

Supplementary Information

Water oxidation by a manganese-potassium cluster: Mn oxide as a kinetically dominant “true” catalyst for water oxidation

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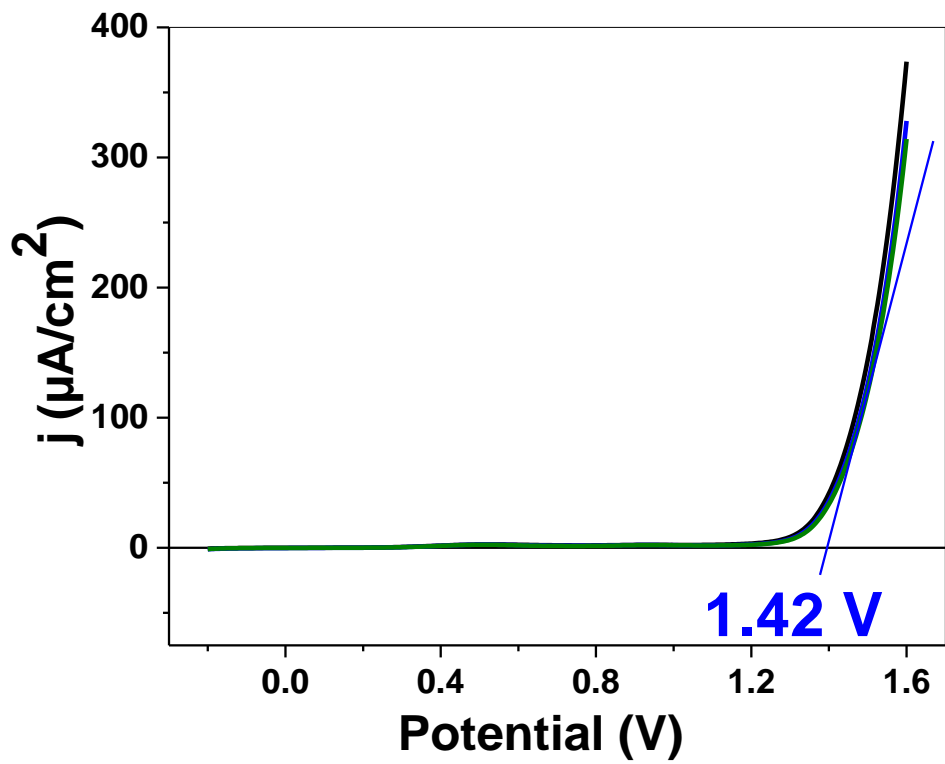


Figure S1 LSV for a fresh FTO in the absence of 1.

