Supplementary Information

{Mo$_4$}-Directed Structural Evolution of Highly Reduced Molybdenum Red Clusters for Efficient Proton Conduction

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Contents

1. Materials

K_2MoO_4 and CH_3COONa were purchased from Adamas, $Na_2MoO_4 \cdot 2H_2O$ was purchased from Sinopharm, Hydrazine dihydrochloride was purchased from Bide Pharmatech Ltd. All reagents were of A.R. grade and used without further purification.

2. Instrumentation

Crystallography: The crystallographic data of compounds were collected using a Bruker D8 venture single crystal diffractometer equipped with a CCD area detector at 1500 W power (50 kV, 30 mA) to generate Mo-Kα radiation (λ=0.71073 Å) at 150 K. The structures were solved by the direct methods and refined with OLEX 2-1.5[1]. All non-hydrogen atoms are anisotropically refined by the least square method except for the guest water molecules. CCDC-2325444 (**1**), CCDC-2325445 (**2**), CCDC-2325443 (**3**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Element Analyses: Element analyses were determined by VARIDEL III Elemental Analyzer.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): Elemental analyses for Mo, Na and K were determined with a Leeman Prodigy Plus inductivity-coupled plasma Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a METTLER TOLEDO TG8000 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of 10 °C·min^{-1}.

Powder X-ray Diffraction (PXRD): Powder XRD of **1**was recorded on a Haoyuan DX-2700B diffractometer equipped with monochromatized Cu-Kα (λ = 1.5418 Å) radiation in the range of $5° \leq 2\theta \leq 50°$, with a scanning rate of 0.02 °s^{-1}. Powder XRD patterns of **2** and **3**were obtained

on D8 Advance diffractometer using Cu Kα radiation (2θ = 5-50°).

Fourier-transform infrared (FT-IR) spectroscopy: The samples were prepared as a KBr pellet and the FT-IR spectrum was collected in transmission mode in the range of 500-4000 cm^{-1} using a NEXUS-670 spectrometer. Wavenumbers are given in cm^{-1}. Intensities are denoted as w = weak, m = medium, s = strong, vs = very strong, br = broad.

Solid-state UV-Vis absorption spectroscopy: All compounds were prepared into powders, which were tested in wavelength mode by integrating sphere attachment in UV3600 UV-Vis spectrometer.

Water adsorption: Water vapor adsorption isotherms were measured at 298.15 K on a BSD-660M A6B6M adsorptometer (Beishide Instruments).

Proton conductivity characterization: The AC impedance test is performed at the electrochemical workstation (CHI 760E) in a standard three-electrode system, with a frequency range of 0.1 Hz-106 Hz and an AC voltage of 50 mV, to test the proton conductivity of **1**, **2** and **3**. As a result of the impedance data being equivalent to the ZSimpWin software, a Nyquist graph can be generated. Measurements were performed at: (1) 25 °C and various humidities (53%-98% RH); (2) 98% RH and various temperatures (25 °C - 70 °C). The proton conductivity was calculated using the following equation.

$$\sigma = \frac{L}{SR}$$

where σ is the ion conductivity, L is the thickness, R is the resistance of the pellet, and S is the area of the pellet. Activation energy (E_a) can be calculated using the formula.

$$\sigma T = \sigma_0 exp(-E_a/k_B T)$$

where σ_0 is the pre-exponential factor, k_B is the Boltzmann constant, and T is the temperature.

3. Synthesis

Synthesis of $K_6Na_8H_2[Mo^V_{12}Mo^{VI}_{16}O_{84}]\cdot30H_2O$ (1).

K_2MoO_4 (0.476 g, 2 mmol) and $N_2H_4\cdot2HCl$ (0.011g 0.1mmol) were added to a solution of CH_3COONa (0.328 g, 4 mmol) in water (3.5 mL). The mixture was then acidified to pH 6.35 with 6 M HCl and stirred for over 30 min. Subsequently, the Mo-containing aqueous solution was transferred to a 10 mL glass vial, which was heated to 80 °C and kept for three days. The reaction mixture was filtered, the filtrate was collected and was kept in an open 15 ml beaker for about two days. The dark red crystals were collected and washed with acetonitrile. Yield: 26 mg (20 % based on Mo). IR (cm^{-1}): 3297(br), 1628 (m), 1552 (m), 1404 (s), 1448 (m), 950 (s), 866 (m), 737 (s), 704 (m), 637 (s), 548 (w). Elemental analysis % calc (found) of **1**: H 1.25 (1.29); K 4.70 (4.58); Na 3.68 (3.72); O 36.54 (36.66); Mo 53.82 (53.75).

Synthesis of $Na_8H_6[Mo^V_{24}Mo^{VI}_6(OH)_{10}O_{80}]\cdot36H_2O$ (2) and
$Na_{14}H_6[Mo^V_{32}Mo^{VI}_8(OH)_{12}O_{108}]\cdot50H_2O$ (3).

Na_2MoO_4 $2H_2O$ (0.484 g, 2 mmol) and $N_2H_4\cdot2HCl$ (0.026g 0.25mmol) were added to a solution of CH_3COONa (0.328 g, 4 mmol) in water (3.5 mL). The mixture was then acidified to pH 6.50 with 6 M HCl and stirred for over 30 min. Subsequently, the Mo-containing aqueous solution was transferred to a 10 mL glass vial, which was heated to 80 °C and kept for two days. On concentration of the mixture, several fractions precipitated: first, a yellow precipitate, then red rod crystals of **2**, followed by dark red diamond crystals of **3**. The mixture was washed several times with isopropanol aqueous solution, and finally dried over air. The individual crystal fractions could only be separated mechanically from one another. Yield: 135 mg (ca. 65% **2** and ca. 35% **3**). IR of **2** (cm^{-1}): 3437 (br), 1621 (m), 1411 (w), 1066 (w), 946 (vs), 889 (w), 835 (w), 744 (m), 701 (m), 578 (w). IR of **3** (cm^{-1}): 3325 (br), 1629 (s), 1551 (m), 1413 (w), 939 (vs), 825 (s), 721 (m), 692 (m), 634 (w), 574 (w). Elemental analysis % calc (found) of **2**: H 1.72 (1.75); Na 3.56 (3.26); O 39.02 (39.27); Mo 55.71 (55.72). Elemental analysis % calc (found) of **3**: H 1.82 (1.79); Na 3.33 (3.42); O 39.34 (39.17); Mo 55.51 (55.62).

