

Designed synthesis of a proton-conductive Ho-MOF with reversible dehydration and hydration

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Experiment methods:

Suitable single crystal of compound **1** was mounted on a loop for the X-ray diffraction. Crystallographic data were collected on an Oxford Diffraction/Agilent SuperNova (dual source) diffractometer equipped with the CrysAlis^{PRO} X-ray crystallography data systems. The data collection for compound **1** was carried out with graphite-monochromated CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. Calculations were performed with SHELXL-2018/1 program package, and the structure was solved by direct method and refined on F² by full-matrix least-squares method. Powder X-ray diffraction (PXRD) were carried out on Rigaku desktop MiniFlex 600 diffractometer with CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). In situ variable-temperature PXRD were carried out at air atmosphere on Rigaku desktop Ultima-IV diffractometer with CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). EDS was determined by using a JSM6700-F microscope. TGA was performed with STA449F3 thermal analysis system. FT-IR spectrum was collected by a VERTEX70 infrared analyzer. Element analysis was measured with a vario MICRO analyzer. Water adsorption isotherm was performed using IGA100B intelligent gravimetric sorption analyser at 298 K with P₀ of 30 mbar. Proton conductivity was measured on Zennium/IM6 impedance analyzer over the frequency ranging from 10⁻¹ Hz to 10⁷ Hz. The relative humidity and temperature were controlled by a STIKCorp CIHI-150BS3 incubator. Operated sample was prepared as a cylindrical pellet of crystalline powder coated with C-pressed electrodes. The bulk conductivity was estimated by semicircle fittings of Nyquist plots.

Synthesis of compound 1:

0.189 g (0.5 mmol) Ho₂O₃ and 0.536 g NaH₂SIP were stocked into a PTFE-lined autoclave, and then 15 ml deionized water was added. After ultrasonic treated for 15 min, the mixture was sealed and heated in an oven at 170 °C for 7 days. After cooling with a programmed procedure for 1 day, crystalline solids were collected by filtration (Yield 90% based on Ho₂O₃). FT-IR (KBr / cm⁻¹): 3387 (br), 1611 (m), 1534 (s), 1453 (s), 1390 (s), 1214 (m), 1173 (m), 1119 (w), 1038 (s), 635 (s). Anal. Calcd (%) for **1**: C 17.40, H 3.47. Found: C 17.28, H 3.42.

Crystal data of 1:

C₈H₁₉O₁₅SHo; Mr = 552.22, monoclinic, P2₁/n, a = 9.4135(3) Å, b = 10.5485(3) Å, c = 17.0809(4) Å, $\beta = 101.273(3)^\circ$, V = 1663.39(8) Å³, Z = 4, $\rho = 2.189 \text{ g cm}^{-3}$, $\mu = 10.812 \text{ mm}^{-1}$, F(000) = 1080.0, GOF = 1.048. A total of 6023 reflections were collected in the range of $9.91^\circ \leq 2\theta \leq 133.19^\circ$, 2935 of which were unique (Rint = 0.0288). Final R indexes for I $\geq 2\sigma(I)$ were R₁ = 0.0288 and wR₂ = 0.0756, and that for all data were R₁ = 0.0324 and wR₂ = 0.0782. CCDC-1886086.

Additional figures and tables:

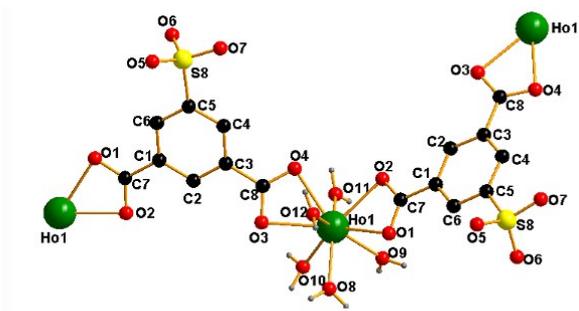


Figure S1 Representative coordination models of the Ho³⁺ ions and SIP ligands in the crystal structure of compound 1.

