Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Polar layered coordination polymers incorporating triazacyclononane-triphosphonate metalloligands

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

Zn1-Cl1	2.189(3)	Zn1-O2	1.964(4)
Zn1-O2C	1.964(5)	Zn1-O2D	1.964(5)
Zn2-O1W	2.009(8)	Zn2-O3	1.901(4)
Zn2-O3F	1.901(7)	Zn2-O3E	1.901(7)
Fe1-O1	1.945(5)	Fe1-N1	2.209(5)
Fe1-O1A	1.945(5)	Fe1-N1A	2.209(5)
Fe1-O1B	1.945(4)	Fe1-N1B	2.209(5)
Cl1-Zn1-O2	116.82(15)	Cl1-Zn1-O2C	116.82(16)
Cl1-Zn1-O2D	116.82(16)	O2-Zn1-O2C	101.2(2)
O2-Zn1-O2D	101.2(2)	O2C-Zn1-O2D	101.2(2)
O1W-Zn2-O3	104.54(12)	O3-Zn2-O3F	113.9(2)
O1-Fe1-N1	83.80(18)	O1-Fe1-O1A	97.9(2)
O1-Fe1-N1A	99.1(2)	O1B-Fe1-N1A	162.60(19)
O1-Fe1-N1B	162.6(2)	O1B-Fe1-N1	162.6(2)
N1-Fe1-N1A	78.84(19)	O1B-Fe1-N1	99.1(2)
N1-Fe1-N1B	78.8(2)	O1A-Fe1-N1A	83.8(2)

Symmetry transformation used to generate equivalent atoms: A: 1-y, -1+x-y, z; B: 2-x+y, 1-x, z; C: 1-x+y, -x, z; D: -y, -1+x-y, z; E: 1-x+y, 1-x, z; F: 1-y, x-y, z.

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

Zn1-O1W	1.953(9)	Zn1-O2	1.929(8)
Zn1-O3A	1.976(8)	Zn1-O5B	1.937(9)
Co1-O1	1.922(7)	Co1-O4	1.943(8)
Co1-O7	1.931(8)	Co1-N1	1.922(10)
Co1-N2	1.953(10)	Co1-N3	1.944(10)
O1W-Zn1-O2	104.5(4)	O1W-Zn1-O3A	111.4(4)
O2-Zn1-O5B	112.5(4)	O2-Zn1-O3A	108.3(3)
O2-Zn1-O5B	112.4(4)	O3A-Zn1-O5B	107.7(4)
O1-Co1-O4	91.9(4)	O1-Co1-O7	90.1(4)
O1-Co1-N1	88.6(4)	O1-Co1-N2	177.4(4)
O1-Co1-N3	91.3(4)	O4-Co1-O7	89.7(3)
O4-Co1-N1	93.0(4)	O4-Co1-N2	89.0(4)
O4-Co1-N3	176.6(4)	O7-Co1-N1	177.1(4)
O7-Co1-N2	92.4(4)	O7-Co1-N3	89.2(4)
N1-Co1-N2	89.0(4)	N1-Co1-N3	88.3(4)
N2-Co1-N3	88.6(4)		

Symmetry transformation used to generate equivalent atoms: A: 0.5-x, y, -0.5+z; B: 0.5-x, -1+y, -0.5+z.

Table S3. Selected Bond Valence Sum (BSV) calculations by using Expo software (version 1.19.09) for **1** and **2**.

1		**2**	
Atom	**BSV**	**Atom**	**BSV**
Fe1	3.04	Co1	3.27
Zn1	2.10	Zn1	2.07
Zn2	2.20	P1	3.83
P1	3.85	P2	3.95
Cl1	0.83	P3	3.91
O1	1.94	O1	2.06
O2	2.06	O2	2.11
O3	2.07	O3	1.89
		O4	1.73
		O5	2.13
		O6	1.83
		O7	1.98
		O8	2.21
		O9	2.08

Table S4. Crystallographic data of randomly selected crystals of **1**. (The structure of D has been deposited in CCDC database)