4. Crystallographic data and crystal structures of 1-3

Table S1 Crystallographic Details for **1**

Compound	1
Empirical formula	$K_6Na_8H_{106}Mo_{28}O_{136}$
Formula weight	5386.66
Crystal system	Triclinic
Space group	P-1
a/Å	11.4876(3)
b/Å	17.1451(6)
c/Å	32.3504(11)
α/°	103
β/°	93
γ/°	102
V/Å^3	6010.1(3)
Z	2
ρ_{calc}/g·cm^{-3}	2.975
μ(MoKα) /mm^{-1}	3.185
F(000)	5138
2θ range /°	1.958 to 25.349°
Index ranges	-13<=h<=13 -20<=k<=20 -38<=l<=38
Reflections collected	134317
Data / restraints / parameters	21788 / 6 / 1559
R_1/wR_2 (I>2σ(I))[a]	0.0398/0.0950
R_1/wR_2 (all data)	0.0532/0.1053
GooF (all data)[b]	1.018
Data completeness	99.0 %

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; w$R_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$
[b] GooF = $\{\sum w[(F_o)^2-(F_c)^2]^2/(n-p)\}^{1/2}$

Table S2 Crystallographic Details for **2**

Compound	**2**
Empirical formula	$Na_8H_{106}Mo_{30}O_{135}$
Formula weight	5328.91
Crystal system	Triclinic
Space group	*P*-1
a/Å	17.5249(13)
b/Å	19.2536(17)
c/Å	20.5386(19)
α/°	117
β/°	92
γ/°	90
V/Å^3	6139.8(9)
Z	2
ρ_{calc}/g·cm^{-3}	2.860
μ(MoKα) /mm^{-1}	3.105
$F(000)$	5016
2θ range /°	1.978 to 25.426°
Index ranges	-21<=h<=20 -23<=k<=23 -24<=l<=24
Reflections collected	145349
Data / restraints / parameters	22517 / 2734 / 1495
R_1/wR_2 (I>2σ(I))[a]	0.0957 / 0.1974
R_1/wR_2 (all data)	0.1087 / 0.2036
GooF (all data)[b]	1.117
Data completeness	99.7 %

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; w$R_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$
[b]GooF $= \{\sum w[(F_o)^2-(F_c)^2]^2/(n-p)\}^{1/2}$

Table S3 Crystallographic Details for **3**

Compound	3
Empirical formula	$Na_{14}H_{140}Mo_{40}O_{181}$
Formula weight	7196.52
Crystal system	Tetragonal
Space group	$I4_1/amd$
a/Å	20.542(4)
b/Å	20.542(4)
c/Å	41.600(8)
α/°	90
β/°	90
γ/°	90
V/Å^3	17548(6)
Z	4
ρ_{calc}/g·cm^{-3}	2.701
μ(MoKα) /mm^{-1}	2.906
$F(000)$	13544
2θ range /°	1.958 to 27.528°
Index ranges	-24<=h<=21 -24<=k<=24 -49<=l<=50
Reflections collected	86489
Data / restraints / parameters	4283 / 23 / 337
R_1/wR_2 (I>2σ(I))[a]	0.0482 / 0.1238
R_1/wR_2 (all data)	0.0585 / 0.1298
GooF (all data)[b]	1.135
Data completeness	99.9 %

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; w$R_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$
[b]GooF $= \{\sum w[(F_o)^2-(F_c)^2]^2/(n-p)\}^{1/2}$

Bond valence calculations were performed for each bond using the bond distance (R) measured and empirical parameters R_0 and B: bond valence = $EXP((R_0-R)/B)$. BVS for each metal centre was then summed from all bond valences of the bonds listed. The parameters R_0 and B were taken from Gagne & Hawthorne. Mo(6+) and Mo(5+) centres were calculated separately using corresponding parameters listed below.

Parameter list:

Bond	R_0	B
Mo(6+)-O	1.903	0.349
Mo(5+)-O	1.888	0.314

Table S4. BVS values for Mo atoms in compound **1**.

Atom	BVS value	Atom	BVS value	Atom	BVS value	Atom	BVS value
Mo1	4.970	Mo2	5.022	Mo3	4.895	Mo4	4.881
Mo5	5.032	Mo6	4.941	Mo7	4.915	Mo8	4.829
Mo9	4.903	Mo10	4.971	Mo11	4.945	Mo12	4.868
Mo13	4.091	Mo14	4.928	Mo15	4.882	Mo16	4.910
Mo17	5.849	Mo18	5.931	Mo19	5.889	Mo20	5.902
Mo21	6.031	Mo22	5.931	Mo23	6.010	Mo24	5.786
Mo25	5.954	Mo26	6.075	Mo27	5.984	Mo28	5.795

Table S5. BVS values for Mo atoms in compound **2**.

Atom	BVS value	Atom	BVS value	Atom	BVS value	Atom	BVS value
Mo1	4.780	Mo2	4.841	Mo3	5.149	Mo4	4.931
Mo5	4.813	Mo6	5.100	Mo7	4.731	Mo8	4.914
Mo9	5.036	Mo10	4.914	Mo11	5.126	Mo12	4.900
Mo13	4.904	Mo14	5.044	Mo15	4.807	Mo16	4.879
Mo17	4.795	Mo18	4.999	Mo19	4.902	Mo20	4.995
Mo21	4.870	Mo22	5.019	Mo23	4.996	Mo24	4.979
Mo25	5.784	Mo26	5.661	Mo27	5.755	Mo28	5.603
Mo29	5.642	Mo30	5.696				

Table S6. BVS values for Mo atoms in compound **3**.

Atom	BVS value	Atom	BVS value	Atom	BVS value	Atom	BVS value
Mo1	5.815	Mo2	4.974	Mo3	4.848	Mo4	4.774
Mo5	4.949	Mo6	5.720				

Table S7. The BVS calculation results of all the protonated oxygen atoms in **2**.
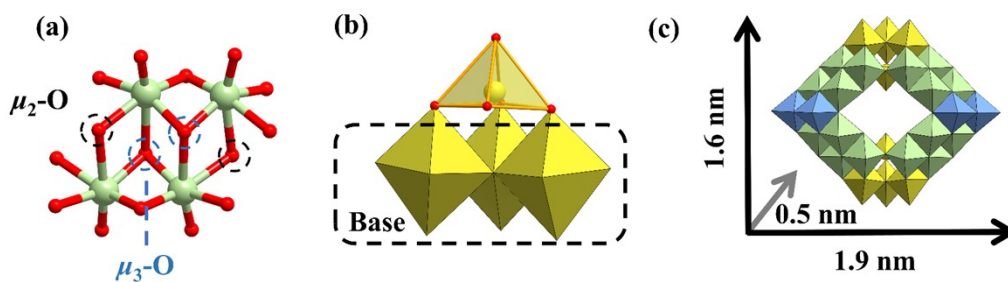
Oxygen Code	BVS value	Oxygen Code	BVS value
O4	1.087	O51	1.061
O6	1.272	O53	1.122
O8	0.988	O58	1.114
O15	1.040	O60	1.205
O17	1.173	O75	1.007

Table S8. The BVS calculation results of all the protonated oxygen atoms in **3**.

