Supporting information

High proton conductivity in an unprecedented anionic metalloring organic framework (MROF) containing novel metalloring clusters with the largest diameter

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Materials and Instrumentation

All reagents were commercially purchased and used without any further purification. The TGA were performed on a TGA/NETZSCH STA449C instrument heated from 40 to 800 ºC under a nitrogen atmosphere at a heating rate of 10 ºC/min. TG-MS was carried out on a STA449C-QMS403C thermal analysis-quadrupole mass spectrometer. Powder X-ray diffraction was recorded on a PANalytical X'pert PRO X-ray Diffractometer using Cu-$K\alpha$ radiation in the 2θ range of 5-50°. The Fourier transform infrared spectrum using KBr pellet was collected on a Spectrum-One FT-IR spectrophotometer in the range of 4000-400 cm^{-1}. Elemental analyses (C, H and N) were measured with an Elemental Vairo EL III Analyzer.

Adsorption Measurement

After the bulk of the solvent was decanted, the freshly prepared sample of **MROF-1** (~0.15 g) was soaked in acetone for 1 hour, and then the solvent was decanted. Following the procedure of acetone soaking and decanting 10 times, the solvent-exchanged samples were activated by vacuum at room temperature for 24 h until a pressure of 5 μm Hg. 196K CO_2 adsorption isotherms were measured on Micromeritics ASAP 2020 HD88 surface area analyzer for the guest-free **MROF-1**.

Proton Conductivity Measurement

AC Impedance Analysis. Proton conductivity testing was carried out on pelletized samples pressed in a cylindrical die (0.25 cm diameter, 0.2~0.3 cm length) at ~0.2 t for 2 minutes to prevent sample decomposition from the high pressure. Impedance analysis was performed on the pellets using a two-probe method with a Solartron SI 1260 Impedance/Gain-Phase Analyzer and 1296 Dielectric Interface Impedance Analyzer from 100 Hz-10 MHz with an input voltage 100 mV. Humidity and temperature were controlled using a XK-CTS80Z humidity control chamber. Measurement were taken in hydrated conditions and done at thermal equilibrium by holding for 20 minutes at each measuring temperature. The resistance value was determined from equivalent circuit fits of the first semi-circle using ZView Software.

Proton conductivity was calculated using the following equation:

$$\sigma = \frac{l}{SR} \qquad (1)$$

where l and S are the length (cm) and cross-sectional area (cm^2) of the samples respectively, and R, which was extracted directly from the impedance plots, is the bulk resistance of the sample (Ω). Activation energy (E_a) for the materials conductivity was estimated from the following equation:

$$\sigma T = \sigma_0 \exp(-\frac{E_a}{k_B T}) \quad (2)$$

where σ is the proton conductivity, σ_0 is the preexponential factor, k_B is the Boltzmann constant, and T is the temperature.

Single-crystal X-ray Diffraction Study

Data collection and structural analysis of crystal **MROF-1** was collected on an Agilent Technologies SuperNova single crystal diffractometer equipped with graphite monochromatic Cu *Kα* radiation (λ = 1.54178 Å). The crystal was kept at room temperature during data collection. Using Olex2, [S1] the structure was solved with the Superflip [S2] structure solution program using charge flipping and refined with the ShelXL [S3] refinement package using least squares minimization. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the ligands were placed in idealized positions and refined using a riding model. Because the partial $(Me_2NH_2)^+$ cations and guest solvent molecules in channels were highly disordered and could not be modelled properly, thus the SQUEEZE routine of PLATON was applied to remove contributions to scattering from $(Me_2NH_2)^+$ and solvent molecules. The reported refinements are of cation- and guest-free structure by SQUEEZE routine.[S4] The detailed crystallographic data and structure refinement parameters for these compounds are summarized in **Tab. S1** (CCDC1029033).

Synthesis of $[Me_2NH_2][In(thb)(pbdc)]\cdot 2.5DMF\cdot 3.5H_2O$ (MROF-1)

A mixture of $In(NO_3)_3\cdot 5H_2O$ (0.50 mmol, 185.00 mg), 4,4'-biphenyldicarboxylic acid (H_2bpdc, 1.0 mmol, 240.00 mg) and 2,5-thiophenedicarboxylic acid (H_2thb, 1.0 mmol, 172.16 mg) was sealed in a 20 mL of Teflon-lined stainless steel vessel with 6 mL of DMF. The mixture was heated to 120 ^oC in 4 h and kept this temperature for 5 days. Then the reaction system was cooled slowly to room temperature during another 3 days. The colourless hexagonal prismatic crystals of **MROF-1** were collected, washed with DMF and ethanol and dried in air (yield 87% based on $In(NO_3)_3\cdot 5H_2O$). Elemental analysis calcd. (%) for $C_{59}H_{85}N_7O_{28}S_2In_2$ (1634.11): C 43.36, H 5.24, N 6.00; found: C 43.62, H 5.01, N 5.86. IR (KBr, cm^{-1}): 3425s, 3067w, 2924w, 1926w, 1771w, 1666s, 1607vs, 1535vs, 1398vs, 1268w, 11822, 1111w, 1007w, 928vw, 877s, 778vs, 688s, 524w, 440s.

