Electronic Supplementary Material (ESI) for Chemical Science.


# Electronic Supplementary Information

## From cubane-assembled Mn-oxo clusters to monodispersed manganese oxide colloidal nanocrystals

Yan He[1], Yang Liu[2], Huijuan Zheng[1], Zhen Xiang[1], Zheng Zhou[1*], Fengting Geng[3], Longlong Geng[3], Evgeny V. Dikarev[4*], Haixiang Han[1*]

[1]*Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China.*

[2]*Department of Material Science, Fudan University, Shanghai 200433, China.*

[3]*Shandong Provincial Key Laboratory of Monocrystalline Silicon Semiconductor Materials and Technology, College of Chemistry and Chemical Engineering, Dezhou University, Dezhou 253023, China.*

[4]*Department of Chemistry, University at Albany, Albany, New York 12222, United States.*

*Author to whom correspondence should be addressed.
E-mail: zhouzheng@tongji.edu.cn, edikarev@albany.edu and hxhan@tongji.edu.cn

# Contents

## Experimental section & general procedures

All manipulations were carried out in a dry, oxygen-free argon atmosphere by employing standard Schlenk and glove box techniques. Manganese(II) perchlorate hexahydrate ($Mn(ClO_4)_2·6H_2O$, 99%), manganese(III) acetate dihydrate ($Mn(OOCCH_3)_3·2H_2O$, 99%), pivalic acid ($C(CH_3)_3COOH$, 99%), triethylamine ($Et_3N$, 99.9%), pyridine (py, 99.5%), methanol (99.9%), ethanol (99.9%), acetonitrile (99.9%), dichloromethane (99.9%) and hexane (99.9%) were purchased from Adamas and used upon received.

**XPS:** X-ray photoelectron spectroscopy (XPS) was recorded on Thermo Scientific K-Alpha spectrometer. Samples were grounded into powder and compressed to flakes, which were then attached to sample plate. Then samples were placed in Thermo Scientific K*α* XPS instrument sample chamber and vacuumed to $2.0 \times 10^{-7}$ mBar. The setting parameters of X-ray irradiation were: Al K*α* radiation ($hv$ = 1486.6 eV), 400 μm beam spot, 12 kV working voltage and 6 mA filament current. Survey spectrum was scanned at the energy of 150 eV with 1 eV per step. High-resolution spectra were scanned at the energy of 50 eV with 0.1 eV per step.

**XANES:** Mn *K*-edge X-ray absorption near edge spectroscopy (XANES) data were collected using a bench-top easyXAFS300+ instrument (easyXAFS, LLC). Spectra were collected using Si (110) spherically bent crystal analyzer and Ag anode X-ray tube, respectively. Spectra were deadtime corrected and the energy was calibrated using a Mn mesh standard.

**Magnetic measurement:** Solid-state DC susceptibility of clusters was measured by American Quantum Design PPMS-9-VSM accessories. The magnetic field was set as 0.1 T; the vibrating frequency was 40 Hz, vibration amplitude was 0.5 mm; the resolution was about $3.5 \times 10^{-6}$ emu; the temperature range was 5−300 K; the maximum magnetic moment was 120 emu. The program was executed and the M-T data were collected in the temperature range of 5−300 K.

**Photocatalytic properties:** The photocatalytic activities of the synthesized clusters were evaluated by degrading tetracycline (TC) with peroxomonosulfate (PMS) as the oxidant. Typically, the cluster (2 mg) was dispersed into a 20 ppm TC solution (10 mL) and stirred for 10 min in a parallel photochemical reaction device (CEL-LAB200E7, Beijing Zhongguo Jinyuan Science and Technology Co., Ltd.) to reach the adsorption-desorption equilibrium. Then PMS (2 mg) was added and irradiated with a visible light from a 30 W LED lamp (400 nm < $\lambda$ < 760 nm) to initiate the photocatalytic degradation reaction. During the reaction progress, 1 mL of the solution was taken and centrifuged at regular intervals, and the concentration of the supernatant was analyzed by UV-visible spectrophotometer. The degradation efficiency of the synthesized catalyst was determined through $A_t/A_0$, and the photocatalytic rate constant was calculated using the equation:

$$\ln\left(\frac{A_t}{A_0}\right) = -kt$$

where $A_0$ and $A_t$ represent the absorbance of TC solution at time 0 and t, respectively.

**TEM:** Transmission electron microscope (TEM) images were collected on a JEOL JEM-2010 at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute nanocrystal dispersion in $CH_2Cl_2$ onto a carbon-coated copper TEM grid and allowing the sample to dry under air.

**X-ray powder diffraction:** X-ray powder diffraction data were collected on a Bruker D2 Advance diffractometer (Cu K*α* focusing Goebel Mirror, LynxEye one-dimensional detector, step of 0.01°, 2$\theta$, 20 °C). The examined crystalline samples were ground, spread on the frosted sample stage and placed into the dome-shaped airtight zero-background holders. Le Bail fit for the powder diffraction patterns has been performed using TOPAS, version 7.13 software package (Bruker AXS, 2006).

## Synthetic procedures

### $Mn_{18}O_{10}(OOCMe)_{12}(OMe)_{14}(py)_2$ ([Mn18-Ac])

$Mn(OAc)_3·2H_2O$ (54 mg, 0.2 mmol) was loaded into a 50 mL tube-like Schlenk flask followed by the addition of 5 mL MeCN, 0.5 mL pyridine and 0.2 mL $Et_3N$. The solution was heated at 60 °C and stirred for 4 h. After the solution cooled down to room temperature, 5 mL MeOH was added, and the resultant dark solution was further stirred for 2 h at room temperature. The solvent was then evaporated off, and the brownish residue was washed with $Et_2O$ for several times. The final residue was obtained after being vacuum dried for several hours to yield a pure, fine brownish powder. The yield is *ca.* 42 %.

### $Mn_{18}O_{14}(OOCCMe_3)_8(OMe)_{14}(MeOH)_5(py)$ ([Mn18-Piv])

$Mn(ClO_4)_2·6H_2O$ (108 mg, 0.3 mmol) and $C(CH_3)_3COOH$ (30.6 mg, 0.3 mmol) were loaded into a 50 mL tube-like Schlenk flask, which was followed by the addition of 5 mL MeOH to dissolve all reagents. After that, 0.5 mL pyridine and 0.2 mL $Et_3N$ were added resulting in an orange solution. After stirring in the open air for 1 h, the color of the solution slowly turned from orange to dark brown. The brown solution was then evaporated under vacuum at room temperature to leave a brownish residue. The residue was then washed with hexanes for several times and vacuum-dried for several hours to yield a pure, dry brownish final product. The yield is *ca.* 66 %.

### 1-$Mn_3O_4$ nanocrystals

50 mg of **[$Mn_{18}$-Ac]** powder was dispersed in 10 mL oleylamine and 2 mL water was added to the suspension. The mixture was slowly heated to 220 °C, and kept at this temperature for 9 hours, and then cooled down to room temperature. After staying undisturbed at room temperature for 10 min, brown precipitate and light-colored supernatant were yielded. The mixture was centrifuged, and the supernatant was discarded. The solid residue was washed with hexanes for several times. The yield is *ca.* 34 %.

### 2-$Mn_3O_4$ nanocrystals

50 mg of **[$Mn_{18}$-Piv]** powder was dispersed in 10 mL oleylamine and 2 mL water was added to the suspension. The mixture was slowly heated to 220 °C, and kept at this temperature for 9 hours and then cooled down to room temperature. After staying undisturbed at room temperature for 10 min, brown precipitate and light-colored supernatant were yielded. The mixture was centrifuged, and the supernatant was discarded. The solid residue was washed with hexanes for several times. The yield is *ca.* 38 %.

## Crystal growth

Brown plate-like crystals of **[$Mn_{18}$-Ac]** and brown block crystals of **[$Mn_{18}$-Piv]** suitable for X-ray single crystal structural measurements were obtained through a low-temperature crystallization process. The saturated solutions of **[$Mn_{18}$-Ac]** in MeOH/MeCN (v:v = 1:1) and **[$Mn_{18}$-Piv]** in MeOH were sealed in glass vials and stored in a 5 °C fridge for one or two weeks to promote crystal growth.

**Table S1**. Single crystal growth conditions.

| **Compound** | **[$Mn_{18}$-Ac]** | **[$Mn_{18}$-Piv]** |
|---|---|---|
| **Shape** | Plate | Block |
| **Color** | Brown | Brown |
| **Method** | Low temp solution crystallization | Low temp solution crystallization |
| **Time** | 2 weeks | 1 week |
| **Temperature** | 5 °C | 5 °C |

## X-ray crystallographic procedures

Data collection of **[$Mn_{18}$-Ac]** was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS detector equipped with a Cu-target. The Incoatec microfocus source IµS X-ray tube ($\lambda$ = 1.5406 Å) at T = 160 K. Data collection of **[$Mn_{18}$-Piv]** was performed on a Rigaku XtaLAB-Synergy-R X-ray diffractometer with PHOTON 100 CMOS detector equipped with a Mo-target. The Incoatec microfocus source IµS X-ray tube ($\lambda$ = 0.71073 Å) at T = 150 K. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).[1] Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).[2] The structure was solved by SHELXT[3] and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2018/3) software package through the OLEX2 graphical interface.[4] All non-hydrogen atoms were refined anisotropically. The H-atoms were included at calculated positions and refined as riders, with $U_{iso}$(H) = 1.2 $U_{eq}$(C). The anisotropic displacement parameters in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å$^2$. They were also restrained to have the same $U_{ij}$ components, with a standard uncertainty of 0.01 Å$^2$. Further crystal and data collection details are listed in Table S2.

