Supporting information

New group IIIA metal phosphate-oxalates containing dimethylammonium cations with proton conductivity

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Characterization Methods.

Powder X-ray diffraction (PXRD) patterns were recorded in the angular range of 2θ = 5–65° on a Rigaku Miniflex II diffractometer with Cu$K\alpha$ radiation (λ = 1.54178 Å). The optical absorption spectra were measured with a Shimadzu 2600 UV/vis spectrometer. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449C instrument from room temperature to 800 °C under N_2 atmosphere at a heating rate of 10 °C/ min. The proton conduction test was performed on a SI 1260 IMPEDANCE/GAINPHASE impedance analyzer. The applied voltage used in the test is 50 mV, and the frequency range is 0.1 Hz~1 MHz.

X-ray Crystallographic Study

Single-crystal X-ray diffraction (SCXRD) data were recorded on a SuperNova CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 292 K for **1** and 100 K for **2**. SCXRD data were collected on a XtaLAB Synergy system with graphite-monochromated Cu$K\alpha$ radiation (λ = 1.54178 Å) at 298 K for **3**. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-2018 program package.[1] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms connected to O atoms in the phosphate groups were located from difference-Fourier maps and their atomic positions were refined. The hydrogen atoms connected to C atoms were located at geometrically calculated positions while those attached to N atoms were located from difference-Fourier maps and their atomic positions were refined. The lattice water molecule in **3** was located from difference-Fourier maps and its atomic positions were refined.

Proton Conductivity Measurement

80 mg of the sample was weighed and ground to a homogeneous powder. Two portions of graphite (70 mg) were also weighed and set aside. The raw materials were added to a mould in the order of graphite-sample-graphite and pressed into a 5 mm diameter cylinder using a tablet press. The proton conductivity was obtained by semicircle fittings of Nyquist plots. The conductivities can be expressed by the equation:

$$\sigma = L/SR \quad \text{(Eq. S1)}$$

where σ represents the conductivity (S cm^{-1}), 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:

$$\ln(\sigma T) = \ln A - E_a/(k_B T) \quad \text{(Eq. S2)}$$

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

Table S1 Crystallographic data and structural refinement details for compounds.

	1	**2**	**3**
Empirical formula	$C_6H_{22}Al_2N_2O_{20}P_4$	$C_6H_{22}Ga_2N_2O_{20}P_4$	$C_6H_{24}N_2O_{21}P_4In_2$
Formula weight	620.09	705.57	813.79
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	8.6163 (14)	8.5858 (10)	8.95360 (10)
b/Å	9.7354 (17)	9.7952 (13)	10.26900 (10)
c/Å	12.3722 (18)	12.5984 (15)	13.16290 (10)
β/°	93.861 (15)	94.080 (12)	95.5430 (10)
V/Å^3	1035.5 (3)	1056.8 (2)	1204.60 (2)
Z	2	2	2
T/K	292 (2)	100 (2)	298 (2)
λ/Å	0.71073	0.71073	1.54178
F(000)	636.0	708.0	800.0
Theta range for data collection	3.2820 to 28.7940°	4.7060 to 29.4700°	3.3560 to 74.7310°
Index ranges	$-8\le h\le 12$, $-13\le k\le 10$, $-17\le l\le 13$	$-11\le h\le 11$, $-11\le k\le 13$, $-13\le l\le 17$	$-11\le h\le 11$, $-12\le k\le 11$, $-16\le l\le 15$
ρ_{calc}/g cm^{-3}	1.989	2.217	2.244
μ/mm^{-1}	0.554	2.954	18.729
Measured refls.	5714	5672	11935
Independent refls.	2509	2566	4430
No. of parameters	165	165	334
R_{int}	0.0431	0.0451	0.0374
R_1 (I>2σ(I))[a]	0.0450	0.0400	0.0305
wR_2(F^2) (I>2σ(I))[b]	0.0995	0.0721	0.0788
GOF	1.022	1.056	1.046

[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 **1**.

