Supporting information

A Polyoxometalate-Based Hydrogen-Bonded Organic Framework as a New Class of Proton Conductive Material

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Experimental Section

Reagents and Apparatus.

All the reagents and solvents used in the experiment were purchased and used without further purification. 2-phenyl-4,5-imidazole dicarboxylic acid (H_3PhIDC) was synthesized according to the reference method [1].

The infrared spectra (IR) spectra were recorded on a NEXUS 470- FTIR infrared spectrophotometer with KBr pellets in the range of $400-4000$ cm^{-1}. Elemental analyses were measured with a FLASH EA 1112 analyzer. Thermogravimetric analysis (TGA) were carried out with a Netzsch STA 409PC differential thermal analyzer from room temperature to 1200 °C under air atmosphere. Powder X-ray diffraction (PXRD) patterns were collected with Panalytical X'pert PRO X-ray diffractometer using Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA.

Synthesis of $[PMo_{12}O_{40}][H_2PhI]_3[HPhI]\cdot 4H_2O$ (PHOF 1)

$[PMo_{12}O_{40}][H_2PhI]_3[HPhI]\cdot 4H_2O$ (PHOF **1**) was prepared by using *in situ* hydrothermal methods. A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (30.8 mg, 0.1 mmol), H_3PhIDC (23.2 mg, 0.1 mmol) and $(NH_4)_3PMo_{12}O_{40}\cdot H_2O$ (18.9 mg, 0.01 mmol) was dissolved in 3 mL acetonitrile and 4 mL water in presence of one drop of triethylamine and stirred at room temperature for 20 min. Then the resulting mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 4 days. After slow cooling to room temperature, yellow block crystals were obtained. Yield 45% (based on Mo). Anal. Calcd for $C_{36}H_{43}Mo_{12}N_8O_{44}P$: C 17.48, H 1.75, N 4.53%. Found: C 17.60, H 1.62, N 4.49%. IR (cm^{-1}, KBr): 3146 (m), 3000 (m), 2742 (m), 1623 (s), 1518 (w), 1478 (w), 1421 (w), 1087 (w), 955 (w), 902 (s), 794 (s), 700 (w), 533 (w), 505 (w).

Single-crystal X-ray Crystallography

Suitable single-crystal of PHOF **1** was collected on an Oxford Xcalibur, Eos, Gemini diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å) at 293K. The structure was solved by direct method with OLEX2 program [2], and refined with

SHELXL-2016 package [3] using full-matrix least-squares methods against F^2. Detailed crystallography data and refinement and hydrogen bonds are given in Tables S1 and S2. CCDC 1989067 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

Proton conductivity measurements.

Electrochemical impedance spectroscopy (EIS) of PHOF **1** was recorded on a Princeton Applied Research PARSTAT 2273 impedance analyser using the typical quasi-four-probe method with Cu electrodes. The frequencies of AC impedance test ranged from 0.1 Hz to 1 MHz with the AC voltage of 100 mV. To prepare circular pellets for measurement, the solid samples were compressed into pellets with 5 mm diameter under a pressure of 2 MPa for 5 minutes. The thickness was measured by Vernier caliper.

The proton conductivity was calculated using the equation: $\sigma = L/(RS)$, where σ (S·cm^{-1}) is the proton conductivity, L (cm) is the thickness of the pellet, S (cm^2) is the surface area of the pellet, and R (Ω) is the bulk resistance. The activation energy (E_a) was calculated from Arrhenius equation: $\ln(\sigma T) = \ln A - E_a/kT$, in which k (eV·K^{-1}) represents the Boltzmann constant, T (K) is the temperature, and A denotes the pre-exponential factor.

Analysis of the Impedance Plots.

