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Supporting information

Comparative study on proton conductivity of a polypyridinyl multicarboxylate-based hydrogen-bonded organic framework and related chitosan composite membrane

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Table S1. Crystallographic data and structure refinement information for HOF **1**.

	HOF **1**
Formula	$C_{24}H_{23}N_3O_{10}$
F_w	513.45
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	7.9842(3)
b (Å)	18.7164(7)
c (Å)	15.8121(5)
α (deg)	90
β (deg)	92.417(3)
γ (deg)	90
V (Å^3)	2360.78(16)
Z	4
ρ_{calc}g/cm^3	1.445
F(000)	1072.0
μ (mm^{-1})	0.971
Theta range for data collection	7.322 to 134.112
Index ranges	$-7 \le h \le 9$, $-22 \le k \le 14$, $-14 \le l \le 18$
Reflections	8515
Data/restraints/parameters	4219/2/346
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0658$, w$R_2 = 0.1769$
Final R indexes [all data]	$R_1 = 0.0899$, w$R_2 = 0.2002$
Dr_{min} and Dr_{max}/e Å^{-3}	0.36/-0.35

Table S2. Selected bond distances (Å) and angles (deg) for **1.**

O(1)-C(1)	1.206(4)	C(6)-C(7)	1.394(4)
O(2)-C(1)	1.303(4)	C(7)-C(8)	1.387(4)
O(3)-C(2)	1.212(4)	C(8)-C(9)	1.397(4)
O(4)-C(2)	1.312(4)	C(9)-C(17)	1.503(4)
O(5)-C(3)	1.245(4)	C(10)-C(11)	1.365(5)
O(6)-C(3)	1.244(4)	C(11)-C(12)	1.380(5)
N(1)-C(10)	1.338(4)	C(12)-C(13)	1.378(5)
N(1)-C(14)	1.344(4)	C(13)-C(14)	1.375(4)
N(2)-C(15)	1.342(4)	C(14)-C(15)	1.484(4)
N(2)-C(19)	1.334(4)	C(15)-C(16)	1.385(4)
N(3)-C(20)	1.361(4)	C(16)-C(17)	1.387(4)
N(3)-C(24)	1.369(4)	C(17)-C(18)	1.384(4)
C(1)-C(4)	1.499(4)	C(18)-C(19)	1.396(4)
C(2)-C(6)	1.496(4)	C(19)-C(20)	1.492(4)
C(3)-C(8)	1.514(4)	C(20)-C(21)	1.353(4)
C(4)-C(5)	1.392(4)	C(21)-C(22)	1.356(5)
C(4)-C(9)	1.397(4)	C(22)-C(23)	1.376(6)
C(5)-C(6)	1.381(4)	C(23)-C(24)	1.366(6)

Table S3. Selected bond distances (Å) and angles (deg) for HOF **1**

C(10)-N(1)-C(14)	123.3(3)	N(1)-C(10)-C(11)	120.0(3)
C(19)-N(2)-C(15)	117.6(2)	C(10)-C(11)-C(12)	118.5(3)
C(20)-N(3)-C(24)	118.7(3)	C(13)-C(12)-C(11)	120.3(3)
O(1)-C(1)-O(2)	123.8(3)	C(14)-C(13)-C(12)	119.8(3)
O(1)-C(1)-C(4)	123.3(3)	N(1)-C(14)-C(13)	118.1(3)
O(2)-C(1)-C(4)	112.9(2)	N(1)-C(14)-C(15)	117.3(3)
O(3)-C(2)-O(4)	123.8(3)	C(13)-C(14)-C(15)	124.6(3)
O(3)-C(2)-C(6）	122.5(3)	N(2)-C(15)-C(14)	115.1(2)
O(4)-C(2)-C(6)	113.7(3)	N(2)-C(15)-C(16)	123.8(3)

O(5)-C(3)-C(8)	116.8(3)	C(16)-C(15)-C(14)	121.2(3)
O(6)-C(3)-O(5)	125.5(3)	C(15) C(16) C(17)	118.2(3)
O(6)-C(3)-C(8)	117.6(3)	C(16)-C(17)-C(9)	121.6(2)
C(5)-C(4)-C(1)	120.2(2)	C(18)-C(17)-C(9)	119.7(2)
C(5)-C(4)-C(9)	119.7(2)	C(18)-C(17)-C(16)	118.7(3)
C(9)-C(4)-C(1)	120.0(2)	C(17)-C(18)-C(19)	119.1(3)
C(6)-C(5)-C(4)	120.9(3)	N(2)-C(19)-C(18)	122.6(3)
C(5)-C(6)-C(2)	119.6(3)	N(2)-C(19)-C(20)	117.2(2)
C(5)-C(6)-C(7)	119.2(3)	C(18)-C(19)-C(20)	120.2(2)
C(7)-C(6)-C(2)	121.1(3)	N(3)-C(20)-C(19)	119.1(3)
C(8)-C(7)-C(6）	120.6(3)	C(21)-C(20)-N(3)	122.2(3)
C(7)-C(8)-C(3)	119.4(2)	C(21)-C(20)-C(19)	118.7(3)
C(7)-C(8)-C(9)	120.1(3)	C(20)-C(21)-C(22)	118.1(3)
C(9)-C(8)-C(3)	120.2(2)	C(21)-C(22)-C(23)	122.1(3)
C(4)-C(9)-C(17)	120.8(2)	C(24)-C(23)-C(22)	118.1(3)
C(8)-C(9)-C(4)	119.4(3)	C(23)-C(24)-N(3)	120.9(3)
C(8)-C(9)-C(17)	119.8(2)		

Table S4. Hydrogen bonding parameters of HOF **1.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
O(2)-H(2)···O(6) #1	0.82	1.76	2.576(3)	175.6
O(7)-H(7B)···O(4)	0.87	1.75	2.592(4)	162.9
O(8)-H(8A)···O(7)	0.85	2.31	2.860(6)	122.7
O(8)-H(8B)···O(6)#2	0.85	1.94	2.790(5)	175.9
O(9)-H(9B)··· O(5)	0.91(2)	2.11(18)	2.849(5)	138(23)
N(1)-H(1)···O(10)#3	0.86	1.94	2.718(4)	150.2
O(10)-H(10B)···O(14)	0.85	2.06	2.837(4)	152.6

Table S5. Proton Conductivities ($S \cdot cm^{-1}$) of HOF **1** at Different RHs and Temperatures.

	RH (%)				
temp (° C)	68	75	85	93	98
30	-	-	-	1.21×10^{-6}	3.54×10^{-6}
40	-	-	-	1.6×10^{-6}	4.6×10^{-6}
50	1.03×10^{-7}	1.56×10^{-7}	2.6×10^{-7}	3.18×10^{-6}	4.96×10^{-6}
60	3.73×10^{-7}	6.66×10^{-7}	8.88×10^{-7}	6.4×10^{-6}	1.84×10^{-5}
70	7.93×10^{-7}	1.56×10^{-7}	2.9×10^{-6}	3.8×10^{-5}	4.16×10^{-5}
80	1.18×10^{-6}	3.23×10^{-6}	4.08×10^{-6}	5.53×10^{-5}	1.48×10^{-4}
90	4.42×10^{-6}	8.7×10^{-6}	1.25×10^{-5}	7.44×10^{-5}	2.08×10^{-4}
100	1.02×10^{-5}	1.82×10^{-5}	8.41×10^{-5}	1.93×10^{-4}	4.83×10^{-4}

s

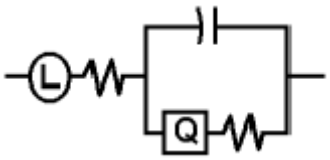
Table S6. The proton conductivities ($S \cdot cm^{-1}$) of **CS/HOF-x** at 98% RH**.**

