**S1**

**Supporting Information**

**General remarks on factors affecting the calculated redox potential.**

**1. atomic charges.** A positive unit charge in the neighborhood of the redox-active cofactor stabilizes (destabilizes) its anionic (cationic) state with respect to the reference state. As a result, in both cases, the presence of a positive charge leads to an up-shift of the redox potential. For instance, the positive unit charge on the non-heme iron in bacterial reaction center (bRC) causes an up-shift in the $Q_B$ redox potential by about 170 mV [1]. Likewise, a negative unit charge causes a down-shift in the redox potential, which can be observed in the case of the iron-sulfur complex $F_X$ in PSI, which carries negative unit charge causing a down-shift of the redox potential of quinones by about 250 mV [2].

**2. H bonds.** The CHARMM [3] force field discriminates between non-polar and polar hydrogen atoms. A polar hydrogen atom possesses a larger atomic partial charge and a smaller atomic radius, compared with non-polar hydrogens. A polar nitrogen or oxygen atom in the neighborhood of a polar hydrogen atom can form an H bond after energy minimization with CHARMM. In our computation, the formation of an H bond with the acceptor group of a redox-active cofactor increases its redox potential due to the positive charge of the polar hydrogen atom. This effect is analogous to the charge influence discussed in the previous paragraph on **atomic charges**. The shift of the redox potential depends on details of the H bond geometry. A strong H bond can increase the cofactor redox potential by about 180 mV (H bond between His-L190 and $Q_B$ in bRC) [1]. The orientation of an H bond can also change the redox potential by about 70 mV (putative H bond from Ser-A692 or Ser-B672 to the quinones in PSI) [2]. On the other hand, a weak H bond often results in a redox potential shift of only 10–20 mV (Ishikita, unpublished data). The present data contain also contributions of H bonds to cofactor redox potentials.

**3. dielectric volume.** The dielectric protein volume refers to the solvent free volume that is occupied by the protein, separating low dielectric (protein, $\varepsilon = 4$) from high dielectric (solvent, $\varepsilon = 80$). Its consideration accounts for protein shape, cofactor location in the protein and possible cofactor solvent exposure. A redox-active group that is in the center of the protein is strongly shielded from the solvent. Thus, charges near to this redox-active group will have a large influence on its redox potential. At a low degree of dielectric shielding inside the protein one often observes non-standard protonation states of titratable residues (i.e. protonation/deprotonation of acidic/basic residues). These may diminish the direct influence of charges on cofactor redox potentials. On the other hand, the solvent exposure of a the redox-active group decreases the influence from protein environment. Thus, a redox-active group near the protein surface will have a tendency to possess a redox potential that is close to the reference value in solution.

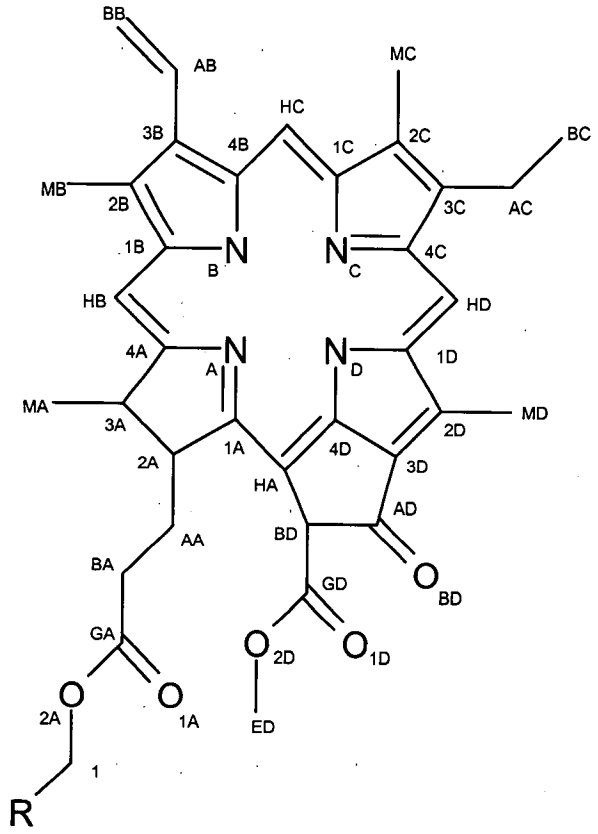
**S2**

Table S1: Atomic partial charges of pheophytin*a*.

