Electronic Supplementary Material (ESI) for Chemical Communications

Anisotropy of Proton Transport in an Organic–inorganic Compound of $[(C_6H_{10}N_2)_2(SO_4)_2{\bullet}3H_2O]_n$ ($C_6H_{10}N_2$= phenylenediammonium dication)

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Experimental section

Synthesis of $[(C_6H_{10}N_2)_2(SO_4)_2{\bullet}3H_2O]_n$ (1)

Compound **1** was synthesized through reaction of ferric sulfate and *o*-phenylenediamine in water as described in the previous literature.[1] Ferric sulfate (2.6 g, 6.5 mmol) was dissolved into 10 mL water and then the 10 mL aqueous solution of *o*-phenylenediamine (2.0 g, 18.5 mmol) was added, while stirring. When pH of the solution was adjusted to 1.2 with concentrated sulfuric acid, the mixture was filtered and the filtrate was kept at room temperature. Colourless crystals were obtained in about 20% yield (based *o*-phenylenediamine) after four days. IR (KBr, cm^{-1}): 3427.6(s), 2853.3(s), 2576.9(s), 1629.4(s), 1571.4(m), 1506.4(s), 1315.3(m), 1168.4(w), 1113.2(s), 1062.9(m), 1050.4(m), 977.4(w), 770.7(m), 760.1(s), 624.0(s), 606.0(m), 513.1(s), 461.0(m) cm^{-1} Anal. Calc for 1: C: 30.89%, N: 12.01%, H: 5.62%. Found: C: 30.85%, N: 11.85%, H: 5.48%.

Single-Crystal Structure Determination

Data were collected with a single-crystal on Oxford Gemini S Ultra CCD area detector using Mo-*K*α radition (λ = 0.71073Å) and equipped with Oxford Instruments at 173 K, 265 K, 280 K, 286 K and 298 K respectively. Absorption corrections were applied by using the multiscan program CrysAlis Red. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL-97 program.[2] The hydrogen atoms of the water molecules were generated geometrically. The hydrogen atoms of organic ligand were located from difference fourier map. CCDC number: 832174-832177 contain the supplementary crystallographic data for this paper as well. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for **1** at 173(2) K, Data were collected on a colorless block-shaped crystal, Monoclinic, space group $P2_1/c$ with a = 27.0203(14) Å, b = 9.5708(5) Å, c = 7.5370(4) Å, β = 93.1(5)°, V = 1946.24(18) Å^3, Mr = 466.49, Z = 4, $\rho_{calcd.}$ = 1.592 g cm^{-3}, μ = 0.340 mm^{-1}. Of the 8759 reflections collected, 3806 are independent (R_{int} = 0.0411) and 2825 are observed [$I > 2\sigma(I)$]. On the basis of all these data and 286 refined parameters, R_1= 0.0598 [$I > 2\sigma(I)$], wR_2 = 0.1571 [all data] are obtained.

Data for **1** at 265(2) K, Monoclinic, space group $P2_1/c$, a = 27.0843(12) Å, b = 9.6042(5) Å, c = 7.5562(4) Å, β = 93.0(4)°, V = 1962.86(17) Å^3, Mr = 466.49, Z = 4, $\rho_{calcd.}$ = 1.579 g cm^{-3}, μ = 0.337 mm^{-1}. Of the 9745 reflections collected, 3847 are independent (R_{int} = 0.0380) and 2797 are observed. R_1 = 0.0657, wR_2 = 0.2139.

Data for **1** at 280(2) K, Monoclinic, space group $P2_1/c$, a = 27.1493(13) Å, b = 9.5940(5) Å, c = 7.5415(4) Å, β = 92.86(4)°, V = 1961.89(17) Å^3, Mr = 466.49, Z = 4, $\rho_{calcd.}$ = 1.579 g cm^{-3}, μ = 0.337 mm^{-1}. Of the 8556 reflections collected, 3842 are independent (R_{int} = 0.0345) and 2765 are observed. R_1= 0.0740, wR_2 = 0.1991.

