Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Lanthanide derivatives of Ta/W mixed-addendum POMs as proton-conducting materials

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SI-1 Experimental Section

1.1 Materials and measurement

The precursor $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]\cdot 17H_2O$ was synthesized according to the procedure described in the literature.[1] All other reagents were readily available from commercial sources and used without further purification. The FTIR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with a VECTOR 22 Bruker spectrophotometer at room temperature. Elemental analyses for P, W, La, Ce, Pr, Nd and Ta were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance Instrument with Cu Kα radiation in the angular range $2\theta = 5–80°$ at 293 K. The thermal behavior of **1-4** was examined by synchronousthermal analyses (TG/DSC, Netzsch 449C Jupiter/QMS 403D). The samples were heated to 700 °C with a heating rate of 5 °C /min, under a flowing N_2 atmosphere. Water vapour adsorption measurements were performed with a Hiden Isochema Intelligent Gravimetric Analyzer (IGA-100B).

1.2 Crystal structure determination

Single crystal XRD analysis of **1-4** were conducted on a Bruker Smart Apex CCD diffractometer with Mo Kα monochromated radiation ($\lambda = 0.71073$ Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography.[2] Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the full matrix least-squares method on F^2 using SHELXS-97.[3] Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception for a few oxygen atoms. Those hydrogen atoms attached to lattice water molecules and coordinated water molecules were not located. Crystallization water molecules were estimated by thermogravimetry and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. The crystal data and structure refinement results of **1–4** are summarized in Table S1. Further details on the crystal structure investigation scan be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data _request/cif on quoting the depository numbers CCDC-1507115 (1), CCDC-1507116 (2), CCDC-1507117 (3), CCDC-1507119 (4).

Table S1. Crystal data and structural refinement for compounds **1-4**.

Compounds	**1**	**2**	**3**	**4**
Formula	$H_{76}O_{100}P_2Ta_3W_{15}La_3$	$H_{76}O_{100}P_2Ta_3W_{15}Ce_3$	$H_{76}O_{100}P_2Ta_3W_{15}Pr_3$	$H_{78}O_{101}P_2Ta_3W_{15}Nd_3$
Formulaweight (g·mol^{-1})	5455.87	5459.50	5461.87	5489.88
T (K)	296 (2)	296 (2)	296 (2)	153
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 21/m	P 21/m	P 21/m	P 21/m
a (Å)	14.3527(3)	14.372(15)	14.2949(15)	14.2909(8)
b (Å)	18.9578(4)	19.14(2)	19.000(2)	18.8295(10)
c (Å)	16.8222(4)	16.770(18)	16.6852(18)	16.7507(9)
α(°)	90	90	90	90
β(°)	109.3113(12)	108.723(12)	108.847(2)	109.2334(15)
γ(°)	90	90	90	90
V(Å^3)	4319.71(17)	4368(8)	4288.7(8)	4255.9(4)
Z	2	2	2	2
D_{calc}(mg m^{-3})	4.195	4.151	4.230	4.284
μ(mm^{-1})	25.276	25.091	25.668	25.981
F(000)	4812.0	4818.0	4824.0	4850.0
Crystalsize (mm)	0.42×0.34×0.02	0.41×0.32×0.04	0.40×0.38×0.03	0.33×0.32×0.04
Goodness−of−fit on F^2	1.054	1.067	1.049	1.068
Final R indices	R_1= 0.0441	R_1= 0.0441	R_1= 0.0607	R_1=0.0761
[I>2σ(I)][a]	wR_2= 0.1073	wR_2= 0.1073	wR_2= 0.1590	wR_2= 0.2365
R indices[a]	R_1 =0.0757	R_1 = 0.0757	R_1 = 0.0968	R_1 = 0.0894
(all data)	wR_2= 0.1420	wR_2= 0.1420	wR_2= 0.1991	wR_2= 0.2545

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

[1] S. Li, S. Liu, S. Liu, Y. Liu, Q. Tang, Z. Shi, S. Ouyang, J. Ye, J Am Chem Soc., 134 (2012) 19716-19721.

[2] International Tables for X-ray Crystallography (Eds.: N. F. M. Henry, K. Lonsdale), Kynoch Press, Birmingham (1952).

[3] G. M. Sheldrick, SHELXS-97: Programs for Crystal Structure Solution, University of Göttingen, Göttingen Germany (1997).

1.3 Proton Conductivity measurement of 1

Ac impedance spectroscopy measurement was performed on a chi660d (Shanghai chenhua) electrochemical impedance analyzer with copper electrodes (the purity of Cu is more than 99.8%) over the frequency range from 105–1 Hz. The powdered crystalline sample of **1** was compressed to 1.0–1.2 mm in thickness and 12.0 mm in diameter under a pressure of 12–14 MPa at room temperature. The conductivities were determined from the Nyquist plots. According to the Nyquist plot for H-**1** at each temperature and humidity, the proton conductivity was calculated as $\sigma = (1/R)\ (h/S)$, where R is the resistance, h is the thickness, and S is the area of the disc. The activation energy was calculated from the Arrhenius plot according to the formula $\sigma T = \sigma_0 \exp(-Ea/k_BT)$. Real (Z′) and imaginary (Z″) parts of the impedance spectra are shown in Figure 3 and Figures S14-S16.

