Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2018

# Supplementary Information

## Superprotonic Conduction through One-dimensional Ordered Alkali Metal Ion Chain in a Lanthanide-Organic Framework

Xia Wang,[a, †] Yanlong Wang,[a, †] Mark A. Silver,[a] Daxiang Gui,[a] Zhuanling Bai,[a] Yaxing Wang,[a] Wei Liu,[a] Lanhua Chen,[a] Juan Diwu,[a] Zhifang Chai,[a] and Shuao Wang*,[a]

a. State Key Laboratory of Radiation Medicine and Protection, School for Radiological and interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, China. E-mail: shuaowang@suda.edu.cn.

# Experimental section

## General

Reagents and solvents employed were commercially available and used as received. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) equipped with a Lynxeye one-dimensional detector. Thermal gravimetric analysis was carried out on a NETZSCH STA 449F3 instrument in the range of 30 – 900 °C under nitrogen flow at a heating rate of 10 °C / min. A Quantachrome Autosorb Gas Sorption analyzer IQ2 was used to perform water vapor adsorption measurements. Scanning electron microscopy images and energy-dispersive spectroscopy data were recorded on a FEI Quanta 200FEG Scanning Electron Microscope with the energy of the electron beam being 30 keV. Samples were mounted directly on the carbon conductive tape with Au coating. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of Li was conducted using a Thermo Finnigan high resolution magnetic sector Element 2 ICP-MS instrument.

## X-ray Crystallography

Data collection was performed on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector at room temperature. The data frames were collected using the program APEX2 and processed using the SAINT routine. The structures were solved by direct methods and refined by the full-matrix least squares on F2 using the SHELXTL-2014 program[1]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic and refinement details are summarized in **Table S1**.

## Proton conductivity measurement

The pelletized samples of **1** for conductivity measurements were attached with two gold electrodes, and then were placed in humidity and temperature controlled chamber (Samples were equilibrated for between 1 to 2 hours after each step in temperature (30 to 90 °C) and for 2 to 3 hours for each step with different relative humidity). Using a vernier caliper the pelletized samples the diameter is 3 mm, and sample thickness is in the range from 0.8 to 2 mm for pelletized compounds. Alternating current impedance of the pelletized samples were carried out on a Solartron SI1260 Impedance/Gain-Phase Analyzer with applied ac voltage amplitude over a frequency range from 4 MHz to 1 Hz with an input voltage amplitude of 500 mV. The conductivity was calculated by the following equation:

$$\sigma = L/RS$$

Where S and L are the cross-sectional area and thickness of the pellet, respectively, and R, which was obtained from the impedance plots, is the value of resistance. The $E_a$ of activation energy for the **1** conductivity was calculated from the following Arrhenius equation:

$$\sigma T = \sigma_0 \exp(-E_a/k_B T)$$

Where σ is the ionic conductivity, $k_B$ is the Boltzmann constant, and $\sigma_0$ is the pre-exponential factor, T is the temperature.

## $Li^+$ exchange experiments

As-synthesized **1** (300 mg) was added into 300 mL saturated lithium chloride aqueous solution. The resulting mixture was mildly stirred for 160 h at room temperature, allowing for sufficient anion exchange. During the process, the old saturated lithium chloride aqueous solution was replaced by fresh saturated lithium chloride aqueous solution every 12 h. After 160 h, the solid in the solution was filtered, soaked in methyl alcohol for 12 hours and rinsed with ethanol, dried in the air, and used for proton conductivity measurement.

## Measurement of $Li^+$ amounts

The samples after $Li^+$ exchange (0.05 mmol) were dissolved in 1 mL $HNO_3$, then gradually dilute to $10^{10}$ times of the pristine solution. After that, the Li amounts of 23.238 ppb was measured by ICP-MS. Finally, we calculated that 33.48% $Na^+$ was replaced by $Li^+$, in consistency with the result of EDS analysis.

## Synthesis of 1

$H_2SDA$ (39.4mg, 0.1mmol) and $Eu(NO_3)_3{\cdot}6H_2O$ (44.6 mg, 0.1 mmol) was dissolved in a mixture with 3 mL DMF and 2 mL $H_2O$, subsequently, 60 mg NaOH was added into the mixture. Then the mixture was sealed in a 20 mL glass vial heated at 100 ℃ for 4 days. The reaction system was cooled gradually to ambient temperature. After filtration and washing three times with ethanol, white block crystals suitable for XRD were collected. Yield: ca. 46% (based on $Eu(NO_3)_2{\cdot}6H_2O$). Elemental analysis calcd (%) for $C_{30.125}H_{20.425}N_{0.375}O_{14.775}S_2EuNa_2$: C, 39.79; H, 2.376; N, 0.6021. Found C, 40.80; H, 2.305; N, 0.5952. CIF information for **1** can be found in the Cambridge Crystallographic Database. (CCDC No. 1817693)

**Table S1.** Crystallographic parameters of **1**.

| | **1** |
|---|---|
| Formula | $Na_2[Eu(SDA)_2(COO)]\cdot 0.375DMF\cdot 0.4H_2O$ |
| Formula weight (mol $g^{-1}$) | 886.10 |
| Crystal system | Orthorhombic |
| *a* (Å) | 26.6907(19) |
| *b* (Å) | 22.7441(16) |
| *c* (Å) | 5.7141(5) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 90 |
| *V* ($Å^3$) | 3468.8(5) |
| *Z* | 4 |
| $D_c$ (g $cm^{-3}$) | 1.697 |
| $\mu$ ($mm^{-1}$) | 2.023 |
| *F* (000) | 1756 |
| T (K) | 168(2) |
| GOF on $F^2$ | 1.121 |
| R1,[a] *w*R2[b] ($I > 2\sigma(I)$) | 0.0415, 0.1076 |
| R1,[a] *w*R2[b] (all data) | 0.0620, 0.1170 |

