Supporting information

Proton conduction in two hydrogen-bonded supramolecular lanthanide–complexes

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Table S1 Selected Bond Lengths (Å) and Angles (deg) for **1**

Eu(1)-O(1)	2.444(4)	Eu(1)-O(15)	2.465(4)
Eu(1)-O(5)	2.300(3)	Eu(1)-O(16)	2.412(4)
Eu(1)-O(13)	2.384(4)	Eu(1)-O(17)	2.396(4)
Eu(1)-O(14)	2.424(4)	Eu(1)-O(18)	2.390(5)
O(1)-Eu(1)-O(15)	128.51(14)	O(14)-Eu(1)-O(1)	133.94(14)
O(5)-Eu(1)-O(1)	142.79(13)	O(14)-Eu(1)-O(15)	75.47(16)
O(5)-Eu(1)-O(13)	140.48(15)	O(16)-Eu(1)-O(1)	74.05(13)
O(5)-Eu(1)-O(14)	75.95(15)	O(16)-Eu(1)-O(14)	69.10(15)
O(5)-Eu(1)-O(15)	73.19(14)	O(16)-Eu(1)-O(15)	142.99(14)
O(5)-Eu(1)-O(16)	107.19(14)	O(17)-Eu(1)-O(1)	71.99(13)
O(5)-Eu(1)-O(17)	71.54(14)	O(17)-Eu(1)-O(14)	126.36(17)
O(5)-Eu(1)-O(18)	95.57(17)	O(17)-Eu(1)-O(15)	130.37(15)
O(13)-Eu(1)-O(1)	75.70(14)	O(17)-Eu(1)-O(16)	81.24(15)

O(13)-Eu(1)-O(14)	77.31(17)	O(18)-Eu(1)-O(1)	71.07(15)
O(13)-Eu(1)-O(15)	72.29(15)	O(18)-Eu(1)-O(14)	145.19(18)
O(13)-Eu(1)-O(16)	89.53(15)	O(18)-Eu(1)-O(15)	69.78(16)
O(13)-Eu(1)-O(17)	147.69(15)	O(18)-Eu(1)-O(16)	144.07(15)
O(13)-Eu(1)-O(18)	90.09(19)	O(18)-Eu(1)-O(17)	80.10(19)

Table S2 Selected Bond Lengths (Å) and Angles (deg) for **2**

Dy(1)-O(1)	2.341(3)	Dy(1)-O(15)	2.345(3)
Dy(1)-O(5)	2.371(3)	Dy(1)-O(16)	2.418(3)
Dy(1)-O(13)	2.363(3)	Dy(1)-O(17)	2.383(3)
Dy(1)-O(14)	2.411(3)	Dy(1)-O(18)	2.348(3)
O(1)-Dy(1)-O(17)	144.17(10)	O(15)-Dy(1)-O(16)	77.38(13)
O(1)-Dy(1)-O(18)	87.55(12)	O(15)-Dy(1)-O(17)	74.00(12)
O(5)-Dy(1)-O(14)	76.19(10)	O(15)-Dy(1)-O(18)	144.57(12)
O(5)-Dy(1)-O(16)	145.85(10)	O(17)-Dy(1)-O(14)	135.41(11)
O(5)-Dy(1)-O(17)	75.53(9)	O(17)-Dy(1)-O(16)	70.43(10)
O(13)-Dy(1)-O(5)	73.40(9)	O(18)-Dy(1)-O(5)	101.37(12)
O(13)-Dy(1)-O(14)	73.27(10)	O(18)-Dy(1)-O(13)	70.23(11)
O(13)-Dy(1)-O(16)	131.87(11)	O(18)-Dy(1)-O(14)	142.40(11)
O(13)-Dy(1)-O(17)	128.57(11)	O(18)-Dy(1)-O(16)	73.92(13)
O(14)-Dy(1)-O(16)	128.15(12)	O(18)-Dy(1)-O(17)	77.10(12)
O(15)-Dy(1)-O(5)	90.87(12)	C(1)-O(1)-Dy(1)	144.8(3)
O(15)-Dy(1)-O(13)	145.03(11)	C(12)-O(5)-Dy(1)	138.9(2)
O(15)-Dy(1)-O(14)	72.70(11)	O(1)-Dy(1)-O(14)	73.44(10)
O(1)-Dy(1)-O(5)	139.86(10)	O(1)-Dy(1)-O(15)	104.28(11)
O(1)-Dy(1)-O(13)	73.16(10)	O(1)-Dy(1)-O(16)	74.28(10)

