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Supporting materials

Generalized Approximate Spin Projection Calculations of Effective Exchange Integrals of the CaMn₄O₅ Cluster in the S₁ and S₃ States of Oxygen Evolving Complex of Photosystem II

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SI Optimized geometrical parameters

Previously we have performed the full geometry optimizations of the right- and left-opened structures of the CaMn₄O₅ cluster by using the highest spin (HS) configuration.⁴² The optimized geometry is usually assumed for other spin configurations in Fig. S2. This approximation is referred to as the vertical approximation in this paper. As a continuation of the previous work, ⁴² we have performed full geometry optimizations of the eight spin configurations, elucidating geometrical relaxation effects for total energies. The vibrational analysis becomes feasible to elucidate the zero-point energy (ZPE) corrections for the optimized geometrical parameters are summarized in Tables S1, S2, S3 and S4. In the supporting section we discuss the optimized geometrical parameters for the eight different spin configurations

in detail.

As discussed in section II, there are two different geometrical structures relating to the structural symmetry breaking (SSB) of the Mn_a -X- Mn_d bond of the CaMn(III)₃Mn(IV)O₅(H₂O)₃Y(Y= H₂O or OH) cluster in the S₁ state as shown in Fig. 1. First of all, we have performed full geometry optimizations of the S_{1a}(R)(X=O;Y= H₂O) structure in Fig. 1A by using the UB3LYP energy gradient method.⁴² The supporting Table S1 summarizes the optimized Mn-Mn and Ca-Mn distances for the eight spin configurations of S_{1a}(R)(X=O;Y=H₂O). From the computational results in Table S1, the geometrical parameters are almost the same among the eight-different spin configurations. Therefore the average values for the eight configurations are also calculated to elucidate general trends for the geometrical parameters.

The average Mn-Mn distances optimized for $S_{1a}(R)(X=O;Y=H_2O)$ indicated a general trend: $R(Mn_a-Mn_b) < R(Mn_b-Mn_c) ~ R(Mn_c-Mn_d) < R(Mn_b-Mn_d) < R(Mn_a-Mn_d)$ (this relationship is the same as the distance rule Ib obtained by the high-spin configuration⁴²). This trend revealed by full geometry optimizations of the eight spin configurations is common under the assumption that the $O_{(5)}$ site is the oxygen dianion. In fact, the rule Ib is applicable to the proposed structures for the S_1 (or S_2) state by other theoretical groups^{41,56-67}, where the $O_{(5)}$ site is assumed to be the oxygen dianion. The average Mn_a-Mn_b , Mn_b-Mn_c , Mn_c-Mn_d , Mn_b-Mn_d and Mn_a-Mn_d distances for $S_{1a}(R)(X=O;Y=H_2O)$ are 2.69(2.71), 2.77(2.81), 2.73(2.72), 3.27(3.26) and 4.78(4.79) (Å), respectively, where the corresponding values by the EXAFS experiments⁸⁴⁻⁸⁹ are given in parentheses, indicating the consistency between theory and experiment. The rule Ib is a general trend for the right-opened structure with O(5)=O⁻².

Next, we have performed full geometry optimizations of the proton-shifted $S_{1b}(C)(X=Y=OH)$ structure in Fig. 1C. Table S2 summarizes the optimized Mn-Mn and Ca-Mn distances of the eight spin configurations of $S_{1b}(C)(X=Y=OH)$. The average Mn-Mn distances indicate the different tendency from the rule Ib: $R(Mn_b-Mn_c) \sim R(Mn_c-Mn_d) < R(Mn_a-Mn_b) < R(Mn_b-Mn_d) < R(Mn_a-Mn_d)$ (this relationship is the same as the distance rule Ia obtained by the high-spin solution) ⁴². The rule Ia is applicable for the optimized structures where the $O_{(5)}$ site is assumed to be protonated, namely hydroxide anion.^{42,43} The average $Mn_a-Mn_b, Mn_b-Mn_c, Mn_c-Mn_d, Mn_b-Mn_d$ and Mn_a-Mn_d distances for $S_{1b}(C)(X=Y=OH)$ are 2.94(2.97), 2.79(2.89), 2.71(2.84), 3.42(3.29) and 5.37(5.00) (Å), respectively, where the corresponding values by the high-resolution XRD experiments are given in parentheses. The calculated Mn_b-Mn_c and Mn_c-Mn_d distances are shorter by 0.1 Å than the corresponding XRD results (see text).

Table S3 summarizes the fully optimized geometrical parameters of the right-opened water-inserted structure $S_{3a}(R)$ -H₂O(X=O, Y=H₂O, W=OH) in the S₃ state of OEC of PSII in Fig. 1C. From Table S3, the geometrical parameters are almost the same among the eight-different spin configurations. The average Mn-Mn distances optimized for $S_{3a}(R)$ -H₂O indicated a general trend Ib in accord with the right-opened structures with X=O²⁻. The average Mn_a-Mn_b, Mn_b-Mn_c, Mn_c-Mn_d, Mn_b-Mn_d and Mn_a-Mn_d distances are 2.70(2.69), 2.78(2.77), 2.73(2.79), 3.27(3.38) and 5.31(4.78) (Å), respectively, where the corresponding values for $S_{1a}(R)(Y=H_2O)$ are given in parentheses. The Mn_c-Mn_d and Mn_a-Mn_d distances are elongated, respectively, by 0.06 and 0.5 (Å) with insertion of water molecule. The calculated Mn-Mn distances for $S_{3a}(R)$ -H₂O are consistent with the model A in the S₃ state proposed by EXAFS,⁸⁹ where the Mn_a-Mn_b, Mn_b-Mn_c, Mn_c-Mn_d distances are 2.75, 2.79, 2.75 and 3.26 (Å), respectively.

Table S4 summarizes the fully optimized geometrical parameters of the left-opened water-inserted structure S_{3a}(L)-H₂O(X=O, Y=H₂O, W=OH) in the S₃ state of OEC of PSII in Fig. 1D. From Table S4, the geometrical parameters are almost the same among the eight-different spin configurations. The average Mn-Mn distances optimized for $S_{3a}(L)-H_2O$ indicated a general trend Ic: $R(Mn_b-Mn_c) \sim R(Mn_c-Mn_d) < R(Mn_b-Mn_d)$ $< R(Mn_a-Mn_b) < R(Mn_a-Mn_d)$ (this relationship is the same as the distance rule Ic obtained by the high-spin solution) 42 . The rule Ic is applicable for the L-type structure with the closed-cubane structure: $Mn(IV)_{b}Mn(IV)_{c}Mn(IV)_{d}$.^{42,43} The average $Mn_{a}-Mn_{b}$, Mn_b-Mn_c , Mn_c-Mn_d , Mn_b-Mn_d and Mn_a-Mn_d distances for $S_{3a}(L)-H_2O$ are 3.22(2.94), 2.73(2.79), 2.72(2.71), 2.84(3.42) and 5.24(5.37) (Å), respectively. The Mn_a-Mn_b distance is elongated by 0.3 Å with insertion of water molecule, whereas the Mn_b-Mn_d distance is shortened by 0.6 Å. Therefore the $Mn(IV)_bMn(IV)_cMn(IV)_d$ triangle in the cubane fragment of $S_{3a}(L)$ -H₂O is almost equilateral because no Jahn-Teller (JT) distortion of the Mn(III) ion as discussed previously:⁴² note that it is obtuse in the XRD structure⁴⁴ because of the JT distortion of Mn(III)_d. Thus general trends Ia-Ic concluded by using the HS solution⁴² are not changed after the full geometry optimizations of all the spin configurations, supporting the HS approximation.

