## Supplementary Information

Anion-Controlled Assembly of Four Manganese Ions: Structural, Magnetic, and Electrochemical Properties of Tetramanganese Complexes Stabilized by Xanthene-Bridged Schiff Base Ligands

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## Experimental

General Procedures. The chemicals for the synthesis of the compounds were purchased from commercial sources and used as received. 3-Amino-1-propanol was purchased from Tokyo Chemical Industry Co., Ltd. 5,5' -(9,9-Dimethylxanthene-4,5diyl)bis(salicylaldehyde) ( $\mathrm{H}_{2}$ xansal) was prepared according to a literature procedure. ${ }^{1}$ NMR spectra were recorded on a Bruker AVANCE 300 FT-NMR spectrometer at room temperature. IR spectra were recorded on a JASCO FT/IR-6200 spectrometer with an attenuated total reflection (ATR) accessory. Electrospray ionization (ESI) mass spectrometry was performed on an Applied Biosystem Mariner time-of-flight mass spectrometer. Elemental analyses were performed by the Analytical Research Service Center at Osaka City University on J-SCIENCE LAB JM10 or FISONS Instrument EA1108 elemental analyzers.

Synthesis of $\mathbf{H}_{4} \mathbf{L}$. To a suspension of $\mathrm{H}_{2}$ xansal ( $0.45 \mathrm{~g}, 1.0 \mathrm{mmol}$ ) in ethanol (10 mL ) was added a solution of 3-amino-1-propanol ( $0.15 \mathrm{~g}, 2.0 \mathrm{mmol}$ ) in ethanol ( 10 mL ). The resulting yellow suspension was refluxed for 30 min , and then cooled to room temperature. The yellow crystalline precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure. Yield: $0.48 \mathrm{~g}(85 \%)$. ${ }^{1} \mathrm{H}$ NMR (300 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.73\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right.$ ), 1.4-2.1 ( $\mathrm{s}, \mathrm{br}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{OH}$ ), 1.98 (tt, $J=6.1,6.5 \mathrm{~Hz}$,
$4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2}$ ), 3.63 (td, $J=6.5,1.0 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{NCH}_{2}$ ), $3.82(\mathrm{t}, J=6.1 \mathrm{~Hz}, 4 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{OH}$ ), 6.89 (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}, 3$-sal), 7.10-7.22 (m, 6H, 6-sal and xan-CH), $7.35-7.45$ (m, 4H, 4-sal and xan-CH), 7.54 (s, br, 2H, N=CH), 13.9 (s, br, 2H, sal-OH). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 32.7,33.2,34.6,54.1,60.0,116.9,117.9,123.4$, 125.1, 127.4, 128.7, 128.8, 130.7, 133.3, 133.9, 147.2, 161.5, 164.9. Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{5}$ : C 74.45, H 6.43, N 4.96. Found: C 74.17, H 6.34, N 4.90. IR (ATR, $\mathrm{cm}^{-1}$ ): 3289, 3064, 2945, 2897, 2850, 1633, 1585, 1497, 1466, 1420, 1397, 1379, 1355, 1280, 1227, 1179, 1135, 1055, 876, 829, 787, 741.

Synthesis of $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mu-\mathrm{OAc})_{2}\right] \cdot \mathbf{1 . 5} \mathbf{C H}_{\mathbf{2}} \mathbf{C l}_{2} \cdot \mathbf{0} . \mathbf{5}^{i} \mathbf{P r O H}$ (1). To a yellow suspension of $\mathrm{H}_{4} \mathrm{~L}(100 \mathrm{mg}, 0.18 \mathrm{mmol})$ in ethanol ( 15 mL ) was added $\mathrm{Mn}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(88 \mathrm{mg}, 0.36 \mathrm{mmol})$. The mixture was stirred at room temperature for 1 h . The resulting dark brown suspension was refluxed for 1 h . After cooling to room temperature, the precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure to afford a moss green powder ( 108 mg ). A dichloromethane solution ( 100 mL ) of the product was layered with 2-propanol ( 75 mL ) and allowed to stand at room temperature for 3 days. Dark brown crystals of $\mathbf{1}$ were deposited, collected by filtration, washed with 2-propanol, and dried under reduced pressure. Yield: 51 mg (36\%). Anal. Calcd for $\mathrm{C}_{74} \mathrm{H}_{70} \mathrm{Mn}_{4} \mathrm{~N}_{4} \mathrm{O}_{14} \cdot 1.5 \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 0.5^{i} \mathrm{PrOH}: \mathrm{C} 57.21, \mathrm{H} 4.80, \mathrm{~N} 3.47$. Found: C $57.39, \mathrm{H}$ 4.69, N 3.57. Four dichloromethane and two 2-propanol molecules of crystallization were found in the crystal structure of $\mathbf{1}$, and were partially lost on drying. IR (ATR, $\mathrm{cm}^{-1}$ ): 1626, 1568, 1541, 1487, 1458, 1431, 1414, 1385, 1315, 1227, 1173, 1134, 1066, 985, 877, 833, 812, 795, 748. UV-Vis: $\lambda_{\max }\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) / \mathrm{nm} 368\left(\varepsilon / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}\right.$ 14700).

