Supplementary Information (SI) for New Journal of Chemistry.

Construction and proton conductivity of a POMs-based compound based on different isomers of $[Mo_8O_{26}]^{4-}$ ions

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Experimental Section

Single Crystal X-ray Diffraction (SC-XRD): SC-XRD data were acquired at 173 K on a Bruker D^8 VENTURE diffractometer equipped with a charge-coupled device detector. The wavelength of the incident beam was 0.71073 Å (λ Mo-Kα). The two-dimensional diffraction image data were processed using the APEX 5 software for data reduction, correction and unit cell refinement. Structure solution and refinement were carried out by SHELXT-2018/3 and SHELXL-2018/3 using Olex [1−2]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic information files of **1** were deposited in the Cambridge Crystallographic Data Centre (CCDC, No. 2497954).

Powder X-ray diffraction (PXRD): Measurements were recorded ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Mo-Kα (λ = 0.71073 Å).

Fourier-transform infrared (FT-IR) spectroscopy: The samples were prepared as KBr pellets and the FT-IR spectrum was collected in transmission mode in the range of 400-4000 cm^{-1} using Nicolet Magna 560 infrared spectrometer.

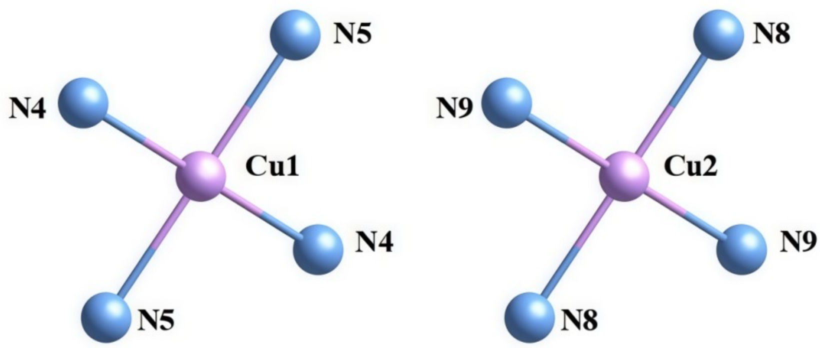

Fig. S1. Ball-and-stick representation of Cu atoms in compound **1**. Color code: Cu, purple; N, blue.

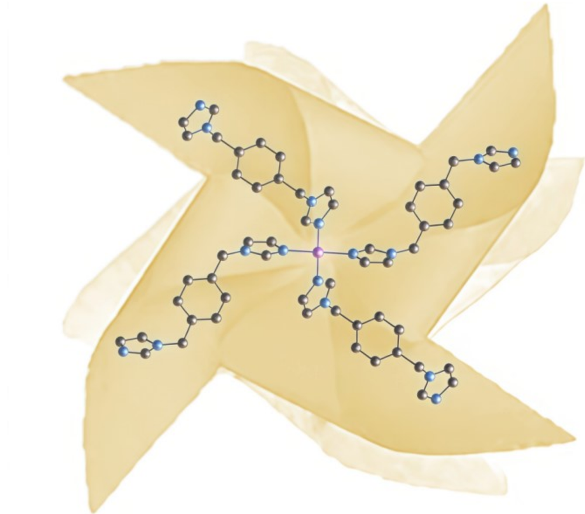

Fig. S2. Ball-and-stick representation of {Cu($C_{14}N_4H_{14}$)$_4$} unit. Color code: Mo = green; C = gray; N = blue; Cu = purple.

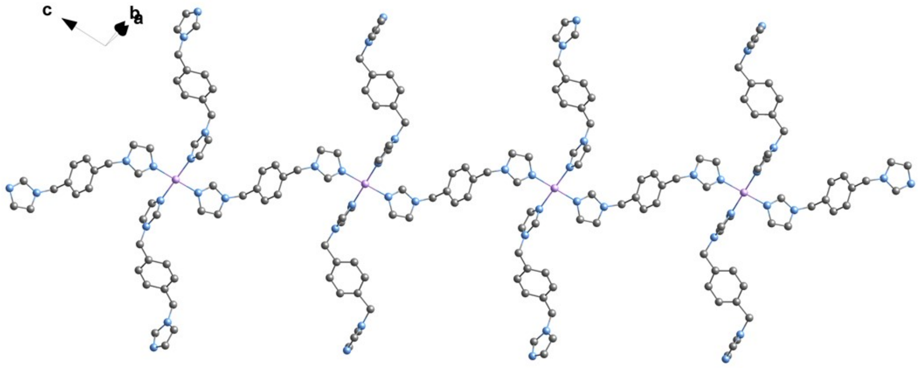

Fig. S3.The 1D chain structure of {Cu($C_{14}N_4H_{14}$)$_4$} unit.

