Supporting Information

Effect of Charge Distribution over a Chlorophyll Dimer on the Redox Potential of P680 in Photosystem II as Studied by Density Functional Theory Calculations

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Computational Method

All calculations were performed on the GAUSSIAN 03 program package (*1*). The atomic coordinates of P680 except for hydrogen atoms were taken from the X-ray crystallographic structure of the PSII core complexes from *T. elongatus* at 3.0 Å resolution by Loll et al. (PDB 2axt) (*2*) and at 3.5 Å resolution by Ferreira et al. (PDB 1s5l) (*3*). The 17-propionic ester groups were replaced with ethyl groups. The coordinates of hydrogen atoms were determined by geometry optimization using the DFT method with fixing the positions of other atoms. This calculation was performed in vacuum using Becke's three parameter hybrid functional (*4*) combined with the Lee-Yang-Parr correlation functional (*5*) (B3LYP) with the 6-31G(d) basis set. Using the optimized geometry obtained for the neutral P680, the electronic energies of the Chl dimer and its monomeric constituents, P_{D1} and P_{D2}, in both of the neutral and cationic states were calculated at the B3LYP/6-311+G(d) level. Calculations were performed in a solvent at ε = 2.2 (benzene) approximated with IEF-PCM (PCM calculation using the integrated equation formalism model) (*6-8*) with UAHF (united atom for Hartree-Fock) radii (*9*). Such a low dielectric environment around P680 was previously predicted to explain the extremely high E_{ox} of P680 and rationalized by the

presence of a much smaller number of polar amino acids around P680 compared with bacterial P870 (*10*). The charge distribution over $P680^+$ was estimated by natural population analysis (*11,12*).

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