<Supporting Information>

Crown-type tetranuclear Ag-POM exhibits excellent proton conductivity performance

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I Materials and methods

All chemicals used in the reaction were purchased commercially and used without further purification. Single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE PHOTON II at 150 K with the graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). FT-IR spectra were recorded on a Bruker VERTEX 70 IR spectrometer via KBr pellets in the range of 400−4000 cm^{-1}. X-ray powder diffraction (PXRD) data were recorded on an X-ray powder diffractometer (Bruker, D8 Advance) using Cu *Kα* radiation (λ = 1.5418 Å) in the 2θ angular range of 5−50° at room temperature. Elemental analysis for Na, As, W and Ag atoms were conducted by Inductively coupled plasma atomic emission spectrometer (ICP-OES) analyses and were recorded on a PerkinElemer Optima 2100 DV spectrometer (PerkinElmer, Waltham, MA). Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449 F5 Jupiter thermal analyzer in a N_2 atmosphere ranging from 25 °C to 800 °C under a heating rate of 10 °C·min^{-1}. Solid-state UV-Vis spectra were collected at room temperature using a HITACHIU-4500UV-Vis-NIR spectrometer equipped with a 60 mm diameter integrating sphere on a finely ground sample. The X-ray photoelectron spectroscopy (XPS) technique was measured on a Thermo Scientific K-Alpha spectrometer with monochromatic Al *Kα* (hν = 1486.6 eV) as the excitation source under 12 kV work pressure. Alternating current (AC) impedance measurements were performed on a Pentium/IM6 impedance analyzer with frequencies ranging from 0.1 Hz to 5 MHz using an applied voltage of 50 mV. The relative humidity (RH) and temperature were controlled by a STIK Corp. CIHI-150B incubator.

X-ray crystallographic

The crystal of compound **1** was mounted on a loop and maintained at 150 K during data collection using a Bruker D8 VENTURE PHOTON II CCD diffractometer with Mo *Kα* radiation (λ = 0.71073 Å). The structure was analyzed using Olex2 and solved with the ShelXT structure solution program. The direct methods were used to refine the text, which was then further refined using the ShelXL-2018/3 refinement package through least squares minimization. In the final refinement, all the nonhydrogen atoms including W, Ag, As, and Na atoms were refined anisotropically. Few lattice water molecules were located by Fourier difference maps; the rest lattice waters were positioned by TG analysis (Figure S3). The crystallographic data of **1** has been deposited in the Cambridge Crystallographic Data Center with the CCDC number: 2443591. Detailed crystallographic data and structure refinement parameters are summarized in the following Table S1.

II Supplementary Structure Figures and Characterizations

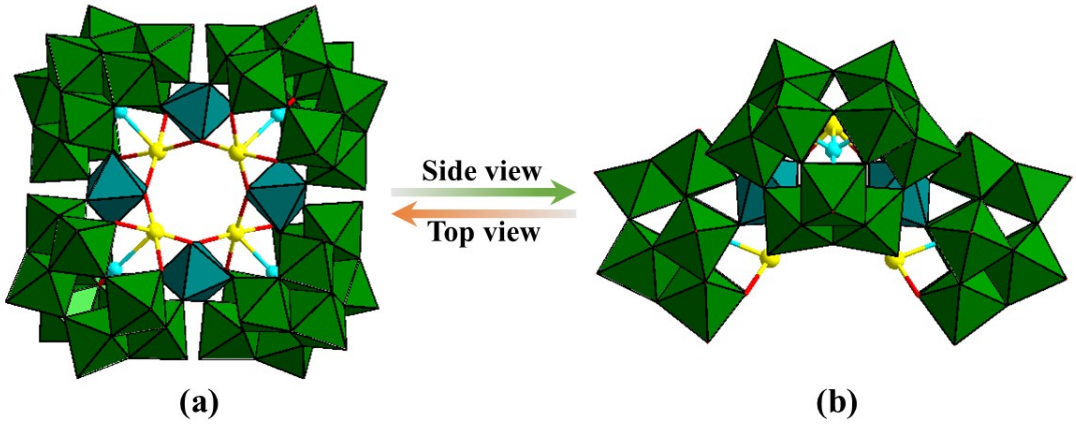

Figure S1. Combined polyhedral/Ball-and-stick representation of **1** from the (a) top view and (b) side view. Color code: W (green/turquoise), Ag/Na (yellow), O (red), As (sky-blue), WO_6 octahedron (green and turquoise).

