Structural Studies of Model Metalloprotein Maquettes Vectorially-Oriented at the Air/Water Interface *	X22B

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De novo synthetic models or "maquettes" of prototypical electron transport membrane proteins based on a 4-helix bundle motif with selected sites for liganding heme groups have been designed and synthesized. Correlated structural and electrochemical studies of such maquettes depend on our ability to orient them vectorially at an interface, preferably with the axis of the bundle more perpendicular than parallel to the interface. While sedimentation and NMR methods suggest that the dihelices spontaneously assemble to form a native four-helix bundle in bulk aqueous solution, X-ray reflectivity studies have shown that the bundle is unstable to an air-water interface with both α-helices of the dihelix lying in the plane of the interface irrespective of the surface pressure in a Langmuir monolayer. Subsequently, a palmitic acid hydrocarbon chain (C_{16}) was covalently linked to the amino-terminus of each helix of the dihelix. The resulting lipopeptide maquette, denoted BBC16, forms more stable monolayers due to its enhanced amphiphilicity. X-ray reflectivity studies of BBC16 alone and of binary mixtures of BBC16 and lipids (palmitic acid or DLPE) show that the α-helices are oriented approximately normal to the air/water interface at higher surface pressures.

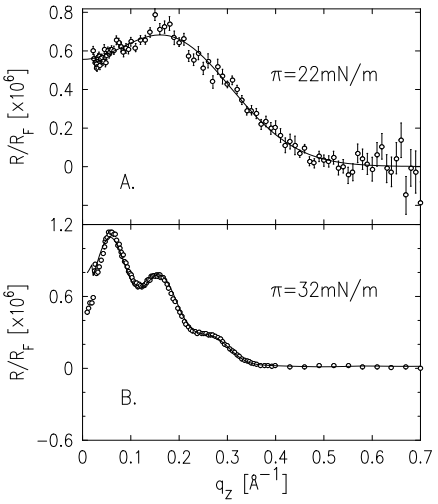

Figure 1. Normalized reflectivities and fits. A. Pure BBC16. B. Palmitic acid and BBC16 (4 PA: 1 α-helix).

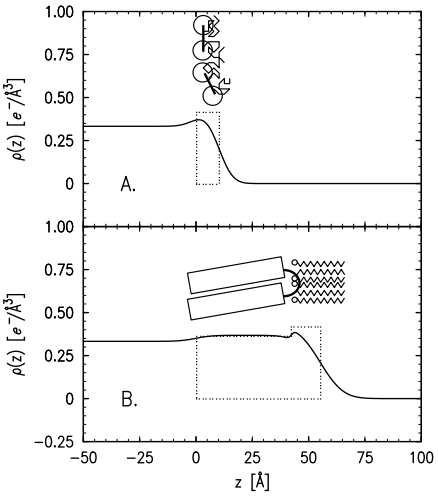

Figure 2. Density profile structures for Fig. 1. As π increases, the α-helix orientation changes from parallel (A) to normal (B) to the air/water interface.

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