Supplementary Information for

Acquirement of water-splitting ability and alteration of charge-separation mechanism in photosynthetic reaction centers

Hiroyuki Tamura, Keisuke Saito and Hiroshi Ishikita *

Hiroshi Ishikita
Email: hiro@appchem.t.u-tokyo.ac.jp

This PDF file includes:

Supplementary text
Figures S1 to S3
Tables S1 to S5
Legends for Datasets S1 to S2
SI References

Other supplementary materials for this manuscript include the following:

Datasets S1 to S2
Supplementary Information Text

**Stretch of the chlorin ring along the Qy transition dipole moment.** From the observation of the PSII crystal structure (1), it seems likely that van der Waals contact of the QA isoprene side chain and P_{D1} make Chl_{D1} deformed along the Qx transition dipole moment, and make it stretched toward the Qy transition dipole moment. Indeed, removal of QA made the N…N distances of Chl_{D1} lengthened toward the Qx transition dipole moment and shortened toward the Qy transition dipole moment (Table S3). It should also be noted that this does not hold for PbRC, because the Q_B isoprene side chain, not the QA isoprene side chain, is oriented toward B_m.
Fig. S1. (a) Orientations of the Qx and Qy transition dipole moments. (b) N...N distances along the Qy transition dipole moments in Å and excitation energies of P_{D1}, P_{D2}, Chl_{D1}, and Chl_{D2} in meV.
Fig. S2. Energy values for electronic excitation and charge-separated states of (B)Chl a and (B)Pheo a in PbRC (left) and PSII (right) in the presence of the intramolecular reorganization energy, calculated using a QM/MM approach, where the interaction between electron and hole was considered quantum-chemically. Thick solid bars indicate the major intermediate states. Red solid bars and arrows indicate major electron transfer in the active branch, and blue solid bars and dotted arrows indicate the corresponding electron transfer in the inactive branch.

Assuming that the excitation energy is 1424 meV (870 nm) for [PLPM]*, the corresponding energies are 1766 meV (702 nm) for BL, and 1763 meV (703 nm) for BM based on Figure S2.

Assuming that the excitation energy is 1822 meV (680 nm) for ChlD1*, the corresponding energies are 1889 meV (656 nm) for PD1, 1895 meV (654 nm) for PD2, and 1849 meV (670 nm) for ChlD2 based on Figure S2.
**Fig. S3.** Contribution of the cationic and anionic species to the energy difference in the charge-separated states between the active and inactive branches in meV.
Table S1. Coupling matrix for the [P<sub>L</sub>P<sub>M</sub>] bacteriochlorophyll pair in PbRC in meV. Values in brackets stand for the excited states calculated as the [P<sub>L</sub>P<sub>M</sub>] dimer bacteriochlorophylls in the PbRC protein environment. Note that values in Figure 2 were calculated as the P<sub>L</sub> and P<sub>M</sub> monomer bacteriochlorophylls, which are essentially the same as shown here.

|          | P<sub>L</sub>* | P<sub>M</sub>* | P<sub>L</sub>*P<sub>M</sub>* | P<sub>L</sub>*P<sub>M</sub>* |
|----------|----------------|----------------|-----------------------------|-----------------------------|
| P<sub>L</sub>* | (1673) | -27 | -136 | -113 |
| P<sub>M</sub>* | (1704) | -120 | -138 |     |
| P<sub>L</sub>*P<sub>M</sub>* | (1739) | 20 |     |     |
| P<sub>L</sub>*P<sub>M</sub>* | (1709) |     |     |     |
Table S2. Coupling matrix for the \([P_{D1}P_{D2}]\) Chl a pair in PSII in meV. Values in brackets stand for the excited states calculated as the \([P_{D1}P_{D2}]\) dimer chlorophylls in the PSII protein environment. Note that values in Figure 2 were calculated as the \(P_{D1}\) and \(P_{D2}\) monomer chlorophylls, which are essentially the same as shown here.

|      | \(P_{D1}^*\) | \(P_{D2}^*\) | \(P_{D1}^{-}\)\(P_{D2}^{-}\) | \(P_{D1}^{-}\)\(P_{D2}^{**}\) |
|------|--------------|--------------|-----------------------------|-----------------------------|
| \(P_{D1}^*\) | (2051)       | -10          | 9                          | 10                          |
| \(P_{D2}^*\) |              | (2071)       | 4                          | 32                          |
| \(P_{D1}^{-}\)\(P_{D2}^{-}\) |            | (2140)       | 4                          |                             |
| \(P_{D1}^{-}\)\(P_{D2}^{**}\) |            |              | (2590)                     |                             |
**Table S3.** N…N distances along the Qx and Qy transition dipole moments in the QM/MM-optimized geometry in Å.

|       | \(P_{D1}\) | \(P_{D2}\) | \(\text{Chl}_{D1}\) | \(Q_{A}\)-depleted \(\text{Chl}_{D1}\) | \(\text{Chl}_{D2}\) |
|-------|-------------|-------------|-----------------|-----------------|-------------|
| Qx    | 4.184       | 4.243       | 4.151           | 4.167           | 4.191       |
| Qy    | 4.030       | 4.040       | 4.063           | 4.057           | 4.061       |
Table S4. Residues and water molecules that decrease the excitation energy of ChlD1 and ChlD2 with respect to P_{D1} and P_{D2} in meV.

|              | P_{D1} | P_{D2} | ChlD1 | ChlD2 |
|--------------|--------|--------|-------|-------|
| D1-His198\(^a\) | 11     |       | 6     |       |
| D2-His197\(^b\) |        | 10     | 7     |       |
| ligand H\(_2\)O for ChlD1\(^c\) |       |       | 8     |       |
| ligand H\(_2\)O for ChlD2\(^d\) |       |       | 10    |       |
| H-bonding H\(_2\)O (W382D)\(^e\) |       | 3     | 15    |       |
| H-bonding H\(_2\)O (W349A)\(^f\) | 7     |       | 13    |       |
| **total**     | 18     | 13     | 30    | 29    |

\(^a\) Serving as a ligand residue for P_{D1} and an H-bond donor to W382D.
\(^b\) Serving as a ligand residue for P_{D2} and an H-bond donor to W424D and the second sphere ligand W1003A.
\(^c\) W1009A and the second sphere ligand W359A.
\(^d\) Donating an H-bond to the ChlD1 keto group and accepting an H-bond from D2-His197.
\(^e\) Donating an H-bond to the ChlD2 keto group and accepting an H-bond from D1-His198.
Table S5. L/M residue pairs that stabilize H$_{L}^{-}$ with respect to H$_{M}^{-}$ (>40 meV) in the LUMO energy level in meV, i.e., corresponding to $E_{m}$ for one-electron reduction.

|       | $E_{m}(H_{L})$ | $E_{m}(H_{M})$ | $E_{m}(H_{L})$ | $E_{m}(H_{M})$ | stabilizing H$_{L}^{-}$ |
|-------|----------------|----------------|----------------|----------------|------------------------|
| Glu-L104 | 128            | 3              | 0              | 8              | 117                    |
| Asp-L218 | -8             | -54            | -3             | 0              | 43                     |
| Tyr-L67  | 3              | 0              | -8             | -46            | 41                     |
Dataset S1 (separate file). QM/MM-optimized atomic coordinates for PbRC.

Dataset S2 (separate file). QM/MM-optimized atomic coordinates for PSII.

References

1. Umena Y, Kawakami K, Shen J-R, & Kamiya N (2011) Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. Nature 473:55-60.