Table S3 Hydrogen bond lengths (Å) and angles (º) for **1**

D–H···A	d(H···A)	d(D···A)	∠DHA
N(4)–H(4)···O(9)#1	2.01	2.854(6)	166.3
O(3)–H(3)···O(2)	1.62	2.436(5)	177.5
O(7)–H(7A)···O(6)	1.66	2.470(5)	171.3
O(13)–H(13B)···O(2)	1.85	2.680(6)	154.5
O(14)–H(14A)···O(4)#2	2.14	2.781(6)	130.7
O(14)–H(14B)···O(22)#3	1.88	2.706(6)	159.3
O(15)–H(15B)···O(12)#4	1.91	2.759(6)	162.5
O(16)–H(16A)···O(3)#2	1.91	2.818(5)	155.5
O(16)–H(16B)···O(10)#5	1.89	2.696(6)	154.8
O(17)–H(17A)···N(3)	2.19	2.881(6)	135.1
O(17)–H(17B)···O(21)#4	1.93	2.746(7)	156.3
O(18)–H(18B)···O(20)	1.92	2.703(8)	142.1
O(18)–H(18B)···O(20A)	2.19	2.87(4)	131.1
N(6)–H(6)···O(8)#6	2.01	2.834(6)	159.9
O(10)–H(10A)···O(11)	1.54(2)	2.435(7)	172(6)
O(19)–H(19A)···N(5)#4	2.02	2.861(7)	170.1
O(19)–H(19B)···O(20)#7	2.19	2.748(15)	115.1
O(20)–H(20A)···O(19)#7	2.10	2.748(15)	131.7
O(20)–H(20B)···O(4)#8	2.15	2.897(10)	146.2
O(21)–H(21A)···O(24)	1.98	2.779(13)	155.9
O(22)–H(22B)···O(6)#9	2.08	2.779(6)	139.0
O(23)–H(23B)···O(22)	2.05	2.856(18)	157.7

Symmetry codes: #1 = *x*, 1 + *y*, +*z*; #2 = –*x*, –*y*, –*z*; #3 = -1 + *x*, *y*, *z*; #4 = 1 – *x*, 1 – *y*, 1 – *z*; #5 = 1 – *x*, –*y*, 1 – *z*; #6 = *x*, -1 + *y*, *z*; #7 = 1 – *x*, 1 – *y*, –*z*; #8 = 1 – *x*, –*y*, –*z*; #9 = 1 + *x*, *y*, *z*.

Table S4 Hydrogen bond lengths (Å) and angles (º) for **2**

D–H···A	d(H···A)	d(D···A)	∠DHA
N(1)–H(1)···O(31)#1	2.16	2.897(4)	143.5
N(3)–H(3)···O(20)	2.09(5)	2.854(4)	148(4)
O(3)–H(3A)···.O(2)	1.70	2.512(4)	172.6
O(7)–H(7A)···O(6)	1.57(2)	2.472(4)	173(6)
O(13)–H(13A)···O(25)	2.18	2.826(5)	130.7
O(13)–H(13B)···O(20)	1.84	2.659(4)	139.0
O(14)–H(14A)···O(29)#1	2.17	2.731(5)	122.6

O(14)–H(14B)···O(31)#1	1.92	2.766(4)	166.7
O(15)–H(15A)···O(23)#1	2.18	2.793(5)	129.7
O(15)–H(15B)···O(26)	1.93	2.765(5)	153.2
O(17)–H(17A)···O(24)#1	2.00	2.785(5)	149.9
O(18)–H(18A)···O(19)	1.97	2.753(5)	147.4
O(18)–H(18B)···O(30)	2.14	2.723(5)	123.1
N(6)–H(6)···O(22)#4	2.11	2.884(5)	149.9
O(10)–H(10A)···O(11)	1.67	2.492(5)	179.0
O(19)–H(19A)···O(27)#1	1.95	2.727(5)	152.1
O(19)–H(19B)···O(12)#5	1.94	2.765(5)	163.0
O(20)–H(20A)···O(21)#6	1.96(6)	2.737(5)	167(6)
O(20)–H(20B)···N(2)#6	2.08(6)	2.893(4)	160(5)
O(21)–H(21A)···O(24)	2.03	2.850(6)	163.6
O(21)–H(21B)···O(26)#1	2.00	2.843(6)	177.8
O(23)–H(23A)···O(8)#7	2.07	2.889(4)	163.7
O(23)–H(23B)···O(11)#8	1.94	2.791(4)	166.7
O(26)–H(26A)···O(12)#9	1.98	2.821(5)	172.6
O(26)–H(26B)···O(3)#10	2.07	2.843(5)	150.7
O(27)–H(27A)···O(9)#9	2.05	2.778(5)	142.6
O(27)–H(27B)···O(29)#9	2.09	2.790(6)	139.3
O(28)–H(28A)···O(19)#2	2.22	2.879(7)	134.3
O(29)–H(29A)···O(8)#7	1.97	2.787(5)	160.3
O(31)–H(31B)···O(21)#11	2.01	2.858(5)	174.5

