Supporting information

New extended poly(oxomolybdophosphates) based on strontium(II) linkers

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1. Structural figures

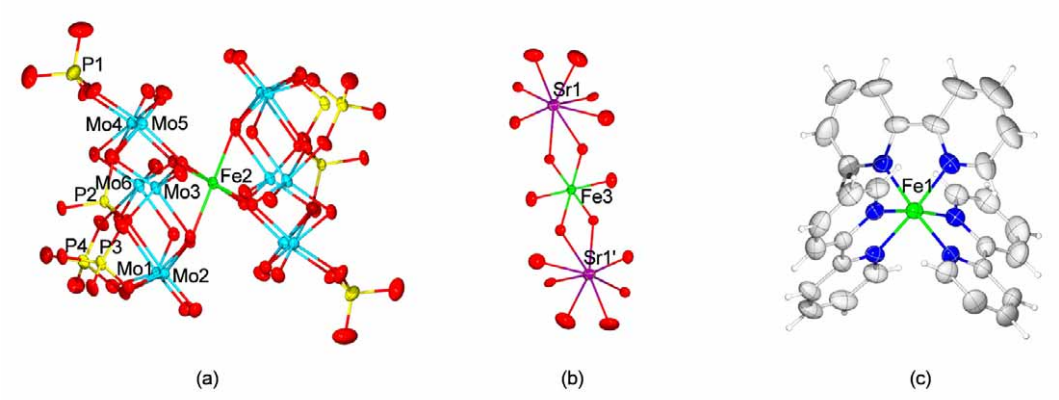

Fig. S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoids: **(a)** the sandwich-type $\{Fe(P_4Mo_6)_2\}$ unit; **(b)** the trinuclear $\{Sr_2Fe\}$ linker; **(c)** the $[Fe(2,2'\text{-bpy})_3]^{3+}$ cationic unit.

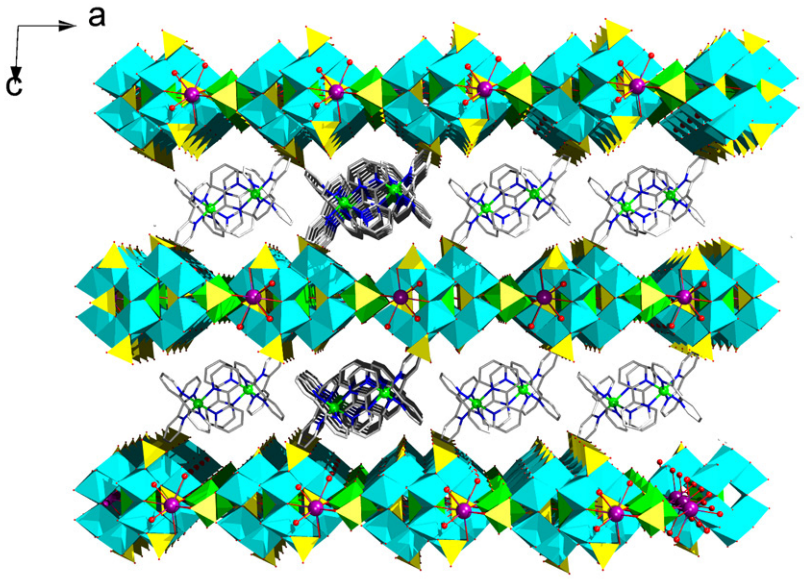

Fig. S2 The packing arrangement of compound **1** viewed along *b* axis. The isolated sodium cations, phosphate anions, and solvent water molecules are omitted for clarity.

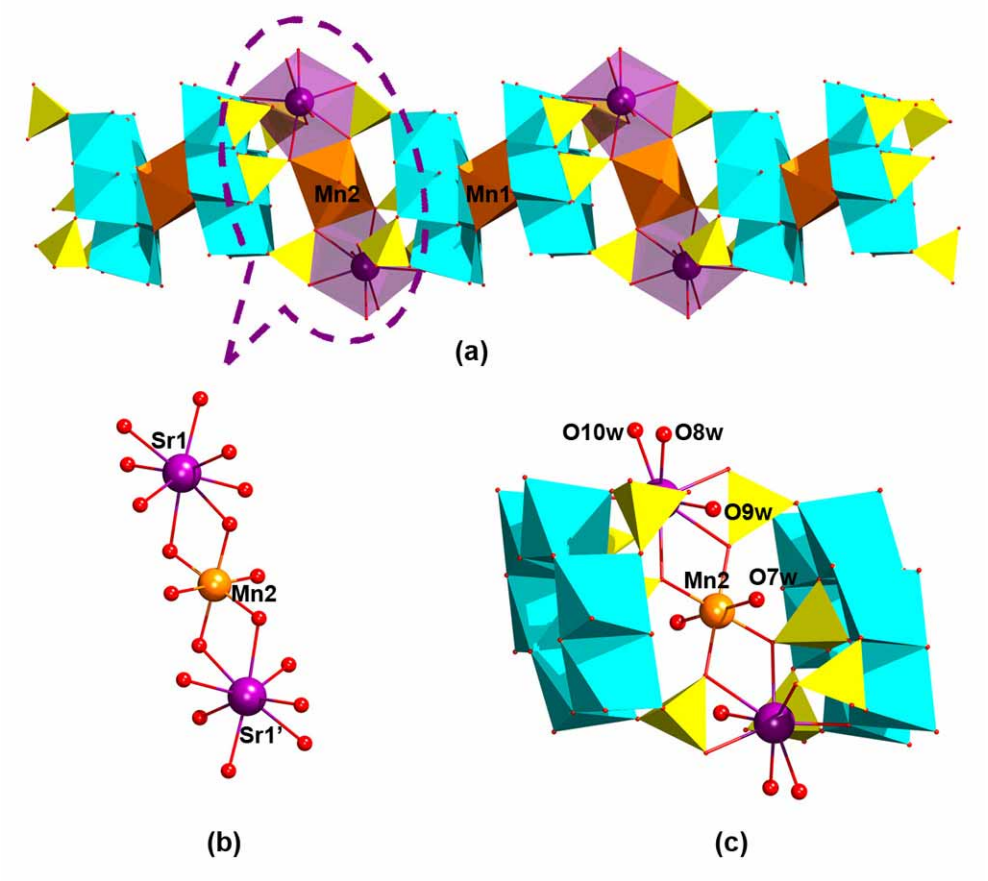

Fig. S3 (a) 1-D chain of the poly(oxomolybdophosphate) based on $\{Mn(P_4Mo_6)_2\}$ units and $\{Sr_2Mn\}$ linkers in **2**; **(b)** The trinuclear linking moiety of $\{Sr_2Mn\}$ in **2**; **(c)** Connection mode between trinuclear $\{Sr_2Mn\}$ unit and its adjacent $\{P_4Mo_6\}$ fragments in **2**.

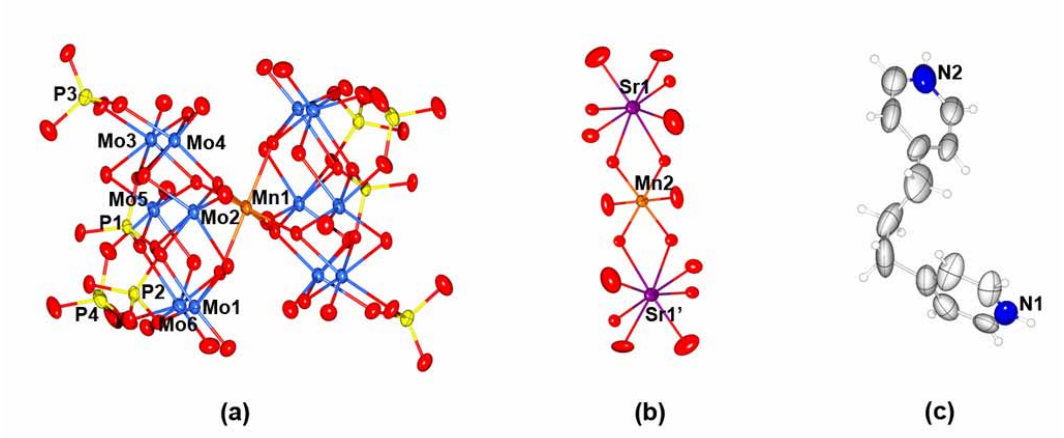

Fig. S4 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoids: **(a)** the sandwich-type $\{Mn(P_4Mo_6)_2\}$ unit; **(b)** the trinuclear $\{Sr_2Mn\}$ linker; **(c)** $[H_2bpp]^{2+}$ protonated ligand.

