

Visualizing Structural Dynamics in Photosynthetic Reaction Centers in the Ultrafast Timescale

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Photosynthetic reaction centers catalyze light-driven electron transfer reactions at remarkably high quantum yield. Attaining such high yields require fine tuning of the cofactor energetics to regulate charge separated states and promote a series of forward electron transfer while preventing energy-wasteful back reactions. Generations of spectroscopic studies using various techniques spanning multiple timescales have expanded our understanding of the initial charge separation processes, as well as the subsequent steps of electron transfer in terms of reaction kinetics, directionality, and redox properties of cofactors. However, many aspects of the formation of the charge separated state still remain unresolved, and one such element revolves around how the protein environment reacts to the charge transfer and regulates interactions with the cofactors. These ultrafast structural motions have been predicted by simulation studies, but only a limited number of experimental data is available.

To determine the subtle structural changes in the environment of the electron transfer cofactors in photosynthetic reaction centers, we have conducted time-resolved optical-pump X-ray diffraction studies on purple bacterial reaction center (pbRC) and photosystem I (PSI) using X-ray free electron lasers (XFELs). The high brilliance and the ultrafast pulses of XFEL enable collection of radiation damage free data of photosynthetic reaction centers at room temperature. By integrating a fs-laser system with the Drop-on-Tape sample delivery system for serial femtosecond crystallography, we collected diffraction data on wild-type and selected mutants of pbRC, and PSI at multiple time points following the excitation. Mutants were chosen that predominantly direct electron transfer along one branch of the electron transport chain. Structural differences were observed between the wild-type and mutants, and also on light illumination. Insights from the preliminary results as well as the specific design of the experiments are discussed.