Oxygen Code	BVS value	Oxygen Code	BVS value
O9	1.240	O13	0.929

Fig. S1 (a) The ball-and-stick representation of $\{Mo^V_4\}$ unit; (b) The polyhedral representation of $\{Mo^{VI}_4\}$ unit, (c) the outer dimensions of **1** at its most extended points.
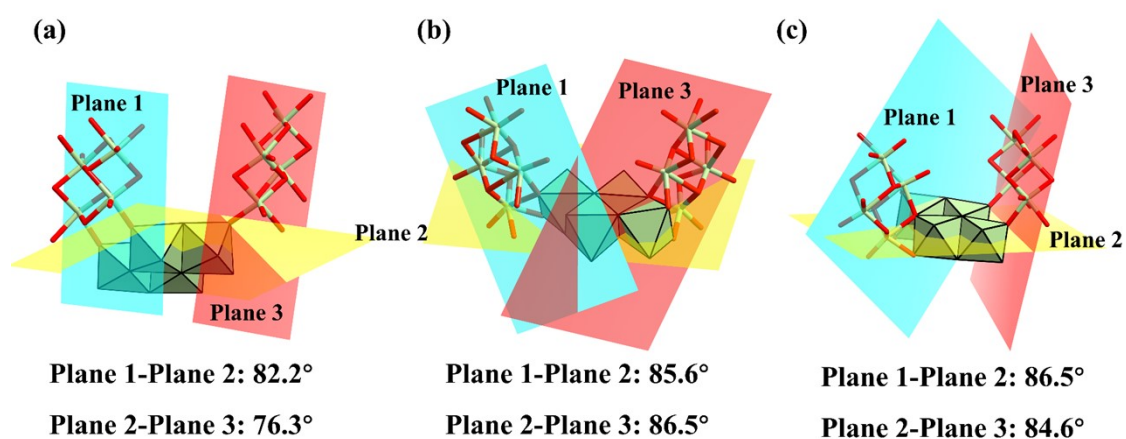
Fig. S2 Combined polyhedral/ball-and-stick representations of the dihedral angle between neighboring planar $\{Mo^V_4\}$ and central $\{Mo^V_4\}$ BBs in **1** (a), **2** (b), and **3** (c).
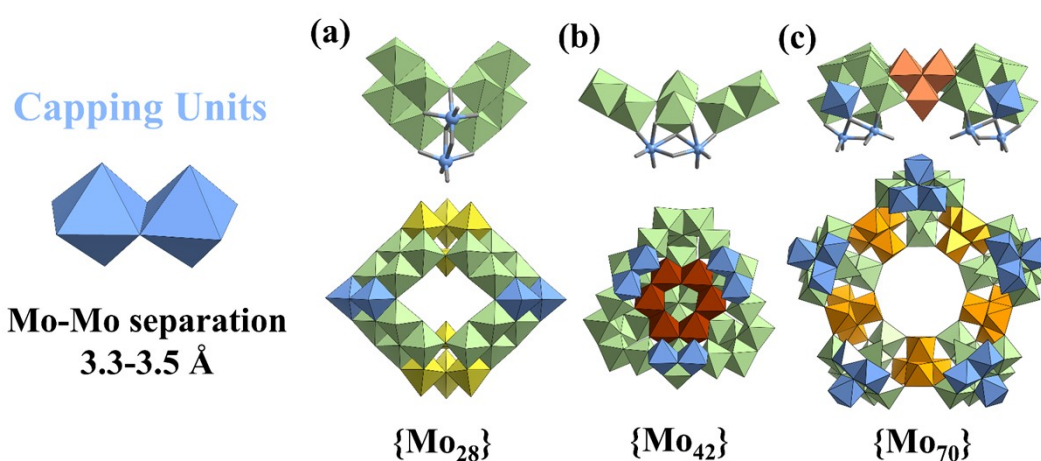
Fig. S3 The capping units in $\{Mo_{28}\}$, $\{Mo_{42}\}$, $\{Mo_{70}\}$. Color code: lime, Mo^V; light blue and yellow, Mo^{VI}; brown, cyclic $\{Mo_6\}$; orange, cross-shaped $\{Mo_4\}$.
