Supporting Information

Understanding Two Different Structures in the Dark Stable State of the Oxygen-Evolving Complex of Photosystem II: Applicability of the Jahn–Teller Deformation Formula

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**SI Structural symmetry breaking of the CaMn₄O₅ cluster in OEC of PSII**

The key concepts for understanding of two S₁ structures[30] in this paper are briefly revisited here. The first DFT calculation[33] based on the high-resolution XRD structure[18] revealed that the Mn₄(a)-O(5)-Mn₁(b) bond of the CaMn₄O₅ cluster in OEC of PSII was labile, indicating the possibility of structural symmetry breaking (SSB) as shown in Fig. S1. The full geometry optimizations of the CaMn₄O₅ cluster by QM[35-37] and QM/MM[37, 38] indeed elucidated the central (C), slightly left (C_L) and right (C_R)-elongated quasi-central structures as well as left (L)- and right (R)-opened structures[39, 48]. The deformation parameter (δ) in eq. (1) in the text was introduced to express the SSB in a quantitative manner[37-39]. The relative stabilities between C_L and C_R or between L and R are highly dependent on the oxidation state (Sₙ, n=0~4)[35-47] and many other factors such as hydrogen bonding interaction (see Fig. 4)[30], pH[54, s37], packing structure[28, 29, s37, s38]. Therefore, realistic theoretical models including these factors were crucial for quantitative discussions on the relative stabilities among the SSB structures in Fig. S1. Large scale QM/MM approach[37, 38] was one of such attempts on the theoretical ground, providing simple equations (1)-(3) for Jahn-Teller (JT) deformations in the SSB structures in Fig. S1.

**Fig. S1** Structural symmetry breaking (SSB) of the CaMn₄O₅ cluster in OEC of PSII[35-39] (see eq. (1) in the text). C_R and C_L denote the slightly right- and left-elongated quasi-central structures respectively. R and L denote the right- and left-opened structures respectively. Sₙ (n=0~4) denotes the n-th state of the Kok cycle for water oxidation in OEC of PSII. Relative stabilities between C_R (R) and C_L (L) are dependent on several environmental conditions.

**SII Jahn-Teller effects of the Mn(III) ion in the CaMn₄O₅ cluster of OEC of PSII**
SII.1 Jahn–Teller deformation formula for SSB structures

The Jahn-Teller (JT) effects of the Mn(III) ion play important roles for subtle geometry changes of the CaMn$_4$O$_5$ clusters with the same valence configurations such as (3443) as illustrated in Fig. S1$^{[39]}$. Our QM and QM/MM computations$^{[33-39]}$ indeed revealed four structures, namely $C_R$, $C_L$, $R$ and $L$, structures of the CaMn$_4$O$_5$ cluster of OEC (see Fig. S1). The relative stabilities among them were variable, depending on the oxidation states ($S_n$ ($n=1$~$4$)) and several environmental conditions as shown in our previous papers (refs. 33-39). The SSB parameter ($\delta$) was defined using the distances of the Mn$_{1(a)}$-O$_{5(5)}$ and Mn$_{4(a)}$-O$_{5(5)}$ bonds as shown in eq. (1)$^{[35-37]}$. The JT deformation formula in eqs. (2) and (3) were found to be reliable for estimations of the geometrical parameters of the CaMn$_4$O$_5$ clusters as shown in previous (refs. 37-39) and present papers.

The elongation axes of the JT effects were variable with the oxidation states of water (O$^{2-}$, OH$^-$ and H$_2$O) at the O$_{5(5)}$ site as illustrated in Fig. 1 in the text and Fig. S2. From Fig. S2, the Mn$_{4(a)}$-O$_{5(5)}$ distances were estimated to be 1.8(2.0), 2.0(2.1), 2.2(2.2), 2.4(2.3) and 2.6(2.4) (Å) for O$_{5(5)}$=O$^{2-}$(OH$^-$) under the assumption of R(Mn$_{4(a)}$-$Mn_{3(b)}$) =2.7, 2.75, 2.8, 2.85 and 2.9 (Å) respectively. The differences of the Mn$_{4(a)}$-O$_{5(5)}$ distance between O$_{5(5)}$=OH$^-$ and O$_{5(5)}$=O$^{2-}$ were 0.2, 0.1, 0.0, -0.1 and -0.2 (Å) respectively for the above Mn$_{4(a)}$-$Mn_{3(b)}$ distances, indicating that the tendency was reversed exceeds through R(Mn$_{4(a)}$-$Mn_{3(b)}$)=2.80 Å (see Fig. S2). Therefore, the discrimination between O$^{2-}$ and OH$^-$ at the O$_{5(5)}$ site was difficult near the crossing region of the two JT deformation curves. The Mn$_{3(b)}$-O$_{5(5)}$ distance was used for the second JT deformation index for discrimination between O$_{5(5)}$=O$^{2-}$ and O$_{5(5)}$=OH$^-$$^{[37]}$ in this region. The first and second JT deformation indices were successfully applied for the extremely low-dose (LD) XRD structures$^{[30]}$ as shown in Table 1 in the text. The reliability and applicability of the JT deformation formula, namely eqs. (1)-(3), were also elucidated in relation to recent SFX results$^{[28, 29]}$ for OEC of PSII in Tables 5, S1 and S7.

The JT deformation eqs. (1)-(3) are applicable to estimation of possible errors of Mn-O distances from the Mn$_{4(a)}$-$Mn_{3(b)}$ distance. The experimental uncertainties by the XRD and SFX methods at 1.9~2.3 Å resolution$^{[11-19]}$ are considered to be relatively small for distances between heavy atoms such as Mn-Mn and Mn-Ca distances as compared with those of the Mn-O distances in the CaMn$_4$O$_5$ cluster of OEC of PSII. Therefore, the Mn$_{4(a)}$-$Mn_{3(b)}$ distances can be used effectively for theoretical estimation of the Mn$_{4(a)}$-O$_{5(5)}$ distance by eq. (3) as shown in the supporting Table S1. The EXAFS results provide several 3D structures using the same Mn-Mn and Mn-O distances as shown in Table S6. The computational results in Table S1 were used for estimation of the Mn$_{4(a)}$-O$_{5(5)}$ distances on the basis of the Mn$_{4(a)}$-$Mn_{3(b)}$ distances observed by several serial femtosecond X-ray (SFX) crystallography in present paper because the Mn$_{4(a)}$-O$_{5(5)}$ distances of the CaMn$_4$O$_5$ cluster by SFX were susceptible to the X-ray damage even by
femtosecond X-ray duration as shown in Table 4. Recently, many papers (s1-s45) were published to elucidate

possible origins of the X-ray damages of the SFX structures[27-29]. The difference between the Mn$_4$(a)-O$_5$(5) distance calculated by eq. (3) using the observed Mn$_4$(a)-Mn$_3$(b) distance and the Mn$_4$(a)-O$_5$(5) distance observed by SFX may be used for estimation of X-ray damage of the SFX structures during femtosecond duration as shown in Table 4 in the text.

SII.2 Geometrical parameters via the mixings of $S_i$ and other states

Exact determinations of geometrical structures of pure $S_i$ (i=0-3) state by XRD and XFEL methods were often difficult because of mixing of other oxidation states as shown in Table S4. The dark stable state without preflash experiments usually consisted of the $S_1$ structure and additional other structures (see Table S4). Geometrical parameters of the CaMn$_4$O$_5$ clusters in the $S_1$ state by XRD and SFX (XFEL) are variable, depending on the partial mixing with other states. Table S2 summarizes the mixing ratios between the $S_1$(R) and $S_0$(C$_X$) (X=L, R) structures for the given Mn$_4$(a)-Mn$_3$(b) distances as well as Mn$_4$(a)-O$_5$(5) and Mn$_3$(b)-O$_5$(5) distances obtained by eqs. (2) and (3) using the Mn$_4$(a)-Mn$_3$(b) distances under the assumption of O$_5$(5)=O$^2_-$ or OH$^-$. The
contamination of the S₂ structure was not negligible for the dark stable state (see Table S4), indicating the
examination of the mixing between the S₁ and S₂ structures. Table S3 summarizes the mixing ratios
Table S1 The Mn₄(a)-O(5) distances of the CaMn₄O₅ cluster estimated by using
the Mn₄(a)-Mn₃(b) distances in the S₁ (3443) state of OEC of PSII

| Cases | Mn₄(a)-Mn₃(b)[a] | Mn₄(a)-O(5)[b] | Δ[c] | O(5)[d] | Mn₃(b)-O(5) | SSB[f] | Type |
|-------|-----------------|----------------|------|---------|------------|--------|------|
| 1     | 2.70            | 1.98(1.78)     | 0.20 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.55(0.75) | R    |
| 2     | 2.71            | 2.00(1.82)     | 0.18 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.53(0.71) | R    |
| 3     | 2.72            | 2.02(1.86)     | 0.16 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.51(0.67) | R    |
| 4     | 2.73            | 2.04(1.90)     | 0.14 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.49(0.63) | R    |
| 5     | 2.74            | 2.06(1.94)     | 0.12 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.47(0.59) | R    |
| 6     | 2.75            | 2.08(1.98)     | 0.10 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.45(0.55) | R    |
| 7     | 2.76            | 2.10(2.02)     | 0.08 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.43(0.51) | R    |
| 8     | 2.77            | 2.12(2.06)     | 0.06 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.41(0.47) | R    |
| 9     | 2.78            | 2.14(2.10)     | 0.04 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.39(0.43) | R    |
| 10    | 2.79            | 2.16(2.14)     | 0.02 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.37(0.39) | R    |
| 11    | 2.80            | 2.18(2.18)     | 0.00 | OH⁻ (O²⁻) | 2.0(1.8)   | 0.35(0.35) | R    |
| 12    | 2.81            | 2.20(2.22)     | -0.02| OH⁻ (O²⁻) | 2.0(1.8)   | 0.33(0.31) | R    |
| 13    | 2.82            | 2.22(2.26)     | -0.04| OH⁻ (O²⁻) | 2.0(1.8)   | 0.31(0.27) | C_R  |
| 14    | 2.83            | 2.24(2.30)     | -0.06| OH⁻ (O²⁻) | 2.0(1.8)   | 0.29(0.23) | C_R  |
| 15    | 2.84            | 2.26(2.34)     | -0.08| OH⁻ (O²⁻) | 2.0(1.8)   | 0.27(0.19) | C_R  |
| 16    | 2.85            | 2.28(2.38)     | -0.10| OH⁻ (O²⁻) | 2.0(1.8)   | 0.25(0.15) | C_R  |

