Two Three-dimensional Fe(II) Frameworks Based on {P_4Mo_6} Tetrameric Clusters Exhibiting Efficient Visible-light Photocatalytic Properties for the Degradation of Cr(VI) and Methylene Blue

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Electronic Supplementary Information

Experimental section

Catalysis Experiments for the Reduction of Cr(VI).

The photocatalytic performances of compounds in Cr(VI) reduction were examined, 20 mg of the photocatalyst was dispersed into a 10 mL of $K_2Cr_2O_7$ aqueous solution (160 mg/L), after which 2-propanol (10 mL) was added. The suspensions were stirred for 30 min in the dark to obtain an absorption equilibrium, then above solution was exposed to visible light irradiation. At given irradiation intervals, 2 mL of the suspension were collected, centrifuged, and measured on an Ultraviolet−visible spectrophotometer. The degradation simulation was performed under the 500 W mercury lamp, a cut-off filter (≥ 420 nm) was placed on the top of the apparatus. The conversion of Cr(VI) was calculated using equation $([C_0] - [C_i]) / C_0 \times 100\%$, where $[C_0]$ and $[C_i]$ are the initial concentration and concentration at each time point, respectively.

Catalysis Experiments for the degradation of MB.

20 mg of the catalyst was placed in a quartz tube with a magnet, 20 mL of 19 mg/L MB aqueous solution. The suspensions were stirred for 30 min in the dark to obtain an absorption equilibrium before irradiation. After the dark reaction, 10 μL of H_2O_2 (AR, 30%) was added to the quartz tube, and the above mixture was stirred and exposed to visible light irradiation. Samples were taken every 30 min, centrifuged, and measured at a maximum absorption wavelength of 664 nm. The calculation of the degradation rate is the same as the above method.

Impedance Measurement.

The samples were compressed into a circular sheet with a diameter of 3 mm and a thickness of 0.7 mm under the pressure of 0.5 MPa at room temperature. Then the pellets were painted on both sides with silver colloids which were fixed on the sample stage with gold wires. The pellet was attached to the surface of the gold electrode. The AC impedance method of the Solartron electrochemical workstation was working in the frequency range of 0.01 Hz to 10 MHz with an input voltage amplitude of 100 mV. The proton conductivity was calculated using the equation:

$$\sigma = L / SR$$

where σ is the conductivity (S cm^{-1}), L is the thickness of the pellet (cm), S is the area of the pellet (cm^2), and R is the body resistance (Ω). The activation energy (E_a) was calculated from the equation

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

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

Preparation of 1−2 modified carbon paste electrodes (CPEs).

The preparation process of **1**-, and **2**-CPE is as follows: crystal sample (20 mg) and graphite powder (40 mg) were mixed in an agate mortar, ground carefully, and a trace amount of paraffin oil was added. Then the mixture was placed into a glass tube with an inner diameter of 2 mm and gently compacted with a copper rod from the other end.

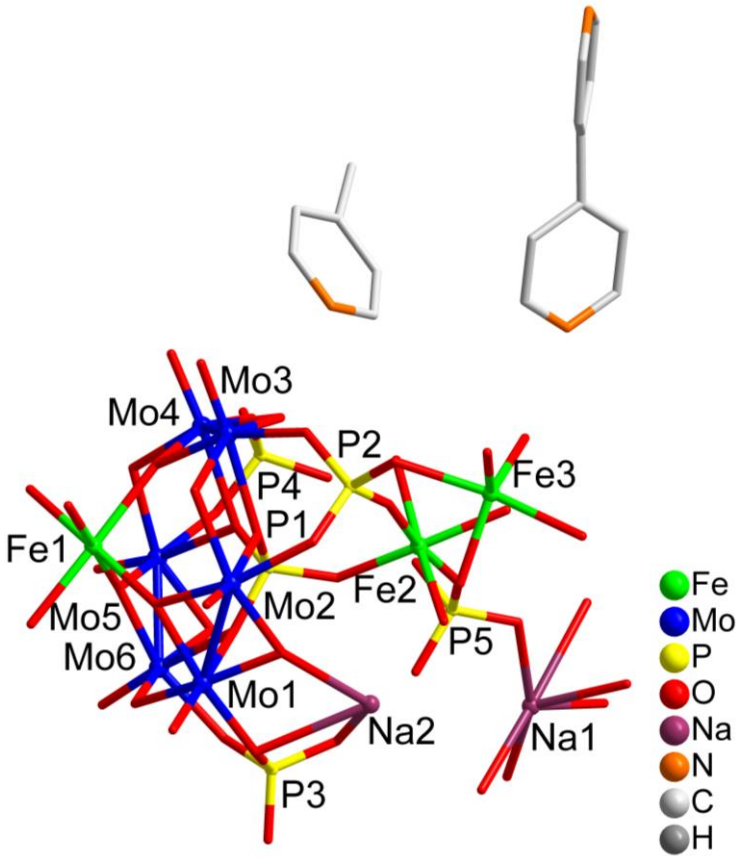

Fig. S1 The asymmetric unit of **1** with H atoms and solvent molecules was omitted for clarity.

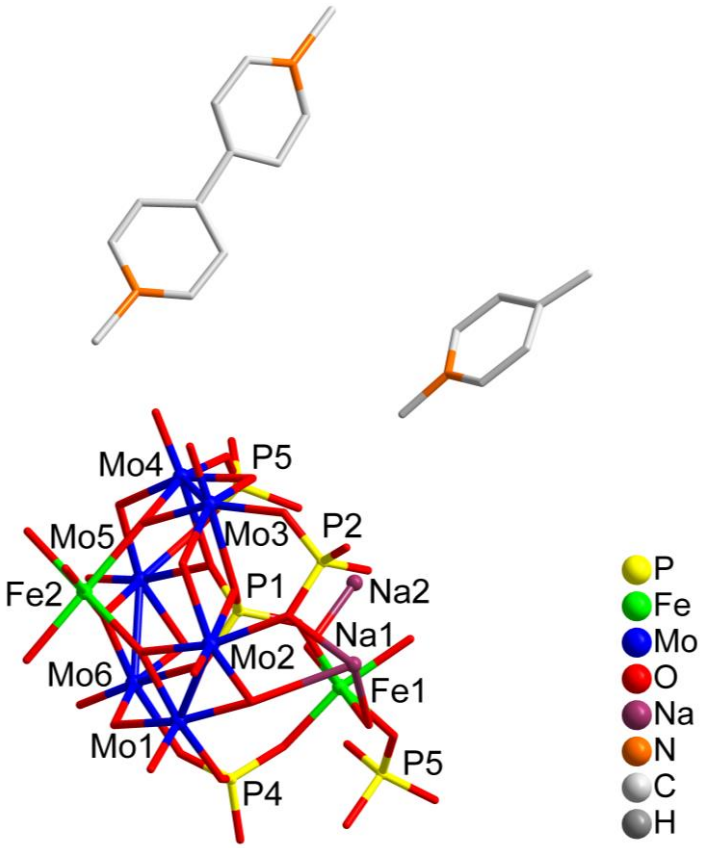

Fig. S2 The asymmetric unit of **2** with H atoms and solvent molecules was omitted for clarity.

