Syntheses, crystal structures, and proton conduction properties of two zirconium fluorophosphonates

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Proton Conductivity Measurement

The proton conductivity of the crystal sample is determined using the following formula:

$$\sigma = \frac{L}{SR}$$ [1] (Eq. S1)

Where σ represents the conductivity (S/cm), R is the resistance value (Ω), L and S are the thickness (cm) of the measured sample and the electrode area (cm^2), respectively.

Arrhenius equation can be described by the equation:

$$ln(\sigma T) = lnA - \frac{E_a}{k_B T}$$ [2, 3] (Eq. S2)

Where σ represents the proton conductivity, E_a represents the proton-transport activation energy, k_B is the Boltzmann constant, and T and A are temperature and pre-exponential factor, respectively.

Table S1. Crystallographic data and structural refinement details for title compounds.

Compound	**1**	**2**
Empirical formula	$C_2H_4O_7F_2P_2K_2Zr$	$C_2H_{12}O_7F_2P_2N_2Zr$
Formula weight	409.41	367.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Crystal size/mm^3	0.10 × 0.05 × 0.05	0.05 × 0.05 × 0.03
a/Å	7.9194(3)	7.9239(2)
b/Å	10.1787(3)	10.2550(3)
c/Å	13.1697(4)	14.1277(4)
β/°	101.289(3)	103.384(3)
V/$Å^3$	1041.06(6)	1116.83(6)
Z	4	4
T/K	100(2)	298
ρ_{calc}/g/cm^3	2.612	2.184
μ/mm^{-1}	2.208	11.360
F(000)	792.0	728.0
λ/Å	0.71073	1.54178
Reflections collected	9960	6968
Independent reflections	2573	2216
No. of parameters	146	173
R_{int}	0.0297	0.0368
R^1 ($I > 2\sigma(I)$)[a]	0.0244	0.0330
wR_2(F^2) ($I > 2\sigma(I)$)[b]	0.0540	0.0880
GOF	1.033	1.046
CCDC	2466567	2466570

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

Table S2. Selected bond lengths (Å) and bond angles (°) for compound **1**.

1			
Zr(1)-F(2)	1.9999(14)	P(1)-O(1)	1.5460(17)
Zr(1)-F(1)	2.0081(14)	P(1)-C(1)	1.848(3)
Zr(1)-O(5)#1	2.0564(17)	P(2)-O(4)	1.4932(18)
Zr(1)-O(2)	2.0650(17)	P(2)-O(5)	1.5468(18)
Zr(1)-O(1)#2	2.0784(16)	P(2)-O(6)	1.5532(16)
Zr(1)-O(6)#2	2.0951(16)	P(2)-C(1)	1.847(3)
P(1)-O(3)	1.4923(18)	O(7)-C(1)	1.462(3)
P(1)-O(2)	1.5409(18)	C(1)-C(2)	1.521(3)
	#1 1+*x*,+*y*,+*z*; #2 1-*x*,-1/2+*y*,1/2-*z*		
F(2)-Zr(1)-F(1)	172.40(6)	O(2)-P(1)-C(1)	106.30(11)
F(2)-Zr(1)-O(5)#1	91.15(7)	O(1)-P(1)-C(1)	107.31(10)
F(1)-Zr(1)-O(5)#1	93.04(6)	O(4)-P(2)-O(5)	114.04(10)
F(2)-Zr(1)-O(2)	86.03(6)	O(4)-P(2)-O(6)	115.05(10)
F(1)-Zr(1)-O(2)	87.40(6)	O(5)-P(2)-O(6)	106.76(9)
O5(1)-Zr(1)-O(2)	93.42(7)	O(4)-P(2)-C(1)	110.94(11)
F(2)-Zr(1)-O(1)#2	87.97(6)	O(5)-P(2)-C(1)	104.48(11)
F(1)-Zr(1)-O(1)#2	88.08(6)	O(6)-P(2)-C(1)	104.63(10)
O(5)#1-Zr1)-O(1)#2	177.61(7)	P(1)-O(1)-Zr(1)#3	141.47(11)
O(2)-Zr(1)-O(1)#2	88.73(7)	P(1)-O(2)-Zr(1)	148.55(11)
F(2)-Zr(1)-O(6)#2	94.87(6)	P(2)-O(5)-Zr(1)#8	144.25(11)
F(1)-Zr(1)-O(6)#2	91.14(6)	P2)-O(6)-Zr(1)#3	131.25(10)
O(5)#1-Zr(1)-O(6)#2	94.11(7)	O(7)-C(1)-C(2)	110.7(2)
O(2)-Zr(1)-O(6)#2	172.39(7)	O(7)-C(1)-P(1)	107.49(16)
O(1)#2-Zr1)-O(6)#2	83.75(7)	C(2)-C(1)-P(1)	111.64(18)
O(3)-P(1)-O(2)	114.43(10)	O(7)-C(1)-P(2)	104.63(16)
O(3)-P(1)-O(1)	113.07(10)	C(2)-C(1)-P(2)	111.64(18)
O(2)-P(1)-O(1)	105.36(10)	P(1)-C(1)-P(2)	110.70(13)
O(3)-P(1)-C(1)	109.89(11)		
Symmetry codes: #1 1+*x*,+*y*,+*z*; #2 1-*x*,-1/2+*y*,1/2-*z*; #3 1-*x*,1/2+*y*,1/2-*z*; #4 2-*x*,-1/2+*y*,1/2-*z*; #5 1-*x*,1-*y*,-*z*; #6 +*x*,3/2-*y*,1/2+*z*; #7 1-*x*,2-*y*,-*z*; #8 -1+*x*,+*y*,+*z*; #9+*x*,3/2-*y*,-1/2+*z*			

