Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Efficient Visible-Light-Driven Reduction of Hexavalent Chromium Catalyzed by Conjugated Organic Species Modified Hourglass-type Phosphomolybdate Hybrids

Hao-Xue Bi, Xiao-Yu Yin, Xiu-Juan Zhang, Yuan-Yuan Ma*, Zhan-Gang Han*

Hebei Key Laboratory of Organic Functional Molecules, National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang, Hebei 050024, People's Republic of China.

Email: mayy334@hebtu.edu.cn; hanzg116@126.com; hanzg116@hebtu.edu.cn

CONTENTS:

1. Experimental Section

1.1 Materials and measurements

All chemical reagents were commercially available. FTIR-8900 infrared spectrometer was used to collect the infrared spectra in the range of 400-4000 cm^{-1} (KBr pellet); Bruker AXS D8 advance X-ray powder diffractometer was used to measure the X-ray powder diffraction; DTG-60A thermogravimetric analyzer was used to characterize the thermogravimetric spectra in the range of room temperature to 600 °C, and cyclic voltammetry curves were performed at CHI760E electrochemical workstation produced by Shanghai Chenhua. The UV-Vis DRS spectra of crystals were determined by Agilent Cary 5000 UV-Vis spectrophotometer ($BaSO_4$ as the standard sample); UV-Vis Spectrum was analyzed by UV-2600 UV-Vis spectrophotometer.

1.2 Single-crystal X-ray diffraction

The crystal diffraction data were collected by using a Smart Apex CCD diffractometer with Mo Kα monochromated radiation (λ = 0.71073 Å) at 296(2) K. The crystal structures of **1–4** were resolved by direct methods and refined by the full matrix least-squares methods on F^2 using the *SHELXTL* crystallographic program package. Except for lattice water, all non-hydrogen atoms were anisotropic. The crystallographic data and structure refinement details for crystals **1–4** (CCDC 2076438, 2076444, 2076445 and 2076446) are summarized in Table S1. Typical bond lengths and angles are also listed in Tables S2-S9.

2. Supplementary Figures

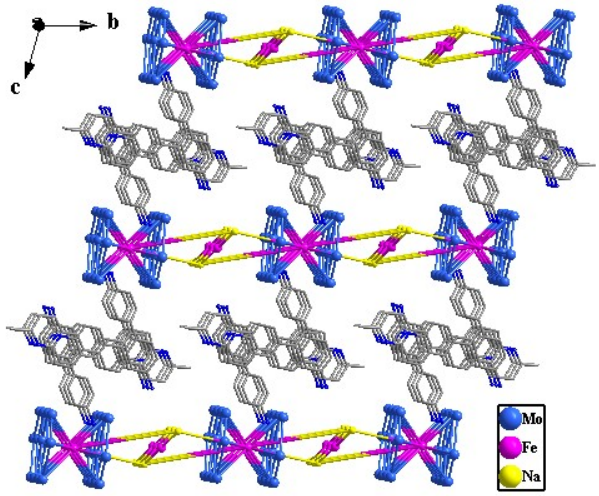


Fig. S1 A simplified diagram of the 3D structure in crystal.

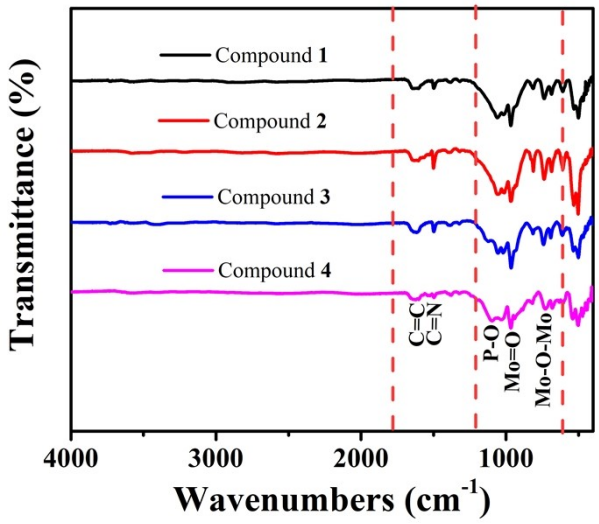
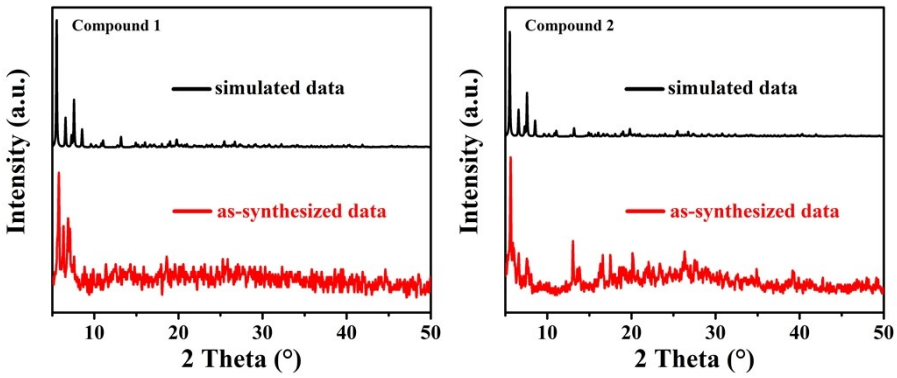


Fig. S2 IR spectra of crystals **1-4** (KBr pellets as background).



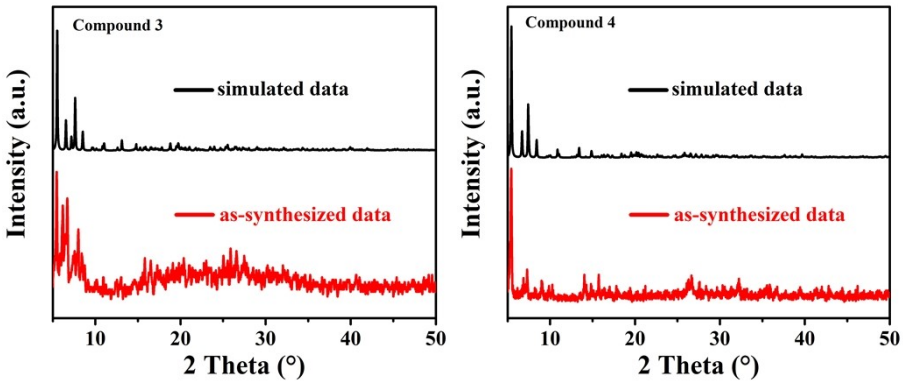


Fig. S3 Powder diffraction patterns of crystals **1-4**.

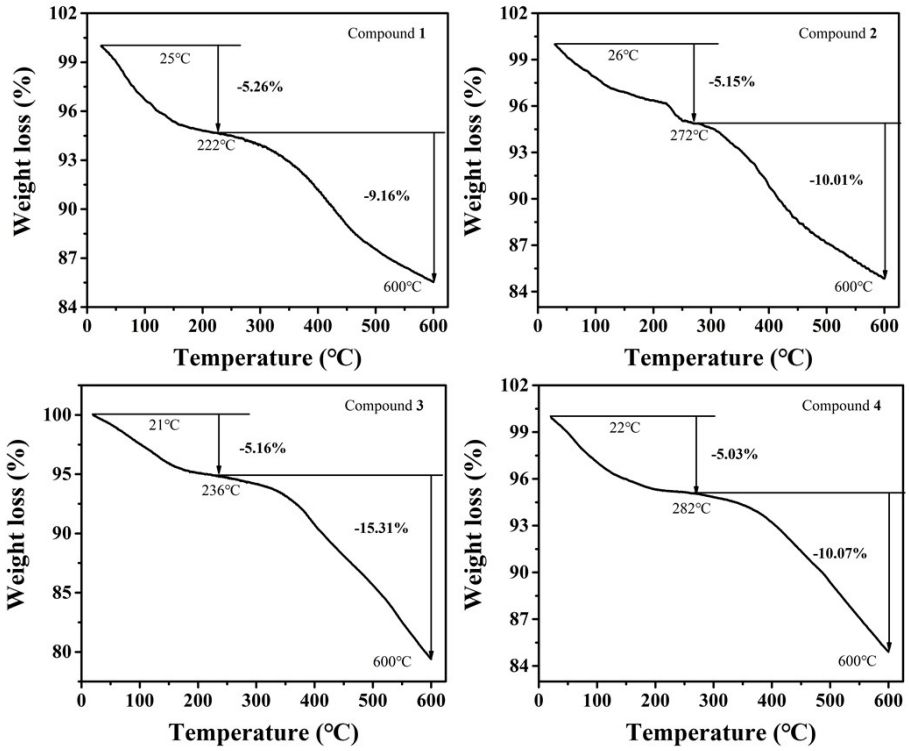
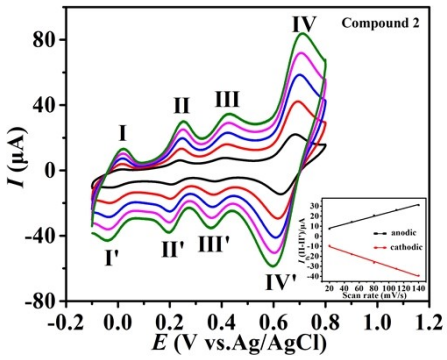


Fig. S4 TG curves of crystals **1-4**.



