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Supporting Information

Title: A water-stable open-framework zirconium(IV) phosphate and its water-assisted high proton conduct

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X-ray crystallography

Single crystal X-ray diffraction data for **ZrP** were collected at 273.15 K using graphite monochromated Mo/Ka radiation (λ=0.71073 Å) on a Bruker Apex III CCD area detector diffractometer. Data reduction and absorption corrections were performed with the SAINT [1] and SADABS [2] software packages, respectively. The structures were solved by a direct method using the SHELXL-2014/7 software package. [3]

The non-hydrogen atoms were anisotropically refined using the full-matrix least-squares method on F2. All the hydrogen atoms were geometrically fixed and placed in ideal positions. CSD 2092514

(ZrP) contain the supplementary crystallographic data for this paper. The details about data collection, structural refinement and crystallography are listed in Table S1.

Table S1. Crystallographic data and structural refinements for **ZrP**.

Formula	$Zr_6N_{10}O_{30}F_{12}\ P_6H_{48}$
Formula weight	1629.62
CSD no.	2092514
Temperature (K)	273.15
Wavelength (Å)	0.71073
Crystal size/mm	0.21 × 0.18 × 0.12
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	15.502(2)
b/Å	7.5316(11)
c/Å	19.141(3)
α/(°)	90
β/(°)	102.593(4)
γ/(°)	90
V/Å^3	2181.0(6)
Z	2
F(000)	1592.0
$\theta_{min,max}$/°	3.072 to 55.286
GOF	1.078
R_1,[a] wR_2 [b] [I > 2σ(I)]	R_1 = 0.0315, wR_2 = 0.1019
Largest diff. peak/hole / e Å^{-3}	0.81/-1.18

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for **ZrP**

	Bond Length/Å		**Bond Length/Å**
Zr(1)-F(1)	2.017(2)	Zr(3)-O(4)^2	2.086(3)
Zr(1)-F(2)	1.994(2)	Zr(3)-O(3)^3	2.106(3)
Zr(1)-O(10)	2.035(3)	Zr(3)-O(3W)	1.957(2)
Zr(1)-O(1)	2.065(3)	P(1)-O(1)	1.515(3)
Zr(1)-O(5)	2.076(3)	P(1)-O(4)	1.524(3)
Zr(1)-O(1W)	1.995(3)	P(1)-O(3)	1.521(3)
Zr(2)-F(4)	2.006(2)	P(1)-O(2)	1.534(3)
Zr(2)-F(3)	2.004(2)	P(2)-O(7)	1.527(3)
Zr(2)-O(7)1	2.089(3)	P(2)-O(6)	1.531(3)
Zr(2)-O(6)	2.048(3)	P(2)-O(8)	1.537(3)
Zr(2)-O(9)	2.040(3)	P(2)-O(5)	1.510(3)

Zr(2)-O(2W)	2.005(2)	P(3)-O(10)	1.530(3)
Zr(3)-F(5)	1.968(2)	P(3)-O(12)	1.494(3)
Zr(3)-F(6)	2.004(2)	P(3)-O(9)	1.531(3)
Zr(3)-O(11)	2.087(3)	P(3)-O(11)	1.538(3)