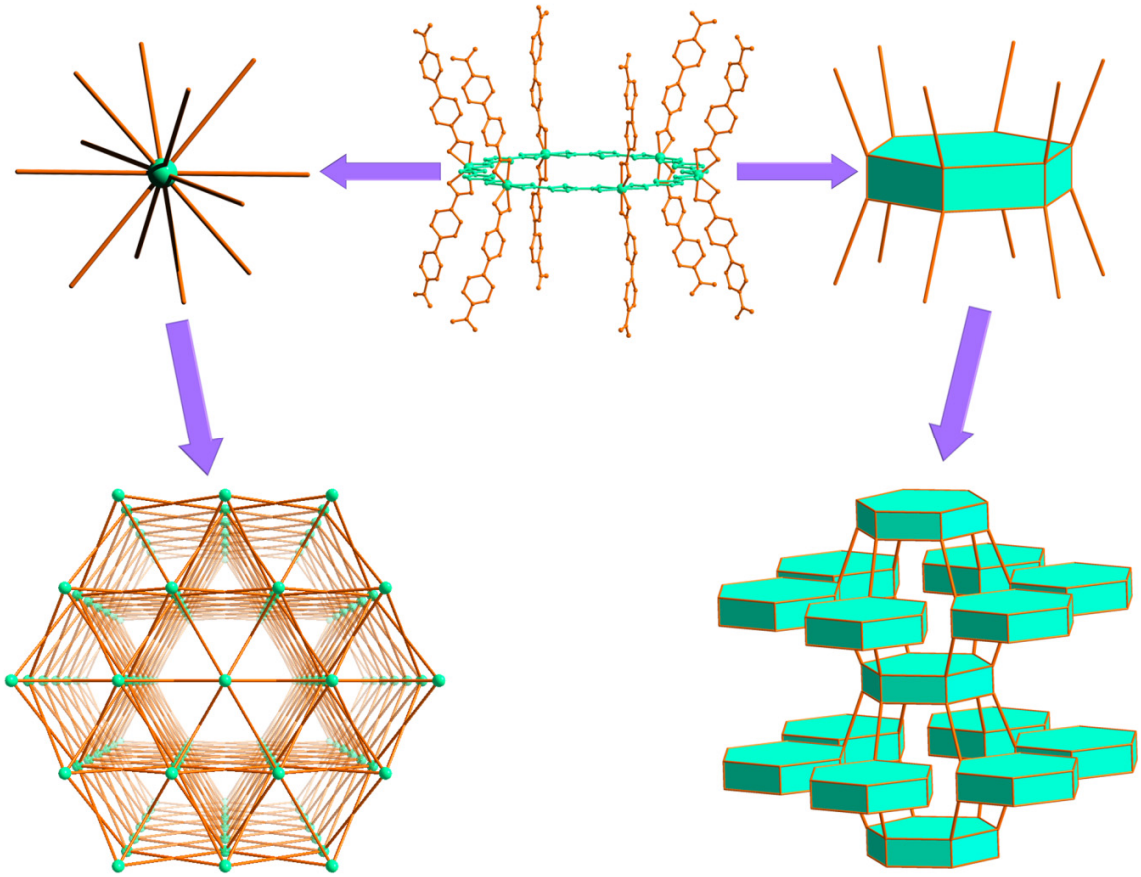


Fig. S1 A novel 12-c topology net is observed in **MROF-1**.