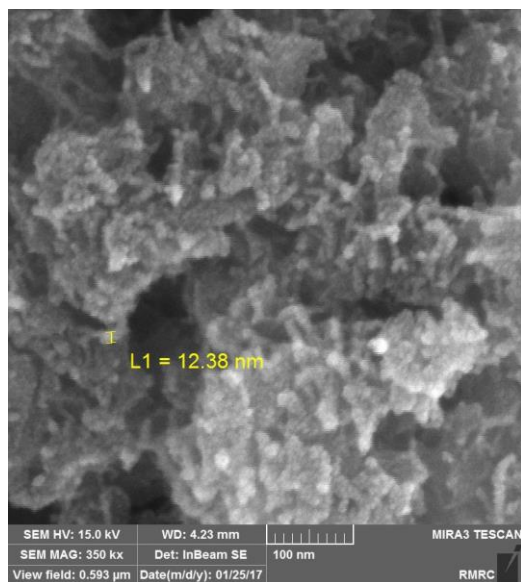
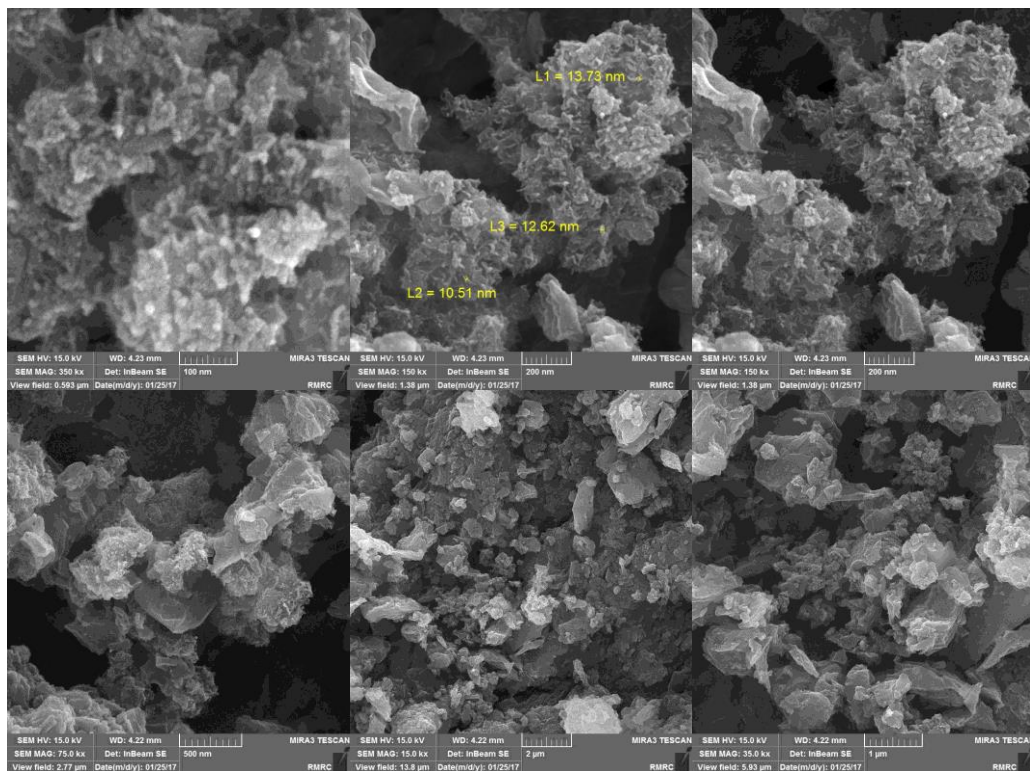


Figure S2 SEM images of **1** before the amperometry at 1.4 V for 2 h in 25.0 mL of phosphate buffer (1.0

M; pH=6.7).

