

Supporting Information

Anhydrous Superprotonic Conductivity of a Uranyl-based MOF from Ambient Temperature to 110 °C

Kun Zhang,^{1, #} Ge-Hua Wen,^{1, #} Xiao-Jing Yang,^{1,2} Dae-Woon Lim,^{3,4} Song-Song Bao,¹ Masaki Donoshita,³ Lan-Qing Wu,¹ Hiroshi Kitagawa,^{3,*} Li-Min Zheng^{1,*}

¹ State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China.

² School of Ocean Science and Technology, Panjin Campus, Dalian University of Technology, Panjin, China.

³ Division of Chemistry, Graduate School of Science Kyoto University Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502 (Japan).

⁴ Current address: Department of Chemistry and Medical Chemistry, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwondo 26493, Republic of Korea

These authors contribute equally.

* Corresponding author.

Methods

Materials. The 2-(phosphonomethyl)benzoic acid (2-pmbH₃) was prepared according to the literature.¹ UO₂(Ac)₂·2H₂O was purchased from HWRK CHEM. All other starting materials were of reagent grade and were used as received from commercial sources without further purification. Caution! Standard procedures for handling radioactive material should be followed, although the uranyl compounds used in the lab contained depleted uranium.

Synthesis of 1. The yellowish crystals of (H₃O)[(UO₂)₄(2-pmb)₃(H₂O)₃]·0.5H₂O (**1**) (2-pmbH₃ = 2-(phosphonomethyl) ben-zoic acid) were prepared by hydrothermal treatment. A mixture of UO₂(CH₃COO)₂·2H₂O (0.0424 g, 0.1 mmol), 2-pmbH₃ (0.0216 g, 0.1 mmol) and 8 mL H₂O as loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C for 5 d. After cooling to room temperature, compound **1** were filtered and washed with distilled water, and further dried in the air. Yield: 0.0201mg (45.7% based on U). Elemental analysis shows that the contents of carbon and hydrogen is 16.07% and 1.75%, which is consistent with the calculated value (16.00% and 1.57%).

Synthesis of LiBr@1. 10 mg compound **1** were put in 2 mL centrifuge tube, and 1 mL saturated LiBr aqueous solution was added. After shaking well, the mixture was standing for 8 hours at room temperature. The solvent was finally removed by centrifugation and the product of **LiBr@1** with formula [(Li(UO₂)₄(2-pmb)₃(H₂O)₃]·0.680LiBr·xH₂O was dried and stored at 80 °C in oven.

Single-crystal X-ray Diffraction. Single crystal of dimensions 0.30×0.20×0.20 mm³ for **1** was used for data collections on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Hemisphere of data were collected in the θ range of 2.65–24.99. The structures were solved by direct method and refined on F² by full-matrix least squares using SHELXTL.² All the non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were either put in calculated positions or found from the difference Fourier maps and refined isotropically. CCDC 2018934 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ionic Conductivity Measurement. Powder **LiBr@1** was pressed into a disk-shaped pellet with a diameter of 5 mm and a thickness of 2.04 mm at a pressure of 1 GPa. The whole process was

completed under the infrared lamp. This pellet was then sandwiched between two electrodes for impedance measurement using a Solartron 1296A electrochemistry workstation. It was tested from 30 to 110 °C for three heating and cooling cycles in a flow of N₂ (50 mL/minute). A small heating station (INSTECH mK2000) is used to control temperature and nitrogen atmosphere and each temperature point is balanced for 20 minutes. Second pellet of **LiBr@1** (1.52 mm thickness, 5 mm diameter) was prepared and tested at 80 and 110 °C in nitrogen for different time. Third pellet of **LiBr@1** (1.80 mm thickness, 5 mm diameter) was cyclically tested from 30 to 180 °C in N₂. The heated sample was also exposed to air at 80 °C for 1 day and was tested for impedance at 30 and 110 °C in N₂. The thickness and diameter of LiBr·xH₂O pellet was 1.49 mm and 6 mm. LiBr·xH₂O was tested from 30 to 180 °C in N₂. **1** was also tested from 30 to 110 °C in N₂ (0.98 mm thickness, 6 mm diameter). Humidity-dependent impedance measurement of **1** (1 mm thickness, 6 mm diameter) is controlled by a constant temperature and humidity chamber. For all the measurements, the range of frequency was set from 1 to 1M Hz with an alternating potential of 100 mV. The ionic conductivity (σ , S cm⁻¹) was estimated by using the equation:

$$\sigma = L / (RS) \quad (2)$$

where L (cm) is the thickness, S (cm²) is the cross-section area and R (Ω) is the measured impedance. Activation energy was fitted by Arrhenius equation:

$$\ln(\sigma T) = \ln A - \frac{E_a}{k_B T} \quad (3)$$

here E_a (eV) is the transport activation energy, k_B is the Boltzmann constant, T (K) is temperature, and A is a pre-exponential factor.

Other Physical Measurements. Mapping and EDS measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope. The inductively coupled plasma mass spectroscopy (ICP-MS) analysis was carried on a PE Optima 5300DV spectrometer. Gas adsorptions were measured on a BELSORP-Max adsorption analyzer. Samples were pretreated under vacuum and 200 °C for 2 hours before adsorption test. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer, operated at 40 kV and 40 mA, with Cu K α radiation ($\lambda = 1.5418$ Å), and the measurement was performed at ambient temperature in the range of $2\theta = 5$ -50 degree with 0.02 degree/step. Synchrotron X-ray diffraction was tested in Shanghai Synchrotron Radiation Facility ($\lambda = 0.6887$ Å), and the data were collected after heating for one and a half hours at 80 °C. Thermo gravimetric analyses (TG) were performed on a Mettler

Toledo TGA/DSC instrument in the range of 25-550 °C under a nitrogen flow (50 mL/min) at a heating rate of 2 °C min⁻¹. For TG, LiBr@1 were first exposed to 25 °C and nitrogen for 5 minutes, and then tested in situ. TG versus time was tested using a heating rate of 20 °C min⁻¹. TG-MS measurement is carried on the NETZSCH STA 449C instrument using a heating rate of 2 °C min⁻¹. The infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer with pressed KBr pellets. X-ray photoelectron spectroscopy (XPS) spectra was obtained on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer. Before XPS test, LiBr and LiBr@1 were heated at 100 °C under vacuum for 30 minutes, then were transferred to the XPS instrument and dried in vacuum for 48 hours. Solid state and PFG NMR measurements were performed using a Bruker Biospin K.K., AVANCE II⁺ 400 spectrometer. Solid state NMR spectra for ⁷Li and ⁷⁹Br were recorded at frequencies of 155.46 and 100.22 MHz, respectively, with a 5 mm SOL H7406 probe using a single $\pi/2$ pulse. Durations of $\pi/2$ pulse for ⁷Li and ⁷⁹Br were 4.0 and 5.7 μ s, and recycle delays for ⁷Li and ⁷⁹Br were 10 and 1 s. ¹H and ⁷Li PFG-NMR measurements were performed at frequencies of 400 MHz and 155.46 MHz with a Diff50 diffusion probe using stimulated echo experiments at 8-16 gradient field strengths. The maximum gradient field was 2290-2410 G cm⁻¹. Durations of $\pi/2$ pulse for ¹H and ⁷Li were 3.75-5.0 and 8.0 μ s. Recycle delays for ¹H and ⁷Li were 15-17 and 175 s. Before single pulse NMR and PFG-NMR test, LiBr and LiBr@1 were remained at 100 °C in oven for 40 minutes, then were transferred to 5 mm NMR tubes and heated to 100 °C under vacuum for 20 minutes. 1 was directly transferred to a 5 mm NMR tube and heated to 85 °C under vacuum for 20 minutes. After that, samples were in situ encapsulation with nitrogen in same NMR tube for test.

