

Support Information

Organic-Inorganic Hybrid Material Based on Basket-like $\{\text{Ca}\text{P}_6\text{Mo}_{18}\text{O}_{73}\}$ cages

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Di Sun^c, Bai-Bin Zhou^{a,b*}

1. Structural figures

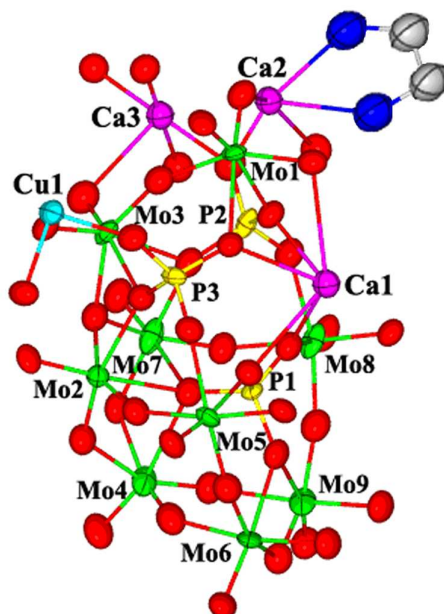


Figure S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoid.

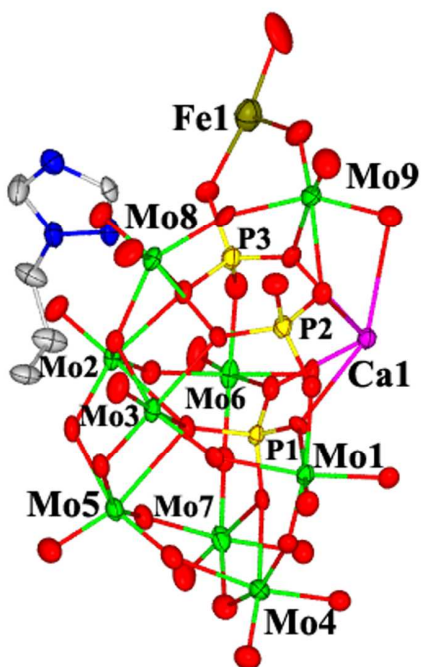


Figure S2 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoid.

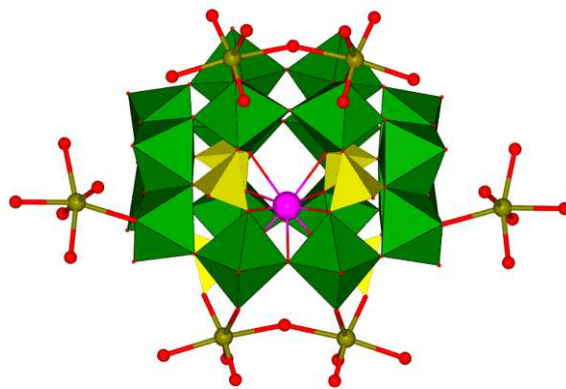


Figure S3 The coordination pattern of $\{P_6Mo_{18}\}$ cluster of compound **2**

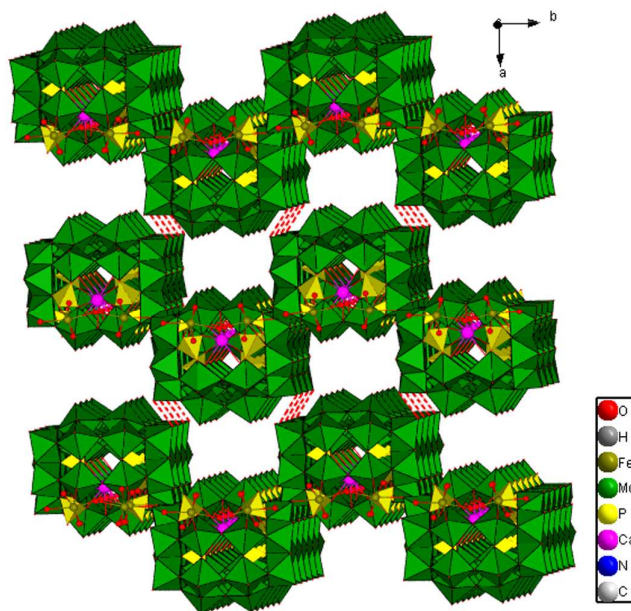


Figure S4 The 3-D supramolecular network on the *ab* plane of compound **2**.

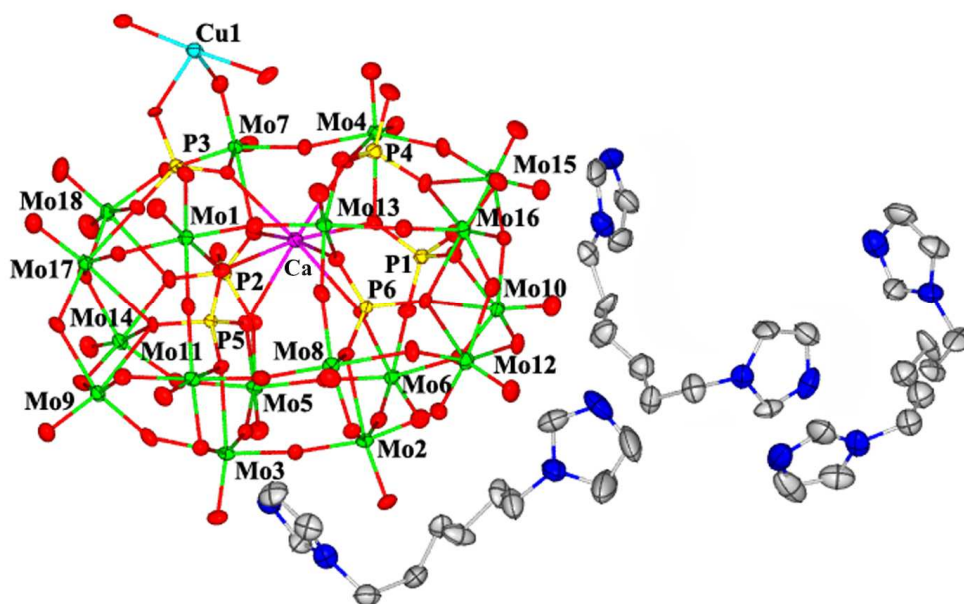


Figure S5 ORTEP view of the basic units in compound **3** with 50% thermal ellipsoid.

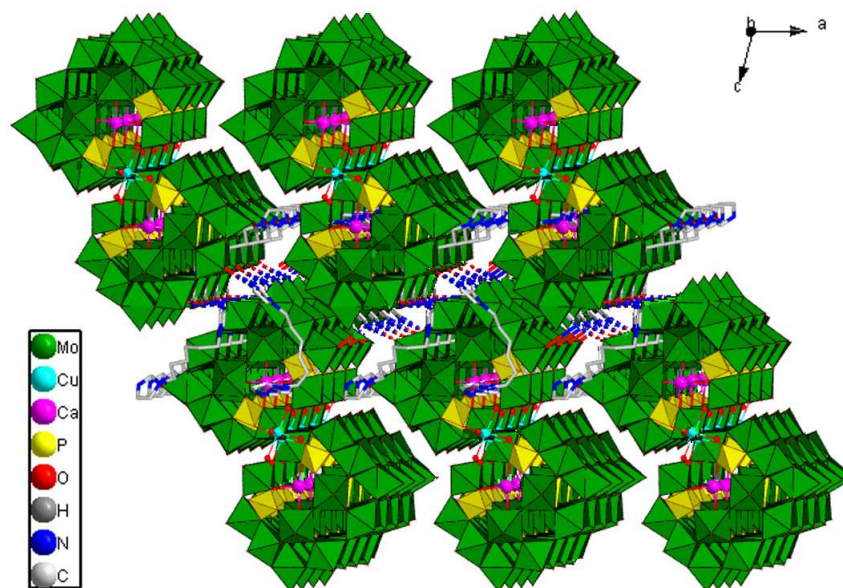


Figure S6 The 3-D supramolecular network on the ab plane of compound **3**.

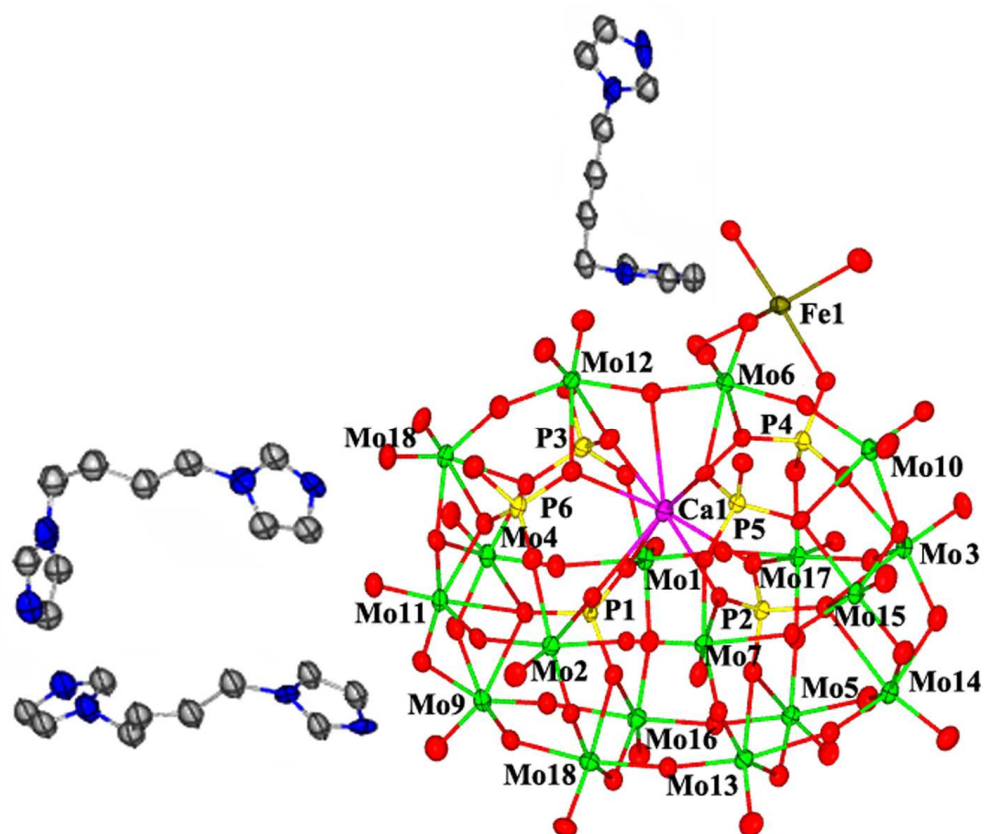


Figure S7 ORTEP view of the basic units in compound **4** with 50% thermal ellipsoid.