[a] Assumed Mn₄(a)-Mn₃(b) distance, [b] Estimated Mn₄(a)-O(5) distances by using Mn₄(a)-Mn₃(b) distance
under the assumption of O(5)= OH⁻ and O₅= O²⁻ (in parentheses), [c] Difference of Mn₄(a)-O(5) distances between O(5)= OH⁻ and O₅= O²⁻, [d] The oxidation state of water at the O(5) site, namely O(5)= OH⁻ and O₅= O²⁻ (in parentheses), [e] Mn₃(b)-O(5) distances of O₅= OH⁻ and O₅= O²⁻ (in parentheses) [f] Structural symmetry breaking (SSB) parameter.

between the S₁(C₉) and S₂(R) structures for the given Mn₄(a)-Mn₃(b) distances as well as Mn₄(a)-O(5) and Mn₃(b)-O(5) distances obtained by eqs. (2) and (3) assuming the Mn₄(a)-Mn₃(b) distances under the assumption of O(5)= O²⁻. Table S4 summarizes the weights of the S₁ (i=0–3) components in the Kok cycle by EXAFS (see ref. 2). The preflash experiments are desirable for purification of the dark stable state before the XRD, SFX and spectroscopic experiments. Table 5 in the text
summarizes the geometrical parameters in the S\(_1\) state determined by SFX with and without preflash\[^{27-29}\]. Available XRD results\[^{18,30}\] and SFX(XFEL)\[^{27-29}\] results were obtained without preflash, indicating the partial contamination of the S\(_0\) or S\(_2\) configurations as shown in Tables S2-S4. Very recently, the SFX results\[^{28}\] for the preflash dark stable state were published. Therefore, the JT deformation formulae were applied to them as shown in Tables 5 and S8 (see below).

Table S2 The Mn\(_4(a)\)-O\(_5\) and Mn\(_3(b)\)-O\(_5\) distances of the CaMn\(_4\)O\(_5\) cluster in the S\(_1\) state of OEC of PSII based on the estimation procedure using the Mn\(_4\)–Mn\(_3\) distance obtained by the mixing of the S\(_1\) (R) (A type in Fig. 1A) and S\(_0\)(C\(_X\)) (X=R or L) structures (eq. 8)

| Structures[^a] | Mn\(_4\)–Mn\(_3\) | \(\alpha(C_X)\) (%)[^b] | Mn\(_4\)–O\(_5\)[^c] | Mn\(_3\)–O\(_5\)[^d] | SSB[^e] | Topology[^f] |
|---------------|----------------|----------------------|----------------|----------------|--------|------------|
| S\(_1\) (Fig. 1A) | 2.70 | 0(0.0) | 1.78(1.78) | 1.80(1.80) | 0.75 | R          |
|               | 2.71 | 5(2.5) | 1.81(1.81) | 1.83(1.82) | 0.72 | R          |
|               | 2.72 | 10(5.0) | 1.84(1.84) | 1.86(1.83) | 0.69 | R          |
|               | 2.73 | 15(7.5) | 1.87(1.87) | 1.89(1.85) | 0.66 | R          |
|               | 2.74 | 20(10.0) | 1.90(1.90) | 1.92(1.86) | 0.63 | R          |
| (1–\(\alpha\)) S\(_1\)(R) | 2.75 | 25(12.5) | 1.93(1.93) | 1.95(1.88) | 0.60 | R          |
| +\(\alpha\) S\(_0\)(C\(_X\)) | 2.76 | 30(15.0) | 1.96(1.96) | 1.98(1.89) | 0.57 | R          |
|               | 2.77 | 35(17.5) | 1.99(1.99) | 2.01(1.91) | 0.54 | R          |
|               | 2.78 | 40(20.0) | 2.02(2.02) | 2.04(1.92) | 0.51 | R          |
|               | 2.79 | 45(22.5) | 2.05(2.05) | 2.07(1.94) | 0.48 | R          |
|               | 2.80 | 50(25.0) | 2.08(2.08) | 2.10(1.95) | 0.45 | R          |

[^a] The Mn\(_4(a)\)-O\(_5\) and Mn\(_3(b)\)-O\(_5\) distances were estimated by using the Mn\(_4(a)\)-Mn\(_3(b)\) distance given by the mixing of the S\(_1\) (R) and S\(_0\)(C\(_X\)) structures.\[^b^\] The mixing ratio \(\alpha\)(R) for the S\(_1\)(C\(_R\)) and S\(_0\)(C\(_R\)) where the corresponding value for the C\(_L\) structure is given in parentheses,\[^c^\] The Mn\(_4(a)\)-O\(_5\) distance for the (1–\(\alpha\))S\(_1\)(R) + \(\alpha\)S\(_0\)(C\(_R\)) structure where the corresponding value for the mixed (1–\(\alpha\))S\(_1\)(R) + \(\alpha\)S\(_0\)(C\(_L\)) structure is given in parentheses,\[^d^\] The Mn\(_3(b)\)-O\(_5\) distance for the mixed (1–\(\alpha\))S\(_1\)(R) + \(\alpha\)S\(_0\)(C\(_R\)) structure where the corresponding value for the mixed (1–\(\alpha\))S\(_1\)(R) + \(\alpha\)S\(_0\)(C\(_L\)) is given in parentheses,\[^e^\] Structural symmetry breaking (SSB) parameter,\[^f^\] the right-opened structure (R).
Table S4 The EXAFS results for the weights of the Si (i=0~3) components for flashes. [a]

| Flashes[a] | S0 (%) | S1(%) | S2(%) | S3(%) |
|------------|--------|-------|-------|-------|
| 0          | 3.0    | 88.0  | 9.0   | 0.0   |
| 1          | 0.3    | 11.5  | 80.1  | 8.1   |
| 2          | 6.9    | 2.8   | 28.4  | 61.8  |
| 3          | 52.9   | 7.5   | 15.7  | 23.9  |

[a] ref. 2.

SIII Damages of redox-active enzymes by SFX (XFEL)

SIII.1 Ab initio molecular dynamics simulation for X-ray damage of SFX structures

Many papers[49-52, s1-s45] have been published for elucidation and explanation of the methodological backgrounds as well as scope and applicability of the serial femtosecond crystallography (SFX)[21-29] using free electron lasers (XFEL)[53]. Here, X-ray-induced atomic displacements within the XFEL pulse durations are discussed in relation to important roles of the low dose (LD) XRD experiments[30]. The distances of the Mn4(a)-O(5) bonds by the LD XRD[30] were about 2.1~2.3 (Å) depending on variation of the hydrogen bonding networks (see Fig. 4), supporting the XFEL structure[27] with the Mn4(a)-O(5) distance with about 2.3 Å. Amin et al.[51, 52] performed ab initio molecular dynamics simulation[s1-s4] of OEC (see text). The computational results showed that the Mn-Mn and Mn-Ca distances were less affected by radiation damage due to their heavy masses, while the O(5) atom moved significantly. The atomic displacements induced
by XFEL at SACLA have been investigated by several groups [49-52, s43, s45]. For example, Inoue et al. [s43] demonstrated no X-ray damage of diamond crystal during 20 fs duration by the use of a pump-probe diffraction method using double XFEL pluses (time delay between them is 0.3 ~ 80 fs) at SACLA [53]. Boudet et al. [s14] observed no significant damage of the XFEL (40fs duration) structure of lysozyme at 1.9 Å resolution at LCLS. However, higher R factors were observed for the SFX data [s14]. Thus, the X-ray damages by XFEL are dependent on systems under investigations [s20, s21]. Recently, Sauter [s15] examined several issues with XFEL data processing that make it difficult to gain accurate measurements of the high resolution signal. Therefore, the high-resolution LD XRD results [30] are very important for examination of possible damages of OEC of PSII [27] by XFEL. The X-ray damage of the XFEL [27] and SFX [28] structures at SACLA [53] were found to be small because of 10fs pulse duration [49, 50]. In fact, the LD XRD [30], XFEL [27] and SFX [28, 29] results for the dark stable state were consistent as discussed in the text (see Tables 4 and 5).

SIII.2 X-ray damages of redox-active enzymes by SFX (XFEL)

Possible damages of the redox active metalloenzymes by strong X-ray radiation were discussed in relation to the radiation damages of the XRD [18], XFEL [27] and SFX [28, 29] structures of the redox-active CaMn₄O₅ cluster of OEC of PSII. Frankel et al. [s5, s6] performed Fourier transform ion cyclotron resonance mass spectrometry to identify damaged amino acid residues by addition of X-ray generated hydroxyl radical ( \( \cdot \) OH ) that were located in second core photosystem II (D1, D2, CP43 and CP47). The majority of the identified oxidized residues (≈75~81 %) were located on the solvent-exposed surface of the complex. A number of buried residues on the proteins were also modified but no indication of the direct radical attack to the CaMn₄O₅ cluster was observed, indicating that the reductions of the Mn ions may be induced by electron transfers of free electrons generated by X-ray radiation.

Wang [s7, s8] also indicated that the damage of amino acid residues occurred even in the case of the SFX by XFEL. Wang et al. investigated possible X-ray damages of OEC of PSII on the theoretical grounds (see text) [46, 52, s9, s10], claiming that the XFEL structure [27] at SACLA corresponds to the S₀ structure. On the other hand, available experimental and theoretical results [49, 50-52, s43] indicated that the X-ray damage by XFEL at SACLA was a few percent because of the 10fs pulse duration. Table 4 summarizes possible elongations of the Mn₄(a)-O(5) bonds of the CaMn₄O₅ cluster. Our conclusion is that the XFEL [27] structure is mainly responsible for the S₁ structure (dx²-JT-type in Fig. 1C) although partial contamination of the S₀ component is inevitable because of no preflash before the SFX experiment [27]. Recent SFX experiments with and without preflash refinement by Suga et al. [28] and Young et al. [29] were summarized in Tables 5 and 5.
The low dose (0.03 MGy) XRD\textsuperscript{[30]} structure elucidated the refined S\textsubscript{1} structure of the CaMn\textsubscript{4}O\textsubscript{5} cluster that was obtained by 5\% reduction of the elongated geometrical parameters of the high-dose (0.43 MGy) XRD structure\textsuperscript{[18]}, indicating the same topological structure between them.

