

## Electronic Supporting Information

# An one-dimensional chain of manganese(II) bridged peroxomolybdate isolated from aqueous Mn-polymolybdate-H<sub>2</sub>O<sub>2</sub> system

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### Materials and methods

(NH<sub>4</sub>)<sub>6</sub>[MnMo<sub>9</sub>O<sub>32</sub>]·6H<sub>2</sub>O was synthesised according to the literature method<sup>1</sup>. All other chemical reagents were commercially available and used without further purification, including MnSO<sub>4</sub>·H<sub>2</sub>O (AR, Aladdin), (NH<sub>4</sub>)<sub>4</sub>[Mo<sub>7</sub>O<sub>24</sub>]·4H<sub>2</sub>O (AR, Aladdin), 30% H<sub>2</sub>O<sub>2</sub> (AR, SCR), CsNO<sub>3</sub> (AR, Aladdin), CH<sub>3</sub>COOH (AR, SCR), CuSO<sub>4</sub>·5H<sub>2</sub>O (AR, SCR). TGA measurements were executed by a SDT Q600 thermogravimetric analyzer in a flowing air atmosphere from 25 to 800°C with a heating rate of 10°C·min<sup>-1</sup>. UV–Vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrophotometer. The concentration of each substance in the TMB and OPD reaction system is: 30 mM TMB/OPD, 300 mM H<sub>2</sub>O<sub>2</sub>, 0.303 mM **Cs-1** (in TMB system), 60.6 μM **Cs-1** (in OPD system), 0.6M acetate buffer with pH 4.5, reaction for 20 min. UV–Vis DRS measurements were executed by a PerkinElmer Lambda 650s spectrophotometer. PXRD patterns collected in the 2θ range from 5° to 50° were acquired on a Bruker D2 Phaser diffractometer with Cu-Kα (λ = 0.15418 nm) radiation. KBr pellets with samples were used to record FT-IR spectra on a Nicolet iS10 spectrometer in the range of 4000 to 400 cm<sup>-1</sup>. Cyclic voltammogram measurements were performed on a BioLogic SP-300 electrochemical workstation in a 0.6 M NaAc-HAc electrolyte solution with pH of 4.5. A three-electrode system was employed with glassy carbon paste electrode as a working electrode, Ag/AgCl electrode as a reference electrode, and Pt as a counter electrode. The carbon paste electrode was prepared as previously described.<sup>2</sup>

### Single crystal X-ray crystallography

Single crystal measurement of **Cs-1** was conducted on a Bruker D8 VENTURE-MetalJet diffractometer equipped with a PHOTON II area detector and HELIOS multilayer optics monochromator using Ga K<sub>α</sub> radiation (λ = 1.34138 Å). Diffraction data reduction was conducted using the APEX III software. The crystal structure of **1** was resolved *via* intrinsic phase method and refined by the full-matrix least-squares method on *F*<sup>2</sup> by SHELXTL-2018/3 crystallographic software package<sup>3</sup>. Anisotropic refinement was applied to all atoms during

the final phase of crystal structure refinement. Visualisation of the crystal structure of **1** was conducted using VESTA software package<sup>4</sup>.

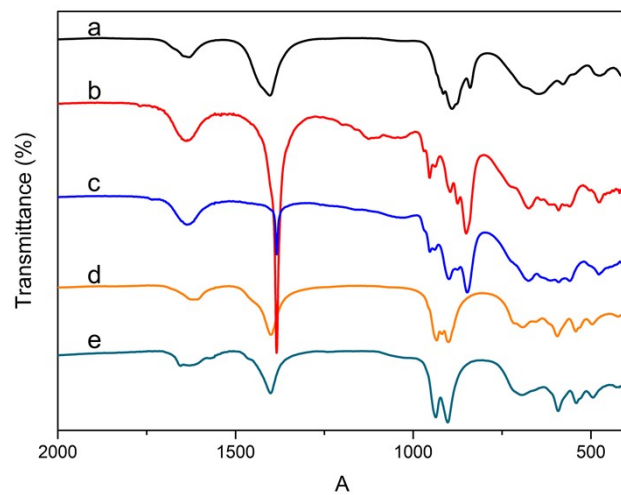
**Table S1.** Crystal data and structural refinements.

