Supporting Information

Coordination Driven Fluorescent J-aggregates in a Perylenetetracarboxylate Based MOF: Permanent Porosity and Proton Conductivity

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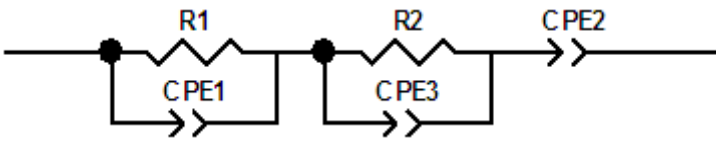
Synthesis of linker PTC:

A mixture of 5.0 g (12.7 mmol) of 3,4,9,10-perylenetetracaboxylicdianhydride and 5.0 g (89.1 mmol) of KOH in 100 mL water is refluxed overnight. A clear solution is obtained which is acidified by conc. HCl followed by formation of dark red precipitate. The precipitate is washed several times with distilled water to remove the extra acid.

Experimental details for impedance measurement

Instrumentation

The ac impedance spectroscopy measurements (for proton conductivity in **1)** were performed on a high performance Frequency analyzer (Novocontrol-Alpha Impedance Analyzer). The temperature variation proton conductivity measurements were obtained by using a Julabo cryostat (Julabo FP50-HL Circulator) coupled with the impedance analyser in the temperature range of 25 °C to 35 °C. The measurements under inert (Ar) atmosphere were performed by evacuating the sample pellet for 5 h to remove the guest water molecules from the crystal structure. Afterwards, the proton conductivity measurements were performed under inert atmosphere at ambient condition and the temperature was varied up to 61 °C. However measurements under humid conditions were performed up to a temperature of 35 °C to maintain the humidified condition.



Scheme S1. Equivalent circuit used for analysing the ambient condition impedance plots of **1**. Here, R1 and R2 correspond to the bulk and grain-boundary resistances respectively and CPE1, CPE2 and CPE3 are constant phase elements.

The proton conductivity of **1** at ambient condition (at 25 ^{o}C) was estimated from the intercept of the low frequency spike with the real axis as obtained from the impedance measurements. The reproducibility of the data and the compound stability were checked by collecting the data for a single set of heating-cooling cycle on the same pellet. The equivalent circuit used for the analysis of the impedance plots recorded at ambient condition (~40% RH) is shown in Scheme S1. The data were fitted to a series combination of two resistances both in turn parallel with constant phase elements (CPE) and a CPE (CPE2) using the ZView^{TM} [Scribner Associates Inc.] software. The proton conductivity (σ) at a particular humidity and temperature was finally calculated using the following equation

$$\sigma = \frac{1}{R} \times \frac{L}{A}$$

where L and A are the thickness (cm) and cross-sectional area (cm^2) of the pellet respectively, and R is the bulk resistivity of the sample.

Table S1: Selected bond lengths (Å) for **1**.

K1- O2	2.599(4)	K3-O5	2.649(3)	K3-O4	2.726(4)
K8- O1	2.706(8)	K3-O10	2.811(4)	K4-O3	2.638(5)
K4- O3	2.638(5)	K6- O3	2.750(4)	K6- O8	2.863(5)
K6-O4	2.965(5)	K6- O1	3.058(4)	K9- O13	2.694(3)
K9- O8	2.884(6)	K9- O8	2.884(6)	K9- O1	2.888(4)
K9-O1	2.888(4)	K4-O12	2.819(4)	K4- O16	2.860(3)
K3- O11	2.855(4)	K3- O12	2.876(5)	K1- O7	2.679(4)
K1-O10	2.773(4)	K1- O6	2.846(3)	K1- O5	2.929(3)
K2- O9	2.649(4)	K2- O7	2.788(4)	K2-O3W	2.911(12)
K2-O3W	2.911(12)	K5- O1WA	2.509(10)	K5- O7	2.894(6)
K7-O9	2.433(7)	K7- O4W	2.62(2)	K7- O6	2.754(6)
K8-O4W	3.03(3)	K8- O2W	2.54(3)		

Table S2: Selected bond angles (º) for **1**.

O2-K1-O7	87.59(15)	O2-K1-O14	108.57(13)	O7-K1-O14	159.95(12)

O2-K1-O10	93.71(16)	O7-K1-O10	97.74(17)	O14-K1-O10	93.08(12)
O2-K1-O6	134.75(14)	O7-K1-O6	66.93(11)	O14-K1-O6	93.04(10)
O10-K1-O6	125.12(10)	O2-K1-O13	82.94(15)	O7-K1-O13	128.43(16)
O14-K1-O13	45.95(10)	O10-K1-O13	133.30(11)	O6- K1-O13	84.94(9)
O2-K1-O5	156.31(13)	O7-K1-O5	70.75(13)	O14-K1-O5	94.69(11)
O10-K1-O5	80.26(10)	O6-K1-O5	44.88(9)	O13-K1-O5	117.84(10)
O2-K1-O8	73.28(15)	O7-K1-O8	42.25(19)	O14-K1-O8	130.04(16)
O10- K1- O8	136.85(17)	O6- K1- O8	62.62(12)	O13- K1- O8	86.78(14)
O5- K1-O8	95.42(10)	O9- K2- O2	93.92(16)	O5- K2- O2	133.52(12)
O4- K2- O2	68.79(14)	O9- K2- O7	88.59(18)	O5- K2- O7	143.78(14)
O4-K2-O7	128.00(19)	O2-K2-O7	82.52(13)	O9-K2-O3W	120.1(2)
O5-K2-O3W	80.5(2)	O4-K2-O3W	99.6(2)	O2-K2-O3W	135.6(2)
O7-K2-O3W	71.6(2)	O1WA-K5-O3W	51.1(3)	O1WA-K5-O15	132.6(2)
O3W-K5-O15	135.5(3)	O1WA-K5-O14	66.2(2)	O3W-K5-O14	82.6(3)
O15-K5-O14	68.96(13)	O1WA-K5-O7	121.5(3)	O3W-K5-O7	74.1(3)
O15-K5-O7	99.29(19)	O14-K5-O7	131.20(17)	O9-K7-O14	140.0(3)
O9-K7-O4W	80.1(6)	O14-K7- O4W	137.8(6)	O9- K7- O6	100.2(2)
O14- K7- O6	98.5(2)	O4W- K7- O6	81.5(6)	O9- K7- O15	92.4(2)
O14- K7- O15	70.25(16)	O4W-K7- O15	102.6(7)	O6- K7- O15	167.3(2)

