Supporting Information File

Copper(II)-coordination polymer based on sulfonic-carboxylic ligand exhibits high water-facilitated proton conductivity

Sakharam B. Tayade,[a] Rajith lllathvalappil,[b,c] Vaidehi A. Lapalikar,[a] Datta Markad,[d] Sreekumar Kurungot,[b,c] Bhalchandra Pujari[e] and Avinash S. Kumbhar*[a]

[a]Department of Chemistry, Savitribai Phule Pune University, Pune-411007, India
[b]Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune- 411007, India
[c]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201 002, India
[d]Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector 81, Manauli PO, S.A.S. Nagar, Mohali, Punjab-140306, India
[e]Centre for Modelling and Simulation, Savitribai Phule Pune University, Pune-411007, India

Email: askum@chem.unipune.ac.in; Tel: +9125601395 Ext. 534

Contents

Section I: Single crystal X-ray structure determination of **1**

Table S1 Crystal structure refinement parameters for **1**

Compound	**1**
Chemical Formula	$C_{42}H_{44}Cu_2N_{12}O_{22}S_2$
Formula Weight (g/mol)	1260.09
Temperature (K)	100.15
Wavelength (Å)	1.54178
Crystal System	Monoclinic
Space Group	$P2_1$ (No. 4)
a (Å)	9.7310(8)
b (Å)	18.7611(16)
c (Å)	13.3099(11)
α (°)	90
β (°)	99.441(2)
γ (°)	90
Z	2
V (Å^3)	2397.0(3)
Density (g/cm^3)	1.746
μ (mm^{-1})	2.791
F (000)	1292.0
Theta (°) Range for Data Coll.	4.11 to 68.433
Reflections Collected	24923
Independent Reflections	8231
Reflections with I >2σ(I)	8021
R_{int}	0.0521
No. of Parameters refined	749
GOF on F^2	1.020
Final R_1[a]/wR_2[b] (I >2σ(I)) R_1/wR_2(all data)	0.0355/0.0924 0.0364/0.0932
Largest diff. peak and hole (eÅ^{-3})	0.41/-0.63
Flack parameter	0.113(18)

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Section II: Packing diagrams of **1**

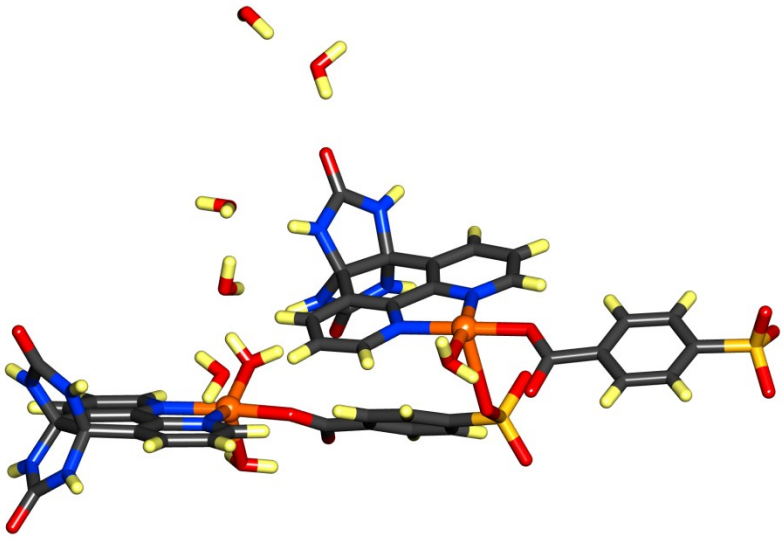

Fig. S1 Asymmetric unit of **1**.

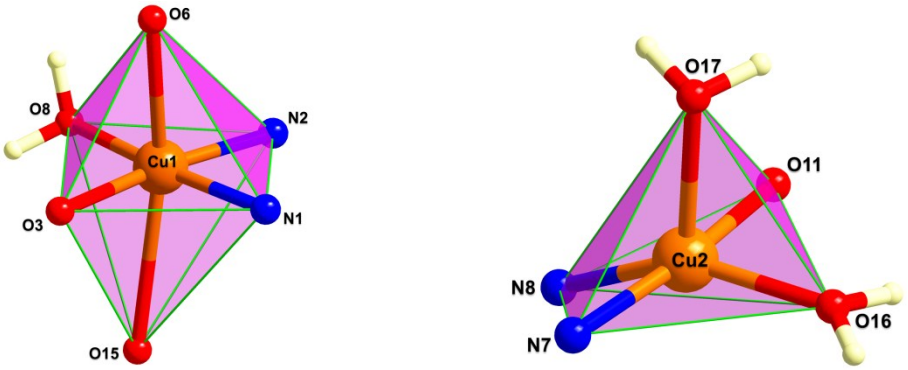

Fig. S2 Polyhedral views of the coordination geometries with atom labeling around Cu(II) centers in **1**.

