A Rh-substituted polyoxometalate with an acetate modified building block $\{As_2W_{22}O_{76}(CH_3COO)_2\}$

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Materials and Syntheses

$Na_2WO_4 \cdot 2H_2O$, $NaAsO_2$, $RhCl_3 \cdot 3H_2O$, dimethylamine hydrochloride and other chemical reagents were acquired from commercial sources and used directly. IR spectra was conducted on a Bruker VERTEX 70 IR spectrometer (KBr pellets) recording in the range of 4000–450 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained by employing a Bruker D8 ADVANCE diffractometer with Cu Kα radiation (the value of λ is 1.54056 Å). TG analyse was measured by a Perkin-Elmer TGA7 instrument under flowing N_2 (heating rate, 10 °C min^{-1}). Elemental analyses (C, H, N) were conducted on an Elementar Vario MICRO analyzer. UV-vis spectrum was tested on the UH4150 UV-Vis spectrophotometer in the range of 180–800 nm (water as solvent). The proton conductivity tests was carried out on AMETEK (GB) LIMITED analyzer by using compacted pellet of the powdered sample of crystalline compound **1**.

Syntheses of 1

Dimethylamine hydrochloride (0.400 g, 4.882 mmol) was added in a 10 mL sodium acetate buffer solution (0.5 mol L^{-1}, pH = 4.5) containing $Na_2WO_4 \cdot 2H_2O$ (1.200 g, 3.638mmol) with stirring. Then, $NaAsO_2$ (1 mol L^{-1}, 0.5 mL) was dropwise added to the solution. $RhCl_3$ (0.050 g, 0.190 mmol) was subsequently added into the reaction mixture. After stirring for 10 min, the pH of the solution was adjusted to about 4.6 with glacial acetic acid. This solution was stirred and heated to 90 °C for 5 h. The resulting solution was cooled and filtered to evaporate at room temperature. The clear filtrate was left for about one week to obtain red stick-shaped crystals. Elemental analysis calcd for **1** (%): H, 1.45; C, 4.56; N, 2.21. Found: H, 1.51; C, 4.39; N, 2.16.

X-ray crystallography

The single crystals **1** was directly fixed on a loop and kept at 150.0 K during data collection on a Bruker D8 VENTURE PHOTON II CCD diffractometer with Mo Kα radiation (the value of λ is 0.71073 Å), After the data reduction,[1] Olex2 was applied to analyse the structures, by which it was first solved with the ShelXT structure solution program by the utilization of direct methods and then refined with the ShelXL-2018/3 refinement package using least squares minimisation.[2] In addition, all the atoms are refined anisotropically in the final refinement cycle, only few harsh constraints have been used in order to eliminate the ADP alert of few atoms. And some lattice water molecules were located by Fourier map, whereas the rest lattice molecules were determined by TGA results and element analyses. All H atoms on water molecules in the molecular formula were directly included. Crystallographic data of **1** has been deposited in the Cambridge Crystallographic Data Center with CCDC numbers: 2093916. Crystal data and structure refinement parameters are detailed in Table S1.

Table S1 Crystallographic data of **1**

	1
Empirical formula	$C_{24}H_{92}As_2N_{10}Na_2O_{85}Rh_2W_{22}$
Formula weight	6327.12
Crystal system	monoclinic
Space group	C2/*c*
a [Å]	40.0469(11)
b [Å]	12.2563(4)
c [Å]	23.2462(6)
α /°	90
β /°	108.0590(10)
γ /°	90
Volume/Å^3	10847.8(5)
Z	4
ρ_{calc} g/cm^3	3.927
μ/mm^{-1}	24.238
F(000)	11320.0
Crystal size/mm^3	0.16 × 0.11 × 0.06
Index ranges	-47 ≤ h ≤ 47, -12 ≤ k ≤ 14, -27 ≤ l ≤ 27
Reflections collected	35713
Data/restraints/ parameters	9618/24/724
R_{int}	0.0343
Goodness-of-fit on F^2	1.031
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0265, 0.0554
R_1, wR_2 [all data]	0.0324, 0.0579

