#### Supporting Information

# 3D POMOF based on {AsW<sub>12</sub>} cluster and Ag-MOF with intersecting channels for large-capacity aqueous asymmetric supercapacitors and highly selective biosensors detecting hydrogen peroxide

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The {AsW<sub>12</sub>O<sub>40</sub>} clusters are grafted into Ag-MOF to yield two 3D polyoxometallate-(POMOFs). based organic frameworks  $(imi)_{2}[Ag_{3}(tpb)_{2}]_{2}$ metal  $(H_2O)$ {AsW<sub>12</sub>O<sub>40</sub>}<sub>2</sub>]·6H<sub>2</sub>O (1) and [(Ag<sub>7</sub>bpy<sub>7</sub>Cl<sub>2</sub>){AsW<sup>V</sup><sub>2</sub>W<sup>VI</sup><sub>10</sub>O<sub>40</sub>}]·H<sub>2</sub>O (2) (imi = imidazole; tpb = 1, 2, 4, 5-tetrakis (4-pyridyl) benzene; bpy = 4, 4'-bipyridyl). Title compounds are complicated 3D networks with intersecting proton channels and novel topology. They exhibit larger capacitance (929.7 and 986.1 F g<sup>-1</sup> at a current density of 3 A  $g^{-1}$ ), superior rate capability, higher capacity retention rate, boosting conductivity and electrocatalytic activities than those of their maternal POM, which can be ascribed to the introduction of Ag-MOF, interpenetrating proton channels, and the unique stability of POMOF. An aqueous asymmetric supercapacitor equipment assembled with 2-CPE displays remarkable energy density (16.1 Wh kg<sup>-1</sup>) with power density 1748.9 W kg<sup>-1</sup> and durable cyclic stability. The practical application capability as a power supply device can be confirmed by lighting up a red light-emitting diode. Moreover, 2-GCE as  $H_2O_2$  biosensor reveals a lower detecting limit (0.48  $\mu$ M), wider linear range (1.43 µM-1.89 mM), high selectivity and reproducibility, which was further confirmed by detecting H<sub>2</sub>O<sub>2</sub> in real blood serum samples.

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#### **1. Experimental Procedures**

#### 1.1 Materials and general methods

All chemicals were commercially purchased and used without further purification. Na<sub>3</sub>AsW<sub>12</sub>O<sub>40</sub> xH<sub>2</sub>O (Noted a-AsW<sub>12</sub>Na) was prepared according to the literature method<sup>[26]</sup> and verified by the IR spectrum. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ag, Al, Cu and W were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. The IR spectrum was recorded in the range 400-4000cm<sup>-1</sup> on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument with a heating rate 10 °C min<sup>-1</sup>. XRD patterns were collected on Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) and 2 $\theta$  ranging from 5 to 50°. The Brunauer-Emmett-Teller (BET) surface area were performed by N<sub>2</sub> adsorption measurements at 77.3 K using a Nova 2000E. The scanning electron microscopy (SEM) images were measured by a Hitachi SU70 SEM coupled with an energy-dispersive X-ray (EDX) detector. X-ray photoelectron spectrum (XPS) analyses were analyzed on an AXIS ULTRA DLD electron spectrometer by an Mg K $\alpha$  (1253.6eV) achromatic X-ray source.

#### 1.2 X-ray crystallography

Single crystal X-ray data of compounds 1 and 2 were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromatized MoK<sub>a</sub> radiation ( $\lambda = 0.71073$  Å). Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct method and refined by the full-matrix least-squares methods on F<sup>2</sup> using the SHELXTL-2014 software package. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon atoms of organic ligands were included at calculated positions and refined with a riding model. The H atoms on water molecules were not included and just put into the final molecular formula. A summary of crystal data and structure refinement for compounds 1 and 2 were provided in Table S1. Crystallographic data for the structures have been deposited in the Cambridge Crystallographic Data Centre. CCDC numbers of compounds 1 and 2 are 2021432 and 2021433, respectively.

#### 1.3 Electrode preparation and electrochemical characterization

The 3mm glassy carbon electrode (GCE) working electrode was polished before each experiment with 1, 0.3, and 0.05 mm alumina power on chamois leather, respectively, rinsed thoroughly with deionized water between each polishing step. In order to prepare the working electrode, **1** or **2** is mixed with acetylene black as a raw material, and ground into a uniform slurry in a 3: 1 ethanol solution. 5  $\mu$ L of well dispersed slurry was dropped onto the glassy carbon surface and dried for 2 hours at room temperature in order to form a uniform thin film. Then, 5  $\mu$ L of Nafion solution (Aldrich) was dropped onto the GCE surface and the electrode was then dried at room temperature.