O9- K7- O5	79.6(2)	O14- K7- O5	91.2(2)	O4W-K7- O5	114.0(7)
O6- K7- O5	42.55(12)	O15- K7- O5	140.3(2)	O9- K7- O16	126.1(2)
O14- K7- O16	60.93(14)	O4W-K7- O16	86.1(7)	O6- K7- O16	128.9(2)
O15- K7- O16	40.74(12)	O5- K7- O16	151.1(2)	O9- K7- O13	178.0(3)
O14- K7- O13	40.58(12)	O4W-K7- O13	99.9(6)	O6- K7- O13	77.78(15)
O15- K7- O13	89.59(15)	O5- K7- O13	98.57(17)	O16-K7- O13	55.85(12)
O2W- K8- O6	130.6(6)	O2W- K8 -O1	116.7(6)	O6- K8 -O1	102.4(2)
O2W-K8- O4W	133.5(8)	O6- K8- O4W	76.5(4)	O1- K8- O4W	84.3(5)
O15- K3- O5	119.83(12)	O15- K3- O4	99.33(14)	O5- K3- O4	80.21(14)
O15- K3- O10	124.46(14)	O5- K3- O10	84.61(11)	O4- K3- O10	135.35(13)
O15- K3- O11	125.64(17)	O5- K3- O11	113.78(16)	O4- K3 -O11	80.92(13)
O10- K3- O11	67.40(12)	O15- K3 -O12	86.54(13)	O5- K3 -O12	150.12(11)
O4- K3- O12	111.09(15)	O10- K3- O12	67.81(11)	O11-K3- O12	45.74(17)
O15- K3- O9	82.66(12)	O5 -K3- O9	107.57(11)	O4- K3- O9	169.82(14)
O10- K3 -O9	41.80(12)	O11- K3- O9	89.80(11)	O12 -K3- O9	58.92(12)
O3 -K4-O3	180.0	O3- K4- O12	77.67(17)	O3- K4- O12	102.33(17)
O3 -K4- O12	102.33(17)	O3- K4 -O12	77.67(17)	O12-K4 -O12	180.0
O3- K4- O16	104.17(14)	O3 -K4- O16	75.83(14)	O12-K4- O16	82.34(12)
O12 -K4 -O16	97.66(12)	O3 -K4- O16	75.83(14)	O3- K4- O16	104.17(14)
O12- K4- O16	97.66(12)	O12 -K4 -O16	82.34(12)	O16-K4- O16	180.00(14)
O11- K6- O13	137.28(13)	O11- K6- O3	91.1(2)	O13- K6- O3	107.46(18)
O11 -K6- O16	77.88(16)	O13 -K6- O16	70.46(10)	O3 -K6- O16	75.62(12)
O11 -K6-O8	102.54(19)	O13- K6 -O8	81.41(17)	O3- K6- O8	148.63(14)

O16 -K6 -O8	134.56(15)	O11 -K6 -O4	81.04(12)	O13 -K6 -O4	138.39(10)
O3 -K6- O4	44.33(16)	O16- K6 -O4	115.24(12)	O8 -K6 -O4	109.57(17)
O11- K6- O1	141.00(13)	O13 -K6 -O1	81.26(11)	O3 -K6- O1	65.92(15)
O16 -K6- O1	121.87(13)	O8- K6- O1	86.57(13)	O4 -K6- O1	60.35(12)
O13 -K9 -O13	180.00(17)	O13- K9- O8	81.15(12)	O13 -K9- O8	98.85(12)
O13 K9 O8	98.85(12)	O13 -K9- O8	81.15(12)	O8 -K9 -O8	180.0
O13 -K9- O1	84.62(12)	O13- K9- O1	95.38(12)	O8- K9- O1	89.47(17)
O8 -K9- O1	90.53(17)	O13 -K9- O1	95.38(12)	O13- K9- O1	84.62(12)
O8 -K9- O1	90.53(17)	O8 -K9- O1	89.47(17)	O1 -K9- O1	180.0