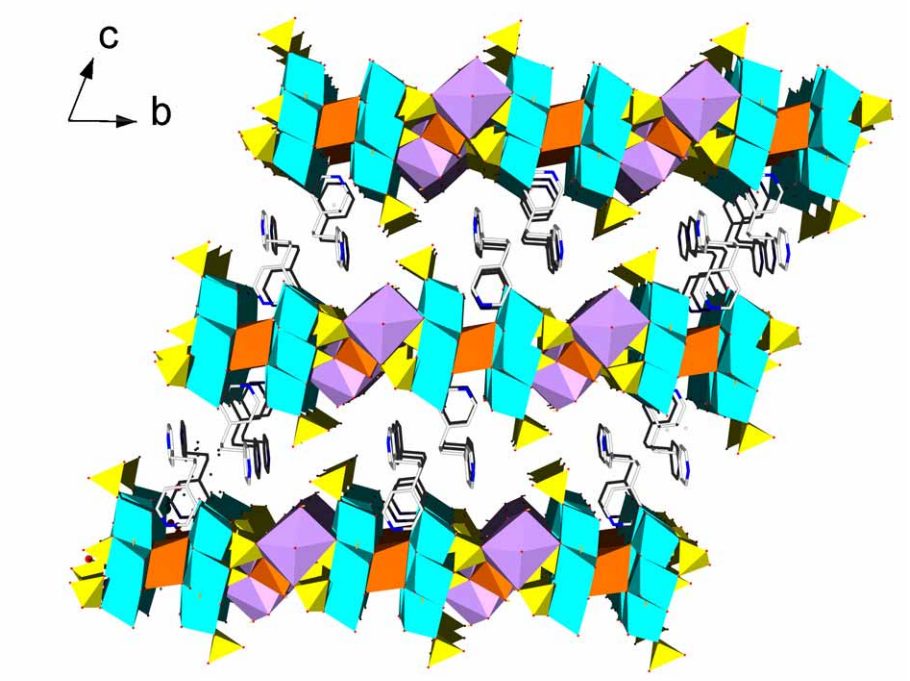

Fig. S5 The packing arrangement of compound **2** viewed along *a* axis. The isolated solvent water molecules are omitted for clarity.

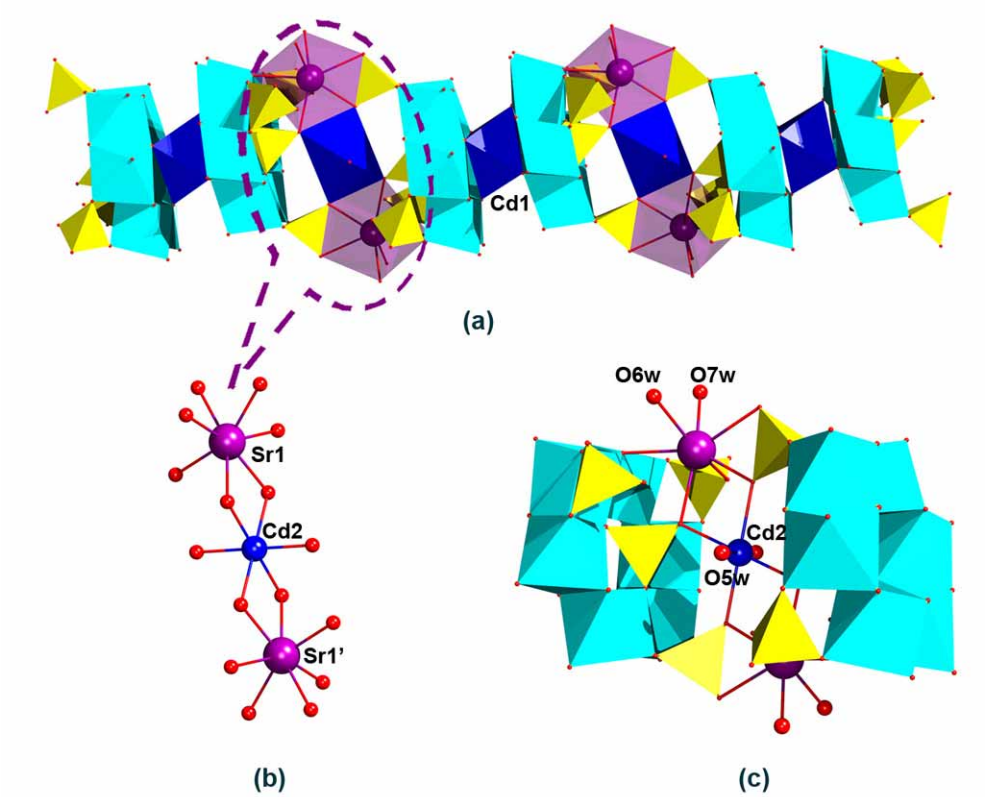

Fig. S6 (a) 1-D chain of the poly(oxomolybdophosphate) based on $\{Cd(P_4Mo_6)_2\}$ units and $\{Sr_2Cd\}$ linkers in **3**; **(b)** The trinuclear linking moiety of $\{Sr_2Cd\}$ in **3**; **(c)** Connection mode between trinuclear $\{Sr_2Cd\}$ unit and its adjacent $\{P_4Mo_6\}$ fragments in **3**.

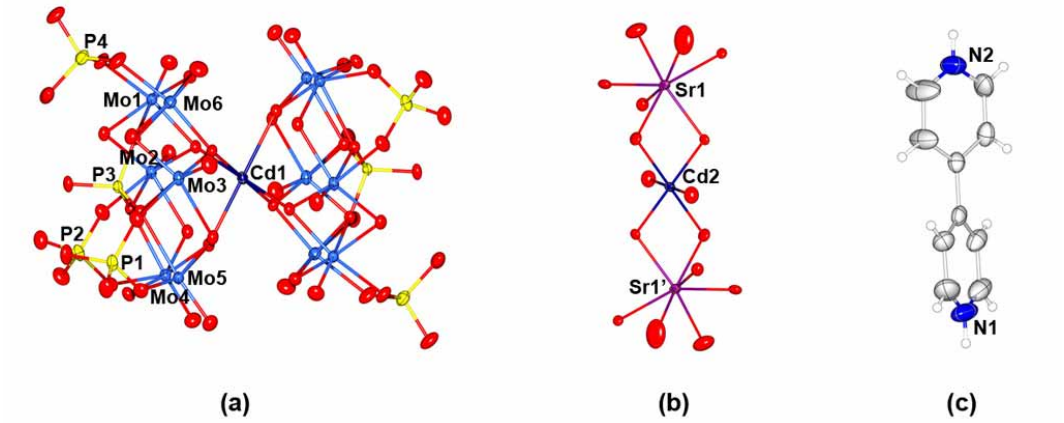

Fig. S7. ORTEP view of the basic units in compound **3** with 50% thermal ellipsoids: **(a)** the sandwich-type $\{Cd(P_4Mo_6)_2\}$ unit; **(b)** the trinuclear $\{Sr_2Cd\}$ linker; **(c)** $[H_2bpy]^{2+}$ protonated ligand.