SI-2 Structures of 1

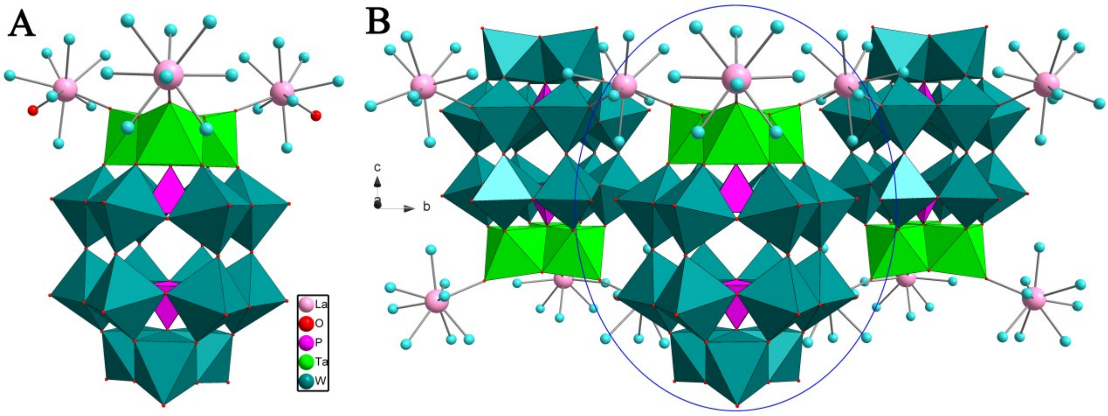


Figure S1. The least asymmetric subunit in **1:** $\{P_2W_{15}Ta_3O_{62}La_3(H_2O)_{22}\}$ (A)**,** and the coordination environment of it (B). The Aqua balls represent coordinated water molecules on La^{3+}.

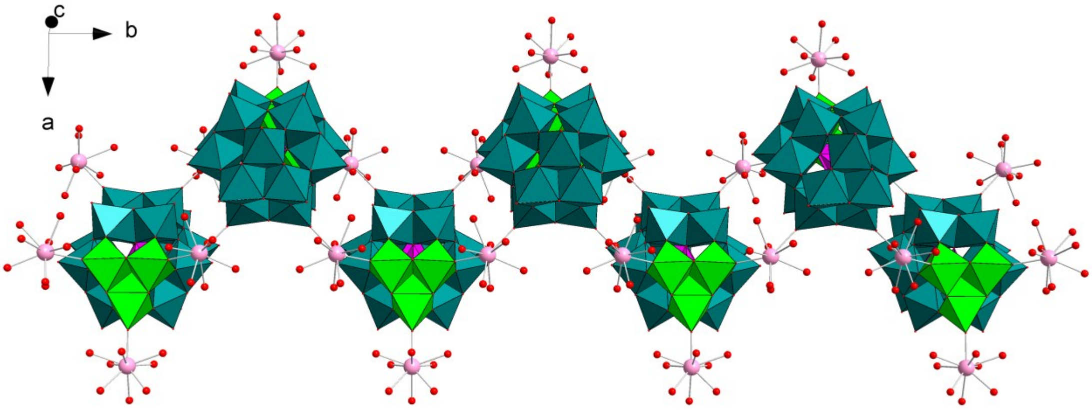


Figure S2. The 1D chain in **1**.