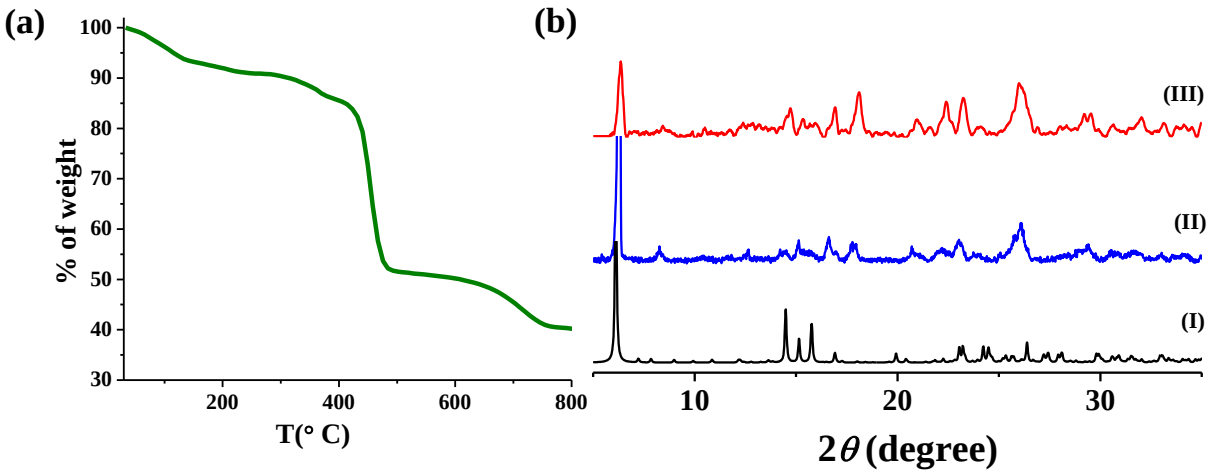


Figure S1. (a) TGA profile of **1** (expt., 9.0 wt% cald., 8.7 wt %; heating rate = 3 °C min^{-1}) in the temperature range of 30 – 800 °C under continuous N_2 flow. (b) PXRD patterns of **1** in different states: (I) simulated, (II) as-synthesized **1,** (III) desolvated **1** (**1′**).

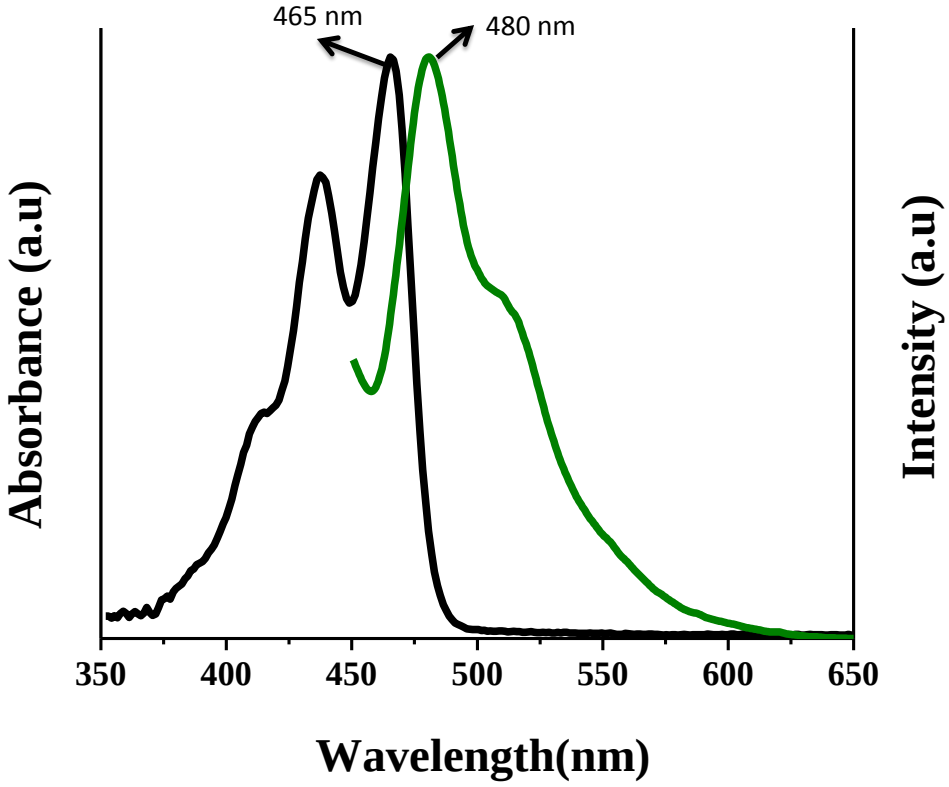


Figure S2. Absorbance (black) and emission (green) spectra (λ_{ex} = 420 nm) of monomer perylene tetracarboxylate in 10^{-6} M KOH solution.

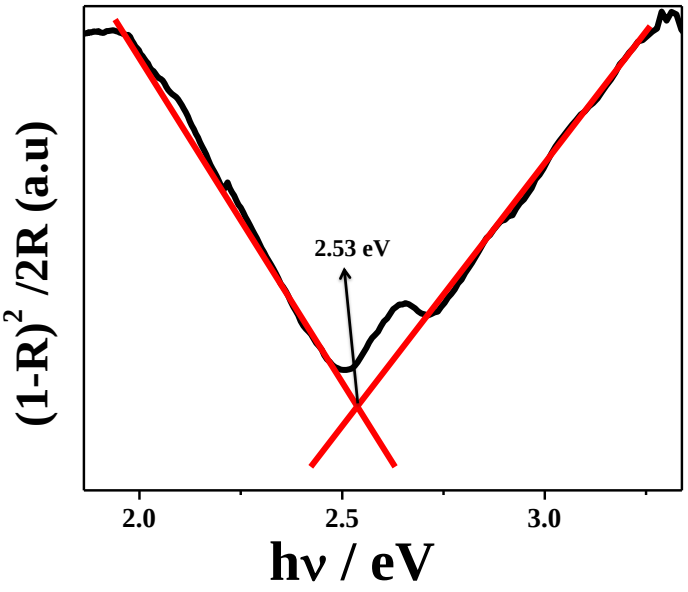


Figure S3. Kubelka-Munk fitting of solid state reflectance spectra of compound **1**.