**Table S2.** Crystal data and structure refinement parameters for **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]**.

| Compound | **[$Mn_{18}$-Ac]** | **[$Mn_{18}$-Piv]** |
|---|---|---|
| CCDC | 2325204 | 2325203 |
| Formula weight | 2450.12 | 2727.72 |
| Temperature (K) | 160 | 150 |
| Wavelength (Å) | 1.54178 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 10.4312(5) | 16.7116(5) |
| $b$ (Å) | 13.1605(6) | 31.6354(5) |
| $c$ (Å) | 16.2948(8) | 23.4460(5) |
| $\alpha$ (°) | 106.181(3) | 90 |
| $\beta$ (°) | 99.194(4) | 110.465(3) |
| $\gamma$ (°) | 90.133(4) | 90 |
| $V$ (Å$^3$) | 2118.14(18) | 11613.1(5) |
| $Z$ | 1 | 4 |
| $\rho_{calcd}$ (g·cm$^{-3}$) | 1.971 | 1.707 |
| $\mu$ (mm$^{-1}$) | 21.854 | 1.958 |
| $F$(000) | 1260 | 6136 |
| θ range for data collection (°) | 2.864–72.628 | 1.963–30.820 |
| Reflections collected | 32244 | 153634 |
| Independent reflections | 8321 ($R_{int}$ = 0.1055) | 30057 ($R_{int}$ = 0.1450) |
| Transmission factors (min/max) | 0.779/0.828 | 0.798/0.891 |
| Data/restraints/params. | 8321/396/518 | 30057/781/1411 |
| $R1$,[a] $wR2$[b] ($I > 2\sigma(I)$) | 0.0707/0.1820 | 0.0958/0.2399 |
| $R1$,[a] $wR2$[b] (all data) | 0.1306/0.2192 | 0.1447/0.2714 |
| Quality-of-fit[c] | 0.928 | 1.028 |
| Largest diff. peak and hole (ē·Å$^{-3}$) | 1.397 and -1.464 | 1.915 and -1.432 |

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.

[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data.

## Solid state structures of [$Mn_{18}$-Ac] and [$Mn_{18}$-Piv]

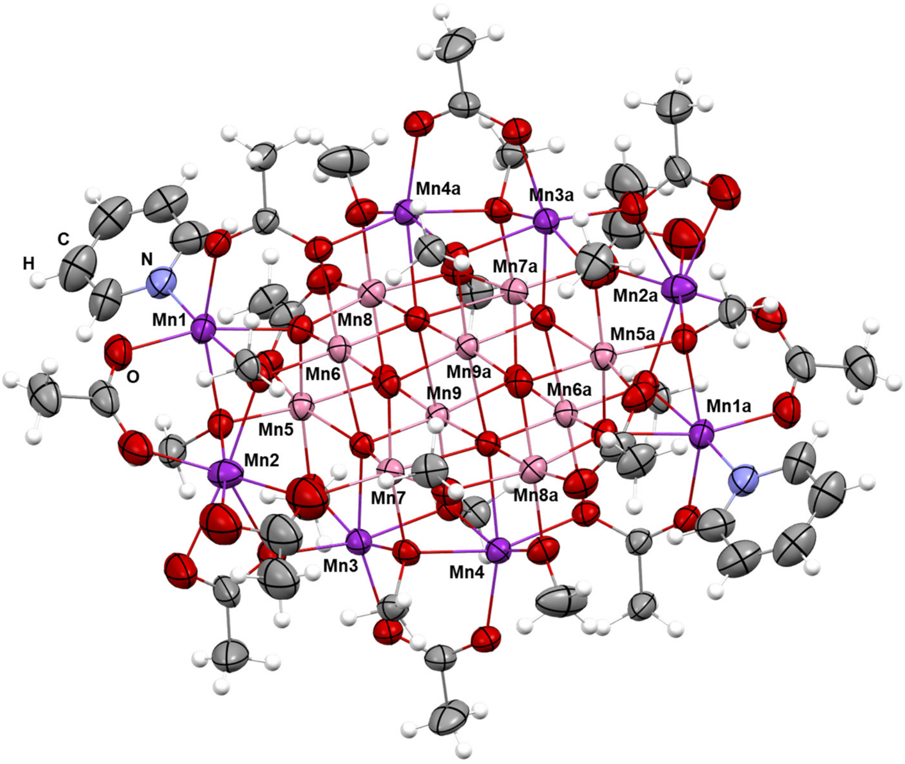



**Figure S1**. Solid state structure of **[$Mn_{18}$-Ac]** drawn with thermal ellipsoids at the 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only metal cations are labeled. $Mn^{II}$, purple; $Mn^{III}$, pink; O, red; N, blue; C, grey; H, white.

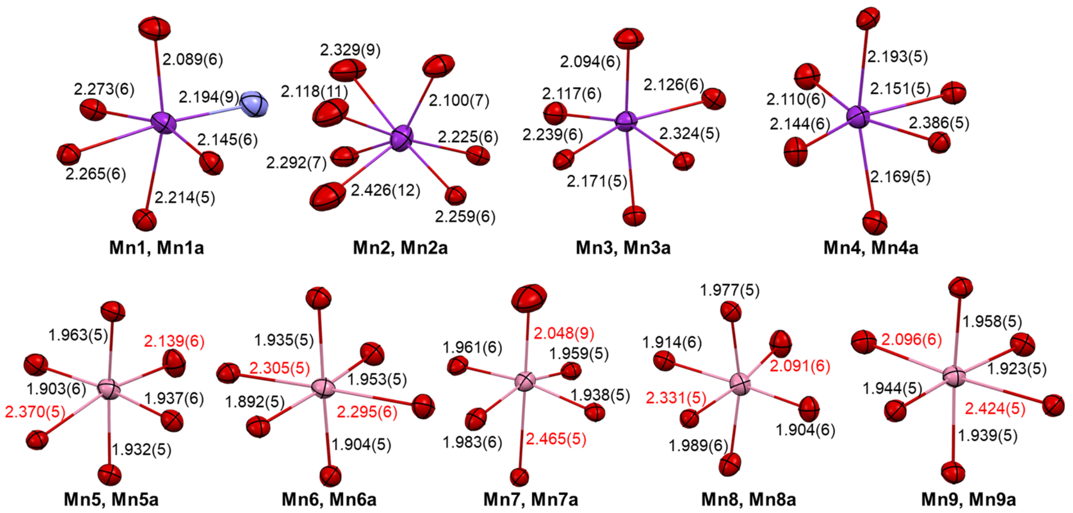



**Figure S2**. Bond lengths (Å) for the Mn ions with nonmetal atoms in structure **[Mn$_{18}$-Ac]**. Red labels represent the Jahn-Teller distorted Mn–O bonds.

**Table S3**. Average bond lengths (Å), oxidation states and JT distortion of all the Mn atoms in the structure of **[$Mn_{18}$-Ac]**.

| Mn atoms | Avg. Mn–O length | Oxidation states of Mn | Jahn-Teller effect |
|---|---|---|---|
| Mn1, Mn1a | 2.197 | +2 | \ |
| Mn2, Mn2a | 2.250 | +2 | \ |
| Mn3, Mn3a | 2.179 | +2 | \ |
| Mn4, Mn4a | 2.192 | +2 | \ |
| Mn5, Mn5a | 2.041 | +3 | Elongated |
| Mn6, Mn6a | 2.034 | +3 | Elongated |
| Mn7, Mn7a | 2.047 | +3 | Elongated |
| Mn8, Mn8a | 2.047 | +3 | Elongated |
| Mn9, Mn9a | 2.059 | +3 | Elongated |

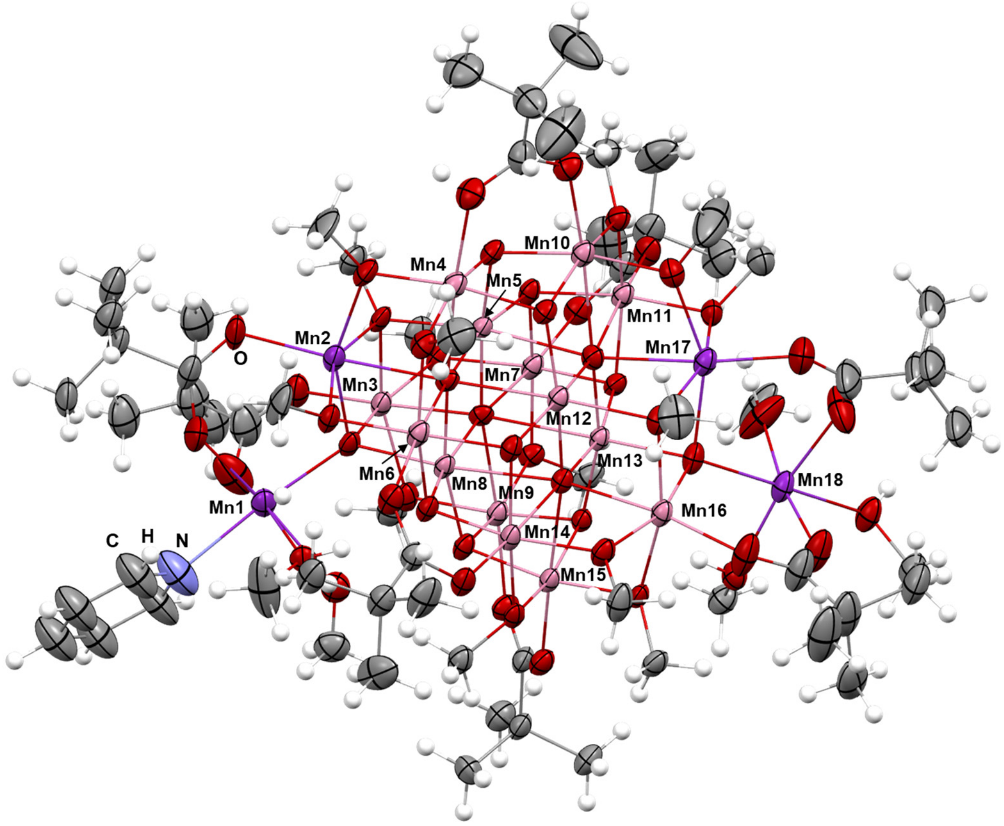



**Figure S3**. Solid state structure of **[$Mn_{18}$-Piv]** drawn with thermal ellipsoids at the 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only metal cations are labeled. $Mn^{II}$, purple; $Mn^{III}$, pink; O, red; N, blue; C, grey; H, white.

