

CsCl-type inorganic cluster-based high-symmetry crystal built from $\{\text{Mo}_{4.55}\text{V}_{7.45}\text{PO}_{40}\}^{10.45-}$ with high ratio of vanadium to molybdenum and $\{(\text{H}_2\text{O})_{0.3}@\text{K}_6(\text{H}_2\text{O})_{12}\}^{6+}$ clusters exhibiting proton conduction below the freezing point of water

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References

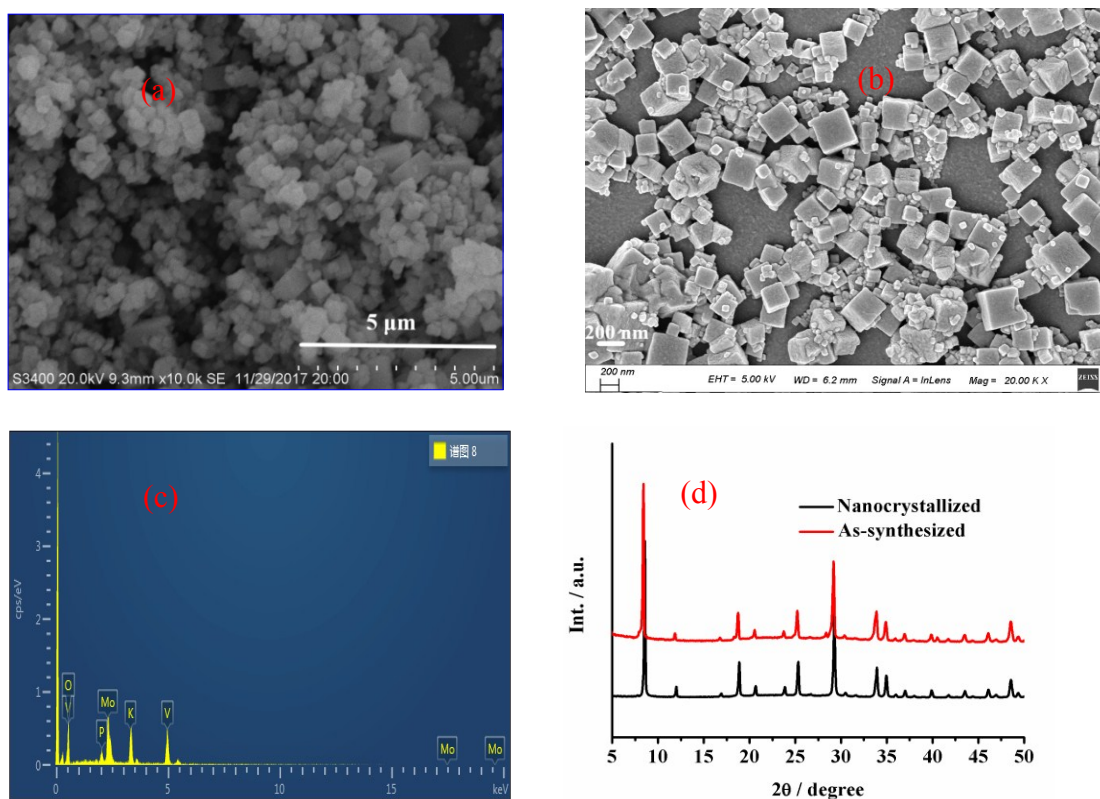


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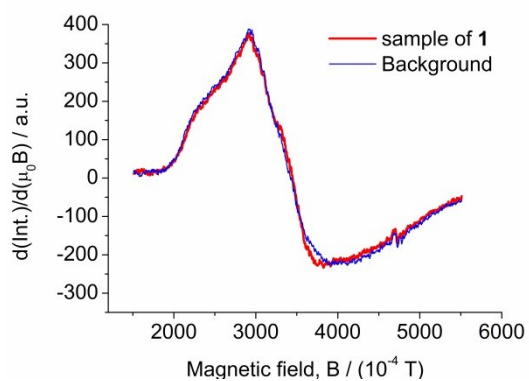


Figure S2: EPR spectrum of **1** at ambient temperature.

