

Inorganic Open Framework based on Lanthanide Ions and Polyoxometalates with High Proton Conductivity

Jia-Xuan Wang, Yi-Di Wang, Mei-Jie Wei, Hua-Qiao Tan, Yong-Hui Wang, Hong-Ying Zang* and
Yang-Guang Li*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate, Science of Ministry of
Education, Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province,
Faculty of Chemistry, Northeast Normal University, Changchun, 130024, Jilin, P. R. China.

E-mail: zanghy100@nenu.edu.cn, liyg658@nenu.edu.cn

Tel: +86 0431-85099108; Fax: +86 0431-85684009

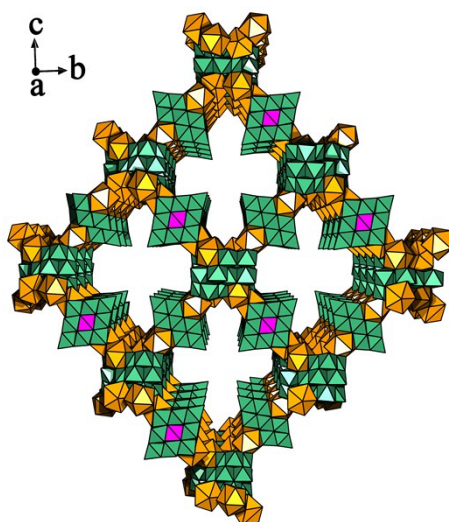


Fig. S1. The polyhedral representation of the 3D framework with channels in compound **1** along the $[100]$ direction. The colors of green and orange 3D polyhedrals representation of the $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ anions and Ce^{3+} cations, respectively.

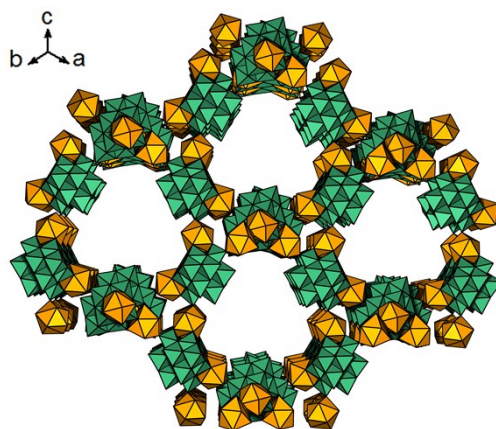


Fig. S2. The polyhedral representation of the 3D framework with channels in compound **1** along the $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ direction. The colors of green and orange 3D polyhedrals representation of the $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ anions and Ce^{3+} cations, respectively.

