Supporting Information for

An acid-stable hexaphosphate ester-based metal-organic framework and its polymer composite as proton exchange membrane

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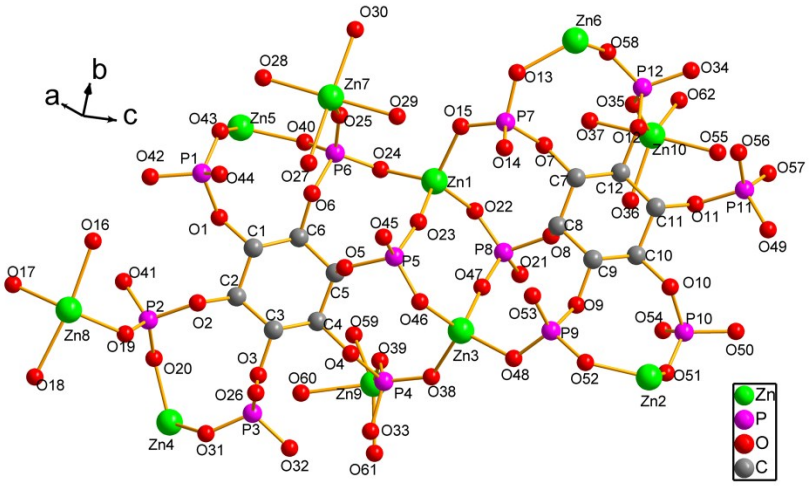

Fig. S1 The asymmetric unit of the JUC-200

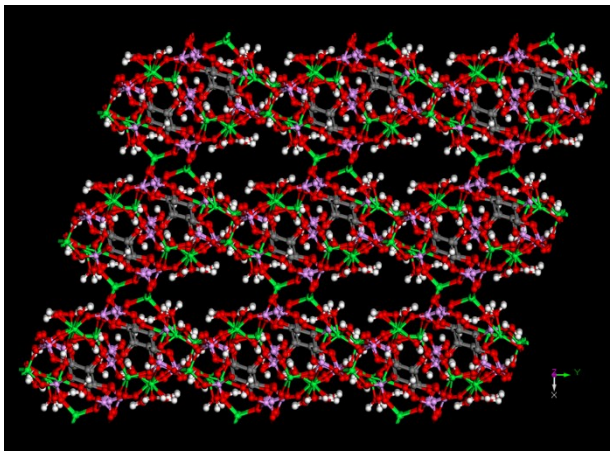

Fig. S2 Viewed along the *c*-axis of the JUC-200 framework

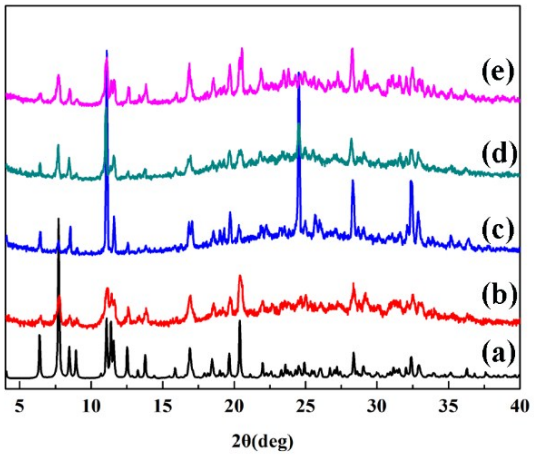

Fig. S3 The PXRD patterns of the JUC-200 immersed in different solvents. (a) The simulated spectrum of the JUC-200. (b) 80 °C water for 3 days. (c) Methanol for 7 days. (d) Ethanol for 1 day. (e) DMF for 1 day.