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

NOTE: Since there are highly disordered solvent molecules in the free space, the SQUEEZE[2] routine in PLATON was applied to remove the diffraction peaks contributed from those highly disordered guest molecules. The chemical formula of **1** was determined by the combination of the crystal data (SQUEEZE result), TGA, and elemental analysis. Based on the SQUEEZE result, the solvent molecules were identified as 0.375 DMF and 0.4 $H_2O$. All disordered molecules have been included in the .ins file, and all parameters of **1** reported in the CIF were changed subsequently, although it was different from the calculated data.

The SQUEEZE results are as follows:

```
# SQUEEZE RESULTS
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   0.118   0.750 -0.012          193          19 ' '
    2   0.382   0.250 -0.074          193          19 ' '
```

| | | | | | |
|---|---|---|---|---|---|
| 3 | 0.618 | 0.750 | -0.055 | 193 | 19 ' ' |
| 4 | 0.882 | 0.250 | -0.043 | 193 | 19 ' ' |

_platon_squeeze_void_probe_radius 1.20

_platon_squeeze_details

As noted above, 76 electrons were removed from the unit cell by the SQUEEZE process. This could correspond with some 76 / 4 = 19 electrons being removed from the asymmetric unit. According to elemental analysis and TGA, we confirm ultimately the removed 19 electrons are from 0.375 DMF (15 electrons) and 0.4 $H_2O$ (4 electrons).

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550

Calculated sin(theta_max)/wavelength = 0.5496

NOTE: Although we have collected crystal data under liquid nitrogen (-105 °C), we haven't got a good high angle crystal date of **1** maybe due to the poor crystal quality. We had tried to add the high angle crystal date into the whole date but failed to determine the crystal structure. Hence, we had to delete the high angle crystal date from the whole date. What's more, we used current crystal date to modulate the PXRD diagram which consistent with the actual PXRD diagram, which confirmed that the solved structure of **1** was correct except lacked some high angle crystal date.