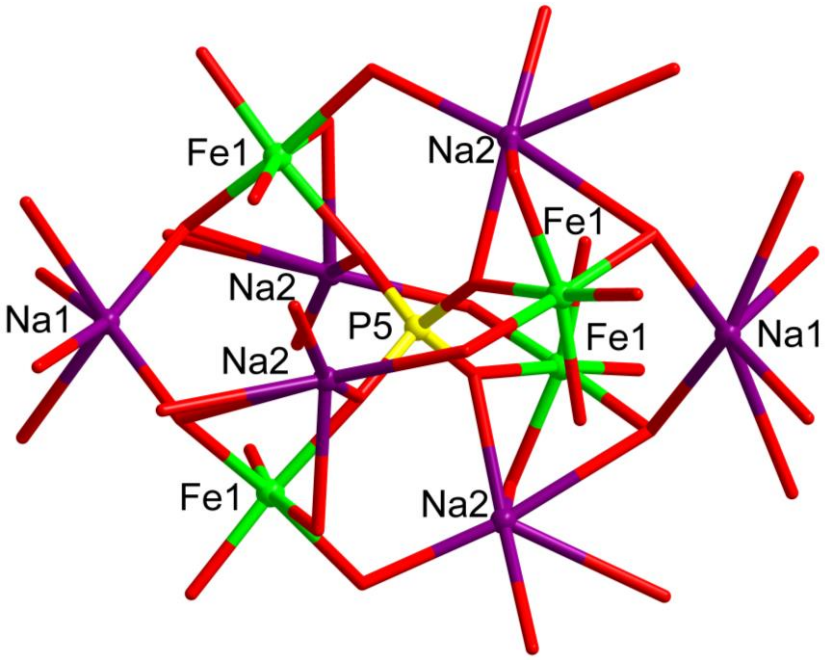

Fig. S3 The shuttle-shaped $\{Na_4Fe_4(PO_4)\}$ (occupancies of 50% for Na2).

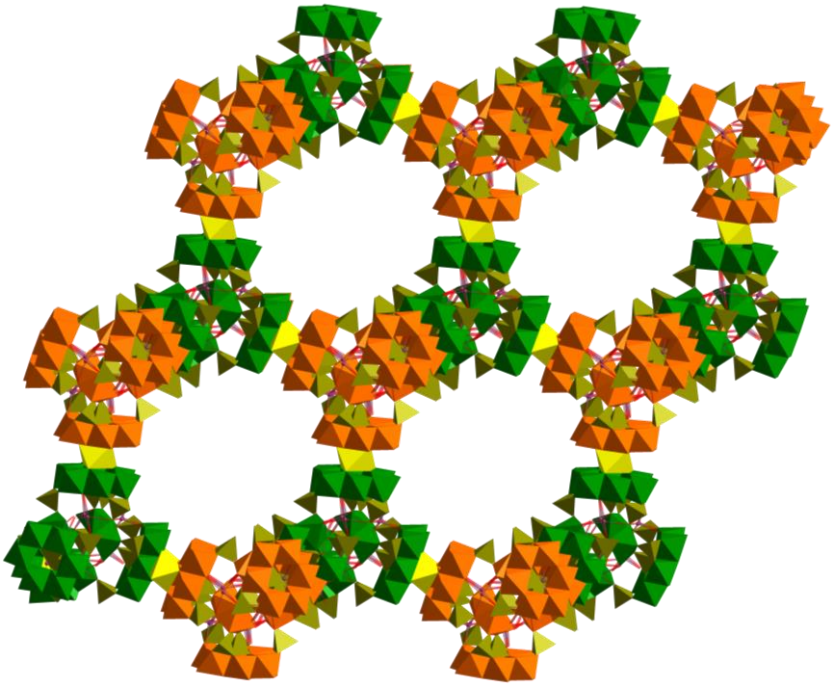

Fig. S4 Anionic network with ca. 21 × 17 Å cavity along *a* direction of **2**.

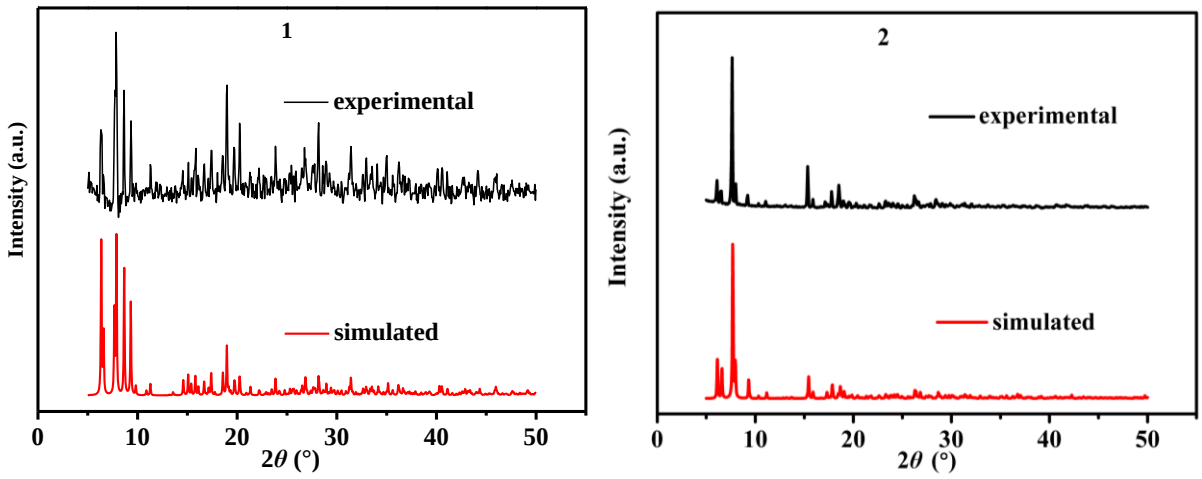

Fig. S5 The PXRD patterns of **1** and **2**.

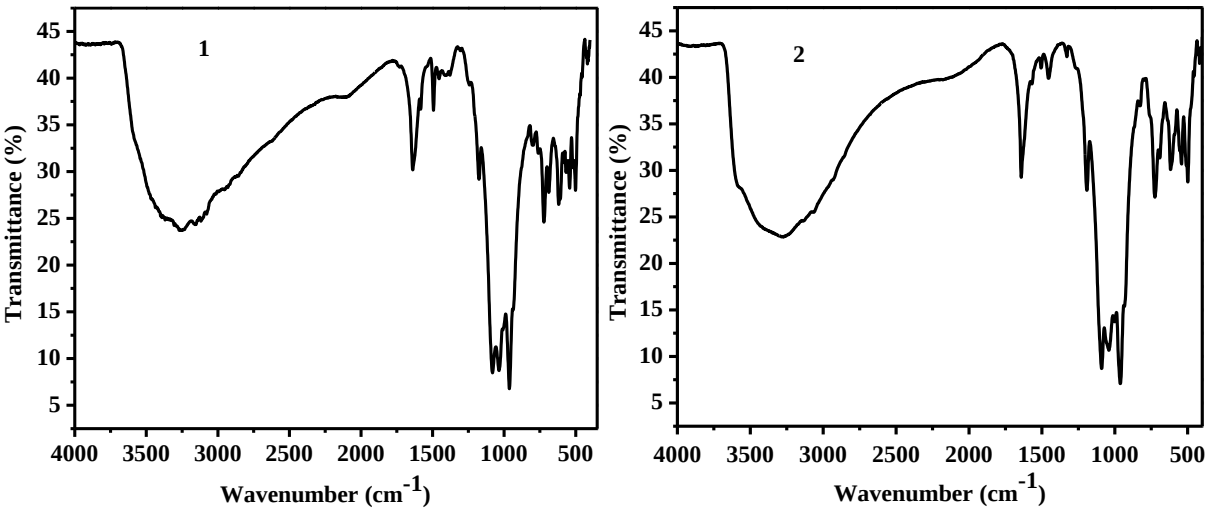

Fig. S6 IR spectra of **1** and **2**.

