Supporting Information

Transition Metal-induced Self-assembly of Small Molybdenum Clusters

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Table S1. Selected Bond lengths (Å) and angles (°) for compounds **1-8.**

Compound **1**			
Mo(1)-V(1)	3.1149(19)	V(3)-O(10)	2.366(12)
Mo(2)-V(1)	3.141(2)	V(1)-O(1W')	1.784(13)
Mo(4)-V(1)	3.151(2)	V(1)-O(1W)	1.791(12)
V(2)-O(3)	1.586(7)	V(1)-O(12')	1.910(13)
V(2)-O(20')	1.840(14)	V(1)-O(21')	1.926(13)
V(2)-O(7)#1	1.917(8)	V(1)-O(9)	1.918(8)
V(2)-O(8)#1	1.928(10)	V(1)-O(11)	1.921(8)
V(2)-O(19)	1.948(14)	V(1)-O(1W)#2	1.986(12)
V(2)-O(19')	1.970(17)	V(1)-O(1W')#2	2.007(13)
V(2)-O(20)	2.067(14)	V(1)-O(21)	2.093(14)
V(2)-O(13)	2.399(11)	V(1)-O(12)	2.12(2)
V(3)-O(2)	1.593(7)	V(1)-V(1)#2	2.909(3)
V(3)-O(17')	1.829(13)	O(1W)-V(1)#2	1.986(12)
V(3)-O(6)#1	1.911(10)	O(1W')-V(1)#2	2.007(13)
V(3)-O(23')	1.926(15)	O(5)-V(3)#1	1.933(8)
V(3)-O(5)#1	1.933(8)	O(6)-V(3)#1	1.911(10)
V(3)-O(23)	2.001(16)	O(7)-V(2)#1	1.917(8)
V(3)-O(17)	2.100(14)	O(8)-V(2)#1	1.928(10)
O(3)-V(2)-O(20')	112.9(5)	O(12')-V(1)-O(21')	59.1(8)
O(3)-V(2)-O(7)#1	102.1(5)	O(1W')-V(1)-O(9)	84.3(5)
O(20')-V(2)-O(7)#1	84.7(5)	O(1W)-V(1)-O(9)	117.7(6)
O(3)-V(2)-O(8)#1	100.3(4)	O(12')-V(1)-O(9)	73.0(6)
O(20')-V(2)-O(8)#1	146.7(5)	O(21')-V(1)-O(9)	110.7(5)
O(7)#1-V(2)-O(8)#1	86.7(4)	O(1W')-V(1)-O(11)	118.6(5)
O(3)-V(2)-O(19)	91.0(11)	O(1W)-V(1)-O(11)	84.6(5)
O(20')-V(2)-O(19)	84.1(6)	O(12')-V(1)-O(11)	108.5(11)
O(7)#1-V(2)-O(19)	165.3(7)	O(21')-V(1)-O(11)	74.6(5)

O(8)#1-V(2)-O(19)	97.6(9)	O(9)-V(1)-O(11)	77.2(3)
O(3)-V(2)-O(19')	110.2(10)	O(1W')-V(1)-O(1W)#2	56.8(6)
O(20')-V(2)-O(19')	88.8(6)	O(1W)-V(1)-O(1W)#2	79.4(6)
O(7)#1-V(2)-O(19')	147.1(11)	O(12')-V(1)-O(1W)#2	86.6(11)
O(8)#1-V(2)-O(19')	81.2(9)	O(21')-V(1)-O(1W)#2	107.1(5)
O(19)-V(2)-O(19')	23.3(4)	O(9)-V(1)-O(1W)#2	117.3(5)
O(3)-V(2)-O(20)	91.9(5)	O(11)-V(1)-O(1W)#2	162.2(5)