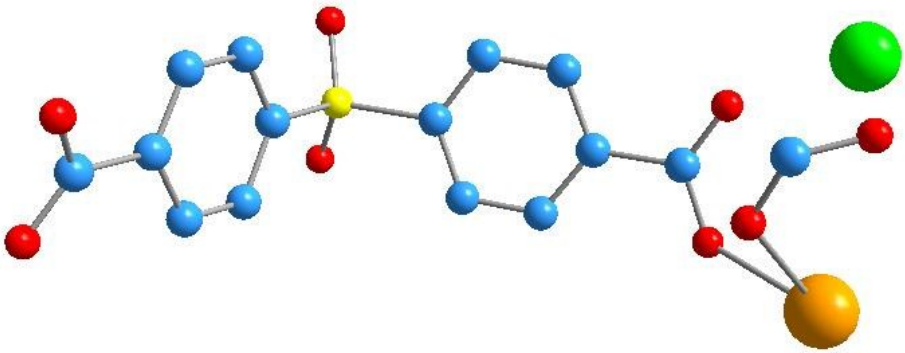

**Fig. S1** The asymmetric unit of **1**.

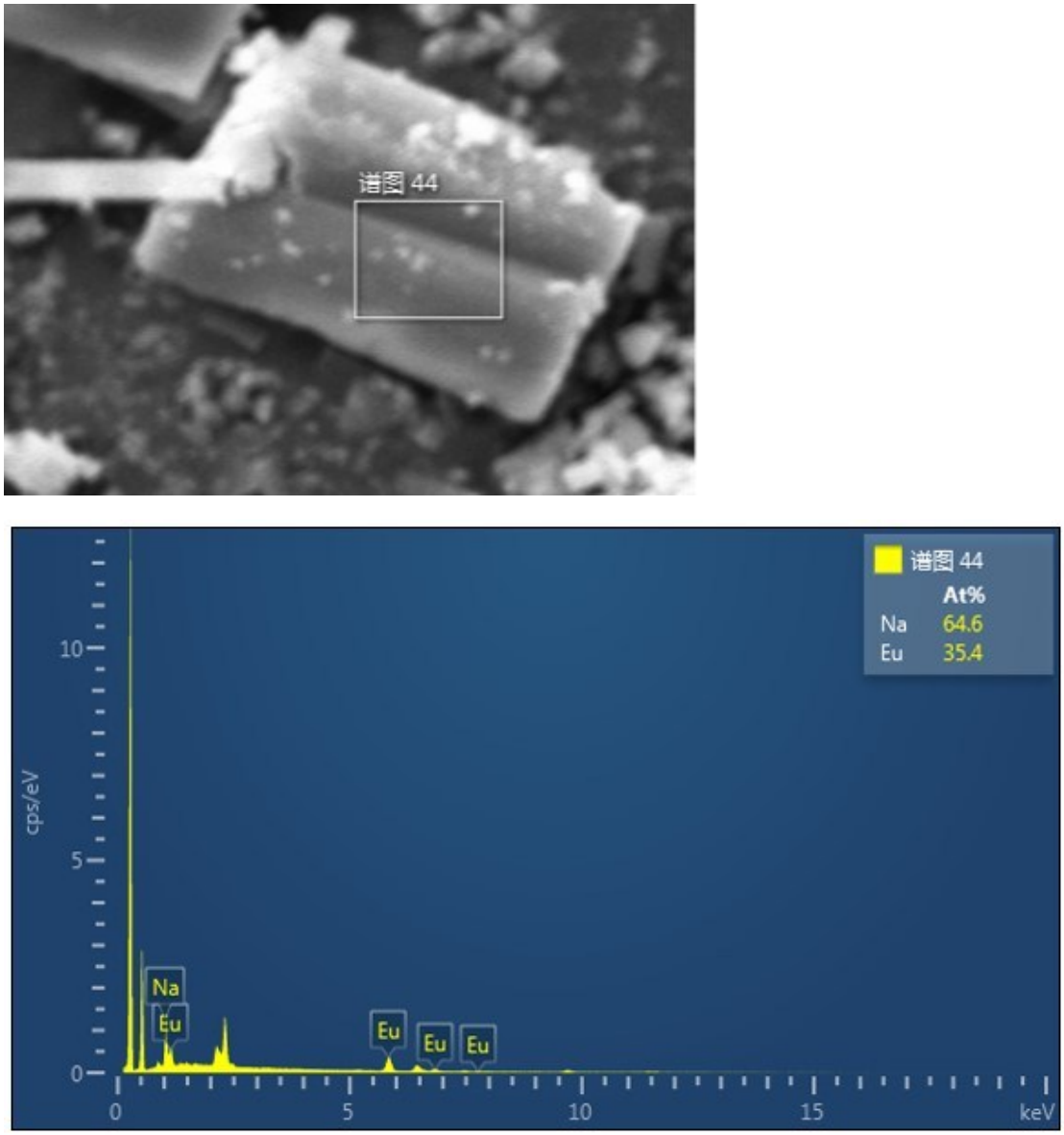


**Fig. S2** SEM and EDS analysis of **1**.

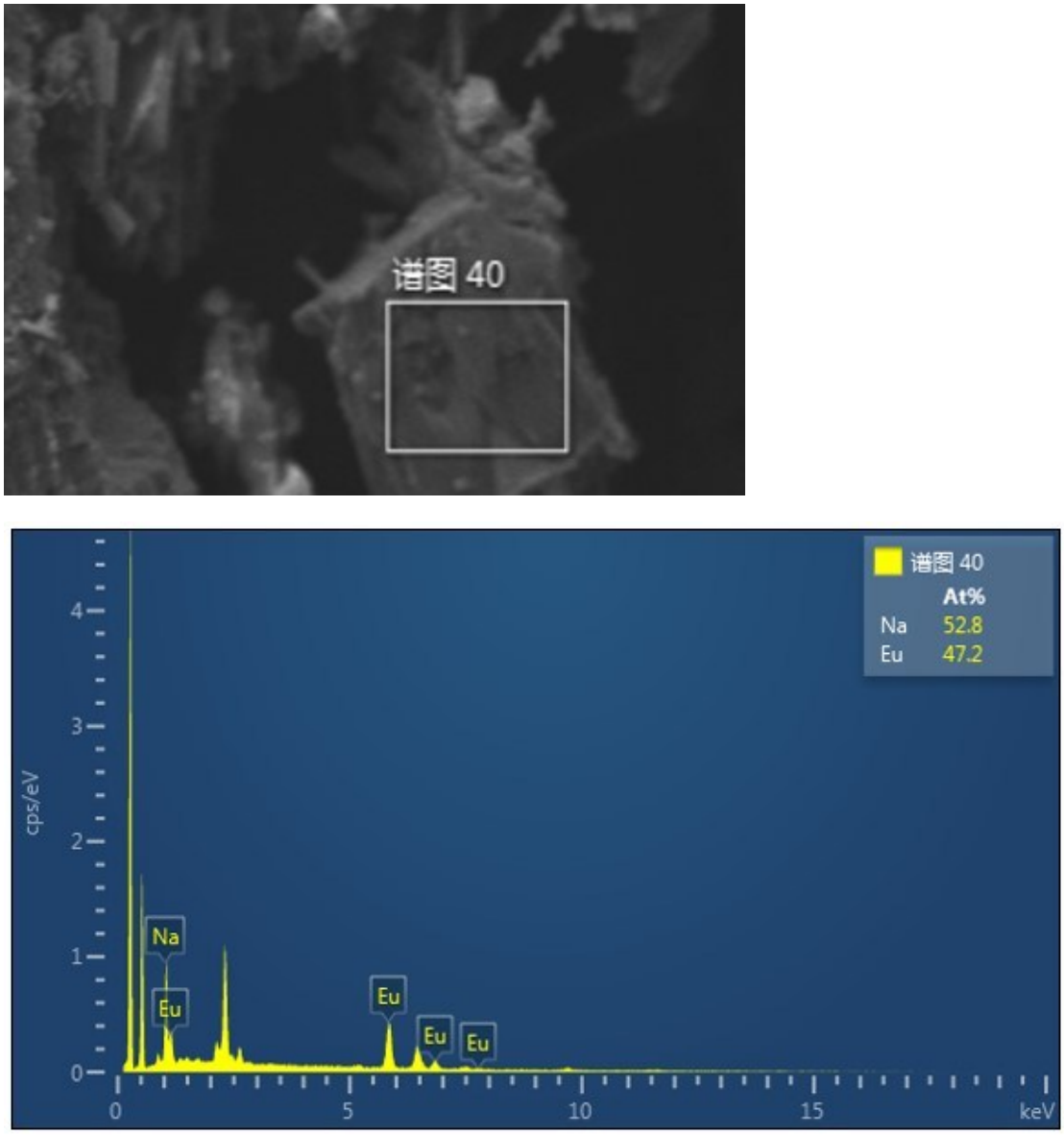


**Fig. S3** SEM and EDS analysis of **1** after $Li^+$ exchange.

**Table S2.** Na/Eu ratio before and after $Li^+$ exchange.

| | Before $Li^+$ exchange | After $Li^+$ exchange |
|---|---|---|
| Na (At%) | 64.6 (1.825) | 52.8 (1.119) |
| Eu (At%) | 35.4 (1.000) | 47.2 (1.000) |

