Continuum Electrostatic Analysis of Variant Chlorophyll Binding in Far-Red Light Acclimated (FarLiP) Photosystem II

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Cyanobacteria are major contributors to global carbon fixation by which solar energy is used to drive oxygenic photosynthesis. Classically, photosynthesis can use wavelengths from 450 to 700 nm but has limited absorption of light at longer wavelengths. In environments where visible light is low, several cyanobacteria strains express different chlorophyll pigments and alternative photosystem subunits to expand the range of usable light into the far-red/near-infrared regime (700 – 750nm). This far-red light photoacclimation (FaRLiP), provides selective growth advantages. During far-red light (FRL) photoacclimation in cyanobacteria, the first complex within the photosynthetic electron transport chain, photosystem II (PSII) is modified to enable the complex to bind several chlorophylls (Chl) *d* and *f* at specific sites, in place of Chl *a.* In cells grown under white light only Chl *a* is found. The variant chlorophylls absorb at a lower energy, but the resultant PSII retains the ability to carry out the difficult reaction of oxidizing water to release O_2. Multi-Conformation Continuum Electrostatics (MCCE) was applied to the cryo-EM crystal structure of apo-PSII monomer (PDB ID: 7SA3) to calculate the relative affinity of each of the 33 Chl binding sites for a specific Chl type via Monte-Carlo sampling. Similar calculations were carried out for the pea (PDB ID: 2bhw) and spinach (PDB ID: 1RWT) LHCII which bind both Chl *a* and Chl *b*. The Chl *b*, *d* and *f* all differ from Chl *a* only due to the presence of a formyl group that can make hydrogen bonds. The conclusions are that in Chl sites which have an opportunity to make a hydrogen bond to the formyl group are always identified by MCCE and the experimental structure to carry a variant Chl. However, a few sites that bind an alternative Chl lack a hydrogen bond donor. MCCE often does not correctly identify the occupant at these sites. In addition, the sites that contain Chl *a* in the experimental structures are often calculated to bind a mixture of Chl types indicating that Chl *a* selection is dependent of other factors, including the higher concentration of Chl *a* in the cell and decisions made upon protein assembly.