Supplementary Information

Mixed-valent nonanuclear [Mn$^{II}_5$Mn$^{III}_4$] molecular cluster with cubic topology of highest symmetry as bifunctional electrocatalyst for efficient water splitting

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Determination of turnover frequency (TOF) of catalyst 1 for OER from the redox features of CV:

Calculated area acquired from C_{dl} curve considering low scan rate of 30 mV/sec = 0.00913 mVAcm^{-2}

Hence, the associated charge = 0.00913 mVAcm^{-2} / 30 mVs^{-1}

$$= 0.0003043 \text{ Ascm}^{-2}$$

$$= \mathbf{0.0003043 \text{ Ccm}^{-2}}$$

Now, the number of electrons transferred = 0.0003043 Ccm^{-2} / 1.602 ×10^{-19} C

$$= \mathbf{0.190 \times 10^{15} \text{ cm}^{-2}}$$

The corresponding expression to determine Turnover Frequency (TOF) from OER current density is,

$$TOF = \frac{j \times N_A}{n \times F \times \tau} \quad \text{.................... (S1)}$$

where, j = current density, N_A = Avogadro number, F = Faraday constant, n = number of electrons for OER = 4, Γ = surface concentration.

Hence, we have,

TOF$_{1.74 \text{ V}}$ = [(0.126) Acm^{-2}(6.023× 10$^{23)}$)] mol^{-1} / [(96485) Cmol^{-1} (4) (0.190 × 10^{15}) cm^{-2}]

$$= \mathbf{1034 \text{ sec}^{-1}}$$

Determination of turnover frequency (TOF) of catalyst 1 for HER from the redox features of CV:

Calculated area acquired from C_{dl} curve considering low scan rate of 30 mV/sec = 0.000836 mVAcm^{-2}

Hence, the associated charge = 0.000836 mVAcm^{-2} / 30 mVs^{-1}

$$= 0.00002786 \text{ Ascm}^{-2}$$

$$= \mathbf{0.\,00002786 \text{ Ccm}^{-2}}$$

Now, the number of electrons transferred = 00002786 Ccm^{-2} / 1.602 ×10^{-19} C

$$= \mathbf{0.174 \times 10^{15} \text{ cm}^{-2}}$$

The corresponding expression to determine Turnover Frequency (TOF) from HER current density is,

$$TOF = \frac{j \times N_A}{n \times F \times \tau} \quad \text{.................... (S1)}$$

where, j = current density, N_A = Avogadro number, F = Faraday constant, n = number of electrons for HER =2, Γ = surface concentration.

Hence, we have,

TOF$_{-0.423 \text{ V}}$ = [(0.078) Acm^{-2}(6.023× 10$^{23)}$] mol^{-1} / [(96485) Cmol^{-1} (2) (0.174 × 10^{15}) cm^{-2}]