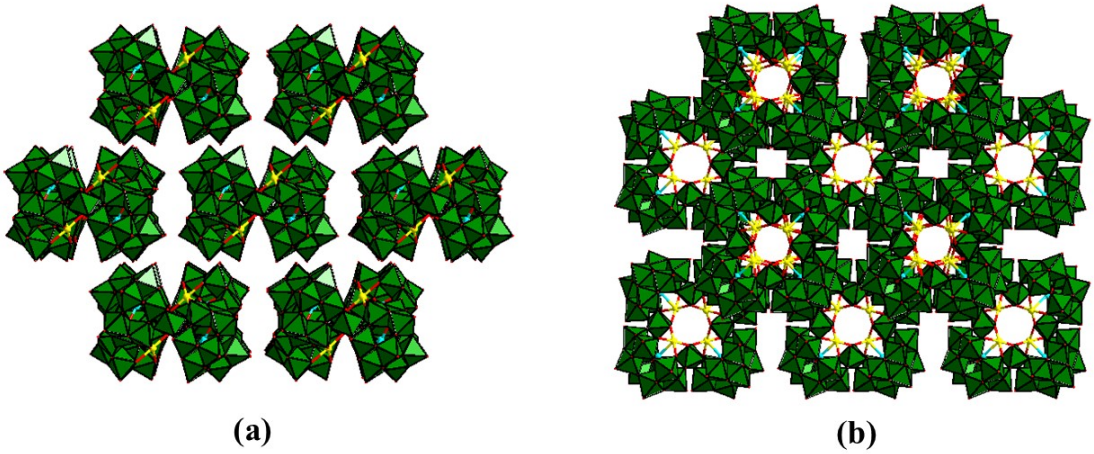

Figure S2. Combined polyhedral/Ball-and-stick representation of compound **1** in two dimensions with (a) y aixs and (b) z aixs. Color code: W (green/turquoise), Ag/Na (yellow), O (red), As (sky-blue), WO_6 octahedron (green and turquoise).

TG Analysis. Thermal weight loss experiments were performed on compound **1** in the temperature range 25−800 °C protected by an N_2 atmosphere at a rate of temperature rise of 10 °C·min^{-1}. The thermogravimetric curve showed that **1** exhibited a two-step weight loss. In the temperature range of 25−400°C, the compound **1** presented a weight loss of 11.10%, corresponding to the release of 82 crystalline water (ca. 11.95%), and as the temperature continued to increase, the POM framework began to disintegrate.[1]

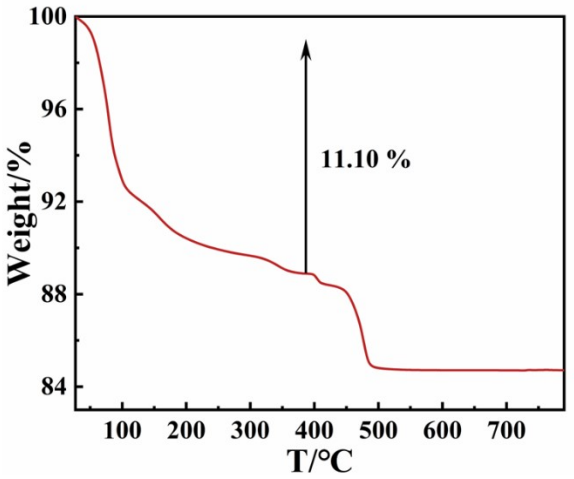

Figure S3. The thermogravimetric curve of **1**.