Data for **1** at 286(2) K, Monoclinic, space group $P2_1/c$, a = 27.1531(13) Å, b = 9.5952(4) Å, c = 7.5456(3) Å, β = 92.84(4)°, V = 1963.52(15) Å^3, Mr = 466.49, Z = 4, $\rho_{calcd.}$ = 1.578 g cm^{-3}, μ = 0.337 mm^{-1}. Of the 8788 reflections collected, 3847 are independent (R_{int} = 0.0350) and 2763 are observed. R_1 = 0.0799, wR_2 = 0.2069.

Data for **1** at 298(2) K, Monoclinic, space group $P2_1/c$, a = 27.1540(15) Å, b = 9.5947(6)Å, c = 7.5549(4) Å, β =

92.828(5)°, V = 1965.91(19) Å^3, Mr = 466.49, Z = 4, $\rho_{calcd.}$ = 1.576 g cm^{-3}, μ = 0.337 mm^{-1}. Of the 8090 reflections collected, 3462 are independent (R_{int} = 0.0350) and 2446 are observed. R_1 = 0.0944, wR_2 = 0.2355.

The Impedence and Dielectric Properties Measurement

Temperature-dependent a.c. impedence plots and dielectric constants were performed on Wayne Kerr 6500B by using two-probe a.c. impendance method in frequency range of 20 Hz to 50 MHz. A single crystal was placed into a cryogenic refrigeration system (Oxford Cyromech). The electric contacts were prepared with gold paste (Tokuriki 8560) to attach 25-μm gold wires to the single crystal.

The DSC, CV and TG Measurements

DSC (differential scanning calorimetry) measurement were performed on the NETZSCH DSC 200F3 with sweeping rate of 10 K/min under nitrogen atmosphere. The cyclic voltammetry curve was performed on CHI760D electrochemical station with the scanning rate 0.1V/s from -1.5 V to 1.5 V. The TG curve was measured on NETZSCH STA 449F3 with sweeping rate of 10 K/min under helium atmosphere.

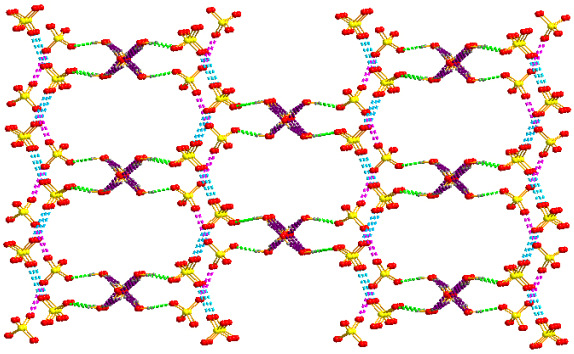

Fig. S1 The 3D structure of **1** viewed as sulfate helices interacting with water chains perpendicular to sulfate helices. The phenylenediammonium dication was omitted for clarity.

