nature catalysis

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41929-017-0004-2

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A bioinspired soluble manganese cluster as a water oxidation electrocatalyst with low overpotential

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Supplementary Information for

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Supplementary Methods

Materials

Manganese (II) acetate tetrahydrate was purchased from Acros organics. Potassium permanganate ($KMnO_4$) was purchased from Fisher chemicals. 3,5-dihydroxybenzoic acid was purchased from Fluka. Water (HPLC grade) and acetonitrile were purchased from Sigma Aldrich. Acetic acid was purchased from Gadot chemicals. THF and diethyl ether were purchased from Bio-Lab. Sodium acetate trihydrate was purchased from Merck. The purchased reagents and solvents were used without additional purification.

Synthesis

$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (**$Mn_{12}Ac$**)[1]: To a stirred solution of $Mn(O_2CMe)_2{\cdot}4H_2O$ (4.0 g, 16.3 mmol) in 60% v/v acetic acid in water (15 mL) was added a solution of

$KMnO_4$ (1.0 g, 6.33 mmol) in 60% v/v acetic acid in water (25 mL). The obtained dark brown solution was left undisturbed in an open flask. After 2 days at room temperature, dark brown crystals $Mn_{12}Ac{\cdot}2MeCO_2H{\cdot}4H_2O$ had grown, and they were collected by filtration, washed with acetone until the washings became colorless, and dried in vacuum. Yield: 50 %. IR (KBr pellet): 3598(w), 1709(w), 1588(m), 1559(m), 1521(m), 1451(s), 1388 (s), 1334(m), 1256(w), 1023(w), 714(m), 675(m), 640(m), 609(m), 563(w), 507(w), 517(w), 410(m) cm^{-1}.

$[Mn_{12}O_{12}(O_2CC_6H_3(OH)_2)_{16}(H_2O)_4]$ $(Mn_{12}DH)$: To a stirred solution of $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]{\cdot}2MeCN{\cdot}4H_2O$ (0.5 g, 0.24 mmol) in acetonitrile (40 mL) was added solid 3,5-dihydroxybenzoic acid (dhbH; 1.54 g, 10 mmol). The obtained solution (both reagents are soluble) was stirred overnight, during which time a brown precipitate had formed. This was collected by vacuum filtration, washed with acetonitrile (3x5 mL), THF (5 mL) and diethyl ether (3x5 mL), and dried in vacuum. Yield: 44%. The solid was analyzed as $[Mn_{12}O_{12}(O_2CC_6H_3(OH)_2)_{16}(H_2O)_4]{\cdot}10H_2O{\cdot}2MeCN$. IR (KBr pellet): 3318(b, vs), 1746(w), 1588(b, s), 1419(b, s), 1155(s), 1042(w), 1008(m), 946(w), 856(m), 783(m), 755(m), 670(m), 610(w), 555(w), 520(w), 440(w) cm^{-1}; UV/Vis: λ_{max} 300 nm; analysis (calcd., found for $C_{116}H_{114}N_2Mn_{12}O_{70}$): C (38.325, 38.465), H (3.160, 3.346), N (0.77, 0.9).

Instrumentation

Elemental analyses (C, H, N or C, H, N, and O) were performed in the in-house facilities of the Chemistry Department at the University of Florida and the in-house facilities of the Shulich Faculty of Chemistry at the Technion, Israel institute of Technology, on a Thermo-Scientific Flash 2000 elemental organic analyzer. At the

Technion, three measurements were performed, and each required 3 mg of the examined cluster. IR spectra (400-4000 cm^{-1}) were recorded on a Nicolet Nexus 670 spectrometer with the samples prepared as KBr pellets (UF instrument), on a "Bruker" FTIR spectrometer and on an "Agilent Cary 630" FTIR spectrometer, equipped with a diamond attenuated total reflection (ATR) instrument, which allows direct measurement with no sample preparation (Technion). UV-Vis spectroscopy measurements (200-800nm) were performed with a Jasco V-570 spectrometer (UF) or an Agilent Cary 60 spectrometer (Technion) at 25°C using a quartz cell with a 1 cm path length. X-ray Photoelectron Spectroscopy (XPS) was performed in the Major Analytical Instrumentation Center at the University of Florida using an XPS/ESCA Perkin-Elmer PHI 5100 ESCA System. Sample preparation was done as follows: a drop from a diluted water solution of the cluster was placed on a silica wafer and dried in air over night to form a monolayer, which was then subjected to XPS measurements. Samples were excited with Al X-ray source; pass energy of 89.45eV and work function of 5.15eV.