Table S2 Selected bond distances (Å) for polyanion **1a**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
O1–W3	1.714(6)	O14–W3	2.372(6)	O27–W9	1.908(6)
O2–W1	1.710(6)	O14–W6	2.301(6)	O28–W8	1.830(6)
O3–W2	1.705(6)	O15–W9	1.728(6)	O28–W9	2.161(6)
O4–W1	1.931(6)	O16–W5	1.926(6)	O29–W7	1.826(6)
O4–W3	1.900(5)	O16–W6	1.939(5)	O30–W9	2.146(6)
O5–W2	1.951(6)	O17–W6	1.710(6)	O31–W9	1.771(6)
O5–W3	1.898(6)	O18–W5	1.712(6)	O32–W7[1]	1.958(5)
O6–W1	1.889(6)	O19–W5	1.822(6)	O32–W11	1.881(6)
O7–W3	1.888(6)	O20–W6	1.824(6)	O33–W3[1]	1.924(6)
O7–W6	1.986(6)	O21–W4	1.896(6)	O33–W11	1.927(6)
O8–W1	1.906(6)	O21–W5	1.985(5)	O34–W11	1.715(6)
O8–W5	1.996(6)	O23–W1	2.394(6)	O35–W6[1]	1.994(6)
O9–W1	1.886(6)	O23–W4	2.433(6)	O35–W11	1.916(6)
O9–W4	1.939(6)	O23–W5	2.283(5)	O36–W10	1.919(6)
O11–W2	1.873(5)	O24–W8	1.704(6)	O36–W11	1.894(6)
O11–W8	1.999(6)	O25–W7	1.918(5)	O37–W10	1.733(6)
O12–W7	1.718(5)	O25–W8	1.967(5)	O38–W10	1.773(6)
O13–W2	2.434(6)	O26–W4	1.916(6)	O39–W10	2.164(6)
O13–W7	2.339(5)	O26–W8	1.904(5)	O40–W9	1.922(5)
O13–W8	2.339(6)	O27–W4	1.882(5)	O40–W10	1.920(5)
Na1–O25, Na1–O25[1]	2.843(7)	Na1–O29, Na1–O29[1]	2.606(6)	Na1–W7, Na1–W7[1]	3.579(3)
Na1–O28, Na1–O28[1]	2.513(5)	Na1–O40, Na1–O40[1]	2.575(7)	Na1–W8, Na1–W8[1]	3.551(3)
Na2–O1[2]	2.457(11)	Na2–O4W	2.59(2)	Na2–O8W[4]	2.520(18)
Na2–O3W	2.440(15)	Na2–O5W[3]	2.882(19)	Na2–O18	2.994(12)
As1–Rh1	2.439(1)	O19–Rh1	2.009(5)	O31–Rh1	1.998(6)
N1–Rh1	2.081(8)	O20–Rh1	1.994(6)	O38–Rh1[1]	1.983(6)

[1]1-X,+Y,3/2-Z; [2]3/2-X,1/2+Y,3/2-Z; [3]3/2-X,3/2-Y,1-Z; [4]1-X,2-Y,1-Z.

Table S3 Selected bond angle (°) for polyanion **1a**.

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O13–As1–Rh1	142.32(19)	O14–As1–Rh1	104.4(2)	O23–As1–Rh1	104.4(2)
C1–N1–Rh1	113.6(6)	C2–N1–Rh1	112.7(6)	W5–O19–Rh1	135.0(3)
W6–O20–Rh1	136.2(3)	W9–O31–Rh1	147.8(3)	N1–Rh1–As1	168.4(2)
O19–Rh1–As1	86.37(17)	O19–Rh1–N1	85.7(3)	O20–Rh1–As1	86.30(18)
O20–Rh1–N1	84.6(3)	O20–Rh1–O19	84.8(2)	O31–Rh1–As1	97.41(18)
O31–Rh1–N1	91.8(3)	O31–Rh1–O19	96.3(2)	O31–Rh1–O20	176.2(3)
O38[1]–Rh1–As1	97.04(19)	O38[1]–Rh1–N1	91.0(3)	O38[1]–Rh1–O19	176.6(3)
O38[1]–Rh1–O20	95.3(2)	O38[1]–Rh1–O31	83.3(2)		

[1]1-X,+Y,3/2-Z.

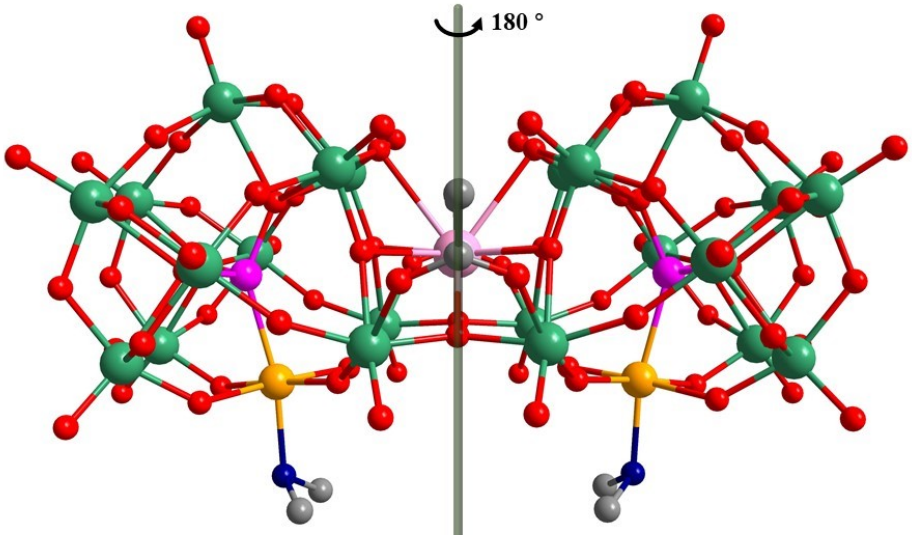

Fig. S1 The *C2* symmetry in **1a**.