	Angle/°		**Angle/°**
F(1)-Zr(1)-O(10)	91.22(12)	F(5)-Zr(3)-O(4)^{2}	91.82(11)
F(1)-Zr(1)-O(1)	86.20(12)	F(5)-Zr(3)-O(3)^{3}	179.71(12)
F(1)-Zr(1)-O(5)	83.72(12)	F(6)-Zr(3)-O(11)	175.73(11)
F(2)-Zr(1)-F(1)	92.43(11)	F(6)-Zr(3)-O(4)^{2}	91.55(11)
F(2)-Zr(1)-O(10)	86.64(12)	F(6)-Zr(3)-O(3)^{3}	88.47(12)
F(2)-Zr(1)-O(1)	87.35(13)	O(11)-Zr(3)-O(3)^{3}	88.44(12)
F(2)-Zr(1)-O(5)	176.05(13)	O(4)2-Zr(3)-O(11)	85.40(11)
F(2)-Zr(1)-O(1W)	94.89(13)	O(4)2-Zr(3)-O(3)^{3}	87.89(12)
O(10)-Zr(1)-O(1)	173.35(13)	O(3W)-Zr(3)-F(5)	93.10(11)
O(10)-Zr(1)-O(5)	92.61(12)	O(3W)-Zr(3)F(6)	92.33(10)
O(1)-Zr(1)-O(5)	93.20(13)	O(3W)-Zr(3)-O(11)	90.45(11)
O(1W)-Zr(1)-F(1)	171.82(12)	O(3W)-Zr(3)-O(4)^{2}	173.65(11)
O(1W)-Zr(1)-O(10)	92.86(14)	O(3W)-Zr(3)-O(3)^{3}	87.19(12)
O(1W)-Zr(1)-O(1)	90.47(14)	O(1)-P(1)-O(4)	110.33(18)
O(1W)-Zr(1)-O(5)	89.02(13)	O(1)-P(1)-O(3)	108.82(18)
F(4)-Zr(2)-O(7)^{1}	86.93(10)	O(1)-P(1)-O(2)	108.31(18)
F(4)-Zr(2)-O(6)	175.24(11)	O(4)-P(1)-O(2)	108.63(17)
F(4)-Zr(2)-O(9)	90.01(11)	O(3)-P(1)-O(4)	109.95(16)
F(3)-Zr(2)-F(4)	91.70(11)	O(3)-P(1)-O(2)	110.79(19)
F(3)-Zr(2)-O(7)^{1}	89.15(11)	O(7)-P(2)-O(6)	109.92(16)
F(3)-Zr(2)-O(6)	91.55(12)	O(7)-P(2)-O(8)	108.98(16)
F(3)-Zr(2)-O(9)	91.79(11)	O(6)-P(2)-O(8)	109.08(18)
F(3)-Zr(2)-O(2W)	175.31(10)	O(5)-P(2)-O(7)	109.57(17)
O(6)-Zr(2)-O(7)^{1}	89.64(11)	O(5)-P(2)-O(6)	109.66(17)
O(9)-Zr(2)-O(7)^{1}	176.82(11)	O(5)-P(2)-O(8)	109.62(19)
O(9)-Zr(2)-O(6)	93.37(12)	O(10)-P(3)-O(9)	108.64(17)
O(2W)-Zr(2)-F(4)	88.19(11)	O(10)-P(3)-O(11)	106.53(17)
O(2W)-Zr(2)-O(7)^{1}	86.16(10)	O(12)-P(3)-O(10)	112.06(19)
O(2W)-Zr(2)-O(6)	88.30(12)	O(12)-P(3)-O(9)	109.75(19)
O(2W)-Zr(2)-O(9)	92.90(11)	O(12)-P(3)-O(11)	111.09(18)
F(5)-Zr(3)-F(6)	91.58(11)	O(9)-P(3)-O(11)	108.65(17)
F(5)-Zr(3)-O(11)	91.49(12)		

Symmetry operators:^{1}1-x,1-y,1-z; ^{2}1/2+x,3/2-y,1/2+z; ^{3}1/2-x,-1/2+y,3/2-z;