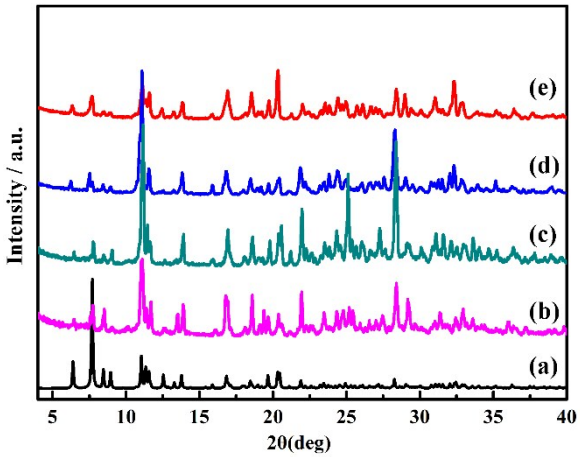

Fig. S4 The PXRD patterns of the JUC-200 soaked in different pH values. (a) The simulated spectrum of the JUC-200. (b) to (e) showed the PXRD of the JUC-200 soaked in different HCl aqueous solution (pH=2, 3, 4, 5) 7 days, respectively.

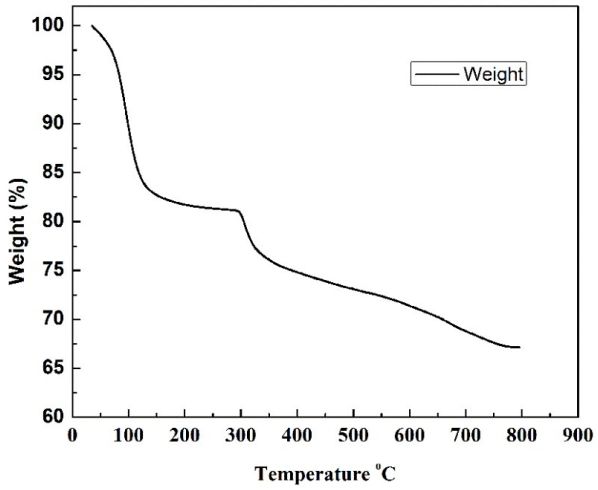

Fig. S5 The TGA curve for JUC-200

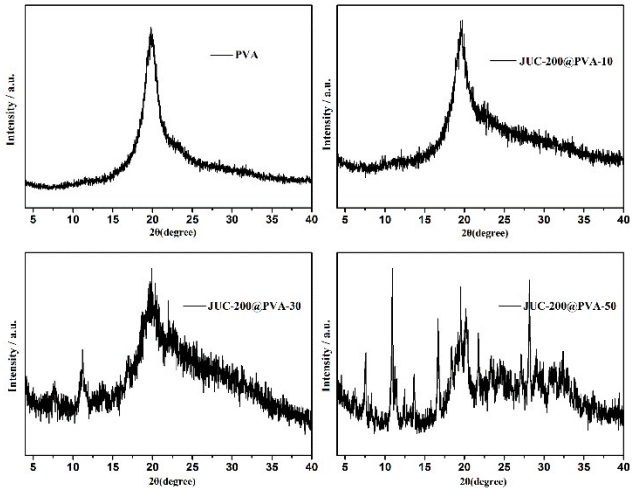

Fig. S6 The PXRD patterns of JUC-200@PVA composite membranes with various contents

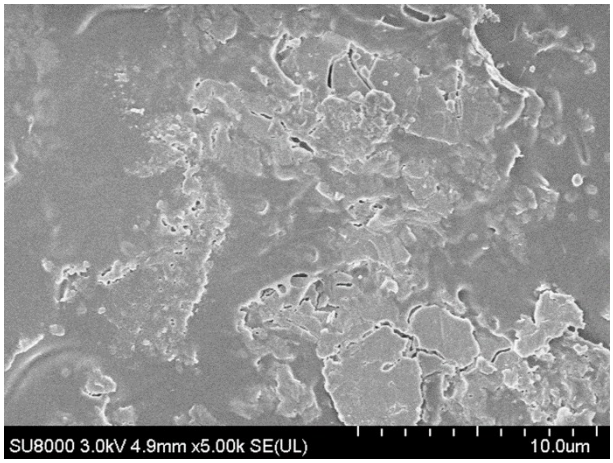

Fig. S7 The SEM images shows the surface of the JUC-200@PVA-50 composite membrane.