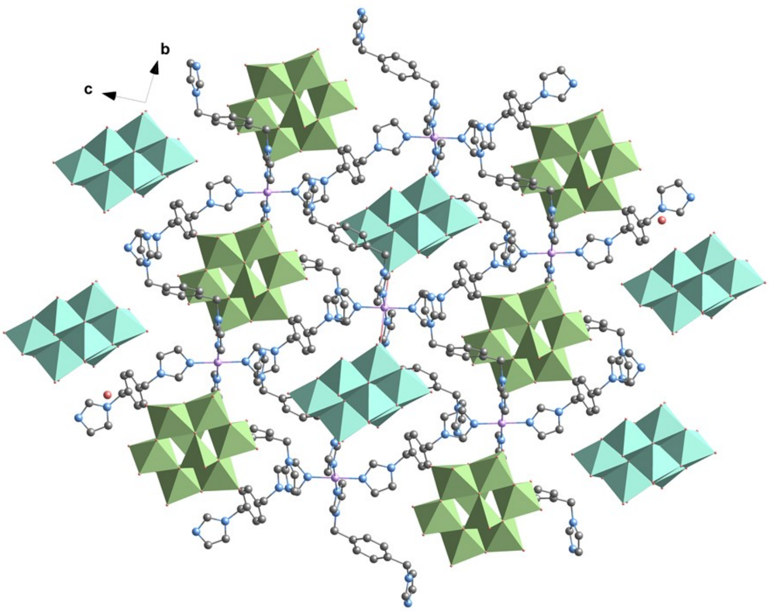

Fig. S4.The 2D supramolecular layer of compound **1** (along the a-axis).

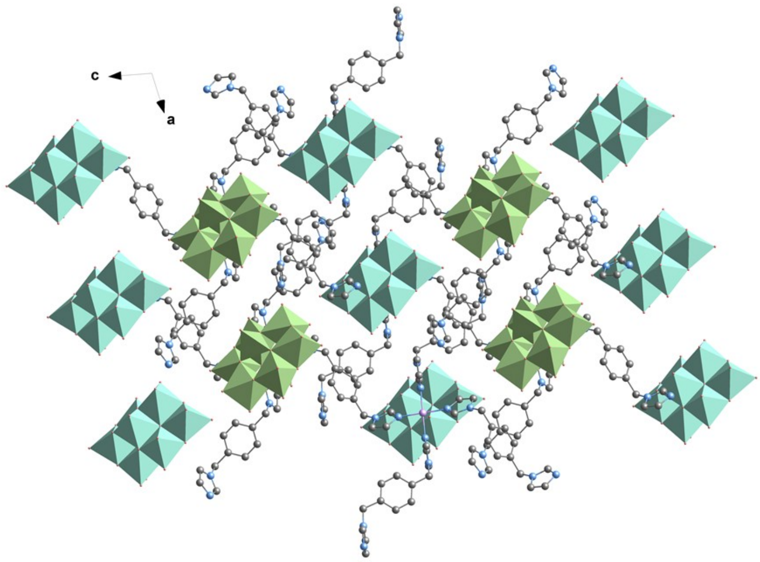

Fig. S5.The 2D supramolecular layer of compound **1** (along the b-axis).

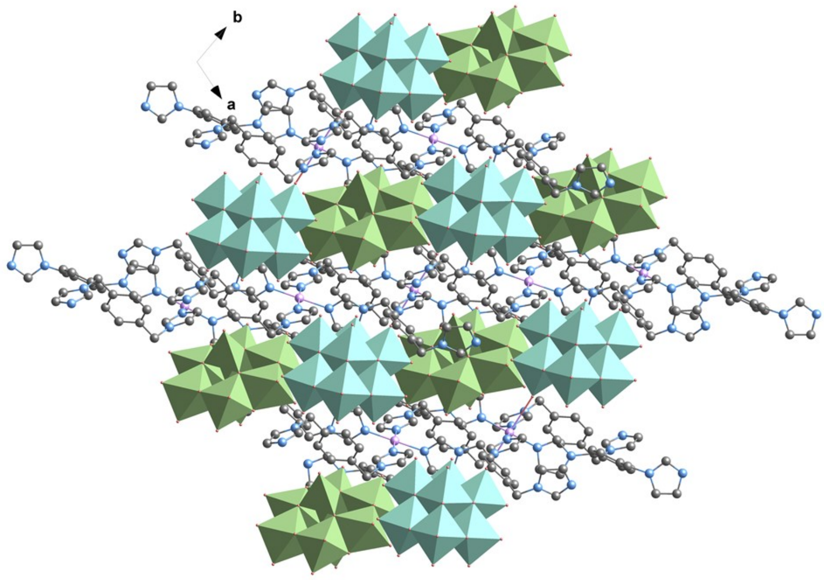

Fig. S6.The 2D supramolecular layer of compound **1** (along the c-axis).

