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Supporting Information

Geometric and electronic structures of the synthetic Mn_4CaO_4 model compound mimicking the photosynthetic oxygen-evolving complex

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Contents

S1. Backgrounds

S1.1 Historical developments of the broken-symmetry methods

S1.2 More general broken-symmetry solutions and recoveries of the broken symmetries

S1.3 Broken-symmetry solutions in the Kohn-Sham density functional theory

S1.4 Spin Hamiltonian models for local spins in diradicals and polyradicals

S1.5 Effective procedures for construction of broken-symmetry solutions

S1.6 Summary of the native OEC structure in the X-ray structures

Figure S1.1 Coordination bond lengths around Mn1 and Mn4

S1.7 Comparison of Zhang model complex with several OEC models of PSII

Figure S1.2 Early structures of PSII-OEC

S2. Results of **1** calculated at the UB3LYP/DZVP level.

Figure S2.1 Superimposed structures of 1 optimized at the UB3LYP/DZVP level.

Figure S2.2 Localized natural orbitals of 1 in the S_0(b) state

Figure S2.3 Localized natural orbitals of 1 in the S_0(a) state

Figure S2.4 Localized natural orbitals of 1 in the S_1 state

Figure S2.5 Localized natural orbitals of 1 in the S_2(R) state

Figure S2.6 Localized natural orbitals of 1 in the S_2(C) state

Figure S2.7 Localized natural orbitals of 1 in the S_3 state

Figure S2.8 low-lying energy levels of 1 calculated at the UB3LYP/DZVP level.

Table S2.1 Bond valence sum calculation

Table S2.2 Local spin correlation factor of 1 calculated the J values at the UB3LYP/DZVP level.

Atomic coordinates of **1** (in XYZ file format) optimized at the UB3LYP/DZVP level in the S_{-1}, S_0(a), S_0(b), S_1(DUUU), S_1(UDUD), S_2(R), S_2(C), S_3 states

S3. Results of **1** calculated at the UBLYP/DZVP level.

Table S3.1 J values of **1** calculated at the UBLYP/DZVP level.

Table S3.2 Low-lying excitation states of **1** evaluated using the J values calculated at the UBLYP/DZVP level.

Figure S3.1 Coordination bond lengths around Mn1 and Mn4

Figure S3.2 Localized natural orbitals related to the Mn Jahn-Teller distortions.
Figure S3.3 Schematic illustration of the magnetic interactions of 1 calculated at the UBLYP/DZVP level.

S4. Results of **2** calculated at the UB3LYP/DZVP and UBLYP/DZVP level .
Table S4.1 Key bond lengths of the Mn_4CaO4 cores of 2 calculated at the UBLYP/DXVP level.
Table S4.2 Mn-O bond lengths of the Mn_4CaO4 cores of 2 calculated at the UBLYP/DXVP level.
Table S4.3 Calculated J values of **2** at the UB3LYP/DZVP (UB3LYP/DZVP) level.
Table S4.4 Low-lying energy levels of 2 calculated at the UB3LYP/DZVP (UBLYP/DZVP) level.
Table S4.5 Local spin correlation factor calculated at the UB3LYP/DZVP (UBLYP/DZVP) level.
Figure S4.1 Superimposed structures of **2**.
Figure S4.2 Localized natural orbitals of 2 in the S0 (b) state
Figure S4.3 Localized natural orbitals of 2 in the S0 (a) state
Figure S4.4 Localized natural orbitals of 2 in the S1 state
Figure S4.5 Localized natural orbitals of 2 in the S2 (R) state
Figure S4.6 Localized natural orbitals of 2 in the S2 (C) state

S5. Theoretical modeling
Figure S5.1 Molecular structures of model $\mathbf{C_a}$ and $\mathbf{C_b}$.
Atomic coordinates of the theoretical models (models A, B, Ca, Cb in XYZ file format) optimized at the UB3LYP/DZVP in the highest spin states (S=7).

S6. Ca substitutions
Table S6.1 Mn-Mn distances of the Ca substituted models
Table S6.2 Mn-O distances of the Ca substituted models
Figure S6.1 Superimposed views of the Ca substituted models (Mn_4AO_4, A=Br, Sr, Ca, Mg, Zn and Mn).

S1. Backgrounds

S1.1 Historical developments of the broken-symmetry methods

According to the suggestion of one of the referees, historical developments of the broken-symmetry (BS) methods are briefly reviewed in the supporting material. In early 1970th the extended Huckel molecular orbital (EHMO) method was useful and handy for theoretical studies of organic molecules. The EHMOs are characterized by the point group symmetry (Pn). Spatial symmetries of EHMOs are theoretical foundations of orbital-symmetry conservation rules for concerted reactions by Woodward-Hoffmann and frontier molecular orbital (HOMO, LUMO) theories for chemical reactions by Fukui. However the EHMO method was insufficient for theoretical studies on spins in molecules.

The Hartree-Fock (HF) MO method takes into account for electron spins in molecules. The spin-restricted Hartree-Fock (RHF) solution is usually reliable for MO description of closed-shell electronic states consisted of even number of electrons. Spatial symmetries of RHF MOs are also theoretical foundations for the Woodward-Hoffmann rules and frontier molecular orbital theories. The HF method utilizes one Slater determinant for many particle (electron) systems, indicating one of the mean field (independent particle) theories. Therefore the HF method permits a bifurcation of the closed-shell singlet pair into the open-shell singlet diradical pair in a certain condition: this condition is referred to as the instability condition (ref. s1). Indeed, the closed-shell RHF solution often suffers from the triplet instability when the HOMO-LUMO energy gap becomes smaller than the on-site Coulomb repulsion integral (U) (ref. s2). The symmetry-adapted molecular orbitals of the unstable RHF solution are inevitably reorganized into the unrestricted Hartree-Fock (UHF) molecular orbitals through the HOMO-LUMO mixing (ref. s2) to reduce the effect of the electron repulsion (U) as follows:

$$\begin{cases} \psi_1^{\alpha} = \cos\theta\ \psi_+ + \sin\theta\ \psi_- \\ \psi_1^{\beta} = \cos\theta\ \psi_+ - \sin\theta\ \psi_- \end{cases} . \qquad (1.1)$$

where the ψ_+ and ψ_- denote the HOMO and LUMO, respectively.

The HOMO and LUMO have usually different special symmetries such as symmetric (S) and anti-symmetric (A). Therefore the alpha and beta spatial orbitals, ψ_1^{α} and ψ_1^{β}, obtained by the HOMO-LUMO mixing inevitably entailed the breakdown of the special symmetry of the molecular orbitals in the UHF solution (ref. s2). Thus the UHF MOs are spatially symmetry-broken in sharp contrast to the RHF orbitals. The HOMO-LUMO crossing often occurs in the course of the symmetry-forbidden

reactions. Therefore the HOMO-LUMO mixing occurs in the orbital crossing region, providing the broken-symmetry (BS) UHF MOs that are responsible for diradical intermediate generated in symmetry-forbidden reactions in organic chemistry. Thus the origin of our concept of the orbital symmetry breaking was closely related to the necessity of the MO-theoretical description of symmetry-forbidden diradical reactions in 1970th (refs. s2 and s8).

The UHF MOs are mainly localized on different spatial region, providing a localized MO picture of diradical electrons, namely local spins, for which chemical notation (・) is often used. Therefore the localized molecular orbitals (LMO) are naturally introduced as the maximum HOMO-LUMO mixing orbitals ($\theta = \pi/4$ in eq. (1.1)) (ref. 17) as

$$\begin{aligned} \psi_+(LMO) &= 1/\sqrt{2}(\psi_+ + \psi_-) \\ \psi_-(LMO) &= 1/\sqrt{2}(\psi_+ + \psi_-) \end{aligned} \qquad (1.2)$$

For example, the LMOs are similar to the atomic 1s orbitals for a dissociating hydrogen molecule: H_a ・ …. ・ H_b since the $\psi_+(LMO)$ and $\psi_-(LMO)$ are largely localized on the x- and y hydrogen atoms, respectively. However, they are not identical to the atomic 1s orbitals in the valence bond (VB) model (see eq. (1.14)) except for the dissociation limit since they have small tails at the y- and x-sites, respectively (ref. 17). On the other hand, the LMOs are orthogonal because of this characteristic property, providing a useful LMO basis for the configuration interaction (CI) approach (ref. 18) starting from the BS MO calculations. The LMO CI provided chemical pictures based on the LMOs instead of the VB model. To this end, the BS MOs in eq. (1.1) are rewritten by the LMOs as

$$\begin{cases} \psi_1^\alpha = \cos\omega\ \psi_+(LMO) + \sin\omega\ \psi_-(LMO) \\ \psi_1^\beta = \cos\omega\ \psi_-(LMO) + \sin\omega\ \psi_+(LMO) \end{cases} \qquad (1.3)$$

where the orbital mixing parameter ω is given by ($\theta + \pi/4$).

The RHF and UHF solutions given by the single Slater determinant can be expanded with the LMOs to obtain the VB picture. For example, the UHF solution is given by

$$\begin{aligned} |\Psi_{UHF1}\rangle &= \left|\psi_1^\alpha \overline{\psi}_1^\beta\right\rangle = \cos\omega^2 \left|\psi_+(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle + \cos\omega\sin\omega\{\left|\psi_+(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle + \\ &\left|\psi_-(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle\} + \sin\omega^2 \left|\psi_-(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle \end{aligned} \qquad (1.4a)$$

$$= \Phi_S + \cos 2\omega \Phi_T + 1/2 \sin 2\omega \{\Phi_{ZWa} + \Phi_{ZWb}\} \qquad (1.5a)$$

where the pure singlet (S), triplet (T) and zwitterionic (ZW) configurations are defined

by using the LMOs as

$$\Phi_S = 1/\sqrt{2}(\left|\psi_+(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle + \left|\psi_-(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle)$$
$$\Phi_T = 1/\sqrt{2}(\left|\psi_+(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle - \left|\psi_-(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle) \quad (1.6)$$

$$\Phi_{ZWa} = \left|\psi_+(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle, \Phi_{ZWa} = \left|\psi_-(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle \quad (1.7)$$

The UHF solution involves the pure triplet component as shown in eq. (1.5a), indicating the mixing of the singlet and triplet states, namely the spin symmetry breaking. In fact, the half and half mixing occurs at the dissociation limit ω=0.

$$\left|\Psi_{UHFI}(\omega = 0)\right\rangle = \Phi_S + \Phi_T \quad (1.8)$$

Such symmetry breaking property of the UHF solution was an origin of the critical opinion for the BS method at that time (1970th).

Quantum mechanics (QM) however teach us to construct the other UHF solution by using the BS orbitals in eq. (1.1) as follows:

$$\left|\Psi_{UHFII}\right\rangle = \left|\psi_1^\beta \overline{\psi}_1^\alpha\right\rangle = \cos\omega^2 \left|\psi_-(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle + \cos\omega\sin\omega\{\left|\psi_-(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle + \left|\psi_+(LMO)^\alpha \overline{\psi_+(LMO)}^\beta\right\rangle\} + \sin\omega^2 \left|\psi_+(LMO)^\alpha \overline{\psi_-(LMO)}^\beta\right\rangle \quad (1.4b)$$

$$= \Phi_S - \cos 2\omega \Phi_T + 1/2 \sin 2\omega\{\Phi_{ZWb} + \Phi_{ZWa}\} \quad (1.5b)$$

The UHFI and UHFII solutions are degenerated in energy, and therefore the quantum-mechanical (QM) resonation between them should occur in the finite diradical systems without the magnetic long-range order, providing the pure singlet and triplet states as follows:

$$\left|\Psi_S\right\rangle = 1/\sqrt{N_S}(\left|\Psi_{UHFI}\right\rangle + \left|\Psi_{UHFII}\right\rangle) = 1/\sqrt{N_S}(2\Phi_S + \sin 2\omega\{\Phi_{ZWb} + \Phi_{ZWa}\}$$
$$\left|\Psi_T\right\rangle = 1/\sqrt{N_T}(\left|\Psi_{UHFI}\right\rangle - \left|\Psi_{UHFII}\right\rangle) = \Phi_T \quad (1.9)$$

where the N_S and N_T denote the normalizing factors (ref. 18). Thus the resonating BS solutions recover the QM requirement (no symmetry breaking), providing the pure singlet and triplet states of diradical states. The pure singlet state in eq. (1.9) can be also obtained by removing out the triplet component from eq. (1.5a or 1.5b), leading to the spin projection (SP) procedure for recovering the spin-symmetry breaking in the BS UHF solution. It is noteworthy that the SP BS solution involves mainly the covalent

term (Φ_S), together with non-negligible zwitterionic terms (Φ_{ZWa} and Φ_{ZWb}) in the LMO CI by the use of two LMOs in eq. (1.2) (ref. 18).

The configuration interaction (CI) by the use of the LMOs has been performed to confirm scope and reliability of the spin projected BS UHF solutions in ref. 18 and related papers in 1970th. It was found that the LMO CI wavefuntion for the singlet ground state mainly involves the singlet wavefunction, together with small correction terms, as

$$\Phi^S_{LMO-CI} = 1/\sqrt{N_S}(|\Psi_S\rangle + (small corrections)\} \\ \Phi^T_{LMO-CI} = 1/\sqrt{N_T}(|\Psi_T\rangle + (small corrections)\} \qquad (1.10).$$

Thus the BS approach followed by the spin projection was applicable to MO-theoretical descriptions of the singlet and triplet diradical ground states. On the other hand, the LMO CI indicated that the excited singlet states are mainly described by the resonating states of the ZW_a and ZW_b configurations. The above results were our early BS approaches to diradical molecules in 1970th.

The above LMO CI scheme for diradical systems was extended for many electron systems, namely polyradicals. To this end, the natural orbital (NO) analysis of the BS solutions was performed to determine the natural molecular orbitals (NO) and their occupation numbers. The active natural orbital space (CAS) for polyradicals are easily selected by using their occupation numbers, leading to the CAS CI for confirmation of the projected BS solutions for the species. The multi-reference (MR) CI by the use of the UHF-NO (=UNO) CAS CI reference was performed for more complex polyradicals systems (ref. s3).

The multiple metal-metal bonds were topic in inorganic chemistry in late 1970th. The triplet instability condition (ref. s1) for the HF solution was also applicable to the Hartree-Fock-Slater (HFS) solutions for the weak metal-metal bonds such as the δ-δ bond of binuclear transition metal complexes with formal quadruple bonds as shown in ref. 19. The HOMO-LUMO mixing in the HFS solution provided the BS orbitals in eq. (1.1) and localized MOs of the HFS solutions like in the case of eq. (1.3). Therefore the same LMO CI-type expansions of the unrestricted HFS (UHFS) solutions were also feasible as shown in ref. 20. However LMO CI was too difficult for large transition-metal clusters at that time. Therefore the many-body perturbations starting from the UHFS solutions were also proposed in relation to the inclusion of dynamical correlations in ref. 20. Nowadays, the double hybrid DFT involving the second-order perturbations (MP2) was developed. Noodleman utilized the localized MOs for analysis of the BS Xα solutions developed by Slater and Johnson in ref. 21.

Our LMO CI approach based on UHF and UHFS crossed the Noodleman's approach near 1980 because the UHFS solution is closely related to the BS Xα solution.

In 1970th, generalized valence bond (GVB) method (ref. s4) was exclusively used for theoretical investigations of diradical species. Therefore Noodelman (ref. 21) used a terminology: Xα valence bond (VB) model for analysis of the BS Xα solution in conformity with the GVB theory. However in 1980th, it was found that the GVB perfect-pairing (PP) method like the VB model could not properly describe the dissociation process of singlet metal-carbene double bond ($M=CH_2$) into two triplet fragments

$$^1M=O\ (^1M=CH_2) \rightarrow {}^1[\cdot M-O\cdot]\ (^1[\cdot M-CH_2\cdot]) \rightarrow {}^3M + {}^3O\ (^3CH_2) \qquad (1.11)$$

The mixing between dπ-pπ HOMO and dπ-pπ* LUMO occurs in an intermediary region, providing BS π-orbitals localized mainly on M and O(CH_2) sites, respectively. Similarly the mixing between dσ-pσ HOMO and dσ-pσ* LUMO occurs in the dissociation region, providing BS σ-type orbitals localized mainly on M and O(CH_2) sites, respectively. Finally two triplet fragments are generated at the dissociation limit. Therefore GVB PP model was broken, leading to the necessity of GVB CI to describe this type of reactions, for example reactions of transition metal oxo complexes. In order to recover the spin symmetry, a kind of spin optimized (SO) procedure (ref. s11) is required for the VB approach by the use of non-orthogonal orbitals. On the other hand, the full CI by the use of complete active space (CAS) is applicable for refinements of the BS solutions if the CAS were constructed by the orthogonal natural orbitals by the BS solutions as shown in ref. s3. Thus we have developed our own UHF-NO (UNO) CI approach for seamless extension from BS (UHF, UHFB) method to symmetry adapted (SA) post BS methods in general.

S1.2 More general broken-symmetry solutions and recovery of the broken symmetries

In the 1960's, the theory of symmetry breaking has been developed in the elementary particle physics by Y. Nambu and in the solid state physics (magnetism) by Nagamiya, Kanamori and Yoshimori in Osaka. Yoshimori discovered the non-collinear helical (rotating) spin structure for the Mn-oxide in 1959 on the basis of the classical Heisenberg model. One of the authors (K.Y) applied the classical spin vector models for radical clusters such as the equilateral H_3 and tetrahedaral H_4 radicals, proposing the triangular (two dimension (2D)) and tetrahedral (three dimension (3D)) spin structures in ref. s5 although the one-dimension (1D) up- and down-spin solutions

in eq. (1.1) were popular in quantum chemistry at that time. The spin structures were characterized by using the magnetic group constructed by the spin rotation (S) and time-reversal (T) symmetries; note that spin is an angular momentum, and therefore the time-reversal (T) operation is necessary for its inversion.

In the field of the theoretical physics, Fukutome developed a general theory of the unrestricted Hartree-Fock (UHF) solutions on the basis of the group-theoretical classification by the use of spin rotation (S) and time-reversal (T) symmetry (ref. s6). The real and complex general spin orbitals (GSO), namely two-component spinors, were introduced, respectively, to describe the 2D and 3D spin structures under the UHF approximation. Later Osaki generalized the Fukutome classification of the UHF solutions by considering the spatial (point group) symmetry (Pn), providing a general UHF theory characterized by the Pn x S x T symmetry operations. Furthermore Ozaki developed the Hartree-Fock-Bogoliubov (HFB) theory by considering the gauge symmetry (ϕ) that describes the superconductivity in general (ref.s7). Therefore general broken-symmetry UHF and unrestricted HFB (UHFB) solutions are characterized by using these symmetry operations in infinite systems, for which various types of phase transitions, namely the long-range orders, are feasible.

We were interested in strong electron correlations effects that entail several types of broken symmetry UHF and UHFB solutions even in finite systems where short-range static correlations (not phase transitions) play significant roles in chemistry. The spin correlation functions were introduced to express short-range spin correlations in refs. s8 and s9, elucidating important roles of spin densities in 1D, 2D and 3D UHF solutions (mathematical derivations are abbreviated here). However, recoveries of broken-symmetries are necessary for quantitative purposes like in the case of eq. (1.9) for diradicals. As an example, we have examined the recovery of the broken-symmetries for the equilateral H_3 radical (a tri-radical) that are described by the GSO under the UHF approximation in ref. s10. We have examined the permutation symmetry (S_N) for recovery of spin symmetry, namely the total spin angular momentum $\langle S^2 \rangle$ and the S_z-componemt of the total wavefunction. The magnetically ordered GSOs for the H_3 radical were also characterized by the time-reversal (T), spin rotation (S) and spatial symmetry (Pn). The total energies of the broken-symmetry (BS) UHF, spin-projected UHF and extended Hartree-Fock (EHF) solutions by the use of the GSOs were obtained analytically by using the Hubbard model, providing the potential curves for the dissociation of the H_3 radical into 3H atoms in ref. s10. The key concept was emerged from these computations, indicating

that the BS solutions provide qualitatively reliable potential curves for the dissociation of covalent bonds.

We have examined the symmetry breaking and recoveries of broken-symmetries in general in ref. s11 by using the symmetry operations, namely S_N, T, S, Pn. These symmetry operations elucidated the interrelationships between several model Hamiltonians used in the field of chemistry as follows:

a) Huckel and extended Huckel models (spatial symmetry characterized by the point group (Pn))

b) Classical Heisenberg model (magnetic group, spin rotation (S) x time reversal (T) symmetry)

c) Quantum Heisenberg model (exchange interaction, permutation group (S_N))

d) Generalized Hartree Fock and Hartree Fock Slater models (magnetic double group, Pn x S x T)

e) Extended Hartree Fock model (a unified theory: S_N x Pn x S x T).

The number density projection of the UHFB solutions was necessary for the recovery of numbers of electrons in finite systems such as fragments of molecular superconductors. Thus we were concerned with the symmetry breaking and recovery of broken symmetry in general before the crossing with the Noodelman' approach based on the Xα model in ref. 21.