Synthesis of $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2} \mathrm{Cl}_{3}\left(\mu_{4}-\mathrm{Cl}\right)\left(\mathbf{O H}_{2}\right)\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (2). To a yellow suspension of $\mathrm{H}_{4} \mathrm{~L}$ ( 20 mg 0.036 mmol ) in ethanol ( 4 mL ) was added an ethanol solution ( 1 mL ) of $\mathrm{MnCl}_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(14 \mathrm{mg}, 0.072 \mathrm{mmol})$. The mixture was stirred at room temperature for 1 h. Triethylamine ( $20 \mu \mathrm{~L}, 0.14 \mathrm{mmol}$ ) in ethanol ( 1 mL ) was added, and the mixture was stirred at room temperature for 1 h . The brown solution was evaporated and recrystallized from a methanol solution by slow diffusion of diethyl ether to give brown crystals of 2. Yield: 19 mg (67\%). Anal. Calcd for $\mathrm{C}_{70} \mathrm{H}_{66} \mathrm{Cl}_{4} \mathrm{Mn}_{4} \mathrm{~N}_{4} \mathrm{O}_{11} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ : C 52.25, H 4.89, N 3.48. Found: C, 52.02; H, 4.92; N, 3.39. Seven water molecules of crystallization were found in the crystal structure of 2 , and were partially lost on drying. IR (ATR, $\mathrm{cm}^{-1}$ ): 1614, 1541, 1453, 1433, 1411, 1384, 1309, 1295, 1236, 1139, 1068,

984, 823, 795,742 . UV-Vis: $\lambda\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) / \mathrm{nm} 410$ (shoulder, $\varepsilon / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1} 11000$ ).

Magnetic Susceptibility Measurements. The magnetic susceptibility measurements were carried out for 1 and 2 by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2) in the temperature range $1.7-300 \mathrm{~K}$ (Figure S1). The applied magnetic field was 1 T . The diamagnetic components were estimated from Pascal's constants.

The $\chi T$ value of 1 at 300 K is $13.34 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$, which is slightly below the spin only value of $14.75 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ expected for two high-spin $\mathrm{Mn}^{\mathrm{II}}$ and two high-spin $\mathrm{Mn}^{\text {III }}$ centers with $g=2.0$. At lower temperature, the $\chi T$ value decreases to $2.23 \mathrm{~cm}^{3} \mathrm{~K}$ $\mathrm{mol}^{-1}$ at 1.7 K . The magnetic susceptibility data of $\mathbf{1}$ was fitted by the Curie-Weiss law $\chi=C /(\mathrm{T}-\theta)$ with $C=13.71 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ and $\theta=-8.9 \mathrm{~K}$.

The magnetic susceptibility data of $\mathbf{2}$ showed that the $\chi T$ values decreases from 7.81 $\mathrm{cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ at 300 K to $0.29 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ at 1.7 K . The $\chi T$ value at 300 K is much smaller than the spin only value of $12.00 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ expected for four high-spin $\mathrm{Mn}^{\text {III }}$ ions with $g=2.0$. The data of 2 were analyzed using the dimer model with a weak interaction between two alkoxo-bridged $\mathrm{Mn}^{\mathrm{III}}{ }_{2}$ units. The Heisenberg Hamiltonian model is given by

$$
H=-2 J\left[S_{\mathrm{Mn} 1} \cdot S_{\mathrm{Mn} 2}+S_{\mathrm{Mn} 3} \cdot S_{\mathrm{Mn} 4}\right],
$$

where $S_{\mathrm{Mn} 1}=S_{\mathrm{Mn} 2}=S_{\mathrm{Mn} 3}=S_{\mathrm{Mn} 4}=2$, and $J$ is the exchange interaction between Mn1 and Mn 2 , or Mn 3 and Mn 4 , bridged by two alkoxide O atoms. A theoretical expression for the molar magnetic susceptibility is derived using the Van Vleck equation, and the interaction between $\mathrm{Mn} 1-\mathrm{Mn} 2$ and $\mathrm{Mn} 3-\mathrm{Mn} 4$ units $\left(T-\theta_{1}\right)$ and a paramagnetic impurity term $\left(\mathrm{C}_{1} /\left(T-\theta_{2}\right)\right)$ are included:

$$
\chi_{\mathrm{mol}}=2 \times 2 N\left(\mathrm{~g}^{2} \mu_{\mathrm{B}}^{2} / k_{\mathrm{B}}\right) \mathrm{F}(\mathrm{X}) /\left(T-\theta_{1}\right)+\mathrm{C}_{1} /\left(T-\theta_{2}\right),
$$