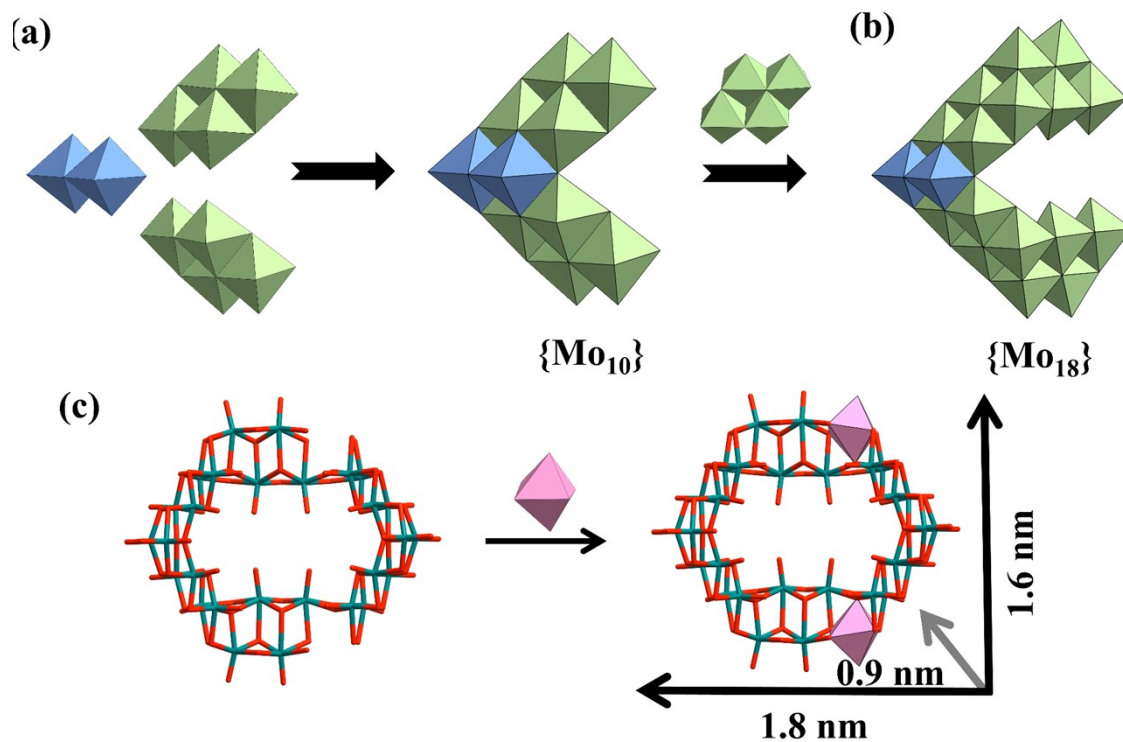
Fig. S4 The polyhedral representation of the assembly diagram of {Mo$_{10}$} (a) and {Mo$_{18}$} motifs (b); (c) the spatial position of {Mo$_1$} add-on units and outer dimensions of **2**.
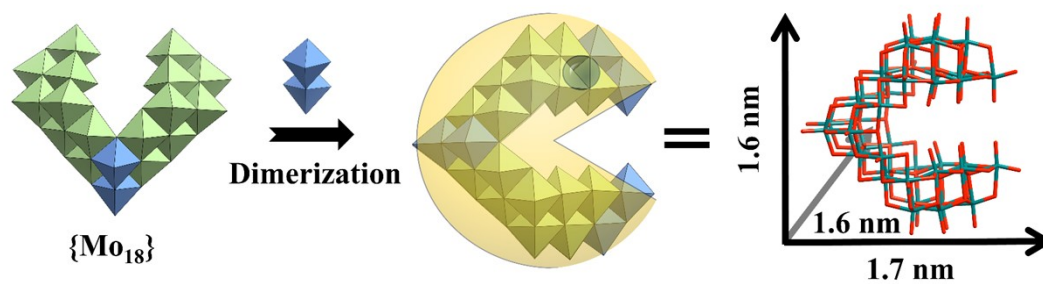
Fig. S5 The outer dimension of PAC-MAN-shaped **3** at its most extended points.
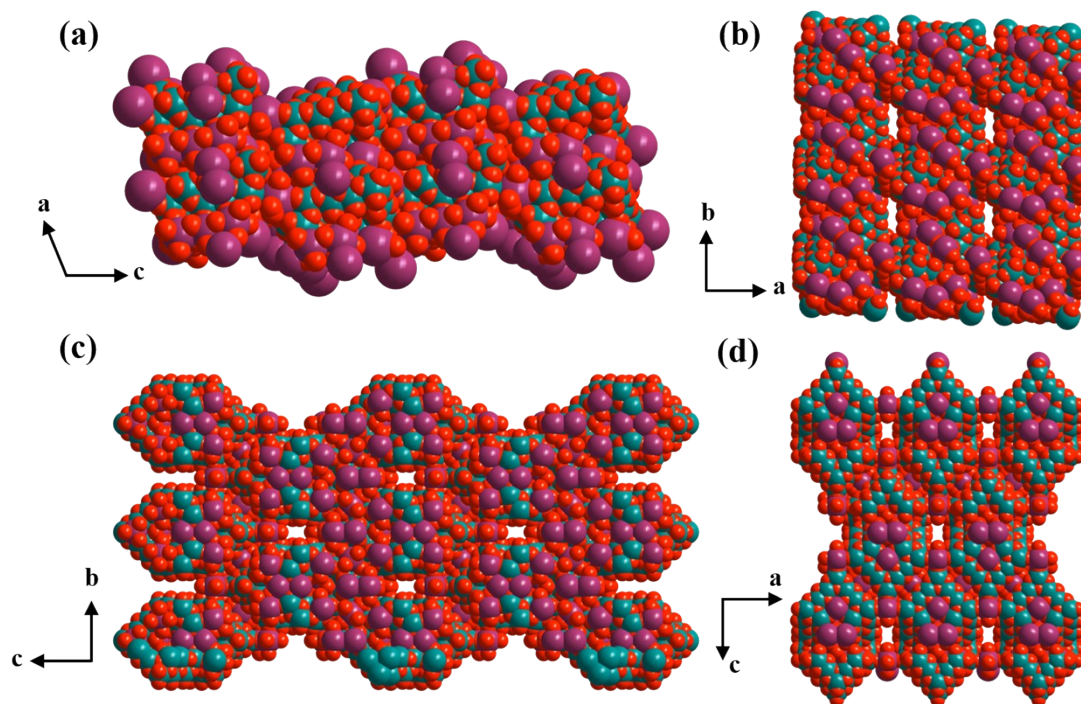
Fig. S6 (a) Packing model of **1** along the b-axis; (b) Packing model of **2** along the c-axis; (c) Packing model of **3** along the a-axis; (d) Packing model of **3** along the b-axis