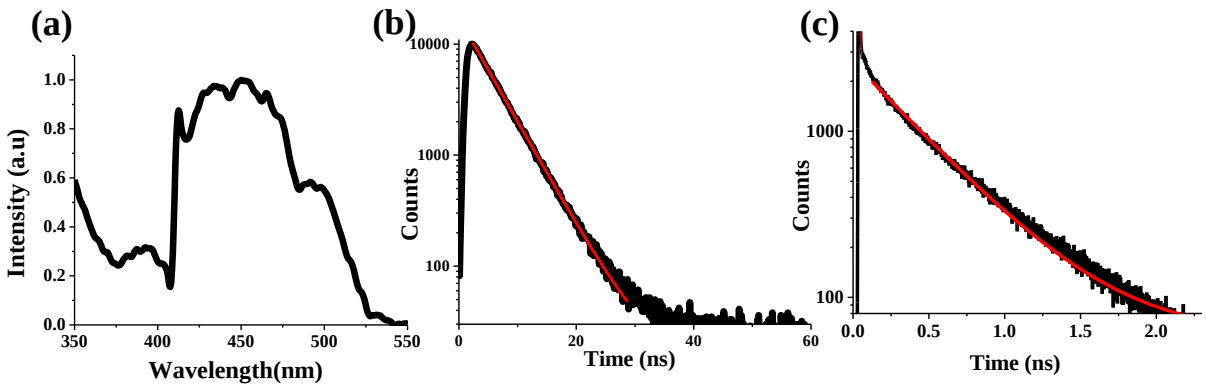


Figure S4. (a) Excitation spectra (λ_{ex} = 675 nm) of compound **1.** (b) Time-resolved fluorescence decay profile of PTC monomer excited at 442 nm and (c) time-resolved fluorescence decay profile of **1** excited at 480 nm.

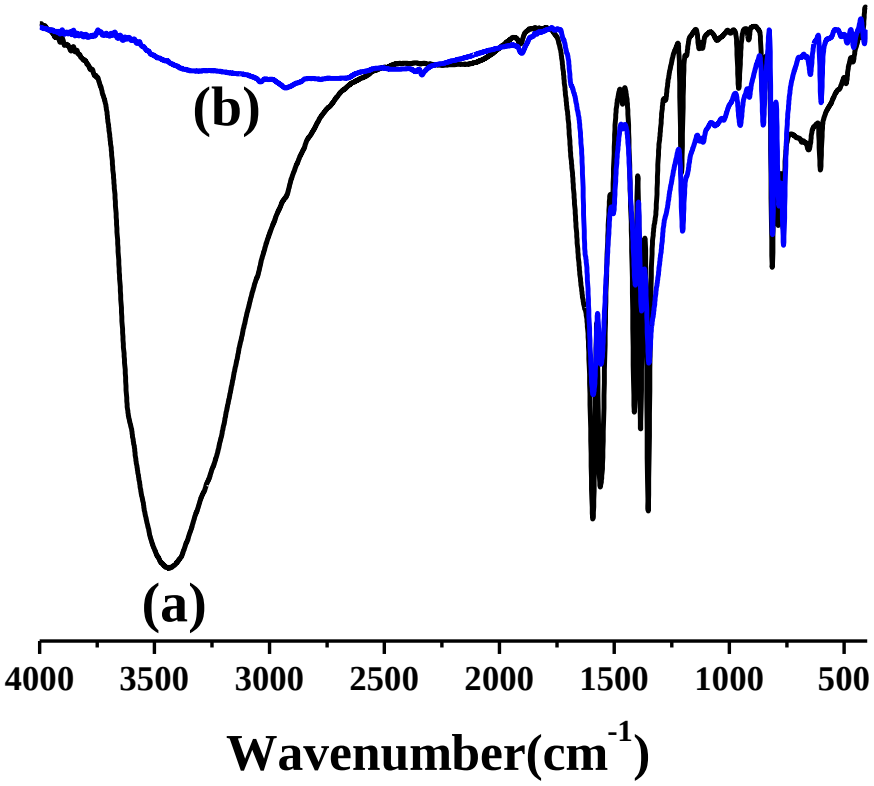


Figure S5. FTIR spectra of **1** recorded in different states (a) as-synthesized crystals (showing broad featureless O-H str. frequency of water molecules) and (b) fully desolvated crystals.

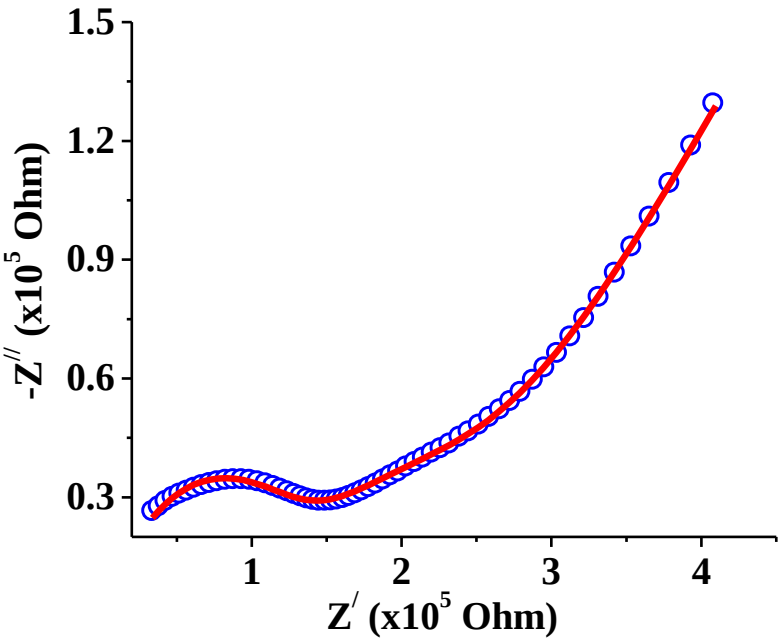


Figure S6. Nyquist plots of **1** at ambient condition (25 °C, 40% RH) before keeping in vacuum; blue circle represents the data and the red line represents fitted data.

