Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information for

Synthesis, characterisation, water adsorption and proton conductivity of three Cd(II) based luminescent metal-organic frameworks

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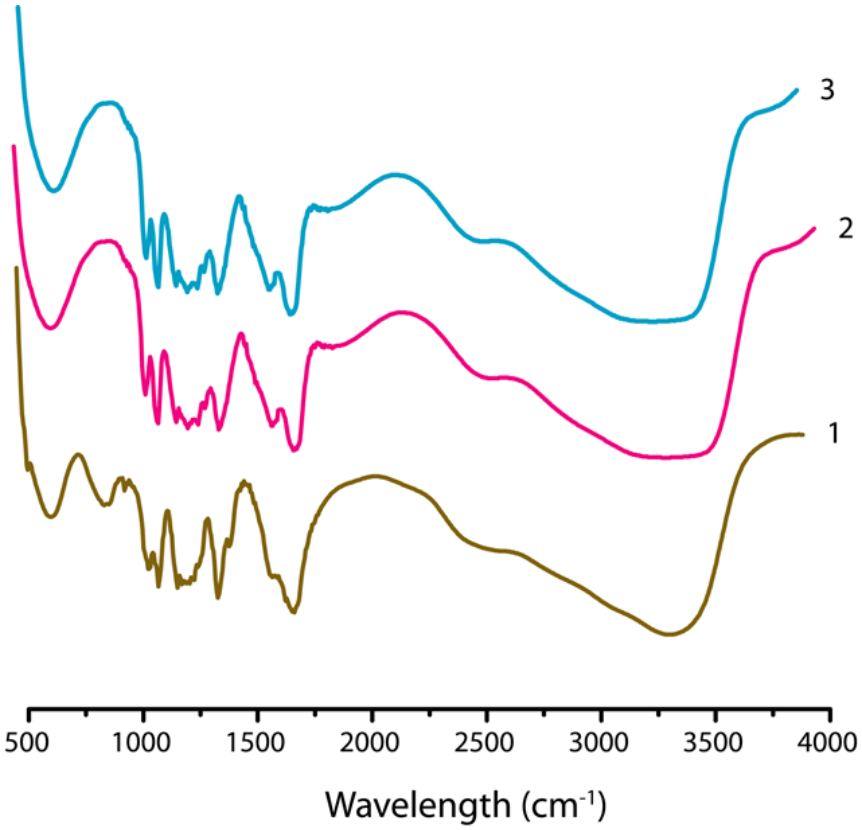
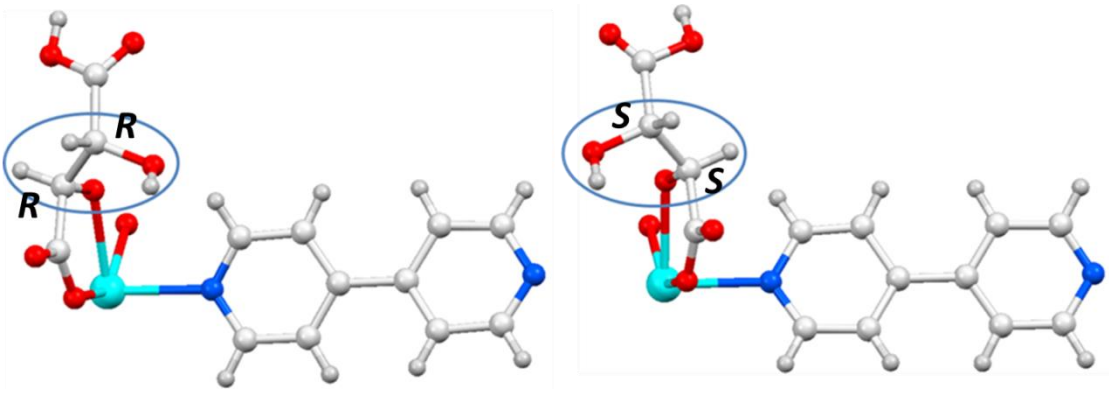


Figure S1. IR spectra of compounds **1-3.**

Table S1. Selected IR bands (cm^{-1}) for the compounds **1-3.**

Compound	ν(OH)	$\nu(COO)_{sym}$	$\nu(COO)_{asym}$	$\Delta\nu$ (ν_{asym}-ν_{sym})
1	3396	1385	1599	214
2	3376	1385	1605	220
3	3376	1392	1612	230



(a) **(b)**

Fig. S2 (a) Asymmetric unit of compound **1**, (b) asymmetric unit of compound **2**. Color code: carbon (light gray), hydrogen (gray), nitrogen (blue), oxygen (red) and cadmium (cyan).

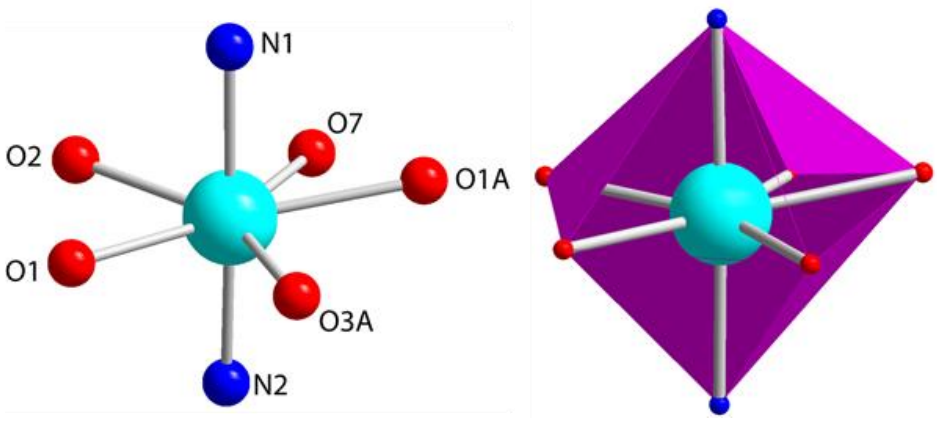


Fig. S3 Pentagonal bipyramidal arrangement of Cd(II) atom in **1**. Color code; same as in Fig. S2.

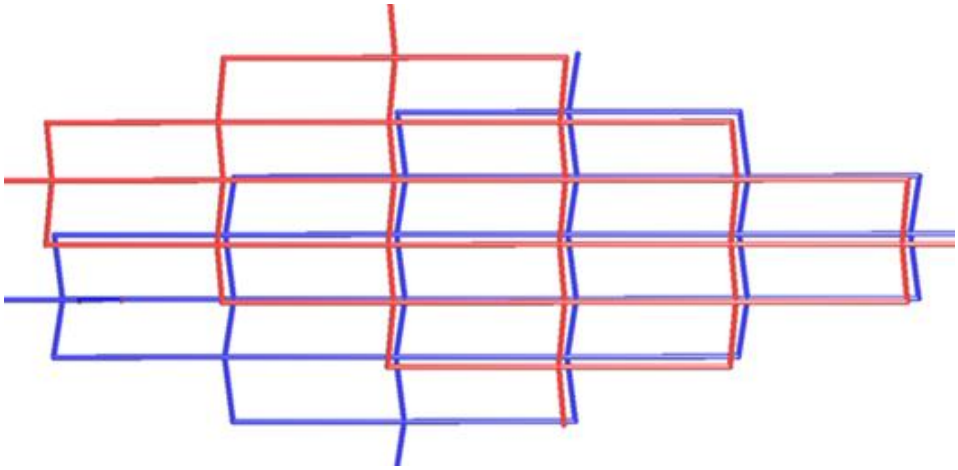


Fig. S4 View of the $\{4^4.6^2\}$ *sql/Shubnikov tetragonal plane* net topology featuring a 4-connected uninodal net.