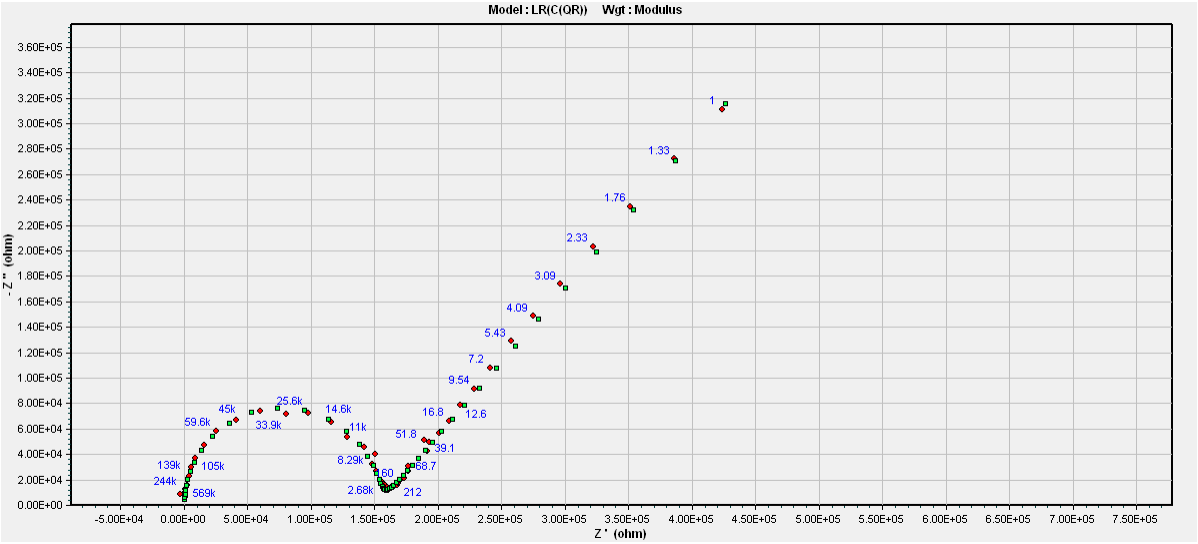
	Wet (%)				
temp (°C)	Pure CS	2%	4%	6%	8%
30	1.42×10^{-3}	3.61×10^{-3}	4.01×10^{-3}	2.05×10^{-3}	1.27×10^{-3}
40	2.01×10^{-3}	4.13×10^{-3}	4.92×10^{-3}	2.15×10^{-3}	1.58×10^{-3}
50	2.46×10^{-3}	4.89×10^{-3}	6.30×10^{-3}	4.22×10^{-3}	2.00×10^{-3}
60	3.40×10^{-3}	5.73×10^{-3}	1.06×10^{-2}	4.80×10^{-3}	2.85×10^{-3}
70	5.38×10^{-3}	1.08×10^{-2}	1.13×10^{-2}	5.26×10^{-3}	4.28×10^{-3}
80	7.10×10^{-3}	1.23×10^{-2}	1.31×10^{-2}	1.14×10^{-2}	6.34×10^{-3}
90	1.04×10^{-2}	1.34×10^{-2}	1.74×10^{-2}	1.53×10^{-2}	1.50×10^{-2}
100	1.25×10^{-2}	1.64×10^{-2}	2.61×10^{-2}	2.10×10^{-2}	1.94×10^{-2}

Table S7. Comparison of theσ of HOF **1** with that of other HOFs.

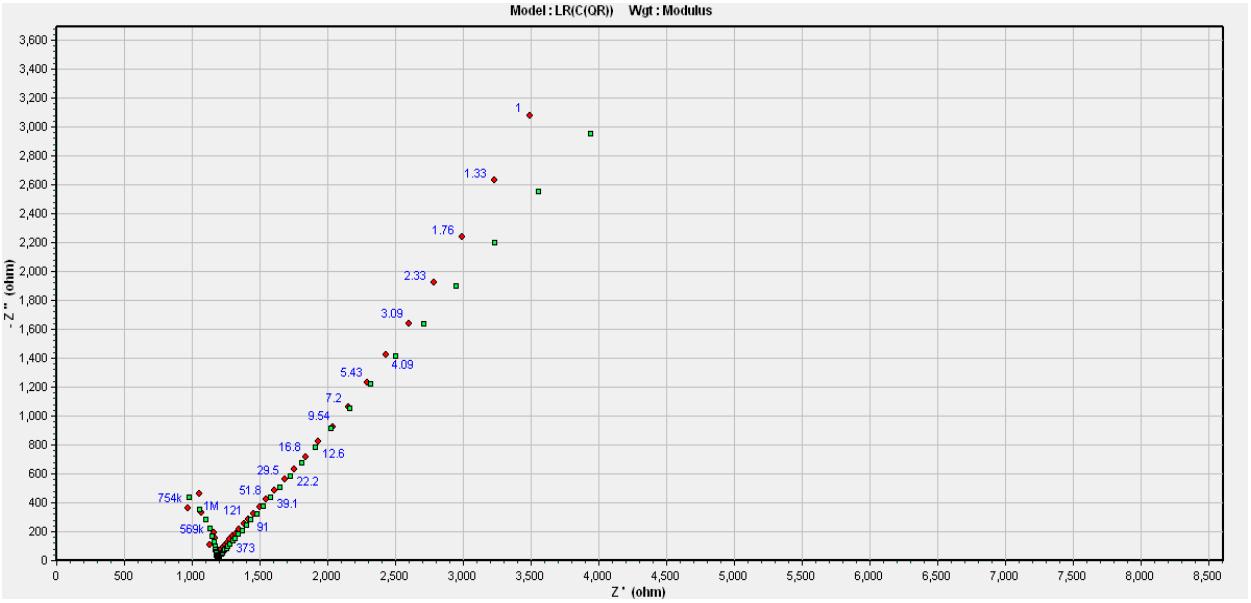
materials	conductivity ($S \cdot cm^{-1}$)	testing conditions
UPC-H3 [1]	9.0×10^{-2}	80 °C and 99% RH
HOF-GS-10 [2]	0.75×10^{-2}	85 °C and 90% RH
HOF-GS-11 [2]	1.80×10^{-2}	30 °C and 95% RH
CPOS-2 [3]	3.7×10^{-3}	100 °C and 98% RH
MHOF-1 [4]	0.75×10^{-3}	80 °C and 98% RH
MHOF-3 [4]	0.97×10^{-3}	80 °C and 98% RH
CPOS-1 [3]	6.0×10^{-4}	30 °C and 98% RH
HOF **1**	4.83×10^{-4}	100 °C and 98% RH
MA-B-BDC [5]	4.32×10^{-4}	50 °C and 98% RH
CPOS-3 [3]	3.7×10^{-4}	30 °C and 98% RH
MHOF-2 [4]	3.5×10^{-4}	80 °C and 98% RH
MA-TMA [5]	3.11×10^{-4}	70 °C and 98% RH
HOF-H_3L [6]	6.91×10^{-5}	30 °C and 98% RH
CPOS-4 [3]	5.6×10^{-5}	30 °C and 98% RH
HOF 6 [7]	3.40×10^{-6}	27 °C and 97% RH
GTUB5 [8]	3.00×10^{-6}	75 °C and 75% RH

Equivalent circuit LR(C(QR)):





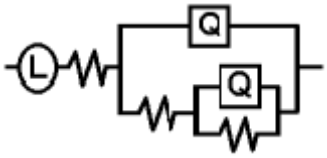
(a)

