Stabilization of Cyclic Water Tetramer and Dimer in the Crystal Host of 2D Coordination Networks: Electrical Conductivity and Dielectric Studies

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Supporting Information

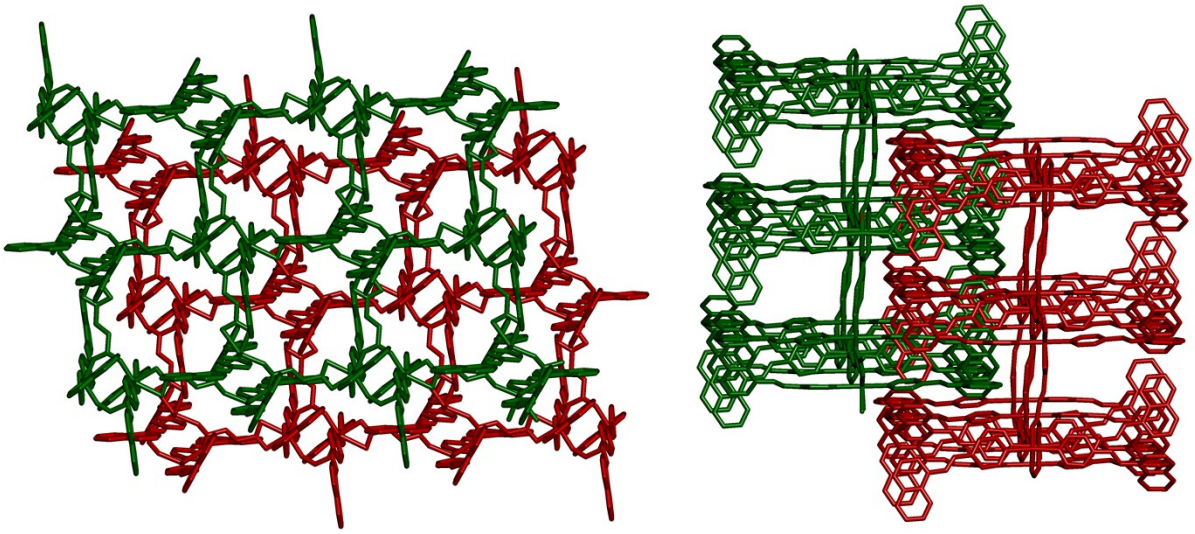

Fig. S1 Side and top views of the 3D interdigitated network of **1**. The hydrogen atoms and solvent molecules are not shown for the clarity.

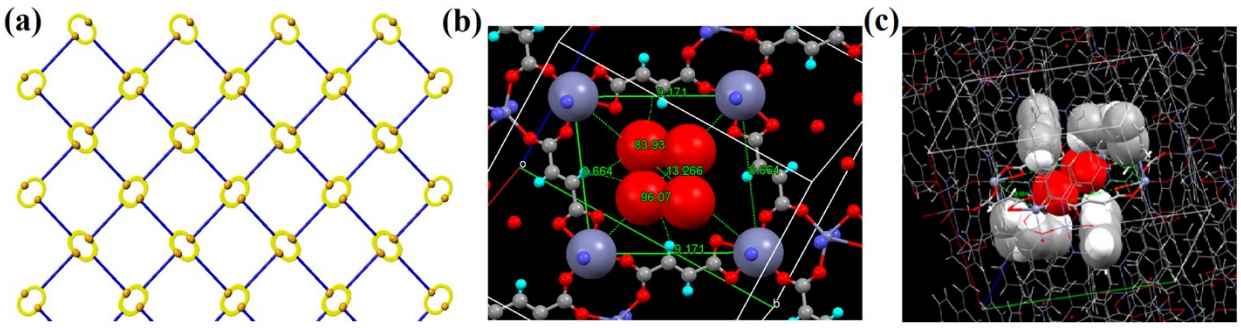

Fig. S2 (a) The topology of the 2D layer of **1** (b) Water tetramer bound to the cage (c) The hydrophobic cavity provided by 4-pvp molecules (Tip of molecules are shown in CPK model).

