

Electronic Supplementary Information (ESI)

**Synthesis, Structure and Electrochemical Characterization of the Isopolytungstate (W_4O_{16})
held by Mn^{II} Anchors within a Superlacunary Crown Heteropolyanion $\{P_8W_{48}\}$**

Masooma Ibrahim^{a*}, Israël M. Mbomekallé^b, Pedro de Oliveira^b, George E. Kostakis^c,
Christopher E. Anson^d

^a Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann von-Helmholtz
Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^b Equipe d'Electrochimie et Photo-électrochimie, Laboratoire de Chimie Physique, Université
Paris-Sud, UMR 8000, CNRS-Université Paris Saclay, Orsay F-91405, France.

^c Chemistry Department, University of Sussex, Sussex House, Falmer Brighton, BN1 9RH
United Kingdom.

^d Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15,
76128 Karlsruhe, Germany.

*Corresponding authors- E-mail: masooma.ibrahim@kit.edu

Methods

Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum One Spectrometer with samples prepared as KBr discs. X-Ray powder diffraction patterns were measured at room temperature using a Stoe STADI-P diffractometer with a Cu-K α radiation at the Institute of Nanotechnology, Karlsruhe Institute of Technology. Elemental compositions were determined by an Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES) at Institutes for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology. Thermogravimetric measurements (TGA) were performed using a NETZSCH STA 409C (TA Instruments). A few milligrams of the material (25 mg) were heated to a temperature of 950 °C at a heating rate of 10 Kmin⁻¹ under nitrogen atmosphere.

Table 1: Selected bond lengths

Bond lengths [Å] W25-O in IsoPOM	
O93	2.078(10)
O94	2.160(12)
O95	2.178(10)
O96	1.739(12)
O97	1.778(13)
O98	1.791(12)
Bond lengths [Å] W26-O in IsoPOM	
O93	2.149(11)
O93	2.124(10)
O94	1.848(12)
O95	2.070(11)
O99	1.768(11)
O10	0 1.764(12)
Bond lengths [Å] Mn1-O (anchor)	
O10	2.235(12)
O14	2.194(12)
O80	2.157(11)
O86	2.170(12)
O96	2.180(12)
O99	2.204(10)
Bond lengths [Å] Mn2-O (anchor)	
O70	2.163(12)
O97	2.087(12)
O10	2.213(14)
O10	2.138(16)
O10	2.206(17)
O10	2.203(14)
Bond lengths [Å] Mn3-O (anchor)	
Cl1	2.365(8)
O71	2.100(13)
O98	2.106(12)
O10	2.149(10)
O10	2.231(14)
O10	2.312(13)