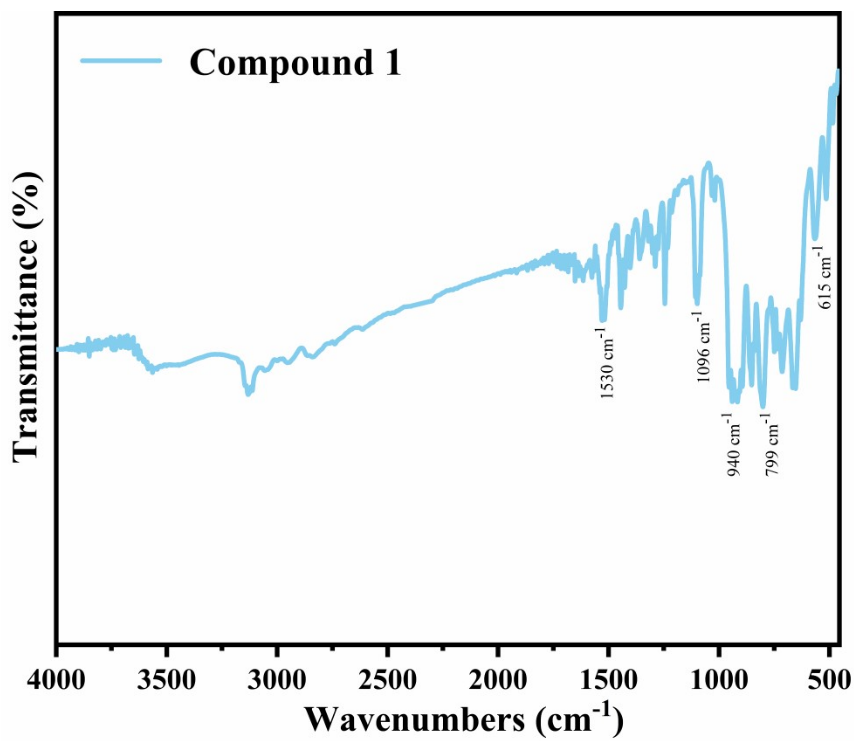

Fig. S7.The IR spectra of compound **1**.

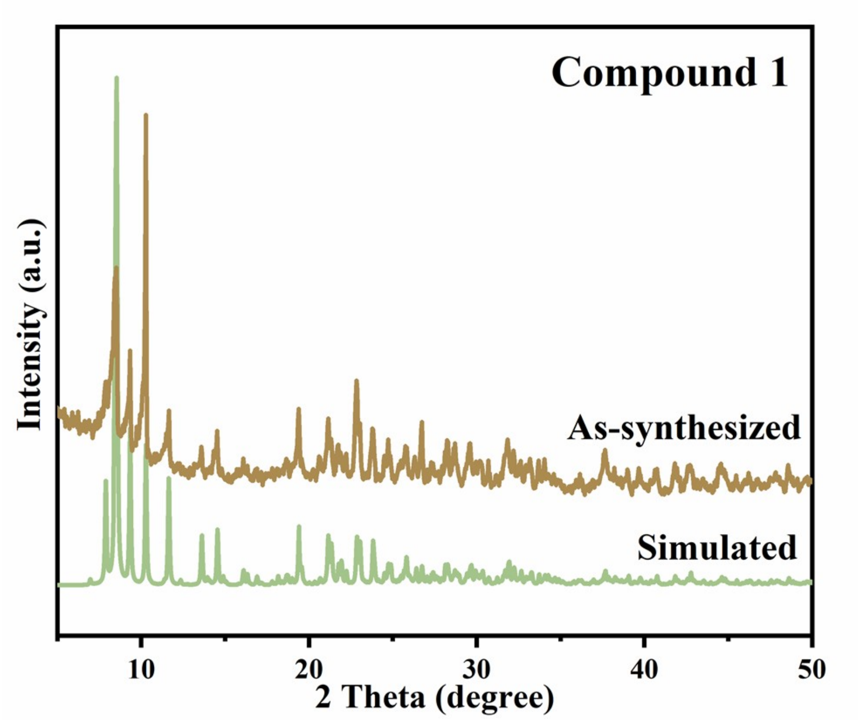

Fig. S8.The PXRD pattern of compound **1**.

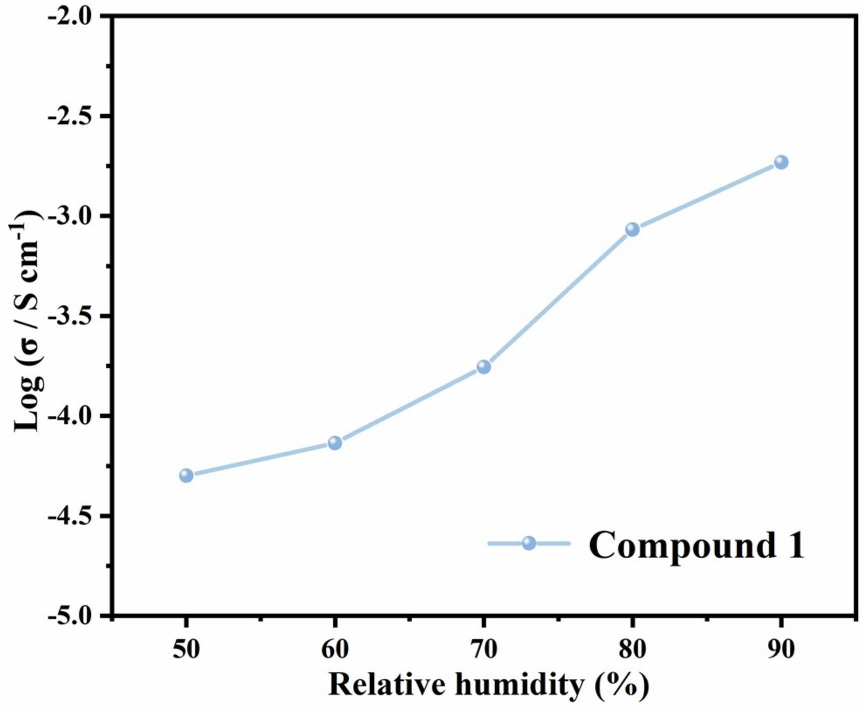

Fig. S9. Humidity-dependent proton conductivities at 30 ℃ for compound **1**.