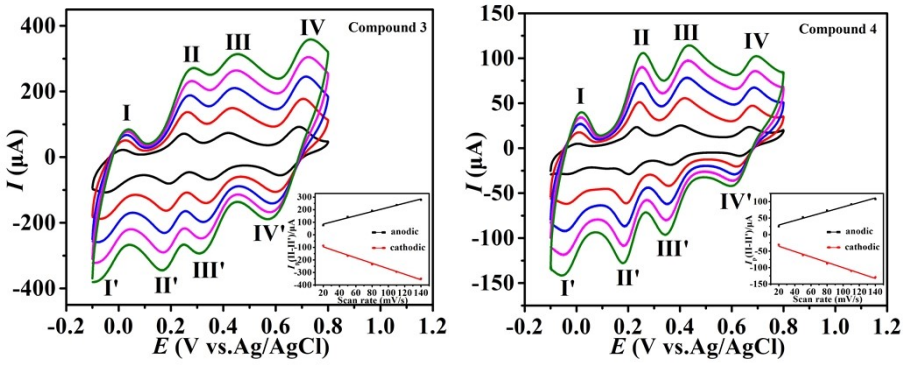


Fig. S5 Cyclic voltammograms of **1**-GCE, **2**-GCE, **3**-GCE and **4**-GCE in the 0.5 M H_2SO_4 solution at different scan rates (20, 50, 80, 110, and 140 $mV \cdot s^{-1}$). The insets are plots of peak current of peak (II–II') versus scan rate.

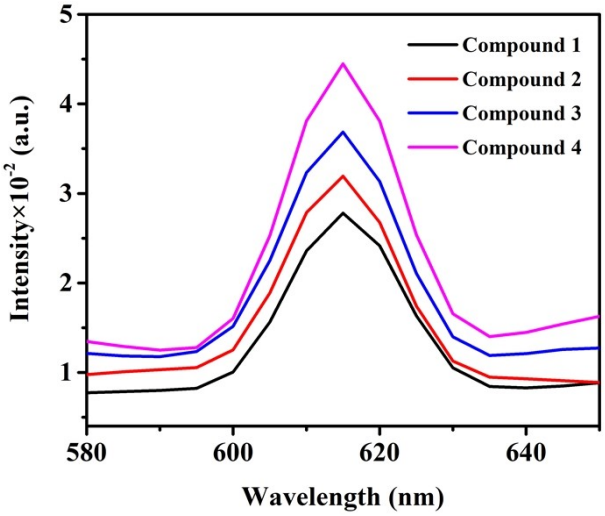
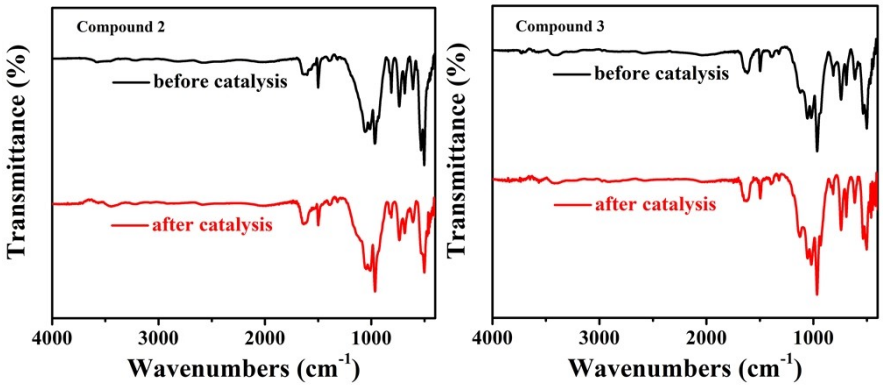


Fig. S6 Solid-state emission spectra of hybrids **1-4**.



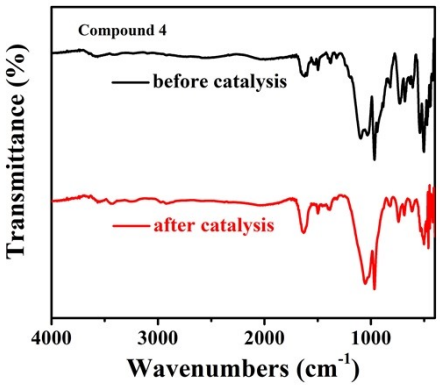


Fig. S7 Comparison of IR spectra of the fresh **2-4** and after catalysis.

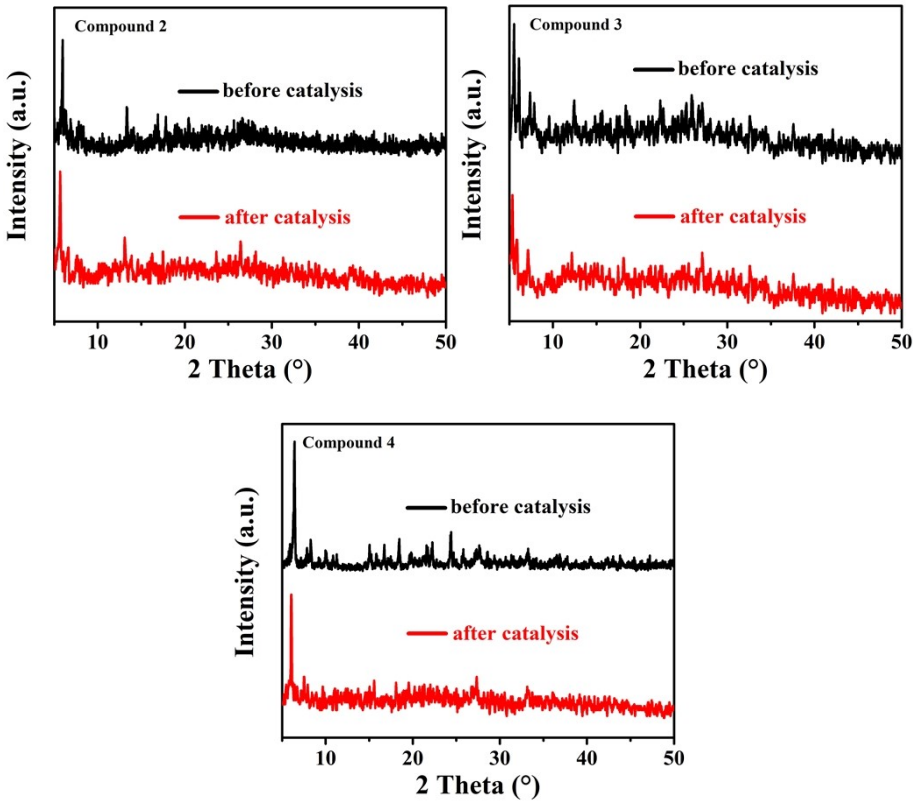


Fig. S8 Comparison of XRD patterns of the fresh **2-4** and after catalysis.

3. Supplementary Tables

Table S1 Crystal data and structural refinement details for crystals **1-4**.

