Using the Non-Heme Iron as an Electron Acceptor for the Photochemical Generation of Chlorophyll and Carotenoid Radical Cations in Photosystem II

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Photosystem II contains in its subunits many chlorophyll and carotenoid molecules. These cofactors absorb light energy and transfer it to P_{680}, the primary electron donor, which is oxidized to initiate the principal redox reactions of the enzyme, leading eventually to the oxidation of water and reduction of a loosely-bound quinone. However, some of these chlorophylls and carotenoids have been found themselves to play a part in electron transfer under conditions in which the catalytic electron transfer pathway is not operating optimally. They can act as alternative electron donors to P_{680}^{+} at low temperatures, when electron donation from water (*via* the oxygen-evolving complex) is slower than P_{680} oxidation, and are hypothesized to do the same at physiological temperatures under high light intensity, in order to protect the protein from oxidative damage.[1,2]

We have used the non-heme iron of photosystem II as an alternative stable electron acceptor for the photochemical generation of chlorophyll and carotenoid radical cations in photosystem II, allowing their investigation as a function of temperature by electron paramagnetic resonance (EPR) spectroscopy. Fe^{2+} has been oxidized to Fe^{3+} in high yield at pH 6.5 by replacing the iron's physiological exogenous ligand, a bicarbonate ion, with a glycolate ion, which was previously found to reduce the iron's reduction potential.[3] Illumination at low temperatures establishes a charge separation in the protein by reducing the iron center and oxidizing chlorophyll and carotenoid cofactors. Fe^{2+} is not readily subsequently reoxidized, so that charge recombination between Fe^{2+} and $Chl^{+\bullet}$, $Car^{+\bullet}$ does not occur. This stability to recombination has allowed us to investigate the temperature-dependent formation and interconversion of chlorophyll and carotenoid radicals in photosystem II, processes which were previously not accessible because of interference from other redox reactions. Supported by DOE DE-FG02-05ER15646.

[1] Schweitzer and Brudvig, Biochemistry **36** (1997) 11351-11359

[2] Frank and Brudvig, Biochemistry **43** (2004) 8607-8615

[3] Deligiannakis *et al.*, Biochim. Biophys. Acta **1188** (1994) 260-270