Supplementary Information

Engineering the Proton Conductivity of Metal-organic Hybrid Materials by Varying Coordination Mode of the Ligand

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Contents:

Selected bond lengths and angles for compounds

Table S1. Selected bond lengths (Å) and angles (deg) of **1**.

Cu(1)-N(3)	1.863(3)	C(17)-N(3)-Cu(1)	131.3(3)
N(7)-Cu(2)-N(5)	175.50(15)	C(17)-N(3)-Cu(1)	131.3(3)

Symmetry transformations used to generate equivalent atoms: #1 -x, y,-z+1/2 #2 -x, y, -z+3/2

Table S2. Selected bond lengths (Å) and angles (deg) of **2.**

Mo(1)-O(3)	2.240(3)	Mo(1)-O(9)	1.708(3)
Mo(1)-O(15)	1.957(3)	Mo(1)-O(16)	1.945(3)
Mo(1)-O(12)	1.688(3)	Mo(1)-O(13)	2.315(3)
Mo(2)-O(8)	1.687(4)	Mo(2)-O(14)	1.958(3)
Mo(2)-O(2)	2.207(3)	Mo(2)-O(15)	2.258(3)
Mo(2)-O(4)	1.712(4)	O(12)-Mo(1)-O(9)	102.83(18)
O(5)-Mo(4)#1	2.272(3)	O(12)-Mo(1)-O(16)	104.57(16)
O(9)-Mo(1)-O(16)	98.59(15)	O(10)-Mo(3)-O(16)#1	105.14(16)
O(8)-Mo(2)-O(4)	102.56(19)	O(11)-Mo(4)-O(6)	102.76(17)
C(20)-O(1)-Mo(3)	133.0(3)	C(10)-O(2)-Mo(2)	133.6(3)
O(11)-Mo(4)-O(14)#2	103.57(16)	C(10)-O(3)-Mo(1)	130.7(3)
Mo(4)-O(13)-Mo(2)	144.99(18)	Mo(4)#1-O(14)-Mo(2)	142.48(18)

Symmetry transformations used to generate equivalent atoms: #1 x-1, y, z, #2 x+1, y, z, #3 -x+1,-y,-z

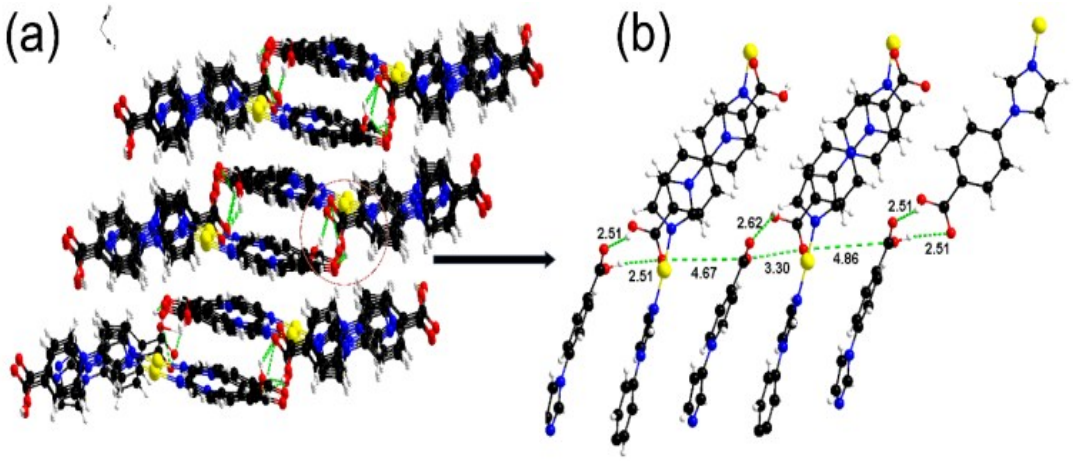


Fig.S1 (a) The packing diagram of compound **1**; (b) The hydrogen bond of intermolecules and possible proton hopping pathway.