O(20')-V(2)-O(20)	21.4(4)	O(1W')-V(1)-O(1W')#2	79.9(6)
O(7)#1-V(2)-O(20)	92.5(5)	O(1W)-V(1)-O(1W')#2	56.3(6)
O(8)#1-V(2)-O(20)	167.7(5)	O(12')-V(1)-O(1W')#2	110.5(7)
O(19)-V(2)-O(20)	80.3(8)	O(21')-V(1)-O(1W')#2	84.2(6)
O(19')-V(2)-O(20)	93.0(8)	O(9)-V(1)-O(1W')#2	163.1(5)
O(3)-V(2)-O(13)	159.0(4)	O(11)-V(1)-O(1W')#2	115.6(5)
O(20')-V(2)-O(13)	52.4(5)	O(1W)#2-V(1)-O(1W')#2	48.2(5)
O(7)#1-V(2)-O(13)	92.0(4)	O(1W')-V(1)-O(21)	144.4(6)
O(8)#1-V(2)-O(13)	95.9(4)	O(1W)-V(1)-O(21)	100.7(6)
O(19)-V(2)-O(13)	73.6(9)	O(12')-V(1)-O(21)	76.3(6)
O(19')-V(2)-O(13)	59.3(8)	O(21')-V(1)-O(21)	21.3(4)
O(20)-V(2)-O(13)	71.8(5)	O(9)-V(1)-O(21)	131.2(5)
O(2)-V(3)-O(17')	113.8(5)	O(11)-V(1)-O(21)	77.9(4)
O(2)-V(3)-O(6)#1	100.9(4)	O(1W)#2-V(1)-O(21)	97.4(5)
O(17')-V(3)-O(6)#1	145.2(5)	O(1W')#2-V(1)-O(21)	64.6(5)
O(2)-V(3)-O(23')	112.5(8)	O(1W')-V(1)-O(12)	100.8(10)
O(17')-V(3)-O(23')	89.9(6)	O(1W)-V(1)-O(12)	144.7(10)
O(6)#1-V(3)-O(23')	79.2(7)	O(12')-V(1)-O(12)	22.4(4)
O(2)-V(3)-O(5)#1	101.7(4)	O(21')-V(1)-O(12)	74.8(9)
O(17')-V(3)-O(5)#1	84.0(5)	O(9)-V(1)-O(12)	78.6(5)
O(6)#1-V(3)-O(5)#1	86.2(4)	O(11)-V(1)-O(12)	130.7(10)
O(23')-V(3)-O(5)#1	144.7(8)	O(1W)#2-V(1)-O(12)	65.4(10)
O(2)-V(3)-O(23)	91.2(8)	O(1W')#2-V(1)-O(12)	98.6(7)
O(17')-V(3)-O(23)	85.1(6)	O(21)-V(1)-O(12)	87.0(7)
O(6)#1-V(3)-O(23)	97.6(7)	O(1W')-V(1)-V(1)#2	42.8(4)
O(23')-V(3)-O(23)	25.9(5)	O(1W)-V(1)-V(1)#2	42.2(4)
O(5)#1-V(3)-O(23)	165.7(6)	O(12')-V(1)-V(1)#2	123.8(10)
O(2)-V(3)-O(17)	90.5(5)	O(21')-V(1)-V(1)#2	121.0(4)
O(17')-V(3)-O(17)	24.2(5)	O(9)-V(1)-V(1)#2	126.8(3)
O(6)#1-V(3)-O(17)	168.2(5)	O(11)-V(1)-V(1)#2	126.3(3)
O(23')-V(3)-O(17)	93.4(7)	O(1W)#2-V(1)-V(1)#2	37.3(4)
O(5)#1-V(3)-O(17)	94.9(5)	O(1W')#2-V(1)-V(1)#2	37.1(4)
O(23)-V(3)-O(17)	78.7(7)	O(21)-V(1)-V(1)#2	101.7(4)
O(2)-V(3)-O(10)	158.3(4)	O(12)-V(1)-V(1)#2	102.6(9)
