Proton conductivity at controlled hydrophilic and hydrophobic surfaces of mesoporous aluminum organophosphonates

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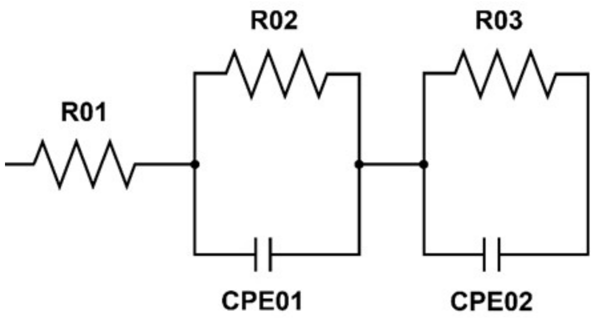

Fig. S1 Equivalent circuit for fitting analysis to calculate proton conductivity**.**

*The equivalent circuit considered the resistance of cables and bulk and grain boundary resistances in the impedance measurement.
*CPE was calculated by following the formula CPE = $\{T(i2\pi f)^{a}\}^{-1}$ ($0 \leq \alpha \leq 1$, $i^2 = -1$), where T and f were a CPE constant and frequency, respectively.

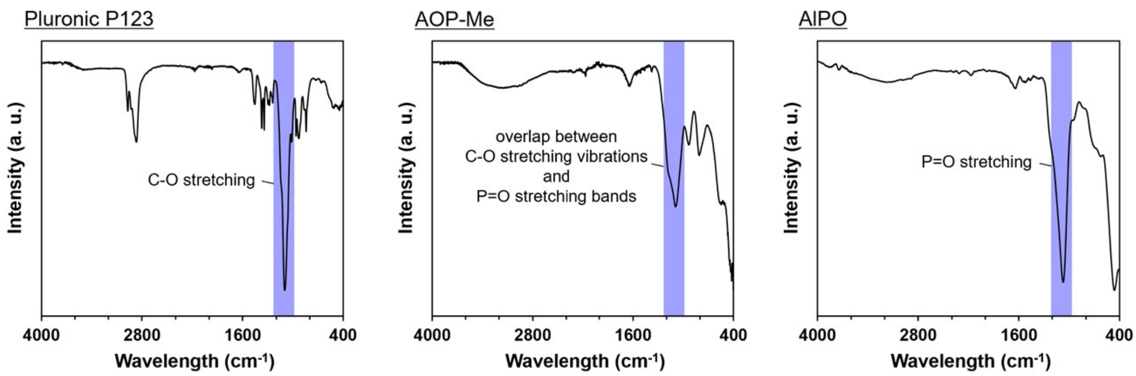

Fig. S2. FT-IR spectra of Pluronic P123 and mesoporous materials such as AOP-Me and AlPO after the extraction of Pluronic P123 by treating in dehydrated acetone.