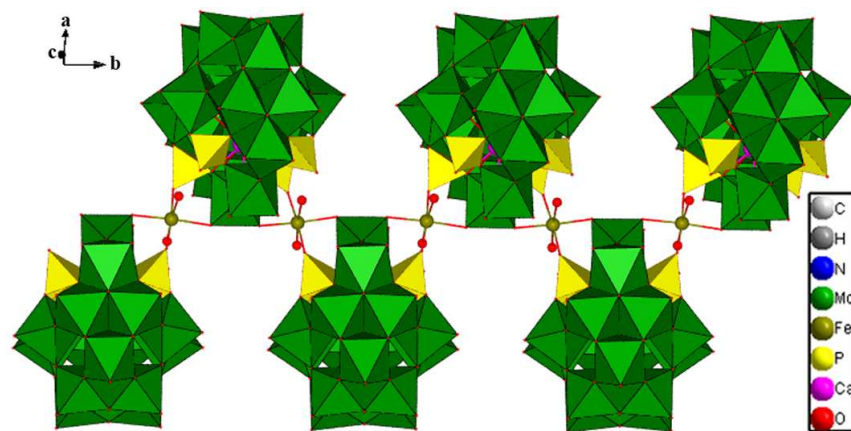


Figure S8 The 1-D zigzag chain of compound **4** based on $\{P_6Mo_{18}\}$ units and $\{Fe(H_2O)_2\}$ linkers.

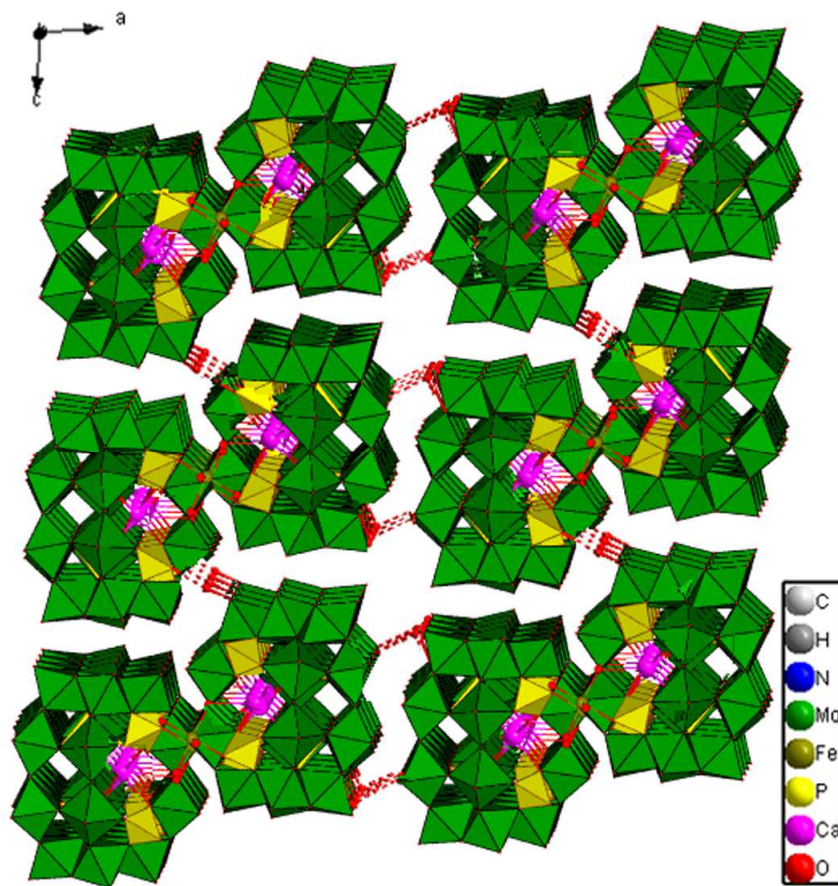


Figure S9 The 3-D supramolecular network on the ab plane of compound **4**.

2. Structural data

Table S1 Selected bond lengths (Å) and bond angles (°) of compound **1**

Mo(1)-O(23)	1.71(2)	Mo(2)-O(27)	1.714(18)	Mo(3)-O(7)	1.701(18)
Mo(1)-O(14)	1.775(17)	Mo(2)-O(19)	1.76(2)	Mo(3)-O(24)	1.74(2)
Mo(1)-O(36)	1.888(4)	Mo(2)-O(4)	1.806(18)	Mo(3)-O(21)	1.86(2)
Mo(1)-O(21)	1.95(2)	Mo(2)-O(20)	2.087(19)	Mo(3)-O(20)	2.035(19)
Mo(1)-O(37)	2.266(17)	Mo(2)-O(35)	2.118(18)	Mo(3)-O(35) (	2.279(19)
Mo(1)-O(28)	2.277(18)	Mo(2)-O(15)	2.442(19)	Mo(3)-O(3)	2.310(18)
Mo(4)-O(38)	1.70(2)	Mo(5)-O(33)	1.690(18)	Mo(6)-O(30)	1.70(2)
Mo(4)-O(31)	1.724(19)	Mo(5)-O(1)	1.860(18)	Mo(6)-O(6)	1.856(19)
Mo(4)-O(8)	1.79(2)	Mo(5)-O(11)	1.88(2)	Mo(6)-O(11)	1.88(2)
Mo(4)-O(4)	2.031(19)	Mo(5)-O(19)	2.03(2)	Mo(6)-O(18)	2.00(3)
Mo(4)-O(29)	2.15(2)	Mo(5)-O(17)	2.23(2)	Mo(6)-O(8)	2.08(2)
Mo(4)-O(15)	2.433(19)	Mo(5)-O(2)	2.239(12)	Mo(6)-O(9)	2.29(2)
Mo(7)-O(32)	1.66(2)	Mo(8)-O(13)	1.67(2)	Mo(9)-O(10)	1.69(2)
Mo(7)-O(5)	1.742(19)	Mo(8)-O(1)#2	1.867(19)	Mo(9)-O(18)	1.82(3)
Mo(7)-O(29)	1.803(19)	Mo(8)-O(12)	1.91(2)	Mo(9)-O(12)	1.87(2)
Mo(7)-O(20)	2.063(19)	Mo(8)-O(5)	2.062(19)	Mo(9)-O(6)#2	1.884(19)
Mo(7)-O(3)	2.14(2)	Mo(8)-O(26)	2.063(19)	Mo(9)-O(31)	2.146(19)
Mo(7)-O(15)	2.42(2)	Mo(8)-O(25)	2.23(2)	Mo(9)-O(9)	2.29(2)
P(1)-O(2)	1.49(2)	P(2)-O(37)	1.46(2)	P(3)-O(22)	1.490(18)
P(1)-O(25)	1.50(2)	P(2)-O(26)	1.543(19)	P(3)-O(28)	1.496(18)
P(1)-O(15)	1.54(2)	P(2)-O(16)	1.56(2)	P(3)-O(17)	1.525(19)
P(1)-O(9)	1.54(2)	P(2)-O(3)	1.57(2)	P(3)-O(35)	1.594(19)
Cu(1)-O(22)	1.92(2)	Ca(1)-O(28)#2	2.535(18)	Ca(1)-O(25)#2	2.63(2)
Cu(1)-O(22)#3	1.92(2)	Ca(1)-O(28)	2.535(18)	Ca(1)-O(25)	2.63(2)
Cu(1)-O(34)	1.962(17)	Ca(1)-O(37)#2	2.539(19)	Ca(1)-O(2)#2	2.66(2)
Cu(1)-O(34)#3	1.962(17)	Ca(1)-O(37)	2.539(19)	Ca(1)-O(2)	2.66(2)
Ca(1)-O(36)	2.83(3)	Ca(2)-O(41)	2.74(4)	Ca(2)-O(42)#1	2.27(3)
Ca(3)-O(40)	2.14(5)	Ca(3)-O(42)#1	2.67(3)	Ca(2)-N(1)	2.49(4)
Ca(2)-N(2)	2.62(4)	Ca(2)-O23	2.63(3)	Ca(2)-O16	2.08(3)
Ca(3)-O24	2.65(4)	Ca(3)-O16	2.16(3)	Cu(1)-O7	2.54(8)
O(23)-Mo(1)-O(14)	106.3(9)	O(27)-Mo(2)-O(19)	106.8(9)	O(7)-Mo(3)-O(24)	102.4(10)
O(23)-Mo(1)-O(36)	101.5(8)	O(27)-Mo(2)-O(4)	102.0(8)	O(7)-Mo(3)-O(21)	102.6(9)
O(23)-Mo(1)-O(21)	95.2(9)	O(27)-Mo(2)-O(20)	95.2(8)	O(7)-Mo(3)-O(20)	98.5(8)
O(23)-Mo(1)-O(37)	89.4(8)	O(27)-Mo(2)-O(35)	97.5(8)	O(7)-Mo(3)-O(35)	85.5(8)
O(23)-Mo(1)-O(28)	164.3(8)	O(27)-Mo(2)-O(15)	168.6(8)	O(7)-Mo(3)-O(3)	166.0(8)
O(38)-Mo(4)-O(31)	103.8(10)	O(33)-Mo(5)-O(1)	97.3(9)	O(30)-Mo(6)-O(6)	101.6(10)
O(38)-Mo(4)-O(8)	104.6(11)	O(33)-Mo(5)-O(11)	101.1(9)	O(30)-Mo(6)-O(11)	101.5(10)
O(38)-Mo(4)-O(4)	97.8(9)	O(33)-Mo(5)-O(19)	96.6(9)	O(30)-Mo(6)-O(18)	103.5(11)
O(38)-Mo(4)-O(29)	94.8(10)	O(33)-Mo(5)-O(17)	97.1(9)	O(30)-Mo(6)-O(8)	92.0(9)
O(38)-Mo(4)-O(15)	164.9(9)	O(33)-Mo(5)-O(2)	173.4(8)	O(30)-Mo(6)-O(9)	169.6(9)
O(32)-Mo(7)-O(5)	104.2(10)	O(13)-Mo(8)-O(1)#2	98.5(9)	O(10)-Mo(9)-O(18)	99.7(12)
O(32)-Mo(7)-O(29)	101.1(10)	O(13)-Mo(8)-O(12)	99.3(9)	O(10)-Mo(9)-O(12)	101.3(11)
O(32)-Mo(7)-O(20)	97.4(9)	O(13)-Mo(8)-O(5)	94.8(9)	O(10)-Mo(9)-O(6)#2	102.7(11)

O(32)-Mo(7)-O(3)	95.6(9)	O(13)-Mo(8)-O(26)	95.6(9)	O(10)-Mo(9)-O(31)	90.8(10)
O(32)-Mo(7)-O(15)	172.2(8)	O(13)-Mo(8)-O(25)	174.8(8)	O(10)-Mo(9)-O(9)	166.8(10)
O(2)-P(1)-O(25)	108.7(11)	O(37)-P(2)-O(26)	114.2(11)	O(22)-P(3)-O(28)	112.5(10)
O(2)-P(1)-O(15)	109.2(11)	O(37)-P(2)-O(16)	113.0(11)	O(22)-P(3)-O(17)	108.4(11)
O(2)-P(1)-O(9)	112.2(11)	O(37)-P(2)-O(3)	107.1(11)	O(22)-P(3)-O(35)	107.6(11)
O(22)-Cu(1)-O(22)#3	179.999(6)	O(28)-Ca(1)-O(37)#2	82.9(6)	O(28)-Ca(1)-O(25)	101.8(6)
O(22)-Cu(1)-O(34)	91.1(8)	O(28)-Ca(1)-O(37)	66.1(6)	O(28)-Ca(1)-O(2)#2	170.7(7)
O(22)-Cu(1)-O(34)#3	88.9(8)	O(28)-Ca(1)-O(25)#2	118.7(6)	O(16)-Ca(2)-O(42)#1	106.2(10)
O(28)-Ca(1)-O(2)	71.4(6)	O(28)-Ca(1)-O(36)	58.8(4)	O(16)-Ca(2)-O(23)	85.8(9)
O(16)-Ca(2)-O(41)	81.6(10)	O(16)-Ca(2)-O(39)	73.6(12)	O(39)-Ca(3)-O(16)	110.7(17)
O(39)-Ca(3)-O(42)	83.2(17)	O(39)-Ca(3)-O(40)	173(2)	O(39)-Ca(3)-O(42)#1	98.5(17)
O(39)-Ca(3)-O(24)	90.2(16)	O(16)-Ca(2)-N(1)	162.0(13)	O(16)-Ca(2)-N(2)	112.6(12)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x+1/2,-y+1/2,-z

