

OA2.1 - Redox potentials of chlorophylls in both electron transfer pathways in photosynthetic reaction centers

Keisuke Kawashima¹ and Hiroshi Ishikita^{1,2}

¹ Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan.

² Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.

We report redox potentials (E_m) for one-electron reduction for all chlorophylls in the two electron-transfer branches of water-oxidizing enzyme photosystem II (PSII), photosystem I (PSI), and purple bacterial photosynthetic reaction centers (PbRC). In PSI, E_m values for the accessory chlorophylls were similar in both electron-transfer branches. In PbRC, the corresponding E_m value was 170 mV less negative in the active L-branch (B_L) than in the inactive M-branch (B_M), favoring $B_L^{\bullet-}$ formation. This contrasted with the corresponding chlorophylls, Chl_{D1} and Chl_{D2} , in PSII, where $E_m(Chl_{D1})$ was 120 mV more negative than $E_m(Chl_{D2})$, implying that to rationalize electron transfer in D1-branch, Chl_{D1} would need to serve as the primary electron donor. Residues that contributed to $E_m(Chl_{D1}) < E_m(Chl_{D2})$ simultaneously played a key role in (i) releasing protons from the substrate water molecules and (ii) contributing to the larger cationic population on the chlorophyll closest to the Mn_4CaO_5 cluster (P_{D1}) (1), favoring electron transfer from water molecules (2).

In PSII, substrate water molecules need to release protons to act as an electron donor; thus, both electron and proton transfer pathways are expected to proceed from the substrate water molecules. The proton transfer pathway from O4 in the Mn_4CaO_5 cluster (3-5) and the electron transfer pathway toward $P_{D1}^{\bullet+}$ go along the same axis in the opposite directions, which allow PSII to use the common protein electrostatic environment for both transfer of electrons (e^-) and protons (H^+) without competing. It seems plausible that $E_m(Chl_{D1}) < E_m(Chl_{D2})$ in PSII, which is obviously inconsistent with $E_m(B_L) > E_m(B_M)$ in PbRC, is due to a compromise between release of protons and release of electrons from the substrate water molecules using the common protein electrostatic environment and could have been overcome i) by uncoupling the P_{D1}/P_{D2} pair and ii) by employing Chl_{D1} as the primary electron donor.

References

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