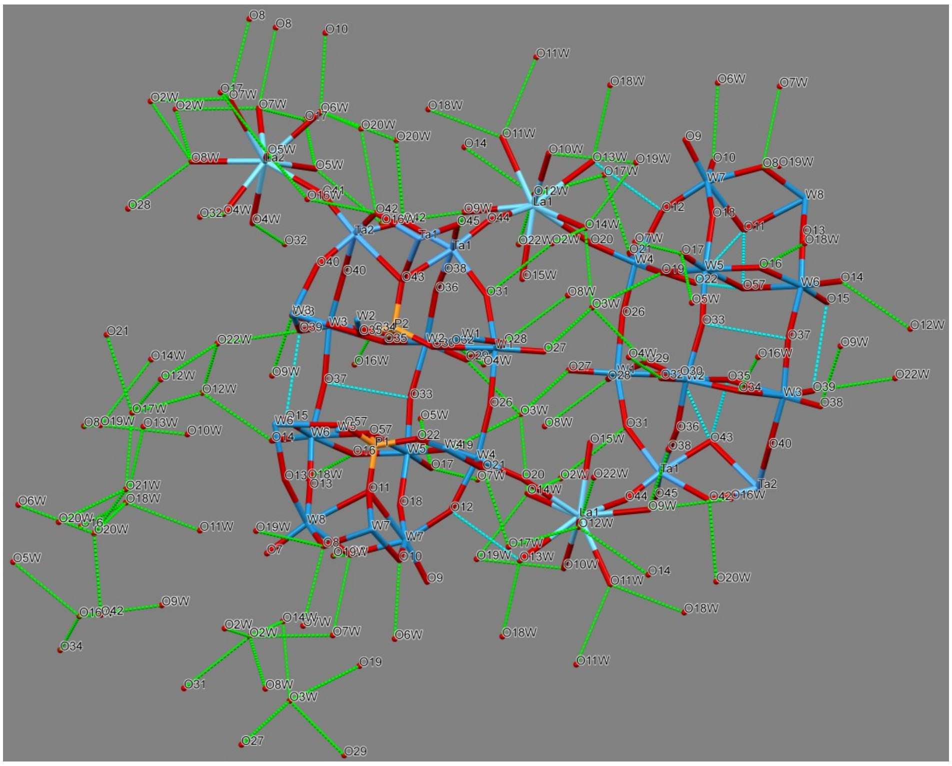


Figure S3. Hydrogen bonding distribution around the minimum structural unit of **1**.

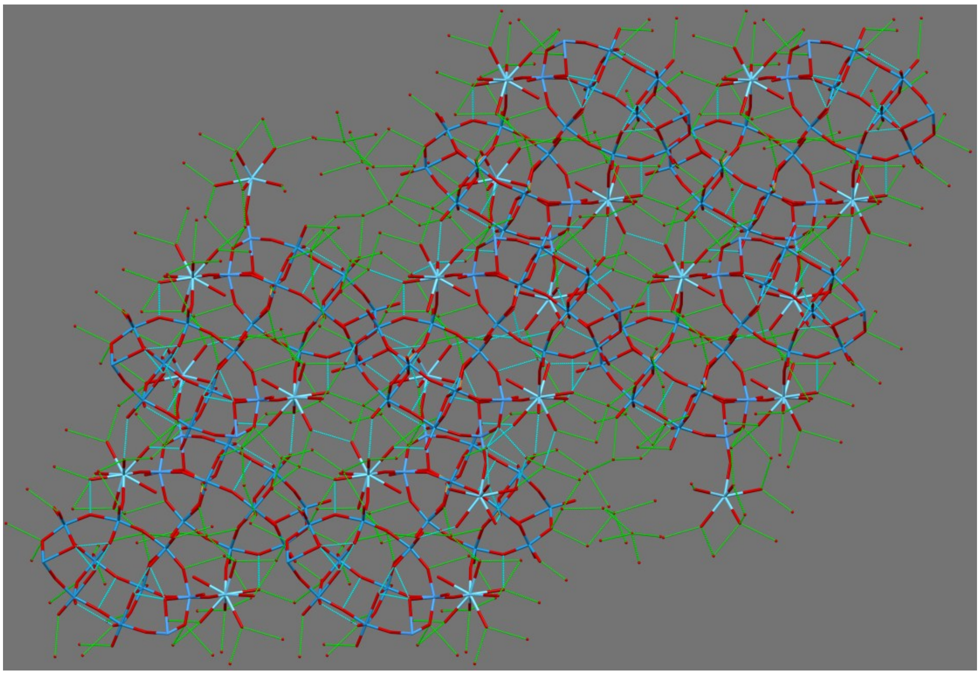


Figure S4. Hydrogen bonding network in **1** view over b axis.

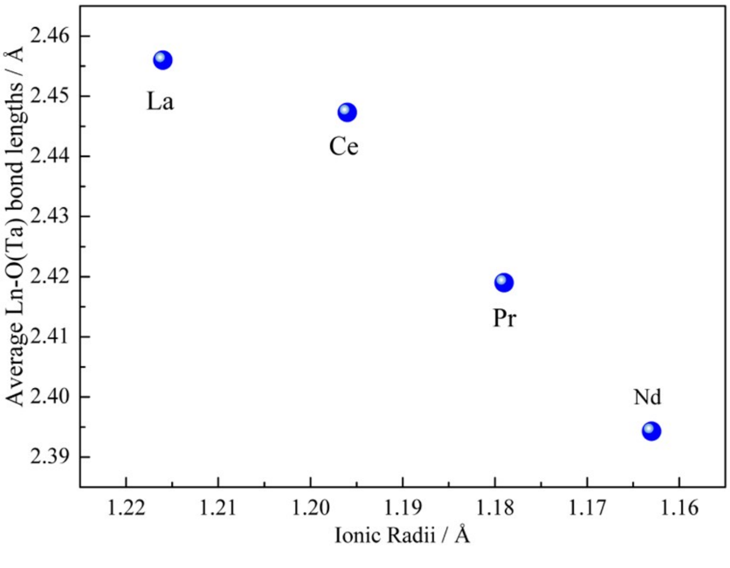


Figure S5. The change in the average Ln-O(Ta) bond lengths with the ionic radii in compounds **1-4.**

