quinones and 3 iron-sulfur clusters. The crystal structure at 3.1 Å resolution reported her add several new features that were not detected in the previous structures. The location of an additional ten β-carotenes as well as five chlorophylls and several loop regions are now modeled. This represents the most complete plant Photosystem I structure obtained thus far, revealing the locations of interactions among 18 protein subunits and 211 non-covalently bound photochemical cofactors. We also detected 12 additional carotenoids especially in the LHC complex as well as structural lipids. The latter suggest evolutionary chemical cofactors. We also detected 12 additional carotenoids especially in the LHC complex as well as structural lipids. The latter suggest evolutionary
differences among the thylakoid membranes of the various cyanobacterial species. In addition we solved the virus-like structure of Psal and Psam minus PSI mutant at 2.8 Å resolution. The novel structure of PSI from mesophilic cyanobacteria is different in several aspects in comparison with the previously published structure of PSI from Thermosynechochoccus elongatus. The common properties of mesophilic cyanobacterial and plant PSI will be discussed.

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Method Dihamed Angles of Ubiquinone Contribute More than 160 mV to the Redox Potential Difference between the Primary (Qα) and Secondary (Qβ) Quinones of the Photosynthetic Reaction Center
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Ubiquinone is an almost universal, membrane-associated redox mediator. Its redox properties are substantially determined by its environment in the binding sites of proteins and by the dihedral angles of the methoxy groups relative to the ring plane. In this work, we use the photosynthetic reaction center as a model system for understanding the role of methoxy conformations in determining the redox potential of the ubiquinone/semiquinone couple. Despite the abundance of X-ray crystal structures for the reaction center, the quinone site resolution has thus far been too low to provide a reliable measure of the methoxy dihedral angles of the primary and secondary quinones, Qα and Qβ. We have performed HYSCORE on isolated reaction centers with ubiquinones 13C-labeled at the headgroup methyl and methoxy groups, and the isotropic and anisotropic hyperfine coupling constants were estimated. Comparison of our data to quantum mechanically derived models and available crystal structures gives a best fit for the 2-methoxy dihedral angle of Qα as 30° more out of plane than in Qβ. This assignment corresponds to a redox potential gap (ΔEm) between Q3 and Q0 of ~180 mV. This is consistent with the failure of a ubiquinone analog lacking the 2-methoxy group to function as Qβ in a mutant reaction center with ΔEm ~160-195 mV. We conclude that the 2-methoxy group of ubiquinone provides an essential mechanism by which the reaction center tunes the redox potential difference necessary for electron transfer. The influence of the methoxy groups on the secondary electron transfer is under investigation through similar EPR studies of the biradical, QαQβ, generated in mutant reaction centers at high pH in wild type reaction centers.

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Characterization of 2- and 3-Methoxy in Ubiquinone Binding and Redox Tuning within the Photosynthetic Reaction Center of Rhodobacter Sphaeroides
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Ubiquinone is a universal, membrane-associated redox mediator. The redox properties of ubiquinone in vivo are closely controlled both by its electrostatic environment within the binding sites of proteins and by steric interactions determining its conformation. Recent experimental work suggests that differences in the angle of the two methoxy side chains with respect to the quinone ring plane dictate the redox potential difference between the two quinone binding sites, however the specific quinone-protein interactions that alter the redox potential could not be identified.

In order to ascertain which specific interactions between the quinones and their environment tune the redox potential, molecular dynamics simulations of ubiquinone bound to the QA and QB sites of the photosynthetic reaction center (RC) of Rhodobacter Sphaeroides were compared with complementary studies done on ubiquinone analogs lacking either the 2- or 3-methoxy group. Since prior ubiquinone parameters were biased towards non-native methoxy angles, systematically parameterized ubiquinone and its analogues to accurately describe the structure and dynamics of the methoxy groups.

The removal any methoxy group showed little impact on the QA binding. However, both the binding conformation and the methoxy dihedral angle distribution in the QB site were significantly altered upon removal of the 2-methoxy group. We observe that the 2-methoxy group in the QB site is oriented approximately normal to the ring plane. This orientation is favored by a weak hydrogen bond between the 2-methoxy oxygen and the amine of GLY225. A mutation out diving methoxy (as imposed by the protein environment) would correspond to a higher electron affinity of QB over QA. We propose this hydrogen bond as the mechanism whereby the redox potential is tuned to promote inter-quinone electron transfer in the RC.

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Tuning Function of the Light-Driven Proteorhodopsin Proton Pump by Formation of Oligomeric and Surfactant-Based Synthetic Complexes
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The Proteorhodopsin (PR) membrane protein equips marine bacteria worldwide with the capability of converting light energy into chemical energy. The proton pump absorbs light via an intrinsic retinal molecule, followed by subsequent conformational changes that store energy in the form of a proton gradient across the bacterial cell membrane. Because PR exists in the complex membrane environment, a multitude of factors could contribute to its light absorption and energy-transducing properties, including protein-protein, protein-lipid, and electrostatic interactions. Here we demonstrate by steady-state and time-resolved optical absorption spectroscopy that there are profound functional effects (e.g. altered activity and photocycle kinetics) modulated by the assembly of PR with other PR molecules to form oligomeric complexes, and by reconstitution in membrane-mimetic surfactant environments with varying chemical and physical characteristics.

We study the molecular-level properties accompanying these functional consequences of environment with magnetic resonance techniques, specifically amino acid side-chain dynamics probed by Electron Paramagnetic Resonance (EPR) and local hydration dynamics by Overhauser Dynamic Nuclear Polarization (ODNP). Such information lends insight into the mechanisms tuning PR function and can be applied towards the design of function-enhancing synthetic environments. For example, surface water diffusion is faster in a model lipid bilayer than in surfactant micelles, concurrent with faster conformational motion, and possibly efficiency (Hussain, et.al, Angew. Chem. 52, 2013). We further have developed a synthetic platform for potential device applications by the insertion of active PR into surfactant-directed mesostructured silica films, in both its hexameric and monomeric forms, and using different surfactants. This provides a unique opportunity to apply results from the biophysical characterization of PR to the design of an optimized solar energy-harvesting biomaterial, tuning molecular interactions to match the desired functional properties.

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The Mitochondrial Tim23 Protein Transport Complex Undergoes Conformational Dynamics Coupled to the Energized State of the Inner Membrane
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The Tim23 Complex of the mitochondrial inner membrane (IM) is a multi-component assembly that mediates the translocation of matrix-targeted precursor proteins as well as the integration of membrane proteins. This complex is energetically coupled to both an ATPase motor and the electrochemical potential across the IM. The central subunit of this complex, Tim23, forms a voltage-gated channel and contains a large soluble domain in the intermembrane space that functions as a substrate receptor. To analyze the structural dynamics that are attendant with changes in the energized state of the membrane, we employed a high-resolution fluorescence mapping approach in which small extrinsic probes were cotranslationally incorporated into the Tim23 transport channels of Tim23 complex that were reconstituted in active mitochondria by steady-state and time-resolved measurements under different physiologically relevant states. Analysis of the channel-facing transmembrane segment (TMS2) of Tim23 revealed that changes in the