Supplementary Information

Self-assembled arrays of Polyoxometalate-based Metal-Organic Nanotubes for proton conduction and magnetism

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1. Materials and Measurements

All the chemicals were obtained from commercial sources, and were used without further purification. The α -K₆P₂W₁₈O₆₂·15H₂O was prepared according to the literature method^{S1} and verified by infrared (IR) spectrum. Elemental analyses (C, N, and H) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; P, Cu and W were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-Ka (1486.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. Diffuse reflectivity was measured from 200 to 800 nm using barium sulfate (BaSO₄) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Magnetic susceptibilities were measured on finely grounded single crystal samples (grease restricted) with the use of a Quantum Design SQUID magnetometer MPMS-XL. Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71069 Å) at 296(2) K. Powder X-ray diffraction measurement was recorded radiation ranging from 5° to 50° at room temperature on a Siemens D5005 diffractometer with Cu-K α (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C under nitrogen at the heating rate of 10 °C ·min⁻¹.

Proton conductivity measurements

The powders were prepared by grinding the sample into a homogeneous powder with a mortar and pestle. With a press and a die measuring 10 mm in diameter and 0.71 mm ($\pm 0.08\%$) in thickness, samples of **1** were pressed into disk-shaped pellets. The impedances were measured with a frequency response analyzer/potentiostat (IviumStat) over a frequency range from 1 Hz to 1 MHz, with a two probe electrochemical cell and an applied ac voltage of 50 mV. Measurements were taken in the temperature range of 25–55 °C with 65% relative humidity and in the relative humidity range of 45%–97% at 25 °C (controlled by using an BPHS-060A incubator), respectively. ZSimpWin software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Nyquist plot and obtain the

resistance values. Conductivity was calculated using the following equation:

 $\sigma = L / RS$

where σ is the conductivity (S cm⁻¹), L is the measured sample thickness (cm), S is the electrode area (cm²) and R is the impedance (Ω).

2. Synthesis

A mixture of α -K₆P₂W₁₈O₆₂·15H₂O (0.25 g, 0.051 mmol), CuCl₂ (0.21 g, 1.56 mmol), and Hatz (0.121 g, 1.44 mmol) was dissolved in 10 mL of distilled water at room temperature. Then the suspension was put into a Teflon-lined autoclave and kept under autogenous pressure at 140 °C for 3 days. After slow cooling to room temperature, green block crystals were filtered and washed with distilled water (40% yield based on W). Elemental analysis (%) calcd for C₁₈H₇₆Cu₉N₃₆O₈₈P₂W₁₈ (6147.97): C 3.52, H 1.25, Cu 9.30, N 8.20, P 1.01, W 53.83; Found: C 3.12, H 0.82.16, Cu 8.94, N 8.53, P 1.45, W 54.76. IR (solid KBr pellet, cm⁻¹): 3432 (w), 3345 (w), 1624 (m), 1555 (m), 1508 (w), 1426 (w), 1286 (w), 1232 (m), 1088 (s), 952 (m), 917 (m), 799 (s), 530 (w).

3. Crystallographic data for 1

The suitable single crystal of compound **1** was glued on a glass fiber. Data collection was performed on a Bruker ApexII CCD diffractometer with Mo K α ($\lambda = 0.71069$ Å) at room temperature. A multiscan correction was applied. The structure was solved by the direct method and refined by full matrix least-squares on F^2 using the SHELXL 97 program.^{S2} During the refinement of these crystal structures, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms for the solvent water molecules in the crystal structure could not be located through Fourier electron density map, although they were included in the molecular formula and molecular mass. The restrains were used to resolve the ADP and NPD errors of some O, C and N atoms by the "SIMU" instructions. The restraint command "DFIX" was used to refine N4 and C1. The "OMIT" order was used to confirm the data completeness. Relevant crystal data and structure refinements of compound **1** are summarized in Table S1. Selected bond lengths (Å) and angles (°) for **1** are listed in the Table S2. Crystallographic data for **1** have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 1043773.



Fig. S1 The TG curve of compound 1.



Fig. S2 The XRD pattern of the simulated pattern (black), as-synthesized (blue), after immersed in boiling water (olive), CH₃OH (magenta), C₂H₅OH (cyan), acetone (orange), acetonitrile (green), DMF (violet) and DMA (dark yellow).



Fig. S3 Two crystallographically unique water molecules are located within the nanotubular structure, forming a 1D hydrogen-bonding water chain.