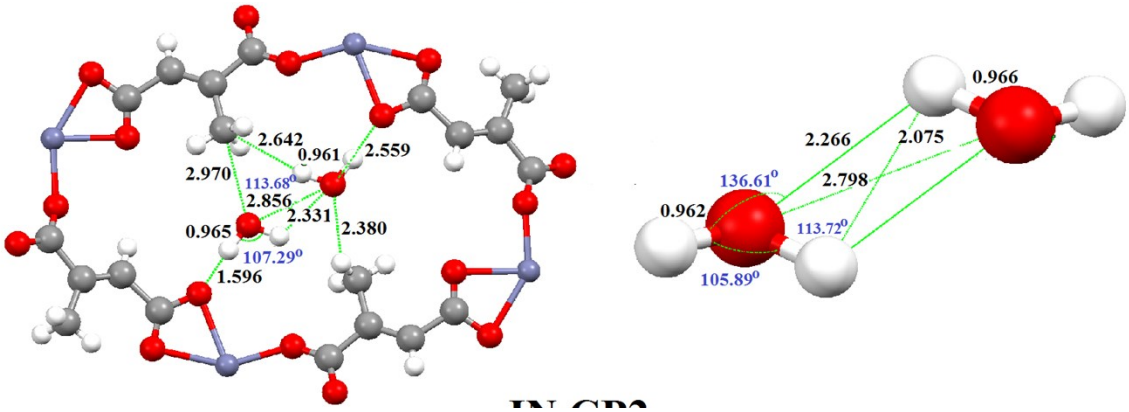

Fig. S3 The optimized geometry water dimer in the cavity of **2** and the corresponding optimized geometry of the free ring dimer.

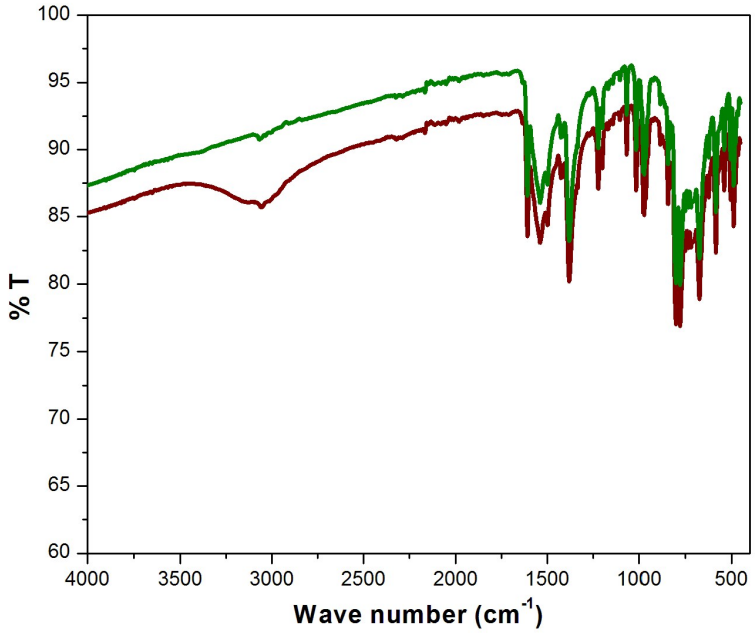

Fig. S4 IR Spectra of as-synthesized **1** (wine) and dehydrated **1** (olive).

