Supporting Information

Assembly of Three Coordination Polymers Based on a Sulfonic-carboxylic Ligand Showing High Proton Conductivity

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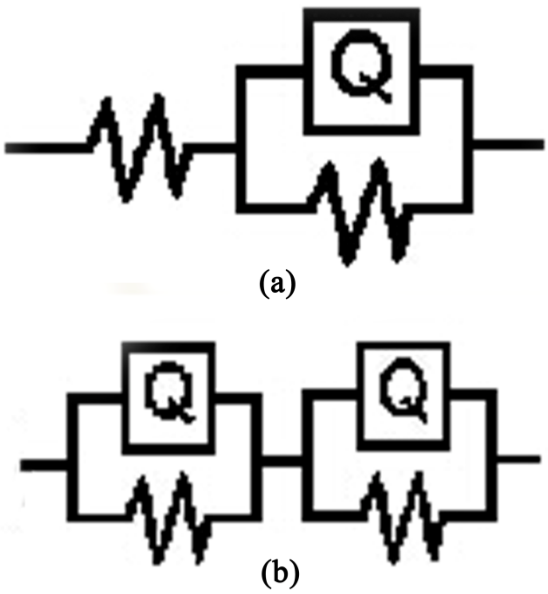
Table S1. Crystal Data and Structure Refinement for Compounds **1−3**

Compound	**1**	**2**	**3**
formula	$CuC_{24}H_{34}N_4O_{14}S_2$	$Ca_2C_{27}H_{37}N_5O_{15}S_2$	$CdC_{13}H_{16}N_2O_7S$
fw	730.21	815.90	456.75
T/K	293(2)	296 (2)	296 (2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	monmclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$C2/c$	P_{nnm}
a (Å)	8.6325(9)	14.4784(15)	13.3226(4)
b (Å)	12.8807(14)	13.8157(15)	16.3848(5)
c (Å)	14.7075(16)	19.3044(19)	6.9437(2)
α (deg)	90	90	90
β (deg)	93.760(2)	104.539(2)	90
γ (deg)	90	90	90
V/Å^3	1631.8(3)	3737.8(7)	1515.73(8)
Z	2	4	4
D_{calcd}.(g·cm^{-3})	1.486	1.450	2.001
F(000)	758	1704	912
$2\theta_{max}$ (°)	49.34	50.54	52.18
GOF	1.06	1.039	1.110
R_1 (I > 2σ(I))[a]	0.0520	0.0528	0.0326
wR_2[b](all data)	0.1481	0.1259	0.1060

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)/\Sigma|F_o|^2]^{1/2}$.

There are four principle elements that contribute to the impedance behavior of a material. Among the principle elements, three are resistors (R), capacitors (C) and inductors (L). The constant phase element (CPE) represented by Q, is the fourth element that can contribute to the overall impedance of a system. The elements R, C, L, and Q can be used to design an equivalent circuit model to represent the impedance behavior of a Nyquist plot. For different Nyquist plots, the fundamental rule of the equivalent circuits is that the deviation of the values for R, C, L, and Q should be less than 10% on the condition of without deviating the basic principles. Thus, in this work, two equivalent circuits were employed to calculate conductivity values for three compounds. The Nyquist plots for compound **1** uses the $R_i(R_bQ_b)$ equivalent circuit, while compound **2** uses the $(R_bQ_b)(R_{gb}Q_{gb})$ equivalent circuit. Compound 3 uses (R_bQ_b) equivalent circuit at 328 K, 338K, and 348K, $(R_bQ_b)(R_{gb}Q_{gb})$ equivalent circuit at 358 K and 368 K.(R_i is the inherent impedance of the circuit, R_b is the resistance of proton transfer in the bulk phase and Q is contributions to account for the depressed, versus perfect, semicircle due to non-ideal capacitance).



Scheme S1: (a) $R_i(R_bQ_b)$ equivalent circuit, (b) $(R_bQ_b)(R_{gb}Q_{gb})$ equivalent circuit.