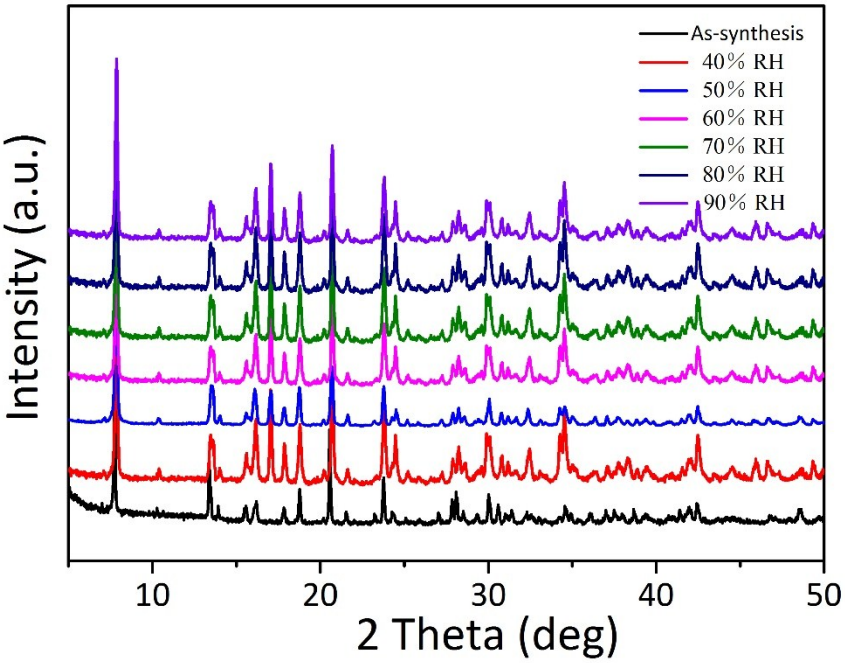


**Fig. S4** PXRD of **1** under different humidity from 40% RH to 90% RH.

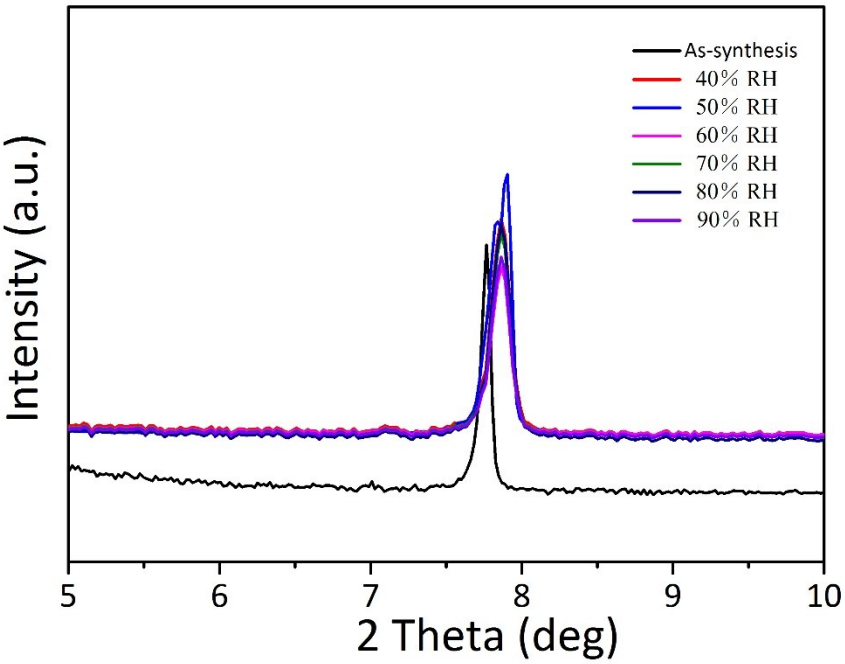


**Fig. S5** Low angle peak positions in the PXRD patterns of **1** under different humidity from 40% RH to 90% RH.

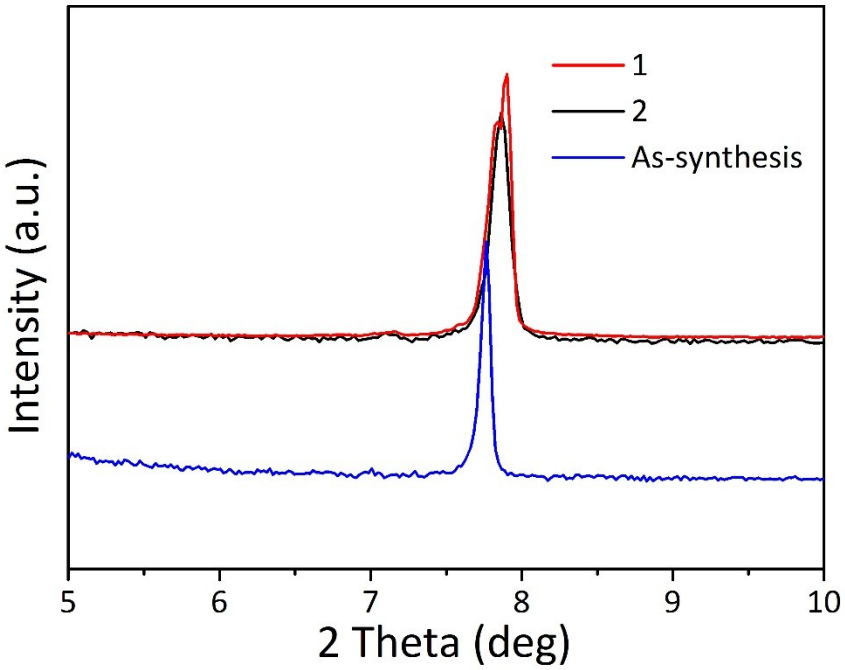


**Fig. S6** Low angle peak positions in the PXRD patterns of as-synthesized sample of **1**, that after water vapor adsorption, and that after proton conduction measurement.