Compound	Cs-1
Empirical formula	Cs <sub>4</sub> MnMo <sub>7</sub> O <sub>32.25</sub>
Formula weight	1774.16
Temperature (K)	173(2)
Wavelength (Å)	1.34138
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> (Å)	23.5716(17)
<i>b</i> (Å)	10.7966(8)
<i>c</i> (Å)	12.5938(9)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	3205.0(4)
<i>Z</i>	4
<i>F</i> (000)	3188
$\vartheta$ range (°)	3.262 to 55.163
Reflections collected	3235
Goof on <i>F</i> <sup>2</sup>	1.081
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0619
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.1673

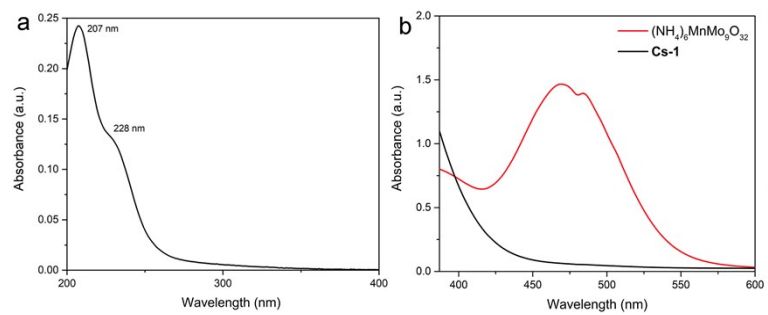
[a]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

**Table S2.** BVS calculation and bond valence calculations of selected atoms in Cs-1.

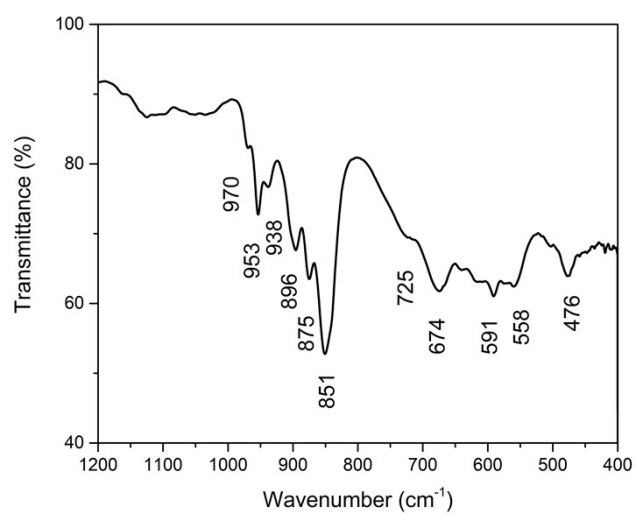
Atom 1	Atom 2	$R_0$ value <sup>5</sup>	$B$ value <sup>5</sup>	Length (Å)	Bond valence	Valence sum
Mn1	O(9)	1.79	0.37	2.118(10)	0.411	2.285
	O(9)#13	1.79	0.37	2.118(10)	0.411	
	O(11)	1.79	0.37	2.128(10)	0.331	
	O((11)#13	1.79	0.37	2.128(10)	0.402	
	O(17)	1.79	0.37	2.203(14)	0.402	
	O(18)	1.79	0.37	2.199(16)	0.328	
Mo1	O(1)	1.907	0.37	2.305(12)	0.341	6.189
	O(2)	1.907	0.37	2.314(12)	0.333	
	O(4)	1.907	0.37	1.858(9)	1.142	
	O(4)#1	1.907	0.37	1.858(9)	1.142	
	O(6)	1.907	0.37	1.734(13)	1.596	
	O(8)	1.907	0.37	1.725(13)	1.644	
Mo2	O(1)	1.907	0.37	2.170(3)	0.49	6.077
	O(3)	1.907	0.37	1.943(9)	0.912	
	O(4)#1	1.907	0.37	2.281(8)	0.364	
	O(5)	1.907	0.37	1.909(9)	0.997	
	O(9)	1.907	0.37	1.760(10)	1.488	
	O(10)	1.907	0.37	1.683(9)	1.827	
Mo3	O(2)	1.907	0.37	2.189(3)	0.467	6.139
	O(4)#1	1.907	0.37	2.260(9)	0.385	
	O(5)	1.907	0.37	1.964(9)	0.855	
	O(7)	1.907	0.37	1.882(10)	1.073	
	O(11)	1.907	0.37	1.742(10)	1.562	
	O(14)	1.907	0.37	1.690(10)	1.793	
Mo4	O(1)	1.907	0.37	2.050(12)	0.681	6.142
	O(3)	1.907	0.37	1.988(10)	0.801	
	O(3)#1	1.907	0.37	1.988(10)	0.801	
	O(8)	1.907	0.37	2.411(12)	0.257	
	O(12)	1.907	0.37	1.676(14)	1.867	
	O(13)	1.907	0.37	1.960(11)	0.874	
Mo5	O(13)#1	1.907	0.37	1.960(11)	0.874	6.331
	O(2)	1.907	0.37	2.060(12)	0.66	
	O(6)	1.907	0.37	2.434(13)	0.241	
	O(7)	1.907	0.37	1.969(9)	0.848	
	O(7)#1	1.907	0.37	1.969(9)	0.846	
	O(15)	1.907	0.37	1.685(14)	1.827	
	O(16)	1.907	0.37	1.923(11)	0.958	
O(16)#1	1.907	0.37	1.923(11)	0.958		