At 100 °C under 98% RH, the impedance plots of PHOF **1** exhibit a single semicircle at high frequency and a spur at low frequency. The Zsimpwin software was used to obtain the equivalent circuit of R(C(R(Q(R((RW))))) with the Nyquist plots. The fitting result is shown in Figure S1.
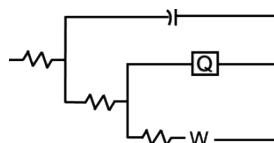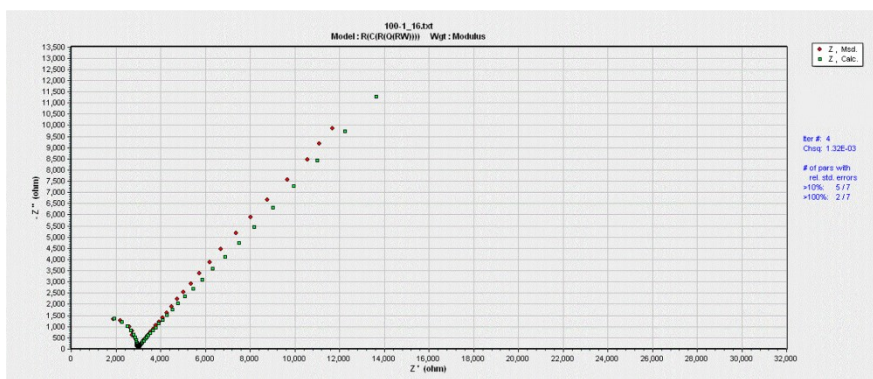

Equivalent circuit R(C(R(Q(R((RW))))):

Fig. S1. Nyquist plots for a polycrystalline sample of PHOF **1** at 100 °C and 98% RH. Red circle and green square are the measured impedance spectroscopy and the fits of the impedance data to the equivalent circuit of R(C(R(Q(R((RW)))).

References

[1] A. V. Lebedev, A. B. Lebedeva, V. D. Sheludyakov, E. A. Kovaleva, O. L. Ustinova and V. V. Shatunov, *Russ. J. Gen. Chem.*, 2007, **77**, 949−953.

[2] L. Palatinus, S. J. Prathapa and S. van. Smaalen, *J. Appl. Cryst.*, 2012, **45**, 575–580.

[3] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **7**, 3–8.

Table S1. Crystal data and structure refinement parameters for PHOF **1**.

Compound	PHOF**1**
Formula	$C_{36}H_{43}Mo_{12}N_8O_{44}P$
Formula weight	2474.03
Crystal system	Triclinic
Space group	P-1
a (Å)	13.1882(4)
b (Å)	14.8316(7)
c (Å)	17.8325(7)
α (°)	90.537(3)
β (°)	104.715(3)
γ (°)	109.659(3)
V (Å^3)	3159.8(2)
Z	2
D (g cm^{-3})	2.600
μ (mm^{-1})	20.071
F(000)	2372
Temperature (K)	293
θ min-max (°)	3.700, 67.076
Tot., uniq. data	24001, 11286
R(int)	0.0509
Observed data [$I > 2\sigma(I)$]	8987
$R_1{}^a$, $wR_2{}^b$ ($I > 2\sigma(I)$)	0.0485, 0.1173
R_1, wR_2 (all data)	0.0633, 0.1296
GOF	1.038
Min. and max resd dens (e·Å^{-3})	-1.696/1.367

[a]$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, [b]$wR_2 = \Sigma[w(F_0{}^2-F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]^{1/2}$; where $w = 1/[\sigma^2(F_o{}^2)+(aP)^2+bP]$, $P = (F_o{}^2+2F_c{}^2)/3$