The optimized Ca-Mn distances obtained for the eight different spin configurations of the right (R)-opened structure, $S_{1a}(R)(X=O;Y=H_2O)$, by UB3LYP in Fig. 1A are quite similar as shown in Table S1. The average optimized Ca-Mn distances have elucidated a general tendency: $R(Ca-Mn_c) < R(Ca-Mn_b) \sim R(Ca-Mn_d) < R(Ca-Mn_a)$. This relationship is the same as the distance rule IIa obtained by the high-spin solution.⁴² The average Ca-Mn_a, Ca-Mn_b, Ca-Mn_c and Ca-Mn_d distances of $S_{1a}(R)(X=O;Y=H_2O)$ are

3.63(4.41), 3.40(3.41), 3.29(3.41) and 3.52(3.41), (Å), respectively, where the corresponding Ca-Mn distances by the EXAFS experiments⁸⁴⁻⁸⁹ are given in parentheses. The Ca-Mn_a distance by EXAFS is elongated as compared with the XRD value in accord with the Berkeley structure⁸⁹.

The average optimized Ca-Mn distances for $S_{1b}(C)$ (X=Y=OH) in Fig. 1B also exhibit the trend IIa as shown in Table S2. The average Ca-Mn_a, Ca-Mn_b, Ca-Mn_c and Ca-Mn_d distances are 3.95(3.82), 3.47(3.55), 3.34(3.25) and 3.59(3.54), (Å), respectively, where the corresponding Ca-Mn distances by the high-resolution XRD structure⁴⁴ are given in parentheses. The calculated Ca-Mn distances are compatible with those of XRD.

The Ca-Mn distances for the left (L)-opened water-inserted structure, $S_{3a}(L)-H_2O(X=O, Y=H_2O, W=OH)$ in the S₃ state of OEC of PSII in Fig. 1D are given in Table S4. From Table S4, the geometrical parameters are almost the same for all the spin configurations. The average optimized Ca-Mn distances have provided the following relationship: R(Ca-Mn_c)~R(Ca-Mn_b)~R(Ca-Mn_d) < R(Ca-Mn_a). The above trend is the same as the distance rule IIb obtained by the high-spin solution.⁴² The average Ca-Mn_a, Ca-Mn_b, Ca-Mn_c and Ca-Mn_d distances of $S_{3a}(L)-H_2O$ are 4.39(3.99), 3.42(3.34), 3.46(3.34) and 3.42(3.34), (Å), respectively, where the corresponding EXAFS values for model A are given in parentheses. The Ca-Mn(IV)_b, Ca-Mn(IV)_c and Ca-Mn(IV)_d distances are similar in accord with the un-distorted cubane structure in the L-type structure without the JT distortion effect.

Christou et al⁷⁴ have synthesized the cubane-like model complex, $Ca_2Mn(IV)_3O_4$ (7b) and have performed the XRD experiments. The Ca-Ca, Ca-Mn_b, Ca-Mn_c and Ca-Mn_d distances of the complex by XRD are 4.20(4.39), 3.42(3.42), 3.39(3.46) and 3.45(3.42), (Å), respectively, where the corresponding calculated values for $S_{3a}(L)$ -H₂O are given in parentheses. The observed and calculated values are similar, indicating the trend Ic. This similarity is consistent with the high-oxidation scenario for $S_{3a}(L)$ -H₂O with the Ca(II)Mn(IV)₄O₄ core.

The optimized $Mn_a-O_{(5)}$ and $Mn_d-O_{(5)}$ distances were quite similar for the eight spin configurations for the right (R)-opened structure, $S_{1a}(R)$ (X=O, Y= H₂O), as shown in Table S1. The average $Mn_a-O_{(5)}$ and $Mn_d-O_{(5)}$ distances were 1.88 and 2.93 (Å), in accord with the R-opened structure with X=O²⁻. The corresponding values are 2.33 and 3.09 (Å), respectively, for $S_{1b}(R)(X=Y=OH)$ as shown in Table S2. The $Mn_a-O_{(5)}$ distance is elongated by 0.45 Å by protonation of the X=O²⁻ site, showing a central (C) structure.⁴²

The optimized $Mn_a-O_{(5)}$ and $Mn_d-O_{(5)}$ distances were almost the same for the eight

spin configurations for the right-opened water-inserted structure, $S_{3a}(R)$ -H₂O(X=O: Y=H₂O:W=OH). The average Mn_a-O₍₅₎ and Mn_d-O₍₅₎ distances were 1.75(1.88) and 3.60(2.93) (Å), respectively, where the corresponding values for $S_{1b}(C)$ are given in parentheses. The Mn_d-O₍₅₎ distance is elongated by 0.7 Å with insertion of water molecule. The average Mn_a-O₍₅₎ and Mn_d-O₍₅₎ distances for the left-opened water-inserted structure, $S_{3a}(L)$ -H₂O(X=O:Y=H₂O:W=OH) in Fig. 1 D are 3.43 and 1.85 (Å), respectively. Therefore the Mn_d-O₍₅₎ distance is elongated by about 0.4 Å with water insertion. The Mn_a-O₍₅₎ and Mn_d-O₍₅₎ distances optimized by large QM Model III are 2.87 and 2.37 (Å) for the left (L) opened S₁-structure $S_{1b}(L)$, respectively. Thus structural symmetry breaking (SSB) is feasible even in the S₁ and S₃ states of OEC.

Present computational results for the eight spin configurations support use of the HS configuration for qualitative discussions of the optimized geometrical parameters.⁴² Here detailed discussions of the optimized geometries have been performed for confirmation of previous conclusions⁴² derived from the HS configuration. It is noteworthy that the adiabatic plus ZPE correction is necessary for reproduction of the thermally excited triplet state for $S_{1a}(R)$, although the optimized geometrical parameters are not so different among the eight spin configurations. The energy levels obtained by the exact diagonsalization are sensitive to subtle geometry changes in the case of $S_{1a}(R)$.

The almost symmetrical $Mn(III)_a-O_{(5)}-Mn(III)_d$ bond of the $CaMn_4O_5$ cluster revealed by the high-resolution XRD experiment⁴⁴ in Fig. 1 is collapsed into the right (R)- and left (L)-opened structures as illustrated in Figs. 1C and 1D. Thus the labile nature of the $Mn(III)_a-O_{(5)}-Mn(III)_d$ bond is a characteristic of active site of water oxidation reaction in OEC of PSII.^{42,43,45-52} Geometrical flexibility is a key concept for lucid understanding of the magneto structural correlations in the $CaMn_4O_5$ cluster of OEC of PSII. Possible explanations of the symmetrical $Mn(III)_a-O_{(5)}-Mn(III)_d$ bond revealed by XRD⁴⁴ have been presented on the basis of a number of DFT computations using different functionals in previous papers.⁴⁵⁻⁵² Therefore they are not repeated here.

Distances	$\uparrow\uparrow\uparrow\uparrow$	↑↓↑↓	$\uparrow \uparrow \downarrow \downarrow$	$\uparrow\downarrow\downarrow\uparrow\uparrow$	↑↑↑↓	↓↑↑↑	↑↑↓↑	↑↓↑↑	Aver. ^{b,c)}
Mna–Mnb	2.69	2.68	2.69	2.68	2.69	2.68	2.69	2.68	2.69(2.71)
Mnb-Mnc	2.77	2.78	2.77	2.77	2.77	2.77	2.77	2.78	2.77(2.81)
Mnc-Mnd	2.74	2.73	2.73	2.72	2.73	2.73	2.73	2.73	2.73(2.72)
Mnb-Mnd	3.23	3.29	3.27	3.29	3.26	3.27	3.25	3.29	3.27(3.26)
Mna-Mnd	4.71	4.82	4.77	4.81	4.75	4.81	4.73	4.82	4.78(4.79)
Ca–Mna	3.62	3.64	3.62	3.64	3.63	3.64	3.63	3.64	3.63(4.41)
Ca-Mn _b	3.41	3.40	3.40	3.41	3.40	3.41	3.40	3.40	3.40(3.41)
Ca–Mnc	3.30	3.29	3.29	3.29	3.29	3.29	3.29	3.29	3.29(3.41)
Ca-Mnd	3.50	3.54	3.51	3.54	3.52	3.53	3.50	3.53	3.52(3.41)
Mna–X	1.89	1.86	1.88	1.86	1.89	1.87	1.89	1.86	1.88
Mnd-X	2.84	2.99	2.92	2.98	2.89	2.97	2.87	2.99	2.93

