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Water-assisted proton conductivity of two highly stable imidazole multi-carboxylate-based MOFs

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Supporting Information

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Table S1. Selected bond distances (Å) and angles (deg) for compound **1**

Mn(1)-N(1)	2.272(2)	Mn(1)-O(7)	2.171(2)
Mn(1)-N(3)	2.219(2)	Mn(1)-O(8)	2.187(2)
Mn(1)-O(1)	2.247(2)	O(5)#2-Mn(1)-O(1)	85.37(8)
Mn(1)-O(5)#2	2.161(2)	O(5)#2-Mn(1)-O7	172.90(8)
N(3)-Mn(1)-N(1)	96.14(9)	O(5)#2-Mn(1)-O(8)	86.54(8)
N(3)-Mn(1)-O(1)	170.04(9)	O(7)-Mn(1)-N(1)	93.47(9)
O(1)-Mn(1)-N(1)	74.38(8)	O(7)-Mn(1)-N(3)	94.71(9)
O(5)#2-Mn(1)-N(1)	89.19(8)	O(7)-Mn(1)-O(1)	89.00(8)
O(5)#2-Mn(1)-N(3)	91.55(9)	O(8)-Mn(1)-N(3)	92.16(9)
O(7)-Mn(1)-O(8)	89.86(9)	O(8)-Mn(1)-O(1)	97.09(8)
O(8)-Mn(1)-N(1)	170.77(8)		

Symmetry codes: #1: -X, 2-Y,1-Z; #2: -X,2-Y,-Z

Table S2. Hydrogen bonding parameters for **1**

D□H...A	d(H...A)	d(D...A)	∠(DHA)
N(2)□H(2)...O(11) #1	2.00	2.850(4)	167.3
O(3)□H(3)...O(2)	1.70(4)	2.516(3)	175(4)
O(7)□H(7A)...O(10) #2	1.93	2.675(4)	142.5
O(7)□H(7B)...O(3) #3	2.87	3.566(3)	154.0
O(7)□H(7B)...O(4) #3	2.12	2.822(3)	153.0
O(8)□H(8B)...O(1) #4	1.95	2.778(3)	159.6
O(10)□H(10A)...O(9)	1.88	2.730(6)	161.9
O(10)□H(10B)...O(2)#5	2.38	3.231(4)	155.7
O(11)□H(11A)...O(6)#1	2.15	2.882(5)	141.4

Symmetry codes: #1：1-X,2-Y,1-Z; #2：1-X,1-Y,1-Z; #3：1-X,2-Y,-Z; #4：-X, 1-Y,-Z; #5 1+X,+Y,1+Z

Table S3. Selected bond distances (Å) and angles (deg) for compound **2**

N(1)-Zn(1)	2.050(2)	O(1)-Zn(1)	2.149(2)
N(2)-Zn(2)	2.000(2)	O(5)-Zn(1)#2	1.956(2)
N(3)-Zn(1)	2.093(3)	O(7)-Zn(2)	2.488(3)
N(4)-Zn(1)	2.144(3)	O(10)-Zn(3)	2.303(2)
N(5)-Zn(2)	2.027(2)	Zn(1)-O(5)#2	1.956(2)
N(6)-Zn(3)	2.045(2)	Zn(3)-N(6)#1	2.045(2)
N(7)-Zn(2)	2.112(3)	Zn(3)-N(9)#1	2.275(7)
N(8)-Zn(2)	2.095(3)	Zn(3)-O(10)#1	2.303(2)
N(9)-Zn(3)	2.275(7)	N(2)-Zn(2)-N(5)	138.94(10)
N(1)-Zn(1)-N(3)	121.80(9)	N(2)-Zn(2)-N(7)	113.73(11)
N(1)-Zn(1)-N(4)	101.69(10)	N(2)-Zn(2)-N(8)	105.42(10)
N(1)-Zn(1)-O(1)	80.21(9)	N(2)-Zn(2)-O(7)	81.95(9)
N(3)-Zn(1)-N(4)	77.06(10)	N(5)-Zn(2)-N(7)	98.24(11)
N(3)-Zn(1)-O(1)	91.00(10)	N(5)-Zn(2)-N(8)	105.89(10)
N(4)-Zn(1)-O(1)	167.06(10)	N(5)-Zn(2)-O(7)	74.45(9)
O(5)#2-Zn(1)-N(1)	106.17(9)	N(7)-Zn(2)-O(7)	86.94(12)
O(5)#2-Zn(1)-N(3)	132.01(10)	N(8)-Zn2-N(7)	78.05(12)
O(5)#2-Zn(1)-N(4)	95.71(11)	N(8)-Zn(2)-O(7)	164.91(11)
O(5)#2-Zn(1)-O(1)	96.02(10)	N(6)1-Zn(3)-O(10)#1	76.85(9)
O(10)1-Zn(3)-O(10)	85.28(14)	N(6)-Zn(3)-N(6)#1	154.29(15)
N(9)-Zn(3)-N(9)#1	105.9(3)	N(6)#1-Zn(3)-N(9)#1	100.74(17)
N(9)#1-Zn(3)-O(10)	84.43(19)	N(6)-Zn(3)-N(9)#1	94.69(17)
N(9)#1-Zn(3)-O(10)#1	169.62(19)	N(6)-Zn(3)-N(9)	100.74(17)
N(9)-Zn(3)-O(10)#1	84.43(19)	N(6)#1-Zn(3)-N(9)	94.69(17)
N(9)-Zn(3)-O(10)	169.62(19)	N(6)-Zn(3)-O(10)	76.85(9)
N(6)-Zn(3)-O(10)#1	84.27(10)	N(6)#1-Zn(3)-O(10)	84.27(10)