SI-3 Powder X-ray diffraction patterns

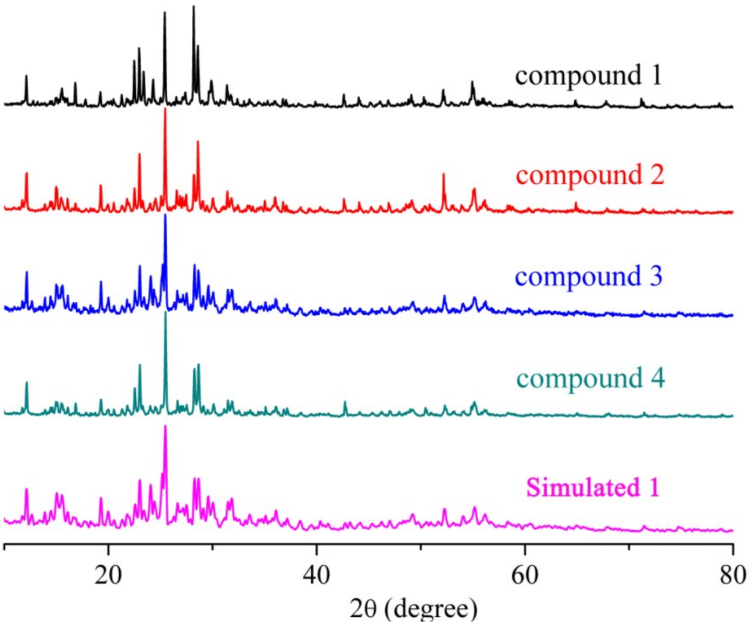


Figure S6. Powder X-ray diffraction patterns of simulated **1** and as-synthesized compounds **1-4.**

SI-4 FTIR Spectroscopy

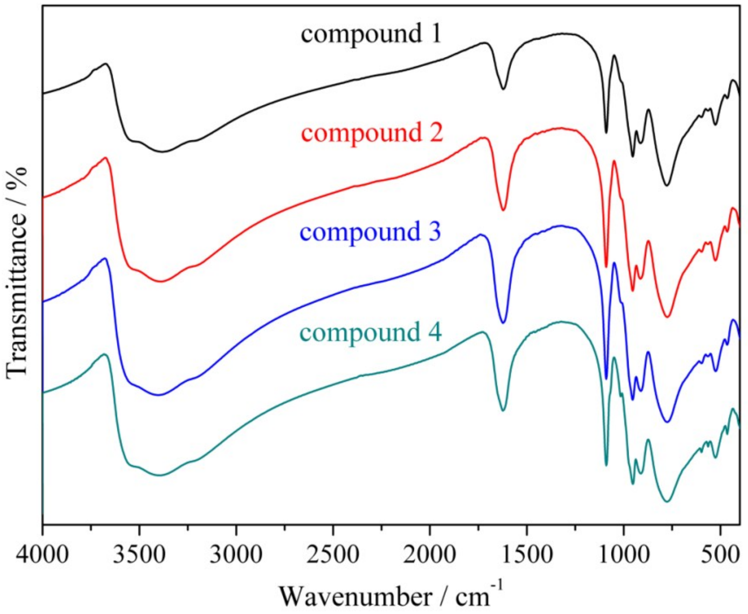


Figure S7. IR spectra of compounds **1-4.**

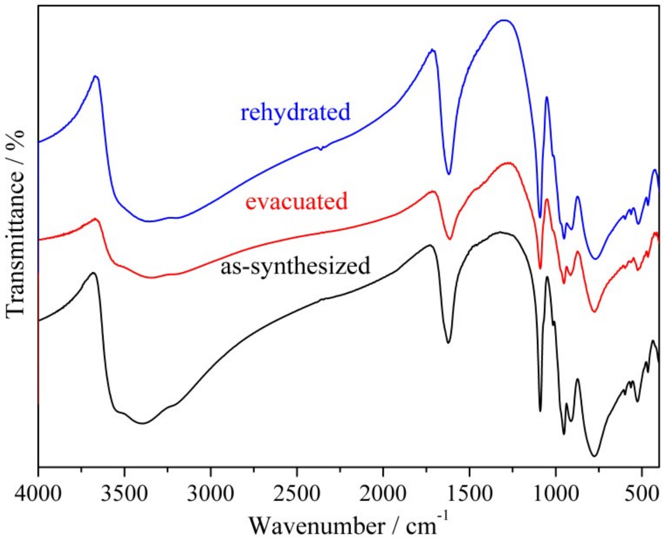


Figure S8. IR spectra of as-synthesized, evacuated and rehydrated samples of **1**.