Table 2: Selected bond angles

Bond angles [°] G-Mn1-O (anchors)		Bond angles [°] G-Mn2-O (anchors)	
O14-Mn1-O10	80.0(4)	O70-Mn2-O101	173.6(5)
O14-Mn1-O99	74.1(4)	O70-Mn2-O103	88.9(5)
O80-Mn1-O10	79.0(4)	O70-Mn2-O104	87.4(5)
O80-Mn1-O14	136.1(4)	O97-Mn2-O70	81.7(5)
O80-Mn1-O86	91.3(4)	O97-Mn2-O101	96.7(5)
O80-Mn1-O96	84.2(4)	O97-Mn2-O102	86.1(5)
O80-Mn1-O99	136.0(5)	O97-Mn2-O103	99.1(5)
O86-Mn1-O10	136.8(4)	O97-Mn2-O104	167.3(6)
O86-Mn1-O14	78.5(4)	O102-Mn2-O70	98.1(6)
O86-Mn1-O96	88.0(5)	O102-Mn2-O101	87.9(7)
O86-Mn1-O99	130.8(5)	O102-Mn2-O103	171.8(6)
O96-Mn1-O10	131.7(5)	O102-Mn2-O104	89.1(7)
O96-Mn1-O14	137.0(5)	O103-Mn2-O101	85.2(6)
O96-Mn1-O99	85.1(4)	O104-Mn2-O101	94.8(5)
O99-Mn1-O10	76.9(4)	O104-Mn2-O103	87.1(6)
Bond angles [°] G-Mn3-O (anchors)			
O71-Mn3-Cl1	92.8(4)		
O71-Mn3-O98	171.4(5)		
O71-Mn3-O100	89.5(5)		
O71-Mn3-O105	90.5(5)		
O71-Mn3-O106	85.8(5)		
O98-Mn3-Cl1	89.8(4)		
O98-Mn3-O100	88.4(4)		
O98-Mn3-O105	97.6(5)		
O98-Mn3-O106	85.6(5)		
O100-Mn3-Cl1	176.4(4)		
O100-Mn3-O105	84.7(5)		
O100-Mn3-O106	81.0(4)		
O105-Mn3-Cl1	92.4(4)		
O105-Mn3-O106	165.2(4)		
O106-Mn3-Cl1	102.0(4)		
Bond angles [°] G-W25-O (IsoPOM)		Bond angles [°] G-W26-O (IsoPOM)	
O94-W25-O95	77.3(4)	O93-W26-O93	73.7(4)
O96-W25-O93	91.5(5)	O94-W26-O93	78.1(5)
O96-W25-O94	87.2(5)	O94-W26-O93	93.2(4)
O96-W25-O95	159.5(4)	O94-W26-O95	159.0(5)
O96-W25-O97	105.2(6)	O95-W26-O93	72.6(4)
O96-W25-O98	103.7(6)	O95-W26-O93	83.0(4)
O97-W25-O93	151.3(5)	O99-W26-O93	159.2(5)
O97-W25-O94	84.3(5)	O99-W26-O93	93.1(5)
O97-W25-O95	86.6(5)	O99-W26-O94	99.9(5)
O97-W25-O98	102.9(5)	O99-W26-O95	90.1(5)
O98-W25-O93	95.3(5)	O100-W26-O93	90.8(5)
O98-W25-O94	164.6(4)	O100-W26-O93	164.1(5)
O98-W25-O95	89.5(5)	O100-W26-O94	99.8(5)
O94-W25-O95	77.3(4)	O100-W26-O95	95.8(5)
O96-W25-O93	91.5(5)	O100-W26-O99	102.7(5)

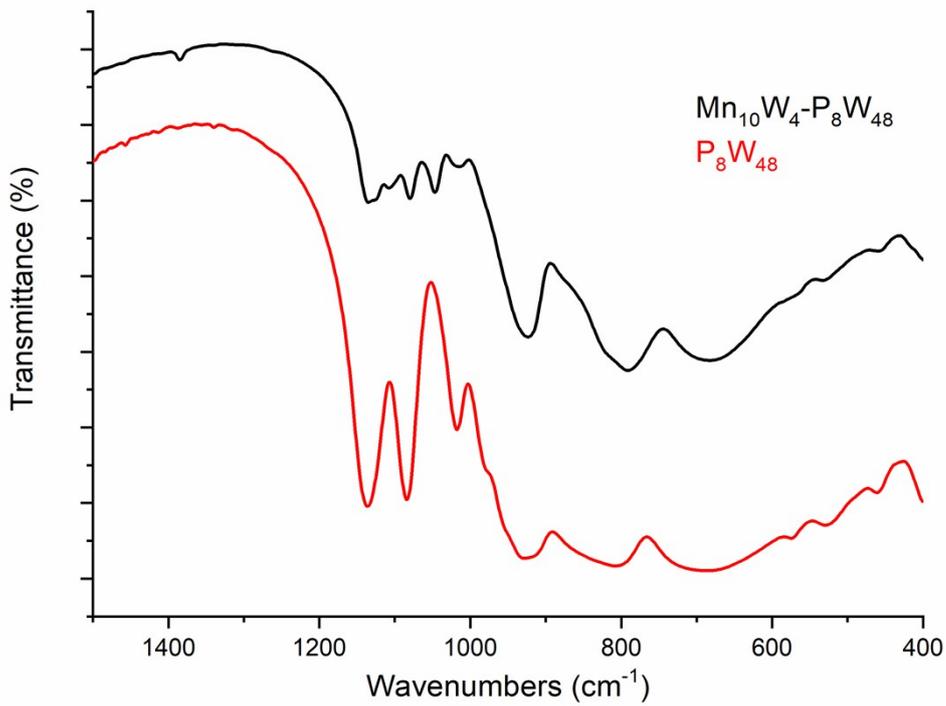


Figure S1. FTIR spectra of precursor $\{\text{P}_8\text{W}_{48}\}$ and **KLiMn-Mn₁₀W₄-P₈W₄₈**