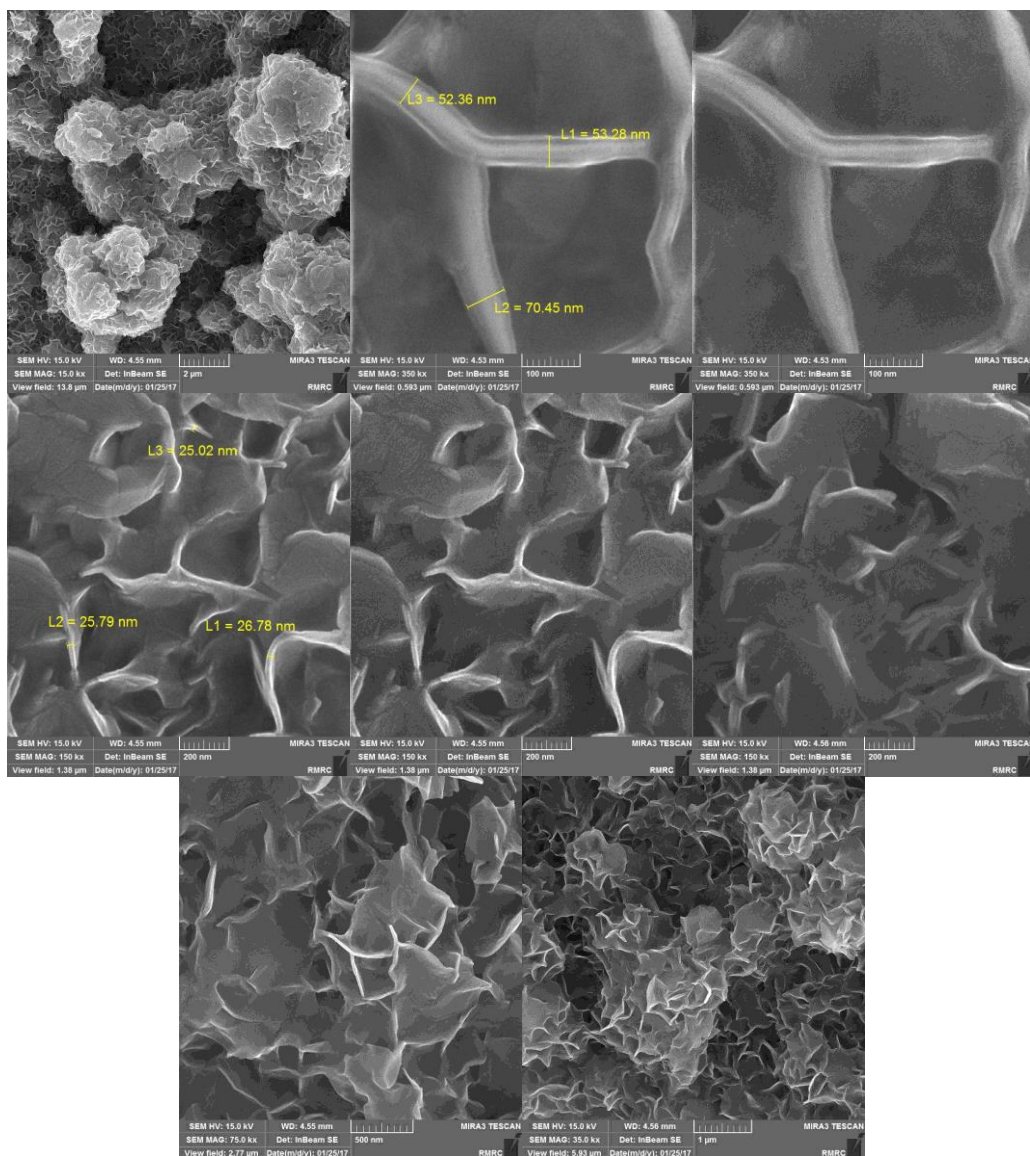


Figure S3 SEM images of **1** after the amperometry at 1.4 V for 2 h in 25.0 mL of phosphate buffer (1.0 M; pH=6.7).