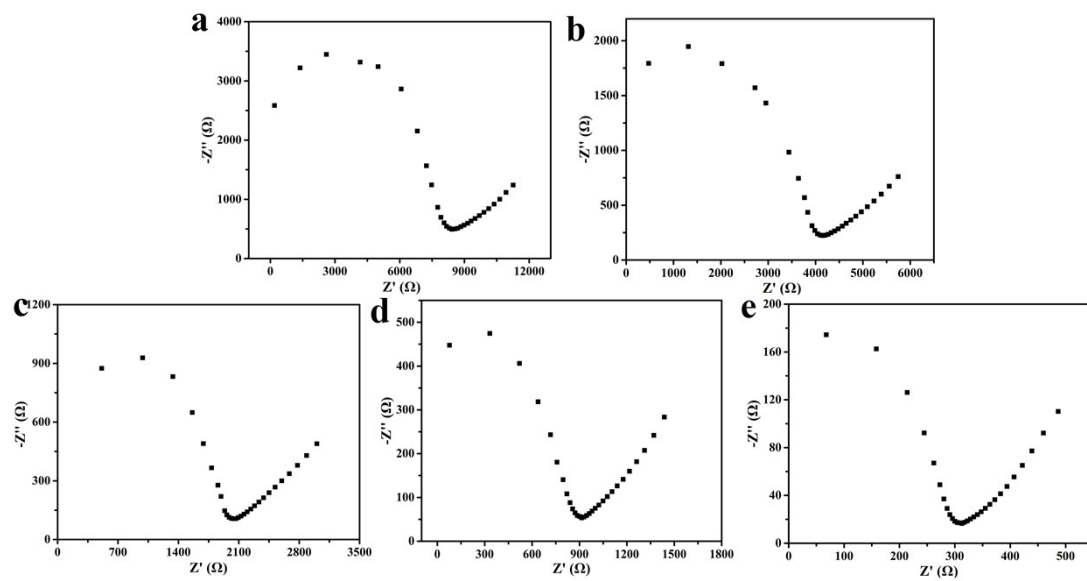


Fig. S3. Nyquist plot of compound **1** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for first time.

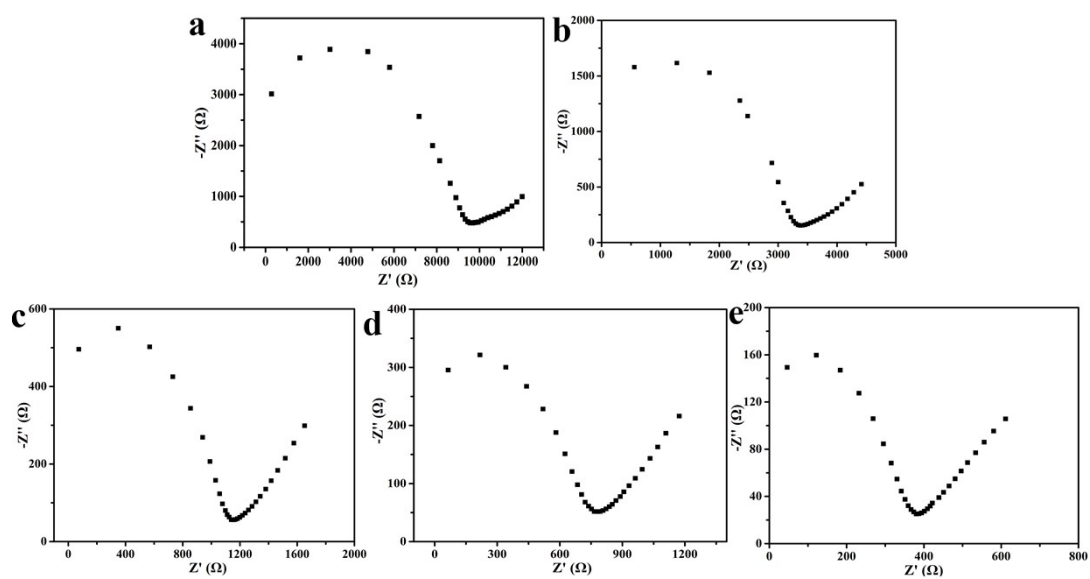


Fig. S4. Nyquist plot of compound **2** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for first time.

