

## **Structural Studies of Model Metalloprotein Maquettes Vectorially Oriented at a Soft Interface**

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*De novo* synthetic models or “maquettes” of prototypical electron transport membrane proteins, based on a four-helix bundle motif with selected positions for liganding one or more prosthetic groups (e.g., heme groups), have been designed and synthesized by Prof. P. L. Dutton’s research group at the University of Pennsylvania. Correlated structural and electrochemical studies of such maquettes depend on our ability to orient them vectorially at an interface with the axis of the bundle perpendicular 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  $\alpha$ -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 (C16) was covalently linked to the amino-terminus of each helix of the dihelix to make the maquette a better amphiphile. X-ray reflectivity studies of this palmitoyl-derivative of the maquette itself and of its binary mixtures with palmitic acid and DMPE have shown that the  $\alpha$ -helices of the dihelix are oriented perpendicular to the air-water interface at higher surface pressures within the Langmuir monolayer. X-ray interferometry studies have shown that these Langmuir monolayers can be transferred via the Langmuir-Blodgett technique to an alkylated inorganic substrate retaining their orientation perpendicular to the substrate plane. Such vectorially oriented single monolayers of these maquettes are ideally suited for resonance x-ray reflectivity and interferometry studies of the metal atom locations of their prosthetic groups and for grazing-incidence x-ray diffraction studies of their secondary/tertiary/quaternary structures.