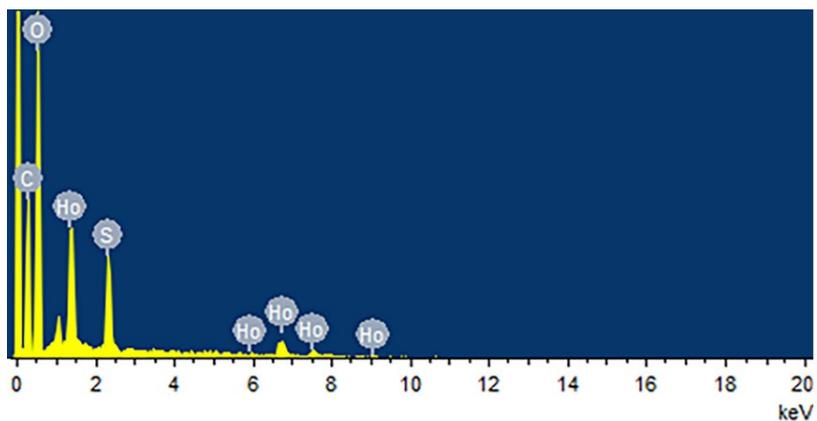


Figure S2 EDS result of compound 1.

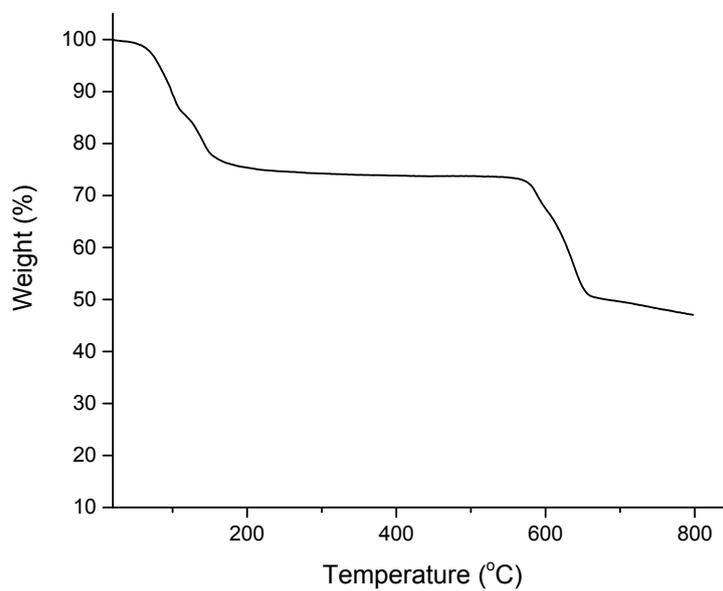


Figure S3 TG curve of compound 1 collected under N₂ atmosphere.

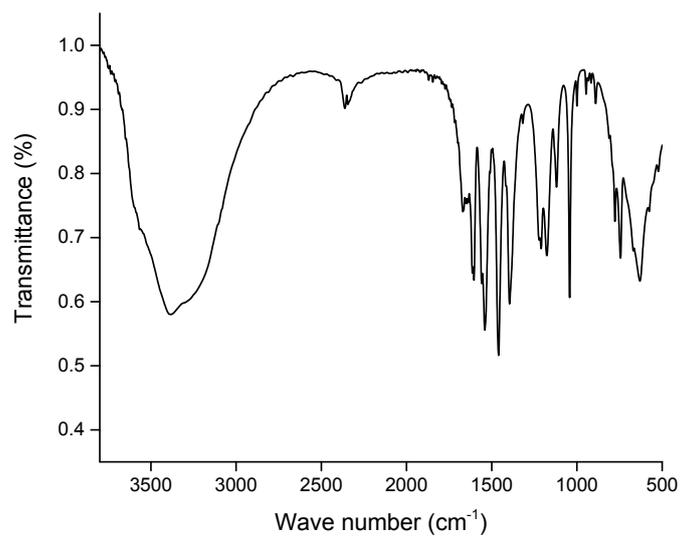


Figure S4 FT-IR spectrum of compound 1.