Electrochemistry

Electrochemical studies, cyclic voltammetry and controlled potential electrolysis, were conducted at room temperature using 563 model "IVIUMSTAT.XRe" potentiostat /galvanostat (Technion) or a CHI 660 potentiostat (ICIQ Tarragona). In ICIQ Tarragona, the CV experiments were performed under N_2 atmosphere inside a MBRAUN GloveBox using a IJ Cambria CHI-660D potentiostat, in a three electrode cell. A glassy carbon (GC) rod (diameter = 1 mm) was used as the working electrode, a platinum wire as the auxiliary electrode, and Ag/Ag+ (0.1 M TBAD-0.01M $AgNO_3$ in MeCN, +0.244V from SCE to NHE) as the reference electrode. CV experiments were recorded at a 10 $mV \cdot s^{-1}$

scan rate. $Mn_{12}Ac$ (8.7 μmol) was dissolved in 5 mL of dry MeCN (final concentration = 1.74 mM) containing the necessary amount of (n-Bu_4N)(PF_6)(TBAH), used as the supporting electrolyte.

Oxygen measurements

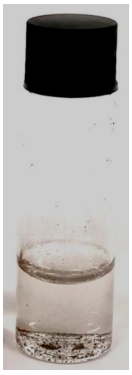
Direct oxygen measurements during bulk electrolysis were conducted using a "PreSens Microx 4" stand-alone optic fiber oxygen meter. The instrument is composed of optic fiber sensor housed inside a needle of a syringe. The needle is inserted to the cell at the anode compartment, and the evolved oxygen is measured at the headspace of the cell. The instrument displays the oxygen levels in μM, and in order to know the absolute amount of oxygen produced, in μmol, a calibration of the instrument was performed. Oxygen sensor calibration: A system containing an H-shaped cell with standard 3 electrodes arrangement was set up. To each compartment 5 ml of pH=6 acetate buffer was added. The system was sealed and degassed for 2 hours using Argon; the 0% oxygen value was then measured. By using Hamilton gas tight™ syringes, a known volume of 100% oxygen was added to the system in increments (0, 100, 250, 500, 750, 1000, 1250, 1500, 1750, 2000 μL) and the oxygen levels (in μM) were monitored over time. Then calibration curve was produced, comparing oxygen volumes to the measured μM values (Supplementary Figure 16). Oxygen volumes were converted to μmols using the RTP values of 24.465 Lit/mol @25°C 1 Atm. μM values can be converted into μmols by using the following equation: $\mu mol\_value = \{(\mu M\_Value - 14.263)/0.1902\}/24.456$

Data processing

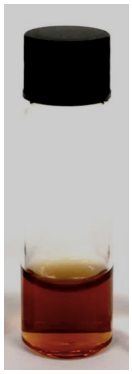
Data processing was done using Excel and graphs were plotted using KaleidaGraph.

