Electronic Supplementary Information

High anhydrous proton conductivity and smart proton transportation approach of a sulfate coordination polymer

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Experimental Details

Synthesis of $\{[(CH_3)_2NH_2]_4Co_2(SO_4)_4\}_n$

$CoCl_2$ (0.2 mmol) and H_2SO_4 (1 mmol) in 13 ml DMF were mixed together and stirred for 40 min at 100°C. The resulting blue solution was then moved into a Teflon-lined steel autoclave, heated at 433 K for 24 h, and then slowly cooled to ambient temperature. The purple needle shaped crystals obtained through filtration are rinsed multiple times with anhydrous ethanol, and the remaining liquid on the surface of the crystals is rinsed clean. They are then placed in a dryer to dry and collected.

Test of single crystal structure

Intensity data were collected at 120.00(10) K on a Bruker Smart APEXII CCD diffractometer for $\{[(CH_3)_2NH_2]_4Co_2(SO_4)_4\}_n$ using graphite monochromated CuK\a radiation (λ = 0.71073 Å), respectively. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full matrix least-squares on F2 using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the nitrogen in the dimethylammonium cation we used theoretical hydrogenation. and the cif files were exported after refinement.

The IR spectra of $[(CH_3)_2NH_2]_4Co_2(SO_4)_4$

Fourier-transform infrared (FT-IR) spectroscopy analysis was carried out using Alpha II Sample Compartment RT-DLaTGS in the400–4000cm^{-1} .

Thermogravimetric (TG) analyses of $[(CH_3)_2NH_2]_4Co_2(SO_4)_4$

Thermogravimetric (TG) analyses were performed on an STA-22-0006 thermogravimetric analyzer under nitrogen 10°C min-1 from 100°C temperature to 800°C.

Test of Impedance

Altering current (AC) impedances were performed for the pellet samples using CorrTest CS chemical Workstation with a conventional two-electrode method; the frequency spans from 1 to 10^6 Hz, and the signal amplitude is 100 mV. The sample was compressed to a pellet under a pressure of 12MPa at room temperature. The thickness of the pellet is 1.64 mm. Clamp the pellet with a self-made fixture, then place it in an oven. Connect the two ends of the platinum

electrode to the equipment through platinum wire, and set the oven temperature to the required temperature for testing. After the temperature reaches the set temperature, keep the sample piece at this temperature for half an hour. The proton conductivity was measured using AC impedance measurement. CS sdudio 5 software was used to simulate impedance data to complete the Nyquist plot and obtain the resistance value. The proton conductivity (σ, S cm^{-1}) of the sample was estimated by using theequation:

$\sigma = L/RS$

where L is the thickness, S is the area of the measured plate; R is the measured impedance.

The activation energy (Ea) is calculated by using the conductivity data between 55 and 175 °Cwith the Arrhenius equation:

$Ln(\sigma T) = lnA - E a/k_B T$

where k_B and A are the Boltzmann constant and the pre-exponential factor, respectively.

Theoretical Calculation Methods

The Gaussian 16 suite of programs[1] was used to optimize the configurations with the M06-2X functional and the def2-SVP basis set (GD3) considering modredundant.

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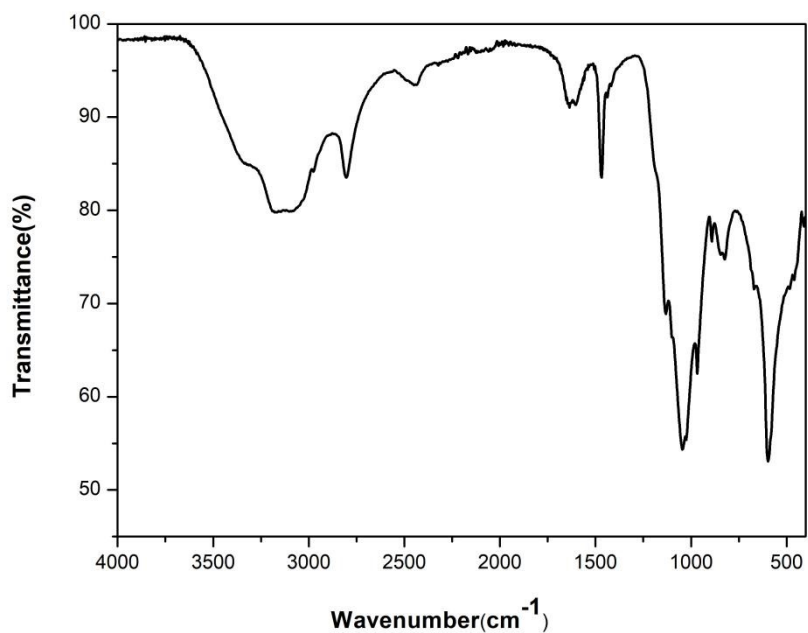
Fig. S1 The IR spectra of $[(CH_3)_2NH_2]_4Co_2(SO_4)_4$;