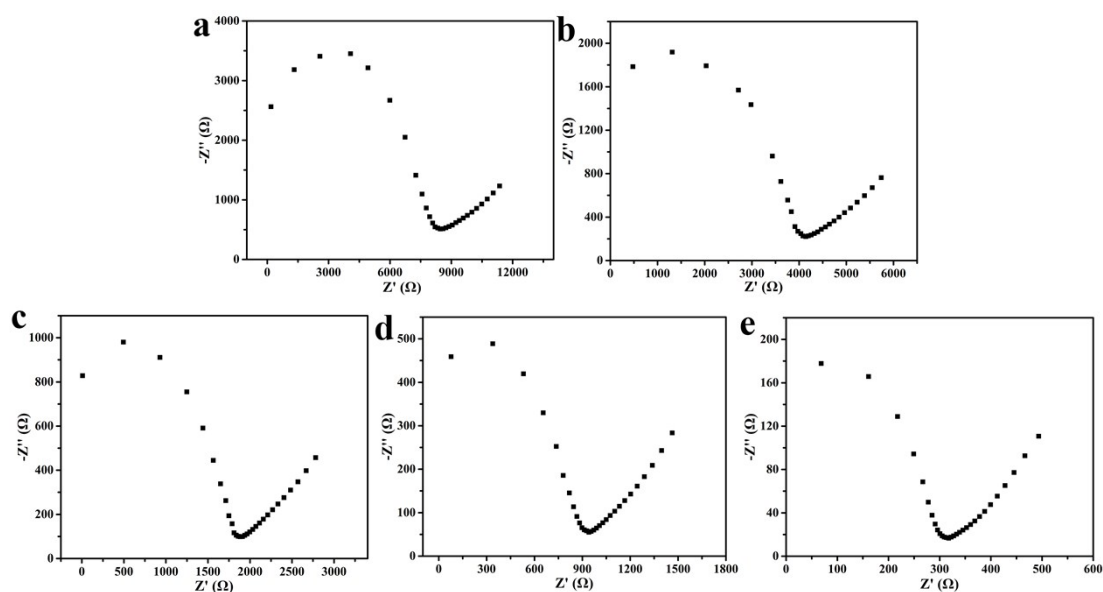


Fig. S5. Nyquist plot of compound **1** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for second time.

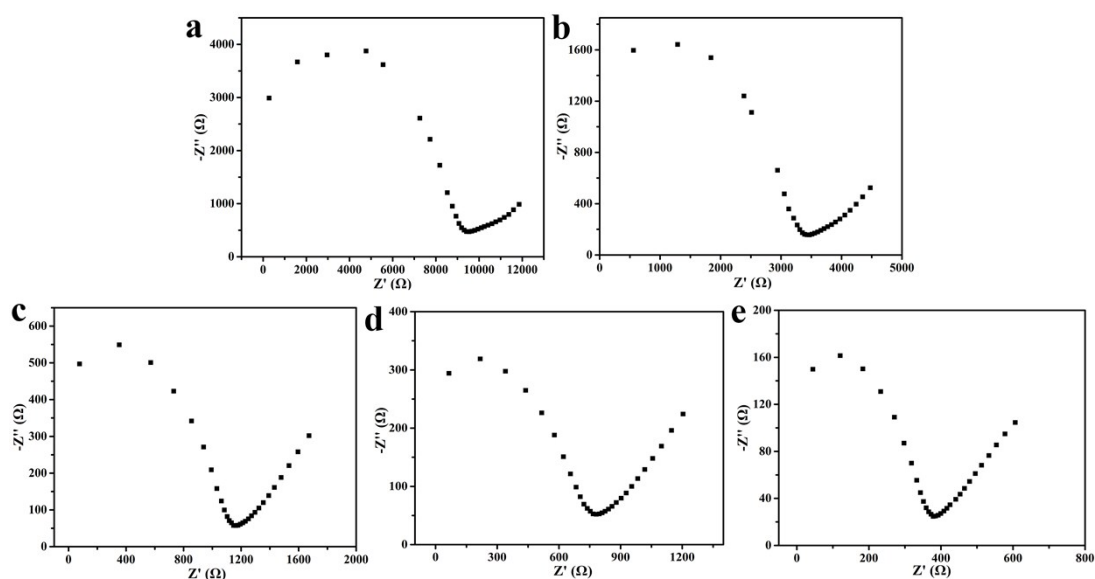


Fig. S6. Nyquist plot of compound **2** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for second time.