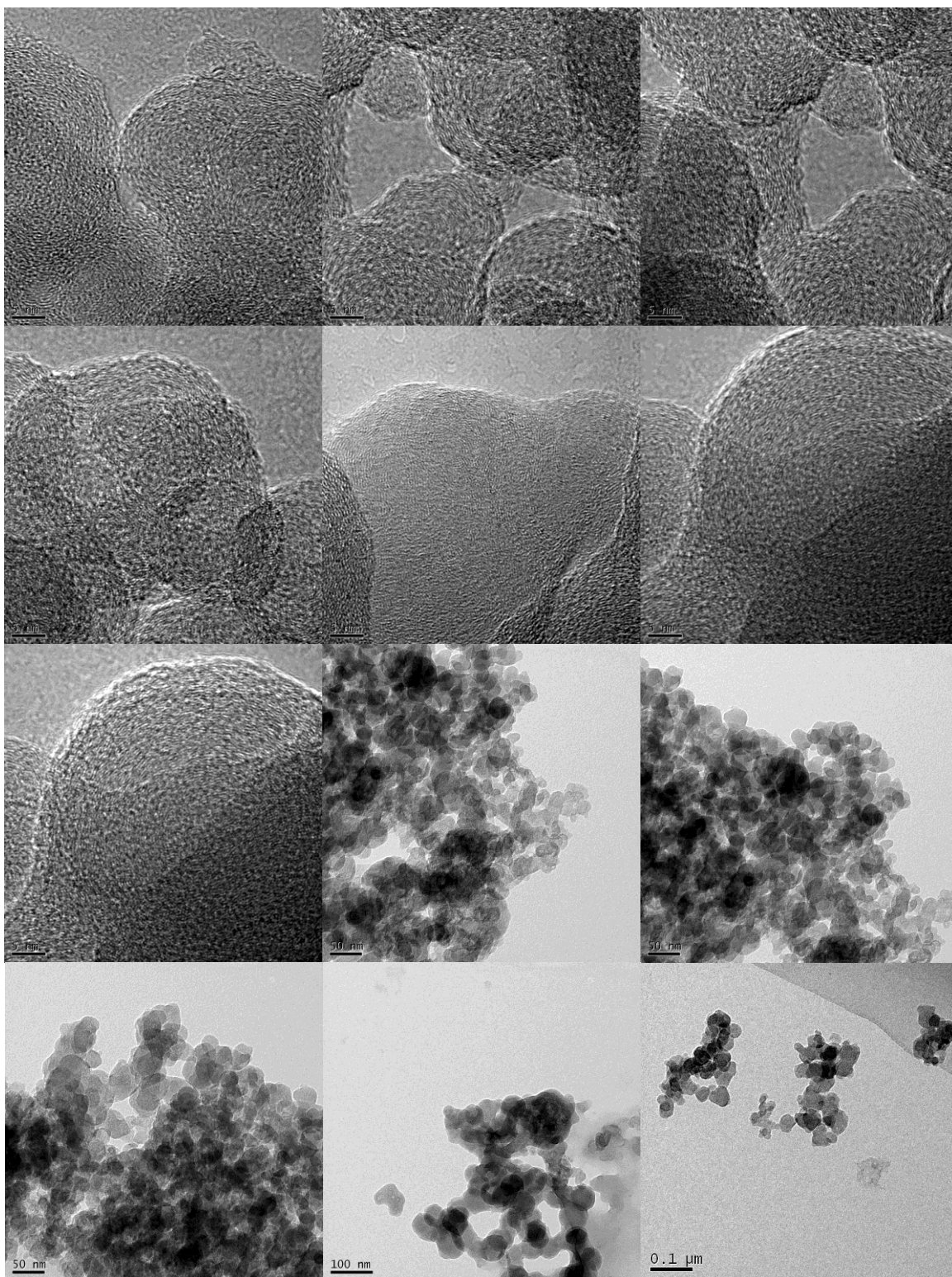


Figure S4 HRTEM images of the mechanically separated solid from the FTO after the amperometry in the presence of **1** at 1.4 V for 2 h (25.0 mL of phosphate buffer (1.0 M; pH=6.7)).