Table S2 Selected bond lengths (Å) and bond angles (°) of compound **2**

Mo(1)-O(31)	1.668(8)	Mo(1)-O(13)	1.834(8)	Mo(1)-O(2)	1.8446(14)
Mo(1)-O(19)	2.001(7)	Mo(1)-O(9)	2.021(8)	Mo(1)-O(7)	2.218(7)
Mo(2)-O(16)	1.666(8)	Mo(2)-O(26)	1.751(8)	Mo(2)-O(10)	1.787(8)
Mo(2)-O(6)	2.019(8)	Mo(2)-O(21)	2.118(8)	Mo(2)-O(17)	2.409(8)
Mo(3)-O(37)	1.660(8)	Mo(3)-O(19)	1.761(8)	Mo(3)-O(4)	1.783(8)
Mo(3)-O(6)	2.048(8)	Mo(3)-O(25)	2.127(8)	Mo(3)-O(17)	2.329(8)
Mo(4)-O(39)	1.661(9)	Mo(4)-O(14)	1.8611(12)	Mo(4)-O(13)	1.865(9)
Mo(4)-O(27)	1.973(9)	Mo(4)-O(34)	2.048(8)	Mo(4)-O(15)	2.274(8)
Mo(5)-O(24)	1.669(9)	Mo(5)-O(34)	1.771(9)	Mo(5)-O(18)	1.798(8)
Mo(5)-O(4)	2.039(8)	Mo(5)-O(10)	2.054(8)	Mo(5)-O(17)	2.315(8)
Mo(6)-O(40)	1.661(9)	Mo(6)-O(3)	1.8377(16)	Mo(6)-O(11)	1.838(9)
Mo(6)-O(26)	2.015(8)	Mo(6)-O(30)	2.019(9)	Mo(6)-O(5)	2.221(8)
Mo(7)-O(38)	1.666(9)	Mo(7)-O(11)	1.861(9)	Mo(7)-O(8)	1.8544(13)
Mo(7)-O(27)	1.958(10)	Mo(7)-O(18)	2.022(8)	Mo(7)-O(15)	2.269(8)
Mo(8)-O(23)	1.665(9)	Mo(8)-O(20)	1.711(9)	Mo(8)-O(29)	1.831(8)
Mo(8)-O(6)	2.018(8)	Mo(8)-O(21)	2.309(8)	Mo(8)-O(25)	2.312(8)
Mo(9)-O(36)	1.679(11)	Mo(9)-O(35)	1.705(10)	Mo(9)-O(1)	1.826(2)
Mo(9)-O(29)	1.961(8)	Mo(9)-O(33)	2.244(8)	Mo(9)-O(22)	2.302(9)
P(1)-O(5)	1.513(8)	P(2)-O(33)	1.515(8)	P(3)-O(22)	1.495(8)
P(1)-O(7)	1.522(8)	P(2)-O(9)	1.523(8)	P(3)-O(30)	1.528(9)
P(1)-O(15)	1.538(8)	P(2)-O(25)	1.544(8)	P(3)-O(21)	1.547(8)
P(1)-O(17)	1.589(8)	P(2)-O(12)	1.559(8)	P(3)-O(32)	1.571(8)
Ca(1)-O(22)#2	2.457(8)	Ca(1)-O(22)	2.457(8)	Ca(1)-O(33)#2	2.503(8)
Ca(1)-O(33)	2.503(8)	Ca(1)-O(7)#2	2.617(7)	Ca(1)-O(7)	2.617(7)
Ca(1)-O(5)	2.643(8)	Ca(1)-O(5)#2	2.643(8)	Ca(1)-O(1)	2.842(12)
Fe(1)-O(32)	1.923(13)	Fe(1)-O(31)#1	2.276(13)	Fe(1)-O(42)	1.91(3)
O(31)-Mo(1)-O(13)	101.7(4)	O(16)-Mo(2)-O(26)	104.8(4)	O(37)-Mo(3)-O(19)	106.0(4)
O(31)-Mo(1)-O(2)	99.5(5)	O(16)-Mo(2)-O(10)	103.0(4)	O(37)-Mo(3)-O(4)	102.4(4)
O(31)-Mo(1)-O(19)	94.0(4)	O(16)-Mo(2)-O(6)	98.5(4)	O(37)-Mo(3)-O(6)	95.2(4)
O(31)-Mo(1)-O(9)	95.0(4)	O(16)-Mo(2)-O(21)	98.4(4)	O(37)-Mo(3)-O(25)	95.7(4)
O(31)-Mo(1)-O(7)	172.4(4)	O(16)-Mo(2)-O(17)	170.0(4)	O(37)-Mo(3)-O(25)	95.7(4)
O(39)-Mo(4)-O(14)	99.8(5)	O(24)-Mo(5)-O(34)	105.0(4)	O(40)-Mo(6)-O(3)	98.3(5)

O(39)-Mo(4)-O(13)	101.5(4)	O(24)-Mo(5)-O(18)	106.4(4)	O(40)-Mo(6)-O(11)	102.0(5)
O(39)-Mo(4)-O(27)	99.1(4)	O(24)-Mo(5)-O(4)	95.1(4)	O(40)-Mo(6)-O(26)	95.0(4)
O(39)-Mo(4)-O(34)	95.8(4)	O(24)-Mo(5)-O(10)	95.7(4)	O(40)-Mo(6)-O(30)	94.9(4)
O(39)-Mo(4)-O(15)	170.9(4)	O(24)-Mo(5)-O(17)	162.1(4)	O(40)-Mo(6)-O(5)	173.0(4)
O(38)-Mo(7)-O(11)	101.9(5)	O(23)-Mo(8)-O(20)	103.3(5)	O(36)-Mo(9)-O(35)	101.4(5)
O(38)-Mo(7)-O(8)	100.7(5)	O(23)-Mo(8)-O(29)	104.3(4)	O(36)-Mo(9)-O(1)	101.1(5)
O(38)-Mo(7)-O(27)	98.5(5)	O(23)-Mo(8)-O(6)	98.7(4)	O(36)-Mo(9)-O(29)	97.2(4)
O(38)-Mo(7)-O(18)	95.1(4)	O(23)-Mo(8)-O(21)	166.3(4)	O(36)-Mo(9)-O(33)	96.3(4)
O(38)-Mo(7)-O(15)	170.1(4)	O(23)-Mo(8)-O(25)	87.8(4)	O(36)-Mo(9)-O(22)	169.4(4)
O(5)-P(1)-O(7)	108.6(4)	O(5)-P(1)-O(15)	111.6(5)	O(5)-P(1)-O(17)	110.1(4)
O(33)-P(2)-O(9)	112.7(4)	O(33)-P(2)-O(25)	109.2(5)	O(33)-P(2)-O(12)	107.8(5)
O(22)-P(3)-O(30)	112.4(5)	O(22)-P(3)-O(21)	109.4(4)	O(22)-P(3)-O(32)	110.3(5)
O(22)#2-Ca(1)-O(22)	81.3(4)	O(22)#2-Ca(1)-O(33)#2	67.1(3)	O(22)-Ca(1)-O(33)#2	116.8(3)
O(22)#2-Ca(1)-O(33)	116.8(3)	O(22)-Ca(1)-O(33)	67.1(3)	O(22)#2-Ca(1)-O(7)#2	102.6(2)
O(22)-Ca(1)-O(7)#2	168.5(3)	O(22)#2-Ca(1)-O(7)	168.5(3)	O(22)-Ca(1)-O(7)	102.6(2)
O(22)#2-Ca(1)-O(5)	116.5(3)	O(22)-Ca(1)-O(5)	71.7(3)	O(22)#2-Ca(1)-O(5)#2	71.7(3)
O(22)-Ca(1)-O(5)#2	116.5(3)	O(22)#2-Ca(1)-O(1)	59.5(3)	O(22)-Ca(1)-O(1)	59.5(3)
O(42)-Fe(1)-O(32)	168.1(11)	O(42)-Fe(1)-O(31)#1	91.6(10)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x+1/2,-y+1/2,-z

Table S3 Selected bond lengths (Å) and bond angles (°) of compound **3**

Mo(1)-O(20)	1.691(6)	Mo(2)-O(6)	1.692(6)	Mo(3)-O(8)	1.672(6)
Mo(1)-O(59)	1.782(5)	Mo(2)-O(60)	1.860(5)	Mo(3)-O(39)	1.873(5)
Mo(1)-O(38)	1.865(6)	Mo(2)-O(34)	1.885(6)	Mo(3)-O(32)	1.888(5)
Mo(1)-O(62)	2.057(5)	Mo(2)-O(49)	1.885(5)	Mo(3)-O(14)	1.939(6)
Mo(1)-O(23)	2.074(6)	Mo(2)-O(46)	2.132(6)	Mo(3)-O(16)	2.121(5)
Mo(1)-O(61)	2.456(5)	Mo(2)-O(40)	2.306(5)	Mo(3)-O(45)	2.297(6)
Mo(4)-O(13)	1.682(6)	Mo(5)-O(3)	1.680(6)	Mo(6)-O(12)	1.682(6)
Mo(4)-O(1)	1.693(6)	Mo(5)-O(60)	1.878(5)	Mo(6)-O(32)	1.872(6)
Mo(4)-O(15)	1.809(5)	Mo(5)-O(39)	1.888(6)	Mo(6)-O(34)	1.877(5)
Mo(4)-O(24)	2.036(5)	Mo(5)-O(29)	1.990(5)	Mo(6)-O(17)	1.908(5)
Mo(4)-O(41)	2.344(6)	Mo(5)-O(21)	2.068(6)	Mo(6)-O(22)	2.098(5)
Mo(4)-O(43)	2.403(6)	Mo(5)-O(31)	2.297(6)	Mo(6)-O(69)	2.314(6)
Mo(7)-O(10)	1.659(6)	Mo(8)-O(4)	1.669(5)	Mo(9)-O(5)	1.665(6)
Mo(7)-O(68)	1.680(6)	Mo(8)-O(26)	1.881(6)	Mo(9)-O(16)	1.861(5)
Mo(7)-O(15)	1.858(6)	Mo(8)-O(25)	1.892(6)	Mo(9)-O(37)	1.868(6)
Mo(7)-O(19)	2.060(6)	Mo(8)-O(17)	2.045(6)	Mo(9)-O(66)	2.011(6)
Mo(7)-O(7)	2.331(5)	Mo(8)-O(28)	2.081(6)	Mo(9)-O(47)	2.065(6)
Mo(7)-O(35)	2.360(5)	Mo(8)-O(69)	2.267(5)	Mo(9)-O(64)	2.239(5)
Mo(10)-O(9)	1.705(6)	Mo(11)-O(11)	1.692(6)	Mo(12)-O(67)	1.702(6)
Mo(10)-O(49)	1.731(6)	Mo(11)-O(26)	1.832(5)	Mo(12)-O(28)	1.791(5)
Mo(10)-O(74)	1.866(6)	Mo(11)-O(38)	1.892(6)	Mo(12)-O(22)	1.792(6)
Mo(10)-O(54)	1.978(6)	Mo(11)-O(14)	2.018(6)	Mo(12)-O(65)	2.062(5)
Mo(10)-O(51)	2.204(5)	Mo(11)-O(37)	2.038(6)	Mo(12)-O(74)	2.062(6)
Mo(10)-O(55)	2.235(5)	Mo(11)-O(45)	2.222(5)	Mo(12)-O(55)	2.439(6)
Mo(13)-O(72)	1.862(6)	Mo(14)-O(36)	1.680(6)	Mo(15)-O(2)	1.694(6)
Mo(13)-O(59)	2.054(6)	Mo(14)-O(29)	1.796(6)	Mo(15)-O(44)	1.700(6)