Crystal	**1**	**2**	**3**	**4**
Empirical formula	$C_{64}H_{64}Fe_2Mo_{12}N_8Na_2O_{71}$	$C_{64}H_{62}Co_2Mo_{12}N_8Na_2O_{70}P_8$	$C_{64}H_{52}Mn_2Mo_{12}N_8Na_2O_{71}P$	$C_{64}H_{54}Zn_2Mo_{12}N_8Na_2O_{70}P_8$
Formula weight	3637.95	3626.09	3654.01	3633.79
Crystal system	Triclinic	Triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a (Å)	11.853(2)	11.8560(10)	11.8092(12)	12.079(2)
b (Å)	14.016(2)	14.0079(12)	14.1430(15)	13.620(2)
c (Å)	16.932(3)	16.8886(14)	17.0587(19)	17.023(3)
α, *β*, *γ* (°)	105.883(3),99.311(3), 92.164(3)	105.9222(13),99.3799(14), 92.0586(15)	106.8435(17),100.0004(16) 91.8117(16)	75.738(3),80.286(3),89.388(3
Volume (Å^3), *Z*	2659.9(8), 1	2651.5(4), 1	2675.3(5), 1	2674.0(8), 1
Density(calculated)(Mg	2.271	2.271	2.268	2.257
Absorption	1.870	1.914	1.831	1.894
$F_{(000)}$	1770.0	1762	1770.0	1766.0
Crystal size (mm^3)	0.2 × 0.15 × 0.1	0.2 x 0.18 x 0.16	0.2 × 0.18 × 0.16	0.2 × 0.18 × 0.16
θ (°)	3.36 to 56.516	1.275 to 25.027	3.02 to 56.562	3.086 to 56.414
Reflections collected	16442	13390	16597	15654
Independent reflections	12017 [$R_{(int)}$= 0.0355]	9277 [$R_{(int)}$ = 0.0238]	12158 [$R_{(int)}$ = 0.0230]	11790 [$R_{(int)}$ = 0.0269]
Max. and min.	0.829 and 0.721	0.7452 and 0.6787	0.746 and 0.700	0.739 and 0.692
Data/restraints/paramet	12017/1020/774	9277/750/744	12158/726/752	11790/840/755
Goodness-of-fit on F^2	1.018	1.022	1.025	1.038
Final *R* indices	R_1= 0.0587, wR_2 = 0.1579	R_1 = 0.0466, wR_2 = 0.1248	R_1 = 0.0483, wR_2 = 0.1311	R_1 = 0.0601, wR_2 = 0.1444
R indices (all data)	R_1= 0.0790, wR_2 = 0.1754	R_1 = 0.0659, wR_2 = 0.1385	R_1 = 0.0681, wR_2 = 0.1451	R_1 = 0.0944, wR_2 = 0.1727

[a] $R_1 = \sum||F_0| - |F_c|| / \sum|F_0|$; $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$.

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

Mo(1)-Mo(4)	2.5932(9)	P(4) -O(30)	1.505(5)
Mo(1)-O(5)	1.974(4)	P(4)-Na(1)^{i}	3.417(6)
Mo(1)-O(8)	2.127(5)	P(3)-O(26)	1.529(5)
Mo(1)-O(11)	1.936(5)	P(3)-O(3)^{i}	1.518(6)
Mo(1)-O(13)^{i}	2.290(4)	P(3)-O(4)	1.514(5)
Mo(1)-O(22)	1.681(5)	P(3)-O(32)	1.573(6)
Mo(1)-O(25)	2.077(5)	P(3)-Na(1)	3.409(5)
Mo(2)-Mo(6)	2.5818(9)	P(1) -O(21)	1.542(6)
Mo(2)-O(6)	1.987(4)	P(1) -O(28)	1.530(6)
Mo(2)-O(8)^{i}	2.146(5)	P(1) -O(2)	1.597(6)
Mo(2)-O(12)	2.067(4)	P(1) -O(31)	1.506(6)
Mo(2)-O(13)	2.267(4)	O(19)-Na(1)^{i}	2.600(7)
Mo(2)-O(14)	1.920(5)	O(24)-Na(1)^{iii}	2.490(7)
Mo(2)-O(15)	1.687(5)	O(27)-Na(1)^{i}	2.643(8)
Mo(3)-Mo(5)	2.5938(9)	O(30)-Na(1)^{i}	2.681(8)
Mo(3)-O(7)	1.973(5)	O(32)-Na(1)	2.426(8)

Mo(3)-O(10)	2.293(4)	N(2)-C(47)	1.451(10)
Mo(3)-O(17)^{i}	2.090(5)	N(1)-C(44)	1.396(11)
Mo(3)-O(18)	1.679(5)	C(40)-C(43)	1.477(11)
Mo(3)-O(19)	1.928(5)	C(40)-C(48)	1.375(11)
Mo(3)-O(3)	2.071(5)	C(40)-C(52)	1.394(12)
Mo(4)-O(5)	1.976(4)	C(41)-C(47)	1.352(12)
Mo(4)-O(10)^{i}	2.297(5)	C(41)-C(48)	1.404(12)
Mo(4)-O(11)	1.946(5)	C(42)-C(43)	1.404(12)
Mo(4)-O(17)	2.105(5)	C(42)-C(60)	1.392(12)
Mo(4)-O(26)	2.065(5)	C(43)-C(50)	1.378(12)
Mo(4)-O(29)	1.668(5)	C(44)-C(55)	1.380(12)
Mo(5)-O(7)	1.975(5)	C(44)-C(60)	1.387(12)
Mo(5)-O(9)	2.104(5)	C(46)-C(47)	1.376(12)
Mo(5)-O(16)	2.250(4)	C(46)-C(52)	1.411(13)
Mo(5)-O(19)	1.942(5)	C(50)-C(55)	1.378(12)
Mo(5)-O(20)	1.668(5)	Na(1)-O(1W)	2.407(11)
Mo(5)-O(21)	2.073(5)	Na(1)-O(4W)	3.00(2)
Mo(6)-O(6)	1.982(5)	N(3)-C(4)	1.378(15)
Mo(6)-O(9)	2.099(4)	N(3)-C(10)	1.337(14)
Mo(6)-O(14)	1.950(5)	C(4)-C(7)	1.402(15)
Mo(6)-O(16)	2.286(4)	C(4)-C(8)	1.424(14)
Mo(6)-O(23)	1.673(5)	C(0AA)-C(6)	1.464(17)
Mo(6)-O(28)	2.037(5)	C(0AA)-C(11)	1.418(15)
Fe(2)-O(27)^{ii}	2.123(5)	C(0AA)-C(12)	1.384(16)
Fe(2)-O(27)	2.123(5)	C(6)-C(15)	1.342(17)
Fe(2)-O(30)^{ii}	2.059(5)	C(6)-C(18)	1.381(16)
Fe(2)-O(30)	2.059(5)	C(7)-C(12)	1.361(16)
Fe(2)-O(1)	2.153(6)	C(8)-C(9)	1.385(15)
Fe(2)-O(1)^{ii}	2.153(6)	C(8)-C(11)	1.386(16)
Fe(1)-O(5)^{i}	2.205(4)	C(9)-C(14)	1.357(17)
Fe(1)-O(5)	2.205(4)	C(10)-C(14)	1.437(16)
Fe(1)-O(6)^{i}	2.130(4)	C(10)-C(19)	1.475(17)
Fe(1)-O(6)	2.130(4)	N(4)-C(16)	1.410(18)
Fe(1)-O(7)	2.205(4)	N(4)-C(17)	1.130(16)
Fe(1)-O(7)^{i}	2.205(4)	C(15)-C(21)	1.439(19)
P(2) -O(12)	1.534(5)	C(16)-C(21)	1.381(19)
P(2) -O(24)	1.585(5)	C(16)-C(22)	1.34(2)
P(2) -O(25)^{i}	1.527(5)	C(17)-C(25)	1.33(2)
P(2) -O(27)^{ii}	1.497(5)	C(17)-C(5)	1.69(2)
P(2) -Na(1)^{iii}	3.184(5)	C(18)-C(22)	1.379(19)
P(4)-O(10)	1.544(5)	C(21)-C(26)	1.312(19)
P(4)-O(13)	1.543(4)	C(25)-C(26)	1.51(2)
P(4) -O(16)	1.555(5)	O(13)-P(4)-O(10)	107.1(3)
O(5)-Mo(1)-Mo(4)	49.01(13)	O(30)-P(4)-O(16)	108.7(3)