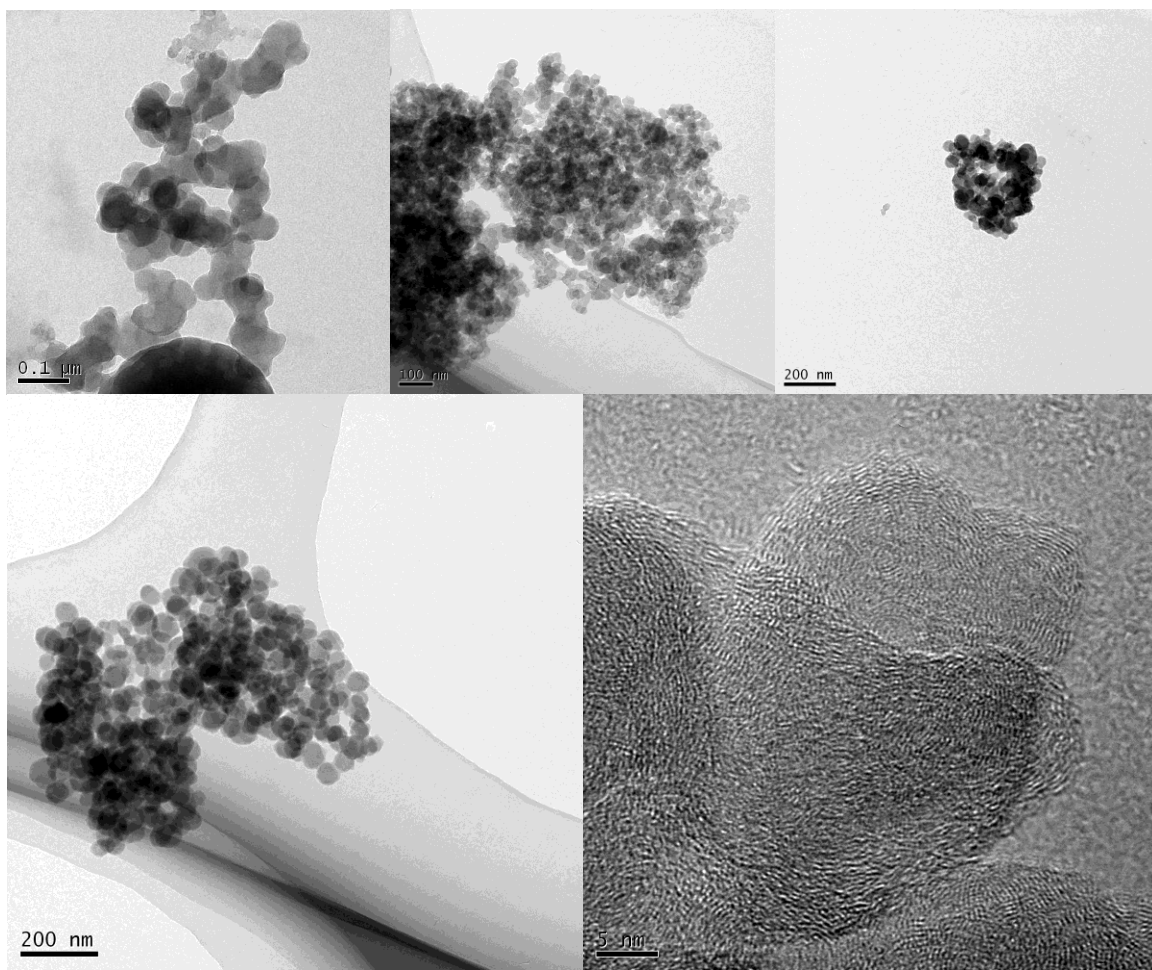


Figure S4 HRTEM images of the mechanically separated solid from the FTO after the amperometry in the presence of **1** at 1.4 V for 2 h (25.0 mL of phosphate buffer (1.0 M; pH=6.7)) (Continue).

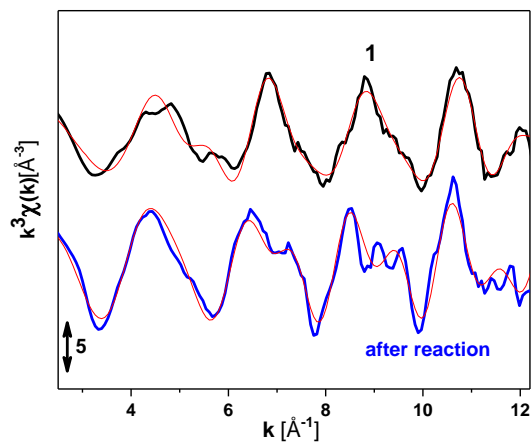


Figure S5 k^3 -weighted $\chi(k)$ of EXAFS spectra of **1** (black) and the obtained compound after the amperometry (blue) at 1.4 V for 2 h in phosphate buffer (1.0 M, pH=6.7). Thick lines show experimental data, thin red lines show simulations. The fit parameters for the simulations are given in **Table 2**. Phase shift not corrected.

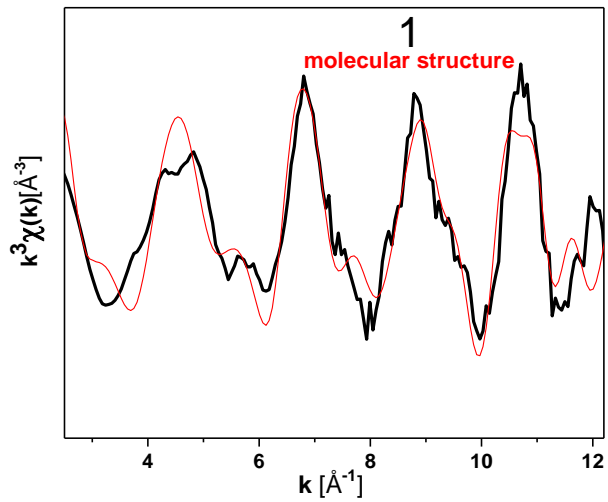
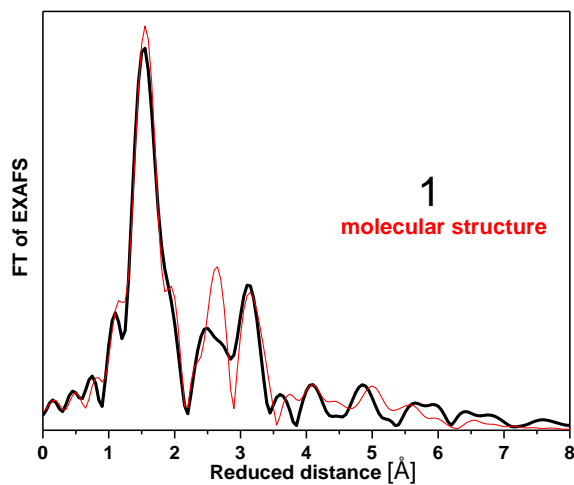
a**b**

