Electronic Supplementary Information (ESI)

A stable polyoxometalate-based porous coordination polymer with highly proton conductivity

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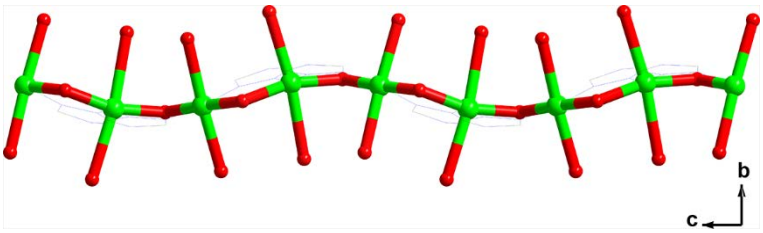

Fig. S1 Cu^{II} ions are connected by μ_2-OH groups to form 1D wave shape Cu-O-Cu chain.

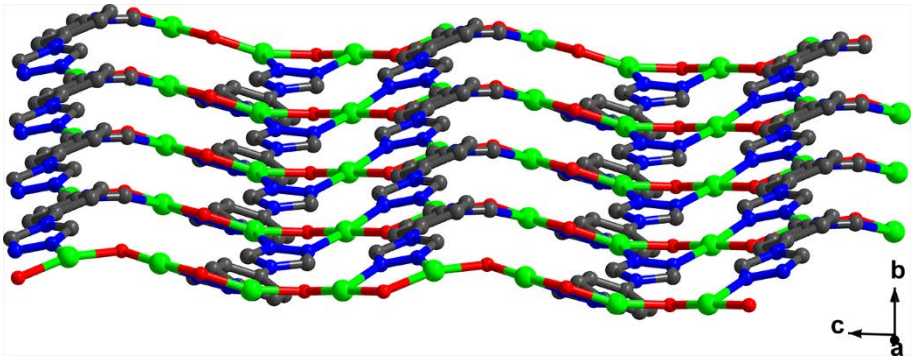

Fig. S2 1D Cu-O-Cu chains are connected by L ligands to generate 2D wavy layer. Coordination water molecules of Cu^{II} ions are omitted for clarify.

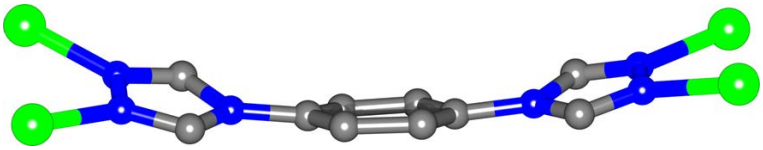

Fig. S3 The L ligands in the framework of **1** are bent into a curved shape.

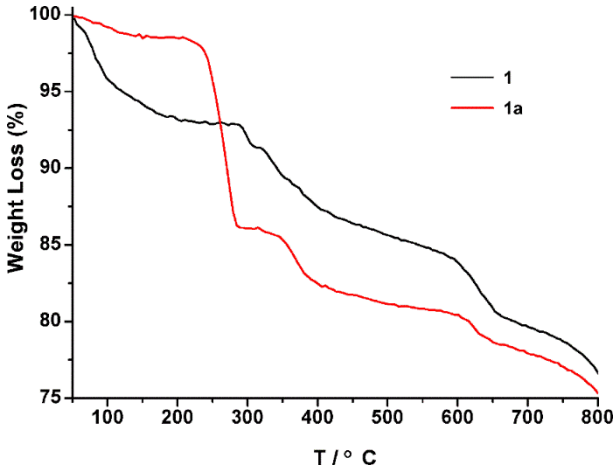

Fig. S5 Thermogravimetric analysis curves of **1** and **1a**.

Elemental analysis of **1a** was performed. Found (%): C, 5.92; H, 1.09; N, 6.05. Thereafter, the loading of $N_2H_4 \cdot H_2SO_4$ was about 5.4 per unit cell. The loaded $N_2H_4 \cdot H_2SO_4$ may presences in both of channels and surface of **1a**. The formula of **1a**

was referred to be $[Cu_4L_2(SiW_{12}O_{40})(OH)_4]\cdot 4H_2O\cdot 2.7N_2H_6SO_4$.

