Supporting Information for

Dynamic water bridging and proton transfer

at a surface carboxylate cluster of photosystem II

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Supporting Information contains:

- Figures S1-S14
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Figure S1. Structural stability of PsbO and PsbU. (A-B) C α RMSD profiles for PsbO and PsbU as monitored from Sim1 (panel A) and Sim2 (panel B). (C) C α -RMSD matrix of the structured regions of PsbO and PsbU computed from Sim3. We used Carma¹ to overlap the structured regions and to calculate the RMSD matrix for Sim3. The overall changes are small, with a maximum RMSD of 2.6 Å. Note that the RMSD matrix in panel C is computed for both PsbO and PsbU, whereas the RMSD profiles from panels A and B are computed separately for PsbO and PsbU.



Figure S2. Secondary structure analyses for PsbO and PsbU as monitored from Sim1 (panel A, D), Sim2 (panel B, E) and Sim3 (panel C, F). All secondary structure analyses were performed using STRIDE.²



Figure S3. Dynamics of the PsbO-PsbU complex. (A-B) Molecular graphics of the PsbO-PsbU complex in Sim1 (panel A) and Sim2 (panel B). We show 5 coordinate snapshots taken from each simulation, overlapped with the starting crystal structure (colored in red). (C-D) Time series of the center-of-mass distances between PsbO and PsbU computed from Sim1 (panel C) and Sim2 (panel D). Data for Sim3 are presented in Figure 2 of the main manuscript. Molecular graphics were prepared using VMD.³



Figure S4. Detailed analyses of water residence times at surface of PsbO and PsbU. (A) Water residence times τ_1 and τ_2 computed with equation (6) for 20 sites of PsbO, and 8 sites of PsbU. (B) Water residence times τ_3 and τ_4 computed with equation (7) for 7 sites of PsbO, and 1 site of PsbU. (C) Water residence times τ_5 computed with equation (8) for 70 sites of PsbO and 31 sites of PsbU. (D) Water residence times τ_6 computed with equation (3) for 126 sites of PsbO and 47 sites of PsbU. Note that for most sites on the surface of PsbO and PsbU (~87% of the sites) we obtain convergence of the water residence time calculations when using the simpler stretched exponential from eq. (3), and the exponential from eq. (8), suggested for waters with short residence times.



Figure S5. Close view of selected PsbO sites with long water residence times. (A) PsbO-A177 and K178 have average water residence times of 204.0 ± 0.2 ps and 114.6 ± 0.1 ps, respectively. (B) PsbO-S191 has the longest average water residence time computed for PsbO and PsbU, 541.3 ± 0.9 ps.



Figure S6. PsbO and PsbU in structures of PSII. (A) B-factor values of PsbO and PsbU as indicated by the crystal structure PDB ID: 3WU2.⁴ (B) Overlap of different S intermediates, labeled according to the number of flashes F used to illuminate the crystal. The crystal structures used are 6DHE,⁵ 6DHF,⁵ 6DHO,⁵ 6DHP,⁵ 3WU2,⁴ 5GTI,⁶ and 5KAI.⁷ Overall the structures show minor differences most notable in an extended loop of PsbO.



Figure S7. Water bridging in the crystal structure. We used the crystal-structure coordinates⁴ of PsbO and PsbU with heavy atoms fixed to the crystal-structure coordinates, and optimized the H atoms coordinates using CHARMM.⁸ Panels A-C illustrate water H bonding to selected charged protein groups at the interface between PsbO and PsbU.



Figure S8. Occupancy of water wires at the interface between PsbO and PsbU as computed from Sim1.



Figure S9. Dynamics of carboxylate groups involved in water bridging. (A) Crosscorrelation for sidechains of PsbO and PsbU. The analyses were performed for pairs of sidechain carbon atoms closest to functional groups that can H-bond, and which are within 22Å within at least 50% of the MD trajectory. (B) Standard deviation of the orientational dynamics of carboxyl groups at the interface between PsbO and PsbU.



Figure S10. Molecular graphics of the QM-optimized reactant states used to compute paths 1-5.



Figure S11. Molecular graphics of the QM-optimized reactant states used to compute paths 6-8.



Figure S12. Molecular graphics illustrating structural changes along selected proton-transfer paths. For clarity we depict only the proton donor and acceptor groups, nearby water molecules and, in panels A-B, PsbO-K123. Dotted lines indicate H bonding in the reactant state of the path. Arrows indicate the approximate direction in which a water molecule or protein group moves along the path. Arrows are color coded green –structural rearrangements that occur prior to proton transfer; orange –structural rearrangements that occur at the first-order saddle point where proton transfer occurs; pink –structural rearrangements that occur after proton transfer is completed. Panels A-D illustrate structural changes along path **1**, path **2**, path **3**, and path **4**, respectively.



Figure S13. Molecular graphics illustrating structural changes along path 5 and path 6. Color codes for arrows are the same as in Figure S9. Panel C shows part of the cluster at the local minimum at $\zeta = 0.4$ from Figure 12D of the main manuscript.



Figure S14. Molecular graphics illustrating structural changes along paths 7 and 8. Color codes for arrows are the same as in Figure S9. Panels B and D illustrate part of the clusters at the corresponding local minima at $\zeta = 0.47$ (Figure 12D of the main manuscript) and at $\zeta = 0.56$ (Figure 12D of the main manuscript).

Supporting References

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