Figure S6 k^3 -weighted $\chi(k)$ (a) and Fourier-transform of EXAFS spectra (b) of **1**. Thick black lines show experimental data, thin red lines show simulation using atom coordinates from the molecular structure (CIF file).

Simulations were performed using the in-house software package SimX¹ and SimXLite.

An EXAFS spectrum $\chi(k)$ is given by the sum of the contributions of n_{shell} 'atomic shells'. A 'shell' is a group of elements with identical atomic number and similar distances from the X-ray absorbing atom (e.g. six oxygen atoms surrounding the absorbing manganese ion). The EXAFS equation is mathematically defined by the following equation:^{2,3}

$$\chi(k) = S_o^2 \sum_i^{n_{shell}} A(R_i, k)_i N_i \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \phi_i)$$

where S_o^2 is the amplitude reduction factor, $A(R_i, k)_i$ is a factor that includes the scattering amplitude and mean-free-path of the photo-electron, ϕ_i the phase correction, N_i the number of atoms in the i^{th} atomic shell, σ_i the Debye-Waller parameter of the i^{th} atomic shell, and R_i the (average) distance between the X-ray absorbing atom and the atoms of the i^{th} atomic shell. The functions A and ϕ were obtained herein from ab-initio calculations using Feff 9.05,⁴ using coordinates from the molecular structure of **1**.

For conversion of the energy axis to a k-vector axis, an E_o of 6547 eV was used. Curve-fitting of the data was accomplished within a k-range of 2.5 Å⁻¹ to 13 Å⁻¹. The amplitude reduction factor, S_o^2 , was 0.7. Parameter error estimation was performed as described in Ref. 5.

As it is well known, distance R is not an independent parameter but strongly coupled with the ΔE_o value. Similarly, the coordination numbers N and Debye-Waller parameters σ are also coupled and need to be separated from each other. Therefore, we first determined ΔE_o and σ from a fit to the initial compound **1** in which the coordination numbers were fixed to the values expected from the molecular structure of **1** (sum of N for Mn-O shells equal to 6, and sum of N for Mn-Mn shells equal to 3.25). We then used these ΔE_o and σ values for the fit of the sample after operation.

Table S1. Crystallographic data of **1**

Compound	1
net formula	C ₈₄ H ₁₅₃ K ₂ Mn ₈ NO ₄₀ ·C ₂ H ₄ O ₂
<i>M_r</i> /g mol ⁻¹	2394.84
crystal size/mm	0.34 × 0.18 × 0.06 mm
<i>T</i> /K	80
Radiation	MoKα
Diffractometer	Xcalibur PX
crystal system	Monoclinic
Crystal shape, color	Plate, red
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	18.998(6)
<i>b</i> /Å	15.678(4)
<i>c</i> /Å	20.236(9)
β/°	100.84(4)
<i>V</i> /Å ³	5920(4)
<i>Z</i>	2
calc. density/g cm ⁻³	1.344
μ/mm ⁻¹	0.97
<i>F</i> (000)	2508
θ range	2.7–31
<i>h, k, l</i>	–26→24, –12→21, –14→28
<i>R</i> _{int}	0.067
<i>R</i> (<i>F</i> _{obs})	0.073
<i>R</i> _w (<i>F</i> ²)	0.149
<i>S</i>	1.05
Absorption correction	Analytical
Hydrogen refinement	Mixed
Measured reflections	32040
Independent reflections	16391
Reflections with <i>I</i> > 2σ(<i>I</i>)	8935
Parameters	667
Max electron density/e Å ⁻³	0.59
Min electron density/e Å ⁻³	–0.60

Table S2. Selected bond angles around the Mn(III) ions in complex **1**.

