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Electronic Supplementary Information

Synthesis of New Mn_{19} Analogues and their Structural, Electrochemical and Catalytic Properties

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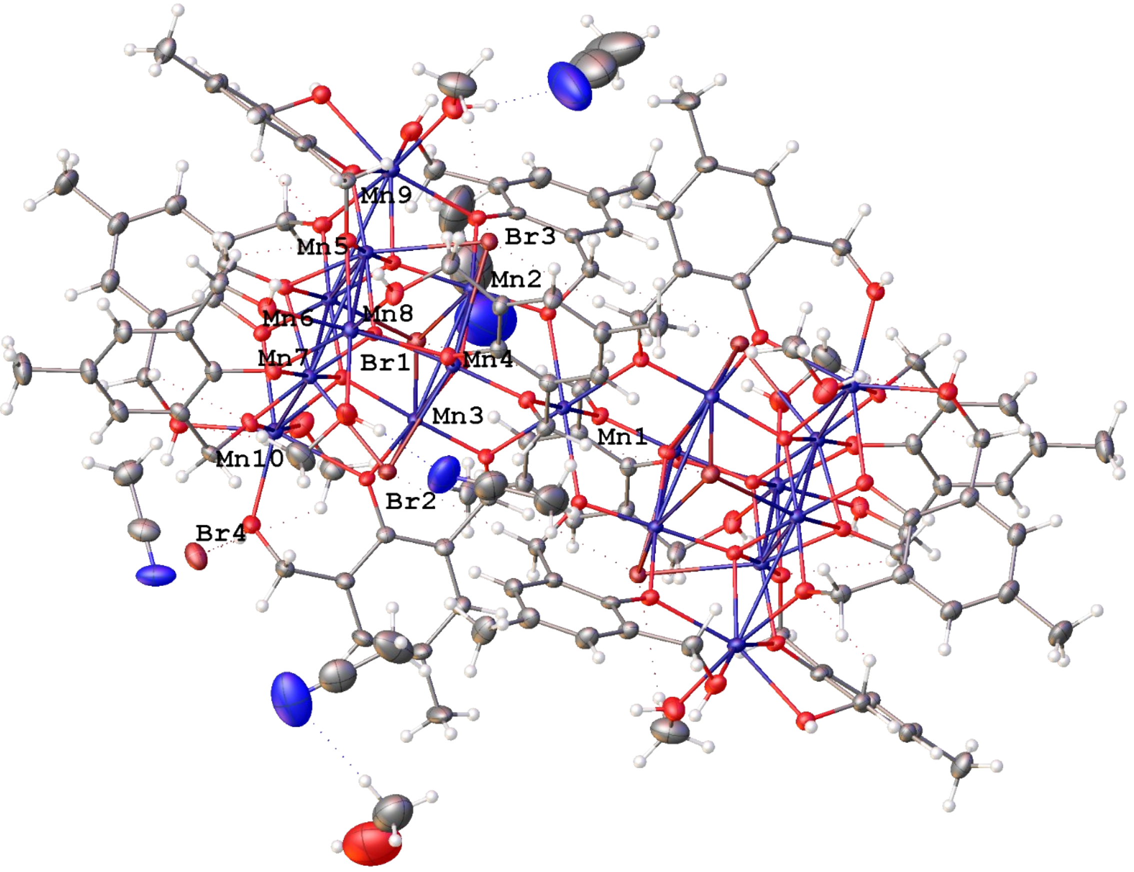
Contents

1.1. Experimental Section

Reagents & analytical methods: All chemicals and solvents were of reagent grade and purchased from Sigma-Aldrich and used without further purification. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using either a universal ATR sampling accessory or a diffuse reflectance sampling accessory. Data were collected and processed using Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. The scan rate was 16 scans per minute with a resolution of 4 scans in the range 4000-500 cm^{-1}. Mass spectroscopy (ESI-MS) was carried out using a TOF-MS (Time-of-Flight–Mass Spectrometer, LCT Premier Instrument) supplied by Waters Corp. UV-vis spectra were performed on a Cary 300 Scan spectrophotometer at 20 ºC using a quartz cell of 1 cm path length. Powder X-ray diffraction (PXRD) studies were carried out using a Bruker D2 Phaser diffractometer using Cu Kα radiation (λ = 1.5418 Å) at room temperature. The slight variation in peak position between the single crystal data collections (100 K) and the powder diffraction data (298 K) are ascribed to the normal unit cell expansion with temperature.