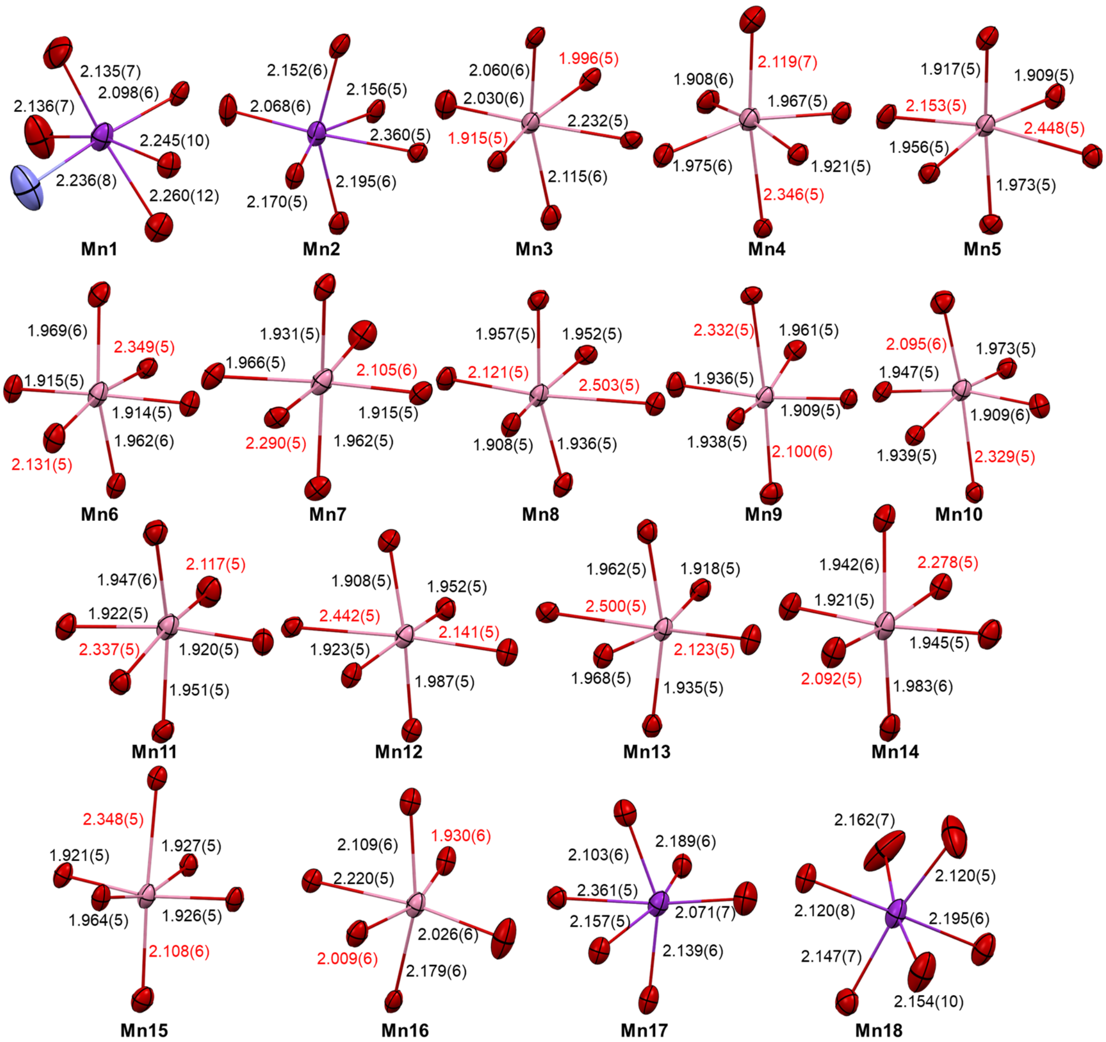
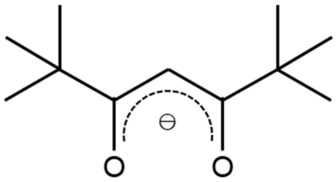
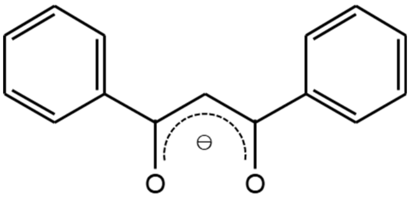
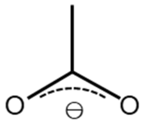
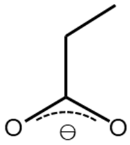
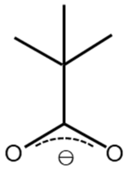
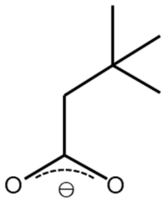
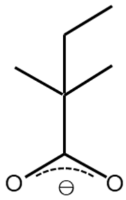


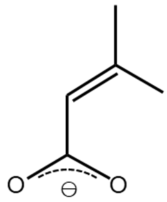
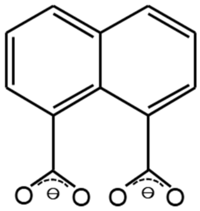
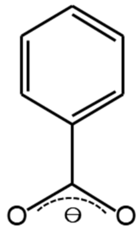
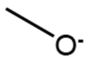
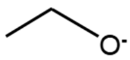
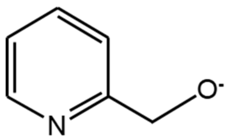
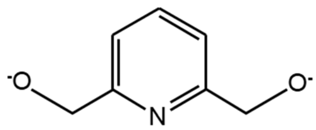
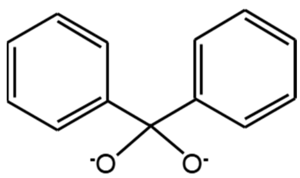

**Figure S4**. Bond lengths (Å) for the Mn ions with nonmetal atoms in structure of **[Mn$_{18}$-Piv]**. Red labels represent the Jahn-Teller distorted Mn–O bonds.

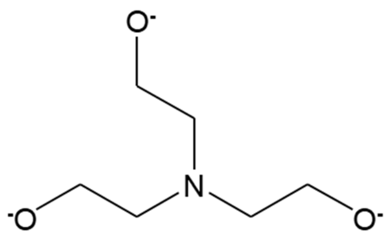
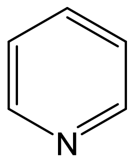
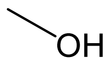
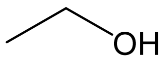
**Table S4**. Average bond lengths (Å), oxidation states and JT distortion for the Mn atoms in the structure of **[$Mn_{18}$-Piv]**.

| Mn atoms | Avg. Mn–O length | Oxidation states of Mn | Jahn-Teller effect |
|---|---|---|---|
| Mn1 | 2.174 | +2 | \ |
| Mn2 | 2.183 | +2 | \ |
| Mn3 | 2.058 | +3 | Compressed |
| Mn4 | 2.038 | +3 | Elongated |
| Mn5 | 2.060 | +3 | Elongated |
| Mn6 | 2.037 | +3 | Elongated |
| Mn7 | 2.027 | +3 | Elongated |
| Mn8 | 2.065 | +3 | Elongated |
| Mn9 | 2.027 | +3 | Elongated |
| Mn10 | 2.031 | +3 | Elongated |
| Mn11 | 2.032 | +3 | Elongated |
| Mn12 | 2.060 | +3 | Elongated |
| Mn13 | 2.068 | +3 | Elongated |
| Mn14 | 2.026 | +3 | Elongated |
| Mn15 | 2.032 | +3 | Elongated |
| Mn16 | 2.079 | +3 | Compressed |
| Mn17 | 2.169 | +2 | \ |
| Mn18 | 2.149 | +2 | \ |