Bond	Angle (°)	Bond	Angle (°)
O1—Mn1—O1 ⁱ	82.12 (12)	O2A—Mn2—O2B ⁱ	177.98 (11)
O1—Mn1—O3	171.65 (11)	O3 ⁱ —Mn3—O1E	90.93 (12)
O1 ⁱ —Mn1—O3	93.45 (11)	O3 ⁱ —Mn3—O2	90.78 (11)
O1—Mn1—O1A	95.09 (11)	O1E—Mn3—O2	177.96 (13)
O1 ⁱ —Mn1—O1A	175.31 (11)	O3 ⁱ —Mn3—O1G	175.28 (11)
O3—Mn1—O1A	89.78 (11)	O1E—Mn3—O1G	85.12 (12)
O1—Mn1—O1B	94.06 (11)	O2—Mn3—O1G	93.12 (12)
O1 ⁱ —Mn1—O1B	91.31 (11)	O3 ⁱ —Mn3—O1F	92.90 (12)
O3—Mn1—O1B	93.10 (11)	O1E—Mn3—O1F	88.82 (11)
O1A—Mn1—O1B	85.11 (11)	O2—Mn3—O1F	92.22 (11)
O1—Mn1—O1C	91.90 (11)	O1G—Mn3—O1F	89.62 (12)
O1 ⁱ —Mn1—O1C	93.88 (11)	O3 ⁱ —Mn3—O2B ⁱ	85.74 (11)
O3—Mn1—O1C	81.31 (11)	O1E—Mn3—O2B ⁱ	98.54 (11)
O1A—Mn1—O1C	89.97 (11)	O2—Mn3—O2B ⁱ	80.48 (10)
O1B—Mn1—O1C	172.58 (10)	O1G—Mn3—O2B ⁱ	92.28 (11)
O2—Mn2—O1	89.29 (12)	O1F—Mn3—O2B ⁱ	172.54 (10)
O2—Mn2—O2C	169.43 (12)	O2—Mn4—O2D	94.81 (12)
O1—Mn2—O2C	99.08 (12)	O2—Mn4—O2F	91.59 (12)
O2—Mn2—O1D	90.20 (12)	O2D—Mn4—O2F	173.31 (12)
O1—Mn2—O1D	175.72 (11)	O2—Mn4—O1H	165.22 (12)
O2C—Mn2—O1D	81.94 (12)	O2D—Mn4—O1H	86.73 (13)
O2—Mn2—O2A	97.39 (11)	O2F—Mn4—O1H	86.58 (12)
O1—Mn2—O2A	85.65 (11)	O2—Mn4—O2G	98.22 (11)
O2C—Mn2—O2A	89.73 (11)	O2D—Mn4—O2G	88.67 (12)
O1D—Mn2—O2A	90.21 (11)	O2F—Mn4—O2G	92.31 (13)
O2—Mn2—O2B ⁱ	81.77 (10)	O1H—Mn4—O2G	96.51 (12)
O1—Mn2—O2B ⁱ	92.50 (10)	O2—Mn4—O2H	105.11 (11)
O2C—Mn2—O2B ⁱ	91.35 (11)	O2D—Mn4—O2H	94.21 (12)
O1D—Mn2—O2B ⁱ	91.63 (11)	O2F—Mn4—O2H	82.25 (12)

Symmetry code: (i) $-x+1, -y, -z+1$.

Table S3 Hydrogen-bond geometry (Å, °) in the crystal structure of **1**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O20—H20···O2E ⁱ	0.84	2.20	2.961 (9)	150
O31—H31···O1H	0.84	2.59	3.42 (2)	170
O32—H32···O32 ⁱⁱ	0.84	2.82	3.48 (5)	137
O32—H32···O42 ⁱⁱ	0.84	1.92	2.76 (4)	173

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x, -y+1, -z+1$.

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