SI-5 Thermal analyses

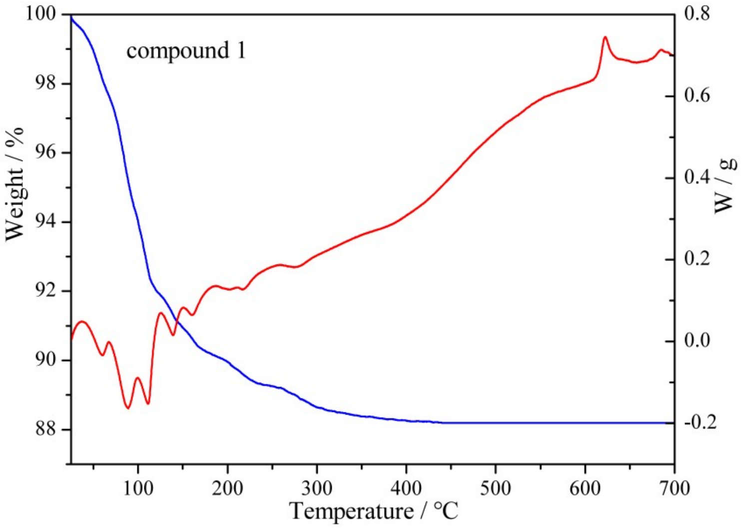


Figure S9. TG\DSC curves of compound **1**.

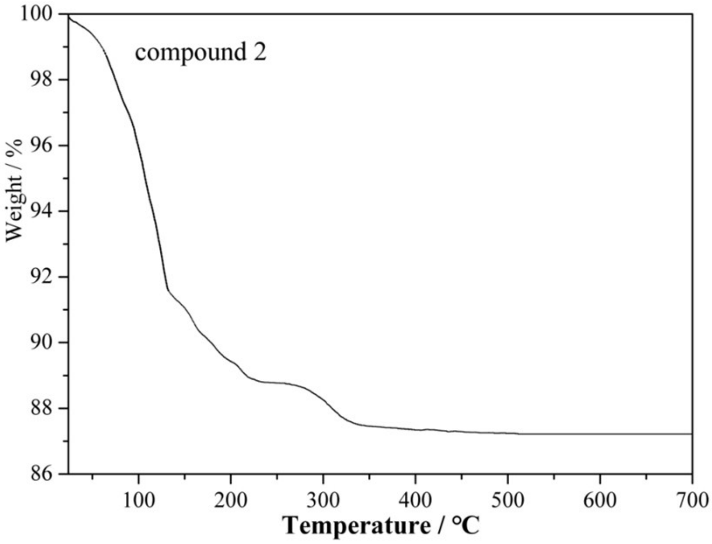


Figure S10. TG curves of compound **2**.

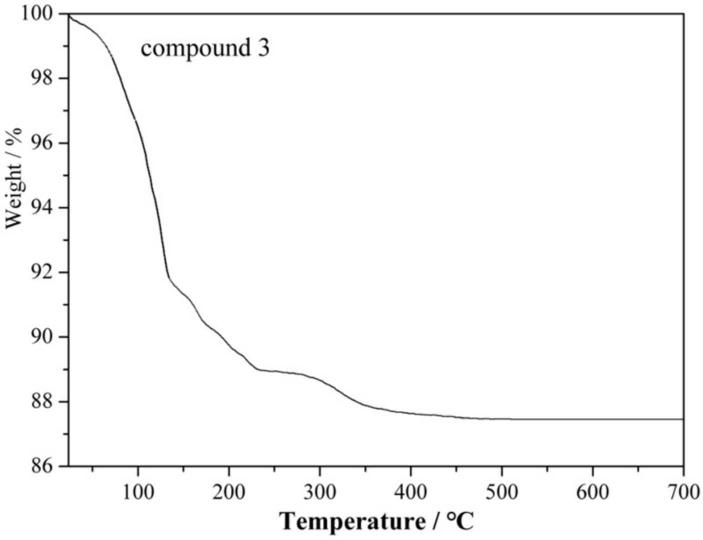


Figure S11. TG curves of compounds **3**.

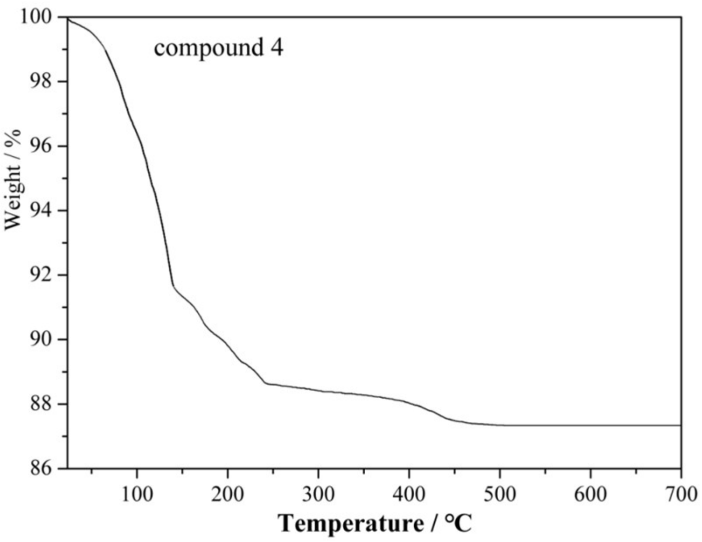


Figure S12. TG curves of compounds **4**.