1			
Al(1)-O(1)	1.899(2)	P(2)-O(5)	1.509(2)
Al(1)-O(2)#1	1.876(2)	P(2)-O(6)	1.5741(19)
Al(1)-O(5)	1.827(2)	P(2)-O(7)	1.516(2)
Al(1)-O(8)#2	1.835(2)	P(2)-O(8)	1.508(2)
Al(1)-O(9)	1.977(2)	O(9)-C(1)	1.248(3)
Al(1)-O(10)#3	1.971(2)	O(10)-C(1)	1.253(3)
P(1)-O(1)	1.4946(19)	C(1)-C(1)#3	1.517(5)
P(1)-O(2)	1.495(2)	N(1)-C(2)	1.467(5)
P(1)-O(3)	1.570(3)	N(1)-C(3)	1.478(5)
P(1)-O(4)	1.526(3)		
Symmetry code: #1 +*x*,1/2-*y*,-1/2+*z*; #2 1-*x*,1-*y*,-*z*; #3 1-*x*,-*y*,-*z*.			
O(1)-Al(1)-O(9)	84.91(9)	O(2)-P(1)-O(4)	111.24(13)
O(1)-Al(1)-O(10)#1	87.48(9)	O(4)-P(1)-O(3)	106.99(19)
O(2)#2-Al(1)-O(1)	174.20(10)	O(5)-P(2)-O(6)	108.45(12)
O(2)#2-Al(1)-O(9)	89.72(9)	O(5)-P(2)-O(7)	110.96(12)
O(2)#2-Al(1)-O(10)#1	89.66(9)	O(7)-P(2)-O(6)	107.06(12)
O(5)-Al(1)-O(1)	88.79(10)	O(8)-P(2)-O(5)	111.55(12)
O(5)-Al(1)-O(2)#2	93.25(10)	O(8)-P(2)-O(6)	104.71(12)
O(5)-Al(1)-O(8)#3	96.79(10)	O(8)-P(2)-O(7)	113.69(12)
O(5)-Al(1)-O(9)	88.10(9)	P(1)-O(1)-Al(1)	135.75(14)
O(5)-Al(1)-O(10)#1	170.43(10)	P(1)-O(2)-Al(1)#4	142.98(14)
O(8)#3-Al(1)-O(1)	90.18(9)	P(2)-O(5)-Al(1)	141.70(14)
O(8)#3-Al(1)-O(2)#2	94.97(9)	P(2)-O(8)-Al(1)#3	145.34(13)
O(8)#3-Al(1)-O(9)	173.01(9)	C(1)-O(9)-Al(1)	112.61(17)
O(8)#3-Al(1)-O(10)#1	92.04(9)	C(1)-O(10)-Al(1)#1	112.55(17)
O(10)#1-Al(1)-O(9)	82.80(9)	O(9)-C(1)-O(10)	128.1(3)
O(1)-P(1)-O(2)	112.13(12)	O(9)-C(1)-C(1)#1	115.8(3)
O(1)-P(1)-O(3)	107.88(13)	O(10)-C(1)-C(1)#1	116.0(3)
O(1)-P(1)-O(4)	110.53(15)	C(2)-N(1)-C(3)	114.1(3)
O(2)-P(1)-O(3)	107.83(14)		
Symmetry code: #1 1-*x*,-*y*,-*z*; #2 +*x*,1/2-*y*,-1/2+*z*; #3 1-*x*,1-*y*,-*z*; #4 +*x*,1/2-*y*,1/2+*z*.			

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**.

2			
Ga(1)-O(1)	1.975(2)	P(2)-O(5)	1.519(2)
Ga(1)-O(2)#1	1.940(2)	P(2)-O(6)	1.577(2)
Ga(1)-O(5)	1.894(2)	P(2)-O(7)	1.518(2)
Ga(1)-O(8)#2	1.911(2)	P(2)-O(8)	1.521(2)
Ga(1)-O(9)	2.032(2)	O(9)-C(1)	1.253(4)
Ga(1)-O(10)#3	2.019(2)	O(10)-C(1)	1.253(4)
P(1)-O(1)	1.503(2)	C(1)-C(1)#3	1.527(6)
P(1)-O(2)	1.511(2)	N(1)-C(2)	1.470(5)
P(1)-O(3)	1.574(3)	N(1)-C(3)	1.491(5)
P(1)-O(4)	1.541(3)		
Symmetry code: #1 +*x*,1/2-*y*,-1/2+*z*; #2 1-*x*,1-*y*,-*z*; #3 1-*x*,-*y*,-*z*.			
O(1)-Ga(1)-O(9)	83.76(9)	O(2)-P(1)-O(4)	110.84(14)
O(1)-Ga(1)-O(10)#1	86.51(9)	O(4)-P(1)-O(3)	107.80(16)
O(2)#2-Ga(1)-O(1)	173.67(10)	O(5)-P(2)-O(6)	108.45(14)
O(2)#2-Ga(1)-O(9)	90.15(9)	O(5)-P(2)-O(8)	112.29(13)
O(2)#2-Ga(1)-O(10)#1	90.96(9)	O(7)-P(2)-O(5)	110.35(13)
O(5)-Ga(1)-O(1)	87.92(9)	O(7)-P(2)-O(6)	107.34(13)
O(5)-Ga(1)-O(2)#2	93.64(9)	O(7)-P(2)-O(8)	113.84(14)
O(5)-Ga(1)-O(8)#3	95.85(10)	O(8)-P(2)-O(6)	104.12(13)
O(5)-Ga(1)-O(9)	88.54(9)	P(1)-O(1)-Ga(1)	133.96(14)
O(5)-Ga(1)-O(10)#1	169.38(9)	P(1)-O(2)-Ga(1)#4	140.27(15)
O(8)#3-Ga(1)-O(1)	89.16(9)	P(2)-O(5)-Ga(1)	136.00(14)
O(8)#3-Ga(1)-O(2)#2	96.78(10)	P(2)-O(8)-Ga(1)#3	138.34(14)
O(8)#3-Ga(1)-O(9)	171.53(9)	C(1)-O(9)-Ga(1)	112.2(2)
O(8)#3-Ga(1)-O(10)#1	93.10(10)	C(1)-O(10)-Ga(1)#1	112.0(2)
O(10)#1-Ga(1)-O(9)	81.88(9)	O(9)-C(1)-O(10)	126.5(3)
O(1)-P(1)-O(2)	111.11(13)	O(9)-C(1)-C(1)#1	116.2(3)
O(1)-P(1)-O(3)	108.42(14)	O(10)-C(1)-C(1)#1	117.3(4)
O(1)-P(1)-O(4)	110.15(14)	C(2)-N(1)-C(3)	114.5(3)
O(2)-P(1)-O(3)	108.42(14)		
Symmetry code: #1 1-*x*,-*y*,-*z*; #2 +*x*,1/2-*y*,-1/2+*z*; #3 1-*x*,1-*y*,-*z*; #4 +*x*,1/2-*y*,1/2+*z*.			