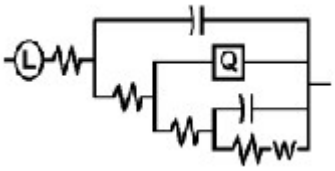
Symmetry transformations used to generate equivalent atoms: #1：+X,3/2-Y,1/2-Z; #2 1/2-X,1-Y,+Z.

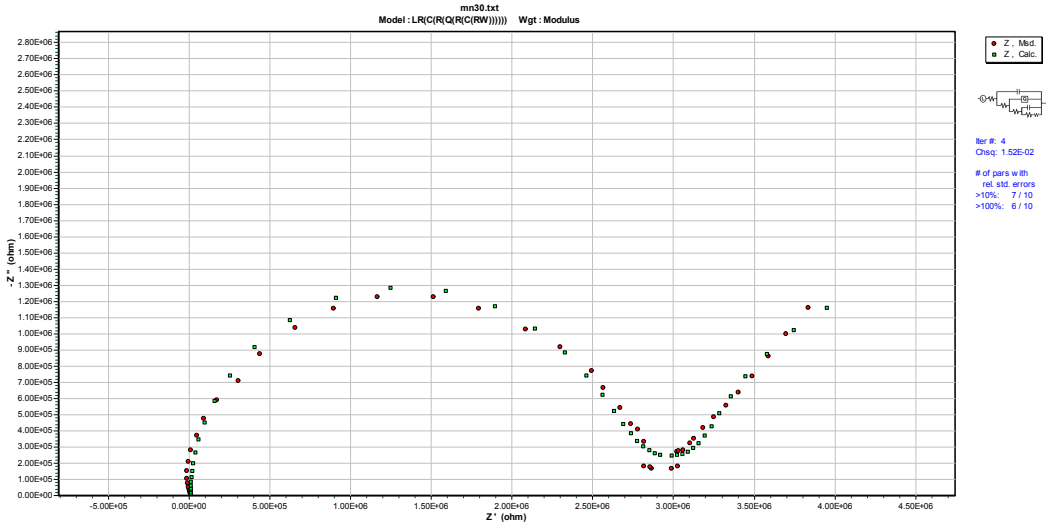
Table S4. Hydrogen bonding parameters for **2**

D□H...A	d(H...A)	d(D...A)	∠(DHA)
O(3)-H(3) ...O(2)	1.61(2)	2.499(3)	176(5)
O(12)-H(12) ...O(8)#1	2.38	3.297(6)	167.5
O(14)-H(14A) ...O(9)#2	1.92	2.751(5)	166.7
O(14)-H(14A) ...O(10)#2	2.81	3.487(5)	137.4
O(14)-H(14B) ...O(15)#1	2.06	2.823(7)	148.6
O(15)-H(15A) ...O(10)#3	2.16	2.958(5)	147.2
O(15)-H(15B) ...O(4)	2.39	3.014(5)	130.8
O(8)-H(8A) ...O(9)	1.62(10)	2.506(4)	160(9)

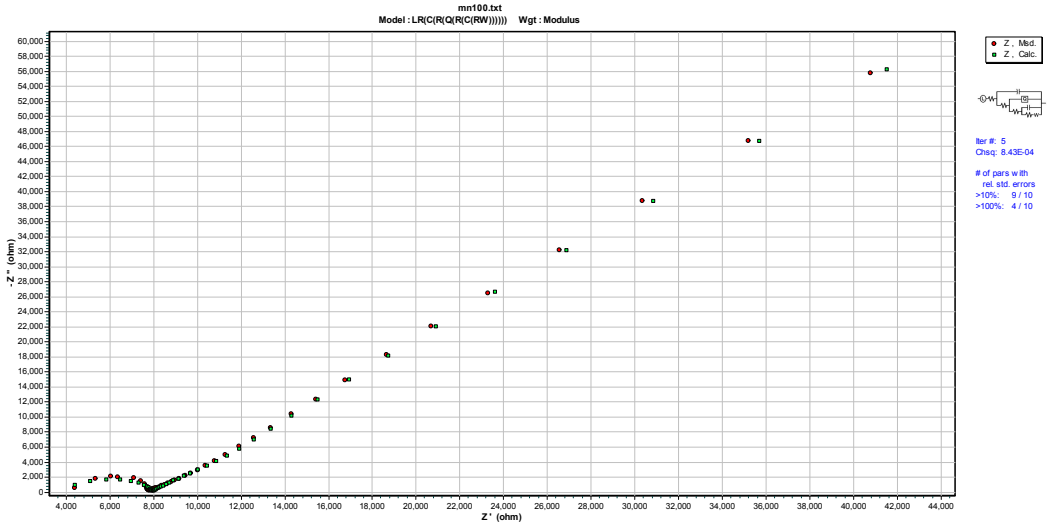
Symmetry codes: #1：1/2+X,+Y,1-Z;#2： 1/2+X,3/2-Y,1/2+Z; #3：+X,3/2-Y,1/2-Z