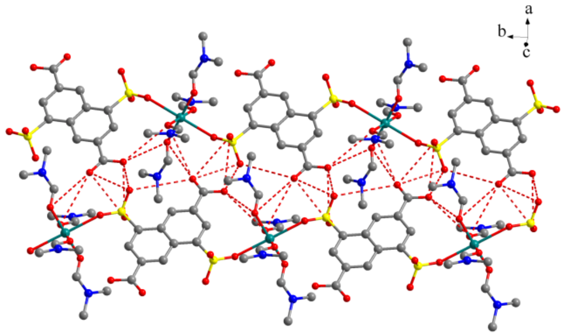


Fig. S1 Hydrogen bonds (red dashed lines) among free carboxylic groups, sulfonic groups and DMF molecules in compound **1**

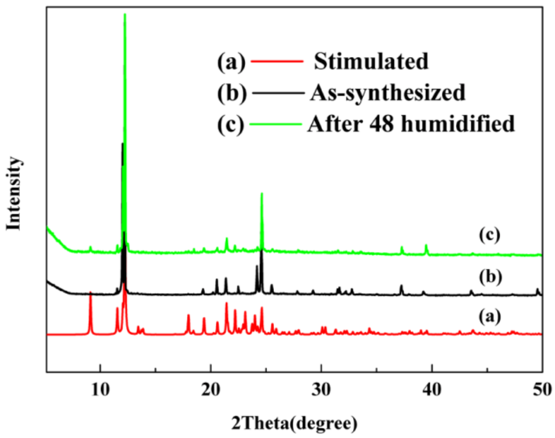


Fig. S2 Powder X-ray diffraction (PXRD) of compound **1**: the humidified samples (humidified for 48 hours, 95% RH), as-synthesized and simulated ones.

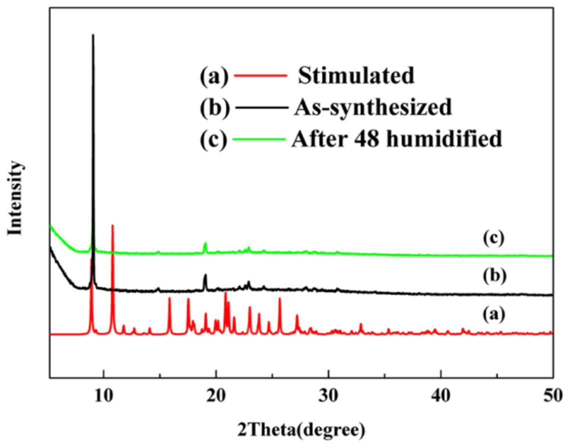


Fig. S3 Powder X-ray diffraction (PXRD) of compound **2**: the humidified samples (humidified for 48 hours, 95% RH), as-synthesized and simulated ones.

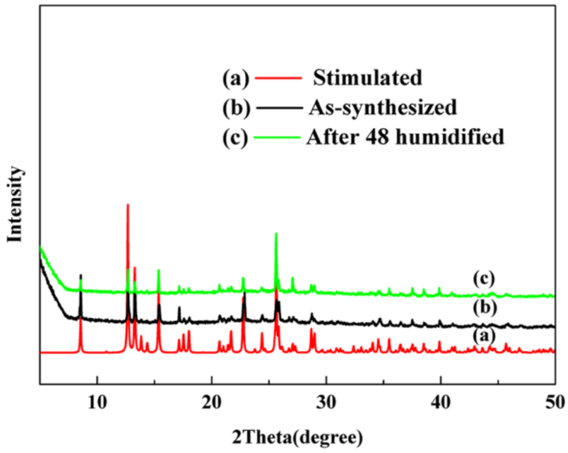


Fig. S4 Powder X-ray diffraction (PXRD) of compound **3**: the humidified samples (humidified for 48 hours, 95% RH), as-synthesized and simulated ones.