Table S4 Selected bond lengths (Å) and bond angles (°) for **3**.

3			
In(1)-O(1)	2.154(5)	P(2)-O(8)	1.563(8)
In(1)-O(5)	2.111(4)	P(3)-O(9)	1.519(5)
In(1)-O(9)	2.097(5)	P(3)-O(10)	1.525(5)
In(1)-O(13)#1	2.065(5)	P(3)-O(11)	1.575(5)
In(1)-O(18)#2	2.213(6)	P(3)-O(12)	1.516(5)
In(1)-O(20)#2	2.186(6)	P(4)-O(13)	1.519(6)
In(2)-O(4)#3	2.105(5)	P(4)-O(14)	1.569(5)
In(2)-O(6)	2.143(5)	P(4)-O(15)	1.526(5)
In(2)-O(10)#2	2.114(5)	P(4)-O(16)	1.507(6)
In(2)-O(16)	2.087(5)	O(17)-C(1)	1.249(9)
In(2)-O(17)	2.186(6)	O(18)-C(1)	1.262(10)
In(2)-O(19)	2.201(5)	O(19)-C(2)	1.247(9)
P(1)-O(1)	1.493(6)	O(20)-C(2)	1.251(9)
P(1)-O(2)	1.554(6)	C(1)-C(2)	1.552(9)
P(1)-O(3)	1.545(7)	N(1)-C(3)	1.456(17)
P(1)-O(4)	1.490(5)	N(1)-C(4)	1.455(15)
P(2)-O(5)	1.496(5)	N(2)-C(5)	1.482(16)
P(2)-O(6)	1.501(5)	N(2)-C(6)	1.460(15)
P(2)-O(7)	1.529(7)		
O(1)-In(1)-O(18)#1	87.0(2)	O(5)-P(2)-O(7)	112.1(4)
O(1)-In(1)-O(20)#1	90.9(2)	O(5)-P(2)-O(8)	107.8(4)
O(5)-In(1)-O(1)	175.72(18)	O(6)-P(2)-O(7)	108.9(4)
O(5)-In(1)-O(18)#1	90.2(2)	O(6)-P(2)-O(8)	108.9(4)
O(5)-In(1)-O(20)#1	91.5(2)	O(7)-P(2)-O(8)	107.2(6)
O(9)-In(1)-O(1)	84.5(2)	O(9)-P(3)-O(10)	111.2(3)
O(9)-In(1)-O(5)	92.1(2)	O(9)-P(3)-O(11)	108.9(3)
O(9)-In(1)-O(18)#1	86.9(2)	O(10)-P(3)-O(11)	104.4(3)
O(9)-In(1)-O(20)#1	162.51(19)	O(12)-P(3)-O(9)	110.5(3)
O(13)#2-In(1)-O(1)	88.1(2)	O(12)-P(3)-O(10)	113.3(3)
O(13)#2-In(1)-O(5)	95.3(2)	O(12)-P(3)-O(11)	108.2(3)
O(13)#2-In(1)-O(9)	102.2(2)	O(13)-P(4)-O(14)	102.8(3)
O(13)#2-In(1)-O(18)#1	169.2(2)	O(13)-P(4)-O(15)	113.1(3)
O(13)#2-In(1)-O(20)#1	94.5(2)	O(15)-P(4)-O(14)	108.7(3)
O(20)#1-In(1)-O(18)#1	76.0(2)	O(16)-P(4)-O(13)	112.7(3)
O(4)#3-In(2)-O(6)	176.4(2)	O(16)-P(4)-O(14)	109.6(4)
O(4)#3-In(2)-O(10)#1	96.7(2)	O(16)-P(4)-O(15)	109.7(3)
O(4)#3-In(2)-O(17)	91.1(2)	P(1)-O(1)-In(1)	138.7(4)
O(4)#3-In(2)-O(19)	93.1(2)	P(1)-O(4)-In(2)#4	147.9(3)
O(6)-In(2)-O(17)	87.7(2)	P(2)-O(5)-In(1)	143.7(3)
O(6)-In(2)-O(19)	83.3(2)	P(2)-O(6)-In(2)	134.6(3)
O(10)#1-In(2)-O(6)	86.9(2)	P(3)-O(9)-In(1)	134.6(3)
O(10)#1-In(2)-O(17)	98.3(2)	P(3)-O(10)-In(2)#2	134.1(3)
O(10)#1-In(2)-O(19)	168.95(19)	P(4)-O(13)-In(1)#1	142.2(3)
O(16)-In(2)-O(4)#3	94.9(2)	P(4)-O(16)-In(2)	133.1(3)
O(16)-In(2)-O(6)	85.3(2)	C(1)-O(17)-In(2)	113.7(5)
O(16)-In(2)-O(10)#1	95.9(2)	C(1)-O(18)-In(1)#2	114.2(4)
O(16)-In(2)-O(17)	163.8(2)	C(2)-O(19)-In(2)	114.1(4)
O(16)-In(2)-O(19)	88.5(2)	C(2)-O(20)-In(1)#2	114.9(5)
O(17)-In(2)-O(19)	76.2(2)	O(17)-C(1)-O(18)	125.0(6)
O(1)-P(1)-O(2)	108.1(3)	O(17)-C(1)-C(2)	118.1(6)
O(1)-P(1)-O(3)	110.3(4)	O(18)-C(1)-C(2)	116.9(6)
O(3)-P(1)-O(2)	104.2(4)	O(19)-C(2)-O(20)	125.1(6)
O(4)-P(1)-O(1)	112.5(3)	O(19)-C(2)-C(1)	116.9(6)