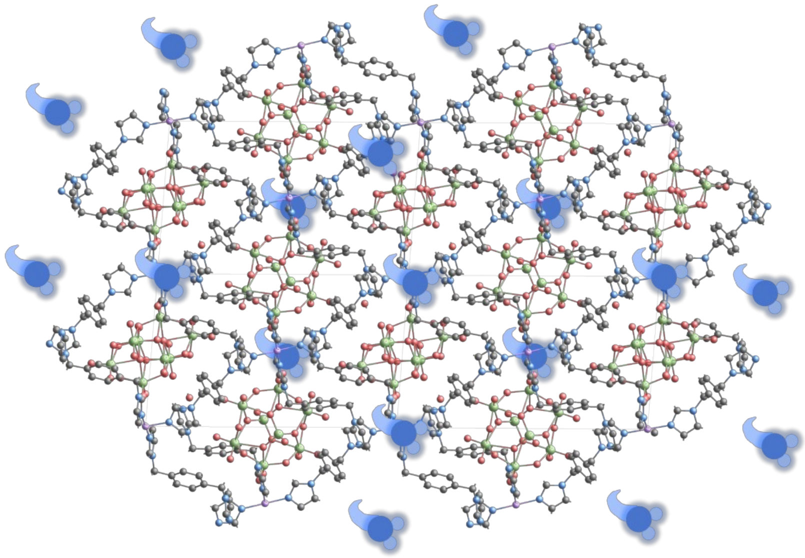

Fig. S10 Possible proton conduction mechanism for compound **1**.

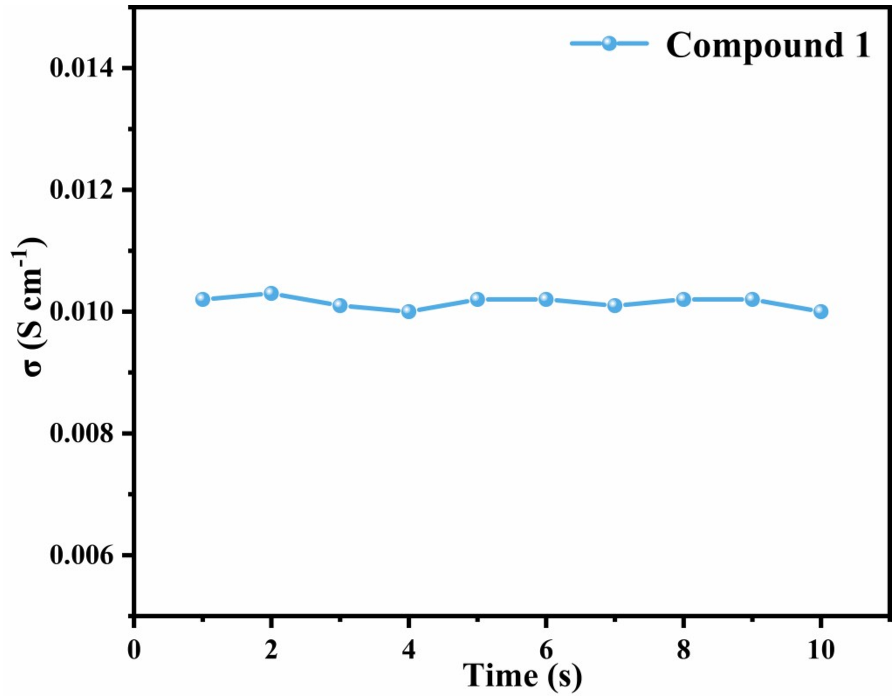

Fig. S11. The Nyquist plot of compound 1 at 80 °C at 90% RH.