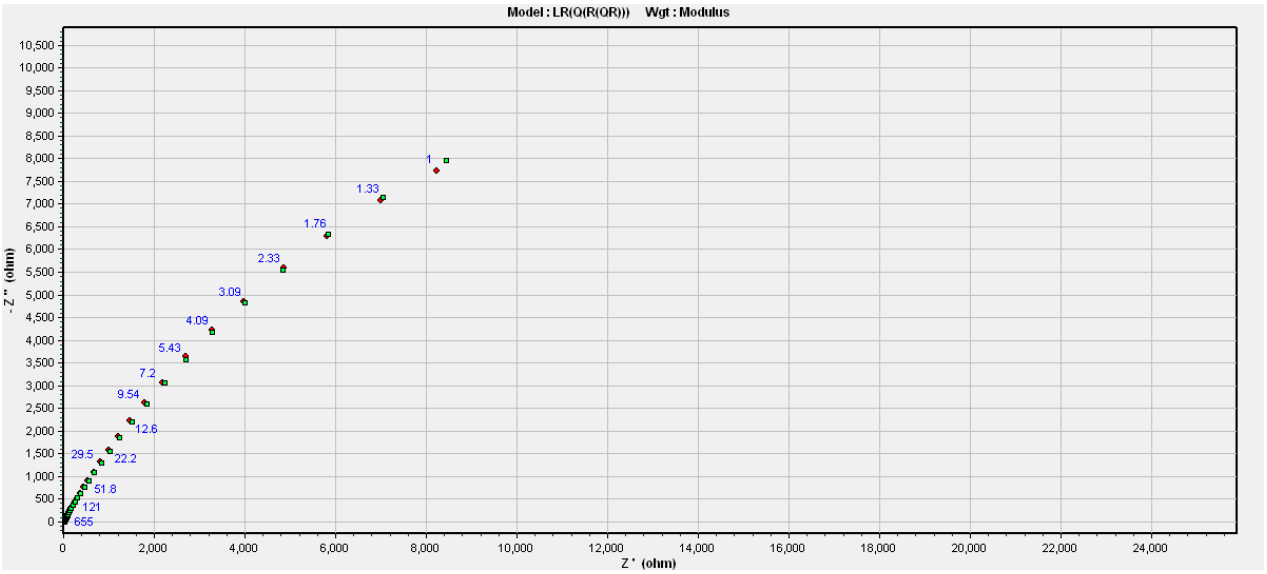


(b)

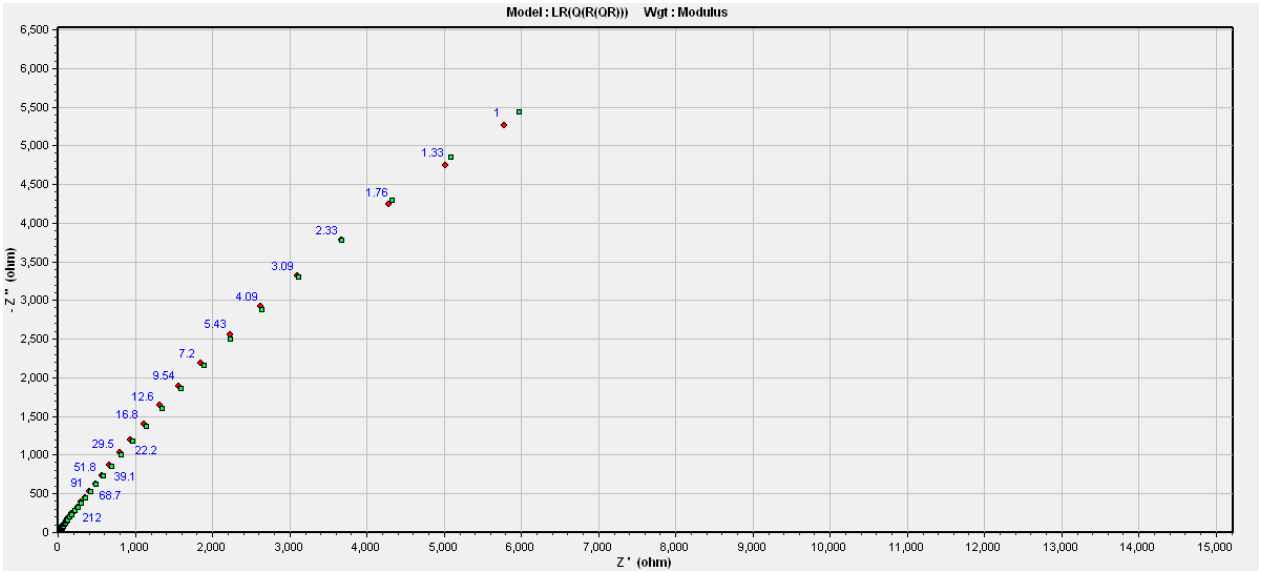
Figure S1. Nyquist plots for a polycrystalline sample of HOF **1** under 30 °C (a) and 100 °C (b) at 98% RH. Red circle and green square are the measured impedance spectroscopy values and the fits of the impedance data to the equivalent circuit of LR(C(QR)).

Equivalent circuit LR(Q(R(QR))):