Table S3. Hydrogen bond parameters of compound **1**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O7-H7A···O4#1	0.90(3)	2.16(3)	2.983(3)	152(3)
C2-H3B···F1#2	0.98	2.55	3.471(3)	156.2

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

Table S4. Selected bond lengths (Å) and bond angles (°) for compound **2**.

2			
Zr(1)-F(1)	1.992(2)	P(1)-O(1)	1.537(3)
Zr(1)-F(2)	2.003(2)	P(1)-C(1)	1.860(4)
Zr(1)-O(5)#1	2.047(3)	P(2)-O(4)	1.485(3)
Zr(1)-O(2)	2.069(2)	P(2)-O(5)	1.539(3)
Zr(1)-O(1)#2	2.090(3)	P(2)-O(6)	1.541(2)
Zr(1)-O(6)#2	2.101(2)	P(2)-C(1)	1.844(4)
P(1)-O(3)	1.500(3)	O(7)-C(1)	1.471(5)
P(1)-O(2)	1.500(3)	C(1)-C(2)	1.504(6)
#1 1+*x*,+*y*,+*z*; #2 1-*x*,-1/2+*y*,1/2-*z*			
F(1)-Zr(1)-F(2)	175.33(10)	O(2)-P(1)-C(1)	107.15(17)
F(1)-Zr(1)-O(5)#1	91.77(11)	O(1)-P(1)-C(1)	107.20(16)
F(2)-Zr(1)-O(5)#1	90.37(11)	O(4)-P(2)-O(5)	113.98(17)
F(1)-Zr(1)-O(2)	88.60(11)	O(4)-P(2)-O(6)	114.35(16)
F(2)-Zr(1)-O(2)	87.13(11)	O(5)-P(2)-O(6)	107.88(15)
O(5)#1-Zr(1)-O(2)	93.62(11)	O(4)-P(2)-C(1)	110.15(19)
F(1)-Zr(1)-O(1)#2	89.21(10)	O(5)-P(2)-C(1)	104.55(16)
F(2)-Zr(1)-O(1)#2	89.21(10)	O(6)-P(2)-C(1)	105.12(17)
O(5)#1-Zr(1)-O(1)#2	176.31(10)	P(1)-O(1)-Zr(1)#3	141.82(16)
O(2)-Zr(1)-O(1)#2	89.96(10)	P(1)-O(2)-Zr(1)	150.26(18)
F(1)-Zr(1)-O(6)#2	91.26(10)	P(2)-O(5)-Zr(1)#4	149.83(19)
F(2)-Zr(1)-O(6)#2	92.77(10)	P(2)-O(6)-Zr(1)#3	131.91(15)
O(5)#1-Zr(1)-O(6)#2	93.11(11)	O(7)-C(1)-C(2)	112.5(4)
O(2)-Zr(1)-O(6)#2	173.26(10)	O(7)-C(1)-P(2)	104.4(3)
O(1)#2-Zr(1)-O(6)#2	83.31(11)	C(2)-C(1)-P(2)	111.9(3)
O(3)-P(1)-O(2)	113.61(16)	O(7)-C(1)-P(1)	106.7(3)
O(3)-P(1)-O(1)	112.45(16)	C(2)-C(1)-P(1)	111.2(3)
O(2)-P(1)-O(1)	107.25(16)	P(2)-C(1)-P(1)	109.84(19)
O(3)-P(1)-C(1)	108.87(17)		
Symmetry codes: #1 1+*x*,+*y*,+*z*; #2 1-*x*,-1/2+*y*,1/2-*z*; #3 1-*x*,1/2+*y*,1/2-*z*; #4 -1+*x*,+*y*,+*z*			

