Cations mediating proton conductivity in an oxalate based microporous coordination polymer

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Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Powder X-ray diffraction (PXRD) were recorded on a Siemens D5005 diffractometer with Cu K_α (λ = 1.5418 Å) radiation. The amount of Ca and Zr was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES).

Synthetic procedures

Synthesis of compound $Ca_2Zr(C_2O_4)_4 \cdot 5.5H_2O$ (1): According to the report procedure,[1] a solution containing 9 $\times 10^{-3}$ mol of oxalic acid dihydrate was introduced dropwise to 20 mL of an aqueous solution containing $CaCl_2$ (4.5 $\times 10^{-3}$ mol) and $ZrCl_4$ (1.5 $\times 10^{-3}$ mol). The solution was heated a few minutes at 90 °C, under stirring, and 30 mL of water were added to slow down the evaporation. After cooling, the solution was filtered off and the white precipitate was washed with water and ethanol and dried at room temperature.

The preparation of 1@NH_4^+

Then about 0.500 g of samples **1** was added to 5 mol/L of NH_4Cl in a solution containing 20 ml of water. The contents were placed in a 20 ml screw-capped vial, which was heated to 45 °C in the water bath for 12 h. A white precipitate was obtained by filtration and washed with water for several times to remove excess NH_4Cl. The solid was then dried overnight under vacuum condition.

The thermal behaviours were studied by TGA. The experiments were performed under a N_2 atmosphere with a heating rate of 10 ºC min^{-1} in temperatures ranging from room temperature to 800 ºC (Fig. S1). The weight loss 16.88% in the temperature range of 31-278 ºC corresponds to the departure of NH_3 in NH_4^+ and water molecules (found: 16.88% calc: 16.76%).

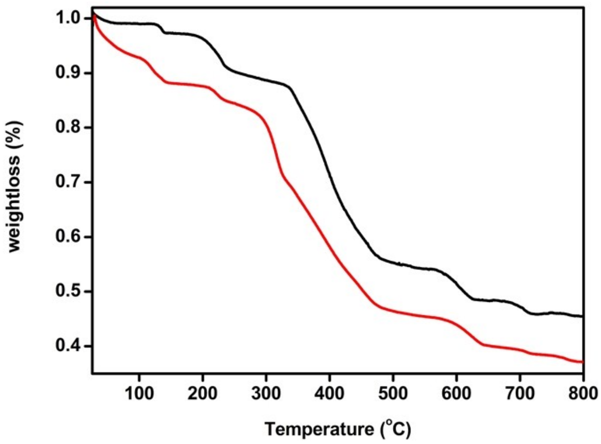

Fig. S1 Thermogravimetric analyses of **1** (black) and **1**@NH_4^+ (red).

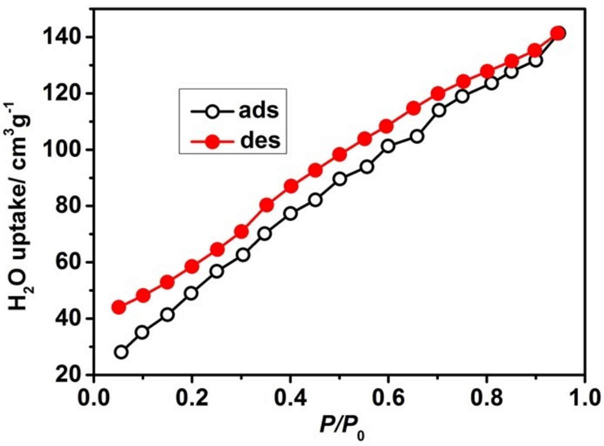

Fig. S2 Water vapor adsorption and desorption isotherms for **1**@NH_4^+.

Proton conductivity measurements

The samples were put into a homemade mould with a radius of 0.2 cm to get circular pellets. The thickness was measured by a vernier caliper. And then the pellets were smeared by silver colloid on two sides which were fixed on the sample stage with gold wires. The proton conductivities were measured using an impedance/gain-phase analyzer (Solartron S1 1260) over a frequency range from 0.1 Hz to 1 MHz with an input voltage of 3000 mV. The temperature and relative humidity are controlled by using an XK-CTS80Z incubator. ZSimpWin software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Niquist plot and obtain the resistance values. The proton conductivity was calculated using the following equation:

$$\sigma = L / RS$$

where σ is the conductivity (S cm^{-1}), L is the measured sample thickness (cm), S is the electrode area (cm^2) and R is the impedance (Ω).

