Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Pivotal role of the redox-active tyrosine in driving the water splitting catalyzed by Photosystem II

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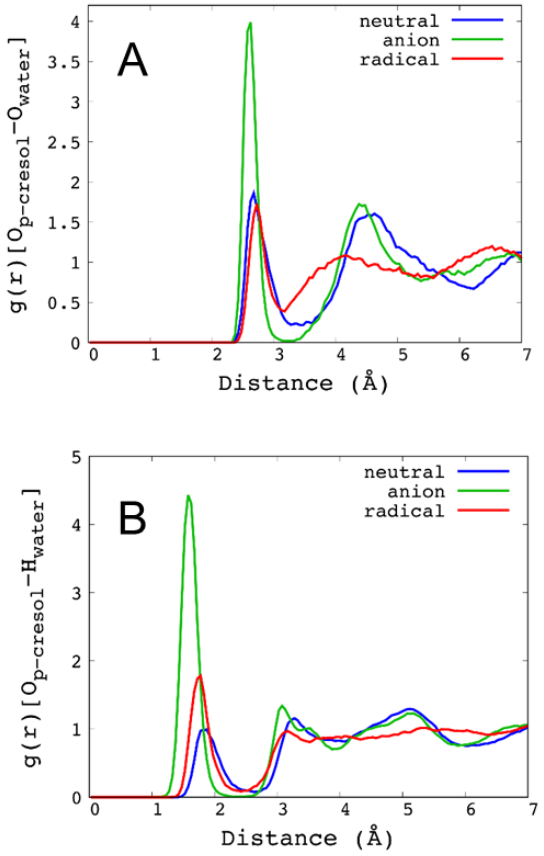

Fig. S1 Radial distribution functions of the oxygen (A) and the hydrogen (B) atoms of water from the phenolic oxygen of *p*-cresol in QM-MD simulations.

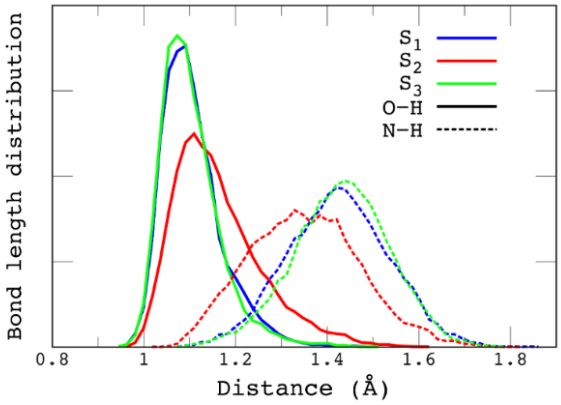

Fig. S2 Distributions of the distances of O-H (solid line) and N-H (dotted line) in the S_1 (blue), S_2 (red), and S_3 (green) state. The distances are designated in Figure 4 (bottom).

