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Electronic Supplementary Information

High proton conduction in an excellent water-stable gadolinium metal-organic framework

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Experimental Section

Materials and Instruments

All chemicals were analytical grade and were obtained from commercially available sources and used as received without further purification. PXRD patterns at room temperature were collected on a Rigaku Miniflex II diffractometer using Cu K_α radiation (λ = 1.540598 Å) at 40 kV and 40 mA ranging from 5° to 50°. Simulated PXRD pattern was obtained from the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury). TG and DSC analysis experiment were carried out on a METTLER TOLEDO thermogravimetrix analyzer in N_2 atmosphere with the sample heated in an Al_2O_3 crucible at a heating rate of 10 K min^{-1}. Elemental analyze was measured on an Elementar Vario EL III microanalyzer. The FT-IR spectrum was obtained on a PerkinElmer Spectrum One Spectrometer using KBr pellet in the 4000–400 cm^{-1} range. The water vapor adsorption/desorption measurements were fulfilled by IGA100B instrument.

Single-crystal X-ray crystallography

Single-crystal X-Ray diffraction data collection of a single crystal of **1** was performed on a Bruker D8 diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å) at 100 K. The structure was solved by direct methods and refined by full-matrix least square on F^2 using the SHELXL software package,[1] with anisotropic thermal parameters for all nonhydrogen atoms. Partial H atoms generated geometrically expect those in the free water and H^+ cannot be defined. The structure was finally verified using the Addsym algorithm from the program PLATON.[2] Crystallographic data and structural refinements for **1** are summarized in Table S1. The main bond lengths and angles for **1** are shown in Table S2. More details on the crystallographic studies as well as atomic displacement parameters are given as cif. The entry of CCDC-1874854 contains the supplementary crystallographic data for **1**.

Synthesis of {$[H_3O][(N(CH_3)_4)_2][Gd_3L_6]$}·$2H_2O$ (1)

A mixture of $Gd(NO_3)_3\cdot 6H_2O$ (89 mg, 0.2 mmol), 5-nitroisophthalic acid (168 mg, 0.8 mmol), CH_3OH (4 mL) and *N*,*N*-dimethylformamide (2 mL) was added into a 23 mL Teflon-lined autoclave. The vessel was sealed and heated to 180 °C in 4 hours, maintained at this temperature for 1 day, and then cooled to room temperature for another 3 days. Bright yellow prismatic crystals of **1** were obtained by filtering the mixed solution, washing with CH_3OH for three times and drying in air. Yield: 54% (based on $Gd(NO_3)_3\cdot 6H_2O$). Anal. Calcd (%) for $Gd_3C_{56}H_{49}O_{39}N_8$: C, 34.84; H, 2.54; N, 5.81) Found: C, 35.71; H, 3.22; N, 6.44. For each of the experiments described in this report, the crystals used for X-ray and other studies were obtained from the same preparation. The resulting bright yellow crystals were obtained by solvothermal method, and powder X-ray diffraction (PXRD) data of as-synthesized sample (Figure 2a) at room temperature matched well with the simulated one from the X-ray single-crystal structure data. This result demonstrated the phase purity of the obtained crystalline product of **1**.

Proton Conductivity Measurements

Proton conductivity measurements were performed using a quasi-four-electrode AC impedance technique with a Solartron 1260 impedance/gain-phase analyzer. For single-crystal measurements, the single-crystal shape is triangular prism, and the cross section sizes are 0.024/0.024/0.04 cm and the length is 0.117 cm, respectively. Gold wires were connected to both ends of the longer axis of each crystal. The single crystal was measured at frequencies ranging from 10^7 to 1 Hz as the temperatures were varied from 25 to 75 °C and the relative humidity (RH) were varied from 70% to 98%. The conductivity of the samples was deduced from the Debye semicircle in the Nyquist plot.

Table S1. Crystallographic data for **1**.

Empirical formula	$Gd_3C_{56}H_{49}O_{39}N_8$
Formula weight	1928.73
Temperature (K)	100
Crystal system	Cubic
Space group	$I\bar{4}3d$
Flack factor	0.000(4)
a **(Å)**	24.9640(3)
α **(°)**	90
V **(Å^3)**	15557.6(6)
Z	8
Crystal size (mm^3)	0.057× 0.031 × 0.025
F**(000)**	7504
θ **range for data collection (°)**	2.58–26.29
D_{calcd} **(g cm^{-3})**	1.642
μ **(mm^{-1})**	2.622
GOF on F^2	0.997
$R_1{}^a$ $[I > 2\sigma(I)]$	0.022
$wR_2{}^b$ $[I > 2\sigma(I)]$	0.067
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	0.73/–0.49

^{a} $R_1 = \sum||F_o|–|F_c||/\sum|F_o|$; ^{b} $wR_2 = \sum[w(F_o{}^2–F_c{}^2)^2]/\sum[w(F_o{}^2)^2]^{1/2}$

Table S2. Selected bond lengths of **1**.