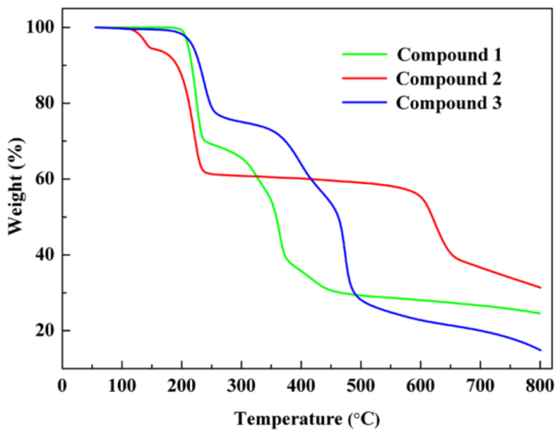


Fig. S5 TGA curve of compounds **1-3**

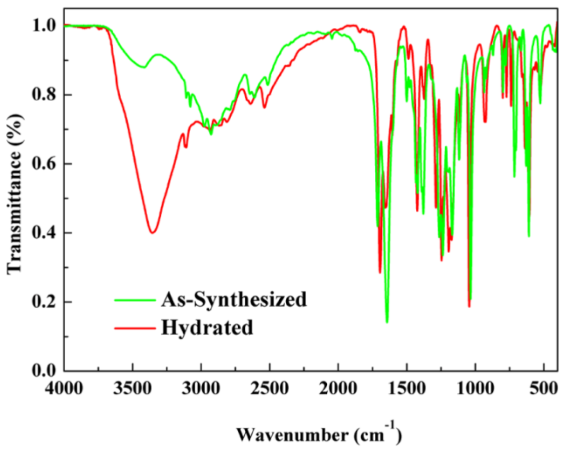


Fig. S6 Comparison of IR spectra of as-synthesized compound **1** with humidified one showing structural retention with inclusion of water molecules.

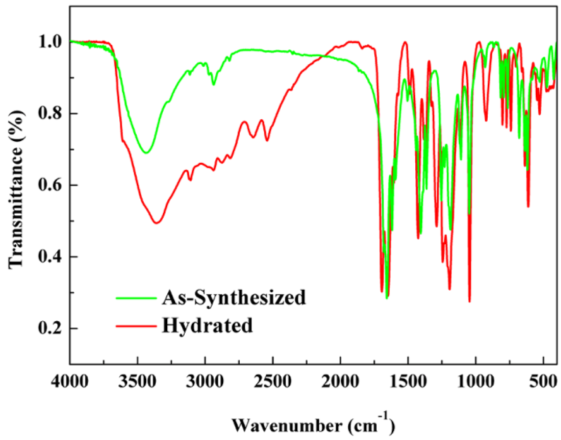


Fig. S7 Comparison of IR spectra of as-synthesized compound **2** with humidified one showing structural retention with inclusion of water molecules.

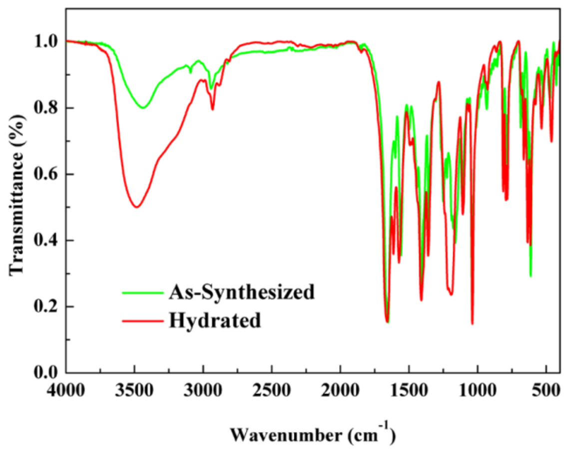


Fig. S8 Comparison of IR spectra of as-synthesized compound **3** with humidified one showing structural retention with inclusion of water molecules

Proton conductivity of compound 1

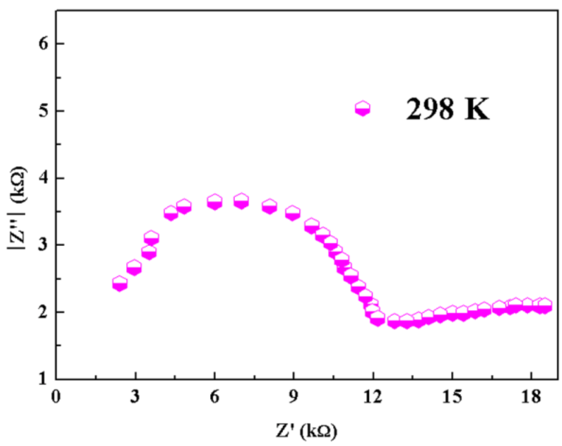


Fig. S9 Nyquist plot of compound **1** at 298 K under 95% RH.