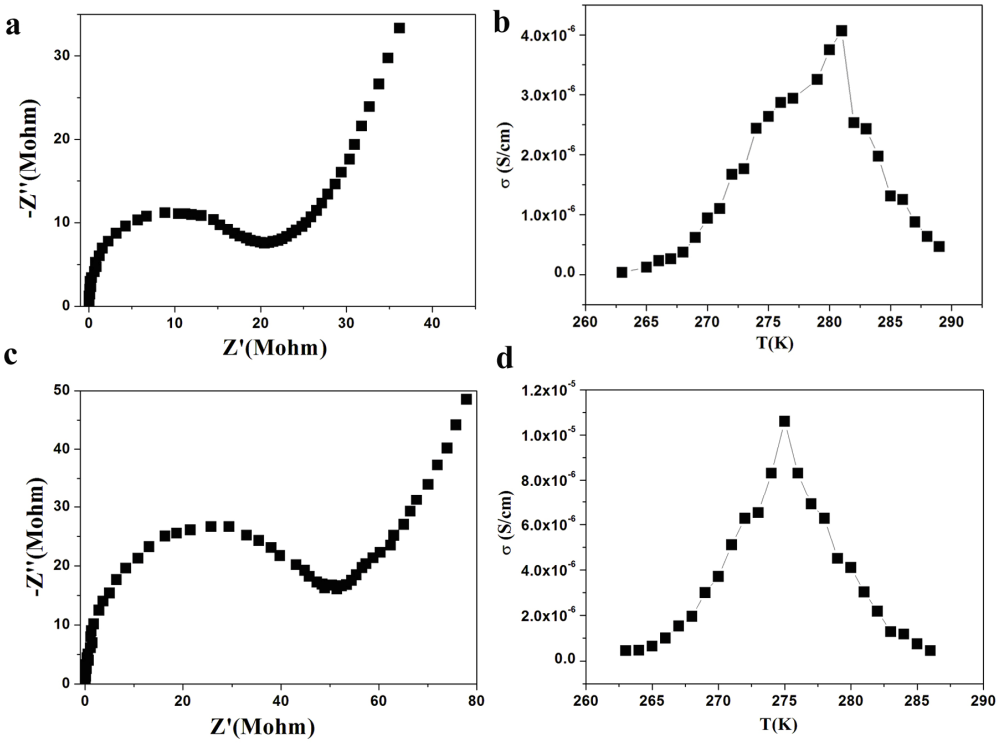

Fig. S2 The impedance plots of **1** measured on a single crystal (a) along *b* axis at 280 K, (c) along *c* axis at 275 K. The temperature-dependent conductivity of **1** on a single crystal (b) along *b* axis, (d) along *c* axis.

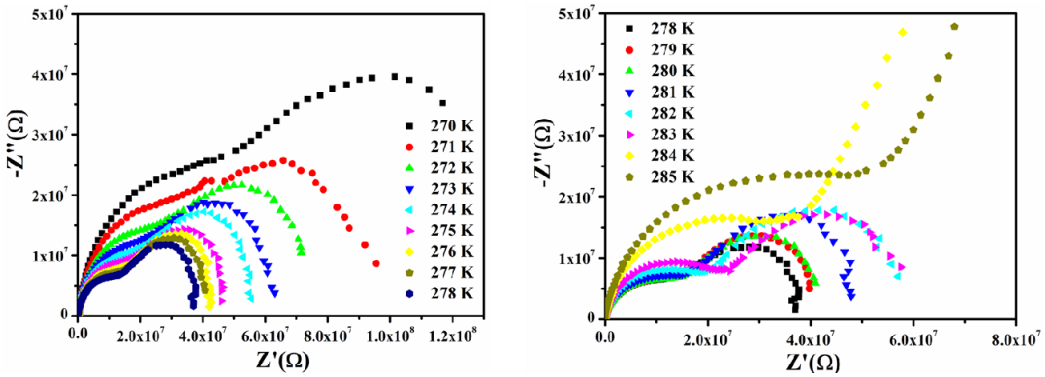

Fig. S3 The impendence plots of **1** at different temperatures based on its single-crystal along *a* axis.

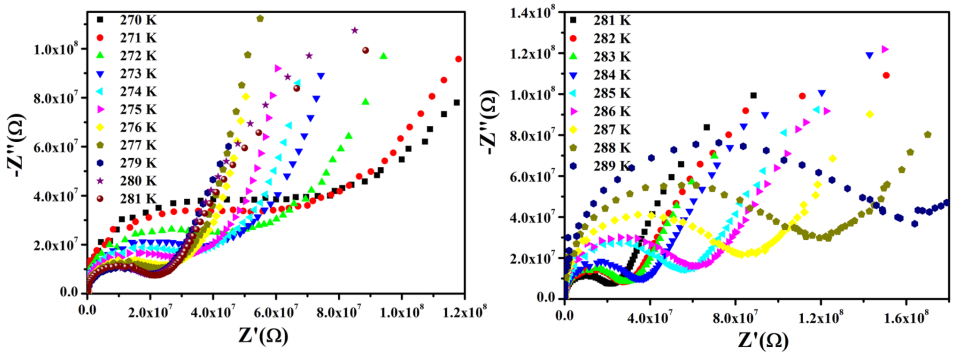

Fig. S4 The impendence plots of **1** at different temperatures based on its single-crystal along *b* axis.

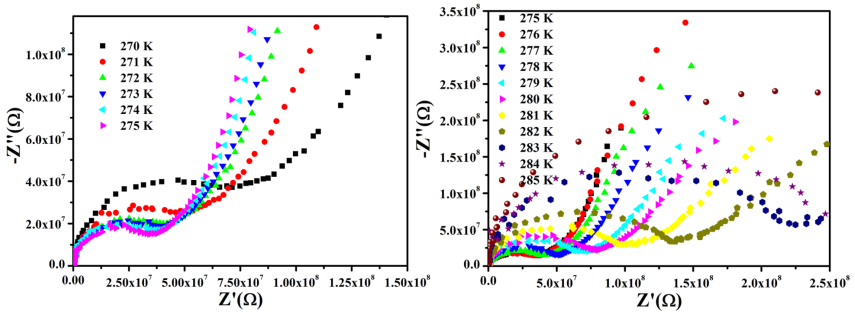

Fig. S5 The impendence plots of **1** at different temperatures based on its single-crystal along *c* axis.