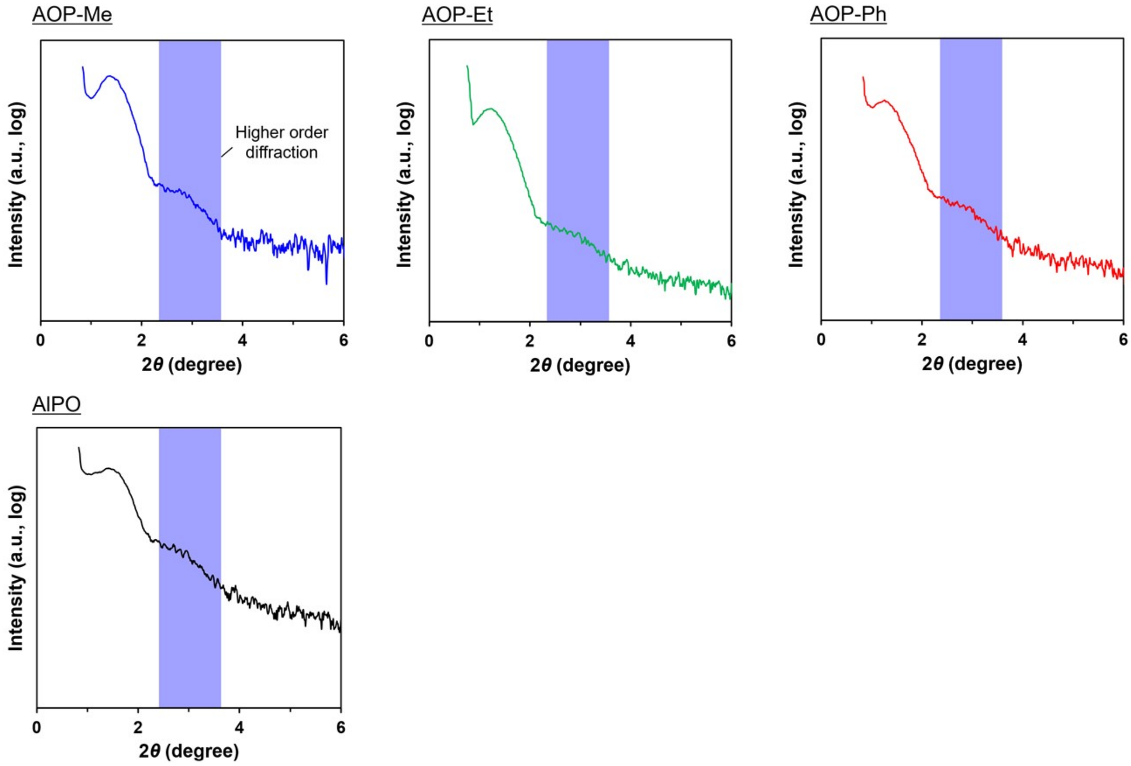

Fig. S3. Low-angle XRD pattern of AOP-Me, AOP-Et, AOP-Ph and AlPO as the log-scale intensity of the *y*-axis.

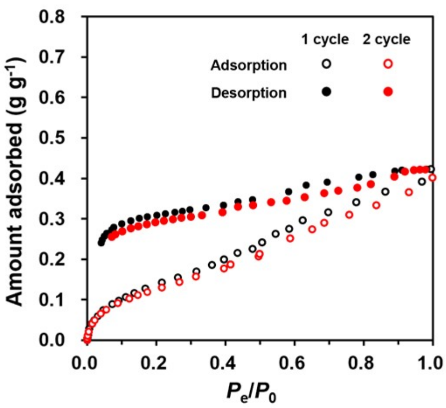

Fig. S4. H_2O adsorption-desorption isotherms of AOP-Me for the first cycle (black) and the second cycle (red).