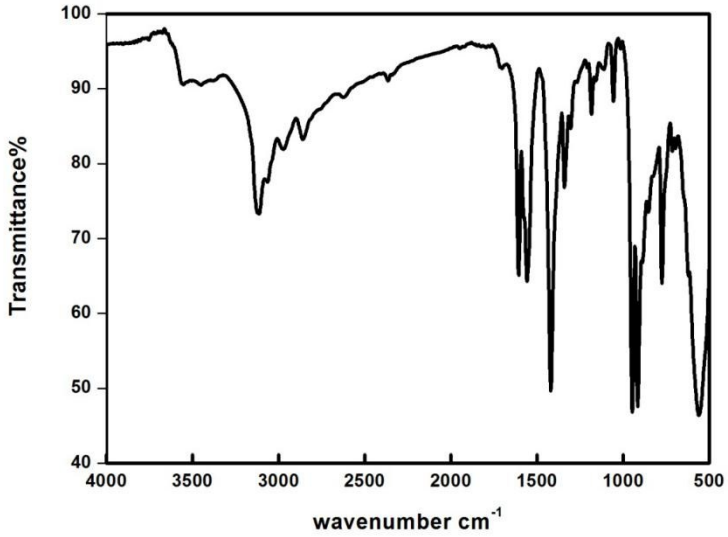


Fig.S2 FT-IR spectroscopy of compound**1**.

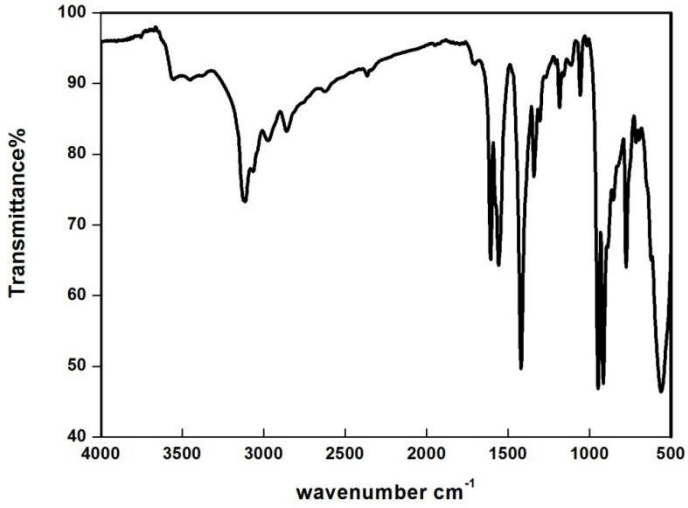


Fig.S3 FT-IR spectroscopy of compound**2**.

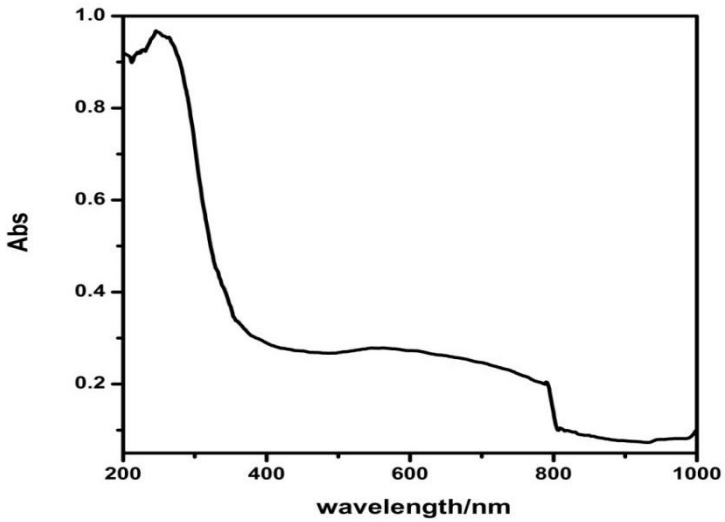
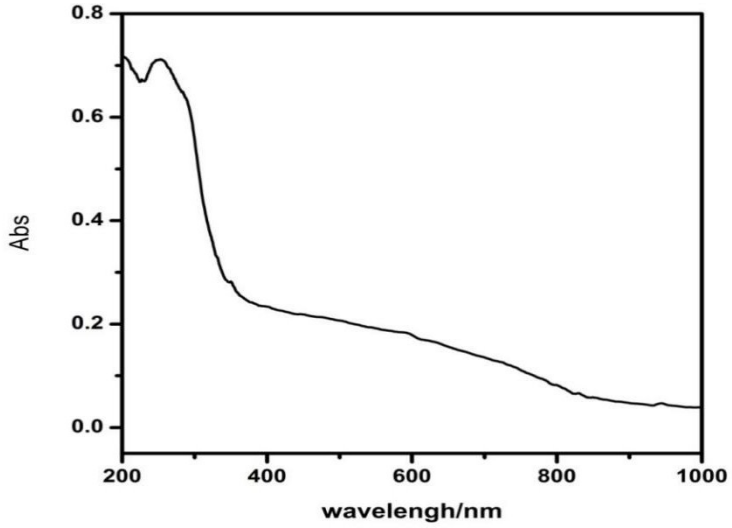