O(4)-P(1)-O(2)	111.1(3)	O(20)-C(2)-C(1)	117.9(6)
O(4)-P(1)-O(3)	110.4(4)	C(4)-N(1)-C(3)	114.4(10)
O(5)-P(2)-O(6)	111.8(3)	C(6)-N(2)-C(5)	114.9(10)

Symmetry code: #1 1-*x*,1/2+*y*,1-*z*; #2 1-*x*,-1/2+*y*,1-*z*; #3 +*x*,+*y*,1+*z*; #4 +*x*,+*y*,-1+*z*.

Table S5 Hydrogen bond parameters of **1**

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O3-H3···O8#1	0.819(10)	2.20(3)	2.860(3)	138
O4-H4···O7#2	0.77(5)	1.73(5)	2.496(3)	170
O6-H6···O7#3	0.815(10)	1.765(11)	2.577(3)	174
N1-H1A···O6#4	0.89	2.00	2.832(4)	154
N1-H1B···O1	0.89	2.04	2.871(4)	155
N1-H1B···O5	0.89	2.57	3.193(4)	128
N1-H1B···O9	0.89	2.51	3.189(4)	134
C2-H2A···O9#4	0.96	2.55	3.483(4)	165
C2-H2B···O4#5	0.96	2.61	3.487(5)	152
C2-H2C···O7	0.96	2.54	3.490(5)	172
C3-H3C···O4#5	0.96	2.49	3.365(6)	152

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

Table S6 Hydrogen bond parameters of **2**

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O3-H3···O8#1	0.814(10)	2.12(3)	2.823(3)	145
O4-H4···O7#2	0.90(4)	1.62(4)	2.511(3)	172
O6-H6···O7#3	0.73(4)	1.83(4)	2.557(3)	174
N1-H1A···O6#4	0.91	1.95	2.816(4)	158
N1-H1B···O1	0.91	1.98	2.843(4)	159
N1-H1B···O5	0.91	2.66	3.207(4)	120
N1-H1B···O9	0.91	2.61	3.284(4)	131
C2-H2A···O9#4	0.98	2.54	3.502(4)	166
C3-H3C···O4#5	0.98	2.48	3.389(4)	154

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

Table S7 Hydrogen bond parameters of **3**

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O2-H2C···O12#1	0.82	1.69	2.507(7)	174
O3-H3D···O21	0.82	2.00	2.801(15)	166
O7-H7A···O15#2	0.82	1.74	2.535(8)	162
O8-H8A···O10#3	0.82	1.99	2.769(8)	158
O11-H11···O15#4	0.821(14)	1.738(18)	2.556(7)	174
O14-H14···O12#5	0.823(14)	1.74(3)	2.550(7)	169
O21-H21A···O13#7	0.826(14)	2.34(7)	3.032(11)	142
O21-H21A···O14#7	0.826(14)	2.44(17)	2.907(11)	116
N1-H1A···O6	0.89	2.06	2.900(9)	156
N1-H1A···O16	0.89	2.56	3.167(10)	126
N1-H1B···O11	0.89	2.05	2.875(10)	153
N2-H2A···O21	0.89	1.96	2.816(16)	160
N2-H2B···O9	0.89	2.05	2.939(11)	173
C4-H4C···O7#6	0.96	2.63	3.564(14)	164