	A	**B**	**C**	**D**
Temperature (K)	193(2)	193(2)	193(2)	193(2)
Crystal size (mm)	0.22×0.10×0.10	0.30×0.14×0.14	0.22×0.12×0.10	0.25×0.12×0.12
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal
Space group	$P6_3$	$P6_3$	$P6_3$	$P6_3$
a (Å)	8.9326(2)	8.9325(2)	8.9385(12)	8.9323(4)
b (Å)	8.9326(2)	8.9325(2)	8.9385(12)	8.9323(4)
c (Å)	13.2641(6)	13.2650(6)	13.2618(17)	13.2617(7)
V (Å^3)	916.57(7)	916.61(7)	917.6(3)	916.34(11)
Z	2	2	2	2
D_c (g cm^{-3})	2.338	2.338	2.336	2.339
μ (mm^{-1})	3.844	3.844	3.840	3.845
F(000)	646	646	646	646
R_{int}	0.045	0.040	0.070	0.044
GOF	1.01	1.01	1.00	1.01
R_1, wR_2 [$I>2\sigma(I)$]	0.0283, 0.0741	0.0271, 0.0670	0.0529, 0.1297	0.0284, 0.0679
R_1, wR_2 (all data)	0.0299, 0.0753	0.0290, 0.0682	0.0567, 0.1325	0.0300, 0.0688
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	1.16, -0.75	0.77, -0.59	1.45, -0.87	0.94, -0.67
Flack	0.07(3)	0.05(3)	0.07(6)	0.05(3)
Configurations of Fe(notp)$^{3-}$	Δ	Δ	Λ	Δ

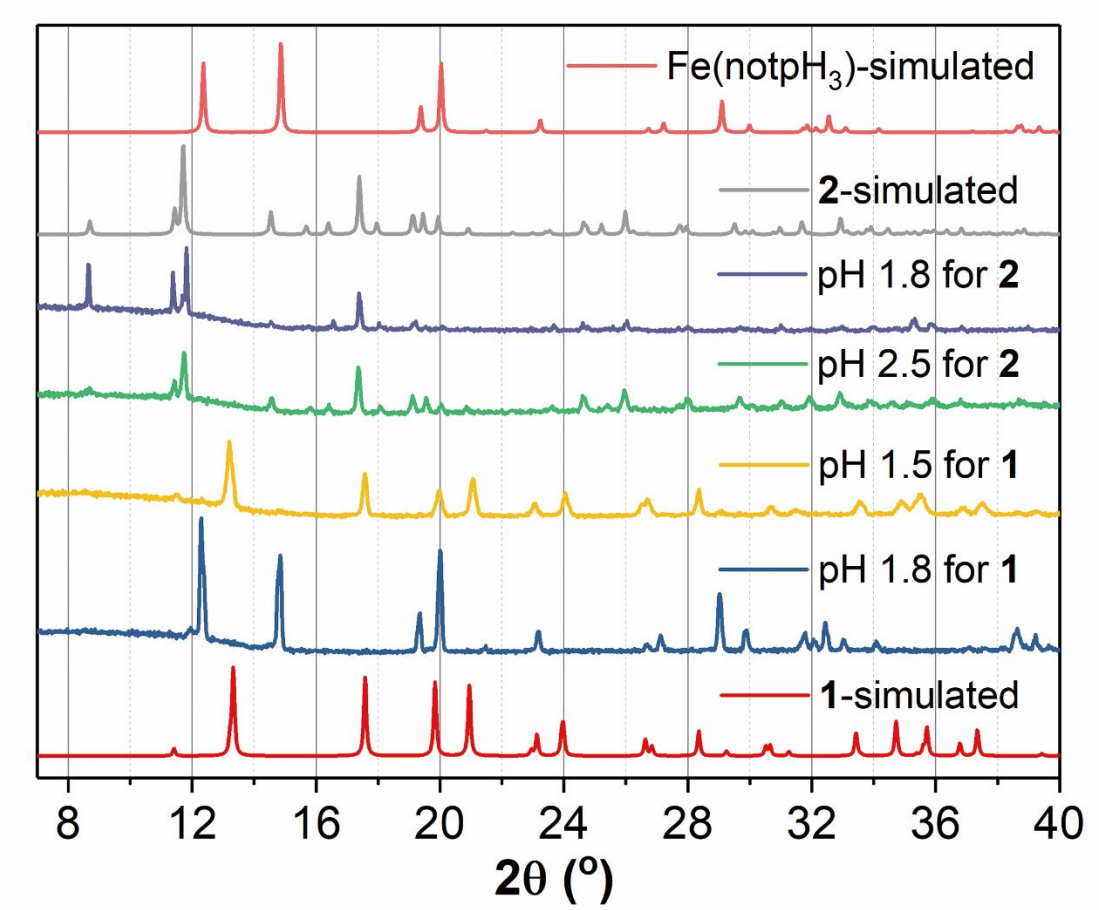

Figure S1. The PXRD patterns for products **1** and **2** at various pH conditions.