**Table S5**. Different types of ligands utilized in the reported Mn-oxo clusters.

| Type | Schematic structure | Ligand |
|---|---|---|
| Diketonates |  | thd[5] |
| |  | dbm[5-7] |
| Carboxylates |  | OOCMe[8-12] |
| |  | OOCEt[13] |
| |  | OOC$^{t}$Bu[14-16] |
| |  | OOC$CH_2{}^{t}$Bu[17, 18] |
| |  | OOC$^{t}$Pe[19] |

| | | |
|---|---|---|
| |  | dma[20] |
| |  | ndc[21] |
| |  | OOCPh[7, 12, 21] |
| Alkoxides |  | OMe[5, 6, 9, 11, 15, 22] |
| |  | OEt (deprotonated)[5, 10] |
| |  | hmp[23, 24] |
| |  | pdm[8, 23] |
| |  | dpkd[16] |

| | | |
|---|---|---|
| |  | tea[25, 26] |
| Neutral molecules |  | py[27] |
| |  | MeOH[5, 11, 28] |
| |  | EtOH[5, 10] |
| | $H_2O$ | $H_2O$[9, 11, 15, 17, 18] |

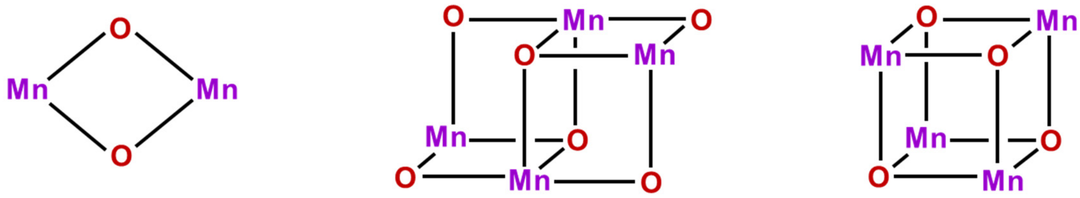



**Figure S5**. Schematic representations of the [$Mn_2O_2$] (left), [$Mn_4O_6$] (middle) and [$Mn_4O_4$] (right) units that have been found both in Mn-oxo clusters and manganese oxide bulk materials.

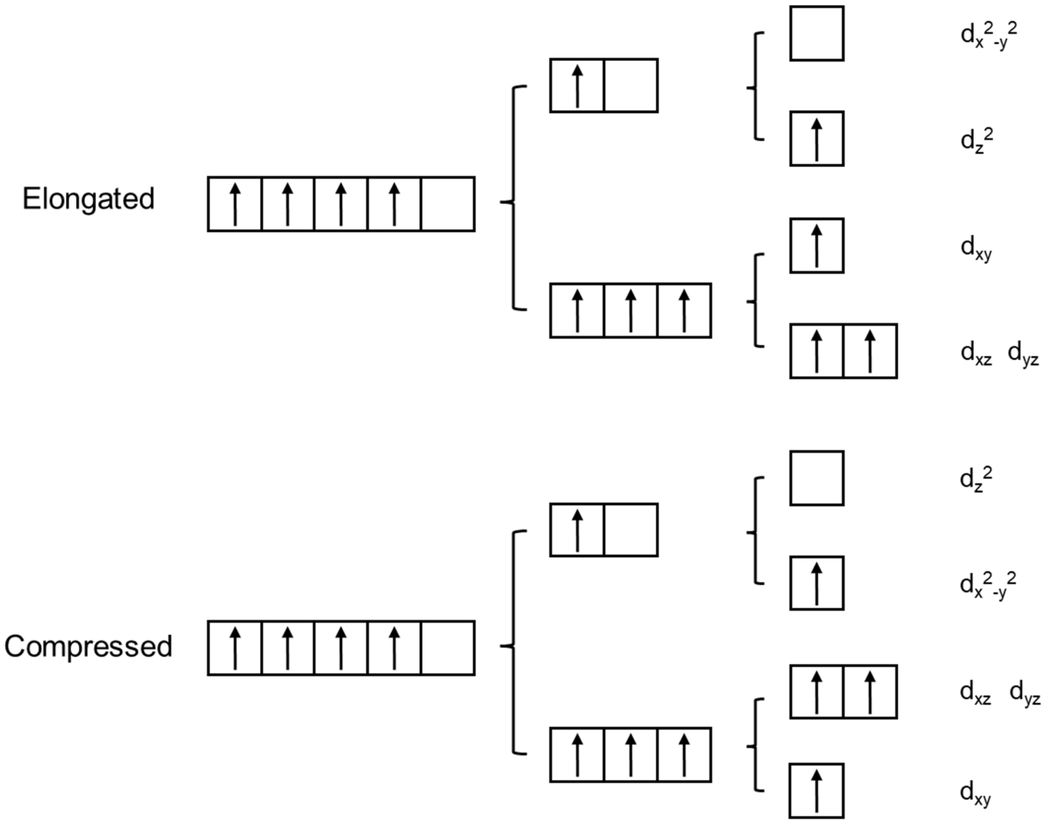



**Figure S6**. Electronic configurations of $Mn^{III}$ 3*d* orbitals in elongated (top) and compressed (bottom) Jahn-Tell manifestations.

## Magnetic properties

The magnetic properties of clusters **[Mn18-Ac]** and **[Mn18-Piv]** were studied in a temperature range of 5–300 K at $H$ = 0.1 T using direct-current (DC) magnet susceptibility measurements in the solid state. At room temperature, the $\chi_M T$ values of **[Mn18-Ac]** and **[Mn18-Piv]** are 39.05 and 116.46 $cm^3 \cdot K \cdot mol^{-1}$, respectively, and the large difference reflects different ratios of $Mn^{II}$ to $Mn^{III}$ ions in two structures. Upon cooling, the $\chi_M T$ values remain constant up to around 40 K, followed by a sharp decrease to reach the final values of 19.54 and 33.38 $cm^3 \cdot K \cdot mol^{-1}$ at 5 K, respectively, where $S$ = 12/2 and 16/2 can be calculated for **[Mn18-Ac]** and **[Mn18-Piv]**. The increase of $\chi_M T$ values around 40 K is attributed to the higher ferromagnetic interactions between Mn ions in both clusters. To be specific, the $\chi_M T$ value is 74.04 $cm^3 \cdot K \cdot mol^{-1}$ for **[Mn18-Ac]** (at 32 K), in contrast, it reaches a value of 186.52 $cm^3 \cdot K \cdot mol^{-1}$ at 46 K. The observed higher $\chi_M T$ values for **[Mn18-Piv]** reflects its higher Mn spins in the structure, which is consistent with the crystallographic and DFT calculations results.

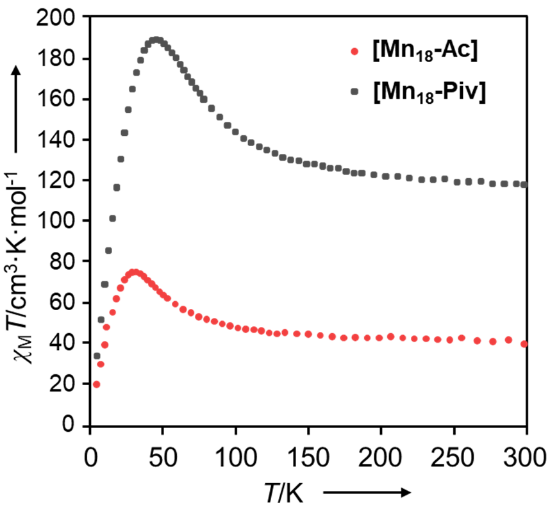



**Figure S7**. Temperature dependence of the $\chi_M T$ product for **[Mn18-Ac]** and **[Mn18-Piv]** at 0.1 T ($\chi_M$, the DC magnetic susceptibility, defined as $M/H$ per mole of complex).

## X-ray photoelectron spectroscopy (XPS)

XPS is a sensitive surface technology that has been widely utilized to determine the binding energy for the elements of interest. Based on the characteristic binding energies of the inner shell electrons, the absolute (typically, extremely difficult) and variation of the oxidation states for metals can be determined. Unfortunately, the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks for $Mn^{II}$ and $Mn^{III}$ cannot be clearly distinguished as they both appear at 641.4 eV and 653.2 eV, respectively.[29] But the observation of shake-up peak at 647 eV is indicative of the presence of $Mn^{II}$, since that signal is absent in $Mn^{III}$ species. In the Mn 2*p* spectra of **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]** (ESI, Figure S8a), their Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks appear at almost identical positions with the splitting energies being all close to 11.8 eV. In addition, shake-up peaks can be observed in the spectra of **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]**. However, the intensities of the shake-up peaks are quite low and there is no significant difference between them. It should be noted here that taking the overall peak profile into account, a single-phase simulation for **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]** single-phase fitting (ESI, Figure S9a, S9b) seems to be less reasonable than introducing the two-phase fitting (ESI, Figure S8b, S8c), which corresponds to the $Mn^{II}$ and $Mn^{III}$ in their structures. In addition, another XPS signature that can be used to discern $Mn^{II}$ and $Mn^{III}$ may be their respective Mn 3*s* orbitals, where the splitting energy for $Mn^{II}$ (5.9 eV) is usually smaller than that for $Mn^{III}$ (5.5 eV).[29] The high-resolution Mn 3*s* spectra of **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]** (ESI, Figure S9c), however, show close and indiscernible splitting energies, which cannot be reliably applied to distinguish $Mn^{II}$ and $Mn^{III}$.[30]

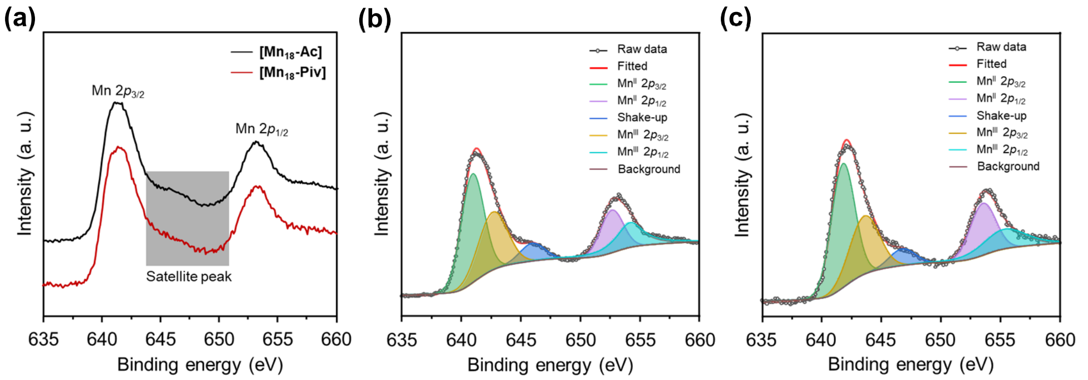



**Figure S8**. High-resolution XPS spectra for Mn 2*p* orbitals of **[Mn18-Ac]** and **[Mn18-Piv]** (a). The $Mn^{II}$ + $Mn^{III}$ double-phase simulation of high-resolution XPS spectra for Mn 2*p* orbitals for **[Mn18-Ac]** (b) and **[Mn18-Piv]** (c).