Symmetry code: #1 1-*x*,1/2+*y*,-*z*; #2 1-*x*,-1/2+*y*,1-*z*; #3 1-*x*,1/2+*y*,1-*z*; #4 2-*x*,-1/2+*y*,1-*z*; #5 2-*x*,1/2+*y*,1-*z*; #6 1+*x*,+*y*,+*z*; #7 +*x*,+*y*,-1+*z*.

Table S8 Summary of counter cations, intra-layered window sizes and the shortest *M-M* distance between the adjacent layers for **1**, **2**, **3**, Hmim·$Fe(HPO_4)(H_2PO_4)(C_2O_4)_{0.5}$ and $CsFe(H_2PO_4)(HPO_4)(C_2O_4)_{0.5}$.

	1	**2**	**3**	Hmim·$Fe(HPO_4)(H_2PO_4)(C_2O_4)_{0.5}$ **2**	$CsFe(H_2PO_4)(HPO_4)(C_2O_4)_{0.5}$ **3**
Counter cations		$[(CH_3)_2NH_2]^+$		N-methylimidazolium	Cs^+
The size of intra-layered windows	7.47 Å × 8.29 Å	7.56 Å × 8.42 Å	7.95 Å × 8.84 Å; 7.87 Å × 8.78 Å	7.64 Å × 8.59 Å	8.02 Å × 8.41 Å; 8.02 Å × 8.73 Å
the shortest *M-M* distance between adjacent layers	8.5858 Å	8.6163 Å	8.9536 Å	9.1586 Å	7.5767 Å

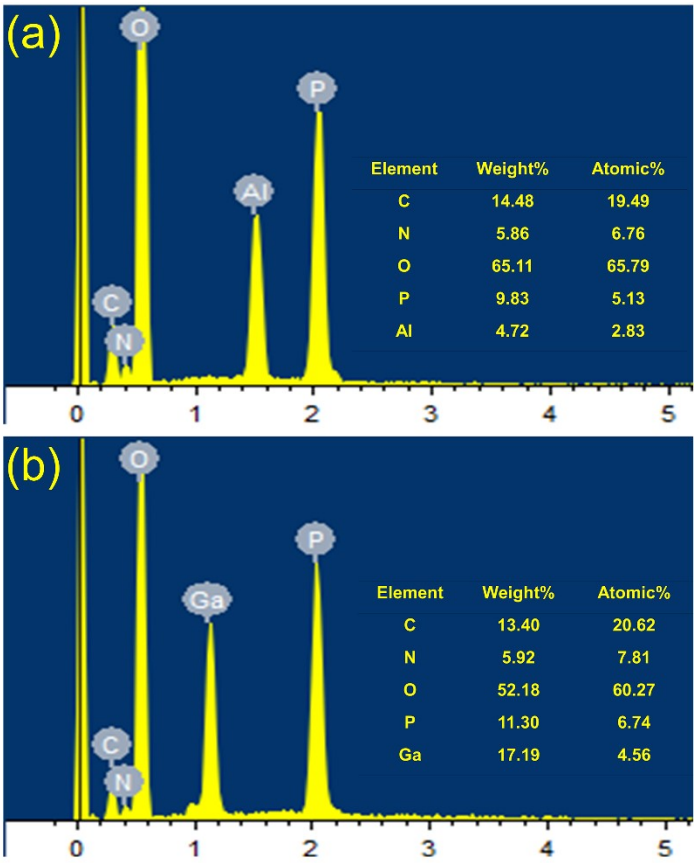

Fig. S1 EDS analysis results of (a) **1** and (b) **2**.

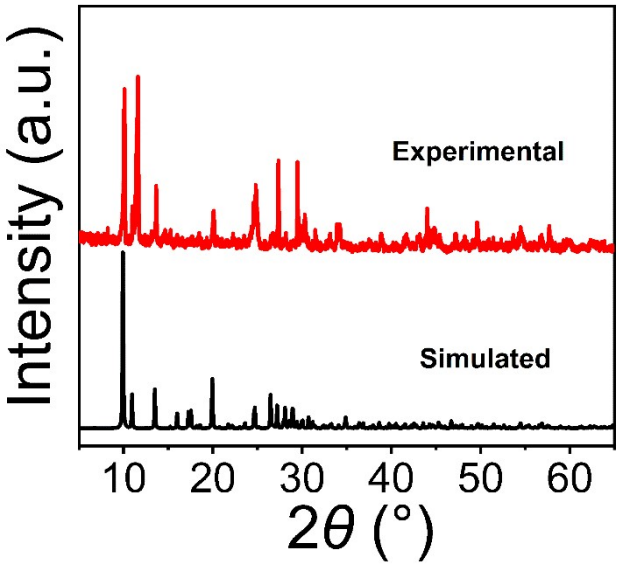

Fig. S2 Comparison of the simulated and experimental PXRD patterns of **3**.