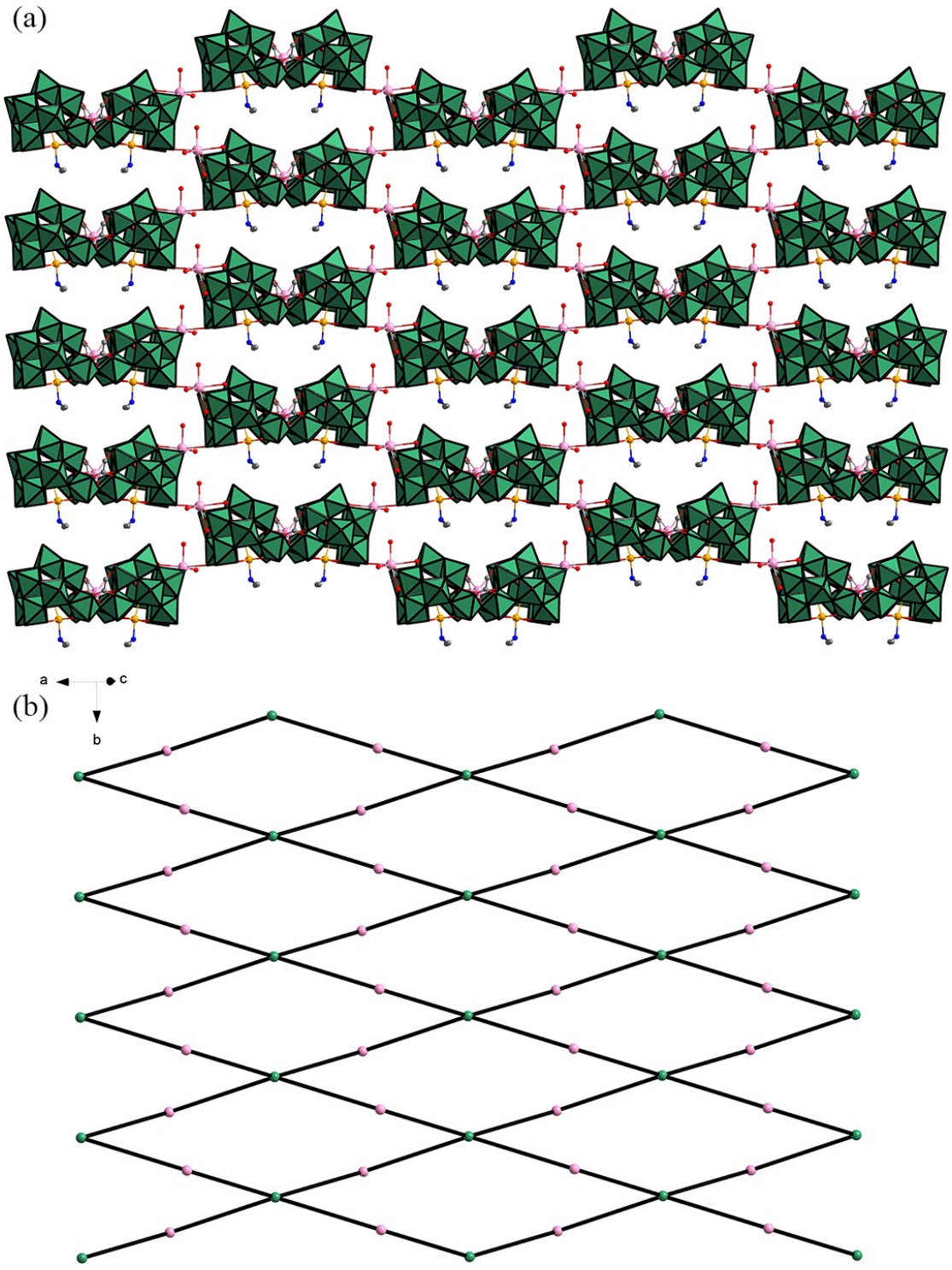

Fig. S2 (a) Combined polyhedral/ball-and-stick, (b) topology representations of 2D network structure along the *c* axis.

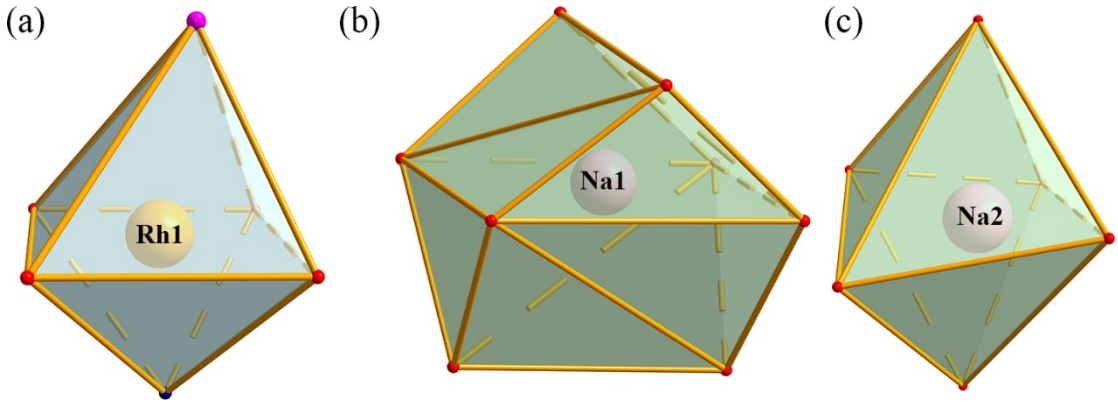

Fig. S3 The coordination geometries of (a) Rh1 in distorted octahedron, (b) central Na1 in distorted dodecahedron configuration and (c) external bridged Na2 in the distorted octahedron configuration.