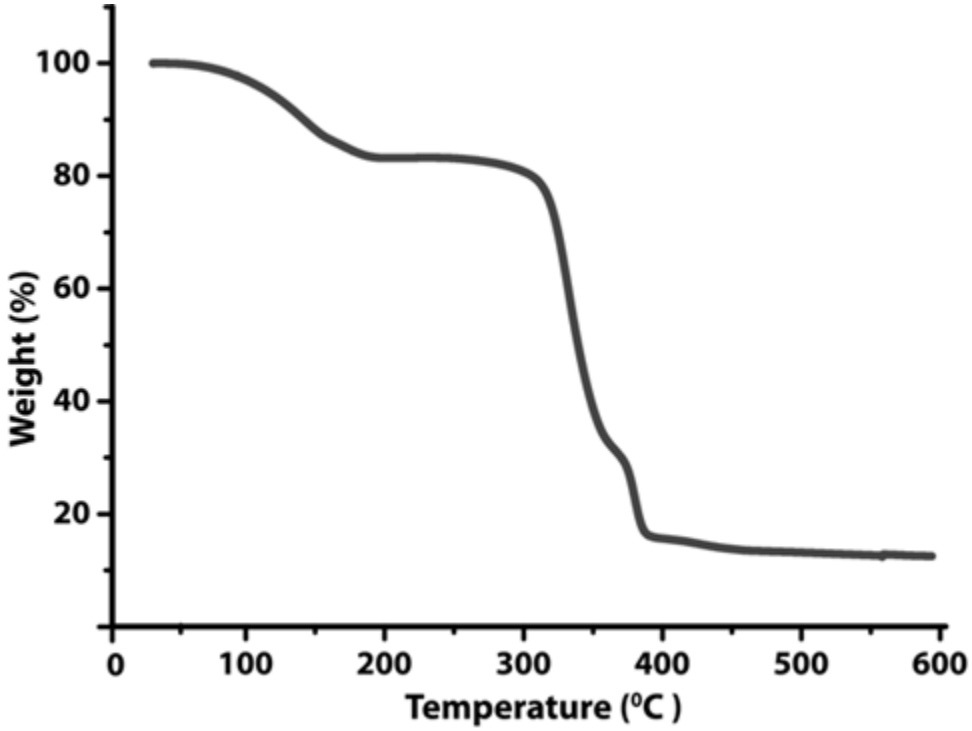


Fig. S5 TGA graph of Compound **1**.

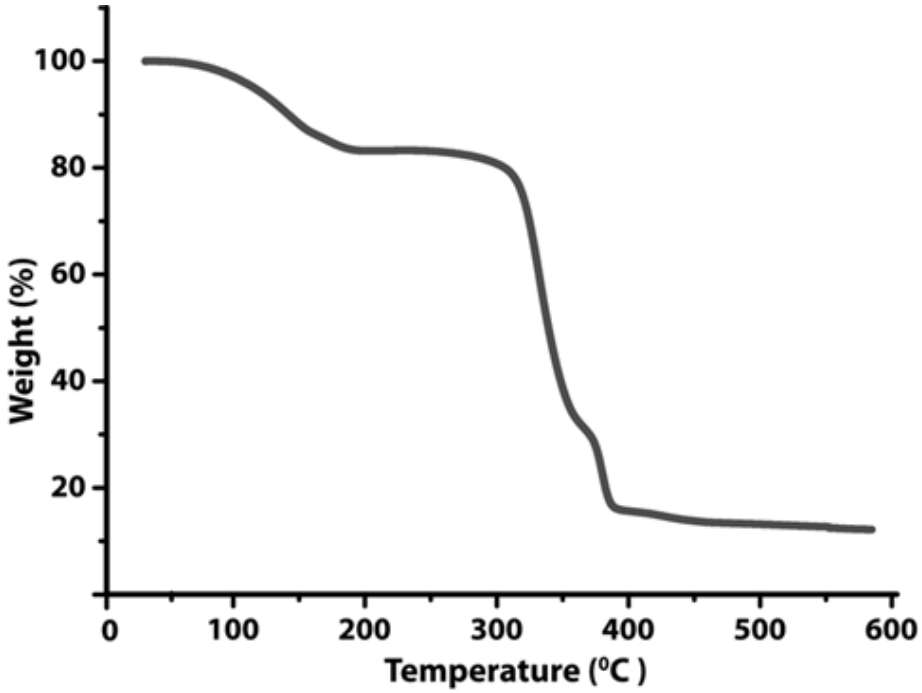


Fig. S6 TGA graph of Compound **2**.

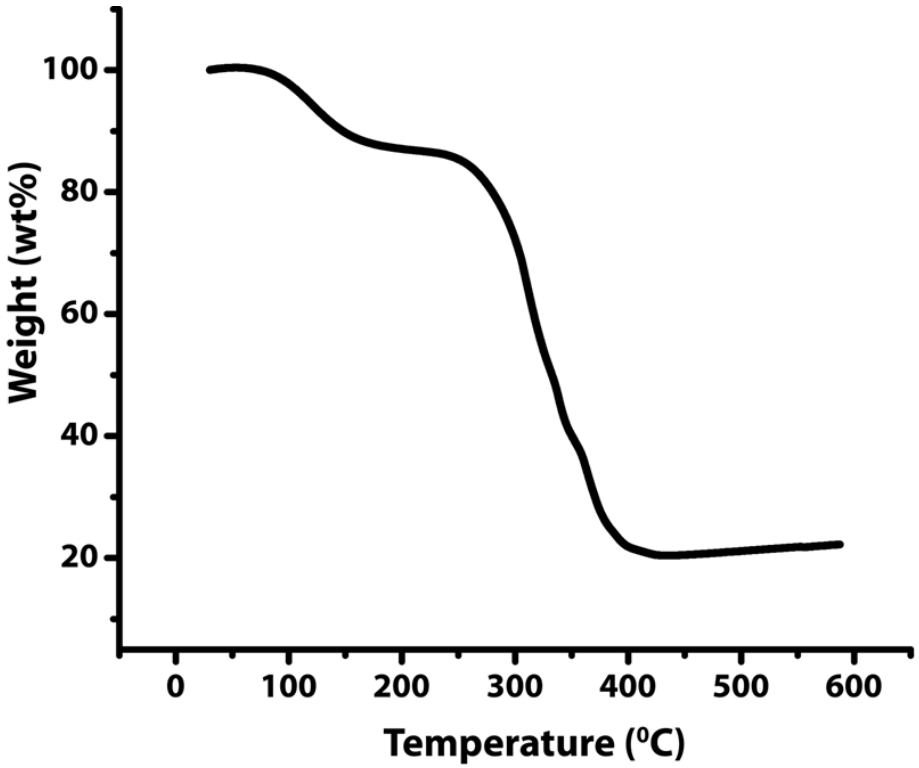


Fig. S7 TGA graph of Compound **3**.