where

$$
\begin{aligned}
& \mathrm{F}(\mathrm{X})=(\exp (18 \mathrm{X})+5 \exp (14 \mathrm{X})+14 \exp (8 \mathrm{X})+30) \\
& \quad /(\exp (20 \mathrm{X})+3 \exp (18 \mathrm{X})+5 \exp (14 \mathrm{X})+7 \exp (8 \mathrm{X})+9)
\end{aligned}
$$

$$
\mathrm{X}=-J / k_{\mathrm{B}} T
$$

The least-squares fitting of the experimental data with this model gives $J=-24.3 \mathrm{~K}$ $\left(-16.9 \mathrm{~cm}^{-1}\right), \theta_{1}=-39.9 \mathrm{~K}, \mathrm{C}_{1}=1.38 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}, \theta_{2}=-6.4 \mathrm{~K}$, and $g=1.88$. The $g$ value may be underestimated by the paramagnetic impurity contribution.

Electrochemistry. Cyclic voltammetric (CV) measurements were performed at room temperature using an ALS/CHI600A voltammetric analyzer (Bioanalytical Systems Inc.). Working, reference, and counter electrodes were a glassy carbon disk
electrode with a diameter of 3 mm (Bioanalytical Systems Inc.), a $\mathrm{Ag} / \mathrm{Ag}^{+}$( 0.01 M $\mathrm{AgNO}_{3}, 1 \mathrm{M}=1 \mathrm{~mol} \mathrm{dm}{ }^{-3}$ ) reference electrode, and a platinum wire, respectively. Sample solutions were prepared in the concentration of $1 \times 10^{-4} \mathrm{M}$ for 1 and $1 \times 10^{-3} \mathrm{M}$ for 2, and contained $0.1 \mathrm{M} \mathrm{Bu}_{4} \mathrm{NPF}_{6}$ or $\mathrm{Bu}_{4} \mathrm{NCl}$ as a supporting electrolyte. The observed potentials were corrected using the redox potential of ferrocenium/ferrocene ( $\mathrm{Fc}^{+} / \mathrm{Fc}$ ) obtained under the same conditions. The cyclic voltammograms of $\mathbf{1}$ and $\mathbf{2}$ are shown in Figures S2 and S3, respectively.

Complex 1 exhibits three redox couples at $-1.08\left(\Delta E_{\mathrm{p}}=131 \mathrm{mV}\right),-0.24\left(\Delta E_{\mathrm{p}}=63\right.$ $\mathrm{mV})$, and $0.17 \mathrm{~V}\left(\Delta E_{\mathrm{p}}=78 \mathrm{mV}\right)\left(E_{1 / 2} \mathrm{vs} E^{0}\left(\mathrm{Fc}^{+/ 0}\right)\right)$. The cathodic peak current at $-1.15 \mathrm{~V}\left(i_{\mathrm{pc}}=2.5 \mu \mathrm{~A}\right)$ is larger by a factor of 1.6 than the anodic peak current at -0.21 $\mathrm{V}\left(i_{\mathrm{pa}}=1.6 \mu \mathrm{~A}\right)$. Furthermore, the second reduction wave was not observed even when swept to -2.4 V (Figure S2). From these results we concluded that the reduction at -1.08 V consists of two overlapped one-electron processes for $\mathrm{Mn}^{\mathrm{III}}{ }_{2} \mathrm{Mn}^{\mathrm{II}} / \mathrm{Mn}^{\mathrm{II}}{ }_{4}$. The two quasi-reversible couples at -0.24 and 0.17 V were assigned to $\mathrm{Mn}^{\mathrm{III}}{ }_{3} \mathrm{Mn}^{\mathrm{II}} / \mathrm{Mn}^{\mathrm{III}}{ }_{2} \mathrm{Mn}^{\mathrm{II}}{ }_{2}$ and $\mathrm{Mn}^{\mathrm{III}} /{ }_{4} \mathrm{Mn}^{\mathrm{III}}{ }_{3} \mathrm{Mn}^{\mathrm{II}}$, respectively, because the anodic peak current at -0.21 V is similar to that of the ferrocenium/ferrocene couple obtained under the same conditions. Complex 2 shows irreversible reduction waves in the range of -1.1 to -0.3 V vs $E^{\circ}{ }^{\prime}\left(\mathrm{Fc}^{+/ 0}\right)$ in the presence of $\mathrm{Bu}_{4} \mathrm{NPF}_{6}$ or $\mathrm{Bu}_{4} \mathrm{NCl}$ as a supporting electrolyte, which are attributable to the reduction from $\mathrm{Mn}^{\mathrm{III}}{ }_{4}$ to $\mathrm{Mn}^{\mathrm{II}}{ }_{4}$ (Figure S3).