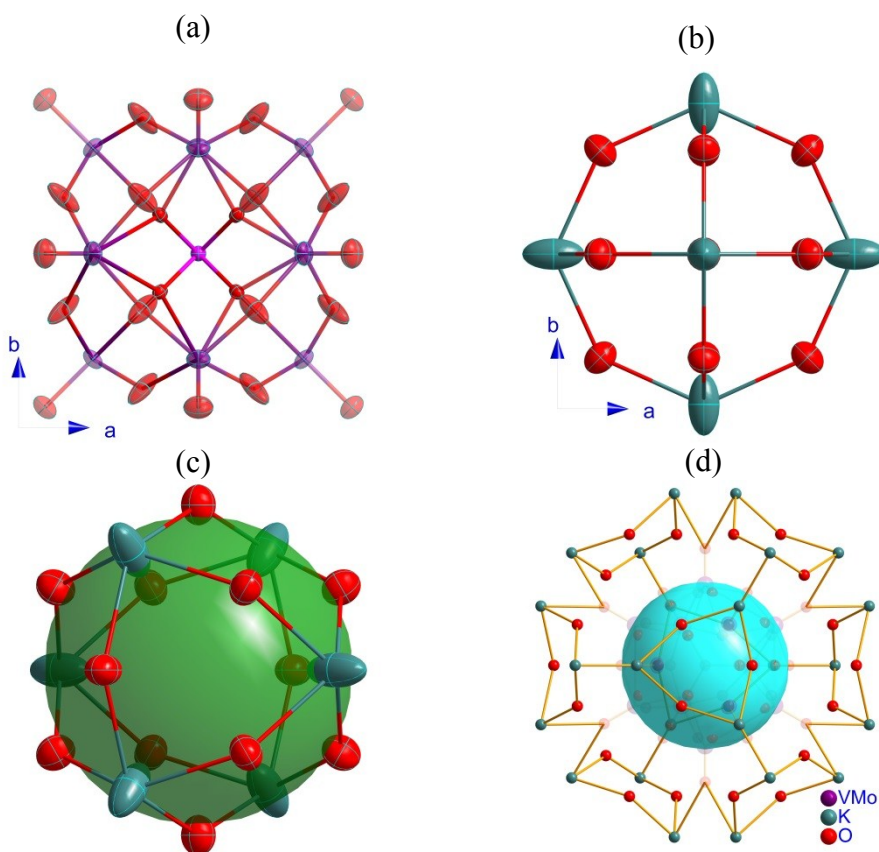


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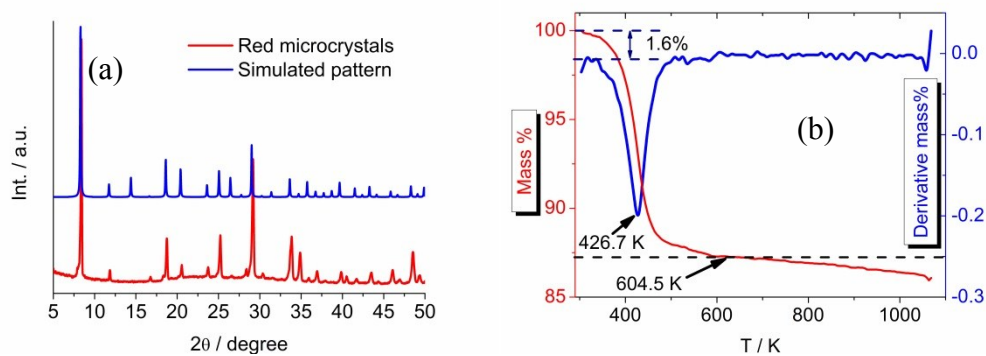


