Electronic Supplementary Information (ESI) for

Porosity regulation of metal-organic frameworks for high proton conductivity by rational ligand design: mono- versus disulfonyl-4,4′-biphenyldicarboxylic acid

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1. The FT-IR and ^{1}HNMR spectra of H_3L

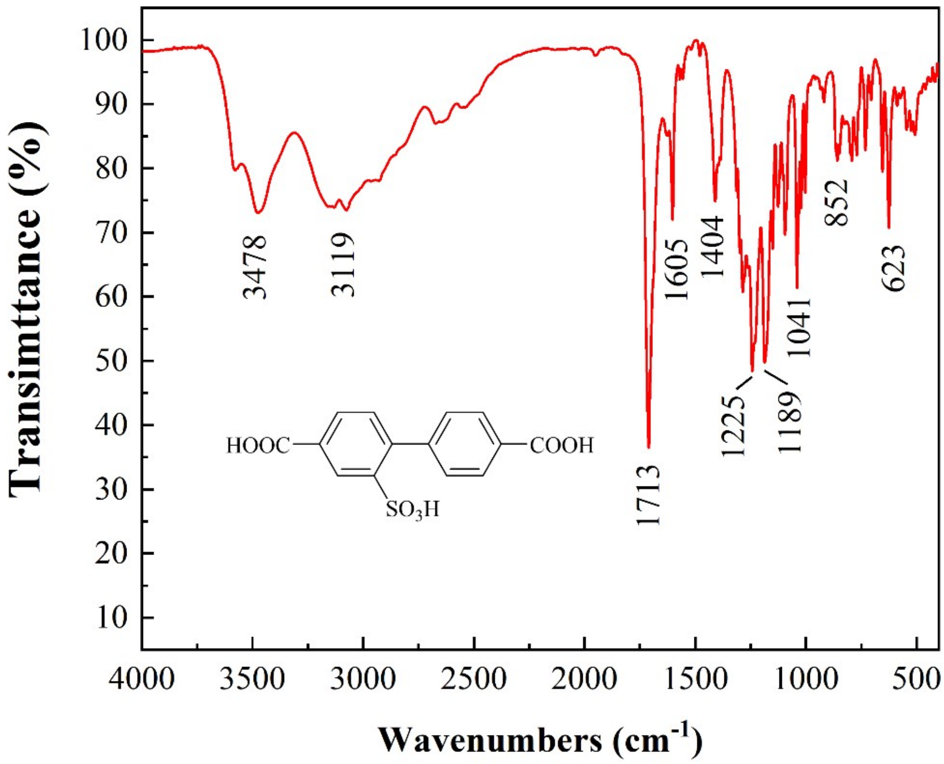

Fig. S1 FT-IR spectra of $\mathbf{H_3L}$.

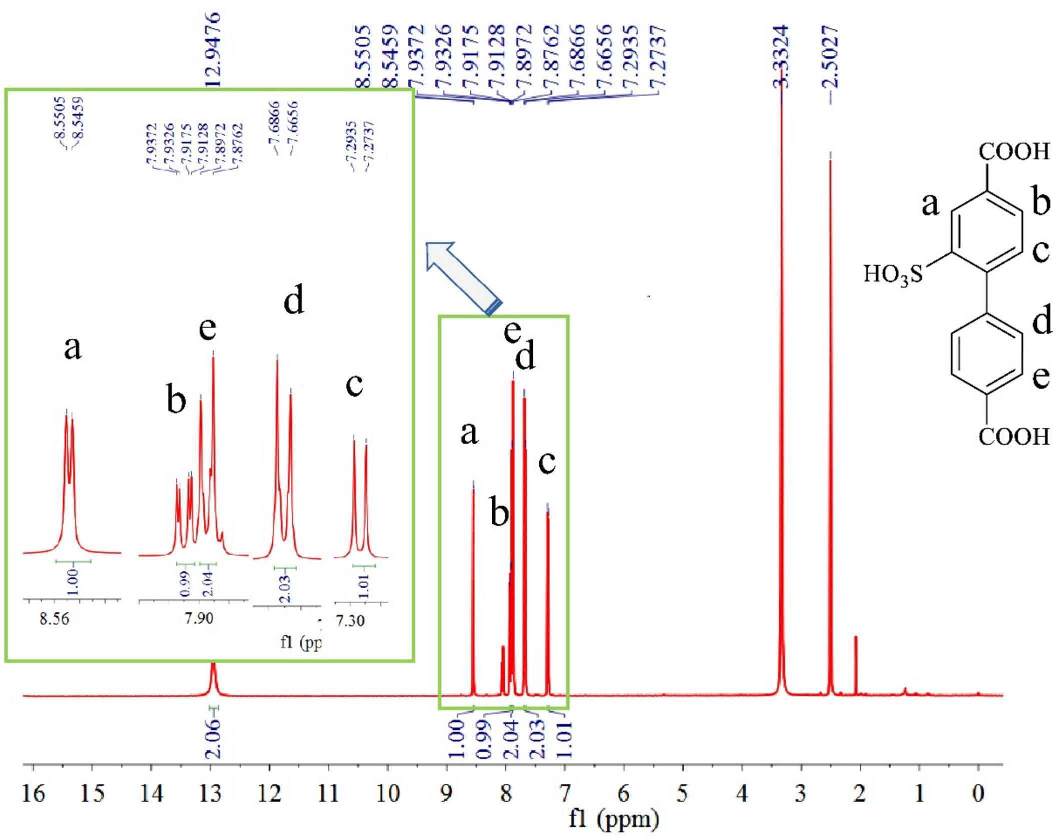

Fig. S2 ^{1}HNMR spectrum of $\mathbf{H_3L}$

2. Molecular structures of MOFs 1-3

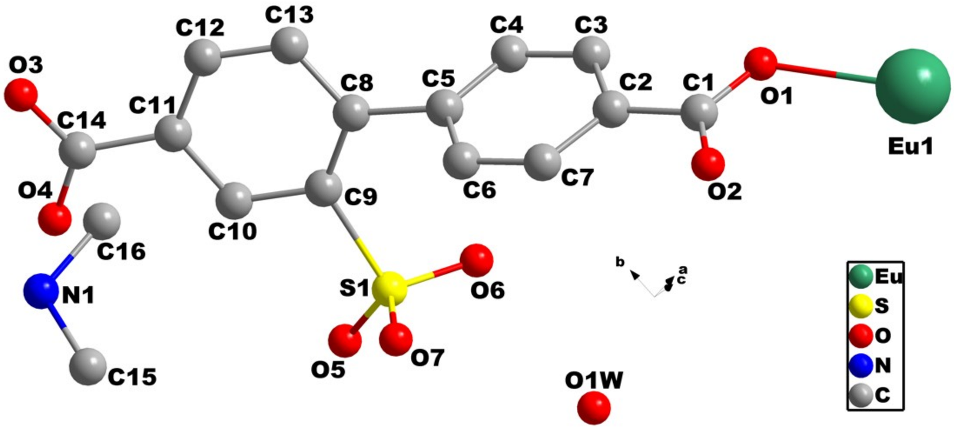

Fig. S3 Asymmetric unit of **1** (H and disordered atoms are omitted for clarity).