1.2 Molecular structures including solvents, crystal data and structural refinement parameters for 2 and 3



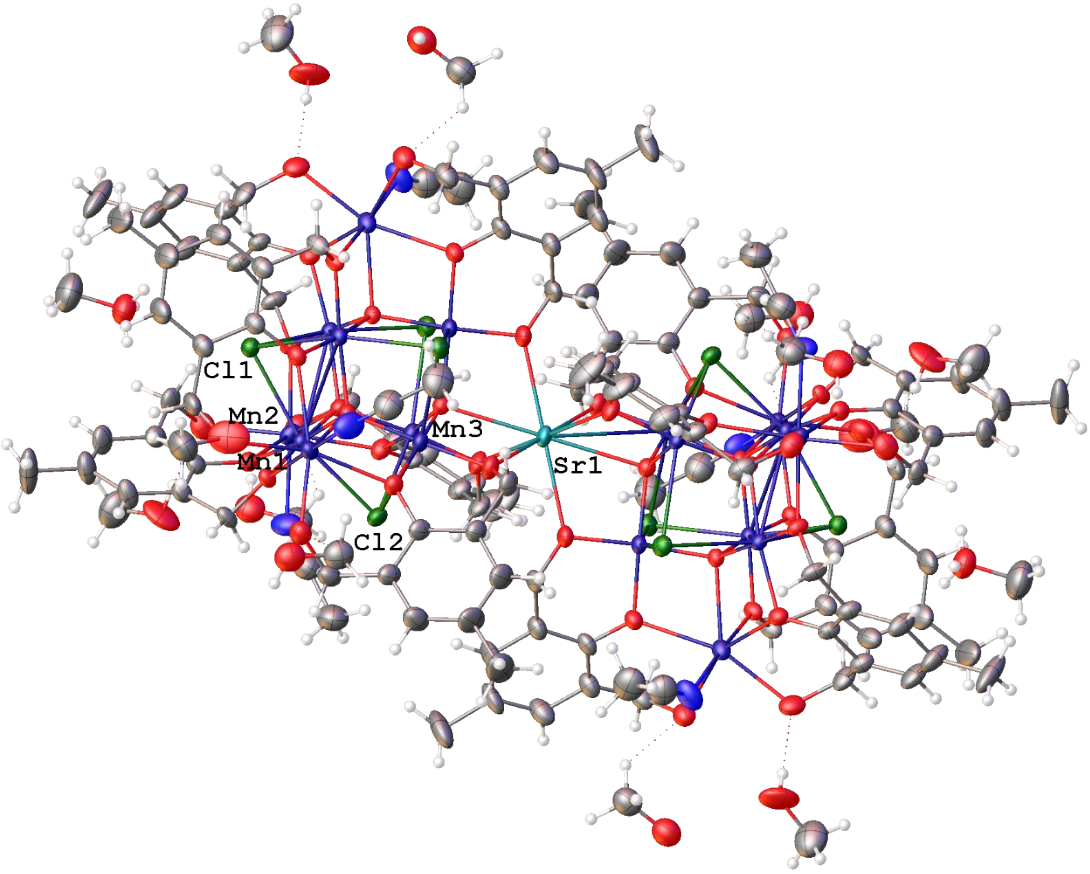


Fig. S1. Symmetry generated full molecular structures including solvents for **2** (top) and **3** (bottom). Only symmetry unique labels are shown for the metals and halides. Atomic displacement shown at 50% probability.

Table S1. Crystal data and structural refinement parameters for 2 and 3.

