

Optically Detected Magnetic Resonance Studies of the Chl F Synthase Enzyme

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Photosynthetic organisms live in a wide variety of environments with very different and variable light conditions. In particular, plants living in the understory can receive relatively little light in the middle of the visible spectrum at times because it is absorbed by the plants above them. It was recently discovered that some oxygenic organisms have a complex set of genes that allow them to adapt to differing light conditions. These genes and the regulatory process associated with them is known as far red light photoacclimation (FaRLiP)[1]. One of the regulatory responses is to synthesize chlorophyll *f*, which absorbs further to red than chlorophyll *a* in a region of the spectrum that is not used under normal light conditions. Once it has been synthesized, the chlorophyll *f* is then incorporated into the antenna systems of Photosystems I and II (PSI and PSII) allowing them to harvest the available light. The pathway by which the chlorophyll *f* is synthesis takes place is not well known. However, it has been demonstrated that chlorophyll *f* synthesis depends on the expression of an unusual gene that shows very high sequence homology to one of the two core proteins of PS II [2]. This gene is a so-called “super-rogue” paralog of the *psbA* gene and the associated protein has been named ChlF synthase. Very little is known about the structure and function of the ChlF enzyme but it has been shown that when it is illuminated at low temperature spin-polarized chlorophyll triplet states are observed. This allows the enzyme to be studied using optically detected magnetic resonance (ODMR) data. Fluorescence detected ODMR measurements reveal the presence of several different types of chlorophyll triplet states with different zero-field splitting parameters and optical properties. The triplet-minus-singlet spectrum obtained from absorption detected ODMR is remarkably similar to the spectrum of the triplet state of the primary donor $^3P_{680}$ of PSII, suggesting that ChlF probably has an electron transfer pathway similar to that of PSII. The ODMR data also reveal the presence of chlorophyll *f* triplet states and carotenoid triplets. These clearly suggest that the enzyme is light activated and has a photoprotection mechanism as well. The site of chlorophyll *f* synthesis remains unknown but the similarity of the data to that of PSII points to the so-called Chl-Z site as a possibility.

[1] F. Gan, S. Zhang, N.C. Rockwell, S.S. Martin, J.C. Lagarias, D.A. Bryant *Science* **345**, 1312-1317 (2014)

[2] M.Y. Ho, G. Shen, D.P. Canniffe, C. Zhao, C., D.A. Bryant *Science*, **353(6302)**, aaf9178 (2016)