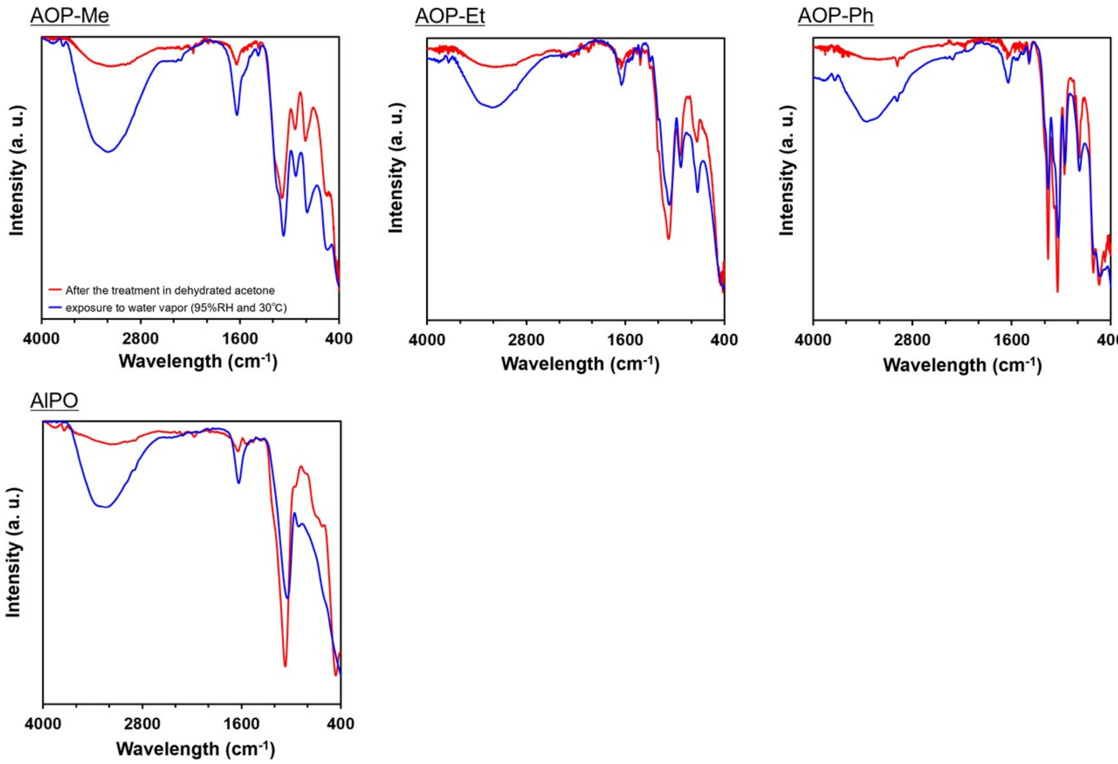

Fig. S5. FT-IR spectra of AOP-Me, AOP-Et, AOP-Ph and AlPO after the treatment in dehydrated acetone and exposure to water vapor (95% RH and 30 °C).

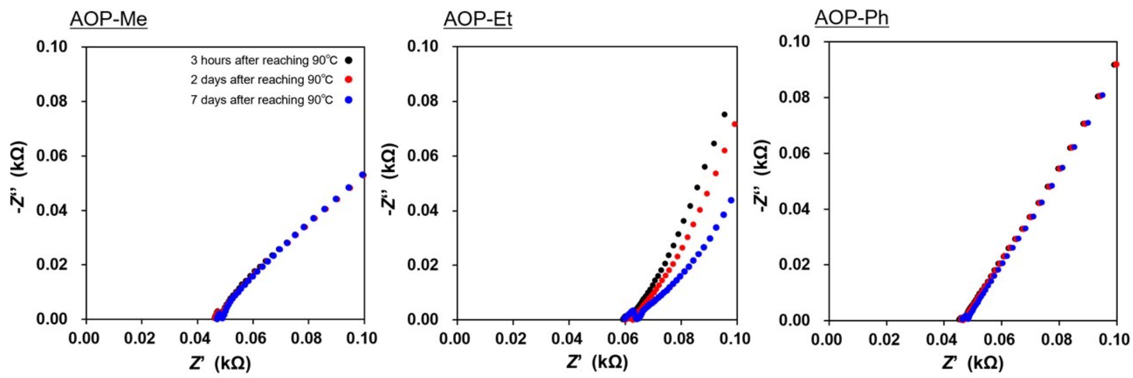

Fig. S6. Impedance spectra of the disk-shaped pellets of AOP-Me, AOP-Et and AOP-Ph under 95% RH at 90 °C after standing for 3 h (black), 2 days (red), and 7 days (blue).

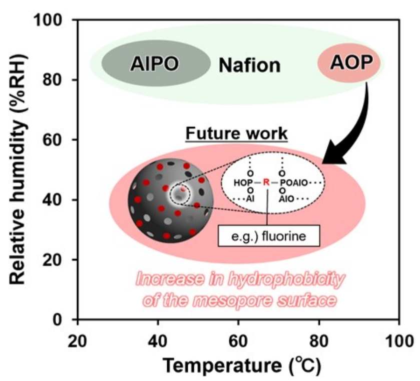

Fig. S7. The operating window of proton conduction with a benchmark material (Nafion): current status and future work of AOP and AlPO type mesoporous materials.

Table S1. Assignments of FT-IR spectra in **Fig. 1a**.