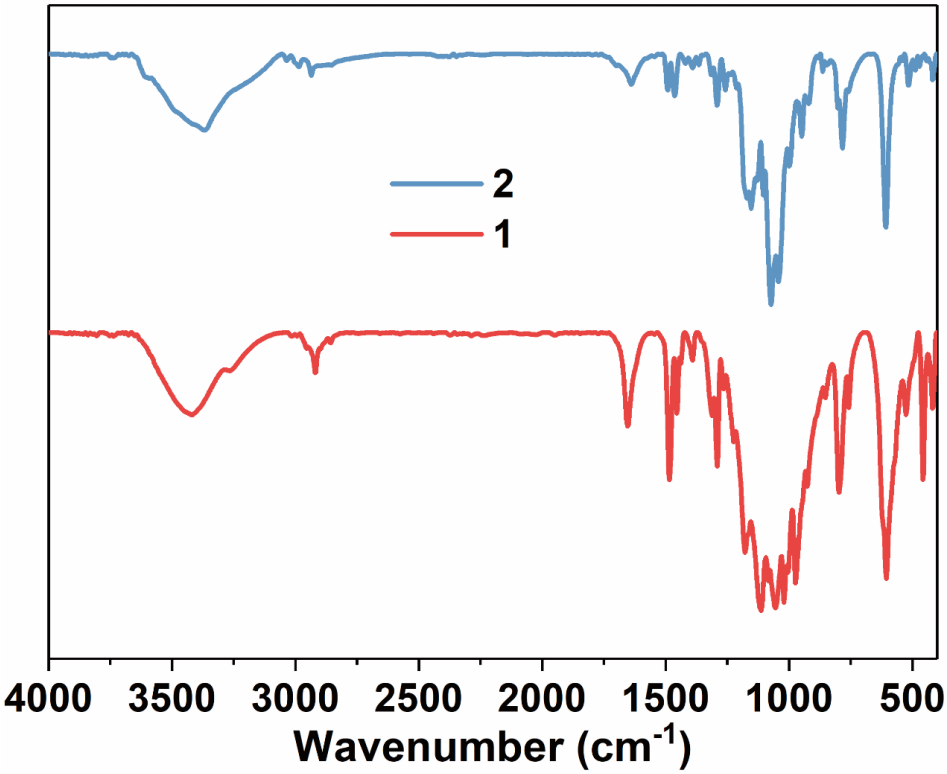

Figure S2. The IR spectra for compounds **1** and **2**.

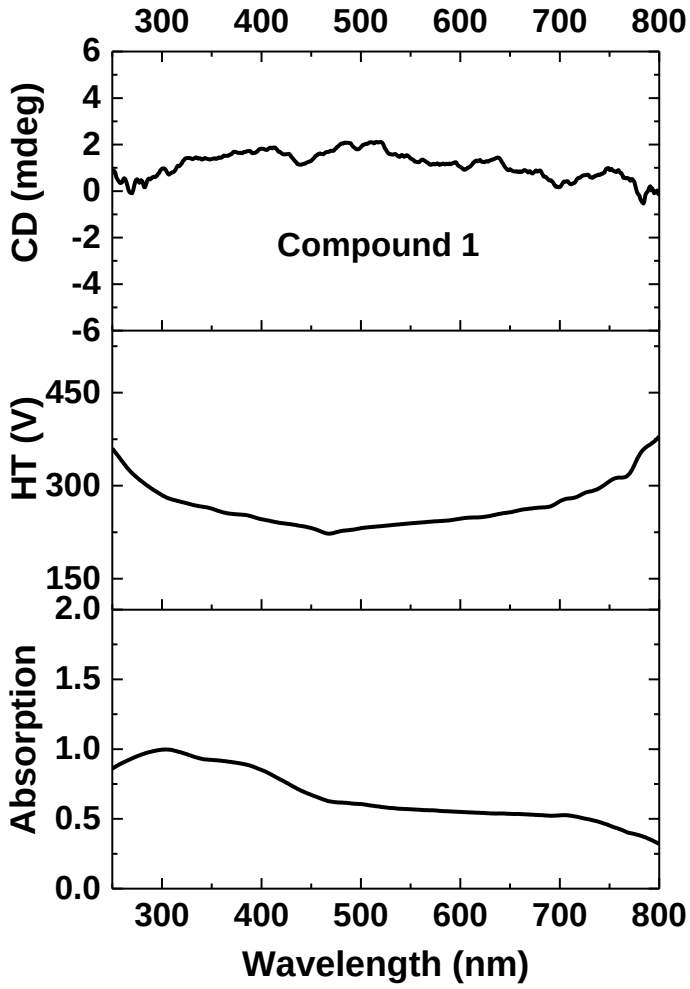

Figure S3. Solid-state circular dichroism spectra for compound 1.