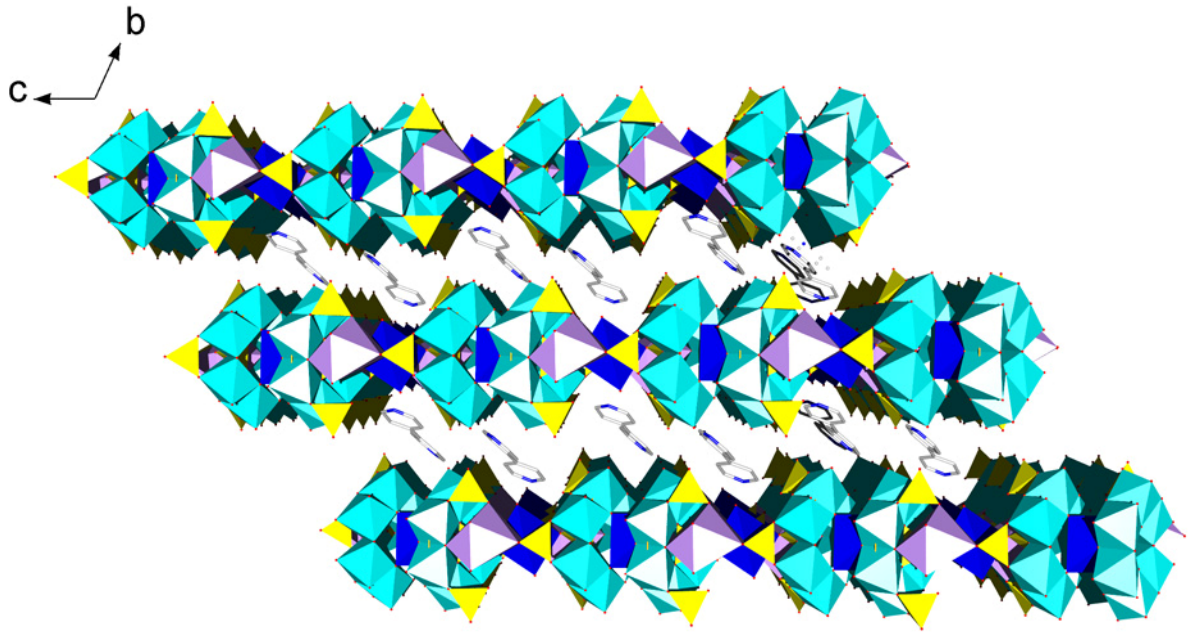

Fig. S8. The packing arrangement of compound **3** viewed along *a* axis. The isolated solvent water molecules are omitted for clarity.

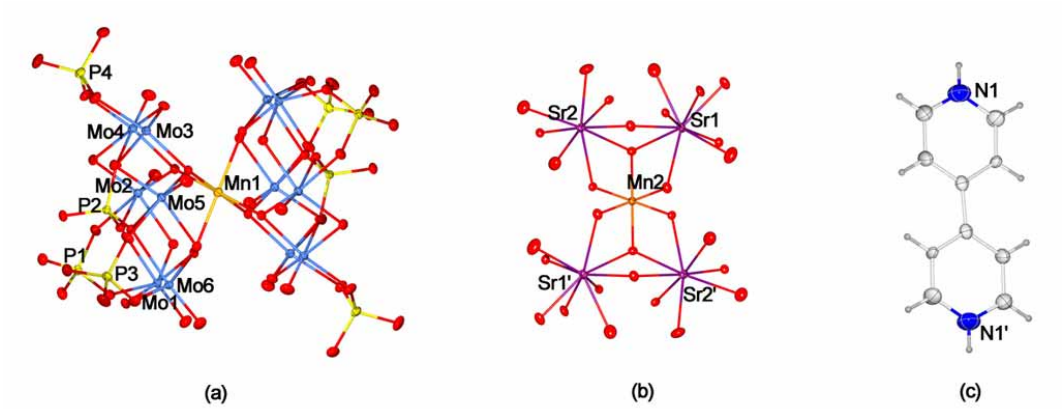

Fig. S9. ORTEP view of the basic units in compound **4** with 50% thermal ellipsoids: **(a)** the sandwich-type $\{Mn(P_4Mo_6)_2\}$ unit; **(b)** the trinuclear $\{Sr_4Mn\}$ linker; **(c)** $[H_2bpy]^{2+}$ protonated ligand.

2. Structural data

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

Mo(1)-O(27)	1.671(3)	Mo(3)-O(18)	1.677(3)	Mo(5)-O(29)	1.674(3)
Mo(1)-O(7)	1.941(3)	Mo(3)-O(14)	1.931(3)	Mo(5)-O(14)	1.933(3)
Mo(1)-O(1)	1.977(3)	Mo(3)-O(3)	1.974(3)	Mo(5)-O(3)	1.983(3)
Mo(1)-O(17)	2.056(3)	Mo(3)-O(10)#1	2.077(3)	Mo(5)-O(20)#1	2.061(3)
Mo(1)-O(13)	2.104(3)	Mo(3)-O(8)#1	2.118(3)	Mo(5)-O(6)#1	2.101(3)
Mo(1)-O(12)	2.302(3)	Mo(3)-O(5)#1	2.289(3)	Mo(5)-O(4)#1	2.301(3)
Mo(2)-O(19)	1.674(3)	Mo(4)-O(24)	1.677(3)	Mo(6)-O(21)	1.681(3)
Mo(2)-O(7)	1.941(3)	Mo(4)-O(16)	1.951(3)	Mo(6)-O(16)	1.942(3)
Mo(2)-O(1)	1.980(3)	Mo(4)-O(2)	1.977(3)	Mo(6)-O(2)	1.975(3)
Mo(2)-O(9)	2.072(3)	Mo(4)-O(22)	2.051(3)	Mo(6)-O(25)	2.038(3)
Mo(2)-O(8)	2.116(3)	Mo(4)-O(6)	2.092(3)	Mo(6)-O(13)	2.081(3)
Mo(2)-O(5)	2.269(3)	Mo(4)-O(4)	2.254(3)	Mo(6)-O(12)	2.291(3)
Mo(1)...Mo(2)	**2.5963(5)**	**Mo(4)...Mo(6)**	**2.5976(5)**	**Mo(3)...Mo(5)**	**2.587(5)**
Sr(1)-O(28)	2.494(4)	Sr(1)-O(15)	2.610(3)	Sr(1)-O(11)#2	2.705(3)
Sr(1)-O(9W)	2.543(5)	Sr(1)-O(16)	2.621(3)	Sr(1)-O(10W)	2.702(5)
Sr(1)-O(26)#2	2.597(3)	Sr(1)-O(8W)	2.655(6)		
Fe(1)-N(6)	1.965(5)	Fe(2)-O(2)#1	2.096(3)	Fe(3)-O(15)#2	2.100(3)
Fe(1)-N(1)	1.968(5)	Fe(2)-O(2)	2.096(3)	Fe(3)-O(15)	2.100(3)
Fe(1)-N(4)	1.966(4)	Fe(2)-O(1)	2.192(3)	Fe(3)-O(7W)#2	2.153(4)
Fe(1)-N(5)	1.968(5)	Fe(2)-O(1)#1	2.192(3)	Fe(3)-O(7W)	2.153(4)
Fe(1)-N(3)	1.969(5)	Fe(2)-O(3)	2.228(3)	Fe(3)-O(11)	2.168(3)
Fe(1)-N(2)	1.970(4)	Fe(2)-O(3)#1	2.228(3)	Fe(3)-O(11)#2	2.168(3)
P(1)-O(23)	1.515(5)	P(2)-O(15)	1.508(3)	P(3)-O(11)	1.499(3)
P(1)-O(22)	1.517(4)	P(2)-O(4)	1.544(3)	P(3)-O(10)	1.529(3)
P(1)-O(20)	1.531(4)	P(2)-O(5)	1.544(3)	P(3)-O(9)	1.536(3)
P(1)-O(31)	1.557(4)	P(2)-O(12)	1.549(3)	P(3)-O(26)	1.591(3)
P(4)-O(28)	1.501(3)	P(4)-O(25)	1.544(3)		
P(4)-O(17)	1.528(3)	P(4)-O(30)	1.574(4)		
O(27)-Mo(1)-O(13)	97.82(14)	O(19)-Mo(2)-O(8)	96.26(14)	O(18)-Mo(3)-O(8)#1	97.18(15)
O(7)-Mo(1)-O(13)	156.35(12)	O(7)-Mo(2)-O(8)	156.89(12)	O(14)-Mo(3)-O(8)#1	155.60(12)
O(1)-Mo(1)-O(13)	85.55(11)	O(1)-Mo(2)-O(8)	86.57(11)	O(3)-Mo(3)-O(8)#1	85.88(11)
O(17)-Mo(1)-O(13)	84.75(12)	O(9)-Mo(2)-O(8)	84.37(12)	O(10)#1-Mo(3)-O(8)#1	85.01(12)
O(13)-Mo(1)-O(12)	73.20(11)	O(8)-Mo(2)-O(5)	72.67(10)	O(10)#1-Mo(3)-O(5)#1	78.57(11)
O(24)-Mo(4)-O(6)	96.54(15)	O(29)-Mo(5)-O(6)#1	98.08(15)	O(21)-Mo(6)-O(13)	99.15(15)
O(16)-Mo(4)-O(6)	157.15(12)	O(14)-Mo(5)-O(6)#1	154.89(13)	O(16)-Mo(6)-O(13)	155.04(12)
O(2)-Mo(4)-O(6)	87.10(12)	O(3)-Mo(5)-O(6)#1	85.69(12)	O(2)-Mo(6)-O(13)	87.19(12)
O(22)-Mo(4)-O(6)	85.83(14)	O(20)#1-Mo(5)-O(6)#1	83.48(13)	O(25)-Mo(6)-O(13)	83.01(13)
O(6)-Mo(4)-O(4)	73.92(11)	O(6)#1-Mo(5)-O(4)#1	72.76(11)	O(13)-Mo(6)-O(12)	73.84(11)
O(28)-Sr(1)-O(9W)	78.47(16)	O(28)-Sr(1)-O(8W)	146.52(17)	O(28)-Sr(1)-O(15)	85.41(12)
O(28)-Sr(1)-O(26)#2	91.50(11)	O(28)-Sr(1)-O(11)#2	76.92(11)	O(28)-Sr(1)-O(16)	98.90(10)
O(28)-Sr(1)-O(10W)	146.20(13)				
N(6)-Fe(1)-N(1)	95.62(19)	O(2)#1-Fe(2)-O(1)	83.59(11)	O(15)#2-Fe(3)-O(7W)	86.57(13)
N(6)-Fe(1)-N(4)	174.8(2)	O(2)-Fe(2)-O(1)	96.41(11)	O(15)-Fe(3)-O(7W)	93.43(13)
N(6)-Fe(1)-N(5)	82.1(2)	O(1)-Fe(2)-O(1)#1	180.00	O(7W)#2-Fe(3)-O(7W)	180.00
N(6)-Fe(1)-N(3)	88.2(2)	O(1)-Fe(2)-O(3)#1	95.44(10)	O(7W)-Fe(3)-O(11)	85.67(13)
N(6)-Fe(1)-N(2)	94.0(2)	O(1)-Fe(2)-O(3)	84.56(10)	O(7W)-Fe(3)-O(11)#2	94.33(13)