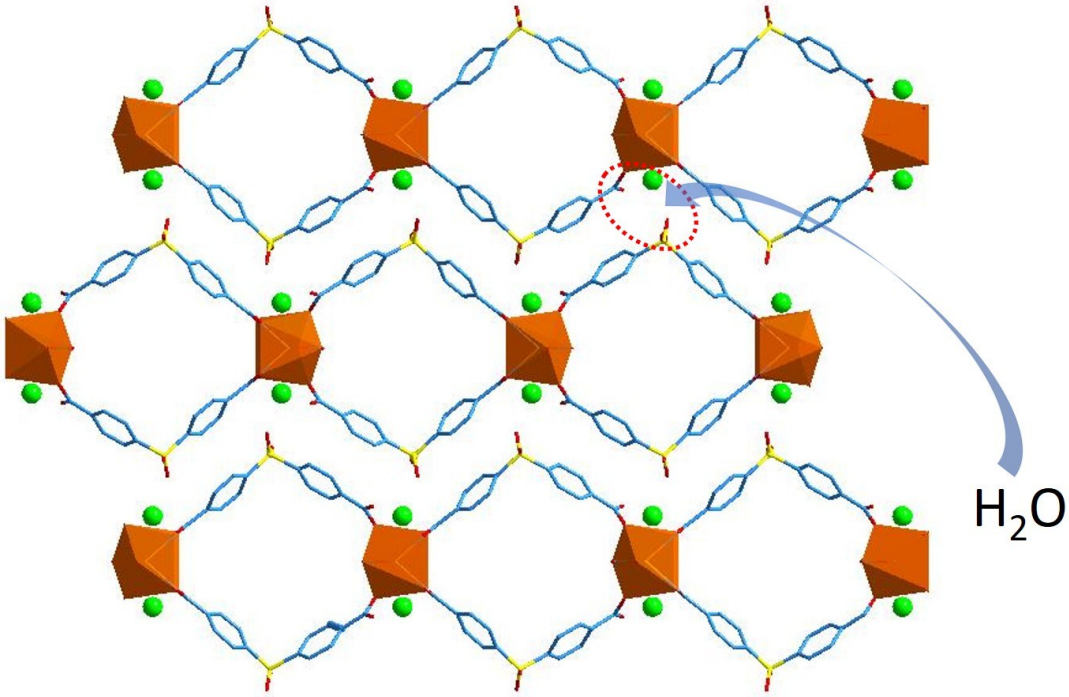


**Fig. S7** Water may exist between the C=O and S=O, coordinating to $Na^+$ and forming the hydrogen bonds.

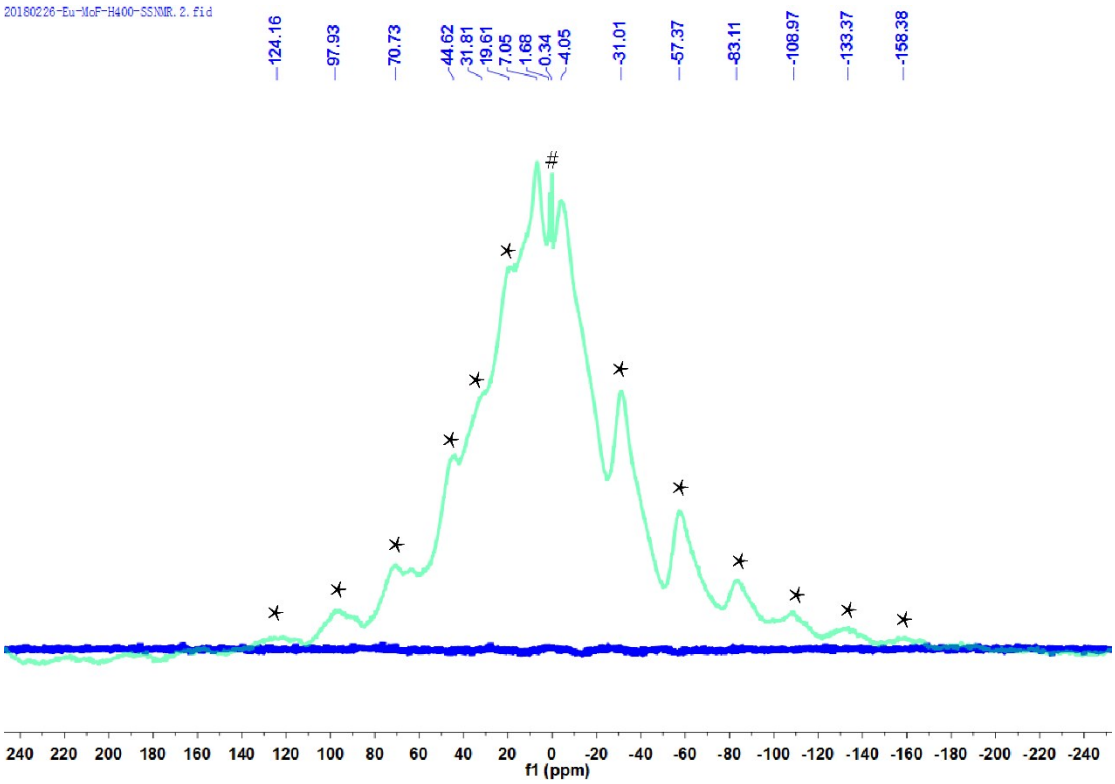


**Fig. S8** Solid-state NMR $^{1}$H spectrum of **1** using one pulse excitation method (green line) and 1D $^{1}$H double quantum filtered spectrum (blue) showing protons in the system are mobile. "*" represent "spinning sidebands"; "#" represent "solvent peak". Two broad resonance peaks appear in the room-temperature SSNMR 1D $^{1}$H spectrum under one-pulse excitation SSNMR test conditions at 7.05 and -4.05 ppm. In addition, the 1D $^{1}$H double-quantum (DQ)-filtered spectrum was also recorded. This type of measurement can clearly discriminate active protons in a flexible environment from those in an inactive rigid environment. Different from the typical $^{1}$H spectrum, the 1D $^{1}$H DQ-filtered method excites only protons with low local mobility. Interestingly, no signal was observed using the DQ-filtered method, which implies the high local mobility of all protons in the system.

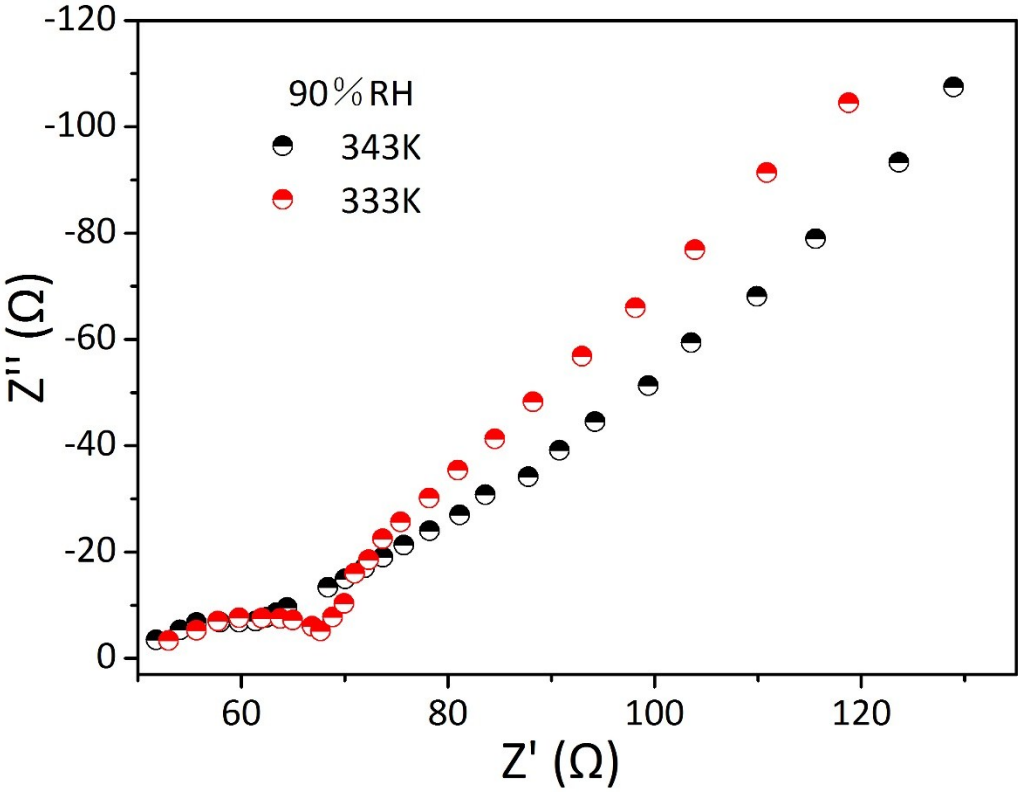


**Fig. S9** Impedance spectrum of **1** at 333 K (δ=1.63 × $10^{-2}$ S $cm^{-1}$) and 343 K (δ=1.86 × $10^{-2}$ S $cm^{-1}$) under 90% RH.