The presence of amine was confirmed by two absorption peaks at 3500-3000 cm^{-1}, The absorption peak at 1600 cm^{-1} is the characteristic absorption peak of N-H bond, The absorption peak of 2850 cm^{-1} confirms the existence of methyl group, and the asymmetric bending vibration of methyl group at 1460 cm^{-1} , The existence of N-H and methyl group confirms existence of Dimethylamine Cations in Pores. The three absorption peaks of 1120 cm^{-1}, 990 cm^{-1}, and 610 cm^{-1} are characteristic absorption peaks of sulfate group, thus confirming the successful coordination of sulfate group.
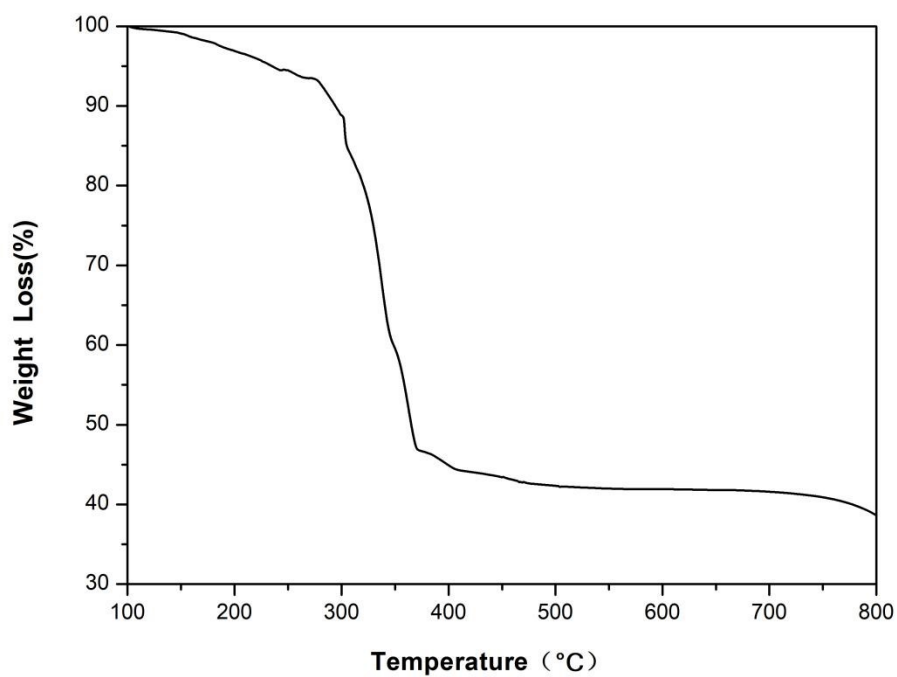
Fig. S2 The thermogravimetric curve of [(CH3)2NH2]4Co2(SO4)4

The thermoweight data of the complex in the range from 100 to 800°C was measured at the N$_2$ atmosphere of 10.0°C/min, and the thermal-weight curve was obtained. The thermal weight curve indicates almost no loss of sample mass at 180°C and continuous weight loss above 300°C. This indicates that the complexes have good thermal stability below 300°C.
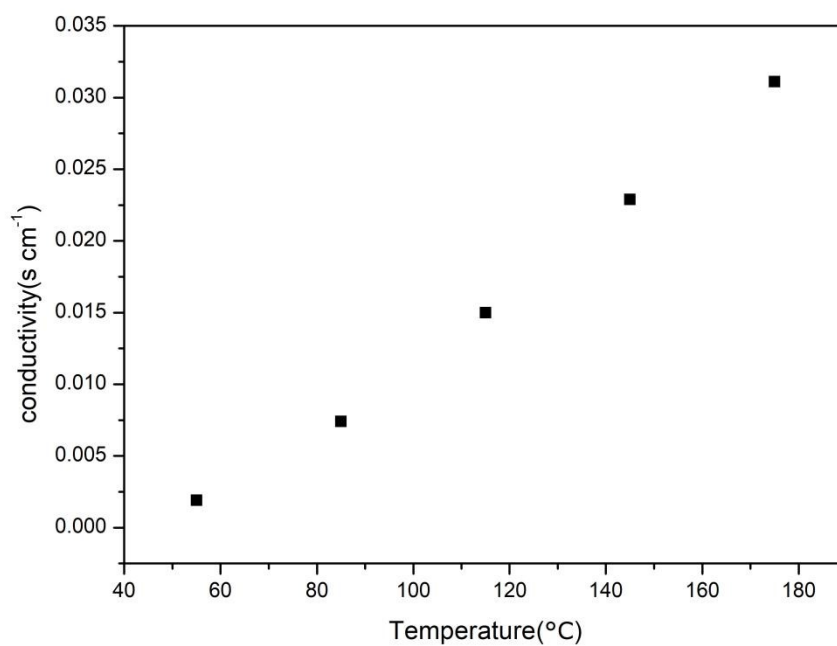
Fig. S3 The change of the conductivity of $[(CH_3)_2NH_2]_4Co_2(SO_4)_4$ with temperature.