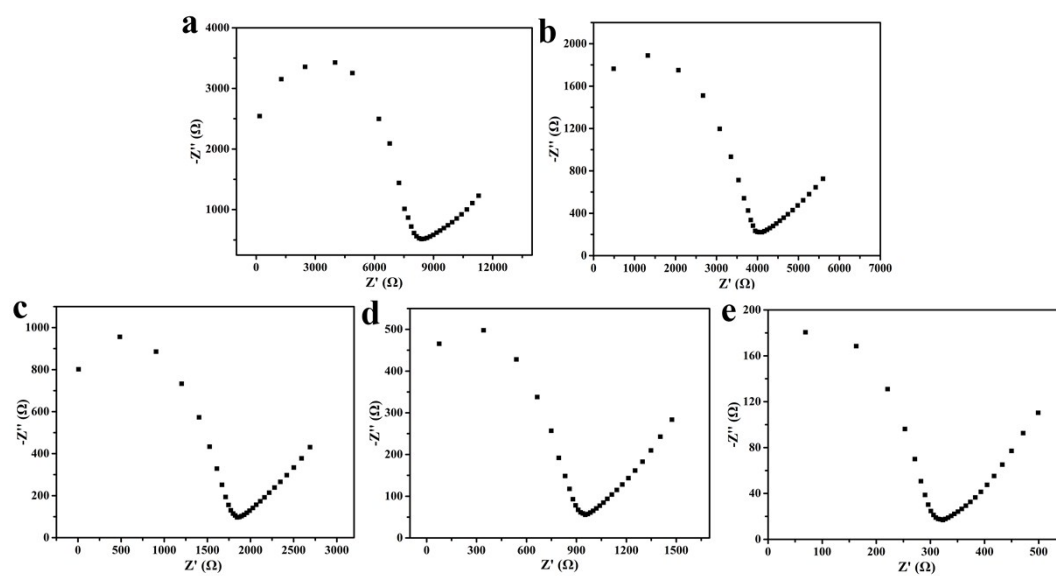


Fig. S7. Nyquist plot of compound **1** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for third time.

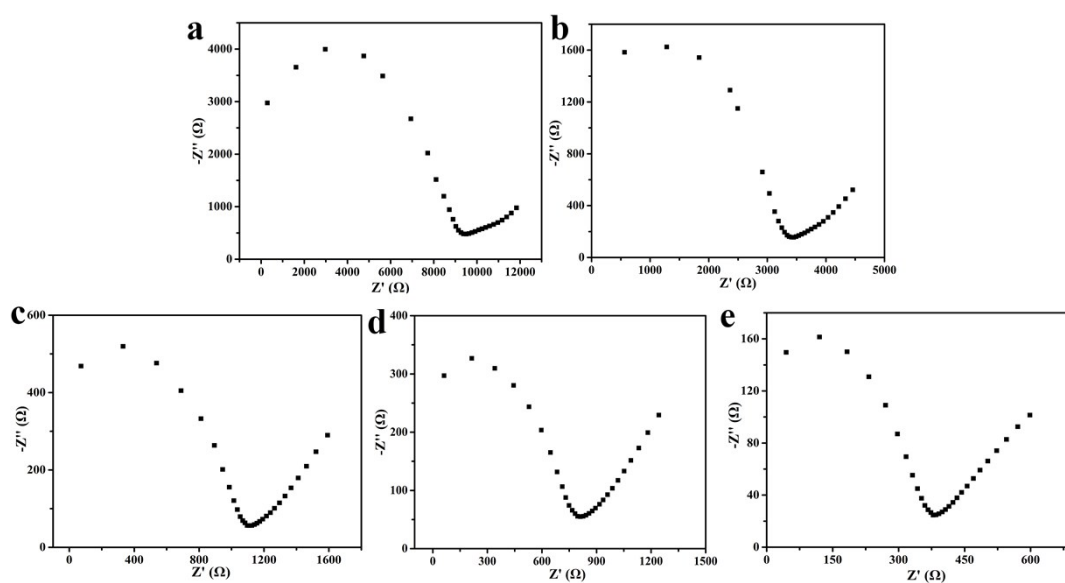


Fig. S8. Nyquist plot of compound **2** at 25 °C and 75% RH (a), 80% RH (b), 85% RH (c), 90% RH (d) and 95% RH (e) for the third time.