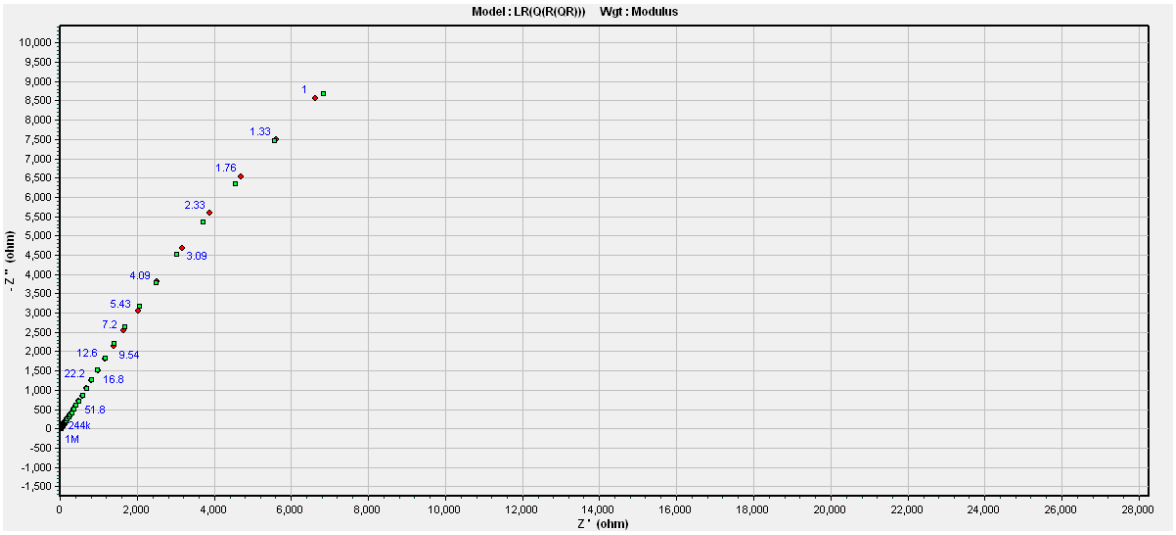




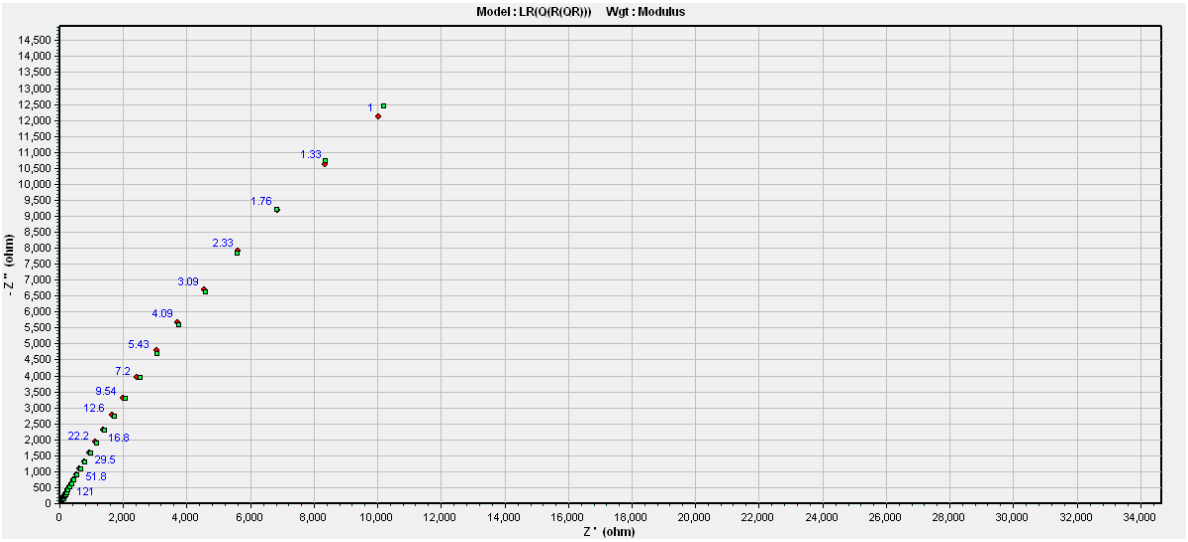
(a)



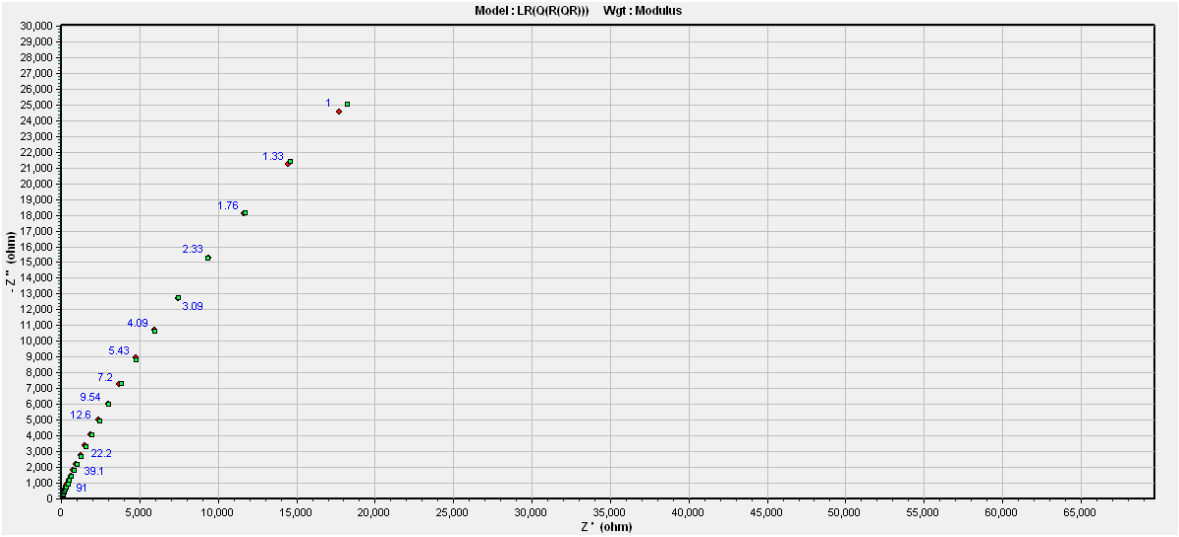
(b)



(c)



(d)



(e)

Figure S2. Nyquist plots for composite membrane samples of Pure CS membrane (a) and **CS/HOF-**

2 (b) and **CS/HOF-4** (c) and **CS/HOF-6** (d) and **CS/HOF-8** (e) under 98% RH and 100 °C. Red circle and green square are the measured impedance spectroscopy values and the fits of the impedance data to the equivalent circuit of LR(Q(R(QR))).

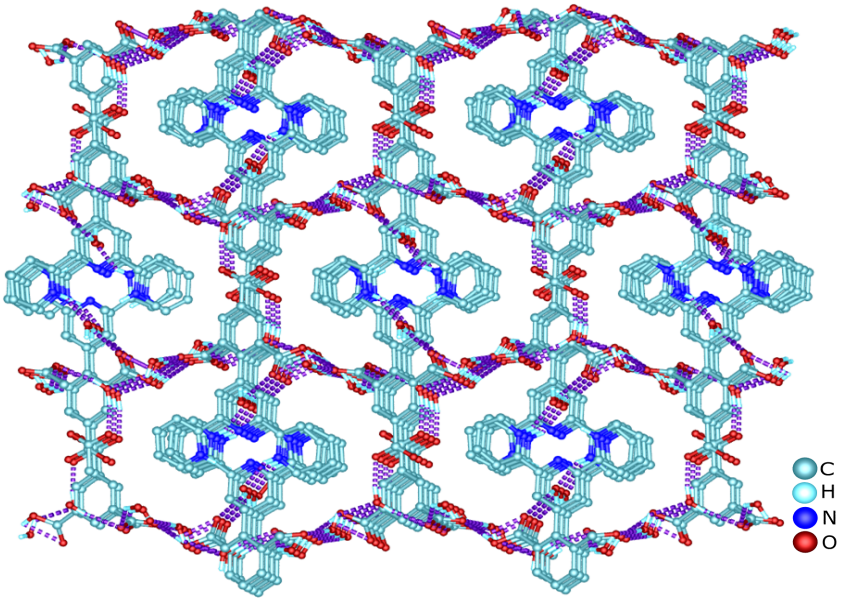


Figure S3. The 3D framework of **1** supported by intermolecular H-bonds and - interactions.

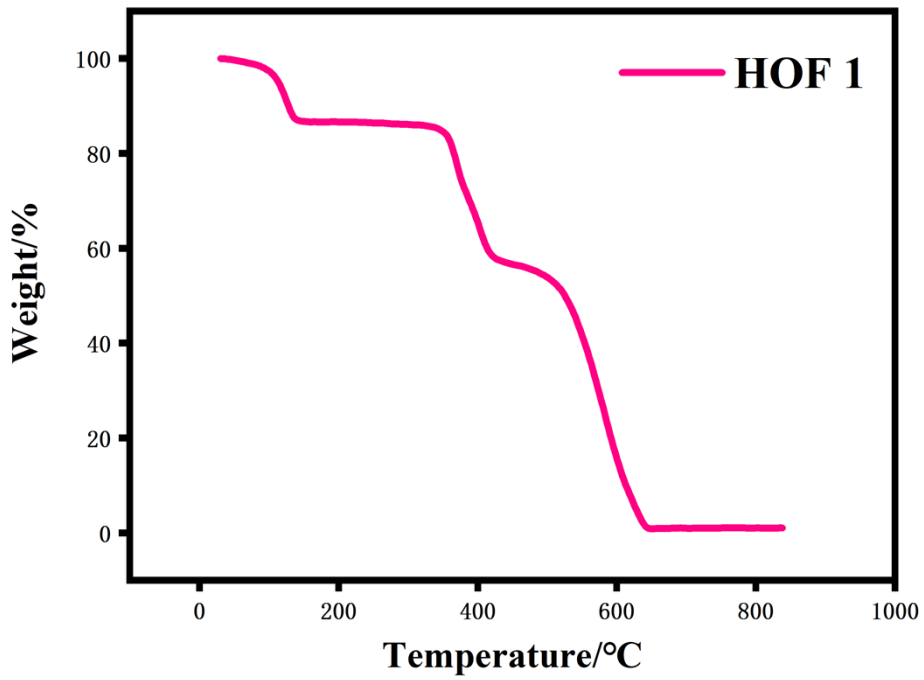


Figure S4. TG analysis profiles of HOF **1**.