Materials	Assignments of vibrations	Wavenumber (nm^{-1})
AOP-Me	C-H stretching	3009, 2970, 2893
	C-H bending	1450, 1372
	P=O stretching	1088
	O-H stretching	3147
	O-H bending	1638
	Al-O-P symmetric stretching	561, 443
	Al-O-P asymmetric stretching	928, 807
AOP-Et	C-H stretching	2968, 2932, 2891
	C-H bending	1453, 1414, 1374
	P=O stretching	1090
	O-H stretching	3178
	O-H bending	1650
	Al-O-P symmetric stretching	433
	Al-O-P asymmetric stretching	932, 838, 768, 723
AOP-Ph	C-H stretching	2974, 2932, 2905
	C-H bending	1475
	C-H stretching (aromatic ring)	1151
	C≃C stretching (aromatic ring)	1388
	P=O stretching	1042
	O-H stretching	3128
	O-H bending	1654
	Al-O-P symmetric stretching	609, 542
	Al-O-P asymmetric stretching	959, 781
AlPO	C-H stretching	2970, 2930, 2870
	C-H bending	1373, 1347
	P=O stretching	1073
	O-H stretching	3154
	O-H bending	1651
	Al-O-P symmetric stretching	638, 465
	Al-O-P asymmetric stretching	933, 834

Table S2. Comparison of performance in proton conduction with reported typical inorganic and inorganic-organic hybrid proton-conducting material.

Name	Proton conductivity (S cm^{-1})	Conditions	E_a (eV)	(Calculated) proton conductivity at 30 °C (S cm^{-1})	Reference
AlPO	1.73×10^{-3}	95% RH 30 °C	0.38	1.73×10^{-3}	This work
AOP-Me	1.35×10^{-4}		-	1.35×10^{-4}	
AOP-Et	4.61×10^{-5}		-	4.61×10^{-5}	
AOP-Ph	2.05×10^{-5}		1.38	2.05×10^{-5}	
BEA	1.5×10^{-4}	100% RH 25 °C	-	-	1
Single-layer GO	2.0×10^{-4}	90% RH 25 °C	0.28	2.4×10^{-4}	2
Colloidal ZrO_2	5.0×10^{-5}	90% RH 20 °C	-	-	3
Zirconium phosphate	4.1×10^{-6}	84% RH 22 °C	-	-	4
ZPGly	5.8×10^{-4}	95% RH 80 °C	0.15	2.6×10^{-4}	5
Ti(PMIDA)	8.0×10^{-5}	100% RH 27 °C	-	-	6
JU102	2.1×10^{-4}	100% RH 20 °C	0.16	2.6×10^{-4}	7
JU102-c	5.3×10^{-4}		0.20	6.9×10^{-4}	
JU103	3.6×10^{-3}	98% RH 20 °C	0.21	4.7×10^{-3}	8
SYSU-1	3.9×10^{-4}	100% RH 55 °C	0.16	2.5×10^{-4}	9
SYSU-1R	5.0×10^{-5}		0.27	2.3×10^{-8}	
AlPO-CJ70	4.2×10^{-4}	100% RH 25 °C	0.16	4.7×10^{-4}	10
$H_2(C_2H_{10}N_2)_2[Co^{II}(H_2O)_2(V^{IV}O)_8(OH)_4(PO_4)_4(HPO_4)_4]$	7.1×10^{-5}	95% RH 25 °C	0.62	1.1×10^{-4}	11
$H_2(C_2H_{10}N_2)_2[Ni^{II}(H_2O)_2(V^{IV}O)_8(OH)_4(PO_4)_4(HPO_4)_4]$	1.0×10^{-4}		0.67	1.6×10^{-4}	
$H_2(C_2H_{10}N_2)_2[Cu^{II}(H_2O)_2(V^{IV}O)_8(OH)_4(PO_4)_4(HPO_4)_4]$	6.3×10^{-4}		0.63	9.4×10^{-4}	
$ZrP\cdot 0.8PrNH_2\cdot 5H_2O$	1.2×10^{-3}	90% RH 20 °C	1.04	4.7×10^{-3}	12
$Zr(P2O7)_{0.81}(O_3POH)_{0.38}$	1.3×10^{-3}		0.19	1.7×10^{-3}	
$(C_2N_2H_{10})_{0.5}CoPO_4$	2.1×10^{-3}	98% RH 56 °C	1.01	9.6×10^{-5}	13
$[Zn(HPSer)]_n$	7.2×10^{-6}	95% RH 80 °C	0.30	1.4×10^{-6}	14
$[Co(HPSer)(H_2O)_2]_n$	2.8×10^{-5}		0.40	3.1×10^{-6}	
$[Mn(HPSer)(H_2O)]_n$	6.5×10^{-6}		0.31	1.2×10^{-6}	
MIL-53(Al)	3.6×10^{-7}	95% RH 80 °C	0.47	2.8×10^{-8}	15
MIL-53(Al)-OH	1.9×10^{-6}		0.27	4.4×10^{-7}	
MIL-53(Al)-NH_2	4.1×10^{-8}		0.45	3.6×10^{-9}	