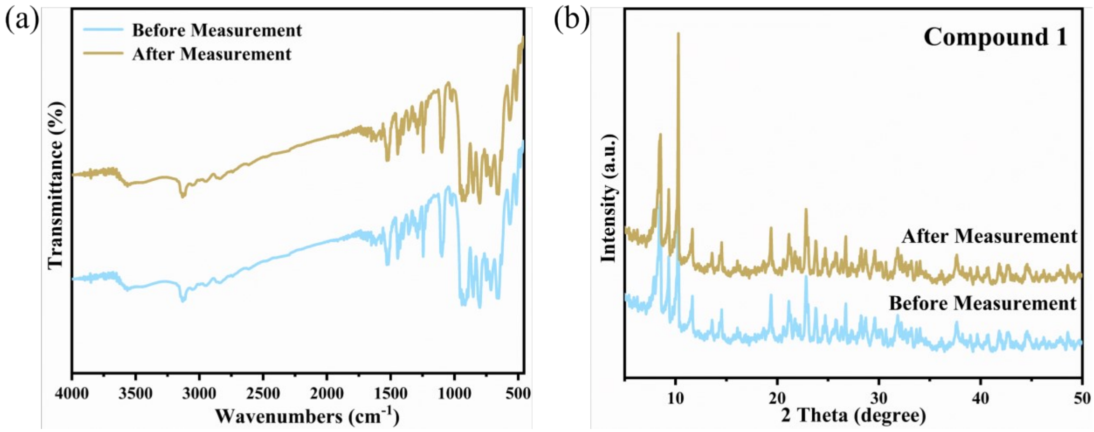

Fig. S12. (a) FT-IR spectra of compound **1** before and after proton conduction testing. (b) PXRD patterns of **1** before and after proton conduction testing.

Supplementary Tables

Table S1. Selected bond length (Å) for Compound **1**.

Complex **1**			
Mo5-Mo6	3.2068(6)	N5-C17	1.358(7)
Mo5-O(16)[1]	2.358(3)	N8-C27	1.374(7)
Mo5-O16	2.138(3)	N8-C28	1.316(6)
Mo5-O18	1.943(3)	N9-C31	1.325(6)

Mo5-O17	1.958(3)	N9-C30	1.386(7)
Mo5-O22	1.743(4)	N10-C32	1.466(6)
Mo5-O21	1.689(3)	N10-C31	1.347(6)
Mo4-O7	1.782(3)	N10-C29	1.360(7)
Mo4-O5	1.784(3)	N7-C28	1.326(7)
Mo4-O4	1.784(3)	N7-C25	1.468(7)
Mo4-O6	1.700(3)	N7-C26	1.360(7)
Mo8-O16	2.335(3)	N11-C42	1.315(8)
Mo8-O(18)[1]	2.334(3)	N11-C39	1.454(7)
Mo8-O17	2.008(3)	N11-C41	1.350(10)
Mo8-O14	1.877(4)	N3-C14	1.344(6)
Mo8-O24	1.706(3)	N3-C11	1.483(6)
Mo8-O23	1.698(3)	N3-C12	1.366(7)
Mo1-O(7)[2]	2.438(3)	N2-C1	1.324(7)
Mo1-O3	1.912(3)	N2-C2	1.366(7)
Mo1-O(13)[2]	1.922(3)	N2-C4	1.476(7)
Mo1-O4	2.383(3)	N6-C15	1.331(7)
Mo1-O1	1.697(4)	N6-C18	1.456(7)
Mo1-O2	1.691(4)	N6-C16	1.344(9)
Mo6-O16	2.346(3)	N1-C1	1.320(8)
Mo6-O18	1.987(3)	N1-C3	1.340(10)
Mo6-O(17)[1]	2.394(3)	C32-C35	1.499(7)
Mo6-O15	1.893(4)	C35-C34	1.377(7)
Mo6-O19	1.698(4)	C35-C36	1.386(7)
Mo6-O20	1.683(4)	C21-C22	1.383(7)
Mo2-O(7)[2]	2.379(3)	C21-C25	1.516(7)
Mo2-O5	2.426(3)	C21-C20	1.369(8)
Mo2-O3	1.904(4)	C24-C23	1.373(8)
Mo2-O10	1.907(4)	C24-C19	1.375(8)
Mo2-O8	1.706(4)	C24-C18	1.526(8)
Mo2-O9	1.694(3)	C23-C22	1.380(8)
Mo7-O16	2.468(3)	C34-C33	1.387(8)
Mo7-O14	1.934(4)	N12-C42	1.301(9)
Mo7-O(22)[1]	2.304(4)	N12-C40	1.350(11)
Mo7-O15	1.922(4)	C29-C30	1.355(7)
Mo7-O25	1.697(4)	C5-C10	1.369(7)
Mo7-O26	1.694(4)	C5-C6	1.387(8)
Mo3-O5	2.436(3)	C27-C26	1.346(8)
Mo3-O13	1.889(4)	C19-C20	1.381(8)
Mo3-O(4)[2]	2.394(3)	C10-C11	1.512(8)
Mo3-O10	1.899(4)	C10-C9	1.388(8)

Mo3-O11	1.705(4)	C6-C7	1.391(8)
Mo3-O12	1.694(4)	C13-C12	1.348(7)
Cu1-N(4)[3]	2.004(4)	C9-C8	1.376(8)
Cu1-N4	2.004(4)	C8-C7	1.375(8)
Cu1-N(5)[3]	2.006(4)	C37-C38	1.383(8)
Cu1-N5	2.006(4)	C37-C36	1.370(8)
Cu2-N(8)[4]	1.987(4)	C7-C4	1.505(8)
Cu2-N8	1.987(4)	C38-C33	1.381(8)
Cu2-N9	2.011(4)	C38-C39	1.515(8)
Cu2-N(9)[4]	2.011(4)	C2-C3	1.334(9)
N4-C14	1.314(6)	C17-C16	1.347(10)
N4-C13	1.380(7)	C40-C41	1.340(11)
N5-C15	1.333(7)		

[1]-X,1-Y,2-Z; [2]1-X,-Y,1-Z; [3]1-X,1-Y,1-Z; [4]-X,-Y,2-Z

Table S2. Selected bond Angle (˚) for Compound **1**.