Table S1. The optimized Mn–Mn, Ca–Mn, and Mn–X distances^{a)} (Å) for the right elongated S_{1a} (R) configuration of OEC of PSII

a) HS UB3LYP/Basis set I, b) average values of **S1a** (R), c)EXAFS (ref.84-89)

Table S2. The optimized Mn–Mn, Ca–Mn, and Mn–X distances^{a)} (Å) for the right elongated S_{1b} (C) configuration of OEC of PSII

Distances	$\uparrow\uparrow\uparrow\uparrow$	↑↓↑↓	↑↑↓↓	$\uparrow\downarrow\downarrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow\downarrow$	$\downarrow \uparrow \uparrow \uparrow$	$\uparrow \uparrow \downarrow \uparrow$	$\uparrow\downarrow\uparrow\uparrow$	Aver. ^{b,c)}
Mna–Mnb	2.93	2.95	2.93	2.95	2.93	2.95	2.93	2.95	2.94(2.97)
$Mn_b - Mn_c$	2.79	2.79	2.79	2.79	2.79	2.79	2.79	2.79	2.79(2.89)
Mnc-Mnd	2.71	2.71	2.71	2.70	2.70	2.71	2.71	2.71	2.71(2.84)
Mnb-Mnd	3.41	3.39	3.41	3.41	3.41	3.38	3.42	3.41	3.42(3.29)
Mna–Mnd	5.35	5.35	5.35	5.37	5.35	5.33	5.37	5.37	5.37(5.00)
Ca–Mna	3.96	3.95	3.95	3.96	3.95	3.96	3.95	3.95	3.95(3.79)
Ca-Mn _b	3.47	3.46	3.47	3.46	3.47	3.46	3.47	3.46	3.47(3.41)
Ca-Mnc	3.35	3.34	3.34	3.34	3.34	3.35	3.34	3.34	3.34(3.36)
Ca-Mnd	3.58	3.58	3.58	3.59	3.59	3.57	3.59	3.58	3.59(3.51)
Mna–X	2.34	2.36	2.32	2.35	2.33	2.36	2.33	2.34	2.33(2.50)
Mnd-X	3.06	3.03	3.07	3.07	3.06	3.01	3.09	3.08	3.09(2.60)

a) HS UB3LYP/Basis set I, b) average values of **S1a** (R), c) XRD values in ref. 44.

Distances	<u> </u>	↑↓↑↓	↑↑↓↓	$\uparrow\downarrow\downarrow\uparrow\uparrow$	↑↑↑↓	$\downarrow \uparrow \uparrow \uparrow$	↑↑↓↑	↑↓↑↑	Aver. b,c)
Mna–Mnb	2.70	2.71	2.70	2.71	2.70	2.71	2.69	2.71	2.70(2.75)
Mnb-Mnc	2.78	2.78	2.78	2.77	2.77	2.78	2.78	2.78	2.78(2.79)
Mnc-Mnd	2.78	2.79	2.78	2.79	2.79	2.78	2.79	2.78	2.79(2.75)
Mnb-Mnd	3.39	3.38	3.38	3.34	3.39	3.39	3.38	3.38	3.38(3.26)
Mna-Mnd	5.31	5.31	5.31	5.30	5.30	5.31	5.31	5.31	5.31
Ca–Mna	3.98	3.98	3.98	3.98	3.97	3.99	3.98	3.99	3.98(3.99)
Ca–Mn _b	3.58	3.57	3.59	3.57	3.58	3.57	3.58	3.58	3.58(3.37)
Ca–Mnc	3.39	3.39	3.39	3.39	3.39	3.39	3.39	3.38	3.39(3.37)
Ca-Mnd	3.39	3.38	3.38	3.34	3.39	3.39	3.38	3.38	3.38(3.37)
Mna–X	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Mnd-X	3.59	3.60	3.60	3.59	3.59	3.60	3.60	3.60	3.60

Table S3. The optimized Mn–Mn, Ca–Mn, and Mn–X distances^{a)} (Å) for the right elongated S_{3a} (R)-H2O configuration of OEC of PSII

a) HS UB3LYP/Basis set I, b) average values of **S1a** (R), c)EXAFS : Model A(ref. 84-89)

Table S4. The optimized Mn–Mn, Ca–Mn, and Mn–X distances^{a)} (Å) for the right elongated S_{3c} (L) –H₂O configuration of OEC of PSII

Distances	<u> </u>	↑↓↑↓	↑↑↓↓	↑↓↓↑	↑↑↑↓	↓↑↑↑	↑↑↓↑	↑↓↑↑	Aver. b,c)
Mn _a –Mn _b	3.21	3.22	3.21	3.22	3.21	3.22	3.21	3.22	3.22(2.82)
Mnb-Mnc	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73(2.72)
Mnc-Mnd	2.72	2.73	2.72	2.72	2.72	2.72	2.72	2.72	2.72(2.72)
Mnb-Mnd	2.84	2.84	2.84	2.85	2.84	2.84	2.84	2.85	2.84(2.82)
Mna-Mnd	5.24	5.24	5.24	5.24	5.24	5.24	5.24	5.24	5.24
Ca–Mna	4.39	4.40	4.39	4.40	4.39	4.40	4.39	4.39	4.39(3.99)
Ca–Mn _b	3.43	3.41	3.43	3.42	3.43	3.42	3.42	3.42	3.42(3.34)
Ca-Mnc	3.46	3.46	3.45	3.46	3.45	3.47	3.46	3.46	3.46(3.34)
Ca-Mnd	3.43	3.42	3.43	3.42	3.42	3.42	3.42	3.43	3.42(3.34)
Mna–X	3.42	3.43	3.42	3.43	3.42	3.43	3.42	3.43	3.43
Mnd-X	1.82	1.85	1.86	1.85	1.86	1.85	1.85	1.85	1.85

a) HS UB3LYP/Basis set I, b) average values of **S1a** (R), c)EXAFS : Model B(ref. 89)

SII. Relative energies of the eight spin configurations.

SII.1 UB3LYP computational results

The eight BS DFT (UB3LYP) solutions for the eight spin configurations have been obtained to elucidate relative stabilities among them. The computational results are summarized in Tables S5 and S6. The optimized geometry of the high-spin (HS) solution has often been assumed for the remaining seven spin configurations. This is referred to as the vertical approximation in this paper. On the other hand, full geometry optimizations have been performed for the eight spin configurations. The energy gaps among them obtained by the procedure are used to determine J values, providing the adiabatic approximation. The zero point energy (ZPE) corrections for the total energies of the optimized geometries are also calculated by the vibrational analysis. This is referred to as the adiabatic plus ZPE correction in Tables S5 and S6. The ZPE correction is not at all trivial because of the quantum nature of molecular spins in finite clusters such as the CaMn₄O₅ cluster. In fact, the ground singlet (S=0) state with the lower-lying triplet (S=1) state for S_{1a}(R)(X=O;Y= H₂O) revealed by the EPR experiment ²¹ cannot be reproduced without the ZPE correction as shown in Fig. 1 (see text) even in the adiabatic energy level.

SII.2 Excitation energies by the exact diagonalization methods

The relative energy levels for the proton-shifted structure $S_{1c}(C)(X=Y=OH)$ based on the BS calculations and the right-opened water-inserted structure $S_{3a}(R)(X=O;$ Y=H₂O;W=OH) obtained by the exact diagonalization method are schematically illustrated in Figs. S1 and S2, respectively.