The LD XRD structure\textsuperscript{[30]} also provided the structural information for examination of possible radiation damages of the XFEL\textsuperscript{[27]} and SFX\textsuperscript{[28, 29]} structures on the theoretical grounds. The present theoretical analysis indicated the reliability of the XFEL\textsuperscript{[27]} and SFX\textsuperscript{[28, 29]} structures for the S\textsubscript{1} state even though several possible partial structural damages were conceivable from the different Fourier maps for OEC of PSII\textsuperscript{[46, 57-60]}. For example, the distances of the Mn\textsubscript{4(a)}-O\textsubscript{5} bonds by the LD XRD\textsuperscript{[30]} were about 2.1~2.3 (Å) because of the coordination of the O\textsubscript{5} site to the Ca(II) ion in the native CaMn\textsubscript{4}O\textsubscript{5} cluster in contradiction to several Mn model clusters examined for early EXAFS experiments\textsuperscript{[6, 7]}. The Mn\textsubscript{4(a)}-Mn\textsubscript{3(b)} length and Mn\textsubscript{4(a)}-O\textsubscript{5} bond lengths are sensitive to the ligand coordination structures of the Ca(II) ion\textsuperscript{[39]}. The XFEL\textsuperscript{[27]} and SFX\textsuperscript{[28]} structures of the CaMn\textsubscript{4}O\textsubscript{5} cluster is compatible with the LD XRD structure\textsuperscript{[30]}; the elongation of 0.4~0.5 Å by the 10fs pulse by SACLA was hardly conceivable\textsuperscript{[49, 50, 63]} as shown in Tables 4 and S5. This in turn supports the assignment of the S\textsubscript{1}(Cr\textsubscript{K}) structure (see Fig. 1B) for the original EXAFS structure\textsuperscript{[10]} as shown in Table S6 in section SIV since too much X-ray reduction (80~90 \%)\textsuperscript{[61]} of the XFEL structure\textsuperscript{[27]} was hardly conceivable from the very recent S\textsubscript{1} structure by SFX by Young et al.\textsuperscript{[29]} and many other XFEL results\textsuperscript{[516-539]}. The SFX results after two flash reported very recently by Suga et al.\textsuperscript{[28]} and Young et al.\textsuperscript{[29]} were discussed in detail in the supporting section SV.

We did not discuss the elongation of the Mn\textsubscript{(III)}\textsubscript{3(b)}-O\textsubscript{5} bond lengths of the CaMn\textsubscript{4}O\textsubscript{5} cluster by strong X-ray pulse of XFEL\textsuperscript{[53]} in the text. In conformity with eq. (11), reduced Mn\textsubscript{(III)}\textsubscript{3(b)}-O\textsubscript{5} bond lengths were estimated using the Coulomb explosion distance (\Delta_{XFEL}) as follows;

\[
R(Mn_{3(b)}-O_5)_{correct} = R(Mn_{3(b)}-O_5)_{XFEL} - \Delta_{XFEL}
\]  

(51)

where \Delta_{XFEL} were given by the above 1.07 (10fs) and 7.49 (50 fs) \% elongations of the Mn\textsubscript{3(b)}-O\textsubscript{5} distance of XFEL\textsuperscript{[27]} and SFX\textsuperscript{[28, 29]} structures. The 2.5 and 5 (\%) elongations were also examined for weak and medium explosions, respectively. Table S5 summarizes the calculated Mn\textsubscript{3(b)}-O\textsubscript{5} distances for Models 1~5 with 2.0~2.4 (Å). The explosion distances (\Delta_{XFEL}) by 10~50 fs durations were about 0.02~0.18 (Å) as shown in Table S5. The elongated Mn\textsubscript{3(b)}-O\textsubscript{5} distances at 10fs pulse duration (SACLA)\textsuperscript{[27]} are shortened by about 0.02~0.03 Å, indicating no significant effect.

The SSB parameters (\delta) were relatively small (0.2~0.3 Å) for the S\textsubscript{1} state because of the homogeneous valence state, namely Mn\textsubscript{(III)}\textsubscript{4(a)}-O\textsubscript{5}+Mn\textsubscript{(III)}\textsubscript{4(a)}, of the CaMn\textsubscript{4}O\textsubscript{5} cluster. The shortening or elongation of the Mn\textsubscript{4(a)}-O\textsubscript{5} bond was predicted theoretically in the S\textsubscript{1} \rightarrow S\textsubscript{2} transition because of the loss of the JT distortion of the Mn\textsubscript{(III)} ion in accord with the Mn\textsubscript{(III)}\textsubscript{4(a)} to Mn\textsubscript{(IV)}\textsubscript{4(a)} or the Mn\textsubscript{(III)}\textsubscript{1(d)} to Mn\textsubscript{(IV)}\textsubscript{1(d)} transition, yielding the R (\delta=0.6~0.7 Å)- or L (\delta=-0.6~0.7 Å)-opened structure\textsuperscript{[35-39]}. The optimized Mn\textsubscript{4(a)}-O\textsubscript{5} bond lengths by large-scale QM/MM\textsuperscript{[37-39]} were 1.82 and 1.80 (Å) respectively for the R-opened S\textsubscript{2} structures with W2=OH\textsuperscript{-} and W2=H\textsubscript{2}O,
indicating the shortening of the Mn$_4$(a)-O(5) length by about 0.4 and 0.2 (Å) in the S$_1$(C$_R$) of Fig. 1B-S$_2$(R) and S$_t$(R) of Fig. 1A)-S$_2$(R) transition respectively. The high-resolution XRD and SFX experiments are necessary for detection of small structural change in the latter case. On the other hand, the optimized Mn$_1$(d)-O(5) bond lengths by large-scale QM/MM were 1.84 and 1.85 (Å) respectively for the L-opened S$_2$ structures with W2=OH$^-$ and W2=H$_2$O, showing the similar shortening in the S$_t$(C$_L$)-S$_2$(L) transition. Unfortunately, the resolution of the latest XFEL structure$^{[23, 25]}$ for the S$_2$ state was 5.9 Å, indicating no information for the precise change of the SSB parameters in the S$_1$ $\rightarrow$ S$_2$ transition. The high-resolution LD XRD structure for the S$_2$ state is also desirable for further discussions. The ultra high-resolution (<1.5 Å) XRD structure of the S$_1$ state is also desirable for discussions of possible disorders of the O$_{(5)}$ site in relation to possible damages of the SFX structures$^{[27-29]}$. The SFX experiments of the S$_3$ state by XFEL$^{[28, 29, s40, s41]}$ elucidated subtle geometrical differences between the A- and B-monomers of OEC of PSII, indicating the necessity of large-scale QM/MM simulations$^{[36, 37]}$ for elucidation of roles of the hydrogen bonding networks$^{[30]}$ for water oxidation.

Table S5 The Mn$_3$(a)-O$_{(5)}$ distances (Å) of the CaMn$_4$O$_5$ cluster of OEC of PSII shortened by the corrections of the XFEL expansions$^{[a]}$

| Structures | Distance$^{[b]}$ | Duration | Time |
|-----------|----------------|----------|------|
| Difference (Å) | | 0 fs | 10 fs | a fs | b fs | 50 fs |
| Model 1 | Mn$_3$(a)-O$_{(5)}$ | 2.00 | 1.98 | 1.95 | 1.90 | 1.85 |
| Model 2 | Mn$_3$(a)-O$_{(5)}$ | 2.10 | 2.08 | 2.05 | 1.99 | 1.94 |
| Model 3 | Mn$_3$(a)-O$_{(5)}$ | 2.20 | 2.18 | 2.14 | 2.07 | 2.04 |
| Model 4 | Mn$_3$(a)-O$_{(5)}$ | 2.30 | 2.28 | 2.24 | 2.18 | 2.13 |
| Model 5 | Mn$_3$(a)-O$_{(5)}$ | 2.40 | 2.37 | 2.34 | 2.28 | 2.22 |

$^{[a]}$The Mn$_3$(a)-O$_{(5)}$ distances of the XFEL structures$^{[27]}$ were estimated by using the Coulomb explosion distance ($\Delta_{XFEL}$) in eq. (11).

[s1] P. V. Parandekar and J. C. Tully, J. Chem. Phys. 2005, 122, 094102.
[s2] J. L. Aloso, A. Castro, P. Echenique, V. Polo, V. Rubio and D. Zueco, N. J. Phys. 2010, 12, 083064.
[s3] B. F. E. Curchod, U. Rothlisberger and I. Tavernelli, ChemPhysChem, 2013, 14, 1314.
[s4] F. Ding, J. J. Goings, H. Liu, D. B. Lingerfelt and X. Li, J. Chem. Phys. 2015, 143, 114105.
[s5] L. K. Frankel, L. Sallans, R. A. Limbach and T. M. Bricker, Biochemistry, 2012, 51, 6371.
[s6] L. K. Frankel, L. Sallans, H. Bellamy, J. S. Goettert, R. A. Limbach and T. M. Bricker,
J. Biol. Chem. **2013**, 288, 23565.

[s7] J. Wang, Protein Science, **2016**, 25, 1407.

[s8] J. Wang, Protein Science, **2016**, 25, 1797.

[s9] M. Askerka, D. J. Vinyard, J. Wang, Q. W. Brudvig and V. S. Batista, Biochemistry, **2015**, 54, 1713.

[s10] O. Einsle, F. A. Tezcan, D. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard and D. C. Rees, Science, **2002**, 297, 1696.

[s11] K. J. Gaffney and H. N. Chapman, Science, **2007**, 316, 1444.

[s12] P. Emma et al., Nat. Photon., **2010**, 4, 641.

[s13] M. Askerka, D. J. Vinyard, J. Wang, Q. W. Brudvig and V. S. Batista, Biochemistry, **2015**, 54, 1713.