The carbon paper electrode of compounds **2** (**2**-CPE): The working electrodes were made by mixing as-synthesized compound (80 wt%), PVDF (10 wt%) and acetylene black (10 wt%) in N-methyl pyrrolidinone, and grinding the compounds for about 30

min to form a slurry, which was then coated on carbon paper  $(1 \text{ cm}^2)$  and dried at 60°C for 12 h. The weight of the as-prepared electrodes was controlled about 1 mg.

The ASC device was prepared by using **2**-CPE as negative electrode and activated carbon (AC) as the positive one. The AC electrode was prepared by pressing a homogeneous paste of 80 % (wt.) active material, 10 % (wt.) carbon black and 10 % (wt.) PVDF onto carbon paper followed by overnight drying at 60°C. 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions were used as the electrolyte, and a porous filter paper as the separator.

The electrochemical measurement was carried out on a CHI660E electrochemical workstation at room temperature. The working electrode was the glassy carbon electrode (GCE) or carbon paper electrode (CPE), a Pt wire was the counter electrode,

and saturated calomel electrode (SCE) was used as a reference electrode. The specific (Cs) capacitances was computed with the equations below:

$$Cs = \frac{2I_m \int V dt}{V^2 \left| \frac{V_f}{V_t} \right|}$$

In which Im=I/m, I (A) is the current for discharge, m (g) is the mass of the electrode material, t (s) is the time discharged, V (V) is the discharge potential range with final value(Vf).

$$C - \times m - \times \varDelta V - = C + \times m + \times \varDelta V +$$

where C-, C+, m+, m-,  $\triangle$  V+ and  $\triangle$  V- are the specifific capacitance, mass and potential range of the negative and positive electrodes.

The energy density E [Wh kg<sup>-1</sup>] and power density P [W kg<sup>-1</sup>] arecomputed according to Equation:

$$E = C \Delta V^2 / 7.2$$

in which C [F  $g^{-1}$ ] is the gravimetric specific capacitance calculated from the discharge curve and V [V] is the potential window during the discharge process.

$$P = 3600 E/\Delta t$$

in which E is the energy density and t is the discharge time.

#### 2. Results and Discussion

#### 2.1 Details of the crystallographic data and structural determination for 1 and 2

Crystallographic data and structure refinement, bond lengths and angles, and

anisotropic displacement parameters have been deposited in the Cambridge

Crystallographic Data Center (CCDC No.2021432 and No. 2021433 for 1 and 2,

### respectively)

Compounds	1	2
Empirical formula	$C_{110}H_{94}Ag_6As_2N_{20}O_{87}W_{24}$	C <sub>70</sub> H <sub>58</sub> AsCl <sub>2</sub> Ag <sub>7</sub> N <sub>14</sub> O <sub>41</sub> W <sub>1</sub>
Formula weight	8297.51	4858.41
T/K	293(2)	296(2)
Crystal. size, mm <sup>3</sup>	0.174 x 0.167 x 0.147 mm	0.169 x 0.154 x 0.145 mm
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a/Å	17.460(2)	12.294(2)
$b/{ m \AA}$	11.4771(15)	13.205(2)
$c/{ m \AA}$	39.016(5)	15.388(3)
$lpha/^{\circ}$	90	98.7733(18)
$eta / ^{\circ}$	97.460(2)	90.5893(18)
$\gamma/^{\circ}$	90	104.7786(17)
$V/\text{\AA}^3$	7752.2(17)	2384.0(7)
Ζ	2	1
$D_{\rm calc}/{ m Mg}~{ m m}^{-3}$	3.555	3.384
$\mu/\mathrm{mm}^{-1}$	18.987	16.298
F(000)	7428	2188
$\theta$ range, deg/°	1.053 to 27.529	1.616 to 24.999
Reflections collected	45739 / 17412	21362 / 8350
R <sub>int</sub>	0.1260	0.0532
Data/restraints/para	17412 / 2215 / 1127	8350 / 1296 / 716
GOF on $F^2$	1.030	1.049
$R_1 / wR_2 [I \ge 2\sigma(I)]^a$	0.0792 / 0.1792	0.0735 /0.1818
$R(F)/wR(F^2)^a$ (all	0.1768 / 0.2018	0.1202 / 0.1987
$\Delta \rho_{\rm max,min}/e{\rm \AA}^{-3}$	3.008 / -3.065	2.663 / -2.320

 Table S1. Crystal data and structure refinement data for 1 and 2.