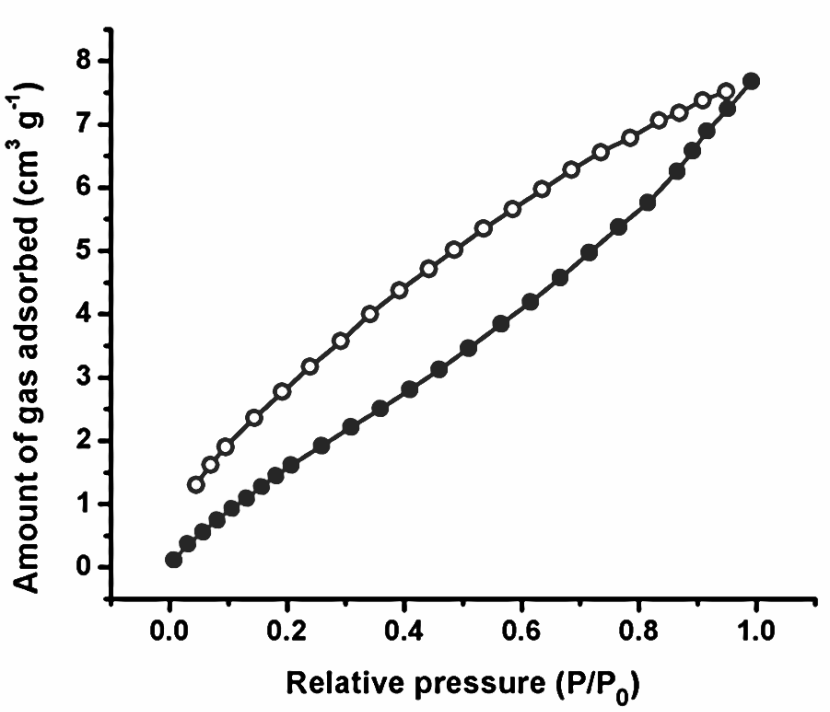


Fig. S8 Carbon dioxide adsorption isotherm of compound **1** at 195 K.

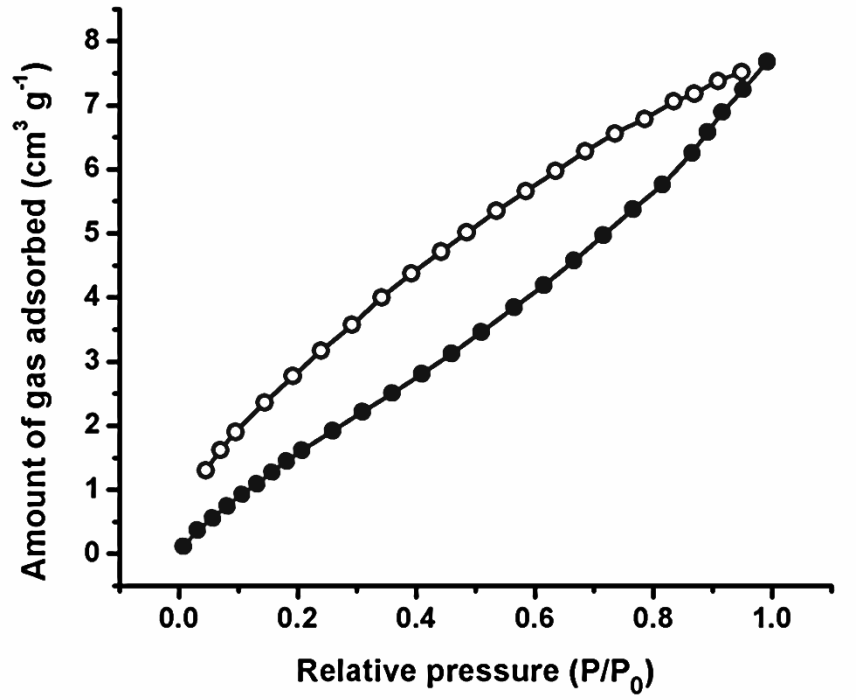


Fig. S9 Carbon dioxide adsorption isotherm of compound **2** at 195 K.

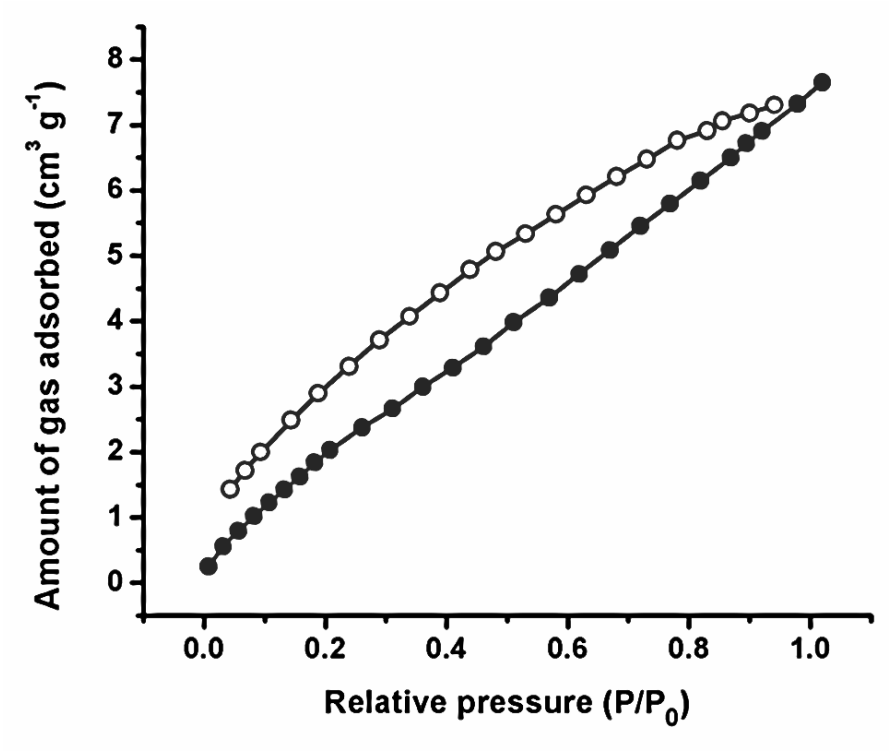


Fig. S10 Carbon dioxide adsorption isotherm of compound **3** at 195 K.

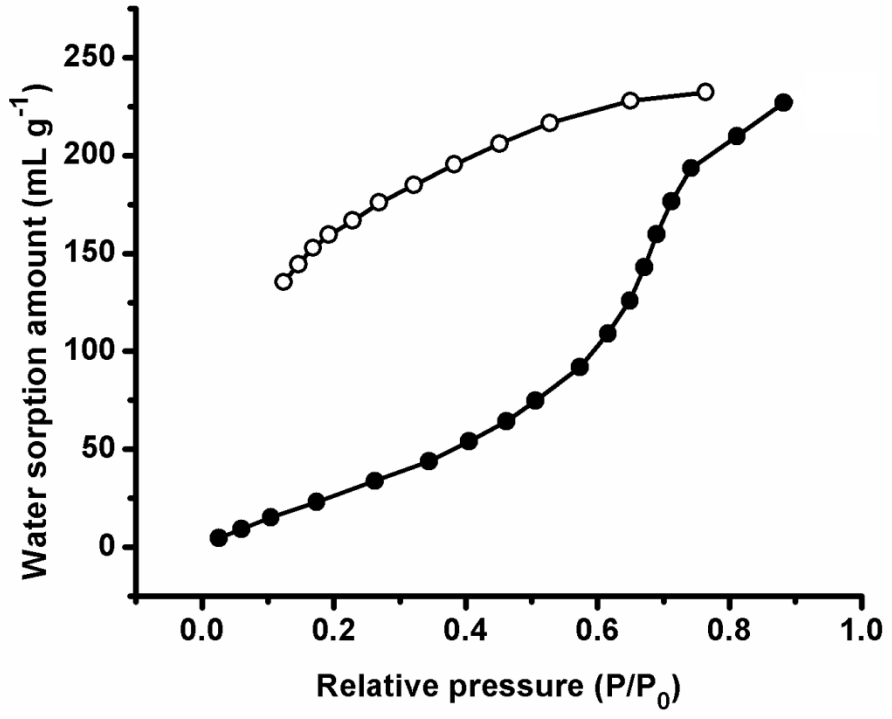


Fig. S11 Water vapour adsorption isotherm of compounds **2** at 298 K.