Supplementary Figures

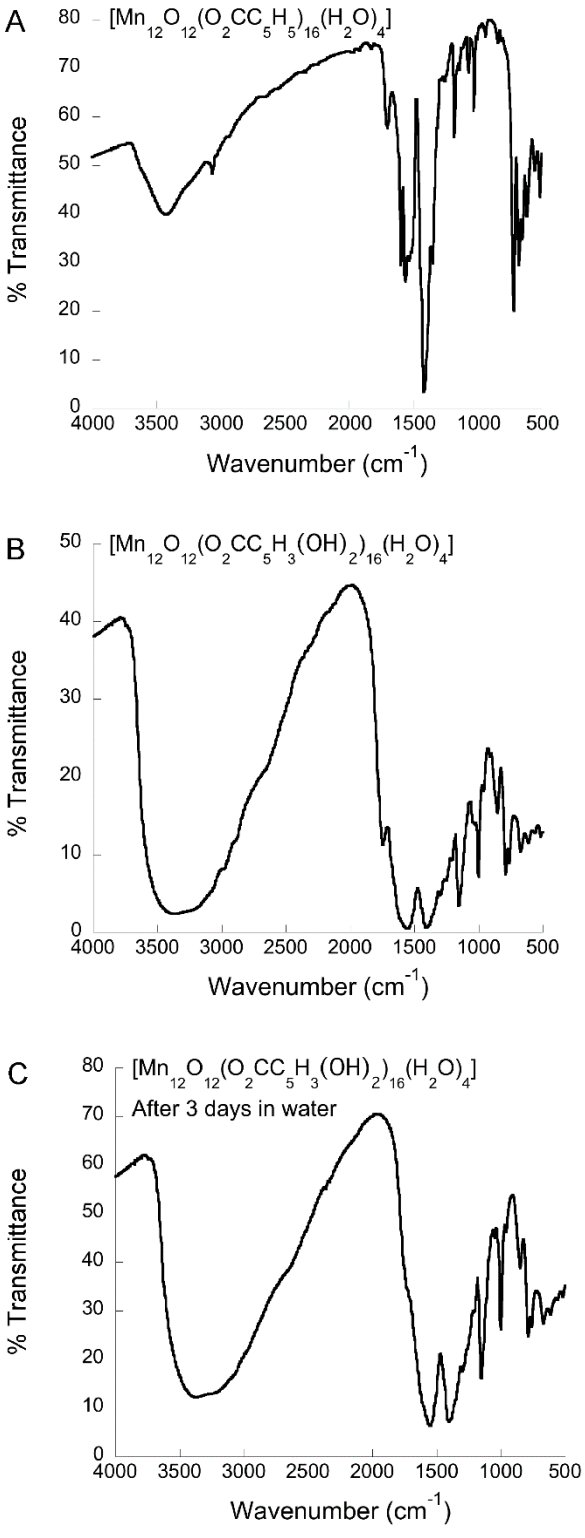
Supplementary Figure 1: Vial containing water and $Mn_{12}Ac$. $Mn_{12}Ac$ is soluble in water but rapidly undergoes hydrolysis to form a brown flocculent precipitate of Mn oxide.



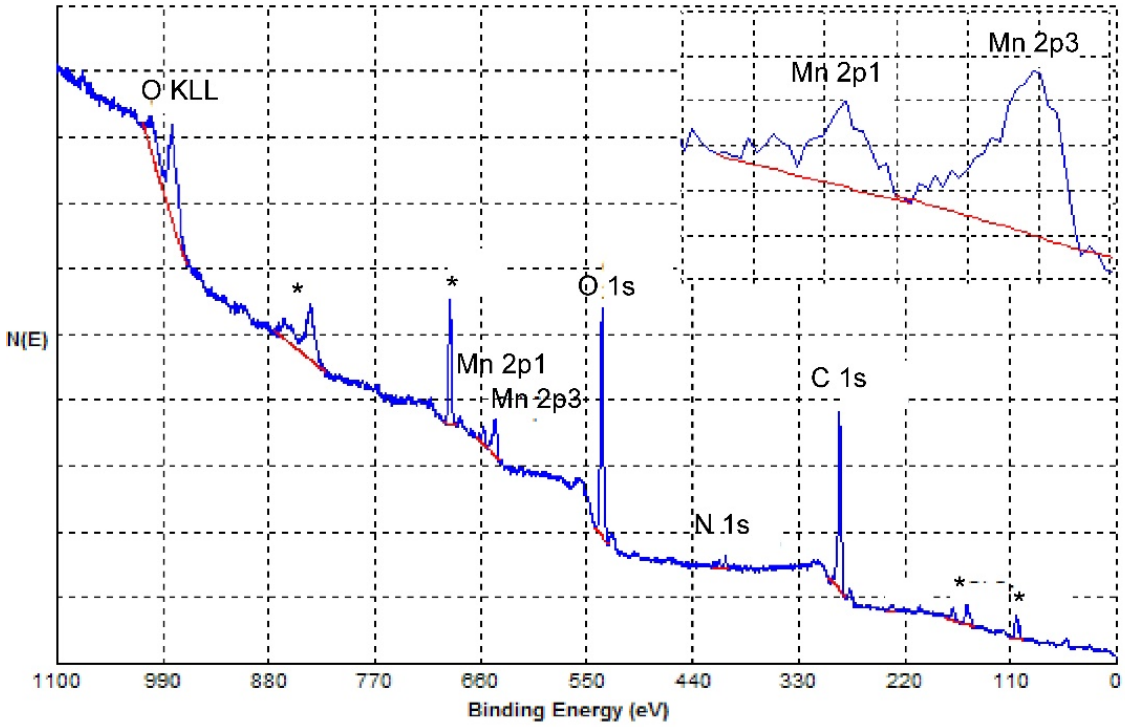
Supplementary Figure 2: Vial containing water and $Mn_{12}Bz$. $Mn_{12}Bz$ is completely insoluble in water.