Equivalent circuit LR(C(R(Q(R(C(RW)))))):



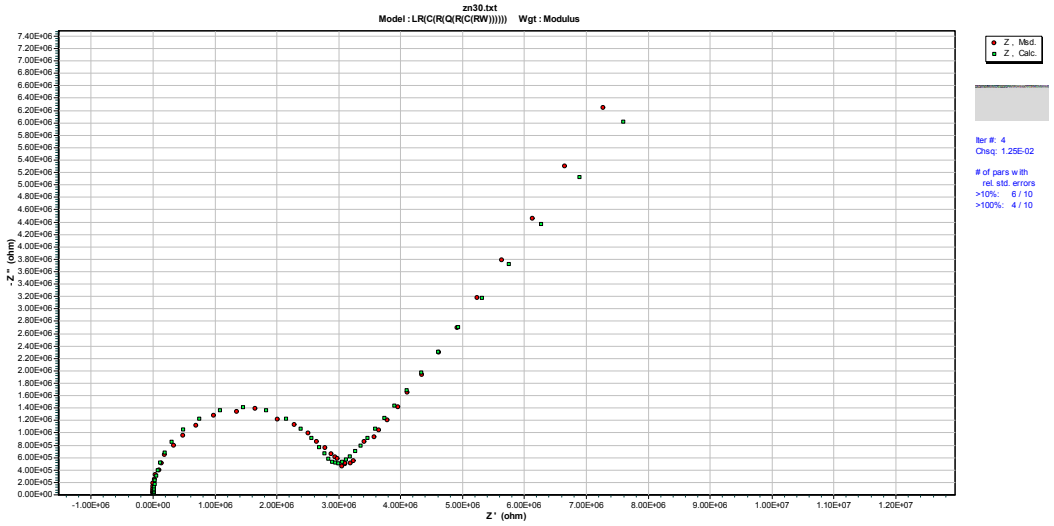


(a)

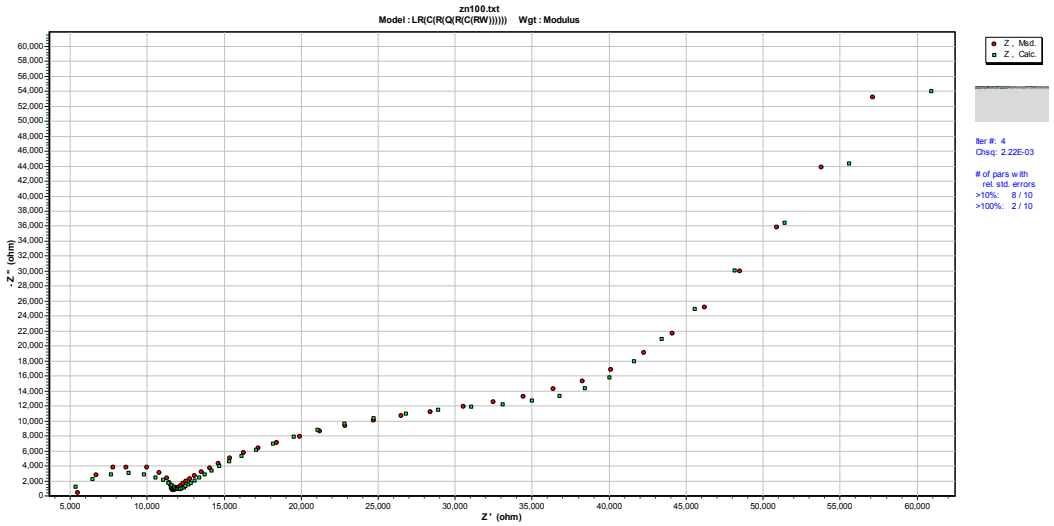


(b)

Fig. S1 Nyquist plots for a polycrystalline sample of **1** at 30 ℃(a) and 100 ℃ (b) and 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(R(Q(R(C(RW)))))).