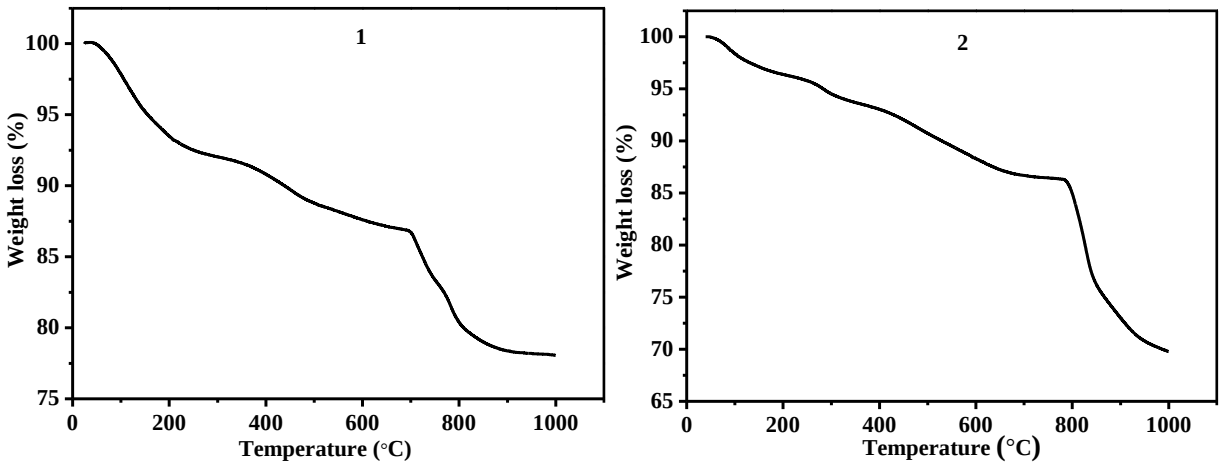

Fig. S7 TG curves for **1** and **2**

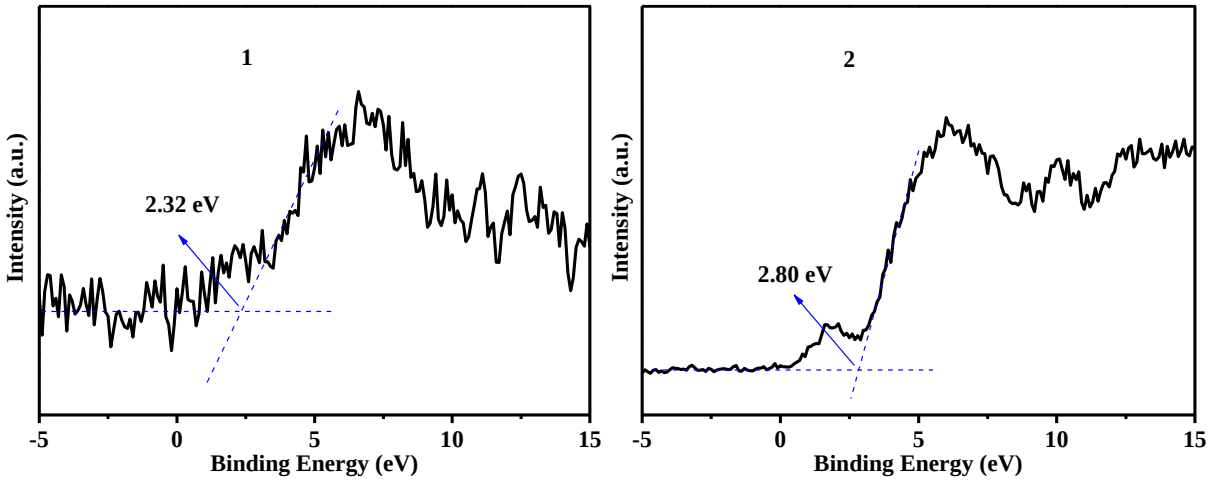

Fig. S8 VB-XPS spectra of **1** and **2**.

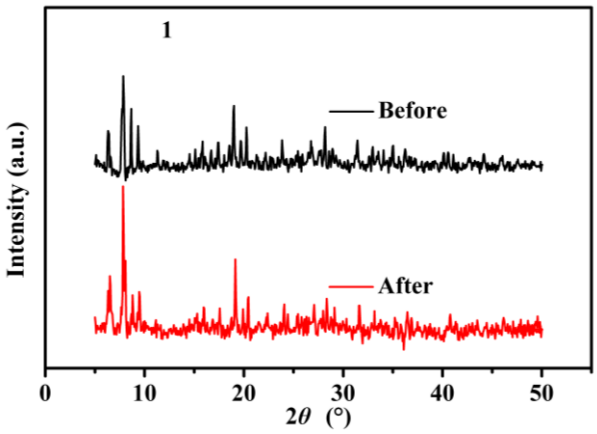

Fig. S9 The PXRD of **1** before and after catalytic reduction Cr(VI) experiments.

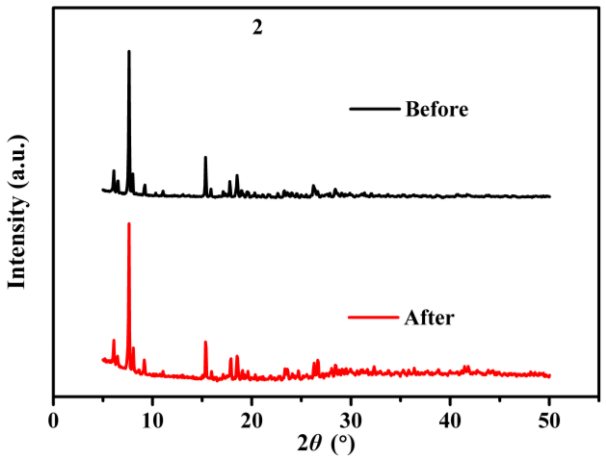

Fig. S10 The PXRD of **2** before and after catalytic oxidation MB experiments.

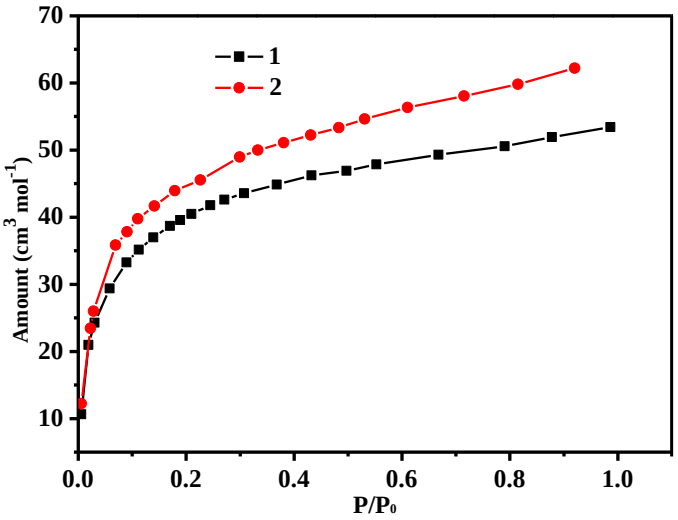

Fig. S11 Water vapor adsorption curves of **1** and **2**.