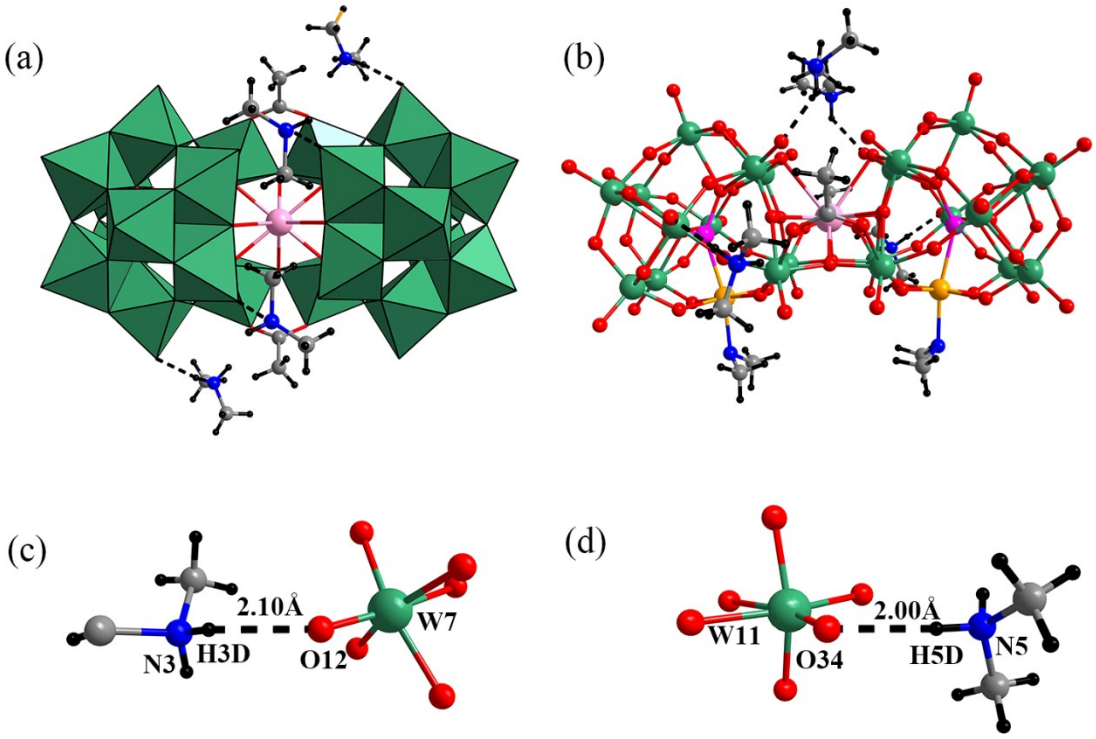

Fig. S4 Hydrogen-bond interactions in **1**.

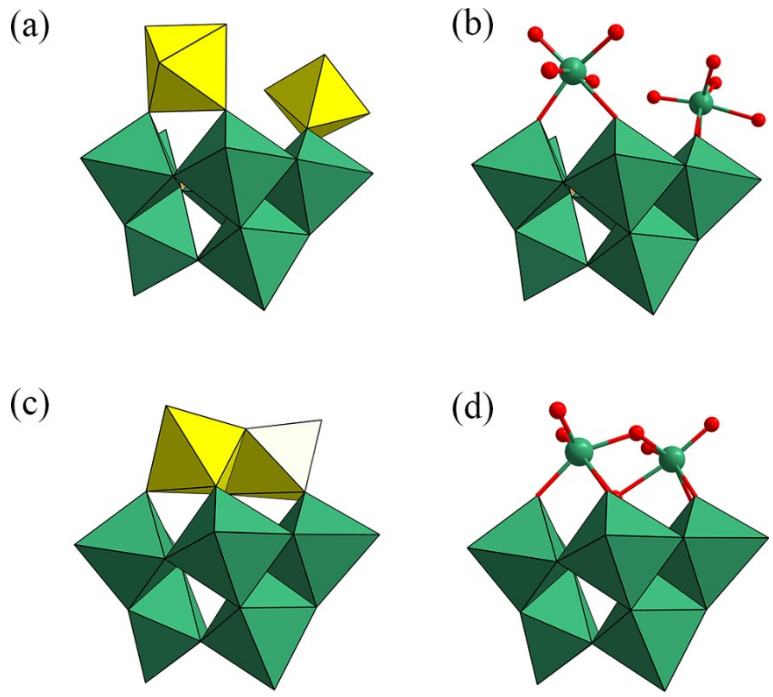

Fig. S5 (a) Polyhedral, (b) combined polyhedral/ball-and-stick representations of the $[AsW_{11}O_{41}]^{13-}$ subunit, (c) Polyhedral, (d) combined polyhedral/ball-and-stick representations of the $[AsW_{11}O_{39}]^{7-}$ subunit.