Fig. S4 XPS spectrum of compound 1.



Fig. S5 The XRD pattern of the simulated pattern (black), as-synthesized (blue), after soaked in water with pH = 2 (wine) and pH = 12 (pink).



Fig. S6 The Thermodiffractograms of the as-synthesized sample. 100 °C (black), 180 °C (blue), 250 °C (olive), 300 °C (magenta), 350 °C (orange).



Fig. S7 Water vapor adsorption isotherm of 1 at 298 K.



Fig. S8 The XRD pattern of the as-synthesized (black), after adsorption experiments (pink).



Fig. S9 Nyquist plot for 1 under different temperatures with 65% RH conditions.



Fig. S10 Nyquist plot for **1** under different RH conditions with T = 25 °C.



Fig. S11 3D H-bonding network constructed by POM oxygen atoms and atz ligands as well as water molecules.

Generally, proton conducting MOFs have been obtained by introducing acidic and/or hydrophilic units or proton carriers into nano-channels to form efficient proton transfer pathways. Hupp *el at.* (JACS, 2012, 134, 51-54) have developed a new approach: a poor proton donor H₂O, is bound to an otherwise open coordination site of a node- or linker-based metal cation. Once the material's channels were infused with MeOH, binding substantially increases the acidity of the incorporated molecule, enabling it to donate a proton to hydroxylic guest molecules (MeOH) and thereby rendering conductive the network of hydrogen-bonded guest molecules filling the framework material's pores and channels. Besides, the measurement was carried out at 296 K under MeOH vapor. So, the proton conductivity of this HKUST-1 is higher, about 1.5×10^{-5} S cm⁻¹. However, as Liu *el at.* (Chem. Commun., 2014, 50, 10023-10026)

reported, the proton conductivity of HKUST-1 is 1.1×10^{-8} S cm⁻¹ at 90 °C under 70 % RH. When POMs were introduced into the framework, a huge enhancement in proton conductivity was observed, approximately 4.8×10^{-5} S cm⁻¹ (90 °C; 70 % RH). So, POMs can strengthen the scaffold, fill void space, provide mobile protons, and improve the hydrophilicity and water retention of the hybrid material. The nanotubes in MOF structure are filled with water molecules, where exists infinite1D hydrogen-bonding water chain as efficient proton transfer pathways, in favor for proton conduction. Besides, as shown in Table S2, multiple hydrogen bonds among POM oxygen atoms and atz ligands as well as water molecules are formed, constructing 3D H-bonding network (Fig. S11), which made this material an attractive candidate for proton conduction. POMs in 1 just act as linkers, holding these MONTs together to form 3D nanotubular arrays. POMs could improve the stability and hydrophilicity of MOFs. As expected, 1 exhibits exceptional chemical and thermal stability.



Fig. S12 UV-vis-NIR absorption spectrum of 1.



Fig. S13 The diffuse reflectance UV-vis-NIR spectra of $(Fhv)^{0.5}$ *vs.* energy (eV) of compound **1**. F = (1-R)*(1-R)/2R; A = log1/R.



Fig. S14 The plot of χ_{M}^{-1} versus *T* in the range 2–300 K (the red line represents the best fit of the data based on the Curie–Weiss law).



Fig. S15 IR spectrum of 1.

Table S1. Crystal Data and Structural Refinement Parameters for Compound 1

	1
empirical formula	$C_{18}H_{76}Cu_9N_{36}O_{88}P_2W_{18}\\$
Formula weight	6147.97
Crystal system	Hexagonal
Space group	<i>P</i> 6 ₃ /m
a (Å)	20.640(4)
b (Å)	20.640(4)
c (Å)	14.742(5)
α (°)	90
β (°)	90

γ (°)	120		
V (Å ³)	5438.84		
Z	2		
D _{calc} (mg m ⁻³)	3.754		
μ (mm ⁻¹)	20.815		
<i>T</i> (K)	296 K		
Reflections collected/ unique	31623/3335		
GOF	1.030		
$\mathbf{R}_{1}/\mathbf{w}\mathbf{R}_{2} \left[\mathbf{I} > 2\sigma(\mathbf{I})\right]$	0.052/0.125		
R ₁ /wR ₂ (all data)	0.078/0.145		

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}wR_{2} = |\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})| / \Sigma |w(F_{o}^{2})^{2}|^{1/2}$