SI-6 Proton Conductivity measurement

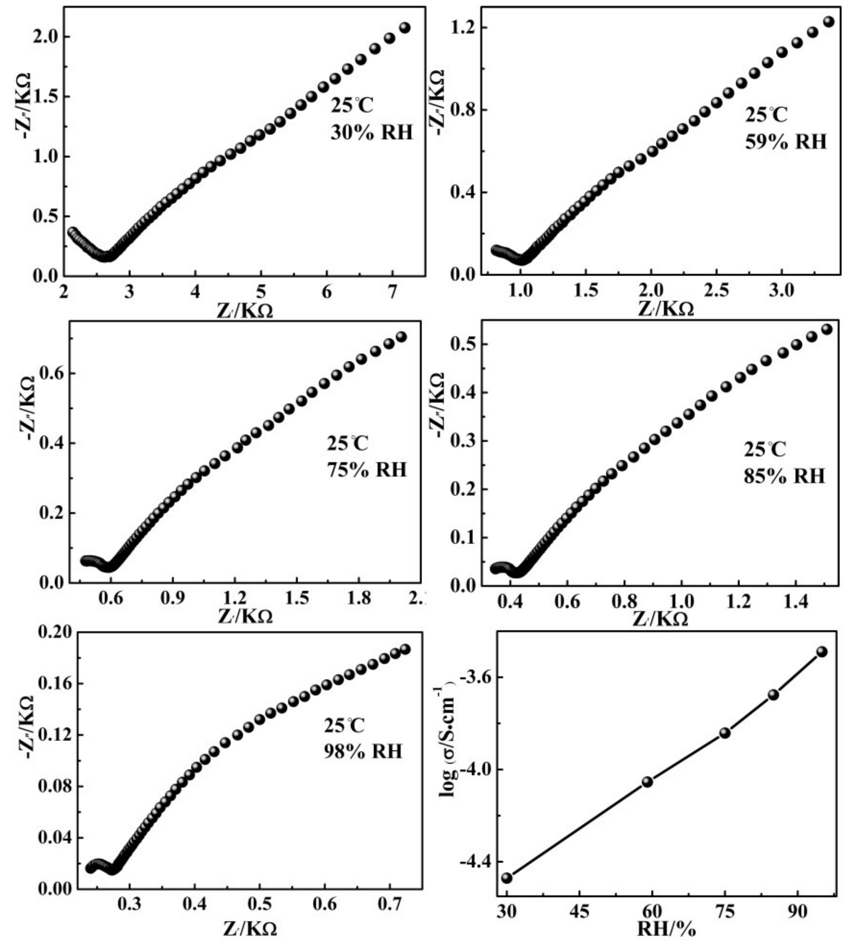


Figure S13. Nyquist plot of proton conduction for **1** at 25℃under 30%, 59%, 75%, 85%, and 98% RH.