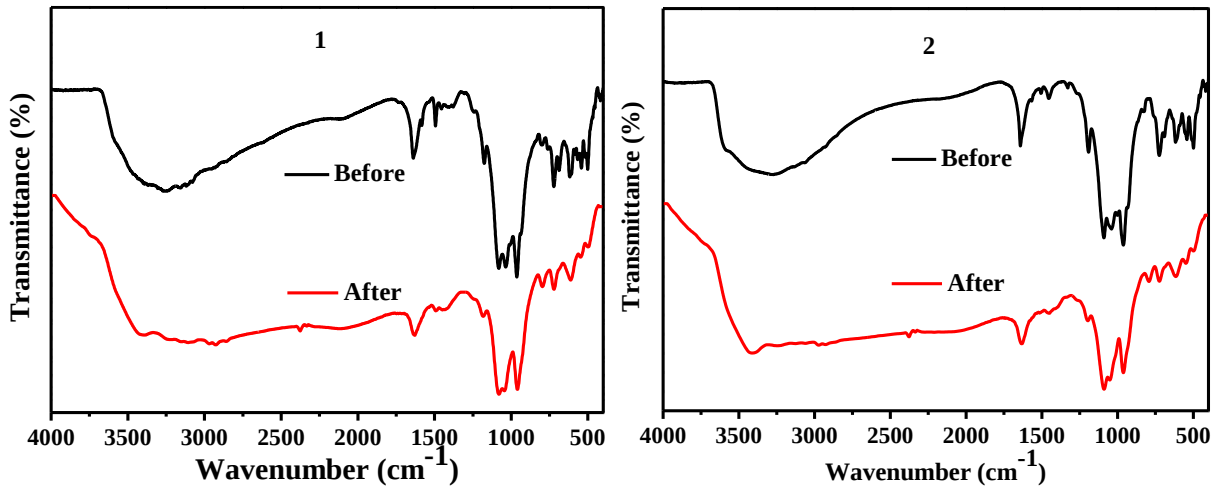

Fig. S12 The IR of **1** and **2** before and after the proton conduction measurement.

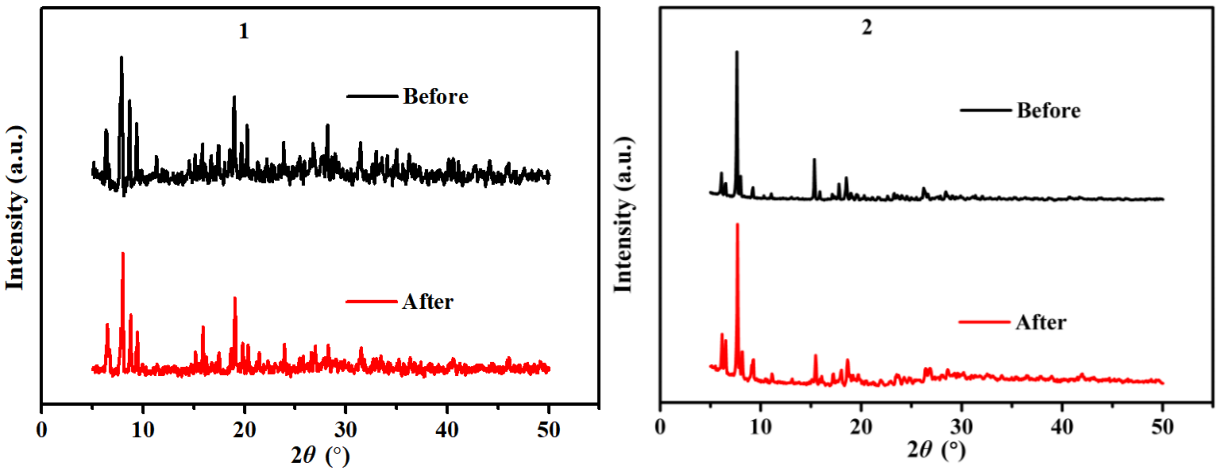

Fig. S13 The PXRD patterns of **1** and **2** before and after the proton conduction measurement.

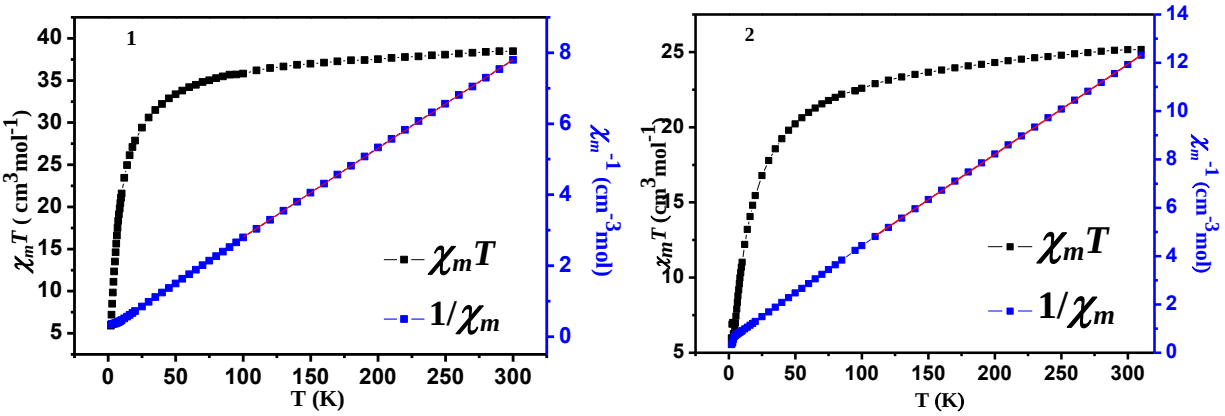

Fig. S14 Temperature dependence of the magnetic susceptibilities of **1** and **2** (Solid lines are generated by the Curie-Weiss expression).

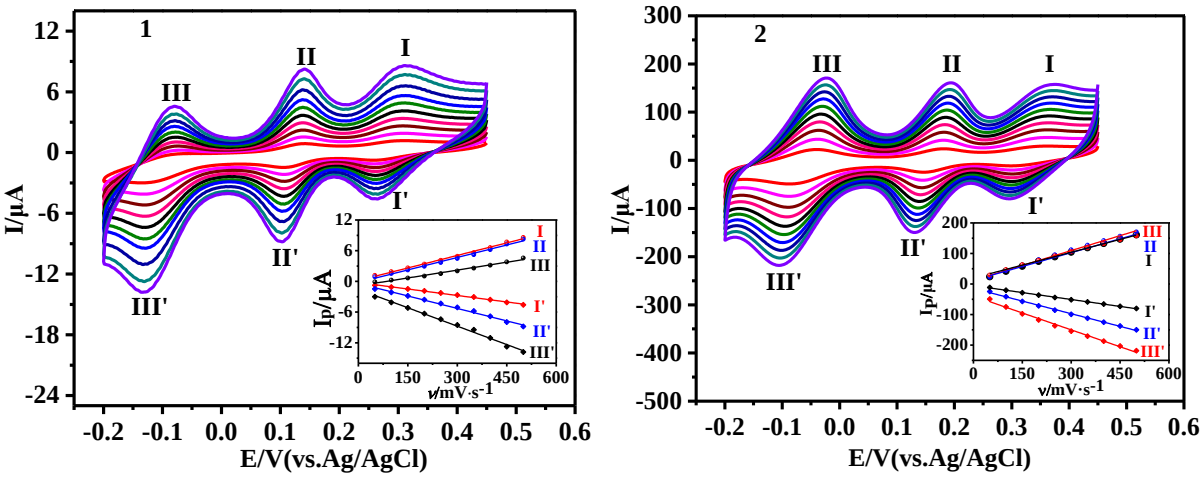

Fig. S15 Cyclic voltammograms of **1**-, **2**-CPEs in 0.1 M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV s^{-1}). Potentials vs. saturated calomel electrode (inset plots: the anodic and cathodic peak currents against the scan rates).