O(17')-V(3)-O(10)	52.1(5)	O(1W')-V(1)-Mo(1)	99.5(4)
O(6)#1-V(3)-O(10)	95.4(4)	O(1W)-V(1)-Mo(1)	99.0(4)
O(23')-V(3)-O(10)	56.7(6)	O(12')-V(1)-Mo(1)	95.5(8)

O(5)#1-V(3)-O(10)	93.5(4)	O(21')-V(1)-Mo(1)	97.7(4)
O(23)-V(3)-O(10)	72.4(7)	O(9)-V(1)-Mo(1)	39.0(2)
O(17)-V(3)-O(10)	72.8(5)	O(11)-V(1)-Mo(1)	38.8(2)
O(1W')-V(1)-O(1W)	54.3(6)	O(1W)#2-V(1)-Mo(1)	152.1(4)
O(1W')-V(1)-O(12')	120.8(10)	O(1W')#2-V(1)-Mo(1)	150.2(4)
O(1W)-V(1)-O(12')	165.3(10)	O(21)-V(1)-Mo(1)	110.1(4)
O(1W')-V(1)-O(21')	162.7(6)	O(12)-V(1)-Mo(1)	110.6(7)
O(1W)-V(1)-O(21')	120.7(6)	V(1)#2-V(1)-Mo(1)	134.44(10)
Compound **2**			
Cr(1)-O(10)	1.960(2)	Cr(1)-O(20)	1.970(2)
Cr(1)-O(6)	1.963(2)	Cr(1)-O(8)	1.972(2)
Cr(1)-O(23)	1.968(2)	Cr(1)-O(19)	1.972(2)
O(10)-Cr(1)-O(6)	94.28(8)	O(23)-Cr(1)-O(8)	83.56(8)
O(10)-Cr(1)-O(23)	95.63(8)	O(20)-Cr(1)-O(8)	97.19(8)
O(6)-Cr(1)-O(23)	96.90(9)	O(10)-Cr(1)-O(19)	85.31(8)
O(10)-Cr(1)-O(20)	83.62(8)	O(6)-Cr(1)-O(19)	179.14(9)
O(6)-Cr(1)-O(20)	82.93(8)	O(23)-Cr(1)-O(19)	83.90(8)
O(23)-Cr(1)-O(20)	179.21(9)	O(20)-Cr(1)-O(19)	96.27(8)
O(10)-Cr(1)-O(8)	178.24(9)	O(8)-Cr(1)-O(19)	96.14(8)
O(6)-Cr(1)-O(8)	84.29(8)		
Compound **3**			
Mn(1)-O(5)#1	2.1563(19)	Mn(1)-O(2)	2.2047(18)
Mn(1)-O(5)	2.1563(19)	Mn(1)-O(1)	2.2174(19)
Mn(1)-O(2)#1	2.2047(18)	Mn(1)-O(1)#1	2.2174(19)
O(5)#1-Mn(1)-O(5)	180	O(2)#1-Mn(1)-O(1)	83.57(7)
O(5)#1-Mn(1)-O(2)#1	97.80(7)	O(2)-Mn(1)-O(1)	96.43(7)
O(5)-Mn(1)-O(2)#1	82.20(7)	O(5)#1-Mn(1)-O(1)#1	96.05(7)
O(5)#1-Mn(1)-O(2)	82.20(7)	O(5)-Mn(1)-O(1)#1	83.95(7)
O(5)-Mn(1)-O(2)	97.80(7)	O(2)#1-Mn(1)-O(1)#1	96.43(7)
O(2)#1-Mn(1)-O(2)	180.000(1)	O(2)-Mn(1)-O(1)#1	83.57(7)
O(5)#1-Mn(1)-O(1)	83.95(7)	O(1)-Mn(1)-O(1)#1	180
O(5)-Mn(1)-O(1)	96.05(7)		
Compound **4**			
Co(1)-O(2)	2.109(3)	Co(2)-O(27)	2.032(3)
Co(1)-O(2)#4	2.109(3)	Co(2)-O(30)	2.071(3)
Co(1)-O(8)#4	2.161(3)	Co(2)-O(32)	2.083(3)
Co(1)-O(8)	2.161(3)	Co(2)-O(24)	2.147(4)