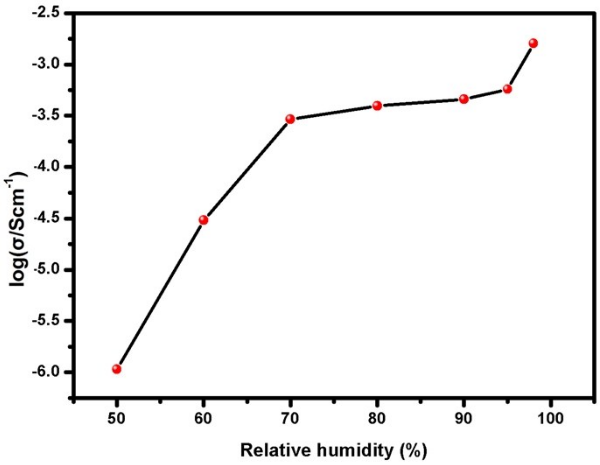

Fig. S3 Proton conductivity (log(σ/S cm^{-1})) of **1**@NH_4^+ at 30°C with different RHs.

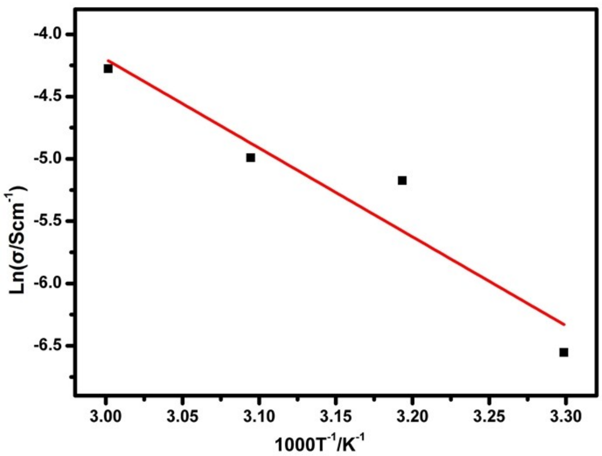

Fig. S4 Arrhenius plot of the proton conductivities of compound **1**@NH_4^+ at 98% RH.

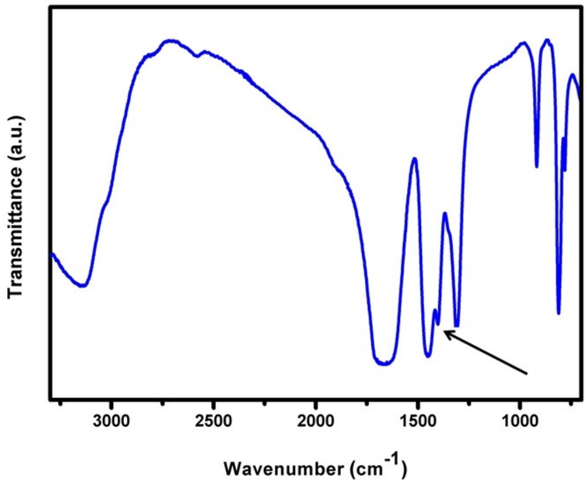

Fig. S5 FTIR spectrum of **1**@NH_4^+ after AC impedance measurement.

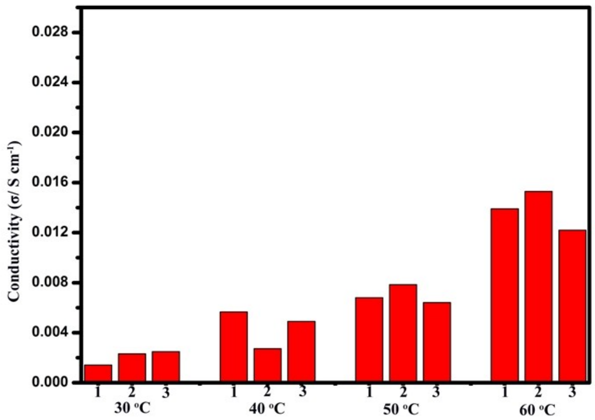

Fig. S6 The proton conductivities (S cm^{-1}) cycle of **1**@NH_4^+ with 98% RH under different temperatures.