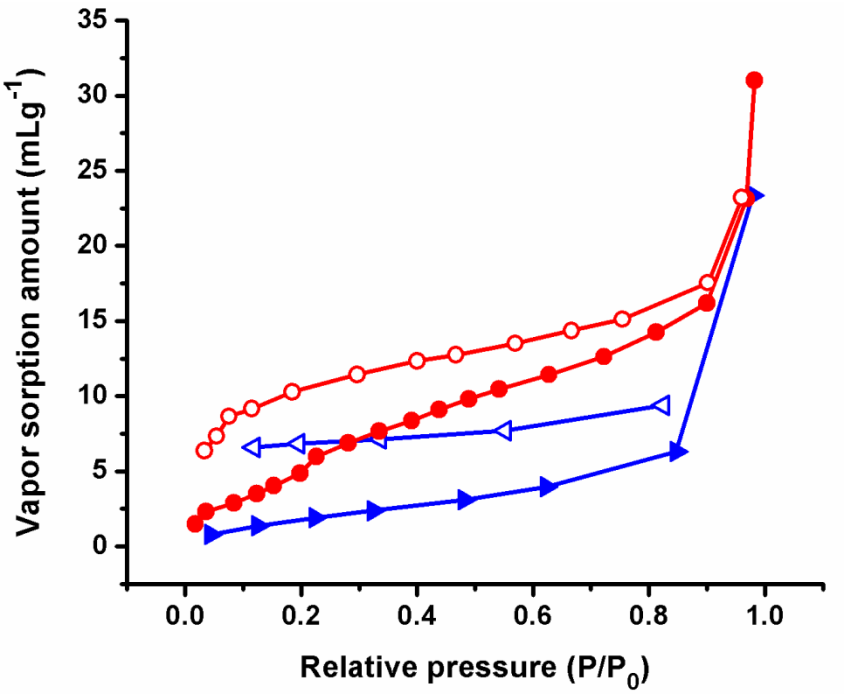


Fig. S12 Vapour adsorption isotherms of compound **1** at 298 K. MeOH (red) and EtOH (blue).

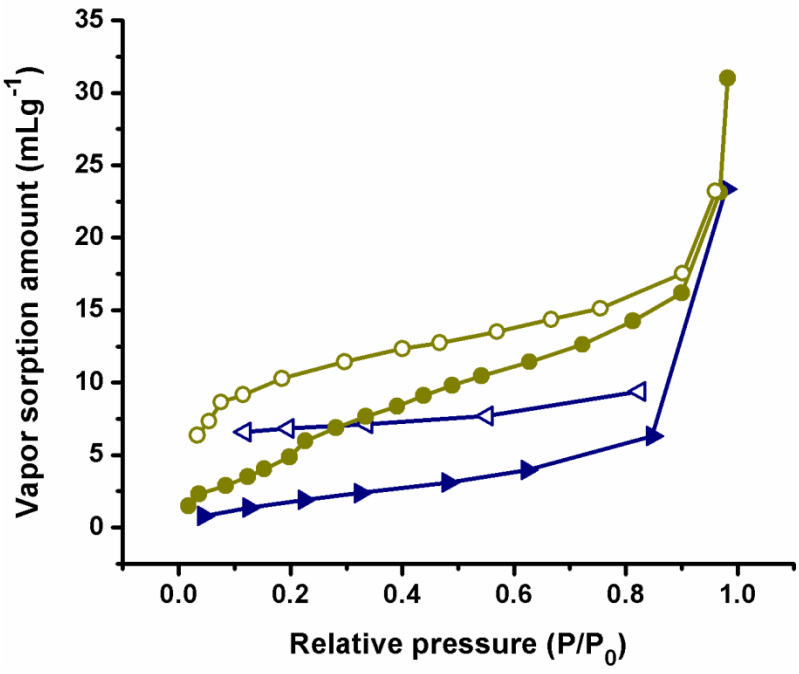


Fig. S13 Vapour adsorption isotherms of compound **2** at 298 K. MeOH (dark-yellow) and EtOH (navy-blue).

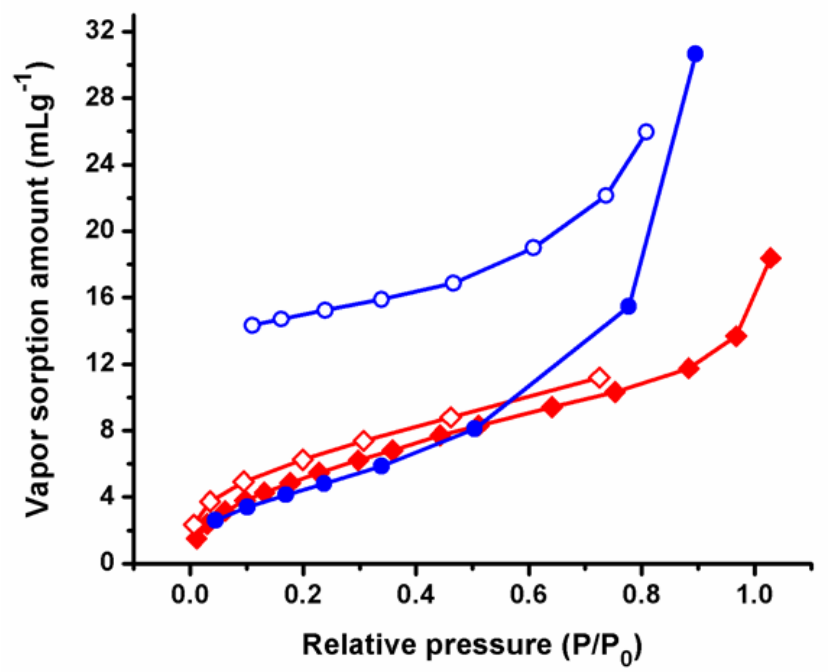


Fig. S14 Vapour adsorption isotherms of compound **3** at 298 K. MeOH (blue) and EtOH (red).

