Electronic Supplementary Information

Proton conductive watery channels constructed by Anderson polyanions and lanthanide coordination cations

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The infrared analyses

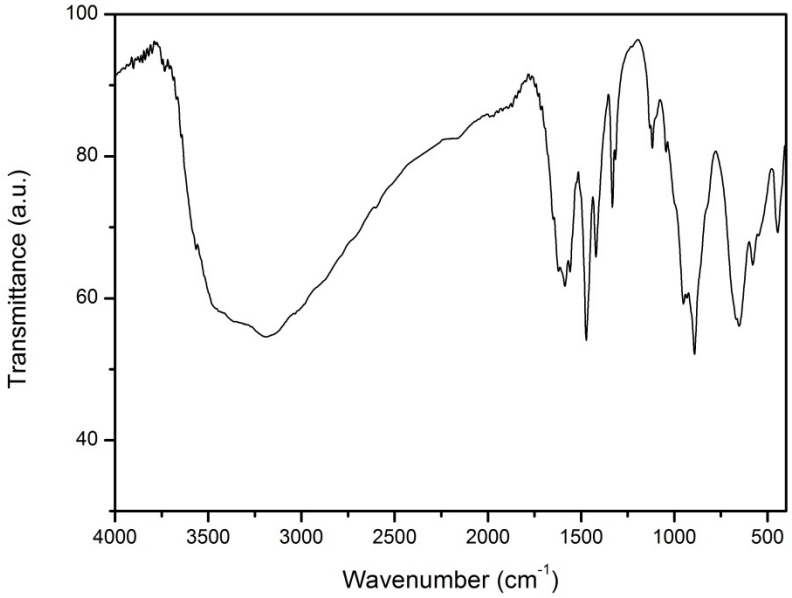

Fig. S1 IR spectrum of **1**.

Thermogravimetric analyses

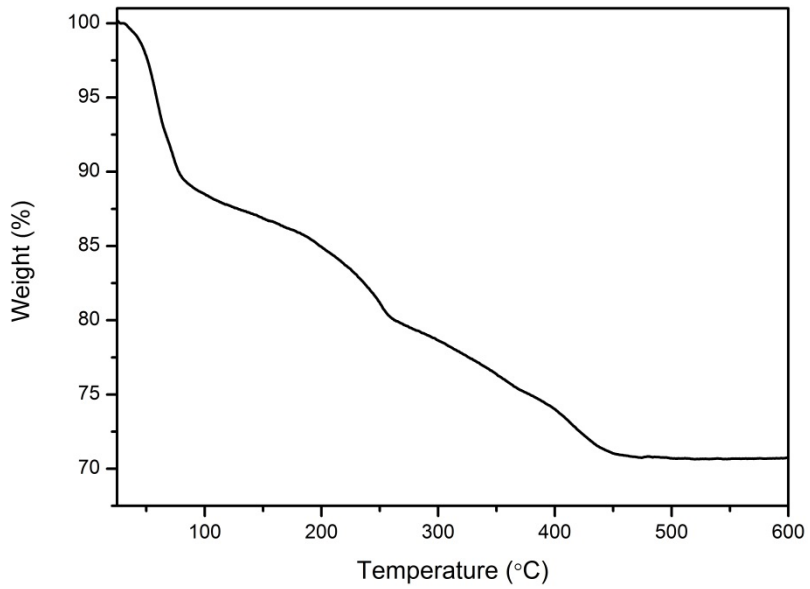

Fig. S2 TGA of **1** under N_2.