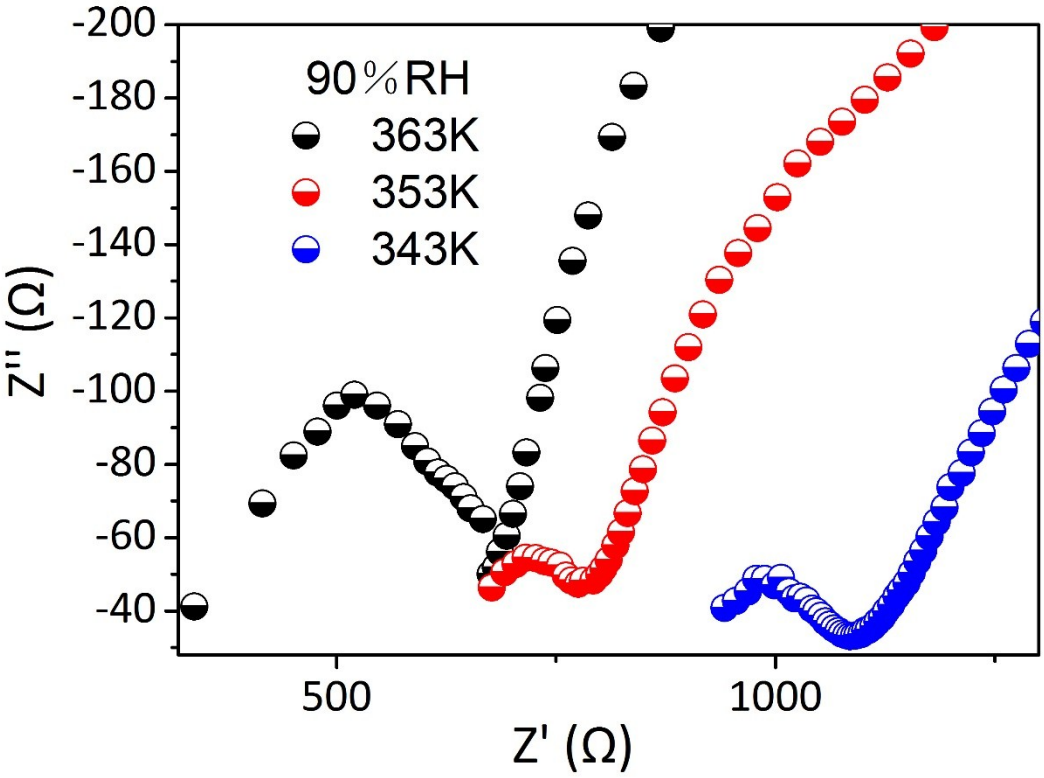

**Fig. S10** Impedance spectrum of **1** after $Li^+$ exchange at 363 K (δ=2.52 × $10^{-3}$ S $cm^{-1}$), 353 K (δ=2.05 × $10^{-3}$ S $cm^{-1}$) and 343 K (δ=1.57 × $10^{-3}$ S $cm^{-1}$) under 90% RH.

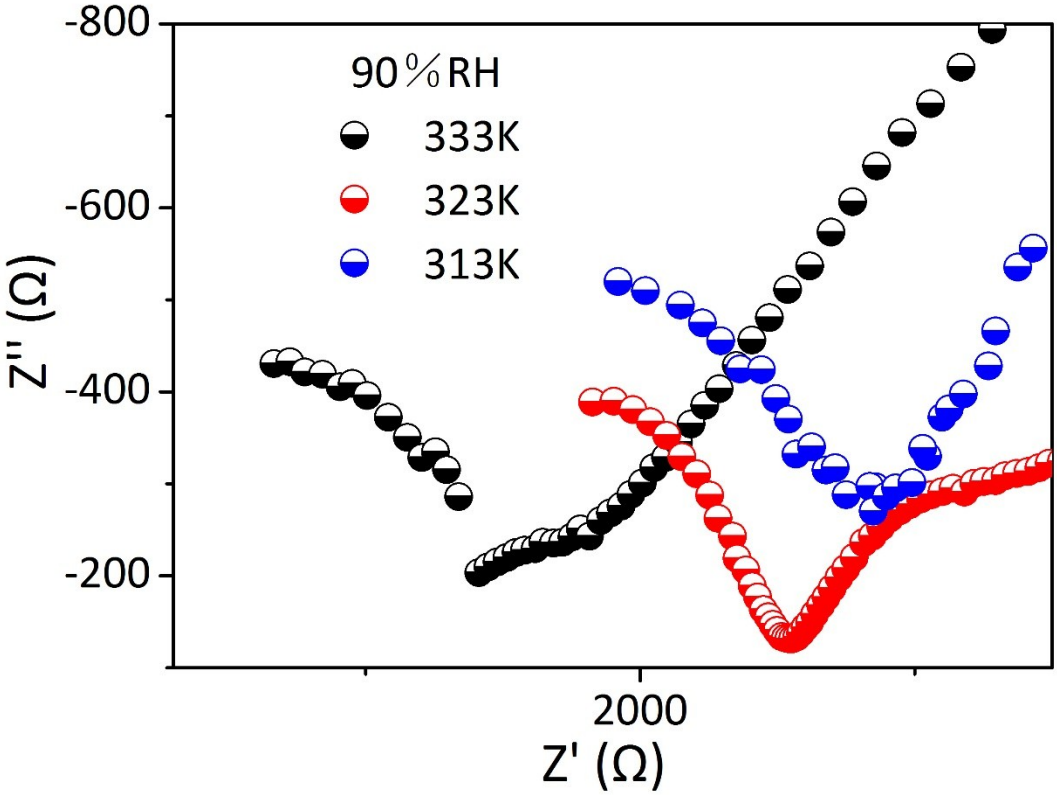


**Fig. S11** Impedance spectrum of **1** after $Li^+$ exchange at 333 K (δ=1.07 × $10^{-3}$ S $cm^{-1}$), 323 K (δ=6.59 × $10^{-4}$ S $cm^{-1}$) and 313 K (δ=5.22 × $10^{-4}$ S $cm^{-1}$) under 90% RH.