We tested the conductivity of the pellet at temperatures of 55, 85, 115, 145, and 175 ℃. The conductivity gradually increases with temperature, and increases by an order of magnitude from 55 ℃ to 175 ℃.

Table S1   Proton conductivities of representative proton conductors under anhydrous conditions.

Composition	Condition	Conductivity(S cm^{-1})	References
COF-3@PA-30	150 °C,anhydrous	1.4	1
COF-3@PA-25	150 °C, anhydrous	5.9×10^{-1}	1
H_3PO_4@TPB-DMeTP-COF	160 °C, anhydrous	1.91×10^{-1}	2
COF-3@PA-20	150 °C, anhydrous	5.2×10^{-2}	1
COF-F6-H	140 °C, anhydrous	4.2×10^{-2}	3
COF-2@PA-20	150 °C, anhydrous	3.9×10^{-2}	1
SiW-4IPS$_{19}$	160 °C, anhydrous	3.4×10^{-2}	4
$[(CH_3)_2NH_2]_4Co_2(SO_4)_4$	175 °C, anhydrous	3.11×10^{-2}	This work
PA@EB-COF	180 °C, anhydrous	2.77×10^{-2}	5
H_3PO_4@NKCOF	160 °C, anhydrous	2.33×10^{-2}	6

References

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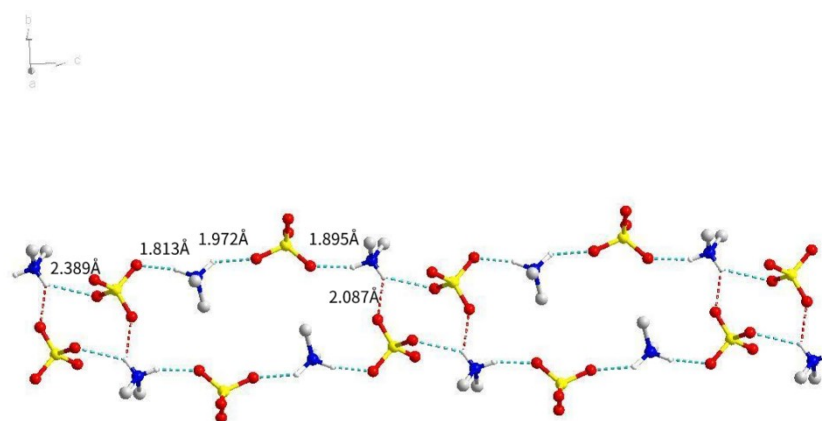
Table S2 The table of the conductivity of $\{[(CH_3)_2NH_2]_4Co_2(SO_4)_4\}_n$

Temperature	55	85	115	145	175
Impedance	107.39	28.06	14.06	9.13	6.72
Conductivity $(S\ cm^{-1})$	1.9×10^{-3}	7.4×10^{-3}	1.5×10^{-2}	2.29×10^{-2}	3.11×10^{-2}

Table S3 The Table of the Hydrogen-bond geometry

hydrogen bond	Hydrogen bond length	bond angle
(N2)H2A...O8	1.813	161.706
(N2)H1B...O6	1.895	156.711
(N2)H2...O4	1.972	156.313
(N1)H1A...O2	2.087	135.770
(N1)H1A...O1	2.389	133.065

Our study is only in one direction, as shown from left to right, We have annotated the five hydrogen bonds listed in the table, as shown in Fig S4.

Fig. S4 Hydrogen bond path diagram