References

- (1) Kaur, K.; Lan, M. J. K.; Pratt, R. F. Mechanism of inhibition of the class C β -lactamase of enterobacter cloacae P99 by cyclic acyl phosph(on)ates: rescue by return. J. Am. Chem. Soc. 2001, 123, 10436-10443.
- (2) SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments, Madison, WI, (1995).

Table S1. Crystal data and structure refinement for **1**

Identification code	1
Formula	C48H56O55P6U8
<i>M</i>	3602.98
temperature	296(2) K
crystal size [mm]	0.30×0.20×0.20
crystal system	Monoclinic
space group	<i>P</i> -3c ₁
<i>a</i> [Å]	15.5212(11)
<i>b</i> [Å]	15.5212(11)
<i>c</i> [Å]	18.712(3)
α [°]	90
β [°]	90
γ [°]	120
<i>V</i> [Å ³]	3903.9(7)
<i>Z</i>	2
<i>D_c</i> [g cm ⁻³]	3.065
μ [mm ⁻¹]	16.764
<i>F</i> (000)	3220
<i>R</i> _{int}	0.0946
GoF on <i>F</i> ²	0.997
<i>R</i> ₁ , <i>wR</i> ₂ ^[a] [<i>I</i> > 2σ(<i>I</i>)]	0.0304, 0.0532
(all data)	0.0491, 0.0569
(Δρ) _{max} , (Δρ) _{min} [e Å ⁻³]	1.078, -0.891
CCDC	2018934

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

Table S2. PFG NMR for LiBr, **1** and **LiBr@1**.

Temperature	LiBr	1	LiBr@1
25 °C	<i>D</i> (⁷ Li) not detected	<i>D</i> (¹ H) 7.5×10 ⁻¹³ m ² s ⁻¹	<i>D</i> (¹ H) 2.9×10 ⁻¹² m ² s ⁻¹ <i>D</i> (⁷ Li) not detected
100 °C	<i>D</i> (⁷ Li) not detected	<i>D</i> (¹ H) 2.7×10 ⁻¹⁰ m ² s ⁻¹	<i>D</i> (¹ H) 3.1×10 ⁻¹⁰ m ² s ⁻¹ <i>D</i> (⁷ Li) 4.3 ×10 ⁻¹⁴ m ² s ⁻¹

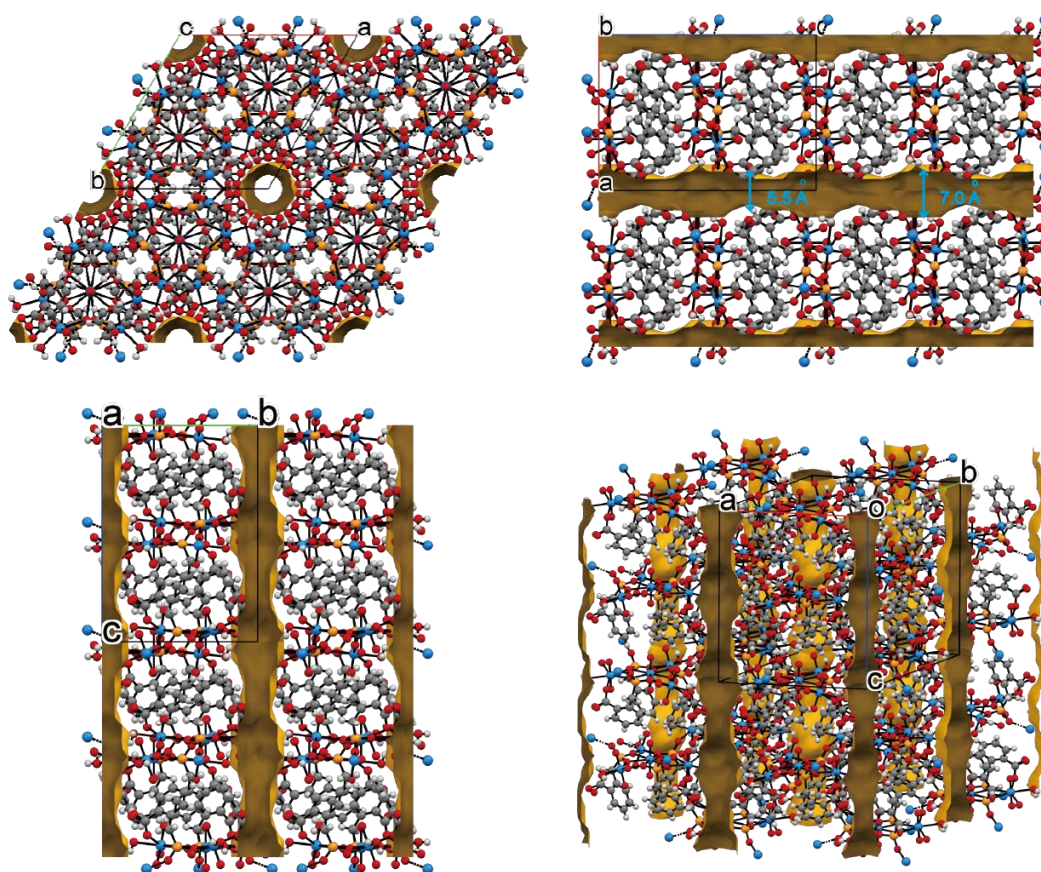


Figure S1. View of empty spaces (voids) in $2 \times 2 \times 2$ unit cell along c , b and a axis (outside, light yellow; inside, dull yellow). All of lattice water molecules ($0.5 \text{ H}_2\text{O}$ and H_3O^+) are squeezed.