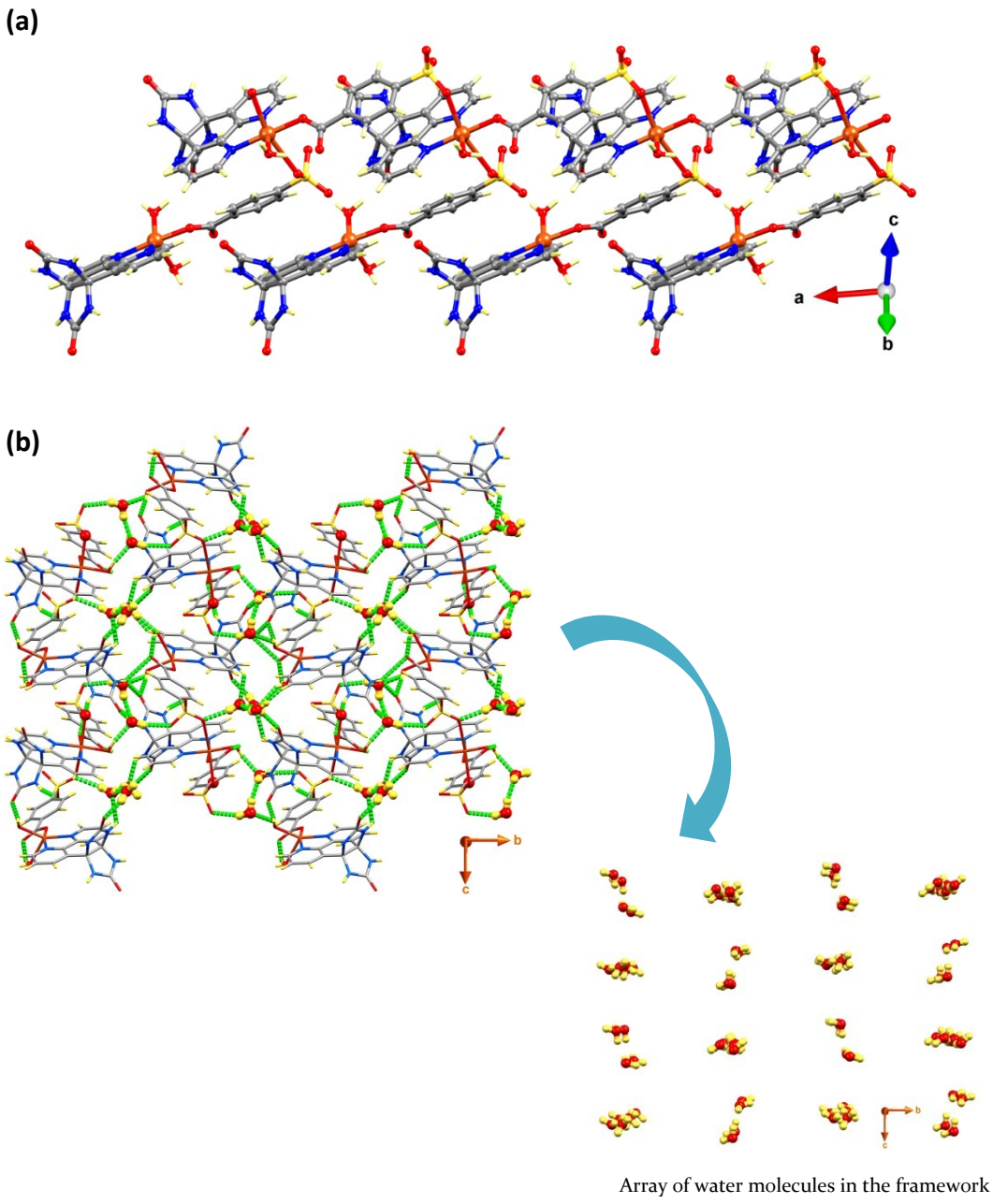

Fig. S3 a) Depiction of 1D infinite chain formed by **1** b) Packing diagram showing array of water molecules in the framework of **1**.

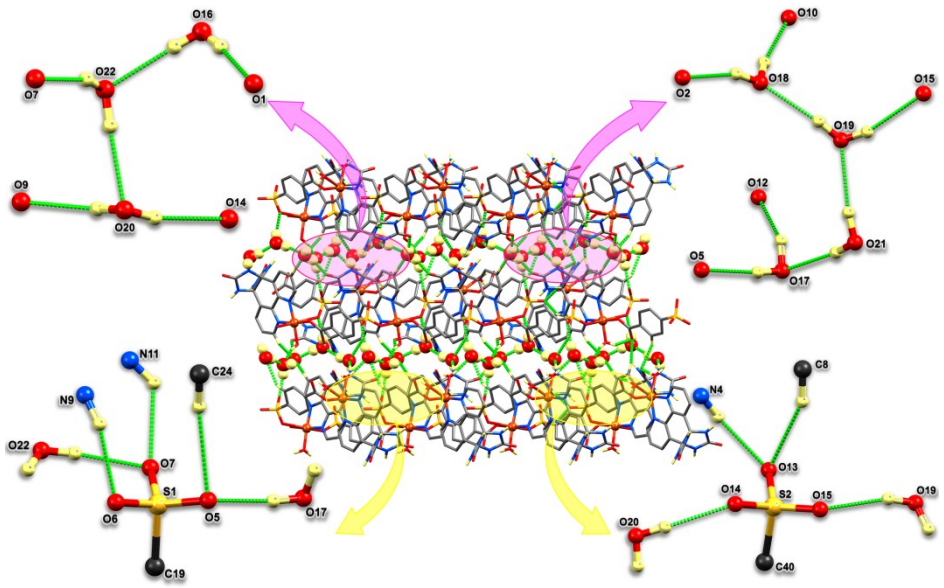

Fig. S4 Packing digram of **1** showing the hydrogen-bonding between water molecules and the adjacent groups in the framework.