[s14] D. M. Fritz et al., Science, **2007**, 315, 633.

[s15] O. Einsle, F. A. Tezcan, D. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard and D. C. Rees, Science, **2002**, 297, 1696.

[s16] K. J. Gaffney and H. N. Chapman, Science, **2007**, 316, 1444.

[s17] R. A. Kirian et al., Opt. Express, **2010**, 18, 5713.

[s18] R. A. Kirian et al., Acta Cryst, **2001**, A63, 131.

[s19] S. Boutet et al., Science, **2010**, 329, 1261 (2012).

[s30] J. Kern et al., Proc. Natl. Acad. Sci. **2012**, 109, 9721 (2012).

[s31] N. K. Sauter, J. Synchrotron Radiat., **2011**, 22, 239 (2015).

[s32] M. S. Hunter and P. Fromme, Methods, **2011**, 55, 387.

[s33] A. Barty et al., Nat. Photonics, **2012**, 6, 35.

[s34] R. Koopmann et al., Nat. Methods, **2012**, 9, 259.

[s35] L. C. Johansson et al., Nat. Methods, **2012**, 9, 263.

[s36] L. Lomb et al, Phys. Rev. B, **2011**, 84, 214111.

[s37] T. A. White, R. A. Kirian, A. V. Martin, A. Aguila, K. Nass, A. Barty and H. N. Chapman, J. Appl. Cryst., **2012**, 45, 335 (CrystFEL)

[s38] N. K. Sauter, J. Hattne, R. W. Grosse-Kunstleve and N. Echols, Acta Cryst. **2013**, 69, 1274.

[s39] J. Tenboer et al, Science, **2013**, 339, 227.

[s40] J. Tenboer et al., Science, **2014**, 346, 1242.

[s41] M. R. Sawara et al, Proc. Natl. Acad. Sci., **2014**, 111, 12769.

[s42] A. E. Cohen et al., Proc. Natl. Acad. Sci., **2014**, 111, 17122.

[s43] J. Hattne et al., Nat. Methods, **2014**, 11, 545 (cctx.xfel).

[s44] W. Kabsch, Acta Cryst., **2014**, D70, 2204.

[s45] R. Neutze, G. Branden and G. F. X. Schertler, Curr. Opinion Struct. Biol. **2015**, 33, 115.

[s46] K. Nass et al., J. Synchrotron Radiat., **2015**, 22, 225.

[s47] I. Schlichiting and J, Miano, J. Synchrotron Radiat., **2015**, 22, 613.

[s48] P. Fromme. Nature Chem. Biol. **2015**, 11, 895.
SIV Three different $S_1$ models for understanding of the EXAFS results

Scope and applicability of the EXAFS methods for the CaMn$_4$O$_5$ cluster in OEC of PSII was examined in previous paper.\cite{39} The EXAFS experiments provided 1D geometrical parameters that were used for constructions of plausible 3D structures.\cite{2,3} The (4433) valence state was employed for the early EXAFS structure by Yachandra et al.\cite{3,4} and the computational model by Siegbahn\cite{40}, indicating no ambiguity for the assignment of the R(Mn(IV)$_{3(b)}$-Mn(IV)$_{4(a)}$=2.70 Å and R(Mn(IV)$_{3(b)}$-O$_{5(5)}$)=1.80 Å. However, the high-resolution XRD\cite{18} revealed the (3443) valence state in the $S_1$ state. The valence state (3443) is now accepted for the CaMn$_4$O$_5$ cluster in the $S_1$ state.\cite{2,3,10,35-37,44-46} Therefore, the JT effect for the Mn(III)$_{4(a)}$ ion plays an important role for the EXAFS structure by Yano et al.\cite{2,10} under the assumption of the (3443) valence structure.\cite{33-39}

According to the JT deformation formula (see eqs. (2) and (3)), the Mn$_{4(a)}$-O$_{5(5)}$ distances were estimated to be 2.02~2.03 (Å) for O$_{5(5)}$= OH$^-$ and 1.86~1.90 (Å) for O$_{5(5)}$=O$^2$ using the Mn$_{3(b)}$-Mn$_{4(a)}$ distance (2.72~2.73 (Å)) as shown in Table S6. The former and latter Mn$_{4(a)}$-O$_{5(5)}$ distances are almost consistent with the Mn-O distances with about 2.0 and 1.8 (Å) by EXAFS respectively.

The observed Mn$_{4(a)}$-O$_{5(5)}$ distances by the LD XRD without the X-ray damage\cite{30} are longer than 2.0 Å. This observation indicates that one of the Mn-O distances with about 2.0 Å by EXAFS\cite{8,10} can be assigned as the Mn$_{4(a)}$-O$_{5(5)}$ distance of the CaMn$_4$O$_5$ cluster in the $S_1$ structure.

The Mn$_{4(a)}$-Mn$_{3(b)}$ distances under this assignment\cite{39} became 2.71 and 2.75 (Å) respectively for O$_{5(5)}$= OH$^-$ and O$^2$. The latter Mn-Mn distance was consistent with that of 5WS5B\cite{28}. However, the observed Mn$_{4(a)}$-O$_{5(5)}$ distance of 5WS5B was 2.29 Å in contradiction to the assigned value (2.0 Å) for EXAFS. The Mn$_{4(a)}$-Mn$_{3(b)}$ distances were successfully estimated to be 2.74-2.78 Å for 5WS5B on the basis of the Mn$_{4(a)}$-O$_{5(5)}$H distances with 2.06-2.14 Å as shown in Table S1. This means that the X-ray damage of the Mn$_{4(a)}$-O$_{5(5)}$ distance of 5WS5B\cite{28} is about 0.1~0.2 Å in accord with the estimated values in Table 4.

The Mn-O distance of 1.8 Å by EXAFS\cite{10} was consistent with the optimized Mn$_{4(a)}$-O$_{5(5)}$ distances by QM and QM/MM\cite{39-46}. The heavy atom distances by EXAFS were wholly

\[ [s39] \] I. Schlichting, Nature, 2015, 517, 26.
\[ [s40] \] C. Kupitz et al., Nature, 2014, 513, 261-265.
\[ [s41] \] N. K. Sauter et al., Nature, 2016, 533, E1-E2.
\[ [s42] \] F. D. Fuller et al, Nat. Methods, 2016, DOI. 10.1038/NMETH.4195.
\[ [s43] \] I. Inoue et al., Proc. Natl. Acad. Sci., 2016, 113, 1492.
\[ [s44] \] C. Gati et al., Proc. Natl. Acad. Sci., 2017, 114, 2253.
\[ [s45] \] T. Takanashi et al., Phys. Chem. Chem Phys. 2017, DOI:10.1039/c7cp01669g.
compatible with those of the $dz^2$-JT type R-structure in Fig. 1A by large scale QM/MM under the assumption of $O_1(5)$=O$^2-$ and W2=H$_2$O$^{[37]}$. The R structures (SSB=0.6~0.7) by QM and QM/MM were often used to emphasize the X-ray damages of the C$_R$ (SSB=0.2~0.3) structure by XFEL$^{[30]}$. The optimized Mn$_{3(b)}$-O$_{(5)}$ distance by QM/MM$^{[35]}$ was 1.78 Å, supporting the assumption in Tables 1-5. However, available XRD$^{[18,30]}$ and SFX$^{[28,29]}$ results revealed that the Mn$_{3(b)}$-O$_{(5)}$ distance is longer than 2.0 Å in contradiction to that of the $dz^2$-JT-type R-structure (see Fig. 1A) at the present stage. The high-resolution (<1.5 Å) low-dose XRD structure is desirable for precise determination of the Mn$_{4(a)}$-O$_{(5)}$ and Mn$_{3(b)}$-O$_{(5)}$ distances for further discussions on the possibility of the $dz^2$-JT-type R-structure with $O_1(5)$=O$^2-$: It is noteworthy that subtle different three structures (A-C) in Fig. 1 are formally geometrical isomers obtained by proton shift from W2 to O$_{(5)}$. Therefore dynamical mutual conversions among them may be feasible depending on proton dynamics in room temperature.

The JT deformation model in Fig. 1B provides the R-structure ($\delta$=0.55) for which the Mn$_{3(b)}$-Mn$_{4(a)}$, Mn$_{4(a)}$-O$_{(5)}$ and Mn$_{3(b)}$-O$_{(5)}$ distances are 2.70, 1.98 and 2.00 (Å), respectively (see Fig. S2). The Mn$_{4(a)}$-O$_{(5)}$ distance by EXAFS can be estimated by the mixing of the Mn$_{4(a)}$-O$_{(5)}$ distances of this B-type S$_1$(R) structure and L-opened S$_0$(C$_L$) structure as follows:

$$R(Mn_{4(a)}-O_{(5)}) = (1-\alpha) \cdot R(Mn_{4(a)}-O_{(5)}) = 1.98 \text{ for } S_1(R) + \alpha \cdot R(Mn_{3(b)}-O_{(5)}) = 2.98 \text{ for } S_0(C_L). \quad (s2)$$

The R(Mn$_{4(a)}$-O$_{(5)}$) value calculated by eq. (s2) can be used for estimation of the Mn$_{3(b)}$-Mn$_{4(a)}$ distance by eq. (2). Table S7 summarizes the calculated results. The Mn$_{3(b)}$-Mn$_{4(a)}$ distances (2.72~2.73 Å) by EXAFS were reproduced by 5~6 % mixing of the S$_0$(C$_L$). The B-type structure with the (dy$^2$) JT deformation (see Fig. 1B) has the Mn$_{3(b)}$-Mn$_{4(a)}$ distances with two 2.7, one 2.8 and null 3.1 (Å), the so-called {2, 1, 0} structure in spite of O$_{(5)}$=OH, supporting the original EXAFS model by Yano et al.$^{[2,3,10]}$. There is no need to assume O$_{(5)}$=O$^2-$ for explanation of the observed {2, 1, 0} structure$^{[39]}$ in agreement with the LD XRD structure$^{[30]}$. According to the JT deformation in Fig. 1 in the text, the discrepancy between the EXAFS$^{[2,3,10]}$ and XRD$^{[30]}$ was removed out although the O$_{(5)}$ was protonated.