Co(1)-O(3)#4	2.182(3)	Co(2)-O(12)	2.151(3)
Co(1)-O(3)	2.182(3)	Co(2)-O(23)	2.259(3)
O(2)-Co(1)-O(2)#4	180.000(2)	O(27)-Co(2)-O(30)	170.49(14)
O(2)-Co(1)-O(8)#4	83.89(12)	O(27)-Co(2)-O(32)	97.54(14)
O(2)#4-Co(1)-O(8)#4	96.11(12)	O(30)-Co(2)-O(32)	87.20(13)
O(2)-Co(1)-O(8)	96.11(12)	O(27)-Co(2)-O(24)	89.39(15)
O(2)#4-Co(1)-O(8)	83.89(12)	O(30)-Co(2)-O(24)	85.12(15)

O(8)#4-Co(1)-O(8)	180.000(1)	O(32)-Co(2)-O(24)	170.93(14)
O(2)-Co(1)-O(3)#4	83.86(12)	O(27)-Co(2)-O(12)	96.36(13)
O(2)#4-Co(1)-O(3)#4	96.14(12)	O(30)-Co(2)-O(12)	92.19(13)
O(8)#4-Co(1)-O(3)#4	96.18(12)	O(32)-Co(2)-O(12)	85.75(13)
O(8)-Co(1)-O(3)#4	83.82(12)	O(24)-Co(2)-O(12)	99.33(14)
O(2)-Co(1)-O(3)	96.14(12)	O(27)-Co(2)-O(23)	84.90(13)
O(2)#4-Co(1)-O(3)	83.86(12)	O(30)-Co(2)-O(23)	87.46(13)
O(8)#4-Co(1)-O(3)	83.82(12)	O(32)-Co(2)-O(23)	83.54(13)
O(8)-Co(1)-O(3)	96.18(12)	O(24)-Co(2)-O(23)	91.31(14)
O(3)#4-Co(1)-O(3)	180.00(17)	O(12)-Co(2)-O(23)	169.29(13)
Compound **5**			
Ni(1)-O(1W)#1	1.997(14)	O(1)-Ni(3)#1	2.151(6)
Ni(1)-O(1W)#2	1.997(14)	O(1)-Ni(2)#1	2.158(6)
Ni(1)-O(1W)	1.997(14)	O(2)-Ni(2)#1	2.061(6)
Ni(1)-O(1W)#3	1.997(14)	O(3)-Ni(8)	1.993(12)
Ni(1)-O(2W)	2.051(16)	O(4)-Ni(2)#1	2.067(6)
Ni(1)-O(2W)#1	2.051(16)	O(13)-Ni(5)#2	2.106(6)
Ni(1)-O(2W)#2	2.051(16)	O(16)-Ni(7)#4	1.990(8)
Ni(1)-O(2W)#3	2.051(16)	O(16)-Ni(7)#5	1.990(8)
Ni(2)-O(21)	2.026(6)	O(20)-Ni(3)#1	2.040(6)
Ni(2)-O(8)	2.048(5)	O(22)-Ni(4)#1	2.132(6)
Ni(2)-O(6)	2.059(6)	O(23)-Ni(6)#6	2.019(6)
Ni(2)-O(2)	2.061(6)	O(23)-Ni(6)	2.019(6)
Ni(2)-O(4)	2.067(6)	O(29)-Ni(4)#1	2.068(6)
Ni(2)-O(1)	2.158(6)	O(30)-Ni(5)#2	2.078(6)
Ni(2)-Ni(2)#1	2.833(2)	O(31)-Ni(5)#1	2.109(6)
Ni(2)-Ni(3)	2.9862(15)	O(40)-Ni(3)#1	2.087(7)
Ni(3)-O(35)	2.012(7)	O(44)-Ni(5)#1	2.189(6)
Ni(3)-O(20)	2.040(6)	O(45)-Ni(7)	1.910(8)
Ni(3)-O(9)	2.046(6)	O(45)-Ni(7)#1	1.910(8)
Ni(3)-O(8)	2.049(6)	O(46)-Ni(8)	1.968(11)