Table S2 Selected bond distances for **1**

Cu1-O3	1.951(3)	Cu2-O11	1.922(3)
Cu1-O6$^{\#1}$	2.433(3)	Cu2-O16	2.014(3)
Cu1-O8	1.968(3)	Cu2-O17	2.311(3)
Cu1-N1	1.989(3)	Cu2-N7	2.002(3)
Cu1-N2	2.014(3)	Cu2-N8	2.000(4)
Cu1-O15	2.738(4)		

Symmetry codes: #1: 1+X,+Y,+Z

Table S3 Selected bond angles for **1**

O3-Cu1-O6$^{\#1}$	84.38(11)	N2-Cu1-O6$^{\#1}$	98.62(11)
O3-Cu1-O8	93.77(12)	N2-Cu1-O15	96.26(12)
O3-Cu1-N1	93.38(13)	O11-Cu2-O16	89.38(13)
O3-Cu1-N2	173.76(15)	O11-Cu2-O17	90.88(13)

O3-Cu1-O15	80.49(11)	O11-Cu2-N7	170.96(15)
$O6^{\#1}$-Cu1-O15	164.74(10)	O11-Cu2-N8	89.77(13)
O8-Cu1-$O6^{\#1}$	94.05(13)	O16-Cu2-O17	86.15(13)
O8-Cu1-N1	172.76(13)	N7-Cu2-O16	99.30(14)
O8-Cu1-N2	91.49(14)	N7-Cu2-O17	92.22(13)
O8-Cu1-O15	88.90(12)	N8-Cu2-O16	151.10(15)
N1-Cu1-$O6^{\#1}$	87.80(12)	N8-Cu2-O17	122.75(13)
N1-Cu1-N2	81.31(14)	N8-Cu2-N7	81.41(14)
N1-Cu1-O15	91.14(12)		

Symmetry codes: #1: 1+X,+Y,+Z

Table S4 Hydrogen bond parameters for **1**

D–H···A	r (D-H) (Å)	r (H···A) (Å)	r (D···A) (Å)	∠D-H···A (º)
N(3)–H(3)···O(9)	0.88	2.00	2.814(5)	153
N(4)–H(4)···O(13)	0.88	2.13	2.976(5)	162
N(5)–H(5)···O(21)	0.88	2.23	2.922(6	136
N(6)–H(6)···O(14)	0.88	2.46	2.919(4)	113
O8–H(8A)···O(20)	0.88	1.96	2.810(5)	162
O8–H(8B)···O(4)	0.88	1.76	2.552(4)	148
N(9)–H(9A)···O(3)	0.88	2.59	3.251(5)	133
N(9)–H(9A)···O(6)	0.88	2.18	2.925(5)	142
N(10)–H(10A)···O(1)	0.88	2.18	2.925(5)	142
N(11)–H(11)···O(7)	0.88	2.22	2.888(5)	132
N(12)–H(12)···O(19)	0.88	2.51	3.148(6)	130
O(16)–H(16A)···O(1)	0.88	1.84	2.722(4)	175
O(16)–H(16B)···O(22)	0.75(8)	1.94(8)	2.683(5)	172(8)
O(17)–H(17A)···O(5)	0.86(4)	1.87(4)	2.729(5)	174(4)
O(17)–H(17B)···O(12)	0.89(4)	1.89(4)	2.670(4)	146(4)
O(18)–H(18A)···O(10)	0.87	1.92	2.766(5)	165
O(18)–H(18B)···O(2)	0.87	1.96	2.792(5)	160
O(19)–H(19A)···O(15)	0.87	2.08	2.920(5	163
O(19)–H(19B)···O(18)	0.87	1.99	2.834(6)	165
O(20)–H(20A)···O(9)	0.87	1.95	2.774(5)	159
O(20)–H(20B)···O(14)	0.87	2.09	2.943(5)	168
O(21)–H(21A)···O(17)	0.87	2.05	2.908(5)	170
O(21)–H(21B)···O(19)	0.87	2.09	2.935(6)	164
O(22)–H(22A)···O(20)	0.87	2.04	2.902(6)	170

O(22)–H(22B)···O(7)	0.87	2.08	2.926(5)	164
C(1)–H(1)···O(3)	0.95	2.50	3.024(5)	115
C(2)–H(2)···O(18)	0.95	2.55	3.479(6)	165
C(3)–H(3)···O(4)	0.95	2.33	3.236(5)	160
C(8)–H(8)···O(13)	0.95	2.48	3.363(5)	154
C(9)–H(9)···O(21)	0.95	2.50	3.428(6)	166
C(10)–H(10)···O(8)	0.95	2.49	3.011(5)	115
C(10)–H(10)···O(18)	0.95	2.48	3.227(5)	135
C(18)–H(18)···O(6)	0.95	2.60	2.918(5)	100
C(23)–H(23)···O(18)	0.95	2.42	3.194(6)	139
C(24)–H(24)···O(5)	0.95	2.58	3.518(5)	170
C(29)–H(29)···O(12)	0.95	2.45	3.373(5)	165
C(31)–H(31)···O(11)		2.40	2.918(5)	114
C(41)–H(41)···O(15)		2.48	2.869(6)	105