This formula was also confirmed by the TGA datum of **1a**. The TGA curve of **1** reveals only one weight loss of 1.52% (calculated 1.78%) from 50 °C till to 200 °C, causing by the loss of water molecules (Fig. S5). The further weight loss from 210 to 300 °C may be attributed to the decomposition of $N_2H_4\cdot H_2SO_4$ and the organic component of the framework. To further confirm the formula of **1a**, we have determined the amount of Cu^{2+} with ICP and the amount of SO_4^{2-} with Ion Chromatography, respectively. For Cu, 100 mg of 1a was heated at 700 °C under air for 4 hours. Thereafter, the residual was dissolved in aqua regia for ICP test. The total amount of Cu was detected to be 12.52 mg. For SO_4^{2-}, 200 mg of **1a** was dissolved in a mixture solution of Na_2EDTA and NaOH, which was diluted before test. The total amount of SO_4^{2-} was detected to be 13.76 mg. The results match well with the formula of **1a**.

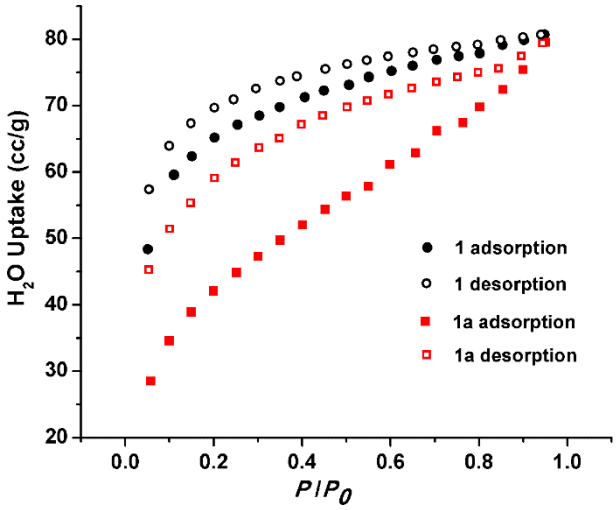

Fig. S6 Water vapor adsorption and desorption isotherms of **1** and **1a**.

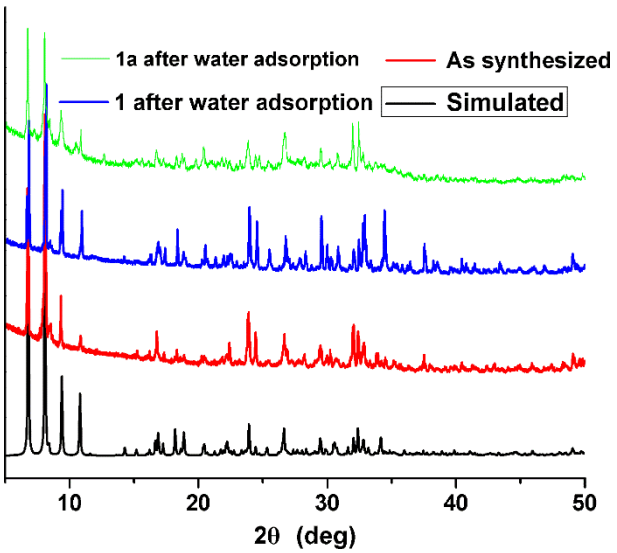

Fig. S7 PXRD patterns for **1** and **1a** after treated under different conditions.