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

#### 2.2 Bond-valence Sums (BVS)

BVS calculations show that all Ag atoms in **1** and **2** of the two compounds are in the +1 oxidation state , while As is in the +5 oxidation state , except that a small part of W in compound **2** is in the +5 oxidation state , and the rest W is in +6 oxidation state.

Atoms	Compound 1	Oxidation state	Compound 2	Oxidation state
W1	6.13	+6	5.98	+6
W2	6.13	+6	6.18	+6
W3	6.17	+6	5.91	+6
W4	6.02	+6	5.43	+5
W5	6.33	+6	5.98	+6
W6	6.18	+6	5.82	+6
W7	6.13	+6		
W8	6.31	+6		
W9	6.33	+6		
W10	6.15	+6		
W11	6.35	+6		
W12	6.34	+6		
As1	5.45	+5	5.42	+5
Ag1	0.91	+1	1.08	+1
Ag2	0.89	+1	1.16	+1
Ag3	0.92	+1	0.95	+1
Ag4			1.24	+1

Table S2. The Bond-valence Sums (BVS) for the W, P and Ag cations of two

# compounds.

# 2.3 Comparison of specific capacitance POM modified nanocomposites

**Table S3** The comparison table of specific capacitance ( $C_s$ ) for reported POM-basedcrystal materials electrode.

Electrode	Specific capacitance [F·g <sup>-1</sup> ]	Current density [A·g <sup>-1</sup> ]	Reference
[Cu <sub>6</sub> (Himi) <sub>6</sub> {As <sup>⊪</sup> W <sub>9</sub> O <sub>33</sub> }₂]·5H <sub>2</sub> O	603.4	2.4	[28]
$(H_2 btp)_4 [Fe^{III}_2 Fe^{III}_2 (H_2 O)_2 (AsW_9 O_{34})_2] \cdot 4H_2 O$	504.6	2.4	[28]
$[H(C_{10}H_{10}N_2)Cu_2][PW_{12}O_{40}]$	153.43	1	[29]
$(H_2bpe)(Hbpe)_2[[Cu(pzta)(H_2O)][P_2W_{18}O_{62}]] \cdot 5H_2O$	168	5	[30]
$[Cu^{l}H_{2}(C_{12}H_{12}N_{6})(PMo_{12}O_{40})]\cdot [(C_{6}H_{15}N)(H_{2}O)_{2}]$	249.0	3	[31]
$[Cu^{II}_{2}(C_{12}H_{12}N_{6})_{4}(PMo^{VI}_{9}Mo^{V}_{3}O_{39})]$	154.5	3	[31]

[Cu <sup>i</sup> (btx)] <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ]	110.3	3	[32]
$[Cu_{^{4}}H_{2}(btx)_{5}(PMo_{12}O_{40})_{2}]\cdot 2H_{2}O$	237.0	2	[33]
$[Cu^{II}Cu^{I}_{3}(btx)_{5}(SiMo^{VI}_{11}Mo^{V}O_{40})]\cdot 4H_{2}O$	138.4	2	[34]
[PW₁1CoO₃9]⁵-@Ru-RGO	624	0.2	[35]
PMoW-PDDA-RGO	279.1	1	[36]
RGO/PMo <sub>12</sub> O <sub>40</sub>	218	1	[37]
Activated carbon/PW <sub>12</sub> O <sub>40</sub>	183	2	[38]
(PMo <sub>12</sub> /PANI/TiN NWA)	469	1	[39]
Activated carbon/P2Mo18	275	6	[40]
PPy-PMo <sub>12</sub> /RGO TNHs	360	0.5	[41]

2.4 Comparison of electrocatalytic performances of the  $H_2O_2$  sensor

Table S4 Comparison of electrocatalytic performances of the H<sub>2</sub>O<sub>2</sub> sensor with other

recently reported GCE electrodes modified.