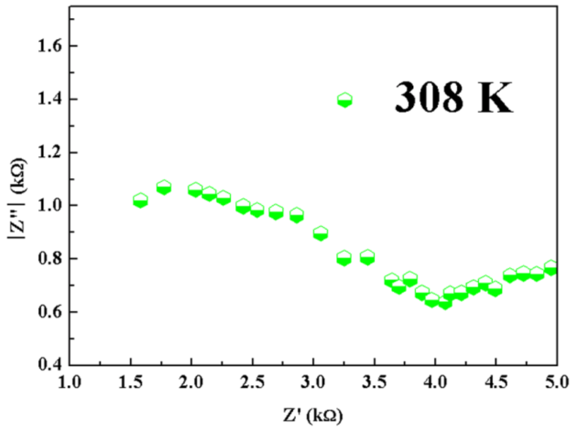


Fig. S10 Nyquist plot of compound **1** at 308 K under 95% RH.

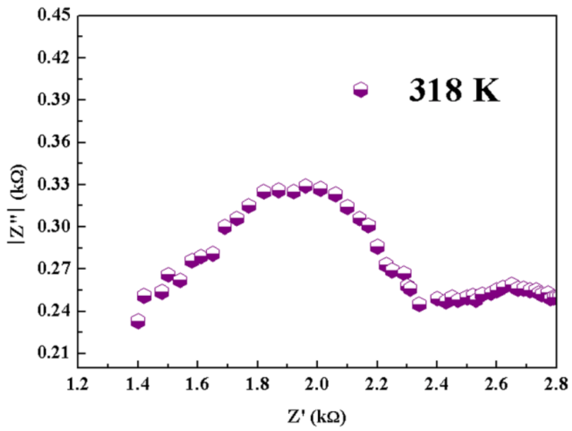


Fig. S11 Nyquist plot of compound **1** at 318 K under 95% RH.

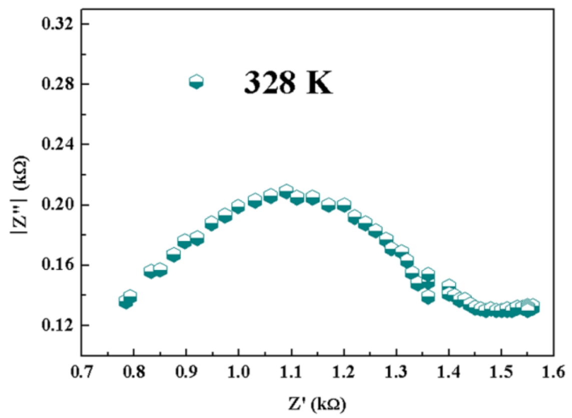


Fig. S12 Nyquist plot of compound **1** at 328 K under 95% RH.

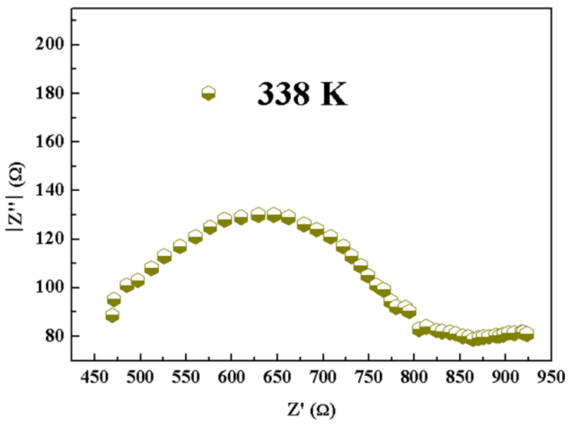


Fig. S13 Nyquist plot of compound **1** at 338 K under 95% RH.