Ni(3)-O(40)	2.087(7)	Ni(6)-O(10W)#7	1.794(19)
Ni(3)-O(1)	2.151(6)	Ni(6)-O(10W)	1.794(19)
Ni(3)-Ni(3)#1	2.823(2)	Ni(6)-O(23)#6	2.019(6)
Ni(4)-O(12)	2.024(6)	Ni(6)-O(11W)	2.03(3)
Ni(4)-O(30)	2.043(6)	Ni(6)-O(11W)#7	2.03(3)
Ni(4)-O(29)	2.068(6)	Ni(7)-O(16)#5	1.990(8)
Ni(4)-O(13)	2.075(6)	Ni(7)-O(5W)	2.09(2)
Ni(4)-O(33)	2.097(7)	Ni(7)-O(6W)	2.10(2)
Ni(4)-O(22)	2.132(6)	Ni(7)-O(4W)	2.131(19)
Ni(5)-O(14)	2.032(6)	Ni(7)-O(3W)	2.210(15)
Ni(5)-O(37)	2.042(8)	Ni(7)-Ni(7)#1	2.281(7)
Ni(5)-O(30)#2	2.078(6)	Ni(8)-O(8W)	2.03(3)
Ni(5)-O(13)#2	2.106(6)	Ni(8)-O(9W)#1	2.11(2)

Ni(5)-O(31)	2.109(6)	Ni(8)-O(9W)	2.11(2)
Ni(5)-O(44)	2.189(6)	O(3W)-Ni(7)#1	2.210(15)
O(1W)#1-Ni(1)-O(1W)#2	180.0(10)	O(8)-Ni(3)-Ni(2)	43.21(15)
O(1W)#1-Ni(1)-O(1W)	83.8(8)	O(40)-Ni(3)-Ni(2)	86.4(3)
O(1W)#2-Ni(1)-O(1W)	96.2(8)	O(1)-Ni(3)-Ni(2)	46.23(16)
O(1W)#1-Ni(1)-O(1W)#3	96.2(8)	Ni(3)#1-Ni(3)-Ni(2)	90.09(3)
O(1W)#2-Ni(1)-O(1W)#3	83.8(8)	O(12)-Ni(4)-O(30)	167.0(3)
O(1W)-Ni(1)-O(1W)#3	180.0(10)	O(12)-Ni(4)-O(29)	98.6(3)
O(1W)#1-Ni(1)-O(2W)	99.1(6)	O(30)-Ni(4)-O(29)	91.1(3)
O(1W)#2-Ni(1)-O(2W)	80.9(6)	O(12)-Ni(4)-O(13)	94.8(2)
O(1W)-Ni(1)-O(2W)	76.3(6)	O(30)-Ni(4)-O(13)	78.8(2)
O(1W)#3-Ni(1)-O(2W)	103.7(6)	O(29)-Ni(4)-O(13)	157.4(3)
O(1W)#1-Ni(1)-O(2W)#1	76.3(6)	O(12)-Ni(4)-O(33)	83.7(3)
O(1W)#2-Ni(1)-O(2W)#1	103.7(6)	O(30)-Ni(4)-O(33)	86.2(3)
O(1W)-Ni(1)-O(2W)#1	99.1(6)	O(29)-Ni(4)-O(33)	99.6(3)
O(1W)#3-Ni(1)-O(2W)#1	80.9(6)	O(13)-Ni(4)-O(33)	99.9(3)
O(2W)-Ni(1)-O(2W)#1	34.4(9)	O(12)-Ni(4)-O(22)	96.6(3)
O(1W)#1-Ni(1)-O(2W)#2	103.7(6)	O(30)-Ni(4)-O(22)	94.2(3)
O(1W)#2-Ni(1)-O(2W)#2	76.3(6)	O(29)-Ni(4)-O(22)	74.2(3)
O(1W)-Ni(1)-O(2W)#2	80.9(6)	O(13)-Ni(4)-O(22)	86.3(3)
O(1W)#3-Ni(1)-O(2W)#2	99.1(6)	O(33)-Ni(4)-O(22)	173.8(3)
O(2W)-Ni(1)-O(2W)#2	145.6(9)	O(14)-Ni(5)-O(37)	86.6(3)
O(2W)#1-Ni(1)-O(2W)#2	180.0(9)	O(14)-Ni(5)-O(30)#2	166.5(3)