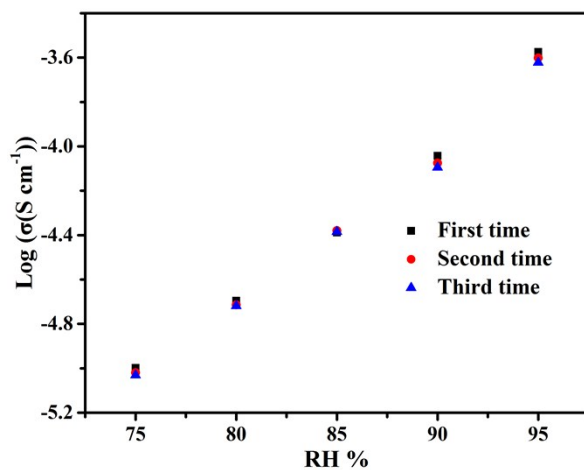


Fig. S9. The variable-humidity reproducibility of the proton conductivity of compound **1** measured for three times.

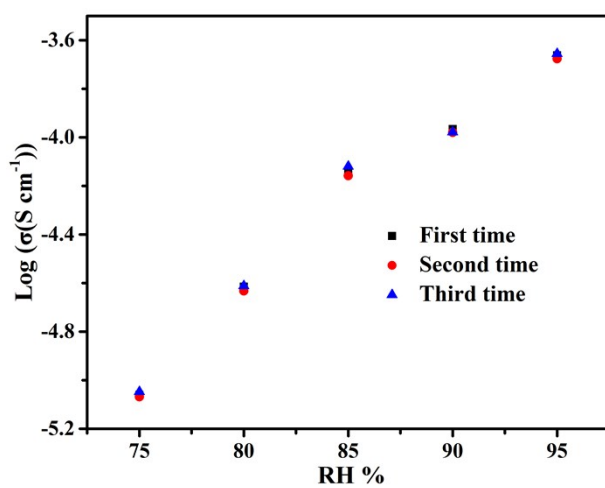


Fig. S10. The variable-humidity reproducibility of the proton conduction data of compound **2** measured for three times.

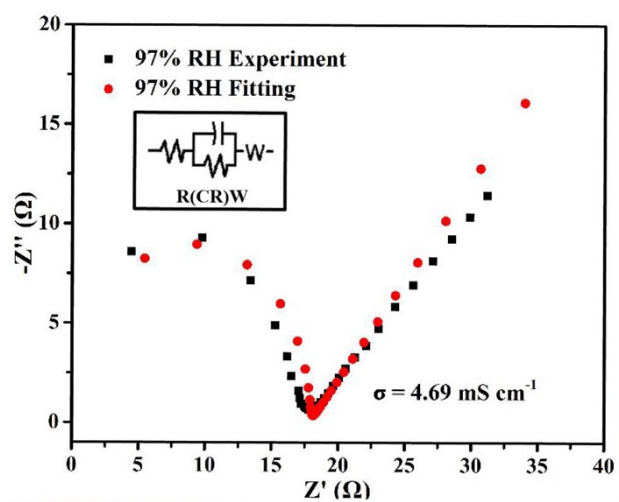


Fig. S11. Nyquist plot of compound **1** at 61 °C under 97% RH.

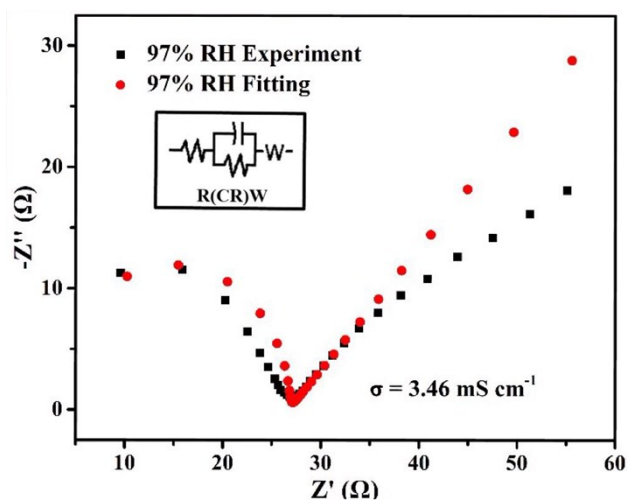


Fig. S12. Nyquist plot of compound **2** at 61 °C under 97% RH.