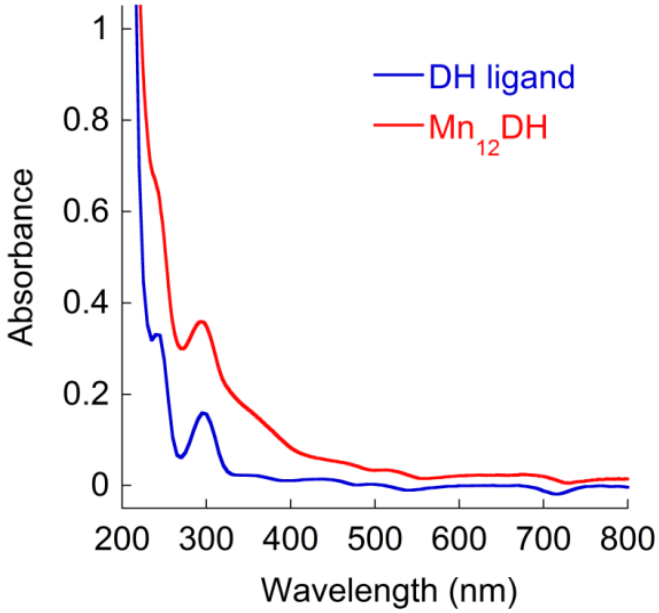
Supplementary Figure 3: Vial containing water and $Mn_{12}DH$. $Mn_{12}DH$ is very soluble in water and gives a persisting brown solution.



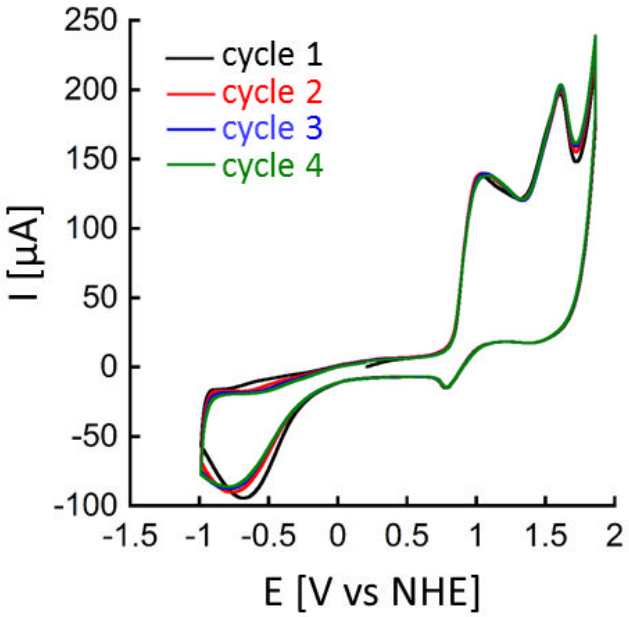
Supplementary Figure 4: FT-IR spectra of (A) $[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]$, (B) $Mn_{12}DH$ and (C) $Mn_{12}DH$ after it was dissolved in water and rest for three days. The spectra were recorded on KBr disks



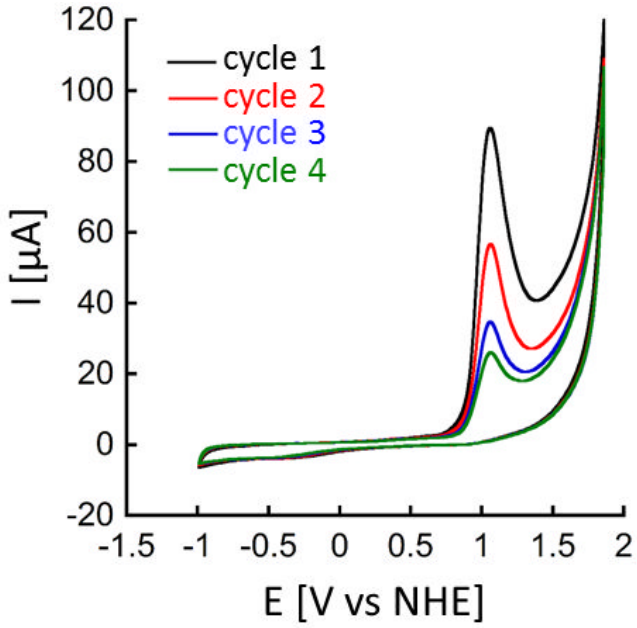
Supplementary Figure 5: X-ray Photoelectron Spectroscopy (XPS) spectrum of $Mn_{12}DH$.