	2	**3**
Empirical formula	$C_{137}H_{184}Br_8Mn_{19}N_{10}O_{53}$	$C_{127}H_{154}Cl_8Mn_{18}N_6O_{51}Sr$
Molecular weight/g mol^{-1}	4502.07	3940.61
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	$R\overline{3}$
a **/Å**	14.5936(5)	20.6642(8)
b **/Å**	33.0583(11)	20.6642(8)
c **/Å**	17.6608(6)	35.2511(15)
α **/deg**	90	90.00
***β*/deg**	92.9610(10)	90.00

γ /deg	90	120.00
V/Å^3	8508.9(5)	13035.9(12)
Z	2	3
ρ_{cal}/g cm^{-1}	1.757	1.506
F(000)	4510	5970
reflections collected/unique	301634/19516	62285/5943
GOF on F^2	1.076	1.064
R_1*[I>2σ(I)]	0.0366	0.0538
wR_2** [I>2σ(I)]	0.0872	0.1569
R indices(all data)	R1 = 0.0512	R1 = = 0.0755
	wR2 = 0.0940	wR2 = 0.1760

$^*R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $^{**}wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

1.3 Electrochemical studies

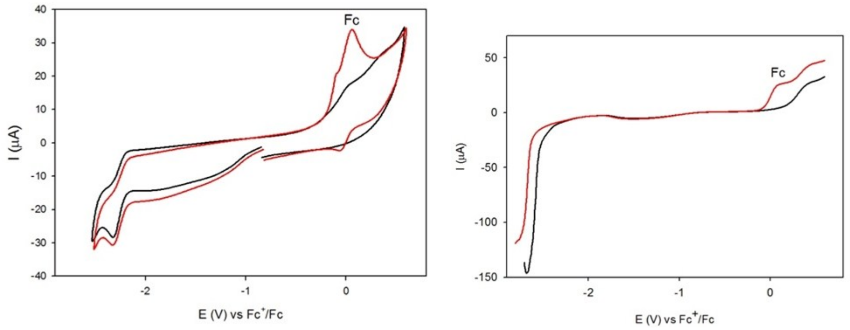


Fig. S2. Cyclic voltammetry (left) at a scan rate of 0.1 Vs^{-1} and (right) RDV at a scan rate of 0.01 Vs^{-1} of **Mn$_{19}$** [**2**, c = 1 mM in DMF, 0.1 M TBAPF$_6$] with Fc (red curve) and without Fc (black curve).

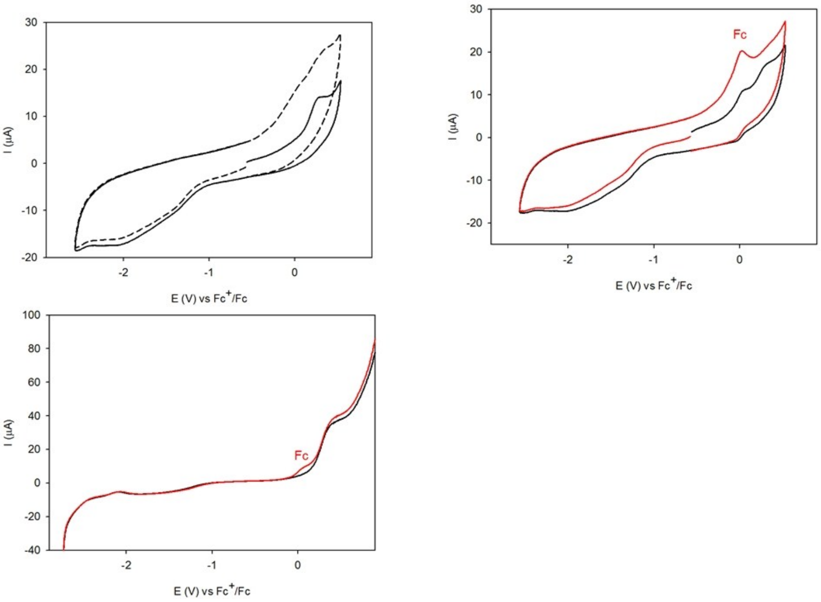


Fig. S3. Electrochemistry of **$Mn_{18}Sr$** [**2**, c = 1 mM in DMF, 0.1 $TBAPF_6$].

1.4 Chemical oxidation studies - GC-MS Analysis

General information

GC-MS analysis was performed on a GC System 7820A (G4320) connected to a MSD block 5977E (G7036A), using Agilent High Resolution Gas Chromatography Column: PN 19091S – 433UI, HP – 5MS UI, 28 mm x 0.250 mm, 0.25 Micron, SN USD 489634H. All samples were prepared in ethyl acetate (200 mL sample volume). Column oven temperature program was as follows: 60 °C for 1 min, ramped at 30 °C/min to 310 °C with 3 min hold, with a total running time of 12.33 min. The mass spectrometer was turned on after 2 min and was operated at the electron ionization mode with quadrupole temperature of 150 °C. Data acquisition was performed in the full-scan mode (50-500). Hydrogen (99.999 % purity) was used as carrier gas at a constant flow rate of 1.5 mL/min.