MIL-53(Al)-$(COOH)_2$	0.7×10^{-5}		0.21	2.2×10^{-6}	
UiO-66(Zr)	7.54×10^{-6}	97% RH 30 °C	0.44	7.5×10^{-6}	16
UiO-66(Zr)-NH_2	1.40×10^{-5}		0.4	1.4×10^{-5}	
UiO-67(Zr)-Br	2.23×10^{-7}		0.78	2.2×10^{-7}	
UiO-66(Zr)-SO_3H	0.34×10^{-2}		0.27	3.4×10^{-3}	
UiO-66(Zr)-$(COOH)_2$	0.10×10^{-2}		0.18	1.0×10^{-3}	
MOF-808(Zr)	3.14×10^{-3}	99% RH 25 °C	0.37	4.0×10^{-3}	17
β-PCMOF2(Na)	5×10^{-6}	90% RH 30 °C	0.28	5.0×10^{-6}	18
PCMOF3(Zn)	3.5×10^{-5}	98% RH 25 °C	0.17	3.9×10^{-5}	19
VNU-17(Zr)	6.65×10^{-5}	98% RH 70 °C	0.47	8.1×10^{-6}	20
VNU-23(Zr)	1.54×10^{-4}	90% RH 70 °C	-	-	21
Cu-SAT	0.53×10^{-3}	98% RH 80 °C	0.23	1.5×10^{-4}	22
MFM-500(Co)	4.4×10^{-5}	98% RH 25 °C	-	4.4×10^{-5}	23
MFM-500(Ni)	4.5×10^{-4}		0.43	5.9×10^{-4}	
Li-HPAA	1.1×10^{-4}	98% RH 24 °C	0.84	2.1×10^{-4}	24
Na-HPAA	5.6×10^{-3}		0.39	7.6×10^{-3}	
K-HPAA	1.3×10^{-3}		0.98	2.8×10^{-3}	
Cs-HPAA	3.5×10^{-5}		0.40	6.0×10^{-4}	
Ca-SBBA	8.58×10^{-6}		0.23	4.8×10^{-5}	25
Sr-SBBA	4.4×10^{-5}		0.56	1.0×10^{-5}	
PCMOF-5(Li)	6.0×10^{-3}	95% RH 85 °C	0.17	2.2×10^{-3}	26
PCMOF-5(Ce)	1.2×10^{-4}		0.20	3.7×10^{-5}	
PCMOF-5(Pr)	3.9×10^{-3}		0.17	1.4×10^{-3}	
PCMOF-5(Nd)	2.1×10^{-4}		0.17	7.7×10^{-5}	
PCMOF-5(Sm)	2.3×10^{-4}		0.24	5.6×10^{-5}	
PCMOF-5(Eu)	1.9×10^{-4}		0.23	4.9×10^{-5}	
PCMOF-5(Gd)	1.5×10^{-4}		0.19	4.9×10^{-5}	
CP-1(Gd)	2.02×10^{-6}	95% RH 80 °C	0.27	4.7×10^{-7}	27
CP-1(Dy)	2.96×10^{-6}		0.25	7.6×10^{-7}	
CP-1(Ho)	4.56×10^{-3}		0.38	5.8×10^{-4}	
CP-1(Er)	6.59×10^{-3}		0.32	1.2×10^{-3}	
HOF	6.91×10^{-5}	98% RH 100 °C	0.68	5.2×10^{-7}	28
Cu-MOF	3.78×10^{-4}		0.63	4.1×10^{-6}	
TMOF-1(Cu)	1.62×10^{-6}	98% RH 90 °C	0.34	1.9×10^{-7}	29
TMOF-2(Cu)	1.23×10^{-4}		0.37	1.2×10^{-5}	
$[Fe(ox)\cdot 2H_2O]$	1.3×10^{-3}	98% RH 25 °C	0.37	1.6×10^{-3}	30
$[Zn(\mathit{l}\text{-}L_{Cl})(Cl)](H_2O)_2$	4.45×10^{-5}	98% RH 31 °C	0.34	4.3×10^{-5}	31
$[Zn(\mathit{d}\text{-}L_{Cl})(Cl)](H_2O)_2$	4.42×10^{-5}		0.36	4.2×10^{-5}	
$(NH_4)_2[Ag_4(mel)$	4.3×10^{-5}	98% RH	0.47	5.3×10^{-5}	32