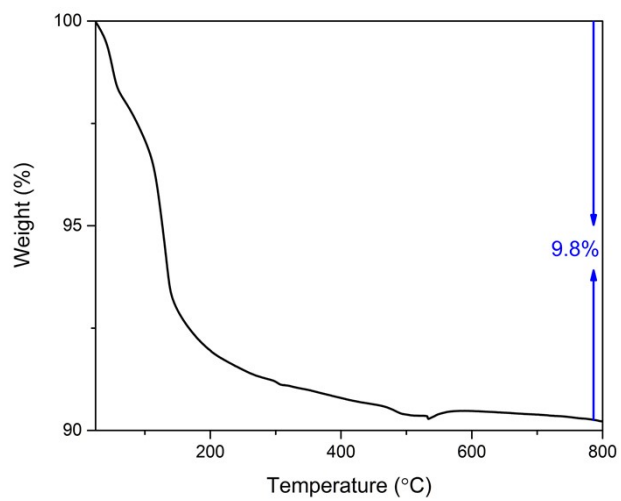
**Figure S1.** IR spectra of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (a), **Cs-1** (b), **Cs-1** converted from  $[\text{MnMo}_9\text{O}_{32}]^{6-}$  (c)  $(\text{NH}_4)_6\text{MnMo}_9\text{O}_{32}\cdot 8\text{H}_2\text{O}$  (d) and the solid sample isolated from the solution of **Cs-1** (e).