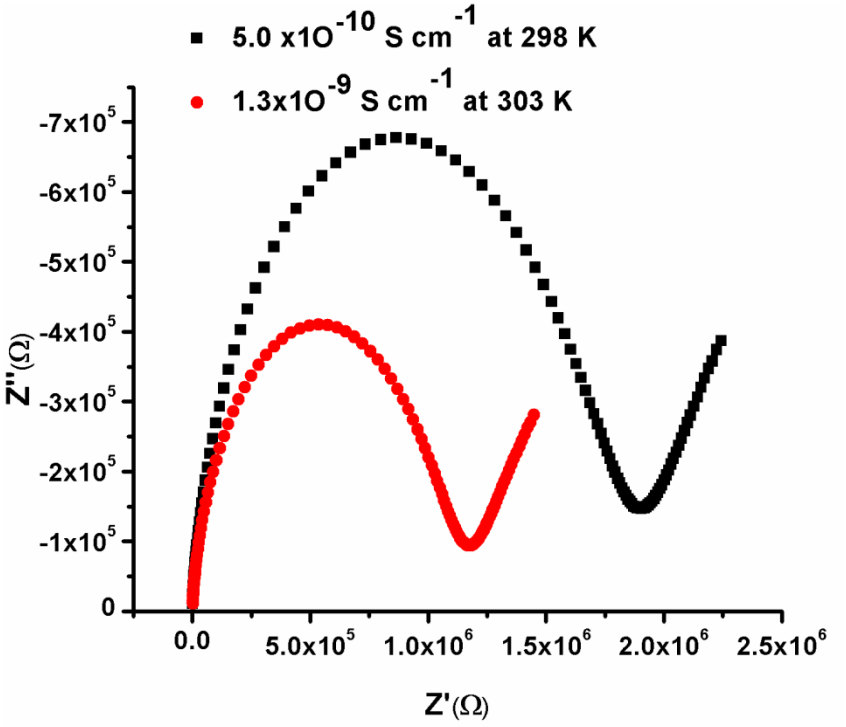


Fig. S15 Nyquist plot of compound **1** at 298 and 303 K, showing increasing trend of proton conductivity values.

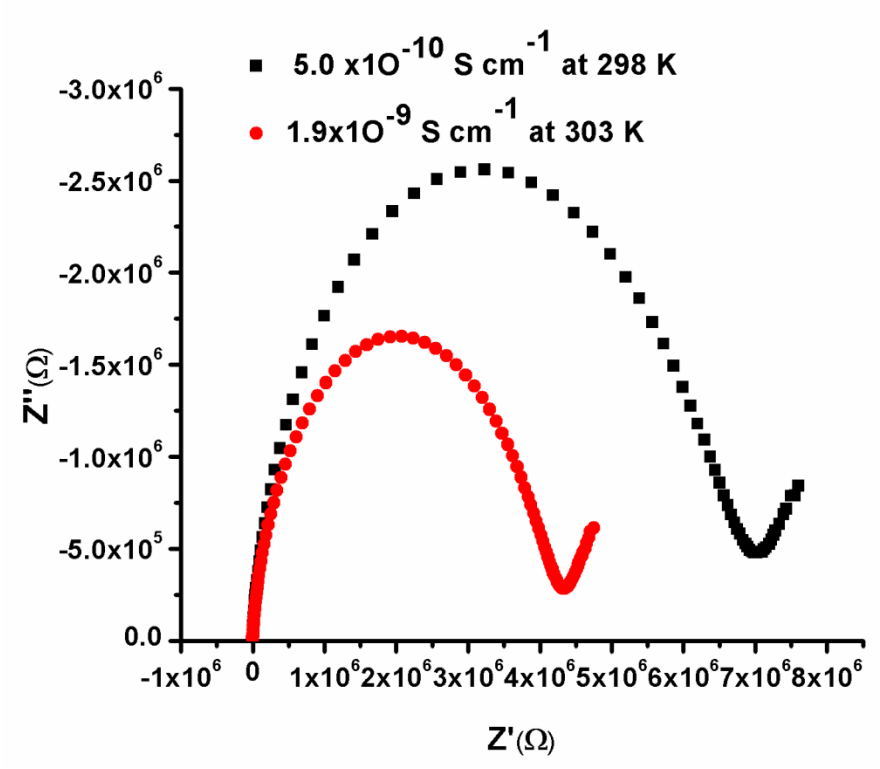


Fig. S16 Nyquist plot of compound **2** at 298 and 303 K, showing increasing trend of proton conductivity values.

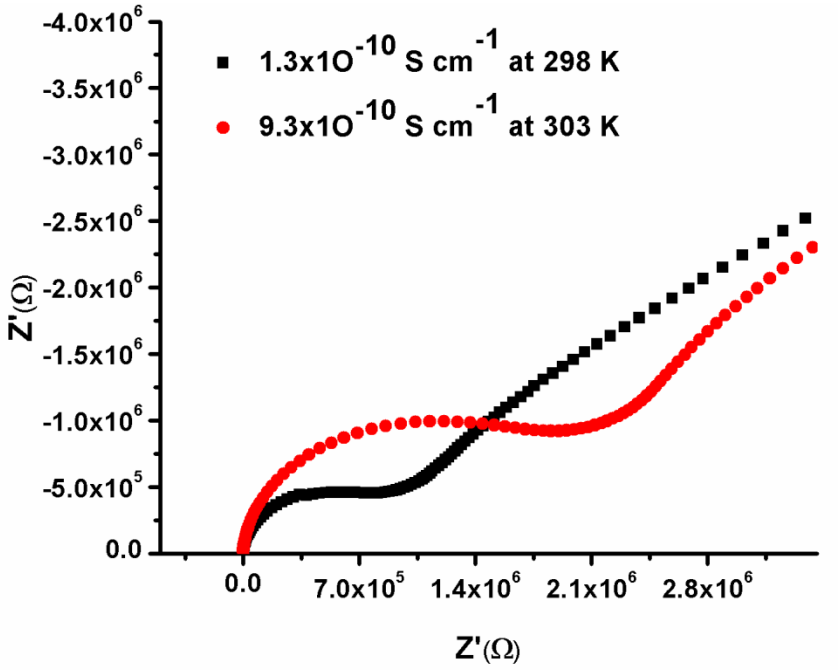


Fig. S17 Nyquist plot of compound **3** at 298 and 303 K, showing increasing trend of proton conductivity values.

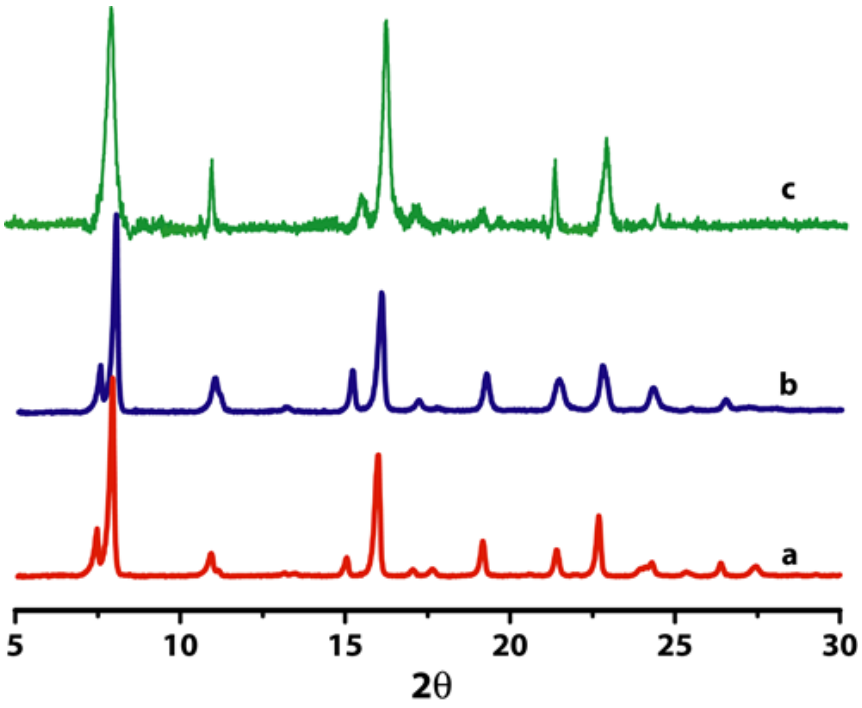


Fig. S18 PXRD pattern of compound **1** and **2**, (a) As synthesized (b) humidified for 24 h at 298 K, (c) humidified for 24 h at 358 K.