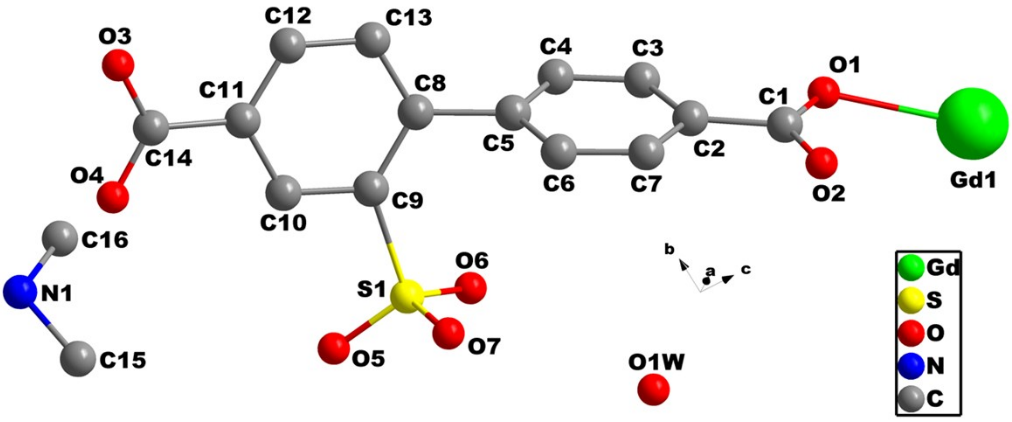

Fig. S4 Asymmetric unit of **2** (H and disordered atoms are omitted for clarity).

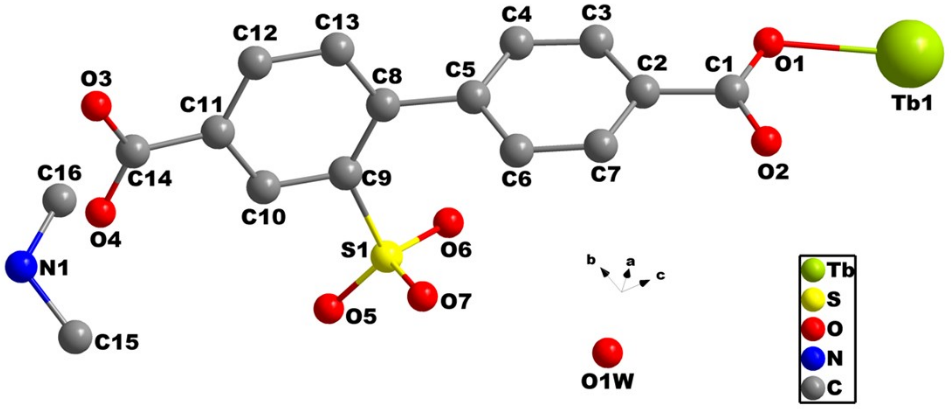

Fig. S5 Asymmetric unit of **3** (H and disordered atoms are omitted for clarity).

3. The FT-IR spectra of MOFs 1-3

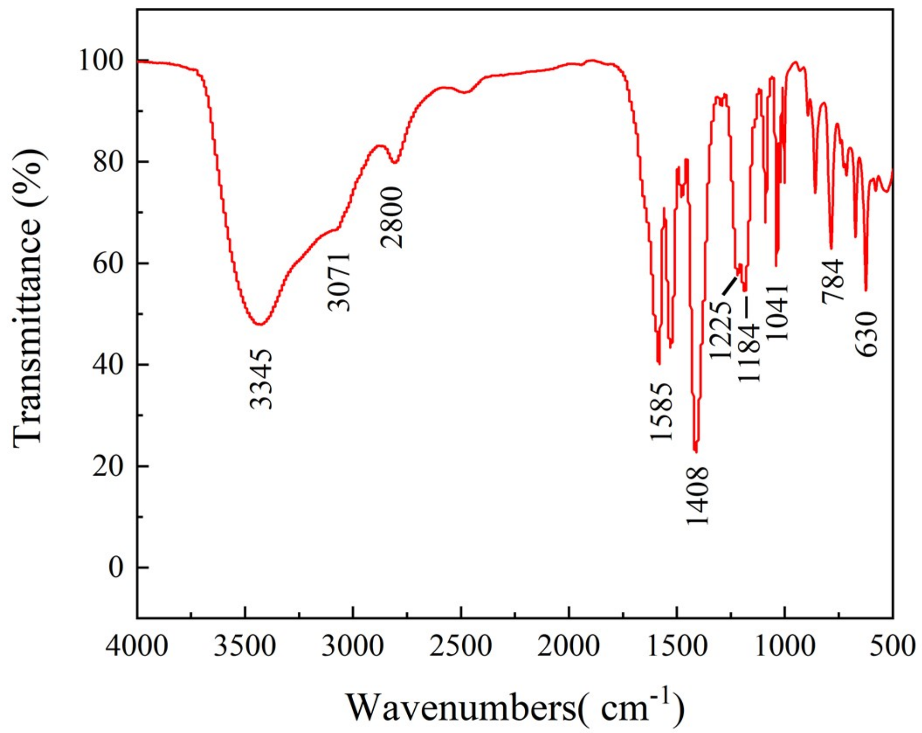

Fig. S6 FT-IR spectra of **1**.