Symmetry codes: (i) 1+x,y,z (ii) -2-x,-1/2+y,-z (iii) -2-x,1/2+y,1-z (iv) 1+x,y,-1+z (v) -2-x,1/2+y,-z (vi) -3-x,-1/2+y,1-z (vii) -2-x,-1/2+y,1-z (viii) 2+x,y,-1+z (ix) -1+x,y,z (x) -1-x,-1/2+y,-z (xi) -1-x,1/2+y,1-z

Section III: Thermal analysis of **1**

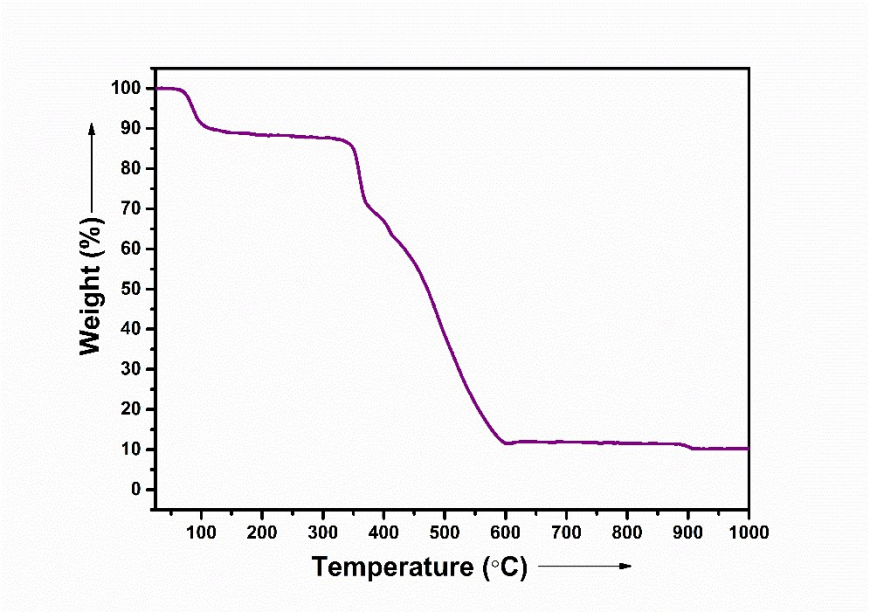

Fig. S5 Thermal gravimetric analysis (TGA) profile of **1** showing the weight loss steps.

Section IV: FTIR Spectroscopy of **1**

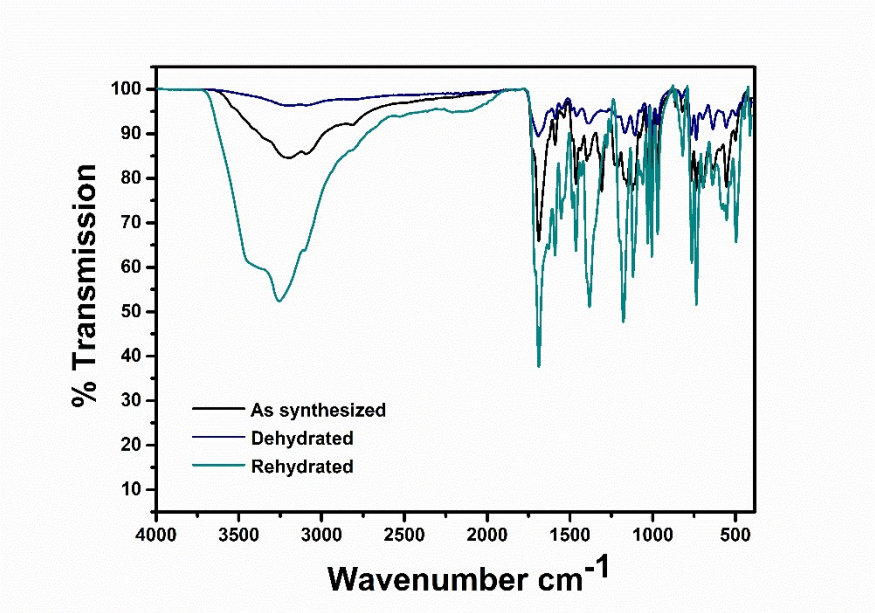

Fig. S6 FTIR spectra of as synthesized, dehydrated and rehydrated sample of **1**.

Section V: Framework stability and Ethanol and Methanol sorption measurements of **1**

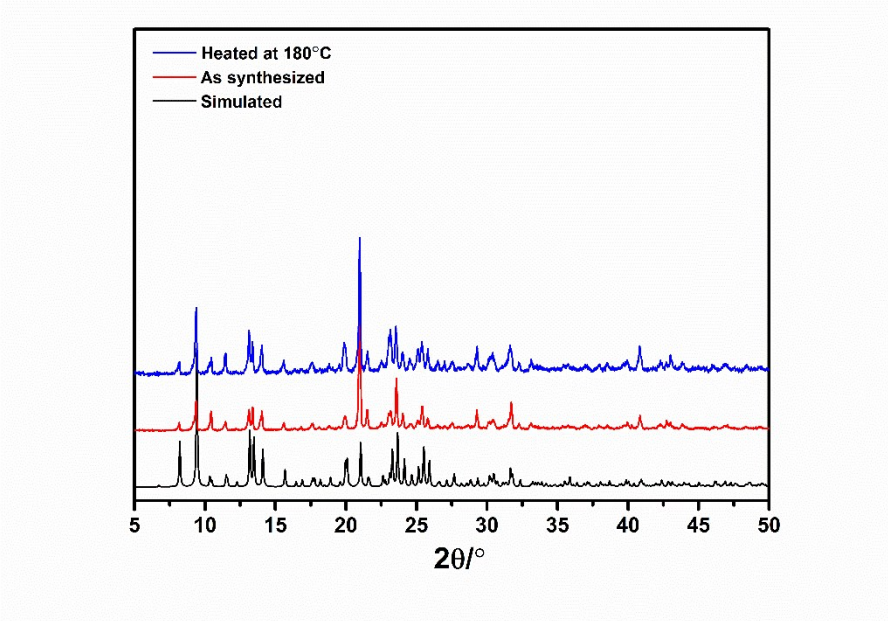

Fig S7 Framework stability of **1** degassed at 180°C before sorption measurements