Water adsorption-desorption study

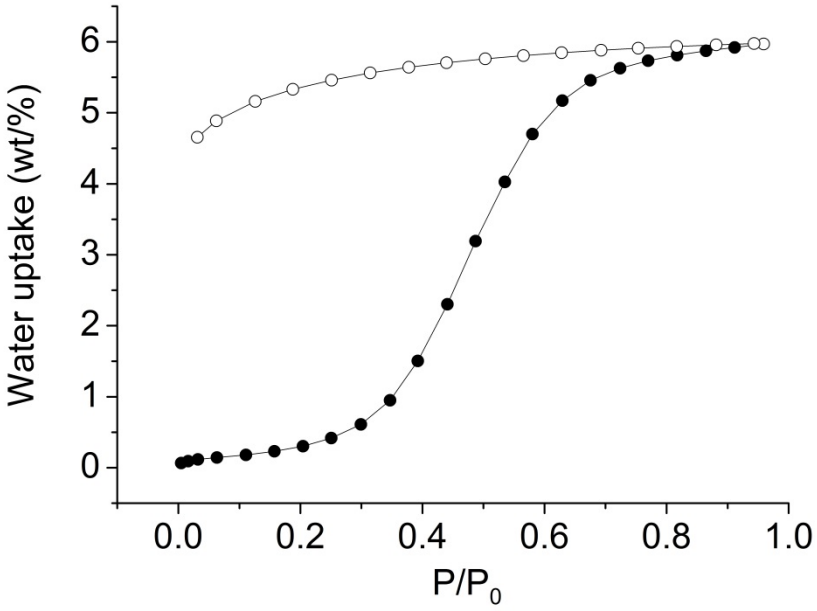

Fig. S3 Water adsorption and desorption isotherm of **1** at 298 K.