Symmetry codes: #1 = 1 – *x*, 1 – *y*, 1 – *z*; #2 = *x*, 3/2 – *y*, -1/2 + *z*; #3 = 1 – *x*, -1/2 + *y*, 3/2 – *z*; #4 = 1/2 – *x*, 1 – *y*, -1/2 + *z*; #5 = *x*, 3/2 – *y*, 1/2 + *z*; #6 = 1 – *x*, 1/2 + *y*, 3/2 – *z*; #7 = -1/2 + *x*, 3/2 – *y*, 1 – *z*; #8 = 1/2 – *x*, 1 – *y*, 1/2 + *z*; #9 = 1/2 + *x*, *y*, 1/2 – *z*; #10 = 1 – *x*, 1/2 + *y*, 1/2 – *z*; #11 = *x*, 1/2 – *y*, -1/2 + *z*.

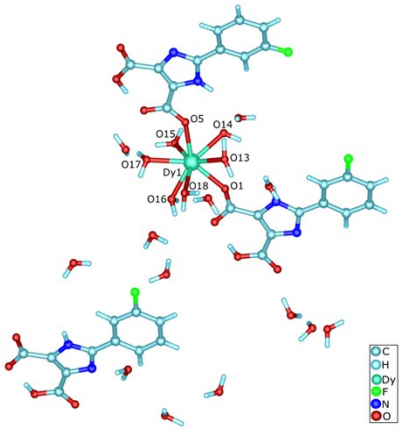


Fig. S1 Coordination environments of Dy^{3+} ion in **2**.

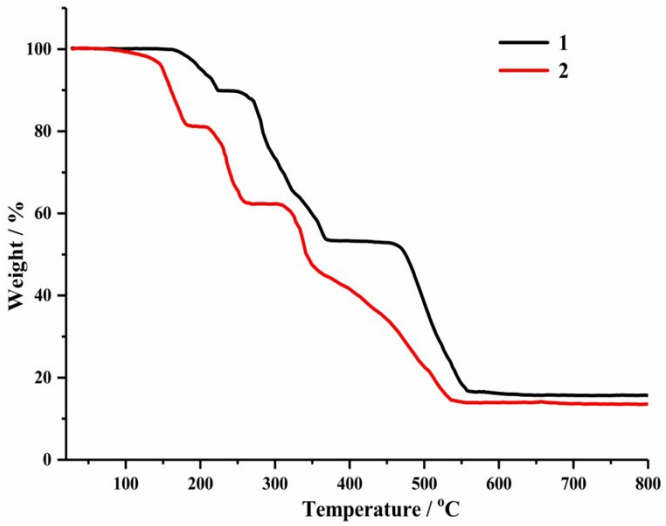
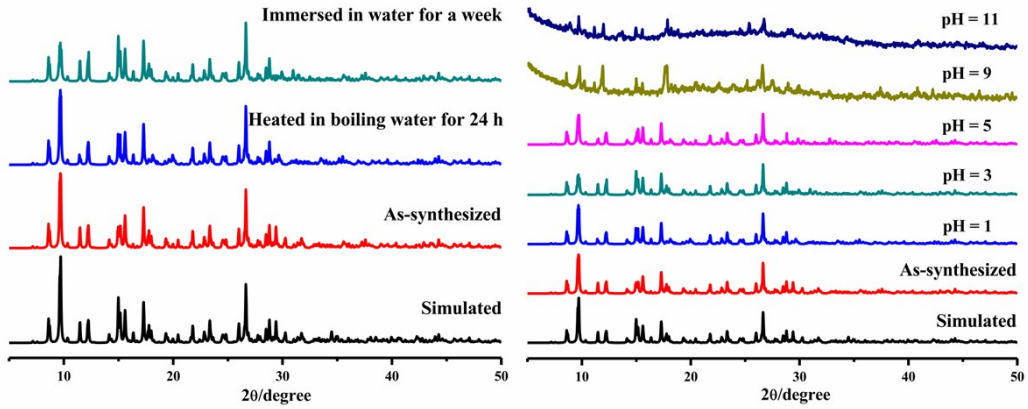


Fig. S2 TG curves of **1** and **2**.



(a) (b)

Fig. **S3**. PXRD patterns of **2** (a) simulated from the single-crystal data, as-synthesized and after water treated samples and (b) after soaked in various pH solutions.