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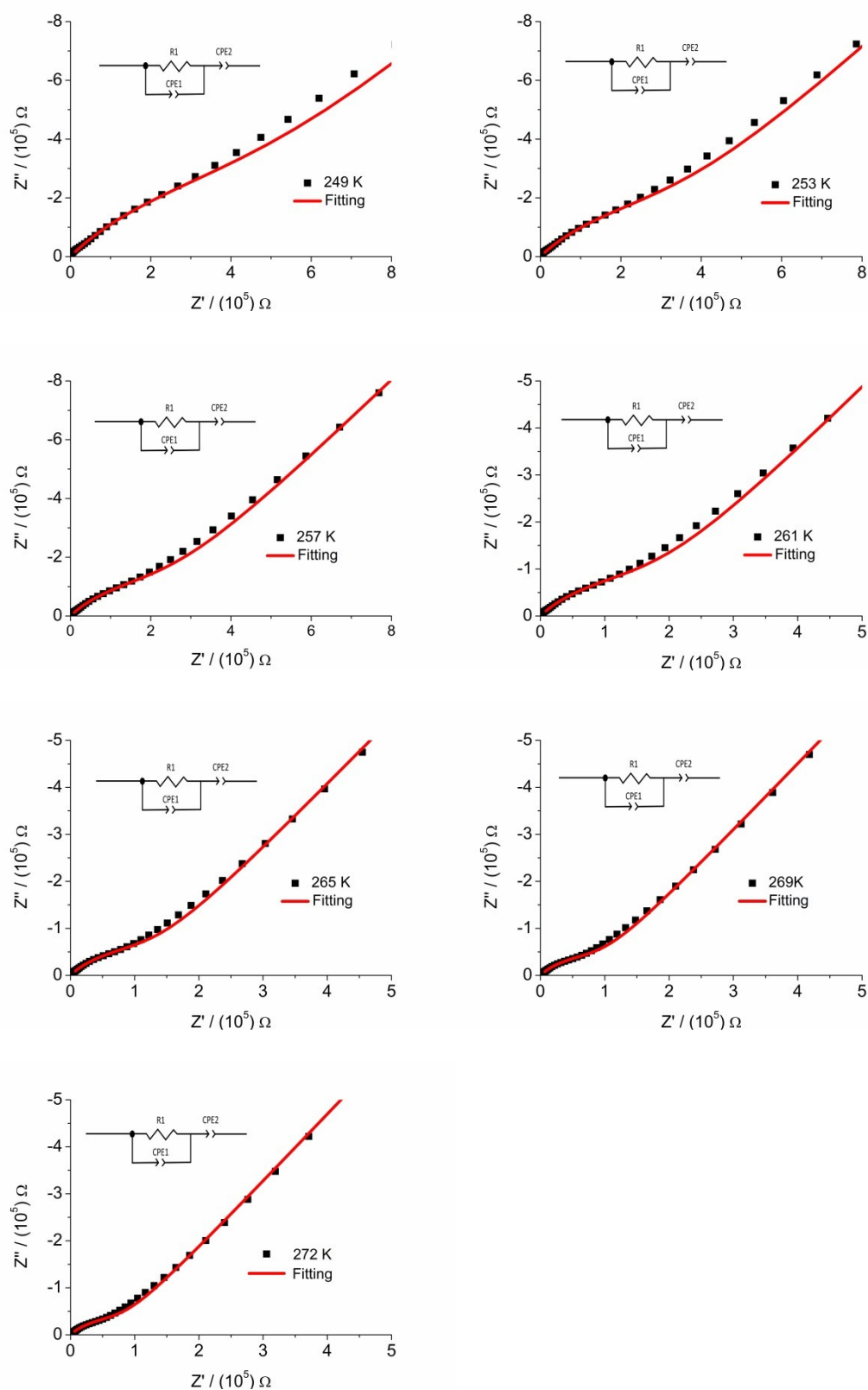


Figure S5: Experimental and fitted impedance spectra of **1** at the selected temperatures (Inset: the equivalent circuit).

Table S1: Selected bond lengths (Å) in **1**

MoV1-O1	2.412(14)	K1-O3#4	2.911(15)	P1-O1#1	1.57(3)
MoV1-O1#1	2.412(14)	K1-O3#5	2.911(15)	P1-O1#10	1.57(3)
MoV1-O2	1.894(5)	K1-O3#6	2.911(15)	P1-O1#11	1.57(3)
MoV1-O2#2	1.894(5)	K1-O4	2.793(12)	P1-O1#12	1.57(3)
MoV1-O2#1	1.894(5)	K1-O4#7	2.793(12)	P1-O1#13	1.57(3)
MoV1-O2#3	1.894(5)	K1-O4#8	2.793(12)	P1-O1#14	1.57(3)
MoV1-O3	1.599(13)	K1-O4#9	2.793(12)	P1-O1#15	1.57(3)
K1-O3	2.911(15)	P1-O1	1.57(3)		