Yield determination and error analysis: GC Calibration

200 μL solutions of benzaldehyde and benzyl alcohol at different concentrations (0.05 M, 0.1 M, 0.2 M, 0.4 M, 0.6 M and 0.8 M) were prepared by diluting 5 M stock solutions of the compounds. For both components, a six-point graph was plotted, correlating the sum of characteristic GC peaks (as integrated automatically by the *Agilent MassHunter Workstation v.B.06.00* software) with substrate concentration. Each data point was obtained from three independent measurements and the correlation line was obtained from the least-squares fitting (intercept = 0). Error bars on graphs are shown as ± standard deviation for each data point. Overall percentage error of the response factor corresponds to ± standard deviation for each slope value.

The yields of products were calculated by comparing the product peak area with the calibration line. For the purpose of this study, reported are not the absolute percentage yields based on the number of moles of the starting materials, but rather percentage contributions to the total composition of the final reaction mixture. Each reaction was performed at least twice to ensure reproducibility, and reported percentage compositions are an average of these two runs.

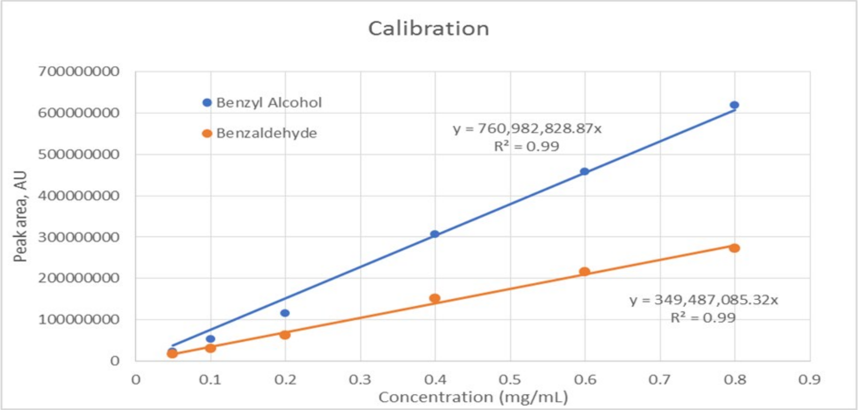


Fig. S4. Correlation between the concentration of an aqueous solution of benzaldehyde or benzyl alcohol and the measured gas chromatography peak area.