Table S5. Hydrogen bond parameters of compound **2**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O7-H7···O4#1	0.827(10)	2.85(5)	3.494(5)	136(6)
N1-H1A···O3	0.84(2)	2.00(2)	2.831(4)	167(4)
N1-H1B···O4#2	0.84(2)	1.94(2)	2.784(4)	173(4)
N1-H1C···F2#1	0.83(2)	2.32(3)	2.945(4)	132(4)
N1-H1C···O3#3	0.83(2)	2.52(4)	3.011(4)	119(3)
N1-H1C···O7#3	0.83(2)	2.52(3)	3.100(5)	127(3)
N1-H1D···O6#4	0.84(2)	2.36(3)	3.032(4)	137(3)
N1-H1D···O7#4	0.84(2)	2.38(3)	3.124(5)	148(4)
N2-H2A···F2#5	0.85(2)	2.14(3)	2.949(5)	161(4)
N2-H2B···O1#5	0.83(2)	2.49(4)	3.097(5)	130(4)
N2-H2B···O2#5	0.83(2)	2.62(4)	3.016(5)	111(3)
N2-H2B···O4#5	0.83(2)	2.21(3)	2.900(5)	141(4)
N2-H2C···F1	0.84(2)	2.52(4)	2.923(4)	111(3)
N2-H2C···F1#6	0.84(2)	2.19(4)	2.786(4)	127(4)
N2-H2D···O3#6	0.84(2)	1.92(2)	2.756(5)	172(4)

Symmetry codes: #1 +*x*,3/2-*y*,-1/2+*z*; #2 1-*x*,1/2+*y*,1/2-*z*; #3 1-*x*,2-*y*,-*z*; #4 1+*x*,+*y*,+*z*; #5 1-*x*,-1/2+*y*,1/2-*z*; #6 1-*x*,1-*y*,-*z*

