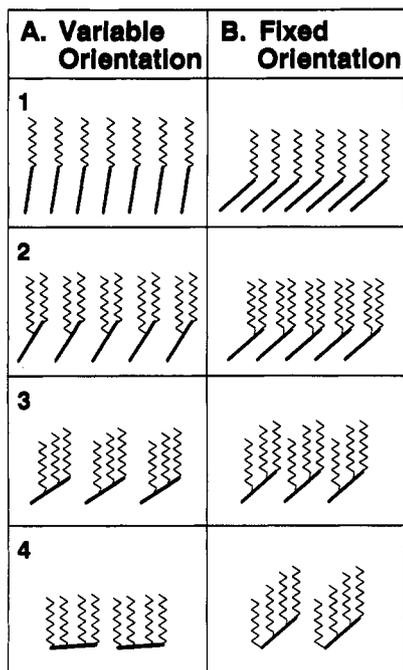
<sup>a</sup> Mean molecular areas (Mma) were determined by extrapolation of the linear region of the isotherms to zero pressure. The Mma of each porphyrin was an average of at least three independent determinations.  $\theta$  is the angle between the mean porphyrin plane and substrate surface. Estimated errors are  $\pm 10$  Å<sup>2</sup> in Mma and  $\pm 4^\circ$  for  $\theta$ .

transfer pressures. The average orientations of the porphyrin plane on the LB trough and on a glass substrate were measured and are compiled in Table 1.<sup>10</sup> In addition, all of these porphyrins show a uniaxial distribution. While similar measurements on several porphyrins have been reported previously,<sup>11</sup> to our knowledge this is the first instance in which the effect of pendant alkyl chains on molecular packing has been systematically studied.

Surprisingly, the number of aliphatic chains attached to the porphyrin has *no significant effect* on the spectroscopically measured tilt angle of the porphyrin macrocycle, either on trough or after transfer to a glass substrate. Within experimental error, the tilt angle of the porphyrin planes is the same on trough for

\* Authors to whom correspondence should be addressed.

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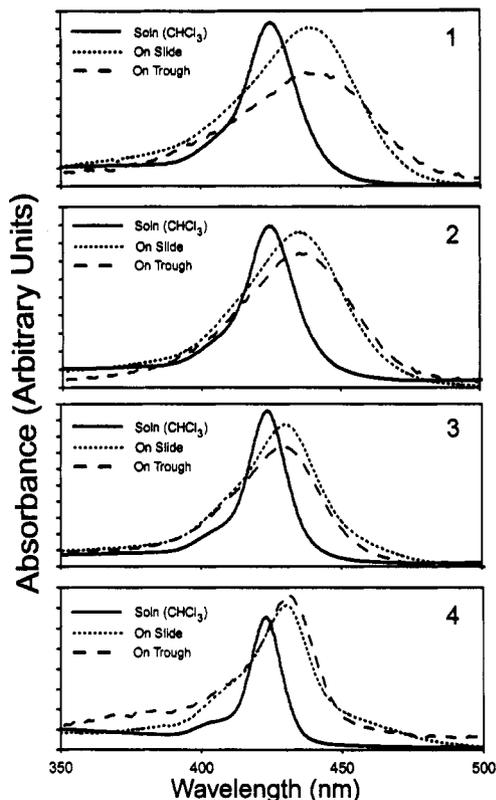
**Figure 2.** Schematic models of Langmuir-Blodgett films. (A) Variable orientation model in which no overlap of porphyrin rings occurs. (B) Fixed orientation model in which porphyrin-porphyrin overlap occurs in the absence of steric constraints from multiple aliphatic chains. The fixed orientation model reconciles the variation of mean molecular areas with the constancy of measured surface tilt angle.

all four porphyrins ( $45 \pm 4^\circ$ ) and is also the same on slide for all four porphyrins ( $33 \pm 4^\circ$ ). This is in contrast to the mean molecular areas, which were greatly affected by the number of aliphatic chains.

Although the on-trough linear dichroism measurements were taken at pressures comparable to transfer pressures, there is a small difference between in the tilt angle on trough compared to on slide ( $45^\circ$  on trough vs  $33^\circ$  on slide). This appears to be the result of a slight relaxation of the porphyrin molecules after transfer to a glass substrate. It is not surprising that slight conformational relaxation should occur in the absence of the trough compression ( $\pi \approx 10\text{--}20$  mN/m).

The apparent discrepancy between the mean molecular area and the linear dichroism measurements can be resolved by a fixed-orientation model in which overlap occurs between adjacent porphyrin rings, as shown schematically in Figure 2B. There is a substantial attractive  $\pi\text{--}\pi$  interaction between porphyrin rings.<sup>12</sup> This attraction is sufficiently strong that significant preaggregation can occur prior to compression of these films.<sup>9e</sup> In the absence of steric constraints from multiple aliphatic chains, porphyrin-porphyrin stacking permits close packing of the rings (Figure 2B, 1 and 2). As the number of aliphatic chains on the porphyrin periphery increases, however, the porphyrin planes must pack more loosely (Figure 2B, 3 and 4). Thus, the porphyrin macrocycle orientation is determined by interactions between porphyrin rings and between porphyrins and the aqueous (or polar glass) surface, while the differences in observed mean molecular area are determined independently by packing constraints imposed by the pendant hydrocarbon chains.