$$= \mathbf{1390 \text{ sec}^{-1}}$$

# Figures with captions
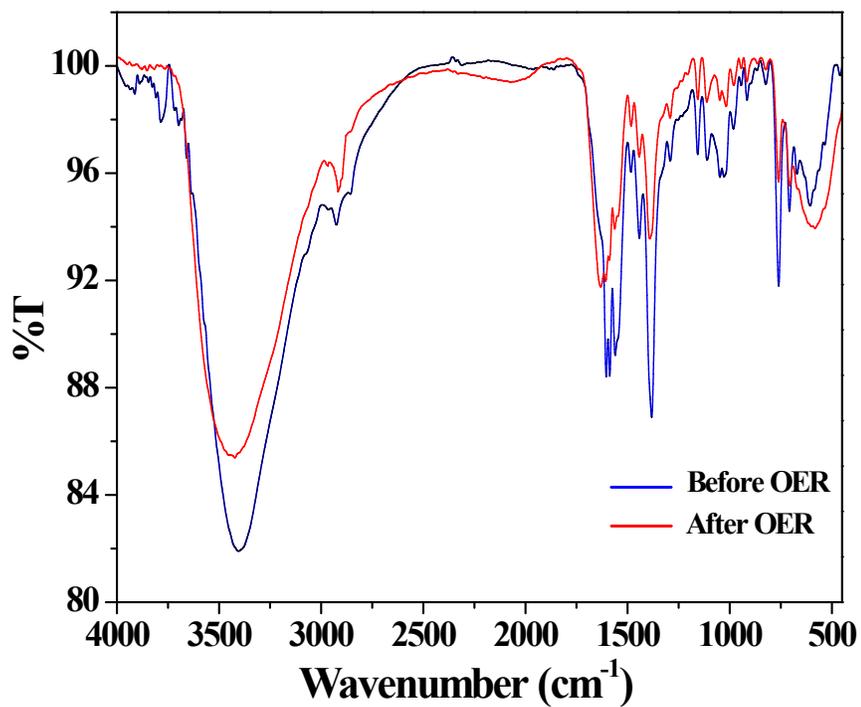
Fig. S1. FTIR spectra of **1** in the region of 4000-450 cm^{-1} before (—) and after (—) OER.
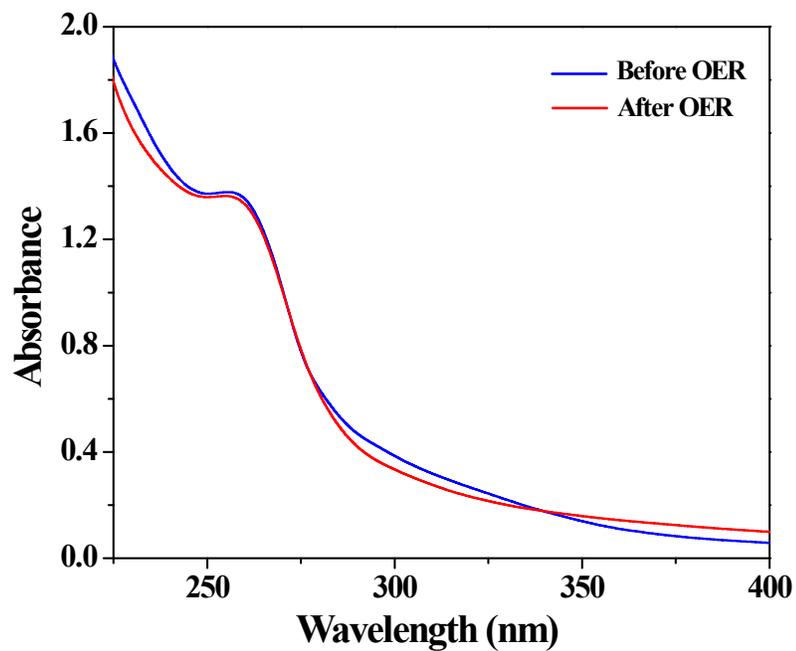
Fig. S2. UV-Vis spectra of **1** at 10^{-4} (M) in aqueous solution before (—) and after (—) OER.
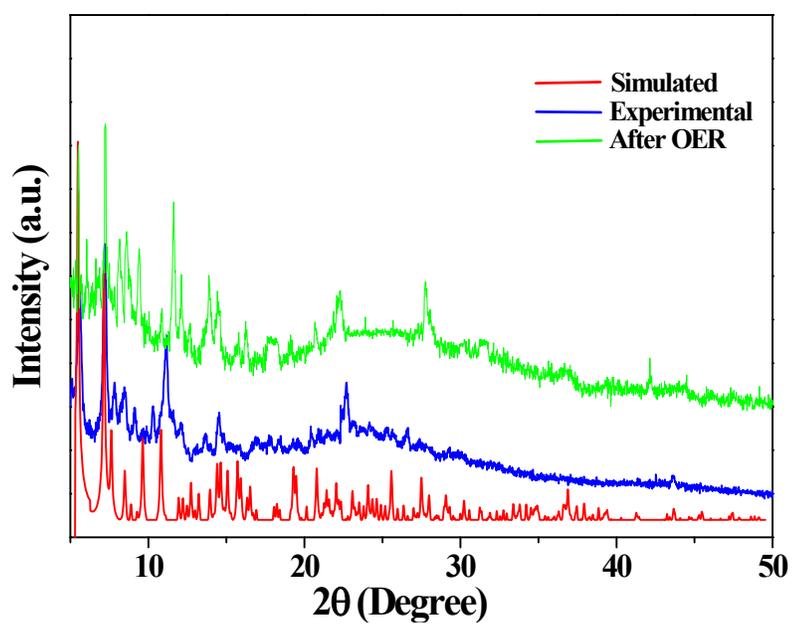

Fig. S3. Powder X-ray diffraction (PXRD) patterns of **1**: simulated PXRD (—), and experimental PXRD before (—) and after (—) OER.
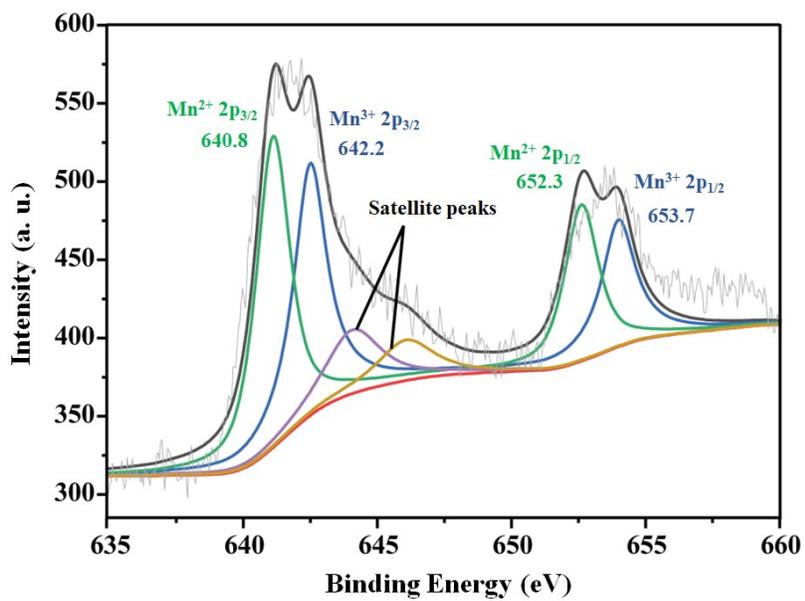
(a)
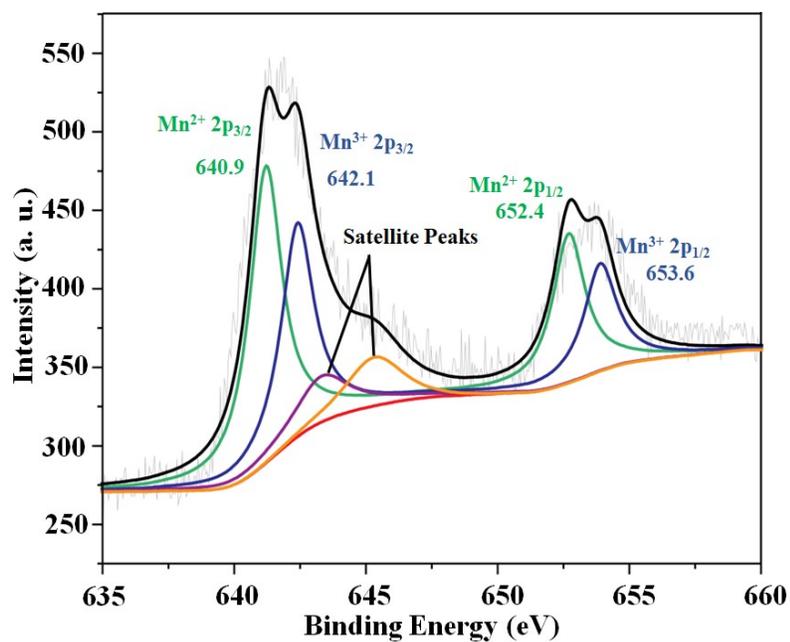
(b)