Mo(13)-O(25)	1.881(6)	Mo(14)-O(47)	1.811(6)	Mo(15)-O(24)	1.921(6)
Mo(13)-O(57)	2.256(6)	Mo(14)-O(70)	2.063(5)	Mo(15)-O(54)	1.930(6)
Mo(13)-O(50)	2.037(6)	Mo(14)-O(73)	2.132(6)	Mo(15)-O(33)	2.287(6)
Mo(13)-O(71)	1.706(6)	Mo(14)-O(64)	2.422(6)	Mo(15)-O(51)	2.313(5)
Mo(16)-O(18)	1.689(6)	Mo(17)-O(30)	1.671(6)	Mo(18)-O(75)	1.664(7)
Mo(16)-O(57)	1.753(6)	Mo(17)-O(62)	1.754(6)	Mo(18)-O(52)	1.775(6)
Mo(16)-O(65)	1.818(6)	Mo(17)-O(66)	1.820(6)	Mo(18)-O(19)	1.841(5)
Mo(16)-O(54)	2.061(5)	Mo(17)-O(70)	2.022(6)	Mo(18)-O(70)	2.059(5)
Mo(16)-O(33)	2.151(6)	Mo(17)-O(56)	2.139(6)	Mo(18)-O(73)	2.099(6)
Mo(16)-O(55)	2.357(5)	Mo(17)-O(64)	2.424(5)	Mo(18)-O(56)	2.420(6)
P(1)-O(43)	1.518(6)	P(2)-O(21)	1.542(6)	P(3)-O(42)	1.530(6)
P(1)-O(46)	1.526(6)	P(2)-O(35)	1.547(6)	P(3)-O(7)	1.555(6)
P(1)-O(51)	1.566(6)	P(2)-O(48)	1.550(6)	P(3)-O(23)	1.563(6)
P(1)-O(58)	1.590(6)	P(2)-O(73)	1.575(6)	P(3)-O(56)	1.576(6)
P(4)-O(50)	1.511(6)	P(5)-O(61)	1.531(6)	P(6)-O(40)	1.537(6)
P(4)-O(41)	1.526(6)	P(5)-O(31)	1.537(6)	P(6)-O(71)	1.537(6)
P(4)-O(33)	1.566(6)	P(5)-O(45)	1.564(5)	P(6)-O(69)	1.547(5)
P(4)-O(27)	1.596(6)	P(5)-O(64)	1.581(5)	P(6)-O(55)	1.600(5)
Cu(1)-O(42)	1.948(6)	Cu(1)-O(48)#1	1.955(6)	Cu(1)-O(53)	2.122(6)
Cu(1)-O(63)	2.194(6)	Cu(1)-O(68)	2.207(6)	Cu(1)-O(10)#1	2.210(6)
Ca(1)-O(35)	2.482(6)	Ca(1)-O(7)	2.497(6)	Ca(1)-O(41)	2.530(6)
Ca(1)-O(31)	2.578(6)	Ca(1)-O(40)	2.596(6)	Ca(1)-O(61)	2.600(6)
Ca(1)-O(43)	2.603(6)	Ca(1)-O(71)	2.615(6)	Ca(1)-O(15)	2.823(6)
O(20)-Mo(1)-O(59)	99.1(3)	O(6)-Mo(2)-O(60)	99.5(3)	O(8)-Mo(3)-O(39)	101.4(3)
O(20)-Mo(1)-O(38)	101.0(3)	O(6)-Mo(2)-O(34)	101.3(3)	O(8)-Mo(3)-O(32)	101.2(3)
O(20)-Mo(1)-O(62)	93.9(3)	O(6)-Mo(2)-O(49)	94.3(3)	O(8)-Mo(3)-O(14)	99.2(3)
O(20)-Mo(1)-O(23)	95.9(3)	O(6)-Mo(2)-O(46)	96.4(3)	O(8)-Mo(3)-O(16)	91.8(3)
O(20)-Mo(1)-O(61)	173.7(3)	O(6)-Mo(2)-O(40)	172.8(3)	O(8)-Mo(3)-O(45)	168.0(2)
O(13)-Mo(4)-O(1)	104.3(3)	O(3)-Mo(5)-O(60)	99.1(3)	O(12)-Mo(6)-O(32)	100.5(3)
O(13)-Mo(4)-O(15)	99.8(3)	O(3)-Mo(5)-O(39)	101.9(3)	O(12)-Mo(6)-O(34)	101.1(3)
O(13)-Mo(4)-O(24)	97.7(3)	O(3)-Mo(5)-O(29)	94.3(3)	O(12)-Mo(6)-O(17)	101.1(3)
O(13)-Mo(4)-O(41)	166.6(3)	O(3)-Mo(5)-O(21)	96.6(3)	O(12)-Mo(6)-O(22)	91.7(3)
O(13)-Mo(4)-O(43)	92.2(3)	O(3)-Mo(5)-O(31)	173.7(3)	O(12)-Mo(6)-O(69)	169.2(2)
O(10)-Mo(7)-O(68)	103.0(3)	O(4)-Mo(8)-O(26)	100.2(3)	O(5)-Mo(9)-O(16)	104.6(3)
O(10)-Mo(7)-O(15)	98.0(3)	O(4)-Mo(8)-O(25)	101.8(3)	O(5)-Mo(9)-O(37)	103.8(3)
O(10)-Mo(7)-O(19)	96.2(3)	O(4)-Mo(8)-O(17)	102.7(3)	O(5)-Mo(9)-O(66)	96.6(3)
O(10)-Mo(7)-O(7)	164.6(2)	O(4)-Mo(8)-O(28)	93.6(3)	O(5)-Mo(9)-O(47)	96.8(3)
O(10)-Mo(7)-O(35)	91.3(2)	O(4)-Mo(8)-O(69)	170.6(2)	O(5)-Mo(9)-O(64)	163.3(2)
O(9)-Mo(10)-O(49)	104.2(3)	O(11)-Mo(11)-O(26)	100.2(3)	O(67)-Mo(12)-O(28)	105.7(3)
O(9)-Mo(10)-O(74)	102.9(3)	O(11)-Mo(11)-O(38)	103.0(3)	O(67)-Mo(12)-O(22)	104.9(3)
O(9)-Mo(10)-O(54)	97.3(3)	O(11)-Mo(11)-O(14)	99.2(3)	O(67)-Mo(12)-O(65)	95.4(3)
O(9)-Mo(10)-O(51)	96.1(3)	O(11)-Mo(11)-O(37)	92.8(3)	O(67)-Mo(12)-O(74)	94.7(3)
O(9)-Mo(10)-O(55)	169.7(3)	O(11)-Mo(11)-O(45)	168.2(2)	O(67)-Mo(12)-O(55)	161.4(2)
O(72)-Mo(13)-O(59)	98.5(3)	O(36)-Mo(14)-O(29)	104.1(3)	O(2)-Mo(15)-O(44)	103.4(3)
O(72)-Mo(13)-O(25)	101.5(3)	O(36)-Mo(14)-O(47)	102.3(3)	O(2)-Mo(15)-O(24)	105.6(3)
O(72)-Mo(13)-O(57)	94.7(3)	O(36)-Mo(14)-O(70)	98.4(3)	O(2)-Mo(15)-O(54)	98.9(3)
O(72)-Mo(13)-O(50)	95.5(3)	O(36)-Mo(14)-O(73)	96.1(3)	O(2)-Mo(15)-O(33)	86.6(3)

O(72)-Mo(13)-O(71)	172.7(3)	O(36)-Mo(14)-O(64)	170.3(2)	O(2)-Mo(15)-O(51)	166.1(3)
O(18)-Mo(16)-O(57)	104.7(3)	O(30)-Mo(17)-O(62)	103.9(3)	O(75)-Mo(18)-O(52)	101.8(3)
O(18)-Mo(16)-O(65)	102.7(3)	O(30)-Mo(17)-O(66)	102.3(3)	O(75)-Mo(18)-O(19)	103.2(3)
O(18)-Mo(16)-O(54)	98.7(3)	O(30)-Mo(17)-O(70)	99.6(3)	O(75)-Mo(18)-O(70)	102.8(3)
O(18)-Mo(16)-O(33)	96.4(3)	O(30)-Mo(17)-O(56)	97.0(3)	O(75)-Mo(18)-O(73)	86.5(3)
O(18)-Mo(16)-O(55)	170.4(2)	O(30)-Mo(17)-O(64)	170.6(3)	O(75)-Mo(18)-O(56)	169.9(3)
O(43)-P(1)-O(46)	112.0(3)	O(21)-P(2)-O(35)	109.8(3)	O(42)-P(3)-O(7)	110.0(3)
O(43)-P(1)-O(51)	110.4(3)	O(21)-P(2)-O(48)	108.3(3)	O(42)-P(3)-O(23)	108.7(3)
O(43)-P(1)-O(58)	106.9(3)	O(21)-P(2)-O(73)	110.7(3)	O(42)-P(3)-O(56)	110.4(3)
O(50)-P(4)-O(41)	113.0(3)	O(61)-P(5)-O(31)	106.6(3)	O(40)-P(6)-O(71)	106.3(3)
O(50)-P(4)-O(33)	112.7(3)	O(61)-P(5)-O(45)	111.4(3)	O(40)-P(6)-O(69)	111.8(3)
O(50)-P(4)-O(27)	105.5(3)	O(61)-P(5)-O(64)	110.6(3)	O(40)-P(6)-O(55)	110.1(3)
O(42)-Cu(1)-O(48)#1	178.6(2)	O(42)-Cu(1)-O(53)	83.5(2)	O(42)-Cu(1)-O(63)	97.9(2)
O(42)-Cu(1)-O(68)	90.5(2)	O(42)-Cu(1)-O(10)#1	89.3(2)	O(35)-Ca(1)-O(7)	65.93(18)
O(35)-Ca(1)-O(41)	114.70(19)	O(35)-Ca(1)-O(31)	73.89(18)	O(35)-Ca(1)-O(40)	119.71(19)
O(35)-Ca(1)-O(61)	103.45(18)	O(35)-Ca(1)-O(43)	79.19(18)	O(35)-Ca(1)-O(71)	173.6(2)
O(35)-Ca(1)-O(15)	57.82(17)				