O(5)-Mo(1)-O(8)	85.74(18)	O(26)-P(3)-O(32)	107.5(3)
O(8)-Mo(1)-Mo(4)	73.24(16)	O(26)-P(3)-Na(1)	114.5(2)
O(8)-Mo(1)-O(13)^{i}	48.25(14)	O(4)-P(3)-O(26)	111.2(3)
O(11)-Mo(1)-Mo(4)	95.50(19)	O(4)-P(3)-O(3)^{i}	109.6(3)
O(11)-Mo(1)-O(5)	156.59(19)	O(4)-P(3)-O(32)	110.7(3)
O(13)^{i}-Mo(1)-Mo(4)	100.64(17)	O(21)-P(1)-O(2)	106.5(3)
O(22)-Mo(1)-Mo(4)	102.8(2)	O(28)-P(1)-O(21)	111.1(3)
O(6)-Mo(2)-Mo(6)	85.90(18)	O(28)-P(1)-O(2)	107.7(3)
O(8)^{i}-Mo(2)-Mo(6)	73.37(17)	O(31)-P(1)-O(2)	106.7(4)
O(12)-Mo(2)-O(13)	90.57(11)	Mo(1)-O(5)-Mo(4)	82.05(17)
O(13)-Mo(2)-Mo(6)	48.66(14)	O(23)-Mo(6)-O(6)	102.4(2)
O(14)-Mo(2)-Mo(6)	96.35(19)	O(23)-Mo(6)-O(9)	97.7(2)
O(15)-Mo(2)-Mo(6)	103.4(2)	O(23)-Mo(6)-O(14)	106.2(2)
O(7)-Mo(3)-Mo(5)	81.54(17)	O(23)-Mo(6)-O(16)	170.1(2)
O(10)-Mo(3)-Mo(5)	134.99(13)	O(23)-Mo(6)-O(28)	95.9(2)
O(17)^{i}-Mo(3)-Mo(5)	73.22(17)	O(28)-Mo(6)-O(9)	83.0(2)
O(18)-Mo(3)-O(3)	48.13(14)	O(28)-Mo(6)-O(16)	81.0(2)
O(19)-Mo(3)-O(7)	81.66(19)	O(27)-Fe(2)-O(27)^{ii}	180.0
O(5)-Mo(4)-O(17)	160.1(2)	O(27)^{ii}-Fe(2)-O(1)^{ii}	93.7(2)
O(5)-Mo(4)-O(26)	88.58(11)	O(27)-Fe(2)-O(1)	93.7(2)
O(17)-Mo(4)-O(10)^{i}	133.44(14)	O(27)-Fe(2)-O(1)^{ii}	86.3(2)
O(26)-Mo(4)-Mo(1)	79.89(19)	O(30)-Fe(2)-O(27)	83.12(19)
O(29)-Mo(4)-O(11)	98.3(2)	O(30)^{ii}-Fe(2)-O(1)^{ii}	87.5(2)
O(20)-Mo(5)-Mo(3)	103.1(2)	O(30)-Fe(2)-O(1)^{ii}	92.5(2)
O(20)-Mo(5)-O(7)	96.9(2)	O(30)-Fe(2)-O(1)	87.5(2)
O(20)-Mo(5)-O(21)	133.64(16)	O(30)^{ii}-Fe(2)-O(1)	92.5(2)
O(21)-Mo(5)-Mo(3)	85.3(2)	O(1)-Fe(2)-O(1)^{ii}	180.0
O(21)-Mo(5)-O(9)	78.47(19)	O(5)^{i}-Fe(1)-O(5)	180.0
O(21)-Mo(5)-O(16)	49.51(13)	O(5)^{i}-Fe(1)-O(7)^{i}	83.98(17)
O(6)-Mo(6)-Mo(2)	87.02(18)	O(5)^{i}-Fe(1)-O(7)	96.02(17)
O(6)-Mo(6)-O(9)	79.73(17)	O(5)-Fe(1)-O(7)	83.98(17)
O(9)-Mo(6)-Mo(2)	72.58(17)	O(5)-Fe(1)-O(7)^{i}	96.02(17)
O(14)-Mo(6)-O(28)	86.5(2)		

Symmetry codes: i = -x, 1-y,-z; ii = -x, 2-y, -z; iii = x, -1+y, z.

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

Mo(1)-Mo(4)	2.5898(9)	P(2)-Na(1)	3.353(5)
Mo(1)-O(7)	1.975(5)	P(2)-O(15)	1.553(5)
Mo(1)-O(8)^{i}	2.111(5)	P(2)-O(25)	1.500(5)
Mo(1)-O(11)	2.286(5)	P(3)-Na(1)	3.423(5)
Mo(1)-O(14)	1.939(5)	P(3)-O(27)^{i}	1.531(6)
Mo(1)-O(23)	1.677(5)	P(3)-O(31)	1.508(6)
Mo(1)-O(32)	2.062(5)	P(3)-O(33)	1.532(6)
Mo(2)-Mo(3)	2.5769(10	P(3)-O(37)	1.584(6)
Mo(2)-O(5)	1.977(5)	P(4)-O(21)	1.540(6)

Mo(2)-O(8)	2.137(5)	P(4)-O(29)	1.534(7)
Mo(2)-O(11)^{i}	2.262(5)	P(4)-O(34)	1.613(7)
Mo(2)-O(12)	1.920(5)	P(4)-O(36)	1.495(6)
Mo(2)-O(16)	2.059(5)	Na(1)-O(19)	2.625(7)
Mo(2)-O(24)	1.674(5)	Na(1)-O(20)	2.554(7)
Mo(3)-O(5)	1.984(5)	Na(1)-O(25)	2.576(7)
Mo(3)-O(9)	2.094(5)	Na(1)-O(26)^{ii}	2.527(7)
Mo(3)-O(12)	1.932(5)	Na(1)-O(37)	2.419(8)
Mo(3)-O(15)	2.285(5)	Na(1)-O(1W)	2.419(10)
Mo(3)-O(28)	1.673(6)	N(2)-C(52)	1.403(12)
Mo(3)-O(29)	2.035(6)	N(1)-C(47)	1.470(11)
Mo(4)-O(7)	1.984(5)	C(41)-C(43)	1.395(13)
Mo(4)-O(10)^{i}	2.293(5)	C(41)-C(57)	1.383(14)
Mo(4)-O(14)	1.941(5)	C(42)-C(45)	1.370(14)
Mo(4)-O(18)	2.099(5)	C(42)-C(47)	1.376(13)
Mo(4)-O(27)	2.056(5)	C(43)-C(44)	1.492(13)
Mo(4)-O(30)	1.665(5)	C(43)-C(48)	1.386(13)
Mo(5)-Mo(6)	2.5899(10	C(44)-C(45)	1.383(13)
Mo(5)-O(6)	1.984(5)	C(44)-C(50)	1.383(13)
Mo(5)-O(9)	2.099(5)	C(46)-C(47)	1.385(13)
Mo(5)-O(15)	2.241(5)	C(46)-C(50)	1.390(14)
Mo(5)-O(19)	1.942(5)	C(48)-C(51)	1.368(14)
Mo(5)-O(21)	2.074(6)	C(49)-C(53)	1.406(16)
Mo(5)-O(22)	1.663(6)	C(49)-N(3)	1.385(16)
Mo(6)-O(6)	1.980(5)	C(49)-C(66)	1.397(17)
Mo(6)-O(10)	2.279(5)	C(51)-C(52)	1.384(14)
Mo(6)-O(17)	1.678(6)	C(52)-C(57)	1.397(14)
Mo(6)-O(18)^{i}	2.086(5)	C(53)-C(61)	1.445(18)
Mo(6)-O(19)	1.931(6)	C(53)-C(70)	1.351(17)
Mo(6)-O(33)	2.062(6)	C(54)-C(65)	1.428(18)
Co(1)-O(5)^{i}	2.121(5)	C(54)-C(70)	1.350(19)
Co(1)-O(5)	2.121(5)	C(55)-C(58)	1.408(18)
Co(1)-O(6)^{i}	2.179(5)	C(55)-C(66)	1.342(19)
Co(1)-O(6)	2.179(5)	N(3)-C(65)	1.326(15)
Co(1)-O(7)^{i}	2.177(5)	C(58)-C(61)	1.372(16)
Co(1)-O(7)	2.177(5)	C(58)-C(69)	1.458(19)
Co(2)-O(20)	2.153(6)	C(62)-C(67)	1.36(2)
Co(2)-O(20)^{ii}	2.152(6)	C(62)-C(69)	1.406(18)
Co(2)-O(25)	2.074(5)	C(64)-C(69)	1.363(18)
Co(2)-O(25)^{ii}	2.074(5)	C(64)-C(8)	1.419(17)
Co(2)-O(35)	2.113(6)	C(65)-C(75)	1.483(19)
Co(2)-O(35)^{ii}	2.113(6)	C(67)-C(4)	1.301(17)
P(1)-Na(1)^{ii}	3.162(5)	C(5)-C(3)	1.61(2)
P(1)-O(16)	1.538(5)	N(4)-C(4)	1.359(6)