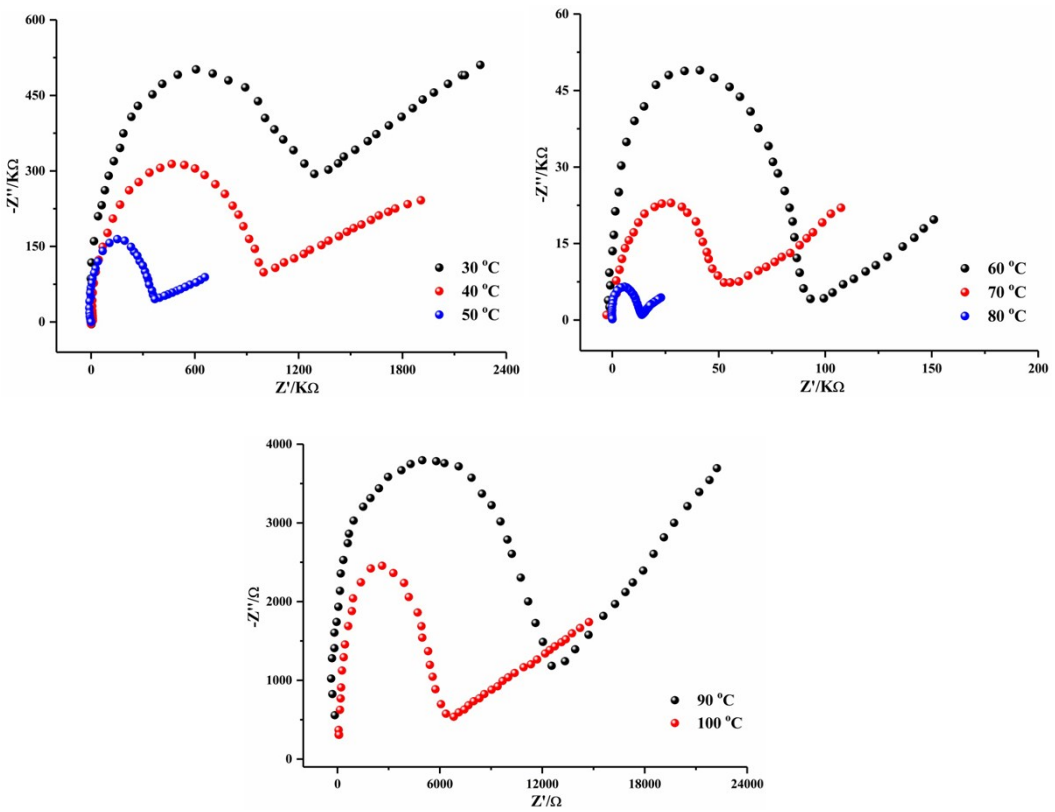


Fig. S4 Impedance spectra of **1** at 93% RH and 30-100 °C.