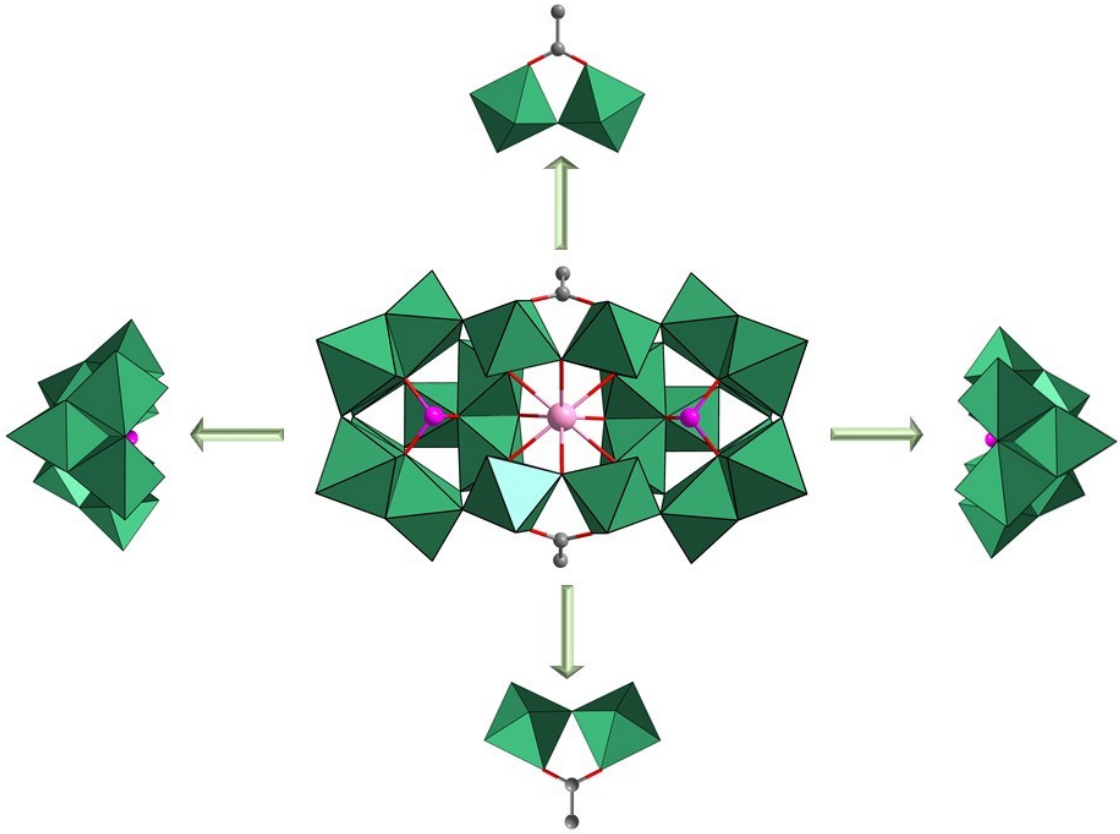

Fig. S6 Assembled scheme of $[NaAs_2W_{22}(CH_3COO)_2O_{76}]^{15-}$.

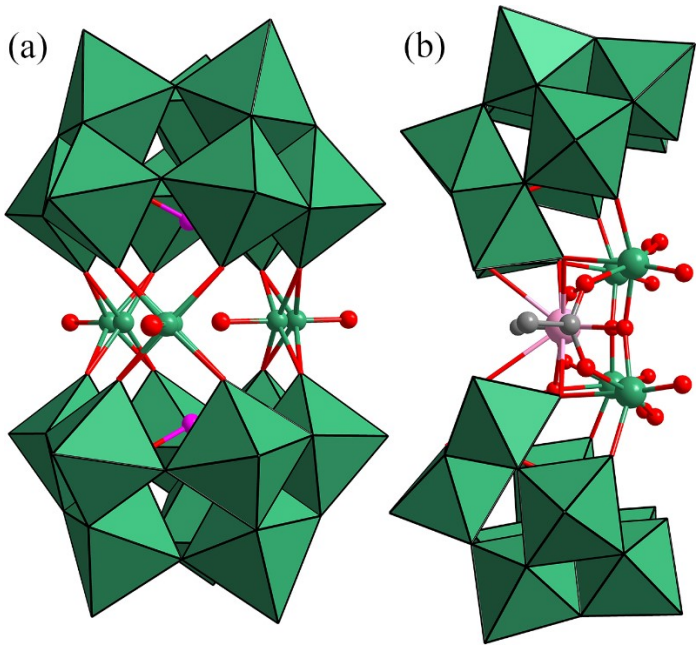

Fig. S7 Combined polyhedral/ball-and-stick representations of (a) $[As_2W_{21}O_{69}(H_2O)]^{6-}$ and (b) $[NaAs_2W_{22}(CH_3COO)_2O_{76}]^{15-}$.