Electronic Absorption Spectroscopy. The absorption spectrum of $\mathbf{1}$ in dichloromethane shows an absorption band at $368 \mathrm{~nm}\left(\varepsilon=14700 \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}\right)$, and a dichloromethane solution of 2 shows a shoulder at $410 \mathrm{~nm}\left(\varepsilon=11000 \mathrm{dm}^{3} \mathrm{~mol}^{-1}\right.$ $\mathrm{cm}^{-1}$ ) (Figure S4). Both spectra did not change with time, suggesting that tetranuclear structures of $\mathbf{1}$ and $\mathbf{2}$ are maintained in the solutions. A toluene solution of $\mathbf{1}$ showed an absorption band at 372 nm similar to that of a dichloromethane solution of $\mathbf{1}$, while such a band was not observed for a methanol solution of $\mathbf{1}$. This suggests that complex $\mathbf{1}$ is not stable in methanol. On the other hand, the absorption spectrum of a methanol solution of 2 gradually changed: the shoulder at 410 nm decreased and a new band appeared at 580 nm after 50 h (Figure S5). The solution behavior of 1 and 2 was further investigated by ESI mass spectrometry (vide infra).

ESI Mass Spectrometry. ESI mass spectra of $\mathbf{1}$ and 2 were measured in dichloromethane, acetonitrile, or methanol in the positive mode. In the ESI mass spectrum of dichloromethane solutions, two low intensity signals were detected for $\mathbf{1}$ (Figure S6). These two signals are assignable to $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mathrm{OAc})\right]^{+}(\mathrm{m} / \mathrm{z} 1399)$ and
$\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mathrm{OAc})_{2}\right]^{+}$( $\mathrm{m} / \mathrm{z} 1458$ ). Complex $\mathbf{1}$ is insoluble in acetonitrile, while 2 is soluble. The ESI mass spectrum of $\mathbf{2}$ in acetonitrile exhibits the signal attributed to the doubly charged ion $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2} \mathrm{Cl}_{2}\right]^{2+}$ at $m / z 705$ (Figure S7). The signal for $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2} \mathrm{Cl}_{3}\right]^{+}$was also observed at $\mathrm{m} / \mathrm{z} 1447$ as the base peak. This suggests that the tetramanganese structure of $\mathbf{2}$ is retained in acetonitrile.

The ESI mass spectrum of $\mathbf{1}$ in methanol shows the signal for $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z}$ 1233), in which two acetate and two manganese ions are removed from 1 (Figure S8). After 7 days, a new signal for $\left[\mathrm{Mn}_{2}(\mathrm{~L})\left(\mathrm{OCH}_{3}\right)\right]^{+}$appeared at $\mathrm{m} / \mathrm{z} 701$ (Figure S9). The ESI mass spectrum of 2 in methanol shows a dominant signal for $\left[\mathrm{Mn}_{2}(\mathrm{~L})\left(\mathrm{OCH}_{3}\right)\right]^{+}$at $\mathrm{m} / \mathrm{z} 701$ (Figure S10), which suggests dissociation of the chloride ligands, followed by monomerization. After 3 days, new signals including $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{2}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 1232)$ and $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 1233)$ were observed (Figure S11). This indicates that the absorption spectral change of a methanol solution of 2 is related to the partial dissociation of manganese ions from the $\mathrm{Mn}_{2}(\mathrm{~L})$ units (vide supra).

X-Ray Crystal Structure Determination of $\mathbf{1}$ and 2. A single crystal of $\mathbf{1}$ or $\mathbf{2}$ was mounted on a glass fiber. The diffraction data were collected on an AFC7/CCD Mercury diffractometer. The data were processed and corrected for Lorentz and polarization effects using CrystalClear software. ${ }^{2}$ Absorption corrections were applied using the Multi Scan method. The structures were solved using direct methods (SIR97 ${ }^{3}$ ) and refined by full-matrix least-squares on $F^{2}$ using SHELXL-97. ${ }^{4}$ Crystallographic data are summarized in Table S1. The structures of $\mathbf{1}$ and $\mathbf{2}$ are shown in Figures S12 and S13, respectively. Selected bond distances and angles for $\mathbf{1}$ and $\mathbf{2}$ are listed in Tables S2 and S3, respectively.

## References

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(2) CrystalClear, Rigaku Corporation, 2001.
(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. J. Appl. Crystallogr. 1999, 32, 115-119.
(4) Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.


Figure S1. Temperature dependence of $\chi T$ for $\mathbf{1}$ (○) and 2 ( $\square$ ). Solid lines represent the least-squares fits of the data to the model described in the text.