Fig. S4. X-ray photoelectron spectra (XPS) of the manganese 2*p* level in **1** (a) before and (b) after OER.
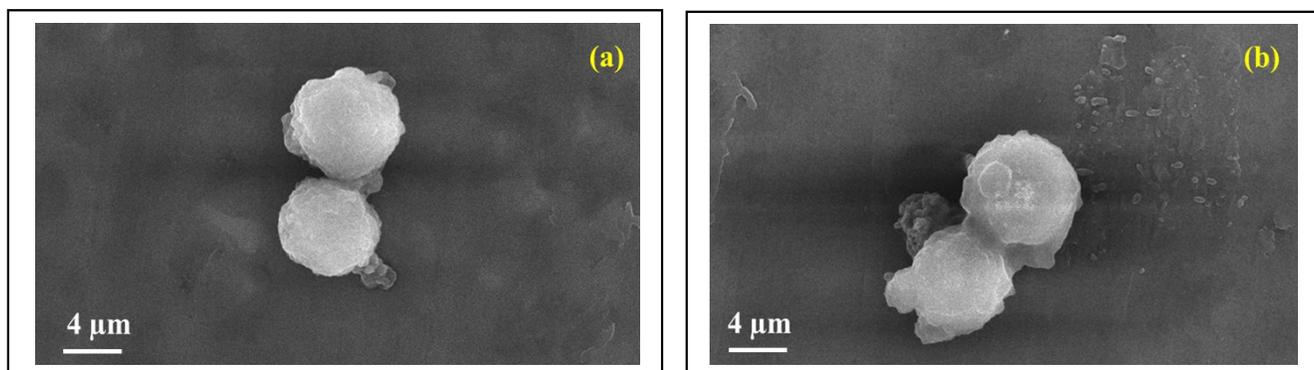
Fig. S5. Field emission scanning electron microscopic (FESEM) images of **1** (a) before and (b) after OER.
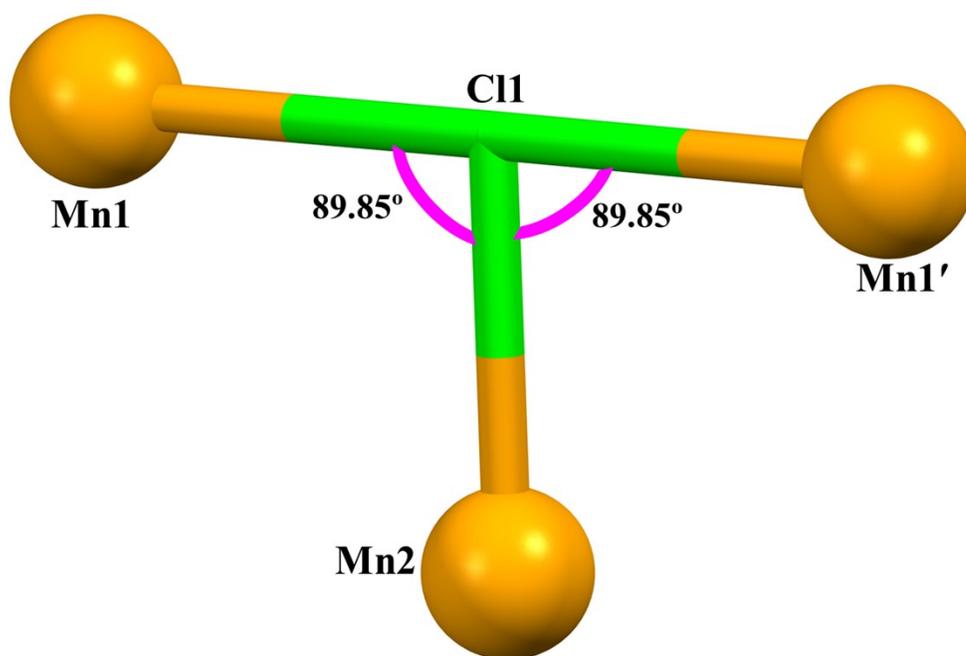