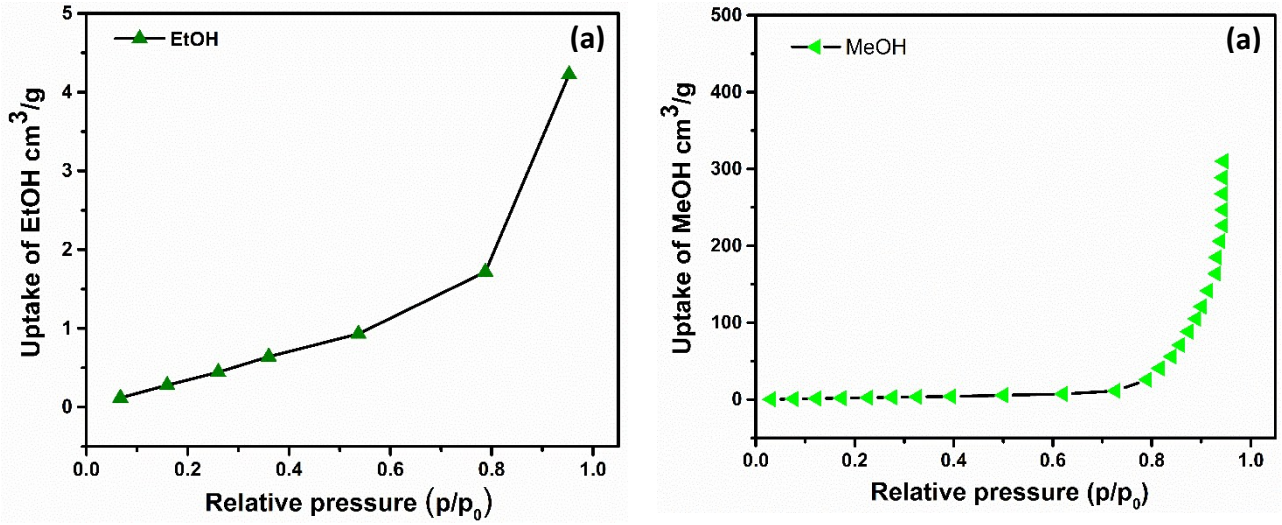

Fig. S8 Ethanol (a) and Methanol (b) sorption isotherms of **1** at 291 K.

Section VI: Impedance measurements of **1**

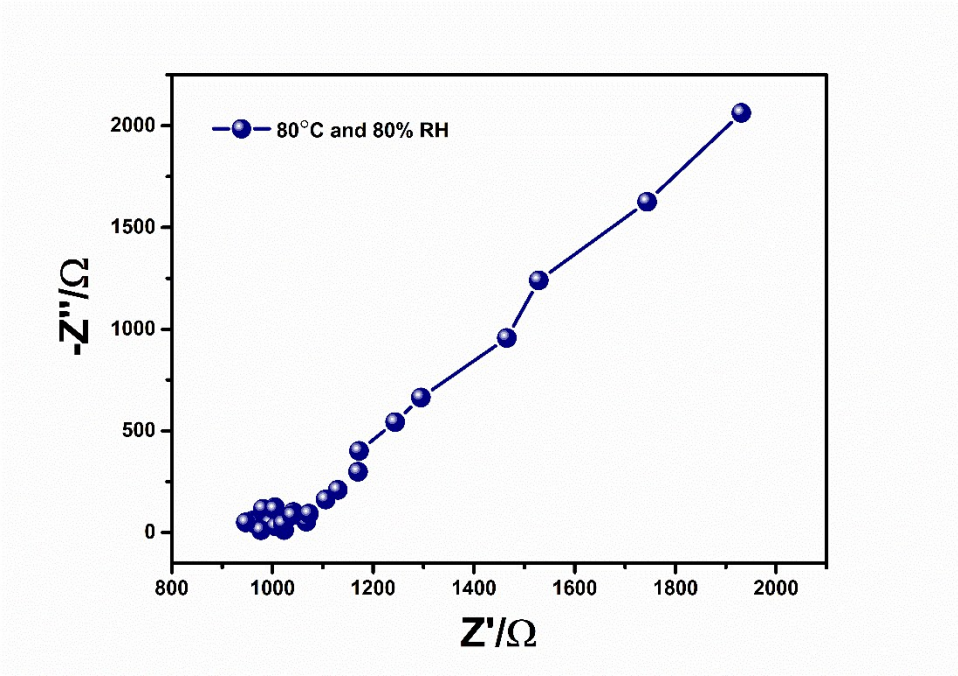

Fig. S9 Nyquist plot of **1** at 80 °C and 80% RH.