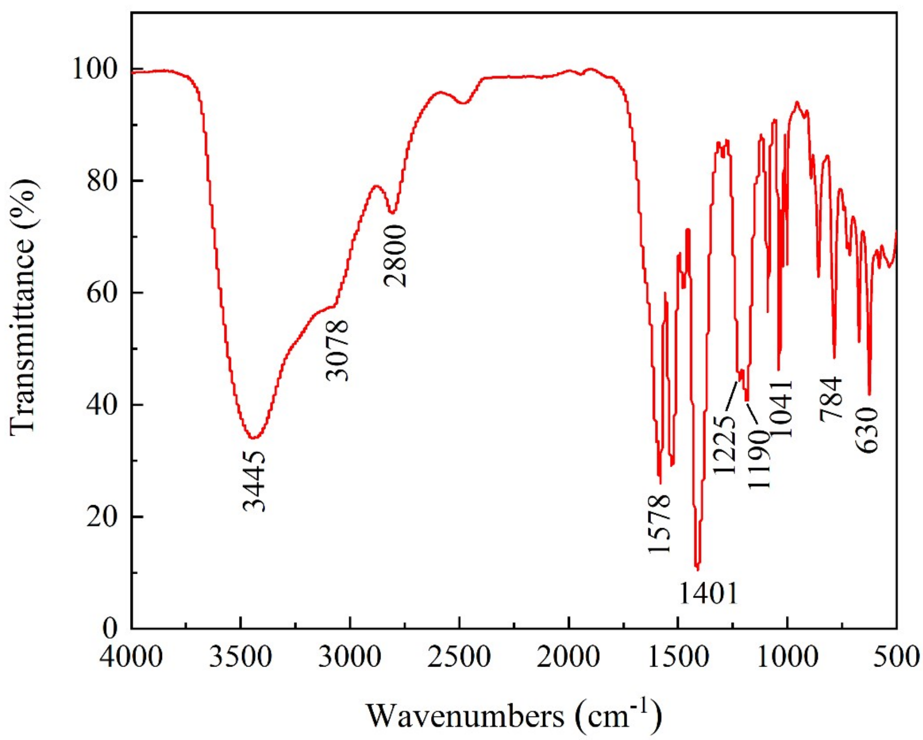

Fig. S7 FT-IR spectra of **2**.

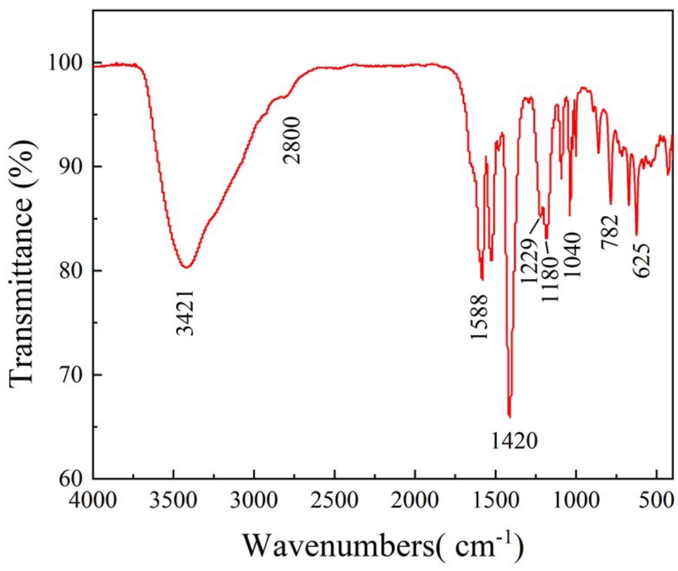

Fig. S8 FT-IR spectra of **3**.

4. The PXRD patterns of MOFs 1-3

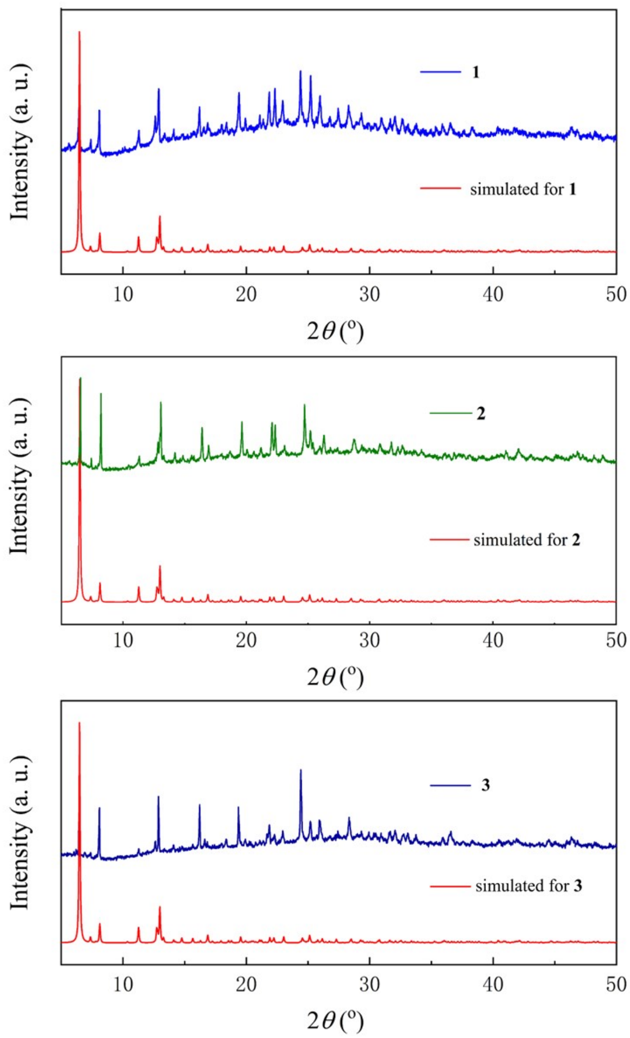

Fig. S9 Experimental and simulated powder X-ray diffraction patterns of MOFs **1**-**3**.