Fig. S6. Arrangement of Mn1, Mn2 and Mn1′ atoms with Cl1 atom in **1** making a T-shaped geometry.
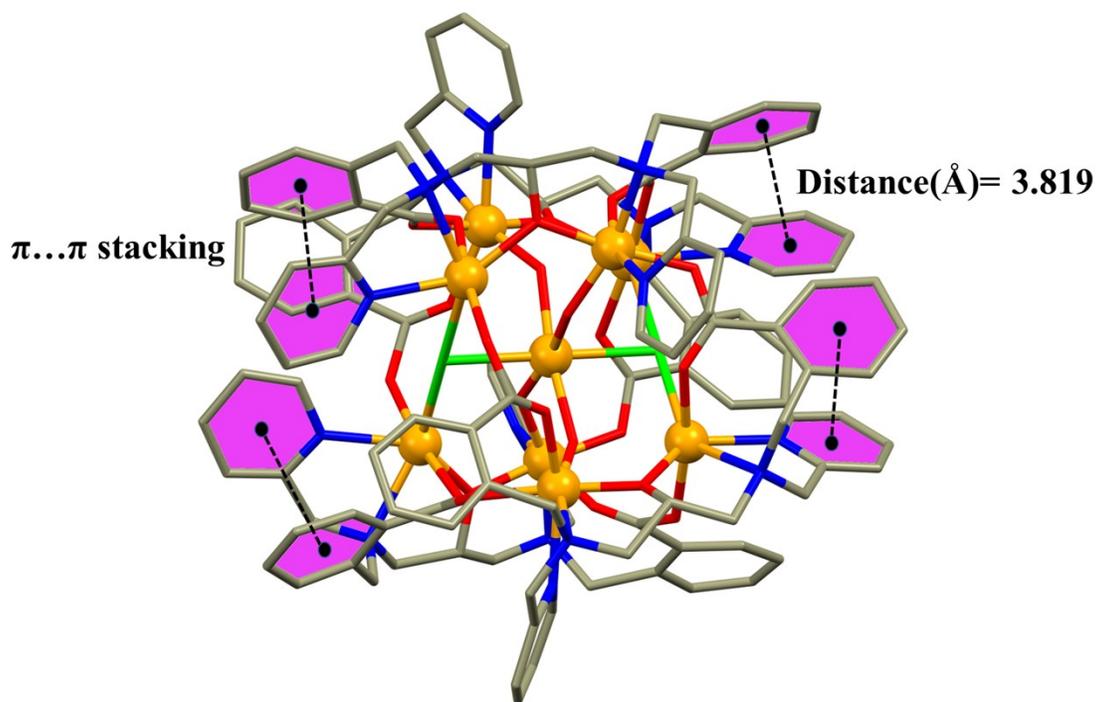
Fig. S7. A view of **1** showing intra-molecular $\pi\cdots\pi$ stacking interactions.
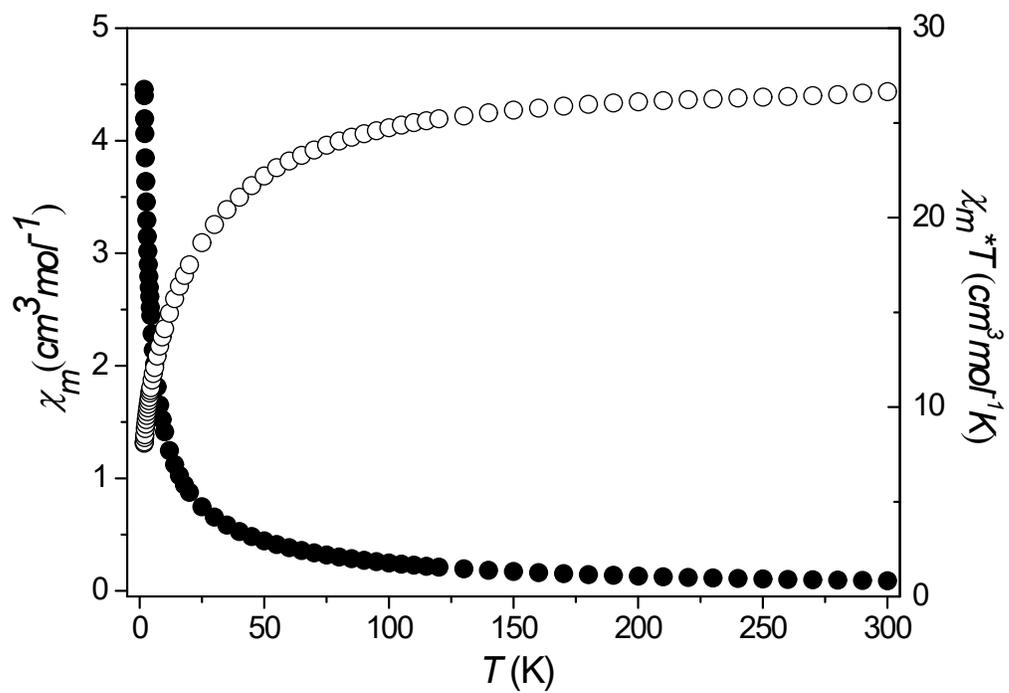
**Fig. S8.** Temperature dependence of χ_m ($\bullet$) and $\chi_m T$ ($\circ$) (χ_m per $Mn^{II}_5Mn^{III}_4$ unit) for **1**.
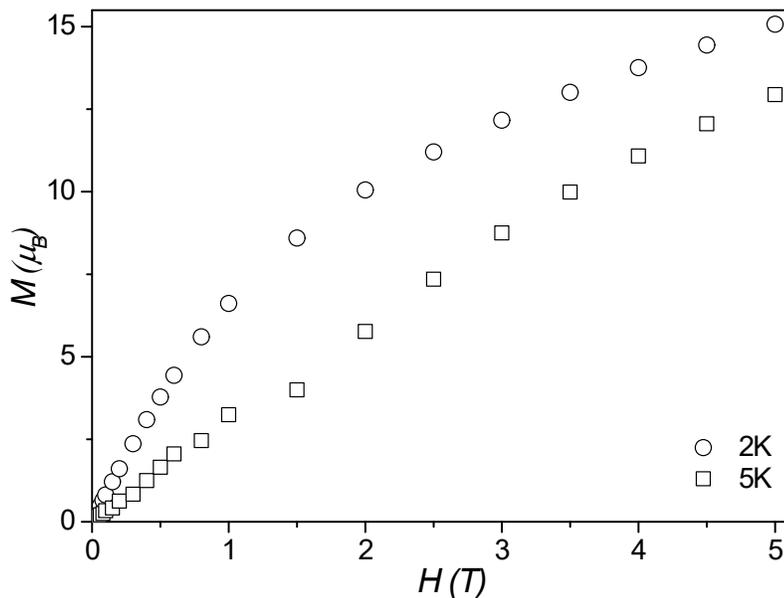