Figure S2. Cyclic voltammograms of $1\left(1 \times 10^{-4} \mathrm{M}\right)$ in dichloromethane containing $0.1 \mathrm{M} \mathrm{Bu}_{4} \mathrm{NPF}_{6}(-,--)$; scan rate, $100 \mathrm{mV} \mathrm{s}{ }^{-1}$; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, $\mathrm{Ag} / \mathrm{Ag}^{+}$.


Figure S3. Cyclic voltammograms of $2\left(1 \times 10^{-3} \mathrm{M}\right)$ in dichloromethane containing 0.1 M Bu ${ }_{4} \mathrm{NPF}_{6}$ (-, ---) and $\mathrm{Bu}_{4} \mathrm{NCl}(-)$; scan rate, $100 \mathrm{mV} \mathrm{s}{ }^{-1}$; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, $\mathrm{Ag} / \mathrm{Ag}^{+}$.


Figure S4. Absorption spectra of $\mathbf{1}(-)$ and $2(-)$ in dichloromethane.


Figure S5. Absorption spectral changes of 2 in methanol: $0 \mathrm{~h}(-)$; 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 26 h (-); 50 h (-).
(a)

(b)

(c)



Figure S6. (a) ESI mass spectrum of 1 in dichloromethane. (b) Expanded view of the region from $\mathrm{m} / \mathrm{z} 1380$ to 1480 . (c) Calculated isotopic distribution patterns for $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mathrm{OAc})\right]^{+}(\mathrm{m} / \mathrm{z} 1399)(\mathrm{left})$ and $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mathrm{OAc})_{2}\right]^{+}(\mathrm{m} / \mathrm{z} 1458)$ (right).
(a)

(b)


(c)



Figure S7. (a) ESI mass spectrum of 2 in acetonitrile. (b) Expanded view of the region from $\mathrm{m} / \mathrm{z} 670$ to 720 (left) and the calculated isotopic distribution pattern for $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2} \mathrm{Cl}_{2}\right]^{2+}(\mathrm{m} / \mathrm{z} 705)$ (right). (c) Expanded view of the signal attributed to $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2} \mathrm{Cl}_{3}\right]^{+}$( $\mathrm{m} / \mathrm{z} 1447$ ) (left) and the calculated isotopic distribution pattern (right).
(a)

(b)



Figure S8. (a) ESI mass spectrum of $\mathbf{1}$ in methanol. (b) Expanded view of the signal attributed to $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z}$ 1233) (left) and the calculated isotopic distribution pattern (right).
(a)

(b)


(c)



Figure S9. (a) ESI mass spectrum of $\mathbf{1}$ in methanol after 7 days. (b) Expanded view of the region from $\mathrm{m} / \mathrm{z} 670$ to 720 (left) and the calculated isotopic distribution pattern for $\left[\mathrm{Mn}_{2}(\mathrm{~L})\left(\mathrm{OCH}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 701)$ (right). (c) Expanded view of the signal attributed to $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{2}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 1232)$ and $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 1233)$ (left) and the calculated isotopic distribution pattern for a 1:3 mixture of $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{2}\right)\right]^{+}$and $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}$(right).
(a)

(b)



Figure S10. (a) ESI mass spectrum of 2 in methanol. (b) Expanded view of the signal attributed to $\left[\mathrm{Mn}_{2}(\mathrm{~L})\left(\mathrm{OCH}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 701)$ (left) and the calculated isotopic distribution pattern (right).
(a)

(b)


(c)



Figure S11. (a) ESI mass spectrum of 2 in methanol after 3 days. (b) Expanded view of the region from $\mathrm{m} / \mathrm{z} 670$ to 720 (left) and the calculated isotopic distribution pattern for $\left[\mathrm{Mn}_{2}(\mathrm{~L})\left(\mathrm{OCH}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 701)$ (right). (c) Expanded view of the signal attributed to $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{2}\right)\right]^{+}(\mathrm{m} / \mathrm{z} 1232)$ and $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}(\mathrm{m} / \mathrm{z}$ 1233) (left) and the calculated isotopic distribution pattern for a $7: 3$ mixture of $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{2}\right)\right]^{+}$and $\left[\mathrm{Mn}_{2}\left(\mathrm{~L}_{2} \mathrm{H}_{3}\right)\right]^{+}$(right).