Table S3. Distances [Å]and angles [°] of selected hydrogen bonding for **ZrP**

D-H…A	d(D-H)	d(H..A)	d(D…A)	<D-H…A
N1-H1A...F1	0.9	1.91	2.806(5)	172
N1-H1B...O8	0.9	2.2	3.099(5)	173
N1-H1D...O2W#1	0.9	2.36	2.869(4)	116
N1-H1D...F6#2	0.9	2.27	2.913(5)	128
O1W-H1W...N1#3	0.85	2.46	2.952(5)	117
N2-H2A...O12	0.9	1.91	2.786(5)	165
N2-H2B...F1	0.9	1.99	2.866(4)	165
N2-H2D...F2#4	0.9	2.44	2.849(4)	108
O2W-H2W...F4	0.85	2.5	2.791(3)	101
N3-H3A...F2	0.9	1.93	2.824(4)	169
N3-H3B...O11	0.9	2.13	3.018(4)	169
N3-H3D...O2#4	0.9	2.1	2.939(5)	154
O3W-H3W...F4	0.85	2.49	3.293(3)	157
N4-H4A...F5	0.9	1.93	2.814(4)	165
N4-H4B...O12	0.9	1.93	2.813(5)	165
N4-H4C...O2W#5	0.85	2.13	2.977(4)	179
N4-H4D...O2#6	0.9	2.38	3.209(5)	153
N5-H5A...F4	0.9	2.02	2.809(4)	146
N5-H5B...O12#3	0.9	2.38	3.058(5)	132
N5-H5C...F4#7	0.9	2.27	2.894(5)	126
N5-H5D...O8#8	0.85	2.53	3.166(5)	132

Symmetry operators: #1: 1-x,2-y,1-z; #2: -1/2+x,3/2-y,-1/2+z; #3: x,-1+y,z; #4: 1/2-x,1/2+y,3/2-z; #5: 3/2-x,1/2+y,3/2-z; #6: 1/2+x,3/2-y,1/2+z; #7: 3/2-x,-1/2+y,3/2-z; #8: 1-x,1-y,1-z.

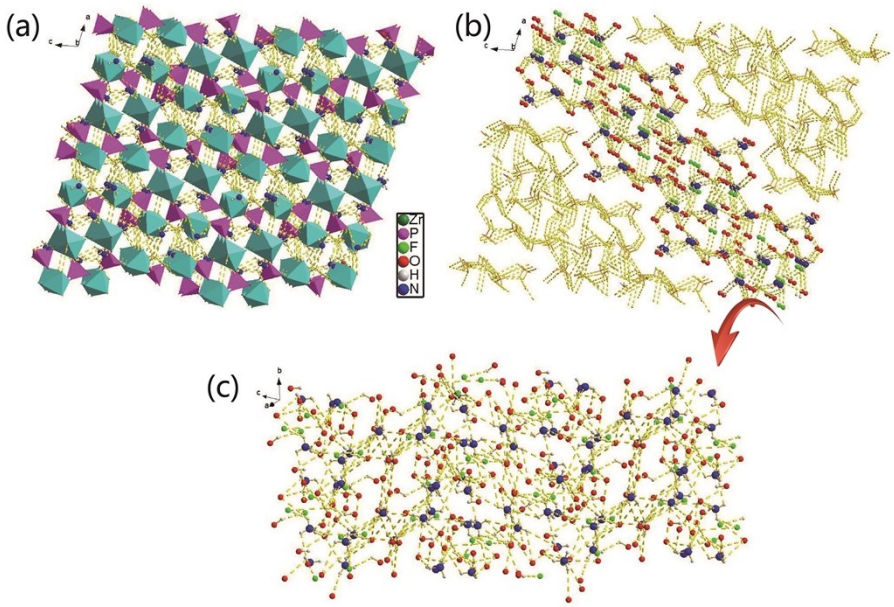


Figure S1. (a) View of the crystal structure of **ZrP** along the *b* axis. ZrO_4F_2 and PO_4 are shown as aqua octahedra and purple tetrahedra respectively. Other atom colour codes: O, red; N, blue; F, green, (b) View of the dense hydrogen-bond network (yellow dash line) in **ZrP** and (c) 2D hydrogen-bond network.