Table S2. Hydrogen bond lengths (Å) and angles (º) for PHOF **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(1W)–H(1WA)···O(19)[i]	0.85	2.25	3.085(12)	167.3
O(1W)–H(1WB)···O(30)[ii]	0.85	2.16	2.999(11)	167.0
O(2W)–H(2WA)···O(16)	0.85	2.42	3.154(10)	144.7
O(2W)–H(2WA)···O(1W)	0.85	2.00	2.761(13)	147.9
O(3W)–H(3WA)···N(1)	0.85	1.99	2.841(12)	176.5
O(3W)–H(3WB)···O(13)	0.85	2.12	2.971(11)	176.4
O(4W)–H(4WA)···O(8)	0.85	2.14	2.930(9)	154.2
O(4W)–H(4WA)···O(9)	0.85	2.48	3.146(9)	136.3
O(4W)–H(4WA)···O(39)[iii]	0.85	2.27	3.046(10)	151.2
N(2)–H(2)···O(25)[iv]	0.86	2.00	2.831(9)	162.6
N(2)–H(3)···O(4W)	0.86	2.02	2.825(11)	155.4
N(4)–H(4)···O(26)[iv]	0.86	1.96	2.769(9)	155.2
N(5)–H(5)···O(7)	0.86	1.98	2.805(9)	161.1
N(6)–H(6)···O(2W)[v]	0.86	1.96	2.802(11)	165.0
N(7)–H(7)···O(5)	0.86	2.19	3.049(10)	177.9
N(8)–H(8)···O(17)[v]	0.86	2.58	3.316(11)	132.4
N(8)–H(8)···O(24)[v]	0.86	2.47	3.114(10)	132.4
C(9)–H(9)···O(29)[vi]	0.93	2.39	3.295(10)	165.0
C(9)–H(9)···O(37)[vi]	0.93	2.45	3.093(11)	126.0
C(12)–H(12)···O(12)[vi]	0.93	2.60	3.319(12)	134.0
C(17)–H(17)···O(33)[iii]	0.93	2.57	3.474(12)	163.3

C(17)–H(17)···O(39)^{iii}	0.93	2.69	3.384(10)	131.8
C(27)–H(27)···O(22)^{iii}	0.93	2.52	3.079(12)	118.8
C(31)–H(31)···O(28)^{vi}	0.93	2.66	3.346(10)	131.2
C(35)–H(35)···O(40)^{iii}	0.93	2.41	3.286(11)	157.1

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+1, y+1, z$; (v) $x, y+1, z$; (vi) $-x+1, -y+1, -z$.

Table S3. Proton conductivities [S·cm^{-1}] for PHOF **1** at different RHs and 40-100°C

	75% RH ^{a}	85% RH ^{a}	93% RH ^{a}	98% RH ^{a}
40 °C ^{b}	5.88×10^{-9}	1.64×10^{-8}	9.68×10^{-8}	2.69×10^{-6}
50 °C ^{b}	4.29×10^{-8}	5.94×10^{-8}	1.20×10^{-6}	3.17×10^{-6}
60 °C ^{b}	5.61×10^{-8}	7.12×10^{-8}	2.67×10^{-6}	4.20×10^{-6}
70 °C ^{b}	7.04×10^{-8}	2.40×10^{-7}	3.75×10^{-6}	5.26×10^{-6}
80 °C ^{b}	2.37×10^{-7}	1.62×10^{-6}	9.58×10^{-6}	1.24×10^{-5}
90 °C ^{b}	2.73×10^{-7}	1.69×10^{-6}	1.85×10^{-5}	2.23×10^{-5}
100 °C ^{b}	1.65×10^{-6}	2.50×10^{-6}	5.26×10^{-5}	2.02×10^{-4}