**Fig. S9.** Field (H) dependence of the magnetization (M) (magnetization per $Mn^{II}_5Mn^{III}_4$ unit) for **1** at 2 and 5 K.
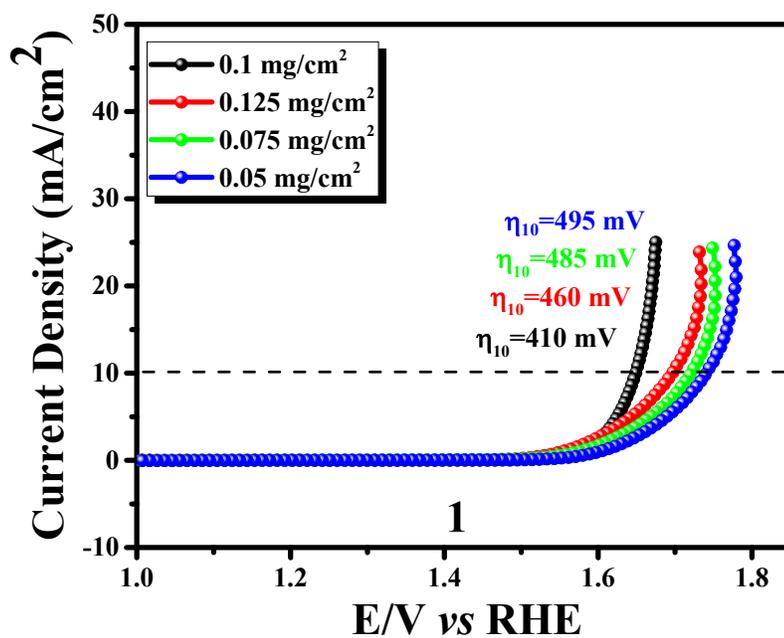
Fig. S10. Mass loading dependency of **1** for OER studies.
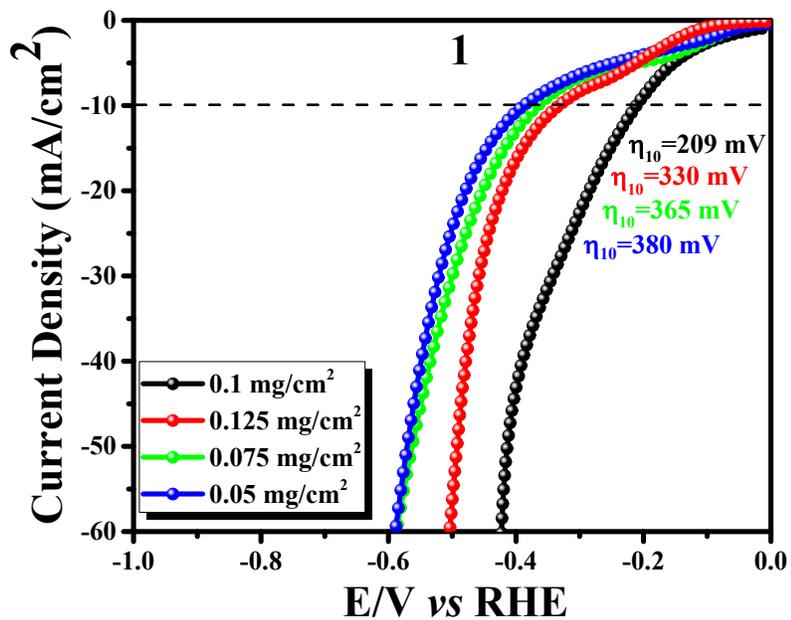
Fig. S11. Mass loading dependency of **1** for HER studies.
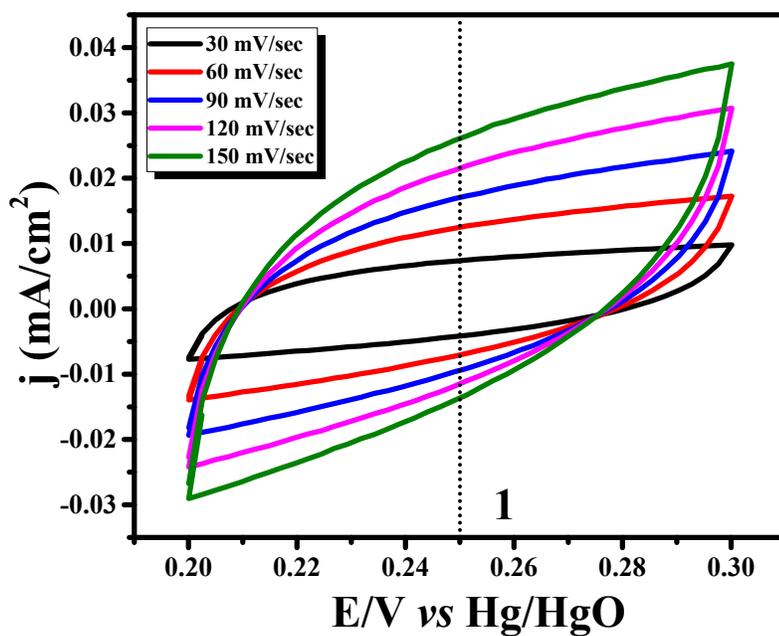
Fig. S12. CV outcomes of **1** under non-Faradaic region with various scan rates in OER studies.
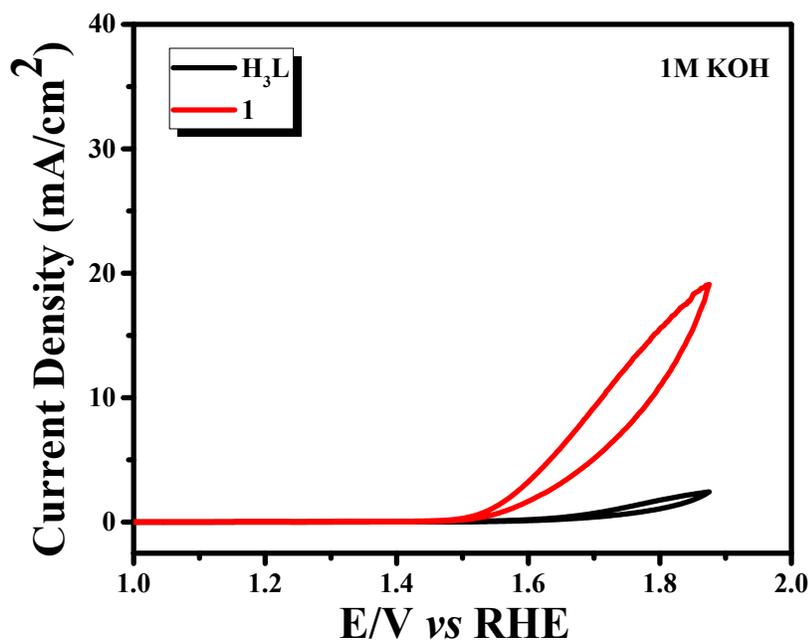
Fig. S13. CV outcomes of **H₃L** and cluster **1** in 1M KOH alkaline medium for OER studies.