The fixed orientation model can be further supported by two pieces of evidence. First, the lower collapse pressures of 3 and 4 compared to 1 and 2 in the isotherms are consistent with the formation of a more loosely packed film in the former cases. Second, the red shift in the peak maximum of the Soret band on slide and on trough compared with the solution spectra in 1 and 2 is significantly greater than in 3 and 4 (13 and 10 nm vs 7 and 7 nm, respectively) as seen in Figure 3. The shift observed in the



**Figure 3.** UV-visible spectra of amphiphilic derivatives of push-pull porphyrins in different environments: in solution, on slide, and on trough.

3 and 4 case of 7 nm may be due to "solvent effects". (Water/quartz is much more polar than chloroform.) The additional shift of 3–6 nm observed for the 1 and 2 case can be attributed to excitonic interactions. Such shifts in the Soret band have been previously observed in the studies of LB porphyrin assemblies and were attributed to excitonic interactions.<sup>9e</sup> Using a simple point dipole model, such as that proposed by McRae and Kasha,<sup>13</sup> the relative distances between the individual porphyrins in each of the four cases can be qualitatively determined. The frequency shift of the aggregate's absorption peak relative to the monomer's absorbance peak is inversely proportional to the cube of the distance between the individual molecules. The spectra in Figure 3 imply that the distance between the porphyrins follows the predicted trend:  $4 \approx 3 > 2 > 1$ .

In summary, this work presents the first study of LB films (both on trough and transferred to a substrate) of tetraarylporphyrins with a varying number of alkyl chains. The results show that the orientation of the porphyrin macrocycle in these systems with respect to the surface is *independent* of the number of aliphatic chains surrounding the macrocycle. The number of aliphatic chains, nonetheless, does determine the packing density between the porphyrin macrocycles. In addition, aggregation is more significant between macrocycles with fewer  $n\text{-C}_{17}\text{H}_{35}$  chains as determined by the red shift of the Soret band (both in the on-trough and the on-slide measurements). Finally, these results emphasize a cautionary note about inferring structural information about monolayers from isotherm data alone. In particular, extreme prudence should be used in interpreting isotherms of amphiphiles containing extended  $\pi$ -systems, since such systems are especially prone to strong intermolecular interactions.

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**Supplementary Material Available:** Spectroscopic and analytical data for compounds 1–4 (3 pages). Ordering information is given on any current masthead page.

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- (4) The amphiphilic derivatives of our “push-pull” porphyrins were synthesized by dissolving each of the parent amino-nitro-substituted phenylporphyrins in a minimal amount of pyridine, slowly adding an excess of stearoyl chloride in  $\text{CH}_2\text{Cl}_2$ , and then stirring for 4 h at room temperature. The reaction mixture was subsequently neutralized with 10%  $\text{NH}_4\text{OH}$  and stirred for another hour. The organic layer was separated and evaporated to dryness and the residue purified by column chromatography; yields ranged from 6 to 40%. As provided in the supplemental material, these porphyrins have been fully characterized by elemental analysis, TLC, FAB-MS, UV-visible, FTIR, and  $^1\text{H}$  NMR spectroscopies.
- (5) Porphyrin films were deposited onto a KSV-2200 or a KSV-5000 Langmuir-Blodgett trough system. The subphase was air-equilibrated, Millipore purified water ( $\Omega = 18.2$  ohms). The surface was compressed at a rate of 3 mm/min, and porphyrin monolayer films were transferred in a z-type fashion onto a glass substrate at surface pressures between 10 and 20 mN/m. The glass was pretreated by dipping three times in concentrated sulfuric acid at 150 °C, followed by 4:1 (v/v)  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ , and dried under  $\text{N}_2$ . Only transferred films with transfer ratios of  $1.0 \pm 0.1$  were used.
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- (10) (a) Linear dichroism measurements were made on slide by taking the absorbance of the transferred porphyrin monolayers with a Varian Cary 3 UV-visible spectrophotometer (fitted with a rotatable slide holder) at 0° and 45° with respect to the incident beam and the plane of the slide. The on-slide measurements were taken within 1 h after transfer. On-trough measurements used an Oriel Xe arc source coupled into a bifurcated fiber optic (Fiberguide Industries). The bifurcated fiber optic was positioned so that the incident beam impinged at 0° and 45° with respect to the normal to the trough surface. Since the porphyrin monolayer was so strongly absorbing, a double pass through the monolayer was sufficient. The polarization was controlled by placing either s- or p-polarized sheet polarizers between the incident beam and the sample. (b) Preliminary  $\chi^{(2)}$  measurements have been made of these films, and significant nonzero responses have been seen in 1, 2, and 3.
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