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 (º) of compound **2**

Mo(1)-O(30)	1.675(5)	Mo(3)-O(15)	1.676(5)	Mo(5)-O(31)	1.677(5)
Mo(1)-O(19)	1.948(5)	Mo(3)-O(11)	1.950(5)	Mo(5)-O(11)	1.949(5)
Mo(1)-O(3)	1.973(5)	Mo(3)-O(1)	1.974(5)	Mo(5)-O(1)	1.976(5)
Mo(1)-O(13)#1	2.077(5)	Mo(3)-O(24)	2.071(5)	Mo(5)-O(20)	2.061(5)
Mo(1)-O(8)	2.103(5)	Mo(3)-O(9)#1	2.094(5)	Mo(5)-O(10)	2.094(5)
Mo(1)-O(2)	2.268(5)	Mo(3)-O(6)	2.266(5)	Mo(5)-O(12)	2.271(5)
Mo(2)-O(25)	1.667(5)	Mo(4)-O(14)	1.671(5)	Mo(6)-O(29)	1.670(6)
Mo(2)-O(7)	1.935(5)	Mo(4)-O(7)	1.938(5)	Mo(6)-O(19)	1.938(5)
Mo(2)-O(4)	1.977(5)	Mo(4)-O(4)	1.987(5)	Mo(6)-O(3)	1.973(5)
Mo(2)-O(5)	2.042(5)	Mo(4)-O(23)#1	2.061(5)	Mo(6)-O(28)	2.062(6)
Mo(2)-O(8)#1	2.104(5)	Mo(4)-O(9)	2.097(5)	Mo(6)-O(10)	2.097(5)
Mo(2)-O(2)#1	2.300(5)	Mo(4)-O(6)#1	2.300(5)	Mo(6)-O(12)	2.272(5)
Mo(1)…Mo(6)	**2.5991(12)**	**Mo(2)…Mo(4)**	**2.6054(10)**	**Mo(3)…Mo(5)**	**2.5976(10)**
Mn(1)-O(4)	2.195(5)	Mn(1)-O(3)	2.214(5)	Mn(1)-O(1)	2.221(5)
Mn(1)-O(4)#1	2.195(5)	Mn(1)-O(3)#1	2.214(5)	Mn(1)-O(1)#1	2.221(5)
Mn(2)-O(16)#2	2.165(5)	Mn(2)-O(17)#3	2.171(5)	Mn(2)-O(7W)	2.222(6)
Mn(2)-O(16)	2.165(5)	Mn(2)-O(17)#1	2.171(5)	Mn(2)-O(7W)#2	2.222(6)
Sr(1)-O(8W)	2.706(14)	Sr(1)-O(18)#3	2.596(5)	Sr(1)-O(21)	2.610(6)
Sr(1)-O(8AW)	2.377(17)	Sr(1)-O(11)	2.600(5)	Sr(1)-O(9W)	2.611(10)
Sr(1)-O(16)	2.638(5)	Sr(1)-O(10W)	2.568(8)	Sr(1)-O(17)#3	2.725(5)
P(1)-O(16)	1.509(5)	P(2)-O(17)	1.509(5)	P(3)-O(22)	1.501(6)
P(1)-O(12)	1.550(5)	P(2)-O(5)	1.535(5)	P(3)-O(24)	1.527(5)
P(1)-O(2)	1.549(5)	P(2)-O(13)	1.536(5)	P(3)-O(23)	1.529(6)
P(1)-O(6)	1.552(5)	P(2)-O(18)	1.566(5)	P(3)-O(21)	1.579(6)
P(4)-O(27)	1.505(6)	P(4)-O(28)	1.534(6)		
P(4)-O(20)	1.525(6)	P(4)-O(26)	1.562(6)		
O(30)-Mo(1)-O(8)	96.9(2)	O(25)-Mo(2)-O(8)#1	98.4(2)	O(15)-Mo(3)-O(9)#1	96.3(2)
O(19)-Mo(1)-O(8)	157.3(2)	O(7)-Mo(2)-O(8)#1	155.0(2)	O(11)-Mo(3)-O(9)#1	155.4(2)
O(3)-Mo(1)-O(8)	85.30(19)	O(4)-Mo(2)-O(8)#1	86.84(19)	O(1)-Mo(3)-O(9)#1	85.99(19)
O(13)#1-Mo(1)-O(8)	85.29(19)	O(5)-Mo(2)-O(8)#1	83.22(19)	O(24)-Mo(3)-O(9)#1	86.1(2)
O(8)-Mo(1)-O(2)	72.78(18)	O(8)#1-Mo(2)-O(2)#1	72.11(17)	O(9)#1-Mo(3)-O(6)	72.89(18)
O(14)-Mo(4)-O(9)	98.7(2)	O(31)-Mo(5)-O(10)	98.2(2)	O(29)-Mo(6)-O(10)	97.9(3)
O(7)-Mo(4)-O(9)	155.0(2)	O(11)-Mo(5)-O(10)	154.6(2)	O(19)-Mo(6)-O(10)	155.3(2)
O(4)-Mo(4)-O(9)	86.08(19)	O(1)-Mo(5)-O(10)	85.59(19)	O(3)-Mo(6)-O(10)	86.2(2)
O(23)#1-Mo(4)-O(9)	84.9(2)	O(20)-Mo(5)-O(10)	85.3(2)	O(28)-Mo(6)-O(10)	84.4(2)
O(9)-Mo(4)-O(6)#1	72.14(18)	O(10)-Mo(5)-O(12)	72.42(18)	O(10)-Mo(6)-O(12)	72.35(18)
O(4)-Mn(1)-O(1)	84.52(17)	O(3)-Mn(1)-O(1)	96.13(17)	O(1)-Mn(1)-O(1)#1	180.00
O(4)#1-Mn(1)-O(1)	95.48(17)	O(3)#1-Mn(1)-O(1)	83.87(17)		
O(16)#2-Mn(2)-O(7)	88.1(2)	O(17)#3-Mn(2)-O(7W)	91.8(2)	O(7W)-Mn(2)-O(7W)#	180.00
O(16)-Mn(2)-O(7W)	91.9(2)	O(17)#1-Mn(2)-O(7W)	88.2(2)		
O(10W)-Sr(1)-O(18)	75.3(2)	O(10W)-Sr(1)-O(9W)	129.8(3)	O(10W)-Sr(1)-O(17)#3	123.7(2)
O(10W)-Sr(1)-O(11)	85.4(2)	O(10W)-Sr(1)-O(16)	160.6(2)		
O(10W)-Sr(1)-O(21)	85.0(2)	O(10W)-Sr(1)-O(8W)	69.9(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+2; #2 -x+2,-y+2,-z+2; #3 x,y+1,z

