Tuning the Low-Energy Fluorescence State in Photosystem II

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Photosystem II (PSII) is a multi-subunit pigment-protein complex that hosts the reaction center where water splitting occurs. The reaction center is surrounded by two core antennas, CP43 and CP47, which possess low-energy fluorescence states. In fluorescence, the CP47 low-energy state results in a 695 nm band that is hypothesized to act as a trap state, but the exact function is unknown. Initially, both, mutagenesis of chlorophyll ligands in CP47 done by Shen and Vermaas and spectroscopic investigation of the isolated CP47 by de Weerd et al. suggested that the chlorophyll ligated to His 114 (Chl B16) is responsible for the low-energy state. Subsequent theoretical and spectroscopic studies variously support or dispute this assignment. A factor for ambiguity in previous mutagenesis studies is the large perturbation in the system, e.g. mutation of the residue ligated to chlorophyll or deletion of the PsbH subunit. This study suggests an *in vivo* approach using site-directed mutagenesis in *Synechocystis sp.* PCC 6803 to perturb the hydrogen bond between Thr5 in the PsbH subunit and Chl B16. To minimize spectral congestion, we developed a PSI knockdown strain combined with phycobilisome deletion (PSI-kd/ΔPBS). We used 77K fluorescence for whole cells to study the site mutations made in the PSI-kd/ΔPBS background. The spectra show an isolated PSII signal that yields conclusive results about the perturbations caused by the change in hydrogen bonding. We observe a red shift in the low-energy band when the Thr5 is replaced by Arg, weakening the hydrogen bond and a blue shift when the Thr5 is replaced by Ala forming no hydrogen bond. 77K emission spectra show that the site mutations made in the PsbH subunit tune the 695nm band suggesting it is Chl B16 responsible for the low-energy state.

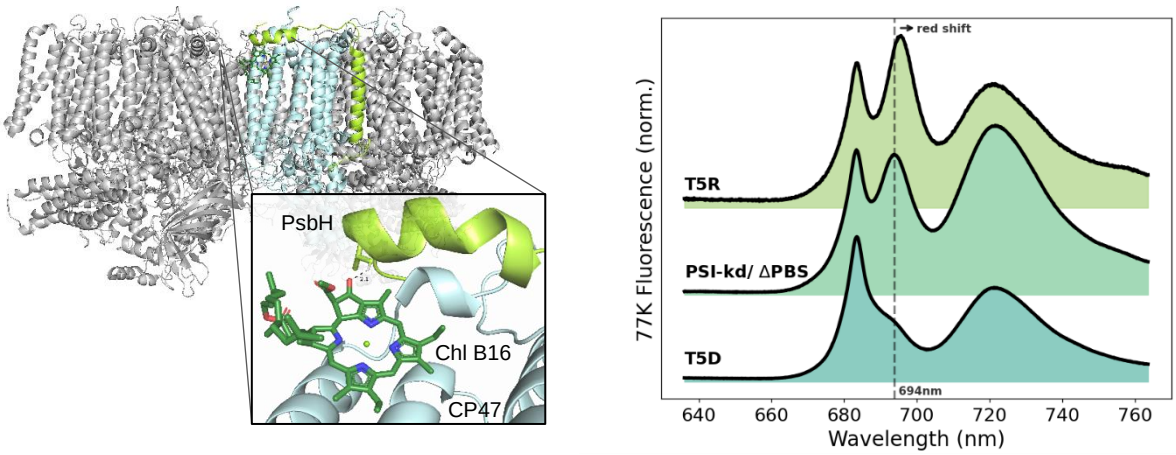

Figure 1: Chl B16 bound to CP47 and PsbH subunit in photosystem II. 77K spectra for site mutants at Thr5 in PSI-kd/ΔPBS background after PSI suppression.