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x+1/2,-y+1/2,-z

Table S4 Selected bond lengths (Å) and bond angles (°) of compound **4**

Mo(1)-O(2)	1.862(9)	Mo(1)-O(46)	1.881(10)	Mo(1)-O(19)	2.037(10)
Mo(1)-O(42)	2.054(9)	Mo(1)-O(13)	2.256(9)	Mo(1)-O(28)	1.706(10)
Mo(2)-O(50)	1.669(9)	Mo(2)-O(7)	1.892(8)	Mo(2)-O(39)	2.081(10)
Mo(2)-O(4)	1.881(10)	Mo(2)-O(54)	2.045(9)	Mo(2)-O(33)	2.267(9)
Mo(3)-O(58)	1.680(9)	Mo(3)-O(60)	1.811(11)	Mo(3)-O(56)	2.132(10)
Mo(3)-O(40)	1.796(9)	Mo(3)-O(35)	2.063(9)	Mo(3)-O(23)	2.422(9)
Mo(4)-O(55)	1.671(9)	Mo(4)-O(61)	1.820(10)	Mo(4)-O(51)	2.139(10)
Mo(4)-O(42)	1.754(9)	Mo(4)-O(44)	2.022(10)	Mo(4)-O(27)	2.424(9)
Mo(5)-O(49)	1.672(10)	Mo(5)-O(12)	1.888(10)	Mo(5)-O(74)	2.121(9)
Mo(5)-O(3)	1.873(9)	Mo(5)-O(11)	1.939(9)	Mo(5)-O(63)	2.297(10)
Mo(6)-O(41)	1.705(9)	Mo(6)-O(5)	1.866(9)	Mo(6)-O(10)	2.204(10)
Mo(6)-O(16)	1.731(9)	Mo(6)-O(20)	1.978(9)	Mo(6)-O(24)#1	2.235(9)
Mo(7)-O(25)	1.692(9)	Mo(7)-O(6)	1.892(10)	Mo(7)-O(8)	2.038(8)
Mo(7)-O(7)	1.832(8)	Mo(7)-O(22)#1	2.018(10)	Mo(7)-O(9)	2.222(9)
Mo(8)-O(75)	1.659(10)	Mo(8)-O(70)	1.858(10)	Mo(8)-O(51)	2.331(9)
Mo(8)-O(72)	1.680(10)	Mo(8)-O(44)	2.060(10)	Mo(8)-O(64)	2.360(9)
Mo(9)-O(62)	1.691(10)	Mo(9)-O(37)	1.865(6)	Mo(9)-O(61)	2.074(10)
Mo(9)-O(57)	1.782(9)	Mo(9)-O(65)	2.057(10)	Mo(9)-O(27)	2.456(10)
Mo(10)-O(36)	1.682(9)	Mo(10)-O(20)	1.809(9)	Mo(10)-O(43)#1	2.344(9)
Mo(10)-O(68)	1.693(10)	Mo(10)-O(35)	2.036(10)	Mo(10)-O(56)	2.403(9)
Mo(11)-O(66)	1.689(10)	Mo(11)-O(65)	1.818(10)	Mo(11)-O(64)	2.151(10)
Mo(11)-O(54)	1.753(9)	Mo(11)-O(44)	2.061(9)	Mo(11)-O(27)	2.357(9)
Mo(12)-O(48)	1.694(11)	Mo(12)-O(5)	1.921(9)	Mo(12)-O(53)	2.287(10)
Mo(12)-O(71)	1.700(10)	Mo(12)-O(70)	1.930(9)	Mo(12)-O(21)	2.313(10)
Mo(13)-O(29)	1.692(11)	Mo(13)-O(6)	1.885(10)	Mo(13)-O(18)	2.132(9)
Mo(13)-O(1)	1.860(8)	Mo(13)-O(11)	1.885(9)	Mo(13)-O(63)	2.306(10)
Mo(14)-O(73)	1.702(10)	Mo(14)-O(18)	1.792(9)	Mo(14)-O(60)	2.062(10)

Mo(14)-O(74)	1.791(10)	Mo(14)-O(47)	2.062(10)	Mo(14)-O(23)	2.439(10)
Mo(15)-O(52)	1.664(9)	Mo(15)-O(47)	1.841(11)	Mo(15)-O(43)#1	2.099(9)
Mo(15)-O(8)	1.775(9)	Mo(15)-O(35)	2.059(9)	Mo(15)-O(23)	2.420(9)
Mo(16)-O(14)	1.682(9)	Mo(16)-O(46)	1.877(10)	Mo(16)-O(57)	2.098(9)
Mo(16)-O(3)	1.872(9)	Mo(16)-O(45)	1.908(9)	Mo(16)-O(34)	2.314(10)
Mo(17)-O(17)	1.665(9)	Mo(17)-O(12)	1.868(10)	Mo(17)-O(30)	2.065(10)
Mo(17)-O(2)	1.861(9)	Mo(17)-O(40)	2.011(9)	Mo(17)-O(15)	2.239(9)
Mo(18)-O(59)	1.680(10)	Mo(18)-O(1)	1.888(9)	Mo(18)-O(37)	2.068(9)
Mo(18)-O(4)	1.878(10)	Mo(18)-O(45)	1.990(9)	Mo(18)-O(34)	2.297(10)
P(1)-O(13)	1.517(9)	P(2)-O(63)	1.522(11)	P(3)-O(21)	1.498(9)
P(1)-O(33)	1.520(10)	P(2)-O(15)	1.523(10)	P(3)-O(19)	1.518(10)
P(1)-O(34)	1.524(10)	P(2)-O(9)	1.525(9)	P(3)-O(51)	1.556(9)
P(1)-O(27)	1.584(9)	P(2)-O(23)	1.560(9)	P(3)-O(31)	1.569(10)
P(4)-O(26)	1.486(10)	P(5)-O(32)	1.511(10)	P(6)-O(39)	1.506(10)
P(4)-O(30)	1.523(10)	P(5)-O(24)	1.526(9)	P(6)-O(53)	1.517(10)
P(4)-O(56)	1.544(9)	P(5)-O(22)	1.538(9)	P(6)-O(64)	1.536(9)
P(4)-O(10)	1.566(9)	P(5)-O(43)	1.582(9)	P(6)-O(67)	1.585(11)
Fe(1)-O(26)	2.032(10)	Fe(1)-O(41)	2.113(9)	Fe(1)-O(69)	2.154(10)
Fe(1)-O(32)	2.045(10)	Fe(1)-O(16)#2	2.128(9)	Fe(1)-O(38)	2.222(9)
Ca(1)-O(24)#1	2.453(9)	Ca(1)-O(10)	2.456(9)	Ca(1)-O(21)	2.521(10)
Ca(1)-O(53)	2.555(10)	Ca(1)-O(33)	2.573(10)	Ca(1)-O(15)	2.577(9)
Ca(1)-O(13)	2.591(9)	Ca(1)-O(9)	2.611(9)	Ca(1)-O(5)	2.827(11)
O(28)-Mo(1)-O(2)	99.3(4)	O(50)-Mo(2)-O(4)	101.5(5)	O(58)-Mo(3)-O(40)	104.3(4)
O(28)-Mo(1)-O(46)	100.4(5)	O(50)-Mo(2)-O(7)	98.6(4)	O(58)-Mo(3)-O(60)	101.8(5)
O(28)-Mo(1)-O(19)	97.3(4)	O(50)-Mo(2)-O(54)	94.3(4)	O(58)-Mo(3)-O(35)	99.4(4)
O(28)-Mo(1)-O(42)	93.6(4)	O(50)-Mo(2)-O(39)	95.9(5)	O(58)-Mo(3)-O(56)	96.7(4)
O(28)-Mo(1)-O(13)	174.4(4)	O(50)-Mo(2)-O(33)	173.1(5)	O(58)-Mo(3)-O(23)	171.4(4)
O(55)-Mo(4)-O(42)	104.2(5)	O(49)-Mo(5)-O(3)	100.5(4)	O(41)-Mo(6)-O(16)	103.4(5)
O(55)-Mo(4)-O(61)	102.2(5)	O(49)-Mo(5)-O(12)	101.4(5)	O(41)-Mo(6)-O(5)	100.1(4)
O(55)-Mo(4)-O(44)	98.7(4)	O(49)-Mo(5)-O(11)	101.3(5)	O(41)-Mo(6)-O(20)	93.7(4)
O(55)-Mo(4)-O(51)	96.6(5)	O(49)-Mo(5)-O(74)	91.4(4)	O(41)-Mo(6)-O(10)	90.7(4)
O(55)-Mo(4)-O(27)	169.9(4)	O(49)-Mo(5)-O(63)	168.5(4)	O(41)-Mo(6)-O(24)#1	164.3(4)
O(25)-Mo(7)-O(7)	99.8(4)	O(75)-Mo(8)-O(72)	103.5(5)	O(62)-Mo(9)-O(57)	104.5(5)
O(25)-Mo(7)-O(6)	100.3(5)	O(75)-Mo(8)-O(70)	106.3(5)	O(62)-Mo(9)-O(37)	104.9(5)
O(25)-Mo(7)-O(22)#1	97.2(4)	O(75)-Mo(8)-O(44)	97.1(5)	O(62)-Mo(9)-O(65)	97.3(5)
O(25)-Mo(7)-O(8)	92.0(4)	O(75)-Mo(8)-O(51)	163.3(5)	O(62)-Mo(9)-O(61)	95.1(5)
O(25)-Mo(7)-O(9)	172.7(4)	O(75)-Mo(8)-O(64)	84.5(4)	O(62)-Mo(9)-O(27)	163.4(4)
O(36)-Mo(10)-O(68)	101.6(5)	O(66)-Mo(11)-O(54)	105.2(4)	O(48)-Mo(12)-O(71)	103.0(5)
O(36)-Mo(10)-O(20)	105.2(4)	O(66)-Mo(11)-O(65)	101.1(5)	O(48)-Mo(12)-O(5)	100.2(4)
O(36)-Mo(10)-O(35)	99.5(4)	O(66)-Mo(11)-O(44)	97.5(4)	O(48)-Mo(12)-O(70)	98.6(4)
O(36)-Mo(10)-O(43)#1	166.8(4)	O(66)-Mo(11)-O(64)	97.4(4)	O(48)-Mo(12)-O(53)	92.3(4)
O(36)-Mo(10)-O(56)	86.2(4)	O(66)-Mo(11)-O(27)	169.2(4)	O(48)-Mo(12)-O(21)	167.0(4)
O(29)-Mo(13)-O(1)	99.5(5)	O(73)-Mo(14)-O(74)	103.5(5)	O(52)-Mo(15)-O(8)	104.7(5)
O(29)-Mo(13)-O(6)	99.8(4)	O(73)-Mo(14)-O(18)	104.8(5)	O(52)-Mo(15)-O(47)	101.1(5)
O(29)-Mo(13)-O(11)	102.1(5)	O(73)-Mo(14)-O(47)	95.1(4)	O(52)-Mo(15)-O(35)	98.6(4)
O(29)-Mo(13)-O(18)	92.4(4)	O(73)-Mo(14)-O(60)	96.0(5)	O(52)-Mo(15)-O(43)#1	98.2(5)
O(29)-Mo(13)-O(63)	169.5(4)	O(73)-Mo(14)-O(23)	163.7(4)	O(52)-Mo(15)-O(23)	170.8(4)