| atom | Pheo (0) | Pheo (–1) | Atom | Pheo (0) | Pheo (–1) |
|---|---|---|---|---|---|
| CHA | -0.049 | -0.156 | CBB | -0.313 | -0.390 |
| CHB | -0.223 | -0.286 | 2 HBB | 0.165 | 0.151 |
| HHB | 0.116 | 0.143 | NC | -0.218 | -0.129 |
| CHC | -0.075 | -0.061 | C1C | 0.038 | 0.001 |
| HHC | 0.089 | 0.091 | C2C | 0.044 | 0.015 |
| CHD | -0.046 | -0.074 | C3C | -0.087 | -0.073 |
| HHD | 0.151 | 0.129 | C4C | -0.021 | -0.002 |
| NA | -0.167 | -0.192 | CMC | -0.106 | -0.125 |
| C1A | 0.002 | 0.033 | 3 HMC | 0.047 | 0.047 |
| C2A | 0.030 | 0.042 | CAC | 0.002 | 0.005 |
| H2A | 0.079 | 0.071 | 2 HAC | 0.025 | 0.011 |
| C3A | 0.162 | 0.122 | CBC | -0.011 | -0.004 |
| H3A | 0.015 | -0.006 | 3 HBC | 0.011 | 0.003 |
| C4A | 0.077 | 0.014 | ND | -0.044 | -0.016 |
| CMA | -0.109 | -0.071 | HND | 0.165 | 0.106 |
| 3 HMA | 0.033 | 0.012 | C1D | -0.070 | -0.085 |
| CAA | -0.098 | -0.058 | C2D | -0.024 | -0.031 |
| 2 HAA | 0.036 | 0.024 | C3D | -0.051 | -0.082 |
| CBA | -0.076 | -0.040 | C4D | -0.093 | -0.098 |
| 2 HBA | 0.021 | 0.002 | CMD | -0.114 | -0.078 |
| CGA | 0.724 | 0.700 | 3 HMD | 0.060 | 0.035 |
| O1A | -0.576 | -0.587 | CAD | 0.419 | 0.366 |
| O2A | -0.350 | -0.317 | OBD | -0.508 | -0.578 |
| NB | -0.015 | -0.065 | CBD | 0.025 | 0.010 |
| HNB | 0.060 | 0.088 | HBD | 0.000 | -0.003 |
| C1B | 0.001 | -0.049 | CGD | 0.781 | 0.805 |
| C2B | 0.044 | -0.006 | O1D | -0.596 | -0.617 |
| C3B | 0.034 | -0.025 | O2D | -0.480 | -0.507 |
| C4B | -0.008 | -0.049 | CED | 0.092 | 0.109 |
| CMB | -0.096 | -0.064 | 3 HED | 0.060 | 0.043 |
| 3 HMB | 0.053 | 0.025 | C1 | -0.057 | -0.104 |
| CAB | -0.158 | -0.070 | 2 H1 | 0.130 | 0.138 |
| HAB | 0.143 | 0.101 | | | |

**S3**

Structure of pheophytin*a*

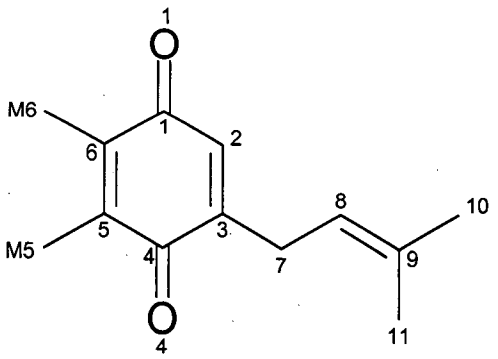



R = phytol chain

**S4**

Table S2: Atomic partial charges of plastoquinone.