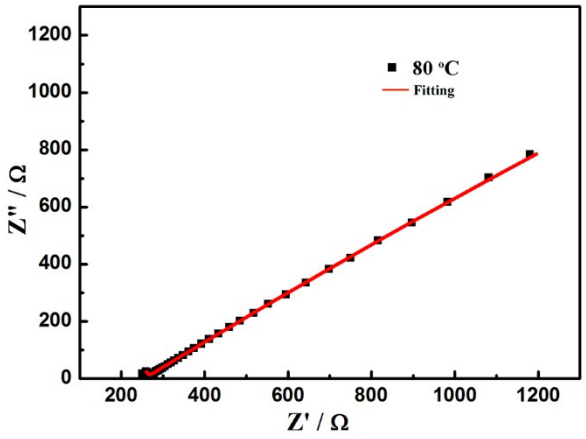

Fig. S8 The Nyquist plot of the JUC-200 at 80 ℃ in the water.

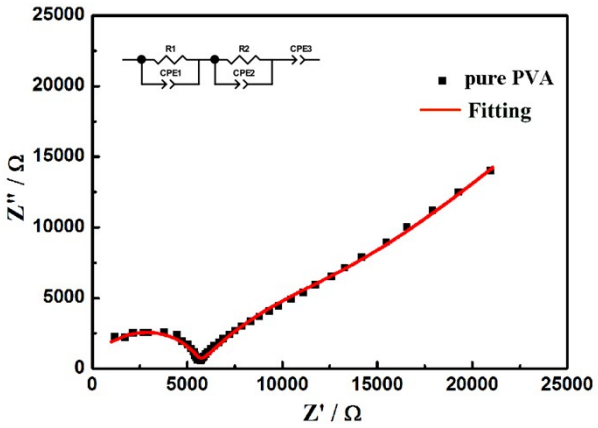

Fig. S9 The Nyquist plot of the pure PVA.