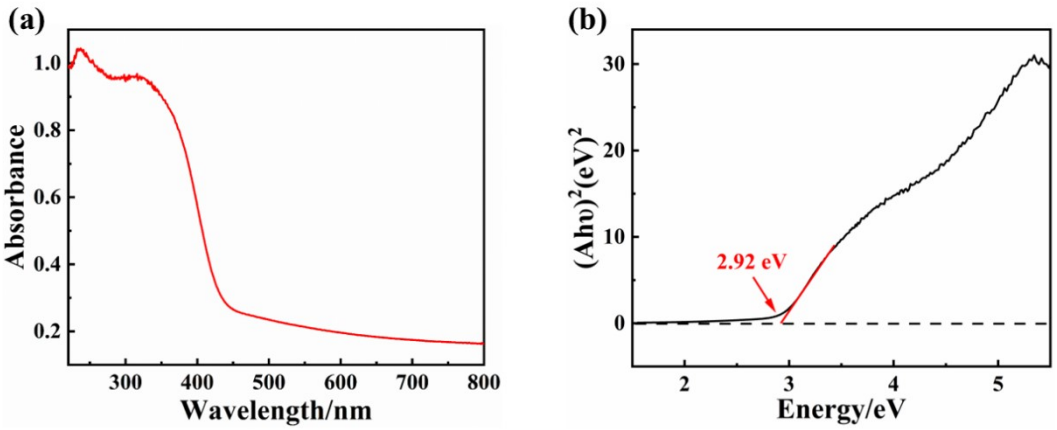

Figure S4. (a) UV-Vis absorption spectra and (b) Tauc plot of **1**.

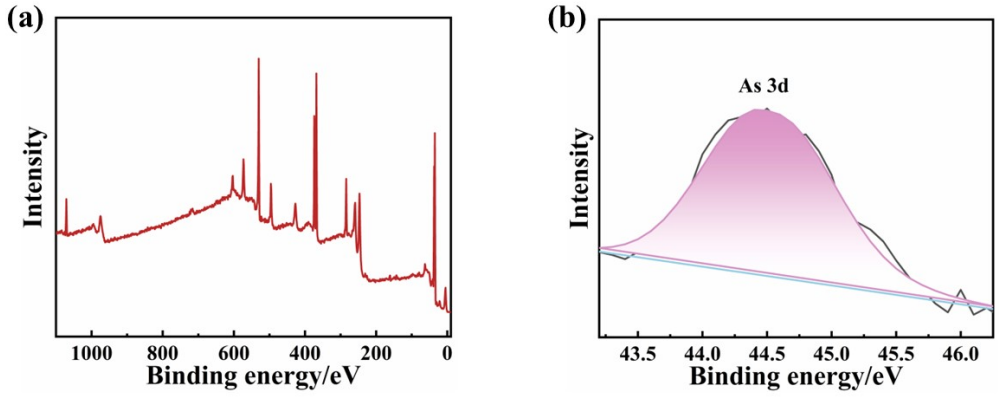

Figure S5. (a) The XPS survey spectra of compound **1**. (b) The XPS spectra of As 3d for **1**.

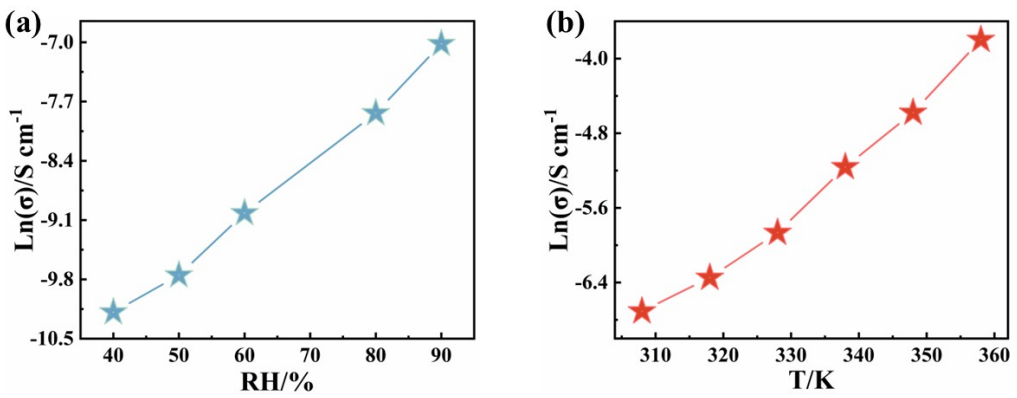

Figure S6. (a) The variation of conductivity with relative humidity for compound **1**; (b) The variation of conductivity with temperature for compound **1**.