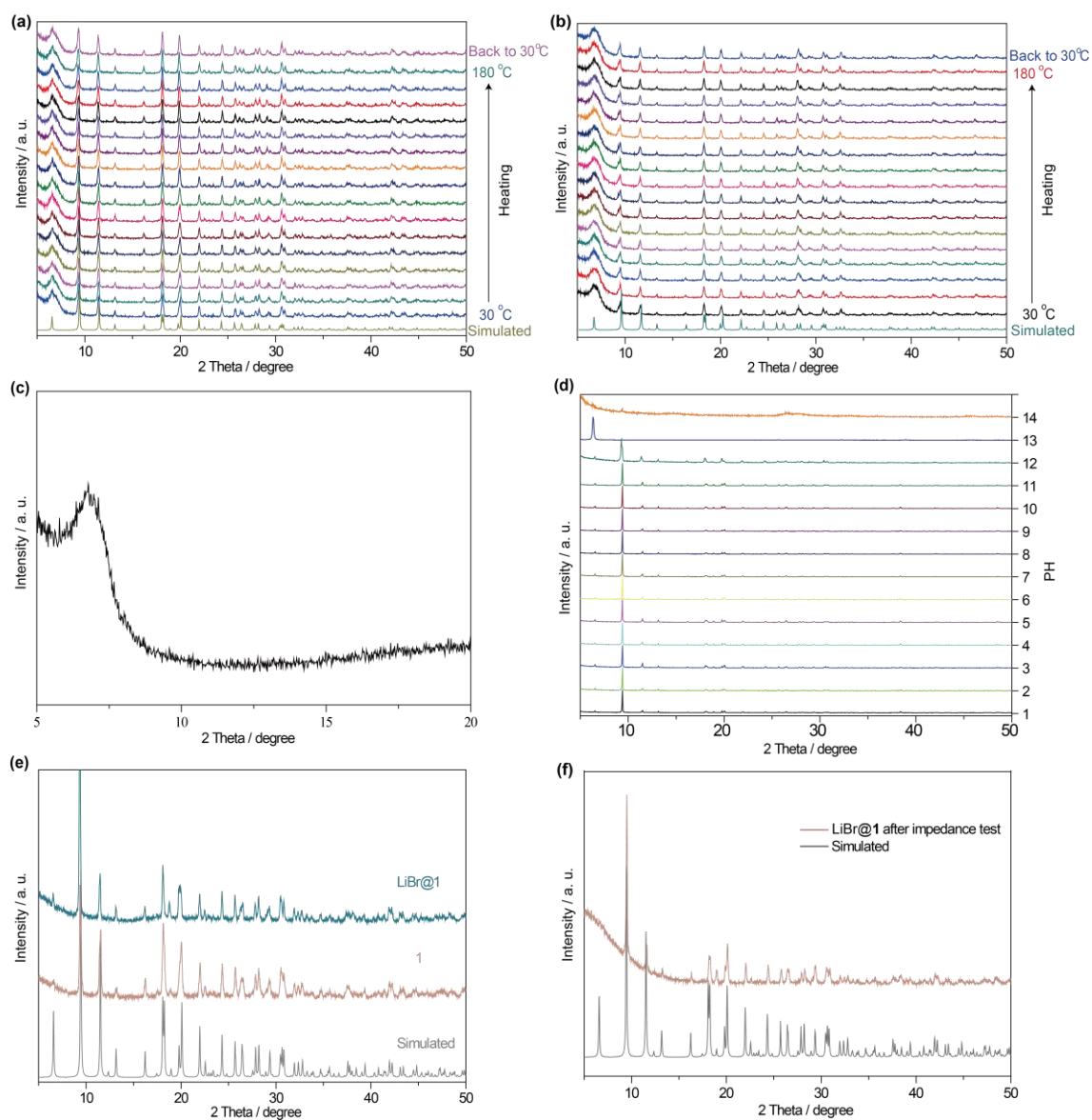


Figure S2. (a) Temperature dependent powder X-ray diffraction (PXRD) for **1**. (b) Temperature dependent PXRD for **LiBr@1**. (c) Baseline for temperature dependent PXRD. (d) PXRD of **1** after soaked in different pH solution. (e) PXRD of **1** and **LiBr@1** after gas absorption. (f) PXRD for **LiBr@1** after impedance test from 30 to 180 °C.

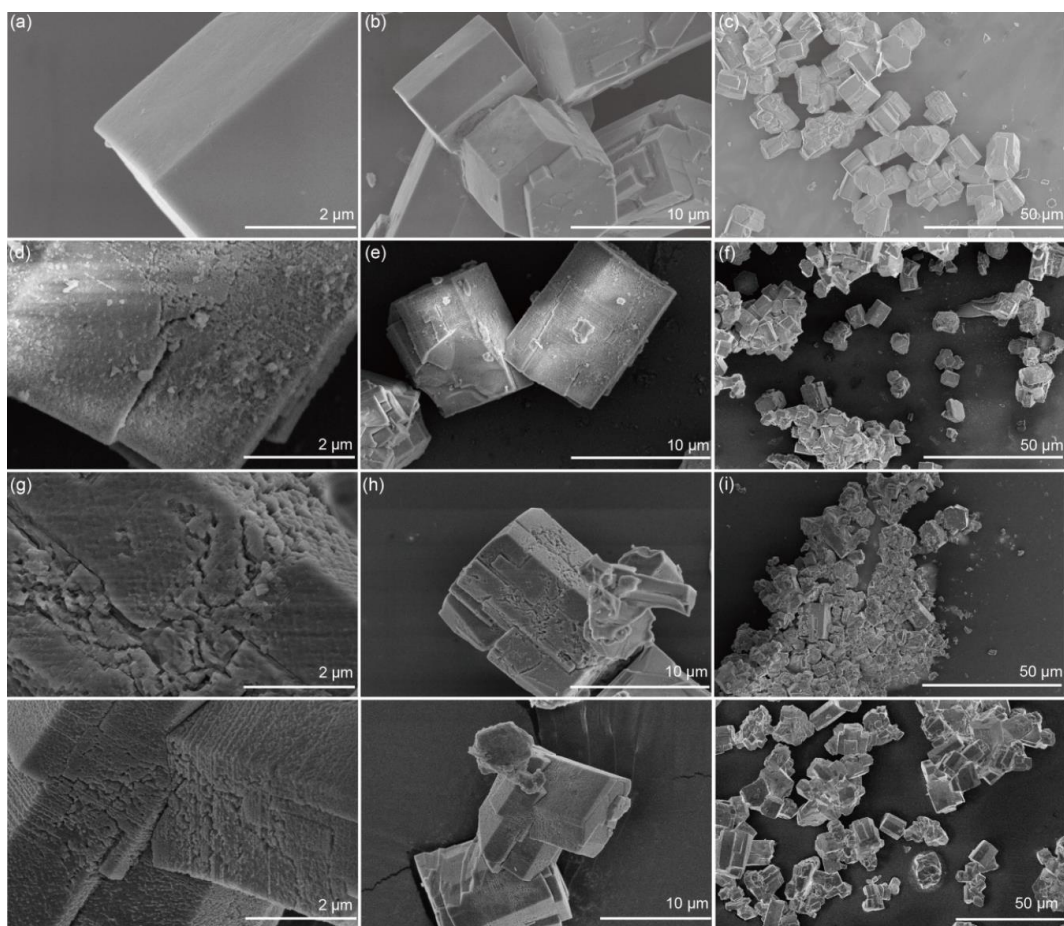


Figure S3. Scanning electron microscopy (SEM) images of different samples. (a)(b)(c) for **1**, (d)(e)(f) for **LiBr@1**, (g)(h)(i) for **LiBr@1** washed with water. (j)(k)(l) for **LiBr@1** after impedance test.