Table S1 X-ray diffraction crystallographic data and structure refinements for **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{67}Fe_{10}Mo_{24}N_4Na_6O_{141}P_{17}$	$C_{48}H_{103}Fe_6Mo_{24}N_8Na_4O_{138}P_{17}$
Formula weight	6145.26	6256.49
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/acd$	$I4_1/acd$
a, Å	26.8287(5)	26.6013(7)
b, Å	26.8287(5)	26.6013(7)
c, Å	40.8233(8)	43.3793(15)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^{-3}	29383.8(12)	30696.4(19)
Z	8	8
μ, mm^{-1}	3.253	2.753
$F(000)$	23456	24176
D_c, g cm^{-3}	2.778	2.711
T, K	296(2)	150(2)
Limiting indices	$-34 \le h \le 22$ $-34 \le k \le 25$ $-52 \le l \le 39$	$-31 \le h \le 30$ $-23 \le k \le 31$ $-41 \le l \le 51$
R_{int}	0.0474	0.1597
Data/restrains/parameters	8425 / 37 / 470	6768 / 35 / 543
GOF on F^2	1.022	1.058
R_1, wR_2 ($I>2\sigma(I)$)[a]	0.0414, 0.1041	0.0656, 0.1606
R_1, wR_2 (all data)	0.0559, 0.1130	0.1089, 0.1911

Table S2 Selected bond lengths (Å) and bond angles (º) of **1**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Fe(2)-O(31)#1	2.130(5)	Fe(2)-O(25)	2.190(4)	Fe(2)-O(28)#1	2.179(5)
Fe(1)-O(12)	1.929(5)	Fe(1)-O(32)	1.970(4)	Fe(1)-O(15)#2	1.998(5)
Fe(1)-O(7)	2.004(5)	Fe(1)-O(19)#3	2.036(5)	Fe(1)-O(2W)#4	2.130(5)
Fe(3)-O(1W)	2.189(7)	Fe(3)-O(20)#3	1.982(5)	Fe(3)-O(17)#2	2.045(5)
Fe(3)-O(11)#5	2.094(5)	Fe(3)-O(11)	2.149(5)	Mo(1)-Mo(2)	2.5902(8)
Mo(1)-O(1)	1.677(5)	Mo(1)-O(24)	1.943(5)	Mo(1)-O(25)	1.969(4)
Mo(1)-O(18)	2.075(5)	Mo(1)-O(23)	2.098(5)	Mo(1)-O(9)	2.285(4)
Mo(2)-O(8)	2.235(4)	Mo(2)-O(2)	1.676(5)	Mo(2)-O(24)	1.946(5)
Mo(2)-O(25)	1.978(4)	Mo(2)-O(13)	2.052(5)	Mo(2)-O(26)	2.120(5)
Mo(3)-Mo(4)	2.5984(8)	Mo(3)-O(3)	1.678(5)	Mo(3)-O(27)	1.955(5)
Mo(3)-O(28)	1.971(5)	Mo(3)-O(14)	2.039(5)	Mo(3)-O(26)	2.101(5)
Mo(3)-O(8)	2.272(4)	Mo(4)-O(10)	2.277(4)	Mo(4)-O(4)	1.674(5)
Mo(4)-O(27)	1.946(5)	Mo(4)-O(28)	1.971(4)	Mo(4)-O(21)	2.067(4)
Mo(4)-O(29)	2.091(5)	Mo(5)-Mo(6)	2.5903(8)	Mo(5)-O(5)	1.669(5)
Mo(5)-O(30)	1.928(5)	Mo(5)-O(31)	1.972(4)	Mo(5)-O(22)	2.049(5)
Mo(5)-O(29)	2.079(5)	Mo(5)-O(10)	2.353(4)	Mo(6)-O(9)	2.288(4)
Mo(6)-O(6)	1.675(5)	Mo(6)-O(30)	1.937(5)	Mo(6)-O(31)	1.975(5)
Mo(6)-O(16)	2.048(5)	Mo(6)-O(23)	2.091(5)	P(1)-O(10)	1.545(5)
P(1)-O(7)	1.514(5)	P(1)-O(8)	1.543(5)	P(1)-O(9)	1.543(5)
P(2)-O(14)	1.542(5)	P(2)-O(12)	1.508(5)	P(2)-O(13)	1.535(5)
P(2)-O(11)	1.535(5)	P(3)-O(18)	1.540(5)	P(3)-O(17)	1.513(5)
P(3)-O(15)	1.537(5)	P(4)-O(20)	1.533(5)	P(3)-O(16)	1.557(5)
P(4)-O(19)	1.516(5)	P(5)-O(32)	1.531(4)	P(4)-O(21)	1.541(5)
P(4)-O(22)	1.552(5)	P(5)-O(32)#4	1.531(4)	O(15)-Na(2)	2.369(5)
O(15)-Na(1)#2	2.683(6)	O(16)-Na(1)#2	2.732(6)	O(18)-Na(2)	2.684(5)
O(19)-Na(1)#4	2.339(6)	O(24)-Na(2)	2.503(5)	O(30)-Na(1)#2	2.249(5)
O(32)-Na(1)	2.280(6)	Na(1)-O(2W)	2.374(6)		
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O(31)#1-Fe(2)-O(31)	84.7(2)	O(31)#1-Fe(2)-O(28)	178.23(17)	O(31)-Fe(2)-O(28)	94.49(17)
O(31)#1-Fe(2)-O(25)	83.85(17)	O(31)-Fe(2)-O(25)	95.43(17)	O(28)-Fe(2)-O(28)#1	86.3(2)
O(28)#1-Fe(2)-O(25)	82.90(16)	O(12)-Fe(1)-O(15)#2	90.7(2)	O(31)-Fe(2)-O(25)#1	83.84(17)
O(12)-Fe(1)-O(32)	173.1(2)	O(32)-Fe(1)-O(7)	86.67(19)	O(25)-Fe(2)-O(25)#1	179.0(2)
O(12)-Fe(1)-O(7)	99.7(2)	O(32)-Fe(1)-O(19)#3	83.79(19)	O(32)-Fe(1)-O(15)#2	90.99(19)
O(12)-Fe(1)-O(19)#3	89.5(2)	O(12)-Fe(1)-O(2W)#4	84.5(2)	O(15)#2-Fe(1)-O(7)	99.1(2)
O(7)-Fe(1)-O(19)#3	168.1(2)	O(7)-Fe(1)-O(2W)#4	85.69(19)	O(15)#2-Fe(1)-O(19)#3	88.20(19)
O(15)#2-Fe(1)-O(2W)#4	173.75(19)	O(20)#3-Fe(3)-O(11)#5	115.4(2)	O(32)-Fe(1)-O(2W)#4	93.32(19)
O(20)#3-Fe(3)-O(17)#2	126.0(2)	O(17)#2-Fe(3)-O(11)	89.91(19)	O(19)#3-Fe(1)-O(2W)#4	87.78(19)
O(20)#3-Fe(3)-O(11)	102.9(2)	O(17)#2-Fe(3)-O(1W)	84.8(2)	O(17)#2-Fe(3)-O(11)#5	118.6(2)
O(20)#3-Fe(3)-O(1W)	92.9(2)	O(1)-Mo(1)-O(24)	105.6(2)	O(11)#5-Fe(3)-O(11)	76.4(2)
O(11)-Fe(3)-O(1W)	163.4(2)	O(1)-Mo(1)-O(18)	96.4(2)	O(11)#5-Fe(3)-O(1W)	92.3(2)
O(24)-Mo(1)-O(25)	95.83(19)	O(1)-Mo(1)-O(23)	97.1(2)	O(1)-Mo(1)-O(25)	102.6(2)
O(25)-Mo(1)-O(18)	159.78(18)	O(18)-Mo(1)-O(23)	84.67(19)	O(24)-Mo(1)-O(18)	85.69(19)
O(25)-Mo(1)-O(23)	86.03(18)	O(25)-Mo(1)-O(9)	81.26(17)	O(24)-Mo(1)-O(23)	156.13(18)