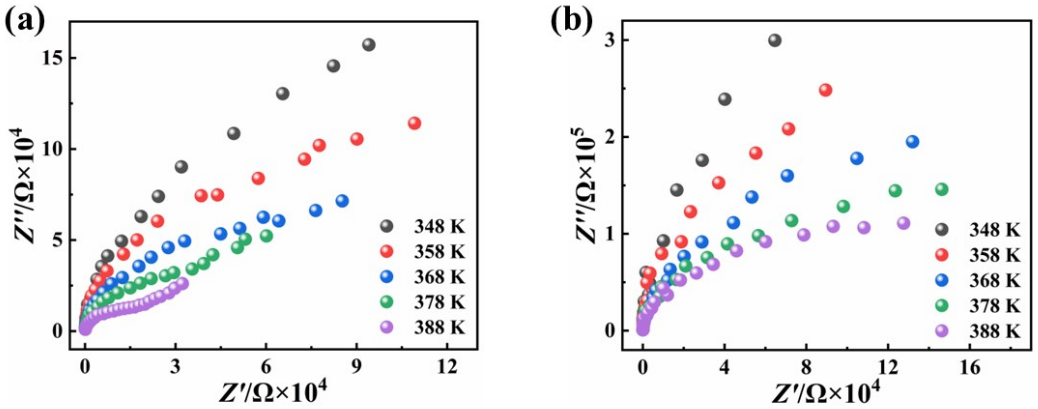

Figure S7. The Nyquist plots of (a) **1** and (b) **1**-dehyd at elevated temperatures.

III Supplementary Tables

Table S1. The proton conductivity of **1** and **1**-dehyd at elevated temperatures.

Temperature/K	σ/ S cm^{-1}	
	1	**1-dehyd**
348	5.91×10^{-6}	9.30×10^{-7}
358	1.04×10^{-5}	2.48×10^{-6}
368	2.10×10^{-5}	3.68×10^{-6}
378	3.48×10^{-5}	6.51×10^{-6}
388	8.50×10^{-5}	8.23×10^{-6}

Table S2. Crystallographic data parameters for **1**.

Compound	**1**
Empirical formula	$H_{24}Ag_{3.4}As_4Na_{24.6}O_{210}W_{40}$
Formula weight	11970.18
temperature (K)	150
Crystal system	Tetragonal
Space group	*I*–4
a [Å]	19.3853(3)
b [Å]	19.3853(3)
c [Å]	26.1587(5)
β /°	90
Volume/Å^3	9830.2(4)
Z	2
ρ_{calc} g/cm^3	4.044
μ/mm^{-1}	24.471
Crystal size/mm^3	0.19 × 0.17 × 0.16
2θ range/deg	4.202 to 50.19
index ranges	−23 ≤ *h* ≤ 23 −20 ≤ *k* ≤ 23 −31 ≤ *l* ≤ 30
Reflections collected	35792
Independent reflections	8753 [R_{int} = 0.0418]
data/restraints/parameters	8753/18/619
GOF on F^2	1.023
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0254, 0.0608
R_1, wR_2 [all data]	0.0270, 0.0617

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

Table S3. The bond lengths of compound **1**.

Bond	Length	Bond	Length	Bond	Length
W1–O1	1.975(12)	W2–O6	1.992(12)	W3–O11	1.995(11)
W1–O5	1.710(12)	W2–O10	1.762(12)	W3–O18	2.322(12)
W1–O23	2.023(12)	W2–O17	1.931(12)	W3–O20	1.762(14)
W1–O26	1.825(11)	W2–O23	1.853(11)	W3–O28	1.728(13)
W1–O27	2.410(11)	W2–O27	2.392(12)	W3–O31	2.108(12)
W1–O35	1.907(12)	W2–O34	1.869(13)	W3–O33	1.900(11)
W4–O4^1	1.922(11)	W5–O1	1.895(12)	W6–O2	2.329(11)
W4–O16^1	2.174(12)	W5–O2	2.333(11)	W6–O4	1.933(11)
W4–O22	1.747(12)	W5–O7	1.741(13)	W6–O8	1.968(11)
W4–O24^1	1.749(14)	W5–O8	1.960(11)	W6–O13	1.885(13)
W4–O26	2.120(11)	W5–O15	1.918(12)	W6–O19	1.908(11)
W4–O29	1.927(12)	W5–O29	1.924(11)	W6–O21	1.728(12)
W7–O3	1.982(13)	W8–O2	2.332(12)	W9–O9	1.760(14)