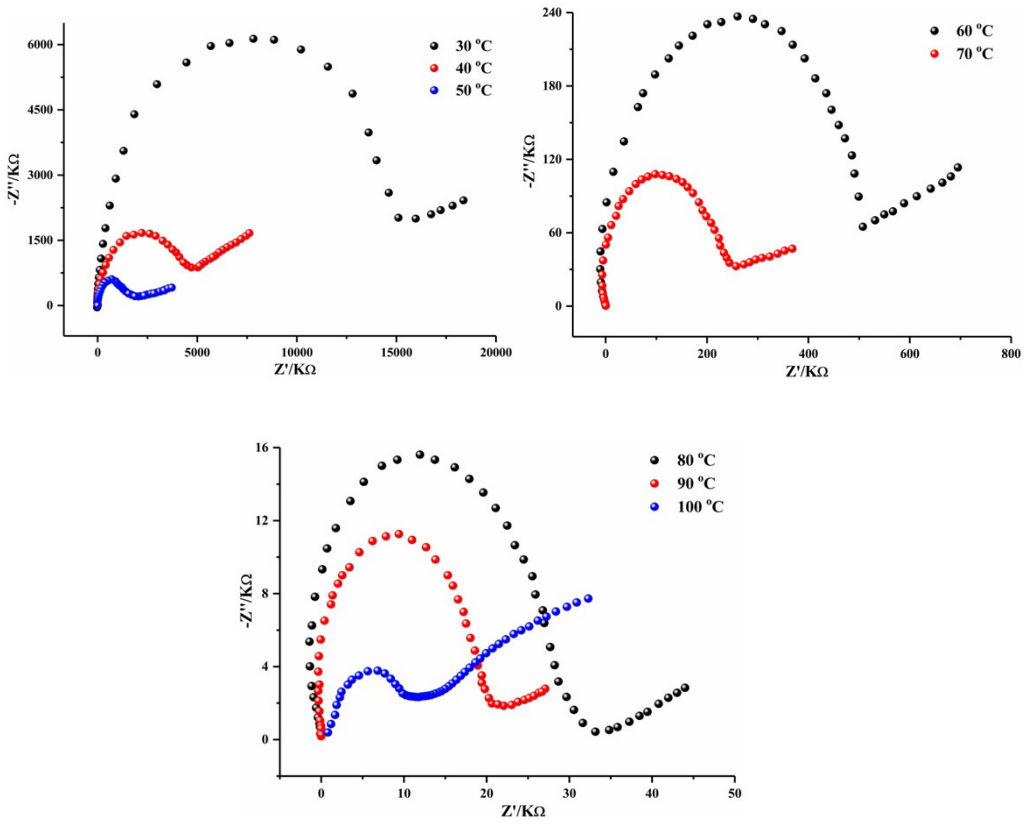


Fig. S5 Impedance spectra of **1** at 85% RH and 30-100 °C.

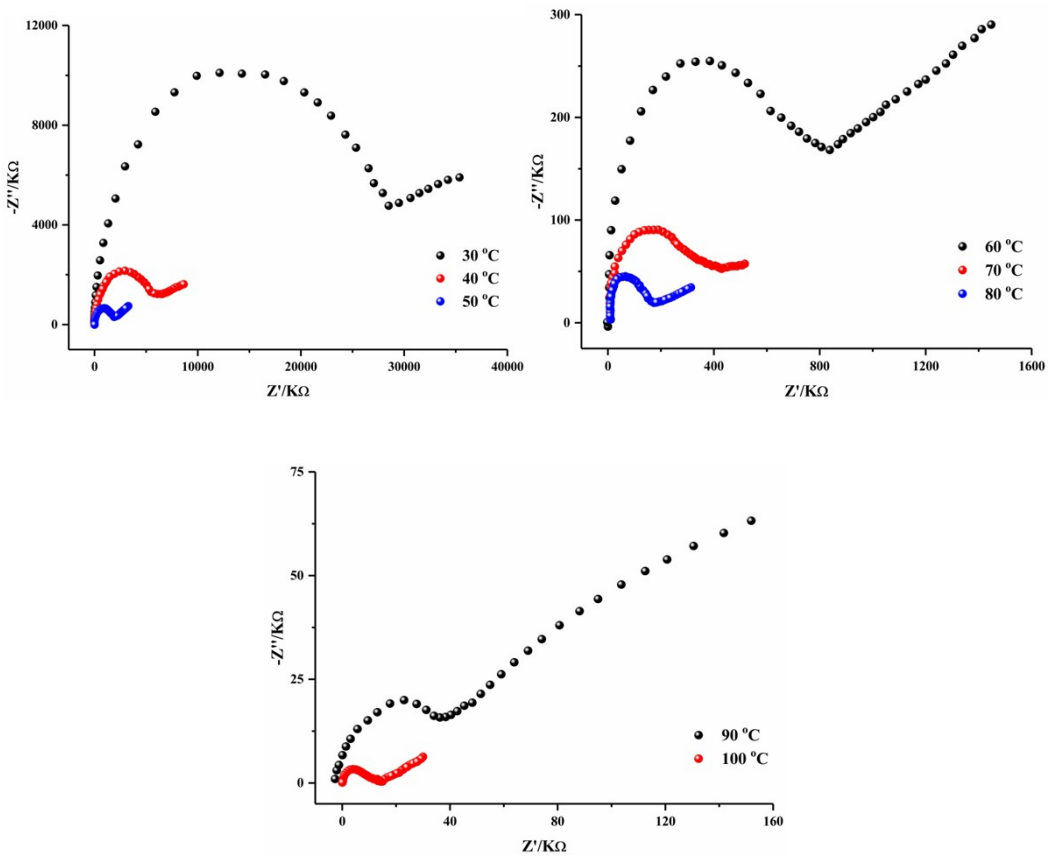


Fig. S6 Impedance spectra of **1** at 75% RH and 30-100 °C.