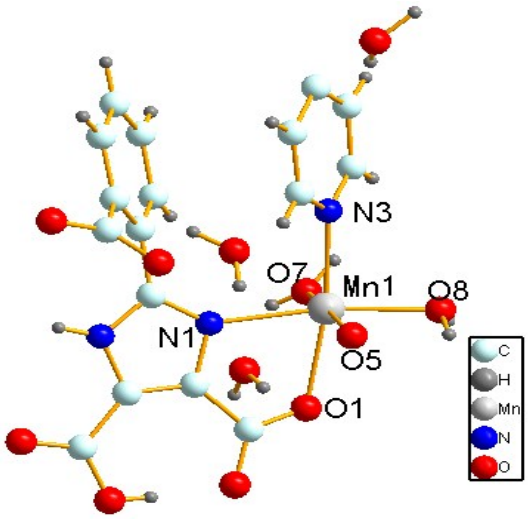


(a)

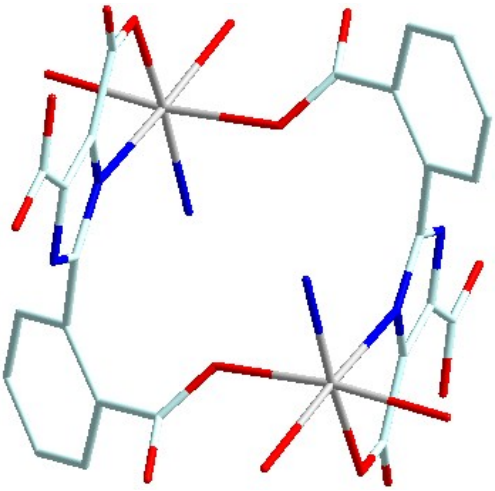


(b)

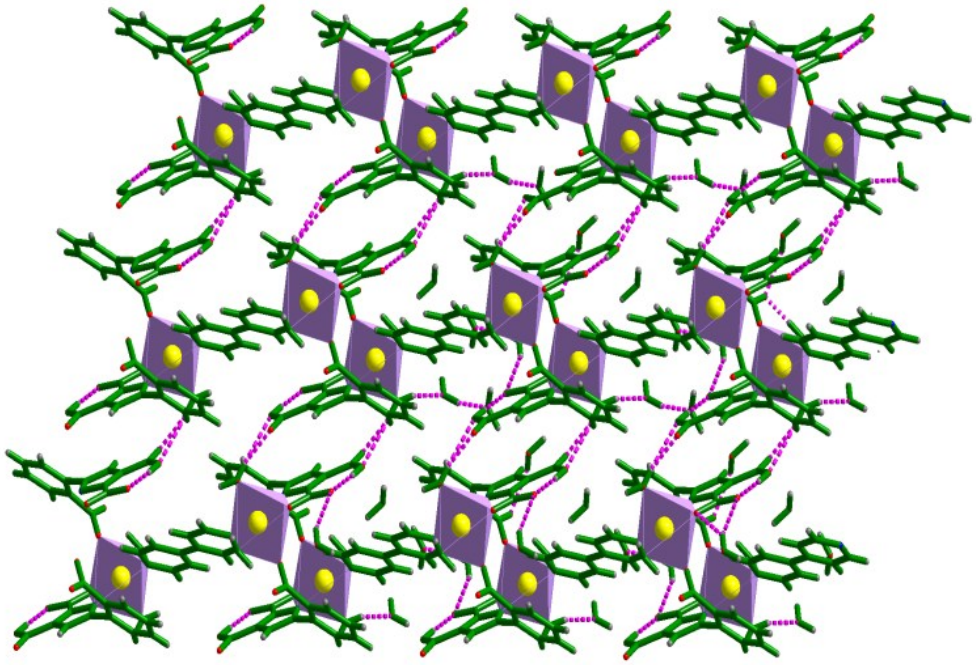
Fig. S2 Nyquist plots for a polycrystalline sample of **1** at 30℃ and 100℃and 98% RH. Red circle and green square are the measured impedance spectroscopy values and the fits of the impedance data to the equivalent circuit of LR(C(R(Q(R(C(RW)))))).



(a)

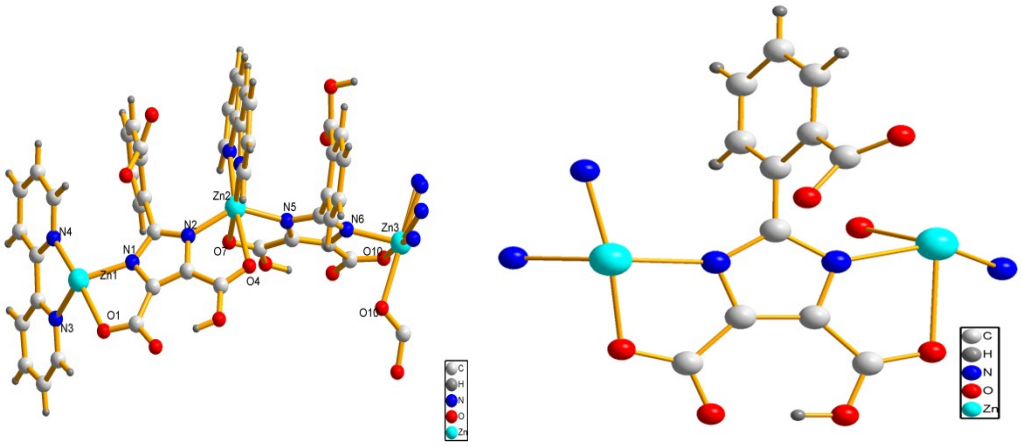


(b)