Proton conductivity

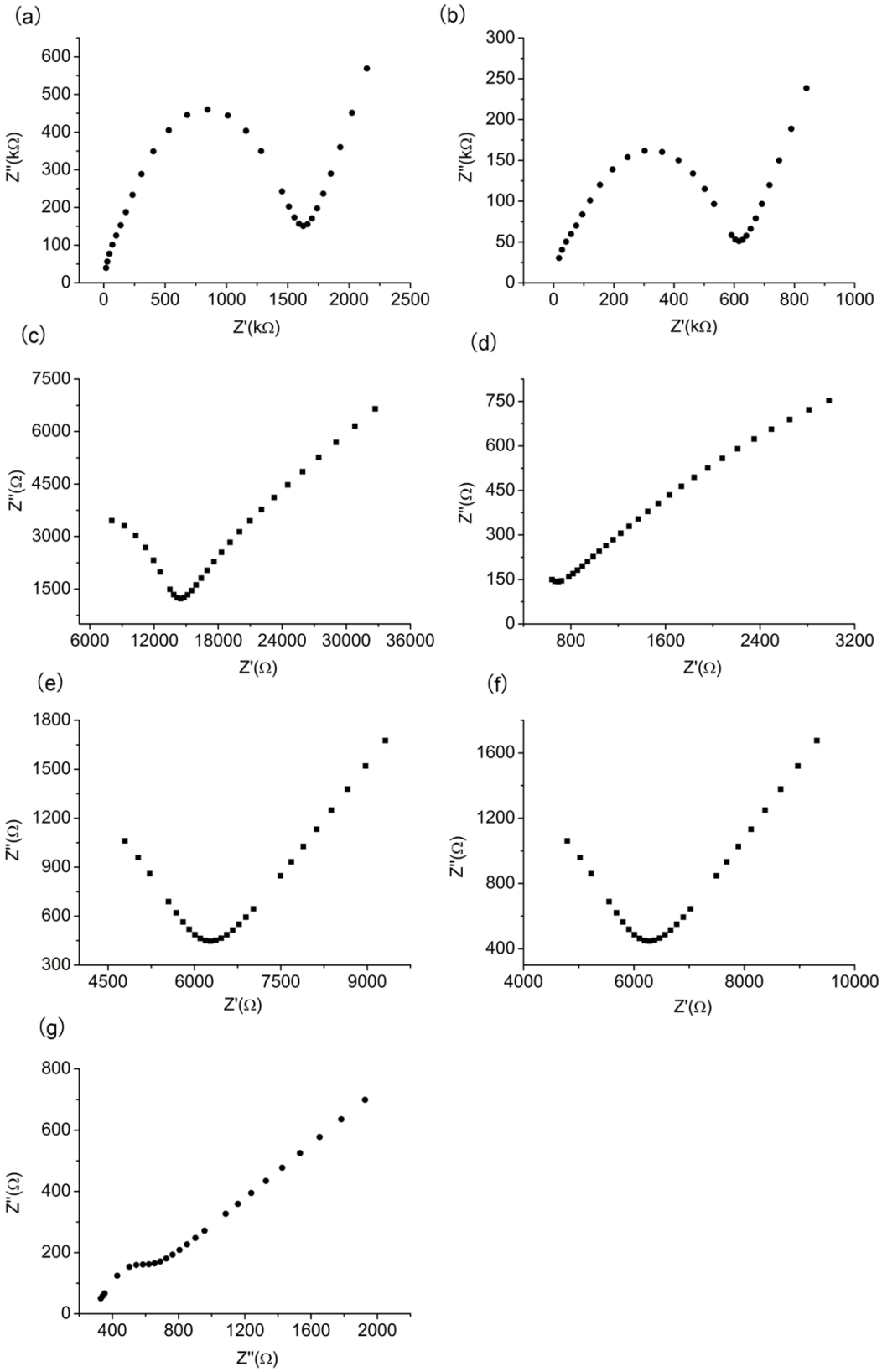

Fig. S4 Nyquist plots for **1** at 25°C (a), 30°C (b), 40°C (c), 50°C (d), 60°C (e), 70°C (f) and 80°C (g) under 95% relative humidity.