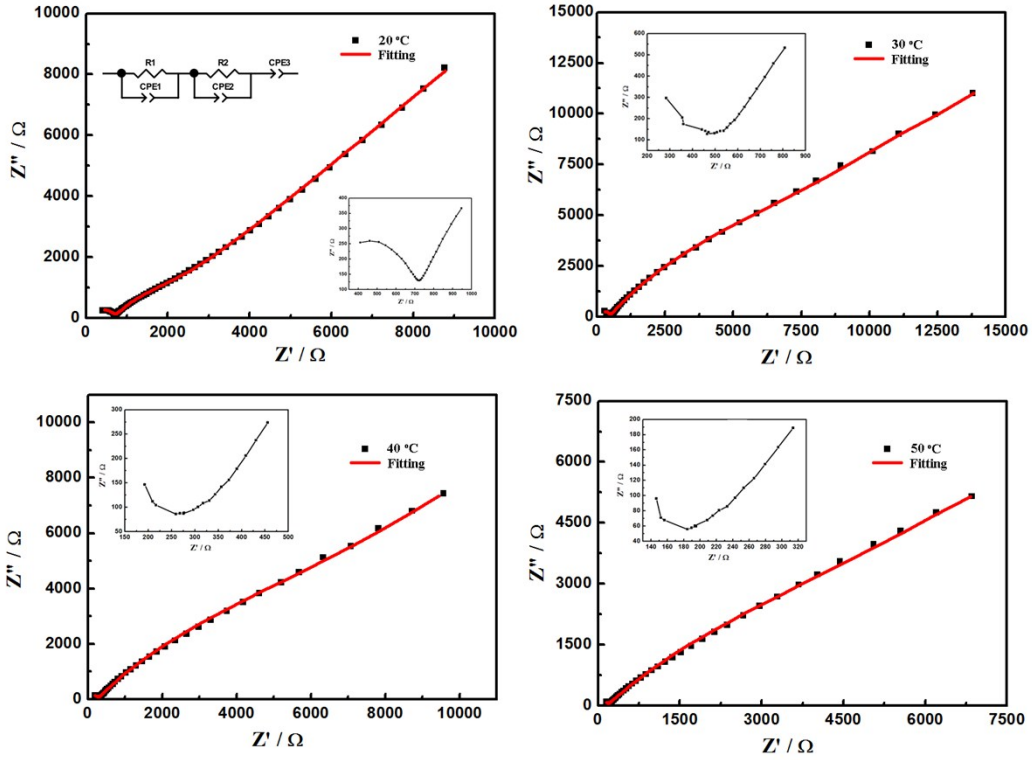

Fig. S10 The Nyquist plot of the JUC-200@PVA-10 with different temperature. The circuit model used for the data fitting of JUC-200@PVA-10 and the enlarged part of the plot were shown as inset.

Table S1. Crystallographic Data and Details of Refinements for JUC-200

Identification code	aaa_sq	
Empirical formula	C12 H44 O62 P12 Zn10	
Formula weight	2205.81	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.962(2) Å	α= 104.12(3)°.
	b = 14.897(3) Å	β= 91.11(3)°.
	c = 22.540(5) Å	γ = 106.09(3)°.
Volume	3726.3(15) $Å^3$	

Z	2
Density (calculated)	1.966 Mg/m^3
Absorption coefficient	3.526 mm^{-1}
F(000)	2184
Crystal size	0.220 x 0.200 x 0.180 mm^3
Theta range for data collection	2.257 to 28.346°.
Index ranges	-15<=h<=15, -19<=k<=19, -30<=l<=30
Reflections collected	85450
Independent reflections	18485 [R(int) = 0.1292]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18485 / 220 / 871
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0786, wR2 = 0.1670
R indices (all data)	R1 = 0.1388, wR2 = 0.1869
Extinction coefficient	n/a
Largest diff. peak and hole	4.057 and -1.520 $e.Å^{-3}$

Table S2. Hydrogen bonds for JUC-200 [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(15)-H(15)...O(61)#6	0.82	2.03	2.848(9)	171.8
O(21)-H(21)...O(15)#6	0.84	1.93	2.450(8)	119.0
O(33)-H(33)...O(45)#5	0.82	1.61	2.426(7)	169.7
O(45)-H(45)...O(52)	0.82	2.61	3.123(7)	121.6
O(49)-H(49A)...O(45)	0.99	1.85	2.790(8)	157.0
O(49)-H(49B)...O(33)	0.99	2.13	3.103(8)	166.4
O(50)-H(50A)...O(42)#5	0.97	1.92	2.840(8)	157.8
O(50)-H(50B)...O(28)	0.98	2.28	2.975(8)	127.6

O(51)-H(51A)...O(58)#2	1.00	2.00	2.976(9)	164.6
O(52)-H(52A)...O(43)	1.00	1.78	2.776(7)	168.5
O(54)-H(54B)...O(25)#2	1.00	1.87	2.788(8)	150.8
O(55)-H(55A)...O(33)	1.00	2.13	2.974(8)	141.2
O(55)-H(55B)...O(41)#5	1.02	2.53	3.210(8)	123.6
O(55)-H(55B)...O(44)#5	1.02	2.38	3.310(8)	152.2
O(56)-H(56A)...O(54)#2	1.01	1.90	2.838(11)	154.2
O(56)-H(56B)...O(42)#7	1.00	2.54	3.298(9)	131.8
O(57)-H(57A)...O(17)#1	1.02	2.45	3.021(12)	114.4
O(58)-H(58A)...O(38)#7	1.02	1.64	2.624(9)	160.7
O(60)-H(60B)...O(19)#6	0.99	1.84	2.768(10)	154.8
O(61)-H(61A)...O(21)#6	1.00	1.72	2.698(8)	164.1
O(61)-H(61B)...O(15)#6	1.01	1.85	2.848(9)	169.1
O(62)-H(62A)...O(34)#6	1.00	1.77	2.736(9)	161.4
O(62)-H(62B)...O(4)	1.00	2.54	3.392(8)	143.8
O(62)-H(62B)...O(23)	1.00	1.84	2.751(9)	150.8
C(3)-H(3)...O(21)	0.98	2.34	2.883(10)	114.5
C(5)-H(5)...O(26)	0.98	2.52	2.997(9)	110.1
C(8)-H(8)...O(57')#6	0.98	2.02	2.76(2)	130.5
C(9)-H(9)...O(39)	0.98	2.43	2.947(10)	112.3
C(9)-H(9)...O(49)#5	0.98	2.60	3.528(9)	158.0
C(11)-H(11)...O(45)	0.98	2.35	2.886(9)	113.3