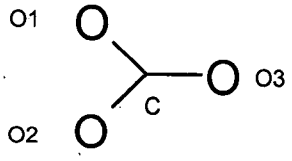
| atom | Plasto-Q (0) | plasto-Q (–1) |
|---|---|---|
| C1 | 0.549 | 0.386 |
| O1 | -0.486 | -0.600 |
| C2 | -0.321 | -0.426 |
| H2 | 0.188 | 0.167 |
| C3 | -0.068 | -0.057 |
| C4 | 0.568 | 0.412 |
| O4 | -0.461 | -0.575 |
| C5 | -0.118 | -0.175 |
| CM5 | -0.087 | -0.033 |
| 3 HM5 | 0.052 | 0.012 |
| C6 | -0.082 | -0.084 |
| CM6 | -0.061 | -0.022 |
| 3 HM6 | 0.048 | 0.009 |
| C7 | -0.025 | -0.017 |
| 2 H7 | 0.069 | 0.044 |
| C8 | -0.292 | -0.303 |
| H8 | 0.140 | 0.156 |
| C9 | 0.068 | 0.063 |
| C10 | -0.058 | -0.055 |
| 3 H10 | 0.036 | 0.021 |
| C11 | -0.124 | -0.123 |
| 2 H11 | 0.062 | 0.036 |




Note that the atomic charges of plasto-Q (–1) were not used in the present computation.

Table S3: Atomic partial charges of bicarbonate.

| atom | deprot. (–1) | prot. (0) |
|---|---|---|
| C | 0.869 | 0.291 |
| O1 | -0.623 | -0.097 |
| O2 | -0.623 | -0.097 |
| O3 | -0.623 | -0.097 |




Note that the atomic charges of protonated bicarbonate [prot. (0)] were not used in the present computation.

**S5**

Table S4: Atomic partial charges of β-carotene.

| atom | β-car (0) | β-car (+1) | atom | β-car (0) | β-car (+1) |
|---|---|---|---|---|---|
| C1 | 0.125 | 0.117 | H21 | 0.155 | 0.150 |
| C2 | -0.028 | -0.027 | C22 | 0.023 | 0.041 |
| 2 H2 | 0.017 | 0.023 | C23 | -0.120 | -0.105 |
| C3 | -0.031 | -0.053 | H23 | 0.107 | 0.106 |
| 2 H3 | 0.012 | 0.024 | C24 | -0.075 | -0.153 |
| C4 | -0.008 | -0.010 | H24 | 0.116 | 0.163 |
| 2 H4 | 0.024 | 0.024 | C25 | -0.149 | -0.107 |
| C5 | 0.030 | 0.054 | C26 | 0.029 | 0.046 |
| C6 | -0.150 | -0.126 | C27 | -0.017 | -0.023 |
| C7 | -0.107 | -0.160 | 2 H27 | 0.025 | 0.033 |
| H7 | 0.141 | 0.161 | C28 | -0.045 | -0.079 |
| C8 | -0.128 | -0.084 | 2 H28 | 0.018 | 0.031 |
| H8 | 0.119 | 0.102 | C29 | -0.031 | -0.011 |
| C9 | 0.018 | 0.026 | 2 H29 | 0.015 | 0.025 |
| C10 | -0.244 | -0.238 | C30 | 0.141 | 0.130 |
| H10 | 0.144 | 0.154 | C31 | -0.167 | -0.148 |
| C11 | -0.095 | -0.077 | 3 H31 | 0.041 | 0.036 |
| H11 | 0.174 | 0.169 | C32 | -0.095 | -0.106 |
| C12 | -0.221 | -0.138 | 3 H32 | 0.025 | 0.030 |
| H12 | 0.153 | 0.131 | C33 | -0.125 | -0.119 |
| C13 | 0.009 | 0.031 | 3 H33 | 0.039 | 0.039 |
| C14 | -0.135 | -0.112 | C34 | -0.044 | -0.046 |
| H14 | 0.111 | 0.137 | 3 H34 | 0.029 | 0.034 |
| C15 | -0.189 | -0.117 | C35 | -0.042 | -0.056 |
| H15 | 0.188 | 0.180 | 3 H35 | 0.030 | 0.048 |
| C16 | -0.176 | -0.062 | C36 | -0.042 | -0.041 |
| H16 | 0.185 | 0.169 | 3 H36 | 0.029 | 0.053 |
| C17 | -0.143 | -0.084 | C37 | -0.042 | -0.053 |
| H17 | 0.111 | 0.141 | 3 H37 | 0.029 | 0.042 |
| C18 | 0.010 | 0.055 | C38 | -0.127 | -0.084 |
| C19 | -0.210 | -0.118 | 3 H38 | 0.039 | 0.035 |
| H19 | 0.148 | 0.151 | C39 | -0.076 | -0.157 |
| C20 | -0.095 | -0.104 | 3 H39 | 0.017 | 0.042 |
| H20 | 0.174 | 0.182 | C40 | -0.147 | -0.096 |
| C21 | -0.262 | -0.168 | 3 H40 | 0.033 | 0.023 |