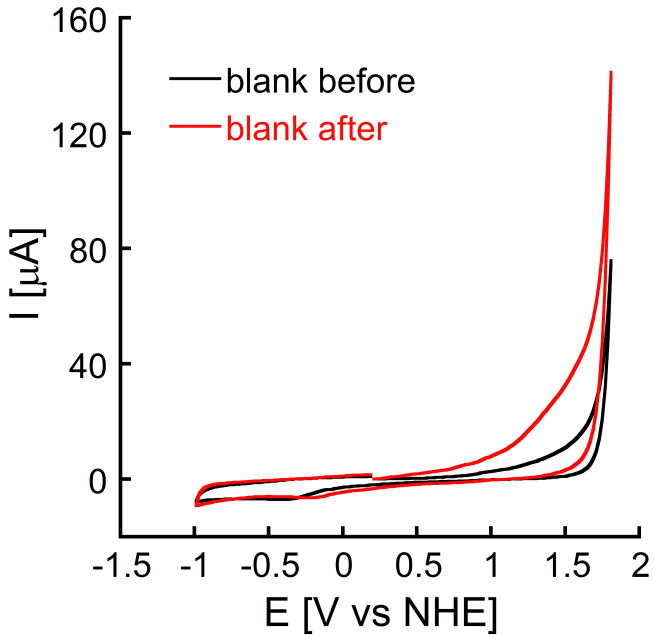
Supplementary Figure 6: UV-vis spectra of dhbH (blue curve) and $Mn_{12}DH$ (red curve) in water.



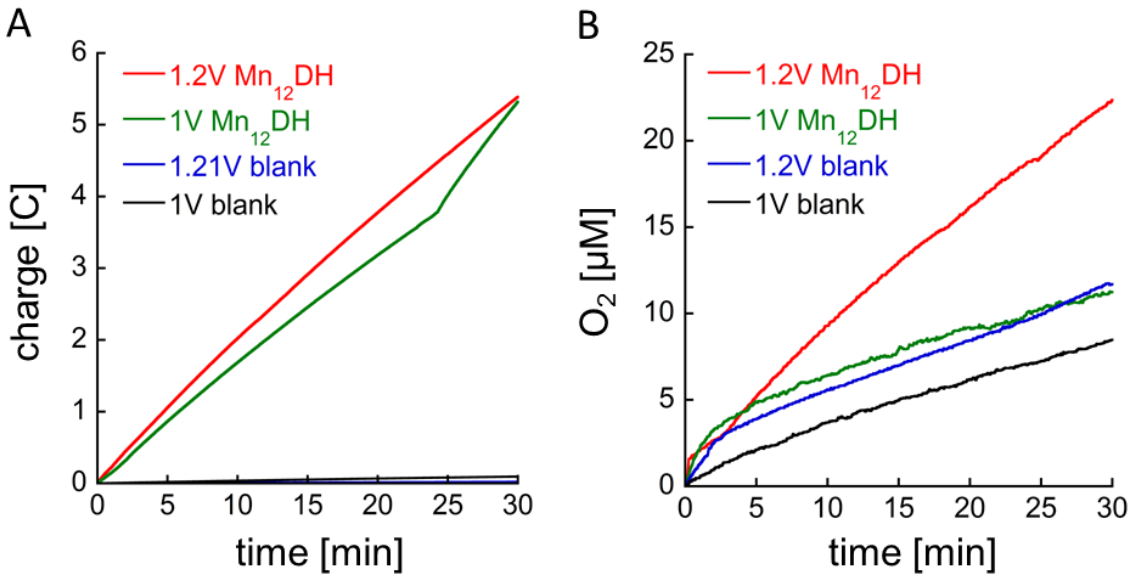
Supplementary Figure 7: Continuous CV scans of Mn_{12}DH over 4 cycles in 0.1 M acetate buffer, pH = 6.