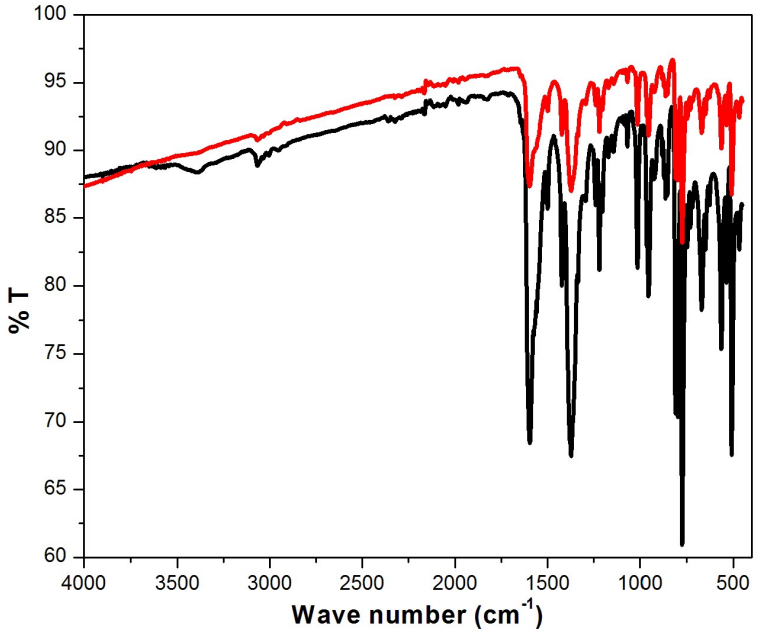

Fig. S5 IR Spectra of as-synthesized **2** (black) and dehydrated **2** (red).

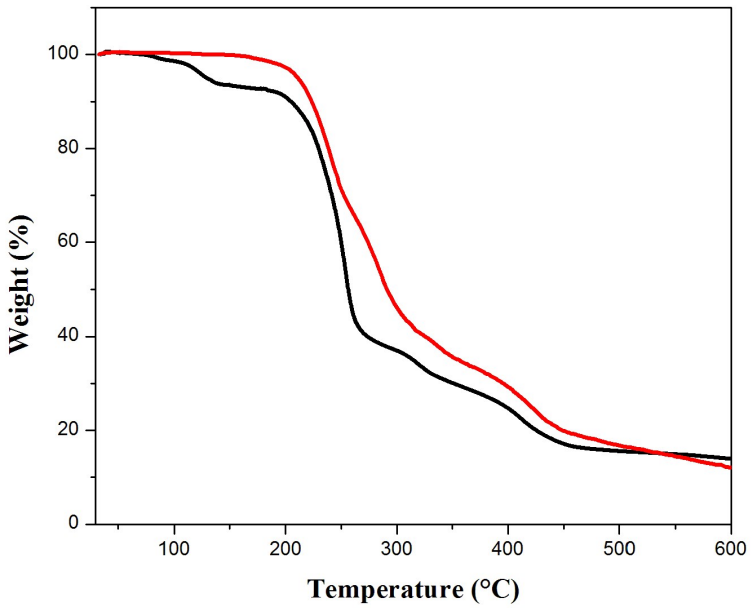

Fig. S6 TGA plots of as-synthesized **1** (black) and dehydrated **1** (red).

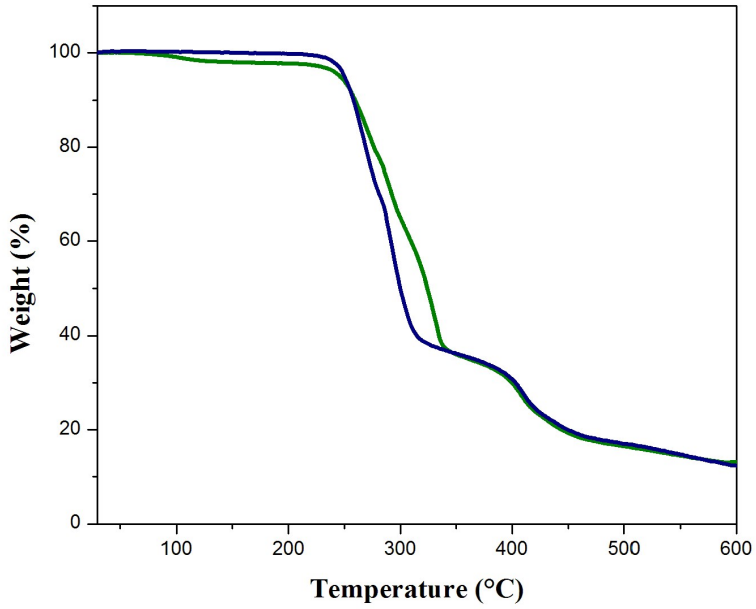

Fig. S7 TGA plots of as-synthesized **2** (blue) and dehydrated **2** (green).