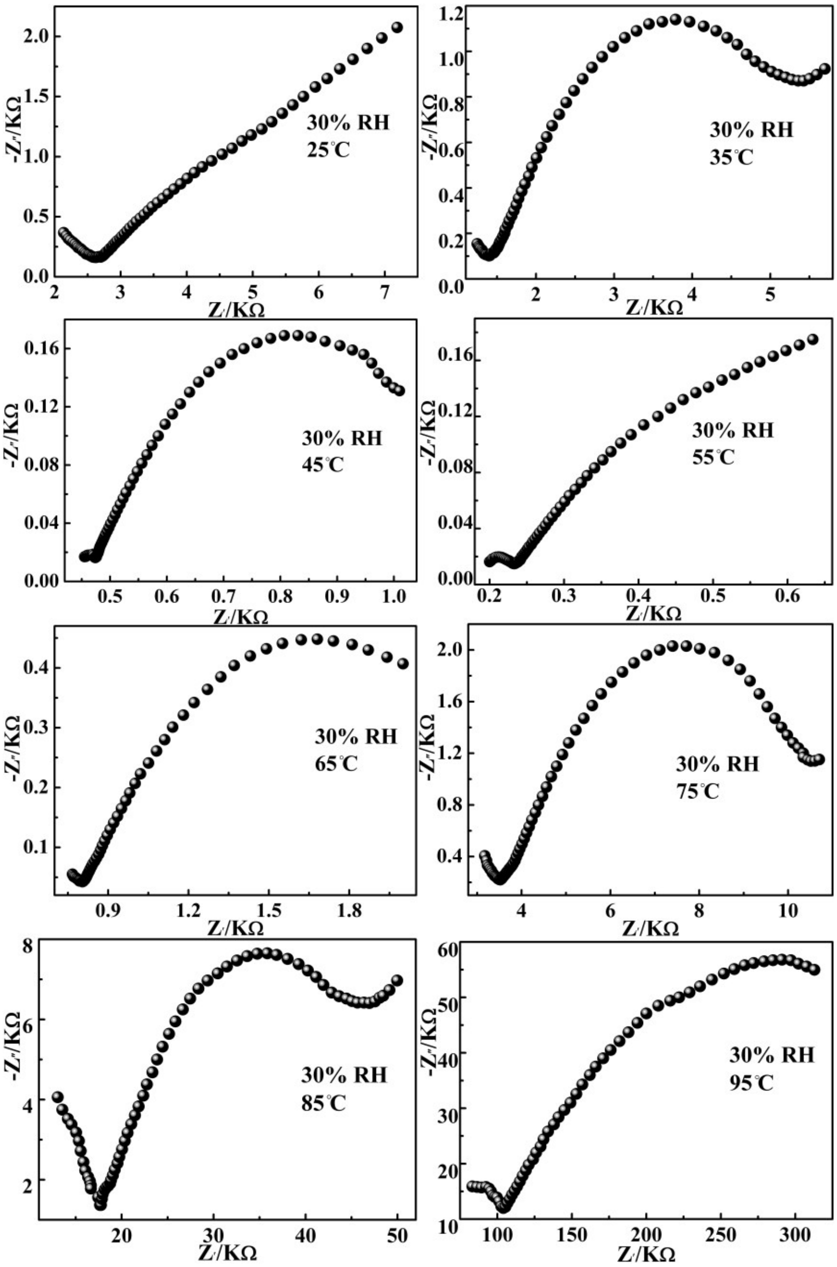


Figure S14. Nyquist plot of proton conduction for **1** under 30% RH at 35℃, 45℃, 55 ℃, 65℃, 75 ℃, 85 and 95℃.

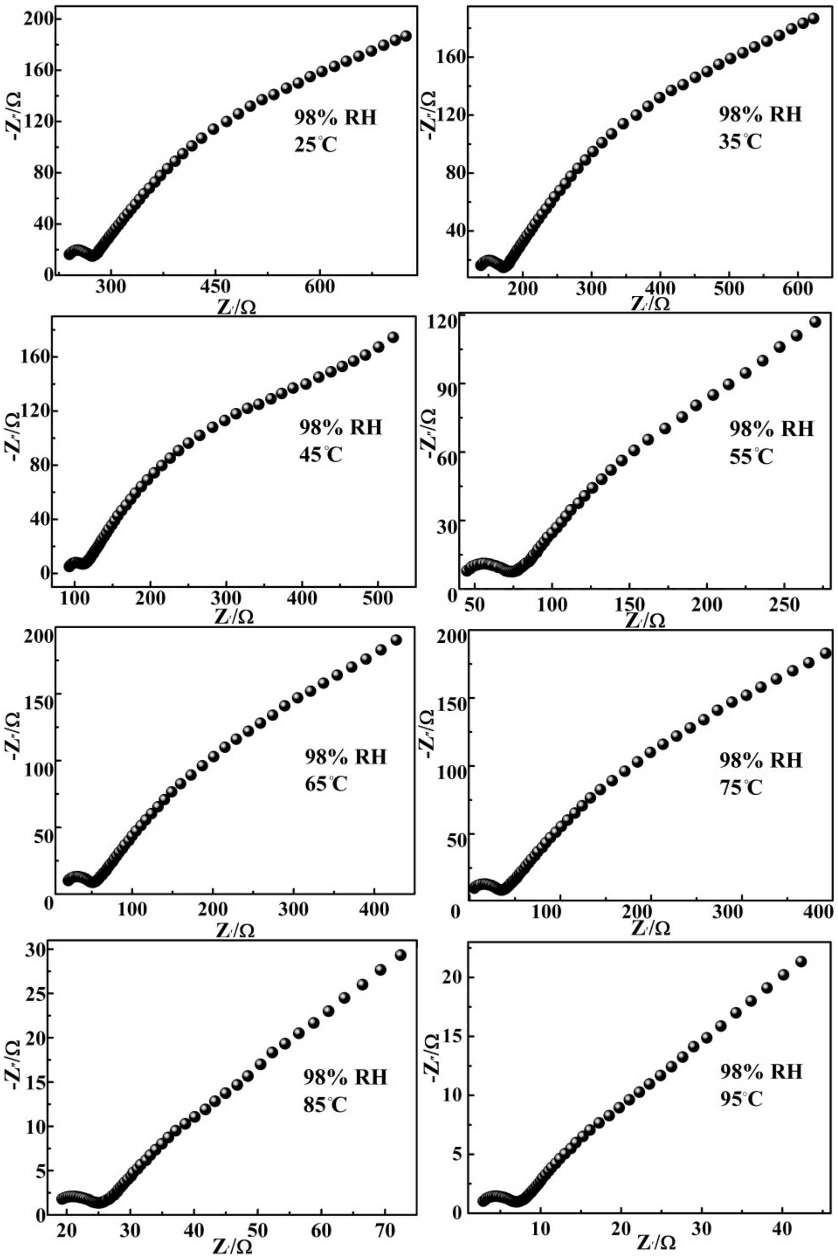
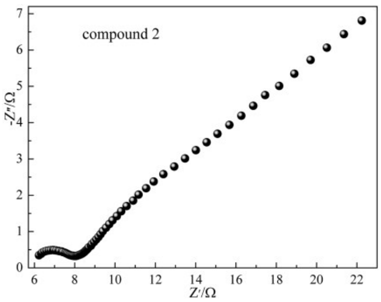
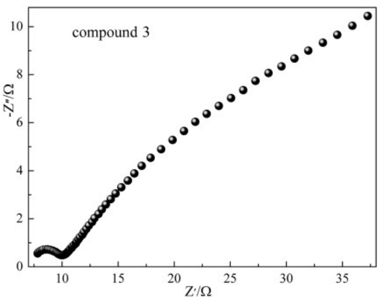