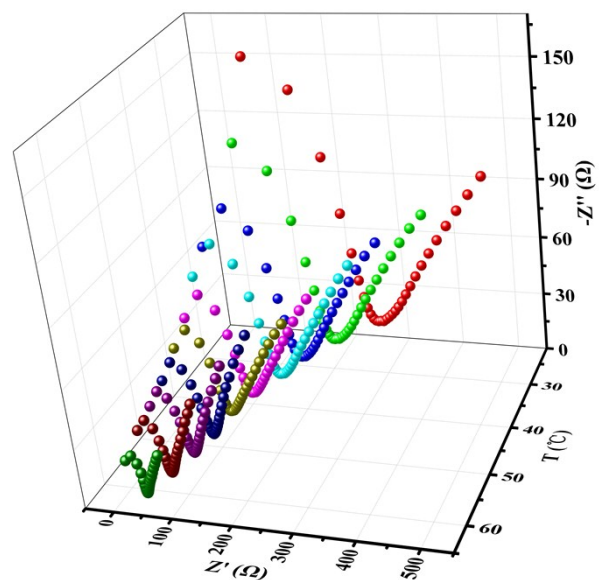


Fig. S13. The reproducibility of Nyquist plots of compound **1** at 97% RH and different temperatures of 25, 29, 33, 37, 41, 45, 49, 53, 57 and 61 °C.

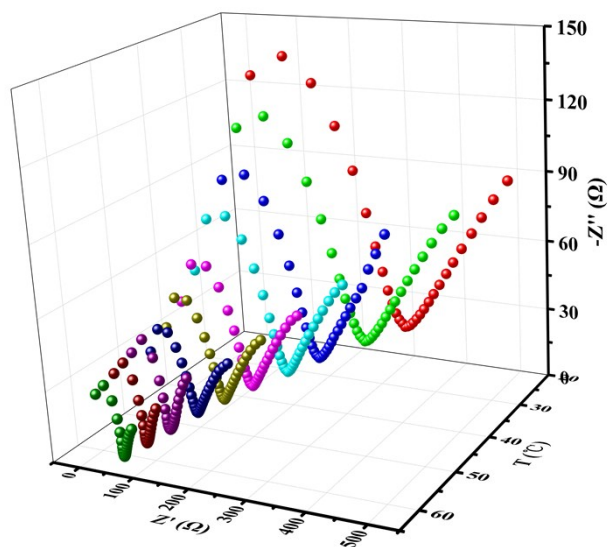


Fig. S14. The reproducibility of Nyquist plots of compound **2** at 97% RH and different temperatures of 25, 29, 33, 37, 41, 45, 49, 53, 57 and 61 °C.

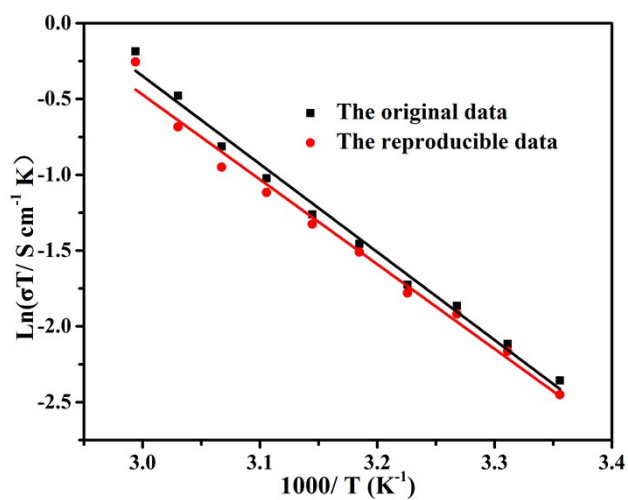


Fig. S15. The reproducibility of Arrhenius plots of the proton conductivity of compound **1** from 25 to 61 °C at 97% RH.