P(1)-O(20)^{ii}	1.488(6)	N(4)-C(3)	1.359(6)
P(1)-O(26)	1.592(5)	C(4)-C(8)	1.359(6)
P(1)-O(32)^{ii}	1.543(6)	C(8)-C(1)	1.359(6)
P(2)-O(10)	1.548(5)	C(1)-C(2)	1.359(6)
P(2)-O(11)^{ii}	1.548(5)	C(2)-C(3)	1.359(6)
O(7)-Mo(1)-O(8)^{ii}	85.5(2)	O(19)-Mo(6)-Mo(5)	95.7(2)
O(7)-Mo(1)-O(11)	80.31(19)	O(31)-P(3)-O(27)#1	111.5(3)
O(7)-Mo(1)-O(32)	158.8(2)	O(31)-P(3)-O(33)	109.7(4)
O(14)-Mo(1)-O(7)	95.7(2)	O(31)-P(3)-O(37)	110.4(4)
O(14)-Mo(1)-O(8)^{ii}	156.7(2)	O(33)-P(3)-O(37)	105.3(4)
O(14)-Mo(1)-O(11)	83.9(2)	O(21)-P(4)-O(34)	106.2(4)
O(14)-Mo(1)-O(32)	86.9(2)	O(29)-P(4)-O(21)	110.9(3)
O(5)-Mo(2)-Mo(3)	49.54(14)	O(29)-P(4)-O(34)	107.1(4)
O(5)-Mo(2)-O(8)	85.6(2)	O(36)-P(4)-O(21)	113.6(4)
O(5)-Mo(2)-O(11)^{i}	81.26(19)	O(36)-P(4)-O(29)	111.3(4)
O(5)-Mo(2)-O(16)	159.4(2)	O(36)-P(4)-O(34)	107.3(4)
O(16)-Mo(2)-O(8)	85.1(2)	Mo(2)-O(5)-Mo(3)	81.17(19)
O(16)-Mo(2)-O(11)^{i}	78.49(19)	Mo(1)^{i}-O(8)-Mo(2)	111.5(2)
O(5)-Mo(3)-O(9)	87.4(2)	Mo(3)-O(9)-Mo(5)	112.5(2)
O(5)-Mo(3)-O(15)	79.81(19)	Mo(6)-O(10)-Mo(4)^{i}	99.69(19)
O(5)-Mo(3)-O(29)	160.2(2)	Mo(2)^{i}-O(11)-Mo(1)	101.07(18)
O(9)-Mo(3)-Mo(2)	135.45(14)	Mo(2)-O(12)-Mo(3)	84.0(2)
O(9)-Mo(3)-O(15)	72.66(19)	O(5)-Co(1)-O(7)^{i}	180.0
O(7)-Mo(4)-O(18)	85.9(2)	O(6)-Co(1)-O(6)^{i}	83.70(19)
O(7)-Mo(4)-O(27)	160.0(2)	O(7)-Co(1)-O(6)	96.30(19)
O(27)-Mo(4)-O(18)	85.2(2)	O(7)-Co(1)-O(6)^{i}	96.30(19)
O(30)-Mo(4)-O(14)	105.0(3)	O(7)^{i}-Co(1)-O(6)	83.70(19)
O(30)-Mo(4)-O(18)	98.2(3)	O(7)^{i}-Co(1)-O(6)^{i}	180.0
O(30)-Mo(4)-O(27)	97.5(3)	O(7)^{i}-Co(1)-O(7)	180.0
O(6)-Mo(5)-Mo(6)	49.14(14)	O(25)-Co(2)-O(20)	180.0
O(6)-Mo(5)-O(9)	85.7(2)	O(25)-Co(2)-O(25)^{i}	87.6(2)
O(9)-Mo(5)-O(15)	73.49(19)	O(25)-Co(2)-O(35)	92.4(2)
O(15)-Mo(5)-Mo(6)	89.75(13)	O(25)-Co(2)-O(35)^{i}	92.4(2)
O(19)-Mo(5)-Mo(6)	47.86(17)	O(25)^{ii}-Co(2)-O(35)	87.6(2)
O(6)-Mo(6)-O(33)	88.07(13)	O(25)^{ii}-Co(2)-O(35)	87.0(2)
O(10)-Mo(6)-Mo(5)	101.3(2)	O(35)-Co(2)-O(20)^{ii}	87.0(2)
O(17)-Mo(6)-Mo(5)	102.0(2)	O(35)^{ii}-Co(2)-O(20)	93.0(2)
O(17)-Mo(6)-O(6)	170.0(2)	O(35)-Co(2)-O(20)	93.0(2)
O(17)-Mo(6)-O(10)	97.2(3)		

Symmetry codes: i = 1-x, 1-y,-z; ii = 1-x, 2-y, -z.

Table S4 Selected bond lengths (Å) and bond angles (°) of compound **3**.

Mo(1)-Mo(5)	2.5919(9)	P(2)-O(20)	1.528(5)
Mo(1)-O(5)	1.981(4)	P(2)-O(27)	1.492(5)
Mo(1)-O(13)	2.243(4)	P(2)-Na(2)	3.207(4)