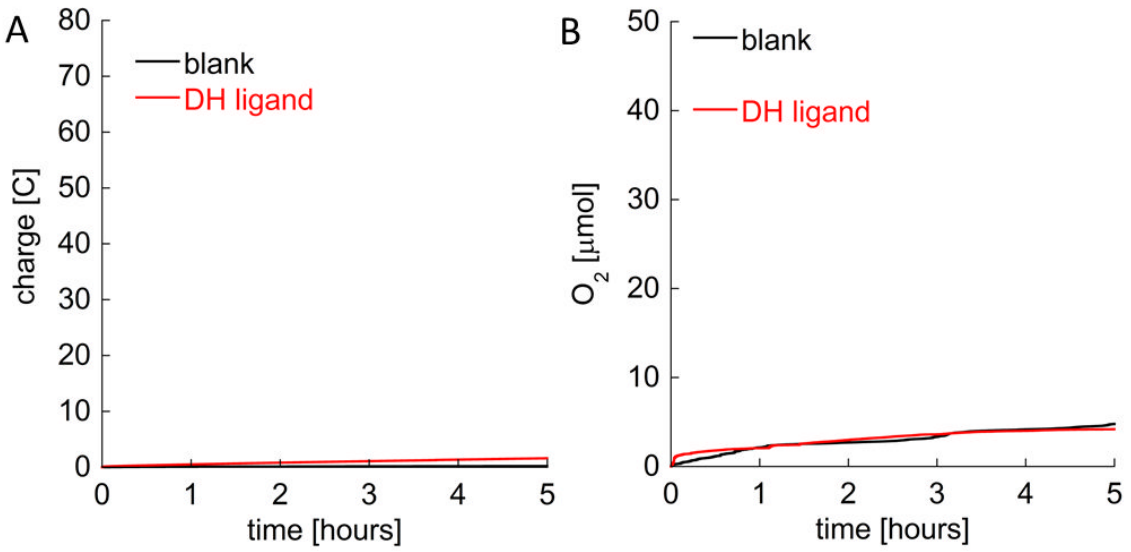
Supplementary Figure 8: Continuous CV scans over 4 cycles of the ligand dhbH in 0.1 M acetate buffer at pH = 6.



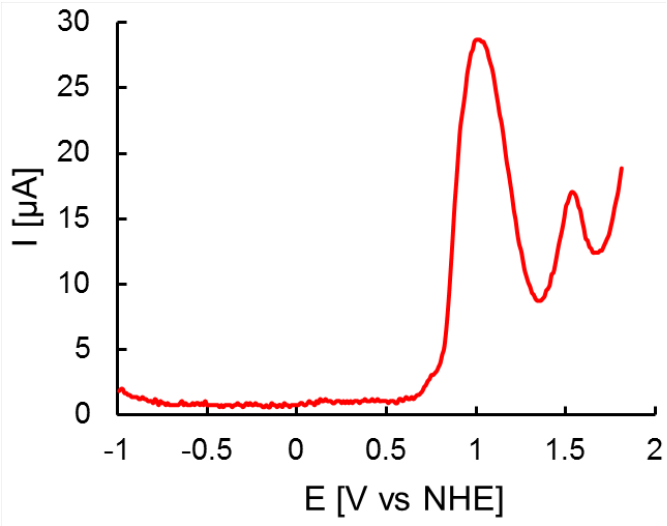
Supplementary Figure 9: CV scan of 0.1 M acetate buffer at pH = 6. Black line: By using a polished GC electrode. Red line: By using an unpolished GC electrode, which was previously used in an experiment were 25 continuous cycles to 1.81 V vs. NHE were done in a solution containing 0.5 mM of Mn_{12}DH at pH = 6, and rinsed with water.



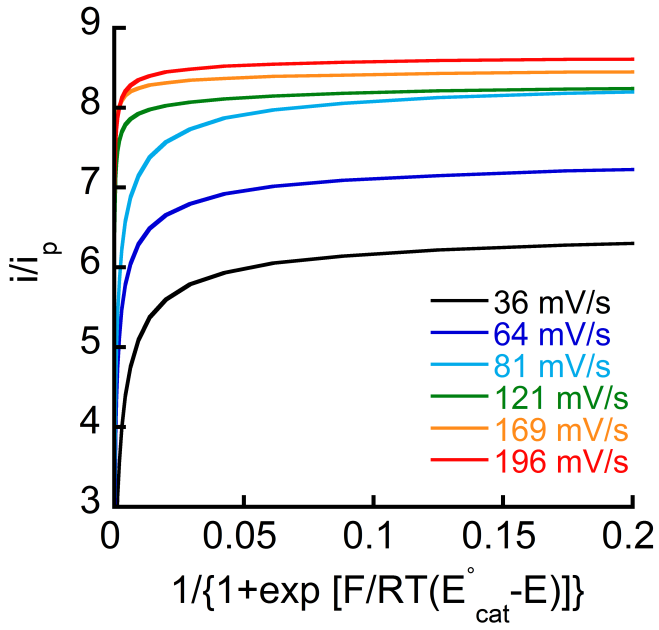
Supplementary Figure 10: Controlled potential electrolysis (CPE) experiments of 2µmol Mn_{12}DH in 0.1 M acetate buffer at pH = 6 at potential of 1.01 V and 1.21 V vs. NHE for 30 minutes.