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

Mo(1)-O(19)	1.676(3)	Mo(3)-O(24)	1.677(3)	Mo(5)-O(29)	1.678(3)
Mo(1)-O(5)	1.951(3)	Mo(3)-O(11)	1.927(3)	Mo(5)-O(12)	1.932(3)
Mo(1)-O(1)	1.968(3)	Mo(3)-O(2)	1.970(3)	Mo(5)-O(4)	1.970(3)
Mo(1)-O(20)	2.073(3)	Mo(3)-O(14)#1	2.066(3)	Mo(5)-O(17)#1	2.034(3)
Mo(1)-O(13)	2.121(3)	Mo(3)-O(3)	2.136(3)	Mo(5)-O(3)	2.111(3)
Mo(1)-O(7)	2.251(3)	Mo(3)-O(10)#2	2.301(3)	Mo(5)-O(10)#2	2.324(3)
Mo(2)-O(22)	1.672(3)	Mo(4)-O(18)	1.678(3)	Mo(6)-O(31)	1.671(4)
Mo(2)-O(5)	1.940(3)	Mo(4)-O(12)	1.940(3)	Mo(6)-O(11)	1.937(3)
Mo(2)-O(1)	1.972(3)	Mo(4)-O(4)	1.970(3)	Mo(6)-O(2)	1.969(3)
Mo(2)-O(6)	2.060(3)	Mo(4)-O(21)#2	2.052(3)	Mo(6)-O(25)#2	2.056(3)
Mo(2)-O(9)	2.116(3)	Mo(4)-O(9)#2	2.148(3)	Mo(6)-O(13)#2	2.125(3)
Mo(2)-O(8)	2.319(3)	Mo(4)-O(8)#2	2.281(3)	Mo(6)-O(7)#2	2.282(3)
Mo(1)...Mo(2)	**2.6160(6)**	**Mo(3)...Mo(6)**	**2.6060(6)**	**Mo(4)...Mo(5)**	**2.5994(6)**
Cd(1)-O(2)	2.268(3)	Cd(1)-O(4)	2.277(3)	Cd(1)-O(1)	2.293(3)
Cd(1)-O(2)#2	2.268(3)	Cd(1)-O(4)#2	2.277(3)	Cd(1)-O(1)#2	2.293(3)
Cd(2)-O(15)	2.243(3)	Cd(2)-O(5W)	2.284(4)	Cd(2)-O(30)#3	2.333(3)
Cd(2)-O(15)#3	2.243(3)	Cd(2)-O(5W)#3	2.284(4)	Cd(2)-O(30)	2.333(3)
Sr(1)-O(26)	2.402(4)	Sr(1)-O(7W)	2.497(7)	Sr(1)-O(27)	2.707(3)
Sr(1)-O(6W)	2.427(5)	Sr(1)-O(15)	2.555(3)		
Sr(1)-O(30)	2.449(4)	Sr(1)-O(5)	2.629(3)		
P(1)-O(30)	1.518(3)	P(2)-O(26)	1.513(4)	P(3)-O(15)	1.517(3)
P(1)-O(17)	1.539(4)	P(2)-O(21)	1.532(4)	P(3)-O(10)	1.539(3)
P(1)-O(27)	1.547(3)	P(2)-O(6)	1.534(3)	P(3)-O(8)	1.546(3)
P(1)-O(14)	1.550(3)	P(2)-O(23)	1.569(3)	P(3)-O(7)	1.546(3)
P(4)-O(28)	1.519(4)	P(4)-O(25)	1.522(4)	P(4)-O(20)	1.530(4)
P(4)-O(16)	1.579(4)				
O(19)-Mo(1)-O(13)	97.90(15)	O(22)-Mo(2)-O(9)	99.91(15)	O(24)-Mo(3)-O(3)	97.24(15)
O(5)-Mo(1)-O(13)	153.45(13)	O(5)-Mo(2)-O(9)	151.00(13)	O(11)-Mo(3)-O(3)	155.81(13)
O(1)-Mo(1)-O(13)	86.68(12)	O(1)-Mo(2)-O(9)	86.53(12)	O(2)-Mo(3)-O(3)	85.66(12)
O(20)-Mo(1)-O(13)	86.08(13)	O(6)-Mo(2)-O(9)	83.78(13)	O(14)#1-Mo(3)-O(3)	85.35(13)
O(13)-Mo(1)-O(7)	70.08(11)	O(9)-Mo(2)-O(8)	71.22(11)	O(3)-Mo(3)-O(10)#2	72.49(12)
O(18)-Mo(4)-O(9)#2	97.44(15)	O(29)-Mo(5)-O(3)	98.73(15)	O(31)-Mo(6)-O(13)#2	100.39(16)
O(12)-Mo(4)-O(9)#2	156.05(13)	O(12)-Mo(5)-O(3)	154.43(13)	O(11)-Mo(6)-O(13)#2	151.93(13)
O(4)-Mo(4)-O(9)#2	85.73(12)	O(4)-Mo(5)-O(3)	86.63(12)	O(2)-Mo(6)-O(13)#2	87.52(13)
O(21)#2-Mo(4)-O(9)#2	85.44(12)	O(17)#1-Mo(5)-O(3)	82.55(13)	O(25)#2-Mo(6)-O(13)#2	83.38(13)
O(9)#2-Mo(4)-O(8)#2	71.43(11)	O(3)-Mo(5)-O(10)#2	72.44(11)	O(13)#2-Mo(6)-O(7)#2	69.41(11)
O(2)-Cd(1)-O(1)	81.05(11)	O(4)-Cd(1)-O(1)	83.66(11)	O(1)-Cd(1)-O(1)#2	180.00
O(2)#2-Cd(1)-O(1)	98.95(11)	O(4)#2-Cd(1)-O(1)	96.34(11)		
O(15)-Cd(2)-O(5W)	93.79(13)	O(5W)-Cd(2)-O(30)	91.27(14)	O(5W)-Cd(2)-O(5W)#3	180.00
O(15)#3-Cd(2)-O(5W)	86.21(13)	O(5W)-Cd(2)-O(30)#3	88.73(14)		
O(26)-Sr(1)-O(6W)	80.37(15)	O(6W)-Sr(1)-O(7W)	75.9(2)	O(6W)-Sr(1)-O(5)	82.59(14)
O(6W)-Sr(1)-O(30)	127.54(15)	O(6W)-Sr(1)-O(15)	155.36(14)	O(6W)-Sr(1)-O(27)	78.11(14)

Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1; #2 -x,-y+1,-z+2; #3 -x,-y+1,-z+1