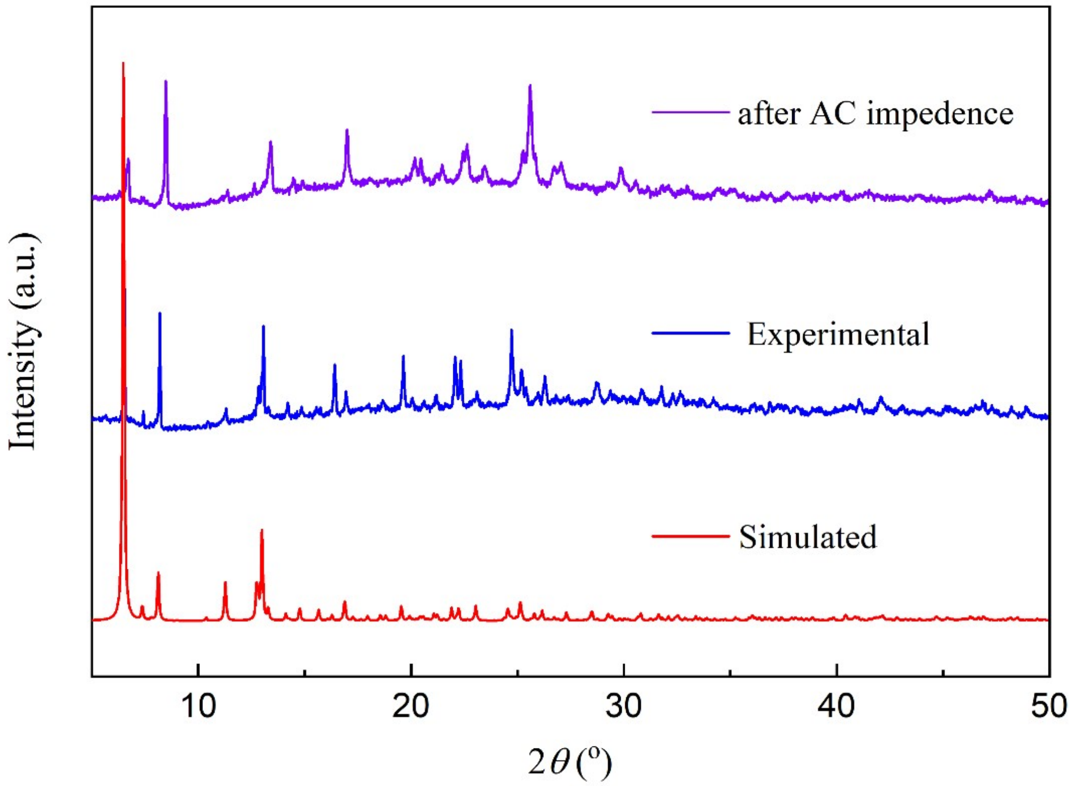

Fig. S10 Experimental and simulated PXRD patterns of **2** and after 72h AC impedance measurements.

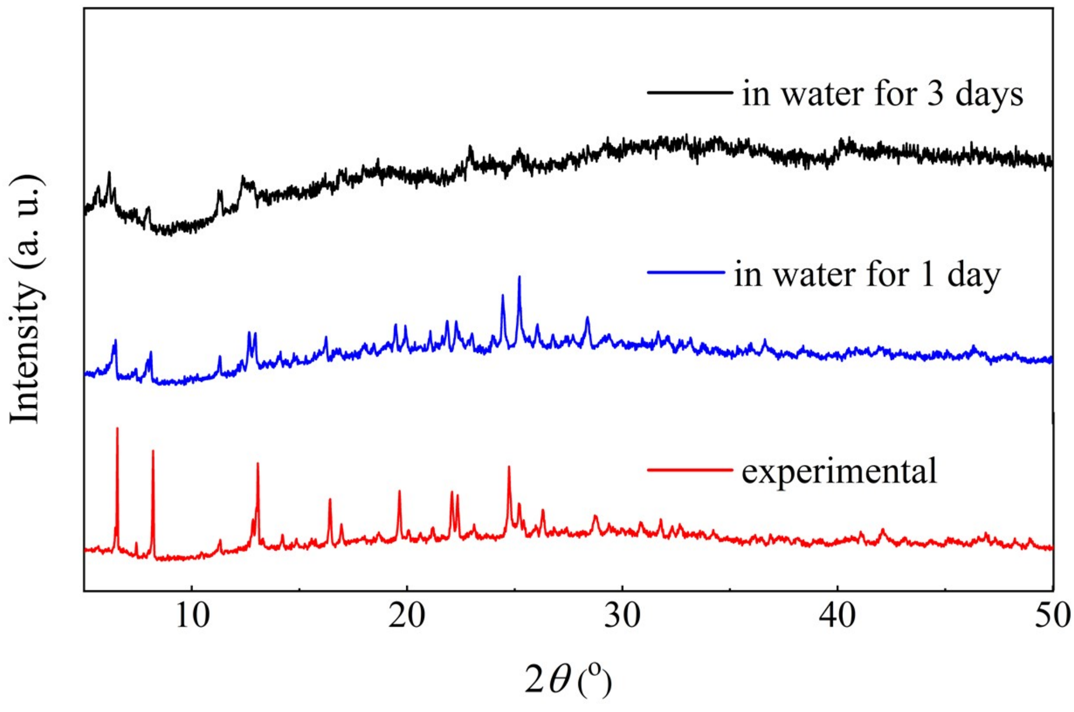

Fig. S11 Experimental PXRD patterns of **2** and after water immersion.