O(14)-Mo(16)-O(3)	101.3(4)	O(17)-Mo(17)-O(2)	98.9(4)	O(59)-Mo(18)-O(4)	102.0(5)
O(14)-Mo(16)-O(46)	100.3(5)	O(17)-Mo(17)-O(12)	101.9(4)	O(59)-Mo(18)-O(1)	99.3(4)
O(14)-Mo(16)-O(45)	101.0(5)	O(17)-Mo(17)-O(40)	92.8(4)	O(59)-Mo(18)-O(45)	100.8(5)
O(14)-Mo(16)-O(57)	91.3(4)	O(17)-Mo(17)-O(30)	94.9(4)	O(59)-Mo(18)-O(37)	92.5(4)
O(14)-Mo(16)-O(34)	168.0(4)	O(17)-Mo(17)-O(15)	171.3(4)	O(59)-Mo(18)-O(34)	169.7(4)
O(13)-P(1)-O(33)	106.7(5)	O(13)-P(1)-O(34)	111.1(5)	O(13)-P(1)-O(27)	111.0(5)
O(63)-P(2)-O(15)	111.6(5)	O(63)-P(2)-O(9)	111.3(5)	O(63)-P(2)-O(23)	107.3(5)
O(21)-P(3)-O(19)	110.5(5)	O(21)-P(3)-O(51)	108.0(5)	O(21)-P(3)-O(31)	112.0(6)
O(26)-P(4)-O(30)	109.1(5)	O(26)-P(4)-O(56)	111.1(5)	O(26)-P(4)-O(10)	109.7(6)
O(32)-P(5)-O(24)	111.1(6)	O(32)-P(5)-O(22)	109.6(5)	O(32)-P(5)-O(43)	109.2(5)
O(39)-P(6)-O(53)	112.2(5)	O(39)-P(6)-O(64)	113.3(6)	O(39)-P(6)-O(67)	107.2(6)
O(26)-Fe(1)-O(32)	175.2(4)	O(26)-Fe(1)-O(41)	88.2(4)	O(26)-Fe(1)-O(16)#2	93.3(4)
O(26)-Fe(1)-O(69)	87.6(4)	O(26)-Fe(1)-O(38)	95.4(4)	O(24)#1-Ca(1)-O(10)	65.7(3)
O(24)#1-Ca(1)-O(21)	117.3(3)	O(24)#1-Ca(1)-O(53)	79.8(3)	O(24)#1-Ca(1)-O(33)	117.6(3)
O(24)#1-Ca(1)-O(15)	102.2(3)	O(24)#1-Ca(1)-O(13)	170.2(3)	O(24)#1-Ca(1)-O(9)	72.2(3)
O(24)#1-Ca(1)-O(5)	59.0(3)				

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x+1/2,-y+1/2,-z

Table S5 Selected Hydrogen Bond Lengths () and Bond Angles (°) of complexes **1-4**

D-H...A	d(D-H)	d(H...A)	<D-H...A	d(D...A)	Symmetry
1					
O4W - H4WA... O27	0.85	3.22	3.41(3)	95.5	
O2W - H2WA... O39	0.85	1.90	2.50(5)	126.6	
O40 - H40A... O41	0.85	2.49	3.14(3)	134.5	
O39 - H39A... O24	0.85	2.48	3.21(5)	144.1	
O39 - H39A... O2W	0.85	2.05	2.50(5)	112.0	
O34 - H34A... O27	0.85	2.71	2.81(2)	88.2	
O34 - H34A... O22	0.85	2.68	2.77(3)	86.7	
O42 - H42A... O40	0.85	2.57	3.02(6)	114.0	
O3W-H3WB... O7	0.85	2.89	3.21(3)	105.2	[-x+1, -y+1, -z+1]
O4W- H4WB...O13	0.85	2.27	2.98(3)	141.2	[x+1/2, -y+1/2, z+1/2]
O2W-H2WB...O34	0.85	2.83	3.03(3)	95.8	[-x+1, -y+1, -z+1]
O2W- H2WA...O30	0.85	2.49	3.02(3)	121.1	[x-1/2, y+1/2, z]
O40- H40B... O16	0.85	2.01	2.50(2)	116.0	[-x, y, -z+1/2]
O40- H40A... O32	0.85	2.62	3.32(5)	141.7	[-x, y, -z+1/2]
O39- H39B... O10	0.85	2.70	3.03(5)	104.7	[-x+1/2, y+1/2, -z+1/2]
O34- H34B... O14	0.85	1.95	2.79(3)	168.9	[-x+1, -y+1, -z+1]
O34- H34A... O2W	0.85	2.66	3.03(3)	107.7	[-x+1, -y+1, -z+1]
O41- H41A... O32	0.85	2.52	3.20(4)	138.0	[-x, y, -z+1/2]
O41- H41A... O24	0.85	2.28	2.96(4)	137.3	[-x, y, -z+1/2]
O42- H42B... O18	0.85	2.44	3.18(4)	144.9	[x-1/2, y+1/2, z]
O42- H42A... O41	0.85	2.49	2.94(4)	113.9	[-x, y, -z+1/2]
O42 - H42A...O16	0.85	2.35	3.19(3)	168.0	[-x, y, -z+1/2]
2					
O2W- H2WA... O1W	0.85	2.15	138.9	2.84(5)	
N2- H2A... O40	0.86	2.53	156.7	3.337(18)	
O1W- H1WB... O31	0.85	2.44	158.6	3.24(2)	[x, -y+3/2, z+1]
O1W- H1WA... O13	0.85	2.80	117.5	3.28(2)	[x, y, z+1]
O2W- H2WB... O42	0.85	2.60	126.6	3.18(4)	[x, -y+3/2, z]
O2W- H2WA... O31	0.85	2.63	115.1	3.086(18)	[x, -y+3/2, z+1]

	N3- H3A... O29	0.86	2.65	165.8	3.489(18)	$[-x+1/2, -y+1, z+1/2]$
	N3- H3A... O36	0.86	2.61	126.5	3.195(18)	$[-x+1/2, -y+1, z+1/2]$
	O42- H42B... O9	0.85	3.17	102.7	3.46(3)	$[x, y, z+1]$
	O42- H42A... O23	0.85	3.09	86.1	3.15(3)	$[-x+1/2, -y+1, z+1/2]$
3	O63-H63A...O1	0.85	2.52	137.7	3.196(9)	
	O63-H63A...O41	0.85	2.38	136.8	3.053(8)	
	O53-H53B...O68	0.85	3.22	85.7	3.273(9)	
	N4-H4A...O14	0.86	2.09	179.4	3.050(10)	
	O63-H63A...O15	0.85	2.57	146.4	3.311(9)	
	N3-H3A...O58	0.86	2.50	112.8	2.944(12)	$[-x+1, y-1/2, -z+1]$
	N3-H3A...O13	0.86	2.47	119.5	2.987(11)	$[-x+1, y-1/2, -z+1]$
	O2W-H2WA...O67	0.85	2.51	122.2	3.050(10)	$[-x+1, y+1/2, -z+1]$
	N8-H8...O14	0.86	2.14	151.7	2.930(11)	$[x+1, y, z]$
	N7-H7A...O23	0.86	2.23	168.3	3.074(11)	$[-x+1, y+1/2, -z+1]$
	O63-H63B...O10	0.85	2.82	91.4	2.969(9)	$[-x+1, y-1/2, -z+2]$
	O53-H53A...O43	0.85	2.31	148.6	3.069(8)	$[-x+1, y-1/2, -z+2]$
4	O38-H38B...O21	0.85	2.26	147.3	3.007(13)	
	O38-H38B...O10	0.85	2.40	120.8	2.926(13)	
	O38-H38B...O5	0.85	2.48	136.9	3.158(13)	
	O69-H69A...O24	0.85	2.47	120.5	2.995(14)	
	O3W-H3WA... O71	0.85	2.45	115.8	2.925(15)	
	O1W-H1WA...O74	0.85	2.68	92.4	2.845(16)	
	O69-H69A... O53	0.85	2.39	156.5	3.187(14)	$[-x+1, y+1/2, -z+1/2]$
	O69-H69B...O4W	0.85	2.40	119.2	2.907(17)	$[-x+1, y+1/2, -z+1/2]$
	O3W-H3WA...O75	0.85	2.42	118.8	2.927(16)	$[-x+1, -y+1, -z+1]$
	O3W-H3WB...O67	0.85	2.62	124.5	3.178(15)	$[-x+1, -y+1, -z+1]$
	O4W-H4WA...O36	0.85	2.27	131.0	2.902(17)	$[-x+1, y-1/2, -z+1/2]$
	O4W-H4WB...O72	0.85	2.52	124.6	3.087(17)	$[-x+1, -y+1, -z+1]$
	O1W-H1WB...O59	0.85	2.53	105.6	2.879(17)	$[-x, y+1/2, -z+1/2]$
	O2W-H2WB...O65	0.85	2.37	159.4	3.184(18)	$[x, -y+1/2, z-1/2]$

Table S6 Bond valence sum calculations for Mo atoms in **1^{III}**

	Mo ^V	Mo ^{VI}	Average
Mo1	5.55	5.82	5.69
Mo2	5.64	5.91	5.78
Mo3	5.58	5.85	5.72
Mo4	5.94	6.22	6.08
Mo5	5.29	5.54	5.42
Mo6	5.45	5.71	5.58
Mo7	5.98	6.26	6.12
Mo8	5.46	5.72	5.59
Mo9	5.81	6.08	5.95
Sum	5.64	5.90	5.78

Table S7 Bond valence sum calculations for Mo atoms in **2^[II]**

	Mo ^V	Mo ^{VI}	Average
Mo1	5.73	5.99	5.86
Mo2	5.90	6.17	6.04
Mo3	5.94	6.22	6.08
Mo4	5.67	5.94	5.81
Mo5	5.86	6.13	6.00
Mo6	5.79	6.06	5.93
Mo7	5.69	5.96	5.83
Mo8	5.90	6.17	6.04
Mo9	5.91	6.18	6.02
Sum	5.82	6.09	5.96

Table S8 Bond valence sum calculations for Mo atoms in **3^[II]**

	Mo ^V	Mo ^{VI}	Average
Mo1	5.58	5.84	5.71
Mo2	5.65	5.92	5.79
Mo3	5.59	5.86	5.73
Mo4	5.91	6.19	6.05
Mo5	5.51	5.64	5.77
Mo6	5.67	5.94	5.81
Mo7	5.94	6.21	6.08
Mo8	5.44	5.57	5.70
Mo9	5.71	5.97	5.84
Mo10	5.85	6.13	5.99
Mo11	5.65	5.92	5.79
Mo12	5.75	6.02	5.89
Mo13	5.43	5.56	5.69
Mo14	5.66	5.93	5.80
Mo15	5.84	6.12	5.98
Mo16	5.79	6.06	5.93
Mo17	5.90	6.18	6.04
Mo18	5.78	6.05	5.92
Sum	5.66	5.93	5.86

Table S9 Bond valence sum calculations for Mo atoms in **4^[II]**

	Mo ^V	Mo ^{VI}	Average
Mo1	5.43	5.69	5.56
Mo2	5.44	5.70	5.57
Mo3	5.67	5.93	5.80
Mo4	5.90	6.18	6.04
Mo5	5.59	5.86	5.73
Mo6	5.85	6.13	5.99
Mo7	5.65	5.92	5.79
Mo8	5.94	6.21	6.08
Mo9	5.58	5.84	5.71
Mo10	5.91	6.19	6.05

Mo11	5.79	6.06	5.93
Mo12	5.84	6.12	5.98
Mo13	5.65	5.92	5.79
Mo14	5.75	6.02	5.89
Mo15	5.78	6.05	5.92
Mo16	5.67	5.94	5.81
Mo17	5.71	5.97	5.84
Mo18	5.51	5.77	5.64
Sum	5.71	6.03	5.87

[1] ref: I. D. Brown, D. Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244–247.