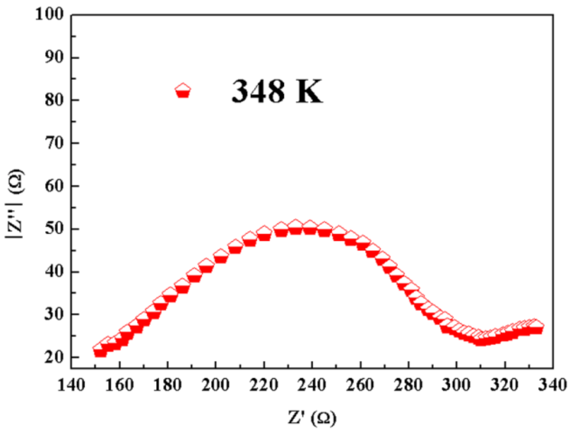


Fig. S14 Nyquist plot of compound **1** at 348 K under 95% RH.

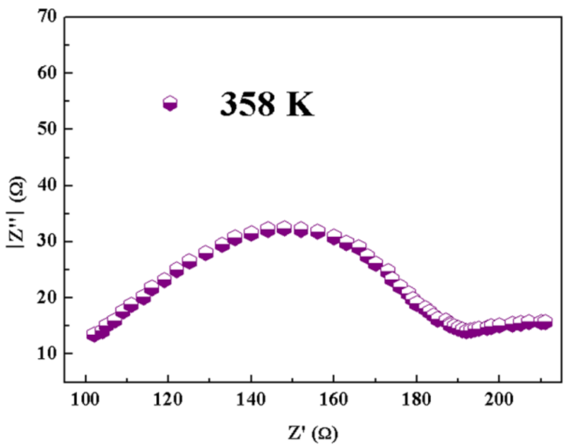


Fig. S15 Nyquist plot of compound **1** at 358 K under 95% RH.

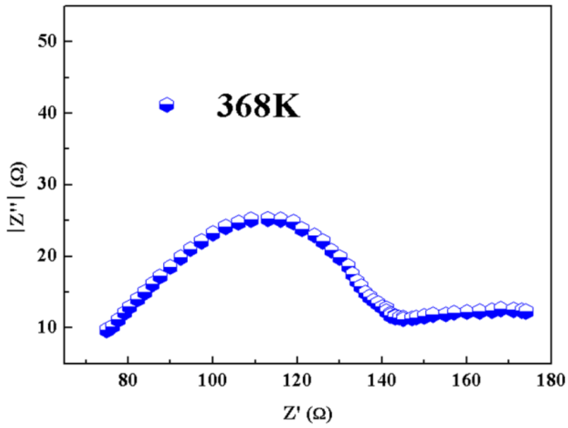


Fig. S16 Nyquist plot of compound **1** at 368 K under 95% RH.

Proton conductivity of compound 2

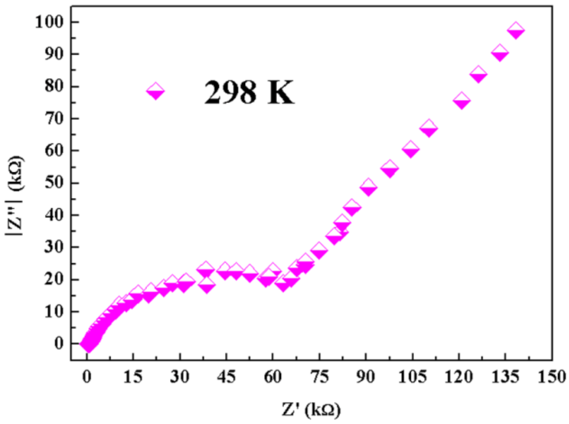


Fig. S17 Nyquist plot of compound **2** at 298 K under 95% RH.

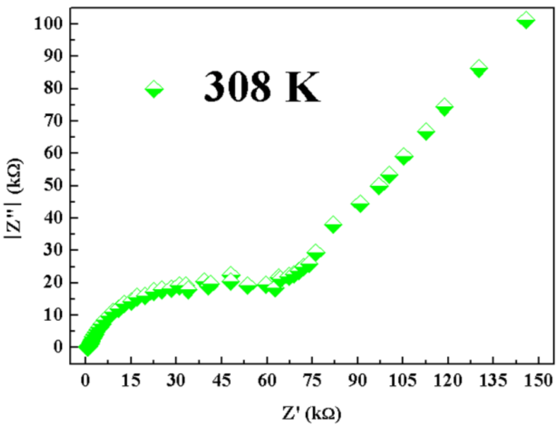


Fig. S18 Nyquist plot of compound **2** at 308 K under 95% RH.