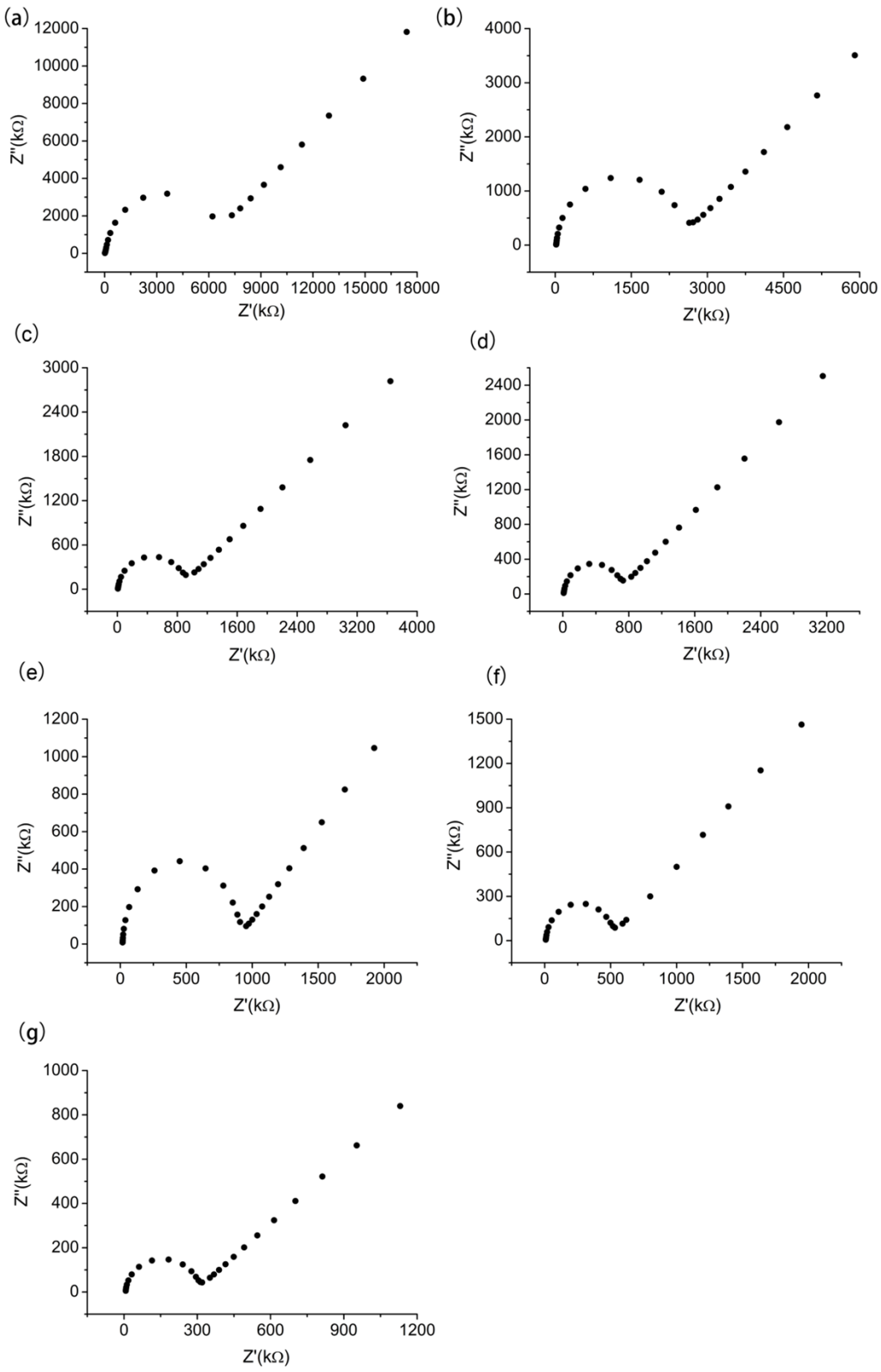

Fig. S5 Nyquist plots for $La(H_2O)_7[Al(OH)_6Mo_6O_{18}] \cdot 4H_2O$ at 25°C (a), 30°C (b), 40°C (c), 50°C (d), 60°C (e), 70°C (f) and 80°C (g) under 95% relative humidity.

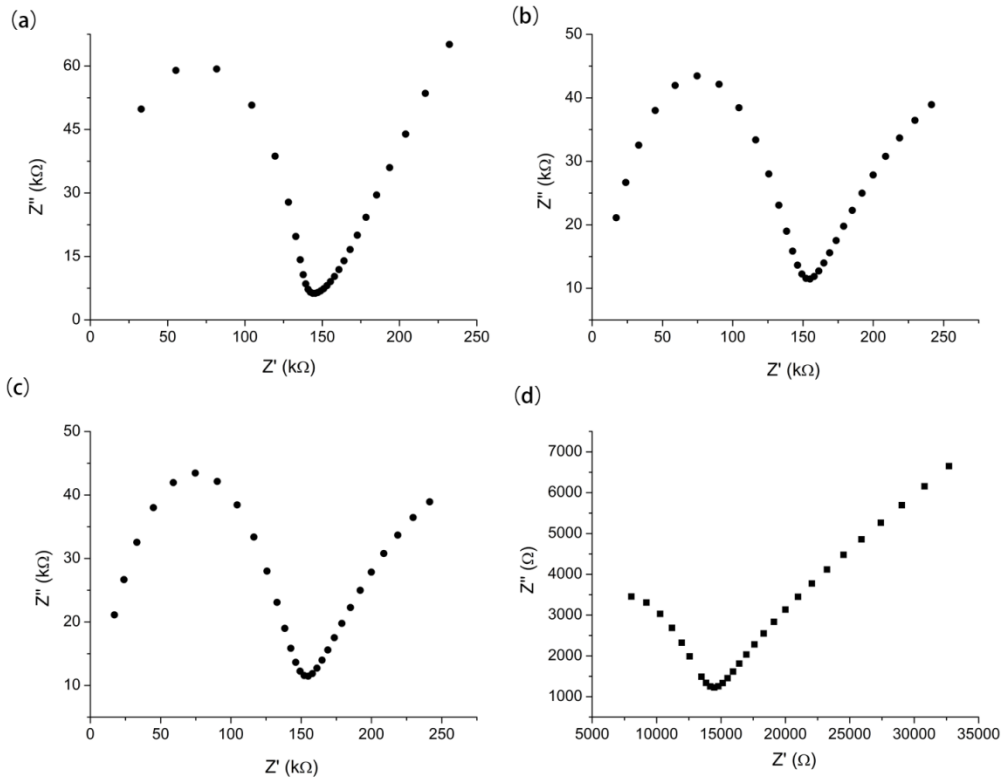

Fig. S6 Nyquist plots for $La(H_2O)_7[Al(OH)_6Mo_6O_{18}] \cdot 4H_2O$ under 35%, 50%, 65% and 80% relative humidity at 80°C.