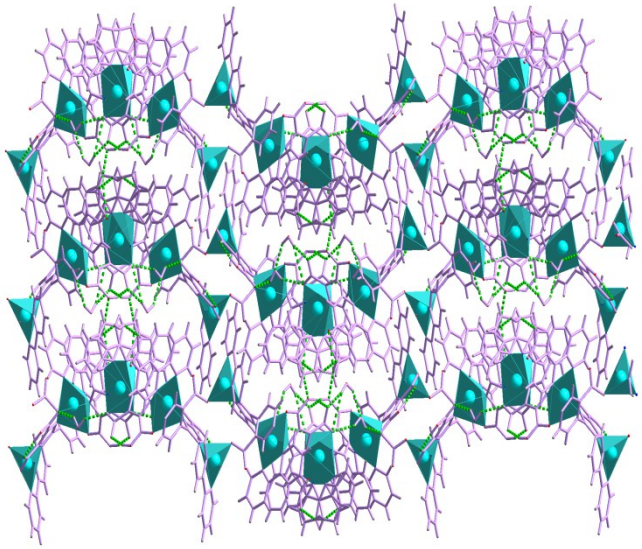


(c)

Fig. S3 (a) Structural unit of **1**. (b) Binary structure of **1** formed by bridging ligands.(c) Two-dimensional sheet of **1** connected by H-bonds.

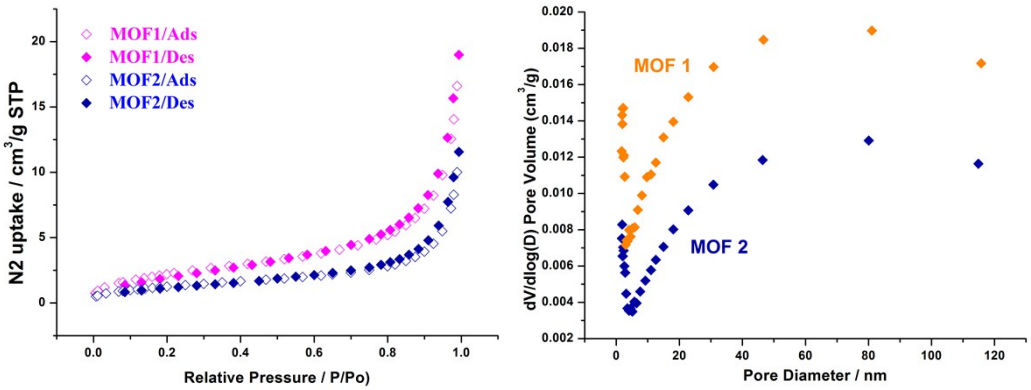


(a) (b)



(c)

Fig. S4 (a) Structural unit of **2**. (b) Coordination mode of the imidazole multi-carboxylate ligand of **2**. (c) Two-dimensional sheet of **2** connected by H-bonds.



(a) (b)

Fig. S5 Nitrogen gas adsorption and desorption isotherms at 77 K (a) and pore size distribution profiles (b) for **1**