O16-Mo5-Mo6	47.00(8)	N(4)[3]-Cu1-N(5)[3]	90.32(16)
O(16)[1]-Mo5-Mo6	86.45(8)	N(4)[3]-Cu1-N5	89.68(16)
O16-Mo5-O(16)[1]	75.79(13)	N5-Cu1-N(5)[3]	180.0
O18-Mo5-Mo6	35.78(10)	N(8)[4]-Cu2-N8	180.00(6)
O18-Mo5-O16	78.77(13)	N(8)[4]-Cu2-N9	91.19(18)
O18-Mo5-O(16)[1]	77.34(12)	N8-Cu2-N(9)[4]	91.19(18)
O18-Mo5-O17	150.42(13)	N(8)[4]-Cu2-N(9)[4]	88.81(18)
O17-Mo5-Mo6	125.34(10)	N8-Cu2-N9	88.81(18)
O17-Mo5-O16	78.34(13)	N9-Cu2-N(9)[4]	180.0(2)
O17-Mo5-O(16)[1]	79.07(12)	Mo5-O16-Mo(5)[1]	104.21(13)
O22-Mo5-Mo6	133.17(11)	Mo5-O16-Mo8	92.91(12)
O22-Mo5-O(16)[1]	81.45(14)	Mo5-O16-Mo6	91.19(11)
O22-Mo5-O16	157.21(14)	Mo5-O16-Mo7	163.85(16)
O22-Mo5-O18	97.40(15)	Mo(5)[1]-O16-Mo7	91.90(11)
O22-Mo5-O17	96.47(15)	Mo8-O16-Mo(5)[1]	97.63(11)
O21-Mo5-Mo6	88.86(12)	Mo8-O16-Mo6	162.33(15)
O21-Mo5-O(16)[1]	174.40(15)	Mo8-O16-Mo7	86.00(10)
O21-Mo5-O16	98.75(15)	Mo6-O16-Mo(5)[1]	98.00(11)
O21-Mo5-O18	100.54(15)	Mo6-O16-Mo7	85.30(10)
O21-Mo5-O17	101.24(15)	Mo5-O18-Mo(8)[1]	111.01(14)
O21-Mo5-O22	104.03(17)	Mo5-O18-Mo6	109.35(15)
O7-Mo4-O5	108.73(16)	Mo6-O18-Mo(8)[1]	105.62(14)
O7-Mo4-O4	109.43(15)	Mo5-O17-Mo8	109.82(15)
O5-Mo4-O4	109.93(16)	Mo5-O17-Mo(6)[1]	108.91(14)
O6-Mo4-O7	108.24(17)	Mo8-O17-Mo(6)[1]	102.82(13)
O6-Mo4-O5	110.54(17)	Mo4-O7-Mo(1)[2]	132.19(17)

O6-Mo4-O4	109.93(17)	Mo4-O7-Mo(2)^{2}	130.55(17)
O(18)^{1}-Mo8-O16	70.87(11)	Mo(2)^{2}-O7-Mo(1)^{2}	88.37(11)
O17-Mo8-O16	72.82(12)	Mo4-O5-Mo2	129.91(17)
O17-Mo8-O(18)^{1}	71.66(12)	Mo4-O5-Mo3	128.99(17)
O14-Mo8-O16	77.22(13)	Mo2-O5-Mo3	87.51(11)
O14-Mo8-O(18)^{1}	84.49(13)	Mo2-O3-Mo1	123.30(18)
O14-Mo8-O17	146.39(14)	Mo3-O13-Mo(1)^{2}	121.84(18)
O24-Mo8-O16	98.18(14)	Mo8-O14-Mo7	118.64(17)
O24-Mo8-O(18)^{1}	165.79(14)	Mo5-O22-Mo(7)^{1}	117.38(17)
O24-Mo8-O17	96.79(15)	Mo4-O4-Mo1	130.35(17)
O24-Mo8-O14	102.27(16)	Mo4-O4-Mo(3)^{2}	130.23(18)
O23-Mo8-O16	157.11(14)	Mo1-O4-Mo(3)^{2}	88.43(11)
O23-Mo8-O(18)^{1}	86.24(14)	Mo3-O10-Mo2	124.06(18)
O23-Mo8-O17	101.00(16)	Mo6-O15-Mo7	117.60(18)
O23-Mo8-O14	100.67(17)	C14-N4-Cu1	124.9(4)
O23-Mo8-O24	104.49(17)	C14-N4-C13	106.4(4)
O3-Mo1-O(7)^{2}	71.06(13)	C13-N4-Cu1	128.7(4)
O3-Mo1-O(13)^{2}	143.26(15)	C15-N5-Cu1	127.3(4)
O3-Mo1-O4	80.46(13)	C15-N5-C17	103.6(5)
O(13)^{2}-Mo1-O(7)^{2}	78.21(13)	C17-N5-Cu1	129.0(4)
O(13)^{2}-Mo1-O4	72.47(13)	C27-N8-Cu2	130.2(4)
O4-Mo1-O(7)^{2}	75.15(12)	C28-N8-Cu2	124.0(4)
O1-Mo1-O(7)^{2}	90.01(16)	C28-N8-C27	105.2(5)
O1-Mo1-O3	101.11(17)	C31-N9-Cu2	130.9(4)
O1-Mo1-O(13)^{2}	98.48(16)	C31-N9-C30	105.3(4)
O1-Mo1-O4	163.80(16)	C30-N9-Cu2	123.7(3)
O2-Mo1-O(7)^{2}	164.01(16)	C31-N10-C32	125.8(4)
O2-Mo1-O3	100.99(17)	C31-N10-C29	107.8(4)
O2-Mo1-O(13)^{2}	103.36(17)	C29-N10-C32	126.1(4)
O2-Mo1-O4	90.03(16)	C28-N7-C25	125.5(4)
O2-Mo1-O1	105.34(19)	C28-N7-C26	106.4(5)
O16-Mo6-Mo5	41.81(8)	C26-N7-C25	128.1(5)
O16-Mo6-O(17)^{1}	71.37(11)	C42-N11-C39	125.4(7)
O18-Mo6-Mo5	34.88(9)	C42-N11-C41	108.9(6)
O18-Mo6-O16	73.03(12)	C41-N11-C39	125.6(7)
O18-Mo6-O(17)^{1}	70.67(12)	C14-N3-C11	125.2(5)
O(17)^{1}-Mo6-Mo5	78.68(8)	C14-N3-C12	107.1(4)
O15-Mo6-Mo5	119.26(11)	C12-N3-C11	127.7(5)
O15-Mo6-O16	77.45(13)	C1-N2-C2	108.5(5)
O15-Mo6-O18	145.35(14)	C1-N2-C4	125.3(6)
O15-Mo6-O(17)^{1}	83.08(14)	C2-N2-C4	126.2(5)
O19-Mo6-Mo5	135.21(14)	C15-N6-C18	128.0(6)
O19-Mo6-O16	160.18(15)	C15-N6-C16	106.6(5)
O19-Mo6-O18	100.40(16)	C16-N6-C18	125.3(6)