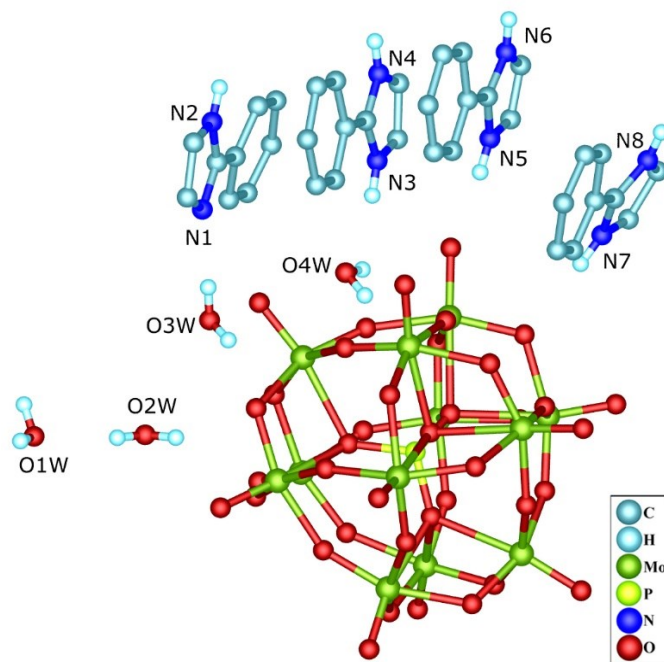^{a} Relative humidity. ^{b} Temperature.

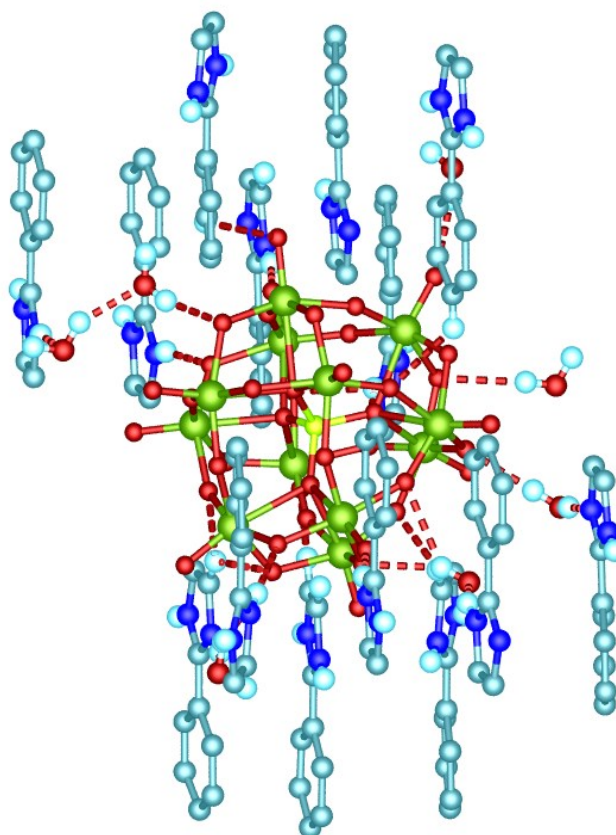**Fig. S2.** The molecular structure of PHOF **1**.