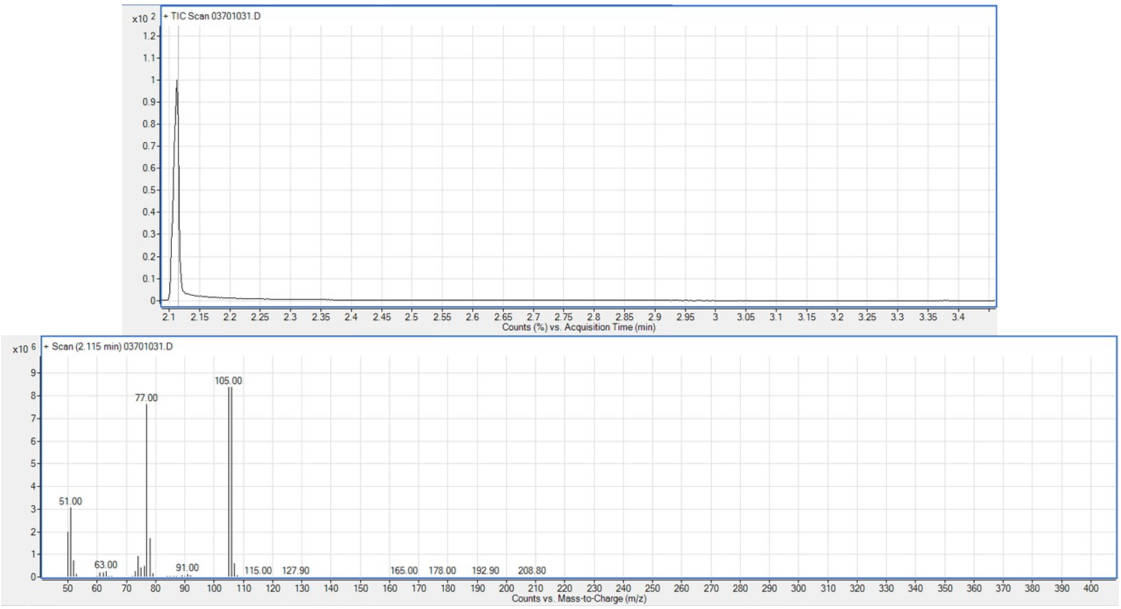


Fig. S5. GC trace and mass spectrum of benzaldehyde characteristic peak.

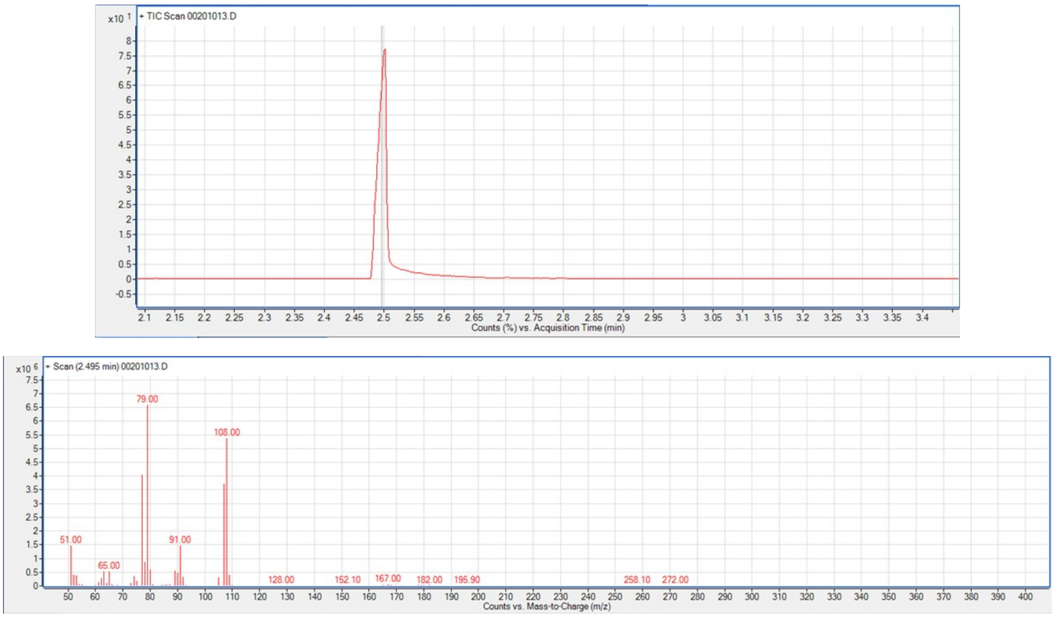


Fig. S6. GC trace and mass spectrum of benzaldehyde characteristic peak.

