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Supplemental Information for:

Rigidly hydrogen-bonded water molecules facilitate proton transfer in photosystem II

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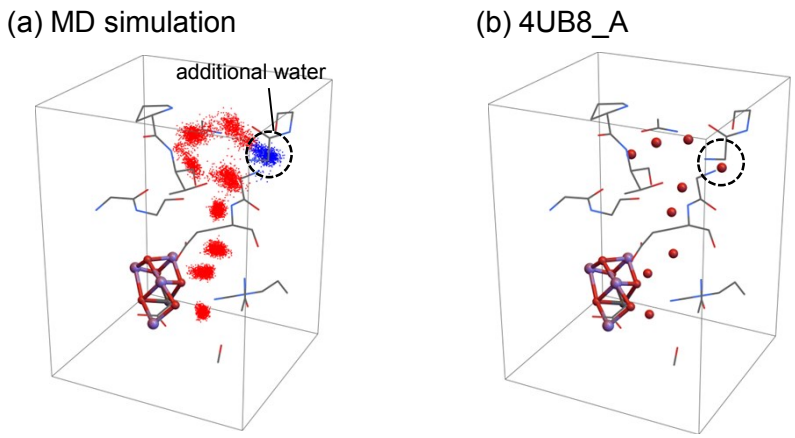


Figure S1. (a) Distribution of the oxygen atoms of water molecules in the MD simulation for PSII. The additional water molecule (blue) entered the channel during the simulation. (b) Oxygen atoms of water molecules in another crystal structure. A water molecule corresponding to the additional water molecule was observed in the X-ray damage-free structure[1] (monomer A in 4UB6 and monomer A/B in 4UB8), whereas this was not observed in the first 1.9-Å structure (3ARC)[2] (see also Table S1).

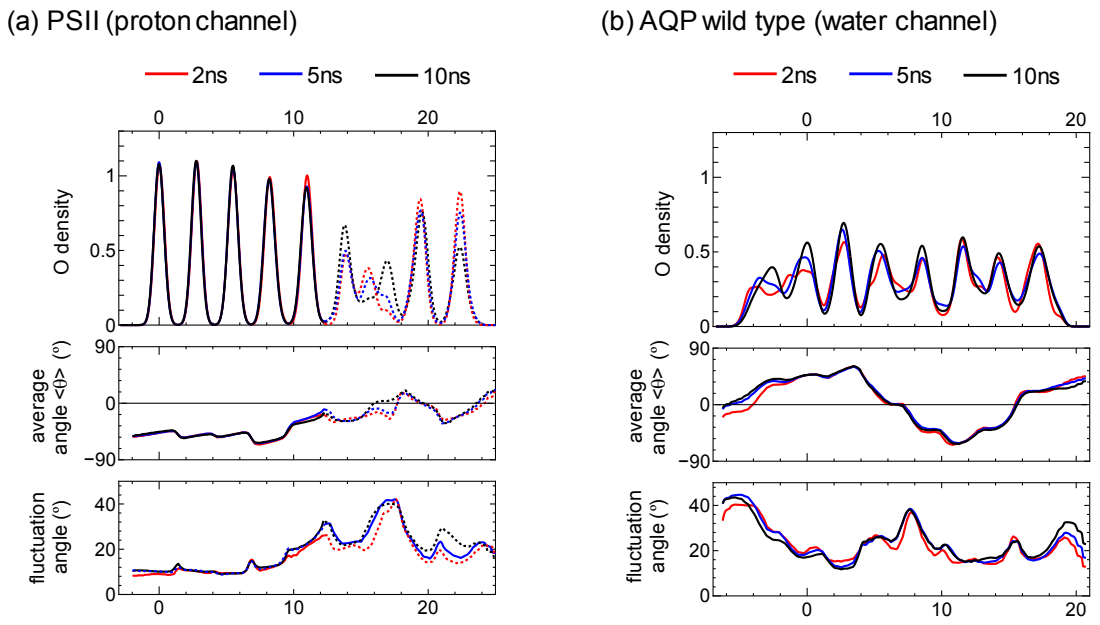


Figure S2. The dependence of the distribution of the water-molecule oxygen atoms (O density); the average angle $<\theta>$, of the water orientation; and angle fluctuation, $<\theta - <\theta>>^2$, on the simulation time in (a) PSII and (b) AQP. Red, blue, and black lines represent distributions in the simulation time of 0-2 ns, 0-5 ns, and 0-10 ns, respectively. See also the figure caption of Figure 5 in the main text.