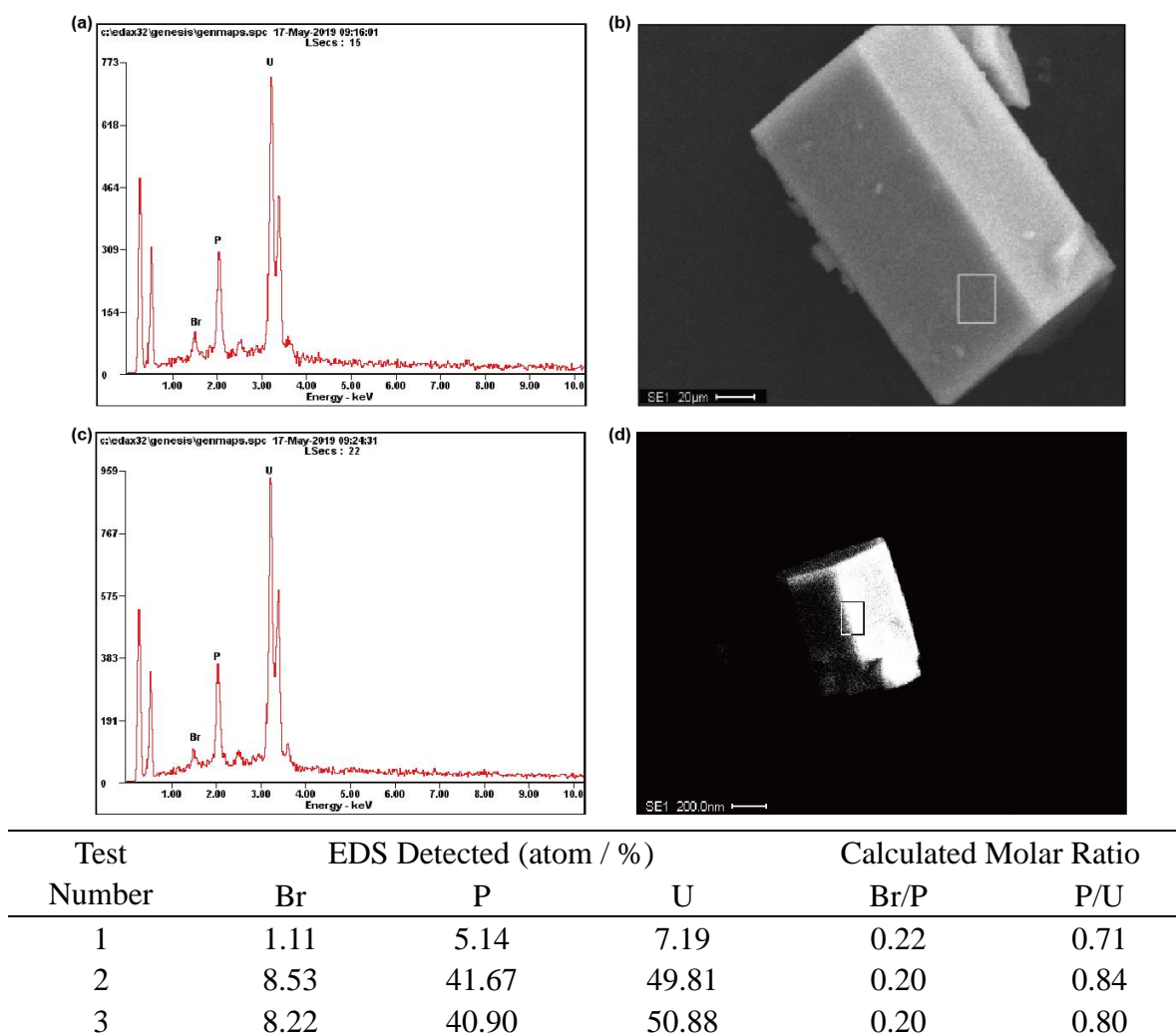


Figure S4. Energy dispersive spectrometer (EDS) analysis of **LiBr@1**. (a)(b) for second test, (c)(d) for third test. The first test is shown in Fig. 2(c). All the test results are summarized in the table.

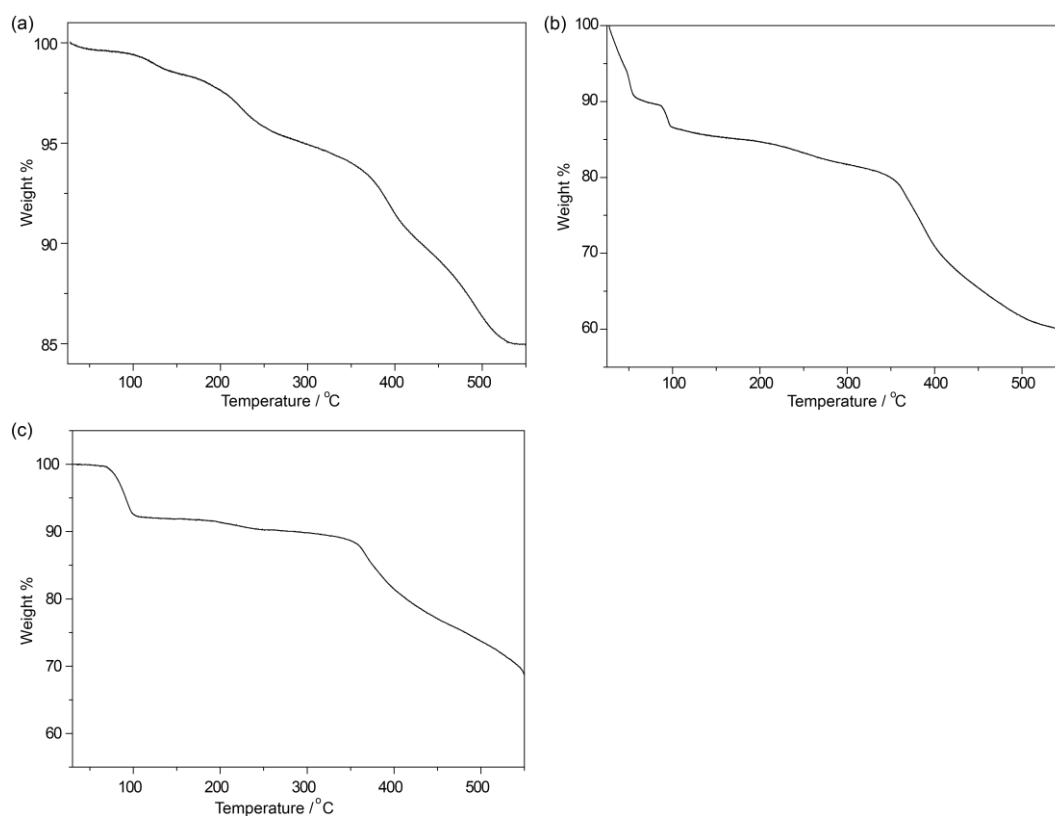


Figure S5. (a) TG plot of **1**. (b) TG plot of **LiBr@1**. (c) TG plot of **LiBr@1** (after impedance test) after exposing to air for 24 h.

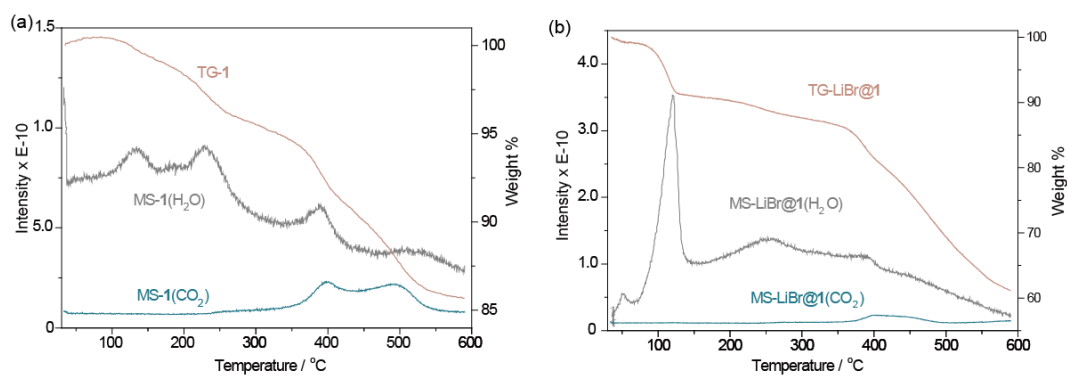


Figure S6. (a) TG-MS plot of **1**. (b) TG-MS plot of **LiBr@1**.

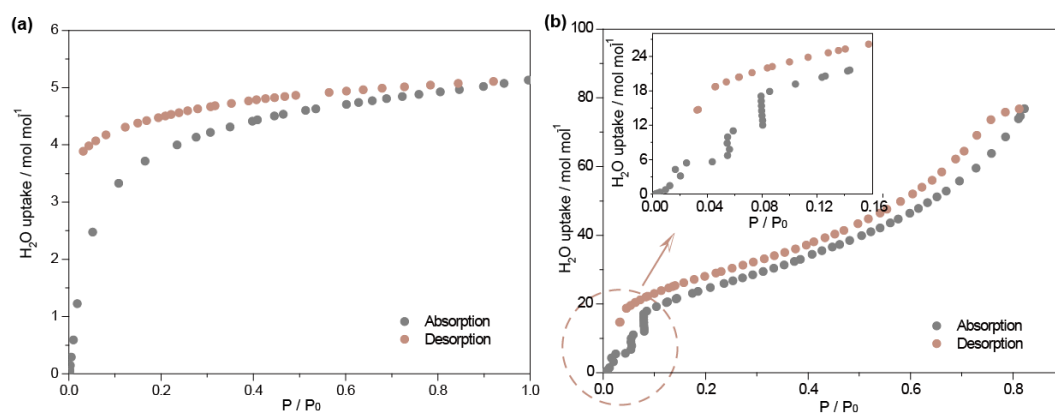


Figure S7. Water sorption isotherms for (a) **1** and (b) **LiBr@1** measured at 25 °C.