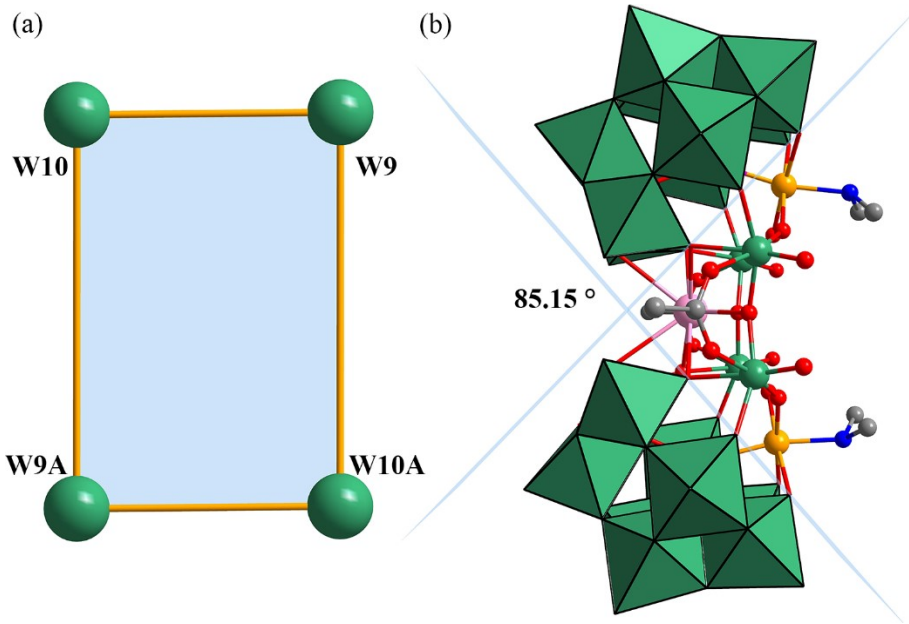

Fig. S8 (a) The plane of four W atoms, (b) the angle of two $[B\text{-}\alpha\text{-}AsW_9O_{33}]^{9-}$ fragments.

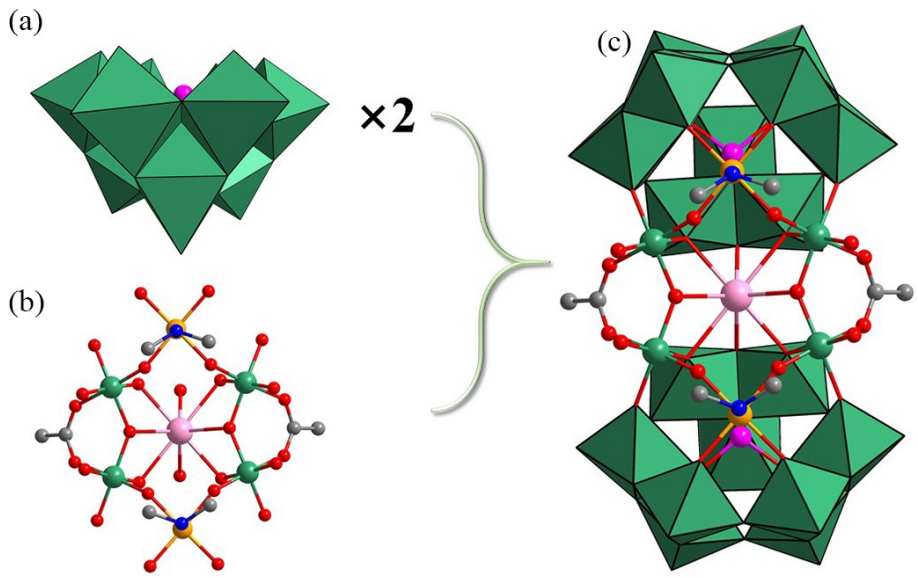

Fig. S9 Assembled scheme of polyanion **1a**.

Table S4 Bond valence sum (BVS) calculations of Rh atoms in **1a**.[3]

Bond	Bond length	Bond Valence	Valence Sum
Rh1–O19	2.011	0.555	Σ(Rh1) = 3.735
Rh1–O20	1.998	0.575	
Rh1–O31	1.987	0.592	
Rh1–O38	1.983	0.598	
Rh1–N1	2.078	0.585	
Rh1–As1	2.439	0.830	

Table S5 Bond valence sum (BVS) calculations of W and As atoms in **1a**.

Atom	BVS	Atom	BVS	Atom	BVS
W1	6.165	W2	6.084	W3	6.202
W4	6.165	W5	6.001	W6	6.011
W7	6.063	W8	6.073	W9	6.212
W10	6.156	W11	6.088	As1	2.606

Table S6 Bond valence sum (BVS) calculations of O atoms in **1a**.