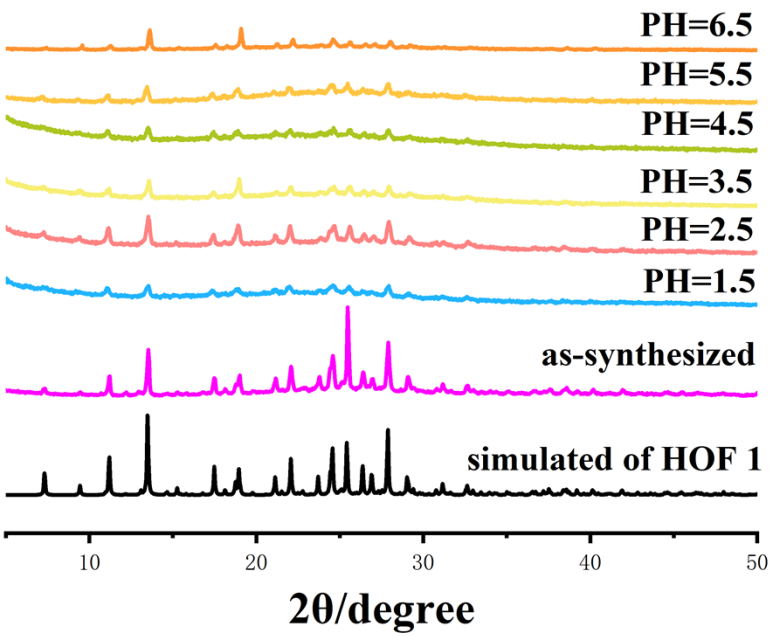


Figure S5. The PXRD patterns of crystals for **1** after soaking in different acidic solutions.

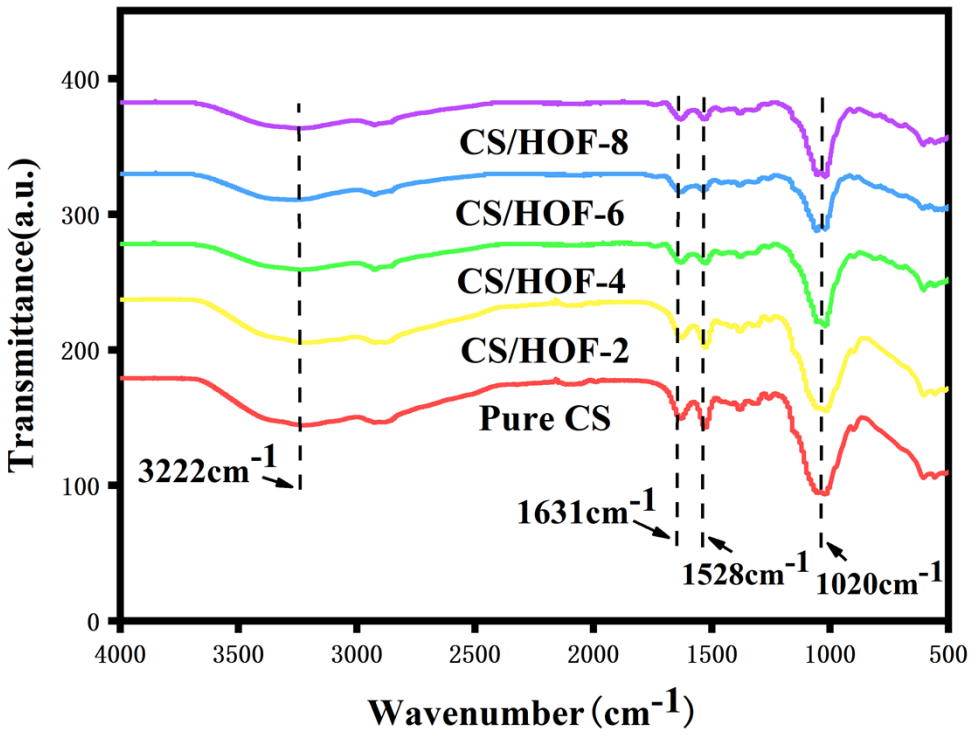


Figure S6. The Fourier Transform Infrared spectra of the **CS/HOF-x**.