Table S1. Crystallographic data for $\mathbf{1}$ and $\mathbf{2}$

|  | 1 | 2 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{84} \mathrm{H}_{94} \mathrm{Cl}_{8} \mathrm{Mn}_{4} \mathrm{~N}_{4} \mathrm{O}_{16}$ | $\mathrm{C}_{70} \mathrm{H}_{80} \mathrm{Cl}_{4} \mathrm{Mn}_{4} \mathrm{~N}_{4} \mathrm{O}_{18}$ |
| Formula weight | 1918.99 | 1626.94 |
| Temperature/K | 163 | 120 |
| Wavelength/ $\AA$ | 0.7107 | 0.7107 |
| Crystal system | triclinic | orthorhombic |
| Space group | $P \overline{1}$ | C222 ${ }_{1}$ |
| $a / \AA$ | 12.384(2) | 13.7200(19) |
| $b / \AA$ | 13.3307(19) | 33.820(5) |
| $c / \AA$ | 15.2393(14) | 15.370(2) |
| $\alpha 1^{\circ}$ | 65.483(11) | 90 |
| $\beta 1{ }^{\circ}$ | 70.914(12) | 90 |
| $\gamma^{\prime}$ | 83.701(15) | 90 |
| $V / \AA^{3}$ | 2162.2(5) | 7131.8(18) |
| Z | 1 | 4 |
| $D_{\text {calcd }} / \mathrm{Mg} \cdot \mathrm{m}^{-3}$ | 1.474 | 1.515 |
| $\mu(\mathrm{Mo} \mathrm{K} \alpha) / \mathrm{mm}^{-1}$ | 0.885 | 0.915 |
| $F(000)$ | 990 | 3360 |
| Crystal size/mm ${ }^{3}$ | $0.37 \times 0.11 \times 0.07$ | $0.15 \times 0.15 \times 0.10$ |
| Reflections collected | 21110 | 26876 |
| Independent reflections | $9306\left(R_{\text {int }}=0.039\right)$ | $7972\left(R_{\text {int }}=0.071\right)$ |
| Completeness to $\theta$ | $95.4 \%\left(\theta=25.0^{\circ}\right)$ | 98.1\% ( $\theta=27.46^{\circ}$ ) |
| Max. and min. transmission | 0.9407 and 0.7355 | 0.9141 and 0.8750 |
| No. of data/restraints/parameters | 9306/1/622 | 7972/0/476 |
| Goodness of fit on $F^{2}$ | 1.087 | 1.161 |
| Final $R$ indices [ $I>2 \sigma(I)$ ] | $\mathrm{R} 1=0.0713$ | $\mathrm{R} 1=0.0795$ |
| $R$ indices (all data) | $\mathrm{wR2}=0.1728$ | $\mathrm{wR} 2=0.1677$ |
| Absolute structure parameter |  | -0.02(3) |
| Largest diff. peak and hole (e $\cdot \AA^{-3}$ ) | 1.50 and -1.18 | 0.402 and -0.644 |

(a)

(b)


Figure S12. ORTEP drawings of $\mathbf{1}$ with thermal ellipsoids at the $50 \%$ probability level. (a) Structure of $\left[\mathrm{Mn}_{4}(\mathrm{~L})_{2}(\mu-\mathrm{OAc})_{2}\right]$. Hydrogen atoms are omitted for clarity. (b) Tetaramanganese core structure in 1. Solid bonds represent the incomplete double-cubane structure of $\mathrm{Mn}_{4} \mathrm{O}_{6}$.