Fig. S3. The O–H⋯O, N–H⋯O, and C–H⋯O interactions between one POM anion, 14 phenyl-imidazoles (including 10 H_2PhI^+ and 4 HPhI) and 7 water molecules.
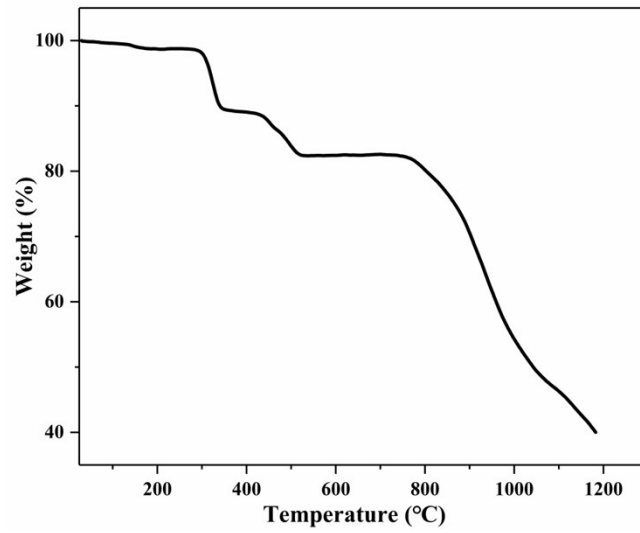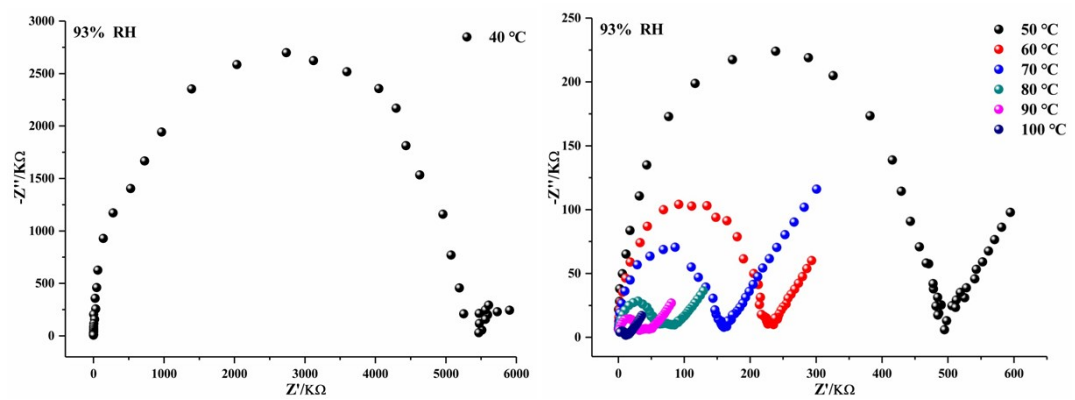
Fig. S4. TG curve of PHOF **1**.

Fig. S5. Impedance spectra of PHOF **1** at 93% RH and 40-100 °C.
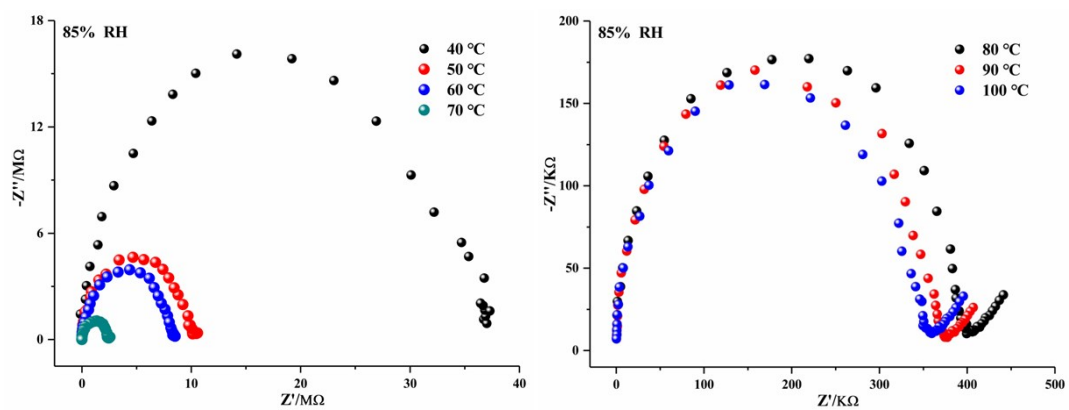