Table S2 Hydrogen bonding geometry (Å, $^\circ)$ for compound 1

D –H···A	D–H	Н…А	D····A	D –Н···A
O(1W)–H(1)…O(2W)	0.85	2.41	3.24(4)	165
O(3W)–H(3)…N(6)	0.96	2.12	3.02(5)	157
O(3W)–H(4)····O(3)	0.96	2.06	2.96(4)	156
N(4)–H(4A)…O(3W)	0.86	2.48	3.23(3)	146
N(4)-H(4B)···O(12)	0.86	2.07	2.90(2)	164
O(4W)–H(5)…O(3)	0.85	2.28	3.13(4)	177
O(4W)–H(6)…O(7)	0.85	2.33	3.18(4)	177
O(4W)–H(6)…O(10)	0.85	2.44	2.88(4)	113
O(5W)–H(7)…N(6)	0.86	1.97	2.79(8)	161

N(7)–H(7A)…N(1)	0.87	2.38	306(4)	135
N(7)-H(7B)····O(7)	0.86	2.42	2.89(4)	115
O(14)–H(14A)····O(4W)	0.85	1.90	2.74(3)	169
O(15)-H(15A)····O(3W)	0.85	1.96	2.77(4)	160
O(15)-H(15B)····O(1W)	0.85	2.09	2.93(3)	170

Table S3 Selected bond distances (Å) and angles (°) for compound 1

	1		
Cu(1)-N(5)	1.977(13)	P(1)-O(9)#4	1.516(11)
Cu(1)-N(3)#1	1.98(3)	P(1)-O(9)	1.516(11)
Cu(1)-N(1)	2.006(15)	P(1)-O(4)	1.565(18)
Cu(1)-O(13)	2.017(8)	W(2)-O(7)	1.684(12)
Cu(2)-N(2)#2	1.95(6)	W(2)-O(8)	1.885(2)
Cu(2)-N(2)#1	1.95(5)	W(2)-O(6)	1.895(11)
Cu(2)-O(13)	2.021(13)	W(2)-O(10)	1.903(12)
Cu(2)-O(14)	2.10(3)	W(2)-O(5)	1.909(14)
Cu(2)-O(15)	2.226(13)	W(2)-O(9)	2.397(11)
P(1)-O(9)#3	1.516(11)	W(3)-O(12)	1.705(11)
W(3)-O(6)#3	1.852(11)	W(1A)-O(4)	2.382(10)
W(3)-O(11)	1.895(3)	W(1B)-O(2)#3	0.91(2)
W(3)-O(1)#3	1.898(13)	W(1B)-O(1)#3	2.020(15)
W(3)-O(10)	1.932(12)	W(1B)-O(5)	2.107(16)
W(3)-O(9)	2.355(11)	W(1B)-O(4)	2.399(12)
W(1A)-O(3)	1.699(18)	N(3)-Cu(1)#5	1.979(9)
W(1A)-O(2)#3	1.89(2)	N(2)-Cu(2)#5	1.951(10)
W(1A)-O(1)	1.923(13)	O(1)-W(3)#4	1.898(13)
W(1A)-O(5)	1.926(15)	O(1)-W(1B)#4	2.020(15)
W(1A)-O(2)	1.96(2)	O(2)-W(1B)#4	0.91(2)
O(2)-W(1A)#4	1.89(2)	O(6)-W(3)#4	1.852(11)
O(4)-W(1B)#4	2.399(12)	O(8)-W(2)#6	1.885(2)