Atom	BVS	Atom	BVS	Atom	BVS
O1	1.905	O2	1.728	O3	1.764
O4	2.009	O5	1.969	O6	2.048
O7	1.916	O8	1.839	O9	2.039
O10	1.907	O11	1.922	O12	1.723
O13	2.060	O14	2.025	O15	1.674
O16	1.924	O17	1.757	O18	1.771
O19	1.849	O20	1.875	O21	1.882
O22	1.804	O23	2.015	O24	1.768
O25	1.929	O26	2.045	O27	2.126
O28	1.933	O29	1.951	O30	1.898
O31	2.071	O32	1.995	O33	1.952
O34	1.727	O35	1.819	O36	2.051
O37	1.645	O38	2.068	O39	1.801
O40	2.100	O3W	0.187	O4W	0.247
O5W	0.052	O8W	0.143		

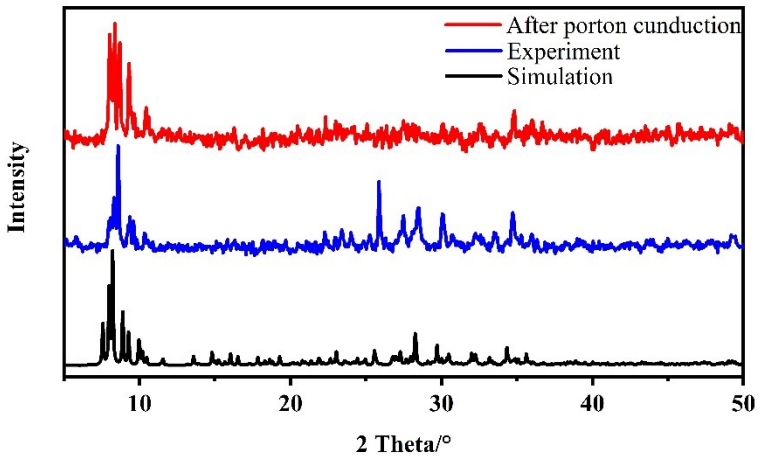

Fig. S10 The PXRD patterns of **1**: experimental, simulated and post proton conduction.

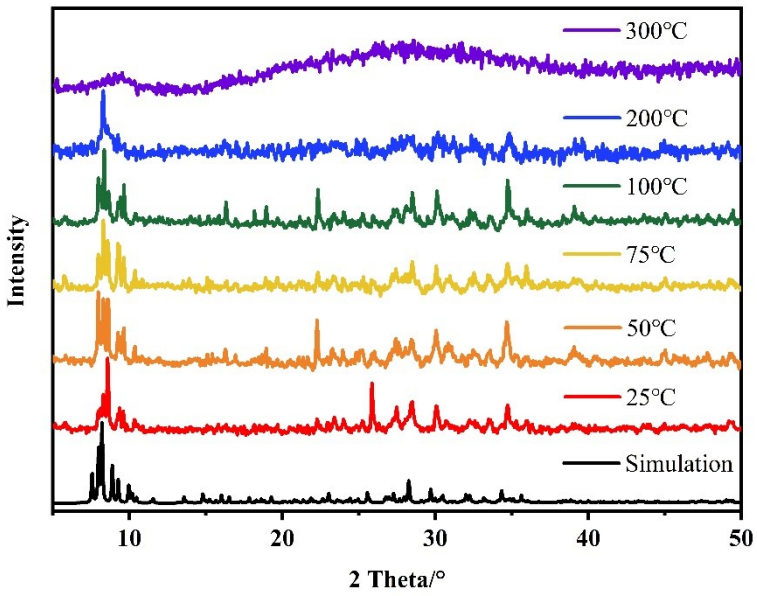

Fig. S11 The PXRD patterns of compound (a) **1** after heated at different temperature in vacuum oven.

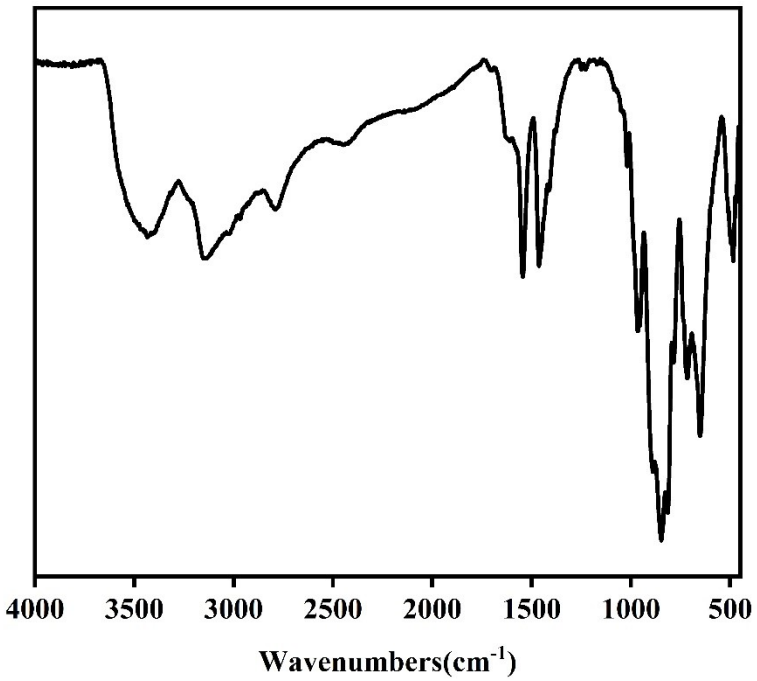

Fig. S12 IR spectra of **1**.