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

Mo(1)-O(4)	1.681(2)	Mo(3)-O(1)	1.672(2)	Mo(5)-O(5)	1.679(2)
Mo(1)-O(20)	1.939(2)	Mo(3)-O(12)	1.954(2)	Mo(5)-O(12)	1.954(2)
Mo(1)-O(6)	1.982(2)	Mo(3)-O(11)	1.978(2)	Mo(5)-O(11)	1.972(2)
Mo(1)-O(16)	2.028(2)	Mo(3)-O(22)	2.066(2)	Mo(5)-O(25)	2.064(2)
Mo(1)-O(7)	2.105(2)	Mo(3)-O(9)	2.093(2)	Mo(5)-O(29)	2.099(2)
Mo(1)-O(14)	2.272(2)	Mo(3)-O(8)	2.264(2)	Mo(5)-O(18)	2.268(2)
Mo(2)-O(2)	1.673(2)	Mo(4)-O(24)	1.679(2)	Mo(6)-O(3)	1.672(2)
Mo(2)-O(19)	1.948(2)	Mo(4)-O(19)	1.940(2)	Mo(6)-O(20)	1.933(2)
Mo(2)-O(10)	1.973(2)	Mo(4)-O(10)	1.978(2)	Mo(6)-O(6)	1.981(2)
Mo(2)-O(15)	2.047(2)	Mo(4)-O(23)	2.064(2)	Mo(6)-O(26)	2.061(2)
Mo(2)-O(7)	2.095(2)	Mo(4)-O(9)	2.114(2)	Mo(6)-O(29)	2.130(2)
Mo(2)-O(14)	2.290(2)	Mo(4)-O(8)	2.261(2)	Mo(6)-O(18)	2.281(2)
Mo(1)...Mo(6)	**2.5924(4)**	**Mo(2)...Mo(4)**	**2.5967(4)**	**Mo(3)…Mo(5)**	**2.6004(4)**
Sr(1)-O(21)#1	2.553(2)	Sr(1)-O(19)	2.642(2)	Sr(1)-O(27)	2.762(2)
Sr(1)-O(8W)	2.571(3)	Sr(1)-O(7W)	2.692(3)	Sr(1)-O(31)#2	2.781(3)
Sr(1)-O(28)#2	2.637(2)	Sr(1)-O(10W)#1	2.719(2)	Sr(1)-O(15)	2.813(2)
Sr(2)-O(17)	2.556(2)	Sr(2)-O(12)#1	2.633(2)	Sr(2)-O(21)#1	2.640(2)
Sr(2)-O(6W)	2.593(3)	Sr(2)-O(5W)	2.681(4)	Sr(2)-O(27)	2.676(2)
Sr(2)-O(13)#1	2.612(2)	Sr(2)-O(5AW)	2.672(12)	Sr(2)-O(9W)	2.718(3)
Mn(1)-O(10)	2.179(2)	Mn(1)-O(6)	2.197(2)	Mn(1)-O(11)	2.248(2)
Mn(1)-O(10)#3	2.179(2)	Mn(1)-O(6)#3	2.197(2)	Mn(1)-O(11)#3	2.248(2)
Mn(2)-O(13)#1	2.136(2)	Mn(2)-O(27)#1	2.194(2)	Mn(2)-O(10W)	2.226(2)
Mn(2)-O(13)	2.136(2)	Mn(2)-O(27)	2.194(2)	Mn(2)-O(10W)#1	2.226(2)
P(1)-O(17)	1.522(2)	P(2)-O(13)	1.509(2)	P(3)-O(21)	1.504(2)
P(1)-O(27)	1.536(2)	P(2)-O(14)	1.540(2)	P(3)-O(25)	1.534(2)
P(1)-O(16)	1.537(2)	P(2)-O(8)	1.547(2)	P(3)-O(26)	1.543(2)
P(1)-O(15)	1.557(2)	P(2)-O(18)	1.552(2)	P(3)-O(30)	1.574(2)
P(4)-O(31)	1.503(2)	P(4)-O(23)	1.541(2)		
P(4)-O(22)	1.533(2)	P(4)-O(28)	1.568(2)		
O(4)-Mo(1)-O(7)	97.25(10)	O(2)-Mo(2)-O(7)	97.18(10)	O(1)-Mo(3)-O(9)	98.70(10)
O(20)-Mo(1)-O(7)	156.51(8)	O(19)-Mo(2)-O(7)	155.27(8)	O(12)-Mo(3)-O(9)	154.55(8)
O(6)-Mo(1)-O(7)	86.34(8)	O(10)-Mo(2)-O(7)	87.32(8)	O(11)-Mo(3)-O(9)	86.06(8)
O(16)-Mo(1)-O(7)	84.63(8)	O(15)-Mo(2)-O(7)	84.88(8)	O(22)-Mo(3)-O(9)	84.90(9)
O(7)-Mo(1)-O(14)	72.81(7)	O(7)-Mo(2)-O(14)	72.60(7)	O(9)-Mo(3)-O(8)	72.18(8)
O(24)-Mo(4)-O(8)	168.54(10)	O(5)-Mo(5)-O(29)	99.76(10)	O(3)-Mo(6)-O(29)	98.55(10)
O(19)-Mo(4)-O(8)	84.96(8)	O(12)-Mo(5)-O(29)	154.55(8)	O(20)-Mo(6)-O(29)	154.86(8)
O(10)-Mo(4)-O(8)	80.70(8)	O(11)-Mo(5)-O(29)	85.84(8)	O(6)-Mo(6)-O(29)	86.68(8)
O(23)-Mo(4)-O(8)	80.38(8)	O(25)-Mo(5)-O(29)	84.96(8)	O(26)-Mo(6)-O(29)	84.10(8)
O(9)-Mo(4)-O(8)	71.91(8)	O(29)-Mo(5)-O(18)	72.98(7)	O(29)-Mo(6)-O(18)	72.17(7)
O(21)#1-Sr(1)-O(8W)	120.69(9)	O(8W)-Sr(1)-O(7W)	140.63(10)	O(8W)-Sr(1)-O(31)#2	74.90(9)
O(8W)-Sr(1)-O(28)#2	75.98(9)	O(8W)-Sr(1)-O(10W)#1	70.26(9)	O(8W)-Sr(1)-O(15)	129.55(8)
O(8W)-Sr(1)-O(19)	70.86(8)	O(8W)-Sr(1)-O(27)	130.38(9)		
O(17)-Sr(2)-O(6W)	73.61(8)	O(6W)-Sr(2)-O(21)#1	74.74(8)	O(6W)-Sr(2)-O(5W)	81.21(12)
O(6W)-Sr(2)-O(13)#1	147.90(8)	O(6W)-Sr(2)-O(27)	113.93(8)	O(6W)-Sr(2)-O(5AW)	70.8(3)
O(6W)-Sr(2)-O(12)#1	86.82(8)	O(6W)-Sr(2)-O(9W)	140.40(9)		
O(13)#1-Mn(2)-O(10	86.46(8)	O(27)#1-Mn(2)-O(10W)	87.57(8)	O(10W)-Mn(2)-O(10W)#1	180.00
O(13)-Mn(2)-O(10W)	93.54(8)	O(27)-Mn(2)-O(10W)	92.43(8)		
O(10)-Mn(1)-O(6)	95.88(8)	O(6)-Mn(1)-O(6)#3	180.00	O(6)-Mn(1)-O(11)#3	83.54(7)
O(10)#3-Mn(1)-O(6)	84.12(7)	O(6)-Mn(1)-O(11)	96.46(7)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1; #2 x,-y+1/2,z-1/2; #3 -x+1,-y+1,-z+1

Table S5. BVS calculations of Mo centers in compounds **1-4**[a]

	1	**2**	**3**	**4**
Mo1	5.23	5.19	5.19	5.25
Mo2	5.19	5.27	5.20	5.25
Mo3	5.19	5.19	5.19	5.22
Mo4	5.25	5.21	5.17	5.20
Mo5	5.22	5.21	5.24	5.20
Mo6	5.26	5.26	5.25	5.09

[a] $V = \sum_{i=1}^{6} \exp(\frac{r_0 - r_i}{0.37})$ (r_0 = 1.907(2) Å, ref: Brown, I. D.; Altermatt, D. *Acta. Crystallogr. Sect. B.* **1985**, *41*, 244-247).