O(4)-W(1A)#4	2.382(10)	O(11)-W(3)#6	1.895(3)
O(4)-W(1A)#3	2.382(10)	O(13)-Cu(1)#6	2.017(8)
O(4)-W(1B)#3	2.399(12)	N(5)-Cu(1)-N(3)#1	174.9(11)
N(2)#1-Cu(2)-O(14)	93.3(16)	N(5)-Cu(1)-N(1)	93.0(6)
O(13)-Cu(2)-O(14)	101.4(10)	N(3)#1-Cu(1)-N(1)	90.4(10)
N(2)#2-Cu(2)-O(15)	90(2)	N(5)-Cu(1)-O(13)	87.5(5)
N(2)#1-Cu(2)-O(15)	90.1(12)	N(3)#1-Cu(1)-O(13)	89.1(10)
O(13)-Cu(2)-O(15)	150.6(6)	N(1)-Cu(1)-O(13)	179.2(6)
O(14)-Cu(2)-O(15)	108.0(10)	N(2)#2-Cu(2)-N(2)#1	173(4)
O(9)#3-P(1)-O(9)#4	111.5(4)	N(2)#2-Cu(2)-O(13)	88.1(17)
O(9)#3-P(1)-O(9)	111.5(4)	N(2)#1-Cu(2)-O(13)	88.1(11)
O(9)#4-P(1)-O(9)	111.5(4)	N(2)#2-Cu(2)-O(14)	93(3)
O(9)#3-P(1)-O(4)	107.3(4)	O(9)#4-P(1)-O(4)	107.3(4)
O(6)-W(2)-O(5)	87.2(6)	O(9)-P(1)-O(4)	107.3(4)
O(10)-W(2)-O(5)	87.9(6)	O(7)-W(2)-O(8)	98.5(7)
O(7)-W(2)-O(9)	170.0(5)	O(7)-W(2)-O(6)	104.9(6)
O(8)-W(2)-O(9)	83.2(5)	O(8)-W(2)-O(6)	86.9(6)
O(6)-W(2)-O(9)	85.0(4)	O(7)-W(2)-O(10)	98.0(6)
O(10)-W(2)-O(9)	72.1(4)	O(8)-W(2)-O(10)	91.5(7)
O(5)-W(2)-O(9)	80.9(5)	O(6)-W(2)-O(10)	157.1(5)
O(12)-W(3)-O(6)#3	103.8(5)	O(7)-W(2)-O(5)	97.9(6)
O(12)-W(3)-O(11)	98.3(6)	O(8)-W(2)-O(5)	163.5(6)
O(6)#3-W(3)-O(11)	88.7(6)	O(12)-W(3)-O(1)#3	97.2(6)
O(1)#3-W(3)-O(9)	81.9(4)	O(6)#3-W(3)-O(1)#3	88.0(5)
O(10)-W(3)-O(9)	72.6(4)	O(11)-W(3)-O(1)#3	164.6(6)
(3)-W(1A)-O(2)#3	101.9(10)	O(12)-W(3)-O(10)	98.4(5)
O(3)-W(1A)-O(1)	100.2(8)	O(6)#3-W(3)-O(10)	157.7(5)
(2)#3-W(1A)-O(1)	157.8(7)	O(11)-W(3)-O(10)	89.3(6)
O(3)-W(1A)-O(5)	101.2(8)	O(1)#3-W(3)-O(10)	88.1(6)

(2)#3-W(1A)-O(5)	90.4(8)	O(12)-W(3)-O(9)	170.9(5)
O(1)-W(1A)-O(5)	87.1(5)	O(6)#3-W(3)-O(9)	85.2(5)
O(3)-W(1A)-O(2)	102.7(10)	O(11)-W(3)-O(9)	82.8(5)
(2)#3-W(1A)-O(2)	82.4(14)	O(1)-W(1A)-O(2)	91.0(8)
O(2)-W(1A)-O(4)	73.2(7)	O(5)-W(1A)-O(2)	156.0(7)
O(2)#3-W(1B)-O(1)#3	138.2(17)	O(3)-W(1A)-O(4)	174.6(8)
O(2)#3-W(1B)-O(5)	122.3(16)	O(2)#3-W(1A)-O(4)	74.3(7)
O(1)#3-W(1B)-O(5)	97.3(6)	O(1)-W(1A)-O(4)	83.5(4)
O(2)#3-W(1B)-O(4)	92.8(15)	O(5)-W(1B)-O(4)	78.9(4)
O(1)#3-W(1B)-O(4)	81.1(4)		

Symmetry transformations used to generate equivalent atoms: #1 x-y,x,-z; #2 xy,x,z+1/2; #3 -y+1,x-y,z; #4 -x+y+1,-x+1,z; #5 y,-x+y,-z; #6 x,y,-z+1/2.

Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
01	2.037	O 6	2.250	011	2.122
02	2.168	07	1.872	012	1.877
03	1.807	08	2.180	013	1.199
04	2.009	09	2.216	014	0.319
05	1.810	O10	1.996	015	0.229

Table S4. The BVS calculation result of all the oxygen atoms in 1

Table S5. The BVS calculation result of W, P and Cu atoms in 1

Code	Bond Valence	Code	Bond Valence
W1	6.026	P1	5.100
W2	6.351	Cu1	1.517
W3	6.348	Cu2	1.667

References

[S1] R. Contant, Inorg. Synth. 1990, 27, 104.

[S2] (a) G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997. (b) G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997. (c) G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467. (d) G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112. (e) L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837; (g) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 1998.