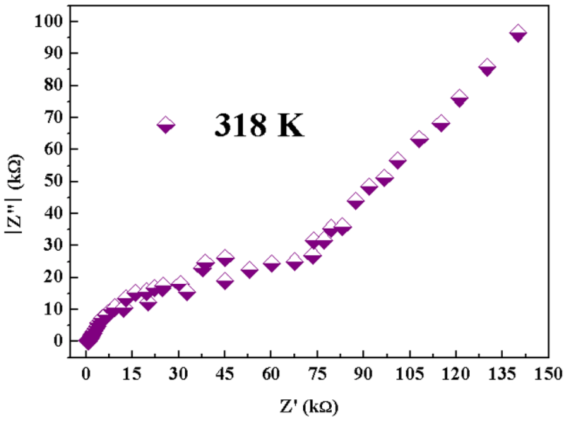


Fig. S19 Nyquist plot of compound **2** at 318 K under 95% RH.

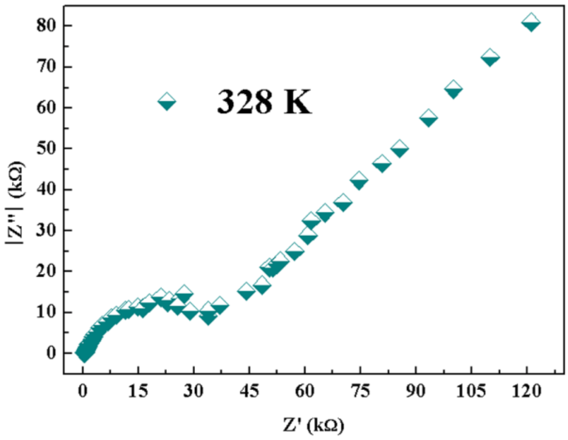


Fig. S20 Nyquist plot of compound **2** at 328 K under 95% RH.

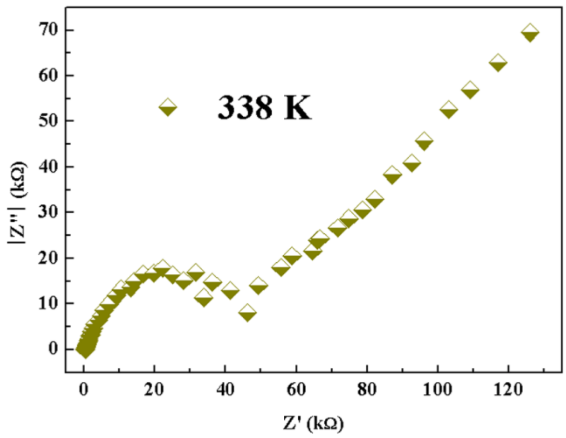


Fig. S21 Nyquist plot of compound **2** at 338 K under 95% RH.

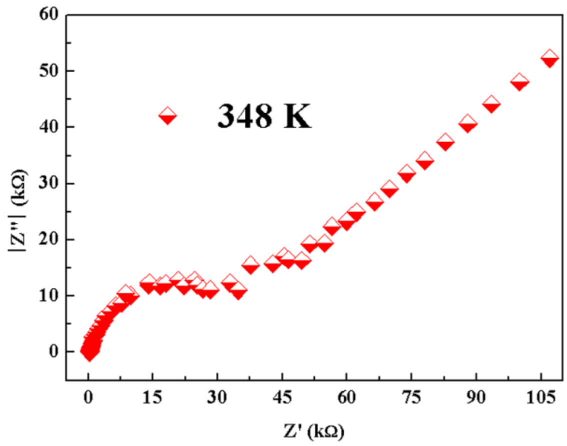


Fig. S22 Nyquist plot of compound **2** at 348 K under 95% RH.