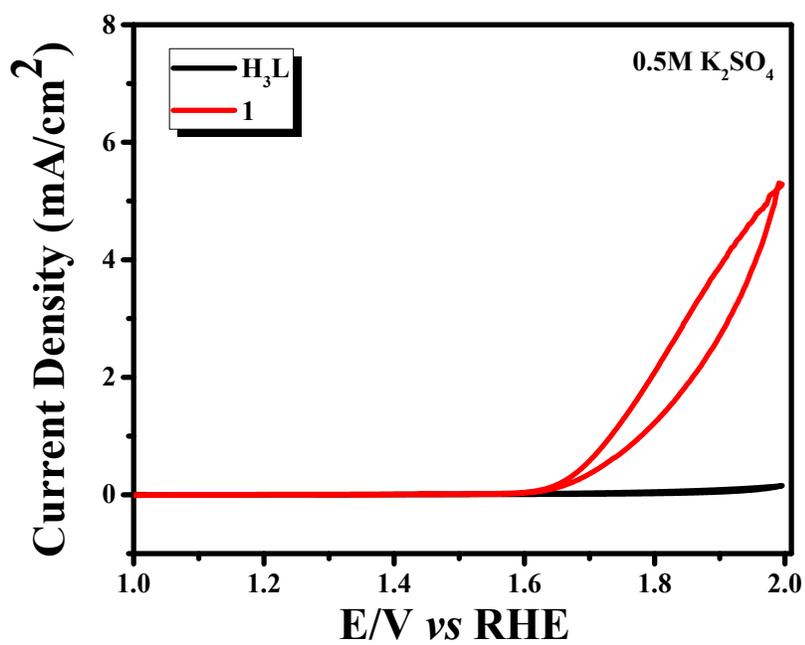
Fig. S14. CV outcomes of **H₃L** and cluster **1** in 0.5M K₂SO₄ neutral medium for OER studies.
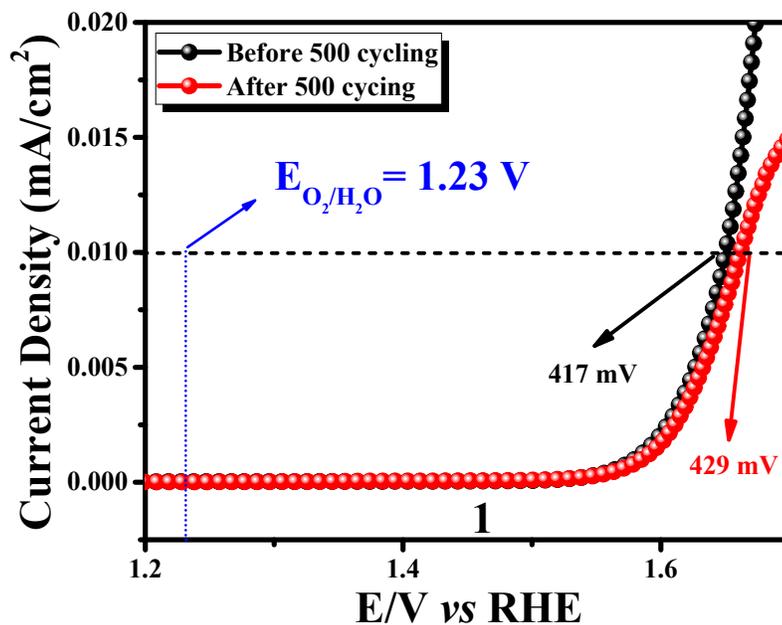
Fig. S15. LSV outcomes of **1** before and after OER AD studies.
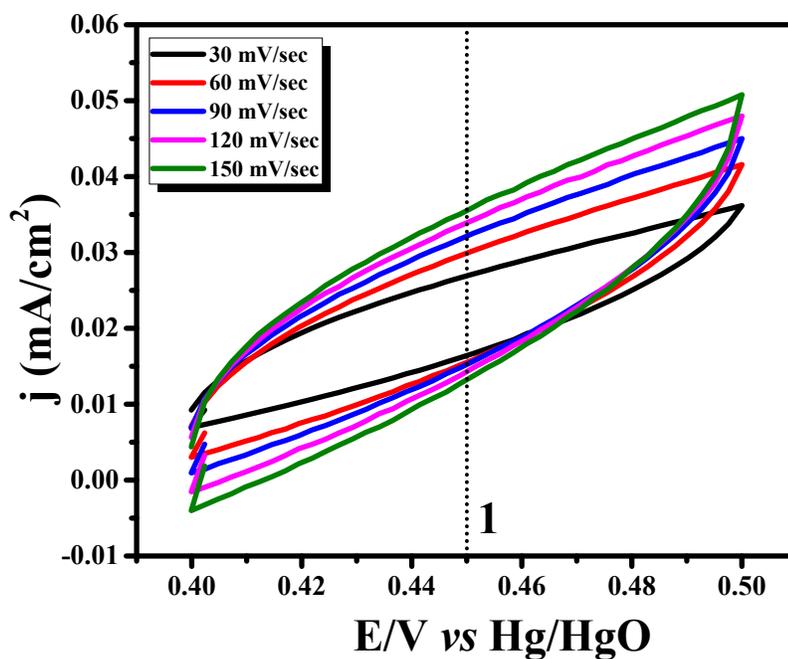
Fig. S16. CV outcomes of **1** under non-Faradaic region with various scan rates in HER studies.
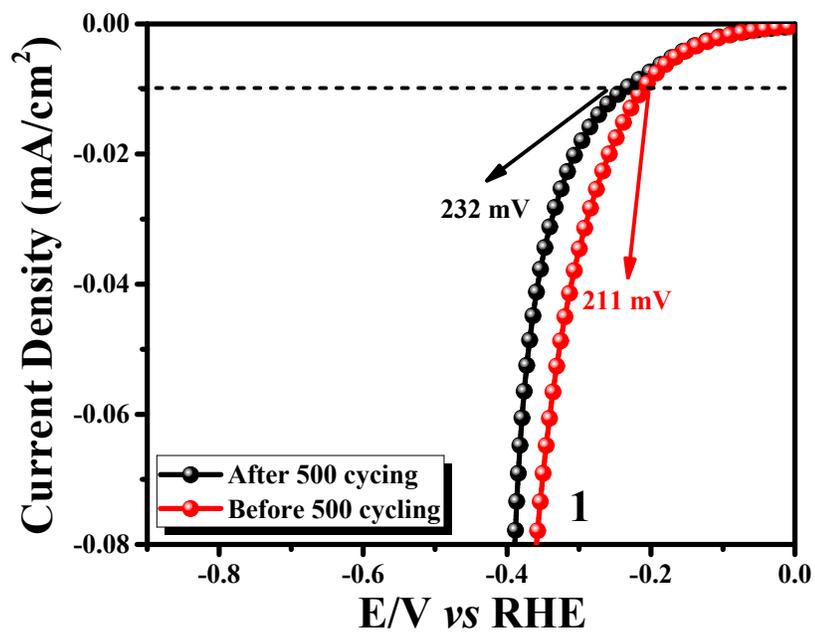
**Fig. S17.** LSV outcomes of **1** before and after HER AD studies.