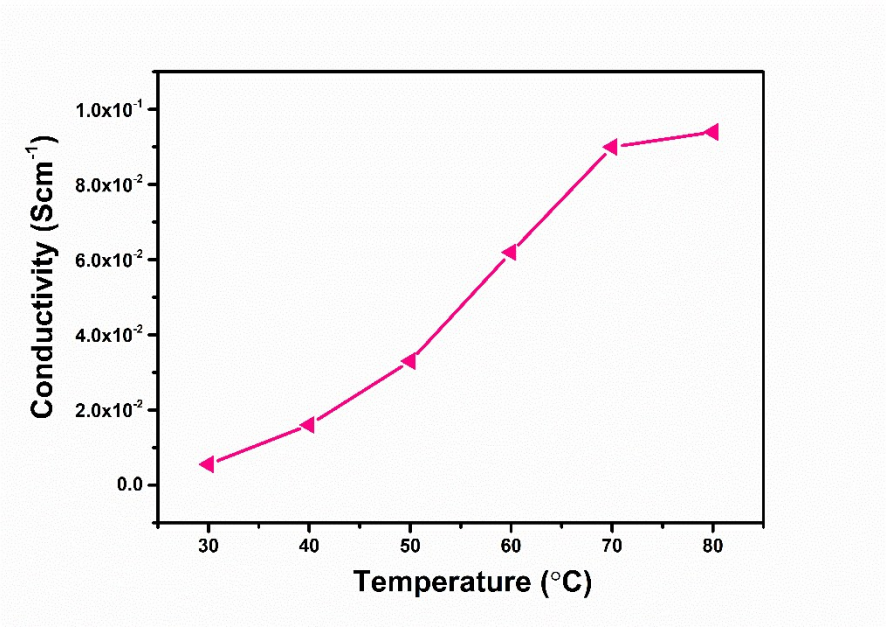

Fig. S10 Plot of conductivity vs temperature at 95% RH of **1**.

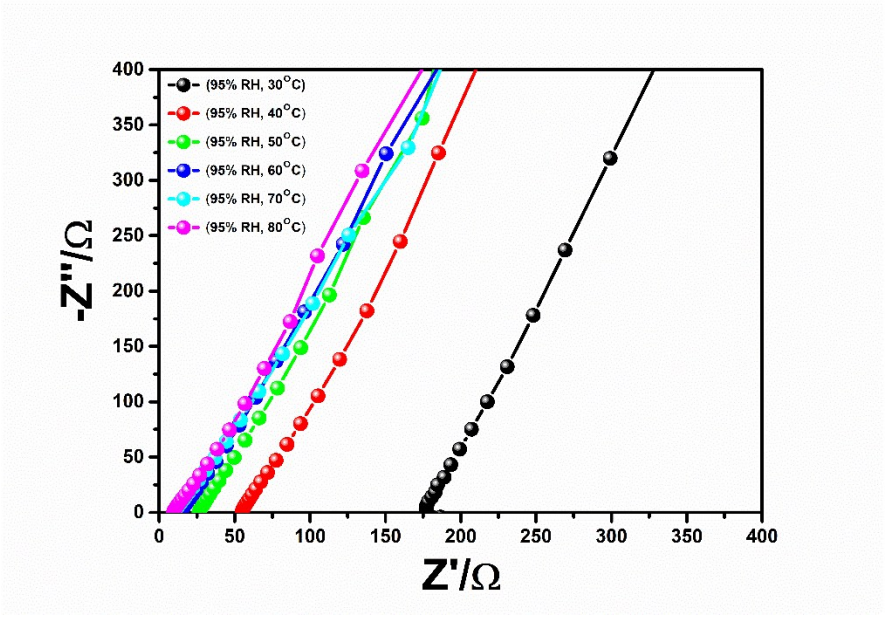

Fig. S11 Nyquist plot of proton conductivities of **1** at variable temperature at 95% RH.

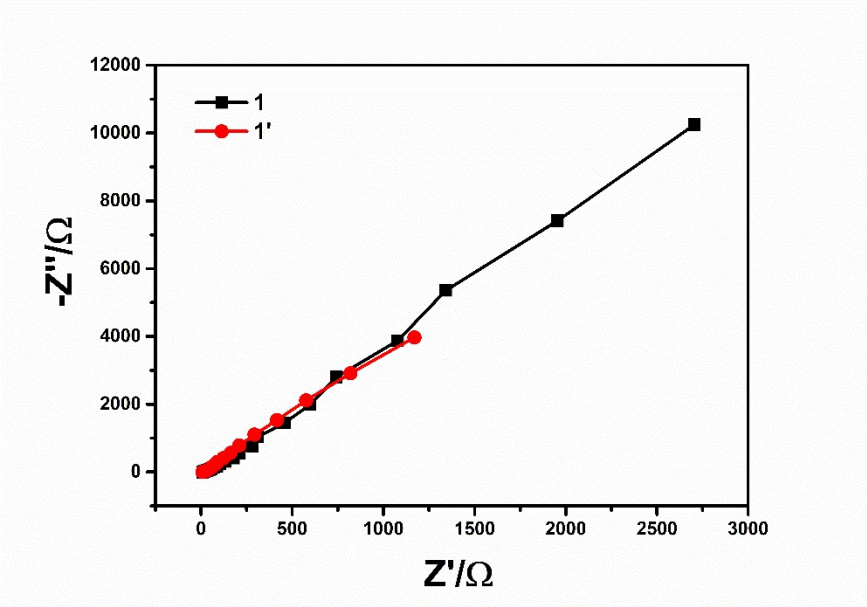

Fig. S12 Nyquist plots of **1** and **1**' at 80 °C and 95% RH exhibiting reproducible proton conductivity.