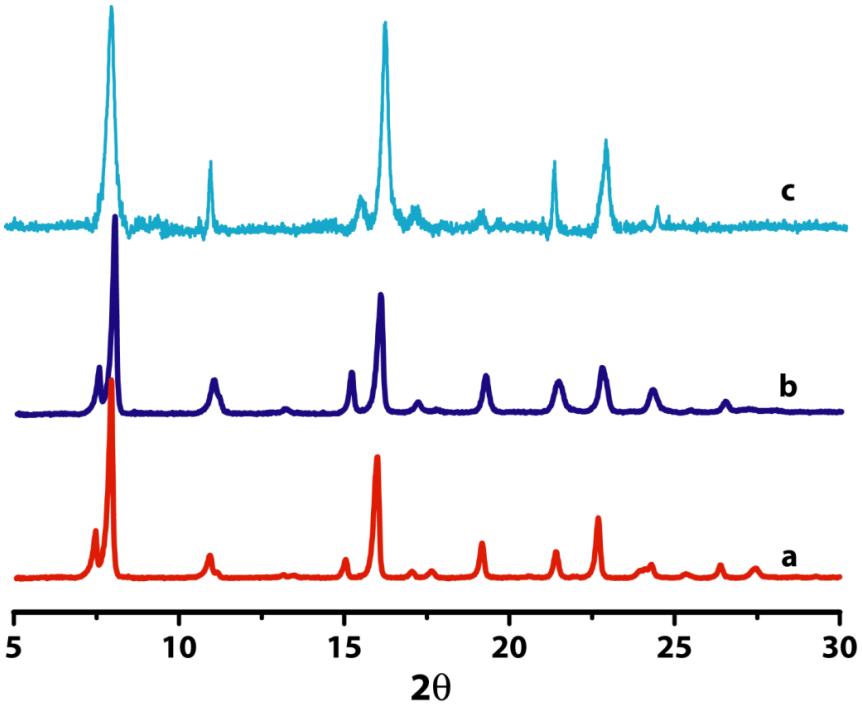


Fig. S19 PXRD pattern of compound **2**, (a) As synthesized (b) humidified for 24 h at 298 K, (c) humidified for 24 h at 358 K.

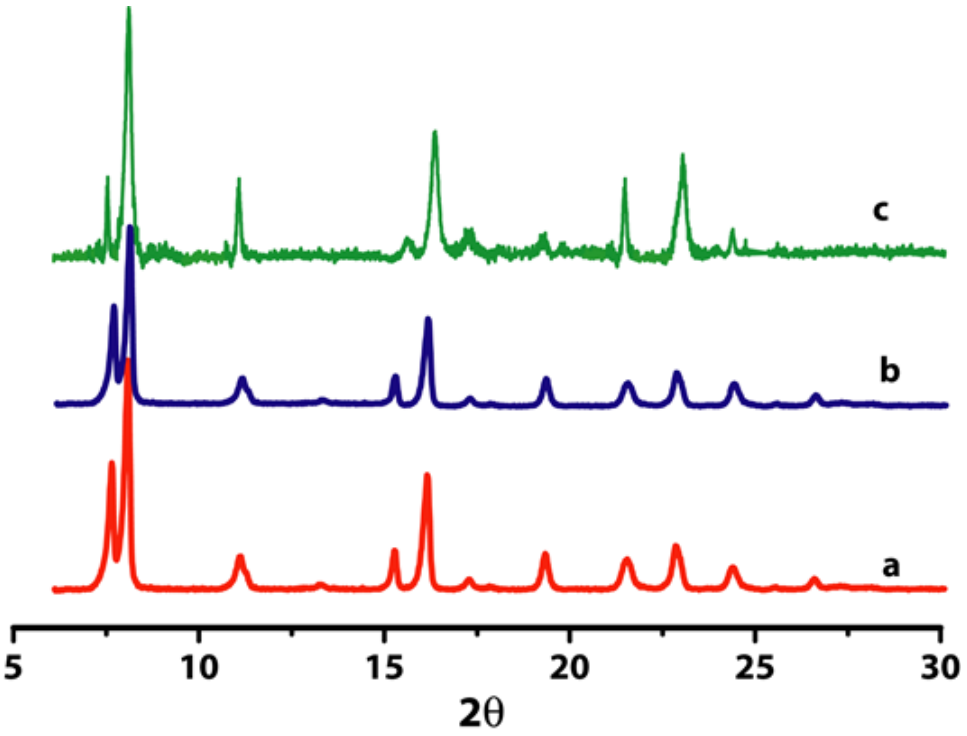


Fig. S20 PXRD pattern of compound **3**, (a) As synthesized (b) humidified for 24 h at 298 K, (c) humidified for 24 h at 353 K.

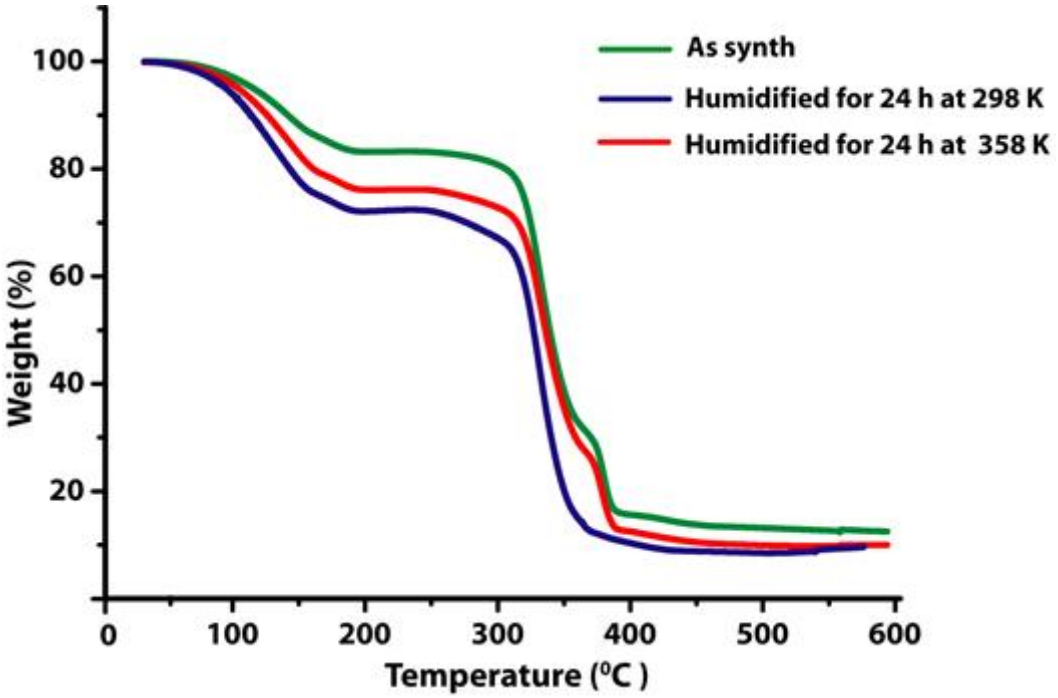


Fig. S21 Thermal Gravimetric Analysis curve for humidified compound **1** at different temperature (at 298 K (navy-blue), at 358 K (red)) in comparison with as-synthesized (green).