Schematic representation of proton conduction

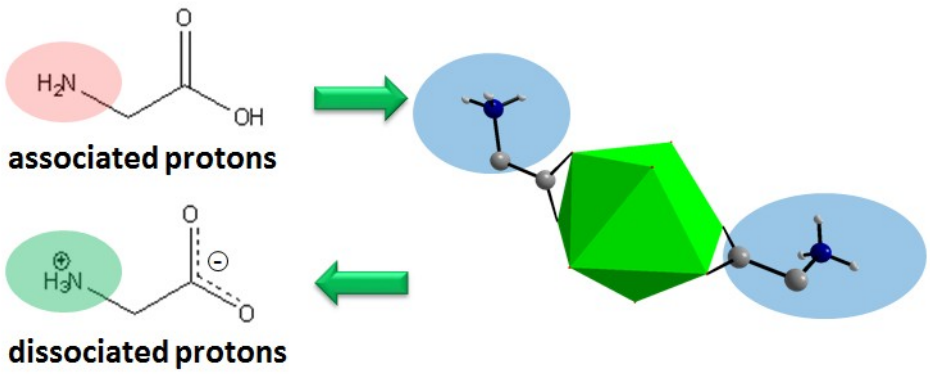

Fig. S7 Distribution of protons from glycine before and after coordination.

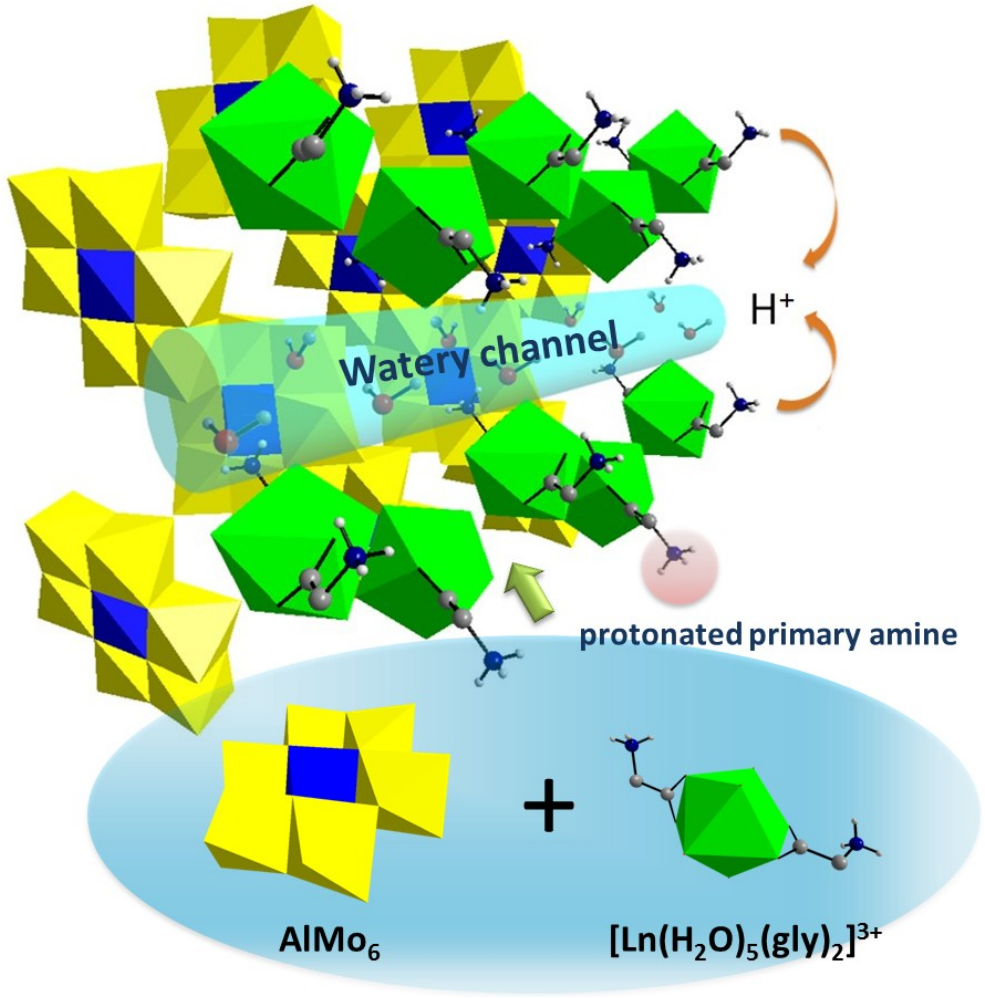

Fig. S8 Schematic representation of proton conduction in the channel of ionic networks constructed by Anderson-type polyanions ($AlMo_6$) and Ln coordination cation, $[Ln(H_2O)_5(gly)_2]^{3+}$. Colour code: Al, blue octahedron; Mo, yellow octahedron; Sm, green polyhedron; N, mazarine; C, gray; O, red.