TG

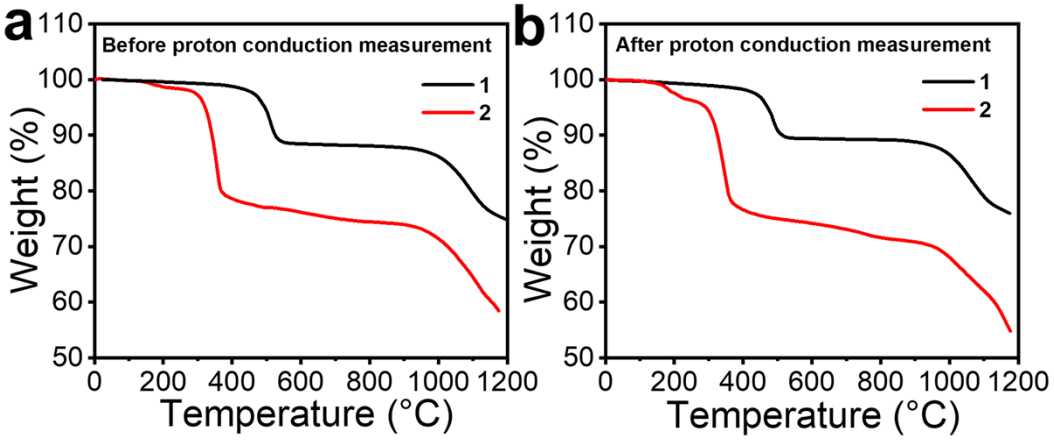

Fig. S1. TG curves for **1** and **2** before (a) and after (b) proton conduction test.

TG analyses of compounds **1** and **2** were performed (Fig. S1). Both compounds show an initial weight loss (2.2% for **1** at 20 - 446 °C and 2.5% for **2** at 20 - 300 °C), which are attributed to the removal of water adsorbed on the surface. For compound **1**, a weight loss of 9.08% (calcd: 8.79%) between 446 and 510 °C is attributed to the escape of HF due to the decomposition of compound. After proton conduction, the TG analysis result of compound **1** is comparable to that before proton conduction, indicating that compound **1** remained stable during proton conduction test. For compound **2**, the weight loss of 19.74% (calcd: 20.15%) observed from 300 to 400 °C results from the release of HF and NH_3.[4] The sample of **2** after proton conduction showed an additional weight loss of 6.40% between 114 and 297 °C, which indicates water adsorption during the proton conduction test.

FTIR

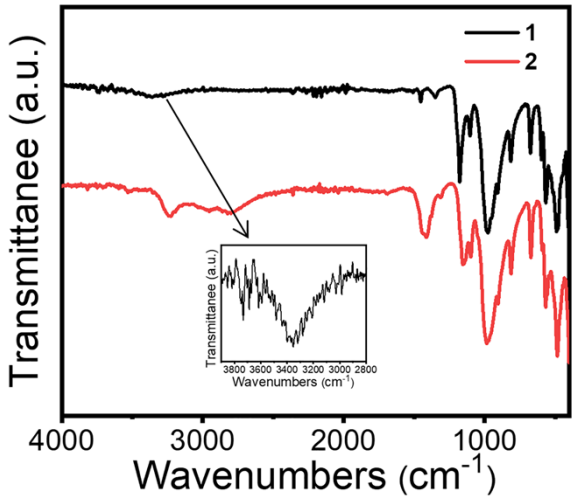

Fig. S2. The FTIR spectra of compounds **1** and **2**.

Fig. S2 shows the FTIR spectra of compounds **1** and **2**. The peaks at 1000 - 1200 cm^{-1} in the FTIR spectra are attributed to the ν(P-O) and ν(P=O).[5] For compound **2**, the strong peak at 1500 cm^{-1} is attributed to the δ(N-H) of NH_4^+. The shoulder peak in the range of 3200 - 2800 cm^{-1} is attributed to the ν(N-H) of NH_4^+ and ν(O-H) of H_2O.[6] A weaker ν(O-H) band of H_2O observed for **1** at 3600 - 3000 cm^{-1} suggests a lower water content, which is consistent with the TG data.