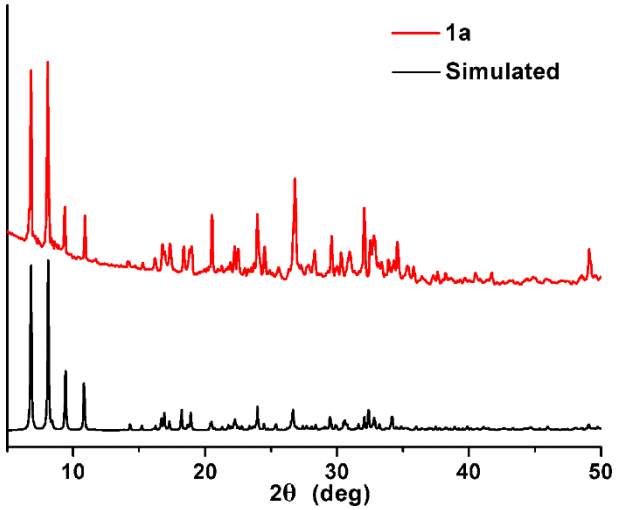

Fig. S8 PXRD patterns of **1a** and simulated **1**.

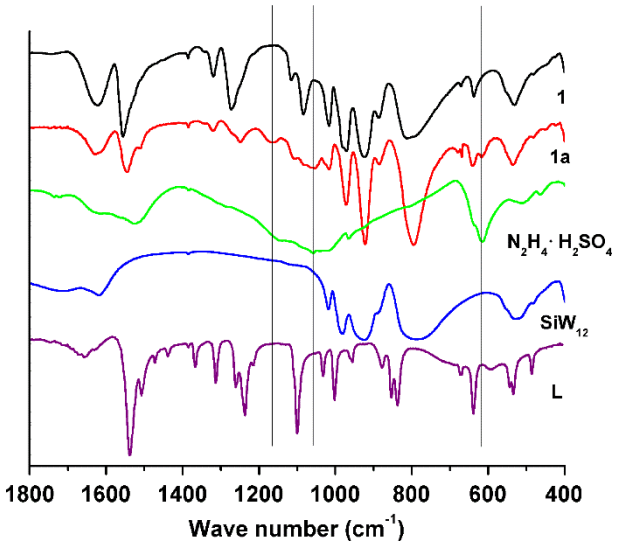

Fig. S9 FT-IR spectrum of **1**, **1a**, $N_2H_4{\cdot}H_2SO_4$, SiW_{12} and **L** ligands. SiW_{12} refers to $H_4SiW_{12}O_{40}{\cdot}xH_2O$.

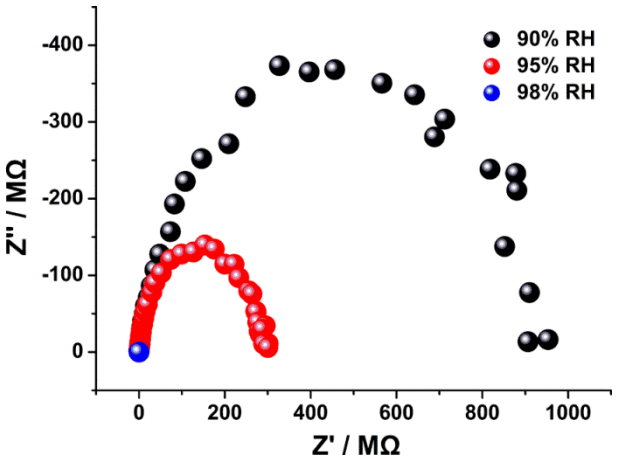

Fig. S10 Impedance spectrum of **1a** at 30 °C with different RHs.

Table S1 Hydrogen-bonding geometry parameters for compound **1**.

D-H···A	Symmetry code	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C1-H1···O14	*x*, *y*, *z*	0.93	2.26	3.18(4)	168
C2-H2···O16	*x*, 1/2-*y*, 1/2+*z*	0.93	2.25	3.16(3)	165
C8-H8···O20	*x*, *y*, 1+*z*	0.93	2.42	3.27(4)	153
C9-H9···O8	1-*x*, 1-*y*, 1-*z*	0.93	2.36	3.29(3)	171

Table S2 Selected bond lengths (Å) and angles (º) of **1**.