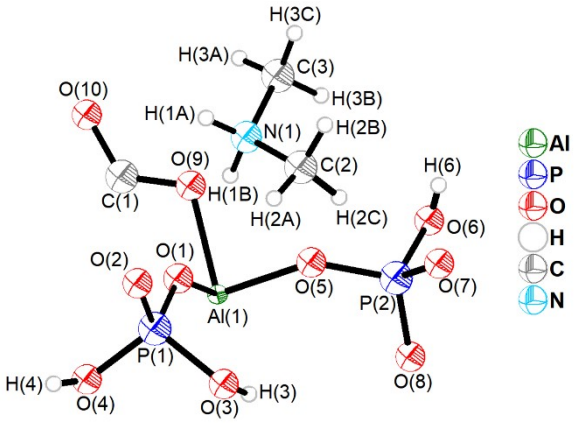

Fig. S3 *ORTEP* plot (50% ellipsoid probability) showing the crystallographically asymmetric unit of **1**.

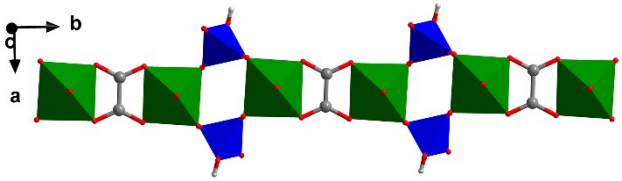

Fig. S4 An infinite chain constructed with the dinuclear $Al_2O_8(C_2O_4)$ units connected by two HPO_4 units in **1**. The green and blue polyhedra represent AlO_6 octahedra and PO_4 tetrahedra, respectively; atom colors: H = white, C = grey.

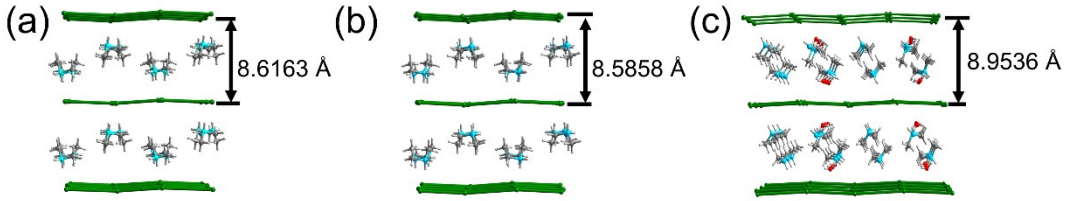

Fig. S5 The shortest *M-M* distance between the adjacent layers of **1** (a), **2** (b) and **3** (c).

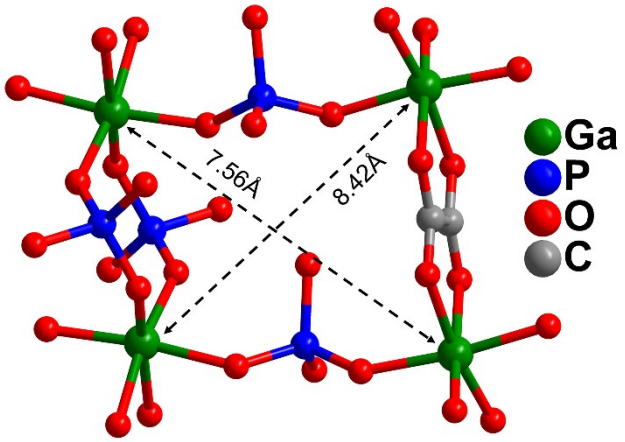

Fig. S6 The ball-and-stick representation of 8-ring window in the anionic layer of **2**.

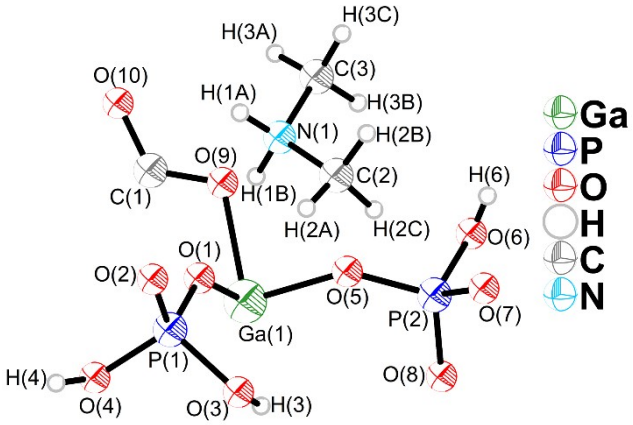

Fig. S7 *ORTEP* plot (50% ellipsoid probability) showing the crystallographically asymmetric unit of **2**.