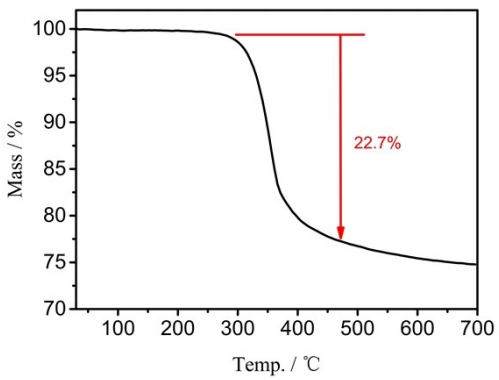
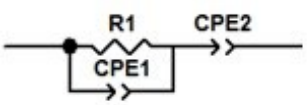


Figure S2. TGA of **ZrP** under nitrogen atmosphere. (471°C)

Calculation of ion conductivity from Impedance spectra by fitting with equivalent circuit (RQ) Q



Scheme S1. Equivalent circuit (RQ)Q.

The possible behaviour of the electrode-electrolyte interfaces can be discussed in terms of blocking or non-blocking character. An interface is blocking concerning the given charge-carrying species in the electrolyte if those species cannot cross the interface or exchange charge (in the electron form) with the electrode; otherwise, it is non-blocking with respect to the given species. For the EIS tests with blocking electrodes, the equivalent circuits are shown in Scheme 1, where R1 represents the bulk resistance, while CPE1 and CPE2 are the constant phase elements for the non-ideal capacitance behaviour of bulk and electrodes, respectively. [4, 5] It consists of the contributions of the bulk and the electrodes, as is reflected in the Nyquist plot that involves a high-frequency semicircle and a low-frequency tail. The bulk resistance R1 can be estimated by either fitting to the equivalent circuit or by the method of low-frequency minimum/intercept along the real Z-axis.

Here we provide the values of R1 by fitting the experimentally obtained data points along with the curve generated by the equivalent circuit mentioned above. The conductivity (σ) was calculated using the equation of σ = L/RS, where the symbols σ, R, L and S represent the conductivity, resistance, thickness and cross-sectional area of the sample, respectively.

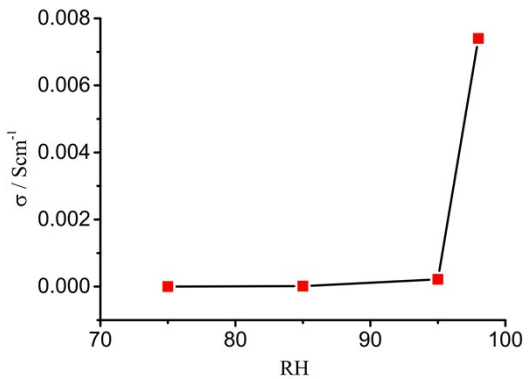


Figure S3. Humidity-dependent proton conductivity of **ZrP** at room temperature.

Table S4. Table of fitting parameters to determine the conductivity of **ZrP** under N_2 atmosphere in various temperatures using ZSimpWin software.

Temp. (K)	Value of R (Ω)	rel. std. error (%)	Conductivity (Scm^{-1})	χ^2 value
293	7.33E+09	50.92	3.10E-11	1.78E-03
303	6.79E+09	54.52	3.34E-11	3.59E-03
313	5.13E+09	45.52	4.42E-11	6.43E-03
323	3.28E+09	26.23	6.92E-11	9.97E-03
333	2.41E+09	18.13	9.40E-11	2.33E-02
343	1.02E+09	11.55	2.21E-10	1.62E-02
353	5.51E+08	9.179	4.12E-10	1.81E-02
363	2.88E+08	7.7	7.88E-10	1.87E-02