3. Physical characterization

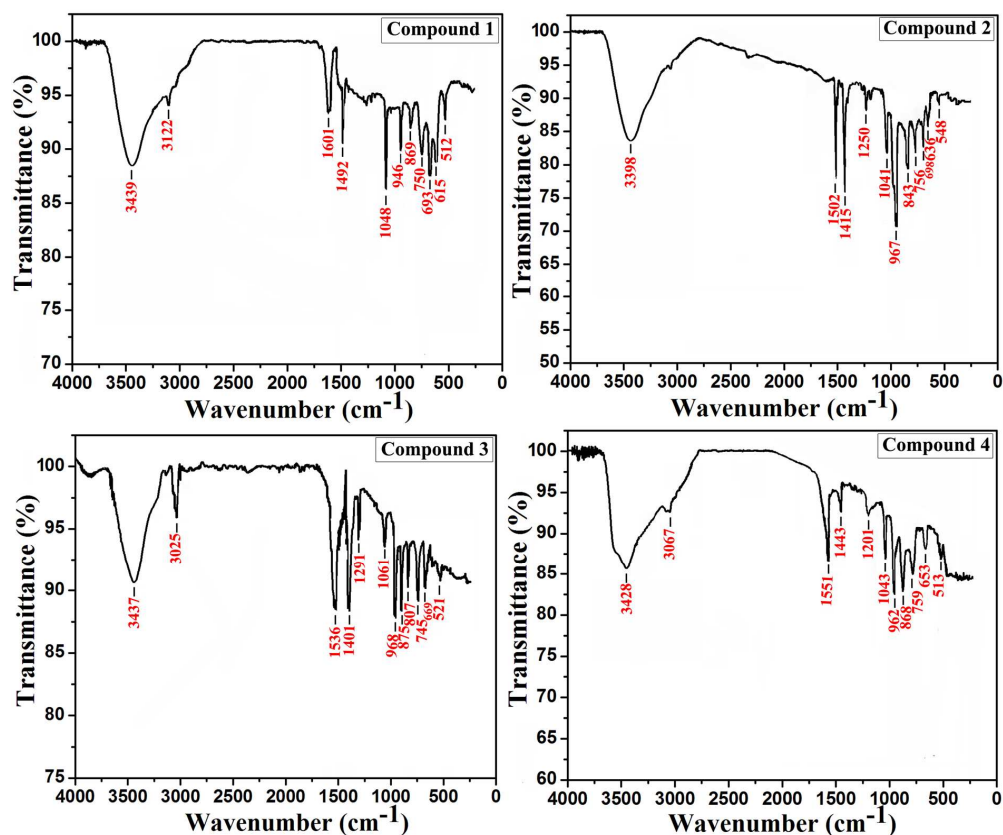


Fig. S10 IR spectra of (a) compound 1, (b) compound 2, (c) compound 3, and compound 4.

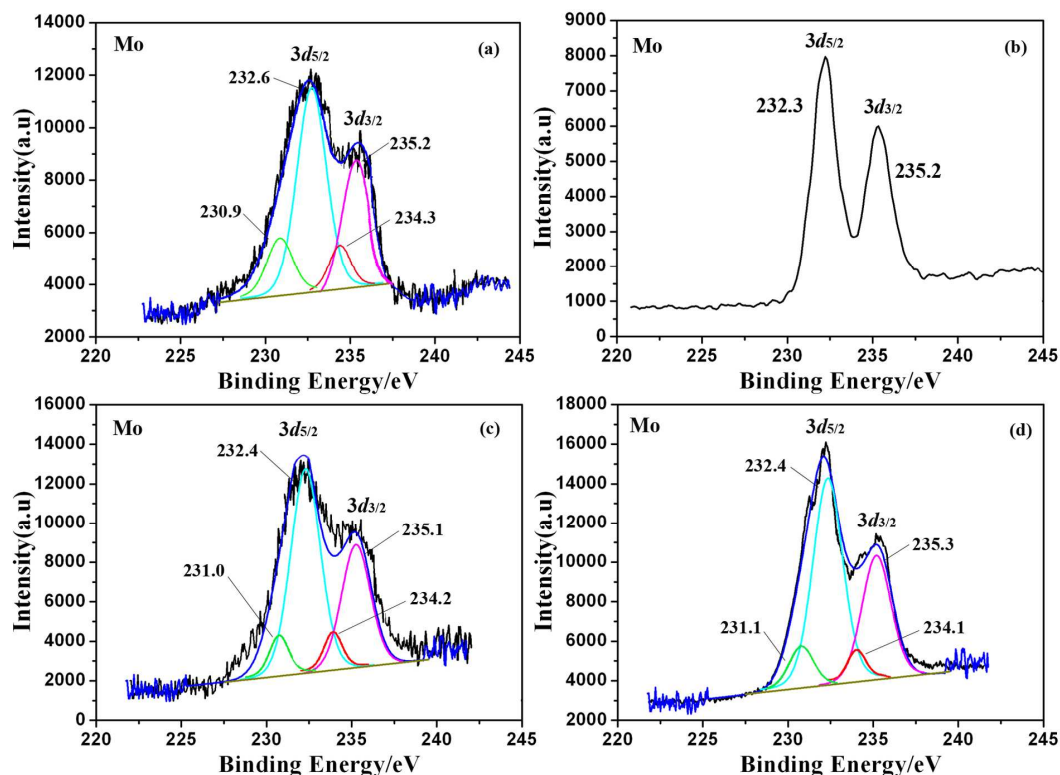


Fig. S11 The XPS spectrum of (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4.

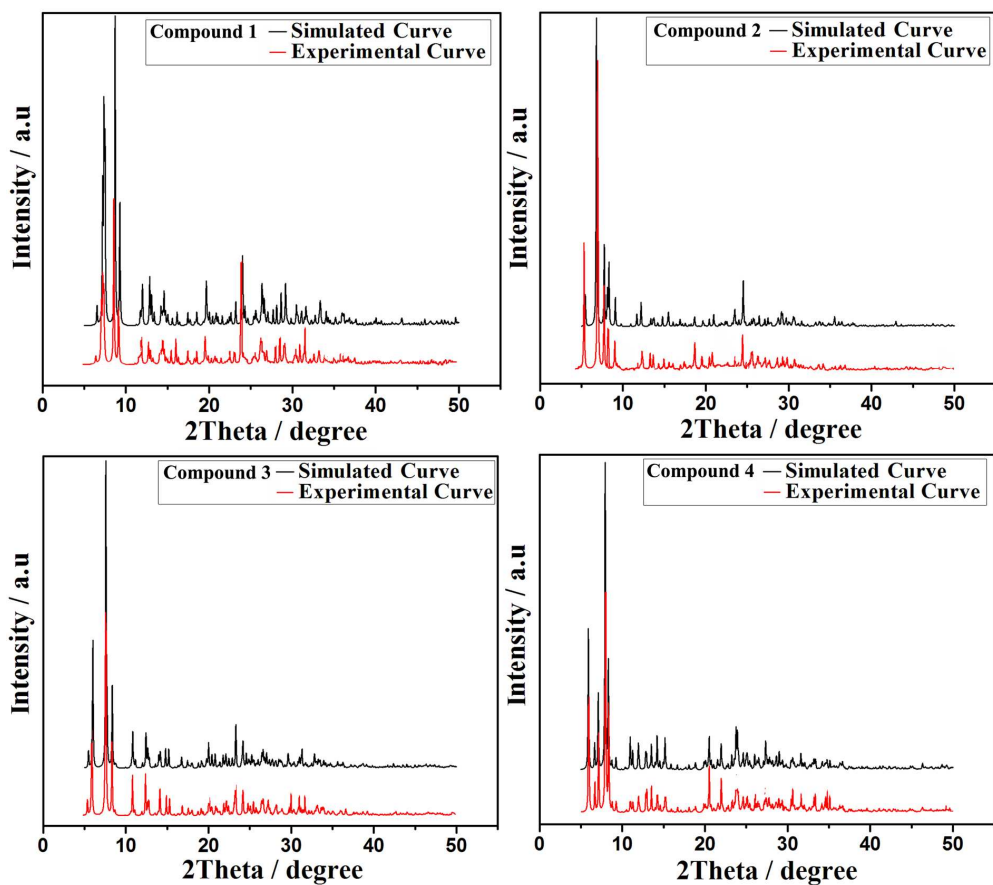


Fig. S12 The PXRD contrast curves of (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4