Table S6. BVS calculations of P centers in compounds **1-4**[a]

	1	**2**	**3**	**4**
P1	5.09	4.91	4.95	4.95
P2	4.98	4.98	4.97	4.97
P3	4.97	5.02	4.97	4.94
P4	4.99	5.05	5.00	4.99

[a] $V = \sum_{i=1}^{4} \exp(\frac{r_0 - r_i}{0.37})$ (r_0 = 1.617(1) Å, ref: Brown, I. D.; Altermatt, D. *Acta. Crystallogr. Sect. B.* **1985**, *41*, 244-247).

Table S7-1. BVS calculations of Fe centers in compounds **1**

	$r_{Fe(II)\text{-}N\ 1.761\ Å}$[a]	$r_{Fe(III)\text{-}N\ 1.815\ Å}$[a]	$r_{Fe(II)\text{-}O\ 1.700Å}$[a]	$r_{Fe(III)\text{-}O\ 1.765Å}$[a]	average
Fe1	3.41	3.97			3.69[b]
Fe2			1.69	2.02	1.85
Fe3			1.83	2.18	2.00

[a] r_o values are originated from the ref: Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102-4105. [b] The calculation result is a little deviated from the true oxidation state, but indicating that Fe1 should possesses the relatively high oxidation state (which is close to +3 oxidation state).

Table S7-2. BVS calculations of transitional metal centers in compounds **2-4**[a]

	2	**3**	**4**
Mn1/Mn2	1.81 / 1.95		
Cd1/Cd2		2.18 / 2.14	
Mn1/Mn2			1.81 / 1.93

[a] $V = \sum_{i=1}^{6} \exp(\frac{r_0 - r_i}{0.37})$ (r_0 (Mn(II)-O) = 1.765(1) Å, r_0 (Mn(II)-O) = 1.904(4) Å, ref: Brown, I. D.; Altermatt, D. *Acta. Crystallogr. Sect. B.* **1985**, *41*, 244-247).

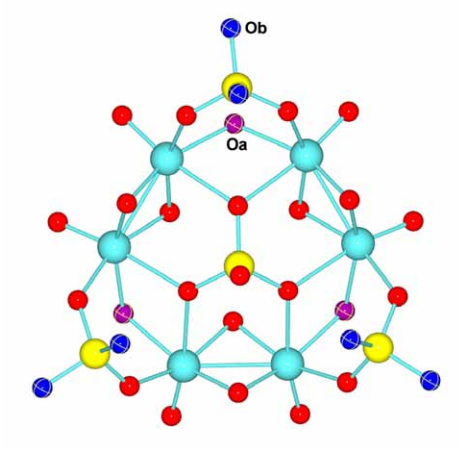

Table S8. BVS calculations of {OH}, {HPO_4} and {H_2PO_4} groups in compounds **1-4**[a]

		1		**2**		**3**		**4**	
Oa	μ-{OH}	O6	1.19	O8	1.17	O3	1.11	O7	1.18
		O8	1.13	O9	1.19	O9	1.09	O9	1.17
		O13	1.21	O10	1.19	O13	1.11	O29	1.14
Ob	{HPO_4}	O30	1.12	O22	1.36	O23	1.13	O28	1.20
								O31	1.36
	{H_2PO_4}	O23	1.32	O26	1.16	O16	1.11		
		O31	1.19	O27	1.36	O28	1.31		

[a] (r_0 (Mo-O) = 1.907(2) Å, r_0 (P-O) = 1.617(1) Å, r_0 (Sr-O) = 2.118(6) Å, ref: Brown, I. D.; Altermatt, D. *Acta. Crystallogr. Sect. B.* **1985**, *41*, 244-247).

3. Physical characterization

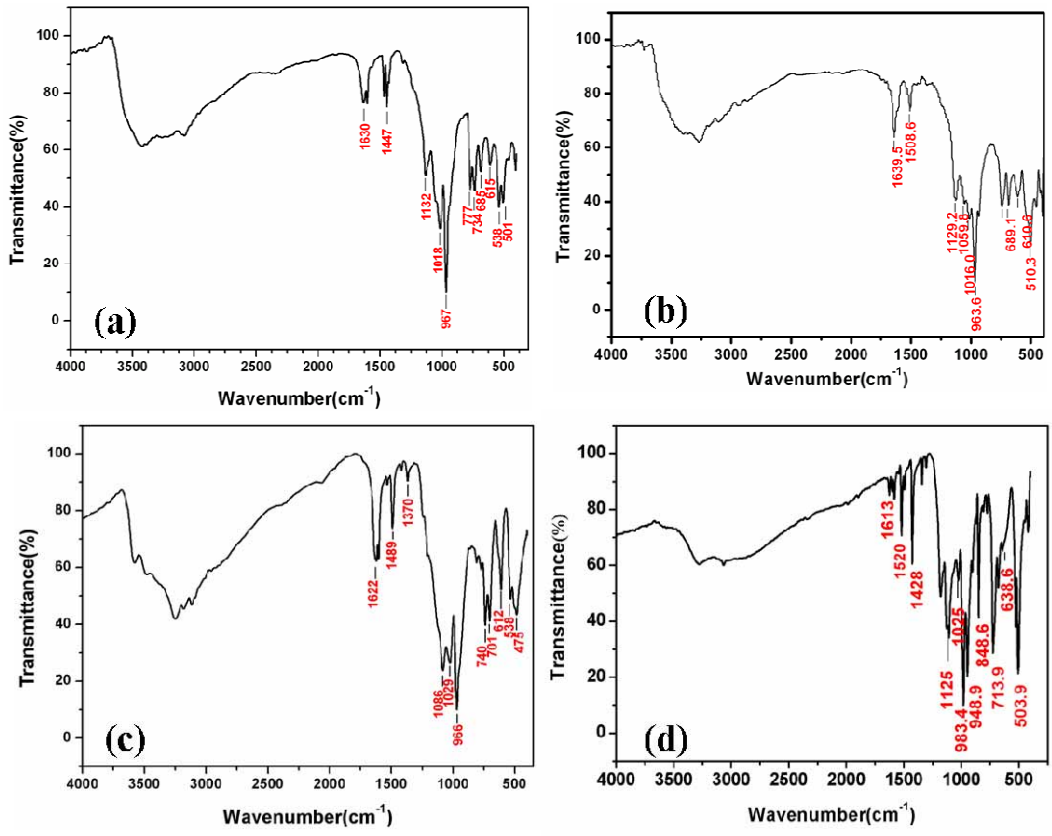

Fig. S10 IR spectra of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **(3)** and **(d)** compound **4**