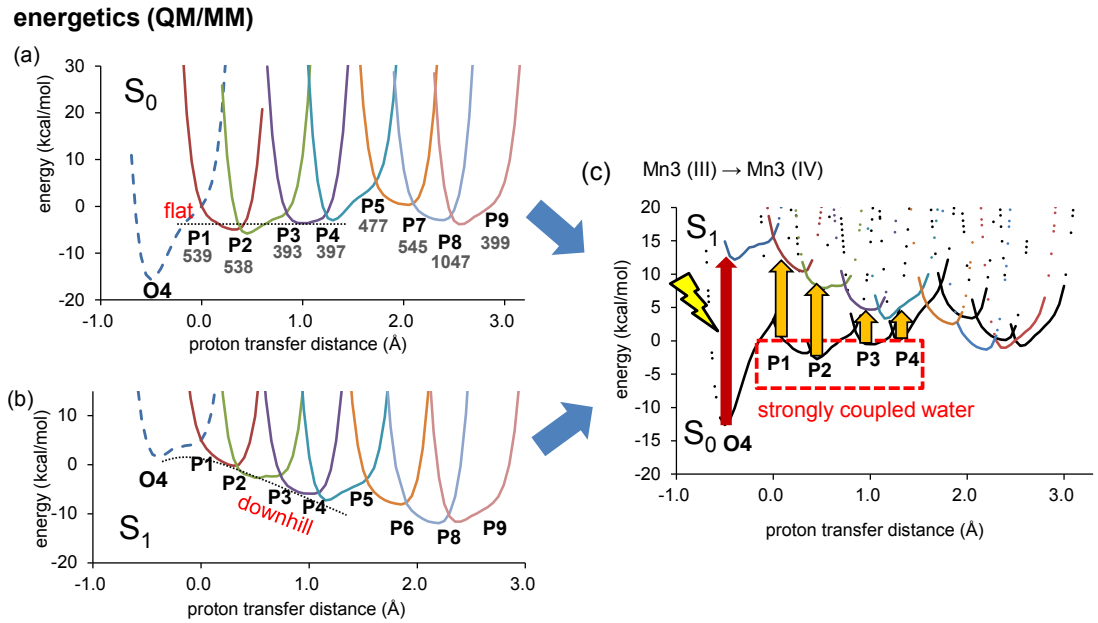
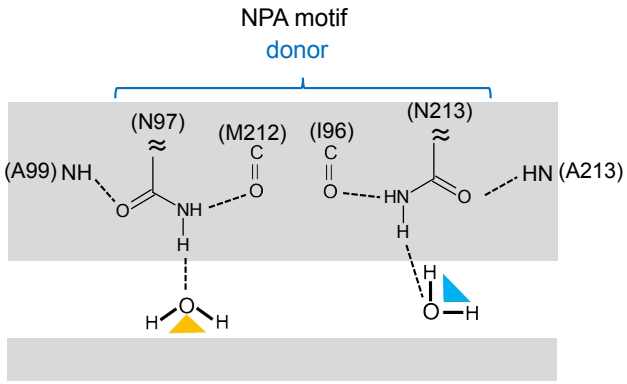
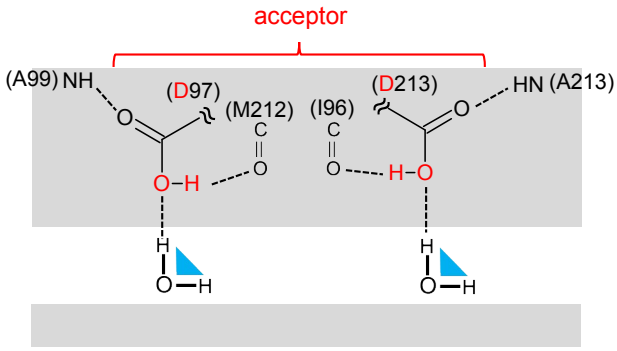


Figure S3. Proton-transfer potential[3] of PSII along the channel in the S_0 (a) (equivalent to Figure 4e) and S_1 states (b). The driving force of proton transfer on O4 of the Mn_4CaO_5 cluster at the S0 → S1 transition by light-energy radiation was propagated to P1–P4 (c).

(a) wildtype (N97 **donor** / N213 **donor**)



(b) N97D (H^+) **acceptor** / N213D (H^+) **acceptor**



(c) N97D (H^+) **acceptor** / N213D (H^+) **donor**

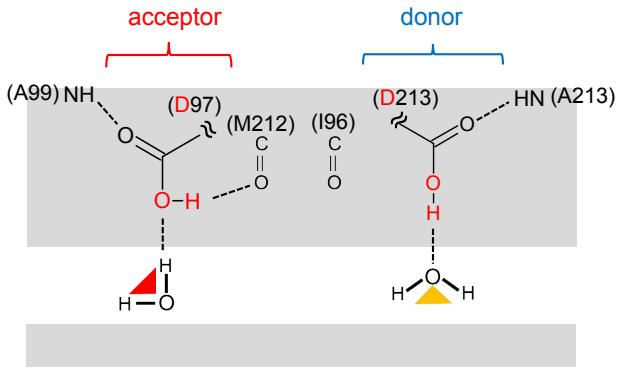


Figure S4. H-bond patterns around the NPA motif appearing in MD simulations using wild-type AQP and the N97D/N213 mutant. We observed only one pattern (a) in the wild type, whereas two patterns were observed in the mutant (b and c).

