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

SI

Substitution of Ca^{2+} and changes in the H-bond network near the oxygen-evolving complex of photosystem II

Manoj Mandal [1]*, Keisuke Saito [2,3], and Hiroshi Ishikita [2,3]*

1) Department of Chemical and Biological Sciences, S. N. Bose National Centre for Basic Sciences, Kolkata 700106, West Bengal, India

2) Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

3) Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan

Table S1. Functional/basis set and calculated distances in the open-cubane S_2 conformation in Å. For efficient analysis, a smaller QM region was adopted (i.e., the Mn_4CaO_5 cluster; the ligand side-chains of D1-Asp170, D1-Glu189, D1-His332, D1-Glu333, D1-Asp342, and CP43-Glu354; ligand carboxy-terminal group of D1-Ala344; and ligand water molecules, W1–W4; and CP43-Arg357): thus, the calculated distances may not be consistent with those calculated using the large QM region (e.g., Figure 1b).

functional	**B3LYP**						**M05**
basis set	**LACVP***	**LACV3P**	**LACV3P***	**LACV3P****	**LACV3P**++**	**LACV3P**++**	**LACVP***
Mn1-Mn2	2.77	2.84	2.80	2.80	2.80	2.80	2.77
Mn1-Mn3	3.18	3.19	3.18	3.18	3.18	3.18	3.18
Mn1-Mn4	4.67	4.68	4.66	4.65	4.66	4.66	4.66
Mn2-Mn3	2.74	2.80	2.76	2.76	2.77	2.77	2.74
Mn3-Mn4	2.72	2.80	2.75	2.75	2.75	2.75	2.72
Mn1-O1	1.83	1.86	1.84	1.84	1.85	1.85	1.82
Mn1-O3	1.90	1.92	1.91	1.91	1.91	1.91	1.90
Mn1-O5	2.71	2.67	2.67	2.68	2.68	2.68	2.71
Mn1-$N_{D1\text{-}His332}$	2.01	1.98	2.00	2.00	2.00	2.00	2.01
Mn1-$O_{D1\text{-}Asp342}$	2.18	2.20	2.20	2.20	2.20	2.20	2.18
Mn1-$O_{D1\text{-}Glu189}$	1.90	1.90	1.91	1.91	1.91	1.91	1.91
Mn2-O1	1.81	1.84	1.83	1.83	1.83	1.83	1.82
Mn2-O2	1.81	1.84	1.82	1.82	1.82	1.82	1.81
Mn2-O3	1.84	1.89	1.87	1.87	1.87	1.87	1.84
Mn2-$O_{D1\text{-}Asp342}$	2.01	1.97	1.99	1.99	1.99	1.99	2.01
Mn2-$O_{D1\text{-}Ala344}$	1.90	1.88	1.90	1.90	1.90	1.90	1.91
Mn2-$O_{CP43\text{-}Glu354}$	2.00	1.98	2.00	1.99	2.00	2.00	2.00
Mn3-O2	1.84	1.88	1.86	1.86	1.86	1.86	1.84
Mn3-O3	1.91	1.92	1.92	1.92	1.92	1.92	1.91
Mn3-O4	1.80	1.82	1.81	1.81	1.81	1.81	1.80
Mn3-O5	1.82	1.87	1.84	1.84	1.84	1.84	1.83
Mn3-$O_{CP43\text{-}Glu354}$	2.06	2.03	2.05	2.05	2.05	2.05	2.08
Mn3-$O_{D1\text{-}Glu333}$	1.99	1.97	1.99	1.99	1.99	1.99	1.99
Mn4-O4	1.77	1.81	1.79	1.79	1.79	1.79	1.77
Mn4-O5	1.97	2.03	1.99	1.99	1.99	1.99	1.97
Mn4-W1	2.17	2.11	2.15	2.17	2.18	2.18	2.19
Mn4-W2	2.05	2.00	2.03	2.04	2.04	2.04	2.06
Mn4-$O_{D1\text{-}Asp170}$	2.16	2.12	2.15	2.14	2.15	2.15	2.17

Mn4-$O_{D1\text{-}Glu333}$	2.08	2.10	2.10	2.09	2.09	2.09	2.08
Ca-O5	2.50	2.53	2.52	2.51	2.52	2.52	2.51
Ca-W3	2.42	2.38	2.41	2.43	2.44	2.44	2.42
Ca-W4	2.42	2.38	2.41	2.42	2.45	2.45	2.43
Ca-$O_{D1\text{-}Glu189}$	3.13	3.17	3.17	3.18	3.17	3.17	3.13

Table S2. Distances in the open-cubane $Mn_4\mathbf{M}O_5$ clusters in S_2 (**M** = Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) in Å using M06 functional (i.e., dispersion correction).

	Mg^{2+}	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**	**Ba^{2+} + water**
ionic radius[a]	0.66	0.99	1.12	1.34	1.34
surface area[b]	0.44	1	1.28	1.83	1.83
W3…**M**	2.08	2.41	2.56	2.66	2.71
W4…**M**	2.12	2.39	2.55	2.69	2.75
O1…**M**	2.16	2.38	2.50	2.65	2.66
O2…**M**	2.25	2.56	2.68	2.81	2.77
O5…**M**	2.89	2.59	2.67	2.78	2.80
O5…Mn1	2.87	3.03	3.06	3.11	3.11
O5…Mn4	1.82	1.83	1.82	1.81	1.82

Table S3. Contributions of the $Mn_4\mathbf{M}O_5$ components to the HOMO of S_2 (%). The component that has the largest contribution to the HOMO is in bold. To specifically focus on the difference in the electronic state of the $Mn_4\mathbf{M}O_5$ cluster, the QM region was defined as $Mn_4\mathbf{M}O_{5;}$ side chains of D1-Asp170, D1-Glu189, D1-His332, D1-Glu333, D1-Asp342, and CP43-Glu354; carboxyl terminal group of D1-Ala344; and water molecules, W1−W4.

	HOMO	**contribution from**								
		Mn1 [a]	**Mn2**	**Mn3**	**Mn4**	**O1**	**O2**	**O3**	**O4**	**O5**
S_2										
	Mg^{2+}-PSII	**86**	0	0	0	3	2	3	0	0
	Ca^{2+}-PSII	**83**	0	0	0	4	2	4	0	0
	Sr^{2+}-PSII	**83**	1	1	0	4	2	5	0	0
	Ba^{2+}-PSII	**82**	1	1	0	4	2	5	0	0

[a] Including ligand residues.