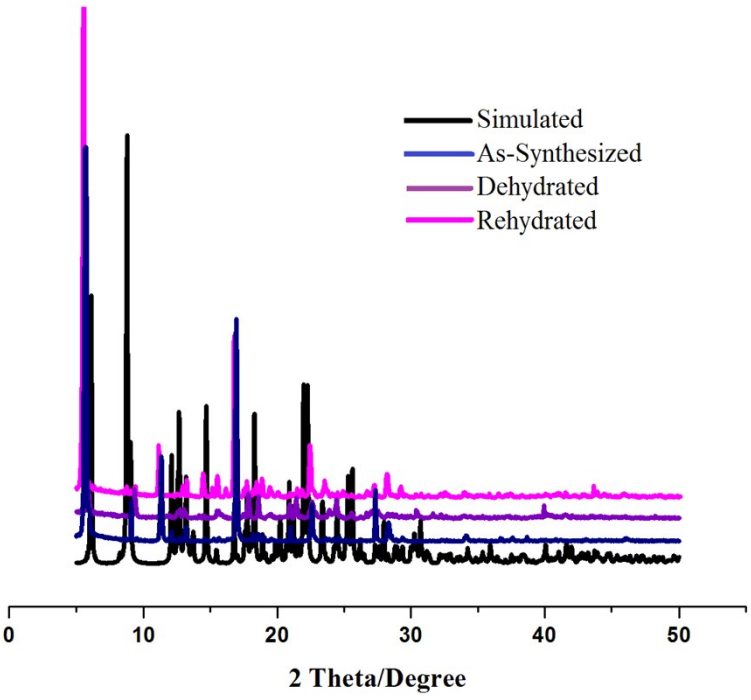

Fig. S8 Powder X-ray diffraction patterns of simulated **1** (black), as-synthesized **1** (green), dehydrated **1** (pink), rehydrated **1** (blue).

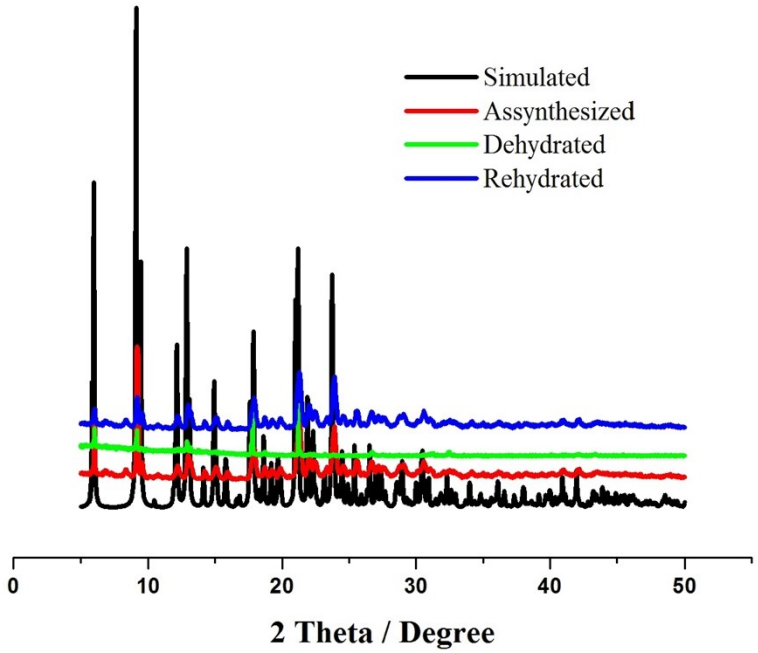

Fig. S9 Powder X-ray diffraction patterns of simulated **1** (black), as-synthesized **1** (red), dehydrated **1** (green), rehydrated **1** (blue).