Fig.S4 The solid state UV-vis spectra of compound **1.**



F**ig.S5** The solid state UV-vis spectra of compound **2.**

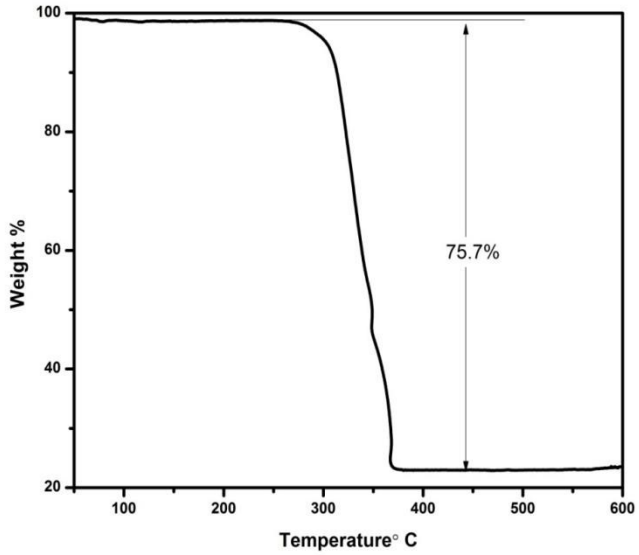


Fig.S6 Thermogravimetric analysis curve for compound **1**

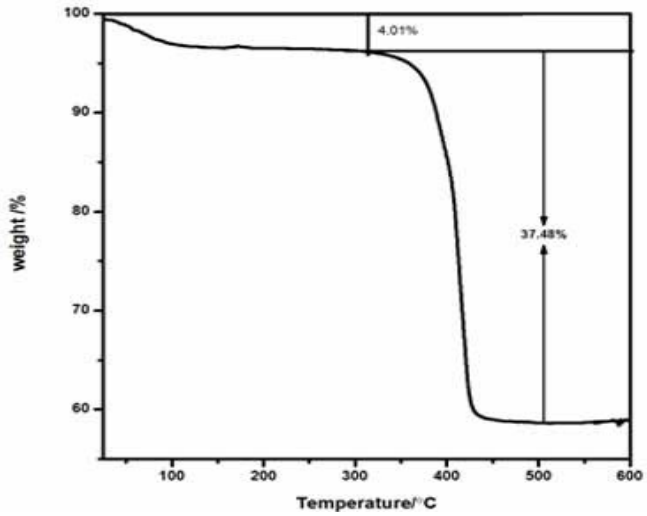


Fig.S7 Thermogravimetric analysis curve for compound **2**.

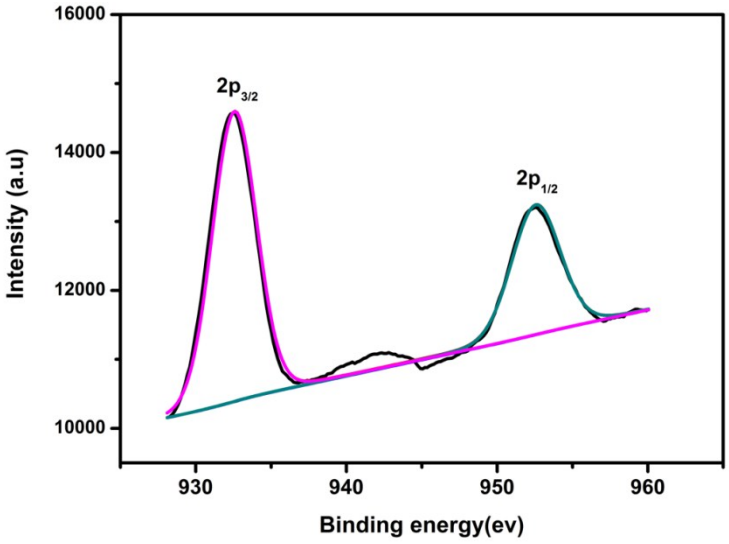


Fig.S8 XPS spectra of Cu^{+} 2p level of compound **1**, showing two partially overlapped peaks. The curve fitting provides peak positions at 932.57eV, 952.57eV, attributed to $2p_{3/2}$, $2p_{1/2}$, respectively.