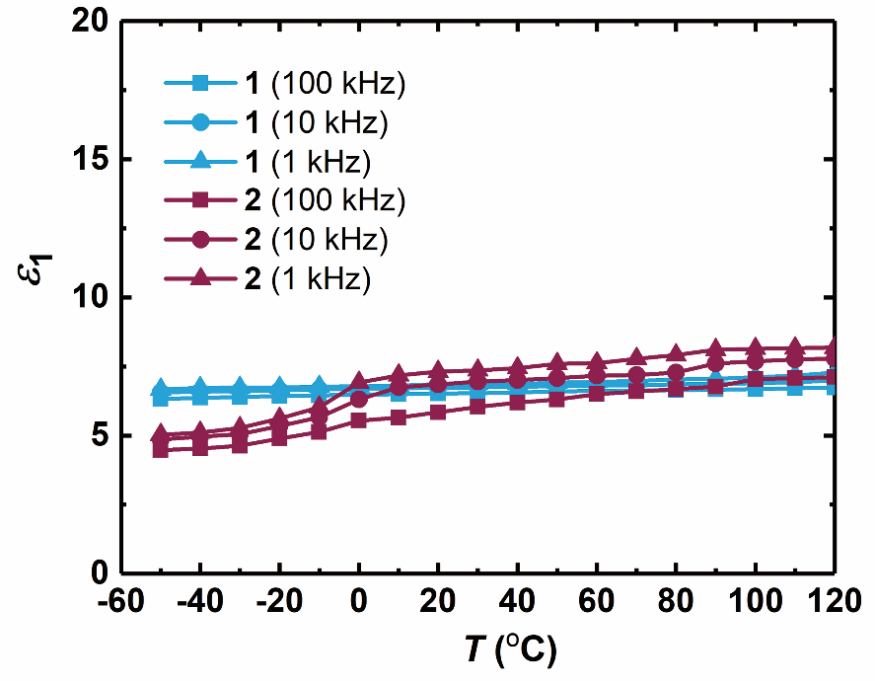

Figure S4. Temperature dependent real part permittivity (ε_1) of pellets **1** and **2**.