MODIFIFIED ELECTRODES	POTENTIAL WORK (V)	LINEAR RANGE (MM)	DETECTION LIMIT (MM)	REF.
CO₃O₄/RGO/GCE	-0.19 (vs SCE)	0.015-0.675	2.40	[48]
FE <sub>2</sub> O <sub>3</sub> /RGO/GCE	-0.6 (vs SCE)	0.05-9.00	6.00	[49]
MNO <sub>2</sub> /RGO/CNT/GCE	0.4 (vs SCE)	0.001-1.03	0.10	[50]
A-MOO₃/GO/GCE	-0.4 (vs SCE)	0.00092-2.46	0.31	[51]
FE₃O₄/NMCMS /GCE	-0.4 (vs SCE)	0.05-33.08	5.89	[52]
CDO/MWCNT /GCE	-1.2 (vs Ag/AgCl)	0.0005-0.20	0.10	[53]
[MO-OXO]N/NMC/RDE	-0.3 ( vs SCE)	0.05-5	0.23	[54]
NENU5-KB-3/GCE	-0.47 (vs Ag/AgCl)	0.01-20	1.03	[55]
CU-ALW <sub>12</sub> /AC/GCE	-0.5 (vs Ag/AgCl)	0.0195-0.9	0.86	[45]
POMOF-2/AC/GCE	-0.4(vs Ag/AgCl)	0.00143-1.89	0.48	This work

<sup>a</sup> rGO: reduced graphene oxide

<sup>b</sup> CNT: carbon nanotubes.

<sup>c</sup>GO: graphene oxide

<sup>d</sup> MNCMs: nitrogen-doped mesoporous carbon microcapsules.

<sup>f</sup>MWCNT: multiwalled carbon nanotubes.

<sup>g</sup>NMC:N, P-dopedconductive mesoporous carbon

<sup>h</sup>KB: ketjenblack carbon.

<sup>i</sup>CNT: carbon nanotubes.

# 2.5 Structure diagram of compounds 1 and 2



Figure S1. ORTEP view of the basic units of 1 with 50% thermal ellipsoids.



**Figure S2.** The 12-membered metal-organic rings consisting of 6 Ag atoms and 6 tpb ligands.



Figure S3. The corrugated metal-organic layer formed by 12-member large rings.



Figure S4. The 3-D topological network of compound 2 with new topology  $\{12^3\}\{4,12^2\}_2$ 



Figure S5. ORTEP view of the basic units of 2 with 50% thermal ellipsoids.



**Figure S6.** Two size of parallelogram rings based on four crystallographic independent Ag and bpy ligand.



Figure S7. 3-D topological network of compound 2 with new topology  $\{12\}$   $\{4.6^4.8\}_2$   $\{4^2.10^2.12^2\}$   $\{6.10.12\}_2$   $\{6.12.14\}_2$   $\{6\}_2$ 

# 2.6 Structural representation (FT-IR, TG, PXRD, SEM, EDS and mapping images)



Figure S8. IR spectra of (a) compounds 1 and (b) 2.

The infrared spectrum of compounds **1-2** clearly shows the stretching vibration peak of a common chemical bond in the Keggin skeleton. The peaks at 913, 985, 854, 787 cm<sup>-1</sup> in **1**, and 904, 989, 816, 753 cm<sup>-1</sup> in **2**, are indicative of the stretching vibration of (As–O<sub>a</sub>),  $v(W=O_d)$ ,  $v(W-O_b)$ , and  $v(W-O_c)$ , respectively. The vibrational signals at 1432 cm<sup>-1</sup> and 1493 cm<sup>-1</sup> are attributed to the vibration of v(N–H) of organic ligands in **1-2**. The broad peaks at 3423 cm<sup>-1</sup> and 3491 cm<sup>-1</sup> are ascribed to the stretching vibration v(O–H) of water molecules.



Figure S9. The PXRD contrast curves of (a) compounds 1 and (b) 2.

The PXRD patterns of compounds 1 and 2 show that the diffraction peaks are consistent with the peak positions of the simulated spectrum, and the results indicate

that compounds 1 and 2 are crystallographic pure phase.



Figure S10. TG curves of (a) compounds 1 and (b) 2.

The TG curve of compounds **1-2** were measured under a N<sub>2</sub> atmosphere of 50 to 750 °C. Compounds **1** and compound **2** are presents two- and one-step weight-loss process, respectively. Compound **1** loses all water molecules (calcd. weight loss 0.87%; found 0.89%) at the first step of weight loss in the temperature range 150-200 °C. The second loss between 300 and 600 °C of 20.40% (calcd 20.32%) attributed to all the loss of organic ligand molecules. The weight loss of compound **2** occurred between 300-650 °C due to the loss of bpy molecules and Cl ions (calcd. weight loss 20.30%; found 20.58%).



**Figure S11.** N<sub>2</sub> adsorption isotherm of (a) compounds 1 and (b) 2 at 77 K ( $P_0 = 1$  atm). Inset: Plot of the linear region for the BET equation.

