

TOWARDS AN ARTIFICIAL PHOTOSYSTEM II: THE SECOND GENERATION OF THE BACTERIOFERRITIN "REACTION CENTRE"

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Introduction. Photosystem II (PSII) of oxygenic photosynthesis has the unique ability to photochemically oxidize water through a Manganese cluster and tyrosine. An engineered bacterioferritin photochemical "reaction centre" (BFR-RC) using a zinc chlorin pigment (ZnCe₆) in place of its native heme has been shown to photo-oxidize bound manganese cluster from Mnⁿ-Mnⁿ to Mnⁿ⁺¹-Mnⁿ⁺¹, thus mimicking a reaction on the electron donor side of PSII (Conlan et al., 2009). However, the full oxidation of water is a four-electron reaction. We studied the influence of axial ligands and carboxyl groups on the oxidation potential of ZnCe₆ using DFT theory, and finally calculated the shift of the redox potential of ZnCe₆ in the BFR-RC protein using the multi-conformational molecular mechanics Poisson-Boltzmann approach. According to our calculations, the redox potential for the first oxidation of ZnCe₆ in the BFR-RC protein is only 0.57 V, too low to oxidize tyrosine and further oxidize the manganese cluster (Mahboob, Vassiliev, Poddutoori, van der Est, & Bruce, 2013). Thus, we aimed to develop a pigment-protein system capable of having a high enough oxidation potential to oxidize a nearby tyrosine. We demonstrate evidence of radical pair formation using Fluorescence Decay Kinetics and Transient EPR.

Materials and Methods. We used Computational Methods and Differential Pulse Voltammetry (DPV) to determine the oxidation potentials of the pigments. Additionally, Transient Electron Paramagnetic Resonance (TR-EPR) and Fluorescence Decay Kinetics were used to examine the formed radical pair. Additionally, Continuous Wave EPR (CW-EPR) was used to characterize the tyrosyl and porphyrin radical.

Results. There is evidence of radical pair through TR-EPR. CW-EPR shows a shoulder feature implying a tyrosyl radical involvement in the radical pair. Furthermore, NAD reduction has been observed.

Conclusions. The pigment-protein system we have developed is one that is suitable for water oxidation through a manganese cluster and a tyrosyl radical. Work is currently done on coupling water oxidation to Carbon Dioxide reduction in an artificial electron transport chain.

References.

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