**S6**

Structure of β-carotene:

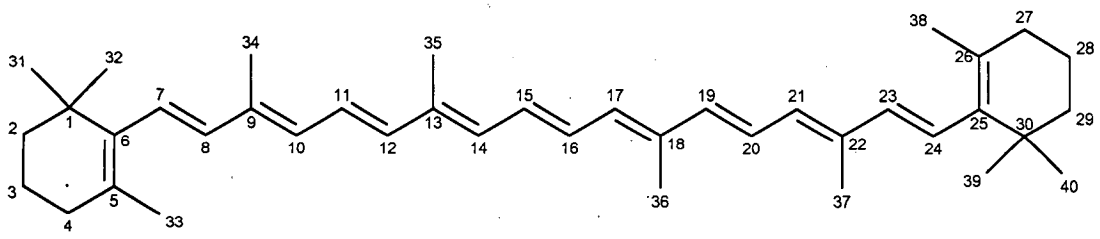



Table S5: Atomic partial charges on the Mn-cluster model.

| component | atomic charge | number | total charge |
|---|---|---|---|
| Mn | +3.25 [a] | 4 | +13 [b] |
| O | –2 | 4 | –8 |
| Ca | +2 | 1 | +2 |
| bicarbonate | –1 | 1 | –1 |
| **Mn-cluster** | | | **+6** |

[a] The total charge $[Mn_4]^{13+}$ was divided by 4 and assigned to each Mn atom.

[b] The total charge of $[Mn_4]^{13+}$ is based on its oxidation state $[Mn_4]$ (II, III, $IV_2$) in state $S_0$ [4].

**S7**

Table S6: Redox potentials of β-car in PSII (left) and PSI (right) in [mV].

PSII

| β-car [a] | $E_m^{ox}$ |
|---|---|
| 48 | +927 |
| 49 | +959 |
| 50 | +905 |
| 51 | +836 |
| 52 | +850 |
| 53 | +911 |
| 54 | +847 |
| **average** | **+891** |

PSI

| β-car [a] | $E_m^{ox}$ | β-car | $E_m^{ox}$ |
|---|---|---|---|
| 4001 | +951 | 4012 | +1119 |
| 4002 | +892 | 4013 | +975 |
| 4003 | +953 | 4014 | +1181 |
| 4004 | +836 | 4015 | +950 |
| 4005 | +965 | 4016 | +857 |
| 4006 | +928 | 4017 | +1049 |
| 4007 | +942 | 4018 | +948 |
| 4008 | +946 | 4019 | +960 |
| (4009) | n.d. [b] | 4020 | +1022 |
| 4010 | +1012 | 4021 | +848 |
| 4011 | +1055 | 4022 | +807 |
| **Average** | | | **+962** |

[a] The numbering of Chl*a* is identical to that used in the crystal structures of PSII [5] (left) and PSI [6] (right).

[b] The redox potential was not calculated due to the incompleteness of the atomic coordinates in the crystal structure.