5. The thermogravimetric analysis of MOFs 1-3

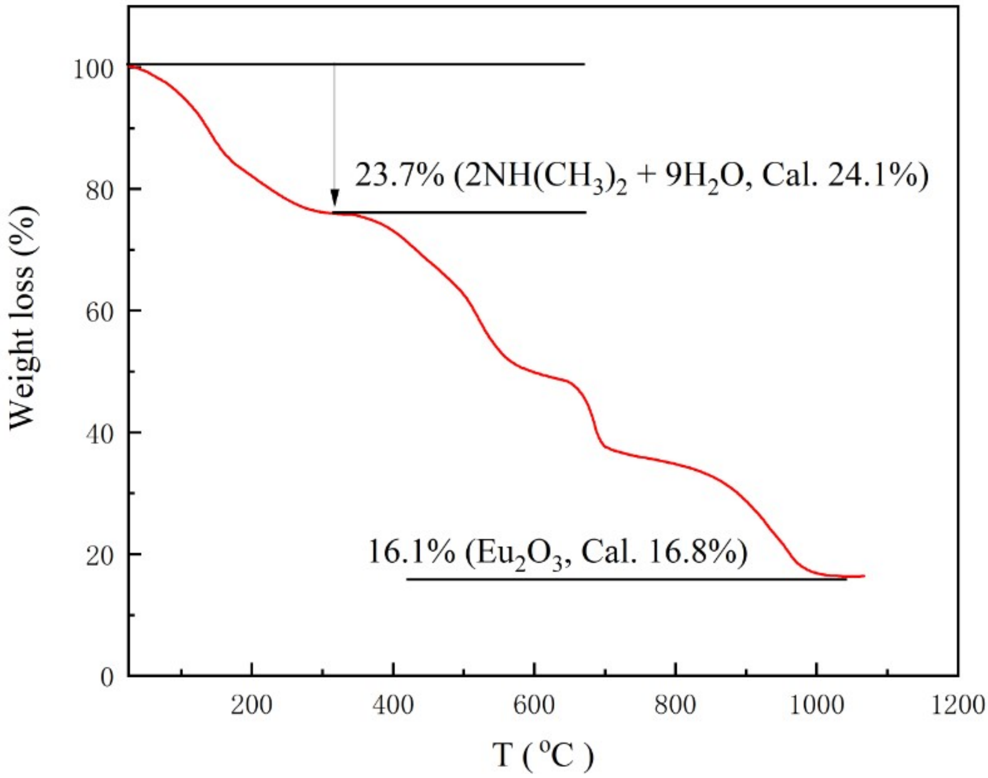

Fig. S12 TGA curve for **1**

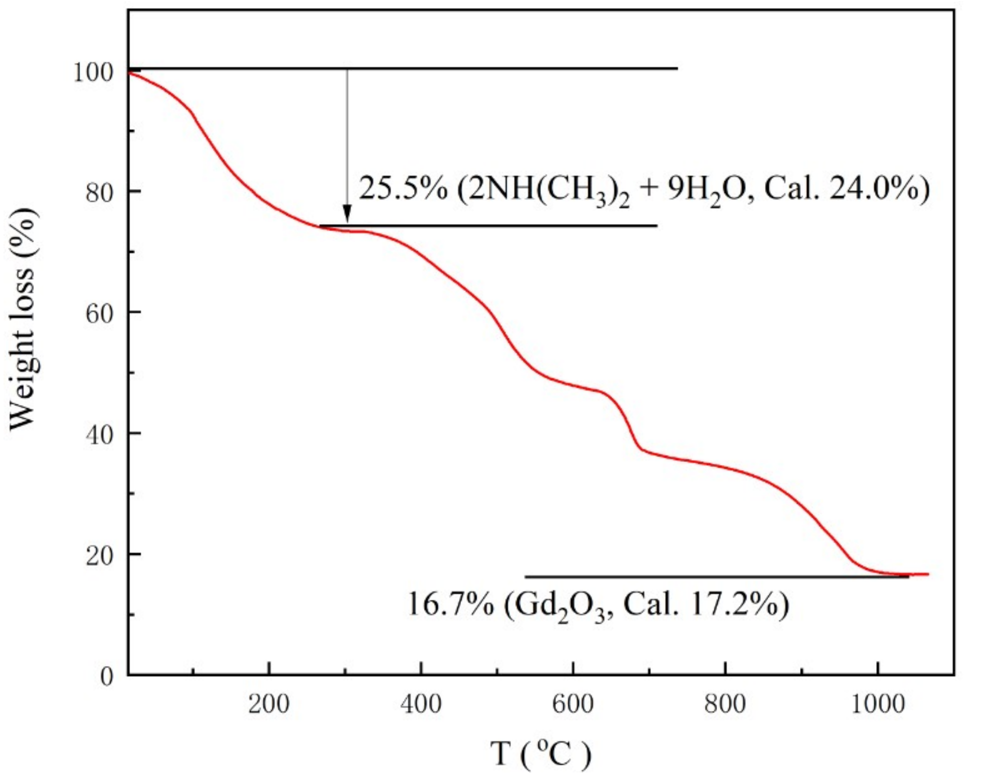

Fig. S13 TGA curve for **2**

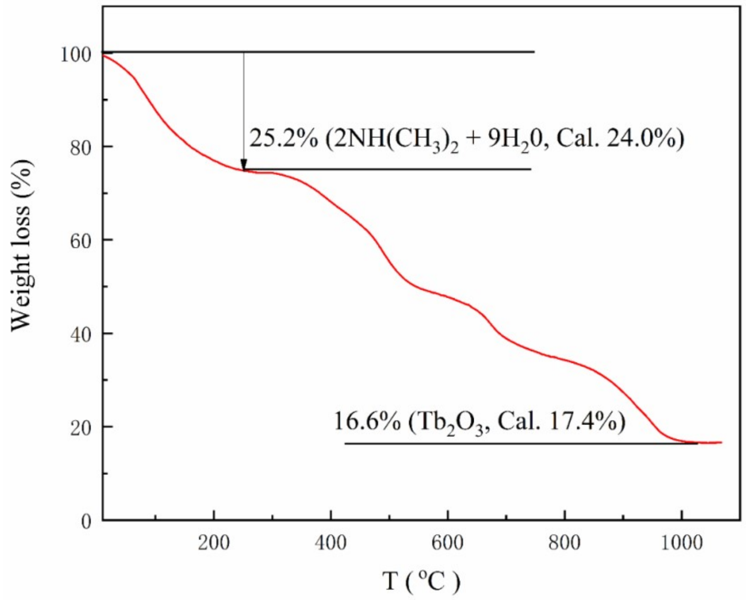

Fig. S14 TGA curve for **3**

6. Crystal structure determination

Table S1 Crystallographic data for **MOFs 1-3**

MOFs	**1**	**2**	**3**
Empirical formula	$C_{32}H_{49}EuN_2O_{23}S_2$	$C_{32}H_{49}GdN_2O_{23}S_2$	$C_{32}H_{49}TbN_2O_{23}S_2$
Formula weight	1045.83	1051.11	1052.79
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnnn*	*Pnnn*	*Pnnn*
a (Å)	14.1253(17)	14.1306(15)	14.1106(8)
b (Å)	17.038(2)	17.0415(18)	17.1352(9)
c (Å)	22.649(3)	22.636(2)	22.4486(12)
V (Å^3)	5450.9(12)	5450.9(10)	5427.8(5)
Z	4	4	4
D_c (g·cm^{-3})	1.096	1.103	1.109
μ (mm^{-1})	1.275	1.341	1.428
F (000)	1808.0	1812.0	1816.0
Crystal size (mm^3)	0.25×0.15×0.10	0.25×0.13×0.10	0.25×0.13×0.10
θ Range (°)	1.496-24.998	1.496-24.998	1.495-25.048
Reflections collected	36995	36891	36784
Independent reflections	4826 [R_{int} = 0.044]	4826 [R_{int} = 0.0268]	4825 [R_{int} = 0.0407]
Reflections observed [$I > 2\sigma(I)$]	3087	3331	3064
Data/restraints/parameters	4826/360/321	4826/216/323	4825/372/321
Goodness-of-fit on F^2	1.090	1.082	1.099
R_1/wR_2 [$I > 2\sigma(I)$]	0.0624/0.2249	0.0597/0.2134	0.0629/0.2261
R_1/wR_2 (all data)	0.0889/0.2503	0.0783/0.2381	0.0905/0.2502
Max., Min. $\Delta\rho$ (e·Å^{-3})	1.325, -0.906	2.156, -0.820	2.001, -0.866