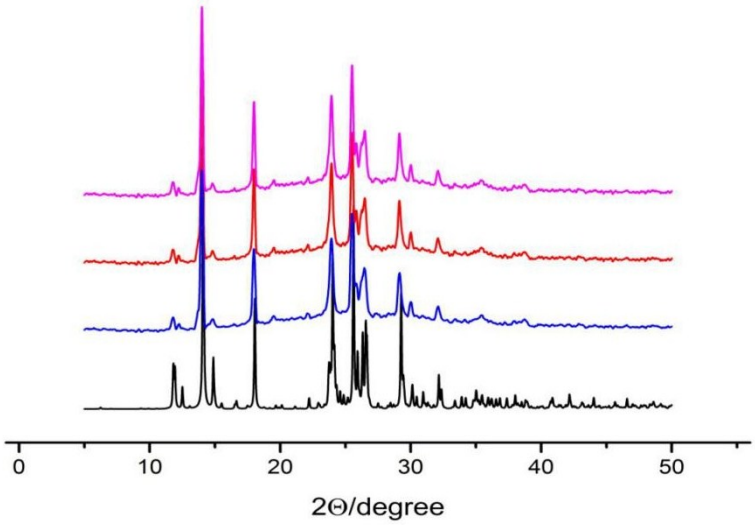


Fig.S9 PXRD patterns of compound **1:** the simulated pattern (black), as-synthesized sample (blue), after boiled in boiling water (red), after proton conductivity measurement under 97% RH at 25℃ (purple curve) are given for comparison.

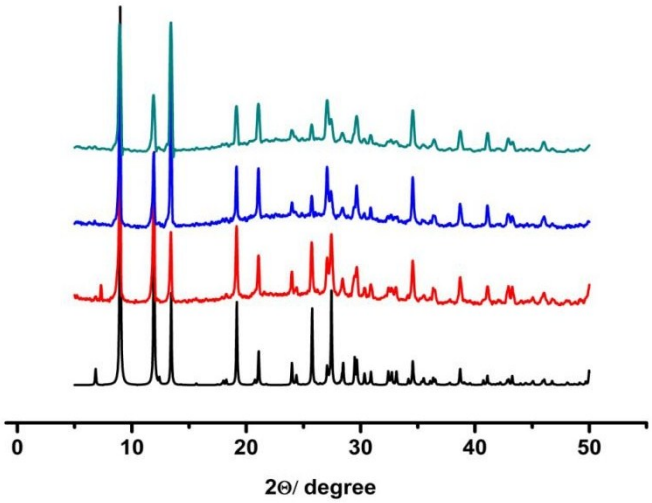


Fig.S10 PXRD patterns of compound **2:** the simulated pattern (black), as-synthesized sample (red), after boiled in boiling water (blue), after proton conductivity measurement under RH 97% at 25 °C (glaucous) are given for comparison.

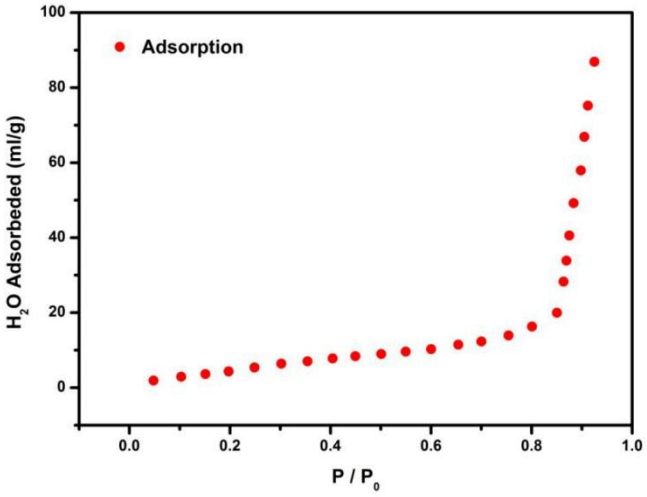


Fig.S11 Water vapor adsorption isotherm for compound **1** at STP.