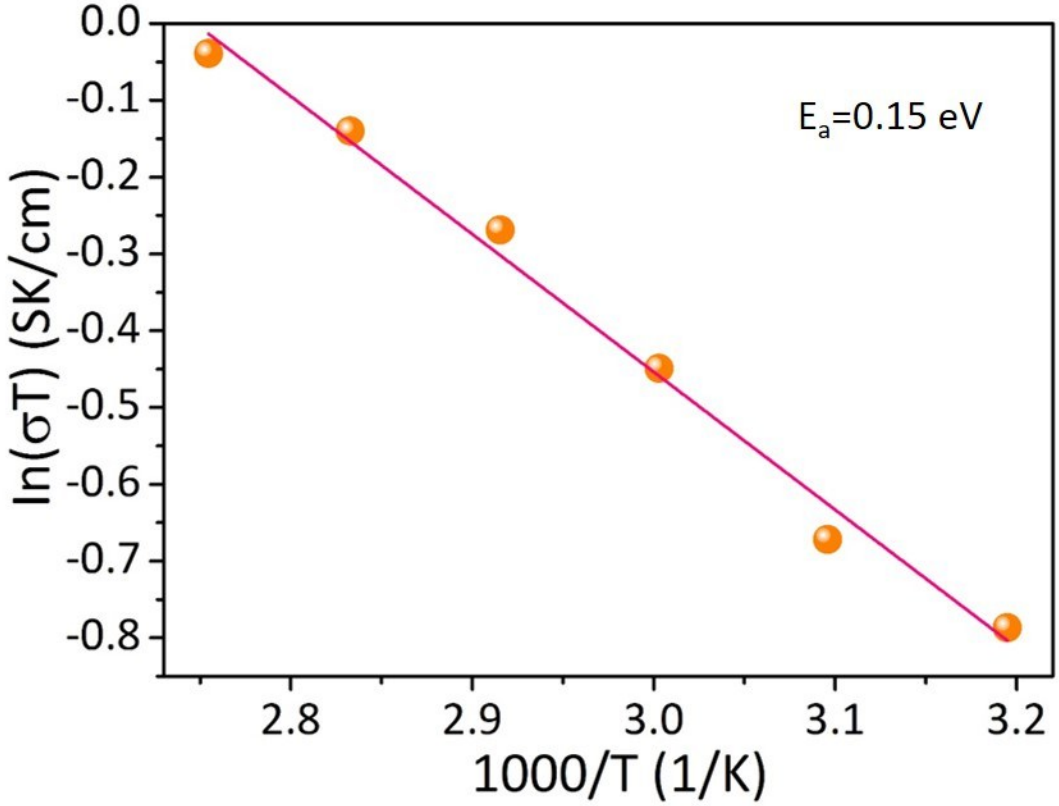

**Fig. S12** Arrhenius plot of the temperature-dependence on proton conductivity in **1** after $Li^+$ exchange at 90% RH.

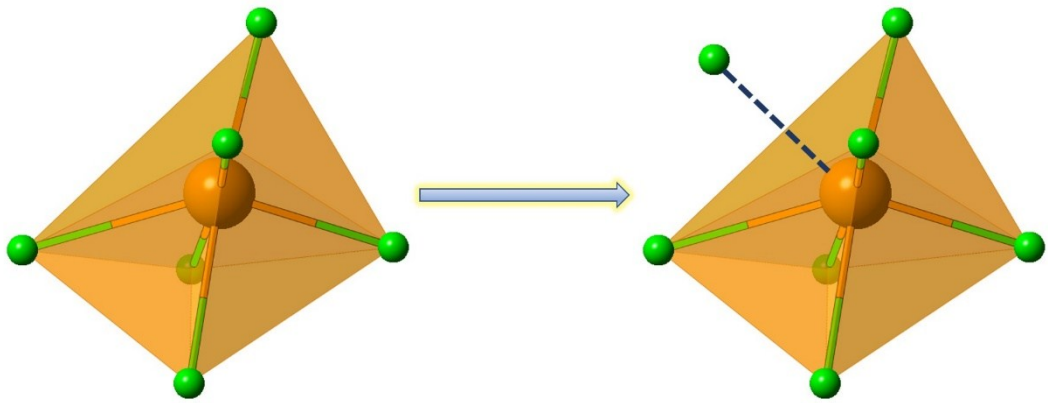

**Fig. S13** Coordination environment of Na+ in 1 showing a highly distorted octahedron geometry with room to locate an additional coordinated water molecule.

**Reference:**


1. Sheldrick, G. M. Acta Cryst., 2015, 71,3−8.
2. Spek, A. L. Acta Cryst., 2015, C71, 9−18.