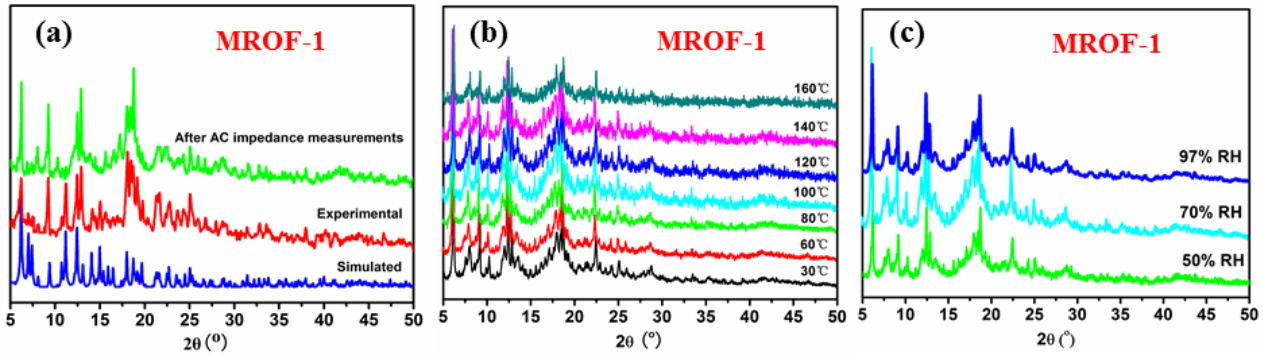


Fig. S2 The PXRD patterns of **MROF-1**at different temperature and ralative humidity.

The stability of the framework was confirmed by the variable temperature and variable humidity powder X-ray diffraction (VT-PXRD and VH-PXRD) technique. As shown in **Fig. S2**, the framework structure of **MROF-1** can be retained at temperatures up to 160 °C, and relative humidity range from 50% to 97%, without any phase change.

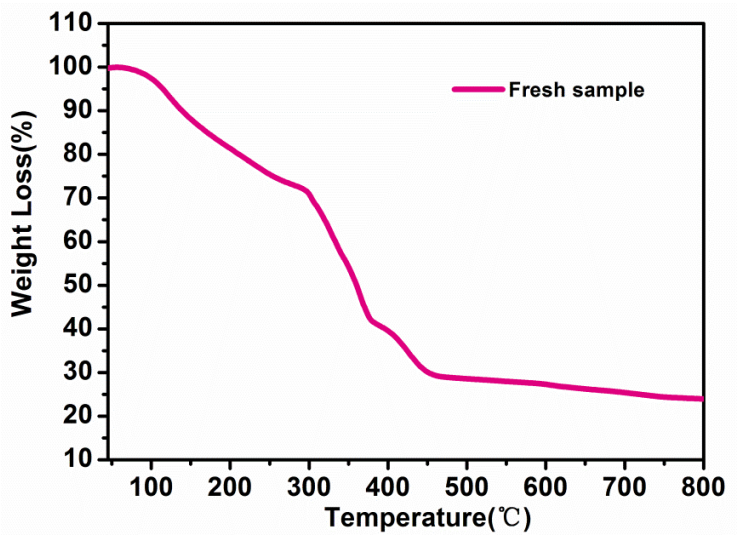


Fig. S3 The TGA curve of **MROF-1**.

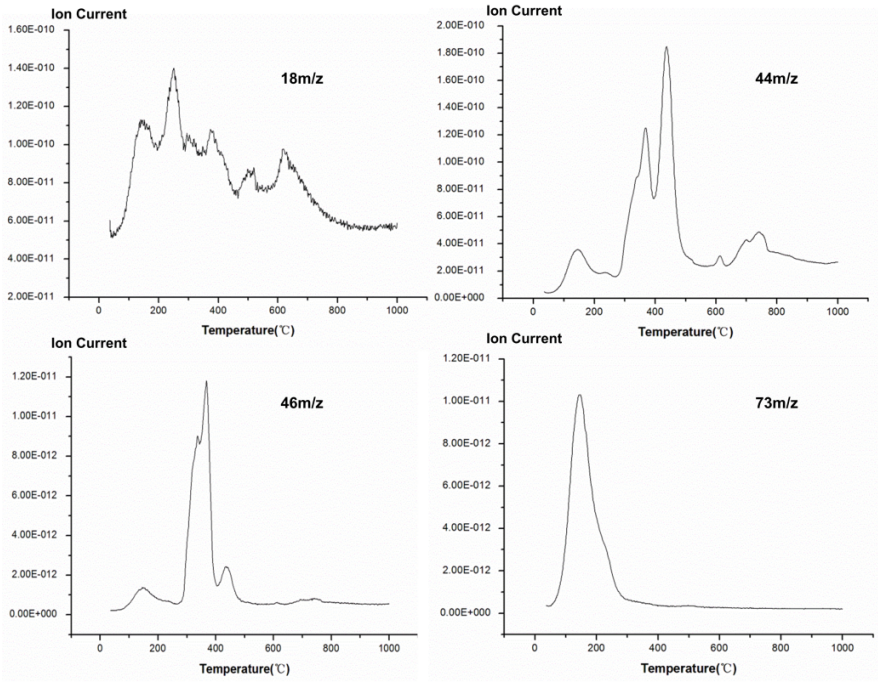


Fig. S4 The MS-TGA curves of **MROF-1**.