The Mn$_{3(b)}$-Mn$_{4(a)}$ distances (2.75~2.77 Å) for the B-monomer of the LD XRD$^{[30]}$ and new SFX structure (5WS5A(B))$^{[28]}$ were also reproduced by 10~15 % mixing of the S$_0$(C$_L$). The estimated Mn$_{4(a)}$-O$_{(5)}$ distances were 2.08~2.13 (Å) in compatible with the observed value for the B-monomer$^{[30]}$ and the 5 % reduced Mn$_{4(a)}$-O$_{(5)}$ distance of 5WS5A(B)$^{[28]}$ SFX structure by correction of the X-ray damage (see Table 4)$^{[51,52]}$. The estimated Mn$_{3(b)}$-O$_{(5)}$ distances are 2.04~2.06 (Å) in agreement with the observed values for the B-monomer$^{[30]}$ and 5WS5A(B) with preflash$^{[28]}$. Thus, the (dy$^2$) JT deformation structure, namely B-structure in Fig. 1B, is in agreement with the original EXAFS$^{[10]}$ structure, the structure of B monomer by LD XRD$^{[30]}$ and SFX(5WS5) structure with preflash$^{[28]}$. The key concept for understanding of the structural deformations of the CaMn$_4$O$_5$ cluster is the JT effect of the Mn(III) ion (see Fig. 1).
The Mn\textsubscript{4(a)}-O(5) distances were estimated to be 2.18–2.22 (Å) for O(5)=OH\textsuperscript{−} and 2.18–2.26 (Å) for O(5)=O\textsuperscript{2−} using the Mn\textsubscript{3(b)}-Mn\textsubscript{4(a)} distance (2.80–2.82 (Å)) under the assumption of the horizontal JT (dx\textsuperscript{2}) deformation as shown in Fig. 1C\textsuperscript{[33, 34]}. The reassigned EXAFS structure\textsuperscript{[35-37]} with R(Mn\textsubscript{3(b)}-Mn\textsubscript{4(a)})=2.80–2.82 Å is consistent with the LD XRD structure of A-monomer\textsuperscript{[28]} in the dimer of OEC of PSI and the 4UB6 structure by the damage-free XFEL method\textsuperscript{[27]}. The reassigned EXAFS structure is also consistent with the recent SFX structure by Young et al.\textsuperscript{[29]} (see Table S6). Thus, no significant structural differences were observed for XRD(A-monomer)\textsuperscript{[30]}, XFEL(4UB6)\textsuperscript{[27]}, reassigned EXAFS\textsuperscript{[37-39]} and SFX\textsuperscript{[29]} structures. The different geometrical structures of the CaMn\textsubscript{4}O\textsubscript{5} cluster in A- and B-monomers by the LD XRD experiments\textsuperscript{[30]} provided experimental foundations for reasonable explanation and understanding of the EXAFS\textsuperscript{[3-10]}, XRD\textsuperscript{[11-19]}, XFEL structures\textsuperscript{[27]}, new SFX structures\textsuperscript{[28, 29]} and theoretical models\textsuperscript{[33-46]} in the S\textsubscript{1} state of OEC of PSI. Small but non-negligible geometry changes in the S\textsubscript{1} state with the (3443) valence state\textsuperscript{[39]} indicate the labile nature\textsuperscript{[33, 36]} of the CaMn\textsubscript{4}O\textsubscript{5} cluster with the JT deformations controlled by strong hydrogen bonding interaction of proteins (see Fig. 4). The QM/MM/MD calculations are necessary for theoretical investigation of subtle geometrical fluctuations induced by proton and protein dynamics in the OEC of PSI\textsuperscript{[37-39]}.

Table S6  The Mn\textsubscript{4(a)}–O(5) and Mn\textsubscript{3(b)}–O(5) distances (Å) of the CaMn\textsubscript{4}O\textsubscript{5} cluster in the states of OEC of PSI by estimation procedure (eqs. (2) and (3)) using the Mn\textsubscript{4}–Mn\textsubscript{3} distance by EXAFS.\textsuperscript{[2, 3 10]}

| Structures               | Mn\textsubscript{4}–Mn\textsubscript{3} | Mn\textsubscript{4}–O(5)\textsuperscript{[a]} | Mn\textsubscript{3}–O(5)\textsuperscript{[b]} | SSB\textsuperscript{[c]} | Topology\textsuperscript{[d,e]} | Ref.\textsuperscript{[f]} |
|-------------------------|---------------------------------------|---------------------------------------------|---------------------------------------------|-----------------|-----------------------------|----------------|
| EXAFS                   | Estimation                            | QM/MM                                       |                                              |                 |                             |                 |
| Berkeley II             | 2.73                                  | 2.04 (1.90)                                 | 2.0 (1.8)                                   | 0.50 (0.63)     | R, \{2, 1, 0\}             | O(5)=OH(O\textsuperscript{2−}) |
| Berkeley IIa            | 2.72                                  | 2.02 (1.86)                                 | 2.0 (1.8)                                   | 0.51 (0.67)     | R, \{2, 1, 0\}             | O(5)=OH(O\textsuperscript{2−}) |
| Berkeley III            | 2.72                                  | 2.02 (1.86)                                 | 2.0 (1.8)                                   | 0.51 (0.67)     | R, \{2, 1, 0\}             | O(5)=OH(O\textsuperscript{2−}) |
| Berkeley III-Cl         | 2.72                                  | 2.02 (1.86)                                 | 2.0 (1.8)                                   | 0.51 (0.67)     | R, \{2, 1, 0\}             | O(5)=OH(O\textsuperscript{2−}) |
| LS QM/MM\textsuperscript{[g]} | 2.71                                  | 1.82(1.82)                                  | 1.77                                        | 0.71            | R, \{2, 1, 0\}             | O(5)=O\textsuperscript{2−}   |
| Reassign. II            | 2.82                                  | 2.22(2.26)                                  | 2.0 (1.8)                                   | 0.33(0.31)      | C\textsubscript{R}, \{2, 1, 0\} | O(5)=OH(O\textsuperscript{2−}) |
| Reassign. Ia            | 2.80                                  | 2.18(2.18)                                  | 2.0 (1.8)                                   | 0.35(0.35)      | C\textsubscript{R}, \{2, 1, 0\} | O(5)=OH(O\textsuperscript{2−}) |
The Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distance was estimated using the Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distance in eqs. (2) and (3) under the assumption of O\(_{\text{S}}\)=OH\(^{-}\) and O\(^{2-}\) (in parentheses). The Mn(IV)\(_{\text{III}}\)-O\(_{\text{S}}\) distance estimated for O\(_{\text{S}}\)=OH\(^{-}\) and O\(^{2-}\) (in parentheses), Structural symmetry breaking (SSB) parameter, Topology, The numbers of the short (2.7 Å), long (2.8 Å) and longer (3.1 Å) Mn-Mn distances are given by \{a, b, c\} (see also Fig. S2), The assignment of the O\(_{\text{S}}\) site, Low spin (LS) QM/MM computational result in ref. [38], XFEL results (see Fig. 1C) in ref. [27] where the estimated values using the Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) or Mn\(_{\text{IV}}\)-Mn\(_{\text{III}}\) distance are given in the parentheses, SFX results (see Fig. 1B) in ref. [28] where the estimated Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distances by using the observed Mn\(_{\text{IV}}\)-Mn\(_{\text{III}}\) as well as the observed Mn\(_{\text{III}}\)-O\(_{\text{S}}\) distances are given.

Table S7 The Mn\(_{\text{IV}}\)-Mn\(_{\text{III}}\) and Mn\(_{\text{III}}\)-O\(_{\text{S}}\) distances of the CaMn\(_{\text{IV}}\) cluster in the S\(_{\text{1}}\) state of OEC of PSII based on the estimation procedure using the Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distance obtained by the mixing of the S\(_{\text{1}}\)(R) (B-type in Fig. 1B) and S\(_{\text{0}}\)(C\(_{\text{X}}\)) structures (eq. s1)

| Structures\(^{[a]}\) | \(\alpha(R)\) (%\(^{[b]}\)) | Mn\(_{\text{IV}}\)-Mn\(_{\text{III}}\) | Mn\(_{\text{IV}}\)-O\(_{\text{S}}\)\(^{[c]}\) | Mn\(_{\text{III}}\)-O\(_{\text{S}}\)\(^{[d]}\) | SSB\(^{[e]}\) | Topology\(^{[f]}\) |
|-------------------|-----------------|----------------|----------------|----------------|---------|----------------|
| S\(_{\text{1}}\)(R) | 0 | 2.70 | 1.98 | 2.00 | 0.55 | R |
|                  | 5 | 2.72 | 2.03 | 2.02 | 0.50 | R |
| (1-\(\alpha\)) S\(_{\text{1}}\)(R) | 10 | 2.75 | 2.08 | 2.04 | 0.45 | R |
| +\(\alpha\) S\(_{\text{0}}\)(C\(_{\text{X}}\)) | 15 | 2.77 | 2.13 | 2.06 | 0.40 | R |
|                  | 20 | 2.80 | 2.18 | 2.08 | 0.35 | C\(_{\text{R}}\) |
|                  | 25 | 2.83 | 2.23 | 2.10 | 0.30 | C\(_{\text{R}}\) |

\(^{[a]}\)The Mn\(_{\text{IV}}\)-Mn\(_{\text{III}}\) and Mn\(_{\text{III}}\)-O\(_{\text{S}}\) distances were estimated by using the Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distance given by the mixing of the S\(_{\text{1}}\)(R) and S\(_{\text{0}}\)(C\(_{\text{X}}\)) structures, \(^{[b]}\)The mixing ratio \(\alpha(C\(_{\text{X}}\))\) for the S\(_{\text{1}}\)(R) and the S\(_{\text{0}}\)(C\(_{\text{X}}\)) structures, \(^{[c]}\)The Mn\(_{\text{IV}}\)-O\(_{\text{S}}\) distance for the (1-\(\alpha\))S\(_{\text{1}}\)(R) + \(\alpha\)S\(_{\text{0}}\)(C\(_{\text{X}}\)) structure, \(^{[d]}\)The Mn\(_{\text{III}}\)-O\(_{\text{S}}\) distance for the mixed (1-\(\alpha\))S\(_{\text{1}}\)(R) + \(\alpha\)S\(_{\text{0}}\)(C\(_{\text{X}}\)) structure, \(^{[e]}\)Structural symmetry breaking (SSB) parameter, \(^{[f]}\)the right-opened structure (R).
SV High and low oxidation paradigms and two flash SFX structures for the OO bonding

The charge degree of freedom is very important for understanding of redox properties of the strongly correlated electron systems (SCES) such as 3d metal clusters[39]. The valence states of Mn ions are variable from Mn(II) to Mn(VII). Therefore, the low- and high-oxidation paradigms[2, 3, 47, s46-s50] have been proposed for valence state of the CaMn$_4$O$_5$ cluster in OEC of PSII. The valence state of the Mn$_{4(a)}$Mn$_{3(b)}$Mn$_{2(c)}$Mn$_{1(d)}$ ions for the S$_0$ state is II, III, III and III, namely (2333), for the low-oxidation (LO) paradigm[47, s49, s50]. Therefore, the valence state of the CaMn$_4$O$_5$ cluster in the S$_1$ and S$_3$ states are (2343) (or (3333)) and (3443) respectively in the LO paradigm[47, s49, s50].