The projection factors obtained for the proton-shifted structure $S_{1b}(C)$ by the exact diagonalizations of the Heisenberg model are summarized in Table S7. The spin densities are obtained by twice of the projection factors in the triplet state (S=1). The topology of the spin density obtained by the exact diagonalization has supported the broken-symmetry (BS) approach as a first step of theoretical elucidation of electronic and spin states of the CaMn₄O₅ cluster.

		vertical		adiabatic		
oxidation	spin		$\langle \mathbf{r}^2 \rangle$	A E d	ΔE +	
state ^a	arrangement ^a	ΔE	$\langle S \rangle$	ΔE^{a}	$\operatorname{ZPE} d$	
abcd		$\mathbf{S}_{1a}(\mathbf{R})(\mathbf{X}=\mathbf{O};\mathbf{Y}=\mathbf{H}_{2}\mathbf{O})$				
3443	$\uparrow \uparrow \uparrow \uparrow$	0.00^{b}	56.23	0.00	0.00	
3443	$\uparrow\downarrow\downarrow\uparrow\uparrow$	-3.19^{b}	8.14	-3.56	-3.59	
3443	$\downarrow \uparrow \downarrow \uparrow$	-3.01^{b}	7.14	-3.40	-3.48	
3443	$\downarrow \downarrow \uparrow \uparrow$	0.89^{b}	7.20	0.80	0.60	
3443	↑↑↑↓	-0.86^{b}	16.19	-0.97	-1.05	
3443	$\uparrow \uparrow \downarrow \uparrow$	-0.54^{b}	23.19	-0.65	-0.76	
3443	$\uparrow \downarrow \uparrow \uparrow$	-1.60^{b}	23.16	-1.93	-2.03	
3443	$\downarrow \uparrow \uparrow \uparrow$	-2.28^{b}	16.17	-2.55	-2.51	
		$\mathbf{S}_{1b}(\mathbf{C})(\mathbf{X}=\mathbf{Y}=\mathbf{OH})$				
3443	$\uparrow \uparrow \uparrow \uparrow$	0.00^{c}	56.21	-0.92	-2.17	
3443	↑↑↓↓	-0.06 ^c	7.18	-1.05	-2.33	
3443	$\uparrow \downarrow \uparrow \downarrow$	-1.37^{c}	7.12	-2.53	-3.86	
3443	$\uparrow \downarrow \downarrow \uparrow$	-1.36^{c}	8.13	-2.51	-3.81	
3443	$\downarrow \uparrow \uparrow \uparrow$	-0.31^{c}	16.17	-1.38	-2.63	
3443	↑↑↑↓	-1.41^{c}	16.16	-2.44	-3.72	
3443	$\uparrow \uparrow \downarrow \uparrow$	-1.01 ^c	23.16	-2.06	-3.38	
3443	$\uparrow\downarrow\uparrow\uparrow$	-0.03^{c}	23.15	-1.17	-2.47	

Table S5. Vertical and adiabatic energy gaps ($\Delta E / \text{kcal mol}^{-1}$) and $\langle S^2 \rangle$ values

for OEC model at the B3LYP/BSI level.

^{*a*} (Mn_a, Mn_b, Mn_c, Mn_d) in ref. 42, ^{*b*} reference to $\mathbf{S}_{1a}(\mathbf{R})(\mathbf{X}=\mathbf{O};\mathbf{Y}=\mathbf{H}_2\mathbf{O})(3443) \uparrow \uparrow \uparrow \uparrow,^c$ reference to $\mathbf{S}_{1b}(\mathbf{C})(\mathbf{X}=\mathbf{Y}=\mathbf{O}\mathbf{H})$ (3443) $\uparrow \uparrow \uparrow \uparrow,^d$ reference to $\mathbf{S}_{1a}(\mathbf{R})(\mathbf{X}=\mathbf{O};\mathbf{Y}=\mathbf{H}_2\mathbf{O})(3443)$ $\uparrow \uparrow \uparrow \uparrow$.

		vertic	al	adi	abatic
oxidation state ^a	spin arrangement ^a	ΔE	$\left\langle S^{2}\right\rangle$	ΔE^{e}	ΔE + ZPE e
abcd		S_{3a} (R)-H ₂ O			
		(X=O;W=OH)			
4444	1111	0.00^{b}	42.26	0.00	0.00
4444	$\uparrow\downarrow\downarrow\uparrow\uparrow$	-0.48^{b}	6.18	-0.77	-0.86
4444	$\downarrow\uparrow\downarrow\uparrow$	-0.09^{b}	6.17	-0.42	-0.53
4444	$\downarrow \downarrow \uparrow \uparrow$	0.27^{b}	6.21	0.19	0.15
4444	↑↑↑↓	0.06^{b}	15.21	-0.06	-0.11
4444	$\uparrow \uparrow \downarrow \uparrow$	0.26^{b}	15.20	0.09	0.03
4444	↑↓↑↑	-0.28^{b}	15.18	-0.53	-0.62
4444	↓↑↑↑	-0.33^{b}	15.21	-0.51	-0.54
		$\mathbf{S}_{3a}(\mathrm{L}) ext{-}\mathrm{H}_{2}\mathrm{O}$			
		(X=O;W=OH)			
4444	1111	0.00^{c}	42.24	0.00	0.00
4444	$\uparrow\uparrow\downarrow\downarrow\downarrow$	1.19^{c}	6.22	1.09	0.89
4444	$\uparrow\downarrow\uparrow\downarrow$	1.80^{c}	6.16	1.38	1.24
4444	$\uparrow\downarrow\downarrow\uparrow\uparrow$	0.53^{c}	6.16	0.04	-0.03
4444	↓↑↑↑	-0.38^{c}	15.18	-0.74	-0.61
4444	↑↑↑↓	1.19^{c}	15.22	1.08	0.86
4444	$\uparrow \uparrow \downarrow \uparrow$	2.31^{c}	15.22	2.23	1.95
4444	$\uparrow \downarrow \uparrow \uparrow$	0.45^{c}	15.16	-0.03	-0.08

Table S6. Vertical and adiabatic energy gaps ($\Delta E / \text{kcal mol}^{-1}$) and $\langle S^2 \rangle$ values

for OEC model at the B3LYP/BSI level.

^{*a*} (Mn_a, Mn_b, Mn_c, Mn_d), ^{*b*} reference to $\mathbf{S}_{3a}(\mathbf{R})(\mathbf{X}=\mathbf{O};\mathbf{W}=\mathbf{OH})(4444)\uparrow\uparrow\uparrow\uparrow,^{$ *c* $}$ reference to $\mathbf{S}_{3a}(\mathbf{L})(\mathbf{X}=\mathbf{O};\mathbf{W}=\mathbf{OH})(4444)\uparrow\uparrow\uparrow\uparrow,^{$ *d* $}$ reference to $\mathbf{S}_{3a}(\mathbf{R})(\mathbf{X}=\mathbf{O};\mathbf{W}=\mathbf{OH})(4444)\uparrow\uparrow\uparrow\uparrow$.



Fig. S1 Excitation energies of the proton-shifted structure $S_{1b}(C)(X=Y=OH)$ in the S_1 state of OEC of PSII by the exact diagonalization of the spin Hamiltonian matrix consisted of the J values determined by three different procedures: (A) vertical approximation where the full geometry optimized structure for the highest spin state is assumed for other seven configurations; (B) adiabatic approximation where full geometry optimizations of all the spin configurations are performed; (C) adiabatic plus zero point energy (ZPE) corrections are performed. The singlet (S=0) state was the ground state by the three procedures.



Figure S2 Excitation energies of the water-inserted structure S_{3a}(R)(X=O,Y=H₂O)-H₂O in the S₃ state of OEC of PSII by the exact diagonalization of the spin Hamiltonian matrix consisted of the J values determined by three different procedures: (A) vertical approximation where the full geometry optimized structure for the highest spin state is assumed for other seven configurations; (B) adiabatic approximation where full geometry optimizations of all the spin configurations are performed; (C) adiabatic plus zero point energy (ZPE) corrections are performed. The singlet (S=0) state was the ground state by the three procedures.