O(1W)#1-Ni(1)-O(2W)#3	80.9(6)	O(37)-Ni(5)-O(30)#2	83.7(3)
O(1W)#2-Ni(1)-O(2W)#3	99.1(6)	O(14)-Ni(5)-O(13)#2	94.7(2)
O(1W)-Ni(1)-O(2W)#3	103.7(6)	O(37)-Ni(5)-O(13)#2	97.3(3)
O(1W)#3-Ni(1)-O(2W)#3	76.3(6)	O(30)#2-Ni(5)-O(13)#2	77.3(2)
O(2W)-Ni(1)-O(2W)#3	180.0(9)	O(14)-Ni(5)-O(31)	92.5(3)
O(2W)#1-Ni(1)-O(2W)#3	145.6(9)	O(37)-Ni(5)-O(31)	172.0(4)
O(2W)#2-Ni(1)-O(2W)#3	34.4(9)	O(30)#2-Ni(5)-O(31)	98.3(3)
O(21)-Ni(2)-O(8)	89.4(3)	O(13)#2-Ni(5)-O(31)	90.7(3)
O(21)-Ni(2)-O(6)	99.3(3)	O(14)-Ni(5)-O(44)	99.3(3)
O(8)-Ni(2)-O(6)	92.7(2)	O(37)-Ni(5)-O(44)	98.9(4)
O(21)-Ni(2)-O(2)	171.0(3)	O(30)#2-Ni(5)-O(44)	91.4(3)
O(8)-Ni(2)-O(2)	91.1(3)	O(13)#2-Ni(5)-O(44)	159.1(3)
O(6)-Ni(2)-O(2)	89.7(3)	O(31)-Ni(5)-O(44)	73.4(3)
O(21)-Ni(2)-O(4)	95.9(3)	O(10W)#7-Ni(6)-O(10W)	164.8(13)
O(8)-Ni(2)-O(4)	164.9(2)	O(10W)#7-Ni(6)-O(23)	95.7(7)
O(6)-Ni(2)-O(4)	100.4(3)	O(10W)-Ni(6)-O(23)	96.0(7)
O(2)-Ni(2)-O(4)	81.5(2)	O(10W)#7-Ni(6)-O(23)#6	96.0(7)
O(21)-Ni(2)-O(1)	93.0(3)	O(10W)-Ni(6)-O(23)#6	95.7(7)
O(8)-Ni(2)-O(1)	87.6(2)	O(23)-Ni(6)-O(23)#6	78.7(4)
O(6)-Ni(2)-O(1)	167.7(2)	O(10W)#7-Ni(6)-O(11W)	82.0(9)
O(2)-Ni(2)-O(1)	78.0(3)	O(10W)-Ni(6)-O(11W)	86.6(9)

O(4)-Ni(2)-O(1)	78.0(2)	O(23)-Ni(6)-O(11W)	99.5(7)
O(21)-Ni(2)-Ni(2)#1	126.1(2)	O(23)#6-Ni(6)-O(11W)	177.2(8)
O(8)-Ni(2)-Ni(2)#1	119.40(18)	O(10W)#7-Ni(6)-O(11W)#7	86.6(9)
O(6)-Ni(2)-Ni(2)#1	121.39(16)	O(10W)-Ni(6)-O(11W)#7	82.0(9)
O(2)-Ni(2)-Ni(2)#1	46.60(15)	O(23)-Ni(6)-O(11W)#7	177.2(8)
O(4)-Ni(2)-Ni(2)#1	46.74(15)	O(23)#6-Ni(6)-O(11W)#7	99.5(7)
O(1)-Ni(2)-Ni(2)#1	48.99(13)	O(11W)-Ni(6)-O(11W)#7	82.4(14)
O(21)-Ni(2)-Ni(3)	82.11(19)	O(45)-Ni(7)-O(16)#5	98.1(4)
O(8)-Ni(2)-Ni(3)	43.21(16)	O(45)-Ni(7)-O(5W)	172.4(6)
O(6)-Ni(2)-Ni(3)	135.85(16)	O(16)#5-Ni(7)-O(5W)	89.4(6)
O(2)-Ni(2)-Ni(3)	92.1(2)	O(45)-Ni(7)-O(6W)	86.7(6)
O(4)-Ni(2)-Ni(3)	123.51(19)	O(16)#5-Ni(7)-O(6W)	173.4(6)
O(1)-Ni(2)-Ni(3)	46.04(16)	O(5W)-Ni(7)-O(6W)	85.7(8)