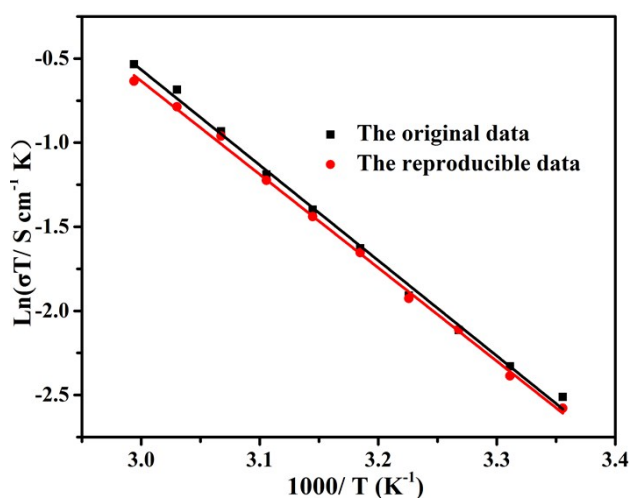


Fig. S16. The reproducibility of Arrhenius plots of the proton conductivity of compound **2** from 25 to 61 °C at 97% RH.

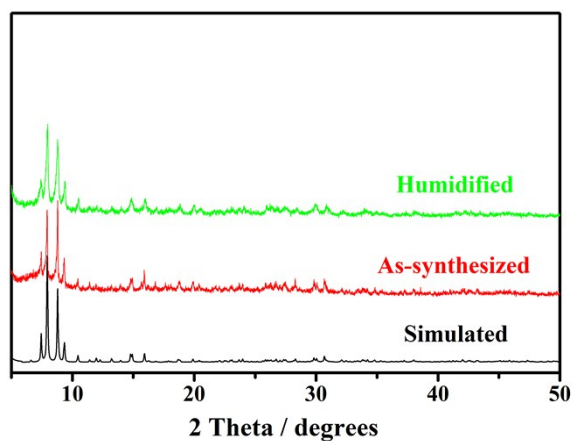


Fig. S17. PXRD patterns of compound **1**; simulated pattern (bottom trace), as-synthesized pattern (middle), and for a sample that was treated after impedance measurement at 61 °C and 97% RH (top).

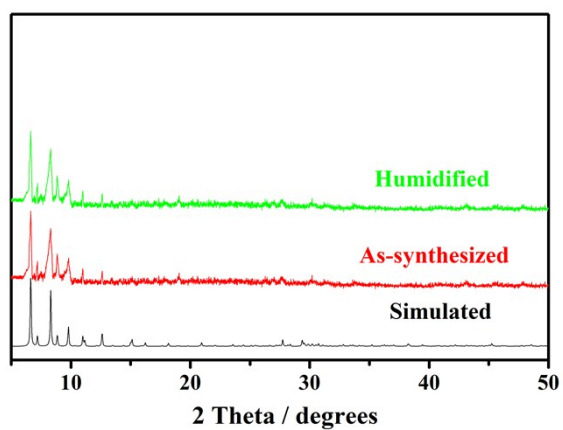


Fig. S18. PXRD patterns of compound **2**; simulated pattern (bottom trace), as-synthesized pattern (middle), and for a sample that was treated after impedance measurement at 61 °C and 97% RH (top).