Methods	Energy(cm-	Mn(III) _a	Mn(IV) _b	Mn(IV) _c	$Mn(III)_d$	
	1)					
$V(1^{th},S=1)^{1,a)}$	2.51	0.87	0.36	0.47	-0.70	
$V(2^{th},S=2)^{1,a)}$	11.3	0.70	0.46	0.36	-0.51	
$V(3^{th},S=1)^{1,c)}$	18.4	1.10	-0.60	-0.43	0.93	
$A(1^{th},S=1)^{2,a)}$	14.0	0.69	0.48	0.39	-0.55	
$A(2^{th},S=1)^{2,b)}$	17.6	1.29	-0.72	-0.37	0.80	
$A(3^{th},S=2)^{2,c)}$	42.6	0.61	0.50	0.31	-0.42	
$ZPE(1^{th},S=1)^{3,a)}$	15.5	0.49	0.41	0.05	0.06	
$ZPE(2^{th},S=1)^{3,b)}$	20.9	1.49	-0.65	-0.03	0.19	
$ZPE(3^{th},S=2)^{3,c)}$	46.5	0.49	0.38	0.03	0.11	

Table S7. The excitation energies and projection factors (spin densities) obtained for the $S_{1b}(C)$ by the exact diagonalyzation of the spin Hamiltonian model

¹⁾Vertical, ²⁾Adiabatic, ³⁾Adiabatic + ZPE, ^{a)}First excited state, ^{b)} Second excited state, ^{c)} Higher excited state.

SIII. Heisenberg model for OEC of PSII

SIII.1 Heisenberg model for the intermediates in the S1 state

Spin Hamiltonian models have been employed for analysis of EPR spectra of the $CaMn_4O_5$ cluster in OEC.¹⁻⁴⁰ The energy levels obtained by the BS DFT (U3LYP) are mapped into the effective exchange integrals (J) in the Heisenberg model^{42, 45-52}, which has been used for analysis of accumulated EPR experimental results.¹⁻⁴⁰ However, the mapping procedures are not described in detail in the text. Here, computational schemes⁴⁹ of J values are briefly given for lucid understanding of our BS DFT approach to biomolecular magnetism in OEC.

The energy expressions for eight spin alignments in Fig. S2 for the right-opened structure $S_{1a}(R)$ (X=O, Y=H₂O) and for the proton-shifted structure $S_{1b}(C)$ (X=Y=OH) are explicitly given under the classical spin approximation (Neel state model) where the magnitude of classical spins are assumed as follows: $M_a(III) = M_d(III) = 4/2$ and $M_b(IV) = M_c(IV) = 3/2$.

$${}^{15} < \mathbf{H} >_{A} = -6J_{ab} - 6J_{ac} - 8J_{ad} - \frac{9}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{7} < \mathbf{H} >_{B} = -6J_{ab} - 6J_{ac} + 8J_{ad} - \frac{9}{2}J_{bc} + 6J_{bd} + 6J_{cd}$$

$${}^{9} < \mathbf{H} >_{C} = -6J_{ab} + 6J_{ac} - 8J_{ad} + \frac{9}{2}J_{bc} - 6J_{bd} + 6J_{cd}$$

$${}^{9} < \mathbf{H} >_{D} = 6J_{ab} - 6J_{ac} - 8J_{ad} + \frac{9}{2}J_{bc} + 6J_{bd} - 6J_{cd}$$

$${}^{9} < \mathbf{H} >_{E} = 6J_{ab} + 6J_{ac} + 8J_{ad} - \frac{9}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{1} < \mathbf{H} >_{F} = -6J_{ab} + 6J_{ac} + 8J_{ad} + \frac{9}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{1} < \mathbf{H} >_{G} = 6J_{ab} - 6J_{ac} + 8J_{ad} + \frac{9}{2}J_{bc} - 6J_{bd} + 6J_{cd}$$

$${}^{3} < \mathbf{H} >_{H} = 6J_{ab} + 6J_{ac} - 8J_{ad} - \frac{9}{2}J_{bc} + 6J_{bd} + 6J_{cd}$$

(s1)

where the constant terms are abbreviated for simplicity. The classical spin model is applicable for systems at the strong correlation limit.⁴⁹

The total energies of eight BS solutions for $S_{1a}(R)$ (X=O, Y=H₂O) (($S_{1b}(R)$ (X=OH, Y=OH)) in Table S5 are mapped into the corresponding total energies of the classical Heisenberg model. The energy differences (kcal/mol) are calculated by setting the total energy of the ferromagnetic configuration (¹⁵A) in Fig. S2 as the reference state.

$$\Delta < \mathbf{H} >_{AB} = < \mathbf{H} >_{B} - < \mathbf{H} >_{A} = 16J_{ad} + 12J_{bd} + 12J_{cd} = -0.86(-1.41)$$

$$\Delta < \mathbf{H} >_{AC} = < \mathbf{H} >_{C} - < \mathbf{H} >_{A} = 12J_{ac} + 9J_{bc} + 12J_{cd} = -0.54(-1.01)$$

$$\Delta < \mathbf{H} >_{D} = < \mathbf{H} >_{D} - < \mathbf{H} >_{A} = 12J_{ab} + 9J_{bc} + 12J_{bd} = -1.60(-0.03)$$

$$\Delta < \mathbf{H} >_{E} = < \mathbf{H} >_{E} - < \mathbf{H} >_{A} = 12J_{ab} + 12J_{ac} + 16J_{ad} = -2.28(-0.31)$$

$$\Delta < \mathbf{H} >_{F} = < \mathbf{H} >_{F} - < \mathbf{H} >_{A} = 12J_{ac} + 16J_{bc} + 9J_{ad} + 12J_{bd} = 0.89(-0.06)$$

$$\Delta < \mathbf{H} >_{G} = < \mathbf{H} >_{G} - < \mathbf{H} >_{A} = 12J_{ab} + 16J_{bc} + 9J_{ad} + 12J_{cd} = -3.01(-1.37)$$

$$\Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{G} - < \mathbf{H} >_{A} = 12J_{ab} + 12J_{bc} + 12J_{ad} + 12J_{cd} = -3.01(-1.37)$$

$$\Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{G} - < \mathbf{H} >_{A} = 12J_{ab} + 12J_{bc} + 12J_{ad} + 12J_{cd} = -3.19(-1.36)$$
(s2)

These equations are utilized for computations of J values (cm⁻¹) under the classical approximation. Seven BS solutions except for the configuration F have been used to obtain analytical expressions of J values as follows:

$$J_{ab} = \frac{1}{24} (-{}^{7} < \mathbf{H} >_{B} - {}^{9} < \mathbf{H} >_{C} + {}^{1} < \mathbf{H} >_{D} + {}^{3} < \mathbf{H} >_{E}) = -36.1(30.3)$$

$$J_{ac} = \frac{1}{24} (-{}^{15} < \mathbf{H} >_{A} + {}^{9} < \mathbf{H} >_{C} + {}^{9} < \mathbf{H} >_{E} - {}^{3} < \mathbf{H} >_{G}) = 2.77(0.73)$$

$$J_{ad} = \frac{1}{32} (-{}^{15} < \mathbf{H} >_{A} + {}^{7} < \mathbf{H} >_{B} + {}^{9} < \mathbf{H} >_{E} - {}^{3} < \mathbf{H} >_{H}) = 0.55(-3.93)$$

$$J_{bc} = \frac{1}{18} (-{}^{15} < \mathbf{H} >_{A} + {}^{9} < \mathbf{H} >_{C} + {}^{9} < \mathbf{H} >_{D} - {}^{3} < \mathbf{H} >_{H}) = 20.4(6.21)$$

$$J_{bd} = \frac{1}{24} (-{}^{15} < \mathbf{H} >_{A} + {}^{7} < \mathbf{H} >_{B} + {}^{9} < \mathbf{H} >_{D} - {}^{3} < \mathbf{H} >_{G}) = 10.6(-1.02)$$

$$J_{cd} = \frac{1}{24} (-{}^{9} < \mathbf{H} >_{D} - {}^{9} < \mathbf{H} >_{E} + {}^{1} < \mathbf{H} >_{G} + {}^{3} < \mathbf{H} >_{H}) = -33.8(-1.16)$$

As expected from the energy differences in Table S5, J_{ab} values are negative and positive in sign for $S_{1a}(R)$ (X=O, Y=H₂O) (($S_{1b}(R)$ (X=OH, Y=OH)).