Ni(2)#1-Ni(2)-Ni(3)	89.91(3)	O(45)-Ni(7)-O(4W)	92.6(6)
O(35)-Ni(3)-O(20)	94.4(3)	O(16)#5-Ni(7)-O(4W)	91.6(6)
O(35)-Ni(3)-O(9)	98.9(3)	O(5W)-Ni(7)-O(4W)	88.0(7)
O(20)-Ni(3)-O(9)	97.4(3)	O(6W)-Ni(7)-O(4W)	92.6(7)
O(35)-Ni(3)-O(8)	92.6(3)	O(45)-Ni(7)-O(3W)	88.1(5)
O(20)-Ni(3)-O(8)	165.1(2)	O(16)#5-Ni(7)-O(3W)	86.2(5)
O(9)-Ni(3)-O(8)	94.4(2)	O(5W)-Ni(7)-O(3W)	91.6(6)
O(35)-Ni(3)-O(40)	168.9(3)	O(6W)-Ni(7)-O(3W)	89.5(7)
O(20)-Ni(3)-O(40)	84.2(3)	O(4W)-Ni(7)-O(3W)	177.8(7)
O(9)-Ni(3)-O(40)	92.2(3)	O(45)-Ni(7)-Ni(7)#1	53.34(19)
O(8)-Ni(3)-O(40)	86.4(3)	O(16)#5-Ni(7)-Ni(7)#1	55.04(18)
O(35)-Ni(3)-O(1)	94.5(3)	O(5W)-Ni(7)-Ni(7)#1	132.3(6)
O(20)-Ni(3)-O(1)	78.6(3)	O(6W)-Ni(7)-Ni(7)#1	126.3(6)
O(9)-Ni(3)-O(1)	166.3(2)	O(4W)-Ni(7)-Ni(7)#1	120.0(5)
O(8)-Ni(3)-O(1)	87.8(2)	O(3W)-Ni(7)-Ni(7)#1	58.9(2)
O(40)-Ni(3)-O(1)	74.4(3)	O(46)-Ni(8)-O(3)	104.2(5)
O(35)-Ni(3)-Ni(3)#1	125.1(2)	O(46)-Ni(8)-O(8W)	171.5(10)
O(20)-Ni(3)-Ni(3)#1	46.21(16)	O(3)-Ni(8)-O(8W)	84.3(10)
O(9)-Ni(3)-Ni(3)#1	119.29(18)	O(46)-Ni(8)-O(9W)#1	85.5(7)
O(8)-Ni(3)-Ni(3)#1	119.55(17)	O(3)-Ni(8)-O(9W)#1	93.9(7)
O(40)-Ni(3)-Ni(3)#1	47.43(17)	O(8W)-Ni(8)-O(9W)#1	94.0(7)
O(1)-Ni(3)-Ni(3)#1	48.99(13)	O(46)-Ni(8)-O(9W)	85.5(7)
O(35)-Ni(3)-Ni(2)	85.32(19)	O(3)-Ni(8)-O(9W)	93.9(7)
O(20)-Ni(3)-Ni(2)	124.4(2)	O(8W)-Ni(8)-O(9W)	94.0(7)
O(9)-Ni(3)-Ni(2)	137.63(18)	O(9W)#1-Ni(8)-O(9W)	169.4(13)
Compound **6**			
Cu(1)-N(2)	2.002(3)	Cu(1)-N(1)	2.012(3)
Cu(1)-N(3)	2.008(3)	Cu(1)-O(6)	2.422(3)
Cu(1)-N(4)	2.010(3)		
N(2)-Cu(1)-N(3)	95.16(14)	N(4)-Cu(1)-N(1)	95.80(13)
N(2)-Cu(1)-N(4)	175.80(14)	N(2)-Cu(1)-O(6)	100.20(12)

N(3)-Cu(1)-N(4)	84.66(14)	N(3)-Cu(1)-O(6)	89.54(12)
N(2)-Cu(1)-N(1)	84.25(14)	N(4)-Cu(1)-O(6)	83.99(13)
N(3)-Cu(1)-N(1)	178.11(15)	N(1)-Cu(1)-O(6)	92.33(13)
Compound **7**			
Cu(1)-N(1)	2.005(5)	Cu(2)-N(4)#2	2.031(6)