and **2.**

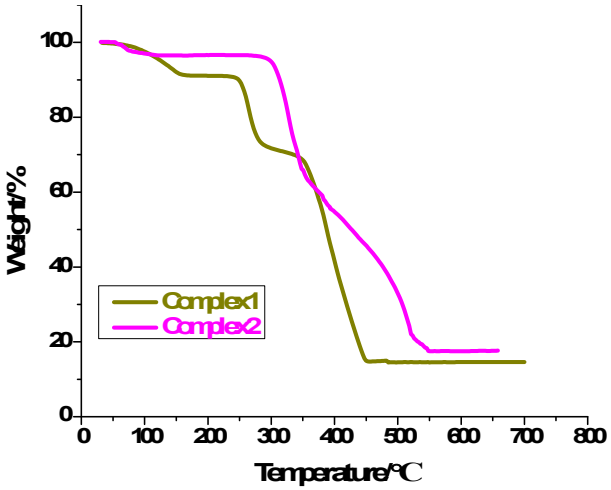
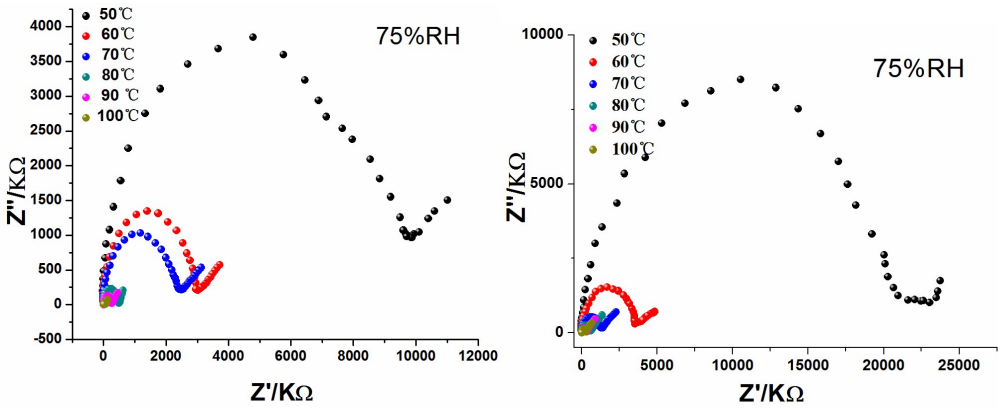
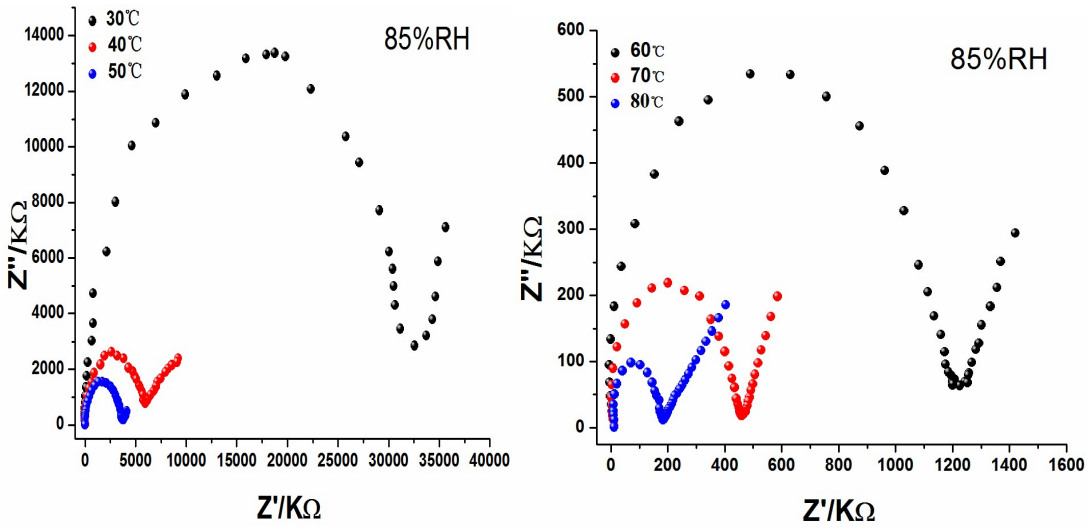


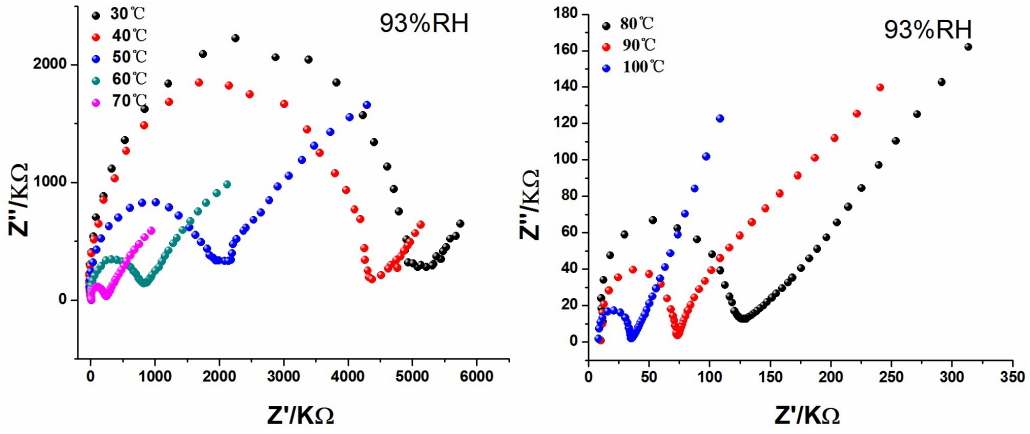
Fig. S6 The TG curves of MOFs **1** and **2**.