Mo(1)-O(14)	2.113(5)	P(3)-O(24)	1.522(5)
Mo(1)-O(22)	1.940(5)	P(3)-O(32)^{i}	1.536(5)
Mo(1)-O(26)	1.667(5)	P(3)-O(34)	1.507(5)
Mo(1)-O(29)	2.067(5)	P(3)-O(35)	1.580(5)
Mo(2)-Mo(4)	2.5887(8)	P(4)-O(29)^{i}	1.539(6)
Mo(2)-O(6)	2.124(4)	P(4)-O(31)	1.523(6)
Mo(2)-O(8)	1.967(4)	P(4)-O(37)	1.594(7)
Mo(2)-O(9)	1.936(4)	P(4)-O(1)	1.498(7)
Mo(2)-O(12)^{i}	2.290(4)	O(16)-Na(2)	2.543(6)
Mo(2)-O(15)	2.064(4)	O(18)-Na(2)	2.635(7)
Mo(2)-O(21)	1.675(5)	O(22)-Na(2)	2.634(6)
Mo(3)-Mo(6)	2.5826(8)	O(27)-Na(2)	2.615(6)
Mo(3)-O(6)	2.143(4)	O(35)-Na(2)	2.423(7)
Mo(3)-O(7)	1.974(4)	N(1)-C(46)	1.479(9)
Mo(3)-O(12)^{i}	2.272(4)	C(38)-C(46)	1.380(11)
Mo(3)-O(17)	1.915(5)	C(38)-C(56)	1.372(11)
Mo(3)-O(20)	2.065(4)	C(39)-C(49)	1.390(11)
Mo(3)-O(23)	1.669(5)	C(39)-C(51)	1.500(11)
Mo(4)-O(8)	1.980(4)	C(39)-C(56)	1.384(11)
Mo(4)-O(9)	1.938(4)	N(2)-C(43)	1.396(10)
Mo(4)-O(11)^{i}	2.289(4)	C(41)-C(48)	1.391(12)
Mo(4)-O(19)	2.116(4)	C(41)-C(51)	1.389(11)
Mo(4)-O(24)	2.061(5)	C(42)-C(46)	1.381(11)
Mo(4)-O(28)	1.678(5)	C(42)-C(49)	1.381(11)
Mo(5)-O(5)	1.964(4)	C(43)-C(47)	1.386(11)
Mo(5)-O(11)	2.283(4)	C(43)-C(48)	1.382(12)
Mo(5)-O(19)^{i}	2.089(5)	C(47)-C(55)	1.393(12)
Mo(5)-O(22)	1.930(5)	C(51)-C(55)	1.365(11)
Mo(5)-O(25)	1.677(5)	Na(2)-O(1W)	2.446(10)
Mo(5)-O(32)	2.068(5)	N(3)-C(0AA)	1.391(14)
Mo(6)-O(7)	1.987(4)	N(3)-C(14)	1.282(14)
Mo(6)-O(13)^{i}	2.279(4)	C(2AA)-C(8)	1.353(15)
Mo(6)-O(14)^{i}	2.109(4)	C(2AA)-C(0AA)	1.381(14)
Mo(6)-O(17)	1.941(5)	C(3AA)-C(0AA)	1.414(15)
Mo(6)-O(30)	1.671(5)	C(3AA)-C(13)	1.428(15)
Mo(6)-O(31)	2.040(5)	C(3AA)-C(1AA)	1.402(15)
Mn(1)-O(5)^{i}	2.226(4)	C(6)-C(7)	1.450(15)
Mn(1)-O(5)	2.226(4)	C(6)-C(8)	1.420(14)
Mn(1)-O(7)^{i}	2.177(4)	C(6)-C(13)	1.359(14)
Mn(1)-O(7)	2.177(4)	C(7)-C(15)	1.405(15)
Mn(1)-O(8)	2.220(4)	C(7)-C(16)	1.378(15)
Mn(1)-O(8)^{i}	2.220(4)	C(14)-C(19)	1.411(17)
Mn(2)-O(18)	2.146(4)	C(14)-C(1)	1.495(17)
Mn(2)-O(18)^{ii}	2.146(4)	C(15)-C(18)	1.395(16)

Mn(2)-O(27)	2.178(5)	C(16)-C(17)	1.441(15)
Mn(2)-O(27)^{ii}	2.178(5)	C(18)-C(4AA)	1.392(14)
Mn(2)-O(33)^{ii}	2.212(6)	C(19)-C(1AA)	1.359(17)
Mn(2)-O(33)	2.212(6)	O(9W)-N(4)	1.668(9)
P(1)-O(11)	1.556(5)	C(3)-C(4)	1.377(5)
P(1)-O(12)	1.550(4)	C(3)-C(5AA)	1.377(5)
P(1)-O(13)	1.549(5)	C(4)-C(17)	1.377(5)
P(1)-O(18)	1.502(4)	C(17)-C(4AA)	1.377(5)
P(1)-Na(2)^{iii}	3.447(5)	C(4AA)-N(4)	1.377(5)
P(2)-O(15)	1.538(5)	N(4)-C(5AA)	1.377(5)
P(2)-O(16)	1.580(5)	C(5AA)-C(2)	1.554(18)
O(5)-Mo(1)-Mo(5)	48.64(12)	O(5)^{i}-Mn(1)-O(5)	180.0
O(5)-Mo(1)-O(13)	80.99(16)	O(7)-Mn(1)-O(5)^{i}	96.58(16)
O(5)-Mo(1)-O(14)	86.42(18)	O(7)^{i}-Mn(1)-O(5)	96.59(16)
O(5)-Mo(1)-O(29)	159.92(19)	O(7)-Mn(1)-O(8)	96.14(15)
O(13)-Mo(1)-Mo(5)	89.50(11)	O(7)-Mn(1)-O(8)^{i}	83.86(15)
O(14)-Mo(1)-Mo(5)	134.16(13)	O(8)^{i}-Mn(1)-O(5)	96.45(16)
O(14)-Mo(1)-O(13)	72.40(16)	O(8)-Mn(1)-O(8)^{i}	180.0
O(6)-Mo(2)-Mo(4)	133.71(12)	O(18)-Mn(2)-O(18)^{ii}	180.0
O(6)-Mo(2)O(12)^{i}	72.76(15)	O(18)^{ii}-Mn(2)-O(27)^{ii}	82.31(17)
O(8)-Mo(2)-Mo(4)	49.22(12)	O(18)-Mn(2)-O(33)^{ii}	90.8(2)
O(8)-Mo(2)-O(6)	85.45(17)	O(27)^{ii}-Mn(2)-O(33)	87.6(2)
O(21)-Mo(2)-O(6)	97.8(2)	O(33)-Mn(2)-O(33)^{ii}	180.0
O(21)-Mo(2)-O(8)	102.9(2)	O(12)-P(1)-O(11)	107.0(2)
O(21)-Mo(2)-O(9)	105.0(2)	O(13)-P(1)-O(11)	108.2(2)
O(7)-Mo(3)-O(6)	85.46(17)	O(13)-P(1)-O(12)	107.5(2)
O(7)-Mo(3)-O(12)^{i}	81.98(16)	O(18)-P(1)-O(11)	111.4(3)
O(7)-Mo(3)-O(20)	159.89(18)	O(18)-P(1)-O(12)	113.8(2)
O(17)-Mo(3)-O(6)	157.62(19)	O(18)-P(1)-O(13)	108.7(3)
O(17)-Mo(3)-O(7)	96.27(18)	O(15)-P(2)-O(16)	107.0(3)
O(17)-Mo(3)-O(20)	86.55(19)	O(20)-P(2)-O(15)	109.1(3)
O(8)-Mo(4)-O(24)	160.1(2)	O(20)-P(2)-O(16)	105.8(3)
O(9)-Mo(4)-O(19)	155.86(19)	O(27)-P(2)-O(15)	113.7(3)
O(9)-Mo(4)-O(24)	85.52(19)	O(27)-P(2)-O(16)	105.0(3)
O(24)-Mo(4)-O(19)	85.51(18)	O(27)-P(2)-O(20)	115.3(3)
O(28)-Mo(4)-O(8)	101.2(2)	O(24)-P(3)-O(32)^{i}	111.5(3)
O(28)-Mo(4)-O(9)	105.2(2)	O(24)-P(3)-O(35)	108.4(3)
O(5)-Mo(5)-O(11)	82.48(16)	O(32)^{i}-P(3)-O(35)	105.7(3)
O(5)-Mo(5)-O(19)^{i}	87.10(18)	O(34)-P(3)-O(24)	111.7(3)
O(5)-Mo(5)-O(32)	161.99(19)	O(34)-P(3)-O(32)^{i}	110.0(3)
O(22)-Mo(5)-O(5)	95.68(19)	O(34)-P(3)-O(35)	109.4(3)
O(22)-Mo(5)-O(11)	81.77(18)	O(29)^{i}-P(4)-O(37)	107.5(4)
O(25)-Mo(5)-O(5)	101.6(2)	O(31)-P(4)-O(29)^{i}	111.2(3)
O(25)-Mo(5)-O(11)	169.4(2)	O(31)-P(4)-O(37)	108.4(3)

O(7)-Mo(6)-Mo(3)	49.10(12)	O(1)-P(4)-O(29)^{i}	111.8(3)
O(7)-Mo(6)-O(13)^{i}	79.40(16)	O(1)-P(4)-O(31)	111.3(4)
O(7)-Mo(6)-O(14)^{i}	87.64(17)	O(1)-P(4)-O(37)	106.4(4)
O(7)-Mo(6)-O(31)	159.6(2)		

Symmetry codes: i = -x, 1-y, 2-z; ii = -x, 2-y, 2-z.

Table S5 Selected bond lengths (Å) and bond angles (°) of compound **4**.