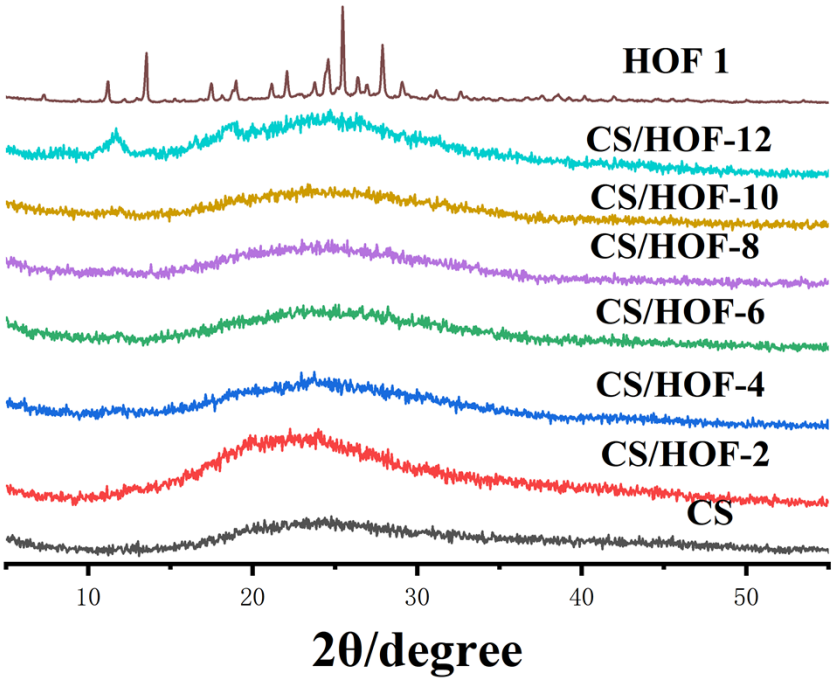


Figure S7. The PXRD patterns of **CS/HOF-x**

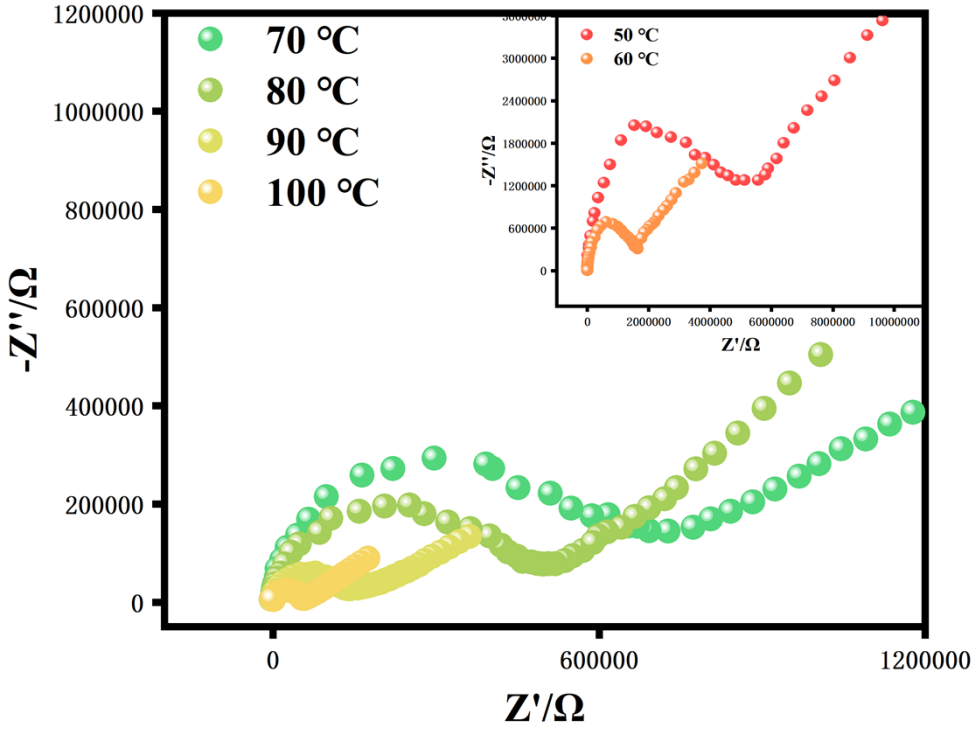


Figure S8. Impedance spectra of HOF **1** at 50-100 °C and 68% RH.

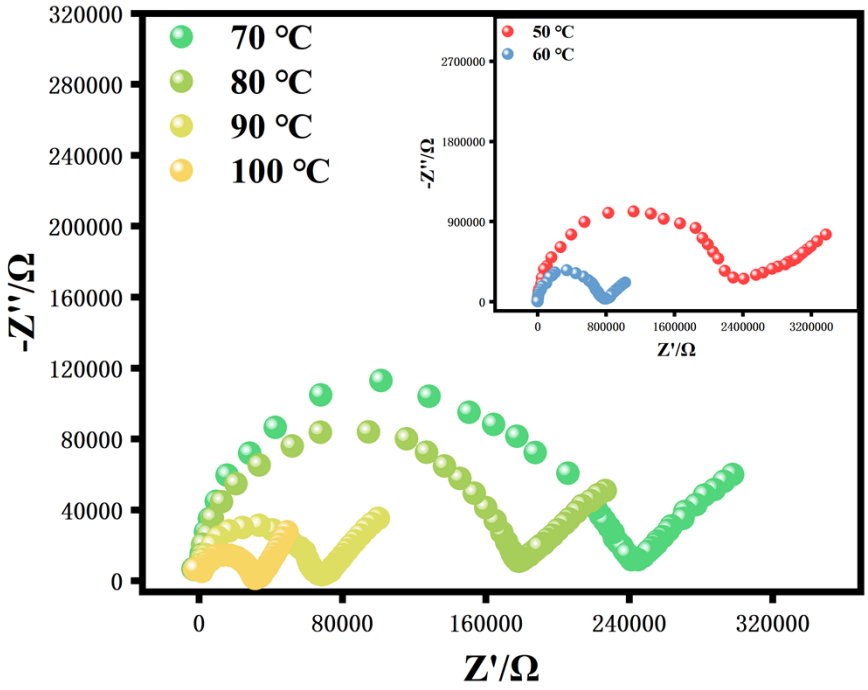


Figure S9. Impedance spectra of HOF **1** at 50-100 °C and 75% RHs.

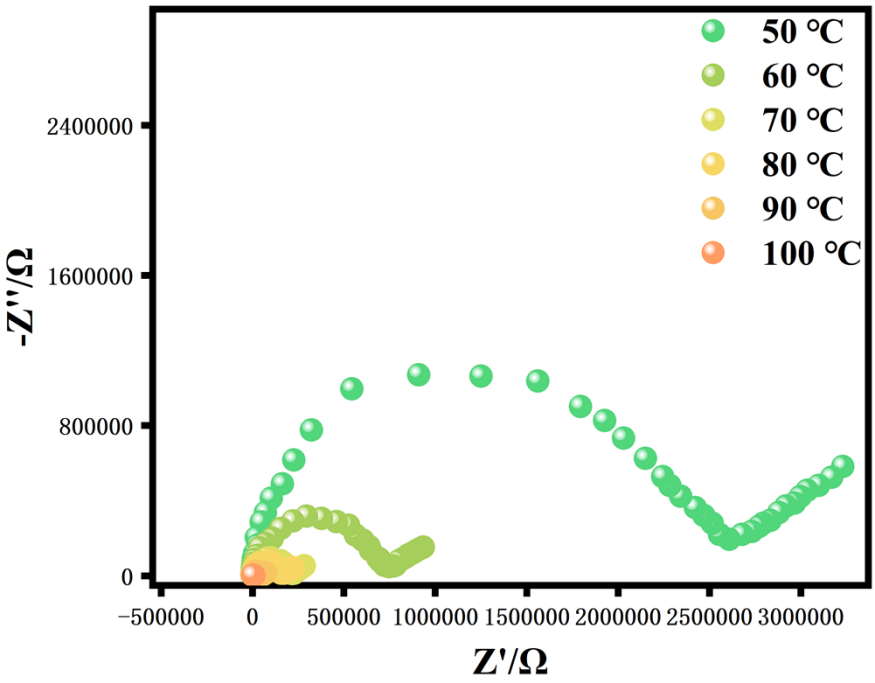


Figure S10. Impedance spectra of HOF **1** at 50-100 °C under 85% RH.

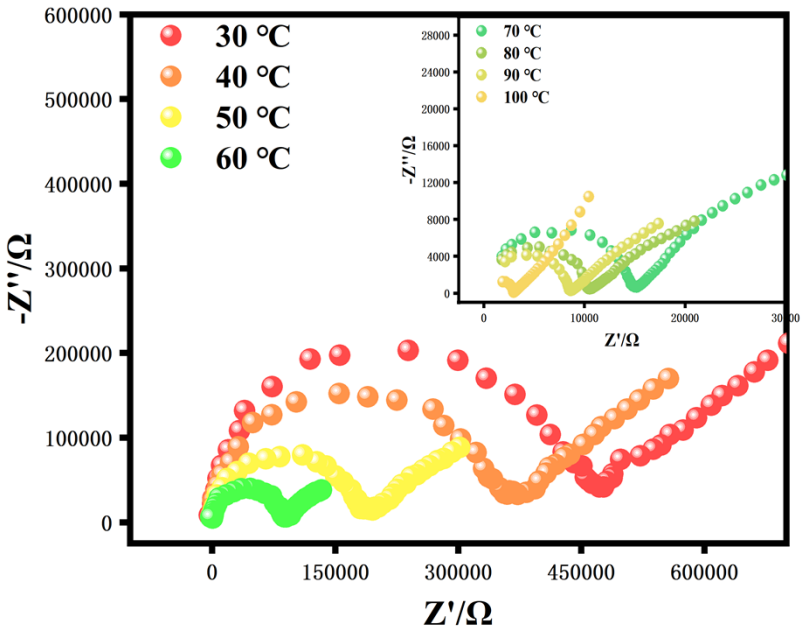


Figure S11. Impedance spectra of HOF **1** at 30-100 °C under 93% RH.