(a)

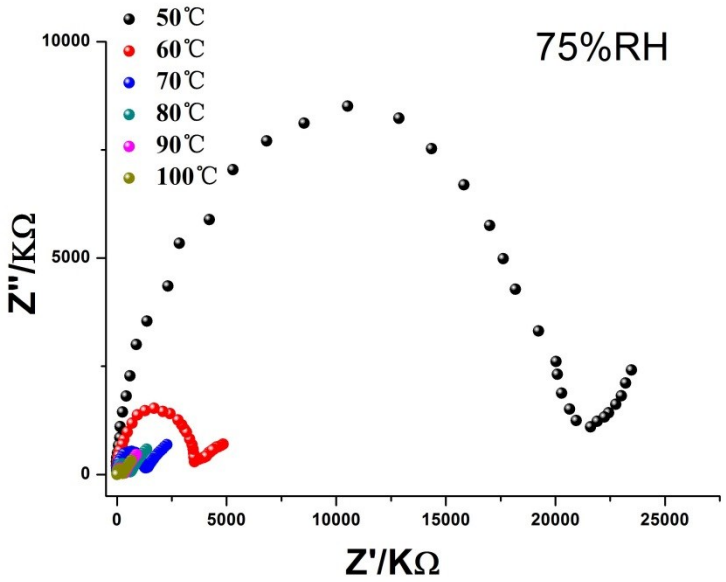


(b)

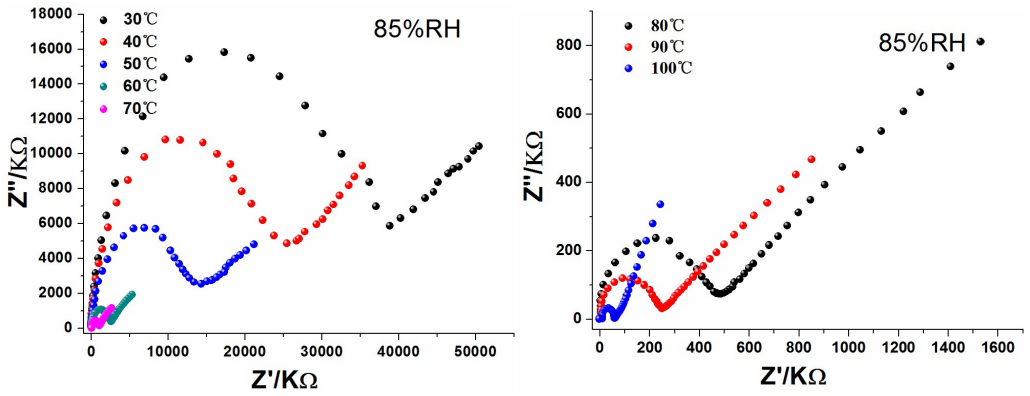


(c)

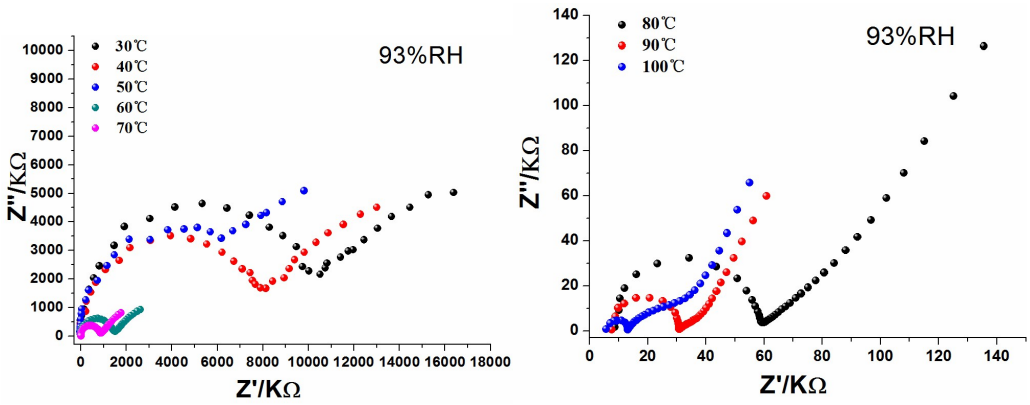
Fig. S7 Impedance spectra of **1** at 75% (a), 85% (b) and 93% RHs (c) and 30-100℃.



(a)

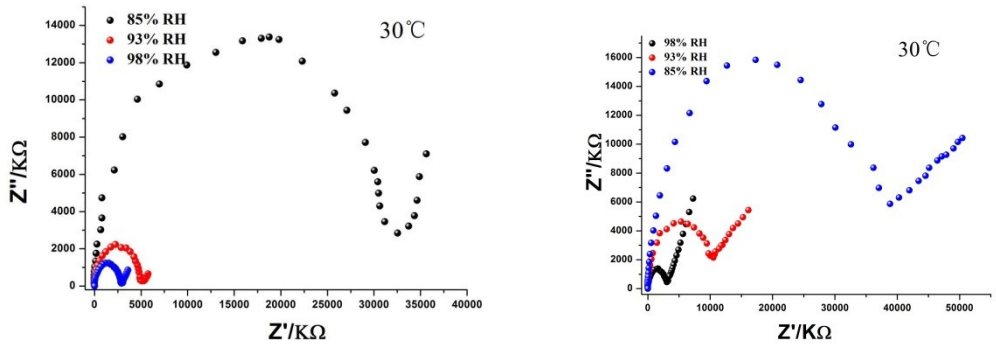


(b)