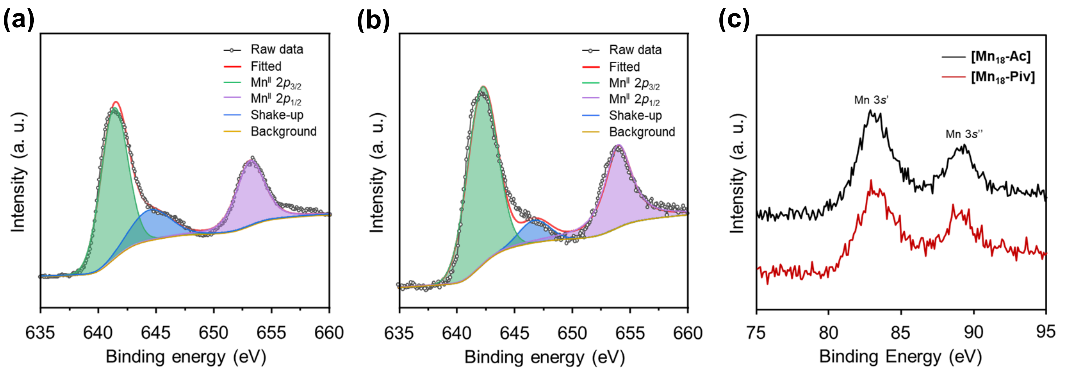



**Figure S9.** $Mn^{II}$ single-phase simulation of high-resolution XPS spectrum for Mn 2*p* orbitals in **[Mn18-Ac]** (a) and **[Mn18-Piv]** (b). High-resolution XPS spectrum for Mn 3*s* orbitals in **[Mn18-Ac]** and **[Mn18-Piv]** (c).

## Synthesis and analysis of $Mn_3O_4$ hausmannite nanocrystals

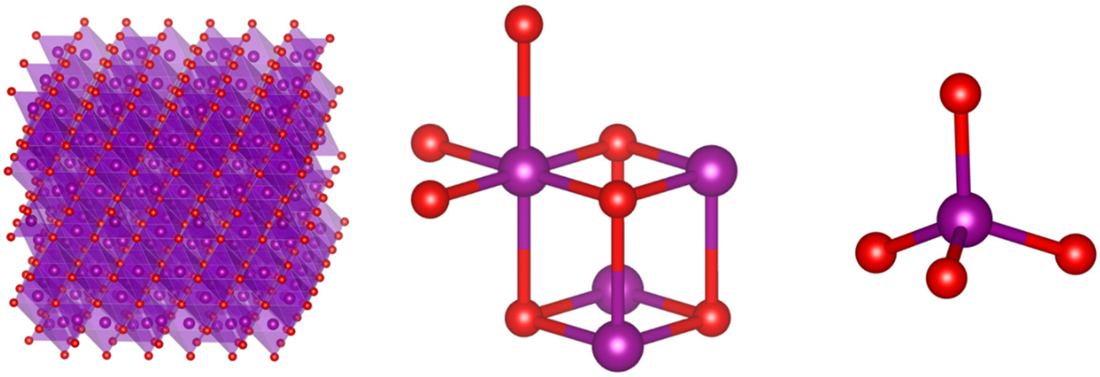


**Figure S10.** Crystal structure of $Mn_3O_4$ hausmannite (left) with the $[Mn_4O_4]$ cubic (center) and $[MnO_4]$ tetrahedron (right) constituent units.

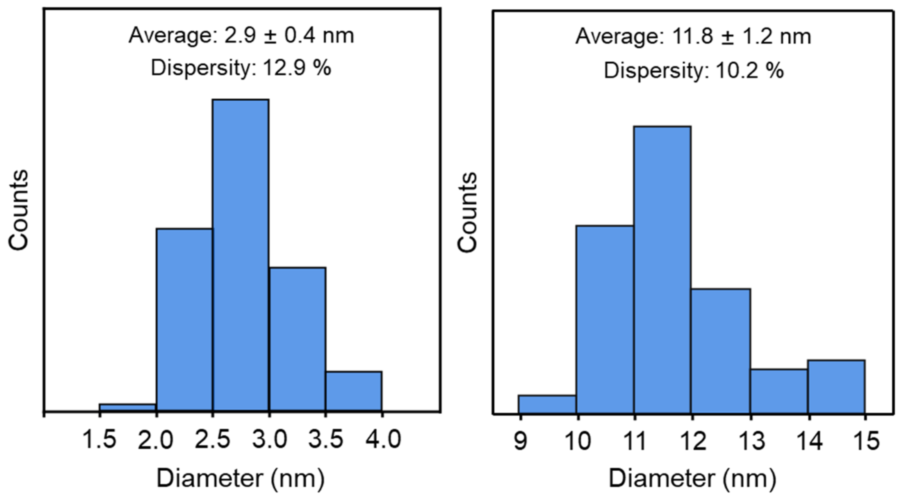



**Figure S11**. Histograms of the statistical size distribution of $Mn_3O_4$ nanocrystals obtained from **[$Mn_{18}$-Ac]** (left) and **[$Mn_{18}$-Piv]** (right) precursors.

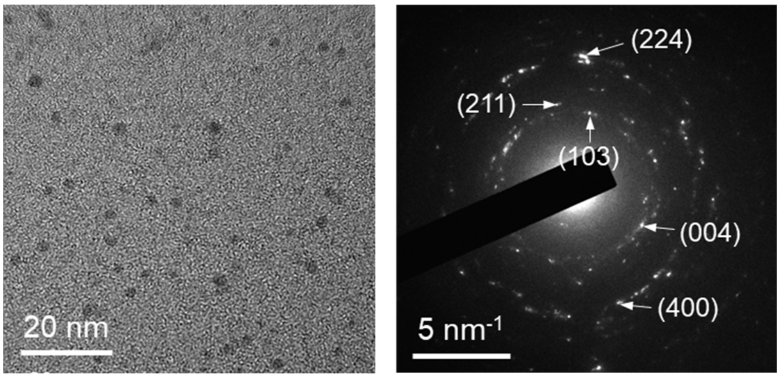



**Figure S12.** TEM micrographs of the **1-$Mn_3O_4$** nanocrystals obtained from **[$Mn_{18}$-Ac]** (left) precursor and the corresponding ring electron diffraction pattern (right).

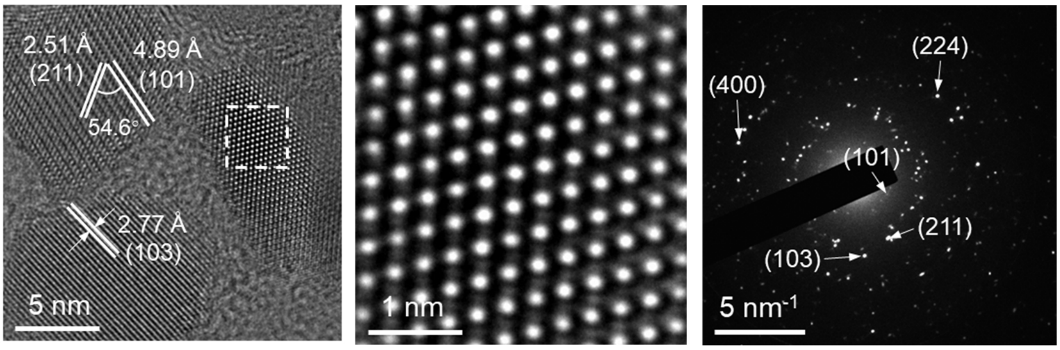



**Figure S13.** TEM micrographs of the **2-$Mn_3O_4$** nanocrystals obtained from **[$Mn_{18}$-Piv]** (left and middle) precursor and the corresponding ring electron diffraction pattern (right). The middle figure is the micrograph of the selected area inside the dashed box in the left micrograph. Figure 7f in manuscript is the fast Fourier transform (FFT) pattern of the middle figure.