Label	Distances (Å)	Label	Distances (Å)
Gd1—O12	2.288 (4)	**O14—C18**	1.270 (8)
Gd1—O12^{i}	2.288 (4)	**O13—C18**	1.270 (7)
Gd1—O11^{ii}	2.406 (4)	**O12—C17**	1.249(7)
Gd1—O11^{iii}	2.406 (4)	**O11—C17**	1.259 (7)
Gd1—O13^{iv}	2.432 (4)	**N11—C15**	1.478 (9)
Gd1—O13^{v}	2.432 (4)	**N11—O16**	1.227 (9)
Gd1—O14^{v}	2.457 (4)	**N21—C22**	1.49 (2)
Gd1—O14^{iv}	2.457 (4)	**N21—C21**^{vii}	1.503 (9)
N11—O15	1.203 (9)	**N21—C21**^{viii}	1.503 (9)
N21—C21^{vii}	1.503 (9)		

Symmetry codes: (i) −x+1, −y−3/2, z; (ii) y+5/4, −x−1/4, −z+1/4; (iii) −y−1/4, x−5/4, −z+1/4; (iv) −z+3/4, y−1/4, −x+1/4; (v) z+1/4, −y−5/4, −x+1/4; (vi) −z+1/4, y+1/4, −x+3/4; (vii) −y−1/2, −z−1, x−1/2; (viii) z+1/2, −x−1/2, −y−1.

Table S3. Proton conduction and measurement conditions for reported single crystal and compound **1**.

Reference samples	**σ (S cm^{-1})**	**Measurement conditions**	**Ref.**
Compound 1	**7.17 x 10^{-2}**	**75 °C 98% RH, single crystal**	**This work**
CB-2	4.3 x 10^{-2}	25 °C 98% RH single crystal	Ref.[27]
CB-1	2.4 x 10^{-2}	25 °C 98% RH single crystal	Ref.[27]
PCC-72	3.4 x 10^{-3}	25 °C 99% RH single crystal	Ref.[28]
$[Cu_2(Htzehp)_2(4,4\text{-}bipy)]\cdot 3H_2O$	1.43 x 10^{-3}	80 °C 95% RH single crystal	Ref.[26]
PCMOF-17	1.25 x 10^{-3}	25 °C 40% RH single crystal	Ref.[23]
$(Me_2NH_2)[Eu(L)]$	1.25 x 10^{-3}	150 °C single crystal	Ref.[24]
$[Zn(H_2PO_4)_2(TzH)_2]_n$	1.1 x 10^{-4}	130 °C single crystal	Ref.[25]
PCMOF10	3.5 x 10^{-2}	70 °C 95% RH pellet	Ref[9]
PCMOF2$^1/_2$	2.1 x 10^{-2}	85 °C 90% RH pellet	Ref[10]
Li-HPAA	1.1 x 10^{-4}	24 °C 98% RH pellet	Ref[12]
Cs-HPAA	3.5 x 10^{-5}	24 °C 98% RH pellet	Ref[12]

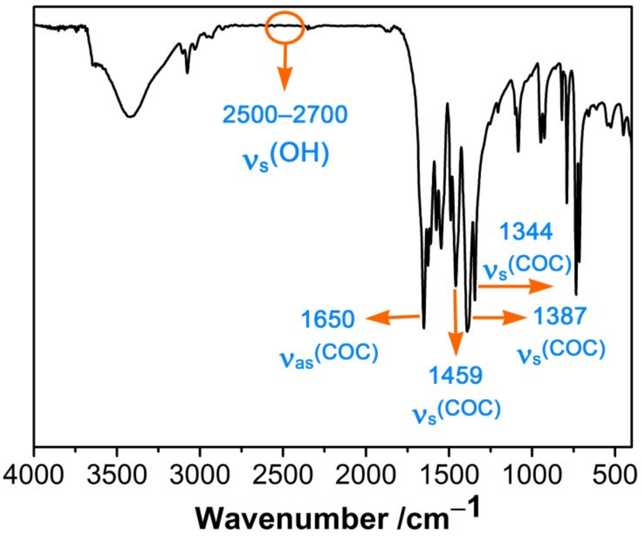

Fig. S1. FT-IR spectrum of **1** in the KBr matrix.