S1.3 Broken-symmetry solutions in the Kohn-Sham density functional theory

The density functional theory (DFT) is the exact theory in principle, and therefore the broken-symmetry (BS) solution should not appear in finite systems without phase transitions. In fact, Becke still stands on this basic position, proposing the symmetry-adapted B13 functional for DFT approaches to strongly correlated electron systems (SCES). On the other hand, the Kohn-Sham (KS) equation permits broken-symmetry (BS) solutions characteristic of the mean field approximation in finite systems with strong electron correlations. Therefore the group-theoretical characterizations mentioned above (section 1.2) are equally applicable to BS KS-DFT solutions and BS hybrid DFT (HDFT) solutions obtained by the mixing of the BS KS DFT and BS HF solutions like in the case of the UB3LYP method (ref. s12). In fact, the natural orbital analysis of the BS HDFT solutions provided the natural molecular orbitals for many electron systems as an extension of LMO in eq. (1.2). Here we do not repeat details. The details are given in our early (ref. s3, s10, s11) and recent papers (refs. 23-25).

S1.4 Spin Hamiltonian models for local spins in diradicals and polyradicals

As shown in sections 1-3, several BS solutions derived from triplet (ref. s1) and

spin-flip (ref. s6) instabilities provide local spins for strongly correlated electron systems (SCES), for which the temperature-dependent magnetism was often observed by the magnetic susceptibility measurements. The observed magnetism of local spins has been investigated on the basis of the Heisenberg spin Hamiltonian model (ref. s4) that involves important parameters (J) responsible for effective exchange interactions between local spins. The newly appeared magnetic energy levels may be regarded as an indication of quasi-phase transitions like in the case of the newly appeared rotational spectra by deformations of nuclear matters. The Bohr-Mottelson theory (ref. s13) for the nuclear deformation was a guiding principle for us at that time (1970th) since the nuclear matters are finite systems like magnetic clusters in chemistry. Thus the temperature-dependent magnetism is a key evidence for existence of local spins in finite systems.

In analogy with the rotational energy levels, the eight energy levels of the ππ, σπ, πσ and σσ diradical configurations of HNOO radical were first obtained as an example of newly appeared spatial and spin-symmetry broken UHF solutions (ref. s14). The successive UHF-NO(UNO) CI calculations were also performed to elucidate singlet and triplet energy gaps for four different diradical structures (ref. s15). For the evaluation of the magnetic interactions (effective exchange J values), three different formulations have been proposed at that time;

$$J_{xy}^{(G)} = \frac{{}^{LS}E_X - {}^{HS}E_X}{S_{max}^2}, \qquad (1.12a)$$

$$J_{xy}^{(N)} = \frac{{}^{LS}E_X - {}^{HS}E_X}{S_{max}(S_{max}+1)}, \qquad (1.12b)$$

$$J_{xy}^{(Y)} = \frac{{}^{LS}E_X - {}^{HS}E_X}{{}^{HS}\langle S^2\rangle_X - {}^{LS}\langle S^2\rangle_X}, \qquad (1.12c)$$

by Ginsberg [s16], Noodleman [s17,s18] and ours [s15,s19-s21], respectively. Our UHF results for HNOO (ref. s14) and UNO-CI results for CH_2OO correspond, respectively, to the Ginsberg scheme (1.12a) and our later scheme (1.12c). These equations are applicable to local spins at sites x and y. The eq. (1.12c) is the approximate spin projection (AP) scheme, and ${}^{Y}E_X$ and ${}^{Y}\langle S^2\rangle_X$ denote the total energy and total squared-magnitude of total spin at the spin state Y by several BS methods X (X=UHF, UMP, UCC, UDFT). The AP procedure is derived from the approximate spin contamination correction of the low spin (BS) state using the Heisenberg spin Hamiltonian ($H = -2J_{x,y}s_x \cdot s_y$) to reproduce the UNO CI results approximately; the triplet component in eq. (1.5a(b)) is replaced with the high-spin (HS) UHF solution for approximate spin projection. On the other hand, the $J^{(G)}$ and $J^{(N)}$ formulations

correspond to the limits of broken diradical bonds and strong covalent bonds, respectively. The $^{LS}\langle S^2\rangle_X$ values at these limits are given by

$$^{LS}\langle S^2\rangle_X = S_{max} \quad \text{for broken diradical bonds,}$$
$$^{LS}\langle S^2\rangle_X = 0 \quad \text{for strong covalent bonds,} \qquad (1.13)$$
$$^{HS}\langle S^2\rangle_X = S_{max}(S_{max}+1).$$

Therefore our scheme in eq. (1.12c) covers both the limits, and moreover it is equally applicable to symmetry-adapted methods such as CAS-CI, CASSCF, UNO(ULO) CI, MR CI (refs. s15 and s19-s21). Many other computational schemes for J values are derived from eq. (1.12c). The total energy of the LS solution after AP is also given by using the J values as

$$^{AP-LS}E_X = {}^{LS}E_X + J_{xy}^{(Y)}({}^{LS}\langle S^2\rangle_X - 0.0) \qquad (1.14)$$

where $^{LS}\langle S^2\rangle$ becomes 0.0 for the exact singlet state although the BS methods X provide non-zero values.

These proposed schemes are, however, limited to two-site systems. For multispin system, we proposed a generalized spin projection (GP) scheme in ref. 28, which is a natural extension of the AP scheme, and properly corresponding to the Heisenberg spin Hamiltonian ($H = \sum_{<x,y>} -2J_{x,y}\, s_x \cdot s_y$). In GP scheme, J values are evaluated as

$$J_{xy}^{(GP)} = \frac{{}^{F}E_X - {}^{AF}E_X}{-2\left({}^{F}\langle s_x \cdot s_y\rangle_X - {}^{AF}\langle s_x \cdot s_y\rangle_X\right)}, \qquad (1.12.d)$$

The energy correction scheme after GP was also derived in ref. 28. In this paper we have used the GP scheme for spin projection for UB3LYP solutions for the Mn_4CaO_4 cluster. Thus our computational formula are applicable for both BS and post BS (symmetry adapted) methods because of symmetry projections in contrast to those of other groups.

s1 J. Cizek and J. Paldus, " Stability conditions for the solutions of the Hartree-Fock equations for atomic and molecular systems. Application to the pi-electron model of cyclic polyenes", J. Chem. Phys. 47, 3976-3985 (1967).

s2 K. Yamaguchi, "The electronic structure of biradicals in the unrestricted Hartree-Fock approximation", Chem. Phys. Lett., 33, 330-335 (1975).

s3 K. Yamaguchi, "Multireference (MR) configuration interaction (CI) approach for quasidegenerate systems", Intern. J. Quant. Chem. S14, 269-284 (l980).

s4 W. A. Goddard, T. H. Dunning, W. J. Hunt and P. J. Hay, “Generalized valence bond description of bonding in low0lying states of molecules “ Accounts Chem. Res. 6, 368-375 (1973).

s5 K. Yamaguchi, “General spin structures of organic radicals”, Chem. Phys. Lett. 30, 288-292 (1975).

s6 H. Fukutome, “Theory of the unrestricted Hartree-Fock equation and its solution. III Classification of instabilities and interconnection relation between the eight classes of UHF solutions” , Prog. Theoret. Phys. 52, 1766-1783 (1974).

s7 M.-A. Ozaki, “Group theoretical analysis of the Hartree-Fock-Bogoiubov equation. I. General theory”, J. Math. Phys. 28, 1514-1520 (1985).

s8 K. Yamaguchi, T. Fueno, “Correlation effects in singlet biradical species”, Chem. Phys. 19, 35-42 (1977).

s9 K. Yamaguchi, “Generalized molecular orbital (GMO) theories of organic reaction mechanisms: orbital symmetry, orbital stability and orbital pairing rules, Chem. Phys. 29, 117-139 (l978).

s10 K. Yamaguchi, Y. Yoshioka and T. Fueno, “Interrelationships between the effective Hamiltonians for the H3 radical”, Chem. Phys. Lett. 46, 360-365 (l977).

s11 K. Yamaguchi, Y. Yoshioka, K. Takatsuka and T. Fueno, “Extended HF theory of chemical reactions II: symmetry properties of the EHF wavefunctions constructed by the magnetically ordered general spin orbitals”, Theoret. Chim. Acta 48, 185-206 (l978).

s12 Becke, J. Chem. Phys, 98, 1372-1377 (1993).

s13 A. Bohr and B. R. Mottelson, “Some current themes in nuclear research”, Physica Scripta , 10A, 13-23 (1974).

s14 K. Yamaguchi, S. Yabushita and T. Fueno, “ Unrestricted Hartree-Fock (UHF) calculations of singlet and triplet diradicala: Nitrene peroxide (HNOO)”, J. Chem. Phys. 71, 2321-2322 (1979).

s15 K. Yamaguchi, S. Yabushita, T. Fueno, S. Kato, K. Morokuma and S. Iwata, “ Ab initio UHF and UHF NO CI approaches for quasi-degenerate systems: methylene peroxide (CH_2OO)”, Chem. Phys. Lett. 71, 563-568 (1980).

s16 A.P. Ginsberg, J. Am. Chem. Soc. 102, 111 (1980).

s17 L. Noodleman, J. Chem. Phys. 74, 5737 (1981).

s18 L. Noodleman, E.R. Davidson, Chem. Phys. 109, 131 (1986).

s19 K. Yamaguchi, Y. Takahara, T. Fueno, in V.H. Smith, Jr., H.F. Scheafer III, K. Morokuma (Eds.), Applied Quantum Chemistry, D.Reidel, Boston, 155 (1986).

Our computational scheme of J was presented at the pacific chem (Hawaii)

meeting in 1984 and in the book “Ryoushi Kagaku Saizensen” (In Japanese, 1985) p19-p29.

s20 K. Yamaguchi, Y. Toyoda, T. Fueno, Synthetic Metals 19, 81 (1987).

s21 S. Yamanaka, T. Kawakami, H. Nagao, K. Yamaguchi, Chem. Phys. Lett. 231, 25 (1994)

S1.5 Effective procedures for construction of broken-symmetry solutions

Broken-symmetry (BS) solutions have been constructed by the HOMO-LUMO mixing procedures in eq. (1.1). However, the SCF processes to obtain the low-spin (LS) BS solutions often exhibit slow convergence or divergence in the case of multi-nuclear transition metal complexes. On the other hand, the highest-spin (HS) solutions are obtained more easily by conventional SCF procedures. Therefore constructions of the trial orbitals for the LS states by using the HS orbitals are practical and convenient for the rapid convergence as shown in ref. 27. To this end localized natural orbital (LNO) transformations were utilized to make good broken-symmetry initial guesses and to clearly depict the Mn d orbitals, which are very variable to understand the Jahn-Teller distorsions. Since the theoretical background and their specific procedures have been described in ref. 27, only the concept and supplemental statements for **1** are given here.

In the two-spin 1/2 system, the bonding and antibonding orbitals are easily obtained by the HS triplet solution as

$$\begin{cases} \psi_+ = \dfrac{1}{\sqrt{2(1+S)}}(\phi_1 + \phi_2) \\ \psi_- = \dfrac{1}{\sqrt{2(1-S)}}(\phi_1 - \phi_2) \end{cases} \qquad (1.15)$$

where ϕ_i is the i-th site atomic orbital and $S = \langle \phi_1 | \phi_2 \rangle$ denotes the overlap integral between them. The broken-symmetry (BS) orbitals are constructed of the mixing of these HS orbitals as shown in eq. (1.1). Using these orbitals, the BS wave function for the low-spin (LS) singlet configuration is given by (see also eq. (1.4a))

$$|\Psi_{\mathrm{BS}}\rangle = \left|\psi_1^{\alpha}\overline{\psi}_1^{\beta}\right\rangle \quad . \qquad (1.16)$$

The total $\langle S^2 \rangle$ value for the LS BS solution are given by

$$\langle S^2 \rangle_{\mathrm{BS}} = 1 - T^2 \qquad (1.17)$$

where T denotes the overlap between the BS orbitals that are non-orthogonal.

$$T = \left\langle \psi_1^{\alpha} \middle| \psi_1^{\beta} \right\rangle = \cos 2\theta . \tag{1.18}$$

In two-spin systems, natural orbitals are same as their molecular orbitals of eq. (1.1). Interestingly, the orbital localization procedure employed here performs the similar orbital mixing procedure as,

$$\begin{cases} \psi_{\mathrm{LNO1}} = \cos\gamma\ \psi_{+} + \sin\gamma\ \psi_{-} \\ \psi_{\mathrm{LNO2}} = -\sin\gamma\ \psi_{+} + \cos\gamma\ \psi_{-} \end{cases} , \tag{1.19}$$

though θ and γ are different in general. However, in two-spin 1/2 systems, $\gamma = \pi/4$ is expected for LNOs, these LNO can be utilized as good BS trials (initial guesses) by

$$\left| \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \right\rangle = \left| \psi_{\mathrm{LNO1}} \overline{\psi}_{\mathrm{LNO2}} \right\rangle . \tag{1.20}$$

It is noted that the initial guess $\left| \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \right\rangle$ is not always the same as the true BS state $\left| \Psi_{\mathrm{BS}} \right\rangle$. The similarity is calculated to be

$$\left| \left\langle \Psi_{\mathrm{BS}} \middle| \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \right\rangle \right| = \sin\left(\theta + \pi/4\right) \tag{1.21}$$

Therefore, if the spin center is completely localized ($\theta = \pi/4$), the LNO guess is equal to the true BS state. Most BS solutions exist near the localized condition ($\theta \approx \pi/4$), the LNO guesses are expected to be good BS trials (initial guesses). Another important point is that their $\left\langle S^2 \right\rangle_{\mathrm{BS}}^{\mathrm{LNO}}$ and $T_{\mathrm{BS}}^{\mathrm{LNO}}$ values can be calculated as

$$\left\langle S^2 \right\rangle_{\mathrm{BS}}^{\mathrm{LNO}} = \left\langle \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \middle| S^2 \middle| \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \right\rangle = 1 \tag{1.22a}$$

$$T_{\mathrm{BS}}^{\mathrm{LNO}} = \left\langle \psi_{\mathrm{LNO1}} \middle| \psi_{\mathrm{LNO2}} \right\rangle = 0 \quad , \tag{1.22b}$$

because the LNOs are orthogonalized to each other.

The HS solutions can be obtained for many electron systems. The natural orbital (NO) analyses of the HS solutions are also feasible to elucidate the orthogonal natural orbitals and their occupation numbers for these systems. Therefore the above localization procedures can be applicable for several bonding and antibonding natural orbital pairs. In general, eq. (1.22a) becomes

$$\left\langle S^2 \right\rangle_{\mathrm{BS}}^{\mathrm{LNO}} = \left\langle \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \middle| S^2 \middle| \Psi_{\mathrm{BS}}^{\mathrm{LNO}} \right\rangle = S(S+1) + N_{\mathrm{LNO},\beta} \quad , \tag{1.23}$$

where $N_{\mathrm{LNO},\beta}$ indicates the number of beta spins in the magnetic orbital space of the

BS state. In the present study, the Pipek-Mezey (PM) localization procedure (ref. s22) was used for many electron systems. In the PM method, 2 × 2 rotational transformations in eq. (1.18) are iteratively performed to maximize the sum of the Mulliken atomic charges. We can construct trial orbitals for LS BS solutions by using the LNOs of the HS solutions as described in ref. 27.

As shown in Figure 4, and SI (Figures S2.2-S2.7,S3.2 and S4.2-S4.6), the LNOs of the HS solutions of the Mn_4CaO_4 cluster are localized on each Mn site according to the orbital symmetry. Therefore, symmetries of the Mn d orbitals, t_{2g} and e_g, are clearly identified from the LNOs. For the Jahn-Teller distortion, orbital distributions of the e_g type are important, LNO transformation is significantly variable as the electronic structure analysis for such complicated multi spin systems (tetra Mn cluster).

s22 J. Pikek and P. G. Mezey, J. Chem. Phys. 90, 4916 (1989).

S1.6 Summary of the native OEC structure in the X-ray structures

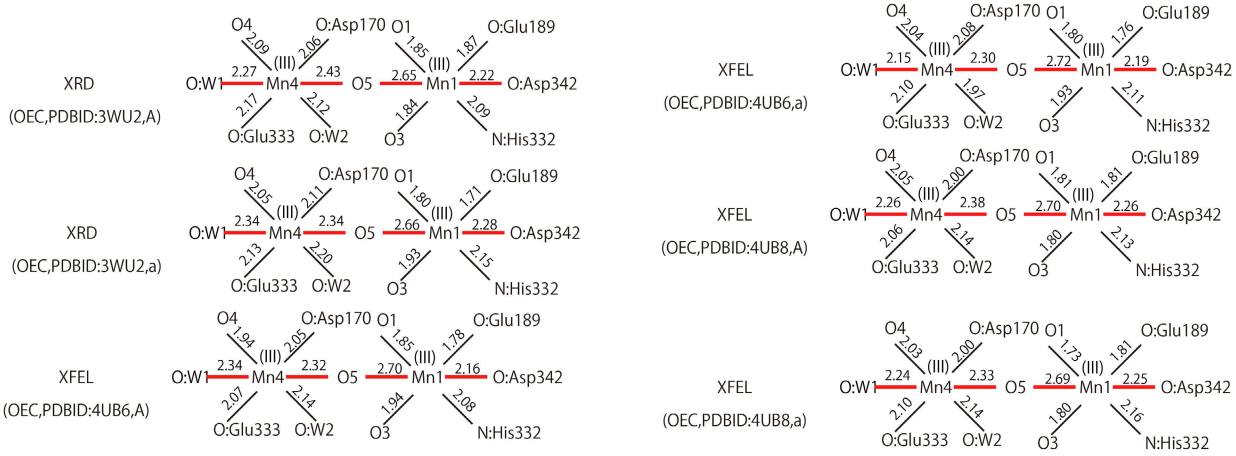

Figure S1.1 Coordination bond lengths around the Mn1 and Mn4 atoms in the native OEC. All the data were taken from X-ray structures. Elongated bonds, expected Jahn-Teller axes, are shown in red line.

S1.7 Comparison of Zhang model complex with several OEC models of PSII

The X-ray structure of the Zhang model complex in ref. 15 is free from the X-ray damage in refs. 5 and 8. Therefore its structure is useful enough for examination of structural characteristics of several model structures reported previously. In fact the Mn-Mn topologies are very important for elucidation of similarity and dissimilarity among the proposed geometrical structures. The London structure in ref. 16 consisted of the $CaMn_4O_4$ core as illustrated in (A) of Fig. S1.2. The Mn_4-Mn_3 and Mn_4-Mn_1 distances of London structure in ref. 16 were about 3.3 Å because of lacking of the $O_{(4)}$ dianion and improper amino acid coordination. In fact they are compatible with the Mn_4-Mn_3 and Mn_4-Mn_1 distances of the Zhang model complex (see Fig. (B) in Fig. S1.2) that also has the $CaMn_4O_4$ core without the $O_{(4)}$ dianion. Dau and Siegbahn proposed possible models of OEC of PSII by addition of the $O_{(4)}$ dianion to the London structure as shown in refs. S23 and S24. The Mn_4-Mn_1 distances were shortened by addition of the $O_{(4)}$ dianion as shown in early Dau model in ref. S23 and early Siegbahn model in ref. 24 that had the $CaMn_4O_5$ core as illustrated in (C) and (D) in Fig. S1.2. On the other hand, the Mn_4-Mn_3 distances were elongated significantly in the Dau and Siegbahn models. However they were still short (about 4.3-4.4 Å) as in the case of model C_a in Fig. 7 due to the bidentate coordination of Glu189 to Mn_1 and Ca as compared with that (4.9 Å) of the XRD in ref. 2 and XFEL in ref. 3, where Glu189 was

mono-dentate to Mn_1. Another difference in the Dau and Siegbahn models is the Mn4 coordination, the bridging ligand between Mn4 and Ca is μ2-OH instead of Asp 170. These differences may lead to an incorrect Mn valence assignment (Mn1(III), Mn2(III), Mn3(IV), Mn4(IV)) in the S1 state.

Very recent QM computational results in refs. S25, S26 and S27 have demonstrated that W3 is one of substrate molecules for water oxidation in OEC of PSII. Thus the proper ligand coordination of Mn_4CaO_5 may be essential for the full functional models of OEC of PSII. It is noteworthy that the large-scale QM/MM calculations in ref. S29 have elucidated importance of several channels for proton release pathways and water inlet pathway and possible geometrical structures of the redox active $CaMn_4O_5$ cluster catalyst for water oxidation. This in turn indicates that early Dau (S23) and Siegbahn (S24) models are regarded as a modified structural and the cluster model, respectively, in comparison with the native PSII-OEC structures reported in ref 2.