$(NH_3)_2]\cdot 3H_2O$		85 °C			
$[Cu_2(Htzehp)_2$ $(4,4'\text{-bipy})]\cdot 3H_2O$	1.39×10^{-4} (*a*-axis)	95% RH 30 °C	0.48	1.4×10^{-4}	33
	1.56×10^{-6} (*b*-axis)		0.56	1.6×10^{-6}	
	1.1×10^{-5} (pellet)		-	1.1×10^{-5}	
Co-MOF-74	8×10^{-6} (*a*-axis)	95% RH 90 °C	-	-	34
	4.5×10^{-3} (*c*-axis)		0.12	2.1×10^{-3}	
	2.5×10^{-7} (pellet)		0.30	3.7×10^{-8}	
$(NH_4)_2(adp)$ $[Zn_2(ox)_3]\cdot 2H_2O$	7×10^{-5}	95% RH 25 °C	0.63	1.0×10^{-4}	35
$K_2(H_2adp)$ $[Zn_2(ox)_3]\cdot 3H_2O$	1.2×10^{-4}	95% RH 25 °C	0.45	1.6×10^{-4}	36
$[In(IA)_2\{(CH_3)_2$ $NH_2\}(H_2O)_2]$	3.4×10^{-3}	98% RH 27 °C	0.61	4.3×10^{-3}	37
$[In(IA)_2\{(CH_3)_2$ $NH_2\}(DMF)]$	4.2×10^{-4}		0.48	5.0×10^{-4}	
$\{[(Me_2NH_2)_3(SO_4)]_2$ $[Zn_2(ox)_3]\}_n$	4.2×10^{-2}	98% RH	0.13	-	38
$[(Cu^I_4Cu^{II}_4L_4)\cdot 3H_2O]_n$	1.13×10^{-2}	98% RH 100 °C	0.37	7.9×10^{-4}	39
$[Cu^I_4Cu^{II}_4L_4]_n\text{-}NH_3$	4.90×10^{-4}		0.39	3.0×10^{-5}	
MIL-101(Cr)-SO_3H	6.32×10^{-5}	90% RH 70 °C	-	-	40
MIL-101(Cr)-NH-$(CH_2)_3SO_3H$	4.8×10^{-3}	95% RH 90 °C	-	-	41
MOF-808(Zr)	1.25×10^{-6}	98% RH 30 °C	0.37	1.3×10^{-6}	42
MOF-808(Zr)-OX	1.54×10^{-6}		0.15	1.5×10^{-6}	
MOF-808(Zr)-EDTA	1.94×10^{-4}		0.14	1.9×10^{-4}	
$\{[Zn(PIP)_2(H_2O)_4]\cdot NDS\}$	5.26×10^{-4}	98% RH 80 °C	0.53	3.0×10^{-5}	43
$\{[Ni(PIP)_2(H_2O)_4]\cdot NDS\}$	2.29×10^{-4}		0.58	9.8×10^{-6}	

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