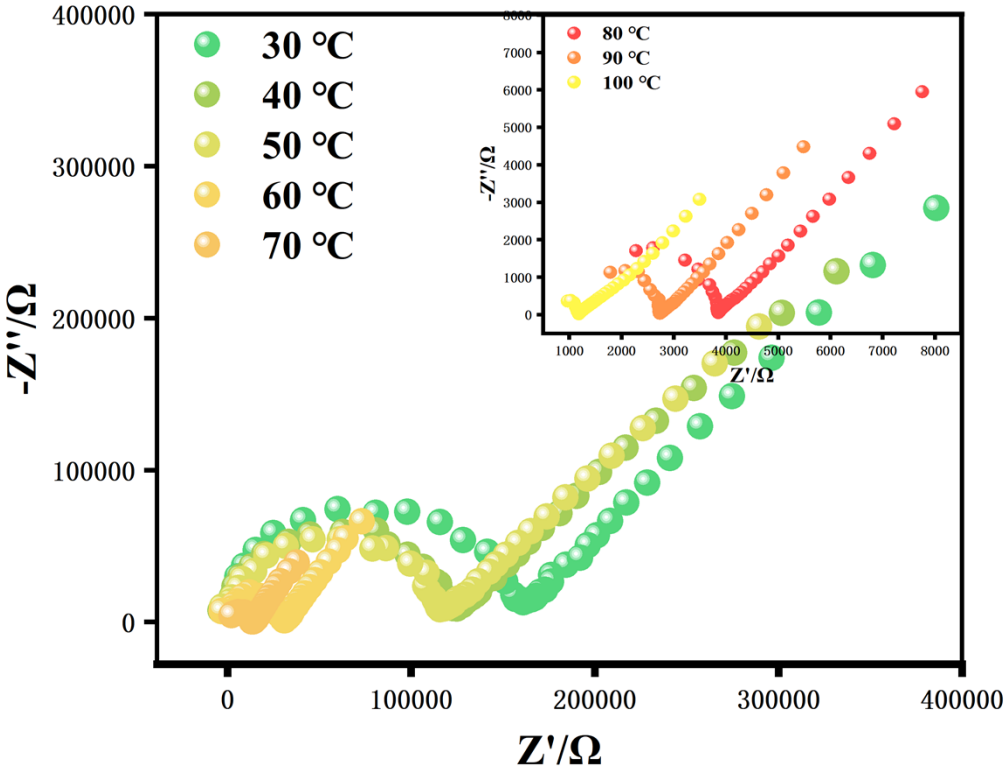


Figure S12. Impedance spectra of HOF **1** at 30-100 °C under 98% RH.

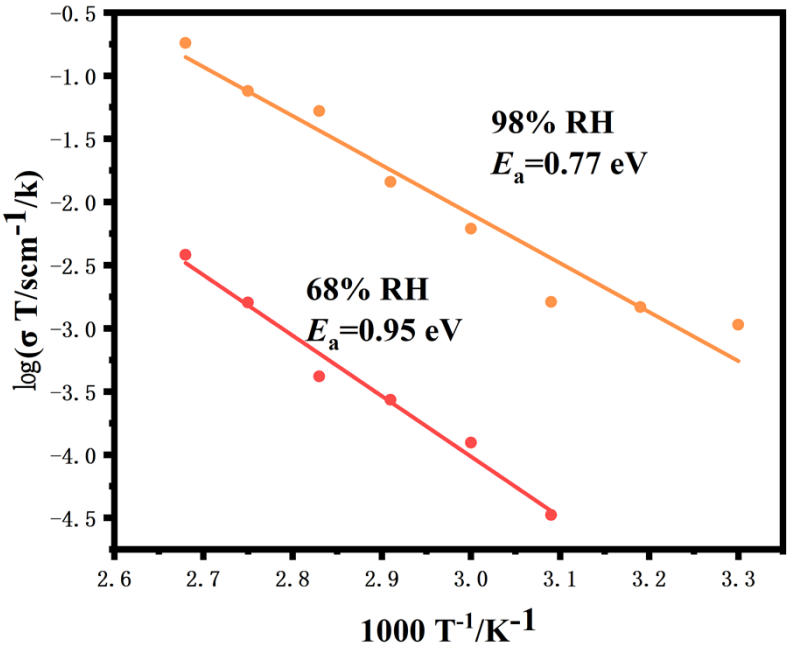


Figure S13. Arrhenius plots of the σ for HOF **1** under 98% and 68% RHs.

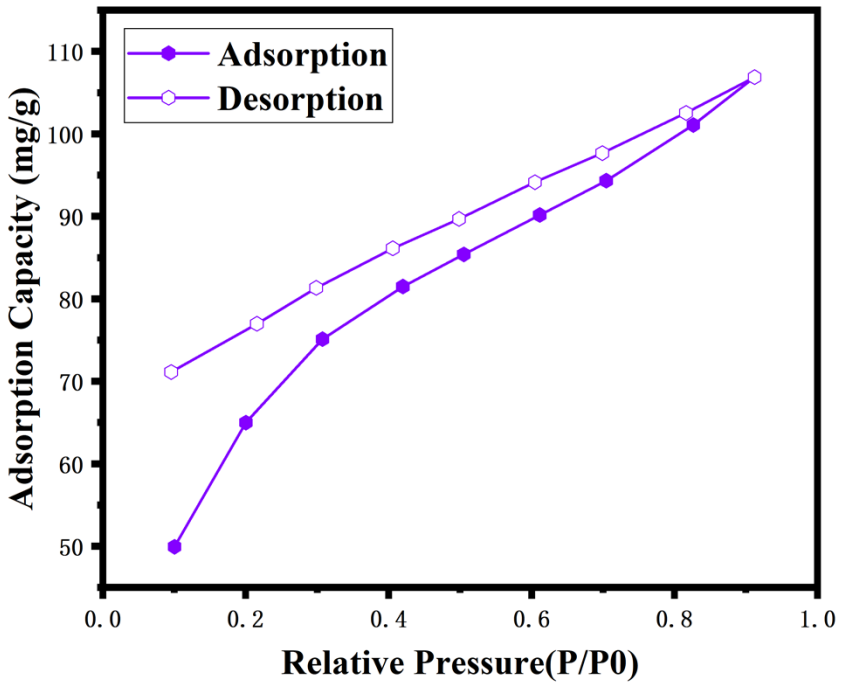


Figure 14. Water vapor adsorption/desorption isotherms of HOF **1** at 25 °C.

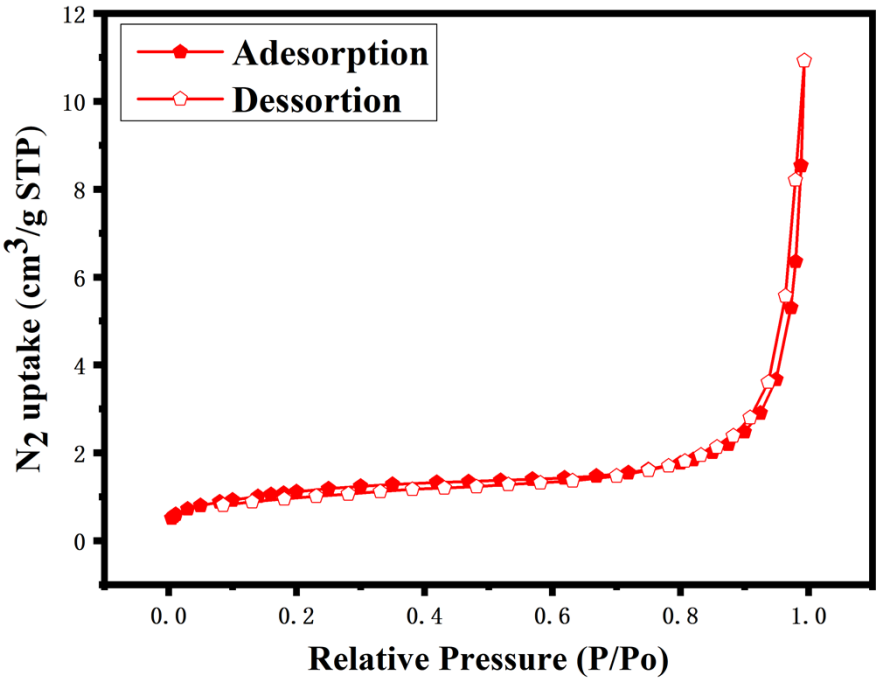


Figure S15. N_2 adsorption−desorption isotherms of HOF **1**.