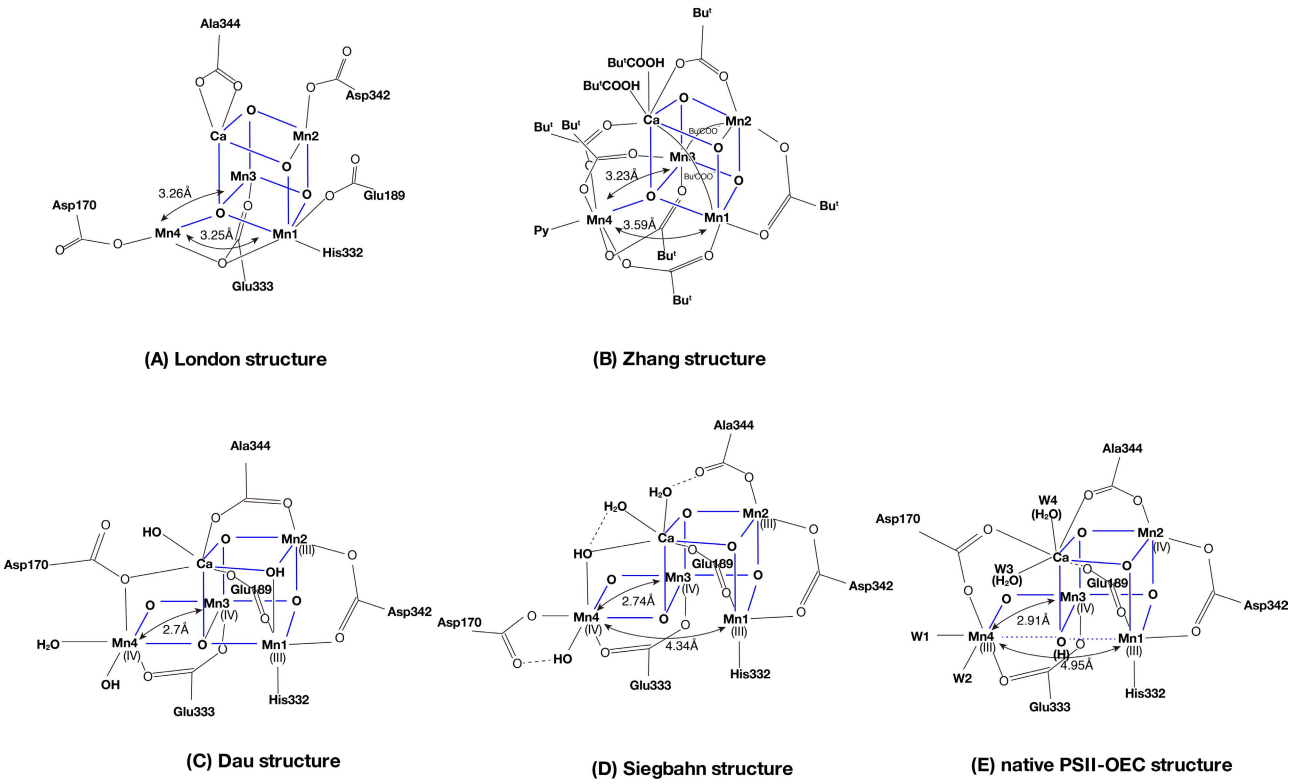

Figure S1.2. Early structures of PSII-OEC: (A) London structure in ref. 16, (B) Zhang structure in ref. 15, (C) Dau structure in ref. 23 and (D) Siegbahn structure in ref. 24. All these models that have shorter Mn4-Mn1 distances than 4.5 Å. (E) Native PSII-OEC (PDBID: 3ARC) in ref. 2

S23) H. Dau, A. Groundmeier, P. Loja, H. Haumann, Phil. Trans. Roy. Soc. B 363 (2008) 1237.

S24) P. E. M. Siegbahn, Chem. Eur. J, 14 (2008) 8290.
S25) M. Shoji, H. Isobe and K. Yamaguchi, Chem. Phys. Lett. 636 (2015) 172.
S26) H. Isobe, M. Shoji. J. –R. Shen and K. Yamaguchi, J. Phys. Chem. B, 119 (2015) 13922.
S27) H. Isobe, M. Shoji, J.-R. Shen, K. Yamaguchi, Inorg. Chem. 55 (2015) 502.
S28) K. Kanda, S. Yamanaka, T. Saito, Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, M. Okumura, H. Nakamura, K. Yamaguchi, Chem. Phys. Lett. 506 (2011) 98.
S29) M. Shoiji, H. Isobe, S. Yamanaka, Y. Umena, K. Kwakami, N. Kamiya, J. –R. Shen, T. Nakajima and K. Yamaguchi, Mol. Phys. 113 (2015) 359.

S2. Results of **1** calculated at the UB3LYP/DZVP level.

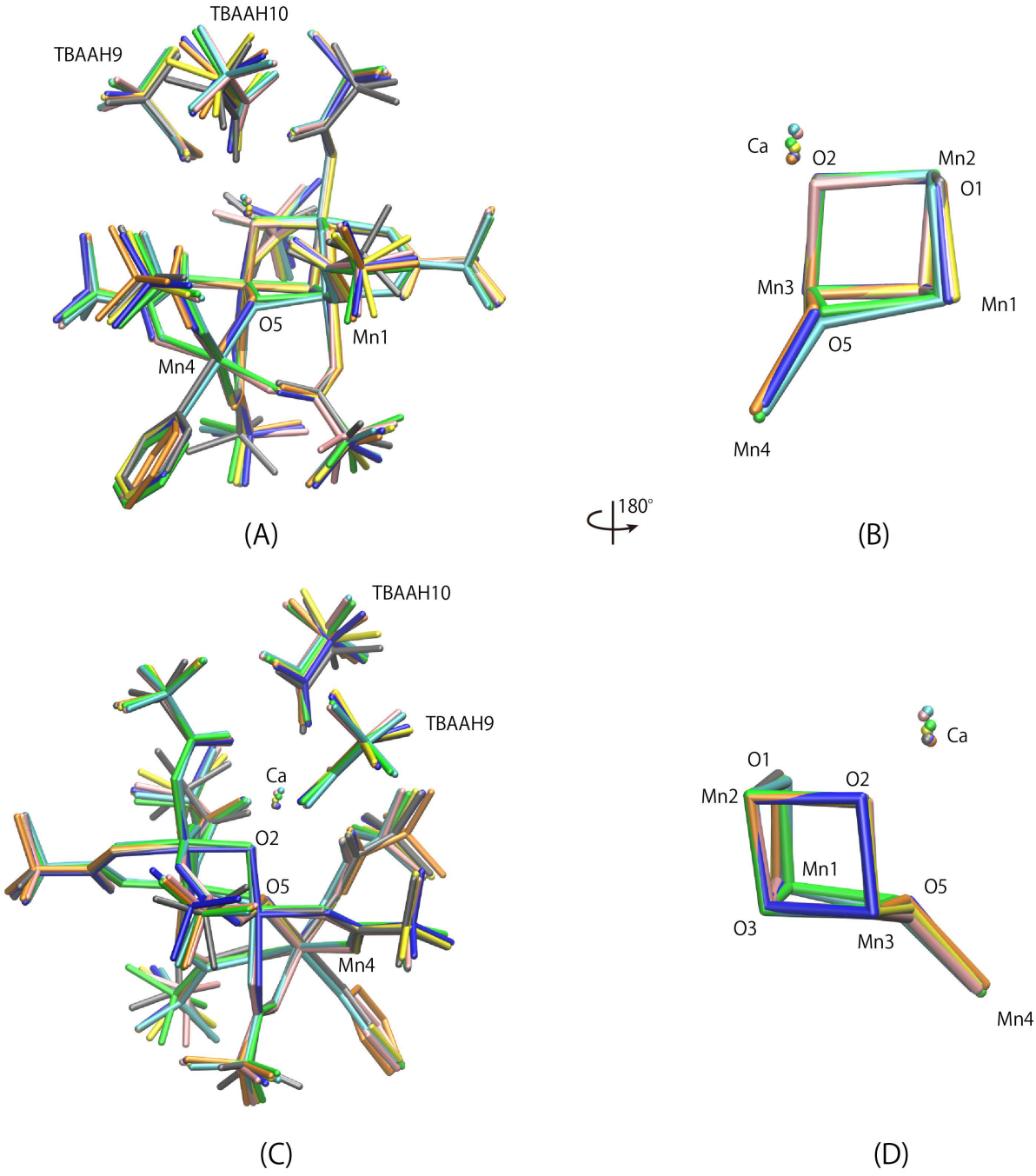

Figure S2.1 Superimposed structures of 1 optimized at the UB3LYP/DZVP level. Structures are colored in gray (X-ray structure), blue (S_0(a)), orange (S_0(b)), yellow (S1), green (S2(C)), pink (S2(R)), and cyan (S3). (A) aligned whole molecular structures of 1 and (B) aligned $CaMn_4O_4$ cores were shown. (C) and (D) are 180 degrees rotated views of (A) and (B). The (B) and (D) drawings show that the Ca atoms becomes far from O5 in the following order; S0(b)(orange), S0(a)(blue), X-ray(gray), S1 (yellow), S_2(C)(green), S_2(R)(pink) and S_3 (cyan). This order is roughly consistent with the RMSD values calculated for the $CaMn_4O_4$ moiety.

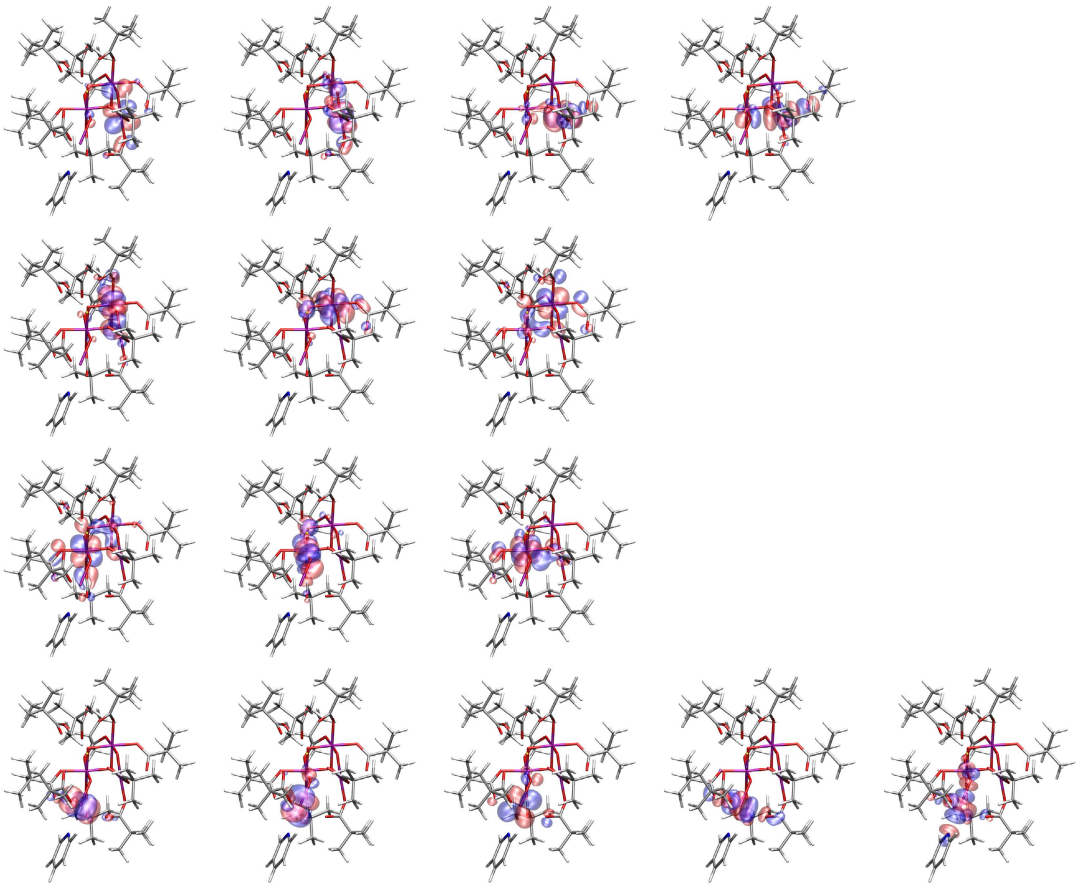

Figure S2.2 Localized natural orbitals of **1** in the highest spin S_0(b) state calculated at the B3LYP/DZVP level. 15 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 5 for Mn4 are shown.

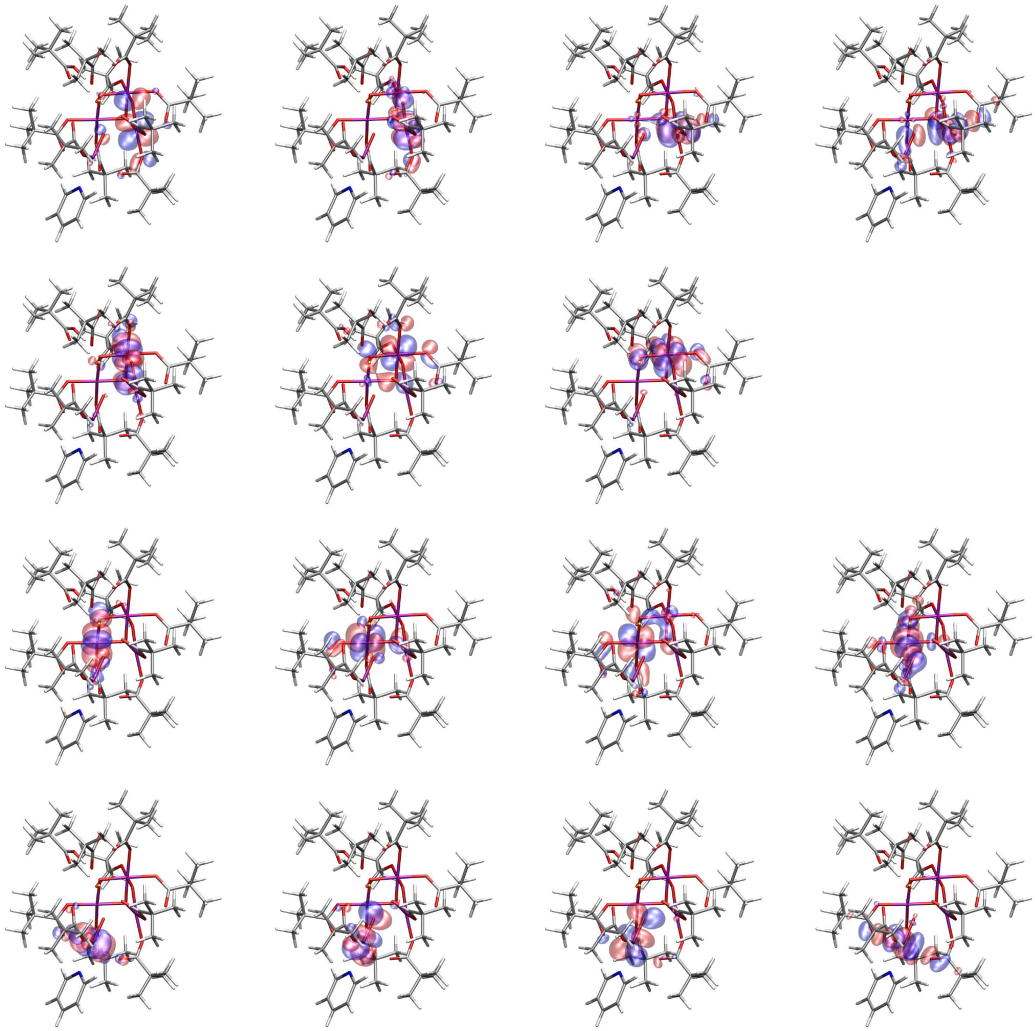

Figure S2.3 Localized natural orbitals of **1** in the highest spin S_0(a) state calculated at the B3LYP/DZVP level. 15 d-type orbitals; 4 for Mn1, 3 for Mn2, 4 for Mn3 and 4 for Mn4 are shown.

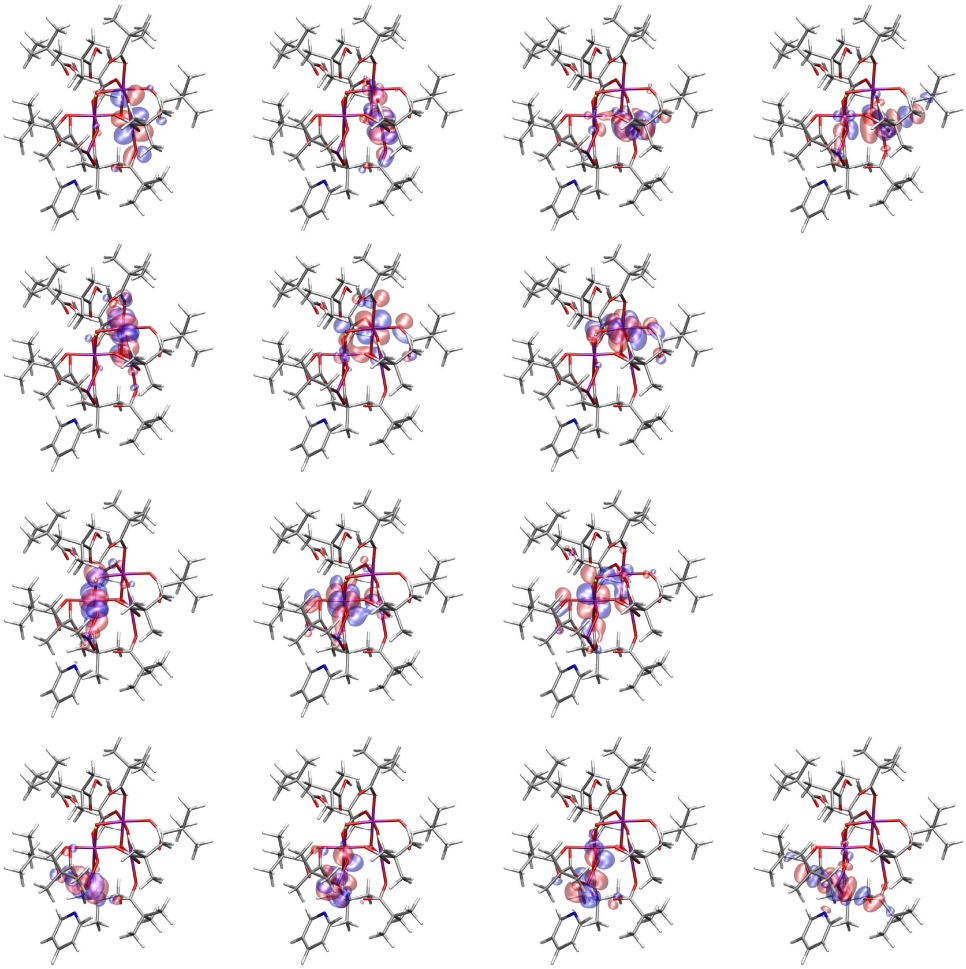

Figure S2.4 Localized natural orbitals of **1** in the highest spin S_1 state calculated at the B3LYP/DZVP level. 14 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 4 for Mn4 are shown.

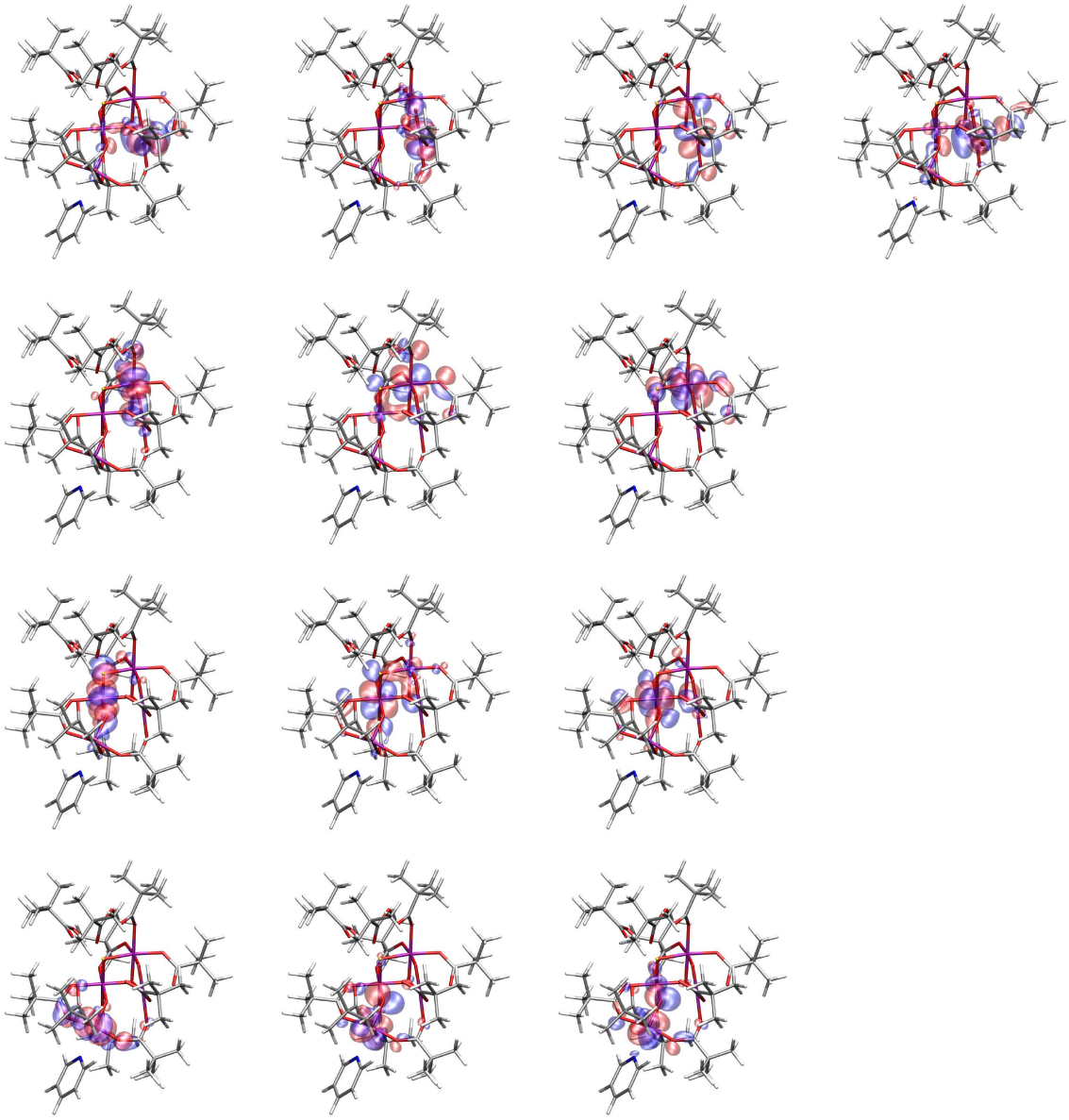

Figure S2.5 Localized natural orbitals of **1** in the highest spin S_2(R) state calculated at the B3LYP/DZVP level. 13 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 3 for Mn4 are shown.