Mo(1)-Mo(2)	2.5972(10)	P (4)-O(41)	1.565(10)
Mo(1)-O(6)	1.971(5)	P(4)-O(42)	1.493(8)
Mo(1)-O(11)	2.104(6)	O(17)-Na(22)	2.388(8)
Mo(1)-O(141)	2.276(6)	O(30)-Zn(21)	1.950(8)
Mo(1)-O(19)	1.945(6)	O(30)-Zn(23)	2.000(8)
Mo(1)-O(21)	2.065(6)	O(30)-Zn(2A)^{iii}	1.866(7)
Mo(1)-O(29)	1.667(6)	O(30)-Zn(2A)^{i}	1.964(7)
Mo(2)-O(6)	1.967(5)	O(32)-Na(2)	2.883(10)
Mo(2)-O(81)	2.129(5)	O(33)-Na(2)	2.411(8)
Mo(2)-O(10)	2.282(5)	O(33)-Zn(2)	2.398(10)
Mo (2)-O(19)	1.933(6)	O(33)-Zn(2A)	1.803(9)
Mo(2)-O(25)	2.074(6)	O(34)-Na(22)	2.739(11)
Mo(2)-O(27)	1.673(6)	O(50)^{ii}-Na(22)	2.858(13)
Mo(3)-Mo(5)	2.5856(11)	N(1)-C(4)	1.473(13)
Mo(3)-O(7)	1.962(5)	C(4)-C(10)	1.350(15)
Mo(3)-O(8)	2.134(5)	C(4)-C(11)	1.364(14)
Mo(3)-O(101)	2.265(5)	O(3W)-Na(2)	2.346(11)
Mo(3)-O(13)	1.935(6)	C (6)-C(11)	1.393(16)
Mo(3)-O(18)	2.079(6)	C(6)-C(12)	1.401(15)
Mo(3)-O(26)	1.680(6)	N(2)-C(19)	1.330(15)
Mo(4)-Mo(6)	2.5878(11)	N(2)-C(26)	1.366(16)
Mo(4)-O(9)	2.098(6)	O(2W)-Zn(21)	2.226(12)
Mo (4)-O(12)	1.986(6)	O(2W)-Zn(2A)^{iii}	2.089(12)
Mo(4)-O(17)	1.930(6)	C(9)-C(12)	1.484(15)
Mo(4)-O(23)	2.306(5)	C(9)-C(17)	1.398(14)
Mo(4)-O(24)	1.679(6)	C(9)-C(20)	1.387(15)
Mo (4)-O(28)	2.076(6)	C(10)-C(15)	1.379(16)
Mo(5)-O(7)	1.976(5)	C(12)-C(15)	1.403(14)
Mo(5)-O(9)	2.097(6)	N(3)-C(14)	1.422(14)
Mo(5)-O(13)	1.939(6)	C(14)-C(21)	1.389(15)
Mo(5)-O(20)	2.054(6)	C(14)-C(25)	1.387(16)
Mo(5)-O(23)	2.304(5)	O (4W) -Na(2)	2.455(14)
Mo(5)-O(31)	1.672(7)	C(17)-C(25)	1.378(16)
Mo(6)-O(111)	2.110(6)	C(19)-C(28)	1.380(17)
Mo(6)-O(12)	1.981(6)	C(19)-C(32)	1.487(19)
Mo(6)-O(14)	2.286(5)	C(20)-C(21)	1.393(16)
Mo(6)-O(17)	1.926(6)	C(22)-C(24)	1.411(17)
Mo (6)-O(22)	1.678(6)	C(22)-C(28)	1.345(18)

Mo(6)-O(34)	2.048(7)	C(23)-C(24)	1.388(18)
Mo(6)-Na(22)	3.652(5)	C(23)-C(30)	1.357(17)
Zn(1)-O(61)	2.227(5)	C(24)-C(26)	1.404(17)
Zn(1)-O(6)	2.227(5)	C(26) -C(31)	1.386(16)
Zn(1)-O(7)	2.187(5)	C(27)-C(30)	1.450(19)
Zn(1)-O(71)	2.187(6)	C(27)-C(31)	1.303(19)
Zn(1)-O(121)	2.178(6)	C(29)-C(30)	1.47(2)
Zn(1)-O (12)	2.177(6)	C(29)-C(33)	1.38(2)
P(1)-O(10)	1.562(6)	C(29)-C(37)	1.38(2)
P(1)-O(141)	1.543(6)	C(33)-C (38)	1.39(2)
P (1)-O(231)	1.540(6)	C(37)-C(36)	1.397(19)
P(1)-O(30)	1.496(6)	C(38)-C (35)	1.29(2)
P(2-)O(18)	1.534(6)	C(1)-C(40)	1.341(7)
P(2)-O(251)	1.530(6)	C(1)-C(34)	1.341(7)
P(2)-O(32)	1.540(7)	C(40)-C(36)	1.341(7)
P(2)-O(33)	1.508(7)	C(36)-C(35)	1.340(7)
P(2)-Na(2)	3.257(5)	C(35)-N(4)	1.341(7)
P(3)-O(211)	1.529(7)	N(4)-C(34)	1.340(7)
P (3)-O(34)	1.518(7)	C(34)-C(2)	1.38(3)
P(3)-O(37)	1.514(8)	Na(2)-Zn (2A)	3.571(6)
P(3)-O(50)	1.542(9)	Zn(2)-Zn(22)	2.455(11)
P(3)-Na(22)	3.456(6)	Zn(2)-O(7W)	1.366(16)
P(4)-O(20)	1.521(7)	Zn(2A)-Zn(2A)	2.256(8)
P(4)-O(28)	1.524(7)	Zn(2A)-O(7W)	2.309(17)
O(6)-Mo(1)-Mo(2)	48.67(16)	O(9)-Mo(5)-O(23)	74.0(2)
O(6)-Mo(1)-O(11)	85.7(2)	O(13)-Mo(5)-O(7)	95.2(2)
O(6)-Mo(1)-O(21)	160.0(2)	O(13)-Mo(5)-O(9)	156.8(2)
O(11)-Mo(1)-O(141)	73.1(2)	O(20)-Mo(5)-O(23)	79.5(2)
O(19)-Mo(1)-Mo(2)	47.76(17)	O(31)-Mo(5)-O(7)	102.4(3)
O(21)-Mo(1)-O(11)	85.1(2)	O(17)-Mo(6)-O(34)	84.1(3)
O(29)-Mo(1)-O(19)	104.9(3)	O(22)-Mo(6)-O(14)	168.6(3)
O(29)-Mo(1)-O(21)	96.7(3)	O(22)-Mo(6)-O(17)	107.3(3)
O(6)-Mo(2)-O(81)	85.9(2)	O(22)-Mo(6)-O(34)	96.8(3)
O(6)-Mo(2)-O(10)	82.0(2)	O(34)-Mo(6)-O(14)	79.1(3)
O(81)-Mo(2)-O(10)	72.7(2)	O(34)-Mo(6)-Na(22)	47.9(3)
O(10)-Mo(2)-Mo(1)	89.32(13)	O(61)-Zn(1)-O(6)	180.0
O(19)-Mo (2)-Mo(1)	48.15(17)	O(7)-Zn(1)-O(61)	96.8(2)
O(25)-Mo(2)-Mo(1)	135.30(17)	O (12)-Zn(1)-O(61)	96.0(2)
O(27)-Mo(2)-O(6)	103.5(3)	O(121)-Zn(1)-O(7)	85.2(2)
O (7)-Mo(3)-O(8)	86.2(2)	O(121)-Zn(1)-O(71)	94.8(2)
O(8)-Mo(3)-O(101)	73.0(2)	O(12)-Zn(1)-O(7)	94.8(2)
O(13)-Mo(3)-O(7)	95.8(2)	O(30)-P (1)-O(10)	109.7(3)
O(18)-Mo(3)-O(8)	84.0(2)	O(30)-P(1)-O(141)	110.4(3)
O(18)-Mo(3)-O(101)	80.2(2)	O(18)-P(2)-O(32)	108.3(4)

O(26)-Mo(3)-O(8)	95.4(3)	O(33)-P(2)-O(32)	105.5(4)
O(9)-Mo(4)-Mo(6)	134.12(16)	O(33)-P(2)-Na(2)	44.0(3)
O(9)-Mo(4)-O(23)	73.9(2)	O(211)-P(3)-O(50)	110.1(4)
O(12)-Mo(4)-O(9)	85.8(2)	O(37)-P(3)-O(211)	111.4(4)
O(12)-Mo(4)-O(23)	81.9(2)	O(37)-P(3)-O34	108.3(5)
O(12)-Mo(4)-O(28)	160.1(2)	O(37)-P(3)-O(50)	109.5(6)
O(17)-Mo(4)-O(28)	86.5(3)	O(20)-P(4)-O(28)	112.6(4)
O(23)-Mo(4)-Mo(6)	89.19(14)	O(20)-P(4)-O(41)	105.9(5)
O(24)-Mo(4)-O(17)	105.1(3)	O(28)-P(4)-O(41)	105.6(5)
O(24)-Mo(4)-O(23)	170.4(3)	O(42)-P(4)-O(20)	113.9(5)
O(24)-Mo(4)-O(28)	96.4(3)	O(42)-P(4)-O(28)	112.3(5)
O(28)-Mo(4)-O(9)	84.9(2)	O(42)-P(4)-O(41)	105.7(6)
O(7)-Mo(5)-O (9)	85.7(2)		

Symmetry codes: i = 1-x, 2-y, 1-z; ii = 1-x, 3-y, 1-z; iii = x, 1+y, z.