Table S2 Selected bond lengths (Å) and angles (°) for **1-3**

		1	
Eu1–O1	2.414(5)	Eu1–O3^{i}	2.477(6)
Eu1–O2^{ii}	2.313(5)	Eu1–O4^{i}	2.487(5)
		2	
Gd1–O1	2.413(4)	Gd1–O3^{i}	2.468(5)
Gd1–O2^{ii}	2.311(4)	Gd1–O4^{i}	2.485(4)
		3	
Tb1–O1	2.373(5)	Tb1–O3^{i}	2.455(5)
Tb1–O2^{ii}	2.289(5)	Tb1–O4^{i}	2.458(5)
		1	
O2–Eu1–O2^{ii}	107.2(3)	O3^{i}–Eu1–O3^{iv}	95.0(3)
O2–Eu1–O1	80.70(18)	O2–Eu1–O4^{i}	156.86(18)
O2^{ii}–Eu1–O1	81.03(19)	O2^{ii}–Eu1–O4^{i}	78.71(18)
O2–Eu1–O1^{iii}	81.03(19)	O1–Eu1–O4^{i}	78.14(17)
O2^{ii}–Eu1–O1^{iii}	80.70(18)	O1^{iii}–Eu1–O4^{i}	122.10(17)
O1–Eu1–O1^{iii}	149.0(2)	O3^{i}–Eu1–O4^{i}	52.45(17)
O2–Eu1–O3^{i}	147.94(18)	O3^{iv}–Eu1–O4^{i}	77.61(18)
O2^{ii}–Eu1–O3^{i}	87.42(19)	O2–Eu1–O4^{iv}	78.71(18)
O1–Eu1–O3^{i}	130.58(18)	O2^{ii}–Eu1–O4^{iv}	156.86(18)
O1^{iii}–Eu1–O3^{i}	73.20(19)	O1–Eu1–O4^{iv}	122.10(17)
O2–Eu1–O3^{iv}	87.42(19)	O1^{iii}–Eu1–O4^{iv}	78.14(17)
O2^{ii}–Eu1–O3^{iv}	147.94(18)	O3^{i}–Eu1–O4^{iv}	77.61(18)
O1–Eu1–O3^{iv}	73.20(19)	O3^{iv}–Eu1–O4^{iv}	52.45(17)
O1^{iii}–Eu1–O3^{iv}	130.58(18)	O4^{i}–Eu1–O4^{iv}	104.9(2)
		2	
O2–Gd1–O2^{ii}	106.7(2)	O3^{i}–Gd1–O3^{iv}	95.2(3)
O2–Gd1–O1	81.13(16)	O2–Gd1–O4^{i}	156.78(15)
O2^{ii}–Gd1–O1	81.13(16)	O2^{ii}–Gd1–O4^{i}	79.03(15)
O2–Gd1–O1^{iii}	81.13(16)	O1–Gd1–O4^{i}	78.14(14)
O2^{ii}–Gd1–O1^{iii}	80.57(15)	O1^{iii}–Gd1–O4^{i}	122.08(14)
O1–Gd1–O1^{iii}	149.1(2)	O3^{i}–Gd1–O4^{i}	52.60(14)
O2–Gd1–O3^{i}	147.97(14)	O3^{iv}–Gd1–O4^{i}	77.49(15)
O2^{ii}–Gd1–O3^{i}	87.54(16)	O2–Gd1–O4^{iv}	79.03(15)
O1–Gd1–O3^{i}	130.72(15)	O2^{ii}–Gd1–O4^{iv}	156.78(15
O1^{iii}–Gd1–O3^{i}	72.98(16)	O1–Gd1–O4^{iv}	78.14(14)
O2–Gd1–O3^{iv}	87.54(16)	O1^{iii}–Gd1–O4^{iv}	122.08(14
O2^{ii}–Gd1–O3^{iv}	147.97(15)	O3^{i}–Gd1–O4^{iv}	77.49(15)
O1–Gd1–O3^{iv}	72.98(16)	O3^{iv}–Gd1–O4^{iv}	52.60(14)
O1^{iii}–Gd1–O3^{iv}	130.72(14)	O4^{i}–Gd1–O4^{iv}	104.7(2)
		3	
O2–Tb1–O2^{ii}	107.2(3)	O3^{i}–Tb1–O3^{iv}	94.6(3)
O2–Tb1–O1	80.12(19)	O2–Tb1–O4^{i}	156.19(18)

O2ⁱⁱ–Tb1–O1	80.90(19)	O2ⁱⁱ–Tb1–O4ⁱ	78.49(18)
O2–Tb1–O1ⁱⁱⁱ	80.9(2)	O1–Tb1–O4ⁱ	77.99(18)
O2ⁱⁱ–Tb1–O1ⁱⁱⁱ	80.12(19)	O1ⁱⁱⁱ–Tb1–O4ⁱ	122.88(18)
O1–Tb1–O1ⁱⁱⁱ	147.7(3)	O3ⁱ–Tb1–O4ⁱ	52.82(18)
O2–Tb1–O3ⁱ	148.32(18)	O3ⁱᵛ–Tb1–O4ⁱ	77.71(18)
O2ⁱⁱ–Tb1–O3ⁱ	87.36(19)	O2–Tb1–O4ⁱᵛ	78.49(18)
O1–Tb1–O3ⁱ	130.79(18)	O2ⁱⁱ–Tb1–O4ⁱᵛ	156.19(18)
O1ⁱⁱⁱ–Tb1–O3ⁱ	73.94(19)	O1–Tb1–O4ⁱᵛ	122.88(18)
O2–Tb1–O3ⁱᵛ	87.36(19)	O1ⁱⁱⁱ–Tb1–O4ⁱᵛ	77.99(18)
O2ⁱⁱ–Tb1–O3ⁱᵛ	148.32(18)	O3ⁱ–Tb1–O4ⁱᵛ	77.71(18)
O1–Tb1–O3ⁱᵛ	73.9(2)	O3ⁱᵛ–Tb1–O4ⁱᵛ	52.82(18)
O1ⁱⁱⁱ–Tb1–O3ⁱᵛ	130.79(18)	O4ⁱ–Tb1–O4ⁱᵛ	105.9(3)

Symmetry codes: (i) 1/2+*x*, 1−*y*, 1/2+*z*; (ii) 1/2−*x*, *y*, 3/2−*z*; (iii) *x*, 1/2−*y*, 3/2−*z*; (iv) 1/2+*x*, 1/2−*y*, 1−*z*.