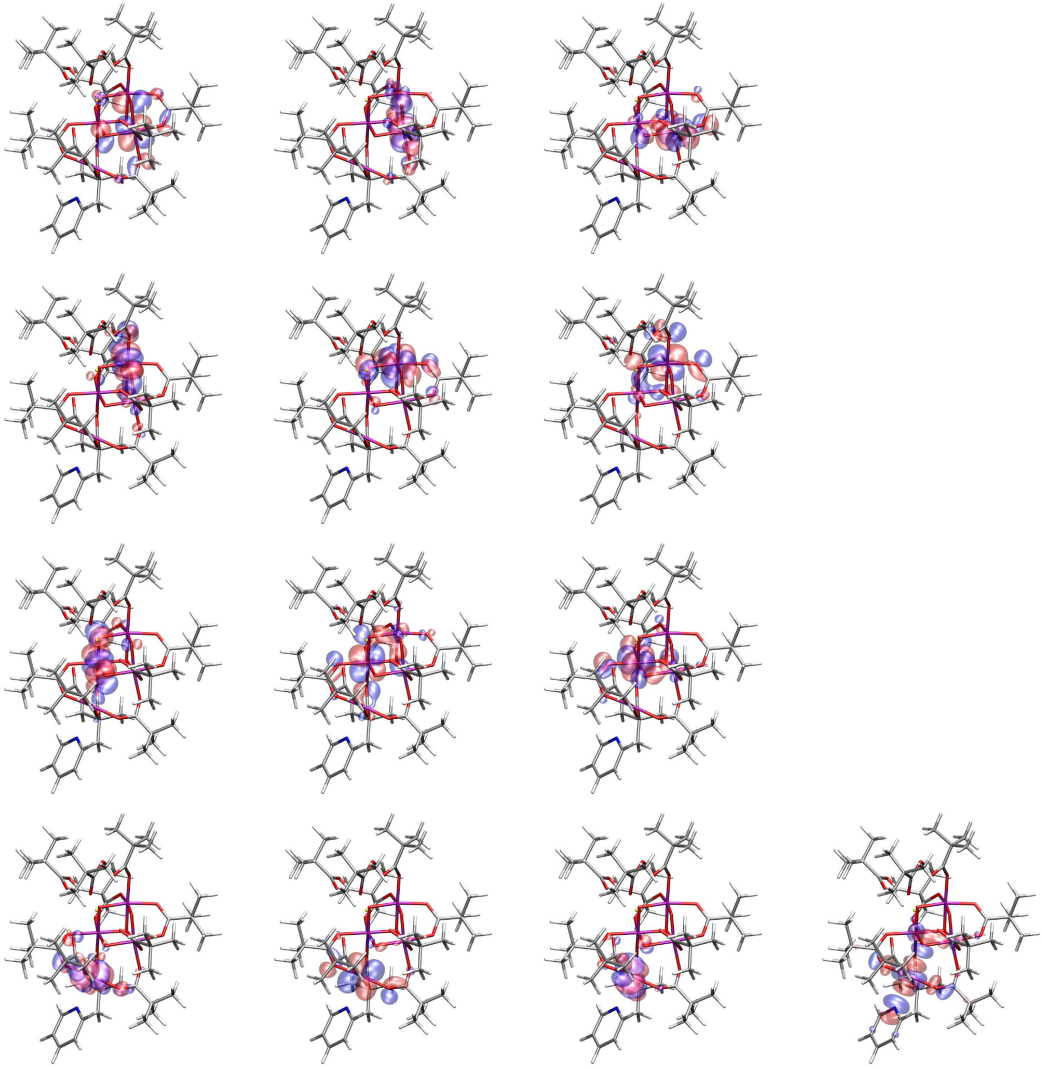

Figure S2.6 Localized natural orbitals of 1 in the highest spin S_2(C) state calculated at the B3LYP/DZVP level. 13 d-type orbitals; 3 for Mn1, 3 for Mn2, 3 for Mn3 and 4 for Mn4 are shown.

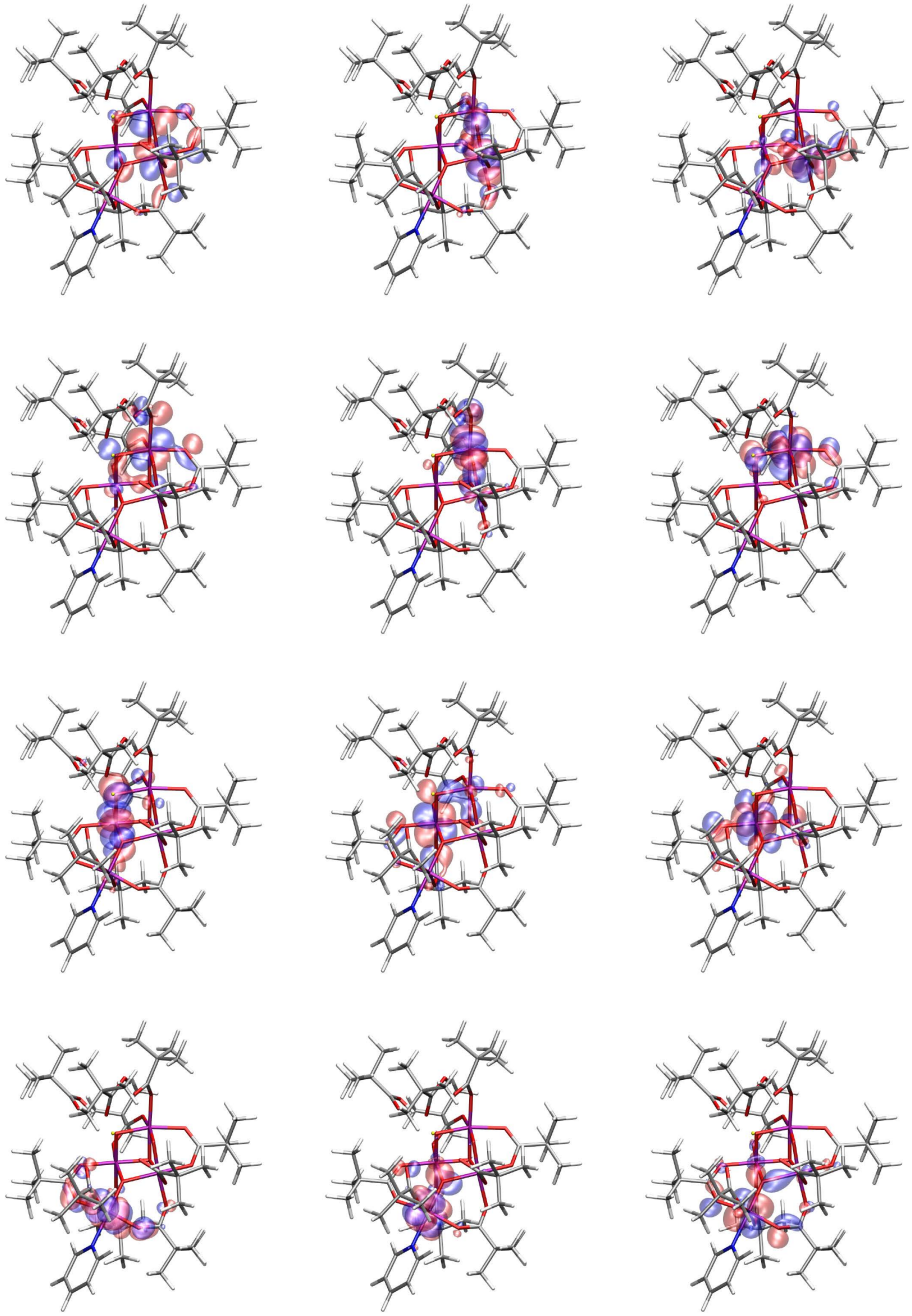

Figure S2.7 Localized natural orbitals of 1 in the highest spin S_3 state calculated at the B3LYP/DZVP level. 12 d-type orbitals; 3 for Mn1, 3 for Mn2, 3 for Mn3 and 3 for Mn4 are shown.

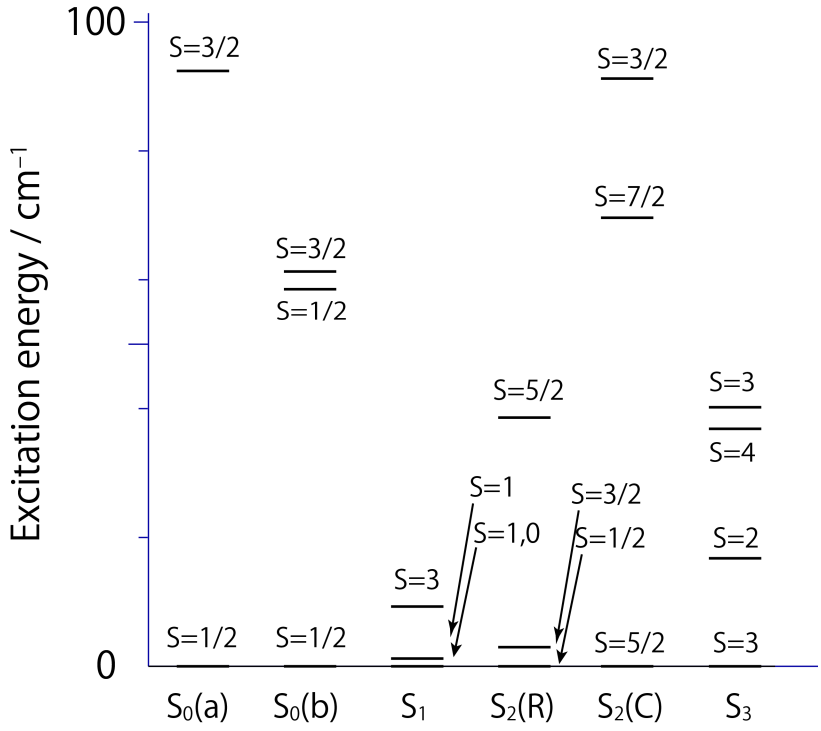

Figure S2.8 Low-lying energy levels of 1 depending on the oxidation states calculated at the B3LYP/DZVP level.

Table S2.1 Bond valence sum (BVS) calculations[a] of **1** at the fully optimized structures

	Mn1	Mn2	Mn3	Mn4
S_0(a)	2.79	4.07	2.88	2.73
S_0(b)	2.80	4.07	3.97	1.94
S_1	2.81	4.08	4.06	2.83
S_2(R)	2.85	4.09	4.08	3.99
S_2(L)	3.99	4.14	4.05	2.82
S_3	3.97	4.14	4.05	3.86

[a] Mn oxidation states were determined by using the bond valence sum (BVS) analysis. The BVS values were evaluated using the BVS parameters determined for the closest Mn formal charge states[S1,S2].

S1. Thorp, H.H. Bond Valence Sum Analysis of Metal-Ligand Bond Lengths in Metalloenzymes and Model Complexes. *Inorg. Chem.* **31**, 1585-1588 (1992).

S2. Liu, W. & Thorp, H.H. Bond Valence Sum Analysis of Metal-Ligand Bond Lengths in Metalloenzymes and Model Complexes. 2. Refined Distances and Other Enzymes. *Inorg. Chem.* **32**, 4102-4105 (1993).

Table S2.2 Local spin correlation factor c for low-lying energy levels of **1** calculated at the UB3LYP/DZP level.[a]

State	Index	S	c_1	c_2	c_3	c_4
S_0(a)[b]	0	1/2	1.760	-0.991	1.558	-1.327
	1	3/2	0.616	-0.154	0.467	0.070
	2	5/2	0.447	-0.030	0.317	0.265
S_0(b)[c]	0	1/2	-0.990	0.691	-0.940	2.239
	1	1/2	1.594	-0.047	0.896	-1.443
	2	3/2	0.260	0.051	-0.204	0.892
S_1	0	1	-0.257	0.380	0.515	0.361
	1	0	–	–	–	–
	2	2	-0.187	0.288	0.478	0.419
S_2(R)	0	1/2	0.958	-0.629	1.617	-0.946
	1	3/2	0.179	0.347	0.735	-0.263
	2	5/2	0.177	0.388	0.515	-0.081
S_2(C)	0	5/2	0.530	0.546	0.485	-0.562
	1	7/2	0.375	0.389	0.320	-0.084
	2	3/2	0.582	0.819	0.377	-0.778
S_3	0	3	0.397	0.466	0.486	-0.349
	1	2	0.361	0.652	0.463	-0.476
	2	4	0.270	0.351	0.371	0.007

[a] $c_i = \langle s_i \cdot S \rangle / \langle S \cdot S \rangle$

[b] Optimized at UDUD spin state at the (B3LYP) method

[b] Optimized at DUDU spin state at the (B3LYP) method

182

S-1, Full, Opted at UB3LYP/DZVP (UUUU)

Mn 14.13647382 4.25171618 15.21347364

Mn 14.82019196 2.64824624 17.53440195

Mn 16.81909905 4.58419222 16.82337174

Mn 15.94722426 7.27879190 15.05078434

Ca 13.52670440 5.71488257 18.40483223

O 13.50726935 3.69750613 16.85804570

O 15.36198167 4.13369322 18.55692339

O 15.92803929 3.07703859 16.17529554

O 15.39093557 5.57311747 16.00276694

O 14.08342469 8.01060909 17.83402722

O 14.48799220 8.71866090 15.70785739

O 17.62360943 6.10784357 17.87105379

O 17.43901296 7.95882612 16.55113163

O 18.40004564 4.71010144 15.30081645

O 17.70309038 6.38874803 13.91430619

O 14.63160735 4.59899413 13.30083081

O 14.80733145 6.86986019 13.15940593

O 15.75981756 4.21792140 21.18882288

O 14.45964995 6.04399930 20.73471730

O 11.49298843 6.70184960 19.79599775

O 10.51421162 4.96158881 20.89564831

O 12.37634769 3.68372632 19.64527046

O 13.64699399 1.89902003 19.04736527

O 16.40085680 1.62123355 18.39576618

O 18.01008098 3.19618185 17.91787639

O 14.20258052 1.06624657 16.46180968

O 13.69249986 2.20151424 14.52930327

O 12.22341041 5.08629072 14.77728825

O 11.65792602 6.03962678 16.77391895

N 16.72708076 9.21292737 13.81079432

C 15.16907316 5.30917124 21.50206448

C 15.37149061 5.78335766 22.99989789

C 16.88254971 6.08825333 23.20215402

C 14.53537285 7.04604911 23.31501509

C 14.95867277 4.62411058 23.94723506

C 10.63476919 6.25792221 20.56869562

C 9.56951620 7.14590016 21.26669619

C 9.72946992 6.99315702 22.80779693

C 8.15621623 6.65443722 20.83573270

C 9.76482957 8.62403293 20.85681880

C 12.71804879 2.45068430 19.72749445

C 11.95408824 1.51897736 20.73084790

C 12.53771598 0.08362205 20.69938679

C 12.10106279 2.10300039 22.16587388

C 10.45262015 1.47579613 20.32126492

C 13.95767433 8.82888517 16.87515035

C 13.05298782 10.10102392 17.08337329

C 12.66298843 10.25918810 18.57255107

C 11.77211126 9.88892923 16.22430805

C 13.80575091 11.36847797 16.59712627

C 11.39055498 5.59951280 15.61785794

C 9.90498580 5.67388096 15.09822243

C 9.45614911 4.23856358 14.70254337

C 8.95870726 6.23703715 16.18552299

C 9.87119094 6.59046971 13.84272340

C 17.77677105 7.36121582 17.61951806

C 18.38561450 8.21193375 18.78375279

C 19.38317913 7.36468126 19.61562836

C 19.09828203 9.46700636 18.21807169

C 17.18709102 8.64877914 19.68075226

C 18.45953825 5.41300747 14.23613060

C 19.60251764 5.00390311 13.23014791

C 19.34768794 3.53241531 12.79580104

C 20.96292246 5.09216203 13.97714904

C 19.62356206 5.92429694 11.98648071

C 17.59173601 2.10723790 18.43819297

C 18.64908988 1.29739348 19.26297758

C 19.88291174 1.02183391 18.35985128

C 19.06551895 2.19391277 20.46677549

C 18.05872816 -0.03766471 19.77926451

C 13.80553138 1.15377806 15.23300907
C 13.44641870 -0.22678954 14.58128414
C 14.73764819 -1.09491755 14.56687838
C 12.92179476 -0.03523317 13.13760328
C 12.36235485 -0.91942021 15.45414392
C 14.67895503 5.71576523 12.65454914
C 14.50199073 5.58800274 11.10094151
C 12.97037519 5.49821455 10.83021029
C 15.19216392 4.29700672 10.58627528
C 15.09200258 6.82755068 10.38356575
C 18.04280217 9.51110992 13.74980985
C 18.53485340 10.63367713 13.06178208
C 17.62192929 11.47757996 12.40750809
C 16.25277269 11.16896682 12.46981912
C 15.85016053 10.02791184 13.18502116
H 18.69961413 8.81286222 14.27237183
H 19.61016509 10.83547095 13.04151683
H 17.97096439 12.35994207 11.85994919
H 15.50555588 11.79785775 11.97622788
H 14.80061748 9.74152132 13.28069814
H 14.71203528 11.54738001 17.20336125
H 14.12014161 11.25867041 15.54841387
H 13.16000272 12.26385498 16.68311269
H 13.55588095 10.40768884 19.20293230
H 11.99791103 11.13505409 18.70440115
H 12.14804409 9.36124782 18.94219266
H 12.03233537 9.79976467 15.15682276
H 11.25778987 8.96047313 16.52362037
H 11.07074083 10.73655301 16.34783675
H 10.76381016 8.98765067 21.14229340
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H 19.79556347 6.97578745 12.26961070
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H 18.38750292 3.44021492 12.25860484
H 20.15203552 3.17617861 12.12342523
H 19.52555091 3.12788312 20.10841559
H 18.18916438 2.46727758 21.07842722
H 19.79320116 1.66168744 21.10873183
H 18.82223670 -0.58918001 20.36073139
H 17.18545695 0.13967086 20.42570023
H 17.72786799 -0.67744191 18.94465520
H 20.68213985 0.52088015 18.93834398

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H 20.27773237 1.96358382 17.94940258
H 15.52501734 -0.61903362 13.95667811
H 15.13022225 -1.22072592 15.58770568
H 14.52788095 -2.09326885 14.13819426
H 12.71918020 -1.04416975 16.48780204
H 11.43610610 -0.31861761 15.48337390
H 12.10994885 -1.91421650 15.04044894
H 13.67168103 0.46637085 12.50625718
H 12.68223358 -1.01762188 12.68795702
H 12.01167493 0.58579246 13.12373396
H 16.17561807 6.91282652 10.57099700
H 14.93383597 6.75097889 9.29089188
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H 12.77539217 5.37106438 9.74821183
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H 12.45670194 6.41466198 11.16730131
H 10.55522866 6.20924210 13.06945027
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H 9.99295445 2.47534284 20.34929335
H 13.60403167 0.08330874 20.97378312
H 11.98906034 -0.56021561 21.41287807
H 12.45830245 -0.35778305 19.69365873
H 13.16405895 2.18333514 22.44764913
H 11.65244793 3.10443575 22.24620705
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182

S0a, Full, Opted at UB3LYP/DZVP (UDUD)

Mn 14.15861710 4.17709055 15.25289822

Mn 14.90747339 2.74369117 17.51675668

Mn 16.74629384 4.73816828 17.07956678

Mn 15.69074102 7.28934445 15.21298637

Ca 13.56151641 5.77305655 18.24667071

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O 15.51905425 4.25551445 18.39921294

O 15.84511852 3.35972693 16.10377715

O 15.15595531 5.92419280 16.14293284

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O 14.33726274 8.63404808 15.82512486

O 17.46004402 6.24706317 18.14165913

O 17.22665640 7.94582371 16.67433693

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O 14.80048075 4.56927235 13.42391359