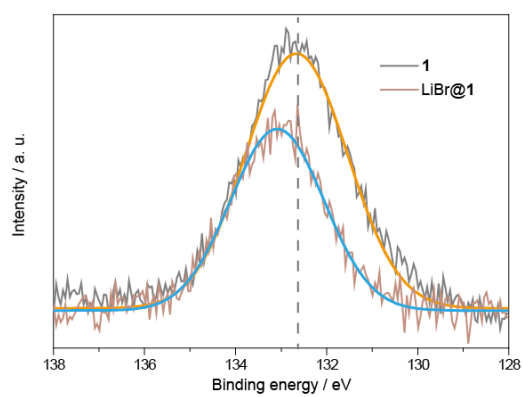


Figure S8. XPS for P of **1** and **LiBr@1**.

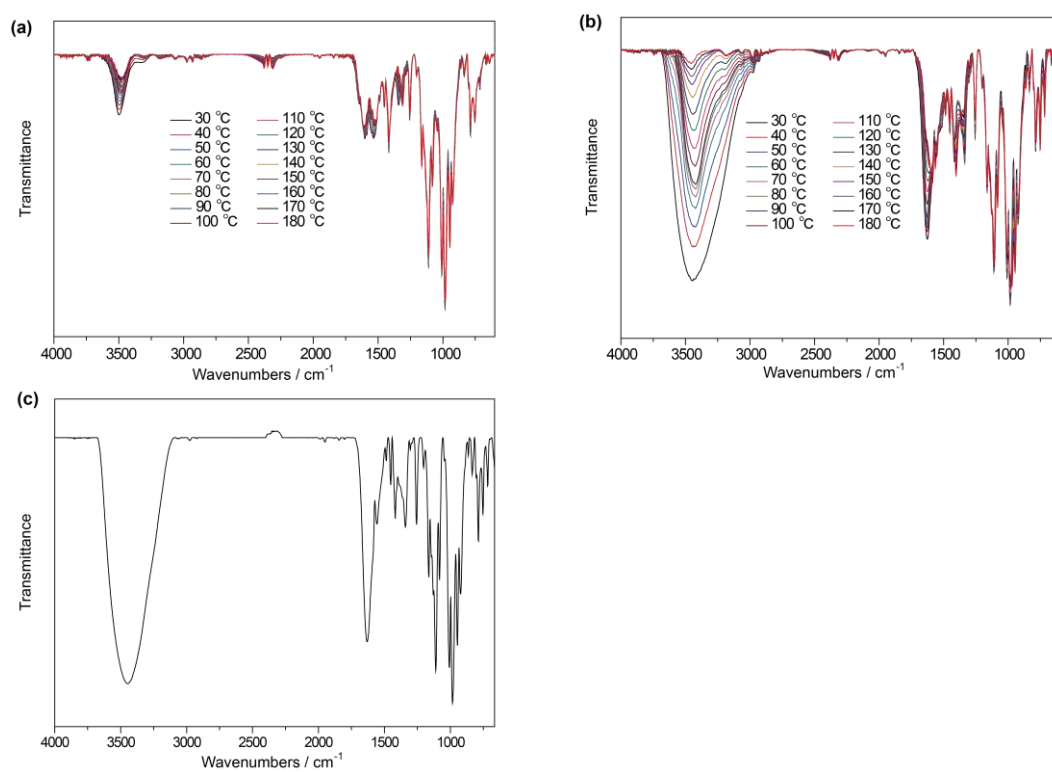
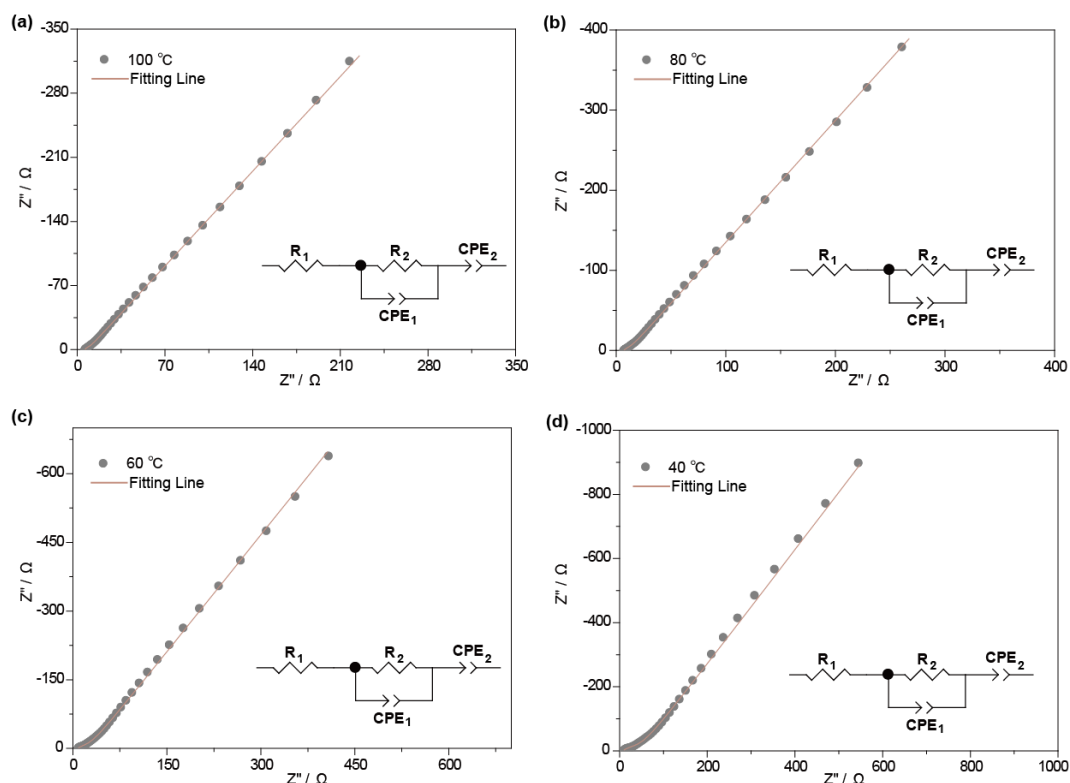


Figure S9. (a) Variable temperature infrared spectra of **1**. (b) Variable temperature infrared spectra of **LiBr@1**. (c) IR spectrum of **LiBr@1** after impedance test.



Temperature / °C	R_1 / Ω	R_2 / Ω	CPE_1		CPE_2		Chi-Squared
			$CPE_1\text{-T}$	$CPE_1\text{-P}$	$CPE_2\text{-T}$	$CPE_2\text{-P}$	
100	6.195	2.097	1.4912e-4	0.82308	8.2393e-4	0.62158	5.9082e-4
80	6.924	4.521	3.8783e-4	0.66055	6.7506e-4	0.62990	5.7308e-4
60	7.305	20.37	5.4617e-4	0.48893	3.9453e-4	0.66278	1.9973e-3
40	8.52	33.55	1.1147e-4	0.58676	2.9394e-4	0.6588	5.2973e-3

Figure S10. The selected impedance fitting result of **LiBr@1** in the third cooling process.