Symmetry codes: #1 =x, -y, z; #2 = y, -z, x; #3 = y, z, x; #4 = x, y, -z+1; #5 = -x+1, -y, -z+1; #6 = -x+1, -y, z; #7 = z, x, y; #8 = -x+1, y, -z+1; #9 = z, x, -y+1; #10 = -x, y, -z; #11 = -x, y, z; #12 = -x, -y, z; #13 = x, y, -z; #14 = -x, -y, -z; #15 = x, -y, -z.

Table S2: Proton-conductivity of POMs around room temperature

Compounds	Conductivity (S cm ⁻¹)	Temperature / humidity	Ref.
[Sm(H ₂ O) ₅ (CO ₂ CH ₂ NH ₃) ₂][Al(OH) ₆ Mo ₆ O ₁₈]·10H ₂ O	4.85 × 10 ⁻⁶	T = 25 °C, 95% RH	1
[Co(H ₂ O) ₈][H(H ₂ O) _{2.5}](HINO) ₄ (PMo ₁₂ O ₄₀)	9.0 × 10 ⁻⁹	T = 25 °C, 35% RH	2
[N(CH ₃) ₄] _{1.5} K _{5.5} Na ₂ [I ₃ C(Mo ^V ₂ O ₂ S ₂) ₈ (Se ^{IV} O ₃) ₈ (OH) ₈]·25 H ₂ O	6.06 × 10 ⁻⁴	T = 20 °C, 97% RH	3
Na ₅ [H ₇ {N(CH ₂ PO ₃) ₃ }Mo ₆ O ₁₆ (OH)(H ₂ O) ₄] ₄ ·18H ₂ O	7.58 × 10 ⁻⁴	T = 30 °C, 98% RH	4
[H ₂ en] ₄ [Ni ₅ (OH) ₃ (trzS) ₃ (en)(H ₂ O)(B-α-PW ₉ O ₃₄)]·6H ₂ O	4.0 × 10 ⁻⁷	T = 25 °C, 98% RH	5
H ₇ SiW ₉ V ₃ O ₄₀ ·9H ₂ O	2.05 × 10 ⁻³	T = 18 °C, 50% RH	6
K ₈ Na ₃ Li ₅ {[Na(NO ₃)(H ₂ O)] ₄ [Al ₁₆ (OH) ₂₄ (H ₂ O) ₈ (P ₈ W ₄₈ O ₁₈₄)] ₂ }·66H ₂ O	4.2 × 10 ⁻³	T = 25 °C, 55% RH	7
(HIm) ₂₄ (NH ₄) ₂₀ [Mo ₇₂ ^{VI} Mo ₆₀ ^{VO} O ₃₇₂ (CH ₃ COO) ₃₀ (H ₂ O) ₇₂]·ca 190H ₂ O	1.26 × 10 ⁻⁶	T = 25 °C, 50% RH	8
H[La(H ₂ O) ₄] ₂ [MnV ₁₃ O ₃₈]·9NMP·17H ₂ O	8.7 × 10 ⁻⁶	T = 25 °C, 75% RH	9
H ₉ P ₂ W ₁₅ V ₃ O ₆₂ ·28H ₂ O	3.64 × 10 ⁻²	T = 26 °C, 75% RH	10
[La ₃ (H ₂ O) ₂₂][P ₂ W ₁₅ Ta ₃ O ₆₂]·nH ₂ O	3.24 × 10 ⁻⁴	T = 25 °C, 98% RH	11
(H ₂ en) ₄ H ₂ [V ₁₂ B ₁₈ O ₅₄ (OH) ₆ (H ₂ O)]·11H ₂ O	3.44 × 10 ⁻⁷	T = 20 °C, 33% RH	12
H ₁₄ [Na ₆ (H ₂ O) ₁₂] ₄ [K ₄₂ Ge ₈ W ₇₂ O ₂₇₂ (H ₂ O) ₆₀]·solvent	4.3 × 10 ⁻⁵	T = 30 °C, 55% RH	13

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