O(24)-Mo(1)-O(9)	83.12(18)	O(2)-Mo(2)-O(24)	106.5(2)	O(1)-Mo(1)-O(9)	169.8(2)
O(23)-Mo(1)-O(9)	73.62(17)	O(2)-Mo(2)-O(13)	96.0(2)	O(18)-Mo(1)-O(9)	78.90(17)
O(24)-Mo(2)-O(25)	95.46(19)	O(2)-Mo(2)-O(26)	95.9(2)	O(2)-Mo(2)-O(25)	101.4(2)
O(25)-Mo(2)-O(13)	160.80(19)	O(13)-Mo(2)-O(26)	83.98(19)	O(24)-Mo(2)-O(13)	87.3(2)
O(25)-Mo(2)-O(26)	86.16(18)	O(25)-Mo(2)-O(8)	80.83(17)	O(24)-Mo(2)-O(26)	156.63(19)
O(24)-Mo(2)-O(8)	85.16(18)	O(3)-Mo(3)-O(27)	105.9(2)	O(2)-Mo(2)-O(8)	167.7(2)
O(26)-Mo(2)-O(8)	72.05(17)	O(3)-Mo(3)-O(14)	94.9(2)	O(13)-Mo(2)-O(8)	80.47(17)
O(27)-Mo(3)-O(28)	94.99(18)	O(3)-Mo(3)-O(26)	100.1(2)	O(3)-Mo(3)-O(28)	101.7(2)
O(28)-Mo(3)-O(14)	161.43(19)	O(14)-Mo(3)-O(26)	81.62(19)	O(27)-Mo(3)-O(14)	88.50(19)
O(28)-Mo(3)-O(26)	87.15(18)	O(28)-Mo(3)-O(8)	79.08(17)	O(27)-Mo(3)-O(26)	152.89(19)
O(27)-Mo(3)-O(8)	82.21(18)	O(4)-Mo(4)-O(27)	105.2(2)	O(3)-Mo(3)-O(8)	171.7(2)
O(26)-Mo(3)-O(8)	71.65(17)	O(4)-Mo(4)-O(21)	95.6(2)	O(14)-Mo(3)-O(8)	83.35(17)
O(27)-Mo(4)-O(28)	95.26(19)	O(4)-Mo(4)-O(29)	95.7(2)	O(4)-Mo(4)-O(28)	102.1(2)
O(28)-Mo(4)-O(21)	159.95(19)	O(21)-Mo(4)-O(29)	84.74(19)	O(27)-Mo(4)-O(21)	89.2(2)
O(28)-Mo(4)-O(29)	84.11(18)	O(28)-Mo(4)-O(10)	82.62(17)	O(27)-Mo(4)-O(29)	158.79(19)
O(27)-Mo(4)-O(10)	83.39(18)	O(5)-Mo(5)-O(30)	105.7(2)	O(4)-Mo(4)-O(10)	169.6(2)
O(29)-Mo(4)-O(10)	75.50(17)	O(5)-Mo(5)-O(22)	96.9(2)	O(21)-Mo(4)-O(10)	78.48(17)
O(30)-Mo(5)-O(31)	95.41(19)	O(5)-Mo(5)-O(29)	97.5(2)	O(5)-Mo(5)-O(31)	101.0(2)
O(31)-Mo(5)-O(22)	160.8(2)	O(22)-Mo(5)-O(29)	84.67(19)	O(30)-Mo(5)-O(22)	86.0(2)
O(31)-Mo(5)-O(29)	86.41(18)	O(31)-Mo(5)-O(10)	80.80(17)	O(30)-Mo(5)-O(29)	155.84(19)
O(30)-Mo(5)-O(10)	82.42(18)	O(7)-P(1)-O(8)	109.7(3)	O(5)-Mo(5)-O(10)	171.4(2)
O(29)-Mo(5)-O(10)	74.07(17)	O(7)-P(1)-O(10)	113.6(3)	O(22)-Mo(5)-O(10)	80.45(17)
O(8)-P(1)-O(9)	109.0(2)	O(12)-P(2)-O(13)	112.5(3)	O(7)-P(1)-O(9)	109.6(3)
O(9)-P(1)-O(10)	106.8(2)	O(12)-P(2)-O(14)	108.7(3)	O(8)-P(1)-O(10)	108.0(3)
O(13)-P(2)-O(11)	108.9(3)	O(17)-P(3)-O(15)	114.2(3)	O(12)-P(2)-O(11)	109.2(3)
O(11)-P(2)-O(14)	107.6(3)	O(17)-P(3)-O(16)	108.0(3)	O(13)-P(2)-O(14)	109.8(3)
O(15)-P(3)-O(18)	105.9(3)	O(19)-P(4)-O(20)	110.8(3)	O(17)-P(3)-O(18)	109.3(3)
O(18)-P(3)-O(16)	111.3(3)	O(19)-P(4)-O(22)	108.7(3)	O(15)-P(3)-O(16)	108.2(3)
O(20)-P(4)-O(21)	109.0(3)	O(32)-P(5)-O(32)#2	111.9(3)	O(19)-P(4)-O(21)	109.9(3)
O(21)-P(4)-O(22)	110.2(3)	O(32)-P(5)-O(32)#4	108.27(17)	O(20)-P(4)-O(22)	108.1(3)
O(32)#2-P(5)-O(32)#3	108.27(17)	Mo(2)-O(8)-Mo(3)	102.48(17)	O(32)-P(5)-O(32)#3	108.27(17)
O(32)#3-P(5)-O(32)#4	111.9(3)	Mo(6)-O(23)-Mo(1)	112.8(2)	O(32)#2-P(5)-O(32)#4	108.27(17)
Mo(4)-O(10)-Mo(5)	97.13(17)	Mo(3)-O(26)-Mo(2)	112.7(2)	Mo(1)-O(9)-Mo(6)	99.46(17)
Mo(1)-O(25)-Mo(2)	82.03(16)	Mo(5)-O(29)-Mo(4)	112.7(2)	Mo(1)-O(24)-Mo(2)	83.52(18)
Mo(3)-O(28)-Mo(4)	82.46(17)	O(30)#2-Na(1)-O(32)	158.1(2)	Mo(4)-O(27)-Mo(3)	83.55(18)
Mo(5)-O(31)-Mo(6)	82.03(17)	O(30)#2-Na(1)-O(2W)	75.18(19)	Mo(5)-O(30)-Mo(6)	84.17(18)
O(32)-Na(1)-O(19)#3	70.79(18)	O(30)#2-Na(1)-O(15)#2	112.63(19)	O(30)#2-Na(1)-O(19)#3	130.8(2)
O(19)#3-Na(1)-O(2W)	108.4(2)	O(2W)-Na(1)-O(15)#2	172.1(2)	O(32)-Na(1)-O(2W)	103.5(2)
O(19)#3-Na(1)-O(15)#2	67.58(17)	O(19)#3-Na(1)-O(16)#2	82.81(18)	O(32)-Na(1)-O(15)#2	68.99(17)
O(32)-Na(1)-O(16)#2	123.83(19)	O(2W)-Na(1)-O(16)#2	132.1(2)	O(30)#2-Na(1)-O(16)#2	63.90(17)
O(15)#2-Na(1)-O(16)#2	55.12(15)	O(15)-Na(2)-O(24)	111.08(15)	O(15)-Na(2)-O(24)#2	97.01(16)
O(15)#2-Na(2)-O(24)#2	111.08(15)	O(15)-Na(2)-O(18)	57.74(14)	O(24)-Na(2)-O(18)#2	94.03(18)
O(24)#2-Na(2)-O(24)	120.4(3)	O(24)-Na(2)-O(18)	63.51(16)	O(15)#2-Na(2)-O(18)	154.15(16)

Symmetry codes: #1 $-x+1/2, y, -z$; #2 $-x, -y+1/2, z$; #3 $y-1/4, -x+1/4, -z-1/4$; #4 $-y+1/4, x+1/4, -z-1/4$; #5 $-x, -y, -z$; #6 $y+1/4, x-1/4, -z-1/4$; #7 $-x, -y-1/2, z$; #8 $-y-1/4, -x-1/4, -z-1/4$.