Table S1. Crystal data and refinement parameters for compound **1**

Formula	$C_{38}H_{32}N_2O_6Zn$ (**1**)	$C_{39}H_{32}N_2O_5Zn$ (**2**)
fw	678.05	673.44
crystsyst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	15.7865(16)	15.7596(17)
b (Å)	15.7979(16)	16.9112(19)
c (Å)	14.0932(15)	12.5653(14)
α(deg)	90	90
β(deg)	113.559(3)	109.196(3)
γ (deg)	90	90
V (Å^3)	3221.8(6)	3162.6(6)
Z	4	4
D_{calcd}(g/cm^3)	1.398	1.389
μ(mm^{-1})	1.477	0.823

λ(Å)	0.71073	0.71073
data[$I > 2\sigma(I)$]/params	5248/436	5555/428
GOF on F^2	1.063	1.071
final R indices[$I > 2\sigma(I)$][a,b]	$R1 = 0.0593$ $wR2 = 0.1322$	$R1 = 0.0660$ $wR2 = 0.1672$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths and bond angles in **1**

Zn1-O2	2.005(3)	O3-Zn1-O4	58.56(10)
Zn1-O1	2.006(3)	N1-Zn1-O4	88.82(11)
Zn-O3	2.103(3)	N2-Zn1-O4	87.32(11)
Zn1-N1	2.152(3)	O2-Zn1-C40)	118.86(12
Zn1-N2	2.167(3)	O1-Zn1-C40	116.80(12)
Zn1-O4	2.382(3)	O3-Zn1-C40	29.42(12)
O2-Zn1-O1	124.10(11)	N1-Zn1-C40	89.87(12)
O2-Zn1-O3	89.46(11)	O 2-Zn1-C40	88.90(12)
O1-Zn1-O3	145.79(11)	O4-Zn1-C40	29.17(11)
O2-Zn1-N1	91.19(12)	C40-O3-Zn1	95.9(2)
O1-Zn1-N1	84.02(12)	C40-O4-Zn1	83.5(2)
O3-Zn1-N1	89.30(11)	C37-O2-Zn1	139.0(2)
O2-Zn1-N2	94.42(12)	C37-O1-Zn1	138.1(3)

O1-Zn1-N2	91.42(12)	C24-N2-C20	117.2(3)
O3-Zn1-N2	92.44(11)	C24-N2-Zn1	121.4(3)
N1-Zn1-N2	174.14(13)	C20-N2-Zn1	121.4(3)
O2-Zn1-O4	148.02(10)	C3-N1-C7	117.0(3)
O1-Zn1-O4	87.71(10)	C3-N1-Zn1	124.9(3)

Symmetry Code: a = 1-x, 1/2+y, 3/2-z;b = 1-x, -y, 1-z; c = x, 1/2-y, -1/2+z; d = x, 1/2-y, 1/2+z

Table S3. Selected bond lengths and bond angles in **2**

Zn01 - O1	2.024(3)	O1 - Zn01 - O3_b	149.7(2)
Zn01 - O4_b	2.302(7)	N1 - Zn01 - N2	178.91(14)
Zn01 - N1	2.179(5)	N1 - Zn01 - O2_c	86.69(14)
Zn01 - O2_c	2.035(4)	N2 - Zn01 - O2_c	94.21(14)
Zn01 - N2	2.174(5)	O4_b - Zn01 - O2_c	146.27(17)
Zn01 - O3_b	2.225(7)	C39- O3 - Zn01_a	92.1(5)
O1 - Zn01 - N1	87.96(13)	Zn01 - N1 - C5	118.9(3)
O1 - Zn01 - O4_b	93.10(17)	Zn01 - N1 - C1	125.3(3)
N1 - Zn01 - O3_b	89.5(2)	C35- O2 - Zn01_c	146.8(3)
N2 - Zn01 - O3_b	91.2(2)	C39- O4 - Zn01_a	86.4(6)
O3_b- Zn01 - O4_b	56.7(2)	Zn01 - O1 - C35	130.7(3)
O1 - Zn01 - N2	91.05(13)	O3_b-Zn01-O1-C35	145.4(5)