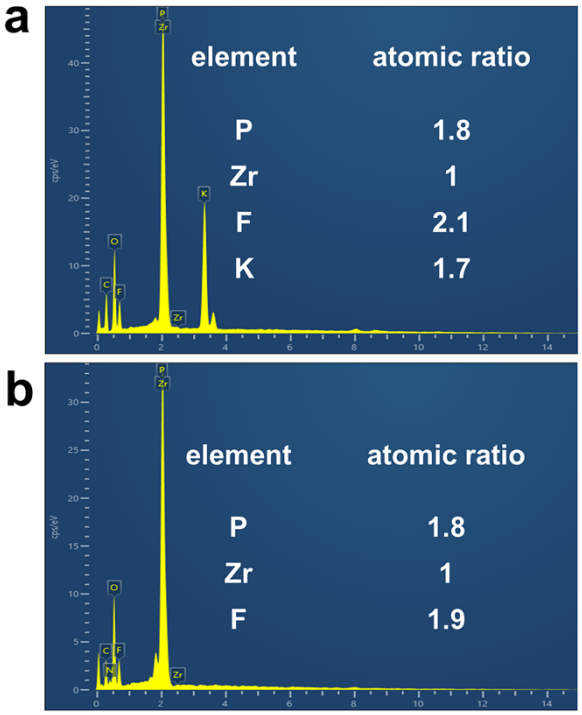

Fig. S3. EDX data of compounds **1** (a) and **2** (b)**.**

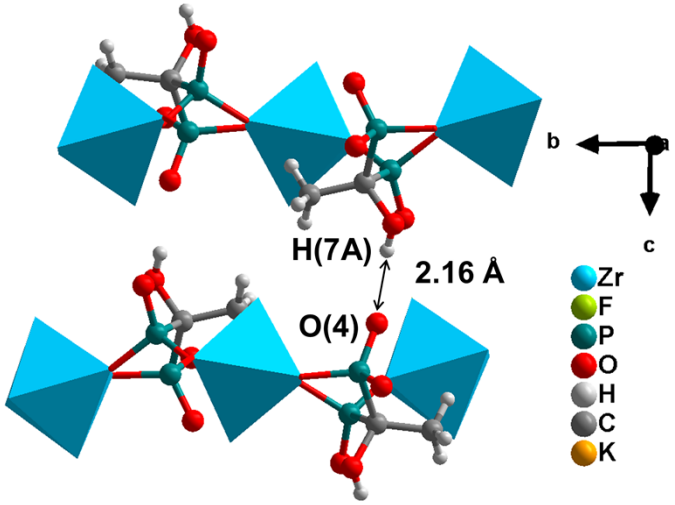

Fig. S4. The distance of O(4)···H(7A) between adjacent layers of compound **1**.

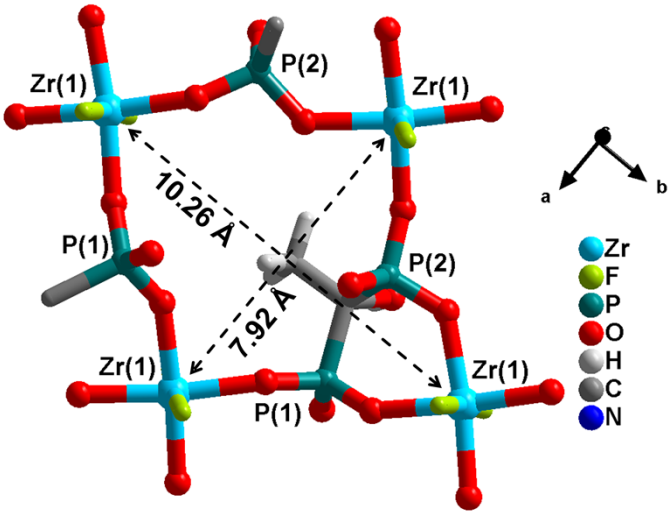

Fig. S5. The ball-and-stick representation of an eight-membered ring in the anionic layer of compound **2**.