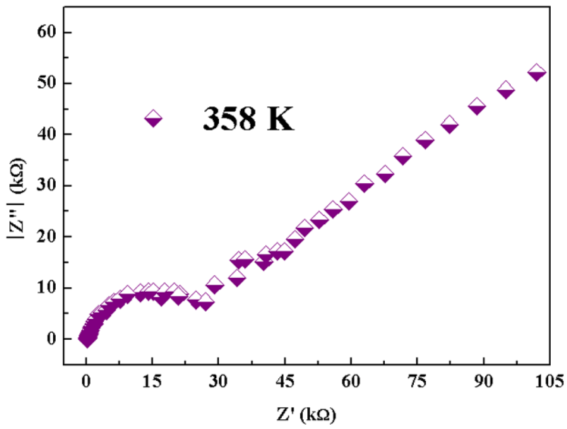


Fig. S23 Nyquist plot of compound **2** at 358 K under 95% RH.

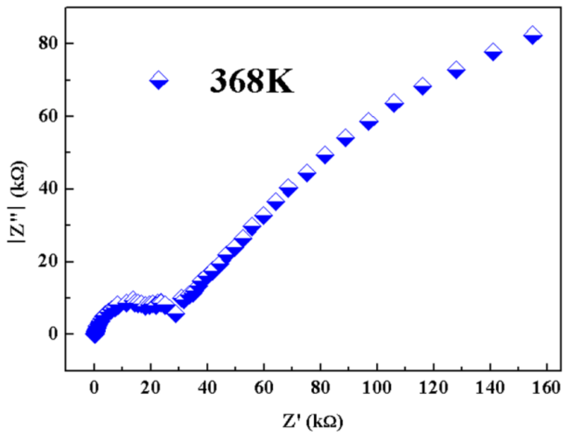


Fig. S24 Nyquist plot of compound **2** at 368 K under 95% RH.

Proton conductivity of compound 3

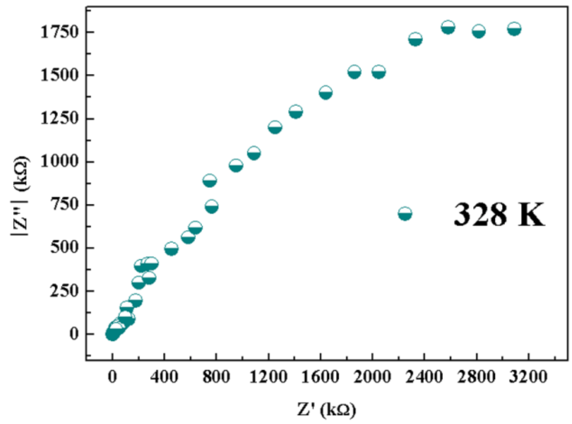


Fig. S25 Nyquist plot of compound **3** at 328 K under 95% RH.

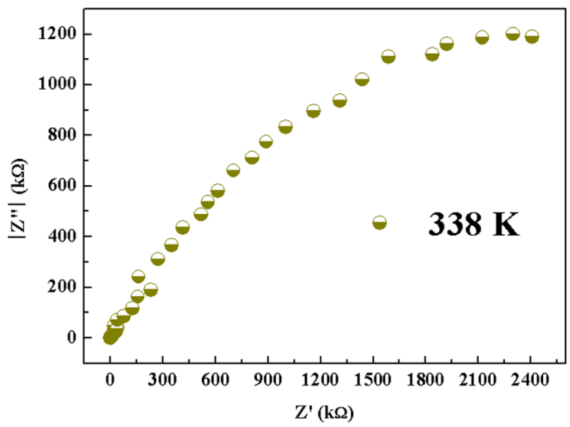


Fig. S26 Nyquist plot of compound **3** at 338 K under 95% RH.

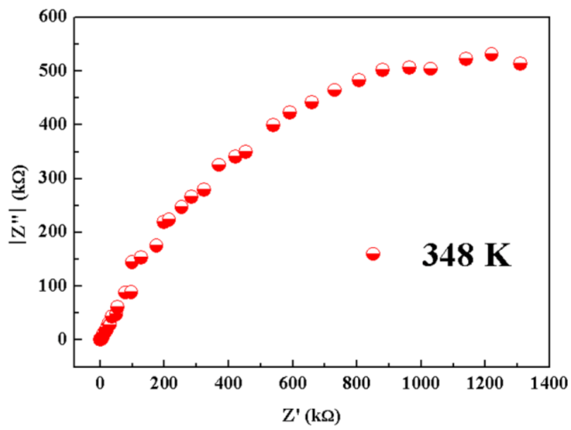


Fig. S27 Nyquist plot of compound **3** at 348 K under 95% RH.