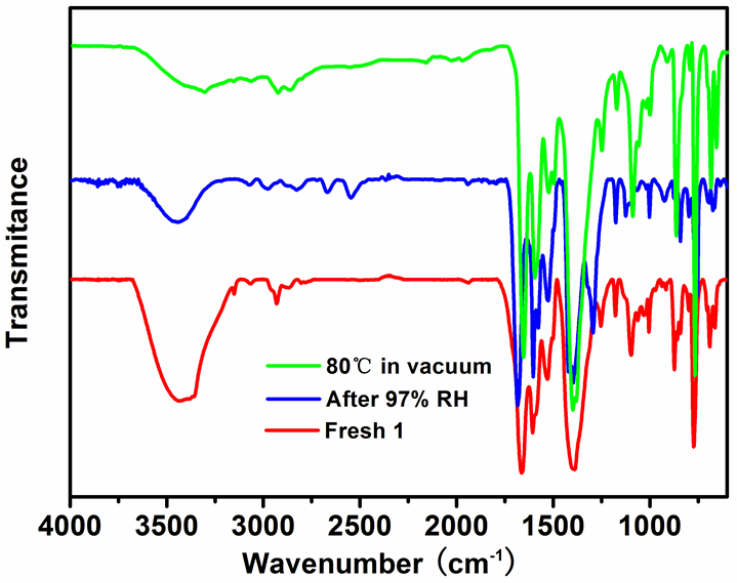


Fig. S5 The FT-IR spectra of ay-synthesized **MROF-1**, after treated in 97% RH and then dried.

The FT-IR spectrum of **MROF-1** shows the characteristic bands of the carboxylic groups in the usual region at 1156-468 cm^{-1} for symmetric vibrations and at 1581-1182 cm^{-1} for asymmetric vibrations. The absence of strong absorption associated with the carboxyl group at around 1607 cm^{-1} indicates that the carboxylic acid ligands are completely deprotonated. As shown in **Fig. S5**, after treated in 97% RH, the FT-IR spectrum of **MROF-1** exhibits two extra peaks (around 2548 and 2672 cm^{-1}), which belong to weak S-H bond vibrations.[S5] And the sample treated in 97% RH was dried at 80 ℃ and in vacuum, the two new peaks disappered. It suggests that the structure of **MROF-1** is intact.

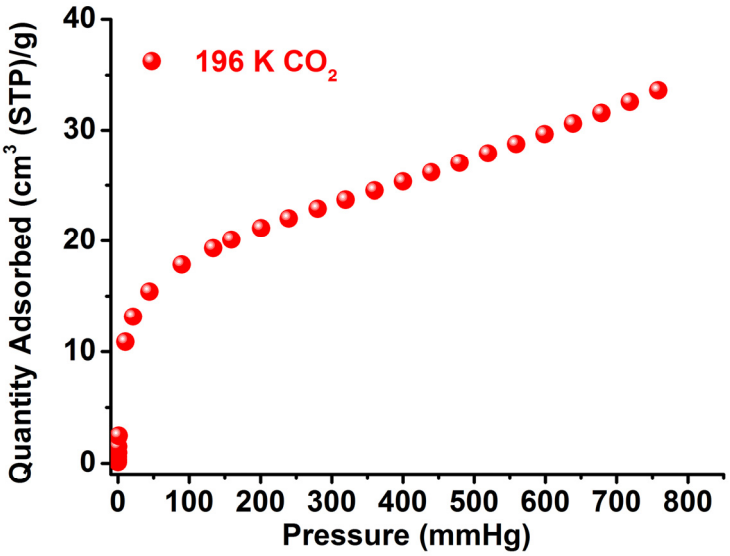


Fig. S6 CO_2 sorption isotherms of **MROF-1a** at 196 K.

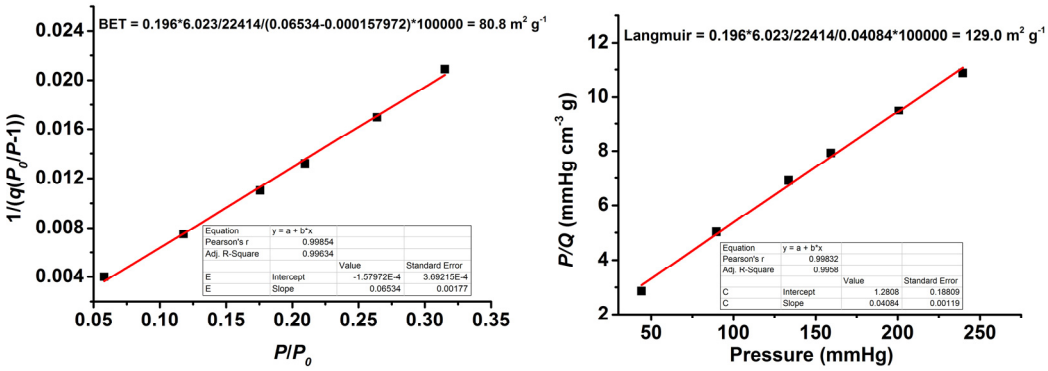


Fig. S7 The surface areas for **MROF-1a** obtained from the adsorption of CO_2 at 196 K**.** The BET (left) and Langmuir (right) surface areas are of 80.8 and 129.0 cm^2/g, respectively.