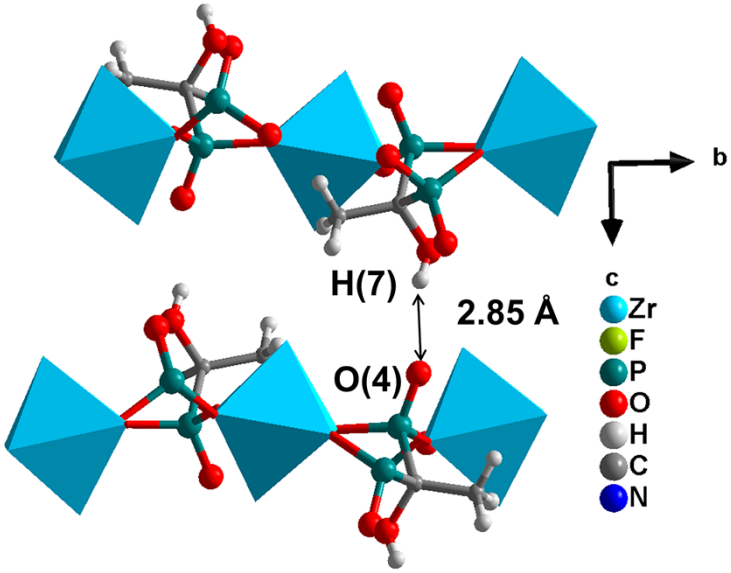

Fig. S6. The distance of O(4)···H(7) between adjacent layers of compound **2**.

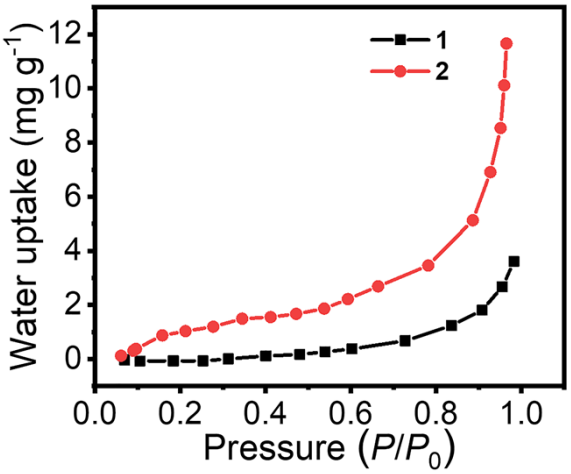

Fig. S7. Water vapor adsorption isotherms of compounds **1** and **2** at 25 °C.

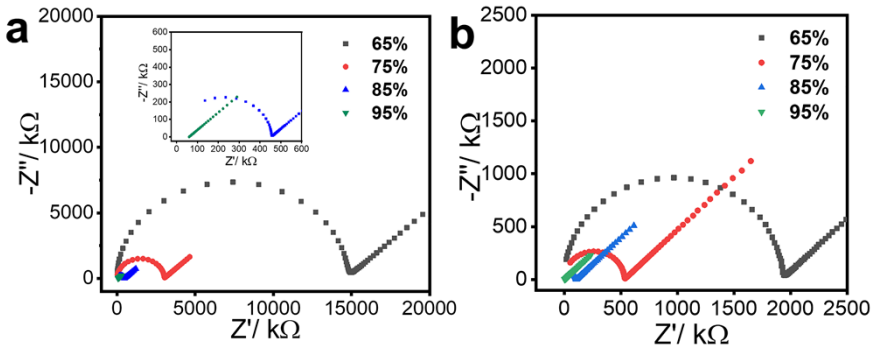

Fig. S8. The Nyquist plots of compounds **1** (a) and **2** (b) under 65 - 95% RH at 25 °C.

SEM

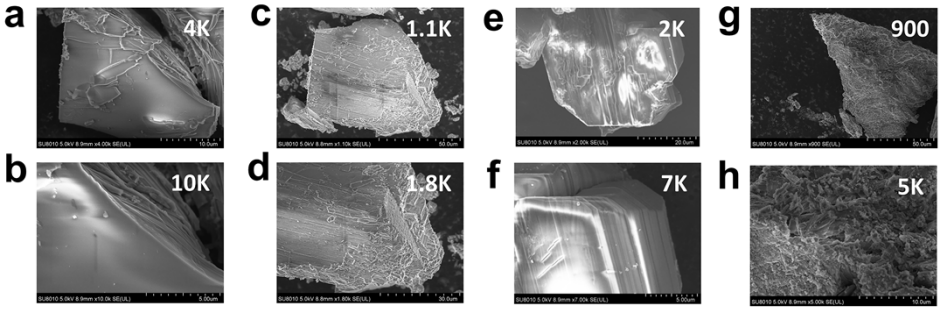

Fig. S9. SEM images of compound **1** before (a, b) and after (c, d) proton conduction test. SEM images of compound **2** before (e, f) and after (g, h) proton conduction test.