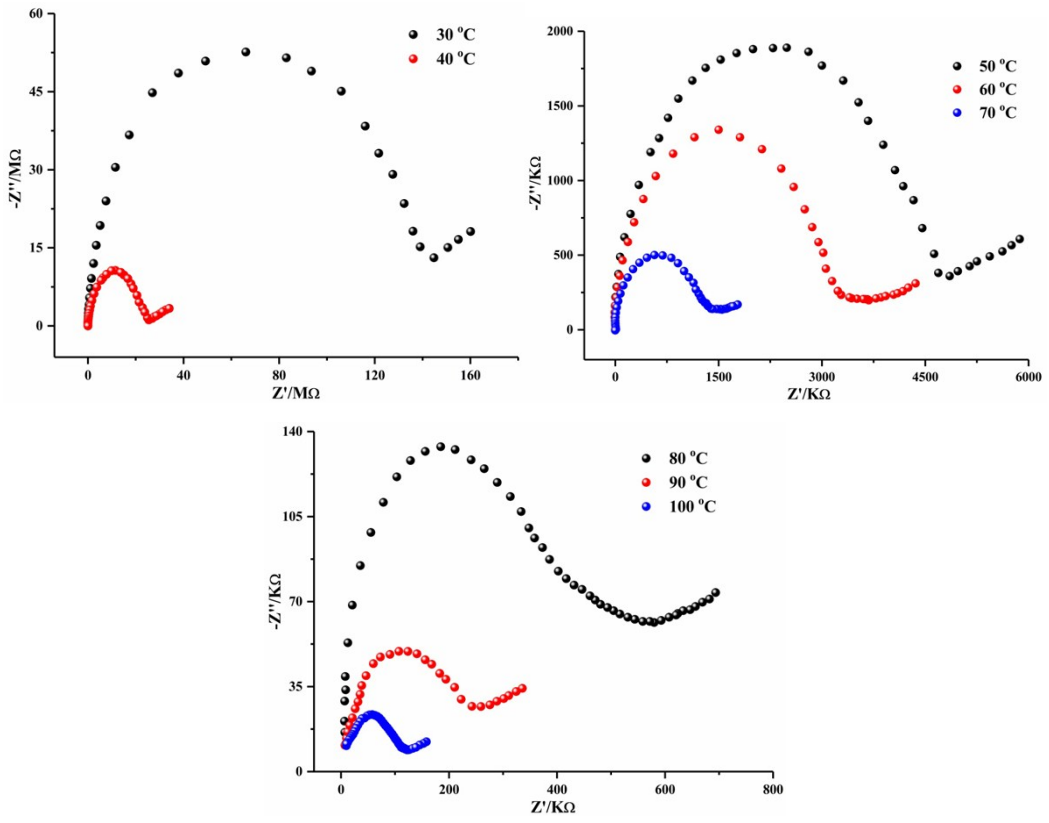


Fig. S7 Impedance spectra of **1** at 68% RH and 30-100 °C.

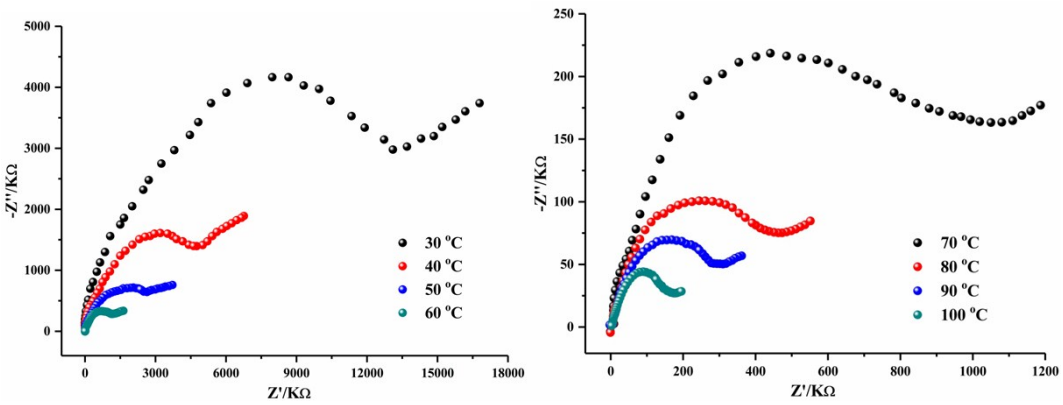


Fig. S8 Impedance spectra of **2** at 93% RH and 30-100 °C.