O19-Mo6-O(17)^{1}	88.82(15)	C1-N1-C3	108.2(6)
O19-Mo6-O15	101.28(17)	N10-C32-C35	112.4(4)
O20-Mo6-Mo5	85.14(14)	N9-C31-N10	110.9(5)
O20-Mo6-O16	94.05(16)	C34-C35-C32	120.3(5)
O20-Mo6-O18	97.94(17)	C34-C35-C36	118.0(5)
O20-Mo6-O(17)^{1}	163.39(16)	C36-C35-C32	121.7(5)
O20-Mo6-O15	101.90(19)	C22-C21-C25	120.4(5)
O20-Mo6-O19	105.5(2)	C20-C21-C22	118.3(5)
O(7)^{2}-Mo2-O5	76.07(11)	C20-C21-C25	121.3(5)
O3-Mo2-O(7)^{2}	72.60(13)	C23-C24-C19	119.4(5)
O3-Mo2-O5	78.39(13)	C23-C24-C18	120.2(6)
O3-Mo2-O10	143.65(15)	C19-C24-C18	120.5(6)
O10-Mo2-O(7)^{2}	79.80(13)	C24-C23-C22	120.8(6)
O10-Mo2-O5	72.26(13)	C35-C34-C33	121.1(5)
O8-Mo2-O(7)^{2}	88.29(14)	C23-C22-C21	120.3(5)
O8-Mo2-O5	163.47(14)	N6-C15-N5	112.4(5)
O8-Mo2-O3	102.25(17)	C42-N12-C40	110.8(6)
O8-Mo2-O10	100.06(17)	C30-C29-N10	106.4(5)
O9-Mo2-O(7)^{2}	166.62(16)	C29-C30-N9	109.5(5)
O9-Mo2-O5	91.60(16)	C10-C5-C6	120.9(5)
O9-Mo2-O3	100.14(17)	C26-C27-N8	108.7(5)
O9-Mo2-O10	101.63(17)	N8-C28-N7	112.3(5)
O9-Mo2-O8	104.42(18)	N7-C25-C21	112.0(5)
O14-Mo7-O16	72.97(12)	C24-C19-C20	119.5(6)
O14-Mo7-O(22)^{1}	77.82(13)	C5-C10-C11	120.5(6)
O(22)^{1}-Mo7-O16	69.27(11)	C5-C10-C9	119.0(5)
O15-Mo7-O16	73.91(13)	C9-C10-C11	120.4(5)
O15-Mo7-O14	144.09(15)	C21-C20-C19	121.8(6)
O15-Mo7-O(22)^{1}	77.84(14)	N4-C14-N3	110.9(5)
O25-Mo7-O16	95.52(18)	C5-C6-C7	120.2(5)
O25-Mo7-O14	96.80(18)	C12-C13-N4	108.6(5)
O25-Mo7-O(22)^{1}	164.73(19)	N3-C11-C10	111.6(5)
O25-Mo7-O15	99.82(18)	N1-C1-N2	108.4(6)
O26-Mo7-O16	159.69(18)	C8-C9-C10	120.0(5)
O26-Mo7-O14	103.59(18)	C27-C26-N7	107.4(5)
O26-Mo7-O(22)^{1}	90.41(19)	C7-C8-C9	121.6(6)
O26-Mo7-O15	102.59(19)	C36-C37-C38	119.9(5)
O26-Mo7-O25	104.8(2)	C6-C7-C4	120.4(5)
O13-Mo3-O5	80.40(14)	C8-C7-C6	118.2(5)
O13-Mo3-O(4)^{2}	72.72(13)	C8-C7-C4	121.3(6)
O13-Mo3-O10	143.89(14)	C37-C38-C39	116.7(5)
O(4)^{2}-Mo3-O5	77.57(11)	C33-C38-C37	119.5(5)
O10-Mo3-O5	72.15(13)	C33-C38-C39	123.8(5)
O10-Mo3-O(4)^{2}	78.72(13)	C3-C2-N2	106.0(6)