W7–O12	1.879(12)	W8–O3	1.880(12)	W9–O25	1.726(13)
W7–O14	1.720(13)	W8–O6	1.866(12)	W9–O27	2.299(11)
W7–O17	1.894(12)	W8–O15	1.998(12)	W9–O33	1.940(11)
W7–O18	2.399(11)	W8–O19	1.984(11)	W9–O34	2.107(12)
W7–O31	1.834(13)	W8–O30	1.728(12)	W9–O35	1.994(12)
W10–O11	1.910(12)	W10–O13	1.969(13)	W10–O18	2.403(11)
W10–O12	2.026(12)	W10–O16	1.790(12)	W10–O32	1.732(12)
Ag1–As1	2.774(3)	Ag1–O22	2.331(13)	Ag1–O20	2.377(13)
Ag1–O9	2.342(13)	Ag1–O24	2.332(14)	As1–O27	1.805(12)
As1–O18	1.785(11)	As1–O2	1.791(11)		

Table S4. The angle values for compound **1**.

Bond	Angle	Bond	Angle	Bond	Angle
O1–W1–O23	81.8(5)	O6–W2–O27	85.8(5)	O11–W3–O18	73.1(4)
O1–W1–O27	82.3(4)	O10–W2–O6	98.8(6)	O11–W3–O31	82.5(5)
O5–W1–O1	101.2(5)	O10–W2–O17	101.0(5)	O20–W3–O11	93.5(5)
O5–W1–O23	95.3(5)	O10–W2–O23	102.0(5)	O20–W3–O18	90.7(5)
O5–W1–O26	103.6(6)	O10–W2–O27	173.6(5)	O20–W3–O31	162.8(6)
O5–W1–O27	165.1(5)	O10–W2–O34	101.2(6)	O20–W3–O33	94.0(5)
O5–W1–O35	102.3(5)	O17–W2–O6	82.4(5)	O28–W3–O11	98.4(5)
O23–W1–O27	70.7(4)	O17–W2–O27	83.9(5)	O28–W3–O18	164.5(5)
O26–W1–O1	86.9(5)	O23–W2–O6	86.1(5)	O28–W3–O20	103.0(6)
O26–W1–O23	159.6(5)	O23–W2–O17	155.6(5)	O28–W3–O31	94.2(6)
O26–W1–O27	91.0(5)	O23–W2–O27	73.8(5)	O28–W3–O33	101.9(6)
O26–W1–O35	97.7(5)	O23–W2–O34	92.9(5)	O31–W3–O18	72.1(4)
O35–W1–O1	154.2(5)	O34–W2–O6	159.8(5)	O33–W3–O11	156.3(5)
O35–W1–O23	85.6(5)	O34–W2–O17	90.6(5)	O33–W3–O18	84.3(5)
O35–W1–O27	72.3(5)	O34–W2–O27	74.6(4)	O33–W3–O31	83.9(5)
$O4^1$–W4–$O16^1$	78.4(5)	O1–W5–O2	87.3(4)	O4–W6–O2	82.9(4)
$O4^1$–W4–O26	82.7(5)	O1–W5–O8	160.6(5)	O4–W6–O8	86.0(5)
$O4^1$–W4–O29	153.7(5)	O1–W5–O15	89.0(5)	O8–W6–O2	73.6(4)
O22–W4–$O4^1$	93.2(5)	O1–W5–O29	88.0(5)	O13–W6–O2	86.6(5)
O22–W4–$O16^1$	171.1(5)	O7–W5–O1	103.2(6)	O13–W6–O4	88.3(5)
O22–W4–$O24^1$	96.1(6)	O7–W5–O2	167.4(5)	O13–W6–O8	159.9(5)
O22–W4–O26	88.3(6)	O7–W5–O8	96.2(6)	O13–W6–O19	89.2(5)
O22–W4–O29	104.3(5)	O7–W5–O15	99.1(5)	O19–W6–O2	74.3(5)
$O24^1$–W4–$O4^1$	104.4(5)	O7–W5–O29	104.5(6)	O19–W6–O4	157.1(5)
$O24^1$–W4–$O16^1$	88.8(5)	O8–W5–O2	73.6(4)	O19–W6–O8	88.6(5)
$O24^1$–W4–O26	171.4(5)	O15–W5–O2	73.9(5)	O21–W6–O2	167.4(5)
$O24^1$–W4–O29	93.3(5)	O15–W5–O8	89.1(5)	O21–W6–O4	104.4(5)
O26–W4–$O16^1$	87.9(4)	O29–W5–O2	156.3(5)	O21–W6–O8	96.5(5)
O29–W4–$O16^1$	82.7(5)	O29–W5–O8	82.5(5)	O21–W6–O13	103.6(6)
O29–W4–O26	78.4(5)	O29–W5–O15	86.0(5)	O21–W6–O19	98.2(5)