Table S3. This represents activation energy and conductivity of **1** at various RHs.

RHs (%)	σ (Scm^{-1}) at 25 °C	σ (Scm^{-1}) at 35 °C	E_a (eV)
Inert atmos.	7.2×10^{-11}	2.4×10^{-10}	0.97
Ambient cond. (40%RH)	1.08×10^{-6}	2.0×10^{-6}	0.47
52	1.2×10^{-6}	2.2×10^{-6}	0.45
75	7.9×10^{-6}	1.2×10^{-5}	0.39
98	1.0×10^{-3}	1.6×10^{-3}	0.23

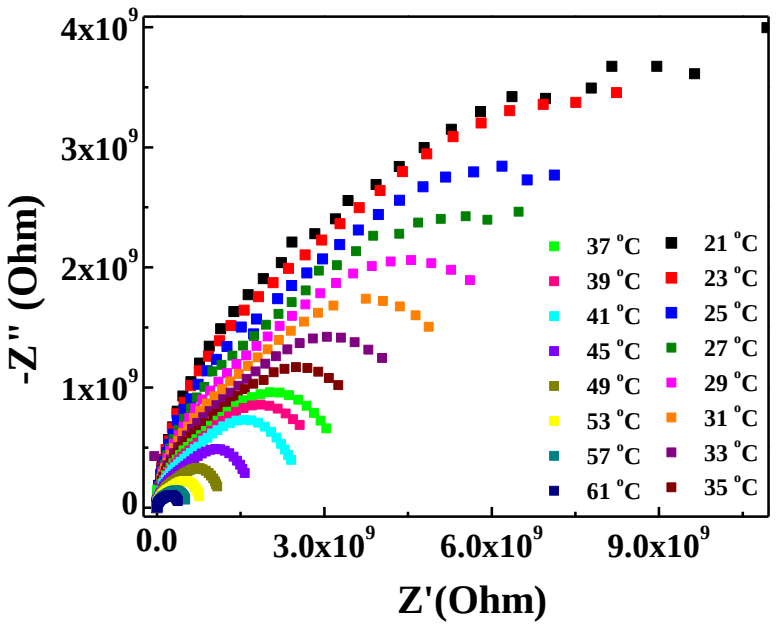


Figure S7. Nyquist plots of **1** under inert (Ar) atmosphere in the temperature range of 21-61 ^{o}C.

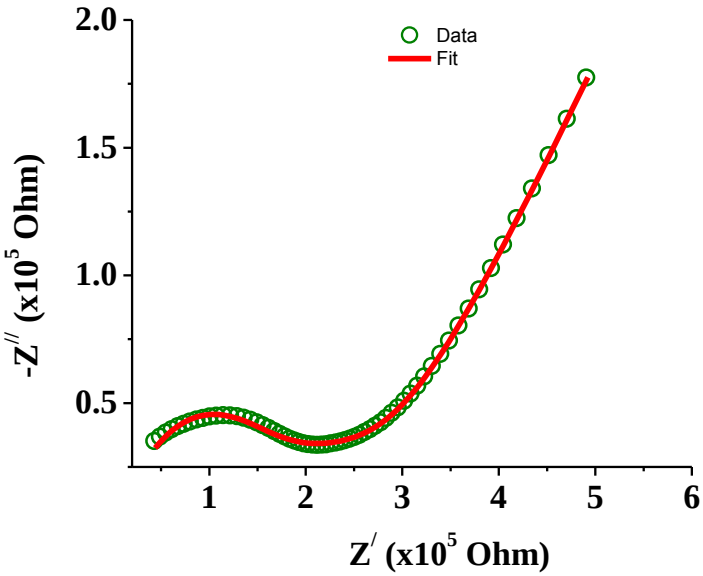


Figure S8. Nyquist plot of **1** at ambient condition (25 °C, 40% RH) after keeping in vacuum; green circle represents the data and the red line represents fitted data.