O 14.63701586 6.81221594 13.33527486

O 15.98463636 4.50015973 20.90069309

O 14.49452033 6.15723735 20.57247045

O 11.57270237 6.73657139 19.63163270

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C 14.37975056 4.76539800 23.50625976

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C 9.81453864 7.26651512 21.23829992

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C 13.91343115 11.36049238 16.54017018

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C 14.95885233 -1.15866481 14.85441435
C 13.16731298 -0.25485636 13.32436984
C 12.58438092 -0.95816788 15.67642115
C 14.69143242 5.67706384 12.79915633
C 14.56960906 5.57386259 11.25834538
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H 20.42324550 0.00394695 18.30581551

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H 20.17149296 1.58092021 17.51592035
H 15.74565415 -0.72364383 14.22593501
H 15.32996718 -1.19956509 15.88256968
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H 11.65411841 -0.37724454 15.64535847
H 12.35730351 -1.97734737 15.33661422
H 13.91573910 0.20524192 12.67193351
H 12.95550876 -1.26650050 12.95314343
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H 15.00313714 6.77400544 9.49758481
H 14.58852473 7.73356412 10.93610871
H 16.39129103 4.40118853 10.94101362
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H 15.18417526 4.24573434 9.65113255
H 12.91310881 5.30768191 9.86373992
H 12.64211933 4.55572890 11.45505989
H 12.50814171 6.31493737 11.26971476
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H 10.35496879 3.77202584 13.74158471
H 9.43517029 7.18241387 16.25422351
H 8.12401944 6.24240619 15.50437511
H 9.08949924 5.54956253 16.82695934
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H 13.36548158 -0.01402639 20.61107455
H 11.66166937 -0.48951575 20.81214920
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H 11.36586042 1.28649805 22.54762368
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182

S0b, Full, Opted at UB3LYP/DZVP (DUDU)

Mn 14.02920429 4.02893395 15.24077549

Mn 14.76806731 2.65542142 17.53418139

Mn 16.46955976 4.72844327 16.95057862

Mn 15.63204882 7.37653642 15.14824233

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O 14.23711514 8.80007416 15.89781539

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C 14.24161430 4.84538689 23.47199145

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H 12.35043047 -2.16637526 15.47094274
H 13.85758812 -0.01699161 12.75353179
H 12.93414681 -1.50397760 13.07363668
H 12.19156009 0.09320250 13.32400429
H 16.38121047 6.83771323 11.09670384
H 15.36294030 6.73238456 9.64078339
H 14.82681225 7.67560913 11.05277469
H 16.42673969 4.23886862 11.13353312
H 14.90470850 3.34539607 11.21387442
H 15.35823088 4.20032226 9.71721474
H 13.13793124 5.41310225 9.73698071
H 12.66434164 4.60620193 11.25016900
H 12.65110614 6.37866342 11.14762836
H 10.91603676 6.13819403 12.83367535
H 9.25387602 6.72168287 13.08561722
H 10.61840929 7.53838367 13.87812081
H 9.41881733 3.56220822 15.15374166
H 8.55799635 4.37135529 13.82897975
H 10.22722437 3.79145916 13.59571323
H 9.46403942 7.20872290 16.15097795
H 8.11338271 6.38012105 15.33924656
H 8.98262222 5.59373946 16.67620170
H 10.38371408 1.52799546 18.98678458
H 9.79017937 1.08674703 20.60028602
H 10.12013908 2.78569025 20.20872276
H 13.36149417 -0.06950456 20.68903087
H 11.66599354 -0.55871658 20.91789157
H 12.29032184 -0.18105903 19.29380846
H 13.03359833 1.80754507 22.41951951
H 11.68073164 2.94405978 22.25320237
H 11.36698019 1.24374013 22.63226794
H 11.57705819 4.55956897 20.66025725
H 15.78587090 4.34786221 19.84099123

182

S1, Full, Opted at UB3LYP/DZVP (DUUU)

Mn 14.03222112 4.11502516 15.17210281

Mn 14.72281950 2.71040156 17.47815086

Mn 16.53986255 4.71050086 17.00152337

Mn 15.80644902 7.28324838 15.20601843

Ca 13.38532422 5.72710708 18.30157582

O 13.37005641 3.66353587 16.82488093

O 15.37358112 4.27496689 18.32065110

O 15.70908418 3.34714668 16.05283913

O 15.31639189 5.83224802 16.17901901

O 14.12174948 7.99480762 18.02386099

O 14.46805380 8.52082707 15.86712534

O 17.34935376 6.10322110 18.08761308

O 17.34197000 7.86606155 16.68403166

O 17.99118354 4.88226626 15.67396886

O 17.30817149 6.40928592 14.17597884

O 14.73345486 4.54049703 13.40830758

O 14.63112855 6.78379470 13.39238443

O 15.94612477 4.55436306 20.88449383

O 14.31862674 6.07525512 20.60145028

O 11.37590750 6.61954006 19.53783510

O 10.84081750 5.16845137 21.16155412

O 12.54039888 3.77977444 19.70371140

O 13.72281849 2.01914107 18.99242436

O 16.34165024 1.74334346 18.20639047

O 17.80875756 3.40924490 17.80286695

O 14.26191029 1.11648408 16.50494038

O 13.72685815 2.04949869 14.52069740

O 12.35187140 4.90323357 14.67058598

O 11.84593824 6.12341527 16.48868697

N 16.43875947 9.00579951 14.08068163

C 15.12889532 5.49707890 21.32500201

C 15.22713234 5.77859954 22.82897350

C 16.61696691 5.42515256 23.38772459

C 14.90951586 7.26290740 23.08617777

C 14.15207246 4.89542438 23.50886490

C 10.71897495 6.33332952 20.53631053

C 9.72551495 7.29230465 21.19666744

C 10.48543817 7.99573453 22.34859946

C 8.51788820 6.52142978 21.76516294

C 9.25193416 8.33362004 20.16955687

C 12.78124814 2.54172120 19.67570733

C 11.91016185 1.56490972 20.49549188

C 12.34841611 0.10922214 20.26496059

C 12.03862258 1.90870473 21.99528745

C 10.44411663 1.74391071 20.03864842

C 14.00079559 8.75695743 17.05011201

C 13.24147509 10.09597945 17.18526546

C 12.78554905 10.29715738 18.63814031

C 12.01372991 10.04296340 16.24944667

C 14.17110653 11.25206579 16.76097544

C 11.53476657 5.57634172 15.41672087

C 10.08396697 5.63565438 14.89486109

C 9.50266672 4.20716877 15.01510473

C 9.25052449 6.61212583 15.73790593

C 10.07451213 6.07108868 13.41668080

C 17.63298091 7.31467047 17.77092178

C 18.41436634 8.09851977 18.84508655

C 19.79579644 7.42669301 19.01177377

C 18.58739130 9.56625422 18.42655368

C 17.63269724 8.01569242 20.17278275

C 18.09408746 5.50263728 14.57525132

C 19.27945214 5.09437124 13.67928847

C 19.00971646 3.64875593 13.20046794

C 20.56981998 5.12620205 14.52578983

C 19.41713513 6.03813331 12.47517431

C 17.49929612 2.24926788 18.23196093

C 18.65628125 1.41409486 18.81203752

C 19.63725517 1.11451291 17.65633031

C 19.36695545 2.25212477 19.89602660

C 18.13173230 0.10147429 19.41432402

C 13.87183662 1.06488829 15.27505318
C 13.58960617 -0.35922153 14.75478976
C 14.90796616 -1.16117668 14.82660103
C 13.07888151 -0.30969098 13.30691732
C 12.53327820 -1.01539511 15.66929053
C 14.65539216 5.67340742 12.80818116
C 14.56192453 5.60269016 11.26925554
C 13.15315571 5.07128788 10.91725243
C 15.61977315 4.61675434 10.73355542
C 14.76866885 6.98984756 10.64308443
C 17.70513814 9.44642630 14.13448431
C 18.13297045 10.55718848 13.41268009
C 17.21505603 11.22932236 12.60631637
C 15.90074155 10.76636025 12.55361452
C 15.54987583 9.65044771 13.30802373
H 18.36937637 8.89250597 14.78603048
H 19.16538447 10.88302271 13.48779237
H 17.51841913 12.09906635 12.03018530
H 15.15274940 11.25557010 11.93821216
H 14.54721670 9.24189965 13.30166151
H 15.06118737 11.30081591 17.40034959
H 14.50193526 11.13582373 15.72517304
H 13.64210785 12.20868415 16.85066421
H 13.64101080 10.35441094 19.31901484
H 12.21437693 11.22977645 18.72380480
H 12.15630021 9.46678511 18.96947869
H 12.32093422 9.91016432 15.20771063
H 11.35345899 9.21088480 16.51713867
H 11.44197297 10.97567334 16.32832560
H 10.08921405 8.90576125 19.76375448
H 8.73512134 7.85595010 19.33006422
H 8.55418130 9.03071530 20.64755691
H 11.35478973 8.54462322 21.97013785
H 9.81940868 8.71104520 22.84489067
H 10.82929901 7.27325686 23.09616553
H 8.82508426 5.78745700 22.51409084
H 7.82226283 7.22623391 22.23501820
H 7.97599857 5.99170984 20.97328428
H 14.15168137 5.08337735 24.58888438
H 13.15362975 5.11942179 23.11911184
H 14.35488579 3.83107501 23.34920200
H 17.40294945 6.02032304 22.91037691
H 16.64197592 5.63374647 24.46375135
H 16.85532117 4.36938135 23.23603036
H 15.65210762 7.91560207 22.61426695
H 13.92691369 7.53071366 22.69009525
H 14.91924422 7.46105187 24.16416142
H 18.15238165 8.59439221 20.94620530
H 16.61989594 8.41899985 20.06082318
H 17.55146183 6.97820743 20.50628943
H 19.14132120 9.65253680 17.48651461
H 17.61911126 10.05861504 18.29078762
H 19.14284411 10.10793522 19.20141847
H 20.36780015 7.93929522 19.79441693
H 19.68676531 6.37468882 19.29051818
H 20.37729249 7.47727322 18.08287858
H 21.41926760 4.79544667 13.91686382
H 20.78783210 6.14073593 14.88226630
H 20.48387224 4.46993611 15.39546982
H 20.26120694 5.71928264 11.85258292
H 18.51481281 6.03761191 11.85768572
H 19.60094645 7.06998212 12.79398628
H 18.92506446 2.96688574 14.05131176
H 18.08112459 3.58726905 12.62281855
H 19.83412440 3.31216721 12.56066827
H 19.75161742 3.18716448 19.47958659
H 18.68298551 2.49997043 20.71616456
H 20.20553566 1.68246129 20.31378069
H 18.97105230 -0.47900402 19.81558557
H 17.42442580 0.29169142 20.22778271
H 17.61766109 -0.50523787 18.66338958
H 20.48953990 0.53697367 18.03350293

H 19.15249180 0.52595783 16.86839970
H 20.01266134 2.04108512 17.21194410
H 15.67966325 -0.70942179 14.19176258
H 15.28657544 -1.19942654 15.85199930
H 14.74030474 -2.18669883 14.47592891
H 12.88544414 -1.06115425 16.70352677
H 11.59100888 -0.45419605 15.65102508
H 12.32381082 -2.03537113 15.32507069
H 13.80975537 0.16178250 12.64316318
H 12.88986263 -1.32836647 12.94718220
H 12.14721740 0.26009159 13.23251391
H 15.75259913 7.39880543 10.89738374
H 14.70025798 6.91866528 9.55084290
H 14.00961177 7.69868181 10.98741204
H 16.63571353 4.96753568 10.94859878
H 15.49593934 3.62869880 11.18388051
H 15.52188795 4.52225975 9.64536576
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H 12.37365749 5.76155251 11.25677565
H 10.64434876 5.37247135 12.79970045
H 9.04351192 6.10478806 13.04379124
H 10.50905418 7.07084811 13.29525420
H 9.49778835 3.86938908 16.05831324
H 8.46846672 4.19311029 14.65006538
H 10.09033251 3.49524629 14.42788014
H 9.63625281 7.63392291 15.65949132
H 8.21120463 6.61219057 15.38721188
H 9.26272096 6.33441273 16.79556386
H 10.33579925 1.52385984 18.97009061
H 9.79892270 1.05184515 20.59236042
H 10.08441971 2.76084727 20.21815034
H 13.38571884 -0.04965709 20.57403540
H 11.70612509 -0.56320557 20.84631182
H 12.27398320 -0.16615324 19.20904208
H 13.07547536 1.80476198 22.33583557
H 11.70307105 2.92549134 22.21641254
H 11.42323208 1.21770031 22.58324871
H 11.49828411 4.59002423 20.65707385
H 15.79727670 4.41039380 19.89239883

182

S1, Full, Opted at UB3LYP/DZVP (UDUD)

Mn 14.03921795 4.11656246 15.17750963

Mn 14.71895946 2.71036389 17.47969548

Mn 16.53335830 4.71920671 17.00021245

Mn 15.81508057 7.29889066 15.20137122

Ca 13.38167978 5.72501642 18.30361130

O 13.36519760 3.65891006 16.82559356

O 15.37186636 4.27544469 18.32116675

O 15.70448513 3.34707888 16.05456874

O 15.34289710 5.84504186 16.17809733

O 14.12306760 7.99032954 18.00983782

O 14.48245681 8.52806696 15.85755346

O 17.36018958 6.09969158 18.08764701

O 17.35767648 7.86838459 16.68942659

O 17.98441548 4.88483872 15.66908302

O 17.30751818 6.42463719 14.18036589

O 14.74624875 4.54530944 13.41853098

O 14.62987225 6.78769224 13.39112288

O 15.94158302 4.55427244 20.88324065

O 14.31620582 6.07862307 20.60072286

O 11.37138859 6.61548396 19.53725763

O 10.83631203 5.16583827 21.16325313

O 12.53678190 3.77933124 19.70756224

O 13.72411896 2.02250285 18.99609330

O 16.34081474 1.74627319 18.20450210

O 17.80866319 3.41206411 17.79226378

O 14.26087406 1.11617709 16.50863138

O 13.71706471 2.05192335 14.52751064

O 12.35218643 4.89955351 14.66405299

O 11.85223557 6.11945913 16.48385628

N 16.45620293 9.01532673 14.08042904

C 15.12657137 5.49883739 21.32385530

C 15.22643852 5.77985089 22.82783278

C 16.61728591 5.42681372 23.38429908

C 14.90852556 7.26379121 23.08661746

C 14.15269541 4.89547457 23.50826210

C 10.71423962 6.32988722 20.53645416

C 9.71946323 7.28825473 21.19567427

C 10.47785680 7.99350036 22.34743474

C 8.51267793 6.51601589 21.76403203

C 9.24462769 8.32820267 20.16777682

C 12.78106144 2.54199576 19.67970280

C 11.91319394 1.56272674 20.49977098

C 12.35674983 0.10855336 20.27043450

C 12.03925819 1.90855822 21.99924781

C 10.44684022 1.73641868 20.04177097

C 14.00636244 8.75667155 17.03995451

C 13.24290463 10.09312700 17.17365445

C 12.77286733 10.28578467 18.62315412

C 12.02448661 10.04205862 16.22571565

C 14.17492960 11.25265878 16.76414721

C 11.53798501 5.57231573 15.41194498

C 10.08458048 5.63323463 14.89646840

C 9.50041024 4.20691524 15.02734994

C 9.25691654 6.61618026 15.73765556

C 10.06910893 6.06022711 13.41600520

C 17.64199583 7.31365955 17.77590084

C 18.41657583 8.09502124 18.85724845

C 19.80023114 7.42784026 19.02402381

C 18.58488836 9.56562211 18.44701755

C 17.63214199 8.00222275 20.18239110

C 18.08988896 5.51139299 14.57589000

C 19.27359510 5.10564438 13.67678477

C 19.00091102 3.66273425 13.19130710

C 20.56429944 5.13088239 14.52298543

C 19.41287945 6.05462807 12.47691156

C 17.49832896 2.25334097 18.22373923

C 18.65773350 1.41785885 18.79986505

C 19.63514060 1.11900847 17.64106290

C 19.37163448 2.25552500 19.88199893

C 18.13559707 0.10494038 19.40340843

C 13.86440122 1.06675843 15.28001364
C 13.57794342 -0.35676598 14.76081317
C 14.89561631 -1.16043805 14.82671576
C 13.06133062 -0.30604751 13.31507311
C 12.52445252 -1.01151217 15.67960681
C 14.65860763 5.67488532 12.81267200
C 14.56026111 5.59495407 11.27455723
C 13.15356183 5.05306031 10.93079060
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C 14.75588863 6.98008132 10.64033095
C 17.72180024 9.45720372 14.14406608
C 18.15509949 10.56467266 13.42065033
C 17.24423016 11.23138954 12.60189628
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H 19.18633658 10.89218562 13.50397759
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H 13.62166927 10.34085404 19.31243896
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H 12.14153021 9.45295526 18.94410302
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H 11.36397386 9.20671658 16.48227331
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H 10.82273112 7.27193202 23.09540609
H 8.82053113 5.78296172 22.51358779
H 7.81577999 7.22007192 22.23309538
H 7.97200099 5.98498309 20.97222239
H 14.15377964 5.08190667 24.58853747
H 13.15358618 5.11969500 23.12029713
H 14.35553968 3.83141250 23.34676798
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H 16.64405020 5.63503102 24.46034541
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H 13.92522156 7.53166696 22.69231346
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H 18.14774243 8.57843863 20.96039303
H 16.61833056 8.40301443 20.07024944
H 17.55341288 6.96269522 20.50968823
H 19.14104575 9.65908619 17.50899952
H 17.61492151 10.05468934 18.31099446
H 19.13582094 10.10572883 19.22618903
H 20.36822679 7.93829954 19.81098690
H 19.69445506 6.37393639 19.29663154
H 20.38391256 7.48582045 18.09694300
H 21.41301322 4.80155465 13.91228708
H 20.78416365 6.14321471 14.88449754
H 20.47728990 4.47056766 15.38948260
H 20.25582576 5.73646459 11.85244726
H 18.51033071 6.05904713 11.85977242
H 19.59943505 7.08455166 12.80027394
H 18.91438496 2.97747656 14.03919166
H 18.07258019 3.60588847 12.61291374
H 19.82502049 3.32723741 12.55057481
H 19.75415474 3.19101989 19.46480260
H 18.69033769 2.50231652 20.70467586
H 20.21203501 1.68613312 20.29651723
H 18.97653710 -0.47550484 19.80136659
H 17.43135889 0.29457308 20.21967420
H 17.61899276 -0.50171465 18.65414750
H 20.48891549 0.54181814 18.01540605

H 19.14811840 0.53035494 16.85461089
H 20.00851344 2.04589224 17.19578995
H 15.66517143 -0.70919935 14.18895303
H 15.27829779 -1.20004310 15.85053440
H 14.72500610 -2.18541289 14.47587491
H 12.88077773 -1.05823063 16.71240358
H 11.58308392 -0.44872328 15.66526720
H 12.31182710 -2.03103146 15.33595452
H 13.79057232 0.16388288 12.64845845
H 12.86876434 -1.32433071 12.95615633
H 12.13060889 0.26566364 13.24445874
H 15.73943050 7.39533842 10.88595422
H 14.68054172 6.90340486 9.54891253
H 13.99560714 7.68658910 10.98658520
H 16.63694283 4.97184524 10.95073260
H 15.50682070 3.62668356 11.19629703
H 15.52229799 4.51251000 9.65319527
H 13.05726856 4.93686607 9.84433635
H 12.98390172 4.08093669 11.40307820
H 12.37141763 5.74084615 11.26899183
H 10.63501175 5.35694960 12.80083168
H 9.03658712 6.09398735 13.04727210
H 10.50523063 7.05834010 13.28682005
H 9.50053594 3.87472670 16.07238250
H 8.46426018 4.19305414 14.66788319
H 10.08357350 3.49052816 14.44107072
H 9.64396831 7.63687998 15.65116902
H 8.21585181 6.61615155 15.39214726
H 9.27407007 6.34496946 16.79693830
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H 10.08369066 2.75231906 20.22014091
H 13.39418348 -0.04661100 20.58099913
H 11.71609207 -0.56580804 20.85134872
H 12.28447380 -0.16755456 19.21456962
H 13.07614937 1.80858810 22.34083747
H 11.69988731 2.92436978 22.21893753
H 11.42571698 1.21605450 22.58734301
H 11.49362529 4.58637522 20.65976131
H 15.79299866 4.40913398 19.89085975

182

S2(R), Full, Opted at UB3LYP/DZVP(UDUD)

Mn 14.07482456 4.11629314 15.26315428
Mn 14.74702585 2.72967177 17.57366010
Mn 16.60392477 4.67840241 17.01444265
Mn 15.97238925 7.24722448 15.14324834
Ca 13.31491717 5.69918729 18.50201401
O 13.40827041 3.69864964 16.90476071
O 15.43020789 4.35481989 18.33503467
O 15.74624956 3.33872716 16.12033289
O 15.48620405 5.84552968 16.06013400
O 14.26798613 7.82154020 17.86070005
O 14.62923698 8.41775081 15.72205481
O 17.42410215 6.19555151 17.97869651
O 17.16708798 7.89238556 16.50702954
O 18.05523209 4.78911176 15.65380285
O 17.45395116 6.39916170 14.20434513
O 14.83388191 4.63874863 13.49663959
O 14.93041727 6.88601551 13.56717494
O 16.10687170 4.62031717 20.92368771
O 14.38777255 6.04252235 20.70246767
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182

S2(C), Full, Opted at UB3LYP/DZVP(UUUD)

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182

S3, Full, Opted at UB3LYP/DZVP(UUUD)

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S3. Results of **1** calculated at the UBLYP/DZVP level.