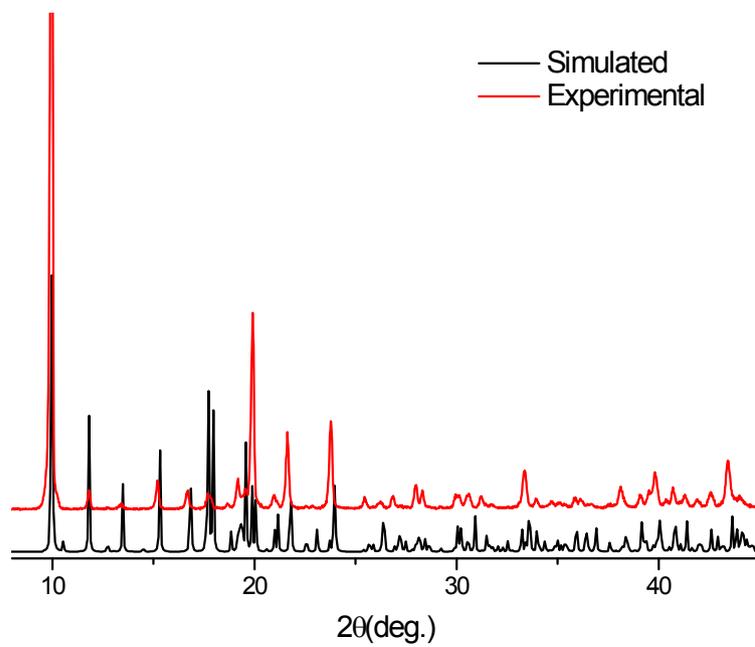


Figure S5 Simulated and experimental PXRD patterns of compound 1.

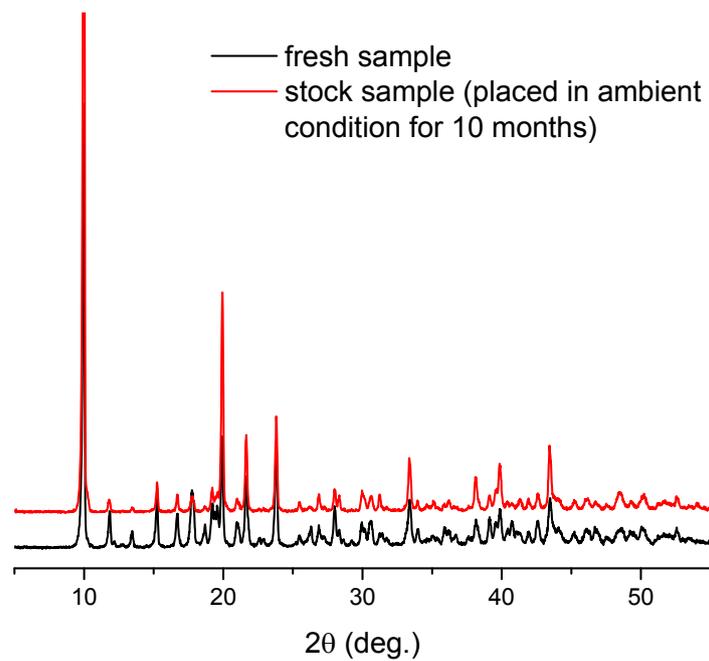


Figure S6 PXRD patterns of fresh and stock sample of 1.