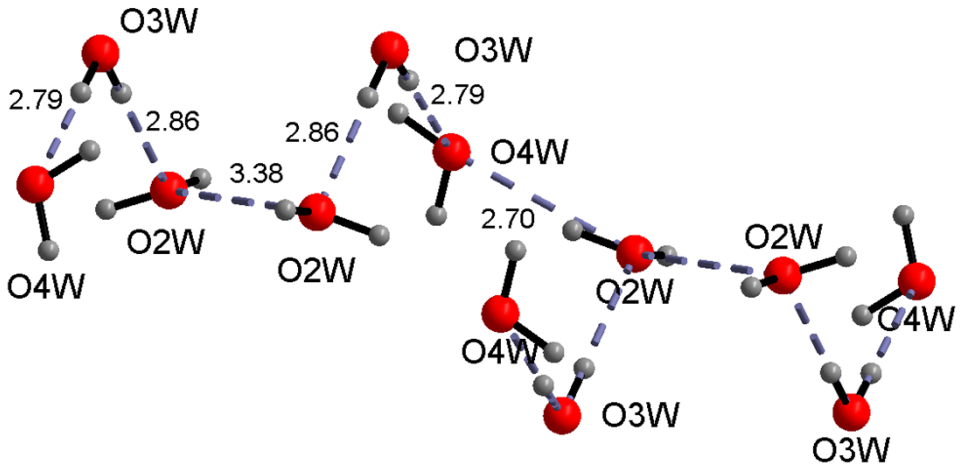

Fig. S9 Close contacts (2.70 Å ~ 3.38 Å) between the O atoms within a water channel.

Additional structural details

The contrasting compound, $La(H_2O)_7[AlMo_6]$ ($[AlMo_6]^{3-}$ = $[Al(OH)_6Mo_6O_{18}]^{3-}$)consists of one-dimensional chains, built by alternating $[AlMo_6]^{3-}$ polyanions and $[La(H_2O)_7]^{3+}$ cations, as shown in Fig. S9. The $[AlMo_6]^{3-}$ acts as a bidentate ligand and two $[La(H_2O)_7]^{3+}$ fragments are coordinated to two terminal oxygen atoms of the polyanion. There are extensive hydrogen bonds among surface of oxygen atoms of the Anderson-type polyanions, coordinated waters, and lattice water molecules.[1]

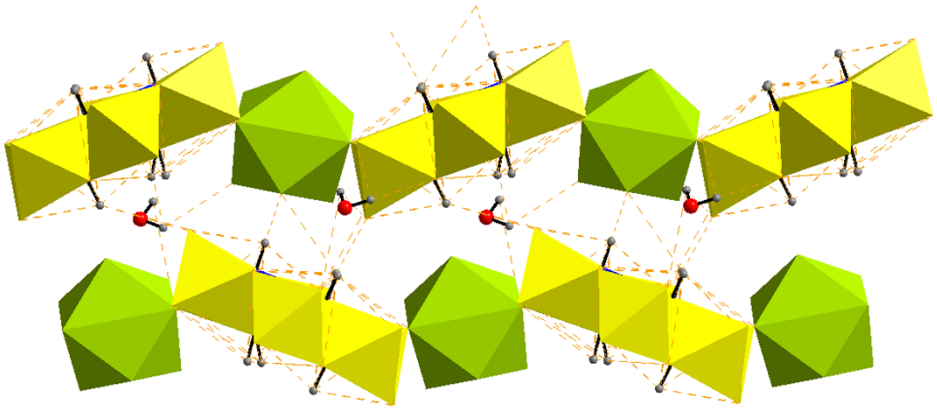

Fig. S10 Hydrogen bonding interactions among surface of oxygen atoms of the Anderson-type polyanions, coordinated waters, and lattice water molecules. Colour code: Al, blue octahedron; Mo, yellow octahedron; La, lime polyhedron; H, grey; O, red.

Reference

1. V. Shivaiah, P. V. Narasimha Reddy, L. Cronin and S. K. Das, *J. Chem. Soc., Dalton Trans.*, 2002, 3781-3782.