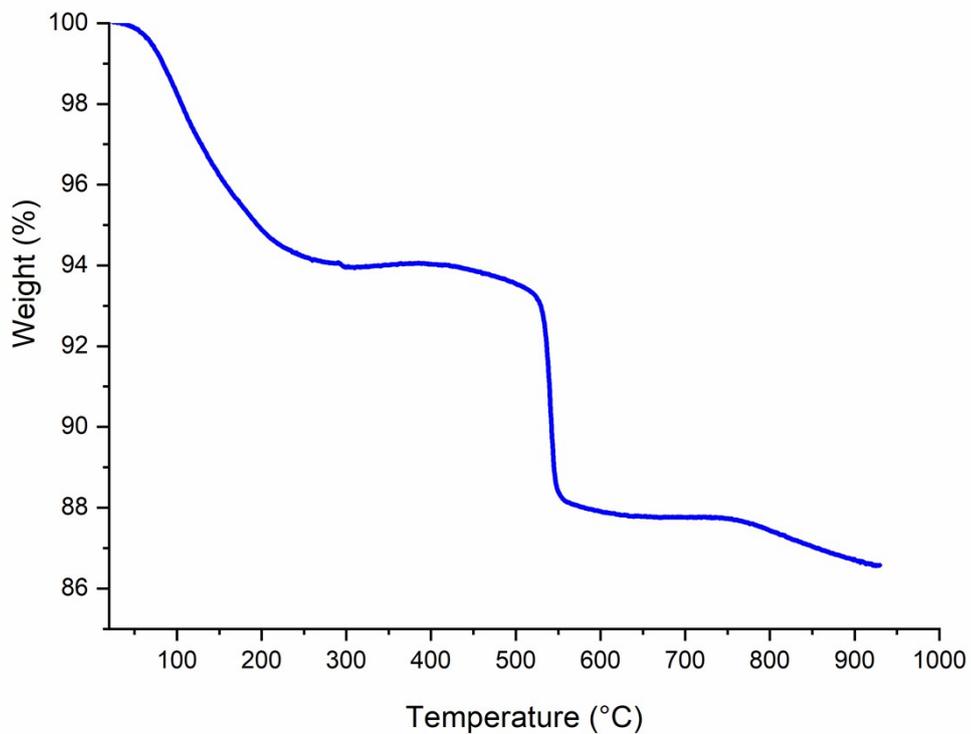


Figure 2. Thermograms of **KLiMn-Mn₁₀W₄-P₈W₄₈** from 25 to 950 °C under N_2 atmosphere.