Table S2. Selected bond distances $/ \AA$ and angles $/{ }^{\circ}$ for 1

| $\mathrm{Mn}(1)-\mathrm{O}(1)$ | $2.073(3)$ | $\mathrm{Mn}(2)-\mathrm{O}(1)$ | $2.360(3)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Mn}(1)-\mathrm{O}(2)$ | $2.124(3)$ | $\mathrm{Mn}(2)-\mathrm{O}(2)^{*}$ | $1.907(3)$ |
| $\mathrm{Mn}(1)-\mathrm{O}(4)$ | $2.317(3)$ | $\mathrm{Mn}(2)-\mathrm{O}(3)$ | $1.868(3)$ |
| $\mathrm{Mn}(1)-\mathrm{O}(4)^{*}$ | $2.234(3)$ | $\mathrm{Mn}(2)-\mathrm{O}(4)$ | $1.947(3)$ |
| $\mathrm{Mn}(1)-\mathrm{O}(6)$ | $2.166(3)$ | $\mathrm{Mn}(2)-\mathrm{O}(7)^{*}$ | $2.207(3)$ |
| $\mathrm{Mn}(1)-\mathrm{N}(1)$ | $2.202(3)$ | $\mathrm{Mn}(2)-\mathrm{N}(2)$ | $2.023(3)$ |
|  |  |  |  |
| $\mathrm{Mn}(1) \cdots \mathrm{Mn}(1)^{*}$ | $3.4020(13)$ | $\mathrm{Mn}(1) \cdots \mathrm{Mn}(2)$ | $3.3780(10)$ |
| $\mathrm{Mn}(1) \cdots \mathrm{Mn}(2)^{*}$ | $3.0963(9)$ | $\mathrm{Mn}(2) \cdots \mathrm{Mn}(2)^{*}$ | $5.5156(14)$ |
|  |  |  |  |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(2)$ | $161.44(11)$ | $\mathrm{O}(1)-\mathrm{Mn}(2)-\mathrm{O}(2)^{*}$ | $90.70(11)$ |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(4)$ | $76.21(10)$ | $\mathrm{O}(1)-\mathrm{Mn}(2)-\mathrm{O}(3)$ | $99.66(11)$ |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(4)^{*}$ | $108.84(10)$ | $\mathrm{O}(1)-\mathrm{Mn}(2)-\mathrm{O}(4)$ | $77.51(11)$ |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(6)$ | $102.85(11)$ | $\mathrm{O}(1)-\mathrm{Mn}(2)-\mathrm{O}(7)^{*}$ | $166.72(11)$ |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | $87.03(11)$ | $\mathrm{O}(1)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | $90.73(12)$ |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{O}(4)$ | $85.92(10)$ | $\mathrm{O}(2)^{*}-\mathrm{Mn}(2)-\mathrm{O}(3)$ | $92.45(12)$ |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{O}(4)^{*}$ | $73.36(10)$ | $\mathrm{O}(2)^{*}-\mathrm{Mn}(2)-\mathrm{O}(4)$ | $85.02(11)$ |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{O}(6)$ | $95.67(11)$ | $\mathrm{O}(2)^{*}-\mathrm{Mn}(2)-\mathrm{O}(7)^{*}$ | $90.76(12)$ |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | $91.87(11)$ | $\mathrm{O}(2)^{*}-\mathrm{Mn}(2)-\mathrm{N}(2)$ | $177.77(13)$ |
| $\mathrm{O}(4)-\mathrm{Mn}(1)-\mathrm{O}(4)^{*}$ | $83.26(10)$ | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{O}(4)$ | $176.16(13)$ |
| $\mathrm{O}(4)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | $101.88(12)$ | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{O}(7)^{*}$ | $93.46(12)$ |
| $\mathrm{O}(4)^{*}-\mathrm{Mn}(1)-\mathrm{N}(1)$ | $164.11(11)$ | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | $89.00(13)$ |
| $\mathrm{O}(6)-\mathrm{Mn}(1)-\mathrm{O}(4)$ | $168.25(10)$ | $\mathrm{O}(4)-\mathrm{Mn}(2)-\mathrm{O}(7)^{*}$ | $89.47(11)$ |
| $\mathrm{O}(6)-\mathrm{Mn}(1)-\mathrm{O}(4)^{*}$ | $86.04(10)$ | $\mathrm{O}(4)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | $93.62(12)$ |
| $\mathrm{O}(6)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | $89.72(12)$ | $\mathrm{O}(7)^{*}-\mathrm{Mn}(2)-\mathrm{N}(2)$ | $87.45(12)$ |
|  |  |  |  |
| $\mathrm{Mn}(1)-\mathrm{O}(1)-\mathrm{Mn}(2)$ | $99.05(11)$ | $\mathrm{Mn}(1)^{*}-\mathrm{O}(4)-\mathrm{Mn}(2)$ | $95.30(11)$ |
| $\mathrm{Mn}(1)-\mathrm{O}(2)-\mathrm{Mn}(2)^{*}$ | $100.25(12)$ | $\mathrm{Mn}(1)-\mathrm{O}(4)-\mathrm{Mn}(2)$ | $104.44(12)$ |
| $\mathrm{Mn}(1)-\mathrm{O}(4)-\mathrm{Mn}(1)^{*}$ | $96.74(10)$ |  |  |
|  |  |  |  |




Figure S13. ORTEP drawings of 2 with thermal ellipsoids at the $50 \%$ probability level. Hydrogen atoms are omitted for clarity. (a) Side and (b) top views. The Cl1 and O1 atoms were found to be split over two positions related by the $C_{2}$ axis, and they were refined with occupancies of 0.5 each.