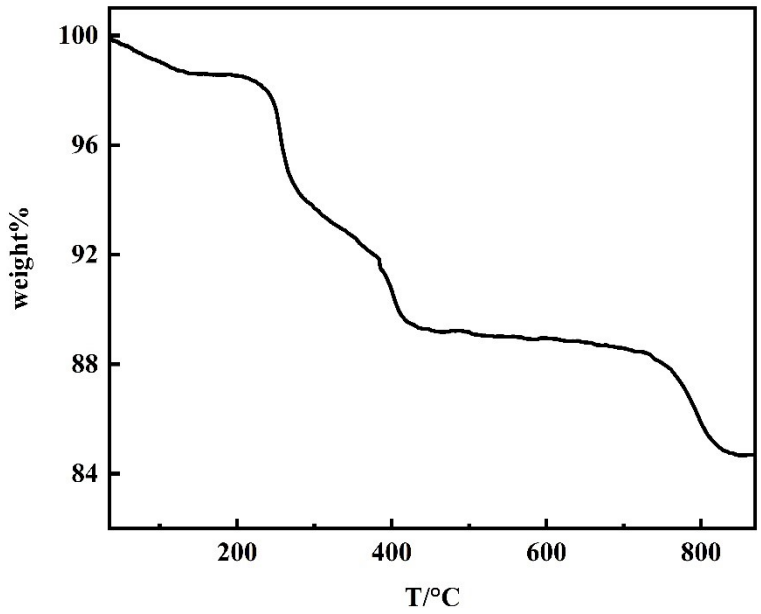

Fig. S13 TGA curve of compound **1.**

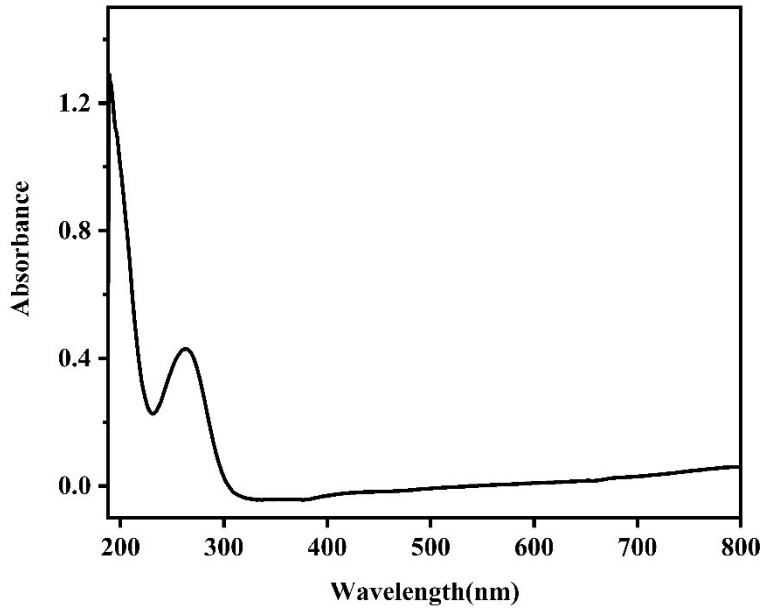

Fig. S14 UV-Vis spectra of **1** in H_2O (1.0×10^{-6} mol/L).

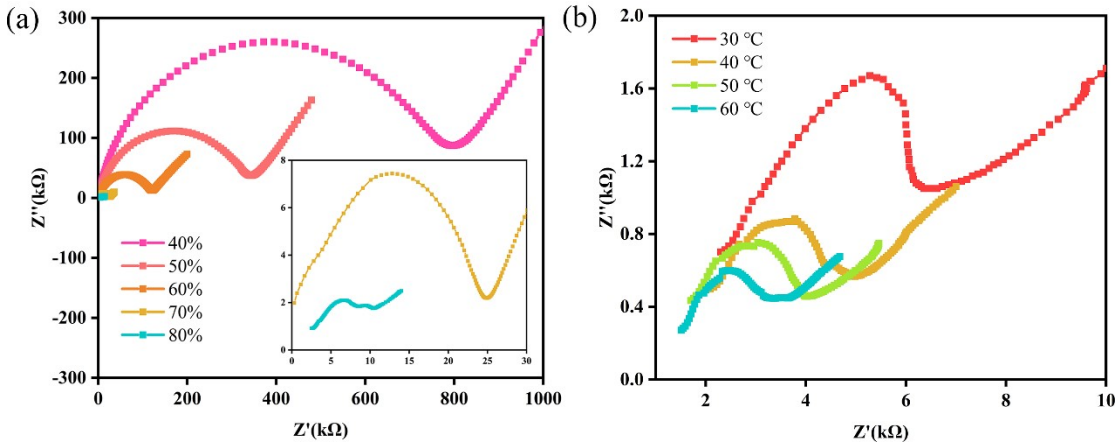

Fig. S15 Nyquist plots of **1** (a) under different RHs at 25 °C, (b) at 80% RH under different temperatures.

(1) SAINT, *Program for Data Extraction and Reduction*, Bruker AXS, Inc., Madison, WI, **2001**.

(2) (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341; (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112−122; (c) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8; (d) G. M. Sheldrick, SHELXL-2018/3, Program for Crystal Structure Refinement, University of Göttingen, Germany, **2018**.

(3) I. D. Brown, D. Altermatt, *Acta Cryst.*, 1985, **B41**, 244–247.