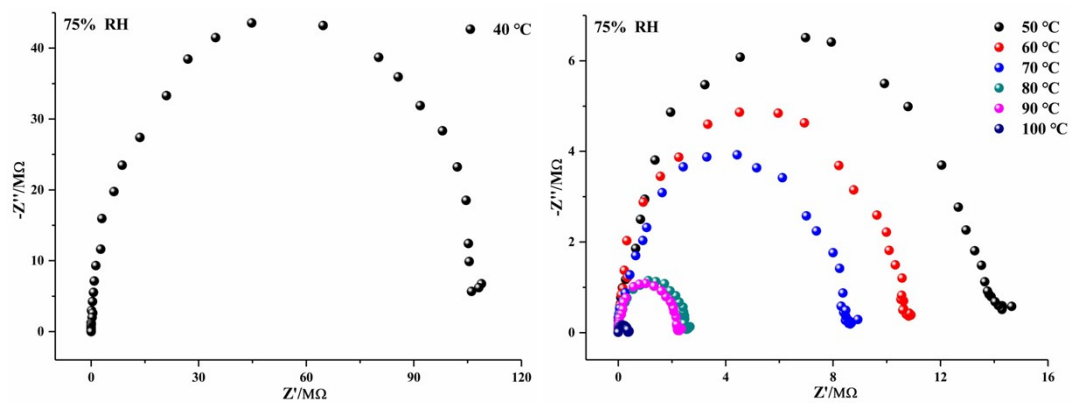**Fig. S6.** Impedance spectra of PHOF **1** at 85% RH and 40-100 °C.

Fig. S7. Impedance spectra of PHOF **1** at 75% RH and 40-100 °C.
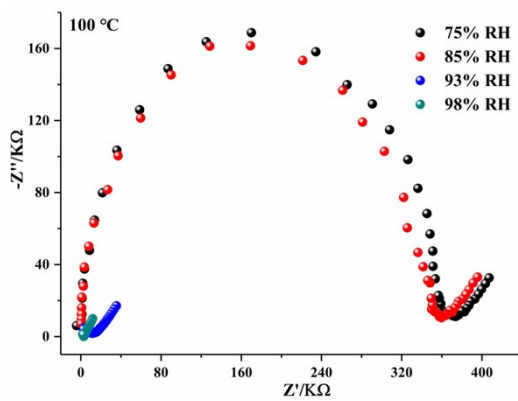

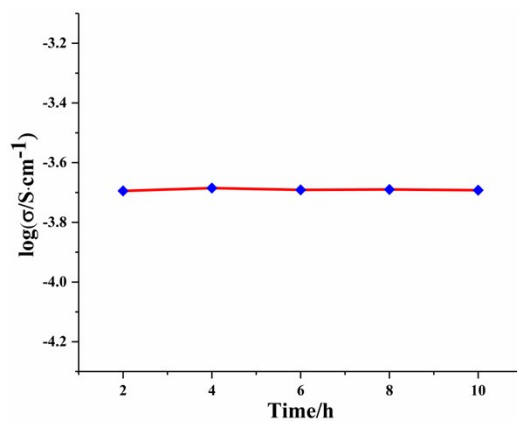**Fig. S8.** Impedance spectra of PHOF **1** at 100 °C and different RHs.

Fig. S9. Time-dependent proton conductivity of PHOF **1** at 100 °C and 98% RH.
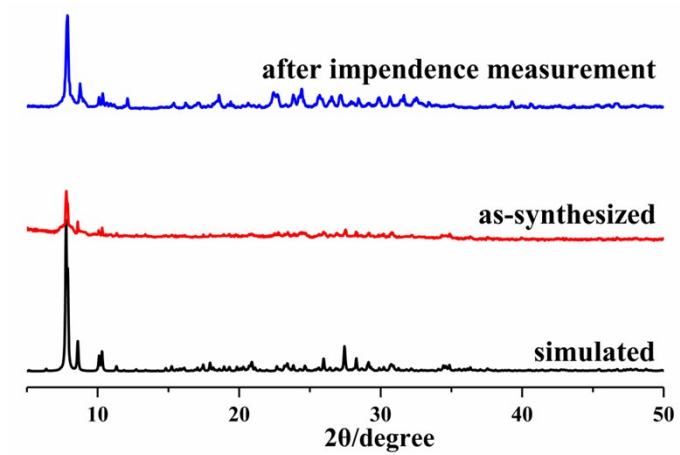
Fig. S10. PXRD patterns of PHOF **1**: the simulated, as-synthesized and after electrochemical test.