## Theoretical calculations

All calculations were performed with ORCA 5.1.0.[31] The geometry optimization of all structures were performed using PBE hybrid functional[32] under def2-SVP level,[33] and the energy was calculated using the same method under def2-TZVP level.[33] For $Mn_{18}$ clusters, the geometries were extracted from crystal structures and the spin numbers were calculated from the SQUID experiments, that are $S$ = 12/2 for **[$Mn_{18}$-Ac]** and $S$ = 16/2 for **[$Mn_{18}$-Piv]**. The MO diagrams were generated by GaussView 6.0. The PDOS plot was generated by Multiwfn 3.8.[34] The oxidation states of Mn ions in **[$Mn_{18}$-Ac]** and **[$Mn_{18}$-Piv]** were calculated in Multiwfn using localized orbital bonding analysis method.[35]

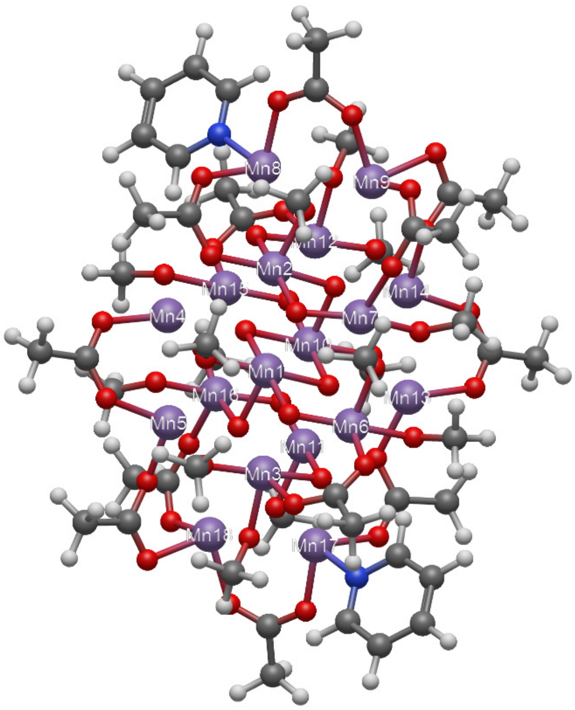



**Table S6**. Oxidation state calculations of Mn atoms in **[$Mn_{18}$-Ac]** along with a labeling scheme.

| Atomic No. | Oxidation state | Atomic No. | Oxidation state |
|---|---|---|---|
| 1 | +3 | 10 | +3 |
| 2 | +3 | 11 | +3 |
| 3 | +3 | 12 | +3 |
| 4 | +2 | 13 | +2 |
| 5 | +2 | 14 | +2 |
| 6 | +3 | 15 | +3 |
| 7 | +3 | 16 | +3 |
| 8 | +2 | 17 | +2 |
| 9 | +2 | 18 | +2 |

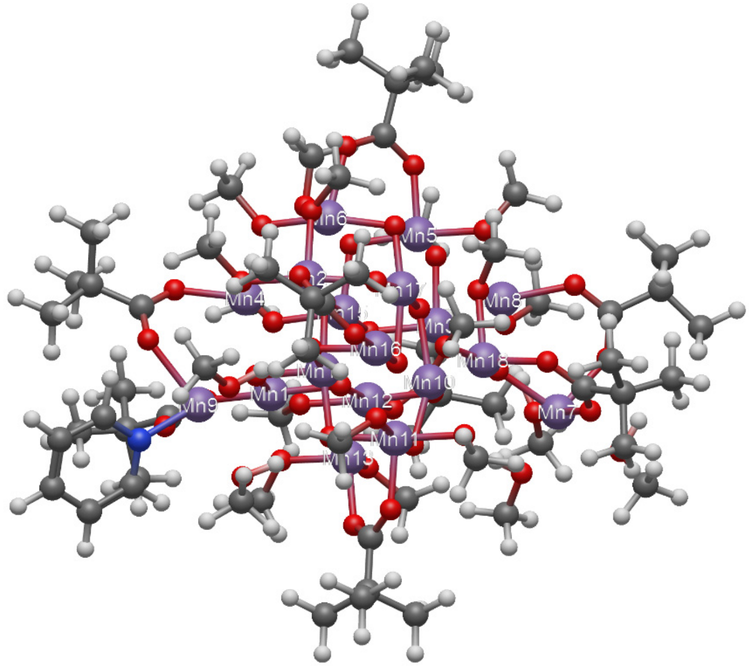



**Table S7.** Oxidation state calculations of Mn atoms in **[Mn$_{18}$-Piv]** along with a labeling scheme.

| Atomic No. | Oxidation state | Atomic No. | Oxidation state |
|---|---|---|---|
| 1 | +3 | 10 | +3 |
| 2 | +3 | 11 | +3 |
| 3 | +3 | 12 | +3 |
| 4 | +2 | 13 | +3 |
| 5 | +3 | 14 | +3 |
| 6 | +3 | 15 | +3 |
| 7 | +2 | 16 | +3 |
| 8 | +2 | 17 | +3 |
| 9 | +2 | 18 | +3 |