5. PXRD spectra of 1-3
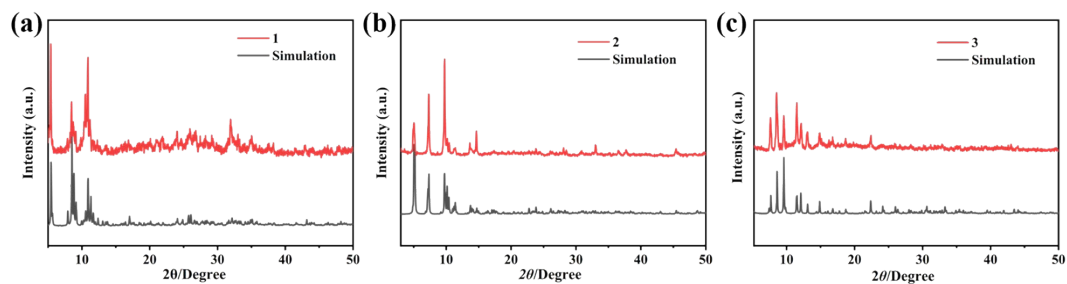
Fig. S7 Experimental and simulated PXRD patterns of **1-3**.

6. TGA results of 1-3
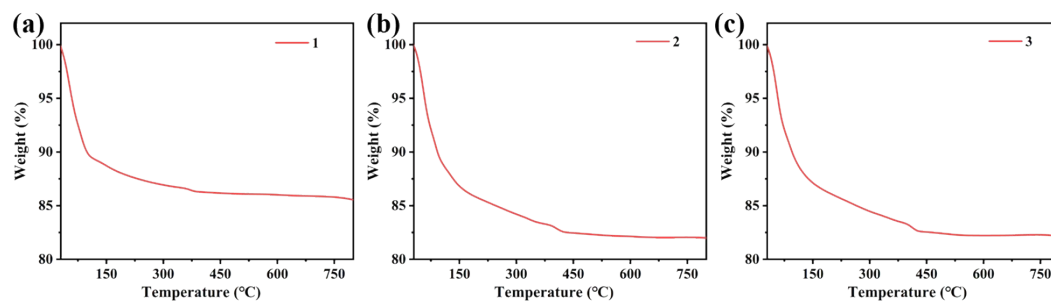
Fig. S8 TGA curves for **1-3**.

7. FT-IR spectra of 1-3
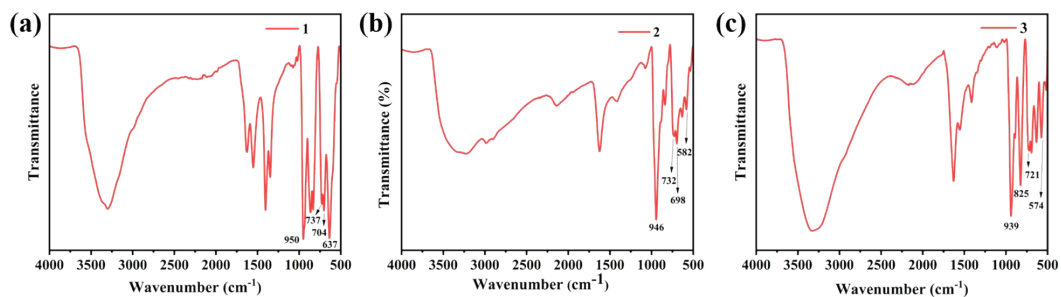
Fig. S9 The FT-IR spectra of **1-3**.

8. Raman spectra of 1-3
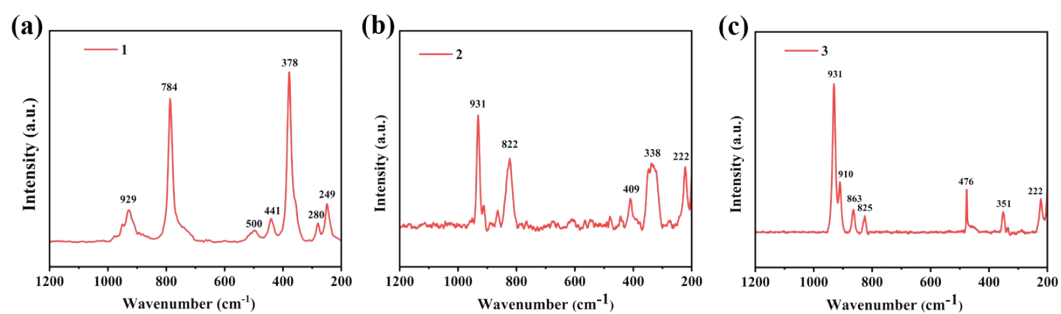
Fig. S10 The Raman spectra of **1-3**.

9. X-ray photoelectron spectra (XPS) of 1-3
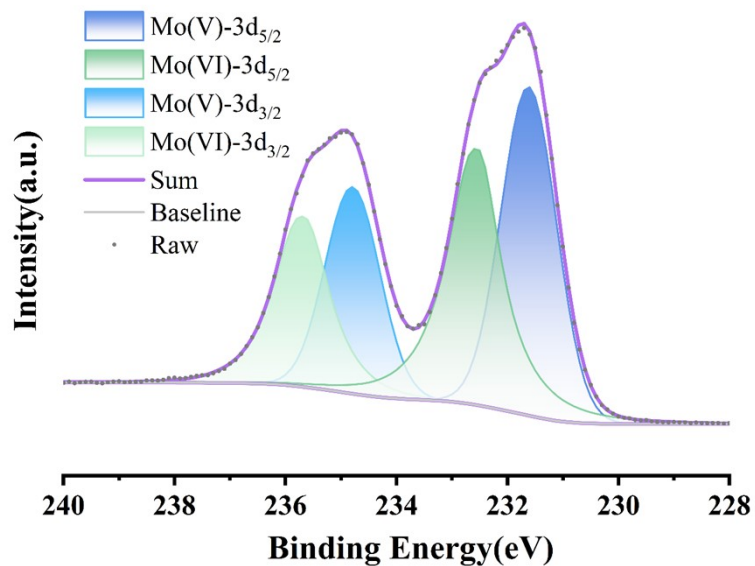
Fig. S11 X-ray photoelectron spectrum of Mo in **1.**
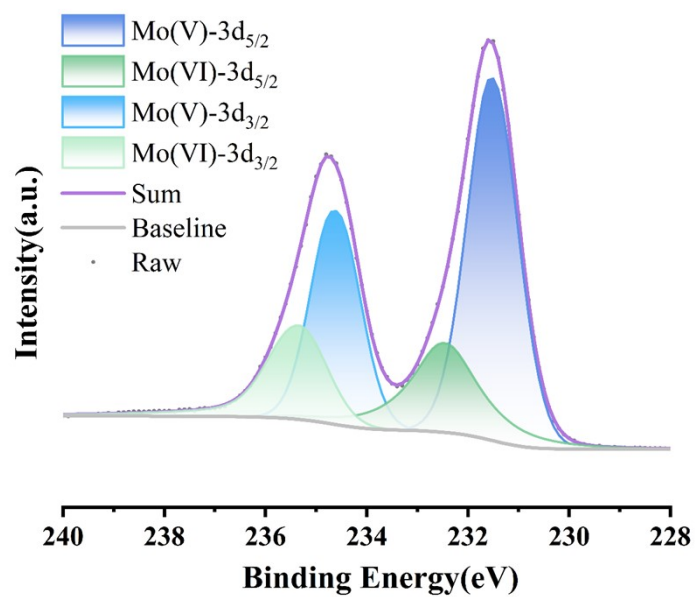
Fig. S12 X-ray photoelectron spectrum of Mo in **2.**
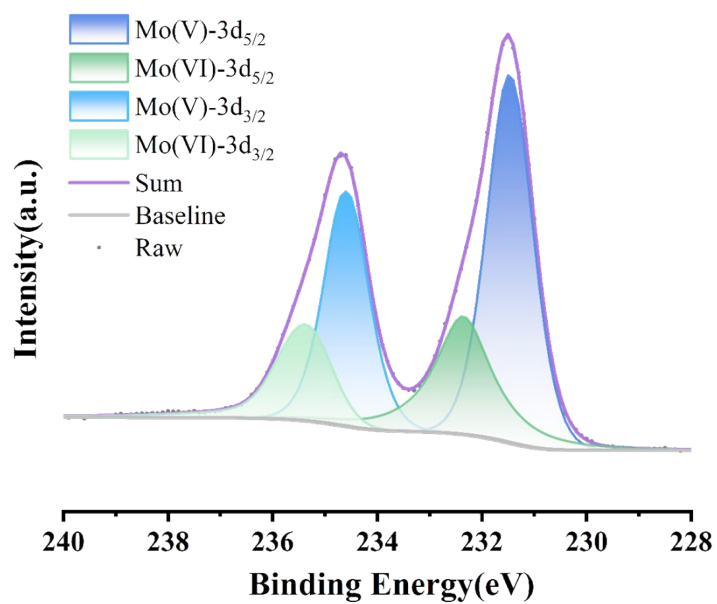
Fig. S13 X-ray photoelectron spectrum of Mo in **3.**