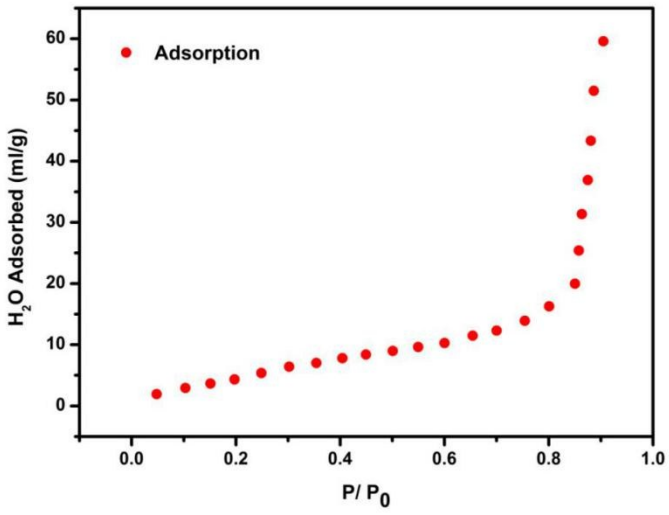


Fig. S12 Water vapor adsorption isotherm for compound **2** at STP.

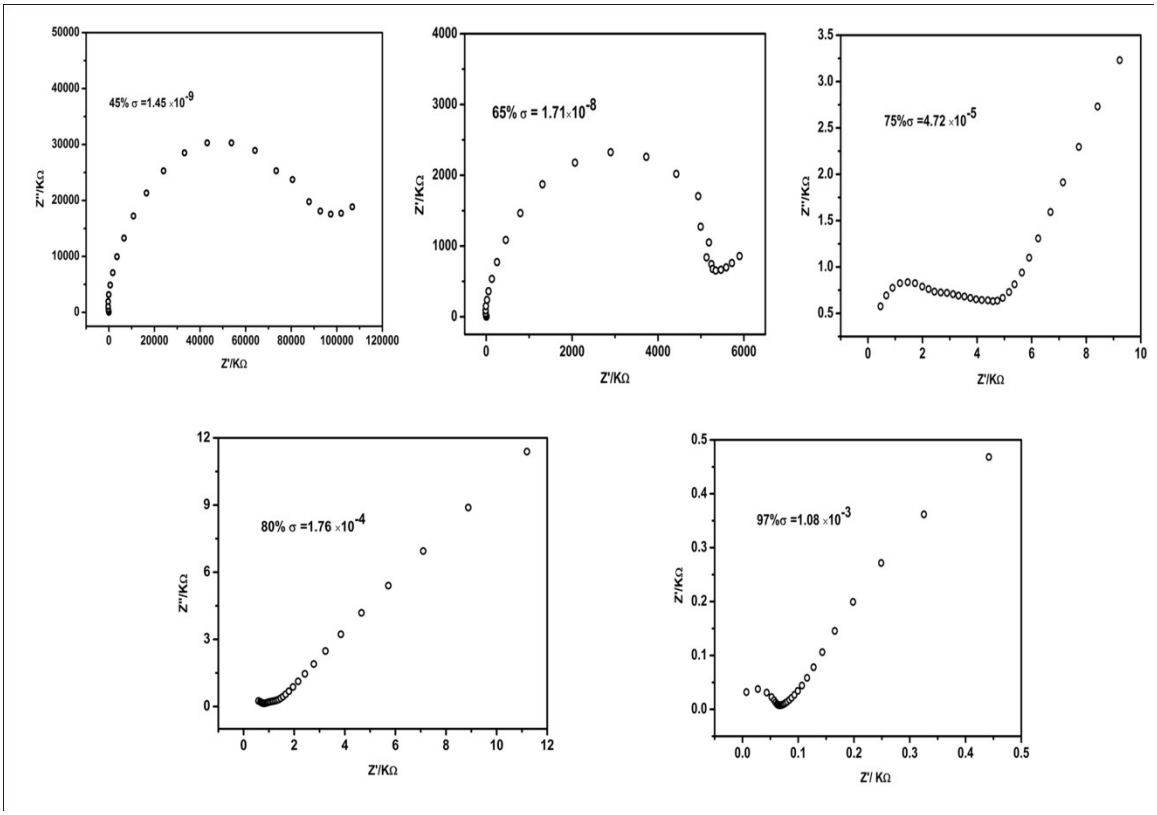


Fig.S13 Nyquist plot of compound **1** at 298K showing decrease in proton conductivity with respect to room temperature. Relative Humidity 45%, $\sigma=1.45\times10^{-9}$ S cm^{-1}; 65%, $\sigma=1.71\times10^{-8}$ S cm^{-1}; Relative Humidity 75%, $\sigma=4.72\times10^{-5}$ S cm^{-1}; Relative Humidity 80%, $\sigma=1.76\times10^{-4}$ S cm^{-1}; Relative Humidity 97%, $\sigma=1.08\times10^{-3}$ S cm^{-1}.