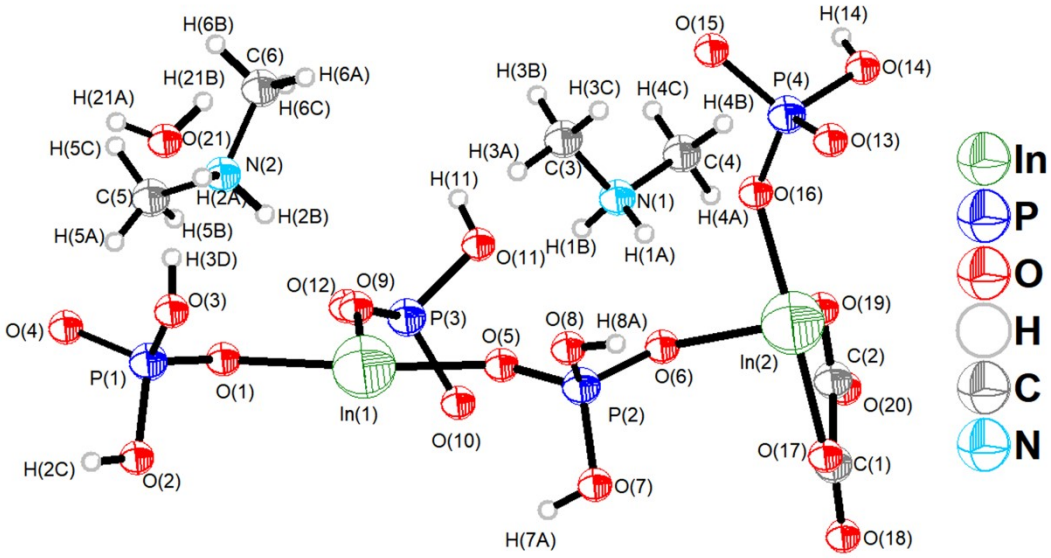

Fig. S8 *ORTEP* plot (50% ellipsoid probability) showing the crystallographically asymmetric unit of **3**.

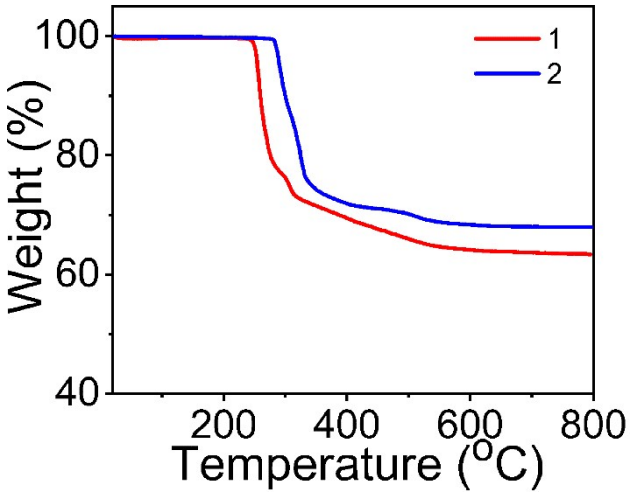

Fig. S9 Thermogravimetric curves for **1** and **2**.

Table S9 Proton conductivity (σ) values of **1** and **2** at 25 °C under varied RH conditions.

1			
RH %	70	85	98
σ (S cm^{-1})	8.35×10^{-7}	4.75×10^{-6}	8.92×10^{-5}
2			
RH %	70	80	85
σ (S cm^{-1})	4.37×10^{-7}	2.40×10^{-6}	5.77×10^{-5}

Table S10 Proton conductivity (σ) values of **1** and **2** under 98% RH and at different temperatures.

1					
T/°C	45	55	65	75	85
σ (S cm^{-1})	1.02×10^{-3}	1.79×10^{-3}	2.87×10^{-3}	5.75×10^{-3}	9.09×10^{-3}
2					
T/°C	45	55	65	75	85
σ (S cm^{-1})	3.71×10^{-4}	4.54×10^{-4}	5.18×10^{-4}	1.3×10^{-3}	6.43×10^{-3}

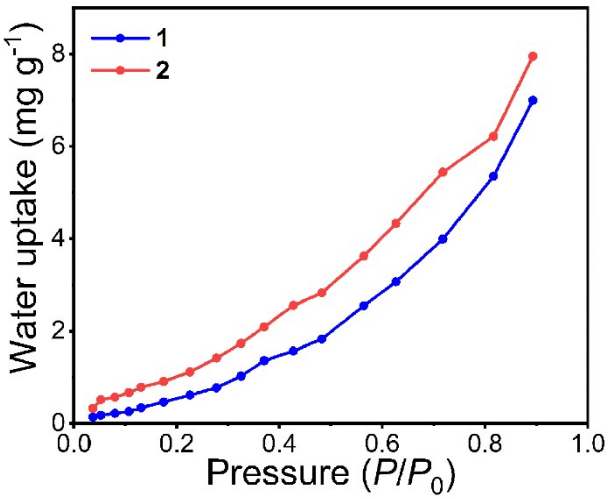

Fig. S10 Water vapor adsorption isotherms of compounds **1** and **2** at 25 °C.