Table S3.1 Calculated effective exchange integrals (J/cm^{-1}) of **1** at the UBLYP/DZVP level.[a]

State	S_0(b)	S_0(a)	S_1	S_2(R)	S_2(C)	S_3
$J_{1,2}$	-84.74	-88.99	–66.85	–58.21	34.78	23.49
$J_{1,3}$	-9.32	-6.31	7.50	–2.30	–10.98	–28.81
$J_{1,4}$	-16.97	-43.41	–10.01	–64.19	–35.41	–34.20
$J_{2,3}$	11.25	-98.67	22.39	15.92	30.80	28.21
$J_{2,4}$	-13.45	-1.51	–2.97	–3.37	–7.22	0.28
$J_{3,4}$	-146.68	-55.44	–39.02	–38.98	–53.73	–24.84

[a] Full geometrical optimizations were also performed at the UBLYP/DZVP level.

Table S3.2 Low-lying excitation states (ΔE /cm^{-1}) of **1** by solving the Heisenberg spin Hamiltonian ($H = -2JSS$) with the calculated J values at the UBLYP/DZVP level.

States	S_0(b)	S_0(a)	S_1	S_2(R)	S_2(C)	S_3
0	S = 1/2	S = 1/2	S = 0	S = 1/2	S = 5/2	S = 2
1	S = 3/2	S = 3/2	S = 1,	S = 3/2,	S = 7/2,	S = 3,
	ΔE =41.0	ΔE =177.8	ΔE =47.7	ΔE =28.9	ΔE =207.3	ΔE =0.1
2	S = 1/2	S = 5/2	S = 1,	S = 5/2,	S = 3/2,	S = 1,
	ΔE =162.7	ΔE =477.4	ΔE =124.0	ΔE =143.2	ΔE =223.9	ΔE =72.6

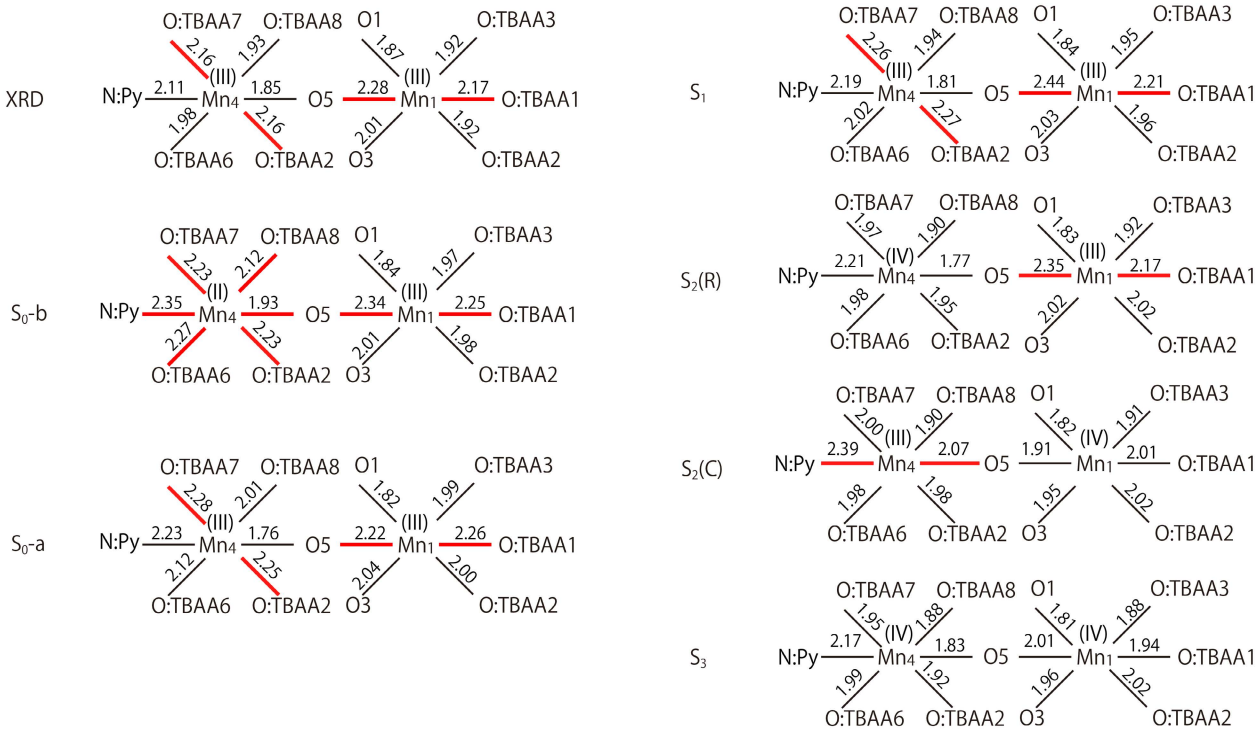

Figure S3.1 The coordination bond lengths of 1 around Mn1 and Mn4 calculated at the UBLYP/DZVP level. The Jahn-Teller axes of Mn(III) atoms are shown as red lines.

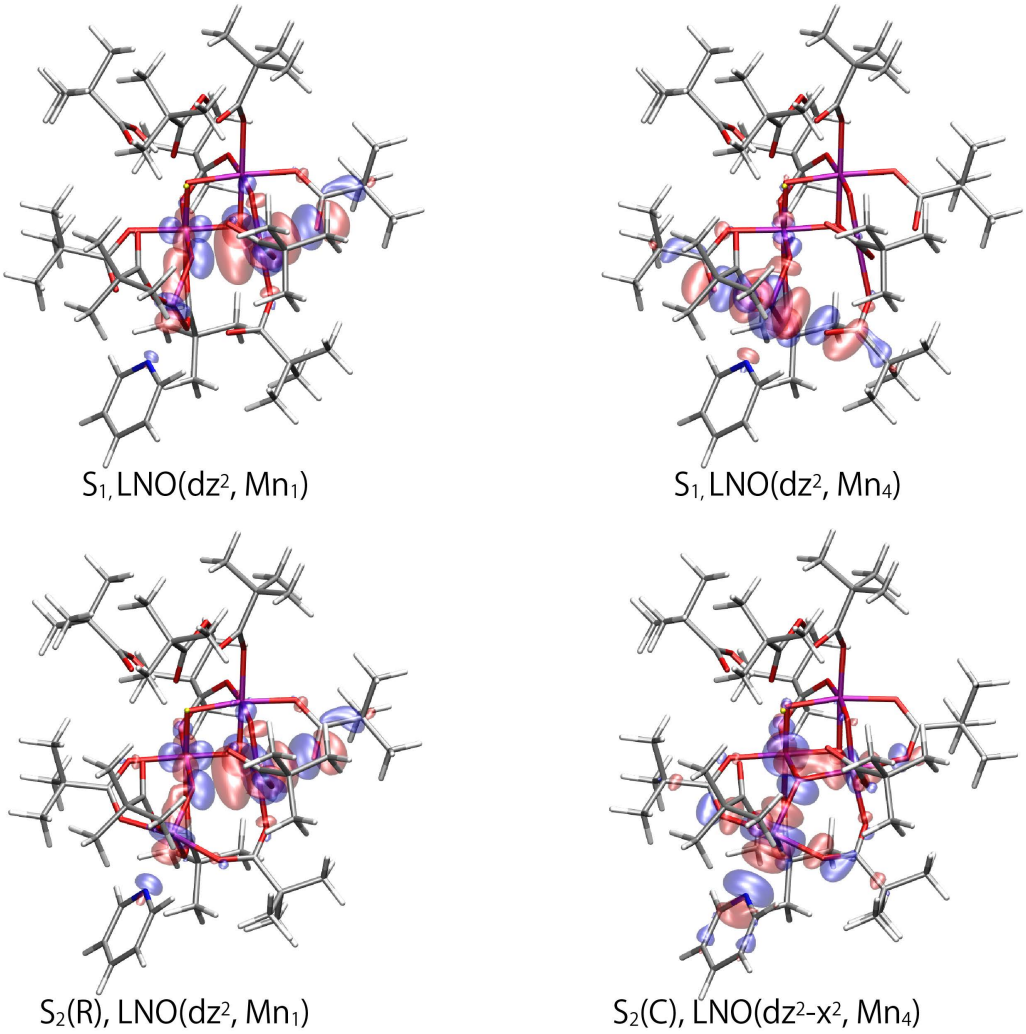

Figure S3.2 Localized natural orbitals (LNOs) mainly contribute to the Mn Jahn-Teller distortions of **1**. These orbitals were calculated at the UBLYP/DZVP level.

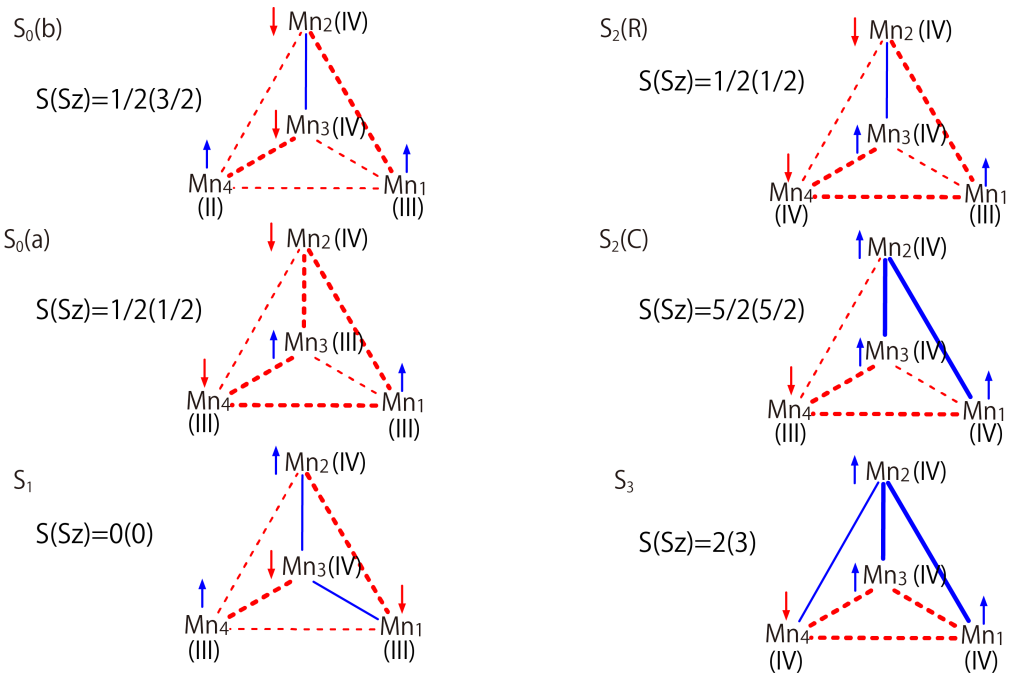

Figure S3.3 Schematic illustrations of the magnetic interactions for the Mn spin sites of **1** in the S_0, S_1, S_2 and S_3 states calculated at the UBLYP/DZVP level. Red dashed lines and blue solid lines represent the antiferromagnetic and ferromagnetic interactions, respectively. Bold and thin lines represent strong and weak magnetic interactions, respectively. All the values of the magnetic interactions are summarized in Table S3.1.

S4. Results of 2 calculated at the UB3LYP/DZVP and UBLYP/DZVP levels.

Table S4.1 Key bond distances /Å of **2** optimized at the UBLYP/DZVP level.

System	Model (**2**)					Native OEC
State	S_1	S_2-R	S_2-L	S_3	XRD	XRD[a]
Mn1–Mn2	2.79	2.78	2.77	2.78	2.77	2.67
Mn1–Mn3	3.18	3.10	2.88	2.97	3.09	3.24
Mn1–Mn4	3.72	3.64	3.51	3.46	3.60	4.95
Mn2–Mn3	2.76	2.76	2.74	2.75	2.74	2.70
Mn2–Mn4	5.28	5.32	5.41	5.30	5.24	5.17
Mn3–Mn4	3.25	3.29	3.39	3.34	3.23	2.86
O5-Mn1	2.49	2.33	1.91	2.01	2.28	2.70
O5-Mn3	1.85	1.91	1.89	1.97	1.86	2.17
O5-Mn4	1.81	1.77	2.06	1.84	1.85	2.32

[a] PDBID: 4UB6, A subunit

Table S4.2 Distances /Å of **2** optimized at the UBLYP/DZVP level.

System			**2**			Native OEC
State	S1	S2-R	S2-L	S3	XRD	XRD[a]
Mn1–O1	1.84	1.82	1.82	1.80	1.87	1.85
Mn1–O3	2.02	2.01	1.94	1.95	2.01	1.94
Mn1-O5	2.49	2.33	1.91	2.01	2.28	2.70
Mn2–O1	1.80	1.80	1.82	1.84	1.78	1.83
Mn2–O2	1.89	1.91	1.86	1.87	1.88	1.90
Mn2–O3	1.87	1.90	1.92	1.93	1.86	1.95
Mn3–O2	1.81	1.79	1.82	1.81	1.84	1.78
Mn3–O3	1.89	1.85	1.87	1.86	1.86	2.08
Mn3–O5	1.85	1.91	1.89	1.97	1.85	2.17
Mn4–O5	1.81	1.77	2.06	1.84	1.85	2.32
Ca-O1	2.55	2.58	2.54	2.59	2.50	2.57
Ca-O2	2.49	2.51	2.53	2.58	2.41	2.67
Ca-O5	2.91	3.23	3.00	3.34	2.70	2.59
Ca-Mn1	3.62	3.69	3.60	3.76	3.46	3.51
Ca-Mn2	3.40	3.43	3.45	3.48	3.36	3.35
Ca-Mn3	3.59	3.73	3.63	3.83	3.44	3.47
Ca-Mn4	4.27	4.53	4.48	4.63	4.06	3.76

Table S4.3 Calculated effective exchange integrals (J /cm^{-1} values) of **2** at the UB3LYP/DZVP (UBLYP/DZVP) level.[a]

	S1	S2-R	S2-L	S3
$J_{1,2}$	–26.1 (-66.28)	–18.44 (-55.77)	39.16 (39.68)	36.04 (29.09)
$J_{1,3}$	15.83 (5.70)	13.26 (–4.80)	–6.80 (–6.48)	–16.01 (–32.86)
$J_{1,4}$	–4.62 (-12.00)	–19.43 (–73.98)	–7.80 (–42.80)	–10.89 (–35.69)
$J_{2,3}$	16.59 (20.58)	14.97 (12.13)	31.31 (35.79)	26.72 (26.26)
$J_{2,4}$	–0.09 (–3.90)	2.54 (–4.39)	–1.17 (–8.61)	1.50 (0.27)
$J_{3,4}$	–2.60 (–38.32)	–8.36 (–27.91)	–10.47 (–49.48)	–5.63 (–24.06)

[a] Geometrical optimizations were performed at the UBLYP/DZP level.

Table S4.4 Low-lying energy levels of **2** by solving the Heisenberg spin Hamiltonian ($H = -2JSS$) using the J values calculated at the UB3LYP/DZVP (UBLYP/DZVP) level.

Energy states	S_1	S_2-R	S_2-L	S_3
0	$S = 0$ ($S = 0$)	$S = 3/2$ ($S = 1/2$)	$S = 5/2$ ($S = 5/2$)	$S = 3$ ($S = 2$)
1	$S = 1$, $\Delta E = 4.03$ ($S = 1$, $\Delta E = 52.74$)	$S = 1/2$, $\Delta E = 4.39$ ($S = 3/2$, $\Delta E = 8.06$)	$S = 7/2$, $\Delta E = 44.13$ ($S = 7/2$, $\Delta E = 223.10$)	$S = 2$, $\Delta E = 22.49$ ($S = 3$, $\Delta E = 17.32$)
2	$S = 2$, $\Delta E = 14.11$ ($S = 1$, $\Delta E = 123.11$)	$S = 5/2$, $\Delta E = 16.69$ ($S = 5/2$, $\Delta E = 70.72$)	$S = 9/2$, $\Delta E = 101.78$ ($S = 3/2$, $\Delta E = 273.82$)	$S = 4$, $\Delta E = 37.51$ ($S = 1$, $\Delta E = 58.21$)

Table S4.5 Local spin correlation factor c for low-lying energy levels at the UB3LYP/DZVP (UBLYP/DZVP) level.[a]

State	Index	S	c_1	c_2	c_3	c_4
S_0(b)[b]	0	(1/2)	(-0.071	-0.194	-0.990	2.255)
	1	(3/2)	(0.843	-0.493	-0.528	1.179)
	2	(5/2)	(0.526	0.058	-0.251	0.666)
S_0(a)[c]	0	(1/2)	(1.739	-0.998	1.585	-1.326)
	1	(3/2)	(0.609	-0.187	0.490	0.087)
	2	(5/2)	(0.442	-0.069	0.341	0.285)
S_1	0	0	–	–	–	–
		(0)	(–	_	_	–)
	1	1	-0.159	0.361	0.489	0.308
		(1)	(0.649	-0.246	-0.031	0.628)
	2	2	-0.084	0.272	0.445	0.367
		(1)	(-0.432	0.297	-0.201	1.336)
S_2(R)	0	3/2	0.170	0.318	0.724	-0.213
		(1/2)	(0.686	-0.593	1.665	-0.759)
	1	1/2	1.068	-0.742	1.609	-0.935
		(3/2)	(-0.171	0.410	0.758	0.002)
	2	5/2	0.121	0.378	0.525	-0.025
		(5/2)	(-0.267	0.437	0.594	0.235)
S_2(C)	0	5/2	0.527	0.537	0.503	-0.568
		(5/2)	(0.509	0.558	0.491	-0.558)
	1	7/2	0.370	0.379	0.342	-0.092
		(7/2)	(0.352	0.400	0.329	-0.082)
	2	9/2	0.297	0.304	0.273	0.123
		(3/2)	(0.495	0.848	0.426	-0.771)
S_3	0	3	0.416	0.467	0.478	-0.361
		(2)	(0.290	0.690	0.467	-0.448)
	1	2	0.387	0.654	0.444	-0.486
		(3)	(0.372	0.482	0.480	-0.335)
	2	4	0.292	0.351	0.364	-0.008
		(1)	(0.320	1.140	0.238	-0.700)

[a] $c_i = \langle s_i \cdot S \rangle / \langle S \cdot S \rangle$

[b] Optimized at UDUD spin state at the (BLYP) method

[b] Optimized at UDDU spin state at the (BLYP) method

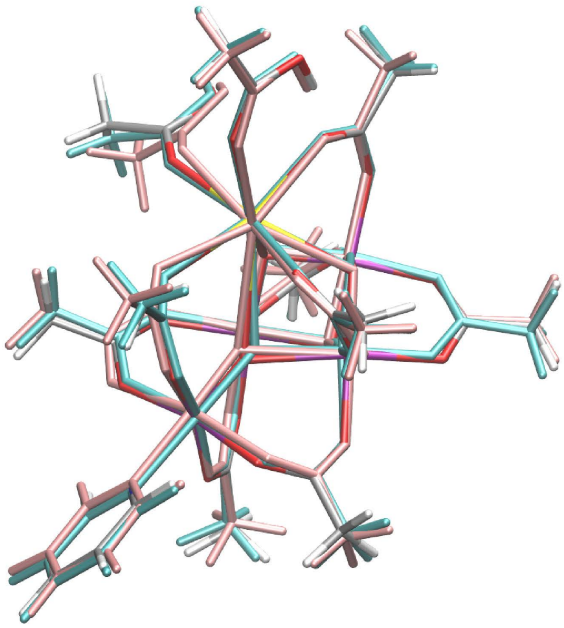

Figure S4.1 Superimposed structures in the S_1(pink), S_2-R(element), S_2-L(cyan) states.

