

Reorientation of the Alpha-Helical Synthetic Peptide ZnPPXBBC16 in a Langmuir Monolayer

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Introduction: Structure of the Langmuir monolayers of porphyrin containing peptides is very important for fundamental biophysical studies and biotechnology applications. To study the orientation of a peptide in the Langmuir monolayer we used X-ray reflectometry (XR), which can determine the electron density profile of a monolayer and polarized epifluorescence (PEF), which provides information about orientational distribution of the porphyrin. The synthetic peptide has two α -helical 31-mer units with a palmitoyl (C16) chain bonded to the N-terminal cysteine to increase the peptide's amphiphilicity. The units dimerize via a disulfide bridge between two cysteines (α -S-S- α) to form two porphyrin-binding sites.

Results: Figure 1 shows x-ray reflectivity data taken at five surface pressure values, namely 5 mN/m, 22 and 27 mN/m, 30 and 34 mN/m. Experimental data are shown by markers, calculated results from Box Refinement are shown by the continuous curves. The electron density profiles obtained via BR show that at lower pressures the monolayer thickness systematically increases from 10 Å for $\pi=5$ mN/m to 15 Å for $\pi=27$ mN/m. At higher pressure the thickness increases drastically up to 50 Å. Orientational distribution curves of the porphyrin obtained via PEF measurements are shown in Figure 2. At the lowest pressure the planes of the porphyrins are oriented on average perpendicular to the monolayer plane with a high degree of orientational ordering, i.e., a relatively narrow distribution width. For $\pi=22$ mN/m the mean tilt angle drops to the value of 65° and the distribution becomes very broad. With further increasing pressure, the tilt angle shifts back towards 90°, and the distribution becomes narrower

Conclusions: XR and PEF data provide strong evidence of the reorientation of the ZnPPIX-BBC16 in the Langmuir monolayer. At lower surface pressure the peptide's di-helices lie in the plane of the surface with a high degree of orientational order. At high pressure they orient perpendicular to the interface but are less well ordered. In the intermediate region the molecules rotate around the di-helical long axis with almost complete loss of orientational order of the porphyrins.

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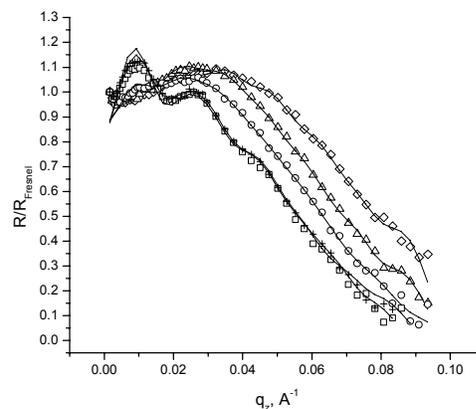


Figure 1. Modules of the x-ray reflectivity divided by the Fresnel reflectivity of pure water vs. surface pressure of the Langmuir monolayer of ZnPPXBBC16. Diamonds - $\pi=5$ mN/m, triangles - $\pi=22$ mN/m, circles - $\pi=27$ mN/m, crosses - $\pi=30$ mN/m and squares - $\pi=34$ mN/m. Experimental data are shown by markers, lines – calculation for the electron density profiles determined via box refinement procedure.

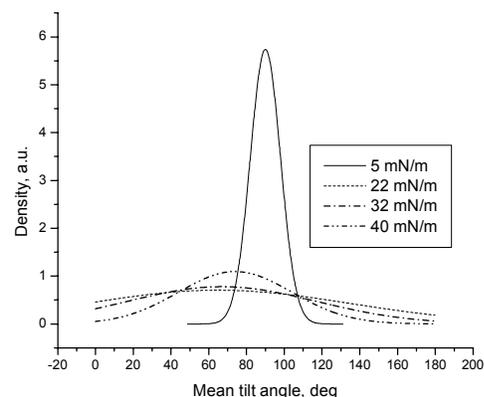


Figure 2. Porphyrin orientation distribution for Langmuir monolayers of ZnPPIX-BBC16 vs. surface pressure as determined from the polarized epifluorescence measurements.