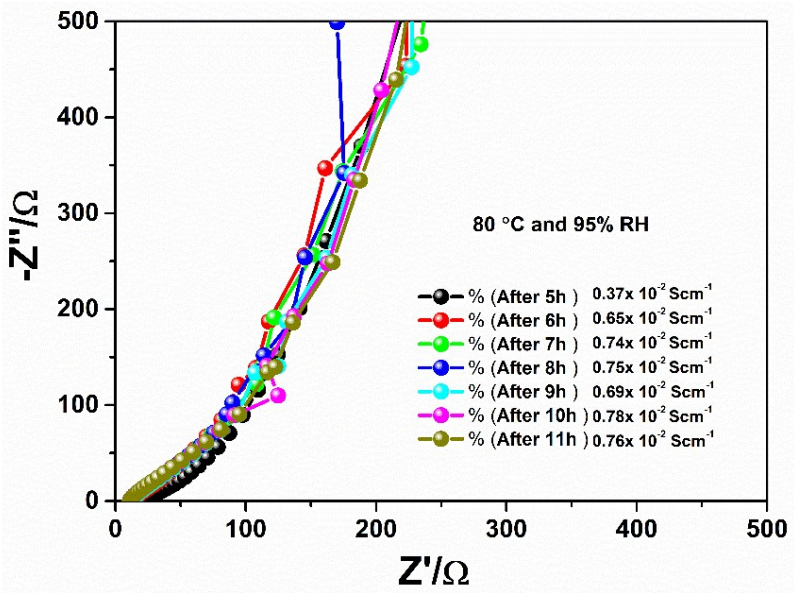

Fig. S13 Nyquist plots of **1** at 80 °C and 95% RH with respect to time.

Section VII: PXRD and IR patterns after impedance measurements of **1**.

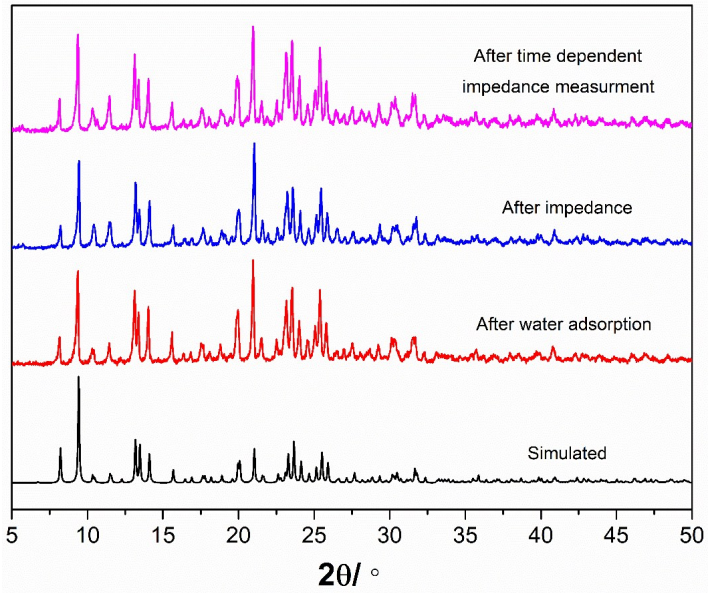

Fig. S14 Powder XRD patterns of simulated, as synthesized, after water sorption, after impedance measurement and time dependent measurements at 80°C and 95% RH of **1**.

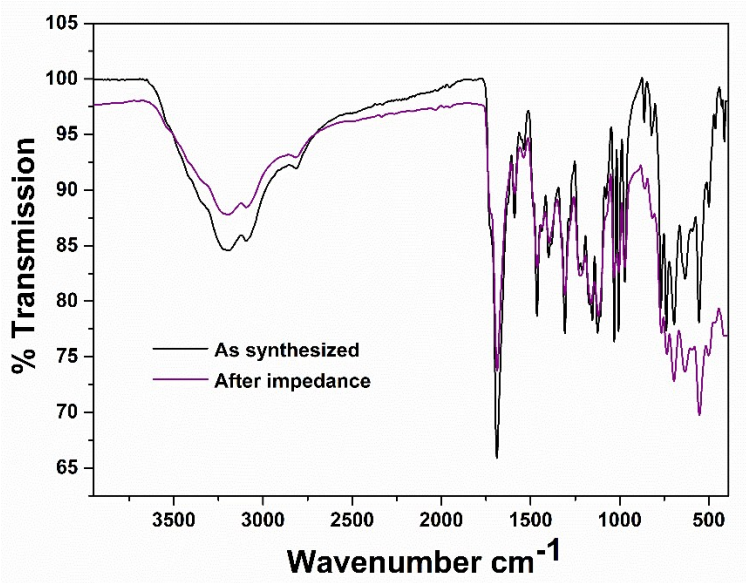

Fig. S15 FTIR patterns of as synthesized and after impedance measurement of **1**.

Section VIII: Computational studies of 1

We first look at all the RMSD, in Fig. S16, we have plotted RMSD of all the atoms for all time frames of MD simulations. Every "pixel" of the image indicates the RMSD value of an atom (with corresponding index on Y-axis) at a given time frame (X axis). The color indicates the deviations in Å. Clearly, there are only certain atoms that show significant deviations. We identify indices corresponding to the atoms that show deviation more than 0.6 Å, they all turned out to be hydrogen atoms attached to the water molecules in the lattice.