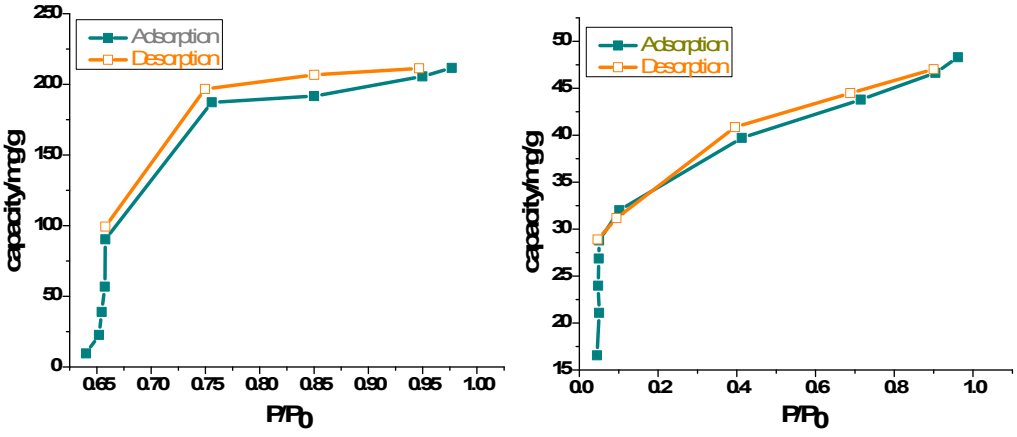
(c)

Fig. S8 Impedance spectra of **2** at 75% (a), 85% (b) and 93% RH (c) and 30-100℃.



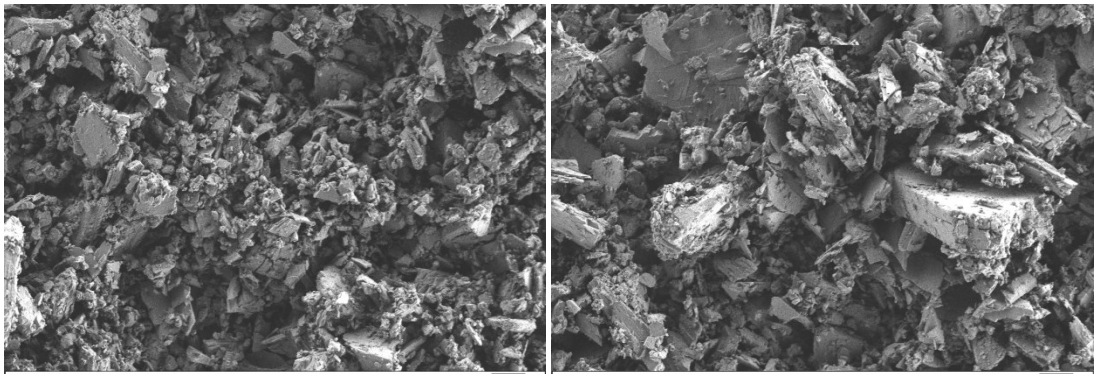
(a) (b)

Fig. S9 Impedance spectra of **1** (a) and **2** (b) at different RHs and 30 °C.



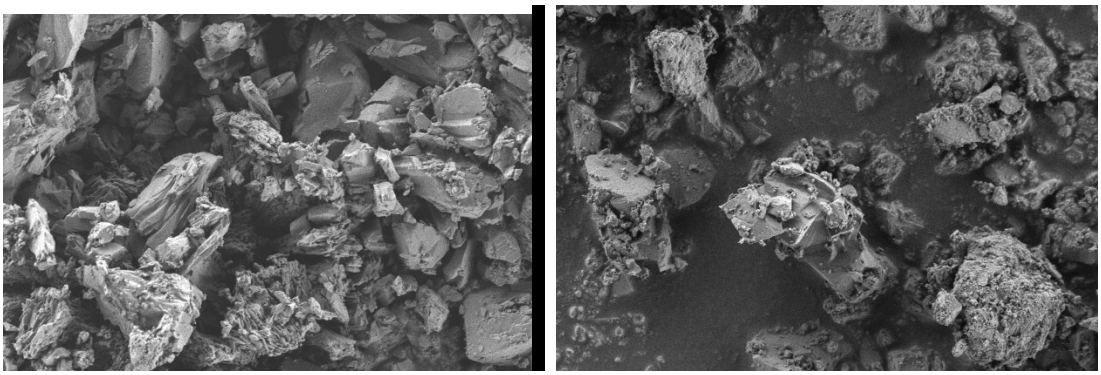
(a) (b)

Fig. S10 The adsorption curves of MOFs **1** and **2.**



(a) (b)

Fig. S11 SEM images for ground powders of **1** before (a) and after (b) impedance test**.**



(a) (b)

Fig. S12 SEM images for ground powders of **2** before (a) and after (b) impedance test**.**