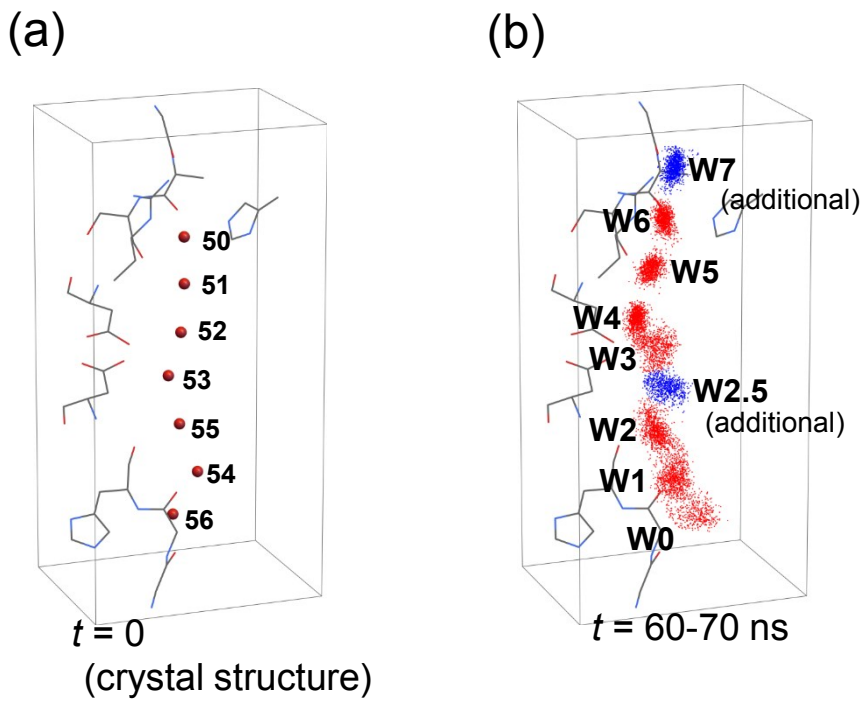


Figure S5. (a) Initial positions of oxygen atoms of water molecules in AQP. (b) Distribution of the oxygen atoms of water molecules in the MD simulation for the N97D/N213D AQP mutant in the N97D acceptor/N213D donor pattern. Positions of spots are same as those observed in simulations using the wild type (Figure 4a), except for W2.5, which entered the channel during the simulation.

Table S1. Water molecules in the proton channel in various crystal structures of PSII. Each crystal structure contains two PSII monomers.

	3ARC (A)			3ARC (B)			4UB6 (A)			4UB6 (B)			4UB8 (A)			4UB8 (B)		
	ID	chain	B-factor	ID	chain	B-factor	ID	chain	B-factor	ID	chain	B-factor	ID	chain	B-factor	ID	chain	B-factor
X1	W539	A	**23.89**	W539	a	25.27	W567	A	**15.58**	W525	a	**20.69**	W568	A	**19.95**	W524	a	**20.25**
X2	W538	C	**24.55**	W538	c	28.16	W665	C	**24.56**	W1060	c	**24.44**	W660	C	33.86	W661	c	26.83
X3	W393	A	**24.15**	W1253	a	**24.36**	W542	A	**17.81**	W619	a	**19.74**	W543	A	**20.76**	W620	a	**21.21**
X4	W397	A	**20.44**	W1255	a	**22.34**	W546	A	**20.37**	W621	a	**21.13**	W547	A	**18.54**	W622	a	28.69
X5	W477	C	48.29	W477	c	44.30	W612	C	28.78	W1010	c	36.93	W608	C	37.36	W608	c	36.74
X6							W806	C	33.58				W796	C	**24.22**	W787	c	34.31
X7	W545	A	35.82	W545	c	39.40	W606	C	31.92	W635	A	35.40	W573	A	29.16	W634	a	35.37
X8	W1047	C	35.35	W1047	c	38.30	W757	C	41.92	W1154	C	39.77	W752	C	37.36	W752	c	40.92
X9	W399	A	34.79	W1257	a	32.61	W548	A	28.11	W623	A	35.89	W549	A	29.78	W624	a	33.86
total	8			8			9			8			9			9		

References

1. M. Suga, F. Akita, K. Hirata, G. Ueno, H. Murakami, Y. Nakajima, T. Shimizu, K. Yamashita, M. Yamamoto, H. Ago and J. R. Shen, *Nature*, 2015, **517**, 99-103.
2. Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55-60.
3. K. Saito, A. W. Rutherford and H. Ishikita, *Nat Commun*, 2015, **6**, 8488.