On the other hand, the eight spin structures are feasible for four spin-site systems such as the CaMn$_4$O$_5$ cluster under the BS approximation.[33-39] On the other hand, the six mixed valence (MV) configurations are possible for the Mn(III)$_2$Mn(IV)$_2$ valence configuration. Therefore, we have constructed total 8 x 6 = 48 BS configurations[35-37] for the CaMn$_4$O$_5$ cluster in the S$_1$ state. The energy diagrams obtained for the 48 BS configurations by UB3LYP under the assumption of the XRD structure at 1.9 Å resolution[18] have shown that the (3443) MV configuration was the ground state in the S$_1$ state. However, the ground spin state of the (3443) configuration was S=3[33-37] in contradiction to the EPR result (S=0)[1, 2]. Therefore, refinements of the XRD structure[18] by full geometry optimization technique have been necessary for reproduction of the S=0 ground spin state[33-39].

Thus, the HO paradigm has been acceptable for the CaMn$_4$O$_5$ cluster on the theoretical ground. Recently, Dau et al. [s51] performed the extensive X-ray emission spectroscopy of the CaMn$_4$O$_5$ cluster in OEC of PSII, supporting the HO paradigm[s52].

Here, the calculated results based on the LO paradigm[s49, s50] are briefly reviewed for comparison.

The low oxidation (LO) S$_{1a}$ model with (2343) valence configuration by Gatt et al. [s49] indicated that the calculated Mn$_{4(a)}$-Mn$_{3(b)}$, Mn$_{4(a)}$-O$_{(5)}$, Mn$_{1(d)}$-O$_{(5)}$ and Mn$_{3(b)}$-O$_{(5)}$ distances were 3.03, 2.60, 2.64 and 2.61 (Å) respectively. Therefore, the estimated Mn$_{4(a)}$-Mn$_{3(b)}$ distances using the Mn$_{4(a)}$-O$_{(5)}$ distance in eq. (3) are 3.01 and 2.91 (Å) for O$_{(5)}$=OH$^-$ and O$^2-$ respectively. The calculated Mn$_{4(a)}$-Mn$_{3(b)}$ by Gatt et al. [s49] is quite similar to the estimated value for O$_{(5)}$=OH$^-$. However, the calculated Mn$_{3(b)}$-O$_{(5)}$ distance is 2.61 Å, indicating that O$_{(5)}$=H$_2$O is rather reasonable for the LO S$_{1a}$ structure because the Mn(III)$_{3(b)}$-O$_{(5)}$H distances are usually shorter than 2.4 Å (see text)[39]. The optimized LO structure was formally similar to the high-dose (0.43 MGy) XRD structure[18]. On the other hand, Yamaguchi at al. [45] have shown that the valence state of the XRD structure[18] was (3333) because of the internal reduction of the Mn(IV)$_{4(a)}$ and Mn(IV)$_{3(b)}$ ions.
via charge transfers from oxygen dianions, indicating formation of two holes at oxygen sites (2O \cdot ) in the HO paradigm.

The LO $S_{1b}$ model with (2343) valence configuration by Petrie et al. [s50] provided that the calculated $Mn_{4(a)}$-$Mn_{3(b)}$, $Mn_{4(a)}$-$O_{(5)}$, $Mn_{1(d)}$-$O_{(5)}$ and $Mn_{3(b)}$-$O_{(5)}$ distances were 2.85, 2.28, 2.66 and 2.37 (Å) respectively. The estimated $Mn_{4(a)}$-$Mn_{3(b)}$ distances using the $Mn_{4(a)}$-$O_{(5)}$ distance were 2.85 and 2.83 (Å) for $O_{(5)}$=OH\textsuperscript{−} and O\textsuperscript{2−} respectively. The calculated $Mn_{4(a)}$-$Mn_{3(b)}$ distance was quite similar to the estimated value for $O_{(5)}$=OH\textsuperscript{−}. The $Mn_{3(b)}$-$O_{(5)}$ distance calculated for LO $S_{1b}$ was 2.37 Å in compatible with the Jahn-Teller (JT) elongated Mn(III)-OH bond. Thus, the LO $S_{1b}$ (2343) structure by Petrie et al. [s49, s50] was compatible with XFEL structure [28] and structure of A-monomer by LD XRD [30], supporting the LO paradigm. The LO $S_{1b}$ (2343) structure is formally regarded as the two-electron reduced state of the HO (3443) structure [s52-s56]. The full optimized structure with the (3443) valence state (namely HO paradigm) under the assumption $O^{\text{5−}}$=OH\textsuperscript{−} was also compatible with the XFEL structure [27, 48]. However, the LO $S_{1b}$ (2343) structure was different from the SFX (preflash 5WS5) [28] and structure of B-monomer by LD XRD [30].

The geometrical structures of the $S_3$ intermediates revealed by the SFX [28, 29] were different between A and B monomers in OEC of PSII. Therefore, the geometrical characteristic is the same as that of the $S_1$ state [30] examined in this paper. Tables S8 summarizes the SFX experimental results after two flash illumination [28, 29]. Suga et al. [28] reported two different (OEX and OYE) SFX structures. The two flash structure of A-monomer of preflash 5WS6(OEX), namely 5WS6A(OEX), by Suga et al. [28] indicated that the $Mn_{4(a)}$-$Mn_{3(b)}$, $Mn_{4(a)}$-$O_{(5)}$, $Mn_{1(d)}$-$O_{(5)}$ and $Mn_{3(b)}$-$O_{(5)}$ distances were 2.84, 2.31, 2.70 and 2.02 (Å) respectively. The estimated $Mn_{4(a)}$-$Mn_{3(b)}$ distances are 2.87 and 2.83 (Å) for $O_{(5)}$=OH\textsuperscript{−} and O\textsuperscript{2−} respectively. The observed structure of 5WS6A(OEX) [28] is rather similar to the $S_1$ structure of A-monomer of low dose (LD) XRD [30] and the XFEL [18] structure. This means that the valence state of the 5WS6A(OEX) structure is similar to the HO(3443) $S_1$ valence state. The internal reduction of the Mn(IV) ion into Mn(III) ion via the charge transfer from dianions might occur in the (4444) configuration to afford the (3443) structure in the HO paradigm. On the other hand, it is noteworthy that the (3443) configuration is responsible for the $S_3$ state in the LO paradigm [47, s49, s50].

The two flash structure of B-monomer of preflash 5WS6(OEX), namely 5WS6B(OEX), by Suga et al. [28] elucidated that the $Mn_{4(a)}$-$Mn_{3(b)}$, $Mn_{4(a)}$-$O_{(5)}$, $Mn_{1(d)}$-$O_{(5)}$ and $Mn_{3(b)}$-$O_{(5)}$ distances were 2.78, 2.30, 2.69 and 2.02 (Å) respectively. The estimated $Mn_{4(a)}$-$Mn_{3(b)}$ distances using the observed $Mn_{4(a)}$-$O_{(5)}$ distance were 2.86 and 2.83 (Å) for $O_{(5)}$=OH\textsuperscript{−} and O\textsuperscript{2−} respectively. On the other hand, the $Mn_{4(a)}$-$O_{(5)}$ distances estimated by the observed $Mn_{4(a)}$-$Mn_{3(b)}$ distance (2.78 Å) were 2.14 and 2.10 (Å) for $O_{(5)}$=OH\textsuperscript{−} and O\textsuperscript{2−}, respectively. The 5WS6B(OEX) structure is rather similar to the $S_1$ structure of B-monomer by LD XRD [30]. This means that the valence state of the
5WS6B(OEX) structure is similar to the (3443) valence state obtained by the internal reduction of the Mn(IV) ion into Mn(III) ion in the S₃ (4444) configuration of the HO paradigm. However, the (3443) configuration is responsible for the S₁ state in the LO paradigm[47, s49, s50] as mentioned above. Therefore, several other explanations of the SFX(5WS6(OEX)) may be feasible in the case of the LO paradigm.