**Figure S2.** UV-Vis spectra of (a) Cs-1 (b) Cs-1 and (NH<sub>4</sub>)<sub>6</sub>MnMo<sub>9</sub>O<sub>32</sub>.

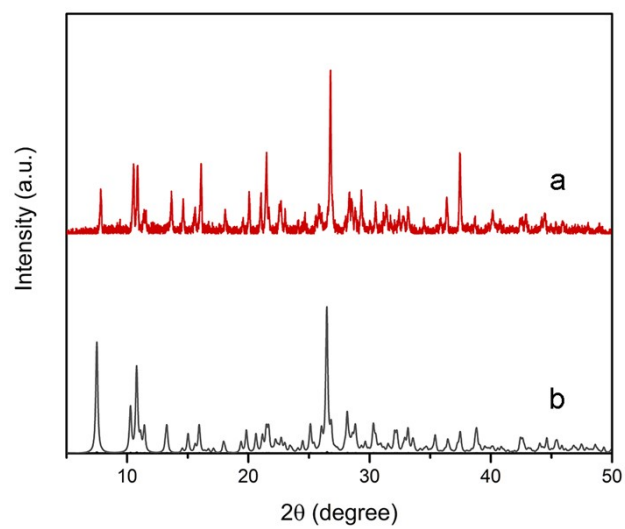


**Figure S3.** IR spectrum of Cs-1.

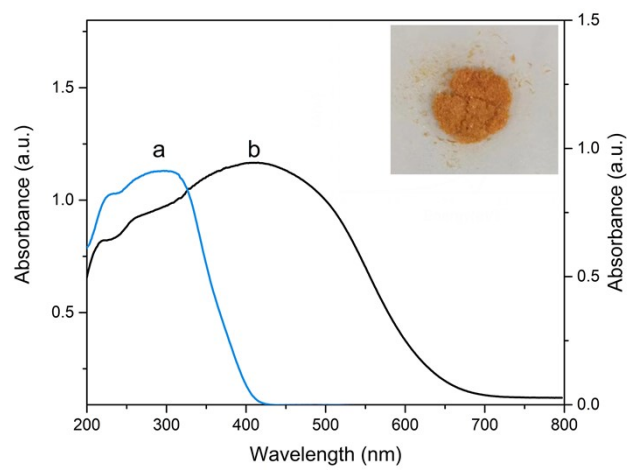


**Figure S4.** The thermogravimetric curve of Cs-1.

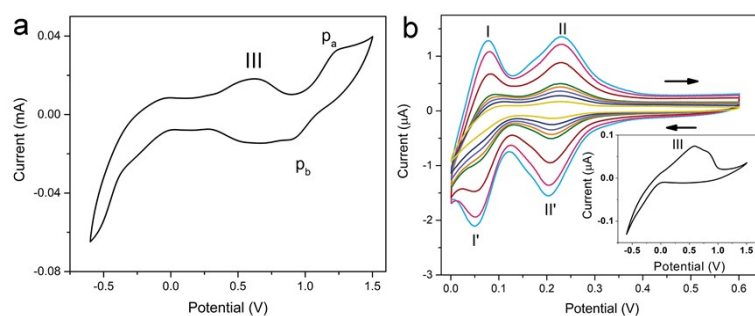




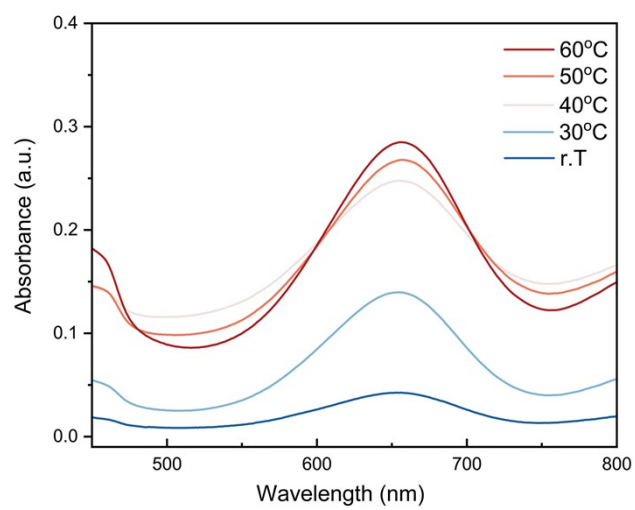
**Figure S5.** (a) Experimental and (b) simulated PXRD patterns of Cs-1.



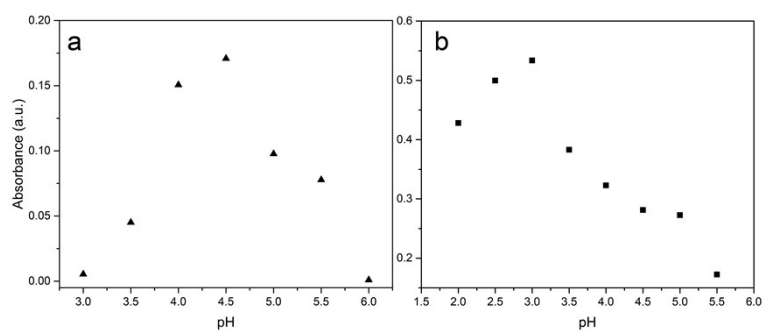
**Figure S6.** UV-Vis DRS of (NH<sub>4</sub>)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub> (a), Cs-1 (b). Insert photograph: the crystal of Cs-1.



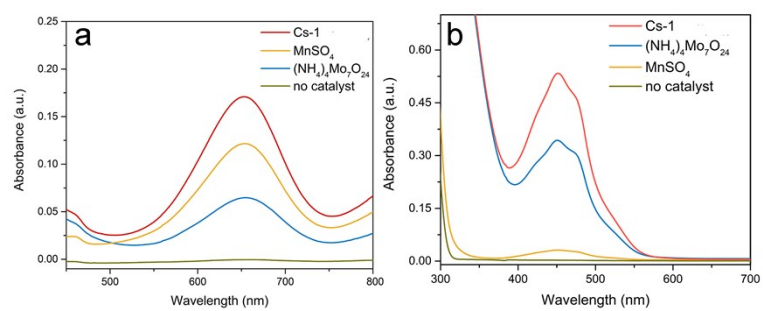
**Figure S7.** CV of **Cs-1** and  $(\text{NH}_4)_4[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$  in aqueous solution. (a) **Cs-1**. III: 0.603 V, the scan rate  $100 \text{ mV}\cdot\text{s}^{-1}$ , in the potential range from +1.5 to  $-0.6 \text{ V}$ . (b)  $(\text{NH}_4)_4[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ . at various scan rates (from inner to outer: 20, 40, 60, 80, 100, 200, 300 and  $400 \text{ mV}\cdot\text{s}^{-1}$ , (I, I': 0.078, 0.052 V; II, II': 0.227, 0.208 V), in the potential range from +0.6 to  $-0.0 \text{ V}$ . (Insert: III: 0.601 V, the scan rate  $100 \text{ mV}\cdot\text{s}^{-1}$ , in the potential range from +1.5 to  $-0.6 \text{ V}$ )



**Figure S8.** UV-Vis spectra of TMB<sup>+</sup> measured at different temperatures.



**Figure S9.** The absorbance of TMB<sup>+</sup> and OPD in their UV-Vis spectra at different pH. (a) 30 mM of TMB, 0.303 mM of Cs-1, 300 mM of H<sub>2</sub>O<sub>2</sub>, (b) 30 mM OPD, 60.6 μM Cs-1, 300 mM of H<sub>2</sub>O<sub>2</sub>, reaction time 20 min.



**Figure S10.** UV-Visible spectra of (a) TMB and (b) OPD systems using Cs-1, MnSO<sub>4</sub>, (NH<sub>4</sub>)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub> as catalysts and blank experiments at optimal pH, respectively.

## SI-8 References

1. John L. T. Waugh, David P. Shoemaker and L. Pauling, *Acta. Cryst.*, 1954, **7**, 438-441.
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