Tables with captions

Table S1. Crystal data and refinement parameters for $[Mn_9L_4(\mu_2\text{-O})_4(\mu_3\text{-Cl})_2]$ (1)	
Empirical formula	$C_{124}H_{116}N_{16}O_{24}Cl_2Mn_9$
Formula weight	2779.689
Crystal system	cubic
Space group	$Ia\text{-}3d$
a, Å	48.362(2)
b, Å	48.362(2)
c, Å	48.362(2)
α, deg	90
β, deg	90
γ, deg	90
Volume, Å^3	113112(9)
Z	24
Density (calculated), Mg/m^3	0.979
Wavelength, Å	1.54178
Temperature, K	154.00
$F(000)$	34152
Absorption coefficient, mm^{-1}	5.414
θ range for data collection, deg	2.238 to 31.362
Reflections collected	1534
Independent reflections	1362
$R(F$ obsd data) [I >2σ(I)]	0.0945
$wR(F^2$ all data)	0.2610
Goodness-of-fit on F^2	1.102
Largest diff. peak and hole, e/Å^3	+0.376 to -0.443

$wR2 = \{\Sigma\ [w(F_o^2 - F_c^2)^2]\ /\ \Sigma\ [w(F_o^2)^2]\}^{1/2}R1 = \Sigma\ ||F_o| - |F_c||\ /\ \Sigma\ |F_o|$