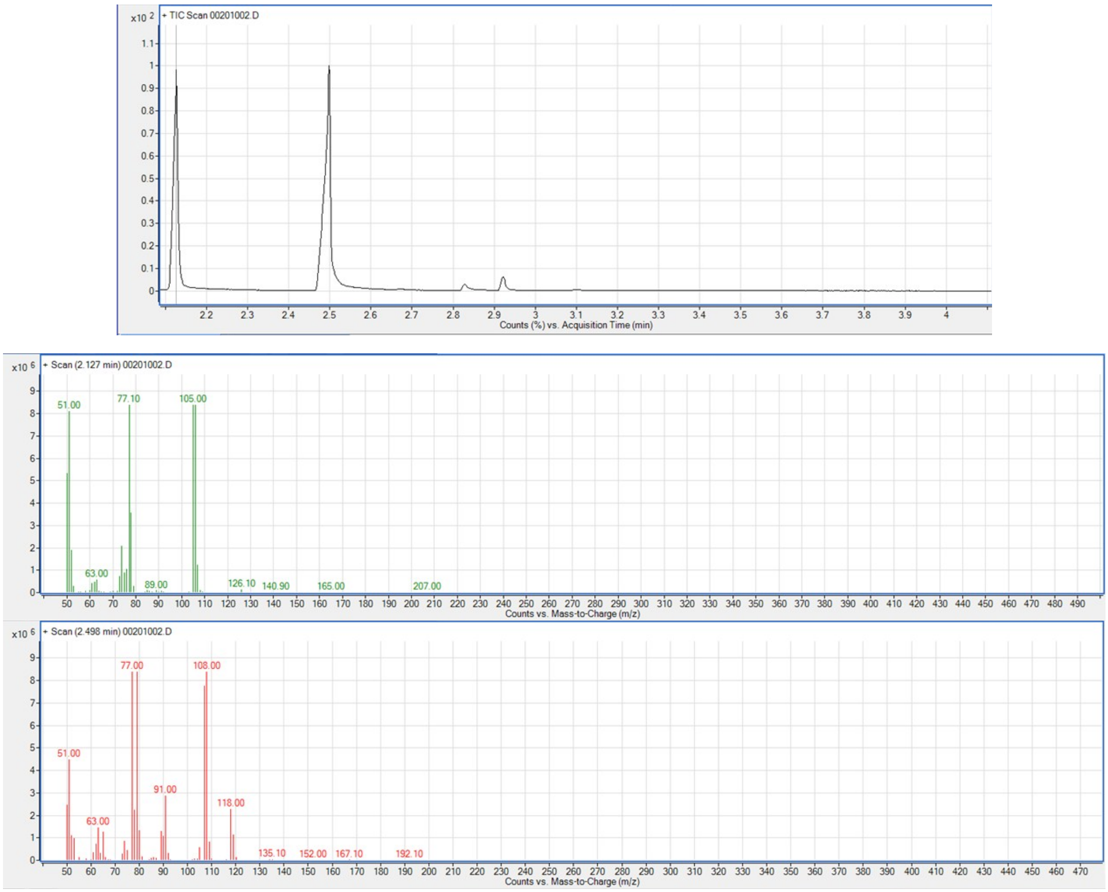


Fig. S7. Typical chromatogram of reaction mixture. (Peaks at 2.82 min and 2.91 min correspond to TEMPO)

Table S2. Solvent screening in the chemical oxidation of benzyl alcohol.

Composition (alcohol/aldehyde/other)*				
Solvent	**Mn_{19}**	**$Mn_{18}Sr$**	**other product**	**Temp. (° C)**
DMF	88/11	98/2	/	100
$CHCl_3$	99/1	99/1	/	65
DMSO	/	/	/	100
Toluene	97/3	98/2	/	100
MeCN	93/6	98/2	/	100
Ethyl Acetate	53/7/40	67/3/30	methyl phenylacetate	100