10. UV-Vis spectra of 1-3
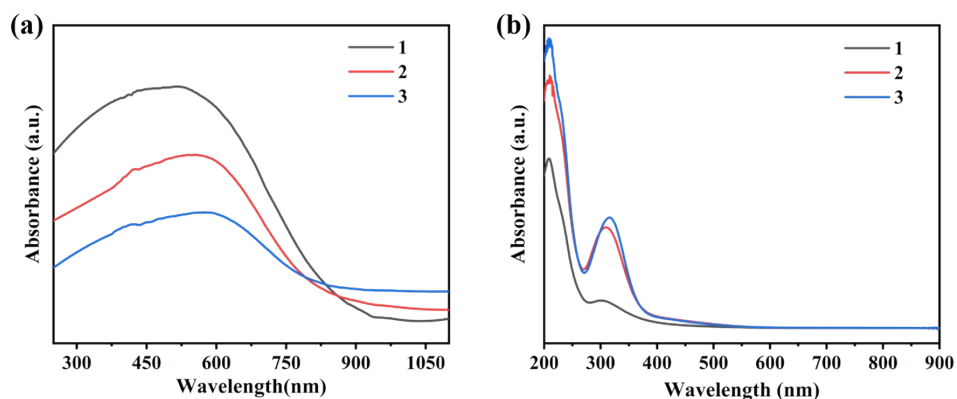
Fig. S14 The Solid (left) and liquid (right) UV-Vis spectra of **1-3**.

11. Proton Conduction Results of 1-3

Table S9 Resistance (R) and proton conductivity (σ) of **1** under different relative humidities and 25°C.

| RH (%)	R (Ω)	σ (S cm^{-1})
53	2.35×10^7	2.17×10^{-8}
68	8.57×10^6	5.95×10^{-7}
75	1.67×10^5	3.05×10^{-6}
85	1.32×10^4	2.44×10^{-5}
98	8.14×10^2	6.27×10^{-4}
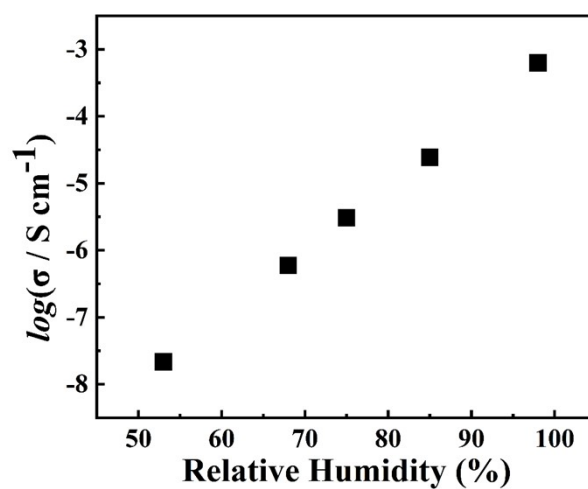
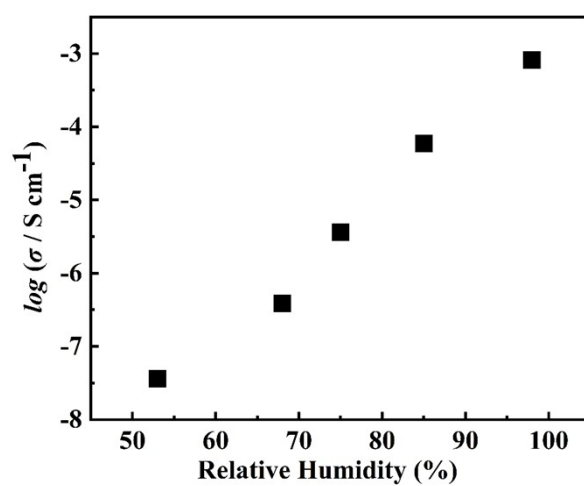**Fig. S15** The scatter plot of the relationship between proton conductivity of compound **1** and different humidities at 25°C.

Table S10 Resistance (R) and proton conductivity (σ) of **2** under different relative humidities and 25°C.

RH (%)	R (Ω)	σ (S cm^{-1})
53	1.56×10^7	3.28×10^{-8}
68	2.49×10^6	2.05×10^{-7}
75	3.52×10^5	1.45×10^{-6}
85	6.86×10^3	7.44×10^{-5}
98	7.06×10^2	7.23×10^{-4}
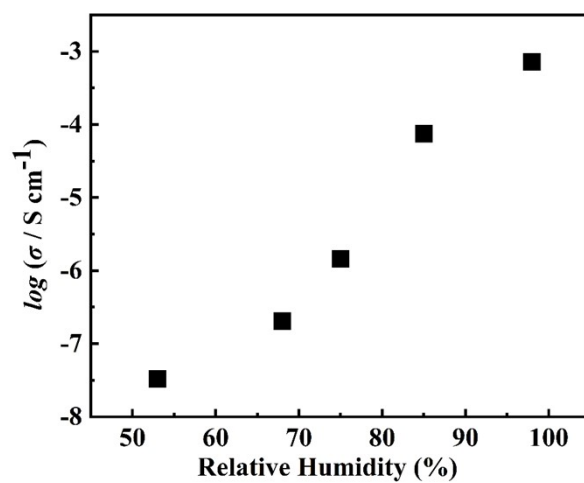
Fig. S16 The scatter plot of the relationship between proton conductivity of compound **2** and different humidities at 25°C.

Table S11 Resistance (R) and proton conductivity (σ) of **3** under different relative humidities and 25°C.

RH (%)	R (Ω)	σ (S cm^{-1})
53	1.40×10^7	3.64×10^{-8}
68	1.32×10^6	3.86×10^{-7}
75	1.41×10^5	3.63×10^{-6}
85	8.68×10^3	5.88×10^{-5}
98	6.25×10^2	8.16×10^{-4}

Fig. S17 The scatter plot of the relationship between proton conductivity of compound **3** and different humidities at 25°C.