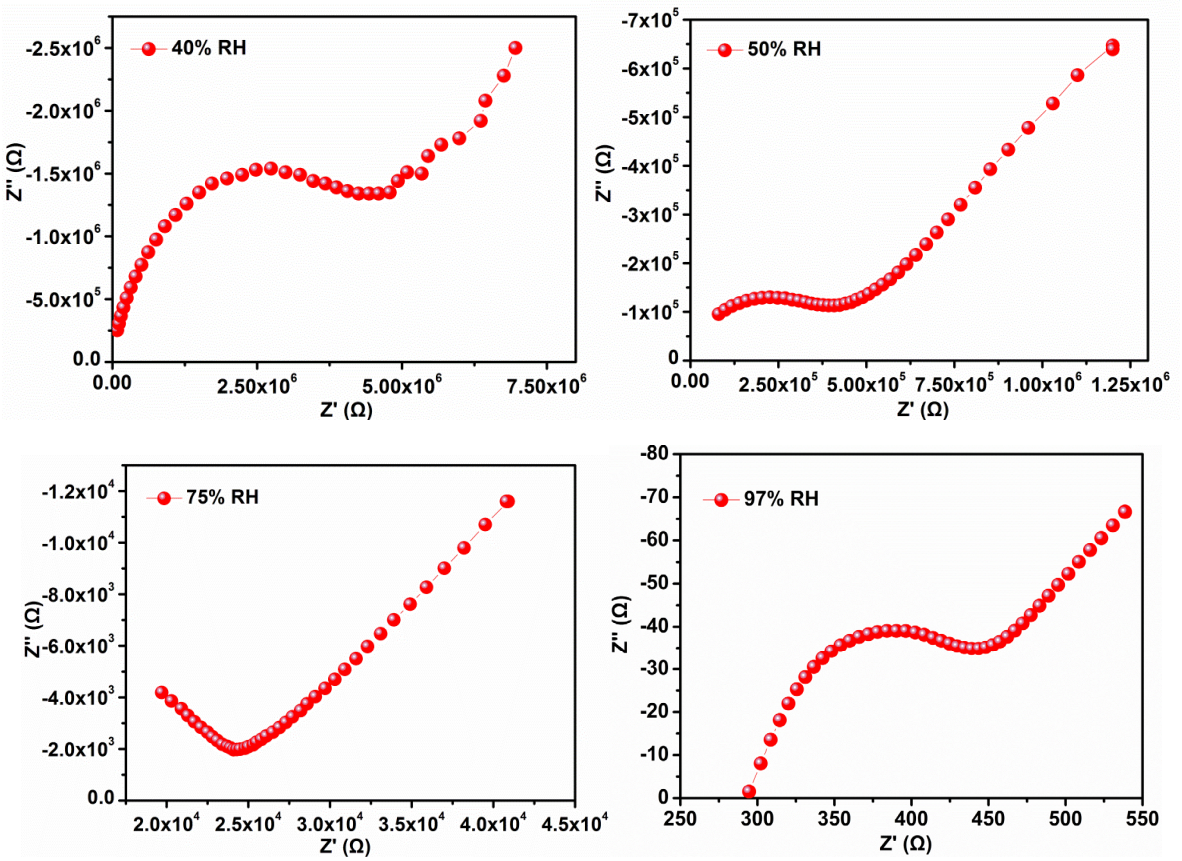


Fig. S8 Nyquist plots of **MROF-1** at 70°C under varying relative humidities.