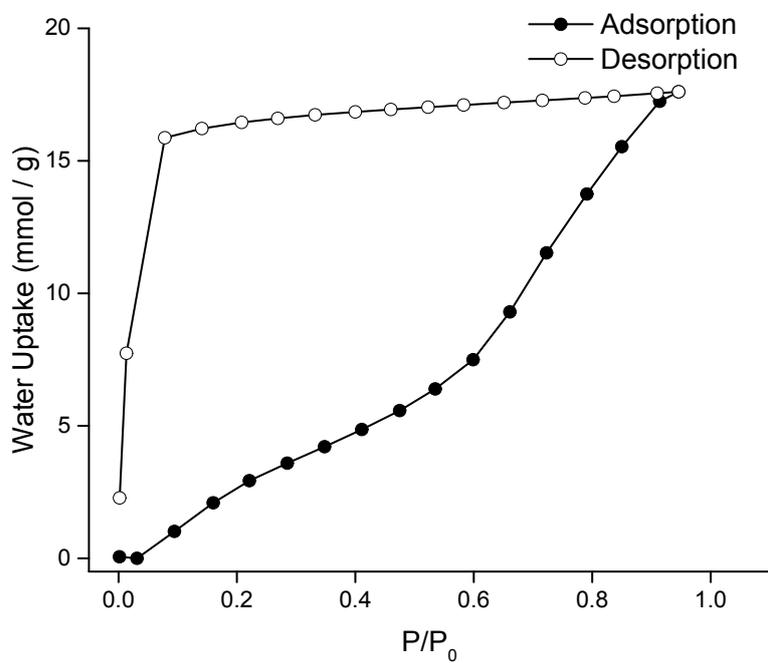
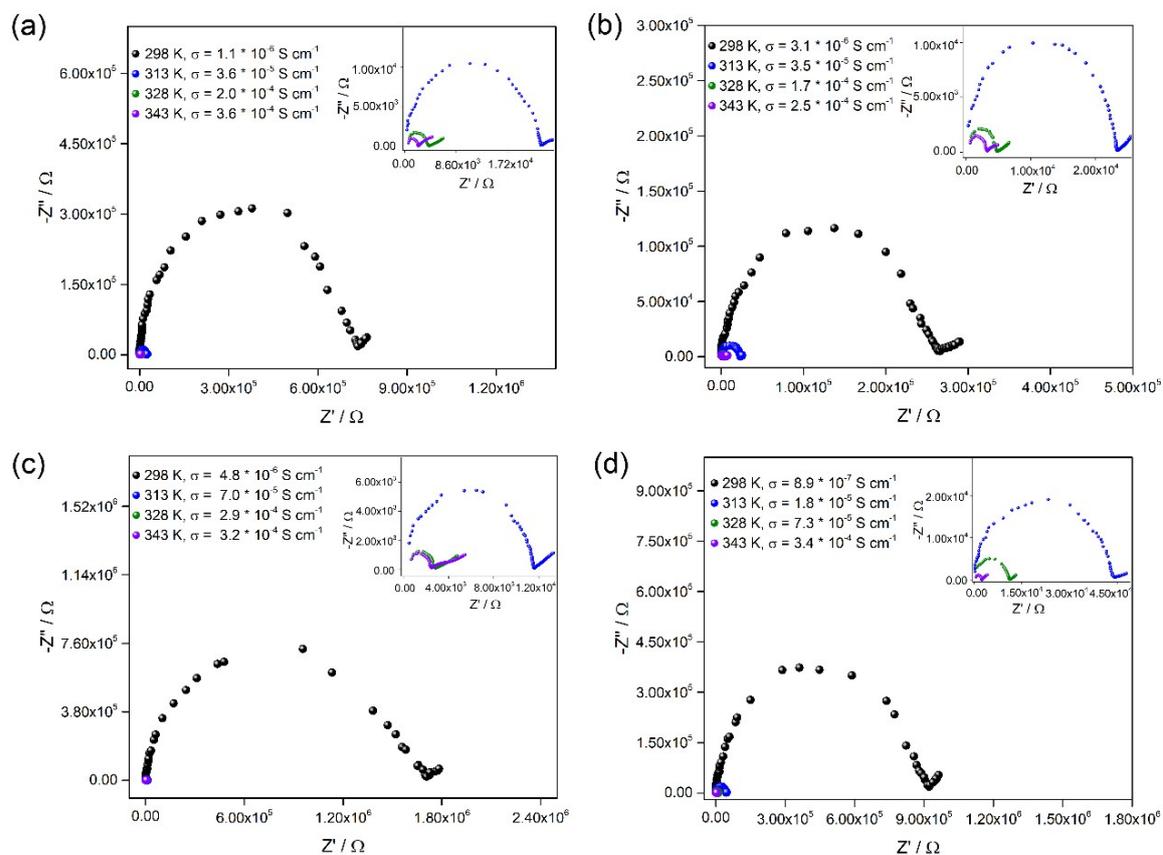


Figure S7 Water vapor adsorption isotherm of compound 1 at 298 K. (P/P_0 : relative pressure of water.)