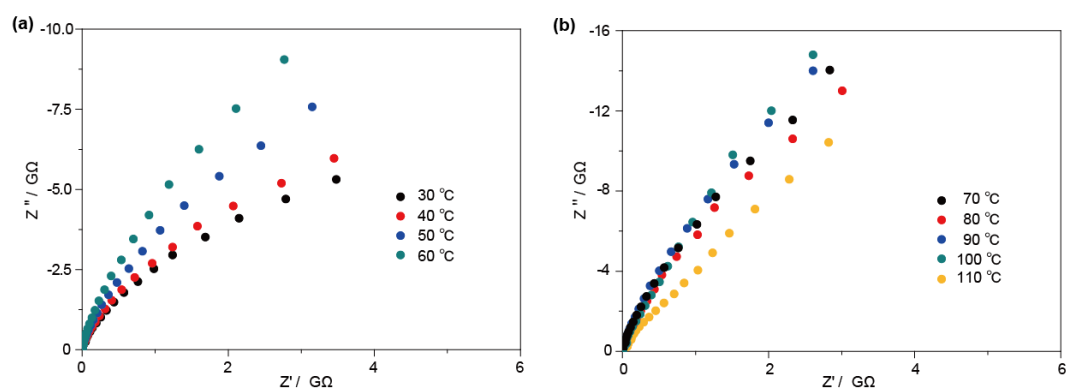


Figure S11. Nyquist plots for **1** under N_2 at selected temperatures.

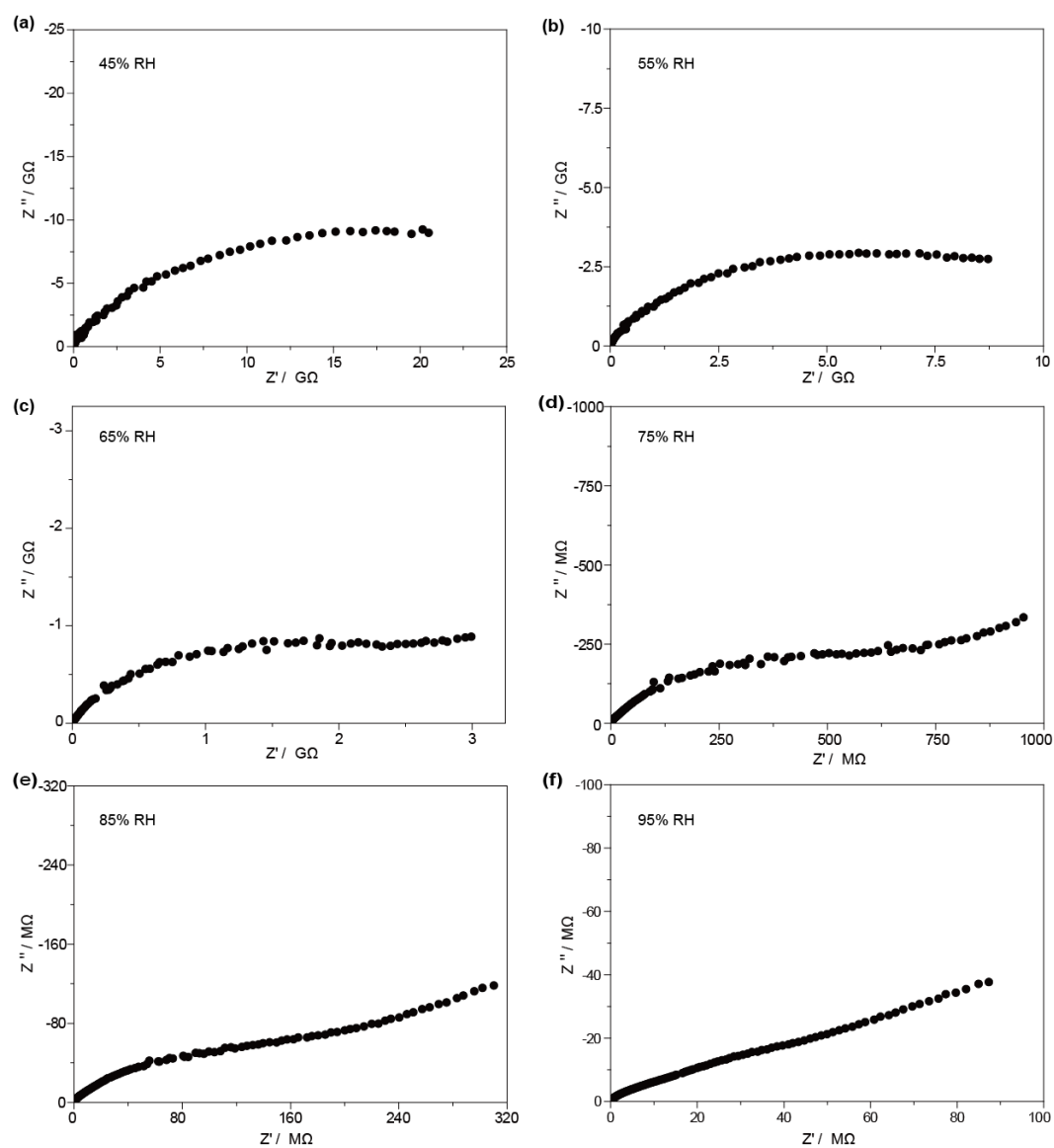


Figure S12. Nyquist plots for **1** at 30 °C under different relative humidity.

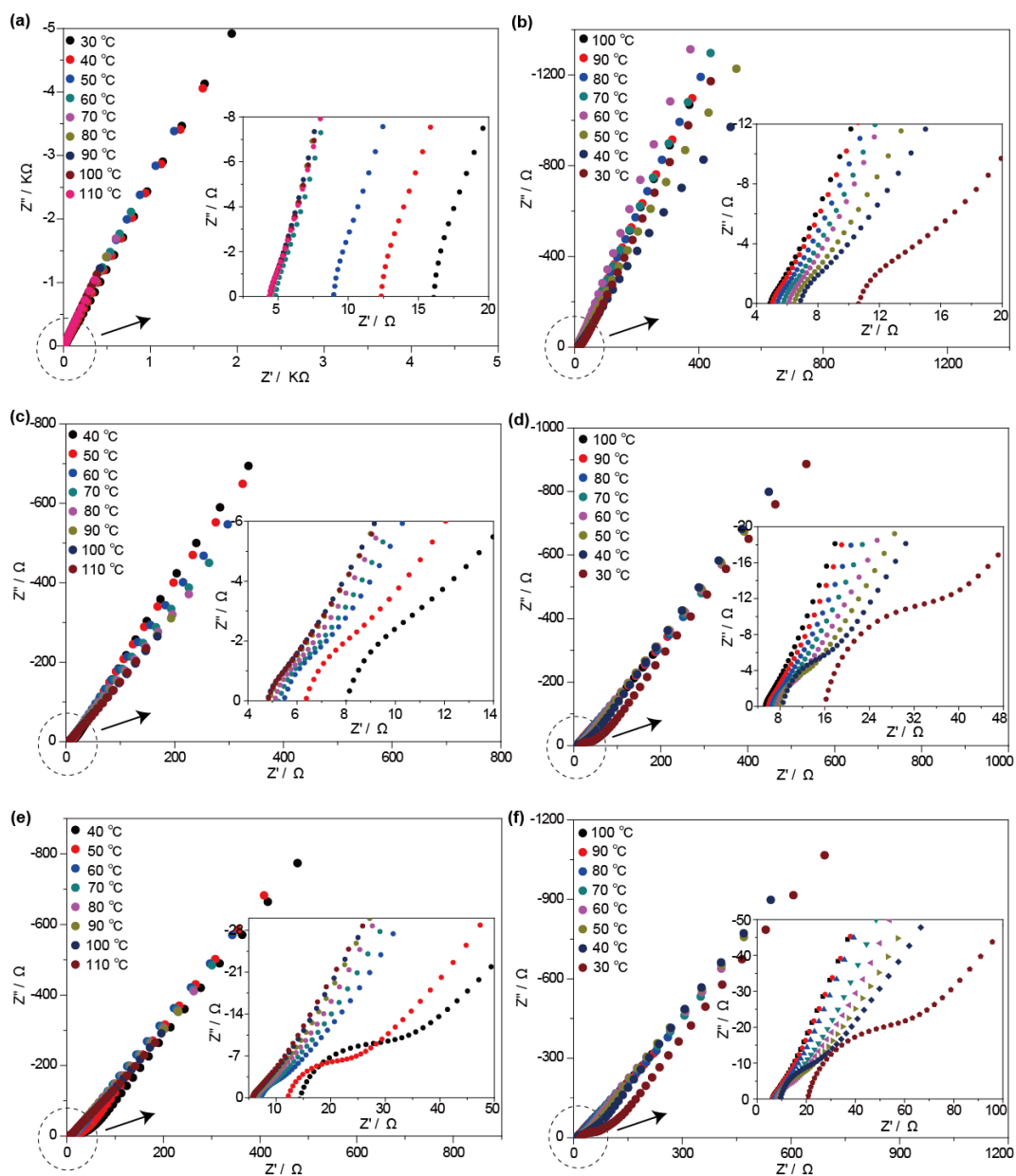


Figure S13. Nyquist plots for **LiBr@1** under N₂ at selected temperatures. (a) The first heating process. (b) The first cooling process. (c) The second heating process. (d) The second cooling process. (e) The third heating process. (f) The third cooling process.