O11-Mo3-O5	87.77(16)	N2-C4-C7	111.8(5)
O11-Mo3-O13	99.83(17)	C38-C33-C34	119.9(5)
O11-Mo3-O(4)[2]	164.41(16)	N12-C42-N11	107.3(7)
O11-Mo3-O10	102.02(17)	N6-C18-C24	113.0(5)
O12-Mo3-O5	166.90(15)	C37-C36-C35	121.6(5)
O12-Mo3-O13	102.01(18)	C13-C12-N3	107.1(5)
O12-Mo3-O(4)[2]	90.77(15)	C2-C3-N1	108.9(6)
O12-Mo3-O10	99.98(17)	N11-C39-C38	113.6(5)
O12-Mo3-O11	104.33(19)	C16-C17-N5	110.6(6)
N(4)[3]-Cu1-N4	180.00(14)	C41-C40-N12	105.4(7)
N4-Cu1-N(5)[3]	89.68(16)	N6-C16-C17	106.8(6)
N4-Cu1-N5	90.32(16)	C40-C41-N11	107.6(8)

[1]-X,1-Y,2-Z; [2]1-X,-Y,1-Z; [3]1-X,1-Y,1-Z; [4]-X,-Y,2-Z

Table S3. A comparison of the proton conductivity (*σ*) of compound **1** with representative POMs-based proton-conductor.

Compounds	*σ* (S/cm)	RH (%)	Temperature (K)	Reference
Compound **1**	$\mathbf{1.02{\times}10^{-2}}$	90	353	-
$[NH_2(CH_3)_2]_{16}KH_7[\{Zr(tarH)O_2\}_4\{As_2W_{19}O_{68}\}_2]\cdot 16H_2O$	3.82×10^{-3}	95	348	3
$K_{11}Eu[KP_5W_{30}O_{110}]\cdot 30H_2O$	2.0×10^{-3}	75	368	4
$Na_8K_{14}H_{10}[Co_{26}@Nb_{36}]\cdot nH_2O$	5.59×10^{-6}	98	348	5
$Li_7KNa_{11}H_6[Si_2Ta_{24}(O_2)_{20}O_{52}(OH)_9]\cdot 85H_2O$	3.63×10^{-3}	95	348	6
$Na_3(H_3O)_2[(HPW_6O_{21})(O_2CC_6H_4NH_2)_3]\cdot 7H_2O$	1.57×10^{-2}	95	368	7
$Cs_{15}(NH_4)[(SiW_9Nb_3O_{40})_4(Mo_4O_6)]\cdot 42H_2O$	1.16×10^{-2}	98	358	8
$[Fe(H_2O)_6]_{14}[W_{72}Fe_{30}O_{252}(H_2O)_{72}(OH)_{60}]\cdot 166H_2O$	1.71×10^{-2}	98	353	9
$K_{11}Li[P_2W_{12}(TaO_2)_6O_{56}]\cdot 19H_2O$	1.13×10^{-2}	90	368	10
$H_7Na_5[Pd(SO_3)_2]_3[Te_4(OH)_2W_6O_{28}]\cdot 20H_2O$	5.8×10^{-3}	98	358	11
$K_{72}[Bi_8(Mo_2O_2S_2)_{24}(HEDP)_{36}]\cdot 500H_2O$	1.83×10^{-2}	95	303	12
$H[Ce(H_2O)_4]_2[MnV_{13}O_{38}]\cdot 9NMP\cdot 17H_2O$	4.68×10^{-3}	97	334	13
$K_{11}Eu[KP_5W_{30}O_{110}]\cdot 30H_2O$	8.3×10^{-3}	75	368	14
$(C_3N_2H_5)_{29}(NH_4)_6H_{12}[(PMo_8O_{27})_8(C_{10}P_4O_{12}N_2H_2O)_4(PO_4)_4Cs(Mo_4O_{10}(H_2O)_4)$	9.70×10^{-3}	98	373	15
$[Ni(Bip)_2(H_2O)_2(\gamma\text{-}Mo_8O_{26})]\cdot 3H_2O$ (CUST-862)	1.97×10^{-3}	98	363	16

Note: The test conditions (temperature, humidity) for different materials vary. The comparison is for reference only.

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