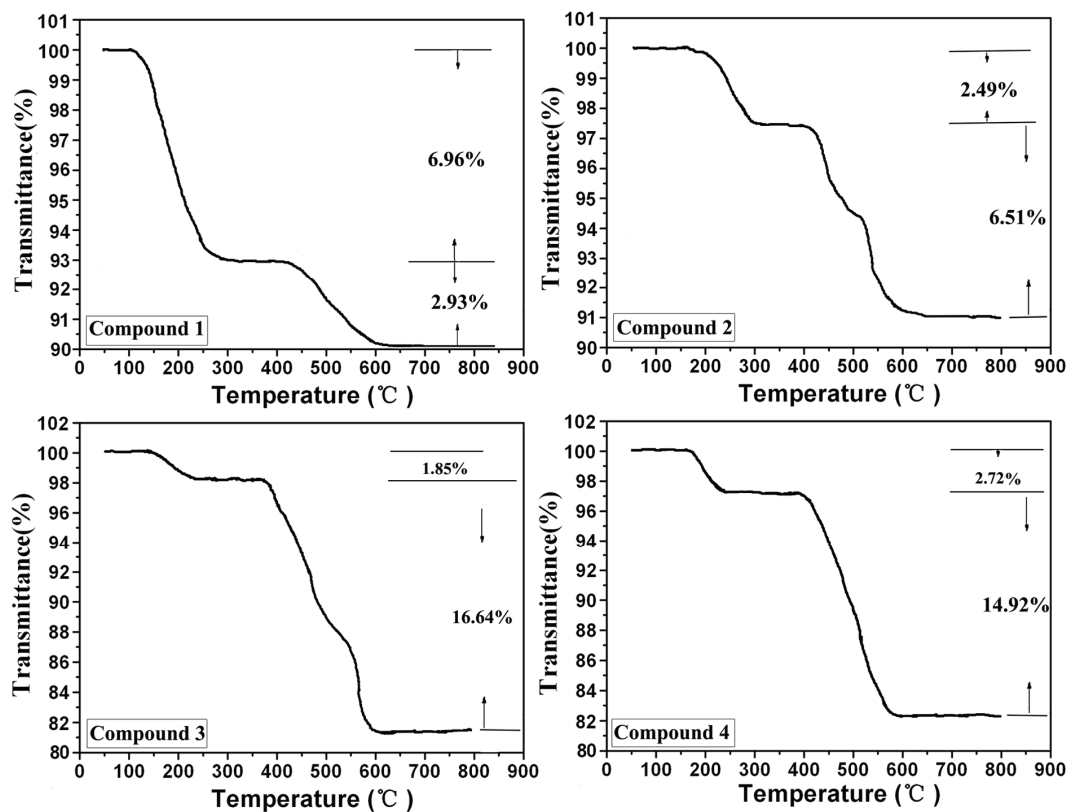


Fig. S13 TG of (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4

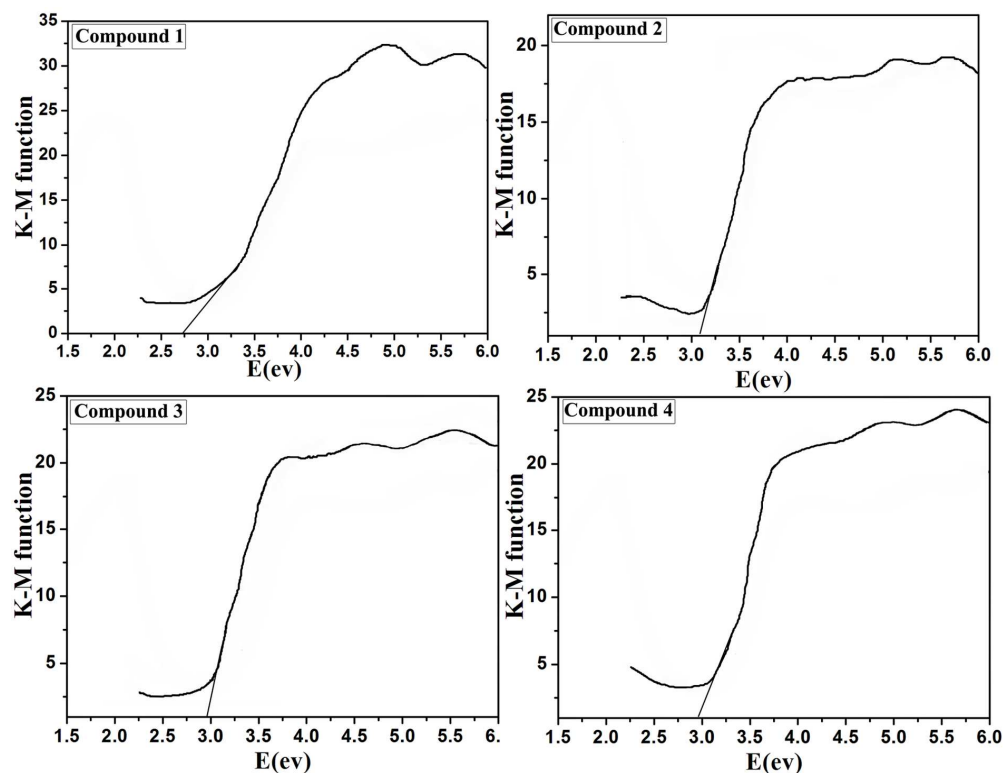


Fig. S14 Kubelka-Munk-transformed diffuse reflectance spectra of (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4. (The band gaps (E_g) were determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka–Munk function F versus energy E ($F = (1 - R)^2/2R$)).

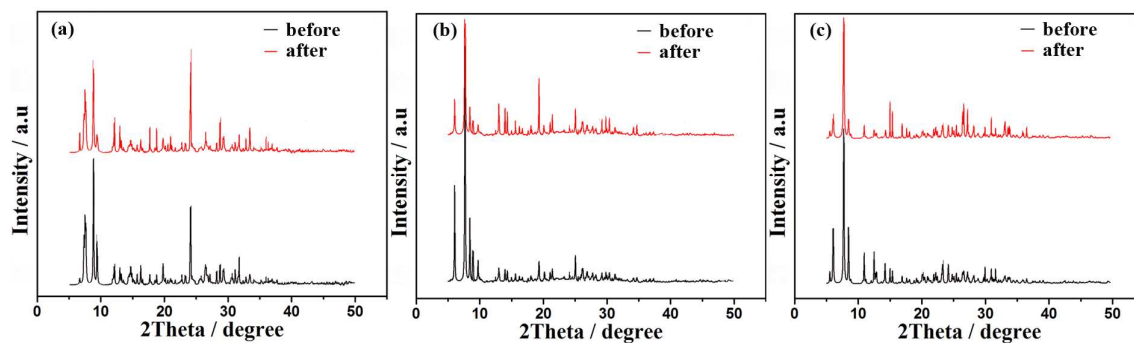


Fig. S15 The XRD patterns of compound **1** (a), compound **2** (b), and compound **3** (c), before and after five cycles.

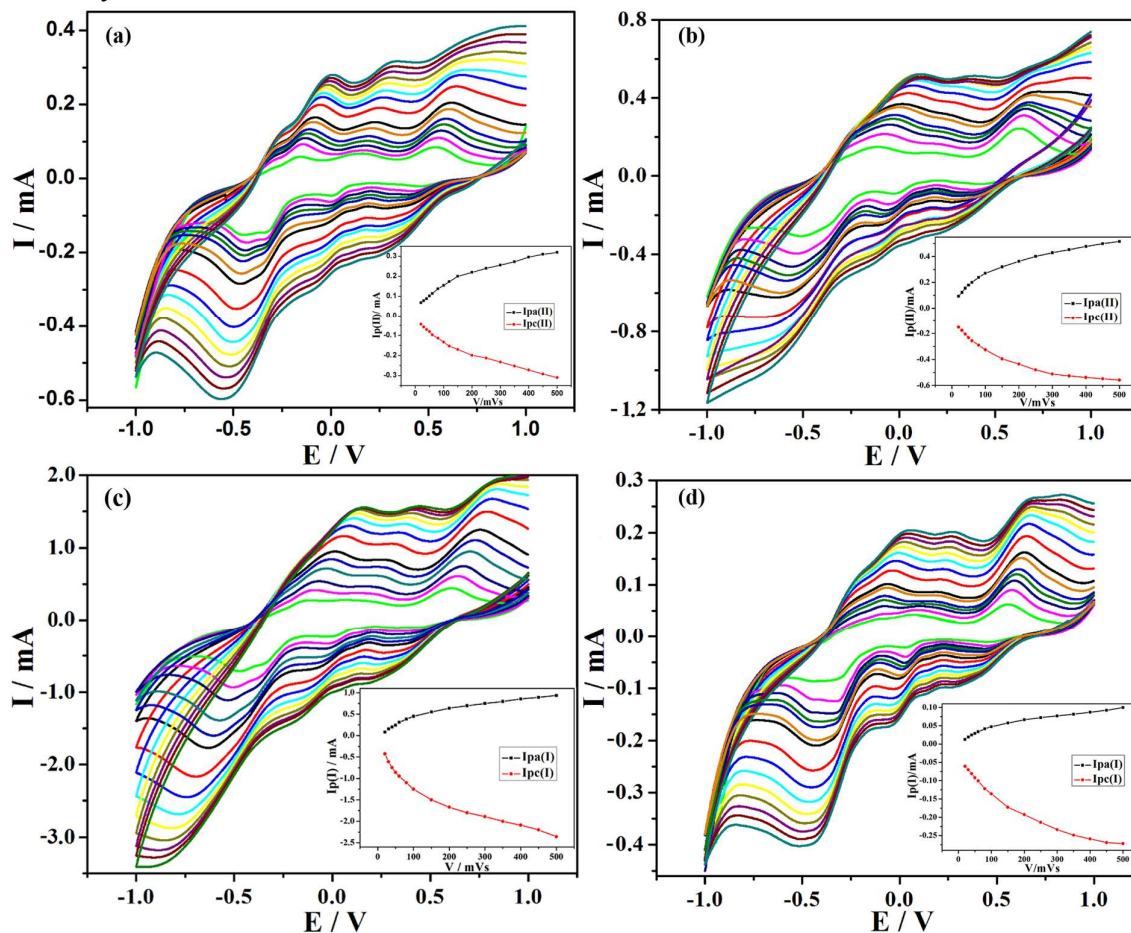


Fig. S16 Cyclic voltammograms of (a) 1-CPE, (b) 2-CPE, (c) 3-CPE, (d) 4-CPE, (e) 5-CPE, and (f) 6-CPE rates (from inner to outer: 20, 30, 40, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}). Potentials vs. SCE. (Insert plots: The dependence of anodic and cathodic peak II current on scan rates.)

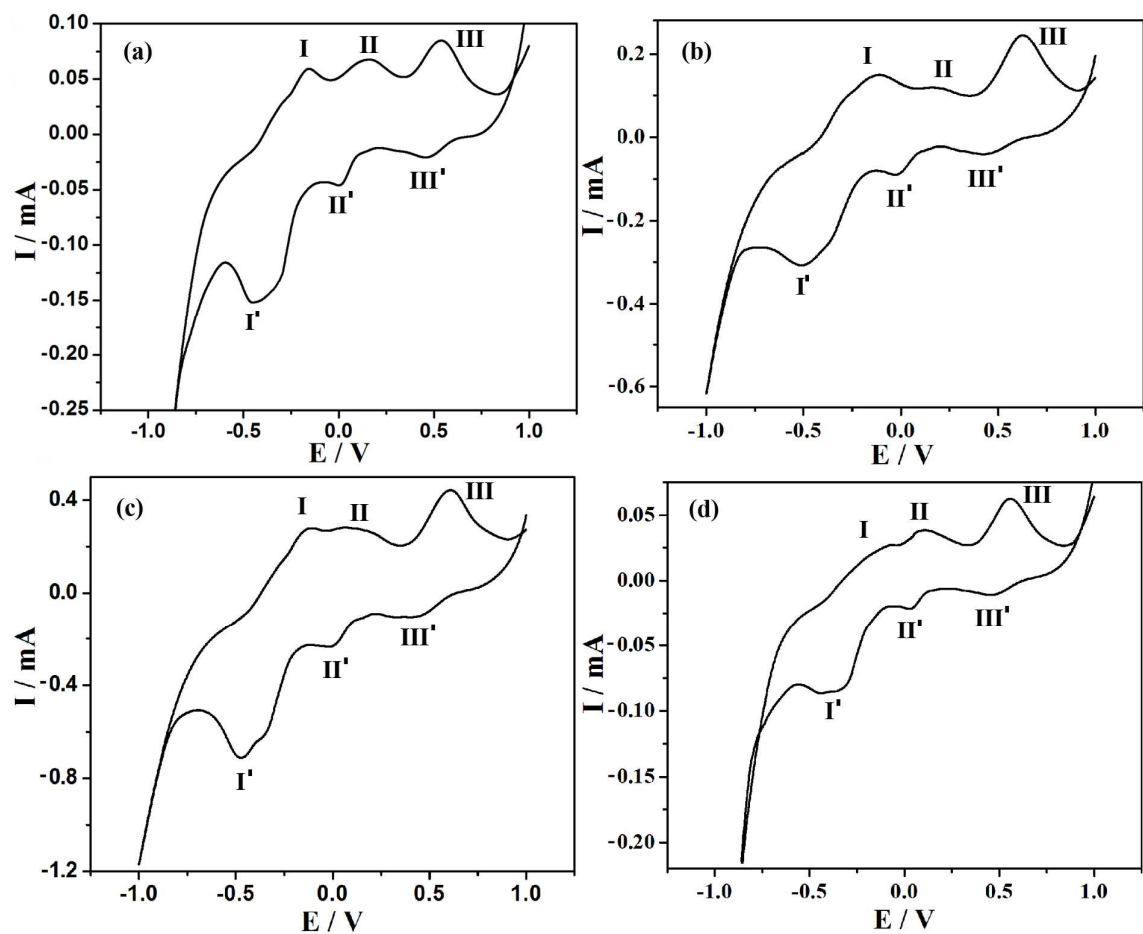


Fig. S17 Cyclic voltammograms of (a) **1-CPE**, (b) **2-CPE**, (c) **3-CPE**, and (d) **4-CPE** in the 1.0 M H_2SO_4 solution at scan rate of 20 mV s^{-1} ; Potentials vs. SCE.