The two flash structure of a monomer of preflash 5WS6A(OEY) by Suga et al. [28] showed that the Mn₄(a)−Mn₃(b), Mn₄(a)−O(5), Mn₁(d)−O(5) and Mn₃(b)−O(5) distances were 2.71, 2.30, 2.80 and 2.02 (Å) respectively. Interestingly, these values were almost the same as those of preflash dark stable S₁ structure (5WS5B). On the other hand, the corresponding optimized parameters for the R-opened hydroxide inserted S₃ structure (S₃abcb) with the HO (4444) valence structure[53] were 2.72, 1.80, 3.51 and 1.83 (Å) respectively. The calculated short Mn₄(a)−O(5) distance (1.80 Å) is well consistent with the general trend; R(Mn(IV)₄(a)−O(5))=1.80 Å in the text. The estimated Mn₄(a)−Mn₃(b) distances using the observed Mn₄(a)−O(5) distance were 2.86 and 2.83 (Å) for O(5)=OH⁻ and O²⁻ respectively. On the other hand, the Mn₄(a)−O(5) distances estimated by the observed Mn₄(a)−Mn₃(b) distance (2.75 Å) were 2.00 and 1.82 (Å) for O(5)=OH⁻ and O²⁻ respectively. The observed Mn₄(a)−Mn₃(b) distance (2.71 Å) for 5WS6A(OEY)[28] was compatible with the corresponding calculated value (2.72 Å) for S₃abcb. However, the estimated Mn₄(a)−O(5) distance by eq. (3) is shorter by 0.50 Å than the observed value[28]. On the other hand, the calculated Mn₁(d)−O(5) distance of the S₃ structure (S₃abcb) is longer by 0.71 Å than the observed value for 5WS6A(OEY)[28] because of the insertion of hydroxide. Nevertheless, the Mn₁(d)−O(5) distance (2.8 Å) by SFX[28] was quite similar to that of the S₁ structure. This means that the SFX (5WS6A(OEY)) structure may be different from the hydroxide-inserted S₃ structure (S₃abcb)[44] with the (4444) valence configuration. The elongated Mn₄(a)−O(5) distance (2.30 Å) of 5WS6A(OEY) may indicate the internal reduction of the Mn(IV)₄(a) into Mn(III)₄(a) ion via charge transfer from the oxygen dianion. This means the formation of the (3444) valence configuration with one active oxygen hole O ⋅ [2, 3] or the (3443) valence configuration with two active oxygen holes (2O ⋅ ⋅ ⋅) [2, 3, s52−s56]. The O–O bond formation via the radical coupling[3, 45, s54−s56] may be feasible in the latter situation. Isobe et al.[s56] already reported the optimized UB3LYP structures of possible nine intermediates such as the peroxide-inserted structure, namely Mn(III)₄(a)−OO−Mn(III)₁(d), in the S₃ state where the Mn(IV) ions are reduced to Mn(III) ions in the formal (4444) S₃ structure. Suga et al.[28] indeed suggested the peroxide-inserted structure for 5WS6A(OEY) under the assumption of water insertion in the S₂ to S₃ transition. However, the (3443) valence state for the peroxide was not consistent with the (4444) valence state revealed for the S₃ state by the XES[51], although the (3443) configuration is responsible for the S₃ state in the LO paradigm[47, s49, s50]. Therefore, several other explanations of the SFX(5WS6A(OEY)) structure may be possible in the case of the LO paradigm by Pace et al.[47].
The two flash structure of B monomer of preflash 5WS6B(OEY) by Suga et al. [28] elucidated that the Mn_{4(a)}-Mn_{3(b)}, Mn_{4(a)}-O(5), Mn_{1(d)}-O(5) and Mn_{3(b)}-O(5) distances were 2.77, 2.29, 2.81 and 1.99 Å respectively. Interestingly, these values were almost the same for those of preflash dark stable S\(_1\) structure (5WS5A) in the dark stable state. The estimated Mn_{4(a)}-Mn_{3(b)} distances using the observed Mn_{4(a)}-O(5) distance are 2.86 and 2.83 Å for O(5)=OH\(^-\) and O\(^2-\), respectively. On the other hand, the Mn_{4(a)}-O(5) distances estimated by the observed Mn_{4(a)}-Mn_{3(b)} distance (2.77 Å) are 2.12 and 2.06 Å for O(5)=OH\(^-\) and O\(^2-\) respectively. The 5WS6B(OEY) structure is rather similar to the S\(_1\) structure of B-monomer of LD XRD[30]. This means that the valence state of the 5WS6B(OEY) structure is similar to the (3443) valence state responsible for the S\(_3\) state in the low oxidation (LO) paradigm[47, s49, s50]. Thus, the two flash SFX structures of A- and B-monomers of 5WS6B(OEY) are a little different like in the case of LD XRD structures[30] for dark stable state discussed in the text. The elongated Mn_{4(a)}-O(5) distance (2.29 Å) of 5WS6B(OEY) suggests the internal reduction of the Mn(IV)\(_{4(a)}\) into Mn(III)\(_{4(a)}\) ion accompanied with formation of oxygen hole \(\text{O}^-\) [s52-s56]. Therefore, the O-O bond formation might be conceivable for 5WS6B(OEY)[28], for which the observed O(5)-O(6) distance was about 1.5 Å. However, the OO bond formation inevitably entailed the (3443) valence state in contradiction to the (4444) valence state by XES [s51].

The two flash structure of A-monomer of no preflash 5TIS by Young et al. [29] indicated that the Mn_{4(a)}-Mn_{3(b)}, Mn_{4(a)}-O(5), Mn_{1(d)}-O(5) and Mn_{3(b)}-O(5) distances were 2.65, 2.25, 2.76 and 2.13 Å respectively. Interestingly, these values are rather similar to the corresponding values of preflash 5WS6A(OEY)[28]. The estimated Mn_{4(a)}-Mn_{3(b)} distances using the observed Mn_{4(a)}-O(5) distance were 2.84 and 2.82 Å for O(5)=OH\(^-\) and O\(^2-\), respectively. On the other hand, the Mn_{4(a)}-O(5) distances estimated by the observed Mn_{4(a)}-Mn_{3(b)} distance (2.65 Å) were 1.88 and 1.58 Å for O(5)=OH\(^-\) and O\(^2-\) respectively. The observed Mn_{4(a)}-Mn_{3(b)} distance for 5TISA was rather similar to the calculated distance for the hydroxide inserted S\(_3\) structure (S_{3abcb}). However, the calculated Mn_{4(a)}-O(5) distance for S_{3abcb} was shorter by 0.45 Å than the observed value for 5TISA [29]. On the other hand, the calculated Mn_{1(d)}-O(5) distance for S_{3abcb} was longer by 0.75 Å than the corresponding value for 5TISA[29] that is quite similar to the Mn_{1(d)}-O(5) distance of the S\(_1\) structure. The structural characteristic is similar between 5WS6A(OEY)[28] and 5TISA[29]. The difference between these structures was only limited to the existence [28] or no existence[29] of the inserted O(6) atom. This means that the SFX structure by 5TISA[29] is largely different from the hydroxide-inserted S\(_3\) structure (S_{3abcb}) with the (4444) configuration although Krewald et al. [44] has proposed the right-opened S\(_3\) structure with hydroxide anion inserted at the Mn_{1(d)} site. It is noteworthy that the observed results for no preflash 5TISB[29] were fully compatible with those of no preflash 5GTIB[28]. The SFX structures [29] of A- and B-monomers by 5TISB were different as shown in Table S8.
As shown in Table S4, the EXAFS experiments elucidated formation of 62% S3 state and 30% S2 state after 2 flash. Therefore, difference Fourier maps were used to elucidate the structural changes by the SFX experiments in the S2 to S3 transition. Young et al. [29] has concluded no water insertion (no O(6) of 5WS6A(OEY)) in the S2 to S3 transition on the basis of the difference Fourier density map for 5TISA. However, Yamaguchi et al. [39] and Shoji et al. [53] elucidated that the optimized structure of the S3 state without hydroxide anion was the left-opened structure (see Fig. S3) instead of the right-opened structure by SFX(5TISA) [29]. Moreover, the long Mn4(a)-O(5) distance (2.25 Å) of 5TISA suggests the internal reduction of the Mn(IV)4(a) into Mn(III)4(a) ion. This means that there remain many other possibilities in the S3 state as mentioned above. Several explanations of the SFX(5TISA) results may be conceivable on the theoretical grounds. In fact, Isobe et al. [56] performed full geometry optimizations of possible nine intermediates with different ground spin states in the S3 state. Several optimized structures among them are possible candidates for the S3 state. For example, the right-opened S3 (4444) structure with the oxo bond inserted at the Mn1(d) site, namely Mn1(d)=O(6), is such a candidate because the O(5)...O(6) distance is shortened to be about 2.0 Å.

Suga et al. [28] and Young et al. [29] have presented different conclusions for two flash SFX results, namely water insertion (O(6)) or no water insertion (no O(6)) in the S2 to S3 transition although the geometrical parameters for 5WS6A(OEY) [28] and 5TISA [29] are not so different. Isobe et al. proposed the chemical equilibrium model for theoretical understanding of the S3 state. Further experimental and theoretical efforts are necessary for elucidation of water insertion or no insertion in the S3 state in the Kok cycle for water oxidation in OEC of PSII. The geometrical parameters, particularly Mn4(a)-O(5), for the two flash structures 5WS6A(OEY) [28] and 5KAIA(B) [29] are rather similar to those of the S1(3443) structure [33-37], suggesting the internal reduction of the oxygen dianions (formation of O ••) [45,54-56] in the high-oxidation paradigm. However, the formation of the radical site is in contradiction of the (4444) valence state by XES [51]. The Mn3(b)-O(5) distances of the SFX structures [28,29] were about 2.0 Å. However, the optimized Mn3(b)-O(5) distances [52-56] were about 1.8 Å under the assumption of O(5)=O2-, suggesting the reduction from Mn(IV)3(b) to Mn(III)3(b) ion. Probably, the experimental uncertainty of SFX structures [28,29] at the 2.2 ~ 2.3 Å resolution is larger than 0.2 Å. Moreover, the damage of SFX structures by strong X-ray pulses of 10 ~ 20 femtosecond durations may be 0.1 ~ 0.2 Å as shown in Table 4. Therefore, the long Mn4(a)-O(5) (2.2~2.3 Å) and Mn3(b)-O(5) (about 2.0 Å) distances by SFX [28,29] may not be conclusive, suggesting possibilities of several intermediates with different O(5)...O(6) distances on the theoretical ground [55-56] in the water-inserted scenario in the S3 state.