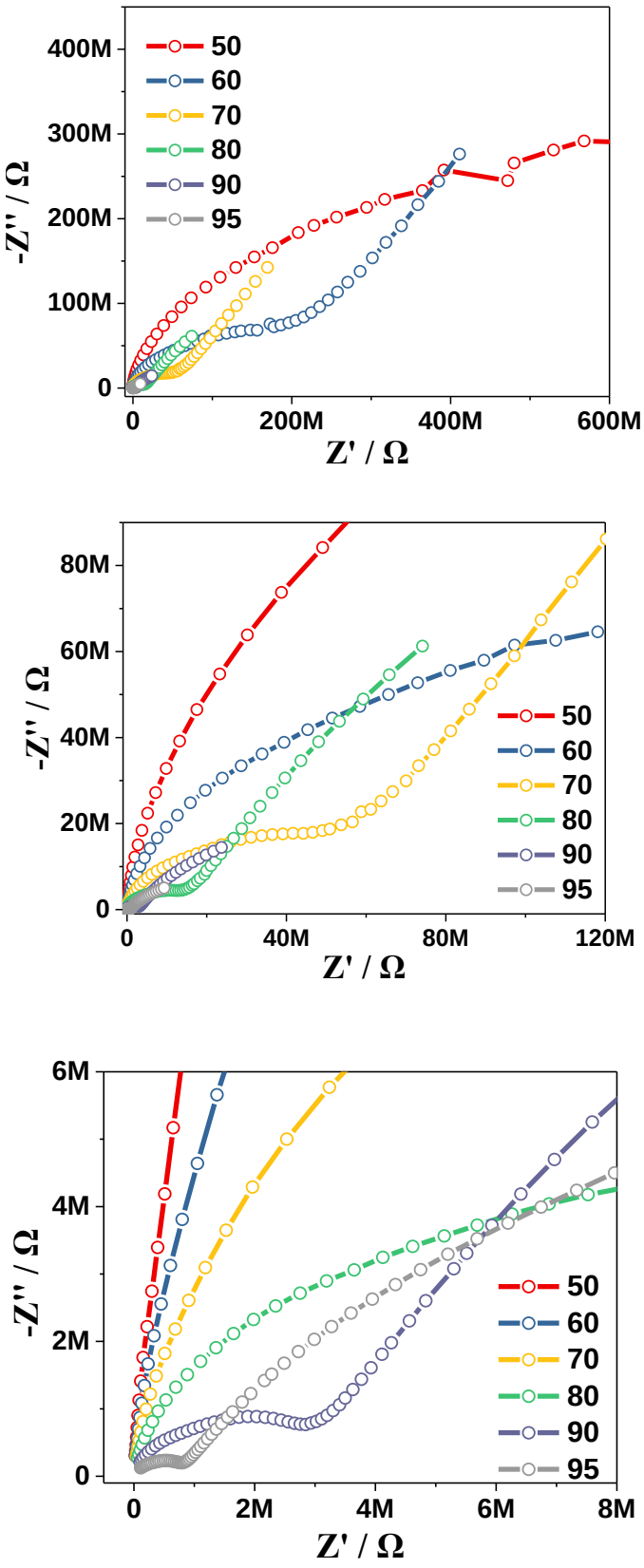

Figure S5. Nyquist plots for the pellet of **1** at 25 ˚C and various RH. Up: RH increases from 40 to 95%; Middle and Bottom: The enlarged view of graph.

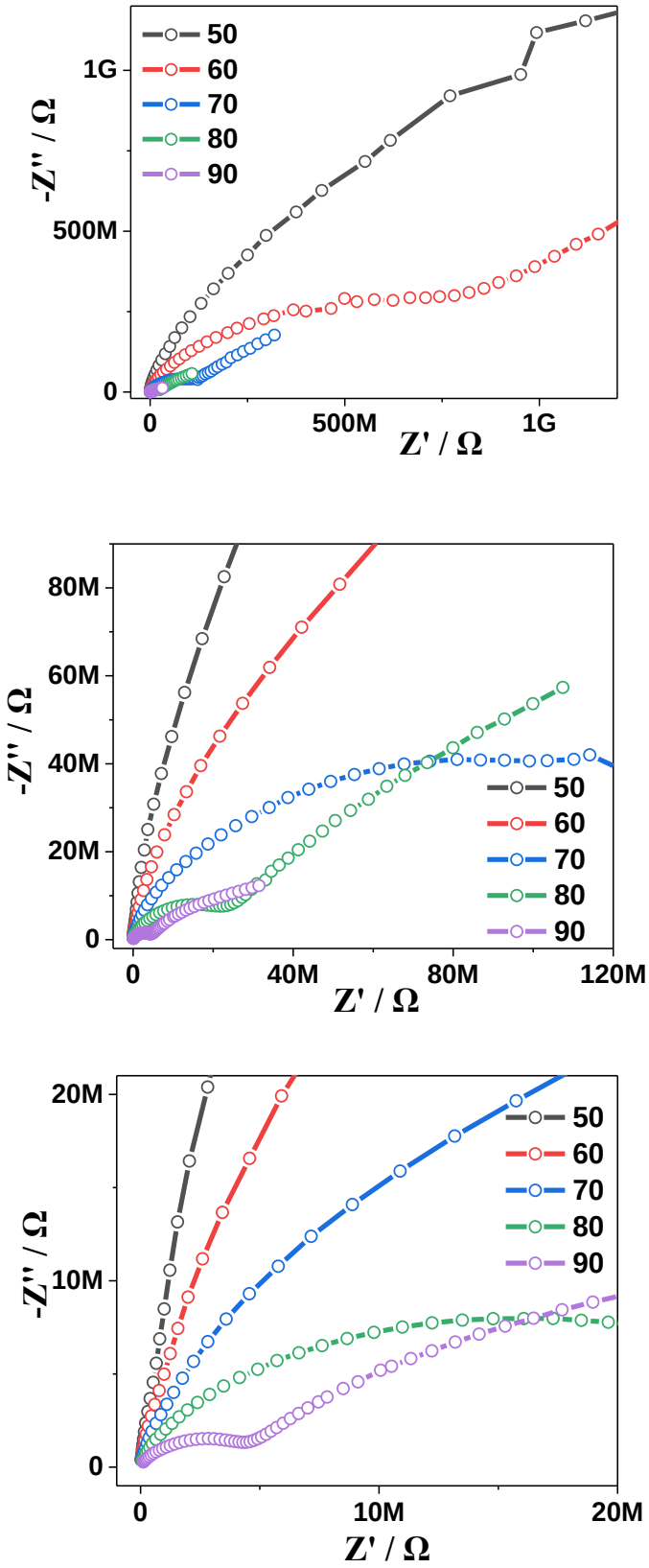

Figure S6. Nyquist plots for the pellet of **1** at 25 ˚C and various RH. Up: RH decreases from 95 to 50%; Middle and Bottom: The enlarged view of graph.