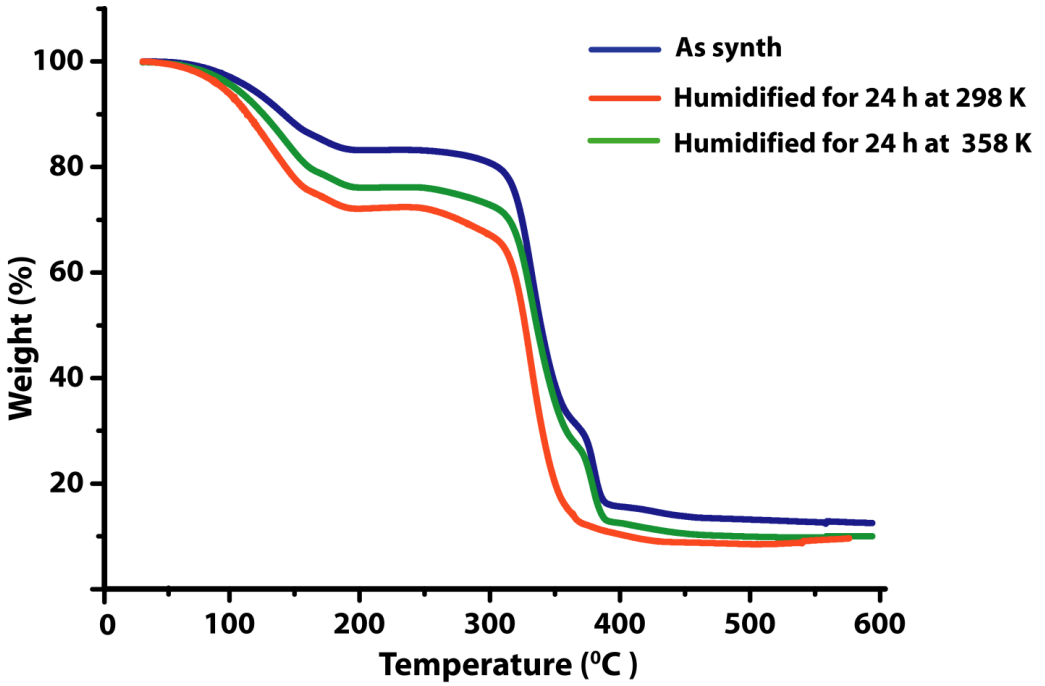


Fig. S22 Thermal Gravimetric Analysis curve for humidified compound **2** at different temperature (at 298 K (red), at 358 K (green)) in comparison with as-synthesized (navy-blue).

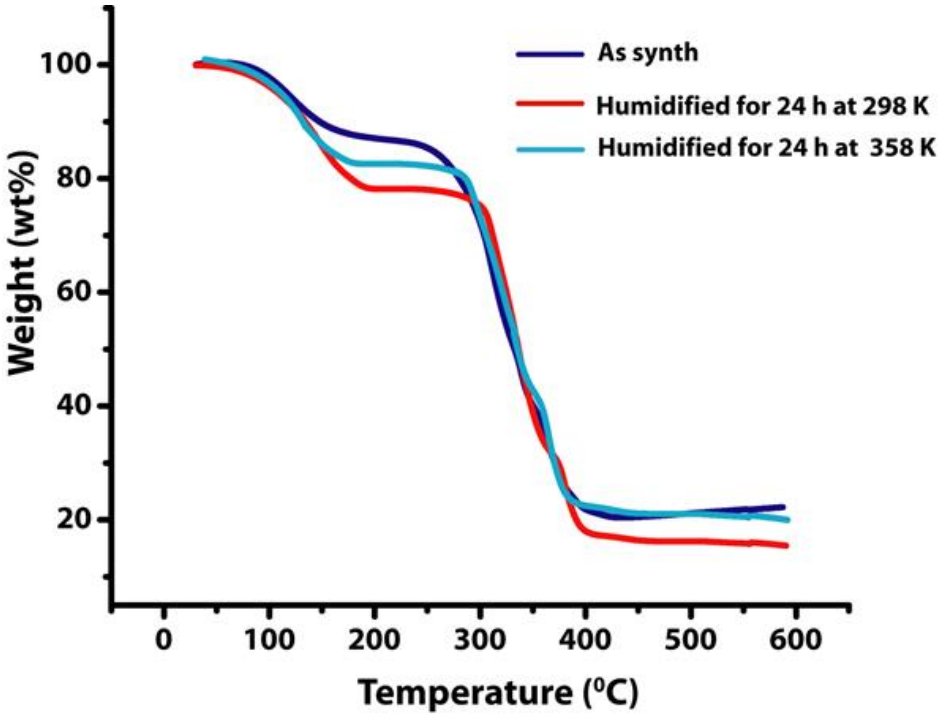


Fig. S23 Thermal Gravimetric Analysis curve for humidified compound **3** at different temperature (at 298 K (red), at 358 K (cyan)) in comparison with as-synthesized (blue).

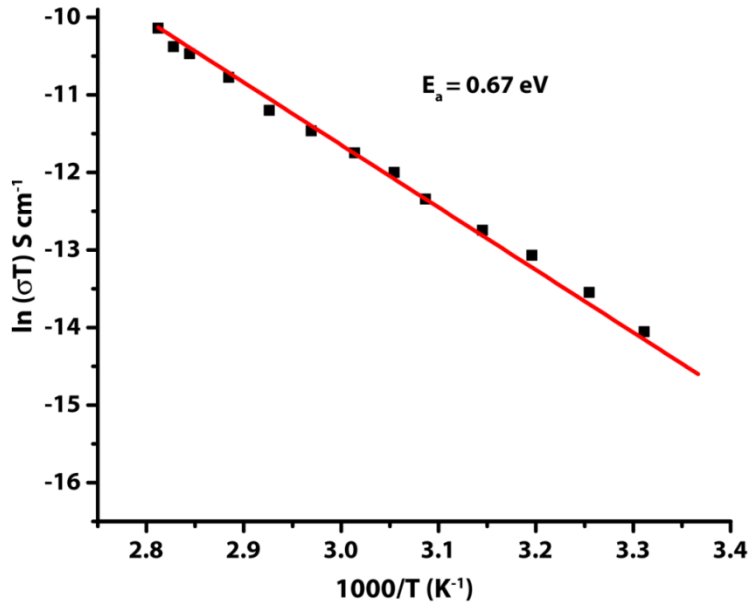


Fig. S24 Arrhenius plot of activation energy for compound **2** showing activation energy (E_a) value of 0.67 eV.