Table S3 Hydrogen-bonding geometry (Å, °) for **2**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
N1–H1A···O4	0.89	2.26	2.893(10)	128
N1–H1B···O5Aⁱ	0.89	1.85	2.604(3)	141
O1W–H1WA···O7	0.85	2.53	3.352(5)	163
O1W–H1WB···O6ⁱⁱ	0.85	2.92	3.751(5)	169
O1W–H1WC···O7Aⁱⁱⁱ	0.85	2.96	3.734(6)	154
O1WA–H1WD···O6	0.85	2.19	3.009(2)	161
O1WA–H1WE···O5ⁱ	0.85	2.50	3.123(4)	131
O1WA–H1WF···O1WAⁱᵛ	0.85	2.39	3.230(7)	170
C15–H15C···O4	0.96	2.48	3.004(2)	115
C16–H16C···π^{i}	0.96	2.67	3.598(3)	162
C6–H6···π^{v}	0.93	3.24	3.943(2)	134

Symmetry codes: (i) 1/2−*x*, *y*, 1/2−*z*; (ii) 1/2−*x*, 1/2−*y*, *z*; (iii) *x*−1/2, *y*−1/2, 1−*z*; (iv) *x*, 1/2−*y*, 1/2−*z*; (v) −*x*, 1−*y*, 1−*z*.