Table S3 Selected bond lengths (Å) and bond angles (º) of **2**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Fe(1)-O(21)	1.968(12)	Fe(1)-O(30)	2.025(10)	Fe(1)-O(19)	2.074(8)
Fe(1)-O(21)	1.968(12)	Fe(1)-O(30)	2.025(10)	Fe(1)-O(19)	2.074(8)
Fe(1)-O(29)	2.091(10)	Fe(1)-O(32)	2.114(10)	Fe(1)-O(31)	2.175(13)
Fe(2)-O(14)	2.134(8)	Fe(2)-O(13)#4	2.152(9)	Fe(2)-O(14)#4	2.134(8)
Fe(2)-O(16)#4	2.208(9)	Mo(1)-O(16)	1.984(9)	Mo(1)-O(1)	1.667(10)
Mo(1)-O(11)	1.938(9)	Mo(1)-O(17)	2.233(8)	Mo(1)-O(12)	2.089(8)
Mo(1)-O(20)	2.117(9)	Mo(2)-O(11)	1.931(9)	Mo(1)-Mo(2)	2.5845(16)
Mo(2)-O(2)	1.673(10)	Mo(2)-O(10)	2.102(9)	Mo(2)-O(16)	1.957(9)
Mo(2)-O(28)	2.068(9)	Mo(3)-O(3)	1.670(8)	Mo(2)-O(15)	2.252(8)
Mo(2)-Na(1)	3.601(5)	Mo(3)-O(26)	2.050(8)	Mo(3)-O(9)	1.937(9)
Mo(3)-O(14)	1.973(8)	Mo(3)-Mo(4)	2.5859(16)	Mo(3)-O(10)	2.088(9)
Mo(3)-O(15)	2.281(8)	Mo(4)-O(9)	1.916(9)	Mo(4)-O(14)	1.998(9)
Mo(4)-O(4)	1.687(8)	Mo(4)-O(8)	2.089(8)	Mo(4)-O(18)	2.324(8)
Mo(4)-O(25)	2.066(9)	Mo(5)-O(7)	1.937(9)	Mo(5)-O(13)	1.965(9)
Mo(5)-O(5)	1.670(9)	Mo(5)-O(8)	2.093(8)	Mo(5)-O(18)	2.308(8)
Mo(5)-O(24)	2.091(9)	Mo(6)-O(6)	1.668(9)	Mo(6)-O(7)	1.933(9)
Mo(5)-Mo(6)	2.5783(17)	Mo(6)-O(23)	2.030(9)	Mo(6)-O(12)	2.101(9)
Mo(6)-O(13)	1.975(8)	Mo(6)-O(17)	2.269(8)	O(11)-Na(1)	2.595(10)
O(9)-Na(2)#2	2.338(15)	O(29)-Na(1)	2.311(9)	O(29)-Na(2)#3	2.630(15)
O(28)-Na(1)	2.515(11)	O(31)-Na(2)	2.09(2)	O(32)-Na(2)#3	2.371(15)
O(30)-Na(2)#3	2.149(16)				
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O(21)-Fe(1)-O(30)	167.4(5)	O(21)-Fe(1)-O(19)	105.2(4)	O(30)-Fe(1)-O(19)	87.4(4)
O(21)-Fe(1)-O(29)	91.1(5)	O(30)-Fe(1)-O(29)	86.8(4)	O(19)-Fe(1)-O(29)	94.3(4)
O(21)-Fe(1)-O(32)	87.1(5)	O(30)-Fe(1)-O(32)	80.6(4)	O(19)-Fe(1)-O(32)	165.5(4)
O(29)-Fe(1)-O(32)	93.1(4)	O(21)-Fe(1)-O(31)	87.8(6)	O(30)-Fe(1)-O(31)	94.6(6)
O(19)-Fe(1)-O(31)	84.1(4)	O(29)-Fe(1)-O(31)	177.8(5)	O(32)-Fe(1)-O(31)	88.8(5)
O(21)-Fe(1)-Na(2)#3	123.1(5)	O(14)#4-Fe(2)-O(14)	180.0	O(14)#4-Fe(2)-O(13)#4	94.5(3)
O(14)-Fe(2)-O(13)#4	85.5(3)	O(14)#4-Fe(2)-O(13)	85.5(3)	O(14)-Fe(2)-O(13)	94.6(3)
O(13)#4-Fe(2)-O(13)	180.0	O(14)#4-Fe(2)-O(16)	84.6(3)	O(14)-Fe(2)-O(16)	95.4(3)
O(13)#4-Fe(2)-O(16)	83.0(3)	O(13)-Fe(2)-O(16)	97.0(3)	O(14)#4-Fe(2)-O(16)#4	95.4(3)
O(14)-Fe(2)-O(16)#4	84.6(3)	O(13)#4-Fe(2)-O(16)#4	97.0(3)	O(13)-Fe(2)-O(16)#4	83.0(3)
O(16)-Fe(2)-O(16)#4	180.0	O(1)-Mo(1)-O(11)	107.3(4)	O(1)-Mo(1)-O(16)	101.5(4)
O(11)-Mo(1)-O(16)	95.1(4)	O(1)-Mo(1)-O(12)	95.1(4)	O(11)-Mo(1)-O(12)	157.0(4)
O(16)-Mo(1)-O(12)	85.2(3)	O(1)-Mo(1)-O(20)	96.0(4)	O(11)-Mo(1)-O(20)	86.6(4)
O(16)-Mo(1)-O(20)	161.0(4)	O(12)-Mo(1)-O(20)	86.0(3)	O(1)-Mo(1)-O(17)	167.3(4)
O(11)-Mo(1)-O(17)	84.6(3)	O(16)-Mo(1)-O(17)	81.3(3)	O(12)-Mo(1)-O(17)	72.7(3)
O(20)-Mo(1)-O(17)	80.1(3)	O(1)-Mo(1)-Mo(2)	102.1(3)	O(11)-Mo(1)-Mo(2)	48.0(3)
O(16)-Mo(1)-Mo(2)	48.6(2)	O(12)-Mo(1)-Mo(2)	132.8(2)	O(20)-Mo(1)-Mo(2)	134.3(3)
O(17)-Mo(1)-Mo(2)	89.1(2)	O(2)-Mo(2)-O(11)	105.7(4)	O(2)-Mo(2)-O(16)	104.1(4)
O(11)-Mo(2)-O(16)	96.2(4)	O(2)-Mo(2)-O(28)	95.2(4)	O(11)-Mo(2)-O(28)	85.0(4)
O(16)-Mo(2)-O(28)	159.5(4)	O(2)-Mo(2)-O(10)	95.9(4)	O(11)-Mo(2)-O(10)	156.9(4)
O(16)-Mo(2)-O(10)	86.1(3)	O(28)-Mo(2)-O(10)	85.1(3)	O(2)-Mo(2)-O(15)	167.5(4)