Table S1 The proton conductivities (S cm^{-1}) of **1**@NH_4^+ at 30°C with different RHs.

Relative humidity (%)	Conductivity (S cm^{-1})
50% RH	1.07×10^{-6}
60% RH	3.05×10^{-5}
70% RH	2.93×10^{-4}
80% RH	3.93×10^{-4}
90% RH	4.57×10^{-4}
95% RH	5.73×10^{-4}

98% RH	1.42 × 10^{-3}

Table S2 The proton conductivities (S cm^{-1}) of **1**@NH_4^+ with 98% RH under different temperatures.

Temperature (°C)	First cycle Conductivity (S cm^{-1})	Second cycle Conductivity (S cm^{-1})	Third cycle Conductivity (S cm^{-1})
30°C	1.42 × 10^{-3}	2.32 × 10^{-3}	2.49 × 10^{-3}
40°C	5.66 × 10^{-3}	2.72× 10^{-3}	4.91 × 10^{-3}
50°C	6.80 × 10^{-3}	7.85 × 10^{-3}	6.41 × 10^{-3}
60°C	1.39 × 10^{-2}	1.53 × 10^{-2}	1.22 × 10^{-2}

Table S3 Proton conductivities (> 10^{-2} S cm^{-1}) of selected MOFs.

Compounds	Conductivity (S cm^{-1})	Experimental condition	Ref.
This work	1.39 × 10^{-2}	60 °C and 98% RH	This work
$Zn_3(bpdc)2(pdc)(DMF)$•6DMF	0.95 × 10^{-2}	60 °C and 97% RH	2
Im-Fe-MOF	1.21 × 10^{-2}	60 °C and 98% RH	3
BUT-83	3.9 × 10^{-2}	80 °C and 97% RH	4
BUT-8(Cr)A	1.27 × 10^{-1}	80 °C and 100% RH	5
BUT-8(Cr)	4.63 × 10^{-2}	80 °C and 100% RH	5
MIL-101-SO_3H	1.16 × 10^{-2}	80 °C and 100% RH	5
$\{[Co_3(m\text{-}ClPhIDC)_2(H_2O)_6]\cdot 2H_2O\}_n$	2.89× 10^{-2}	100 °C; water and aqua−ammonia vapors ($NH_3 \cdot H_2O$ concentration of 7.40 M)	6
$\{[Co_3(p\text{-}ClPhHIDC)_3(H_2O)_3]\cdot 6H_2O\}_n$	4.25× 10^{-2}	100 °C; water and aqua−ammonia vapors ($NH_3 \cdot H_2O$ concentration of 7.40 M)	6
UiO-66(-$SO_3H)_2$	8.4 × 10^{-2}	80 °C and 90% RH	7
TfOH@MIL-101	8×10^{-2}	60 °C and 15% RH	8
Fe-CAT-5	5× 10^{-2}	25 °C and 98% RH	9
$[(Me_2NH_2)_3(SO_4)]2[Zn_2(ox)_3]_n$	4.2 × 10^{-2}	80 °C and 95% RH	10
PCMOF-10	3.55 × 10^{-2}	70 °C and 95% RH	11

VNU-15	2.90×10^{-2}	95 °C and 60% RH	12
$H^+@Ni_2(dobdc)(H_2O)_2$ (pH = 1.8)	2.2×10^{-2}	80 °C and 95% RH	13
$PCMOF2_{1/2}$	2.1×10^{-2}	85 °C and 90% RH	14
$[ImH][Cu(HPO_4)_{1.5}(HPO_4)_{0.5}\cdot Cl_{0.5}]$	2.0×10^{-2}	130 °C and 0 RH	15
HOF-GS-11	1.8×10^{-2}	30 °C and 95% RH	16
H_3PO_4@MIL-101	1.0×10^{-2}	140 °C and 1.1% RH	17
H_2SO_4@MIL-101	1.0×10^{-2}	150 °C and 0.13% RH	18
$CsHSO_4$@Cr-MIL-101	10^{-2}	200 °C and 0 RH	18
$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$	10^{-2}	ambient temperature	19

Table S4 ICP-AES results of the compound **1** and **1**@NH_4^+

Compounds	Ca (umol/mL)	Zr (umol/mL)	the reduction of calcium in 1 mol sample (mol)
1	5.464	2.57	0.14723004
1@NH_4^+	4.676	2.363	

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