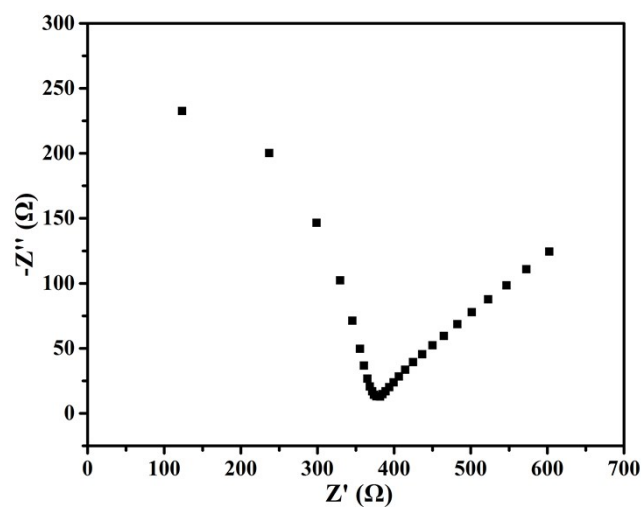


Fig. S19. Nyquist plot of compound **1** in the presence of D_2O at 25 °C under 97% RH.

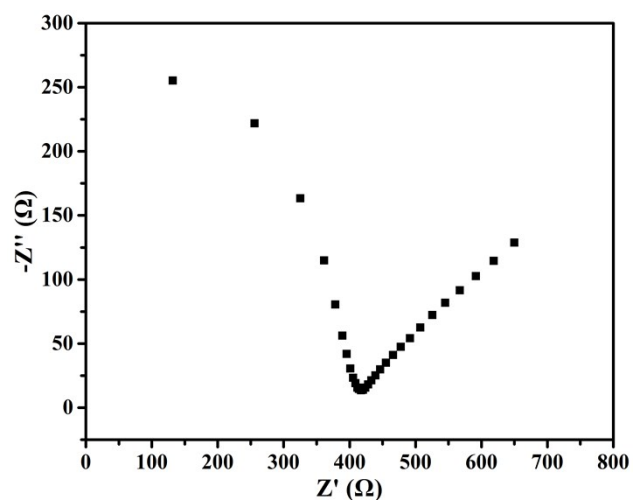


Fig. S20. Nyquist plot of compound **2** in the presence of D_2O at 25 °C under 97% RH.

Table. S1. Comparison of proton conductivity of lanthanide-based proton conductors.

Compounds	T (°C)	RH (%)	Proton conductivity (S cm ⁻¹)	Reference
La _{1.96} Ca _{0.04} Sn ₂ O _{7-δ}	300	/	9.50×10 ⁻⁹	<i>Solid State Ionics.</i> , 2010, 181 , 1258–1263.
Sm _{1.96} Ca _{0.04} Sn ₂ O _{7-δ}	300	/	7.4× 10 ⁻⁹	<i>Solid State Ionics.</i> , 2010, 181 , 1258–1263
LaM; M = Cr, Co,	25	95	1 × 10 ⁻⁵	<i>Inorg. Chem.</i> , 2015, 54 , 8529–8535
{[LnK(BPDSDC)(DMF)(H ₂ O)]·x(solvent)} _n	80	98	1.11 × 10 ⁻³	<i>Inorg. Chem.</i> , 2016, 55 , 6271–6277
[LnL(H ₂ O) ₃] · 2H ₂ O	75	97	1.6 × 10 ⁻⁵	<i>Chem. Commun.</i> , 2014, 50 , 1912–1914
[Sm(H ₂ O) ₅ (CO ₂ CH ₂ NH ₃) ₂] [Al(OH) ₆ Mo ₆ O ₁₈]·10H ₂ O	80	95	4.53 × 10 ⁻³	<i>Dalton Trans.</i> , 2014, 43 , 14749–14755
[La(H ₅ L)(H ₂ O) ₄]	60	98	4 × 10 ⁻³	<i>J. Am. Chem. Soc.</i> , 2013, 135 , 1193–1196
[Eu ₂ (CO ₃)(ox) ₂ (H ₂ O) ₂]·4H ₂ O	150	/	2.08 × 10 ⁻³	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 12444–12449.