Table S6 The hydrogen bond lengths (Å) and angles (°) in compound **1**.

Donor-H···Acceptor	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
N(1)-H(1B)···O(1W)	0.86	2.13	2.877(13)	145
N(2)-H(2A)···O(18)	0.89	2.55	3.370(8)	154
N(3)-H(3)···O(31)	0.86	1.88	2.732(11)	170
N(4)-H(4)···O(2W)	0.86	1.77	2.63(2)	172
C(5)-H(5C)···O(2W)	0.96	2.48	3.27(2)	139
C(7)-H(7)···O(28)	0.93	2.41	3.317(14)	164
C(12)-H(12)···O(29)	0.93	2.53	3.367(12)	150
C(14)-H(14)···O(3W)	0.93	2.59	3.400(19)	146
C(18)-H(18)···O(29)	0.93	2.41	3.190(14)	142
C(19)-H(19A)···O(31)	0.96	2.55	3.363(12)	143
C(41)-H(41)···O(15)	0.93	2.55	3.432(10)	158

Table S7 The hydrogen bond lengths (Å) and angles (°) in compound **2**.

Donor-H···Acceptor	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
N(1)-H(1A)···O(17)	0.89	2.60	3.387(10)	149
N(2)-H(2A)···O(34)	0.86	2.27	2.982(12)	140
N(3)-H(3)···O(36)	0.86	1.89	2.737(13)	170
N(4)-H(4)···O(2W)	0.86	1.75	2.606(19)	173
C(2)-H(2)···O(21)	0.93	2.38	3.115(13)	136
C(42)-H(42)···O(24)	0.93	2.55	3.430(13)	158
C(55)-H(55)···O(30)	0.93	2.54	3.357(15)	146
C(62)-H(62)···O(30)	0.93	2.45	3.219(15)	140
C(64)-H(64)···O(23)	0.93	2.56	3.391(15)	149
C(66)-H(66)···O(29)	0.93	2.41	3.317(15)	164
C(75)-H(75B)···O(36)	0.96	2.55	3.361(14)	143

Table S8 The hydrogen bond lengths (Å) and angles (°) of compound **3**.

Donor-H···Acceptor	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
N(1)-H(1D)···O(32)	0.89	2.24	2.968(8)	139
N(2)-H(2A)···O(37)	0.87	2.23	2.997(11)	146
N(3)-H(3A)···O(3W)	0.93	2.54	3.351(18)	146
C(3)-H(6)···O(4W)	0.93	2.38	3.292(14)	168
C(8)-H(8)···O(28)	0.93	2.44	3.187(13)	137
C(19)-H(19)···O(29)	0.93	2.46	3.257(15)	143
C(38)-H(38)···O(23)	0.93	2.54	3.435(10)	161
C(48)-H(48)···O(1)	0.93	2.43	3.350(12)	171

Table S9 The hydrogen bond lengths (Å) and angles (°) of compound **4**.

Donor-H···Acceptor	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
N(1)-H(1A)···O(22)	0.89	2.42	2.982(12)	121
N(2)-H(2)···O(42)	0.86	1.78	2.631(14)	168
N(3)-H(3A)···O(25)	0.88	2.17	2.986(13)	156
C(1)-H(1)···O(28)	0.93	2.57	3.283(16)	134
C(10)-H(10)···O(26)	0.93	2.54	3.419(14)	158
C(22)-H(22)···O(19)	0.93	2.53	3.444(14)	167
C(27)-H(27)···O(29)	0.93	2.53	3.310(15)	142
C(32)-H(32A)···O(42)	0.96	2.60	3.372(16)	138
C(37)-H(37)···O(27)	0.93	2.56	3.394(19)	149

Table S10 BVS results of Mo atoms and M centers in **1-4**.

	compound **1**	compound **2**	compound **3**	compound **4**
Mo1	5.144	5.198	5.264	5.266
Mo2	5.135	5.249	5.207	5.221
Mo3	5.236	5.302	5.297	5.179
Mo4	5.224	5.259	5.186	5.177
Mo5	5.263	5.298	5.281	5.248
Mo6	5.249	5.255	5.250	5.242
M(Fe, Co, Mn, Zn)	1.806	1.703	1.947	1.583

Table S11 Peak potential data (mV) for **1-4** at a sweep rate of 140 $mV \cdot s^{-1}$.

Scan rate 140 mV s^{-1}	*E*a/*E*c (I) / mV $E_{1/2}$	*E*a/*E*c (II) / mV $E_{1/2}$	*E*a/*E*c (III) / mV $E_{1/2}$	*E*a/*E*c (III) / mV $E_{1/2}$
compound **1**	30 / -50 -10	260 / 190 225	430 / 350 390	720 / 590 655
compound **2**	19 / -43 -12	250 / 190 220	430 / 360 395	710 / 600 655

compound **3**	34 / -66 -16	280 / 167 223.5	453 / 316 384.5	729 / 581 655
compound **4**	17 / -43 -13	257 / 180 218.5	435 / 345 390	691 / 608 649.5

Table S12 Performance comparison of typical photocatalysts for Cr(VI) reduction.

photocatalysts	light source	dose (mg)	V (mL)	C (mg/L)	time (min)	R (%)	K (min^{-1})	Ref.
GO/g-C_3N_4/MoS_2	300 W Xe lamp	20	50	10	60	88	0.0123	1
carbon/SnS_2/MCS	300 W Xe lamp	50	100	50	120	63.2	0.00656	2
CdS/$P_2Mo_xW_{18-x}$	500 W Xe lamp	30	30	40	100	64	0.0102	3
Ag/AgCl/NH_2-UiO-66	300 W Xe lamp	25	100	20	150	93	0.0177	4
[Zn(mbpy)] {$Zn[P_4Mo_6O_{31}]_2$}	10 W LED	20	15	118	180	94.7	0.0163	5
crystal **1**	10 W LED	20	15	118	120	86	0.016	This work
crystal **2**	10 W LED	20	15	118	120	82	0.014	This work
crystal **3**	10 W LED	20	15	118	120	76	0.011	This work
crystal **4**	10 W LED	20	15	118	120	72	0.010	This work

Reference:

1 M. H. Wu, L. Li, Y. C. Xue, G. Xu, L. Tang, N. Liu and W. Y. Huang, *Appl. Catal., B*, 2018, **228**, 103-112.

2 L. Han, Y. L. Zhong, Y. Su, L. T. Wang, L. S. Zhu, X. F. Fei, Y. Z. Dong, G. Hong, Y. T. Zhou and D. Fang, *Chem. Eng. J.*, 2019, **369**, 1138-1149.

3 C. X. Liu, W. C. Fang, Y. T. Song, F. Y. Li, Z. X. Sun and L. Xu, *Mater. Sci. Semicond. Process.*, 2020, **120**, 105276.

4 Z. G. Zhang, S. Q. Wang, M. Bao, J. Ren, S. Pei, S. Yu and J. Ke, *J. Colloid Interface Sci.*, 2019, **555**, 342-351.

5 L. Hou, Y. Zhang, Y. Ma, Y. Wang, Z. Hu, Y. Gao and Z. Han, *Inorg. Chem.*, 2019, **58**, 16667-16675.