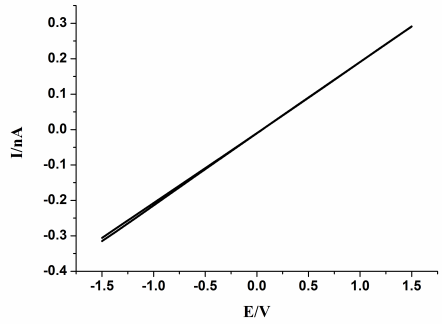

Fig. S6 The electrochemical CV curves of **1**.

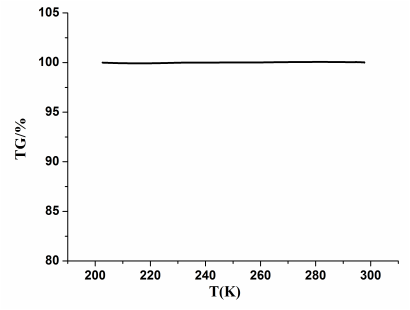

Fig. S7 The TG curves of **1** from 203 K to 298 K.

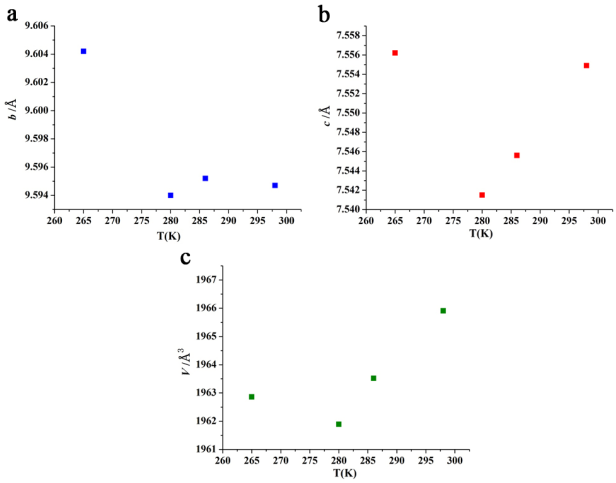

Fig. S8 The cell parameters change with the change of the measured temperatures for *b* axis (a), *c* axis (b) and cell volume (c).

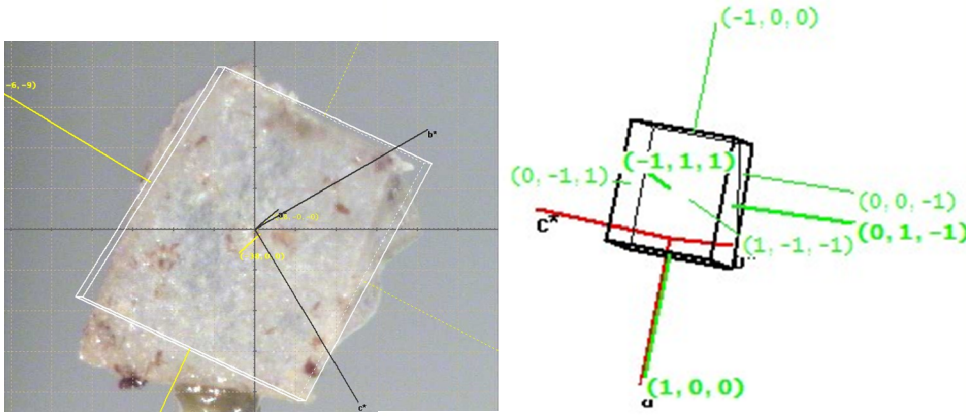

Fig. S9 The determination of *a*, *b* and *c* axes.

References

1. P. Raghavaiah, S. Supriya and S. K. Das, *Chem. Commun.*, 2006, 2762.
2. *SHELXTL 6.10*, Bruker Analytical Intrumentation, Madison, WI, 2000.