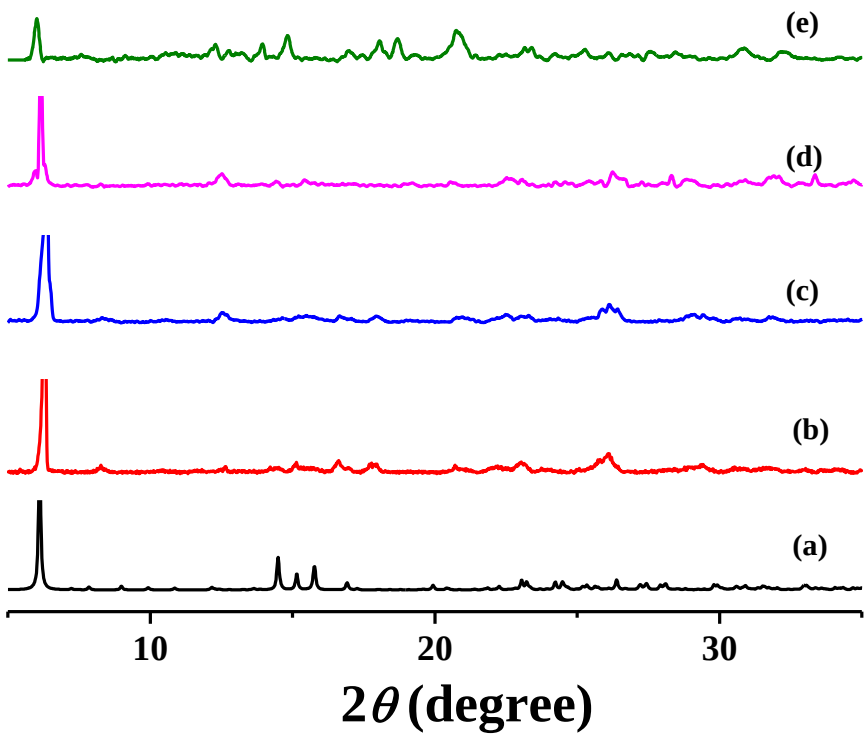


Figure S9. PXRD patterns of **1** in different states showing the structural stability in different relative humidities (RH) (a) simulated (b) 40% RH (ambient condition) (c) 52% RH (d) 75% RH and (e) 98% RH.

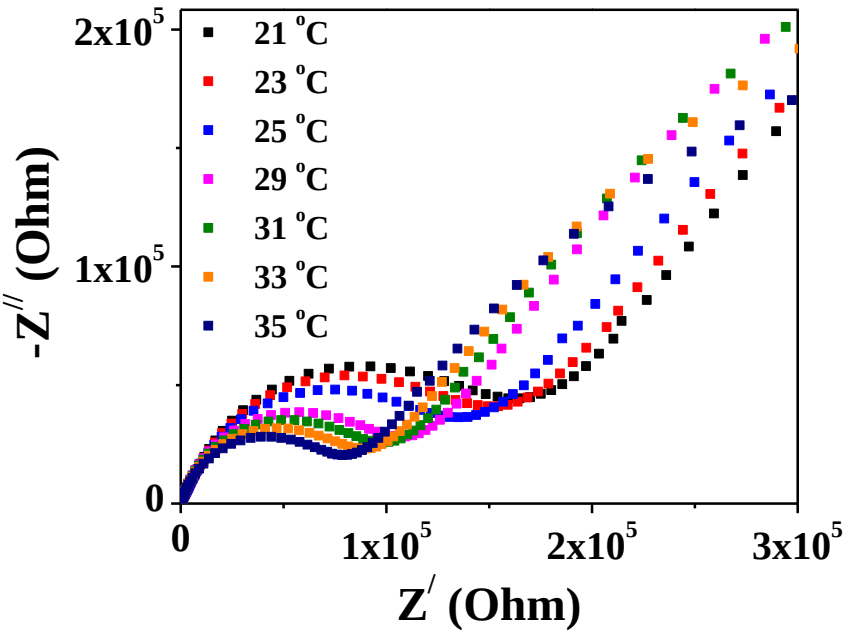


Figure S10. Nyquist plots of **1** at ambient condition (RH 52%) in the temperature range of 21-35 °C.

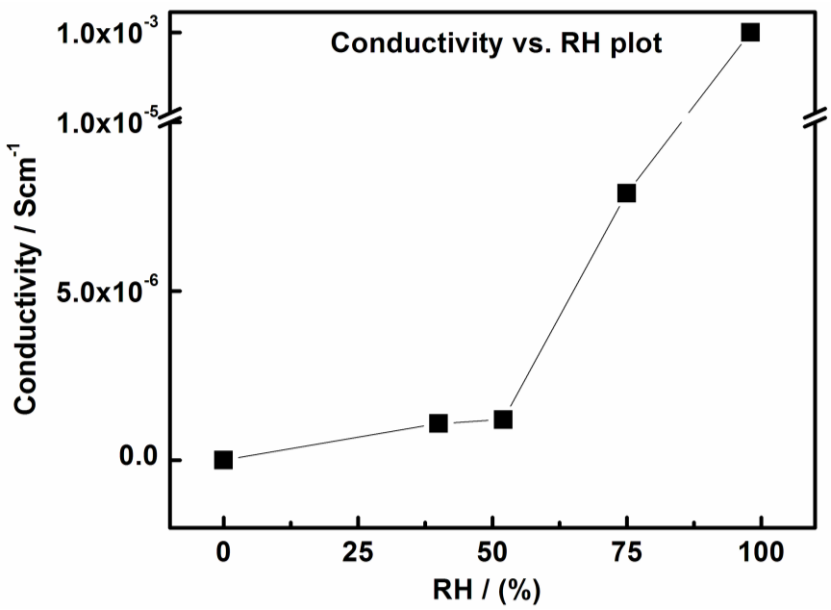


Figure S11. Plot of proton conductivity of **1** (Scm^{-1}) vs. RH (%).