12. Water adsorption–desorption isotherms of 1-3
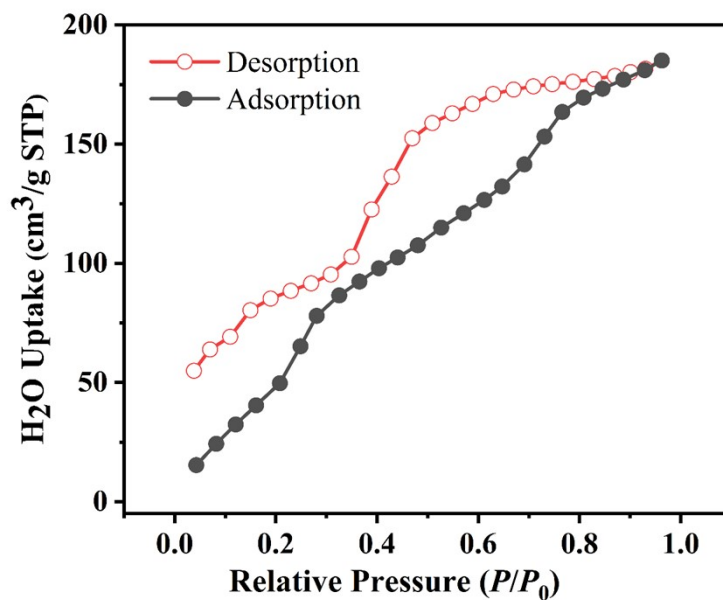
Fig. S18 Water vapor sorption isotherms of **1**.
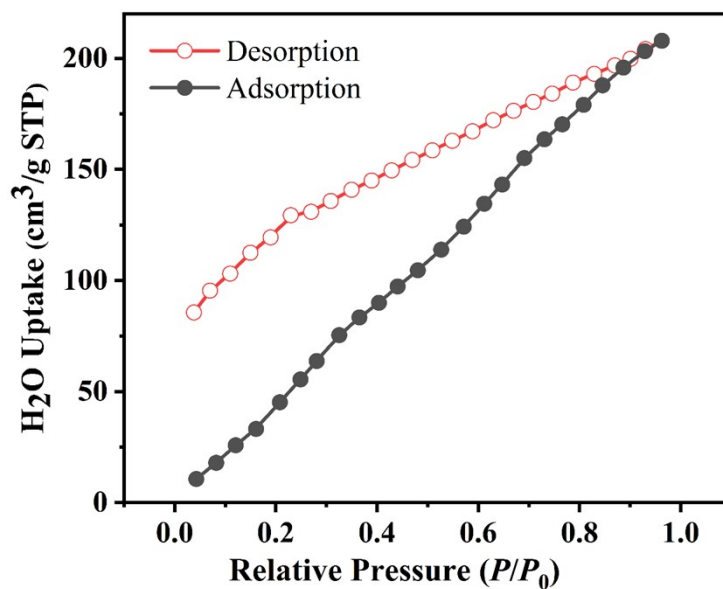
Fig. S19 Water vapor sorption isotherms of **2**.
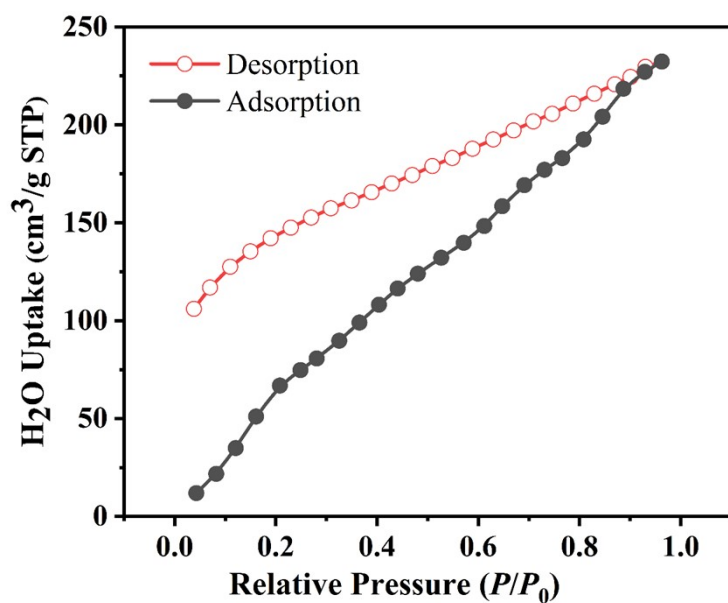
Fig. S20 Water vapor sorption isotherms of **3**.