The molecular spins are quantum spins in finite systems. Therefore quantum Heisenberg model is often necessary for quantitative purpose. The total energies of the quantum Heisenberg model correspond, respectively, to those of spin-projected eight BS solutions for $S_{1a}(R)$ (X=O, Y=H₂O) (($S_{1b}(R)$ (X=OH, Y=OH)) in Table S5.

$${}^{15} < \mathbf{H} >_{A} = -6J_{ab} - 6J_{ac} - 8J_{ad} - \frac{9}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{7} < \mathbf{H} >_{B} = -6J_{ab} - 6J_{ac} + 12J_{ad} - \frac{9}{2}J_{bc} + 9J_{bd} + 9J_{cd}$$

$${}^{9} < \mathbf{H} >_{C} = -6J_{ab} + 9J_{ac} - 8J_{ad} + \frac{15}{2}J_{bc} - 6J_{bd} + 9J_{cd}$$

$${}^{9} < \mathbf{H} >_{D} = 9J_{ab} - 6J_{ac} - 8J_{ad} + \frac{15}{2}J_{bc} + 9J_{bd} - 6J_{cd}$$

$${}^{9} < \mathbf{H} >_{E} = 9J_{ab} + 9J_{ac} + 12J_{ad} - \frac{9}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{1} < \mathbf{H} >_{F} = -6J_{ab} + 9J_{ac} + 12J_{ad} + \frac{15}{2}J_{bc} - 6J_{bd} - 6J_{cd}$$

$${}^{1} < \mathbf{H} >_{G} = 9J_{ab} - 6J_{ac} + 12J_{ad} + \frac{15}{2}J_{bc} - 6J_{bd} + 9J_{cd}$$

$${}^{3} < \mathbf{H} >_{H} = 9J_{ab} + 9J_{ac} - 8J_{ad} - \frac{9}{2}J_{bc} + 9J_{bd} + 9J_{cd}$$
(s4)

where the constant terms are abbreviated for simplicity.

The quantum energy corrections (kcal/mole) are calculated by setting the total energy of the ferromagnetic configuration (¹⁵A) as the reference. Seven BS solutions except have been used to obtain analytical expressions of J values as follows:

$$\Delta < \mathbf{H} >_{B} = <\mathbf{H} >_{B} - <\mathbf{H} >_{A} = (12 - 8p_{ad})J_{ad} + (9 - 6p_{bd})J_{bd} + (9 - 6p_{cd})J_{cd}$$

$$\Delta < \mathbf{H} >_{C} = <\mathbf{H} >_{C} - <\mathbf{H} >_{A} = (9 - 6p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (9 - 6p_{cd})J_{cd}$$

$$\Delta < \mathbf{H} >_{D} = <\mathbf{H} >_{D} - <\mathbf{H} >_{A} = (9 - 6p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (9 - 6p_{bd})J_{bd}$$

$$\Delta < \mathbf{H} >_{E} = <\mathbf{H} >_{E} - <\mathbf{H} >_{A} = (9 - 6p_{ab})J_{ab} + (9 - 6p_{ac})J_{ac} + (12 - 8p_{ad})J_{ad}$$

$$\Delta < \mathbf{H} >_{F} = <\mathbf{H} >_{F} - <\mathbf{H} >_{A} = (9 - 6p_{ac})J_{ac} + (12 - 8p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (9 - 6p_{bd})J_{bd}$$

$$\Delta < \mathbf{H} >_{F} = <\mathbf{H} >_{F} - <\mathbf{H} >_{A} = (9 - 6p_{ac})J_{ac} + (12 - 8p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (9 - 6p_{bd})J_{bd}$$

$$\Delta < \mathbf{H} >_{G} = <\mathbf{H} >_{G} - <\mathbf{H} >_{A} = (9 - 6p_{ab})J_{ab} + (12 - 8p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (9 - 6p_{cd})J_{cd}$$

$$\Delta < \mathbf{H} >_{H} = <\mathbf{H} >_{H} - <\mathbf{H} >_{A} = (9 - 6p_{ab})J_{ab} + (9 - 6p_{ac})J_{ac} + (9 - 6p_{bd})J_{bd} + (9 - 6p_{cd})J_{cd}$$
(s5)

These equations are utilized for computations of energy levels after spin projection (cm $^{-1}$) under the generalized approximate spin projection (GAP). The p_{ij} coefficients for the antiferromagnetic pair (ij) have been determined using the total spin quantum numbers obtained by the broken-symmetry (BS) calculations. The magnitude of the p_{ij} value becomes larger than the classical limit (1.0) under the BS approximation.

$${}^{15} < S_{total}^{2} = 19.5 + (6 + 6 + 8 + \frac{9}{2} + 6 + 6)$$

$${}^{7} < S_{total}^{2} = 19.5 + (6 + 6 + 8p_{ad} + \frac{9}{2} + 6p_{bd} + 6p_{cd})$$

$${}^{9} < S_{total}^{2} = 19.5 + (6 + 6p_{ac} + 8 + \frac{9}{2}p_{bc} + 6 + 6p_{cd})$$

$${}^{9} < S_{total}^{2} = 19.5 + (6p_{ab} + 6 + 8 + \frac{9}{2}p_{bc} + 6p_{bd} + 6)$$

$${}^{7} < S_{total}^{2} = 19.5 + (6p_{ab} + 6p_{ac} + 8p_{ad} + \frac{9}{2} + 6 + 6)$$

$${}^{1} < S_{total}^{2} = 19.5 + (6 + 6p_{ac} + 8p_{ad} + \frac{9}{2}p_{bc} + 6p_{bd} + 6)$$

$${}^{1} < S_{total}^{2} = 19.5 + (6p_{ab} + 6 + 8p_{ad} + \frac{9}{2}p_{bc} + 6p_{bd} + 6)$$

$${}^{1} < S_{total}^{2} = 19.5 + (6p_{ab} + 6 + 8p_{ad} + \frac{9}{2}p_{bc} + 6 + 6p_{cd})$$

$${}^{3} < S_{total}^{2} = 19.5 + (6p_{ab} + 6p_{ac} + 8 + \frac{9}{2} + 6p_{bd} + 6p_{cd})$$

The energy corrections for the BS solutions in eq. (S5) are nothing but for the qualitative purpose to elucidate approximated quantum corrections by using total spin angular momentums of the broken-symmetry (BS) solutions in eq. (S6). The magnitude of total spin angular momentums in eq. (S6) is variable under the BS approximation depending on the strength of static electron correlations.⁴⁵⁻⁵² The BS energy levels based on the hybrid DFT solutions correspond to those of the mean-field approximation ($S_a \cdot S_b \rightarrow S_a \langle S_b \rangle$) of the quantum Heisenberg model. The GAP procedure for multi-nuclear transition-metal complexes is the direct generalization of the AP procedure for binuclear transition-metal complexes under the mean field hybrid DFT approximation. On the other hand, the classical spin vector models corresponds to classical approximation ($S_a \langle S_b \rangle \rightarrow \langle S_a \rangle \langle S_b \rangle$) where $\langle S_a \rangle$ means axial spin vector instead of spin operator. The magnitude of $\langle S_a \rangle$ is usually given by the classical value, for example, $\langle S_a \rangle = S_a = 4/2$ for Mn_a(III) in the analytical expression.

