Supplemental Materials

Electrostatic influence of PsaC protein binding to the PsaA/PsaB heterodimer in Photosystem I

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Supplemental Discussion

Difference between the Henderson-Hasselbalch and the effective pK_a. The difference between the Henderson-Hasselbalch pK_a and the effective pK_a is pronounced especially for strong electrostatic coupling between different titratable residues. The latter pK_a relates directly to measurable protonation probability of the considered residue. For instance, we obtained a protonation probability of 0.27 H^+ for Asp-B575 in the A_{1B}^- state of the P700-F_X core at pH 7 (see main text). This protonation probability yields the effective pK_a value of 6.6 for this residue according to the following equation (1)

$$pK_a = pH + \frac{1}{\ln 10} \ln \frac{< x >}{1 - < x >} \qquad \text{(eq. S1)}$$

where <x> is the protonation probability of the considered titratable residue. In cases where pK_a and solvent pH differ too much, the protonation probability <x> is close to zero or one. Under such circumstances the evaluated pK_a is error prone, since the numerical accuracies of the computed probabilities <x> are too low. In this case, the Henderson-Hasselbalch pK_a definition becomes more useful. Although, it is an invasive method, since it changes the protonation state of the considered residue by using a bias potential.

For the same charge state A_{1B}^-, the Henderson-Hasselbalch pK_a of Asp-B575 in the P700-F_X core evaluated with application of a bias potential is 6.9 (Table 1 in the main text), which differs by 0.3 pK_a units (corresponding to an energy of 18 meV) from that obtained with eq. S1. Asp-B575 is located in the inner water network between $A_{1A/B}$ and F_X (2). When we constrain the protonation state of Asp-B575 to be 0.5 H^+ as is done with a bias potential (i.e. using the definition of the Henderson-Hasselbalch pK_a), we simultaneously obtain tiny changes of the protonation pattern of nearby titratable residues, namely deprotonation at Asp-B555, Asp-B558, Glu-B682 and Glu-F98 (see Fig. 1A in the main text). These local deprotonations induced by constraining Asp-B575 to be half protonated are the main source that yields different values for the Henderson-Hasselbalch and the effective pK_a.

Supplemental References

1. Ullmann, G.M., and E.W. Knapp. 1999. Electrostatic models for computing protonation and redox equilibria in proteins. *Eur. Bophys. J.* 28:533-551.
2. Jordan, P., P. Fromme, H.T. Witt, O. Klukas, W. Saenger, and N. Krauß. 2001. Three-dimensional structure of cyanobacterial photosystem I at 2.5 Å resolution. *Nature* 411:909-917.

Supplemental Table

Table S1: Calculated pK_a values of residues for the native PSI complex and the P700-F_X core in the P_B^0 state.

residues of PsaA	redox state[a]	native PSI	P700-F_X core	residues of PsaB	redox state[a]	native PSI	P700-F_X core
Asp-A568		3.9	4.7	Asp-B555		4.1	5.6
(Asn-A571)[b]				Asp-B558		8.5	5.7
Asp-A579		–0.2	2.0	Asp-B566		–4.8	3.2
Arg-A583		22.3	13.6	Arg-B570		21.4	15.5
(Gln-A588)[b]				Asp-B575		5.4	5.1
					A_{1A}^-	8.9	8.3
					A_{1B}^-	7.4	7.0
					F_X^-	9.4	8.6
Glu-A699		–2.6	–2.4	Glu-B679		–4.2	–4.3
	A_{1A}^-	–2.7	–2.5		A_{1B}^-	–3.9	–3.9
Glu-A702		–1.3	2.6	Glu-B682		4.8	5.2
	A_{1A}^-	–1.3	2.8		A_{1B}^-	6.3	5.9
(Gln-A718)[b]				Lys-B702		16.4	10.0

[a] If no redox state is indicated all redox active cofactors are in the neutral charge state.

[b] Non-titratable residue in PsaA, which is symmetry related to a titratable residue in PsaB.