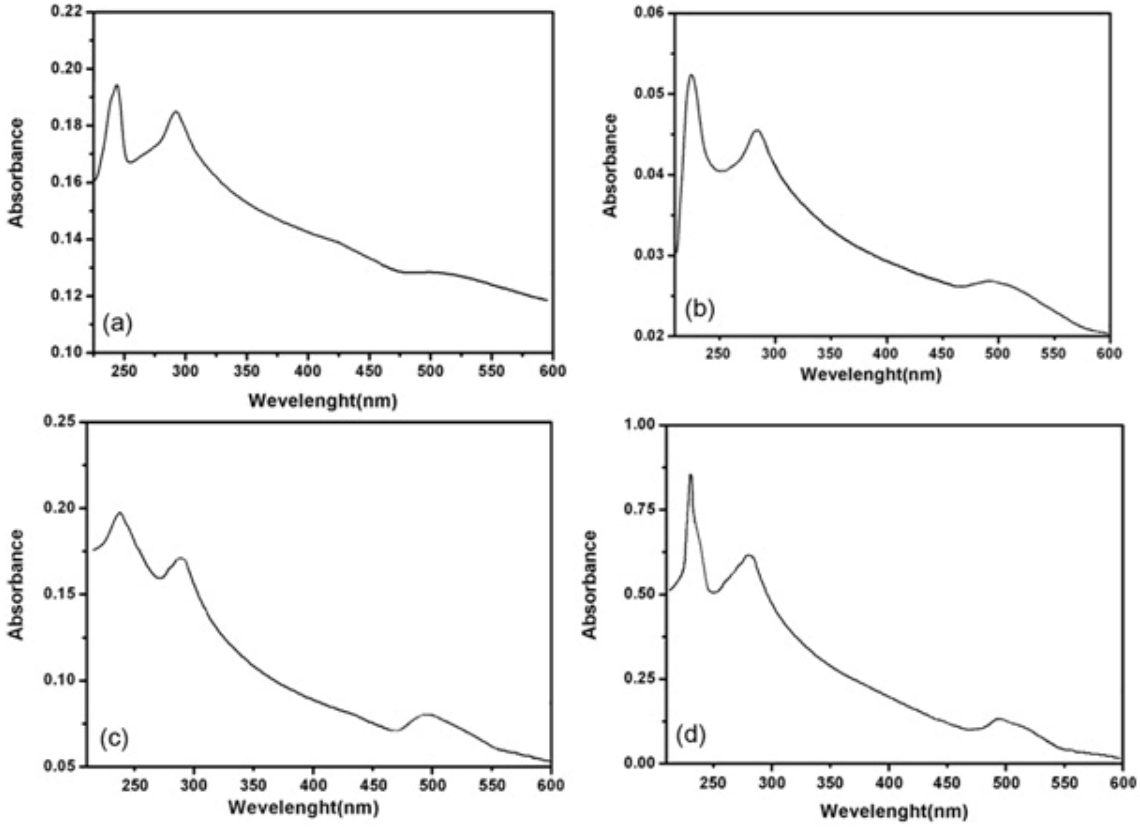

Fig. S11 Solid state UV-vis spectra of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **3** and **(d)** compound **4**

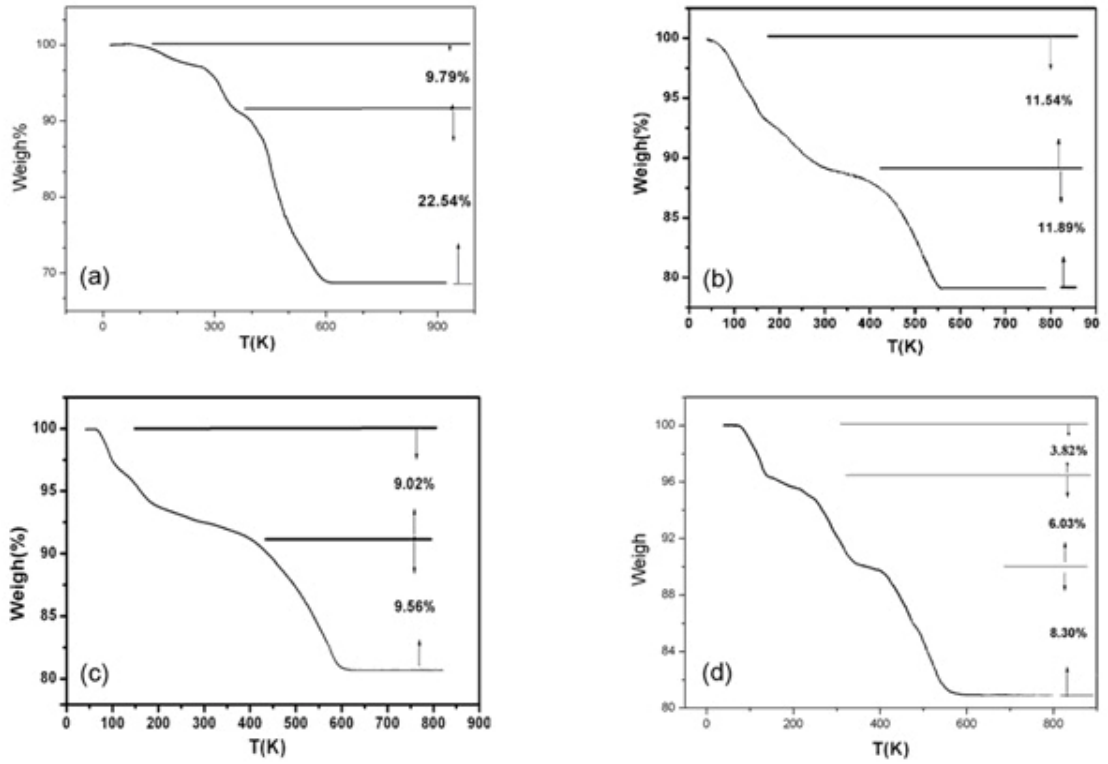

Fig. S12 TG of **(a)** compound **1**, **(b)** compound **2**, **(c)** compound **3** and **(d)** compound **4**

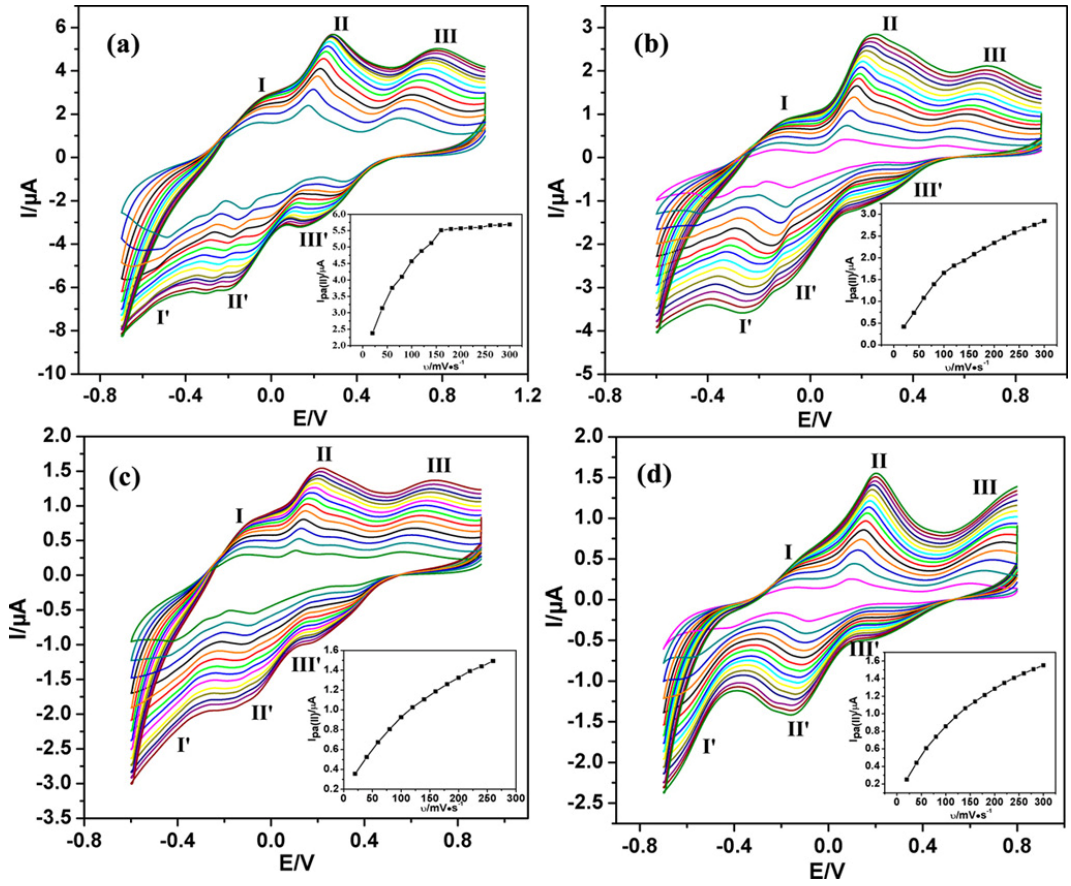

Fig. S13 Cyclic voltammograms of **(a) 1-CPE, (b) 2-CPE, (c) 3-CPE, and (d) 4-CPE** in the 1.0 M H_2SO_4 solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 mV s^{-1}). Potentials vs. SCE. (Insert plots: The dependence of anodic peak II current on scan rates.)