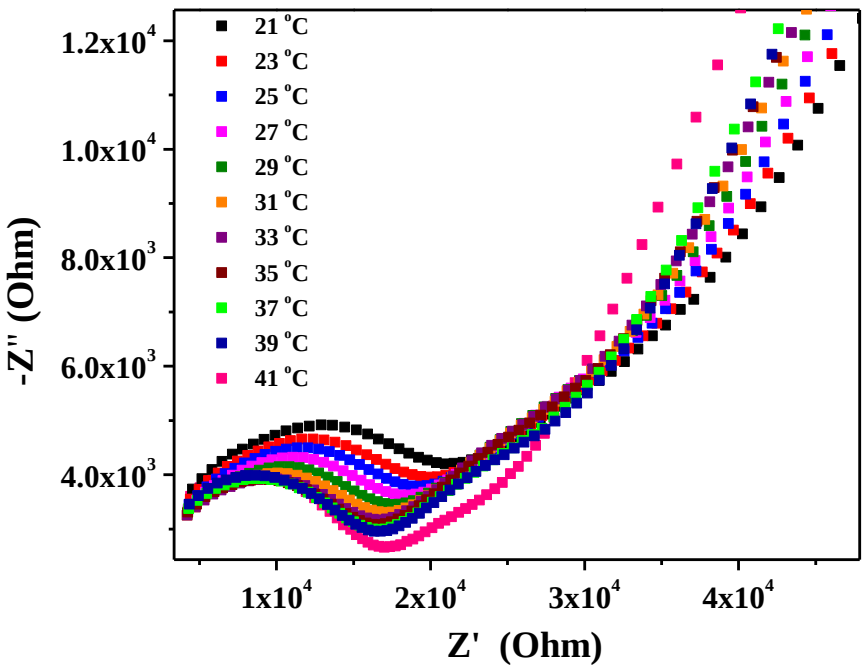


Figure S12. Nyquist plots of **1** at ambient condition (RH 40%) in the temperature range of 21-41° C.

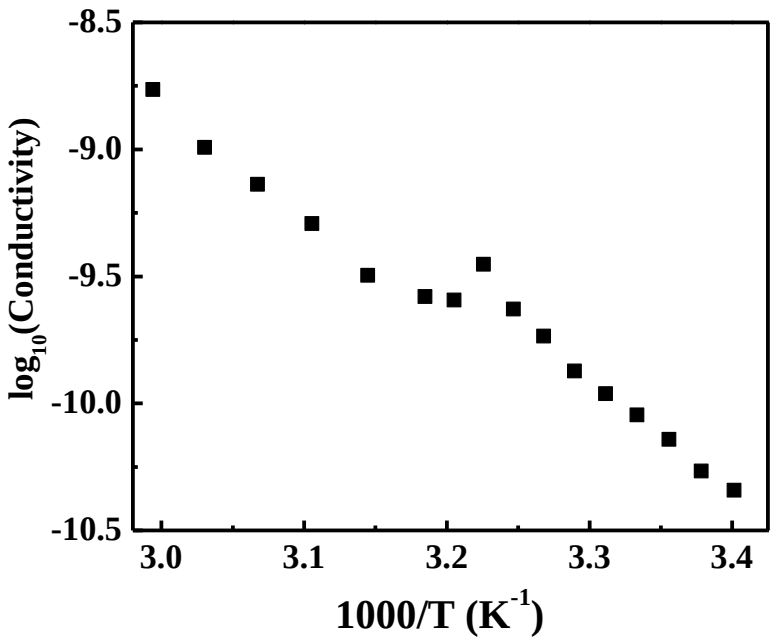


Figure S13. Arrhenius plot of **1** under inert (argon) atmosphere after evacuating the pellet for 5 h.

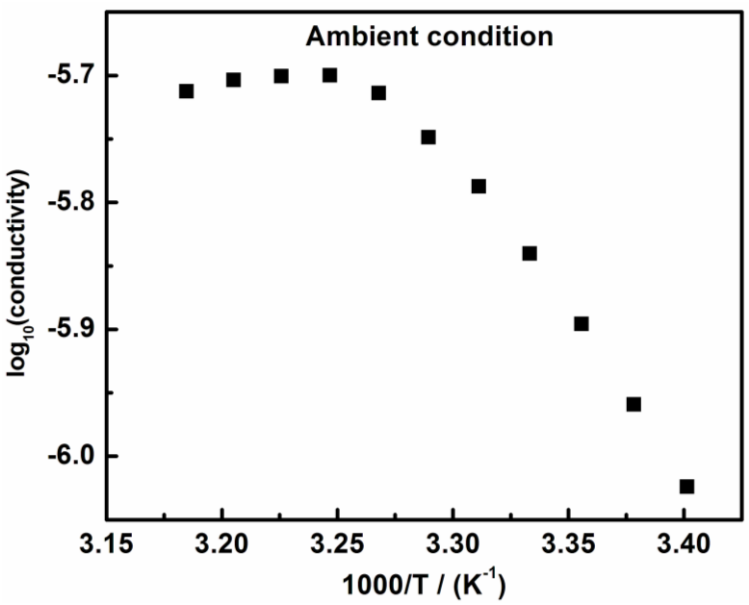


Figure S14. Arrhenius plot of **1** at ambient condition (RH = 40%) in the temperature range of 21-41 °C.

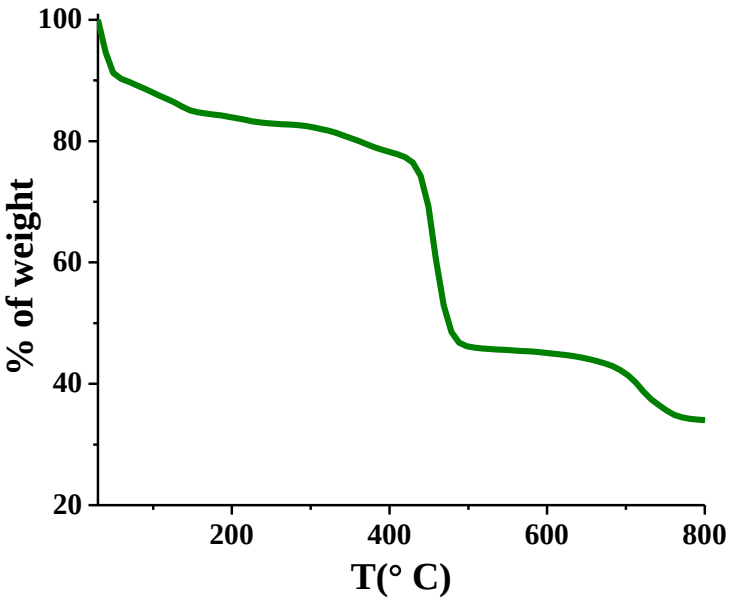


Figure S15. TGA profile of **1** recorded after keeping the crystals in 98% RH for 3 days.