O1 - Zn01 - O2_c	120.31(14)	O4_b-Zn01-O1-C35	140.6(4)
N1- Zn01 - O4_b	90.3(2)	N2-Zn01-O1-C35	51.2(4)
N2- Zn01 - O4_b	89.3(2)	O1-Zn01-N1-C5	174.8(4)
O3_b- Zn01 - O2_c	89.6(2)	O4_b-Zn01 -N1-C1	88.0(4)
O2_c-Zn01-N2 -C18	147.6(4)	O3_b-Zn01-N1-C1	144.8(4)

Symmetry Code: a = 1-x, -1/2+y, 3/2-z; b = 1-x, 1/2+y, 3/2-z; c = 1-x, 1-y, 1-z; d = x, 1/2-y, -1/2+z

Binding Energy Calculations:

Binding Energy Calculations with BSSE for tetramer in 1:

a. **Binding Energy of water in the crystal cavity**

Energy of Cavity + Water = - 9241.8351418 a.u.

Energy of water = - 305.8804259 a.u.

Energy of cavity = -8935.9330248 a.u.

Hence, Binding Energy = -0.0216911 a.u. = -13.6113626 kcal/mol

BSSE error = 02.4110827 kcal/mol

Corrected Binding Energy = -11.2002799 kcal/mol

b. **Binding Energy of water molecules in the water tetramer of the crystal cavity**

Energy of cavity water tetramer = -305.8804259 a.u.

Total energy of four individual water = (-76.4579984 -76.4581029 -76.4581013 -76.4579962) = -305.8321988

Hence, Binding energy= -0.0482271 a.u. = -30.2629393 kcal/mol

BSSE error = 03.2835336 kcal/mol

Corrected Binding Energy = -26.9794057 kcal/mol

c. Binding Energy of water molecules in the optimized water tetramer

Energy of cavity water tetramer = -305.8815081 a.u.

Total energy of four individual water = (-76.4580699 – 76.4580582 -76.4580699 – 76.4580582) a.u. = -305.8322562 a.u.

Hence, Binding Energy = -0.0492519 a.u. = -30.92551919469 kcal/mol

BSSE error = 03.4375898 kcal/mol

Corrected Binding Energy = -27.4879294 kcal/mol

Binding Energy Calculations with BSSE error for ring dimer in 2:

a. Binding Energy of water in the crystal cavity

Energy of Cavity + Water = -9246.0228706 a.u.

Energy of water = -152.9239036 a.u.

Energy of cavity = -9093.0950119 a.u.

Hence, Binding Energy = 0.0039551 a.u. = -2.481861241 kcal/mol

BSSE error = 1.944350087 kcal/mol

Corrected Binding Energy = -0.53751115441 kcal/mol

b. Binding Energy of water molecules in the water dimer of the crystal cavity

Energy of cavity water dimer = -152.9239036 a.u.

Total energy of two individual water = (-76.458402 + -76.458402) a.u. = -152.916804 a.u.

Hence, Binding Energy = -0.0070996 a.u. = - 4.455063606 kcal/mol

BSSE error = 0.333904819 kcal/mol

Corrected Binding Energy = - 4.1211588 kcal/mol

c. Binding Energy of water molecules in the optimized water dimer

Energy of optimized water dimer = - 152.9242714 a.u.

Total energy of two individual water =(-76.4585002 + -76.4585002) a.u. = -152.9170004 a.u.