13. FT-IR spectra of 1-3 after measurement
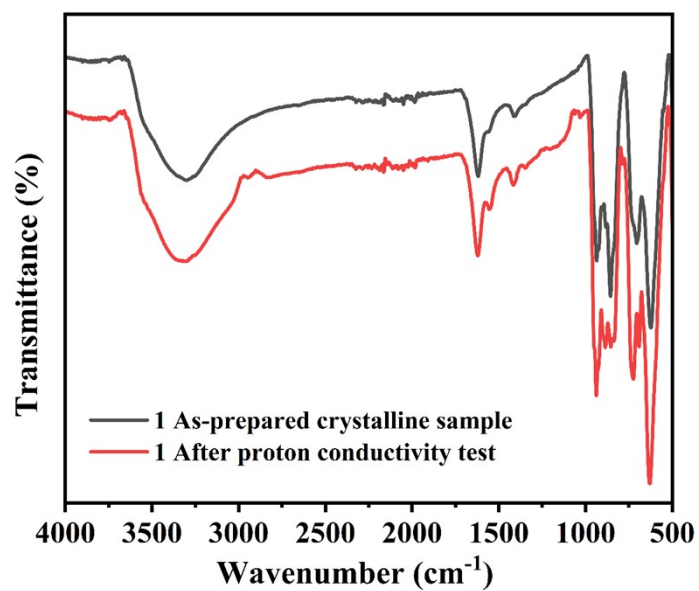

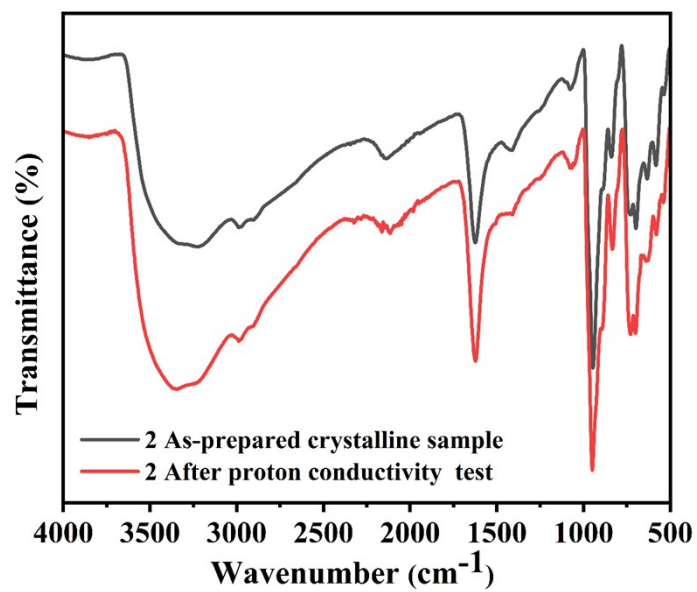**Fig. S21** FT-IR spectra of **1** before and after measurement.
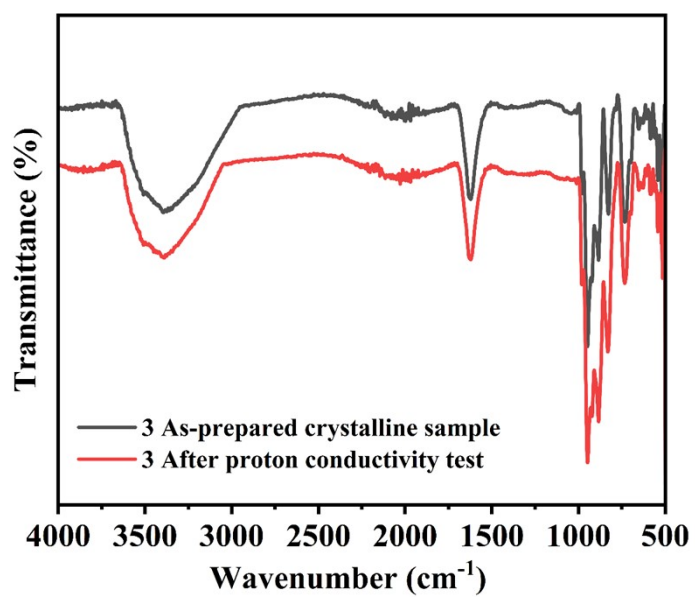
Fig. S22 FT-IR spectra of **2** before and after measurement.

Fig. S23 FT-IR spectra of **3** before and after measurement.
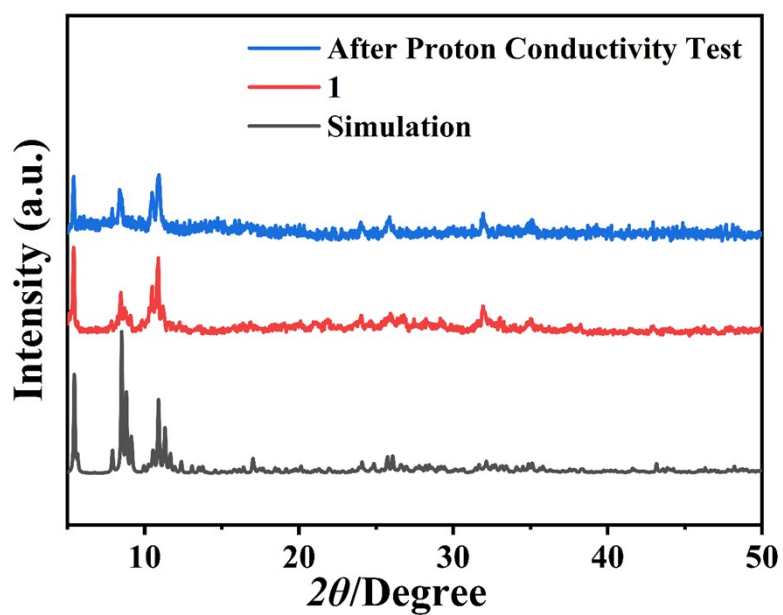
14. XRD spectra of 1-3 after measurement

Fig. S24 XRD spectra of **1** before and after measurement.
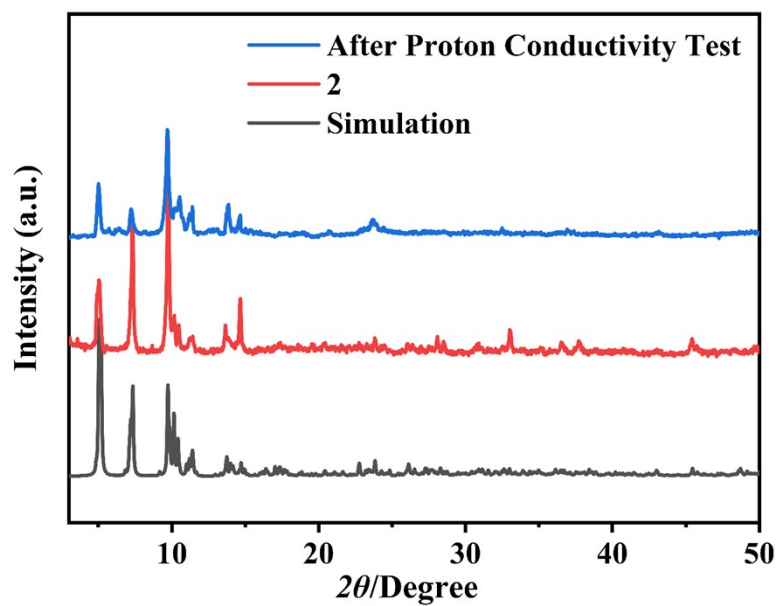

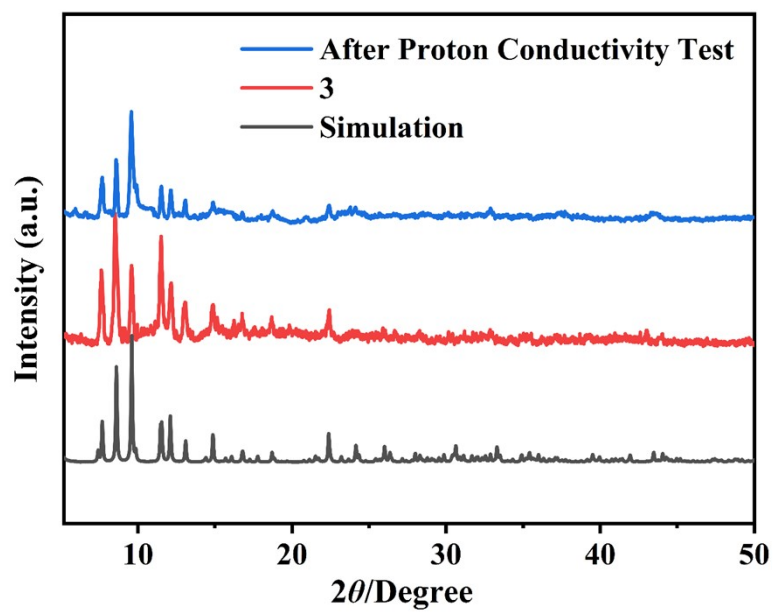**Fig. S25** XRD spectra of **2** before and after measurement.

Fig. S26 XRD spectra of **3** before and after measurement.

15. References

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. "OLEX2:

a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* 2009,**42**,

339-341.