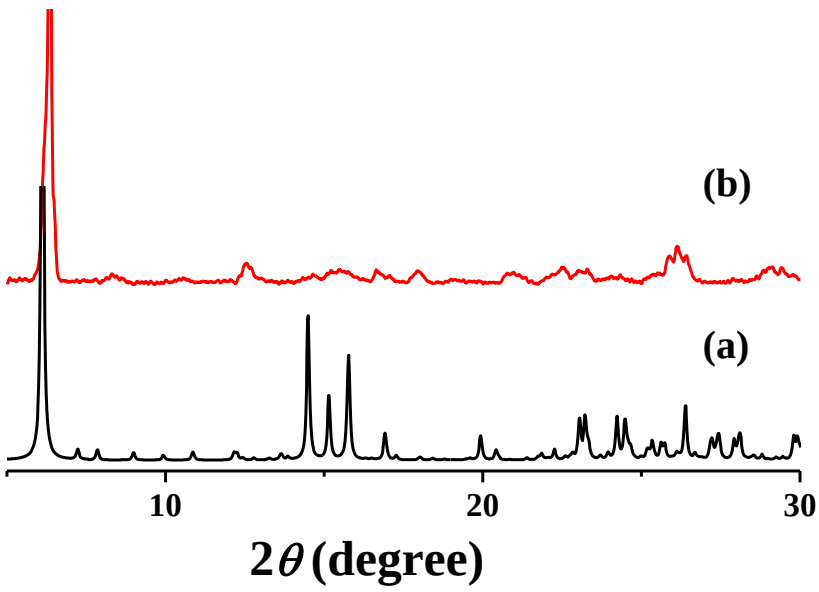


Figure S16. PXRD patterns of (a) simulated and (b) **1** after keeping in vacuum.

Table S4. Comparison of proton conductivities based on only water channel mediated pathway in MOFs.

Framework	Conductivity	Activation energy (eV)	Measurement condition	Ref.
1	1.0×10^{-3}	0.23	25°C, 98% RH	This work
$[Mn(dhbq)\cdot H_2O]$	4×10^{-5}	0.26	RT, 98% RH	1
$[Mo_5P_2O_{23}][Cu(phen)(H_2O)]\cdot3.5H_2O$	2.2×10^{-5}	0.23	28°C, 98% RH	
$[(HOC_2H_4)_2(dtoa)Cu]$	5×10^{-6}	0.16	25°C 98% RH	

$\{NH(prol)_3\}[MCr(ox)_3]$	1×10^{-4}	n/a	25°C 98% RH	
$[NMe_3(CH_2CO_2H)][FeCr(ox)_3]$	0.8×10^{-4}	n/a	RT 65% RH	
PCMOF-3	3.5×10^{-5}	0.17	RT 98% RH	
Fe(OH)(bdc-COOH) (10-COOH)	2.0×10^{-5}	0.21	25°C 98% RH	
HKUST-1-H_2O (11-H_2O)	1.5×10^{-5}	n/a	RT methanol vapor	
$[Zn(l\text{-}Lcl)(Cl)]\cdot H_2O$	4.45×10^{-5}	0.35	30°C 98% RH	
$La(H_5DTMP)\cdot7H_2O$	8×10^{-3}	0.25	24°C, 98% RH	2
$(NH_4)_2(H_2adp)[Zn_2(ox)_3]\cdot3H_2O$	8×10^{-3}	0.63	25°C, 98% RH	
Ca-PiPhtA-NH_3	6.6×10^{-3}	0.4	24°C, 98% RH	
PCMOF-5	4×10^{-3}	0.16	62°C, 98% RH	
Cu−TCPP nanosheet	3.9×10^{-3}	0.28	25°C, 98% RH	

Cd-5TIA	3.61 x 10^{-3}	0.16	28°C, 98% RH	
In-IA-2D-1	3.4 x 10^{-3}	0.61	27°C, 98% RH	
Sulfonated MIL-53(Al)	~3 x 10^{-3}	NA	~65°C, <10	
$V^{II}[Cr^{III}(CN)_6]_{2/3} \cdot 4.2H_2O$	2.6 x 10^{-3}	0.10, 0.19	50°C 100% RH	
$[\{(Zn_{0.25})_8(O)\}Zn_6(L)_{12}(H_2O)_{29}(DMF)_{69}(NO_3)_2]_n$	2.3 x 10^{-3}	0.22	25°C, 95% RH	
Histamine@$[Al(\mu_2\text{-}OH)(1,4\text{-}NDC)]_n$	1.7 x 10^{-3}	0.25	150°C 0% RH	
$(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$	1.7 x 10^{-3}	0.23	40°C, 96% RH	
$Co^{II}[Cr^{III}(CN)_6]_{2/3} \cdot 4.8H_2O$	1.7 x 10^{-3}	0.22	35°C, 100% RH	
$MgH_6ODTMP\cdot 6H_2O$	1.6 x 10^{-3}	0.31	19 °C, 100% RH	
β-PCMOF2	1.3 x 10^{-3}	0.28	85°C, 90% RH	

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