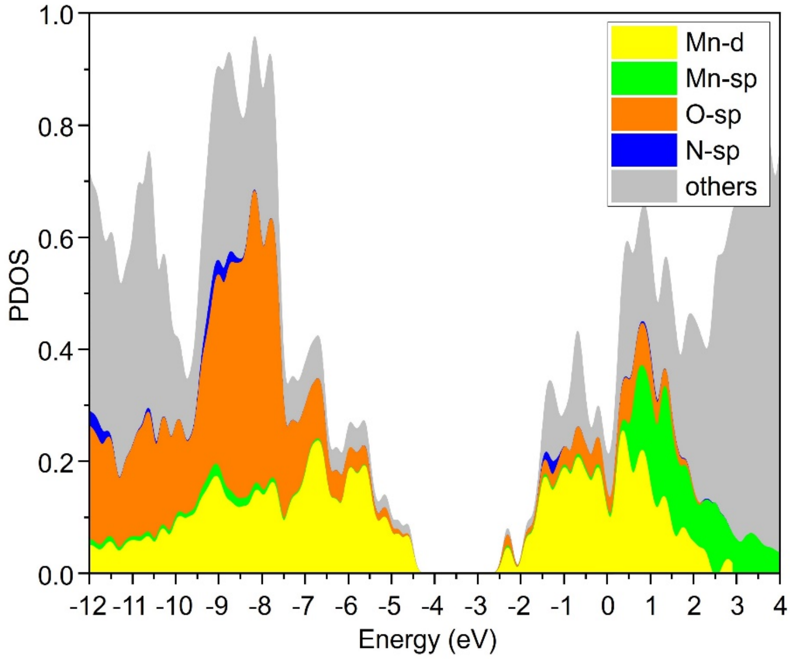



**Figure S14.** Partial density of states (PDOS) of alpha orbitals in **[$Mn_{18}$-Ac]**.

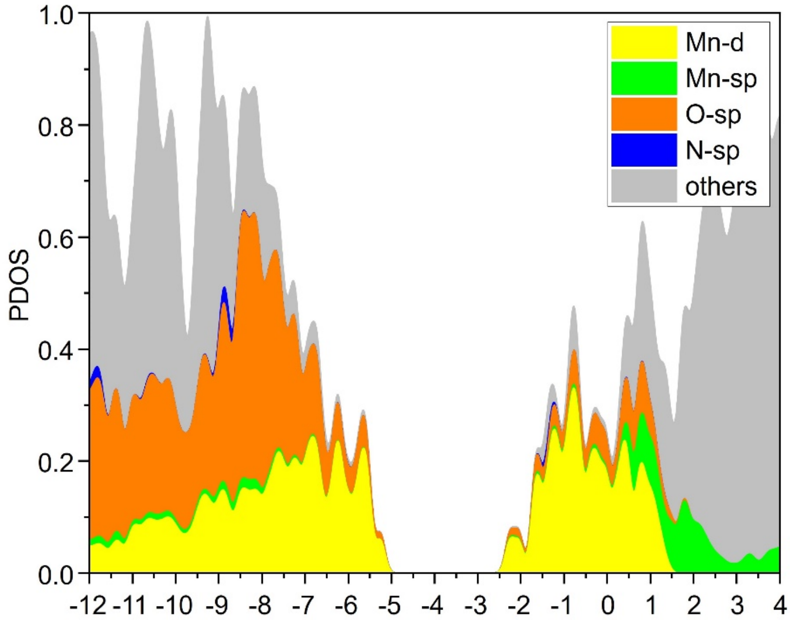



**Figure S15.** Partial density of states (PDOS) of alpha orbitals in **[$Mn_{18}$-Piv]**.

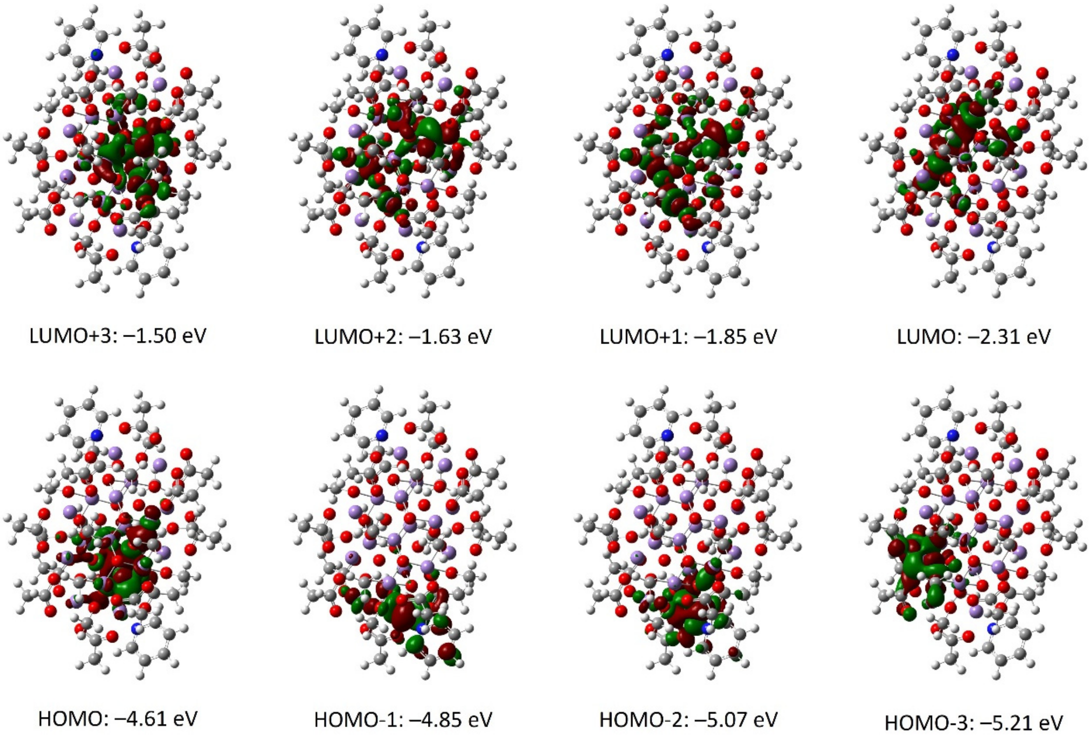



**Figure S16.** Selected active molecular orbitals in **[$Mn_{18}$-Ac]**.

**Table S8.** Orbital composition analysis by Hirsfeld method in **[$Mn_{18}$-Ac]**.

| MO | Orbital No. | Contributions from Mn atoms |
|---|---|---|
| LUMO+3 | 622a | Mn7: 39.0%, Mn16: 18.9%, Mn2: 7.0%, Mn3: 6.2% |
| LUMO+2 | 621a | Mn16: 24.6%, Mn7: 20.7%, Mn3: 16.2%, Mn1: 4.2% |
| LUMO+1 | 620a | Mn16: 42.7%, Mn2: 22.7% |
| LUMO | 619a | Mn11: 51.7% |
| HOMO | 618a | Mn17: 74.6% |
| HOMO-1 | 617a | Mn17: 75.6% |
| HOMO-2 | 616a | Mn5: 73.8% |
| HOMO-3 | 615a | Mn5: 72.5, Mn1: 4.4% |

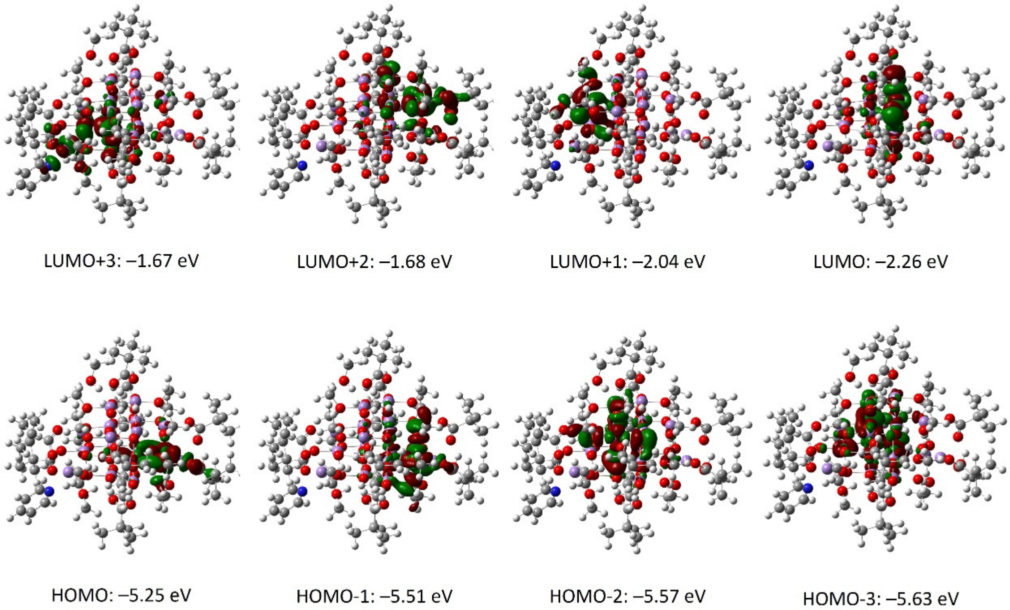



**Figure S17.** Selected active molecular orbitals in **[$Mn_{18}$-Piv]**.

**Table S9**. Orbital composition analysis by Hirsfeld method in **[$Mn_{18}$-Piv]**.

| MO | Orbital No. | Contributions from Mn atoms |
|---|---|---|
| LUMO+3 | 707a | Mn2: 36.5%, Mn17: 17.8, Mn6: 4.0% |
| LUMO+2 | 706a | Mn17: 29.1%, Mn18: 18.3%, Mn11: 15.3% |
| LUMO+1 | 705a | Mn18: 45.3%, Mn17: 18.7%, Mn11: 4.0% |
| LUMO | 704a | Mn18: 62.2% |
| HOMO | 703a | Mn5: 70.7% |
| HOMO-1 | 702a | Mn3: 58.0%, Mn10: 10.0% |
| HOMO-2 | 701a | Mn8: 42.1%, Mn15: 15.6, Mn3: 5.1% |
| HOMO-3 | 700a | Mn15: 29.3%, Mn4: 28.3% |

**Table S10.** Cartesian coordinates of **[$Mn_{18}$-Ac]**.

Total energy: -26315.135597754812 Hartree.