Finally, different explanations of the SFX results [28,29] are conceivable in the scenario of no water insertion. [29,53] For example, the large-scale QM/MM calculations [53] indicated possibility of a disorder structure consisted of superposition (mixing) of the right-opened (R) S2(R) structure
and the left-opened (L) S₃(L) structure in this scenario at the S₂ to S₃ transition (see Table S4). The Mn₄(a)-O(5) distances by SFX²⁸,²⁹ were supposed to be determined by the mixing of the short and long Mn₄(a)-O(5) distances of the R- and L-opened structures.[s53]

\[
R(\text{Mn}_{4(a)}-\text{O}(5)) = (1 - \alpha) \{R(\text{Mn}_{4(a)}-\text{O}(5)) = 1.80 \text{ for S}_2(R)\} + \alpha \{R(\text{Mn}_{3(b)}-\text{O}(5)) = 3.10 \text{ for S}_3(L)\}. \tag{s3}
\]

The distance between the O(5) for S₂(R) and O(5) (=O(6)) for S₃(L) was calculated to be about 1.3 Å as illustrated in Fig. S3.[s53] The estimated O(5)-O(6) distance is rather consistent with the observed value (1.5 Å) by SFX²⁸,²⁹. The magnitude of the densities on the O(5) and O(6) sites may be different depending of the ratio of the S₂(R) and S₃(L) structures in this disordered structure. The positions of the Mn₄(a) and O(4) ions are also shifted significantly in the disordered structure in Fig. S3. The SFX structures²⁸,²⁹ at higher resolution than about 2.3 Å are really desirable for further theoretical discussions.

The (3443) valence state corresponds to the S₃ state of the LO paradigm⁴⁷,⁴⁹,⁵⁰, providing possibility of different explanations of the SFX structures after two flash illuminations. In this paper two different S₁ structures discovered by Tanaka et al. [³⁰] were mainly examined by using the JT deformation formulae based on the HO paradigm in the text. The SFX results²⁸,²⁹ also indicated the subtle geometry differences between the A and B monomers in the S₃ state. Further spectroscopic investigations on the valence states of four Mn ions of the CaMn₄O₅ cluster are inevitable for elucidation of scope and applicability of the low⁴⁷,⁴⁹,⁵⁰- and high²,³,⁴⁶-oxidation paradigms for valence states of the CaMn₄O₅ cluster in OEC of PSII. Moreover, the LD XRD, SFX, XES and EPR experiments together with computational studies are necessary for elucidation of the geometrical, electronic and spin structures of the S₃ intermediate in detail.

[s46] I. Zaharieva, P. Chernev, G. Berggren, M. Anderlund, S. Styring, H. Dau and M. Haumann, Biochemistry, 2016, 55, 4197-4311.

[s47] C. J. Pollock, M. U. Delgado-Jaime, M. Atanasov, F. Neese and S. DeBeer, J. Am. Chem. Soc., 2014, 136, 9453-9463.

[s48] K. M. Davis, M. C. Palenik, L. Yan, P. F. Smith, G. T. Seidler, G. C. Dismukes and Y. N. Pushkar, J. Phys. Chem. C, 2016, 120, 3326-3333.

[s49] P. Gatt, S. Petrie, R. Stranger and R. J. Pace, Angew. Chem. Int. Ed., 2012, 51, 12025-12028.

[s50] S. Petrie, R. J. Pace and R. Stranger, Angew. Chem. Int. Ed., 2015, 54, 7120-7124.

[s51] I. Zaharieva, P. Chernev, G. Berggren, M. Anderlund, S. Styring, H. Dau and M. Haumann, Biochemistry, 2016, 55, 4197-4211.

[s52] K. Yamaguchi, S. Yamanaka, H. Isobe, T. Saito, K. Kanda, Y. Umena, K. Kawakami, J. –R. Shen, N. Kamiya, M. Okumura, H. Nakamura, M. Shoji and Y. Yoshioka, Int. J. Quant. Chem., 2013, 113, 453-473.

[s53] M. Shoji, H. Isobe, T. Nakajima, Y. Shigeta, M. Suga, F. Akita, J.-R. Shen and
Table S8  The Mn$_4$-Mn$_3$ distances of the CaMn$_4$O$_5$ cluster in the two flash states of OEC of PSII by SFX methods$^{[28,29]}$ and estimation procedure (eqs. 2 and 3)

| Structures   | Mn$_4$–Mn$_3$ | Mn$_4$–Mn$_3$[a] | Mn$_4$–O$_{(5)}$[b] | Mn$_3$–O$_{(5)}$[c] | O$_{(5)}$[d] | SSB[e] | Topology[f] |
|--------------|---------------|------------------|--------------------|---------------------|-------------|-------|-------------|
|              | XRD           | (Estimation)     | Exp.(Est.)         | Exp.                |             |       |             |
| 5GTIA        | 2.94          | (2.88)$^{[a1]}$ | 2.34               | 2.02                | O$_{(5)}$=OH$^-$| 0.19  | C$_R$       |
| (no preflash)|               | (2.84)           | 2.34               | 2.02                | O$_{(5)}$=O$^{2-}$| 0.19  | C$_R$       |
| two flash)   | 2.94          | (2.46)           | (2.0)              | O$_{(5)}$=OH$^-$    | 0.07        | C     |
|              | 2.94          | (2.74)           | (1.8)              | O$_{(5)}$=O$^{2-}$  | -0.21       | C$_L$ |
| 5GTIB        | 2.83          | (2.88)$^{[a1]}$ | 2.34               | 2.02                | O$_{(5)}$=OH$^-$| 0.19  | C$_R$       |
| (no preflash)|               | (2.84)           | 2.34               | 2.02                | O$_{(5)}$=O$^{2-}$| 0.19  | C$_R$       |
| two flash)   | 2.83          | (2.24)           | (2.0)              | O$_{(5)}$=OH$^-$    | 0.29        | C$_R$ |
|              | 2.83          | (2.30)           | (1.8)              | O$_{(5)}$=O$^{2-}$  | 0.23        | C$_R$ |
| 5WS6A        | 2.84          | (2.87)$^{[a1]}$ | 2.31               | 2.02                | O$_{(5)}$=OH$^-$| 0.22  | C$_R$       |
| (OEX)        |               | (2.83)$^{[a2]}$ | 2.31               | 2.02                | O$_{(5)}$=O$^{2-}$| 0.22  | C$_R$       |
| (preflash)   | 2.84          | (2.26)$^{[b1]}$ | (2.0)$^{[c1]}$     | O$_{(5)}$=OH$^-$    | 0.27        | C$_R$ |
| two flash)   | 2.84          | (2.34)$^{[b2]}$ | (1.8)$^{[c2]}$     | O$_{(5)}$=O$^{2-}$  | 0.19        | C$_R$ |
| 5WS6B        | 2.78          | (2.86)$^{[a1]}$ | 2.30               | 2.02                | O$_{(5)}$=OH$^-$| 0.23  | C$_R$       |
| (OEX)        |               | (2.83)$^{[a2]}$ | 2.30               | 2.02                | O$_{(5)}$=O$^{2-}$| 0.23  | C$_R$       |
| (preflash)   | 2.78          | (2.14)$^{[b1]}$ | (2.0)$^{[c1]}$     | O$_{(5)}$=OH$^-$    | 0.39        | R     |
| two flash)   | 2.78          | (2.10)$^{[b2]}$ | (1.8)$^{[c2]}$     | O$_{(5)}$=O$^{2-}$  | 0.43        | R     |
| 5WS6A        | 2.71          | (2.86)$^{[a1]}$ | 2.30               | 2.02                | O$_{(5)}$=OH$^-$| 0.23  | C$_R$       |
| (OEX)        |               | (2.83)$^{[a2]}$ | 2.30               | 2.02                | O$_{(5)}$=O$^{2-}$| 0.23  | C$_R$       |
| (preflash)   | 2.71          | (2.00)$^{[b1]}$ | (2.0)$^{[c1]}$     | O$_{(5)}$=OH$^-$    | 0.53        | R     |
| two flash)   | 2.71          | (1.82)$^{[b2]}$ | (1.8)$^{[c2]}$     | O$_{(5)}$=O$^{2-}$  | 0.71        | R     |
| 5WS6B        | 2.77          | (2.86)$^{[a1]}$ | 2.29               | 1.99                | O$_{(5)}$=OH$^-$| 0.23  | C$_R$       |
| (OEX)        |               | (2.83)$^{[a2]}$ | 2.29               | 1.99                | O$_{(5)}$=O$^{2-}$| 0.23  | C$_R$       |
| (preflash) two flash) | 2.77 | (2.12)^[b1] | (2.0)^[c1] | O(5)=OH^− | 0.41 | R |
| SKAIA(B) | 2.87 | 2.33 | 2.20 | O(5)=OH^− | 0.20 | C_R |
| (no preflash) two flash, NH₃ | 2.87 | 2.33 | 2.20 | O(5)=O^{2−} | 0.20 | C_R |
| STISA | 2.65 | (2.84) | 2.25 | 2.13 | O(5)=OH^− | 0.28 | C_R |
| (no preflash) two flash) | 2.65 | (2.82) | 2.25 | 2.13 | O(5)=O^{2−} | 0.28 | C_R |
| STISB | 2.83 | (2.91) | 2.39 | 2.15 | O(5)=OH^− | 0.14 | C_R |
| (no preflash) two flash) | 2.83 | (2.85) | 2.39 | 2.15 | O(5)=O^{2−} | 0.14 | C_R |
| S₃abcb(R) (hydroxide inserted) | 2.72 | (2.61) | 1.80 | 1.83 | O(5)=OH^− | 0.73 | R |
| 2.72 | (2.71) | 1.80 | 1.83 | O(5)=O^{2−} | 0.73 | R |
| 2.72 | (2.02) | (2.0) | O(5)=OH^− | 0.51 | R |
| 2.72 | (1.86) | (1.8) | O(5)=O^{2−} | 0.67 | R |

^[a]The Mn₄(a)-Mn₃(b) distances were estimated by using the experimental Mn₄(a)-O(5) distance in eqs. (2) and (3) under the assumption of a1) O(5)=OH^− and a2) O^{2−}; [b] The Mn₄(a)-O(5) distances were estimated by using the experimental Mn₄(a)-Mn₃(b) distance in eqs. (2) and (3) under the assumption of b1) O(5)=OH^− and b2) O^{2−}; [c] The Mn₃(b)-O(5) distances were estimated to be 2.0 and 1.8 for c1) O(5)=OH^− and c2) O^{2−} respectively; [d] Assignment of the O(5) site; [e] Structural symmetry breaking (SSB) parameter; [f] Topology.
Fig. S3  The superposed (mixed) structure of the S_2(R) (yellow) and S_3(L) (red) structure where O(5)(S_2(R))-O(5)(S_3(L)) distance was about 1.3 Å.