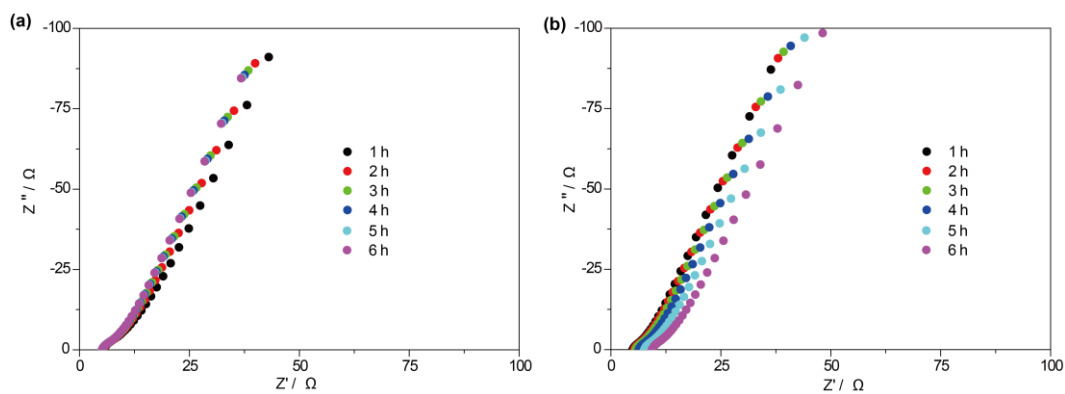


Figure S14. Time dependent Nyquist plots of **LiBr@1** in N_2 at different temperature, (a) for 80 °C and (b) for 110 °C.

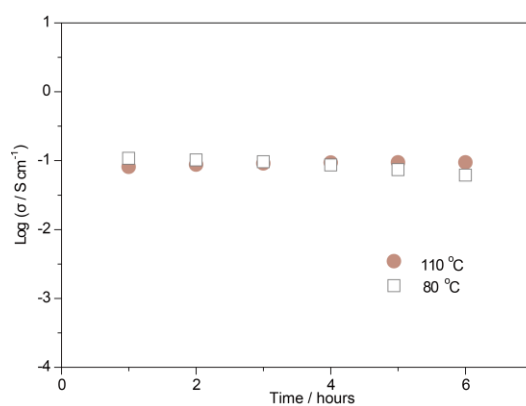


Figure S15. Proton conductivity of **LiBr@1** in the form of $\log(\sigma)$ versus time under various temperatures and nitrogen. The sample was firstly heated to 80 °C and maintained for 6 hours, and then heated to 110 °C and maintained for another 6 hours.

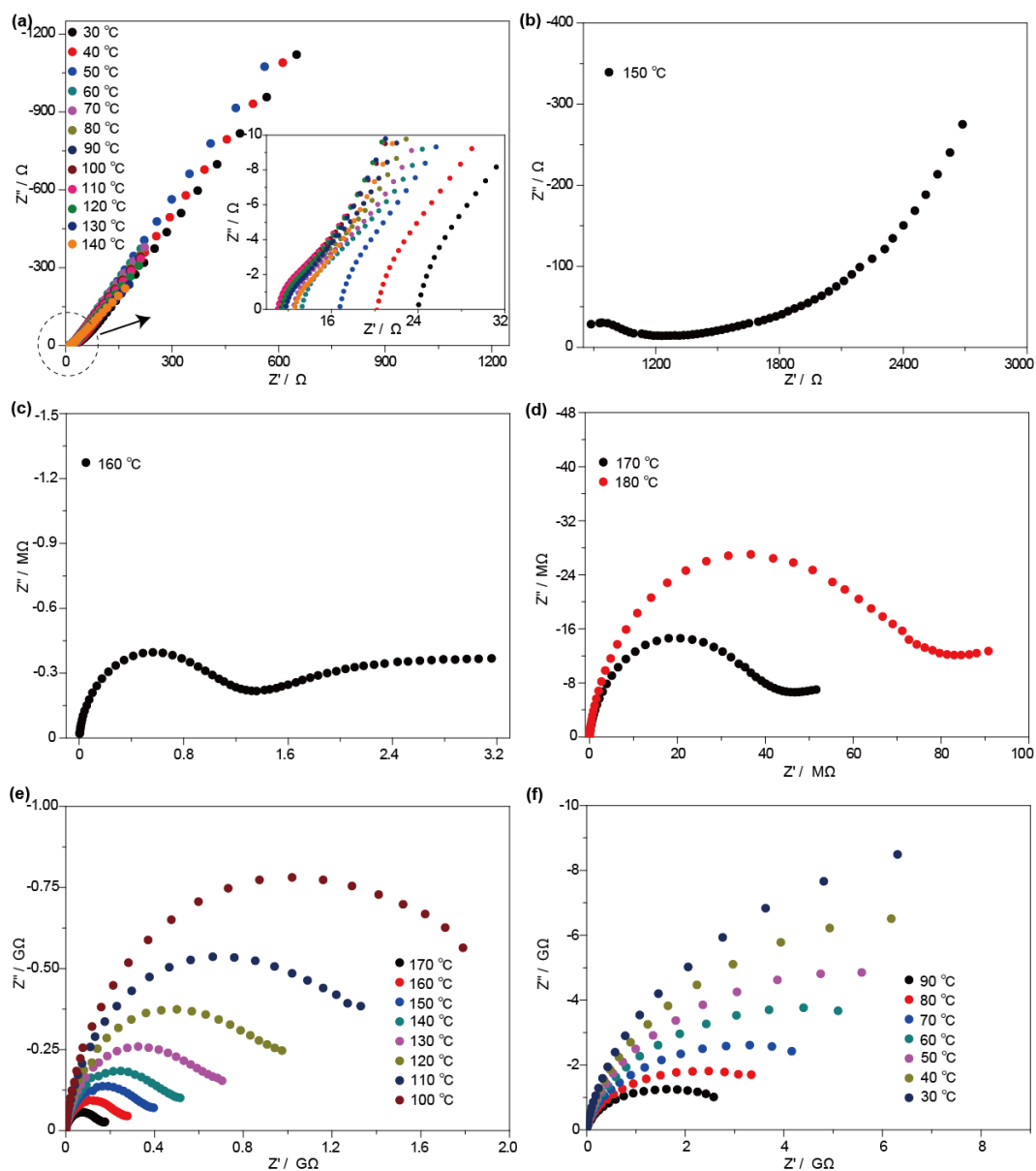


Figure S16. Nyquist plots for **LiBr@1** under N₂ at selected temperatures. (a), (b), (c) and (d) for the heating process. (e) and (f) for the cooling process.