The effective exchange integrals (J) between Mn ions (a and b) obtained by the GAP procedure using the BS approximation are orbital-averaged values instead of each orbital value (J_{ij}). The exact diagonalization method of the spin Hamiltonian matrix is necessary to obtain the energy levels at the exact quantum level under the assumption of the orbital-averaged J values. The calculated spin densities (projection factors) have elucidated topological patterns of spin populations in the ground and lower-lying excited states. The spin densities obtained by the exact diagonalization are in turn used for elucidation of scope and reliability of the BS solutions with classical spin structures as discussed in the text. Therefore the energy levels by the exact diagonalizations and the BS approximations exhibit one to one correspondence as follows: [Fig. 4 -> Fig. 2] for $S_{1a}(R)$ and [Fig. S1 -> Fig. 3] for $S_{1b}(C)$.

The energy levels obtained by the exact diagonalization in Fig. 4 and Fig. S1 can be used for analysis of the EPR spectra of OEC of PSII.¹⁻⁴⁰ On the other hand, the energy levels in Fig. 2 and Fig. 3 obtained by the broken-symmetry calculations provide qualitative (mean-field) pictures of relative stabilities of eight spin configurations that are expressed by single Slater determinant under the BS approximation. Therefore Figs. 2 and 3 are given in this paper for qualitative purpose. Tables 3 and S7 summarizes the projection factors (spin densities) for quantitative discussions of the topology of spin polarizations.

SIII.2 Heisenberg model for the intermediates in the S3 state

The energy expressions for eight spin alignments for $S_{3a}(R)$ (X=O, Y=H₂O, W=OH) (($S_{3a}(L)$ (X=OH, Y=H₂O, W=OH)) where $M_a(IV) = M_d(IV) = M_b(IV) = M_c(IV) = 3/2$ are explicitly given under the classical approximation as⁴⁵⁻⁵²

$$^{13} < \mathbf{H} >_{A} = \frac{9}{2} (-J_{ab} - J_{ac} - J_{ad} - J_{bc} - J_{bd} - J_{cd})$$

$$^{7} < \mathbf{H} >_{B} = \frac{9}{2} (-J_{ab} - J_{ac} + J_{ad} - J_{bc} + J_{bd} + J_{cd})$$

$$^{7} < \mathbf{H} >_{C} = \frac{9}{2} (-J_{ab} + J_{ac} - J_{ad} + J_{bc} - J_{bd} + J_{cd})$$

$$^{7} < \mathbf{H} >_{D} = \frac{9}{2} (J_{ab} - J_{ac} - J_{ad} + J_{bc} + J_{bd} - J_{cd})$$

$$^{7} < \mathbf{H} >_{E} = \frac{9}{2} (J_{ab} + J_{ac} + J_{ad} - J_{bc} - J_{bd} - J_{cd})$$

$$^{1} < \mathbf{H} >_{F} = \frac{9}{2} (-J_{ab} + J_{ac} + J_{ad} + J_{bc} + J_{bd} - J_{cd})$$

$$^{1} < \mathbf{H} >_{G} = \frac{9}{2} (J_{ab} - J_{ac} + J_{ad} + J_{bc} - J_{bd} + J_{cd})$$

$$^{1} < \mathbf{H} >_{H} = \frac{9}{2} (J_{ab} - J_{ac} + J_{ad} - J_{bc} - J_{bd} + J_{cd})$$

(s7)

where the constant terms are abbreviated for simplicity.

The total energies of eight BS solutions for $S_{3a}(R)$ (X=O, Y=H₂O, W=OH) (($S_{3a}(L)$ (X=OH, Y=H₂O, W=OH)) in Table S6 are mapped into the corresponding total energies of the classical Heisenberg model. The energy differences (kcal/mol) are calculated by setting the total energy of the ferromagnetic configuration (¹⁵A) as the reference. Seven BS solutions except for the configuration F have been used to obtain analytical expressions of J values as follows:

$$\Delta < \mathbf{H} >_{AB} = <\mathbf{H} >_{B} - <\mathbf{H} >_{A} = 9(J_{ad} + J_{bd} + J_{cd}) = -0.11(0.86)$$

$$\Delta < \mathbf{H} >_{AC} = <\mathbf{H} >_{C} - <\mathbf{H} >_{A} = 9(J_{ac} + J_{bc} + J_{cd}) = 0.03(1.95)$$

$$\Delta < \mathbf{H} >_{AD} = <\mathbf{H} >_{D} - <\mathbf{H} >_{A} = 9(J_{ab} + J_{bc} + J_{bd}) = -0.62(-0.08)$$

$$\Delta < \mathbf{H} >_{AE} = <\mathbf{H} >_{E} - <\mathbf{H} >_{A} = 9(J_{ab} + J_{ac} + J_{ad}) = -0.54(-0.61)$$

$$\Delta < \mathbf{H} >_{AF} = <\mathbf{H} >_{F} - <\mathbf{H} >_{A} = 9(J_{ac} + J_{bc} + J_{ad} + J_{bd}) = 0.15(0.89)$$

$$\Delta < \mathbf{H} >_{AG} = <\mathbf{H} >_{G} - <\mathbf{H} >_{A} = 9(J_{ab} + J_{bc} + J_{ad} + J_{cd}) = -0.53(1.24)$$

$$\Delta < \mathbf{H} >_{AH} = <\mathbf{H} >_{G} - <\mathbf{H} >_{A} = 9(J_{ab} + J_{bc} + J_{ad} + J_{cd}) = -0.86(-0.03)$$
(s8)

These equations are utilized for computations of J values (cm⁻¹) under the classical approximation.

$$J_{ab} = \frac{1}{18} (-^{7} < \mathbf{H} >_{B} - ^{7} < \mathbf{H} >_{C} + ^{1} < \mathbf{H} >_{D} + ^{1} < \mathbf{H} >_{E}) = -25.4(-30.7)$$

$$J_{ac} = \frac{1}{18} (-^{13} < \mathbf{H} >_{A} + ^{7} < \mathbf{H} >_{C} + ^{7} < \mathbf{H} >_{E} - ^{1} < \mathbf{H} >_{G}) = 0.39(1.75)$$

$$J_{ad} = \frac{1}{18} (-^{13} < \mathbf{H} >_{A} + ^{7} < \mathbf{H} >_{B} + ^{7} < \mathbf{H} >_{E} - ^{1} < \mathbf{H} >_{H}) = 4.08(5.25)$$

$$J_{bc} = \frac{1}{18} (-^{13} < \mathbf{H} >_{A} + ^{7} < \mathbf{H} >_{C} + ^{7} < \mathbf{H} >_{D} - ^{1} < \mathbf{H} >_{H}) = 5.23(36.7)$$

$$J_{bd} = \frac{1}{18} (-^{13} < \mathbf{H} >_{A} + ^{7} < \mathbf{H} >_{B} + ^{7} < \mathbf{H} >_{D} - ^{1} < \mathbf{H} >_{G}) = -3.88(-9.12)$$

$$J_{cd} = \frac{1}{18} (-^{7} < \mathbf{H} >_{D} - ^{7} < \mathbf{H} >_{E} + ^{1} < \mathbf{H} >_{G} + ^{1} < \mathbf{H} >_{H}) = -4.46(37.1)$$

As expected from the energy differences in Table S6, J_{ab} values are negative and positive in sign for $S_{3a}(R)$ (X=O, Y=H₂O, W=OH) (($S_{3a}(L)$ (X=OH, Y=H₂O, W=OH)).