**S8**

Table S7: Redox potentials of Chl*a* calculated in the absence of protein charges in [mV].

| CP47 | | | | | | CP43 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Chl*a*** [a] | **ligand** [b] | $E_m^{red}$ | $\Delta E_m^{red}$ [c] | $E_m^{ox}$ | $\Delta E_m^{ox}$ [c] | **Chl*a*** [a] | **ligand** [b] | $E_m^{red}$ | $\Delta E_m^{red}$ [c] | $E_m^{ox}$ | $\Delta E_m^{ox}$ [c] |
| 10 | D2-117 | –1004 | +63 | +863 | +53 | 9 | D1-118 | –1037 | +44 | +859 | +61 |
| 25 | B23 | –1081 | +138 | +986 | +123 | 15 | C53 | –1078 | +118 | +976 | +83 |
| 24 | B26 | –1079 | +68 | +977 | +69 | 13 | C56 | –1061 | +91 | +977 | +86 |
| 30 | B100 | –1045 | +30 | +931 | +40 | 17 | C118 | –1018 | +37 | +907 | –62 |
| 37 | B114 | –915 | –13 | +911 | –33 | 21 | C132 | –937 | –71 | +874 | –41 |
| 34 | B142 | –1039 | +52 | +852 | +71 | 19 | C164 | –1067 | –13 | +875 | –15 |
| 29 | B202 | –1104 | +50 | +972 | +25 | 16 | C237 | –1053 | –31 | +967 | –119 |
| 23 | B216 | –991 | +115 | +940 | +111 | 11 | C251 | –1032 | +36 | +895 | +26 |
| 28 | B455 | –1111 | +97 | +982 | +117 | 18 | C430 | –1087 | +66 | +984 | –86 |
| 31 | B466 | –1013 | +95 | +919 | +89 | 14 | C441 | –1020 | +200 | +955 | +76 |
| 35 | B469 | –1008 | +218 | +938 | +175 | 20 | C444 | –977 | +99 | +943 | +112 |
| 32 | B9 | –980 | +73 | +914 | +51 | 44 | (C39) [e] | –989 | +247 | +962 | +216 |
| 27 [d] | B157 | –937 | +49 | +901 | +65 | | (Phe-C181) | | | | |
| 33 [d] | B201 | –1096 | +113 | +948 | +115 | | (Gly-C236) | | | | |
| 26 [f] | | –989 | –2 | +912 | +2 | 12 [f] | | –959 | +4 | +896 | –17 |
| 36 [f] | | –1071 | +95 | +977 | +121 | 22 [f] | | –1098 | +56 | +966 | +33 |
| 46 [f] | | –903 | –21 | +856 | –28 | 47 [f] | | –1074 | +53 | +926 | –11 |
| average [g] | | –1023 | | +932 | | | | –1032 | | +936 | |

**S9**

[a] The numbering of Chl*a* is identical to that in the crystal structure [5]. Each line shows a pair of Chl*a*, which are symmetry counterparts with respect to the sequence between PsbB (CP47) and PsbC (CP43). Note that the $Chl_Z$ do not belong to the antenna complex.

[b] The axial ligand of Chl*a* is a histidine, if not otherwise specified.

[c] Redox potential difference of $E_m$(charged – zero) corresponding to the direct influence of all atomic charges of PSII.

[d] According to the crystal structure [5] no Chl*a* was found to be ligated to the appropriate residue in sequence PsbC.

[e] The Chl*a* has an Asn as axial ligand.

[f] No axial ligand was found for this Chl*a*.

[g] The average of the redox potentials were evaluated without considering $Chl_Z$.

**References to Supporting Information**

(1) Ishikita, H., Morra, G., and Knapp, E. W. *Biochemistry* **2003**, *42*, 3882-3892.

(2) Ishikita, H., and Knapp, E. W. *J. Biol. Chem.* **2003**, *278*, 52002-52011.

(3) Brooks, B. R., Bruccoleri, R. E., Olafson, B. D., States, D. J., Swaminathan, S., and Karplus, M. *J. Comp. Chem.* **1983**, *4*, 187-217.

(4) Yachandra, V. K., Sauer, K., and Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927-2950.

(5) Ferreira, K. N., Iverson, T. M., Maghlaoui, K., Barber, J., and Iwata, S. *Science* **2004**, *303*, 1831-1838.

(6) Jordan, P., Fromme, P., Witt, H. T., Klukas, O., Saenger, W., and Krauß, N. *Nature* **2001**, *411*, 909-917.