O3–W7–O18	85.8(4)	O3–W8–O2	86.9(4)	O9–W9–O27	91.0(5)
O12–W7–O3	85.2(5)	O3–W8–O15	159.5(5)	O9–W9–O33	94.0(5)
O12–W7–O17	155.6(5)	O3–W8–O19	90.6(5)	O9–W9–O34	163.6(5)
O12–W7–O18	73.9(5)	O6–W8–O2	85.5(4)	O9–W9–O35	92.4(5)
O14–W7–O3	99.1(6)	O6–W8–O3	91.4(5)	O25–W9–O9	104.1(6)
O14–W7–O12	101.5(6)	O6–W8–O15	87.7(5)	O25–W9–O27	163.2(6)
O14–W7–O17	101.2(6)	O6–W8–O19	158.2(5)	O25–W9–O33	101.2(6)
O14–W7–O18	173.1(5)	O15–W8–O2	72.6(4)	O25–W9–O34	92.0(6)
O14–W7–O31	100.5(6)	O19–W8–O2	73.0(4)	O25–W9–O35	98.3(5)
O17–W7–O3	82.4(5)	O19–W8–O15	82.9(5)	O33–W9–O27	84.7(5)
O17–W7–O18	84.2(5)	O30–W8–O2	167.4(5)	O33–W9–O34	85.3(5)
O31–W7–O3	160.2(5)	O30–W8–O3	102.4(6)	O33–W9–O35	157.3(5)
O31–W7–O12	93.8(5)	O30–W8–O6	102.5(6)	O34–W9–O27	72.6(5)
O31–W7–O17	90.9(5)	O30–W8–O15	97.8(6)	O35–W9–O27	73.4(4)
O31–W7–O18	74.9(5)	O30–W8–O19	98.3(5)	O35–W9–O34	82.4(5)
O11–W10–O12	85.0(5)	O13–W10–O18	81.2(4)	O32–W10–O11	103.2(5)
O11–W10–O13	153.5(5)	O16–W10–O11	97.7(5)	O32–W10–O12	94.3(5)
O11–W10–O18	72.7(4)	O16–W10–O12	160.8(5)	O32–W10–O13	100.9(5)
O12–W10–O18	71.5(4)	O16–W10–O13	87.1(5)	O32–W10–O16	103.5(6)
O13–W10–O12	82.4(5)	O16–W10–O18	91.1(4)	O32–W10–O18	165.3(5)
O9–Ag1–As1	81.4(3)	O24–Ag1–As1	94.9(3)	O2–As1–O27	96.7(5)
O9–Ag1–O20	79.8(4)	O24–Ag1–O9	176.0(5)	O18–As1–O2	97.2(5)
O20–Ag1–As1	80.8(3)	O24–Ag1–O20	98.2(5)	O18–As1–O27	101.2(5)
O22–Ag1–As1	95.6(3)	O24–Ag1–O22	82.1(4)	O22–Ag1–O20	176.4(5)
O22–Ag1–O9	99.6(4)				