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x+1,-y+2,-z+1 #3 -x+1,-y,-z

#4 -x+2,-y+1,-z #5 -x+1,-y+1,-z #6 -x+1,-y+1,-z+1 #7 x,y+1,z+1

Table S3. List of some proton conduction compounds

Compounds	Conductivity ($S \cdot cm^{-1}$)	Analysis conditions	Stability	Ref.
UiO-66$(SO_3H)_2$	8.4×10^{-2}	80 °C, 90 RH%	postsynthetic in 0.02M H_2SO_4	1
H^+@Ni(dobdc)	2.2×10^{-2}	80 °C, 95 RH%	pH=1.8	2
TfOH@MIL-101	8×10^{-2}	60 °C, 15 RH%	anhydrous acid	3
JUC-200	1.62×10^{-3}	80 °C, 100RH%	water and acid	this work
PCMOF-10	3.55×10^{-2}	70 °C, 95 RH%	water	4
PCMOF-5	4×10^{-3}	60 °C, 98 RH%	water	5
PCMOF2$^1/_2$	2.1×10^{-2}	85 °C, 90 RH%	-----	6
La(H_5DTMP)·$7H_2O$	8×10^{-3}	24 °C, 98 RH%	-----	7
$(NH_4)_2$(adp)[$Zn_2(ox)_3$]·$3H_2O$	8×10^{-3}	25 °C, 98 RH%	-----	8
Cu−TCPP nanosheet	3.9×10^{-3}	25 °C, 98 RH%	-----	9

Cd-5TIA	3.61×10^{-3}	28 °C, 98 RH%	-----	10
In-IA-2D-1	3.4×10^{-3}	27 °C, 98 RH%	-----	11
$V^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.2H_2O$	2.6×10^{-3}	50 °C, 100 RH%	-----	12
$[\{(Zn_{0.25})_8(O)\}Zn_6(L)_{12}(H_2O)_{29}(DMF)_{69}(NO_3)_2]_n$	2.3×10^{-3}	25 °C, 95 RH%	-----	13
$Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$	1.7×10^{-3}	35 °C, 100 RH%	-----	12
$MgH_6ODTMP\cdot 6H_2O$	1.6×10^{-3}	19 °C, 100 RH%	-----	14
β-PCMOF2	1.3×10^{-3}	85 °C, 90 RH%	-----	6
$Fe(Ox)\cdot 2H_2O$	1.3×10^{-3}	25 °C, 98 RH%	-----	15
$\{[Ca(D\text{-}Hpmpc)(H_2O)_2]\cdot 2HO_{0.5}\}_n$	8.9×10^{-4}	60 °C, 97 RH%	-----	16
Ca-PiPhtA-I	5.7×10^{-4}	24 °C, 98 RH%	-----	17
In-IA-2D-2	4.2×10^{-4}	27 °C, 98 RH%	-----	11
GdHPA-II	3.2×10^{-4}	21 °C, 98 RH%	water	18

Note: the "-----" shows that the article does not report the stability of the compound.

Reference:

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