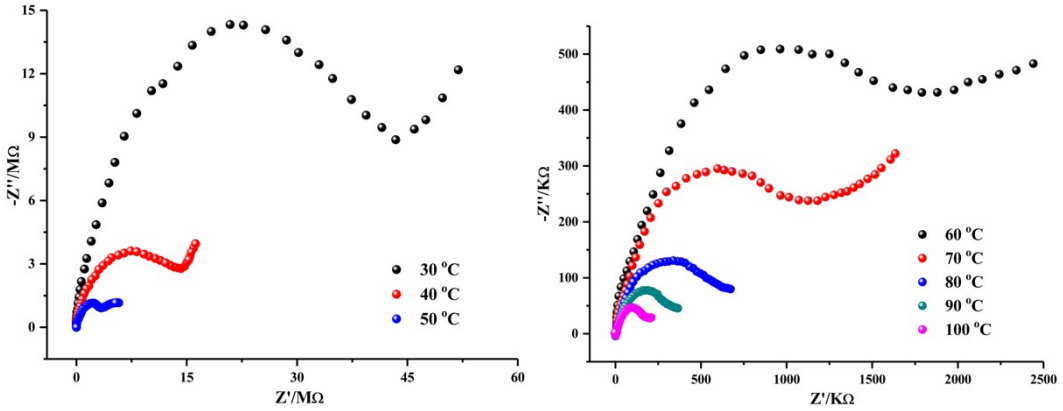


Fig. S9 Impedance spectra of **2** at 85% RH and 30-100 °C.

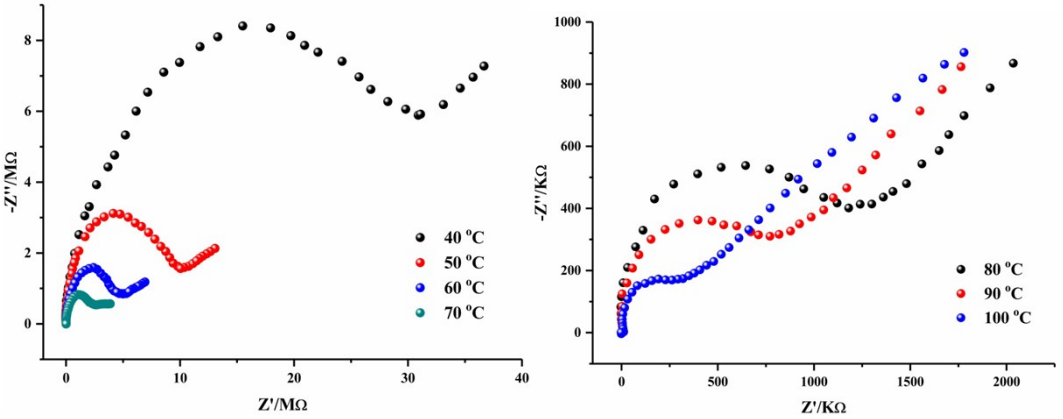


Fig. S10 Impedance spectra of **2** at 75% RH and 30-100 °C.

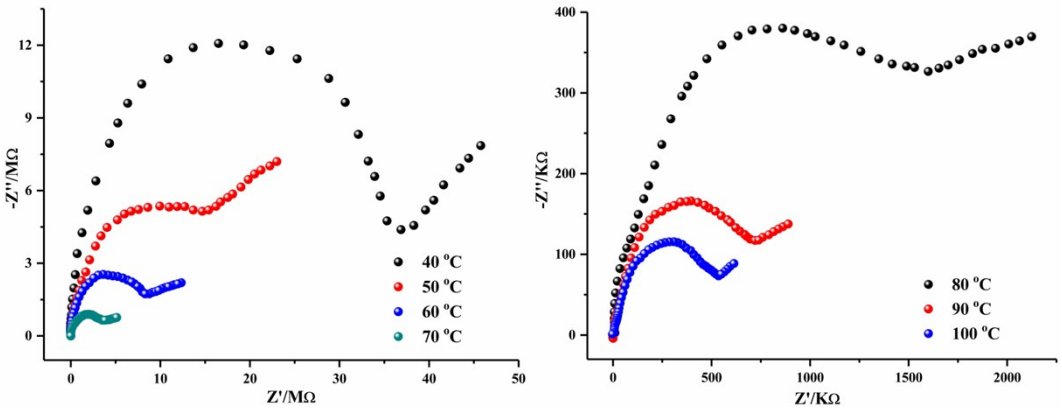


Fig. S11 Impedance spectra of **2** at 68% RH and 30-100 °C.