The total energies of the quantum Heisenberg model correspond, respectively, to those of spin-projected eight BS solutions for $S_{3a}(R)$ (X=O, Y=H₂O, W=OH) (($S_{3a}(L)$ (X=OH, Y=H₂O, W=OH)).

$${}^{13} < \mathbf{H} >_{A} = \frac{9}{2} (-J_{ab} - J_{ac} - J_{ad} - J_{bc} - J_{bd} - J_{cd})$$

$${}^{7} < \mathbf{H} >_{B} = \frac{9}{2} (-J_{ab} - J_{ac} - J_{bc}) + \frac{15}{2} (J_{ad} + J_{bd} + J_{cd})$$

$${}^{7} < \mathbf{H} >_{C} = \frac{9}{2} (-J_{ad} - J_{ab} - J_{bd}) + \frac{15}{2} (J_{ac} + J_{bc} + J_{cd})$$

$${}^{7} < \mathbf{H} >_{D} = \frac{9}{2} (-J_{ac} - J_{ad} - J_{cd}) + \frac{15}{2} (J_{ab} + J_{bc} + J_{bd})$$

$${}^{7} < \mathbf{H} >_{E} = \frac{9}{2} (-J_{bc} - J_{bd} - J_{cd}) + \frac{15}{2} (J_{ab} + J_{ac} + J_{ad})$$

$${}^{1} < \mathbf{H} >_{F} = \frac{9}{2} (-J_{ab} - J_{cd}) + \frac{15}{2} (J_{ac} + J_{ad} + J_{bc} + J_{bd})$$

$${}^{1} < \mathbf{H} >_{G} = \frac{9}{2} (-J_{ac} - J_{bd}) + \frac{15}{2} (J_{ab} + J_{ad} + J_{bc} + J_{cd})$$

$${}^{1} < \mathbf{H} >_{H} = \frac{9}{2} (-J_{ad} - J_{bc}) + \frac{15}{2} (J_{ab} + J_{ad} + J_{bc} + J_{cd})$$

where the constant terms are abbreviated for simplicity.

The quantum energy corrections (kcal/mole) are calculated by setting the total energy of the ferromagnetic configuration (¹⁵A) as the reference. Seven BS solutions except the configuration ¹⁵A (no correction for this state) have been used to obtain

analytical expressions of J values as follows:

$$\begin{split} \Delta < \mathbf{H} >_{B} = < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{C} = < \mathbf{H} >_{C} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{D} = < \mathbf{H} >_{D} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} \\ \Delta < \mathbf{H} >_{D} = < \mathbf{H} >_{D} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} \\ \Delta < \mathbf{H} >_{E} = < \mathbf{H} >_{E} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{ad} \\ \Delta < \mathbf{H} >_{F} = < \mathbf{H} >_{F} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} \\ \Delta < \mathbf{H} >_{E} = < \mathbf{H} >_{F} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} \\ \Delta < \mathbf{H} >_{E} = < \mathbf{H} >_{G} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ad})J_{ad} + (\frac{15}{2} - \frac{9}{2}p_{bc})J_{bc} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{H} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{H} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{H} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} + (\frac{15}{2} - \frac{9}{2}p_{cd})J_{cd} \\ \Delta < \mathbf{H} >_{H} = < \mathbf{H} >_{H} - < \mathbf{H} >_{A} = (\frac{15}{2} - \frac{9}{2}p_{ab})J_{ab} + (\frac{15}{2} - \frac{9}{2}p_{ac})J_{ac} + (\frac{15}{2} - \frac{9}{2}p_{bd})J_{bd} + (\frac{15}{2} - \frac{9}{2}p_{b$$

(s11)

These equations are utilized for computations of energy levels after spin projection (cm ⁻¹) under the quantum approximation. The pij coefficients for the antiferromagnetic pair have been determined using the total spin quantum numbers obtained by the broken-symmetry calculations.

$${}^{13} < S_{total A}^{2} = 15.0 + \left(\frac{9}{2} + \frac{9}{2} + \frac{9}{2} + \frac{9}{2} + \frac{9}{2} + \frac{9}{2} + \frac{9}{2}\right)$$

$${}^{7} < S_{total B}^{2} = 15.0 + \left(\frac{9}{2} + \frac{9}{2} + \frac{9}{2}p_{ad} + \frac{9}{2} + \frac{9}{2}p_{bd} + \frac{9}{2}p_{cd}\right)$$

$${}^{7} < S_{total C}^{2} = 15.0 + \left(\frac{9}{2} + \frac{9}{2}p_{ac} + \frac{9}{2} + \frac{9}{2}p_{bc} + \frac{9}{2} + \frac{9}{2}p_{cd}\right)$$

$${}^{7} < S_{total C}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2} + \frac{9}{2} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}\right)$$

$${}^{7} < S_{total D}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ac} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}\right)$$

$${}^{1} < S_{total F}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ac} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}\right)$$

$${}^{1} < S_{total G}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ac} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}\right)$$

$${}^{1} < S_{total G}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ac} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}\right)$$

$${}^{1} < S_{total G}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}p_{cd}\right)$$

$${}^{1} < S_{total H}^{2} = 15.0 + \left(\frac{9}{2}p_{ab} + \frac{9}{2}p_{ac} + \frac{9}{2}p_{ad} + \frac{9}{2}p_{bc} + \frac{9}{2}p_{bd} + \frac{9}{2}p_{cd}\right)$$

The energy corrections for the BS solutions in eq. (S11) are nothing but for the

qualitative purpose to elucidate quantum corrections for BS energy levels. Therefore the energy revels by the exact diagonalizations and the BS approximations exhibit one to one correspondence as follows:

[Fig. S2 -> Fig. 5] for $S_{3a}(R)$ -H₂O and [Fig. 7 -> Fig. 6] for $S_{3a}(L)$ -H₂O. The energy levels obtained by the exact diagonalization in Fig. 7 and Fig. S2 can be used for analysis of the EPR spectra of OEC of PSII.¹⁻⁴⁰ On the other hand, the energy levels in Fig. 5 and Fig. 6 obtained by broken-symmetry approximation provide qualitative pictures of relative stabilities of eight spin configurations that are expressed by single Slater determinant under the mean-field approximation. Therefore Figs. 5 and 6 are given in this paper for qualitative purpose.

SIII.3 Heisenberg model for synthetic model compounds

The magnetic susceptibility experiments have been performed to elucidate effective exchange integrals (J) for synthetic Mn_4 model clusters. The observed J values for Christou complex⁷⁴ have been compared with the calculated J values for $S_{3a}(L)$ -H₂O in the text. Kanady et al^{S1)} have performed the magnetic susceptibility measurements of their synthetic model complex; $Mn(III)_2Mn(IV)_2$. The observed J values are as follows: $J_{ab}=J_{ac}=J_{bd}=J_{cd}=J_1 = -13.9 \text{ (cm}^{-1})$; $J_{ad}=J_2 = -6.13 \text{ (cm}^{-1})$; $J_{bc}=J_3 = -18.2 \text{ (cm}^{-1})$. The total energies of the eight spin configurations are given by the quantum Heisenberg model in eq. (s3). The computational results are shown in eq. (s13). The triplet state is the ground state for $Mn(III)_2Mn(IV)_2$ in accord with the EPR experiment, showing the up-, up-down-down spin structure for the mixed–valence $Mn(III)_aMn_d(III)Mn(IV)_b$ $Mn(IV)_c$ state. The computational results for the model complex $Mn(III)_2Mn(IV)_2$ support the present theoretical formulations for the four-site spin systems.

$${}^{15} < H_{total A} = -24J_1 - 8J_2 - \frac{9}{2}J_3 = 465.9$$

$${}^{7} < H_{total B} = 6J_1 + 12J_2 - \frac{9}{2}J_3 = -77.1$$

$${}^{9} < H_{total C} = 6J_1 - 8J_2 + \frac{15}{2}J_3 = -169.5$$

$${}^{9} < H_{total D} = 6J_1 - 8J_2 + \frac{15}{2}J_3 = -169.5$$

$${}^{7} < H_{total E} = 6J_1 + 12J_2 - \frac{9}{2}J_3 = -77.1$$

$${}^{1} < H_{total F} = 6J_1 + 12J_2 + \frac{15}{2}J_3 = -295.5$$

$${}^{1} < H_{total G} = 6J_1 + 12J_2 + \frac{15}{2}J_3 = -295.5$$

$${}^{3} < H_{total H} = 36J_1 - 8J_2 - \frac{9}{2}J_3 = -368.1$$

(s13)

S1) J. S. Knady, R. Tran, J. A. Stull, L. Liu, T. A. Stich, M. W. Day, J. Yano, R. D. Britt, T. Agapie, Chem. Sci. 2013, 4, 3986.