Cu1-O23	1.90(2)	Cu1-N5#2	2.06(2)
Cu1-O24	1.92(2)	Cu1-O1W	2.49(4)
Cu1-N1	1.97(3)	Cu1-O2W	2.44(4)
Cu2-O23	1.93(2)	Cu2-N4#1	1.99(2)
Cu2-O24#3	1.94(2)	Cu2-O3W	2.73(6)
Cu2-N2	1.98(2)	Cu2-O4W	2.57(7)
O23-Cu1-O24	176.6(12)	O23-Cu1-N1	89.0(10)
O24-Cu1-N1	93.1(11)	O23-Cu1-N5#2	90.0(9)
O24-Cu1-N5#2	88.1(10)	N1-Cu1-N5#2	174.7(11)
N1-Cu1-O2W	89.4(17)	N5#2-Cu1-O2W	95.9(16)
O23-Cu1-O1W	93.1(15)	O24-Cu1-O1W	89.5(17)
N1-Cu1-O1W	88.4(16)	N5#2-Cu1-O1W	86.4(16)
O2W-Cu1-O1W	174(2)	O24-Cu1-O2W	85.5(19)
O23-Cu1-O2W	91.9(17)		
O23-Cu2-O24#3	163.2(14)	O23-Cu2-N2	88.1(10)
O24#3-Cu2-N2	93.9(11)	O23-Cu2-N4#1	92.3(10)
O24#3-Cu2-N4#1	89.4(11)	N2-Cu2-N4#1	167.1(14)
O23-Cu2-O4W	103.8(19)	O24#2-Cu2-O4W	93(2)
N2-Cu2-O4W	84.4(18)	N4#1-Cu2-O4W	83.0(17)
O23-Cu2-O3W	82.3(15)	O24#2-Cu2-O3W	81.0(17)
N2-Cu2-O3W	103.1(17)	N4#1-Cu2-O3W	89.7(16)
O4W-Cu2-O3W	171(2)		

Symmetry codes: #1, -1+*x*, +*y*, +*z*, #2, -1+*x*, 1/2-*y*, -1/2+*z*; #3, +*x*, 1/2-*y*, 1/2+*z*.

Table S3 The proton conductivities of a part of POM-based polymer.