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| Mn | 2.761811 | 4.808272 | 6.918577 | Mn | 5.021584 | 3.900124 | 8.490542 |
| Mn | 2.516990 | 4.789515 | 9.837530 | Mn | 5.329091 | 3.866519 | 5.610857 |
| Mn | 3.018228 | 4.703553 | 3.997005 | Mn | 4.802144 | 3.941826 | 11.442888 |
| Mn | 2.681367 | 7.681251 | 8.366898 | Mn | 5.075080 | 1.031157 | 7.098729 |
| Mn | 2.894648 | 7.428265 | 5.300516 | Mn | 4.886440 | 1.280410 | 10.144846 |
| Mn | 2.831889 | 2.331722 | 5.450997 | Mn | 4.991671 | 6.352039 | 10.002030 |
| Mn | 2.377905 | 2.274589 | 8.492967 | Mn | 5.317424 | 6.411500 | 7.000141 |
| Mn | 2.359597 | 5.300748 | 12.736669 | Mn | 5.486800 | 3.323060 | 2.769905 |
| Mn | 1.994476 | 2.217029 | 12.348577 | Mn | 5.855872 | 6.339201 | 3.055324 |
| O | 1.714934 | 4.005724 | 8.321966 | O | 6.091652 | 4.683277 | 7.106243 |
| O | 2.002093 | 4.013009 | 5.419859 | O | 5.799654 | 4.653131 | 9.989505 |
| O | 4.180576 | 3.187048 | 4.302220 | O | 3.673109 | 5.476337 | 11.152591 |
| O | 4.032470 | 5.598955 | 5.646345 | O | 3.683436 | 3.187363 | 9.772818 |
| O | 1.749110 | 6.430265 | 6.858071 | O | 5.987267 | 2.228739 | 8.563077 |
| O | 1.483473 | 6.491757 | 9.787499 | O | 6.312863 | 1.907690 | 5.671958 |
| O | 3.887448 | 5.589412 | 8.425402 | O | 3.937508 | 3.168697 | 6.955585 |
| O | 3.569010 | 0.701823 | 8.536222 | O | 4.230531 | 8.015474 | 6.905934 |
| O | 1.422178 | 3.965333 | 11.207514 | O | 6.449797 | 4.615121 | 4.132440 |
| O | 4.310760 | 5.077549 | 2.504943 | O | 3.566249 | 3.481345 | 12.923226 |
| O | 1.600176 | 1.693160 | 6.789277 | O | 6.192651 | 6.976078 | 8.622211 |
| O | 2.034632 | 6.309791 | 3.815408 | O | 5.796945 | 2.342504 | 11.607782 |
| O | 1.652871 | 9.380146 | 7.749980 | O | 6.071863 | -0.701334 | 7.790966 |
| O | 3.823722 | 0.671438 | 5.516529 | O | 3.986671 | 7.996659 | 9.985010 |
| O | 1.702680 | 9.110070 | 5.528523 | O | 6.073405 | -0.392264 | 10.005529 |
| O | 1.187298 | 6.879988 | 11.970804 | O | 6.581483 | 1.705477 | 3.467458 |
| O | 1.897475 | 3.673257 | 2.758709 | O | 5.944485 | 4.985730 | 12.657999 |
| O | 1.746688 | 1.767646 | 3.944989 | O | 6.101139 | 6.905766 | 11.503371 |
| O | 4.304389 | 8.045578 | 4.003934 | O | 3.441331 | 0.773293 | 11.467042 |
| O | 1.152590 | 4.912868 | 14.296324 | O | 6.741138 | 3.583756 | 1.246545 |
| O | 0.684606 | 2.783026 | 13.817870 | O | 7.182818 | 5.756917 | 1.478244 |
| O | 0.878562 | 1.357292 | 9.509146 | O | 6.762589 | 7.204110 | 5.976250 |
| N | 3.289072 | 6.694764 | 13.933510 | N | 4.554753 | 2.018537 | 1.584773 |
| C | 0.974622 | 7.142169 | 10.785289 | C | 6.702223 | 1.272090 | 4.619401 |
| C | 1.506837 | 2.489918 | 2.939957 | C | 6.344340 | 6.165283 | 12.496722 |
| C | 1.352474 | 9.717824 | 6.564958 | C | 6.402209 | -1.018002 | 8.965476 |
| C | 0.020425 | 4.040426 | 11.013120 | C | 7.847577 | 4.552793 | 4.360726 |
| H | -0.362614 | 5.049306 | 11.232782 | H | 8.197782 | 3.508957 | 4.343615 |
| H | -0.473941 | 3.331899 | 11.693370 | H | 8.374348 | 5.114343 | 3.574947 |
| H | -0.228935 | 3.776265 | 9.974178 | H | 8.081467 | 4.995723 | 5.341618 |
| C | 2.972103 | -0.576184 | 8.656268 | C | 4.844253 | 9.280334 | 6.799019 |
| H | 2.038752 | -0.609742 | 8.076483 | H | 5.770219 | 9.302682 | 7.392641 |
| H | 2.744906 | -0.782399 | 9.712690 | H | 5.082602 | 9.492228 | 5.745652 |
| H | 3.665627 | -1.340318 | 8.273701 | H | 4.159684 | 10.057796 | 7.175480 |
| C | 0.347133 | 6.304160 | 6.791754 | C | 7.396496 | 2.330593 | 8.586288 |
| H | 0.073473 | 5.529926 | 6.059482 | H | 7.696137 | 3.145674 | 9.260504 |
| H | -0.095932 | 7.263358 | 6.477690 | H | 7.827730 | 1.384924 | 8.950784 |
| H | -0.052401 | 6.013894 | 7.776118 | H | 7.775221 | 2.544652 | 7.576179 |
| C | 0.219872 | 1.845848 | 6.575713 | C | 7.573356 | 6.792589 | 8.787784 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.054303 | 2.912563 | 6.524276 | H | 7.839687 | 5.725530 | 8.713967 |
| H | -0.327766 | 1.372050 | 7.403713 | H | 8.111640 | 7.348016 | 8.006205 |
| H | -0.055473 | 1.361371 | 5.625673 | H | 7.871085 | 7.170784 | 9.778175 |
| C | 0.045278 | 8.262798 | 10.419947 | C | 7.389468 | -0.042784 | 4.844887 |
| H | 0.506921 | 8.946338 | 9.690883 | H | 6.850387 | -0.647059 | 5.588081 |
| H | -0.263474 | 8.807286 | 11.318815 | H | 7.505870 | -0.581618 | 3.898055 |
| H | -0.839007 | 7.828777 | 9.927749 | H | 8.385232 | 0.160560 | 5.269964 |
| C | 0.730625 | 6.350931 | 3.327183 | C | 7.137655 | 2.320184 | 11.992450 |
| H | 0.704072 | 6.154148 | 2.240250 | H | 7.233641 | 2.469523 | 13.082540 |
| H | 0.298608 | 7.351303 | 3.507369 | H | 7.578692 | 1.341757 | 11.735262 |
| H | 0.079196 | 5.603503 | 3.815515 | H | 7.723715 | 3.110883 | 11.492417 |
| C | 3.720836 | 5.409738 | 1.262933 | C | 4.153485 | 3.171773 | 14.169018 |
| H | 3.104183 | 4.575209 | 0.899395 | H | 4.729570 | 4.029929 | 14.548609 |
| H | 4.509854 | 5.645202 | 0.531921 | H | 3.367997 | 2.897779 | 14.890453 |
| H | 3.080498 | 6.296696 | 1.373953 | H | 4.837080 | 2.315162 | 14.064731 |
| C | 0.301961 | 0.771675 | 10.466937 | C | 7.386215 | 7.794536 | 5.047923 |
| C | 0.676422 | 1.891558 | 1.840254 | C | 7.174688 | 6.749053 | 13.605524 |
| H | -0.171653 | 2.556469 | 1.624387 | H | 7.959728 | 6.036439 | 13.892662 |
| H | 0.321775 | 0.890708 | 2.109782 | H | 7.610783 | 7.709264 | 13.308649 |
| H | 1.290634 | 1.835566 | 0.929192 | H | 6.526996 | 6.897390 | 14.482952 |
| C | 0.530882 | 3.824297 | 14.485577 | C | 7.364720 | 4.643512 | 0.946813 |
| C | 4.313052 | 8.474529 | 2.805790 | C | 3.504155 | 0.165971 | 12.603096 |
| O | 5.059780 | 7.943707 | 1.962748 | O | 2.802155 | 0.576863 | 13.535170 |
| C | 3.701356 | 7.833629 | 13.361406 | C | 4.114820 | 0.873477 | 2.130634 |
| H | 3.607094 | 7.880974 | 12.272986 | H | 4.180201 | 0.809336 | 3.218882 |
| C | -0.493142 | 3.818567 | 15.591155 | C | 8.427899 | 4.524471 | -0.116895 |
| H | -0.119310 | 4.375499 | 16.460840 | H | 8.217150 | 3.686038 | -0.792431 |
| H | -0.762309 | 2.792471 | 15.867811 | H | 8.523693 | 5.467242 | -0.670061 |
| H | -1.394244 | 4.340410 | 15.232447 | H | 9.390185 | 4.326331 | 0.381407 |
| C | 0.495961 | 10.948611 | 6.413845 | C | 7.274599 | -2.237103 | 9.127884 |
| H | -0.488667 | 10.755990 | 6.866415 | H | 8.277039 | -2.008620 | 8.734169 |
| H | 0.369292 | 11.217886 | 5.359022 | H | 7.358251 | -2.530832 | 10.180752 |
| H | 0.946690 | 11.782497 | 6.970566 | H | 6.873439 | -3.064591 | 8.526418 |
| C | 3.390595 | 6.557198 | 15.260908 | C | 4.479727 | 2.164077 | 0.253582 |
| H | 3.007493 | 5.620538 | 15.670276 | H | 4.876444 | 3.098032 | -0.144772 |
| C | 4.225304 | 8.885793 | 14.104750 | C | 3.599400 | -0.166013 | 1.366074 |
| H | 4.543277 | 9.798070 | 13.597548 | H | 3.260865 | -1.078043 | 1.860577 |
| C | 4.338094 | 8.745846 | 15.485348 | C | 3.519565 | -0.016977 | -0.016186 |
| H | 4.747593 | 9.553978 | 16.096203 | H | 3.118559 | -0.815994 | -0.644069 |
| C | 3.153788 | -0.541927 | 5.333928 | C | 4.656858 | 9.209629 | 10.177411 |
| H | 3.818383 | -1.383376 | 5.598269 | H | 3.989297 | 10.055732 | 9.934055 |
| H | 2.847386 | -0.662786 | 4.280226 | H | 4.982671 | 9.319807 | 11.226505 |
| H | 2.241492 | -0.606811 | 5.949083 | H | 5.558548 | 9.284291 | 9.547379 |
| C | 3.395425 | 9.599558 | 2.427189 | C | 4.410571 | -1.017485 | 12.742093 |
| H | 2.361691 | 9.220382 | 2.441200 | H | 4.368927 | -1.412743 | 13.763023 |
| H | 3.633188 | 9.981745 | 1.427965 | H | 4.108208 | -1.794310 | 12.024390 |
| H | 3.448927 | 10.401178 | 3.176411 | H | 5.437702 | -0.731633 | 12.474460 |
| C | 3.916344 | 7.554966 | 16.073262 | C | 3.966055 | 1.177235 | -0.578400 |
| H | 3.980110 | 7.398693 | 17.151512 | H | 3.930680 | 1.346831 | -1.656008 |
| O | 0.528719 | 0.984200 | 11.672891 | O | 7.232639 | 7.578308 | 3.834208 |
| C | -0.759016 | -0.237329 | 10.104467 | C | 8.428274 | 8.798753 | 5.468778 |
| H | -1.119535 | -0.767376 | 10.993476 | H | 8.789634 | 9.369027 | 4.605464 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.358563 | -0.948738 | 9.367824 | H | 8.016813 | 9.472058 | 6.233410 |
| H | -1.599520 | 0.286180 | 9.623317 | H | 9.273162 | 8.261561 | 5.927080 |

**Table S11**. Cartesian coordinates of **[Mn$_{18}$-Piv]**.

Total energy: -27090.917966193294 Hartree.

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| Mn | 6.080821 | 21.652887 | 4.731320 | H | 1.984152 | 14.772056 | 8.754526 |
| Mn | 3.646437 | 16.911260 | 3.858054 | C | -1.421618 | 23.402882 | 6.472129 |
| Mn | 1.300953 | 22.924304 | 5.641274 | H | -1.183958 | 24.462464 | 6.281031 |
| Mn | 5.235066 | 19.368219 | 2.716043 | H | -2.120282 | 23.348269 | 7.323092 |
| Mn | 0.334392 | 20.842439 | 3.743926 | H | -1.897568 | 22.978408 | 5.575124 |
| Mn | 2.195356 | 19.206812 | 2.426576 | C | 1.140540 | 24.422160 | 9.508630 |
| Mn | 0.353628 | 21.257014 | 10.069365 | H | 0.487892 | 25.293279 | 9.325076 |
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