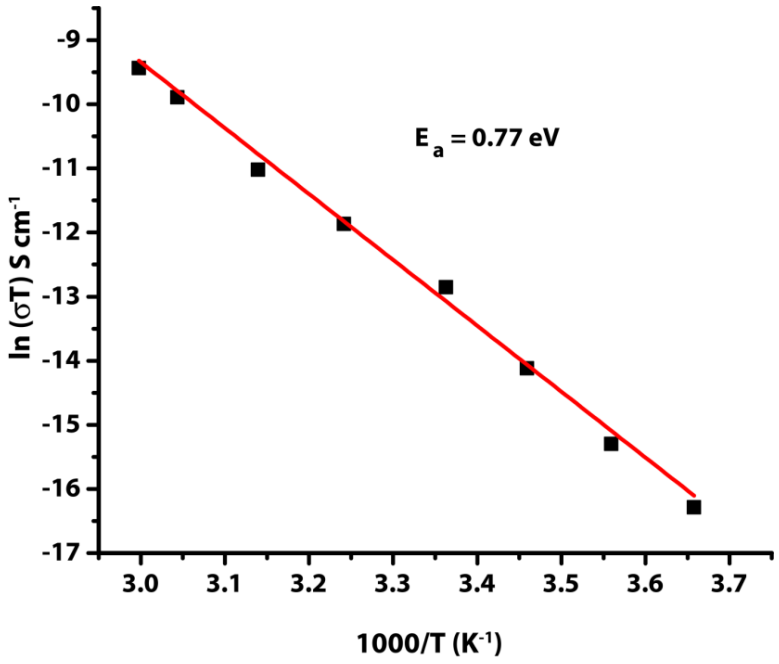


Fig. S25 Arrhenius plot of activation energy for compound **3** showing activation energy (E_a) value of 0.71 eV.

Table S2. H-bonding table for compound **1**.

Donor-H⋯Acceptor	**D – H(Å)**	**H...A(Å)**	**D...A (Å)**	**D - H...A(°)**
O4-H4 ⋯O3[a]	0.820(8)	2.753(4)	3.221(8)	115
C1-H1⋯O2[a]	0.930(8)	2.684(5)	3.338(1)	125
C13-H13⋯O6[a]	0.980(5)	2.588(7)	2.824(7)	91
C14-H14⋯O3[a]	0.980(7)	2.548(.003)	2.858(.007)	96
C15-H6A⋯O7[b]	1.612(7)	2.354(4)	3.268(6)	120
O6-H6A⋯O2[b]	0.820(8)	2.054(3)	2.772(11)	143
C1-H1⋯O5[b]	0.930(8)	2.841(13)	3.632(15)	141
O6-H6A⋯O7[b]	0.820(8)	2.354(4)	2.962(.9)	129
C15-H6A⋯O2[b]	1.612(7)	2.054(3)	3.373(6)	142
C10-H10⋯O4[c]	0.930(7)	2.776(7)	3.478(11)	130
C5-H5⋯O3[c]	0.930(9)	2.496(4)	3.154(11)	125
C10-H10⋯O3[c]	0.930(7)	2.718(4)	3.394(8)	127
C14-H14⋯O7[d]	0.980(7)	2.897(3)	3.743(7)	143

Equivalent positions:

(a) x,y,z, (b) -x,-y+2,+z, (c) -x+1/2,+y+1/2,-z+1, (d) x,+y-1,+z

Table S3. H-bonding table for compound **2**.

Donor-H···Acceptor	**D – H(Å)**	**H...A(Å)**	**D...A (Å)**	**D - H...A(°)**
O5-H5···O1[a]	0.820(9)	2.759(4)	3.226(10)	115.71
C1-H1···O3[a]	0.930(1)	2.974(7)	3.485(14)	113.46
C10-H10···O4[a]	0.930(9)	2.697(6)	3.335(12)	123.86
C12-H12···O7[a]	0.980(6)	2.546(8)	2.817(9)	93.43
C13-H13···O1[a]	0.980(9)	2.559(4)	2.862(9)	95.59
C5-H5A···O1[b]	0.930(8)	2.731(5)	3.403(8)	127.35
C5-H5A···O5[b]	0.930(8)	2.772(9)	3.487(12)	132.07
C9-H9···O1[b]	0.930(11)	2.507(5)	3.161(12)	124.70
C10-H10···O6[c]	0.930(9)	2.767(15)	3.603(17)	148.50
O7-H7···O4[c]	0.820(12)	1.966(4)	2.778(14)	169.81
O7-H7···O3[c]	0.820(12)	2.593(4)	2.981(11)	108.08
O7-H7···O7c	0.820(12)	2.979(6)	3.143(5)	91.66
C13-H13···O3[d]	0.980(9)	2.895(4)	3.738(9)	143.48

Equivalent positions:

(a) x,y,z. (b) -x+1/2,+y+1/2,-z. (c) -x,-y+2,+z. (d) x,+y-1,+z.

Table S4. Humidity sweep impedance measurement at constant temperature (298 K).

Humidity (%)	**Compound 1**	**Compound 2**	**Compound 3**
35% RH	5.7×10^{-11}	5.7×10^{-11}	2.3×10^{-11}
50% RH	5.7×10^{-11}	5.9×10^{-11}	2.5×10^{-11}
65% RH	9.2×10^{-11}	8.4×10^{-11}	2.6×10^{-11}
80% RH	1.2×10^{-10}	1.7×10^{-10}	8.3×10^{-11}
95% RH	5.0×10^{-10}	5.2×10^{-10}	1.3×10^{-10}

Table S5. Selected bond lengths (Å) and bond angles (°) of compounds **1** and **2**.

Compound 1		**Compound 2**	
Cd1 -O1	2.309(3)	Cd1-O2	2.310(4)
Cd1-O2	2.411(3)	Cd1-O4	2.405(4)
Cd1-O7	2.265(4)	Cd1-N1	2.324(5)
Cd1-N2	2.316(5)	Cd1-O3	2.264(4)
Cd1-O1A	2.495(3)	Cd1-O2	2.495(4)
Cd1-N1	2.325(5)	Cd1-N2	2.316(6)
Cd1-O3	2.414(3)	Cd1-O1	2.411(4)
O1-Cd1-O2	67.5(1)	O1-Cd1-O2	53.2(1)
O1-Cd1-O7	144.5(2)	O2-Cd1-O4	67.6(1)
O1-Cd1-N2	93.3(2)	O2-Cd1-N1	84.0(2)
O1-Cd1-O1	133.4(1)	O2-Cd1-O3	144.3(2)
O1-Cd1-O3	82.6(1)	O2-Cd1-O1	82.5(1)
O1-Cd1-N1	84.1(1)	O2-Cd1-O2	133.2(1)
O2-Cd1-O7	77.1(2)	O2-Cd1-N2	93.4(2)
O2-Cd1-N2	90.3(2)	O4-Cd1-N1	90.4(2)
O2-Cd1-O1	157.2(1)	O4-Cd1-O3	76.9(2)
O2-Cd1-O3	149.5(1)	O4-Cd1-O1	149.4(1)
O2-Cd1-N1	90.3(2)	O4-Cd1-O2	157.3(1)
O7-Cd1-N2	90.2(2)	O4-Cd1-N2	90.0(2)
O7-Cd1-O1	81.1(1)	N1-Cd1-O3	92.3(2)
O7-Cd1-O3	133.0(1)	N1-Cd1-O1	92.8(2)
O7-Cd1-N1	92.9(2)	N1-Cd1-O2	84.1(2)
N2-Cd1-O1	96.5(1)	N1-Cd1-N2	177.1(2)
N2-Cd1-O3	85.4(2)	O3-Cd1-O1	133.3(2)
N2-Cd1-N1	176.9(2)	O3-Cd1-O2	81.3(2)
O1-Cd1-O3	53.2(1)	O3-Cd1-N2	90.6(2)
O1-Cd1-N1	84.1(1)	O1-Cd1-N2	85.4(2)
O3-Cd1-N1	92.5(1)	O2-Cd1-N2	96.7(2)