Hence, Binding energy= -0.007271 a.u. = -4.562618666 kcal/mol

BSSE error = 0.40031809 kcal/mol

Corrected Binding Energy = -4.162300576 kcal/mol

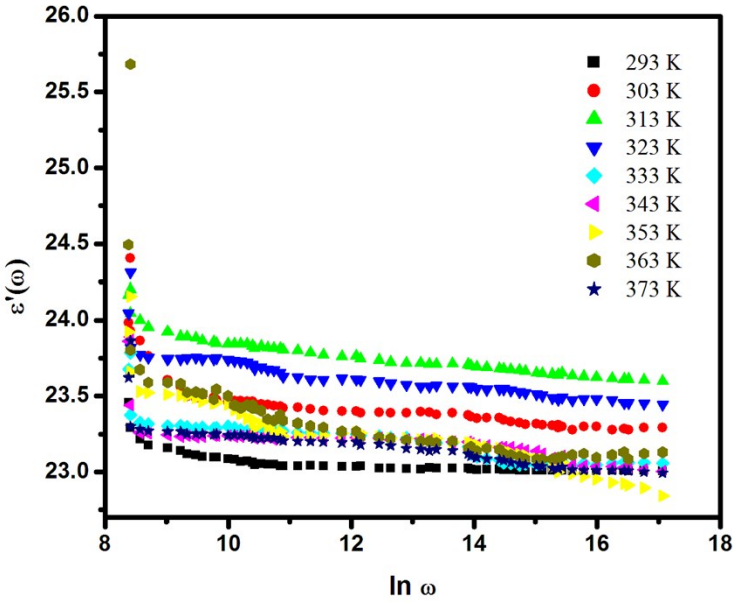

Fig. S10 ε′(ω) vs logω plot of **1** at various temperatures.

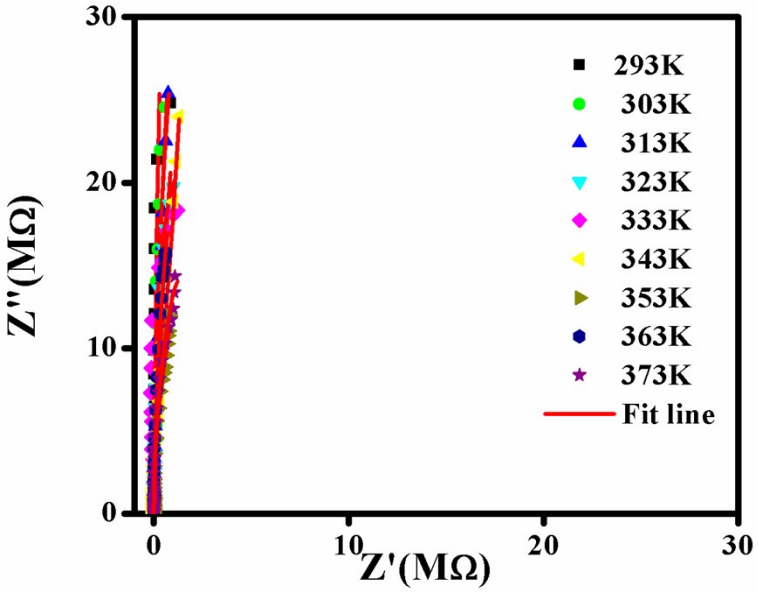

Fig. S11 Cole-Cole plots of **2** at various temperatures.