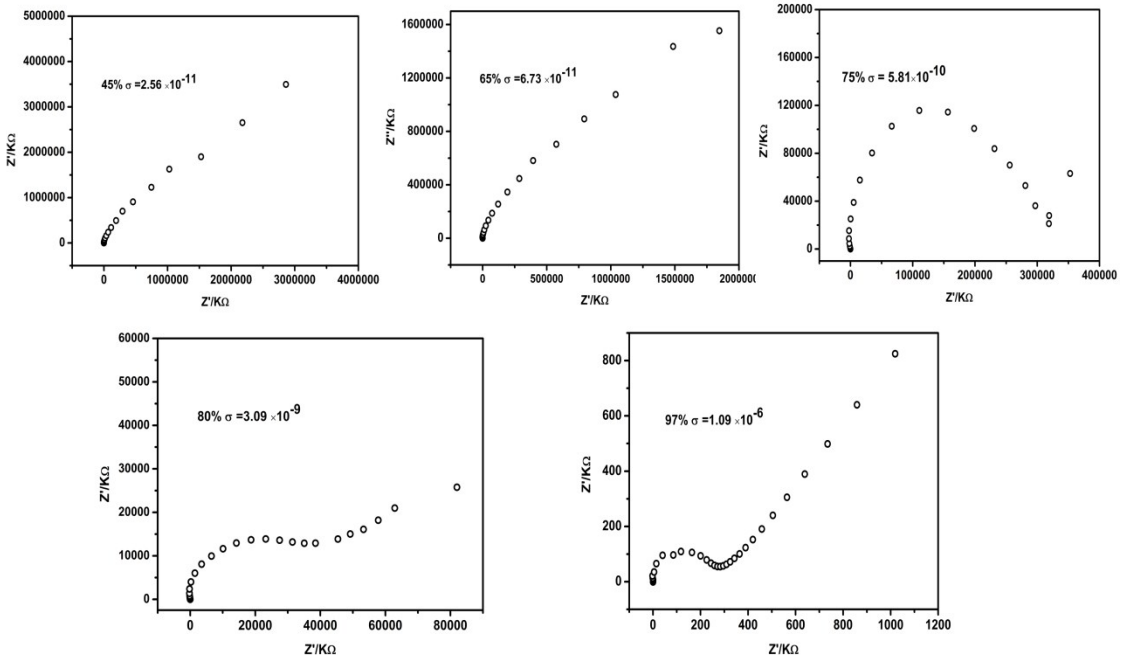


Fig.S14 Nyquist plot of compound **2** at 298K showing decrease in proton conductivity with respect to room temperature. Relative Humidity 45%, σ=2.56×10^{-11} S cm^{-1}; Relative Humidity 65%, σ=6.73×10^{-11}S cm^{-1}; Relative Humidity 75%, σ=5.81×10^{-10} S cm^{-1}; Relative Humidity80%, σ=3.09×10^{-9} S cm^{-1}; Relative Humidity 97%, σ=1.09×10^{-6} S cm^{-1};