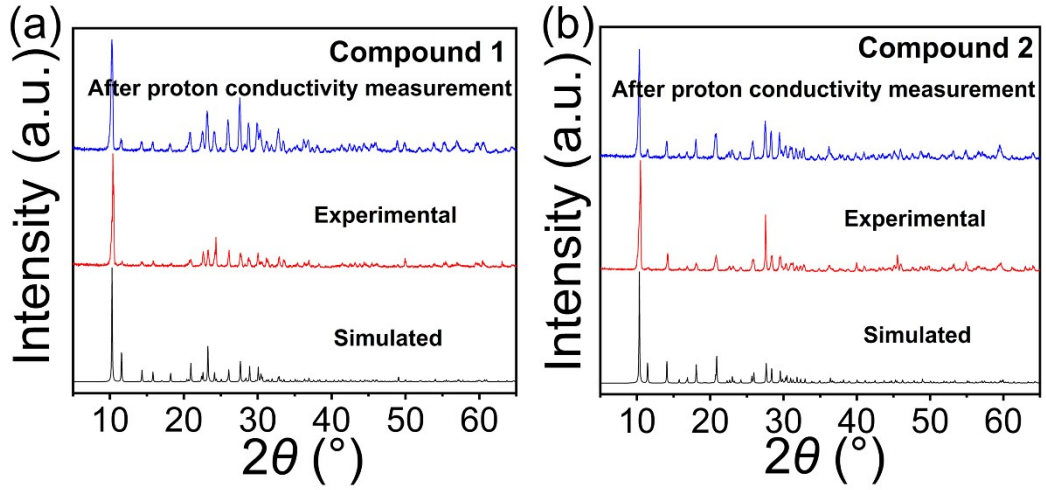

Fig. S11 PXRD patterns of **1** (a), **2** (b) and both samples after proton conductivity measurement. All are in good agreement with the corresponding simulated PXRD pattern calculated from single crystal X-ray data. All lines are refined compared with that in Fig. 3.

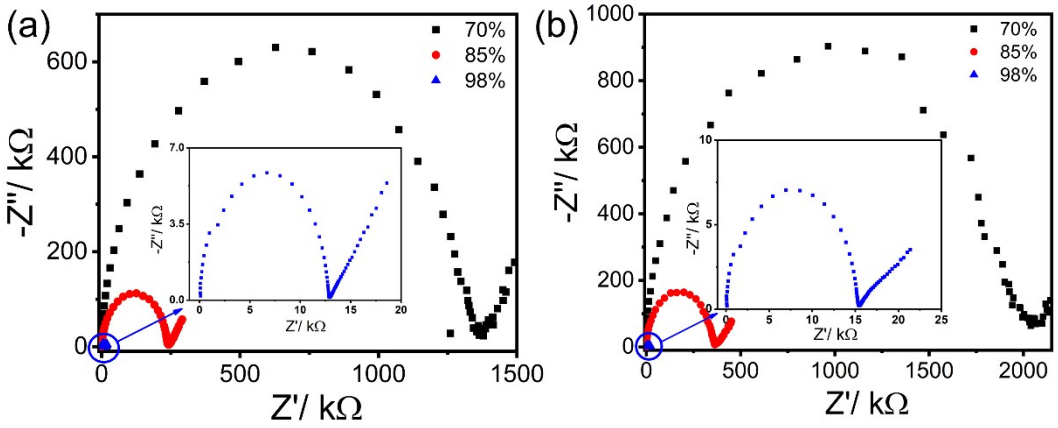

Fig. S12 The Nyquist plots of **1** (a) and **2** (b) under 70-98% RH at 25°C.

References

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2. J. Zhang, Q. Lei, L. Luan, H. Zeng, G. Zou and Z. Lin, N-methylimidazolium containing metal phosphate–oxalates: solvent-free synthesis, crystal structure, and proton conduction, *CrystEngComm*, 2022, **24**, 743-746.

3. C. Y. Sheu, S. F. Lee and K. H. Lii, Ionic liquid of choline chloride/malonic acid as a solvent in the synthesis of open-framework iron oxalatophosphates, *Inorg. Chem.*, 2006, **45**, 1891-1893.