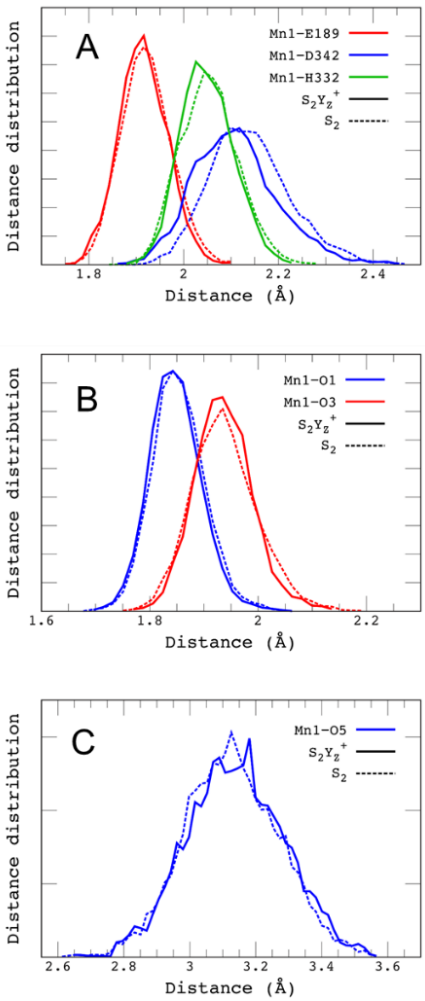

Fig. S3 Distributions of the distance between the Mn1 and oxygen atoms of carboxylate ligands (A), and Mn1 and μ-oxo (B; for O1 and O3, C; for O5) in the S_2 (dotted line), and the $S_2Y_Z^+$ (solid line) state.

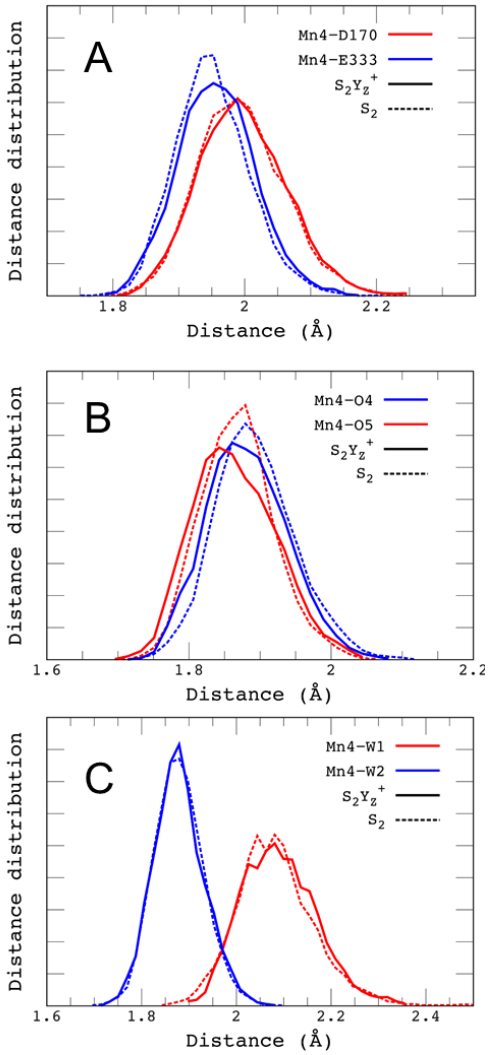

Fig. S4 Distributions of the distance between the Mn4 and oxygen atoms of carboxylate ligands (A), Mn4 and μ-oxo (B), and Mn4 and water ligands (C) in the S_2 (dotted line), and the $S_2Y_Z^+$ (solid line) state.

Table S1 Averaged Mulliken spin populations of each Mn ions in the Mn_4Ca cluster in each S state in QM/MM-MD simulations together with those errors estimated by standard deviation.

	S_1	S_2	S_3
Mn1	4.04 ± 0.04	3.99 ± 0.04	3.18 ± 0.06
Mn2	–3.13 ± 0.06	–3.16 ± 0.06	3.22 ± 0.07
Mn3	3.06 ± 0.06	–3.14 ± 0.07	3.17 ± 0.07
Mn4	–3.98 ± 0.04	3.14 ± 0.06	–3.10 ± 0.05

Table S2 Averaged interatomic distances (Å) in the Mn_4Ca cluster in each S state obtained by QM/MM-MD simulations and averaged distances (Å) between two monomers in previously reported X-ray structures