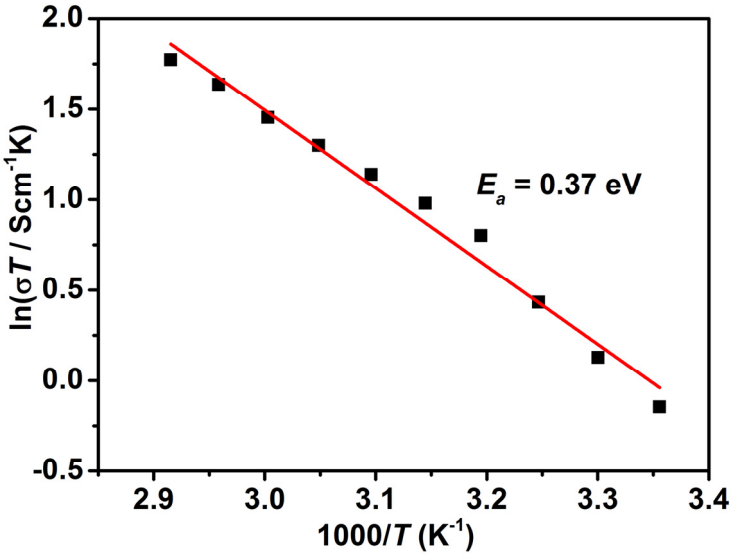


Fig. S9 Arrhenius plot of **MROF-1** between 20-70 °C at 97% RH.

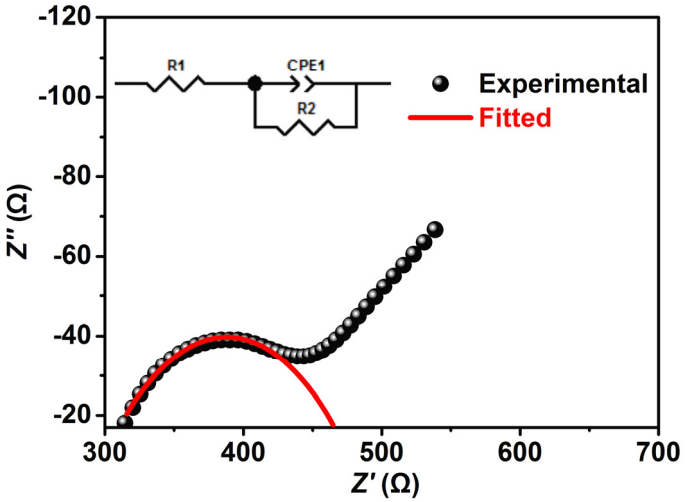


Fig. S10 Fitting for the Nyquist plot of **MROF-1** at 70°C and 97%RH, with circuit model used for the data fitting shown as an inset.

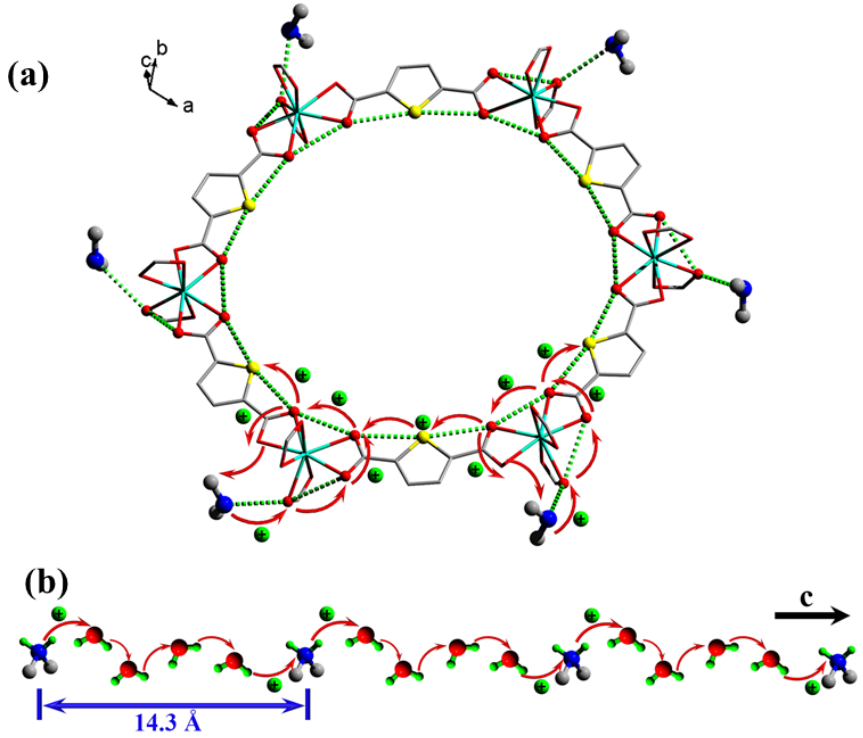


Fig. S11 Speculative proton pathway conduction for **MROF-1** based on single crystal X-ray data showing the actual positions of partial dimethyl ammonium cations within the structure. The green dashed lines represent the hydrogen-bonding interactions, and the red arrows indicate the possible movement of the H^+.