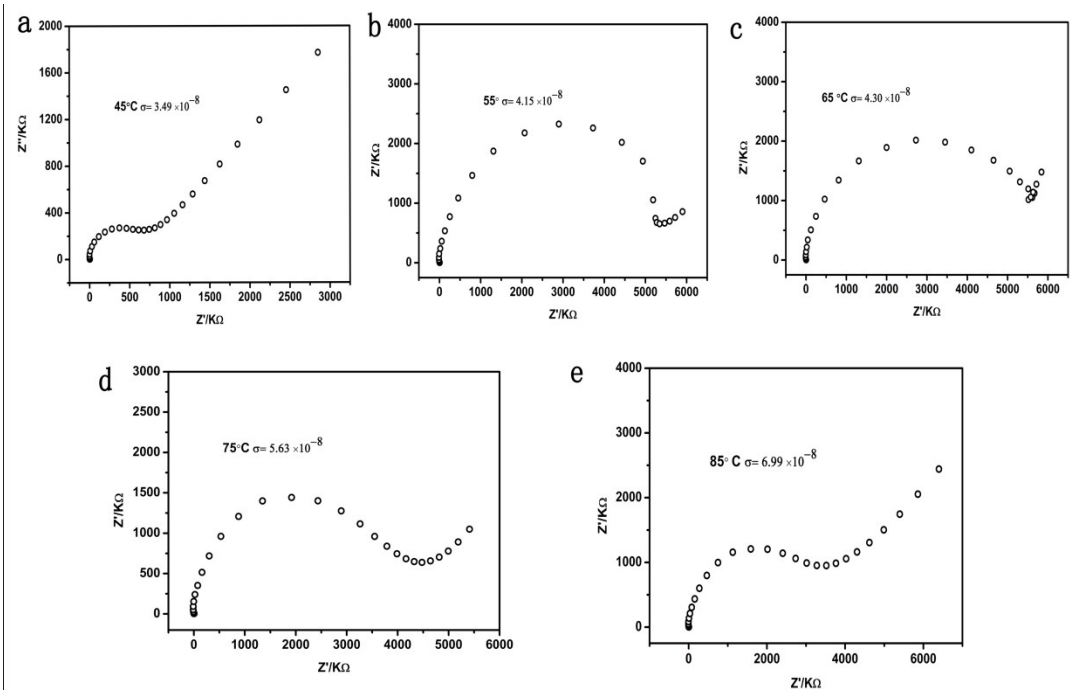


Fig.S15 Impedance plots of compound **1** from 45 to 85 °Cat relative humidity 65%.

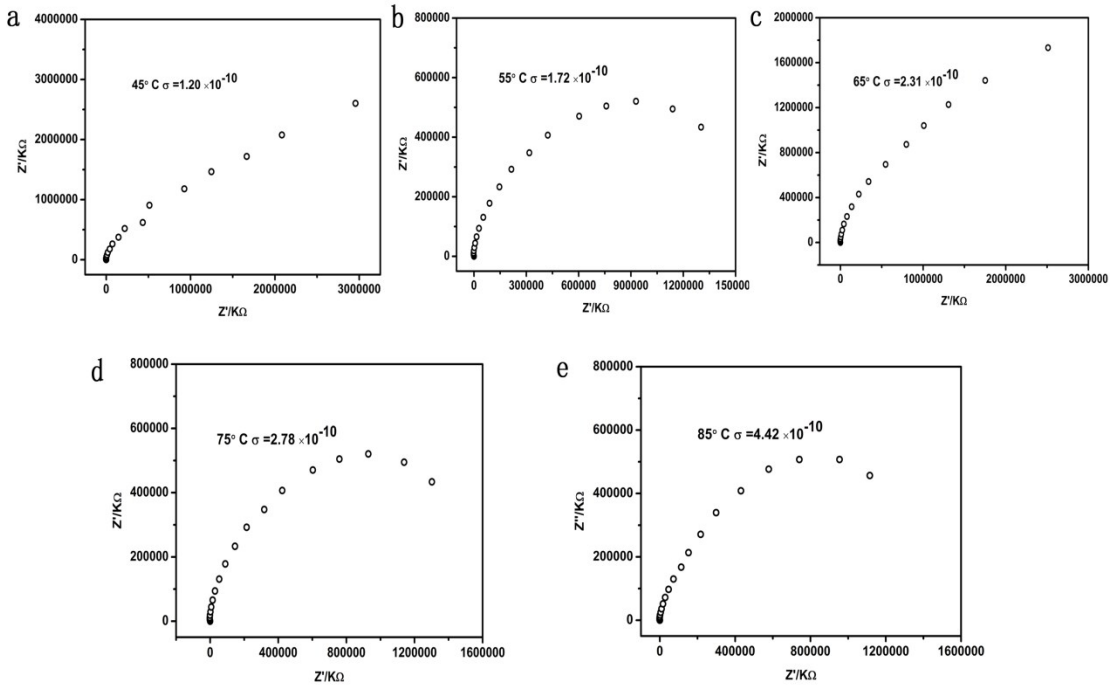


Fig.S16 Impedance plots of compound **2** from 45 to 85 °C under relative humidity 65%.