The N<sub>2</sub> adsorption-desorption isotherms of compounds **1** and **2** were conducted for the activated solid samples at 77 K. The absorption isotherms in the P/P<sub>0</sub> range of 0.05-0.30 were treated in a straight line by the term  $1/[V(p_0/p-1)]$  to obtain the slope (k) and intercept (b) of the straight line. The specific surface areas were calculated by the BET formula. The BET surface area of compounds **1** and **2** are 52.02 and 64.43 m<sup>2</sup> g<sup>-1</sup>, which far greater than that of matrix POM.



**Figure S12.** EDS elemental mappings of (a) W, O, Ag, As, N, and C for compound 1; (b) W, O, Ag, As, N, Cl, and C for compound **2**.

The surface morphology and elemental composition of compounds 1 and 2 were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The compounds 1 and 2 are block crystals having a regular shape and have a size of about  $250 \times 200 \times 40$  and  $200 \times 150 \times 50$  um<sup>3</sup>, respectively. The EDS mapping and microanalysis results of the compounds indicate that the compound **1** contains the elements C, N, O, As, W, Ag and the compound **2** contains the elements C, N, O, As, W, Ag and Cl. At the same time, each element is evenly distributed in the compound .



Figure S13. The EDS microanalysis of compounds 1 and 2.



Figure S14. The XPS of W, As, and Ag in compound 1.



Figure S15. The XPS of W, As, and Ag in compound 2.

As shown in Fig.S11, S12, two peaks at 35.1 and 37.2 eV for compound 1 attribute to

the W4f<sub>7/2</sub> and W4f<sub>5/2</sub> of W<sup>6+</sup>. Four overlapped peaks at 34.5, 35.3, 36.6, and 37.4 eV in the W4f region of compound **2**, which should be ascribed to the mixture of W<sup>5+</sup> and W<sup>6+</sup>, respectively. Two peaks at 40.1, 44.7 eV for compound **1** and 40.2, 44.9 eV for compound **2** may ascribe to the As3d<sub>5/2</sub> and As3d<sub>3/2</sub> of As<sup>5+</sup>. Two peaks at 40.1, 44.7 eV for compound **1** and 40.2, 44.9 eV for compound **2** may be assigned to the Ag3d<sub>5/2</sub> and Ag3d<sub>3/2</sub> of Ag<sup>+</sup>.

#### 2.7 Electrochemical properties test



Figure S16. The plots of the anodic and cathodic peak currents vs scan rates



Figure S17. GCD curves of the 1-GCE at different current densities



Figure S18. The Degradation of the capacitance of  $\{AsW_{12}Na\}$ -GCE during 5000 cycles at a current density of 3.6 A/g



Figure S19. EIS control spectra of 1-GCE (a) and 2-GCE (b) before and after circulation (Inset: the magnification part of the high frequency range for the EIS spectra).



Figure S20. (a) The CV at different scanning speeds and (b) GCD under diverse current densities of 2-CPE.



**Figure S21.** (a) The CV curves of AC-CPE at different scanning speeds; (b) GCD of AC-CPE under diverse current densities; (c) The specific capacitance of AC-CPE at different current densities; (d) EIS spectra of AC-CPE (The inset shows a magnified part of the high-frequency range for the EIS spectra).



**Figure S22.** CV curves of the **2**-CPE and the AC-CPE in separate potential windows at a scan rate of 20 mV s<sup>-1</sup>.



**Figure S23.** (a) The EIS plot of the AC//2-CPE ASC (The inset shows a magnified part of the high-frequency range for the EIS spectra); (b) The cycling stability of the AC//2-CPE ASC.



**Figure S24.** Cyclic voltammograms of **1**-GCE (a) and **2**-GCE (b) in 0.5 M  $H_2SO_4$  solution containing AA at different concentrations (from bottom to top: 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mM; at scan rate: 50 mV s<sup>-1</sup>)



Figure S25. The plots of the cathodic peak currents vs concentrations of  $H_2O_2$ 



Figure S26. Cyclic voltammograms of  $\{AsW_{12}Na\}$ -GCE (b) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing H<sub>2</sub>O<sub>2</sub> at different concentrations (from bottom to top: 0, 0.5, 1.0, 1.5, and 2.0 mM; at scan rate: 50 mV s<sup>-1</sup>)



**Figure S27.** (a) The plots of the anodic and cathodic peak currents vs scan rates; (b) Reproducibility of the same electrode with the determination towards 0.05 mM  $H_2O_2$ ; (c) The stability study of the **2**-GCE.