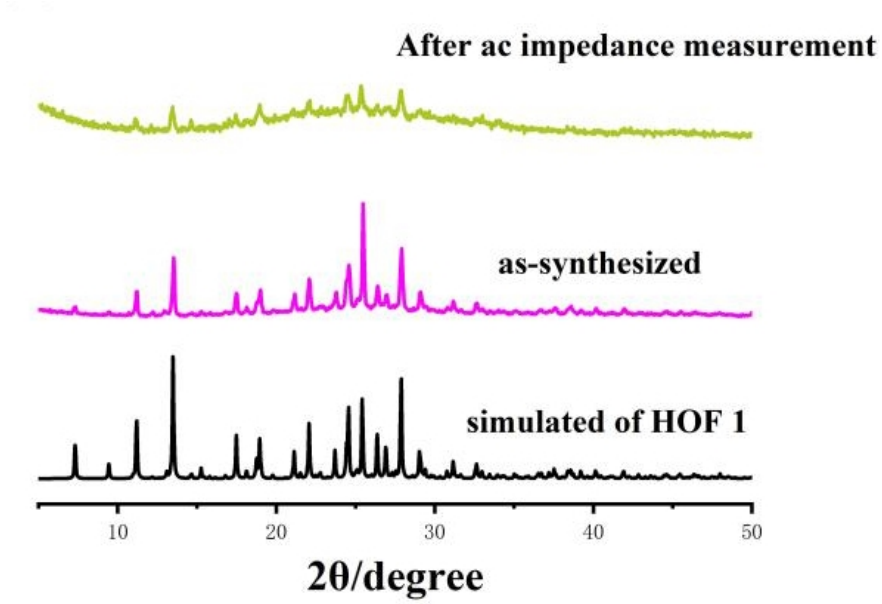
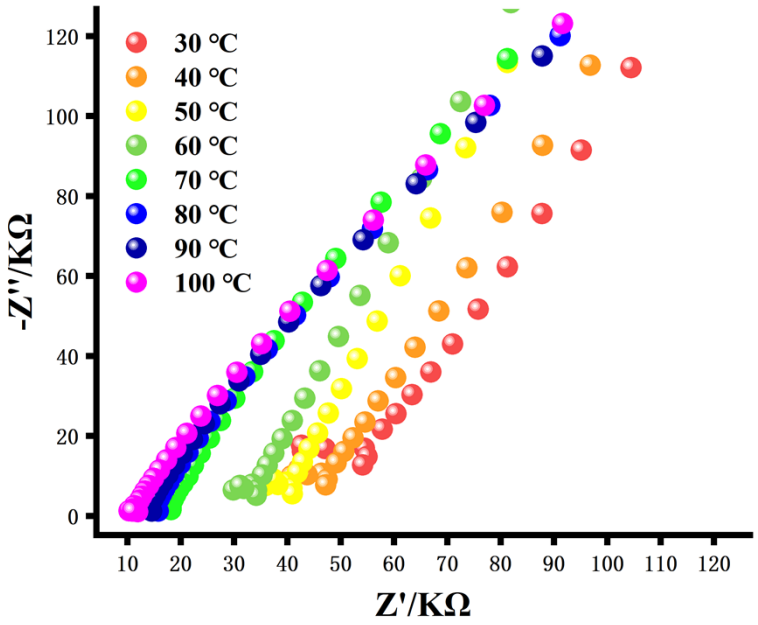
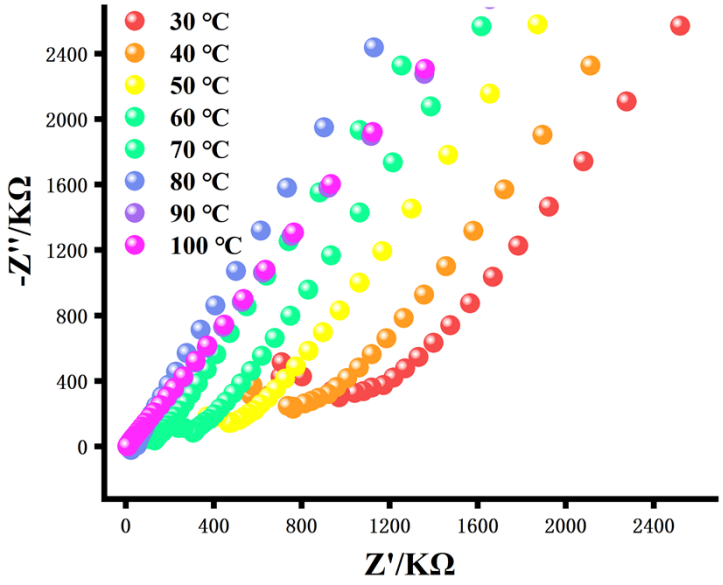


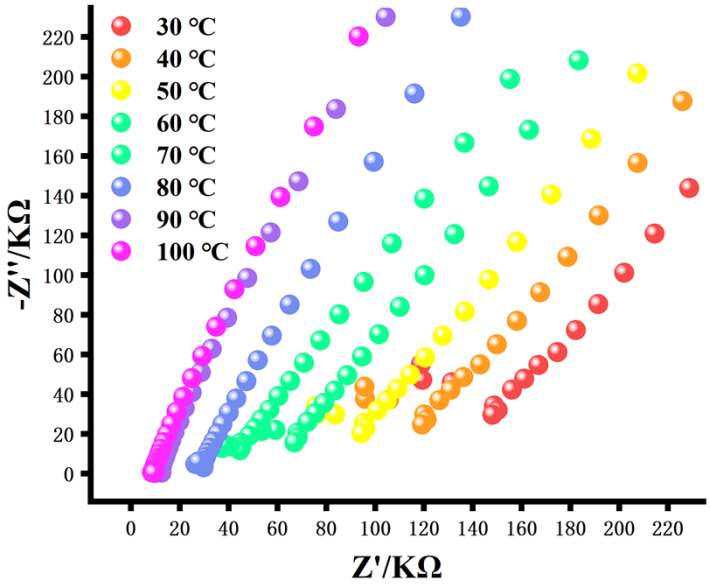
Figure S16. The PXRD patterns of HOF **1** before and after impedance measurement.


30 °C
40 °C
50 °C
60 °C
70 °C
80 °C
90 °C
100 °C
-Z''/KΩ
Z'/KΩ
0
20
40
60
80
100
120
10
20
30
40
50
60
70
80
90
100
110
120

(a)


30 °C
40 °C
50 °C
60 °C
70 °C
80 °C
90 °C
100 °C
-Z''/KΩ
Z'/KΩ
0
400
800
1200
1600
2000
2400

(b)



(c)

Figure S17. Impedance spectra of **CS/HOF-x** at 98% RH and 30-100 °C.(a) **CS/HOF-2** (b) **CS/HOF-6** (c) **CS/HOF-8**

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