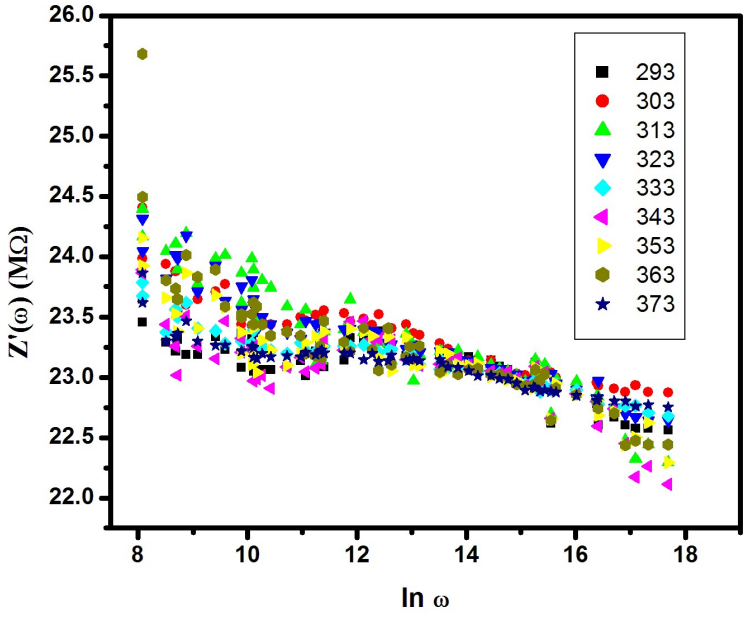

Fig. S12 Z′(ω) vs logω plot of **2**.

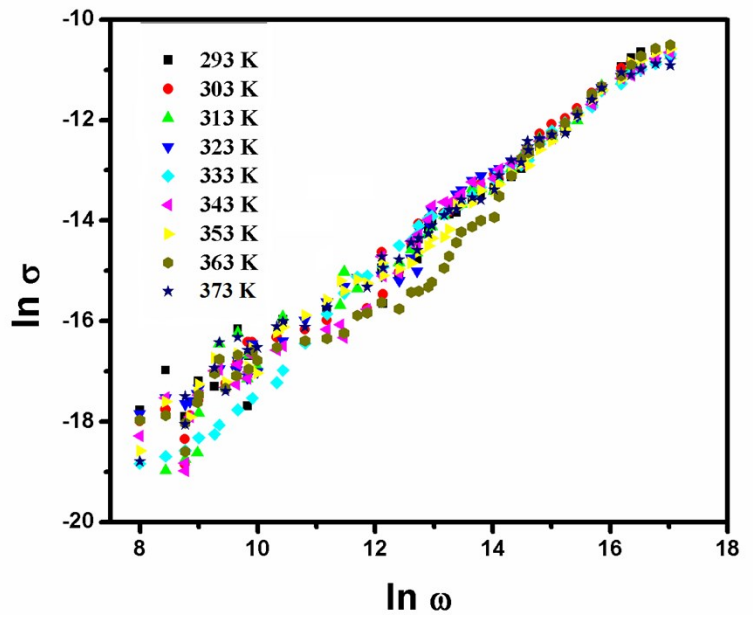

Fig. S13 Frequency dependent ac conductivity ($\ln\sigma_{ac}$) plot of **2** at various temperatures.

Table S4. The variation of resistance and capacitance values of **1** at various temperatures.

Temperature(K)	R_g (MΩ)	C_g (pF)	R_{gb} (MΩ)	C_g (pF)	Fitting goodness factor χ2
293	2593	12.53	0.455	0.6647	0.0178
303	841.2	12.54	217.2	14.4	0.0788
313	642.4	12.5	640.2	17.19	0.221
323	386	13.91	2.124	0.158	0.194
333	36.18	20.51	15.53	31.82	0.267
343	1.248	150.3	1458	13.66	0.2663
353	11.25	23.22	11.52	26.73	0.289
363	18.22	25.94	17.86	23.91	0.254
373	14.74	22.83	13.51	27.37	0.235

Table S5. The variation of resistance and capacitance values of **2** at various temperatures.

Temperature (K)	R_g (MΩ)	C_g (pF)	R_{gb} (MΩ)	C_g (pF)	Fitting goodness factor χ2
293	63.35	19.25	1.148	77.51	0.05888
303	32.95	20.93	1.054	60.87	0.05582
313	39.3	19.78	0.825	71.04	0.05729
323	76.85	19.22	1.475	76.85	0.06285
333	0.838	97.01	81.44	17.95	0.06283
343	0.129	15.83	0.053	283	0.02668
353	81.53	18.52	0.581	124.4	0.09980
363	51.42	19.87	1.0	81.49	0.07000
373	1.401	42.28	11.55	28.58	0.07010