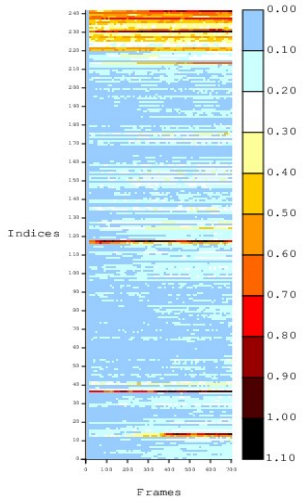

Fig. S16 RMSD of all the atoms for all time frames of MD simulation.

Hydrogen bonds in the framework as a function of MD simulation time is shown in Fig. S17. Plot indicates, throughout the simulation run, the network of hydrogen bonds is maintained, indicating a sustained pathway for H^+ hopping.

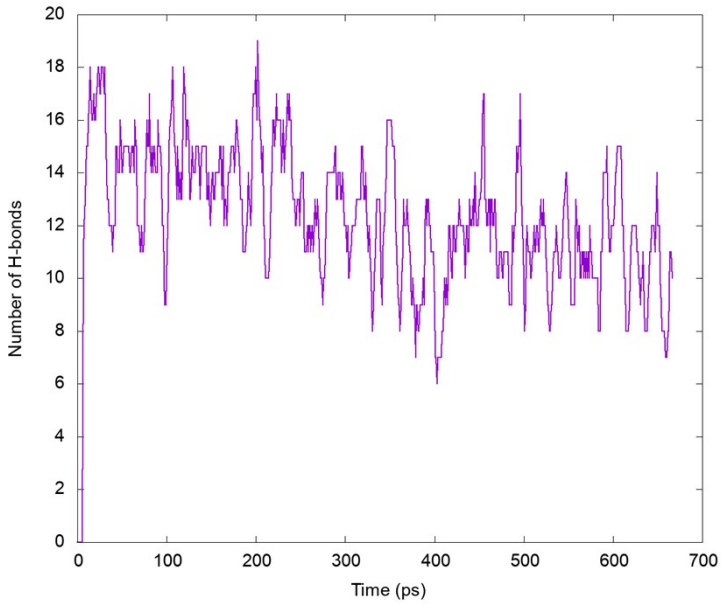

Fig. S16 Hydrogen bonds in the framework as a function of MD simulation time.

References:

1 T. Yamada, M. Sadakiyo and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 3144–3145.
2 C. Dey, T. Kundu and R. Banerjee, *Chem. Commun.*, 2012, **48**, 266–268.
3 S. Kim, K. W. Dawson, B. S. Gelfand, J. M. Taylor, G. K. H. Shimizu and B. S. Gelfand, *J. Am. Chem. Soc.*, 2013, **135**, 963–966.
4 J. M. Taylor, R. K. Mah, I. L. Moudrakovski, C. I. Ratcliffe, R. Vaidhyanathan and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2010, **132**, 14055–14057.
5 S. Morikawa, T. Yamada and H. Kitagawa, *Chem. Lett.*, 2009, **38**, 654–655.
6 A. Shigematsu, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 2034–2036.
7 S. C. Sahoo, T. Kundu and R. Banerjee, *J. Am. Chem. Soc.*, 2011, **133**, 17950–17958.
8 R. M. P. Colodrero, P. Olivera-Pastor, E. R. Losilla, M. A. G. Aranda, L. Leon-Reina, M. Papadaki, A. C. McKinlay, R. E. Morris, K. D. Demadis and A. Cabeza, *Dalton Trans.*, 2012, **41**, 4045–4051.
9 W. J. Phang, H. Jo, W. R. Lee, J. H. Song, K. Yoo, B. Kim and C. S. Hong, *Angew. Chem., Int. Ed.*, 2015, **54**, 5142–5146.
10 M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 9906–9907.
11 K. Kanaizuka, S. Iwakiri, T. Yamada and H. Kitagawa, *Chem. Lett.*, 2010, **39**, 28–29.
12 S. S. Nagarkar, S. M. Unni, A. Sharma, S. Kurungot and S. K. Ghosh, *Angew. Chem., Int. Ed.*, 2014, **53**, 2638–2642.
13 A. Shigematsu, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 2034–2036.
14 W. J. Phang, W. R. Lee, K. Yoo, B. Kim and C. S. Hong, *Dalton Trans.*, 2013, **42**, 7850–7853.
15 H. Okawa, A. Shigematsu, M. Sadakiyo, T. Miyagawa, K. Yoneda, M. Ohba and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 13516–13522.
16 T. Kundu, S. C. Sahoo and R. Banerjee, *Chem. Commun.*, 2012, **48**, 4998–5000.
17 R. M. P. Colodrero, P. Olivera-Pastor, E. R. Losilla, D. Hernández-Alonso, M. A. G. Aranda, L. Leon-Reina, J. Rius, K. D. Demadis, B. Moreau, D. Villemin, M. Palomino, F. Rey and A. Cabeza, *Inorg. Chem.*, 2012, **51**, 7689–7698.
18 A. Mallick, T. Kundu and R. Banerjee, *Chem. Commun.*, 2012, **48**, 8829–8831.