Table S3. Selected bond distances $/ \AA$ and angles $/{ }^{\circ}$ for 2

| $\mathrm{Mn}(1)-\mathrm{O}(1)$ | 2.032(14) | $\mathrm{Mn}(2)-\mathrm{O}(3)$ | 1.971(4) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Mn}(1)-\mathrm{O}(2)$ | 1.882(4) | $\mathrm{Mn}(2)-\mathrm{O}(4)$ | 1.863(4) |
| $\mathrm{Mn}(1)-\mathrm{O}(3)$ | 1.935(4) | $\mathrm{Mn}(2)-\mathrm{O}(5)$ | 1.939(4) |
| $\mathrm{Mn}(1)-\mathrm{O}(5)$ | 1.943(4) | $\mathrm{Mn}(2)-\mathrm{N}(2)$ | 2.010(5) |
| $\mathrm{Mn}(1)-\mathrm{N}(1)$ | 2.021(5) | $\mathrm{Mn}(2)-\mathrm{Cl}(2)$ | 2.4572(18) |
| $\mathrm{Mn}(1)-\mathrm{Cl}(1)$ | 2.582(6) | $\mathrm{Mn}(2)-\mathrm{Cl}(3)$ | 2.9374(15) |
| $\mathrm{Mn}(1)-\mathrm{Cl}(3)$ | 2.7355(16) |  |  |
| $\mathrm{Mn}(1)-\mathrm{Mn}(2)$ | 2.9137(12) | $\mathrm{Mn}(1)-\mathrm{Mn}(2) *$ | 5.6689(14) |
| $\mathrm{Mn}(1)-\mathrm{Mn}(1)^{*}$ | 4.768(2) | $\mathrm{Mn}(2)-\mathrm{Mn}(2) *$ | 4.9697(19) |
| $\mathrm{Cl}(1)-\mathrm{Mn}(1)-\mathrm{Cl}(3)$ | 170.16(14) | $\mathrm{Cl}(2)-\mathrm{Mn}(2)-\mathrm{Cl}(3)$ | 168.54(6) |
| $\mathrm{Cl}(1)-\mathrm{Mn}(1)-\mathrm{O}(2)$ | 95.8(2) | $\mathrm{Cl}(2)-\mathrm{Mn}(2)-\mathrm{O}(3)$ | 96.68(12) |
| $\mathrm{Cl}(1)-\mathrm{Mn}(1)-\mathrm{O}(3)$ | 90.73(18) | $\mathrm{Cl}(2)-\mathrm{Mn}(2)-\mathrm{O}(4)$ | 97.98(14) |
| $\mathrm{Cl}(1)-\mathrm{Mn}(1)-\mathrm{O}(5)$ | 96.44(17) | $\mathrm{Cl}(2)-\mathrm{Mn}(2)-\mathrm{O}(5)$ | 95.44(13) |
| $\mathrm{Cl}(1)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 88.83(19) | $\mathrm{Cl}(2)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | 93.16(16) |
| $\mathrm{Cl}(3)-\mathrm{Mn}(1)-\mathrm{O}(2)$ | 93.97(16) | $\mathrm{Cl}(3)-\mathrm{Mn}(2)-\mathrm{O}(3)$ | 73.80(11) |
| $\mathrm{Cl}(3)-\mathrm{Mn}(1)-\mathrm{O}(3)$ | 79.43(12) | $\mathrm{Cl}(3)-\mathrm{Mn}(2)-\mathrm{O}(4)$ | 89.02(14) |
| $\mathrm{Cl}(3)-\mathrm{Mn}(1)-\mathrm{O}(5)$ | 81.79(13) | $\mathrm{Cl}(3)-\mathrm{Mn}(2)-\mathrm{O}(5)$ | 76.56(12) |
| $\mathrm{Cl}(3)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 92.20(15) | $\mathrm{Cl}(3)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | 95.74(15) |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{O}(3)$ | 169.96(18) | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{O}(4)$ | 92.95(17) |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{O}(5)$ | 92.92(18) | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{O}(5)$ | 77.93(16) |
| $\mathrm{O}(2)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 91.30(19) | $\mathrm{O}(3)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | 168.59(18) |
| $\mathrm{O}(3)-\mathrm{Mn}(1)-\mathrm{O}(5)$ | 78.73(16) | $\mathrm{O}(4)-\mathrm{Mn}(2)-\mathrm{O}(5)$ | 164.57(19) |
| $\mathrm{O}(3)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 96.48(18) | $\mathrm{O}(4)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | 91.37(19) |
| $\mathrm{O}(5)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 172.88(19) | $\mathrm{O}(5)-\mathrm{Mn}(2)-\mathrm{N}(2)$ | 95.45(18) |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{Cl}(3)$ | 171.7(4) |  |  |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(2)$ | 89.7(4) | $\mathrm{Mn}(1)-\mathrm{O}(5)-\mathrm{Mn}(2)$ | 97.30(17) |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(3)$ | 95.9(4) | $\mathrm{Mn}(1)-\mathrm{Cl}(3)-\mathrm{Mn}(1)^{*}$ | 121.28(9) |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{O}(5)$ | 90.7(4) | $\mathrm{Mn}(1)-\mathrm{Cl}(3)-\mathrm{Mn}(2)$ | 61.69(3) |
| $\mathrm{O}(1)-\mathrm{Mn}(1)-\mathrm{N}(1)$ | 95.1(4) | $\mathrm{Mn}(1)-\mathrm{Cl}(3)-\mathrm{Mn}(1)^{*}$ | 121.28(9) |
|  |  | $\mathrm{Mn}(1)-\mathrm{Cl}(3)-\mathrm{Mn}(2) *$ | 175.70(6) |
| $\mathrm{Mn}(1)-\mathrm{O}(3)-\mathrm{Mn}(2)$ | 96.48(15) | $\mathrm{Mn}(2)-\mathrm{Cl}(3)-\mathrm{Mn}(2) *$ | 115.54(8) |