**DMF appears to be the best solvent for the experiment.*

1.5 IR Spectroscopy

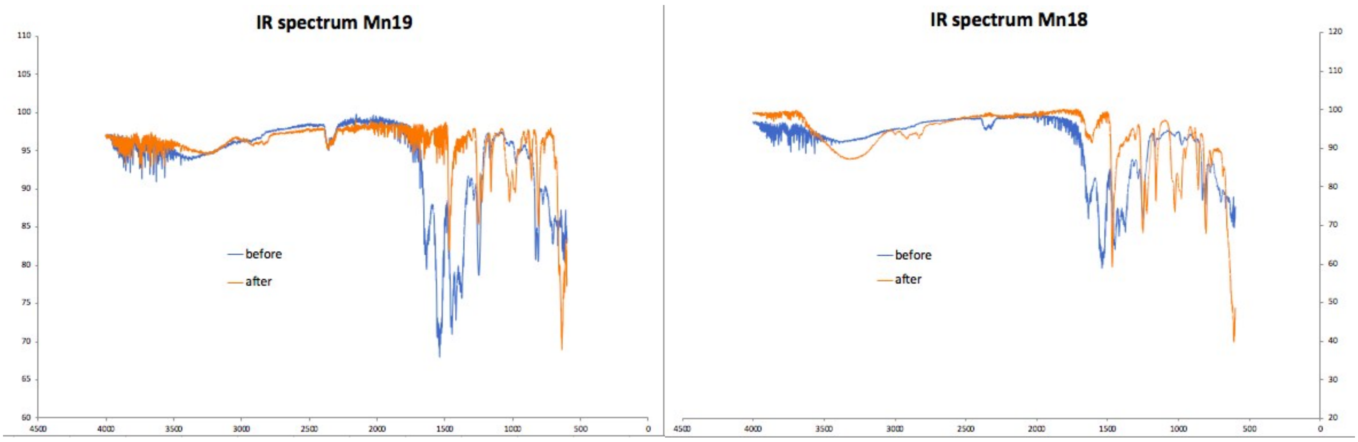


Fig. S08. IR spectra of catalysts Mn_{19} (**2**) (left) and $Mn_{18}Sr$ (**4**) (right) before and after chemical oxidation of Benzyl alcohol.

1.6 UV-Vis Spectroscopy

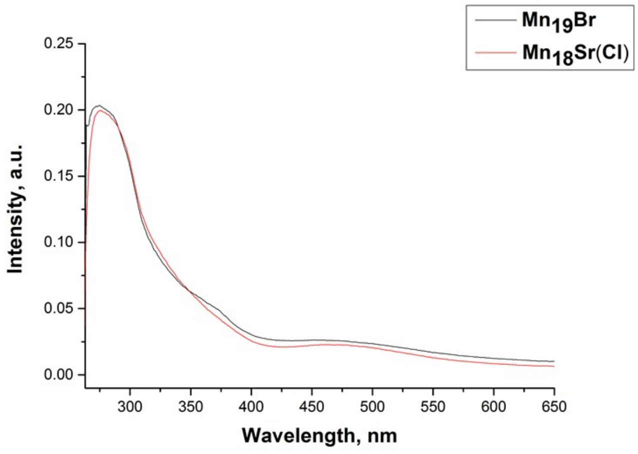


Fig. S09. UV-Vis spectrum of **2** (grey) and **3** (red) in DMF (10^{-5}M), λ_{max}=278 nm.

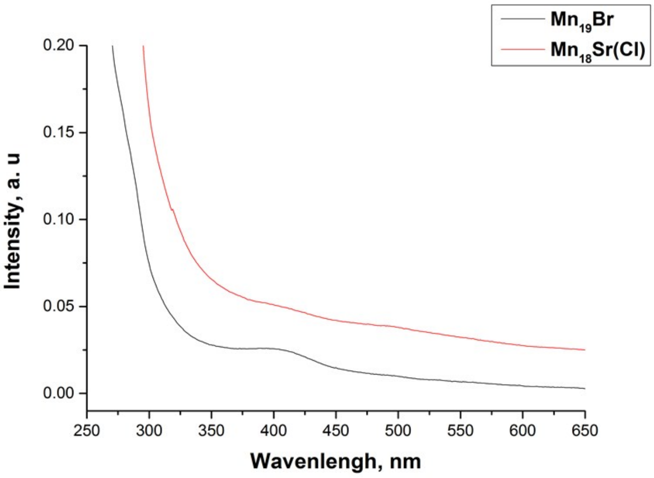


Fig. S10. UV-Vis spectrum of **2** (grey) and **3** (red) in DMF<<<< phosphate buffer (10^{-5}M), λ_{max}=278 nm.