Figure S15. Nyquist plot of proton conduction for **1** under 98% RH at 35℃, 45℃, 55 ℃, 65℃, 75 ℃, 85 and 95℃.





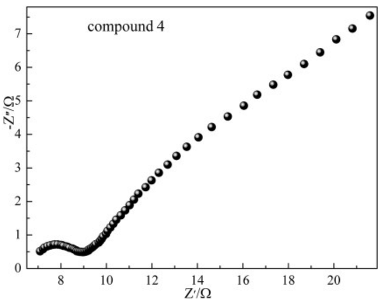


Figure S16. Nyquist plot of proton conduction for compounds **2, 3** and **4** at 95℃ under 98% RH.

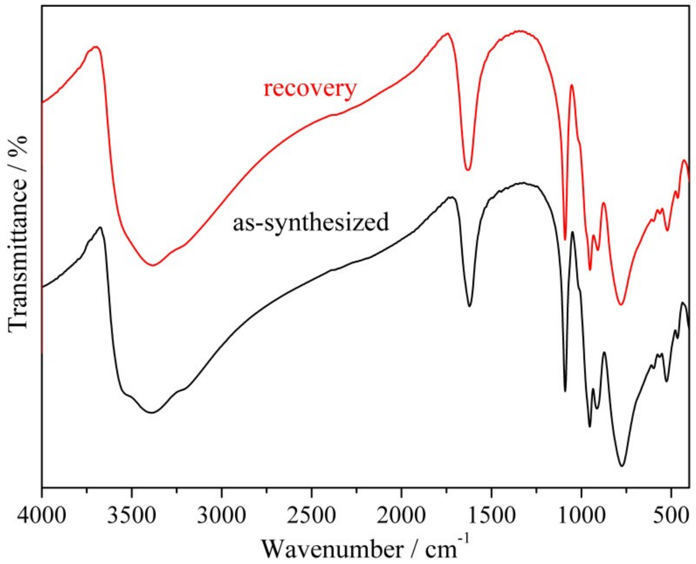


Figure S17. IR spectra of compound **1** before (black) and after (red) the proton conductive measurement.

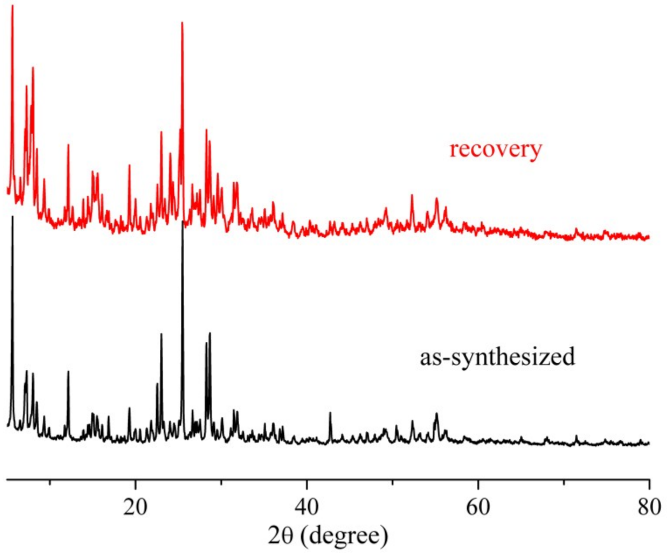


Figure S18. Powder X-ray diffraction patterns of **1** before (black) and after (blue) the proton conductive measurement.