Table S5. Bond valence sum calculations of W, Ag, As and O atoms of compound **1**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
Ag1	1.03	As1	2.96	W1	5.93	W2	5.90
W3	5.98	W4	6.19	W5	5.86	W6	5.94
W7	6.24	W8	5.88	W9	5.91	W10	5.96
O1	1.92	O2	1.97	O3	1.94	O4	1.94
O5	1.75	O6	1.96	O7	1.61	O8	1.76
O9	1.79	O10	1.52	O11	1.83	O12	1.85
O13	1.96	O14	1.70	O15	1.80	O16	1.91
O17	2.03	O18	1.89	O19	1.86	O20	1.76
O21	1.67	O22	1.85	O23	1.94	O24	1.84
O25	1.68	O26	1.86	O27	1.85	O28	1.67
O29	1.95	O30	1.67	O31	1.85	O32	1.65
O33	1.99	O34	1.74	O35	1.84		

Table S6. Comparison of the macrocyclic POM-based materials on proton conductivity.

Compounds	Conductivity (S cm^{-1})	Relative humidity (%)	Temperature (K)	Reference
$Na_{24}[Ag_{3.4}Na_{0.6}(As_4W_{40}O_{140})]\cdot 82H_2O$	**2.24×10^{-2}**	**90**	**358**	**This work**
$Cs_{15}(NH_4)[(SiW_9Nb_3O_{40})_4(Mo_4O_6)]\cdot 42H_2O$	1.16×10^{-2}	98	358	2
$Na_6K_6H_{25}[(P_6W_{37}O_{127})\{Ag_2(Ag_6O_{19})\}]\cdot 53H_2O$	3.0×10^{-2}	98	368	3
$K_8Na_3Li_5\{[Na(NO_3)(H_2O)]_4[Al_{16}(OH)_{24}(H_2O)_8(P_8W_{48}O_{184})]\}\cdot 66H_2O$	4.5×10^{-2}	70	358	4
$(Me_2NH_2)_{13}K_7Na_2Li_{10}[\{As^{III}_5O_4(OH)_3\}_2(P_8W_{48}O_{184})]\cdot 32H_2O$	1.2×10^{-2}	70	358	5
$[N(CH_3)_4]_2K_{16}Na_{10\cdot5}H_{10\cdot5}[\{Zr(C_2O_4)_2\}_3(PO_4)(P_6W_{39}O_{150})]\cdot 45H_2O$	1.18×10^{-2}	95	368	6
$K_4Na_4H_{11}[KCo_2(H_2O)_{10}P_4W_{24}O_{92}\{(PhPO)_2\}]\cdot 48H_2O$	1.59×10^{-2}	95	318	7
$\{P_5W_{30}\}_2\subset\{Mo_{22}Fe_8\}$	1.7×10^{-2}	90	368	8
$H_2(C_2H_{10}N_2)_2[M^{II}(H_2O)_2(V^{IV}O)_8(OH)_4(PO_4)_4(HPO_4)_4]$	1.0×10^{-2}	97	358	9
$Zr_{70}(SO_4)_{58}(O/OH)_{146}\cdot x(H_2O)\cdot[Mg(H_2O)_6]_y$	5.24×10^{-3}	98	343	10
$K_{12}\{(Mo_2O_2S_2)_8(OH)_{12}[N_2C_2H_4(CH_2PO_3)_4]_2\}\cdot 40H_2O$	4.17×10^{-3}	80	358	11

Table S7. Comparison of different type materials on proton conductivity.

Compounds	Conductivity (S cm^{-1})	Relative humidity (%)	Temperature (K)	Type
$Na_{24}[Ag_{3.4}Na_{0.6}(As_4W_{40}O_{140})]\cdot 82H_2O$	**2.24×10^{-2}**	**90**	**358**	**This work**
10HSA@MOF-808-(bSA)$_2$[12]	2.47×10^{-1}	98	358	MOFs
$[Tb_2(TPTC)_2(H_2O)_2][(CH_3)_2NH_2]_2$[13]	1.62×10^{-2}	100	353	
PA@MTI-DAPy-COF[14]	3.68×10^{-2}	anhydrous	423	COFs
Im-CH_3@COF[15]	2.40×10^{-3}	100	343	
iHOF-45[16]	5.25×10^{-3}	98	373	HOFs

$[(TSM)(DBpy)_2 \cdot 2(H_2O)]_n$[17]	1.23×10^{-2}	98	373

IV Reference

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