373	2.20E+08	10.58	1.03E-09	6.85E-02
383	8.48E+07	6.209	2.68E-09	1.78E-02
393	4.67E+07	5.69	4.85E-09	1.64E-02
403	2.67E+07	5.359	8.48E-09	1.52E-02
413	1.55E+07	5.189	1.46E-08	1.44E-02
433	5.50E+06	6.246	4.12E-08	1.97E-02
443	3.38E+06	7.564	6.71E-08	2.81E-02
453	2.12E+06	9.075	1.07E-07	3.95E-02
463	1.37E+06	10.59	1.66E-07	5.22E-02
473	8.97E+05	12.05	2.53E-07	6.52E-02
483	5.78E+05	13.5	3.93E-07	7.74E-02
493	2.93E+05	15.62	7.73E-07	8.74E-02

Table S5. Table of fitting parameters to determine the conductivity of **ZrP** under various RH at room temperature (25 ^{o}C) using Gamry Echem Analyst software.

RH(%)	Value of R1 (Ω)	Error(Ω)	Conductivity (Scm^{-1})	Goodness of Fit
75	8.47E+04	420	1.90E-06	3.08E-03
85	1.13E+04	82.01	1.42E-05	7.53E-04
95	7.45E+02	3.753	2.15E-04	1.33E-04
98	2.17E+01	2.58E-01	7.40E-03	1.79E-02

Table S6. Table of proton conductivity of **ZrP** under 98%RH_in various temperatures using Gamry Echem Analyst software.

Temp (K)	Value of R1 (Ω)	Error(Ω)	Conductivity (Scm^{-1})	Goodness of Fit
298	2.18E+01	1.27E-01	7.36E-03	1.76E-02
303	1.90E+01	1.94E-01	8.45E-03	2.22E-02
308	1.59E+01	8.13E-02	1.01E-02	2.72E-02
313	1.24E+01	6.72E-02	1.29E-02	4.00E-02
318	8.782	4.97E-02	1.83E-02	9.17E-02
323	6.458	4.18E-02	2.49E-02	9.17E-02
328	4.888	3.16E-02	3.28E-02	1.19E-01
333	3.64	2.44E-02	4.41E-02	1.50E-01

Table S7. List of proton conducting materials reported under high humidity at ambient temperature.

Compound	**Proton conductivity ($S\ cm^{-1}$)**	**Ea (eV)**	**Conditions**	**Ref**
H_2SO_4@MIL-101-SO_3H (3 M)	1.82	0.39	70 °C, 90% RH	6
BUT-8(Cr)	1.27×10^{-1}	0.11	80 °C, 100 % RH	7
PCMOF2½(Triazole)	1.17×10^{-1}	0.22	85 °C, 90 % RH	8
UiO-66-$(SO_3H)_2$	8.4×10^{-2}	0.32	80 °C, 90 % RH	9
Nafion	7.8×10^{-2}	0.22	25 °C, 100 % RH	10
TfOH@MIL-101	8.0×10^{-2}	0.23	15 °C, 60 % RH	11

$(NH_4)_5[Zr_3(OH)_3F_6(PO_4)_2(HPO_4)]$	4.41×10^{-2}	0.33	60 °C, 98% RH	This work
$\{[(Me_2NH_2)_3(SO_4)]_2[Zn(ox)_3]\}_n$	4.2×10^{-2}	0.13	25 °C, 98 % RH	12
PCMOF10	3.6×10^{-2}	0.4	70 °C, 95 % RH	13
VNU-15	2.9×10^{-2}	0.22	95 °C, 60 % RH	14
$(NMe_4{\cdot}Zn[HPO_4][H_2PO_4]$	1.30×10^{-2}	--	60 °C, 98 % RH	15
$(NH_4)_3Zr(H_{2/3}PO_4)_3$	1.21×10^{-2}	0.30	90 °C, 95 % RH	16
MIP-202(Zr)	1.10×10^{-2}	0.22	90 °C, 95 % RH	17
CPM-103a	1.0×10^{-2}	0.66	22.5 °C, 75 % RH	18
UiO-66(Zr)-$(CO_2H)_2$	2.3×10^{-3}	0.17	90 °C, 95 % RH	19

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