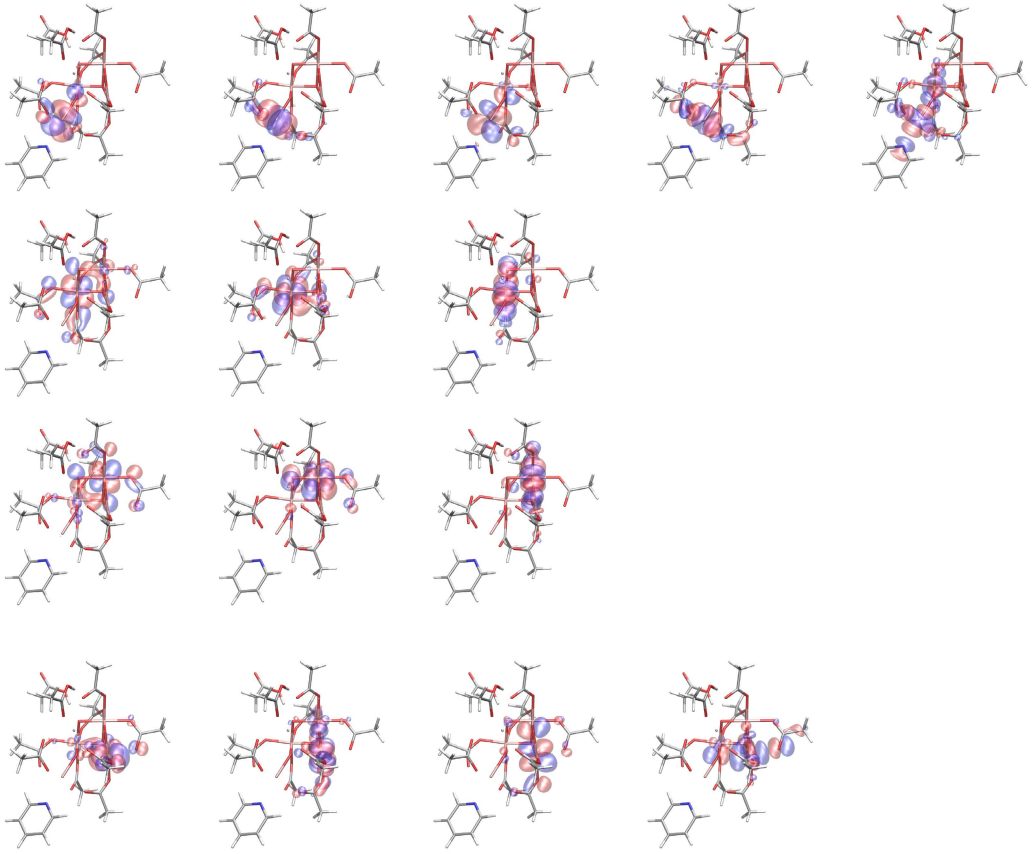

Figure S4.2 Localized natural orbitals of **2** in the highest spin S_0(b) state calculated at the BLYP/DZVP level. 14 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 5 for Mn4 are shown.

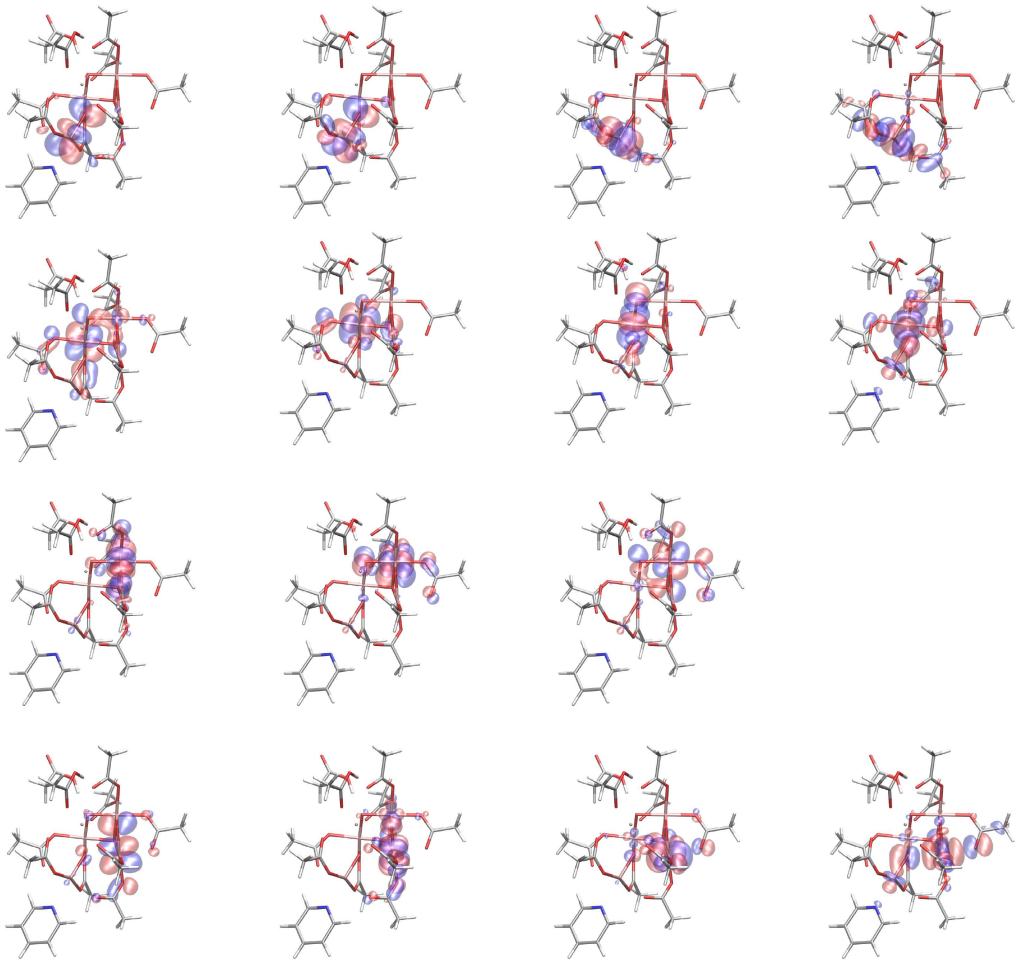

Figure S4.3 Localized natural orbitals of **2** in the highest spin S_0(a) state calculated at the BLYP/DZVP level. 15 d-type orbitals; 4 for Mn1, 3 for Mn2, 4 for Mn3 and 4 for Mn4 are shown.

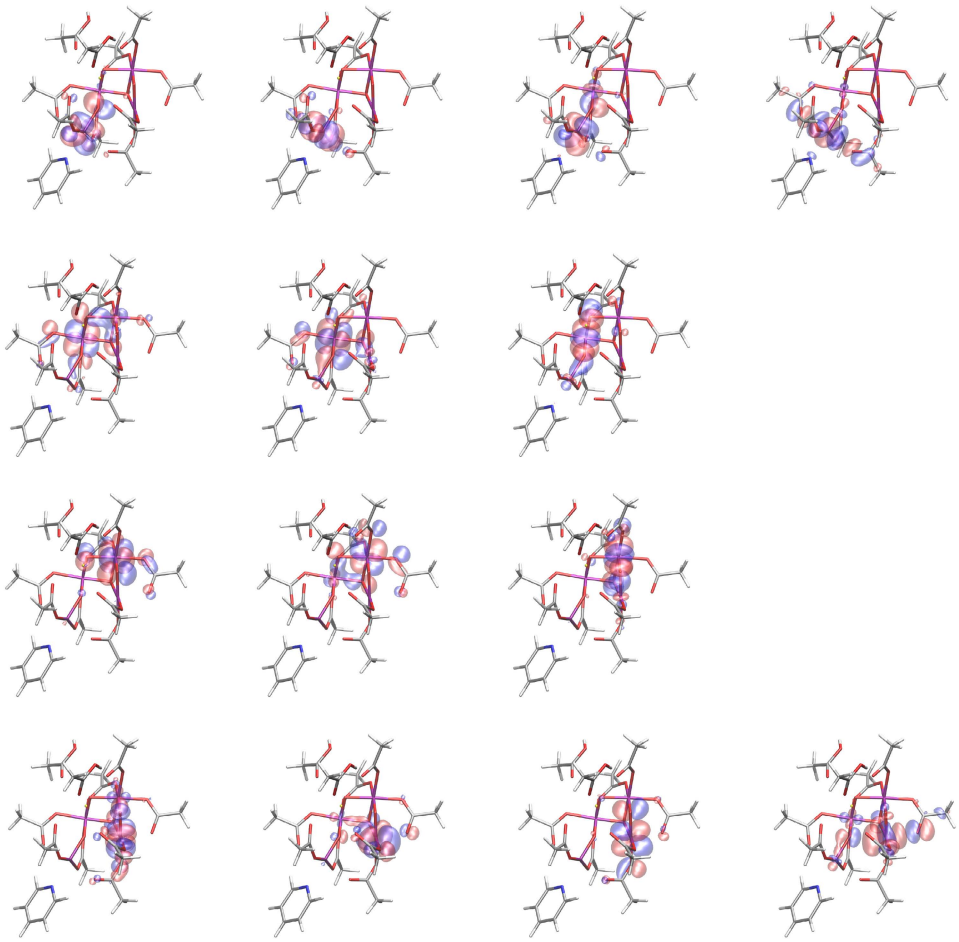

Figure S4.4 Localized natural orbitals of **2** in the highest spin S_1 state calculated at the BLYP/DZVP level. 14 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 4 for Mn4 are shown.

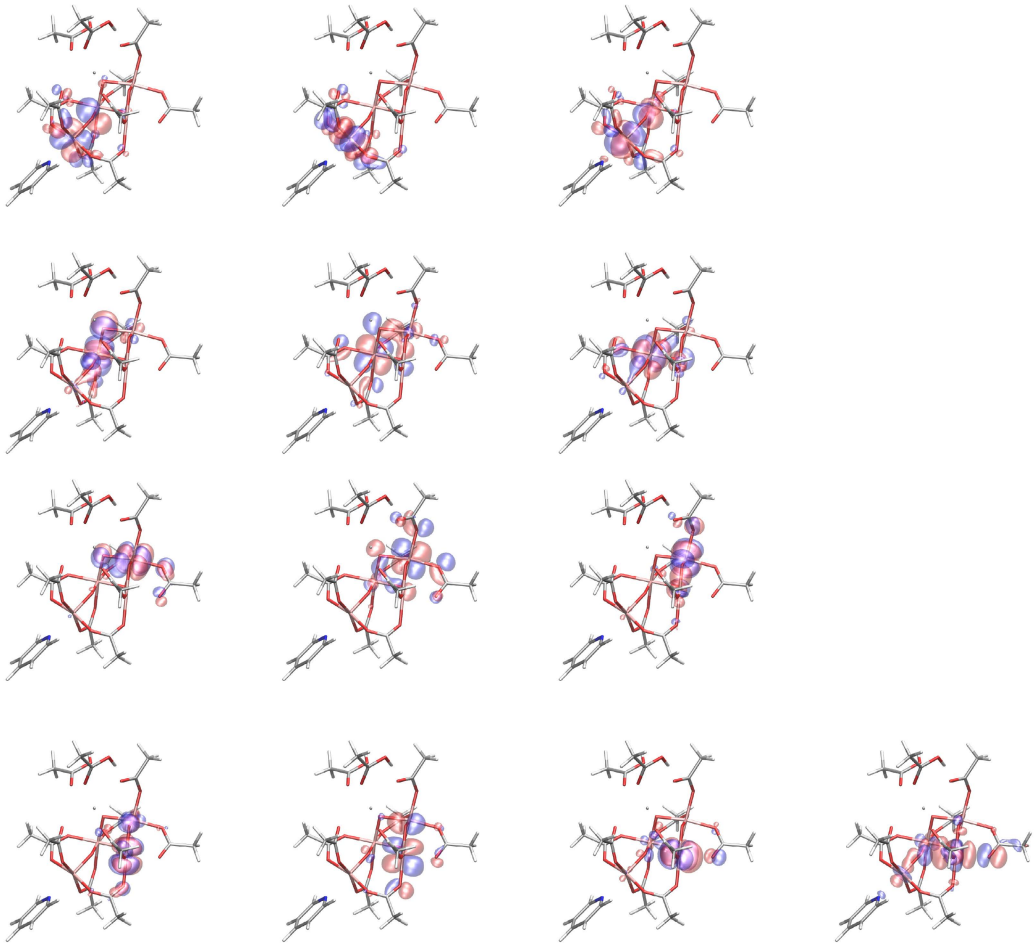

Figure S6. mshoji et al

Figure S4.5 Localized natural orbitals of **2** in the highest spin S_2–R state calculated at the BLYP/DZVP level. 13 d-type orbitals; 4 for Mn1, 3 for Mn2, 3 for Mn3 and 3 for Mn4 are shown.

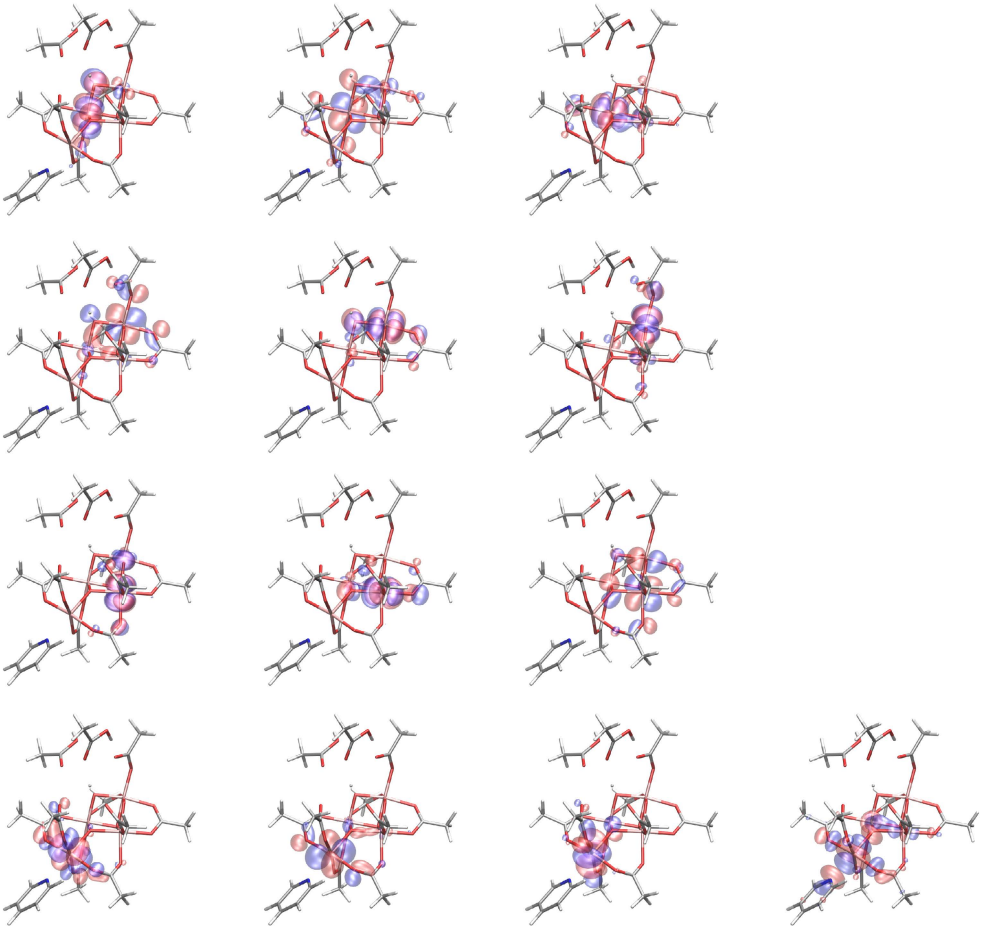

Figure S4.6 Localized natural orbitals of 2 in the highest spin S_2–C state calculated at the BLYP/DZVP level. 13 d-type orbitals; 3 for Mn1, 3 for Mn2, 3 for Mn3 and 4 for Mn4 are shown.

S5. Theoretical modeling of the synthetic model (**2**)

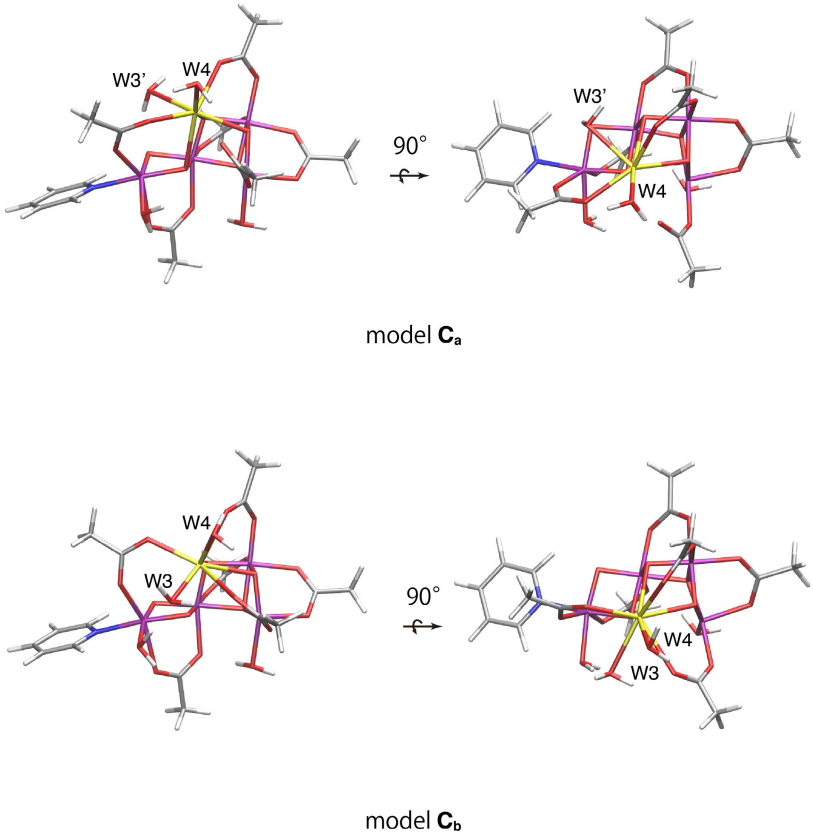

Figure S5.1 Molecular structures of the model **Ca** and model **Cb**.

92

2, S1, Opted at UB3LYP/DZVP(UUUU)

Mn 14.10881401 4.07108691 15.24148354

Mn 14.75926136 2.71783845 17.59840256

Mn 16.54640248 4.72021313 17.14373855

Mn 15.79044508 7.28776382 15.32446540

Ca 13.37399506 5.70764149 18.33108805

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C 13.82906620 8.65960406 17.06386007

C 12.79977788 9.77460731 17.11238953

C 11.71031547 5.74537364 15.31706838

C 10.46876809 6.17568967 14.55459547

C 17.48880840 7.40247143 17.94777422

C 18.03261974 8.27706600 19.06245664

C 18.09288441 5.52201988 14.71565204

C 19.18232289 5.07966356 13.76087036

C 17.53300308 2.28720576 18.38324111

C 18.67709099 1.43856656 18.90233224

C 13.95143402 1.04885473 15.39817805

C 13.64652174 -0.34430654 14.88216971

C 14.77288794 5.62755703 12.91260135

C 14.76310581 5.55884570 11.39797028

C 17.64081599 9.49344147 14.26930259

C 18.05144894 10.61066354 13.54792419

C 17.12893173 11.25505067 12.72450315

C 15.82740542 10.75949004 12.65472755

C 15.49259486 9.63985234 13.41048981

H 18.30910133 8.95722494 14.93208040

H 19.07421322 10.96259777 13.63618880

H 17.41915877 12.12892053 12.14771683

H 15.07712837 11.22726834 12.02548641

H 14.50056767 9.20622536 13.39408431

H 18.68353687 7.70728483 19.72973273

H 18.56710246 9.13354113 18.64586286

H 17.18087684 8.65228000 19.64271417

H 19.41519128 5.86688925 13.04109655

H 20.07484506 4.78266412 14.31645778

H 18.81742130 4.20087991 13.21583470

H 14.76115125 6.55907835 10.96087865

H 15.63667144 4.99842512 11.04988171

H 13.87409922 5.00809503 11.07111478

H 9.80793398 6.76131839 15.19616781

H 10.76945280 6.77853023 13.69012933

H 9.94250852 5.29605299 14.17119542

H 13.38799986 -0.31134516 13.82266427

H 14.51570909 -0.99116007 15.03862488

H 12.81545805 -0.76920195 15.45530319

H 12.46079483 0.72272874 20.76937964

H 10.99398612 1.72583962 20.56518613

H 12.20974873 2.18925939 21.76244436

H 8.66509790 6.89823672 21.04852282

H 9.93816769 7.40965687 22.15779083

H 9.73772341 8.26328765 20.60047950

H 11.81791676 9.32512587 16.92166042

H 12.78114587 10.22393355 18.10783714

H 12.99080989 10.53230501 16.34874334

H 17.12022257 4.73101676 22.03478180

H 16.68874529 6.45186571 21.86754948

H 17.01500809 5.49337186 20.41597644

H 19.39235780 2.05612821 19.45153991

H 18.29973285 0.62792178 19.52870118

H 19.20083629 1.00257512 18.04337529

H 11.23487386 4.51965993 20.46728240

H 15.38185995 3.48395544 22.16354458

91

A, S1, Opted at UB3LYP/DZVP(UUUU)