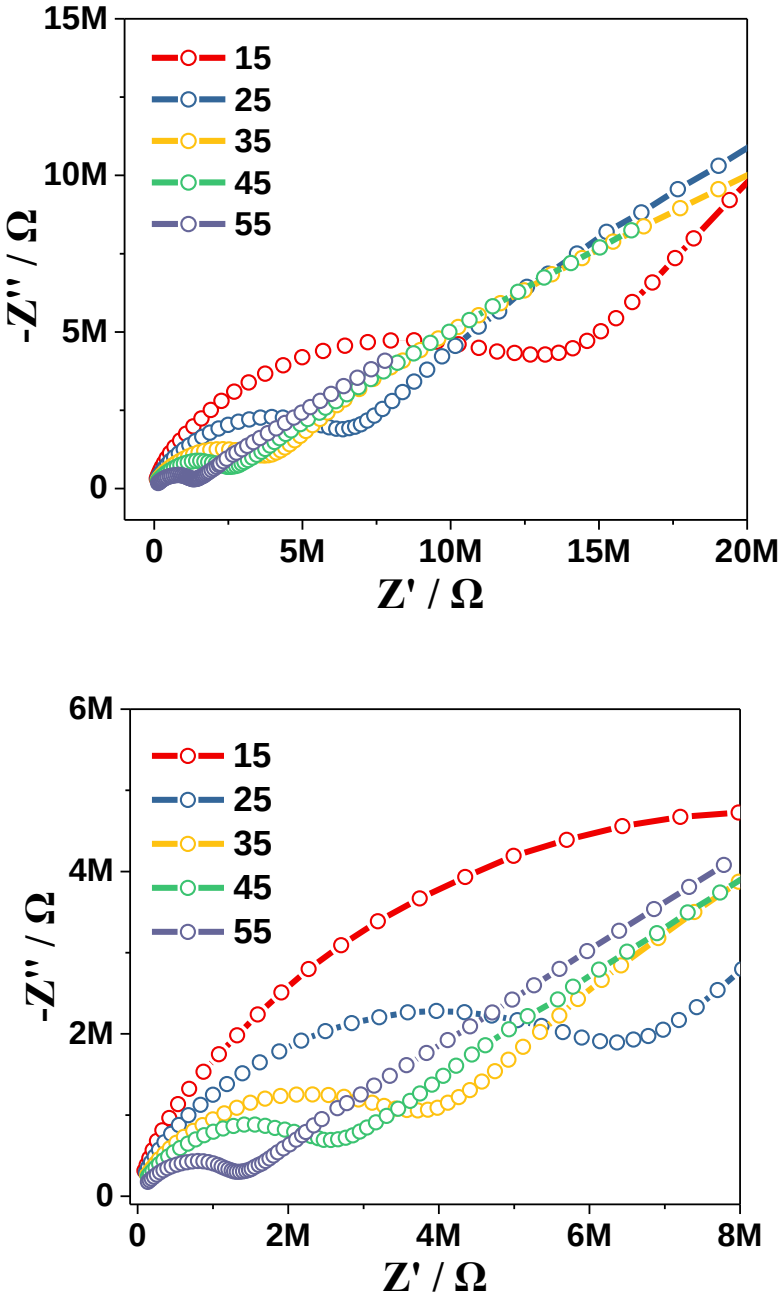

Figure S7. Nyquist plots for the pellet of **1** at 95% RH and various temperatures. Bottom: The enlarged view of graph.