Table S1 Hydrogen bonds for compound **1**.

D-H...A	d(D-H) / Å	d(H...A) / Å	d(D...A) / Å	<(DHA) / °
O(8)-H(8A)...O(2) ^a	0.85	1.956	2.804	174.30
O(8)-H(8B)...O(6) ^b	0.85	1.834	2.681	174.21
O(9)-H(9A)...O(4) ^a	0.85	1.892	2.742	179.13
O(9)-H(9B)...O(13) ^c	0.85	1.887	2.737	178.90
O(10)-H(10A)...O(6) ^d	0.85	2.094	2.920	163.90
O(10)-H(10B)...O(3) ^c	0.85	2.064	2.890	163.77
O(11)-H(11A)...O(1) ^d	0.85	1.870	2.720	178.63
O(11)-H(11B)...O(14)	0.85	1.859	2.709	178.59
O(12)-H(12A)...O(5) ^e	0.85	1.965	2.809	171.89
O(12)-H(12B)...O(15)	0.85	1.919	2.763	171.95
O(13)-H(13A)...O(5) ^f	0.85	2.228	2.966	145.31
O(13)-H(13B)...O(15) ^f	0.85	2.072	2.809	144.70
O(15)-H(15A)...O(7) ^b	0.85	1.922	2.766	171.49
O(15)-H(15B)...O(3) ^f	0.85	2.452	3.296	172.06

Symmetry transformation used to generate equivalent atoms: a: [-x+3/2, y+1/2, -z+1/2]; b: [x+1/2, -y+3/2, z+1/2]; c: [-x+2, -y+1, -z+1]; d: [-x+3/2, y-1/2, -z+1/2]; e: [-x+1/2, y-1/2, -z+1/2]; f: [-x+1, -y+1, -z+1]

**Figure S8** Proton conductivity of as-prepared **1** under different pH. (a) pH = 2; (b) pH = 4; (c) pH = 6; (d) pH = 8.

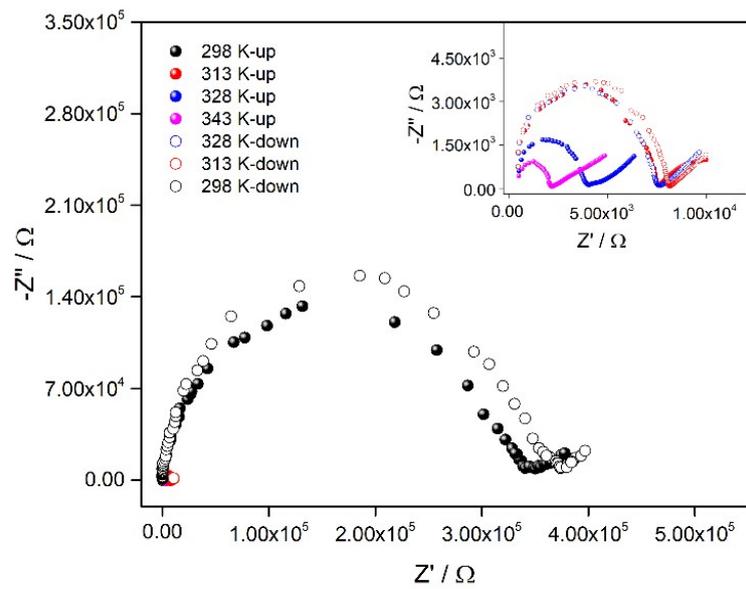


Figure S9 Proton conductivity of compound **1** as increasing temperature from 298 K to 343 K and decreasing temperature from 343 K to 298 K (up: increasing temperature process; down: decreasing temperature process).