To account for the high proton conductivity of **MROF-1**, we speculate a possible Grotthuss mechanism for proton hopping within the metalloring cluster and along the 1D channel. Firstly, water molecules were adsorbed during humidification of as-synthesized sample by strong hydrogen bonding with dimethyl ammonium cations, thiophene sulphurs and In(III) bound carboxylate moieties. The $(Me_2NH_2)^+$ is known to provide easily dissociable protons in the presence of water molecule, so the H^+ from $(Me_2NH_2)^+$ was easy transferred to In(III) bound carboxylate moiety via hydrogen-bonding interactions. Again it further transferred to next carboxylate moiety or thiophene sulfurs via hydrogen-bonding interactions. Finally, this proton moved to another $(Me_2NH_2)^+$ and the hopping goes on within metalloring cluster (**Fig. S11a**). Furthermore, the proton from dimethyl ammonium also easy transferred to adjacent another $(Me_2NH_2)^+$ via adsorbed water molecule along ***c*** axis direction (**Fig. S11b**). Combining the two types of proton hopping mechanism, a complete proton conducting pathway can be formed.

Tab. S1. Crystallographic data and structure refinement details for **MROF-1**.

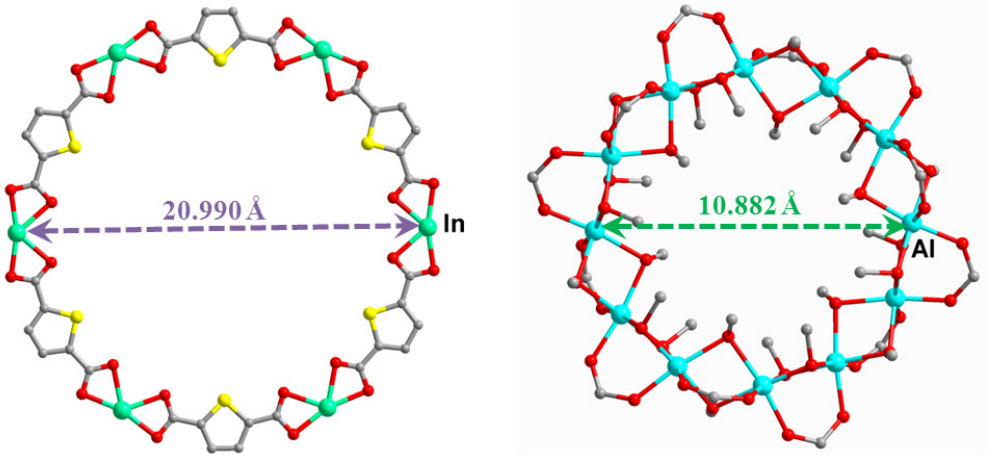
Compound	**MROF-1**
Empirical formula	$C_{20.67}H_{10}InN_{0.33}O_8S$
Formula weight	537.84
Crystal system	hexagonal
space group	*P6/mcc*
$a = b$, Å	25.0980(2)
c, Å	28.4464(3)
γ, °	120
V, Å^3	15518.0(3)
Z	12
D_{calcd}, g cm^{-3}	0.691
μ, mm^{-1}	4.201
F(000)	3184.0
Radiation	Cu $K\alpha$ (λ =1.54178Å)
GOF	1.082
Final R indexes [I>=2σ (I)][a]	R_1= 0.0414, wR_2= 0.1090
Final R indexes [all data][a]	R_1= 0.0489, wR_2=0.1164
CCDC	1029033

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Tab. S2 Compare the diameter of the metalloring in **MROF-1** with that of reported MROF materials.

Compounds	ligands	Cluster type	Diameter (Å)[a]	ref
CAU-1	NH_2-H_2BDC	$Al_8(OH)_4(OCH_3)_8$	8.114	S6
MIL-125	H_2BDC	$Ti_8(O)_8(OH)_4$	8.247	S7
MIL-125-NH_2	NH_2-BDC	$Ti_8(O)_8(OH)_4$	8.269	S8
MOF-520	H_3BTB	$Al_8(OH)_8$ $(HCOO)_4$	8.670	S9
$Be_{12}(OH)_{12}(BTB)_4$	H_3BTB	$Be_{12}(OH)_{12}$	8.994	S10
CAU-3-BDC-NH_2	NH_2-H_2BDC	$Al_{12}(OCH_3)_{24}$	10.449	S11
CAU-3-BDC	H_2BDC	$Al_{12}(OCH_3)_{24}$	10.770	S11
CAU-3-NDC	H_2NDC	$Al_{12}(OCH_3)_{24}$	10.882	S11
$H_2Na_4[Cu_{12}(OH)_6(pz)_6(BTC)_6]$	H_3BTC, pz	$Cu_{12}(OH)_6(pz)_6$	12.185	S12
MROF-1	**H_2thb, H_2pbdc**	**$In_6(thb)_6$**	**20.990**	**This work**

[a] The diameter of the metalloring cluster for the above MROF materials, as shown in the following figure, corresponding to the diagonal distance.