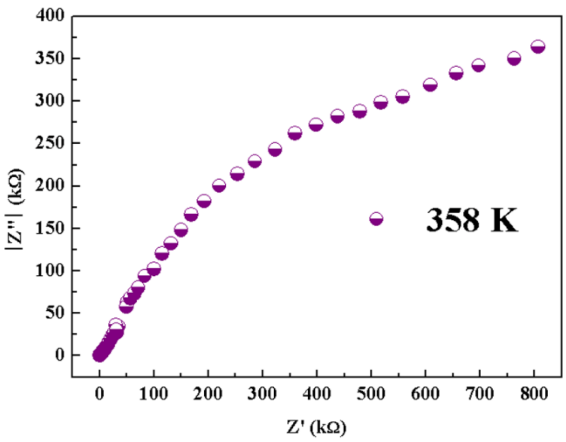


Fig. S28 Nyquist plot of compound **3** at 358 K under 95% RH.

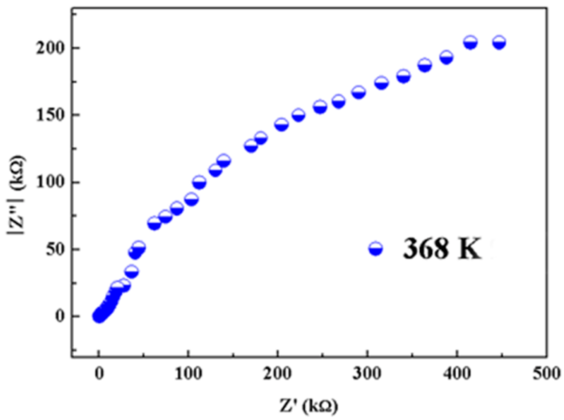


Fig. S29 Nyquist plot of compound **3** at 368 K under 95% RH.

Table S2. Proton conductivities of compounds **1-3** at different temperatures under relative humidity 95%

Temperature (K)	Proton conductivity at 95% RH (Scm^{-1})		
	1	2	3
298	3.05E-5	4.04E-6	/
308	4.32E-5	4.40E-6	/
318	1.54E-4	5.33E-6	/
328	2.41E-4	6.54E-6	2.77E-8
338	3.80E-4	7.88E-6	4.55E-8
348	1.28E-3	9.90E-6	1.02E-7
358	2.71E-3	1.22E-5	1.68E-7
368	3.46E-3	1.27E-5	2.49E-7

Table S3. Impedance values used to fit the equivalent circuit of compound **1** at different temperatures under relative humidity 95%

Temperature (K)	R_i (Ω)	Error%	R_b (Ω)	Error%
298	1512.32	8.76	9475.58	5.59
308	866.93	6.28	6861.27	7.66
318	573.42	5.26	1872.46	8.32
328	385.17	7.56	1200.04	2.18
338	254.76	7.62	759.33	4.41
348	115.23	6.46	209.37	9.35
358	83.29	3.95	113.25	8.26
368	63.47	3.67	84.92	6.15

Table S4. Impedance values used to fit the equivalent circuit of compound **2** at different temperatures under relative humidity 95%

Temperature (K)	R_b (Ω)	Error%	R_{gb} (Ω)	Error%
298	6.79E4	5.08	6.60E5	8.77
308	6.12E4	9.18	6.02E5	6.46
318	5.65E4	8.52	5.55E5	5.10
328	4.57E4	7.11	5.12E5	6.65
338	3.79E4	7.72	4.50E5	5.60
348	3.02E4	8.45	3.49E5	8.32
358	2.44E4	7.70	2.97E5	7.72
368	2.35E4	5.65	2.50E5	9.36

Table S5. Impedance values used to fit the equivalent circuit of compound **3** at different temperatures under relative humidity 95%

Temperature (K)	R_b (Ω)	Error%
328	7.76E6	4.18
338	4.73E6	9.83
348	2.10E6	3.12
358	1.28E6	8.62
368	8.64E5	8.75