Mn 14.06870948 4.11402047 15.26149347

Mn 14.70537549 2.71978665 17.54242954

Mn 16.48273909 4.75120424 17.11079726

Mn 15.75303259 7.34523403 15.31470683

Ca 13.28540075 5.72137716 18.38764153

O 13.33220087 3.67892169 16.82449672

O 15.30559586 4.26769540 18.36309826

O 15.73740853 3.37984532 16.11652332

O 15.23282949 5.85400305 16.22574338

O 14.04696186 7.97242967 18.10050760

O 14.40825991 8.55594803 15.95893510

O 17.23242893 6.17050291 18.21343575

O 17.32332454 7.82200218 16.68304996

O 18.00305278 5.03873217 15.77817716

O 17.03036536 6.20894235 14.12073311

O 14.70020970 4.14502194 21.81963746

O 14.37191774 5.97279566 20.61920135

O 11.32606519 6.58684488 19.57846570

O 10.46780820 5.02507131 20.94741765

O 12.37732858 3.73990176 19.56421543

O 13.72595886 2.03093904 19.01474268

O 16.32141987 1.77763460 18.22761010

O 17.76679433 3.48384697 17.88201675

O 14.25113124 1.14077013 16.49875200

O 13.87029992 2.12884381 14.50230238

O 12.58507174 5.18064543 14.59842366

O 11.80809011 6.12847049 16.48739636

N 16.44229650 9.02064644 14.17892597

C 15.11947142 5.32578777 21.32766460

C 16.52327452 5.76711759 21.66214358

C 10.53129343 6.25349476 20.45821776

C 9.55192959 7.20318288 21.09191805

C 12.76828464 2.55718593 19.69450124

C 12.09417401 1.63647395 20.68629651

C 13.90189604 8.74470800 17.14149501

C 13.05974376 9.99775022 17.27305659

C 11.65267852 5.77390885 15.31614004

C 10.34873220 5.99987460 14.58613549

C 17.54764522 7.35124954 17.82821981

C 18.21893032 8.22719274 18.86201066

C 18.01339870 5.54832328 14.63296133

C 19.24847662 5.38272394 13.77791122

C 17.47307747 2.30145317 18.26365526

C 18.61146890 1.47322557 18.81275103

C 13.94905532 1.11621387 15.25335611

C 13.65799042 -0.25267431 14.68239828

C 17.75419803 9.30681806 14.09973432

C 18.23329005 10.40017532 13.38710074

C 17.32133722 11.22879814 12.73324293

C 15.96137814 10.93448779 12.82327517

C 15.55889320 9.82449597 13.55898182

H 18.41968356 8.64905416 14.64497420

H 19.30002873 10.59525646 13.35373376

H 17.66449108 12.09063240 12.16845590

H 15.21543202 11.55389846 12.33657022

H 14.51688760 9.55308008 13.66812991

H 18.90644334 7.64207235 19.47743441

H 18.74427611 9.05296687 18.37933384

H 17.44267015 8.64249098 19.51594162

H 19.71299066 6.36378732 13.62664256

H 19.96197090 4.70857615 14.25244650

H 18.97129277 5.00620750 12.78800444

H 9.70970184 6.68172663 15.14870446

H 10.52883504 6.38604709 13.57859519

H 9.83831787 5.03570743 14.47524879

H 13.52860689 -0.20142779 13.60041196

H 14.46738790 -0.94207412 14.93975251

H 12.74198506 -0.64078603 15.14141001

H 12.69227407 0.74177441 20.86330937

H 11.12124892 1.33537219 20.27970362

H 11.91518457 2.16880220 21.62461938

H 8.56387939 6.74020618 21.16304510

H 9.88160559 7.42956457 22.11249467

H 9.50193171 8.12773034 20.51647821

H 12.04911340 9.77409688 16.91023283

H 12.99069830 10.29317352 18.32144388

H 13.46416514 10.81242978 16.66751734

H 16.91958046 5.30698665 22.57227194

H 16.53588402 6.85348605 21.76858668

H 17.16392413 5.50668312 20.81116697

H 18.96262344 1.92050760 19.74933018

H 18.28667032 0.44813103 18.99436984

H 19.44850084 1.48927926 18.10864419

H 11.15475703 4.45974164 20.48695176

H 15.39179352 3.73192197 22.36312941

O 15.07017394 4.35886153 13.43193946

H 15.89659262 4.87921721 13.58228141

H 15.31166377 3.44805825 13.18233768

O 14.28744729 7.08144553 13.50130824

H 13.55601275 6.48105743 13.77911684

H 14.66554828 6.65297701 12.71703136

85

B, S1, Opted at UB3LYP/DZVP(UUUU)

Mn 13.57355751 3.77899561 15.28536082

Mn 14.67324340 2.93548352 17.63881983

Mn 16.14105091 5.03858711 16.63525343

Mn 15.81429616 7.69264257 16.33741770

Ca 12.96613552 5.86088011 18.06289579

O 13.09580513 3.63494376 17.02091314

O 15.27930026 4.56166435 18.17272223

O 15.30126855 3.41969878 15.97698251

O 14.74654859 6.14562053 16.20551412

O 13.02072530 8.33423275 17.69462992

O 15.12939858 8.97376571 18.06331922

O 16.98335522 6.55531340 17.12140307

O 16.83380272 5.12763535 14.66235632

O 16.62034323 7.34147988 14.26803829

O 15.25998672 5.15960196 21.40973167

O 14.19691804 6.62483425 20.14540500

O 10.93636640 6.53420295 19.34457908

O 10.65358946 5.23338906 21.15851540

O 12.58714882 4.07358499 19.81619427

O 14.02813557 2.40373372 19.38439188

O 16.47684548 2.16457638 18.05092165

O 17.68790391 3.85661542 17.14328706

O 14.16069568 1.12477246 16.93800940

O 13.40862077 1.68003579 14.87431539

O 11.96308776 4.49264000 14.56745611

O 11.36557504 5.90741929 16.21425606

N 17.26886555 9.27202508 16.25840604

C 15.25929133 6.24008760 20.60503159

C 16.57765629 6.91048815 20.32861573

C 10.33846490 6.25695179 20.38206415

C 9.16762421 7.05733125 20.89389131

C 13.15111315 2.98859006 20.10715278

C 12.82007326 2.30882876 21.42120884

C 13.89992583 8.99228217 18.35033839

C 13.43278992 9.82270781 19.53015307

C 11.14093076 5.31642395 15.14821627

C 9.83440265 5.52029296 14.40586045

C 16.96159333 6.18660255 13.93567529

C 17.54596674 5.95787517 12.55093397

C 17.56350103 2.72533795 17.70646607

C 18.83930900 1.94933436 17.96847071

C 13.68487085 0.84905965 15.78857196

C 13.39690608 -0.61821820 15.52885777

C 18.56670308 8.98072147 16.43763688

C 19.55812294 9.95495607 16.35865847

C 19.18798461 11.27040507 16.08127418

C 17.83755712 11.56657268 15.89504803

C 16.90667346 10.53700740 15.99531963

H 18.78020464 7.93846596 16.65497741

H 20.59659269 9.68074536 16.51422113

H 19.93840744 12.05321685 16.01247088

H 17.50463580 12.57633461 15.67773480

H 15.84395203 10.70892744 15.86373472

H 17.82260284 6.90786222 12.09039697

H 18.41349776 5.29443925 12.61073438

H 16.79481872 5.46636496 11.92057328

H 9.23824443 6.29635112 14.88824521

H 10.03326747 5.78724005 13.36300823

H 9.27573785 4.57764688 14.39705298

H 13.38274021 -0.82349402 14.45635056

H 14.13156203 -1.24862919 16.03519824

H 12.40803206 -0.85576884 15.93946687

H 13.17401464 1.27684809 21.43044096

H 11.74164397 2.34095940 21.60281679

H 13.31194302 2.86595858 22.22725159

H 8.29113972 6.40870877 20.99373977

H 9.39612943 7.45020667 21.89027137

H 8.95037558 7.87744433 20.20933272

H 12.48736691 10.31736403 19.29218511

H 13.25427821 9.14458161 20.37201311

H 14.18862193 10.55663496 19.81880562

H 17.34706148 6.66565554 21.06818803

H 16.42265782 7.99052479 20.28920426

H 16.90933382 6.60719021 19.32532686

H 19.67019665 2.63357501 18.15528246

H 18.70473346 1.26084095 18.80525174

H 19.07694840 1.36196633 17.07337330

H 11.42878301 4.74147849 20.73231819

H 16.17302544 4.90999942 21.62835366

O 14.62599263 3.93564273 13.45700667

H 15.52685237 4.17218233 13.80793208

H 14.68190084 3.00032594 13.18942359

O 14.24947210 8.73806560 15.38258402

H 13.56610834 8.58839435 16.10959638

H 13.99284103 8.15759485 14.64535533

75

Ca, S1, Opted at UB3LYP/DZVP(UUUU)

Mn 13.53028411 3.83193132 15.24287942

Mn 14.76622535 2.87658255 17.48772911

Mn 16.13573685 5.00064347 16.38768220

Mn 15.60067606 7.61966284 15.87481822

Ca 13.19220169 5.81779660 18.06713020

O 13.16037205 3.60645546 16.99818142

O 15.39372241 4.52636517 17.95535487

O 15.29561448 3.38390816 15.77321883

O 14.63256166 6.01143977 15.89188633

O 12.67589095 8.18734932 17.89395846

O 14.55439919 9.05223596 17.03774733

O 16.78655817 6.63187225 16.85596137

O 16.86679613 5.01369041 14.40860321

O 16.60818822 7.16967408 13.81977671

O 15.18539075 6.85821135 19.32642443

O 10.93614640 6.51053352 19.06928070

O 13.35052557 4.32728035 19.98191392

O 14.24651561 2.38748386 19.24637707

O 16.63233695 2.17534707 17.77780926

O 17.72848514 3.93838919 16.85546027

O 14.21986536 1.10307577 16.79457298

O 13.31289123 1.71180901 14.80735248

O 11.83639994 4.50169061 14.66091480

O 11.21907292 5.70223034 16.45793312

N 17.00536150 9.23422631 15.75948472

C 13.67578568 3.13864767 20.13848008

C 13.40382171 2.42845884 21.45124590

C 13.47541311 9.13957347 17.70625811

C 13.15468853 10.50750965 18.28959985

C 10.96590625 5.14289960 15.37646487

C 9.56693370 5.17132163 14.79389212

C 17.03765230 6.00578670 13.61788560

C 17.84500534 5.73574259 12.35944571

C 17.67744451 2.80204719 17.43330758

C 19.01091102 2.15673850 17.74798880

C 13.66084664 0.85806213 15.67141491

C 13.38246222 -0.60778745 15.39643170

C 18.30183217 9.00465908 16.02326334

C 19.26266303 10.00640032 15.91864797

C 18.86438086 11.28262405 15.52270139

C 17.51581045 11.51508246 15.25222610

C 16.61435400 10.46384951 15.38777538

H 18.53697643 7.99165907 16.33476991

H 20.29975917 9.78256663 16.14656387

H 19.59171566 12.08453903 15.43063075

H 17.16032312 12.49378928 14.94667164

H 15.55233667 10.59001841 15.21245845

H 17.53486600 6.40239258 11.55154527

H 18.90031460 5.93794403 12.58063991

H 17.76371594 4.69097941 12.05116538

H 8.93017911 5.86418111 15.34658429

H 9.60395575 5.45121391 13.73683000

H 9.14014822 4.16317383 14.84712515

H 13.08993442 -0.75883042 14.35580798

H 14.26352102 -1.20851117 15.63939240

H 12.56825687 -0.94003200 16.05074896

H 14.30408115 1.90900067 21.79304679

H 12.63004447 1.66891913 21.29182823

H 13.06300799 3.14113445 22.20401295

H 12.97964629 11.21972766 17.47480385

H 12.27115627 10.46765729 18.92923701

H 14.01254165 10.87189603 18.86336280

H 19.50431252 2.73127248 18.54017189

H 18.87094190 1.12699981 18.07994765

H 19.65544201 2.19043586 16.86483796

O 14.42326200 3.95421787 13.32086621

H 15.35963296 4.10490973 13.60447246

H 14.38003538 3.01902496 13.04739790

O 14.31049805 8.36364467 14.25481149

H 13.50153273 7.83288618 14.35977740

H 14.83299038 7.92282328 13.55260491

H 11.17107116 7.44787218 18.91574531

H 10.45243660 6.26816720 18.25684405

H 15.87642009 6.92662742 18.62947852

H 15.43246609 6.03900498 19.78856112

75

Cb, S1, Opted at UB3LYP/DZVP(UUUU)

Mn 13.68997817 3.08343140 14.98307146
Mn 14.68315433 2.99647455 17.52612647
Mn 16.02507272 4.95229353 16.09909821
Mn 15.50395486 7.46726724 15.27938792
Ca 12.86106942 5.74261611 17.11577527
O 13.09193754 3.35613998 16.65884478
O 15.10106270 4.74914510 17.66217575
O 15.37037780 3.13386848 15.80402943
O 14.57909281 5.81655068 15.36540929
O 13.15317404 7.87403110 18.10783726
O 14.49171774 8.83637876 16.58377856
O 16.71221884 6.59307396 16.28609441
O 16.80685367 4.68736988 14.17114858
O 16.45211661 6.75340740 13.32209547
O 11.83858972 7.49762445 15.33292670
O 10.43078878 5.82946481 17.82062067
O 12.40862089 4.55581662 19.23344127
O 13.91421199 2.87443090 19.27868726
O 16.49513128 2.55246612 18.19550346
O 17.61724462 4.07078549 16.93564068
O 14.39456990 1.01824941 17.26779279
O 13.73428657 0.95980017 15.10184672
O 12.02411636 3.36755210 14.02745193
O 11.05031990 4.98484594 15.24711345
N 16.85631991 9.11122240 15.00656334
C 12.96437789 3.58283208 19.78586915
C 12.54680526 3.15053249 21.17926570
C 13.88666992 8.81394659 17.70452267
C 14.07589412 10.01316847 18.62300423
C 11.03373945 4.12040909 14.33510850
C 9.78384369 3.91280158 13.50100672
C 16.90694175 5.59134994 13.25393713
C 17.65353103 5.15911073 12.00134141
C 17.55023166 3.13937831 17.79417843
C 18.85126488 2.69957383 18.43259770
C 14.04378000 0.41464274 16.20395732
C 14.00696888 -1.10026003 16.29079160
C 18.14660871 8.96524095 15.34798940
C 19.06941739 9.99696279 15.19751951
C 18.63781600 11.21566116 14.67576160
C 17.29548818 11.36165617 14.32487256
C 16.43434335 10.28434466 14.50879868
H 18.40868886 7.99483921 15.75856231
H 20.10288595 9.84071016 15.48940780
H 19.33446097 12.03952345 14.54698139
H 16.91573513 12.29320252 13.91774517
H 15.38079304 10.34183794 14.25927234
H 18.69833213 4.95468837 12.26051639
H 17.22958412 4.23027858 11.60541881
H 17.61111236 5.93843388 11.23865487
H 8.99442629 4.60627244 13.79639350
H 10.02196665 4.04727962 12.44075583
H 9.43521627 2.88172634 13.62285819
H 13.62788864 -1.53497375 15.36438826
H 15.01693928 -1.47456798 16.49066236
H 13.37738661 -1.40299695 17.13334240
H 13.38161956 3.31450107 21.86946977
H 12.32519107 2.07890333 21.18704722
H 11.67951665 3.72097607 21.51638798
H 14.46727769 10.87550409 18.07886811
H 13.13355201 10.26617008 19.11685939
H 14.79282524 9.73874159 19.40632427
H 19.02976925 3.32294781 19.31707520
H 18.78687155 1.65785173 18.75344002
H 19.68245684 2.84299290 17.73873793
O 14.83088109 2.98958924 13.20704660
H 15.05011644 2.04302521 13.14366539
H 15.66328410 3.44334961 13.51754542
O 14.08225583 8.19913733 13.88109631
H 13.21364027 8.00530875 14.31933537

H 14.18385897 7.55923091 13.15477853

H 10.61627765 5.31665156 18.63199396

H 10.07158843 5.19751337 17.17340686

H 11.37832288 8.12571589 15.91215565

H 11.20301821 6.78862955 15.08842579

S6. Ca substitutions of the synthetic model (**2**)

Table S6.1 Key bond distances /Å of the model complex (**Mn_4AO_4**) in the S1 state.

	Model (**MMn_4O_4**)							Native OEC
	A=Ba	A=Mg	A=Mn	A=Sr	A=Zn	A=Ca	A=Ca XRD	XRD[a]
Mn1–Mn2	2.80	2.83	2.81	2.79	2.82	2.79	2.77	2.67
Mn1–Mn3	3.17	3.15	3.14	3.16	3.14	3.18	3.09	3.24
Mn1–Mn4	3.66	3.59	3.64	3.64	3.60	3.72	3.60	4.95
Mn2–Mn3	2.72	2.71	2.73	2.72	2.71	2.76	2.74	2.70
Mn2–Mn4	5.22	5.20	5.22	5.21	5.21	5.28	5.24	5.17
Mn3–Mn4	3.24	3.21	3.23	3.24	3.21	3.25	3.23	2.86
O5-Mn1	2.41	2.21	2.27	2.39	2.22	2.49	2.28	2.70
O5-Mn3	1.86	1.84	1.84	1.86	1.83	1.85	1.86	2.17
O5-Mn4	1.82	1.80	1.81	1.82	1.81	1.81	1.85	2.32

[a] PDBID: 4UB6, A subunit

Table S6.2 Distances /Å of the model complex (Mn_4AO_4) in the S1 state.

	Model (Mn_4AO_4)							Native OEC XRD[a]
	A=Ba	A=Mg	A=Mn	A=Sr	A=Zn	A=Ca	A=Ca XRD	
Mn1–O1	1.82	1.81	1.83	1.83	1.82	1.84	1.87	1.85
Mn1–O3	2.08	2.17	2.10	2.07	2.15	2.02	2.01	1.94
Mn1-O5	2.41	2.21	2.27	2.39	2.22	2.49	2.28	2.70
Mn2–O1	1.79	1.81	1.80	1.79	1.81	1.80	1.78	1.83
Mn2–O2	1.85	1.84	1.86	1.85	1.87	1.89	1.88	1.90
Mn2–O3	1.85	1.83	1.85	1.85	1.83	1.87	1.86	1.95
Mn3–O2	1.79	1.82	1.82	1.79	1.82	1.81	1.84	1.78
Mn3–O3	1.83	1.85	1.85	1.84	1.84	1.89	1.86	2.08
Mn3–O5	1.86	1.84	1.84	1.86	1.83	1.85	1.85	2.17
Mn4–O5	1.82	1.80	1.81	1.82	1.81	1.81	1.85	2.32
A-O1	2.80	2.19	2.24	2.66	2.25	2.55	2.50	2.57
A-O2	2.73	2.24	2.29	2.58	2.21	2.49	2.41	2.67
A-O5	3.00	3.02	2.88	2.90	2.99	2.91	2.70	2.59
A-Mn1	3.79	3.35	3.35	3.69	3.37	3.62	3.46	3.51
A-Mn2	3.66	3.10	3.13	3.49	3.12	3.40	3.36	3.35
A-Mn3	3.74	3.49	3.46	3.63	3.45	3.59	3.44	3.47
A-Mn4	4.29	4.31	4.17	4.22	4.28	4.27	4.06	3.76

[a] PDBID: 4UB6, A subunit

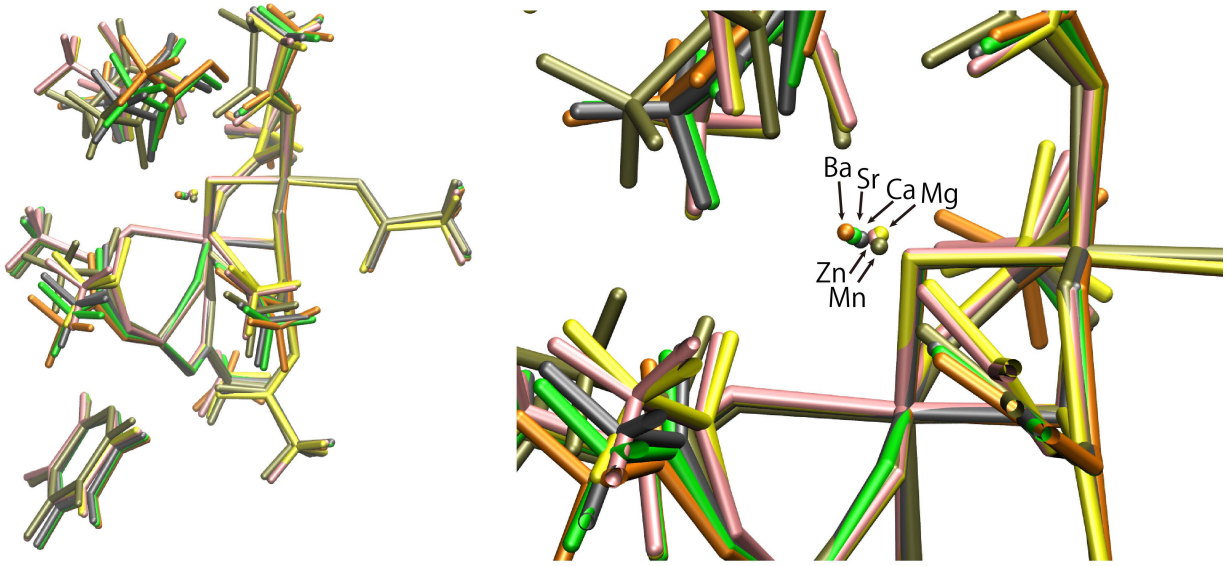

Figure S6.1 Superimposed views of the Ca substituted models (Mn_4AO_4) optimized at the UB3LYP/DZVP level. Structures are colored in orange (A=Ba), green (A=Sr), gray (A=Ca), yellow (A=Mg), pink (A=Zn) and tan (A=Mn). (A) whole molecular structures and (B) enlarged view for the Mn_4AO_4 cores are shown.