MROF-1 **CAU-3-NDC**

H_2BDC = terephthalic acid; NH_2-H_2BDC = 2-aminoterephthalic acid; H_2NDC = 2,6-naphthalenedicarboxylic acid; H_3BTC = 1,3,5-Benzenetricarboxylic acid; H_3BTB = 1,3,5-benzenetribenzoic acid; pz = pyrazol; H_2thb = 2,5-thiophenedicarboxylic acid; H_2pbdc = 4,4'-biphenyldicarboxylic acid.

Tab. S3 Compare proton conductivity of CPs or MOFs containing dimethyl ammonium and other representative proton conductors with that of **MROF-1**.

Compounds	**Guests**	**Proton Conductivity** ($S \cdot cm^{-1}$)	**RH** (%)	**T** (^oC)	E_a (eV)	**Ref**
Nafion	H_2O	1×10^{-1}	98	80	0.22	S13
UiO-66$(SO_3H)_2$	H_2O	8.4×10^{-2}	90	80	0.32	S14
H_2SO_4@MIL-101	H_2SO_4, H_2O	6.0×10^{-2}	20	80	0.42	S15
Fe-CAT-5	$Me_2NH_2^+$, H_2O	5.0×10^{-2}	98	25	0.24	S16
$\{[Me_2NH_2)_3(SO_4)]_2[Zn_2(ox)_3]\}_n$	$Me_2NH_2^+$, SO_4^{2-}	4.2×10^{-2}	98	25	NA	S17
PCMOF-10	H_2O	3.55×10^{-2}	95	70	0.4	S18
VNU-15	DMF, H_2O, $Me_2NH_2^+$	2.90×10^{-2}	60	95	0.22	S19
HOF-GS-11	$C(NH_2)_3^+$	1.8×10^{-2}	95	30	0.13	S20
MROF-1	**$Me_2NH_2^+$, H_2O**	**1.72×10^{-2}**	**97**	**70**	**0.37**	**This work**
$(NH_4)_2(H_2adp)[Zn_2(ox)_3]\cdot3H_2O$	H_2adp, NH_4^+	8×10^{-3}	98	25	0.63	S21
Ca-PiPhtA-NH_3	NH_3, H_2O	6.6×10^{-3}	98	24	0.4	S22
Cd-5TIA	$Me_2NH_2^+$	3.6×10^{-3}	98	28	0.163	S23
$Na_6[(AlPO_4)_8(OH)_6]\cdot8H_2O$	Na^+, H_2O	3.59×10^{-3}	98	20	0.21	S24
In-IA-2D-1	$Me_2NH_2^+$, H_2O	3.4×10^{-3}	98	27	0.61	S25
PCMOF-5	H_2O	2.5×10^{-3}	98	60	0.16	S26
$[\{(Zn_{0.25})_8(O)\}Zn_6(L)_{12}(H_2O)_{29}(DMF)_{69}$	H_2O, DMF	2.3×10^{-3}	95	25	0.22	S27

$(NO_3)_2]_n$						
$(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$	H_2O, NH_4^+	1.7×10^{-3}	96	40	0.23	S28
Eu-MOF	$Me_2NH_2^+$, H_2O	1.1×10^{-3}	98	100	0.97	S29
PA@Tp-Azo	H_3PO_4,H_2O	9.9×10^{-4}	98	59	0.11	S30
CoLaII-SC	H_2O	3.05×10^{-4}	95	25	0.42	S31
$\{[Gd_4(R\text{-}ttpc)_2(R\text{-}Httpc)_2(HCOO)_2(H_2O)_8]\cdot 4H_2O\}_n$	H_2O	1.5×10^{-4}	97	50	0.32	S32
$[NH_2(CH_3)_2][In(FDA)_2]$	$Me_2NH_2^+$	1.0×10^{-4}	99.5	30.5	/	S33
$[Zn_3(5\text{-}sip)_2(5\text{-}sipH)(bpy)](DMF)2(DMA)$	$Me_2NH_2^+$, DMF	8.7×10^{-5}	60	25	/	S34
In-5TIA	$Me_2NH_2^+$	5.35×10^{-5}	98	28	0.137	S23
In-IA-2D-2	$Me_2NH_2^+$, DMF	1.5×10^{-5}	0	120	0.48	S25
$[MIL\text{-}53(Fe)(COOH)_2]$	H_2O	7×10^{-6}	95	80	0.21	S35
$[(CH_3)_2NH_2][Zn_3Na_2(cpida)_3]2.5DMF$	$Me_2NH_2^+$, H_2O	2.1×10^{-6}	97	95	0.81	S36

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