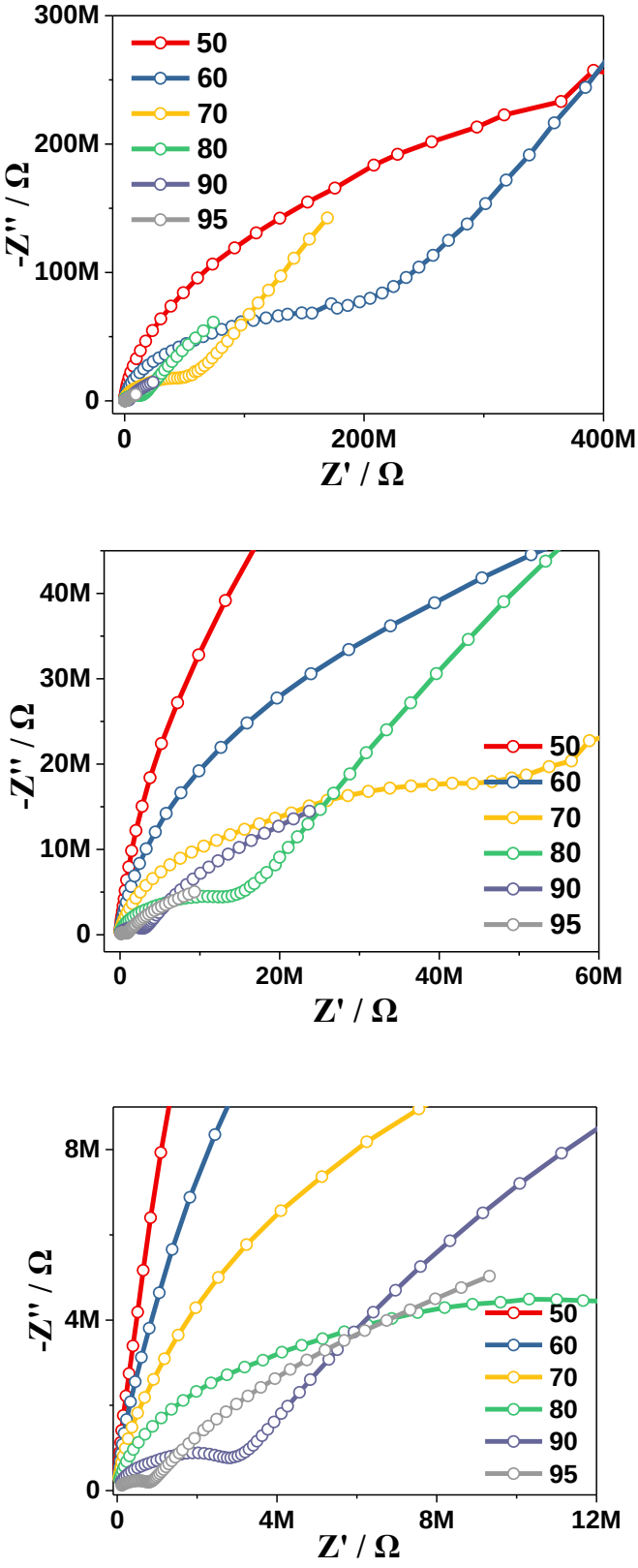

Figure S8. Nyquist plots for the pellet of **2** at 25 ˚C and various RH. Up: RH increases from 40 to 95%; Middle and Bottom: The enlarged view of graph.