1.7 Mass Spectroscopy

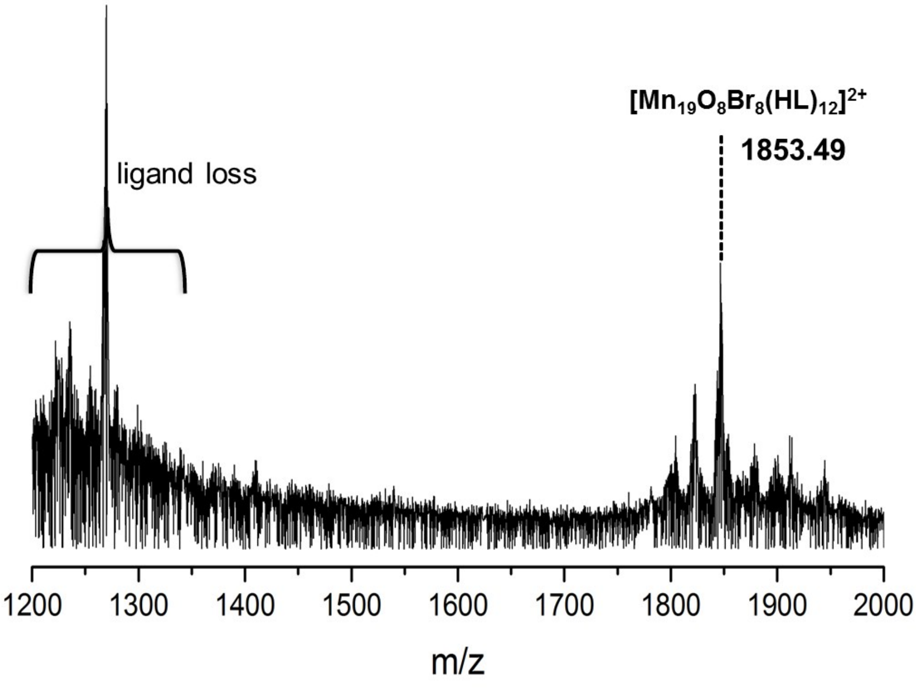


Fig. S11. ESI-MS of [Mn_{19}] (**2**) in DMF, featuring dication without apical MeOH solvents (**1853.49**).

$[Mn_{18}Sr(\mu_4\text{-}O)_8(\mu_3\text{-}Cl)_8(HL)_{12}(MeCN)_6]Cl_2$ = **4011.62**

$[C_{127}H_{154}Cl_8Mn_{18}N_6O_{51}Sr]^{2+}$ = **3940.72**; m/z = **1970.36**

Apical ligands are **MeCN** but these could exchange with **H_2O**

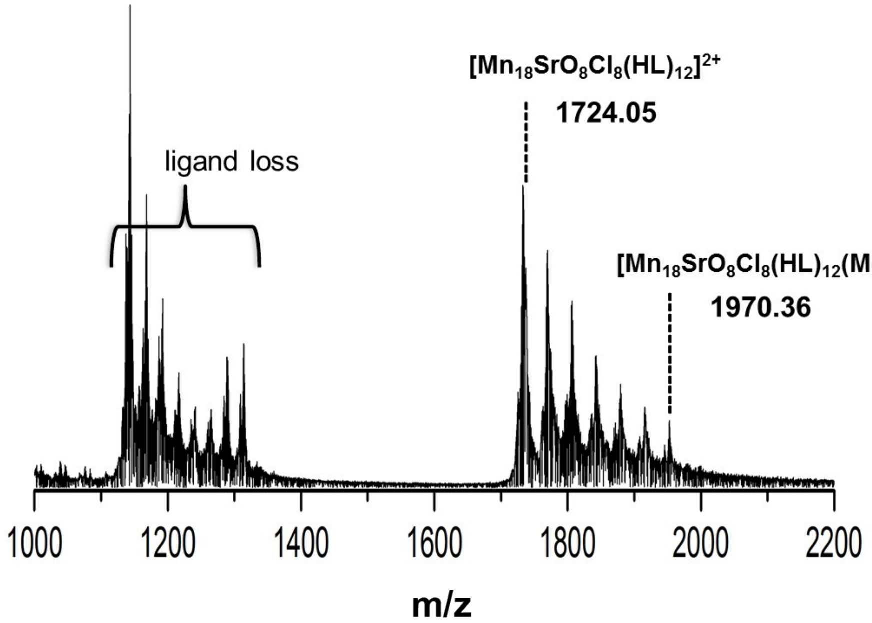


Fig. S12. ESI-MS of $[Mn_{18}Sr]$ (**3**) in DMF, featuring dication with (**1970.36**) or without (**1724.05**) MeCN apical solvents in DMF.

NOTE: For corresponding half fragment.Mn_{10}: $[Mn^{II}_4Mn^{III}_6(\mu_4\text{-}O)_4(\mu_3\text{-}OMe)(\mu_3\text{-}Br)_3(HL^{Me})_6(MeOH)_3]Br_2$ $\{Mn_{10}C_{58}H_{73}Br_3O_{26}\}$; M/z Dication 987.63855