7. Proton conductivity measurement

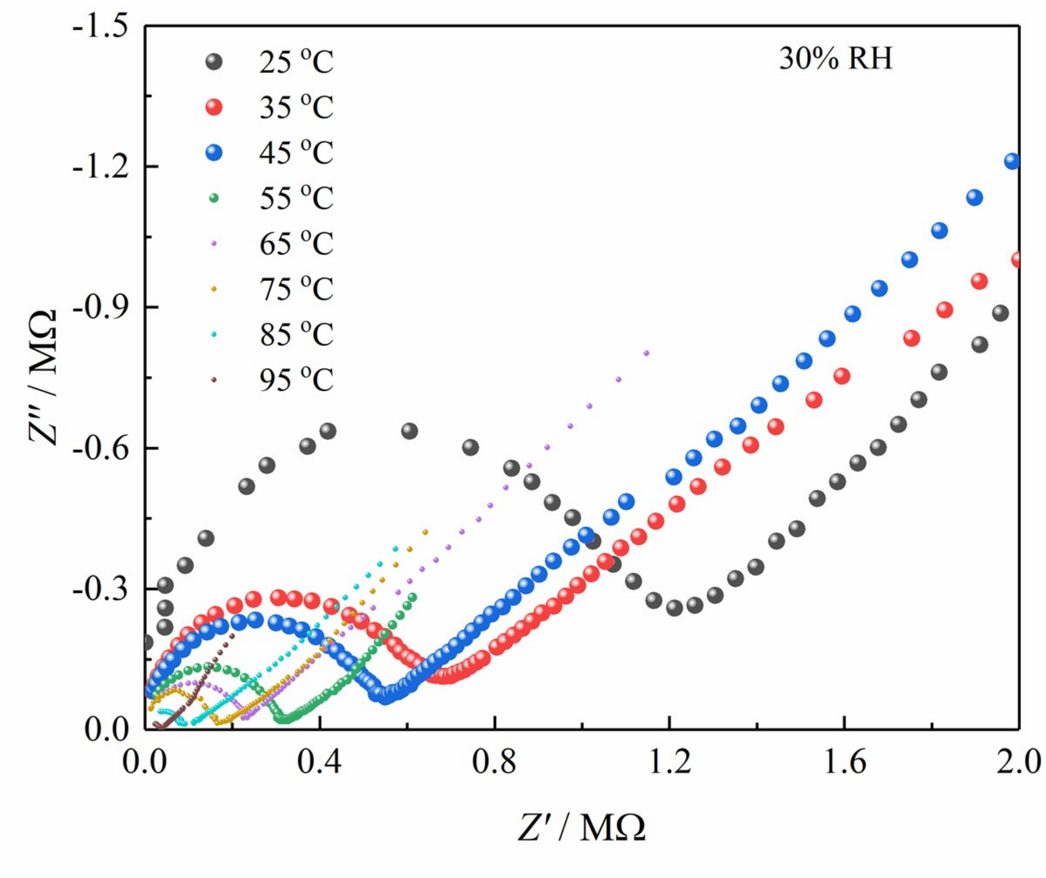

Fig. S15 Temperature-dependent Nyquist plots of **2** under 30% RH

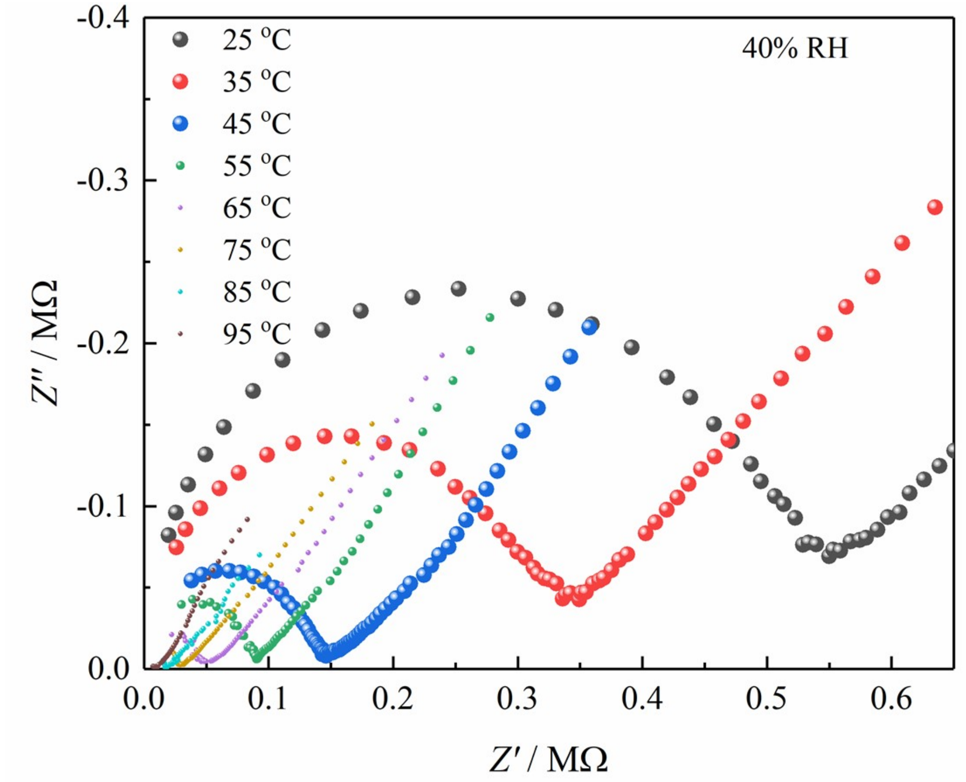

Fig. S16 Temperature-dependent Nyquist plots of **2** under 40% RH

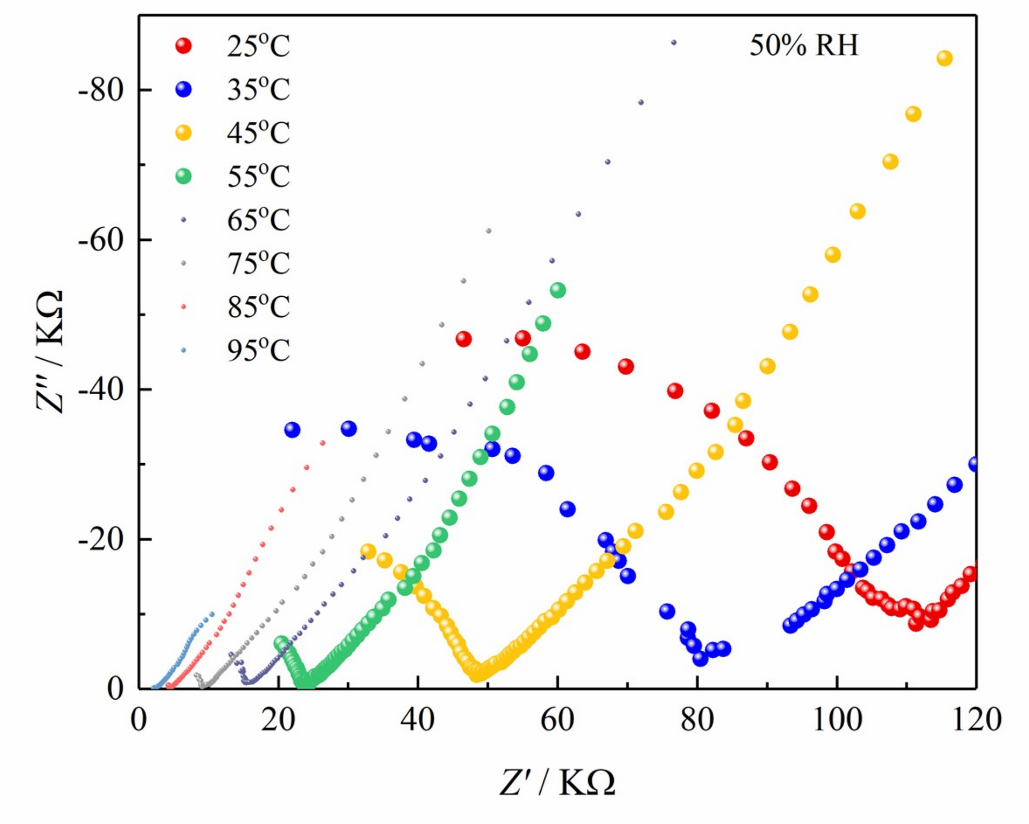

Fig. S17 Temperature-dependent Nyquist plots of **2** under 50% RH

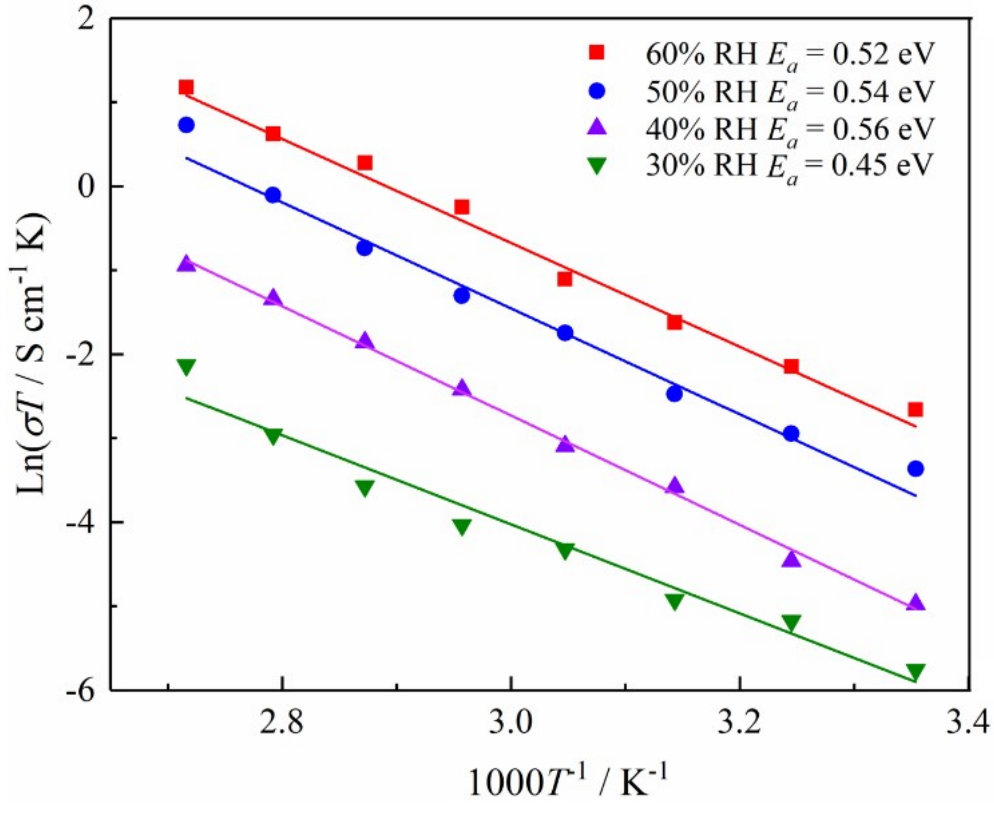

Fig. S18 Arrhenius plot of **2** at 30-60% RH

Table S4 Proton conductivities for **2** at various RH and temperature

T (°C)	σ (S cm^{-1})			
	30% RH	40% RH	50% RH	60% RH
25	1.06×10^{-5}	2.32×10^{-5}	1.16×10^{-4}	2.35×10^{-4}
35	1.84×10^{-5}	3.75×10^{-5}	1.70×10^{-4}	3.80×10^{-4}
45	2.28×10^{-5}	8.76×10^{-5}	2.65×10^{-4}	6.20×10^{-4}
55	4.04×10^{-5}	1.38×10^{-4}	5.32×10^{-4}	1.01×10^{-3}
65	5.23×10^{-5}	2.63×10^{-4}	8.04×10^{-4}	2.31×10^{-3}
75	8.06×10^{-5}	4.50×10^{-4}	1.38×10^{-3}	3.80×10^{-3}
85	1.45×10^{-4}	7.28×10^{-4}	2.51×10^{-3}	5.22×10^{-3}
95	3.22×10^{-4}	1.06×10^{-3}	5.62×10^{-3}	8.83×10^{-3}