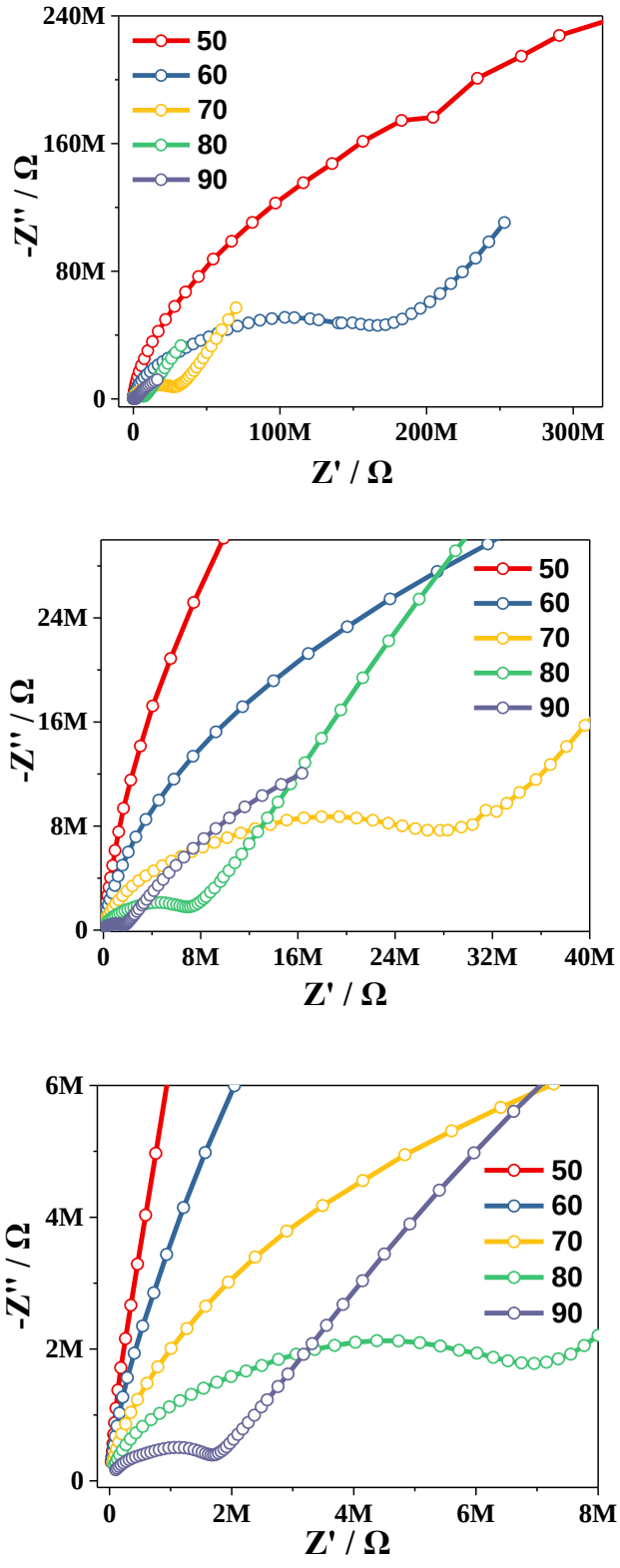

Figure S9. Nyquist plots for the pellet of **2** at 25 ˚C and various RH. Up: RH decreases from 95 to 50%; Middle and Bottom: The enlarged view of graph.

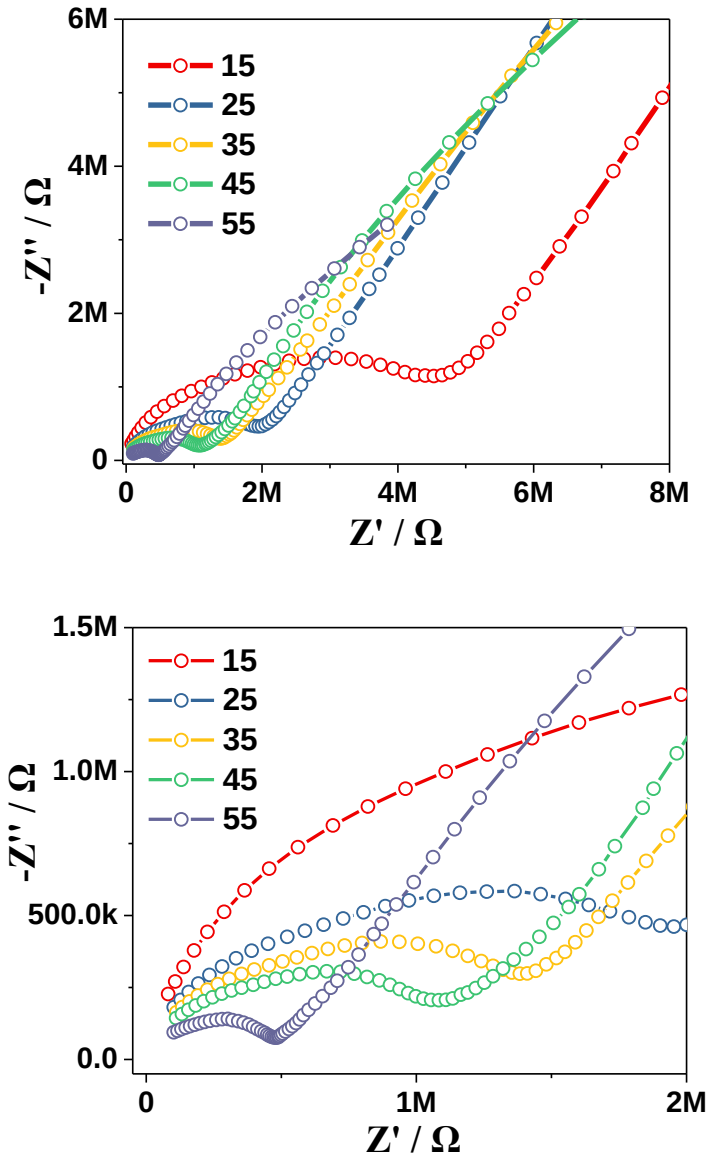

Figure S10. Nyquist plots for the pellet of **2** at 95% RH and various temperatures. Bottom: The enlarged view of graph.