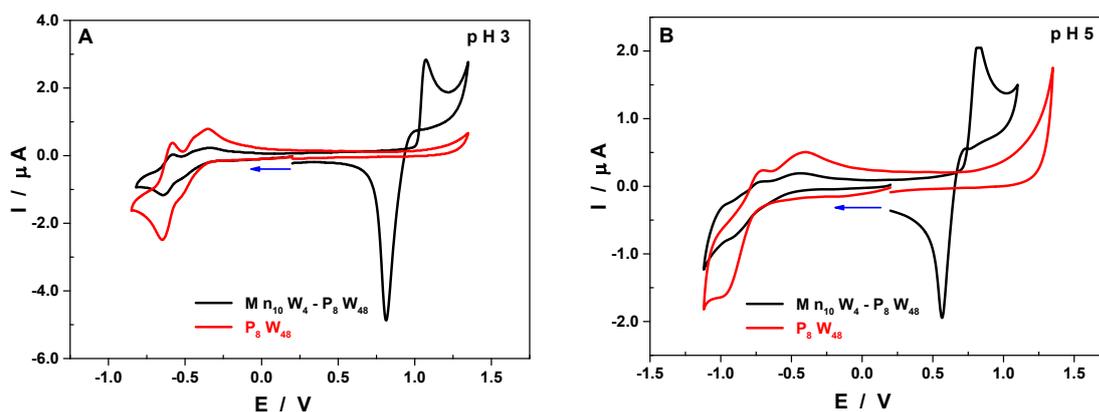


Figure S3. CVs of $\text{Mn}_{10}\text{W}_4\text{-P}_8\text{W}_{48}$ (black) and P_8W_{48} (red), (A) in 0.5 M $\text{Li}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ / pH 3.0 and (B) in 1.0 M $\text{LiCH}_3\text{CO}_2 + \text{CH}_3\text{CO}_2\text{H}$ / pH 5.0. In (A), the potential range is comprised between 1.35 V and -0.82 V. The scan was started at +0.2 V towards the negative potentials. In (B), the potential range is comprised between either 1.35 V or 1.10 V and -0.40 V. The scan was started at +0.2 V towards the negative potentials. Working electrode: EPG; counter electrode: Pt wire; reference electrode: SCE. Scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$. POM concentrations: 0.07 mM for $\text{Mn}_{10}\text{W}_4\text{-P}_8\text{W}_{48}$ and 0.08 mM for P_8W_{48} .

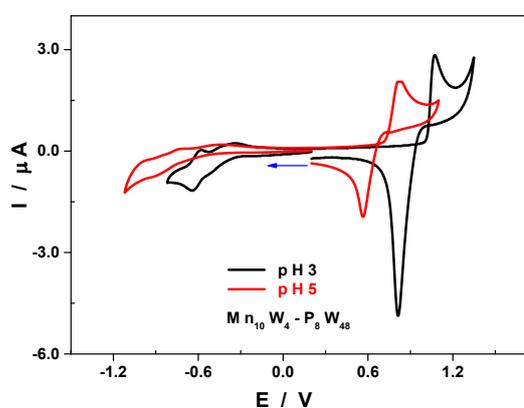


Figure S4. CVs of $\text{Mn}_{10}\text{W}_4\text{-P}_8\text{W}_{48}$ in 0.5 M $\text{Li}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ / pH 3.0 (black) and in 1.0 M $\text{LiCH}_3\text{CO}_2 + \text{CH}_3\text{CO}_2\text{H}$ / pH 5.0 (red). Working electrode: EPG; counter electrode: Pt wire; reference electrode: SCE. Scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$. POM concentration: 0.07 mM.

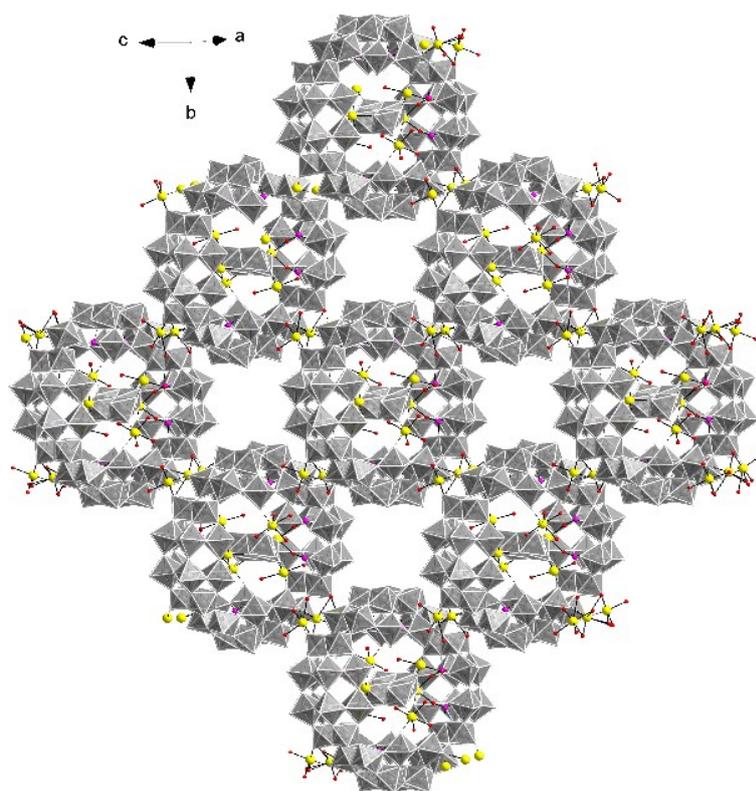


Figure S5. Combined polyhedral/ball-and-stick representation of the crystal packing arrangement in $\mathbf{Mn}_{10}\mathbf{W}_4\mathbf{-P}_8\mathbf{W}_{48}$. Alkali metal cations omitted for clarity. WO_6 octahedra (gray), O (red), P (pink), Mn (yellow).