SEM images (Fig. S9) reveal that the sample surfaces of compounds **1** and **2** after the proton conduction test became rougher, indicating that water vapor permeation occurred during the test process.

Table S6. Proton conductivity (σ) values of compounds **1** and **2** at 25 °C under varing RH conditions.

		1		
RH%	65	75	85	95
σ (S cm^{-1})	1.61×10^{-7}	7.88×10^{-7}	5.25×10^{-6}	3.96×10^{-5}
		2		
RH%	65	75	85	95
σ (S cm^{-1})	1.40×10^{-6}	5.07×10^{-6}	2.55×10^{-5}	5.88×10^{-4}

Table S7. Proton conductivity (σ) values of compounds **1** and **2** under 95% RH and at different temperatures.

			1		
T/°C	45	55	65	75	85
σ (S cm^{-1})	3.67×10^{-4}	3.98×10^{-4}	4.95×10^{-4}	5.50×10^{-5}	6.37×10^{-4}
			2		
T/°C	35	55	65	75	85
σ (S cm^{-1})	3.11×10^{-3}	4.68×10^{-3}	7.45×10^{-3}	1.03×10^{-2}	1.27×10^{-2}

Table S8. The σ of phosphonic MOFs with proton-conducting properties.

Compound	Condition (T/°C, RH%)	σ (S cm^{-1})	Ref.
$Zr(O_3PCH_2)_2N\text{-}C_6H_{10}\text{-}N(O_3CH_2P)_2X_{2-x}H_{2+x}\cdot nH_2O$ (X = H, Li, Na, K, $0 < x < 1$,$4 < n < 7.5$)	80 °C, 95%	5.4×10^{-5}	[7]
$Zr_2(PO_4)H_5(L)_2\cdot H_2O$ (L = $(O_3PCH_2)_2NCH_2COO$)	140 °C, 95%	1×10^{-3}	[8]
$(DMA)_3[Zr(HL)F_2]$ (DMA = dimethylammonium, H_6L = 2,4,6-tris(4-phosphonophenyl) pyridine)	70 °C, 95%	8×10^{-3}	[9]
PCMOF20	85 °C, 95%	1.3×10^{-2}	
$(Me_2NH_2)[Eu(L)]$ (H_4L = 5(phosphonomethyl)isophthalic acid)	100 °C, 100%	3.76×10^{-3}	[10]
Na-MOF	60 °C, 98%	1.03×10^{-1}	[11]
ICR-11	25 °C, 100%	4.26×10^{-4}	[12]
PGM-L3	80 °C, 100%	1.26×10^{-2}	[13]
PGMH1	60 °C, 75%	9.8×10^{-3}	
$[Cd_2(L^1)_2(Bib)_2(H_2O)]\cdot 4.5H_2O$ (L^1 = 4-carboxyphenylmethylphosphonate ethyl ester)	95 °C, 95%	3.51×10^{-5}	[14]
$[Cd(L^2)(Bib)]\cdot 3H_2O$ (L^2 = 3-carboxyphenylmethylphosphonate ethyl ester, Bib = 1,4-bis-(1H-imidazol-1-yl)benzene	95 °C, 95%	1.21×10^{-5}	
$[Tb(H_2L)(H_2bts)(H_2O)]\cdot H_2O$ (H_3bts = 5-sulfoisophthalic acid, H_4L = bismethylenephosphonic acid)	95 °C, 95%	2.3×10^{-4}	[15]
$KZn_6(OOCCH(OH)PO_3)_4(OH)\cdot 5H_2O$	80 °C, 95 %	1.6×10^{-6}	[16]
$NH_4Zn(OOCCH(OH)PO_3)$	80 °C, 95 %	1.4×10^{-4}	

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