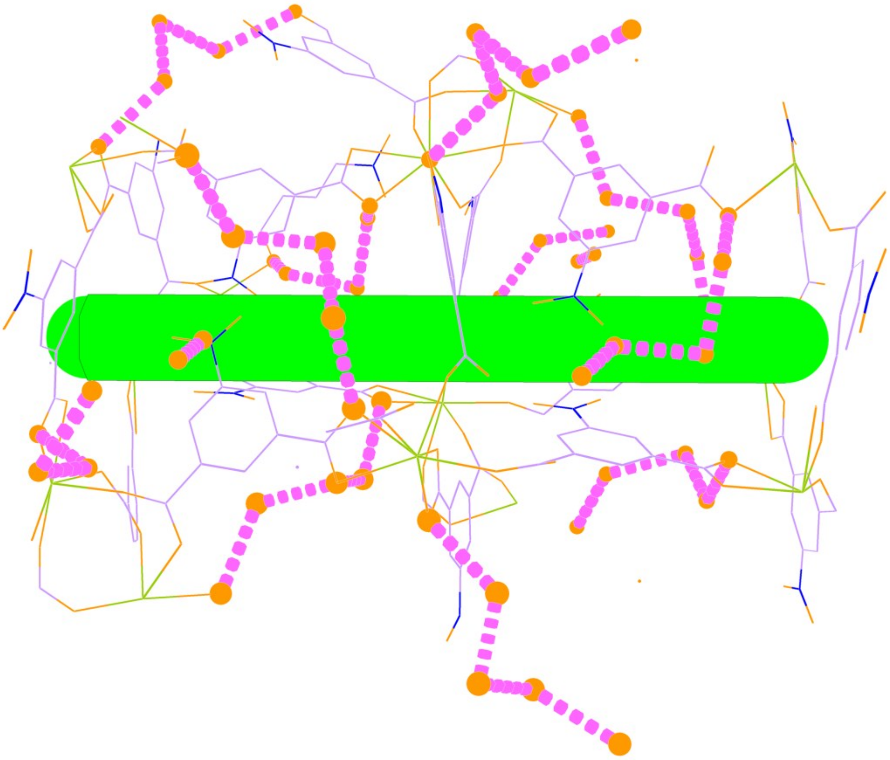

Fig. S2. Hydrogen bonds in the channel of **1**.

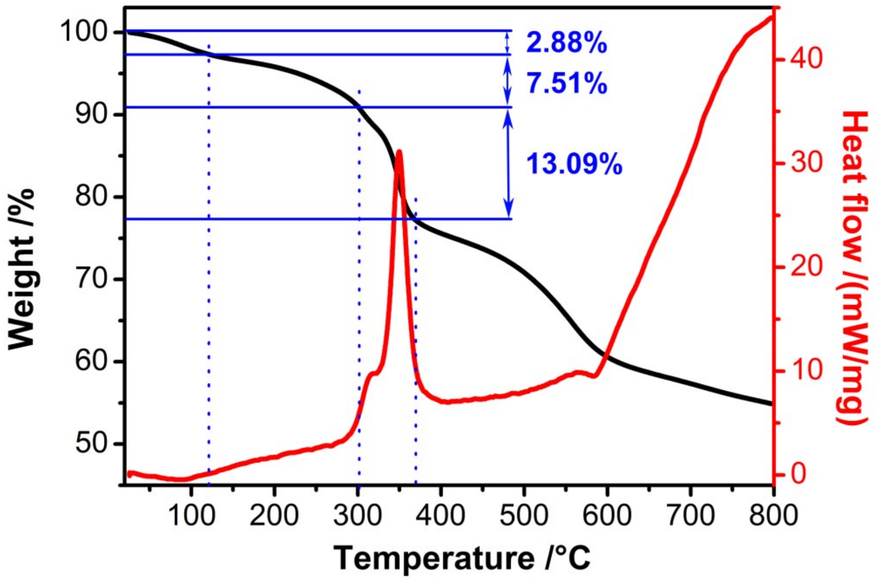

Fig. S3. TGA and DSC curves of **1** in N_2. The weight loss in the range of 30–120 °C is ~2.88%, corresponding to the content of three lattice water molecules per molecule (2.85%, calculated). The weight loss between 120 and 300 °C is ~7.51%, closing to a calculated weight loss of ~7.67% with the tetramethylammonium cations; the weight loss of 13.09% in the range of 300–370 °C was caused by the fall off of $–NO_2$ group of NIPA ligand (14.47%, calculated). After 370 °C, the framework began to decompose owning to the decomposition of NIPA. Until the end of 800 °C, the weight stable in about 50 % account for the formation of final products gadolinium oxide.

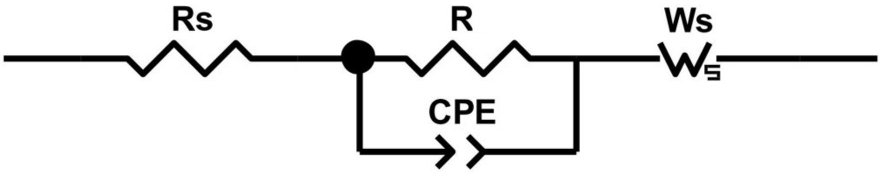

Fig. S4. The equivalent circuit used for fitting the impedance spectra.

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