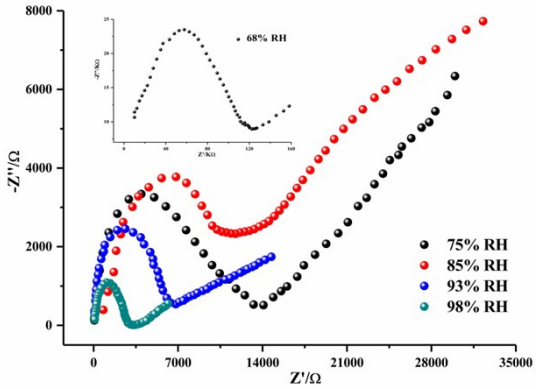
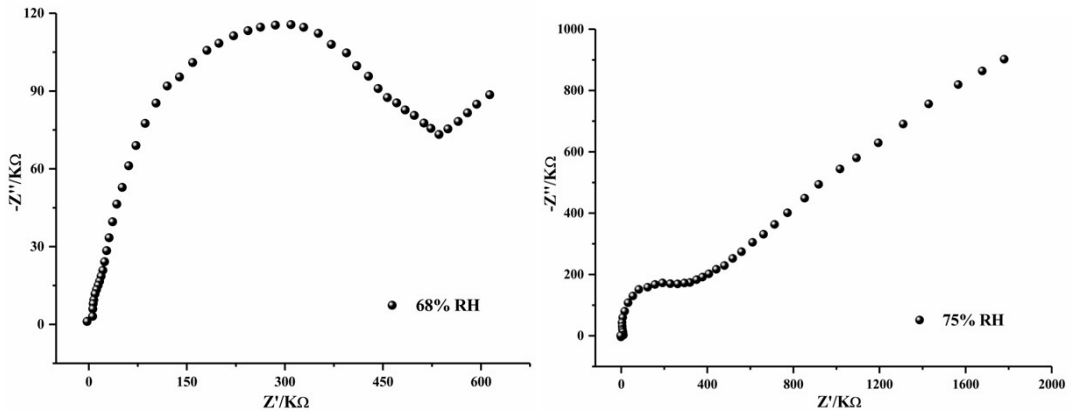


Fig. S12 Impedance spectra of **1** at 100 °C and different RHs.



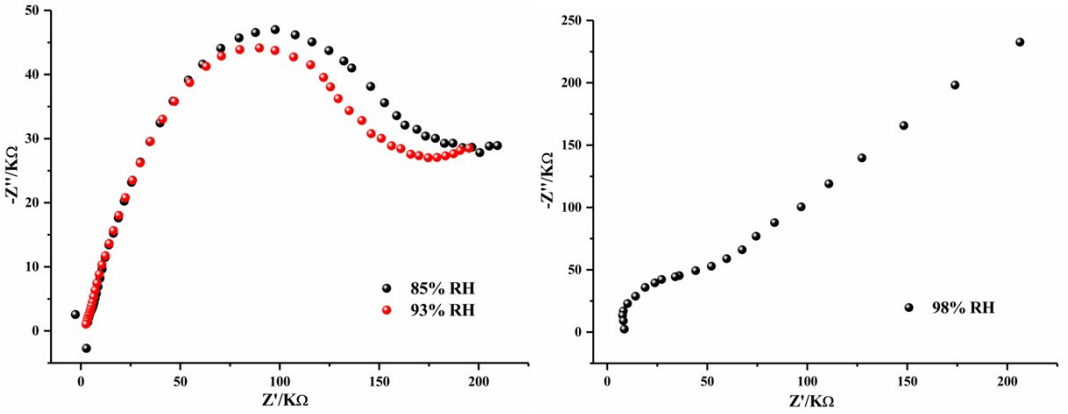
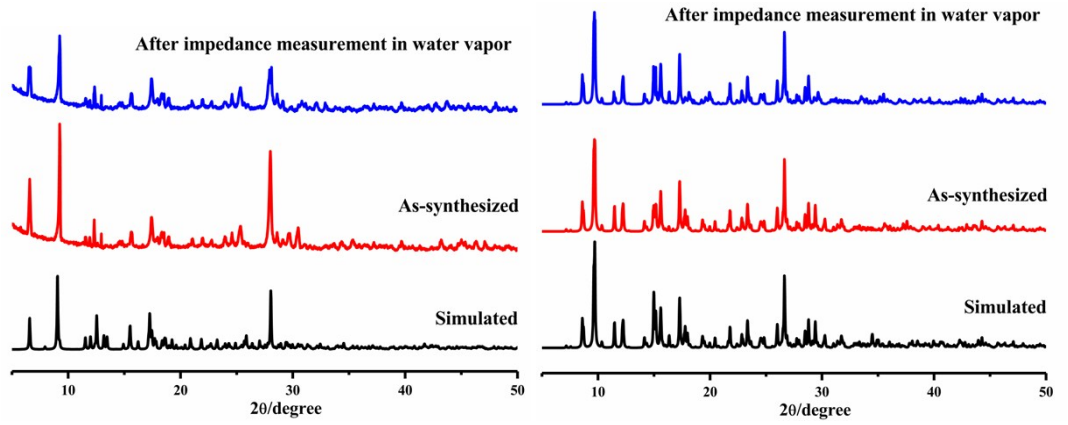


Fig. S13 Impedance spectra of **2** at 100 °C and different RHs.



(a) (b)

Fig. S14 PXRD patterns of **1** (a) and **2** (b): the simulated, as-synthesized and after electrochemical test