Table S2. Selected bond distances (Å) and angles (deg) for [Mn$_9$(L)$_4$(μ_2-O)$_4$(μ_3-Cl)$_2$] (**1**)

Bond distances (Å)			
Mn(1)-O(1)	2.103(16)	Mn(2)-Cl(1)	2.537(10)
Mn(1)-O(2)	2.178(18)	Mn(3)-O(1)	1.890(17)
Mn(1)-O(5)	2.19(2)	Mn(3)-O(3)	1.89(2)
Mn(1)-N(1)	2.44(2)	Mn(3)-O(4)	2.176(17)
Mn(1)-N(2)	2.33(2)	Mn(3)-O(6)	1.921(15)
Mn(1)-Cl(1)	2.777(4)	Mn(3)-N(3)	2.13(2)
Mn(2)-O(6)	2.192(13)	Mn(3)-N(4)	2.29(2)
Bond angles (deg)			
O(1)-Mn(1)-O(2)	84.2(6)	O(6)-Mn(2)-O(6′)	90.29(5)
O(1)-Mn(1)-O(5)	92.5(6)	Cl(1)-Mn(2)-Cl(1′)	180.0
O(1)-Mn(1)-N(1)	71.5(7)	O(1)-Mn(3)-O(3)	173.1(8)
O(1)-Mn(1)-N(2)	138.3(8)	O(1)-Mn(3)-O(4)	94.9(6)
O(1)-Mn(1)-Cl(1)	135.3(5)	O(1)-Mn(3)-O(6)	82.4(7)
O(2)-Mn(1)-O(5)	173.3(7)	O(1)-Mn(3)-N(3)	82.0(8)
O(2)-Mn(1)-N(1)	79.2(7)	O(1)-Mn(3)-N(4)	96.3(7)
O(2)-Mn(1)-N(2)	105.5(7)	O(3)-Mn(3)-O(4)	84.9(7)
O(2)-Mn(1)-Cl(1)	79.1(5)	O(3)-Mn(3)-O(6)	104.5(7)
O(5)-Mn(1)-N(1)	105.3(8)	O(3)-Mn(3)-N(3)	91.1(8)
O(5)-Mn(1)-N(2)	80.9(7)	O(3)-Mn(3)-N(4)	81.9(7)
O(5)-Mn(1)-Cl(1)	99.5(6)	O(4)-Mn(3)-O(6)	93.8(6)
N(1)-Mn(1)-N(2)	70.8(9)	O(4)-Mn(3)-N(3)	87.6(8)
N(1)-Mn(1)-Cl(1)	142.6(6)	O(4)-Mn(3)-N(4)	159.0(7)
N(2)-Mn(1)-Cl(1)	86.3(7)	O(6)-Mn(3)-N(3)	164.3(8)
O(6)-Mn(2)-Cl(1)	94.1(4)	O(6)-Mn(3)-N(4)	105.3(7)
O(6′)-Mn(2)-Cl(1)	85.9(4)	N(3)-Mn(3)-N(4)	76.4(8)

Table S3. Overpotential (η) and current density (j) values of some reported metal oxide- or metal chelate-based electrocatalysts towards oxygen evolution reaction (OER)

Sl. No.	Metal Oxide/Metal Chelate-Based Elecrocatalysts	Overpotential (η) (mV)	Current Density (j) (mA/cm^2)	Ref.
1.	MnO_2-$Ni_{0.002(M)}$	445	10	53
2.	Carbon Dots 0.15-MnO2	343	10	54
3.	urchin-like α-MnO_2	640	-	55
4.	Co-intercalated layered MnO_2	360	10	56
5.	α-MnO_2-SF	490	10	57
6.	$(NMe_4)[Cu^{III}(L_1)]$	560	-	58
7.	$[Fe^{III}(dpaq)(H_2O)](ClO_4)_2$	200-250	-	59
8.	$[Mn_9L_4(\mu_2\text{-}O)_4(\mu_3\text{-}Cl)_2]$	410	10	This Work

Table S4 Overpotential (η) and current density (j) values of some reported metal oxide- or metal chelate-based electrocatalysts towards hydrogen evolution reaction (HER)

Sl. No.	Metal Oxide/Metal Chelate-Based Elecrocatalysts	Overpotential (η) (mV)	Current Density (j) (mA/cm^2)	Ref.
1.	Ni@NiL1-Sal	384	10	66
2.	$[Mo_3S_{13}]^{2-}$ Cluster	220	10	67
3.	$[Ag_4(S_2PFc(OMe)_4]$	932	5	68
4.	$[MnBr(pybz)(CO)_3]$	280	10	69
5.	$[\{Cu^{II}(2,2'\text{-bpy})(H_2O)_2\}][\{Co^{II}W^{VI}_{12}O_{40}\}\{Cu^{II}(2,2'\text{-bpy})(H_2O)\}\{Cu^{II}(2,2'\text{-bpy})\}]\cdot 2H_2O$	520	1	70
6.	$[(UO_2)_2(\mu\text{-L})_2]$	274	-	71
7.	$K_{10}[\{K_4(H_2O)_6\}\{UO_2\}_2(\alpha\text{-}PW_9O_{34})_2]\cdot 13H_2O$	115	1	72
8.	MnO$_x$/Ti	240	100	73
9.	$[Mn_9L_4(\mu_2\text{-O})_4(\mu_3\text{-Cl})_2]$	**209**	**10**	**This Work**