O(11)-Mo(2)-O(15)	84.1(3)	O(16)-Mo(2)-O(15)	82.2(3)	O(28)-Mo(2)-O(15)	77.6(3)
O(10)-Mo(2)-O(15)	73.4(3)	O(3)-Mo(3)-O(9)	105.5(4)	O(3)-Mo(3)-O(14)	102.9(4)
O(9)-Mo(3)-O(14)	95.4(4)	O(3)-Mo(3)-O(26)	94.8(4)	O(9)-Mo(3)-O(26)	87.3(4)
O(14)-Mo(3)-O(26)	160.6(3)	O(3)-Mo(3)-O(10)	98.4(4)	O(9)-Mo(3)-O(10)	154.8(3)
O(14)-Mo(3)-O(10)	86.8(3)	O(26)-Mo(3)-O(10)	82.8(3)	O(3)-Mo(3)-O(15)	171.0(4)
O(9)-Mo(3)-O(15)	82.6(3)	O(14)-Mo(3)-O(15)	79.9(3)	O(26)-Mo(3)-O(15)	81.5(3)
O(10)-Mo(3)-O(15)	73.0(3)	O(4)-Mo(4)-O(9)	105.1(4)	O(4)-Mo(4)-O(14)	102.9(4)
O(9)-Mo(4)-O(14)	95.2(4)	O(4)-Mo(4)-O(25)	95.9(4)	O(9)-Mo(4)-O(25)	85.9(4)
O(14)-Mo(4)-O(25)	160.2(3)	O(4)-Mo(4)-O(8)	97.5(4)	O(9)-Mo(4)-O(8)	156.7(3)
O(14)-Mo(4)-O(8)	85.1(3)	O(25)-Mo(4)-O(8)	86.2(3)	O(4)-Mo(4)-O(18)	170.7(4)
O(9)-Mo(4)-O(18)	82.5(3)	O(14)-Mo(4)-O(18)	81.4(3)	O(25)-Mo(4)-O(18)	79.1(3)
O(8)-Mo(4)-O(18)	74.5(3)	O(5)-Mo(5)-O(7)	105.3(4)	O(5)-Mo(5)-O(13)	103.1(4)
O(7)-Mo(5)-O(13)	95.6(4)	O(5)-Mo(5)-O(24)	95.1(4)	O(7)-Mo(5)-O(24)	88.8(4)
O(13)-Mo(5)-O(24)	159.4(3)	O(5)-Mo(5)-O(8)	96.5(4)	O(7)-Mo(5)-O(8)	157.6(3)
O(13)-Mo(5)-O(8)	84.1(3)	O(24)-Mo(5)-O(8)	84.3(4)	O(5)-Mo(5)-O(18)	169.4(4)
O(7)-Mo(5)-O(18)	83.0(3)	O(13)-Mo(5)-O(18)	82.2(3)	O(24)-Mo(5)-O(18)	78.3(3)
O(8)-Mo(5)-O(18)	74.8(3)	O(6)-Mo(6)-O(7)	106.9(4)	O(6)-Mo(6)-O(13)	101.2(4)
O(7)-Mo(6)-O(13)	95.4(4)	O(6)-Mo(6)-O(23)	95.1(4)	O(7)-Mo(6)-O(23)	87.9(4)
O(13)-Mo(6)-O(23)	161.5(4)	O(6)-Mo(6)-O(12)	98.8(4)	O(7)-Mo(6)-O(12)	153.1(3)
O(13)-Mo(6)-O(12)	87.3(3)	O(23)-Mo(6)-O(12)	81.8(3)	O(6)-Mo(6)-O(17)	170.4(4)
O(7)-Mo(6)-O(17)	82.3(3)	O(13)-Mo(6)-O(17)	80.0(3)	O(23)-Mo(6)-O(17)	82.5(3)
O(12)-Mo(6)-O(17)	71.7(3)	Mo(6)-O(7)-Mo(5)	83.6(4)	Mo(4)-O(8)-Mo(5)	112.7(4)
Mo(4)-O(9)-Mo(3)	84.3(3)	Mo(3)-O(10)-Mo(2)	112.5(4)	Mo(2)-O(11)-Mo(1)	83.8(3)
Mo(1)-O(12)-Mo(6)	112.8(4)	Mo(5)-O(13)-Mo(6)	81.7(3)	Mo(3)-O(14)-Mo(4)	81.2(3)
Mo(2)-O(15)-Mo(3)	100.5(3)	Mo(2)-O(16)-Mo(1)	82.0(3)	Mo(1)-O(17)-Mo(6)	101.7(3)
Mo(5)-O(18)-Mo(4)	97.5(3)	O(29)#1-Na(1)-O(29)	136.2(6)	O(29)#1-Na(1)-O(28)	61.8(3)
O(29)-Na(1)-O(28)	150.7(3)	O(29)#1-Na(1)-O(28)#1	150.7(3)	O(29)-Na(1)-O(28)#1	61.8(3)
O(28)-Na(1)-O(28)#1	115.2(6)	O(29)#1-Na(1)-O(11)#1	87.5(3)	O(29)-Na(1)-O(11)#1	117.9(3)
O(28)-Na(1)-O(11)#1	80.4(3)	O(28)#1-Na(1)-O(11)#1	63.9(3)	O(29)#1-Na(1)-O(11)	117.9(3)
O(29)-Na(1)-O(11)	87.5(3)	O(11)#1-Na(1)-O(11)	110.8(5)	O(28)#1-Na(1)-O(11)	80.3(3)

Symmetry codes: #1 – *x* + 1, – *y* + 1/2, *z*; #2 *y* + 1/4, – *x* + 3/4, – *z* + 1/4; #3 – *y* + 3/4, *x* – 1/4, – *z* + 1/4; #4 – *x* + 3/2, – *y* + 1/2, – *z* + 1/2; #5 – *y* + 3/4, – *x* + 3/4, – *z* – 1/4; #6 – *x* + 3/2, *y*, – *z*; #7 *y* + 3/4, *x* – 3/4, – *z* + 1/4

Table S4 Hydrogen bond parameters (Å, º) of **1**.

D–H···A	D(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(2)–H(2A)···O(5)#1	0.93	2.08	2.960(19)	157

Symmetry codes: #1 – *x*, 1/2 – *y*, *z*

Table S5 Hydrogen bond parameters (Å, º) of **2**.

D–H···A	D(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(4)–H(4A)···O(2)	0.95	2.38	3.31(18)	165
C(5)–H(5A)···O(28)	0.95	2.21	3.156(19)	173
C(6)–H(6C)···O(27)	0.98	2.58	3.41(2)	143
C(12)–H(12B)···O(4)	0.98	2.56	3.34(2)	136
C(12)–H(12B)···O(12)#2	0.98	2.25	2.99(2)	132
C(16)–H(16A)···N(2)	0.96	2.06	2.69(4)	122
C(16)–H(16A)···O(6)#1	0.96	2.22	2.76(4)	114
C(17)–H(17A)···O(6)#1	0.95	2.26	2.81(4)	116

Symmetry codes: #1 *x*, 1/2 + *y*, – *z*; #2 3/2 – *x*, 1/2 – *y*, 1/2 – *z*

Table S6 BVS calculations of P, Mo, and Fe in compounds **1** and **2**.

	1	**2**		**1**	**2**
P1	4.98	4.91	Mo1	5.21	5.23
P2	4.36	4.35	Mo2	5.54	5.57
P3	4.97	5.02	Mo3	5.24	5.31
P4	4.99	4.98	Mo4	5.24	5.15
P5	5.05	5.40	Mo5	5.29	5.23
Fe1	2.47	2.43	Mo6	5.27	5.36
Fe2	1.87	1.88	Fe3	1.94	