Compound	Condition (Temp., RH)	Conductivity [S cm^{-1}]	Ref.
$N_2H_6SO_4$@$[Cu_4(C_{10}H_{10}N_6)_2(SiW_{12}O_{40})(OH)_4(H_2O)_8]\cdot 8H_2O$	338K, 98%	3.9×10^{-3}	**This work**
$[Cu_4(C_{10}H_{10}N_6)_2(SiW_{12}O_{40})(OH)_4(H_2O)_8]\cdot 8H_2O$	338K, 98%	1.4×10^{-4}	**This work**
$[Sm(H_2O)_5(CO_2CH_2NH_3)_2][Al(OH)_6Mo_6O_{18}]\cdot 10H_2O$	353K, 95%	4.53×10^{-3}	[1]
H_3(3-PyBim)$_2$][$PMo_{12}O_{40}$]·3.5H_2O·CH_3CN·CH_3OH	373K, 98%	3.34×10^{-3}	[2]
$[Co(bpz)(Hbpz)][Co(SO4)_{0.5}(H_2O)_2(bpz)]_4[PMo^{VI}_8Mo^{V}_4V^{IV}O_{42}]\cdot 13H_2O$（NENU-530）	348K, 98%	1.5×10^{-3}	[3]
$[M(H_2O)_8][H(H_2O)_2](HINO)_4[PXO_{40}]$ M=Zn, Mn, Cu;	373K, 98%	1.3×10^{-3}	[4]
$[P_2Mo_5O_{23}][C_7H_7N_2]_6\cdot H_2O$ (NNU-6)	323K, 98%	1.21×10^{-3}	[5]
$[H_3$(3-PyBim)$_2$][$PMo_{12}O_{40}$]·4H_2O·CH_3CN	373K, 98%	1.36×10^{-3}	[2]
{H[Ni(Hbpdc)$(H_2O)_2]_2[PW_{12}O_{40}]\cdot 8H_2O$}n	373K, 98%	1.35×10^{-3}	[6]
H[Cu(Hbpdc)$(H_2O)_2]_2[PM_{12}O_{40}]$ M = Mo, W	373K, 98%	10^{-4}-10^{-3}	[6]
{$[Cu_3(L)_2(H_2O)_4][Cu(DMF)_4(SiW_{12}O_{40})]\cdot 9H_2O$}n	373K, 98%	5.97×10^{-4}	[7]
$Na_5[H_7\{N(CH_2PO_3)_3\}Mo_6O_{16}(OH)(H_2O)_4]_4$	303 K, 98%	7.6×10^{-4}	[8]
$[PMo_{11.04}V_{0.96}O_{40}][C_3H_5N_2]_4\cdot H_2O$ (NNU-8)	323K, 98%	4.45×10^{-4}	[5]
{$H_6[(H_2O)_{1.5}(H_2biim)_2(CH_3OH)]_2[(H_2biim)(CH_3OH)_2]$	373 K, 98%	3.1×10^{-4}	[9]
$[Ni_2(bpz)(Hbpz)_3(H_2O)_2][PMo^{VI}_8Mo^{V}_4V^{IV}O_{44}]\cdot 8H_2O$（NENU-531）	358K, 98%	2.8×10^{-4}	[3]
$(TMA)_{14}H_2[Ce^{III}(H_2O)_6]\{[Ce^{IV}Ce^{III}O_6(OH)_6(CO_3)(H_2O)_{11}][(P_2W_{16}O_{59})]_3\}\cdot 41H_2O$	373K, 98%	2.65×10^{-4}	[10]
$[Zn_{12}(trz)_{20}][SiW_{12}O_{40}]\cdot 11H_2O$	368 K, 95%	1.2×10^{-4}	[11]
$[Cu_{12}(BTC)_8(H_2O)_{12}][H_3PW_{12}O_{40}]\cdot nH_2O$	363K, 70%	4.76×10^{-5}	[12]
$[H_2EN]_5[NiMo_{12}O_{30}(PO_4)_8]\cdot 5.5H_2O$	300K, 98%	2.25×10^{-5}	[13]
$[Cu(phen)(H_2O)]_3[P_2Mo_5O_{23}]\cdot 5H_2O$	301 K, 98%	2.2×10^{-5}	[14]
$[H_2en]_4[Ni_5(OH)_3(trzS)_3(en)(H_2O)(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 6H_2O$	358K, 98%	1.3×10^{-5}	[15]
$[PMo_{12}O_{40}][C_7H_7N_2]_3\cdot 2H_2O$ (NNU-7)	323K, 98%	6.87×10^{-6}	[5]
$[Cu_3(\mu_3\text{-}OH)(H_2O)_3(atz)_3]_3[P_2W_{18}O_{62}]\cdot 14H_2O$	298K, 97%	4.4×10^{-6}	[16]
$Cu_6(Trz)_{10}(H_2O)_4[H_2SiW_{12}O_{40}]\cdot 8H_2O$	368K, 95%	1.84×10^{-6}	[17]

Table S4 Bond valence for Cu ions of compound **1**.

bond	Bond distance	Bond valence	Sum of bond valence
Cu1-O23	1.90	0.647177	Cu1 = 2.27
Cu1-O24	1.92	0.613123	
Cu1-N1	1.97	0.487279	
Cu1-N5	2.06	0.382066	
Cu1-O1W	2.49	0.067485	
Cu1-O2W	2.44	0.073185	
Cu2-O23	1.93	0.596774	Cu2 = 2.18
Cu2-O24	1.94	0.580861	
Cu2-N2	1.98	0.474285	
Cu2-N4	1.99	0.461639	
Cu2-O3W	2.73	0.029187	
Cu2-O4W	2.57	0.041488	

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