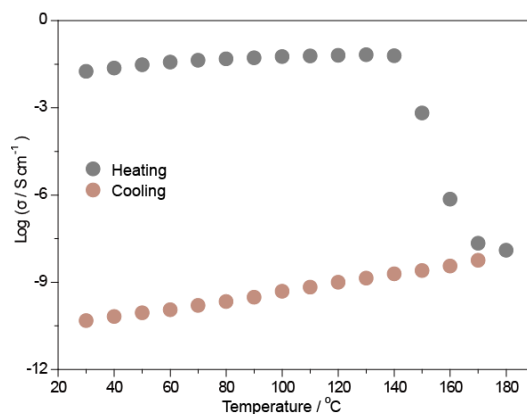


Figure S17. Proton conductivity of **LiBr@1** in the form of log(σ) versus temperature under N₂.

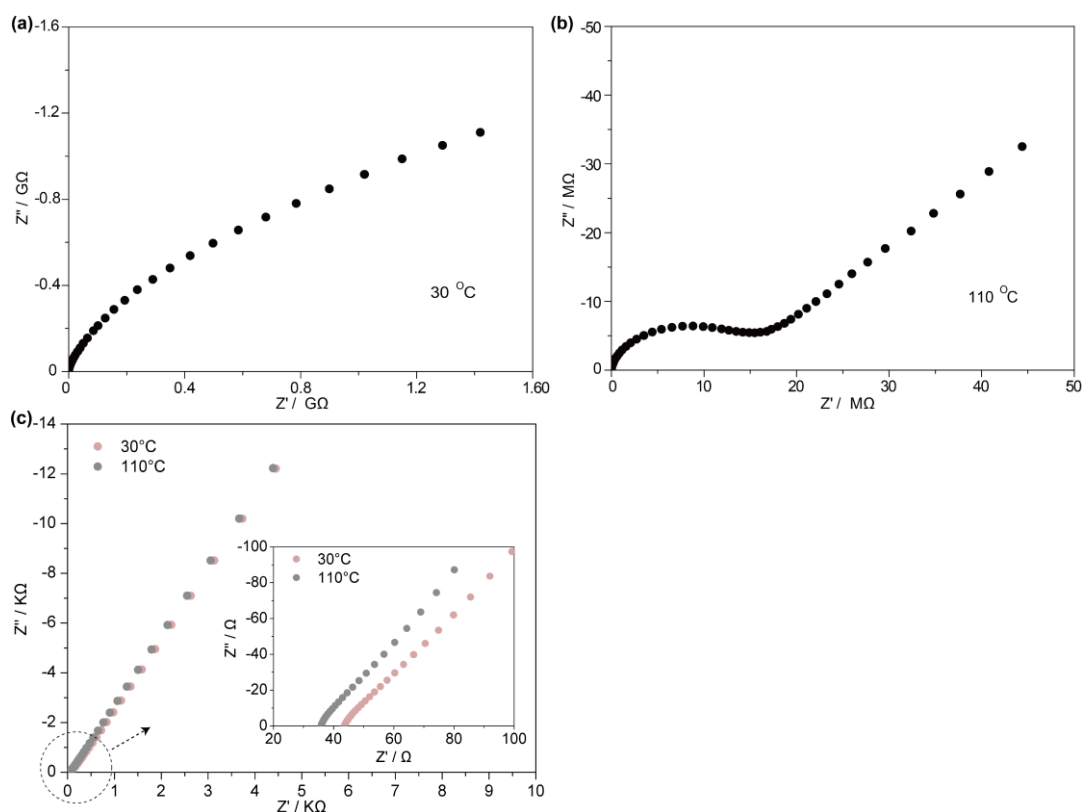


Figure S18. (a)(b) Nyquist plots for **LiBr@1** (after exposing the anhydrous sample to air for one day) under N_2 . (c) Nyquist plots for the rehydrated **LiBr@1** (after immersing the anhydrous sample in the saturated solution of LiBr for 8 h) under N_2 . The pellet for the measurements has 1.67 mm in thickness and 5 mm in diameter.

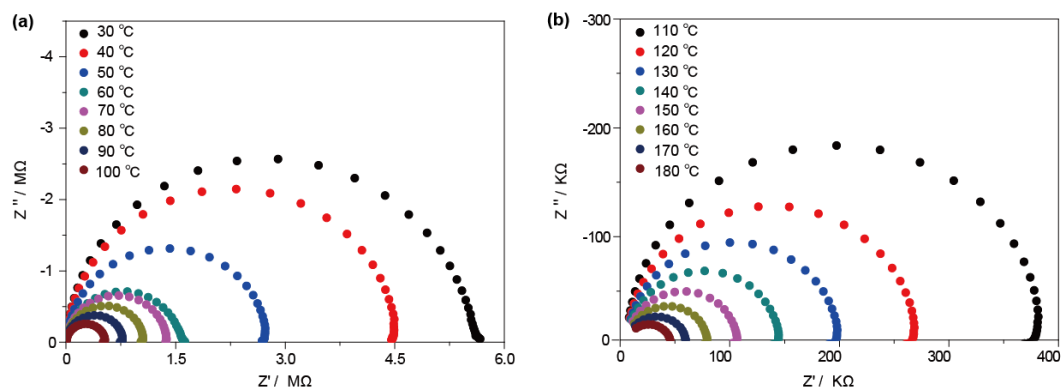


Figure S19. Nyquist plots for $LiBr \cdot xH_2O$ under N_2 at selected temperatures.

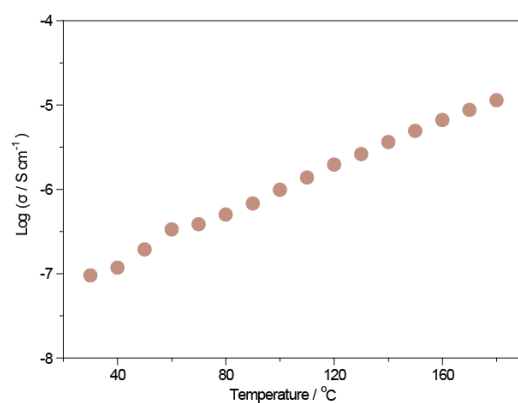


Figure S20. Ionic conductivity of $\text{LiBr} \cdot x\text{H}_2\text{O}$ in the form of $\log(\sigma)$ versus temperature from 30 to 180 °C.

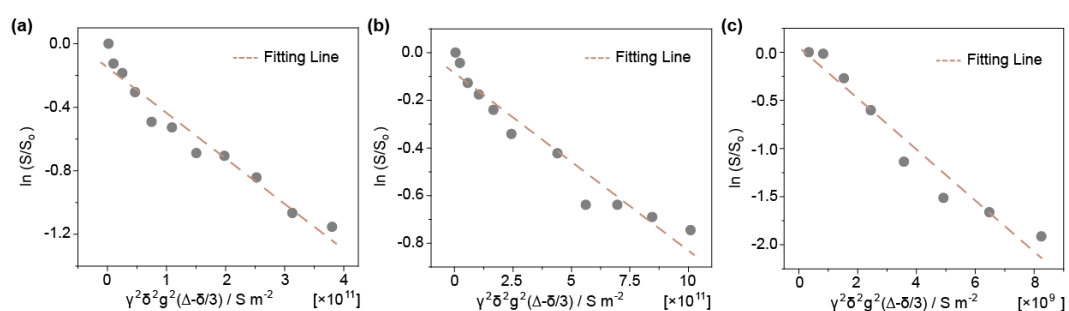


Figure S21. (a) $D(^1\text{H})$ for $\text{LiBr}@\mathbf{1}$ at 25 °C. (b) $D(^1\text{H})$ for $\mathbf{1}$ at 25 °C. (c) $D(^1\text{H})$ for $\mathbf{1}$ at 100 °C.