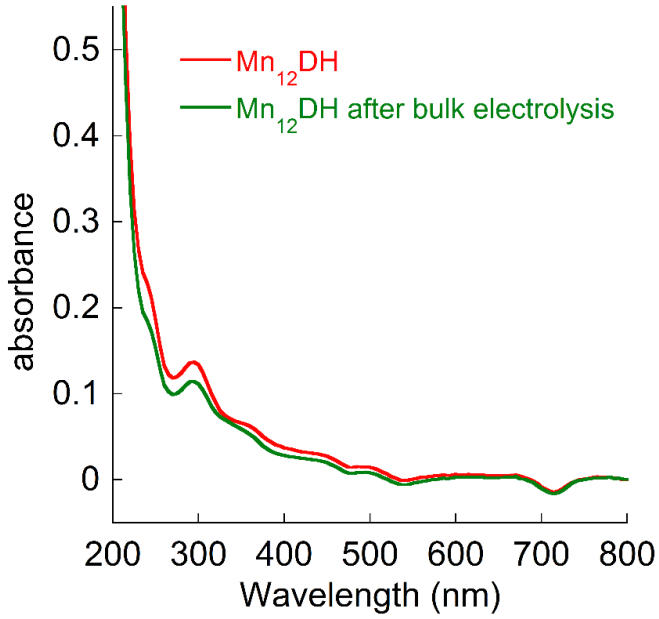
Supplementary Figure 11: Controlled potential electrolysis (CPE) experiments of 40 µmol dhbH in 0.1 M acetate buffer at pH = 6 at potential of 1.21 V vs. NHE for five hours.



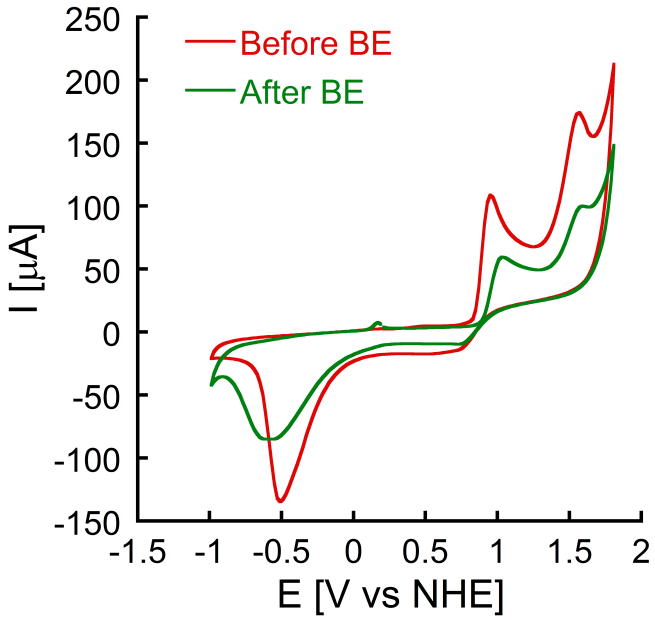
Supplementary Figure 12: DPV scan for 0.5mM Mn_{12}DH in pH = 6 acetate buffer.