	This work				Suga et al.		Kern et al.			
Distance (Å)	S_1	S_2	$S_2Y_Z^+$	S_3	0F (4UB6)[a]	2F (5WS6)[a]	0F (6DHE)[a]	1F (6DHF)[a]	1F(150 μs) (6DHG)[a]	2F (6DHO)[a]
Mn1-Mn2	2.79	2.77	2.77	2.81	2.68	2.63	2.78	2.81	2.81	2.75
Mn1-Mn3	3.21	3.39	3.40	3.56	3.20	3.26	3.25	3.26	3.35	3.33
Mn1-Mn4	4.76	4.96	4.97	5.31	4.95	5.03	4.86	4.86	5.02	5.06
Mn1-Ca	3.54	3.57	3.58	3.40	3.47	3.43	3.43	3.42	3.42	3.37
Mn2-Mn3	2.80	2.81	2.80	2.85	2.70	2.80	2.85	2.84	2.84	2.86
Mn2-Mn4	5.14	5.19	5.17	5.32	5.21	5.24	5.21	5.24	5.26	5.25
Mn2-Ca	3.40	3.37	3.38	3.39	3.32	3.39	3.38	3.41	3.41	3.33
Mn3-Mn4	2.78	2.78	2.76	2.81	2.87	2.74	2.74	2.74	2.74	2.77
Mn3-Ca	3.51	3.51	3.56	3.53	3.40	3.53	3.51	3.52	3.50	3.57
Mn4-Ca	3.67	3.81	3.86	4.02	3.77	4.03	3.83	3.90	3.93	4.01

[a]PDB cords that we referred to summarize the atomic distances [4UB6; Suga et al., (2015) *Nature* 517(7532):99-103, 5WS6; Suga et al., (2017) *Nature* 543(7643);131-135, and 6DHE, 6DHF, 6DHG, and 6DHO; Kern et al., (2018) *Nature* 563(7731);421-425].

Table S3 Averaged hydrogen bond distances (Å) around the Mn_4Ca cluster in each S state obtained by QM/MM-MD simulations together with the averaged distances (Å) between two monomers in previously reported X-ray structures

	This work				Suga et al.		Kern et al.			
Distance (Å)	S_1	S_2	$S_2Y_Z^+$	S_3	0F (4UB6)[a]	2F (5WS6)[a]	0F (6DHE)[a]	1F (6DHF)[a]	1F(150 μs) (6DHG)[a]	2F (6DHO)[a]
W1-D61	2.71	2.70	2.77	2.58	2.65	2.33	2.74	2.69	2.61	2.60
W2-W5	2.73	2.80	2.79	2.82	2.76	2.61	2.75	2.60	2.54	2.61
W3-W5	3.79	3.46	3.44	3.68	2.90	2.90	2.70	2.80	2.66	2.74
W3-W7	2.92	2.83	2.81	2.80	2.92	2.65	2.79	2.71	2.61	2.64
W5-W6	2.82	2.95	2.95	2.94	2.70	2.81	2.68	2.95	3.02	2.82
W6-W7	2.73	2.83	2.87	2.77	2.94	2.95	2.83	2.70	2.76	2.72
W7-Y_Z	2.81	2.74	2.73	2.84	2.52	2.42	2.56	2.57	2.97	2.60
W4-Y_Z	3.03	2.74	3.09	2.74	2.77	2.67	2.66	2.60	2.72	2.74
W4-Wa	2.71	3.54	2.95	4.13	3.57	(3.50)[b]	3.53	3.19	3.43	3.50
Wa-Wb	2.68	2.85	2.77	-	2.68	(2.54)[b]	2.46	2.54	2.71	2.36
Wb-O1	2.92	3.55	4.41	-	2.49	2.88	2.98	3.34	3.84	3.51
Wc-O4	2.61	2.70	2.71	2.65	2.59	2.33	2.59	2.54	2.52	2.48
Wc-D61	2.69	2.68	3.15	3.48	2.69	2.73	2.90	2.82	2.81	2.84
Wc-Wd	2.79	2.75	2.77	2.75	2.85	(2.43)[b]	3.10	-	-	-

[a]PDB cords that we referred to summarize the atomic distances [4UB6; Suga et al., (2015) *Nature* 517(7532):99-103, 5WS6; Suga et al., (2017) *Nature* 543(7643);131-135, and 6DHE, 6DHF, 6DHG, and 6DHO; Kern et al., (2018) *Nature* 563(7731);421-425]. [b]The distances are calculated from one monomer. Wa and Wd disappeared in another monomer.