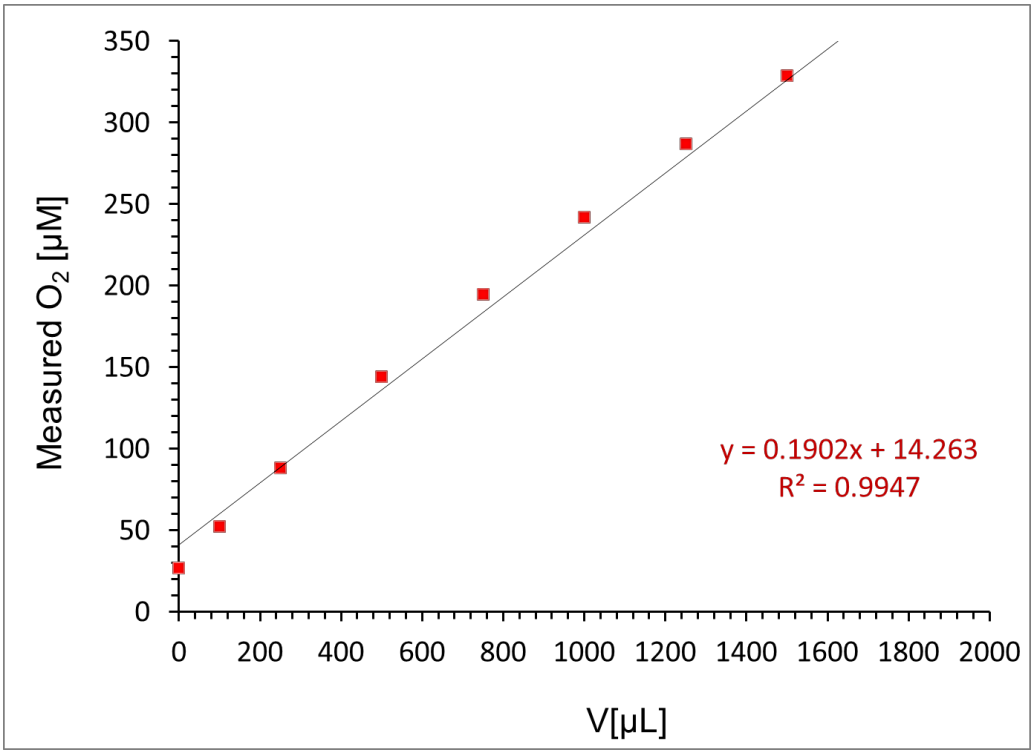
Supplementary Figure 13: Foot-of-the-wave analysis (FOWA) plotting i_{cat}/i_p vs. $1/(1+\exp[(F/RT)(E_{cat}-E)])$ at each scan rate. k_{obs} was extracted from the slope of the plot.[2,3,4]



Supplementary Figure 14: UV-Vis spectrum of the cluster $Mn_{12}DH$ in water before and after 5 hours controlled potential electrolysis (bulk electrolysis) at 1.21 V vs. NHE.



Supplementary Figure 15: CV scans before and after 5 hours controlled potential electrolysis (bulk electrolysis) of 0.5mM Mn_{12}DH in 0.1 M pH=6 acetate buffer.



Supplementary Figure 16: Oxygen calibration curve, used to convert µM values into µL and later to µmols.

Supplementary Equations:

$$\frac{i_{cat}}{i_p} = \frac{n \cdot 2.24\sqrt{\frac{RT \cdot K_{obs}}{F\nu}}}{1 + \exp\left[\frac{F}{RT} \cdot (E_{cat} - E)\right]}$$

Supplementary Equation 1: The formula used to obtain K_{obs} by Foot-of-the-wave analysis (FOWA).[5]

- E_{cat} - the standard potential for the catalysis-initiating redox couple (1.01V vs. NHE calculated from DPV, (see Supplementary Figure 14)
- i_{cat} –the catalytic current intensity in the presence of substrate.
- i_p - the non-catalytic current intensity (here we approximate this current to the current associated with the Mn^{III} reduction).
- n=4 (for water oxidation) the number of electrons in the reaction,
- F=96485 C·mol^{-1}, R=8.314 J·mol^{-1}K^{-1}, T=298K, ν - scan rate in V/s.

$$TON = \frac{t \cdot K_{obs}}{1+\exp\left[\frac{F}{RT} \cdot (E°_{cat} - E)\right]} = 628.61$$

Supplementary Equation 2: The equation used to calculate the turn over number (TON)[5]

- t- Bulk electrolysis duration, 18000s (5 hr).
- K_{obs} – averaged K_{obs} value obtained. (0.034937 s^{-1})
- E_{cat} - the standard potential for the catalysis-initiating redox couple (1.01V vs. NHE calculated from DPV, (see Supplementary Figure 14)
- E- BE operating potential 1.21V vs NHE.
- F=96485 C·mol^{-1}, R=8.314 J·mol^{-1}K^{-1}, T=298K.

Supplementary Tables:

Supplementary Table 1: Summary of the curve's slope presented in Supplementary Figure 15 and the K_{obs} obtained at each scan rate.

Rate (mV/s)	Slope	K_{obs} (s^{-1})
196	0.3846	0.014063
169	0.3639	0.010856
121	0.5870	0.020225
81	1.3622	0.07291
64	1.2916	0.051791
36	1.5093	0.039781
	Average:	0.034937

Supplementary References:

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