Cu(1)-N(1)#1	2.005(5)	Cu(2)-N(4)	2.031(6)
Cu(1)-N(2)	2.012(5)	Cu(2)-N(3)	2.044(6)
Cu(1)-N(2)#1	2.012(5)	Cu(2)-N(3)#2	2.044(6)
Cu(1)-O(2)	2.502(3)	Cu(2)-O(1)	2.510(4)
N(1)-Cu(1)-N(1)#1	180	N(4)#2-Cu(2)-N(4)	180.000(1)
N(1)-Cu(1)-N(2)	84.98(18)	N(4)#2-Cu(2)-N(3)	97.9(3)
N(1)#1-Cu(1)-N(2)	95.02(19)	N(4)-Cu(2)-N(3)	82.1(3)
N(1)-Cu(1)-N(2)#1	95.02(19)	N(4)#2-Cu(2)-N(3)#2	82.1(3)
N(1)#1-Cu(1)-N(2)#1	84.98(18)	N(4)-Cu(2)-N(3)#2	97.9(3)
N(2)-Cu(1)-N(2)#1	180	N(3)-Cu(2)-N(3)#2	180.000(1)
N(1)-Cu(1)-O(2)	96.80(15)	N(4)#2-Cu(2)-O(1)	95.3(2)
N(1)#1-Cu(1)-O(2)	83.20(15)	N(4)-Cu(2)-O(1)	84.7(2)
N(2)-Cu(1)-O(2)	90.76(14)	N(3)-Cu(2)-O(1)	97.11(18)
N(2)#1-Cu(1)-O(2)	89.24(14)	N(3)#2-Cu(2)-O(1)	82.89(18)
Compound **8**			
Zn(1)-O(55)	1.892(5)	Zn(2)-O(52)	1.879(5)
Zn(1)-O(28)	1.948(5)	Zn(2)-O(63)	1.946(5)
Zn(1)-O(30)	1.949(5)	Zn(2)-O(58)	1.954(5)
Zn(1)-O(23)	1.969(5)	Zn(2)-O(27)	1.961(5)
O(55)-Zn(1)-O(28)	128.4(2)	O(52)-Zn(2)-O(63)	109.6(2)
O(55)-Zn(1)-O(30)	107.4(2)	O(52)-Zn(2)-O(58)	101.2(2)
O(28)-Zn(1)-O(30)	98.9(2)	O(63)-Zn(2)-O(58)	116.0(2)
O(55)-Zn(1)-O(23)	103.7(2)	O(52)-Zn(2)-O(27)	124.1(2)
O(28)-Zn(1)-O(23)	102.0(2)	O(63)-Zn(2)-O(27)	105.6(2)
O(30)-Zn(1)-O(23)	117.4(2)	O(58)-Zn(2)-O(27)	100.5(2)

Symmetry code: for **1**: #1 -x+1,-y+1,-z+1; #2 -x,-y+1,-z+1; for **3**: #1 -x, -y+1, -z+1; for **4**: #4 -x+1, -y+1, -z+2; for **5**: #1 x, y, -z; #2 -x+1/2, -y+1/2, z; #3 -x+1/2, -y+1/2, -z; #4 -x, -y, z; #5 -x, -y, -z; #6 -x+1, -y, -z; #7 -x+1, -y, z; for **7**: #1 -x, -y+2, -z; #2 -x, -y+1, -z+1.

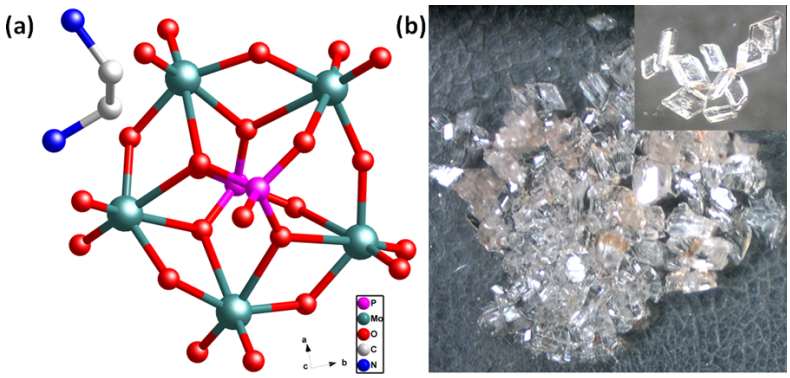


Figure S1. Ball-stick view of the asymmetric unit (a) of $[(HPO_4)_2Mo_5O_{15}]\cdot 2(en)$ [1] (H atoms are omitted for clarity) with its crystal photographs (b).

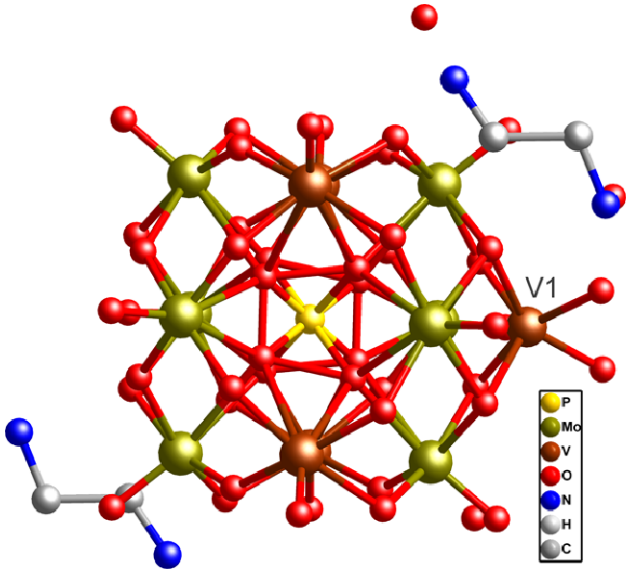


Figure S2. Ball-stick view of the asymmetric unit of **1**. Hydrogen atoms are omitted for clarity.

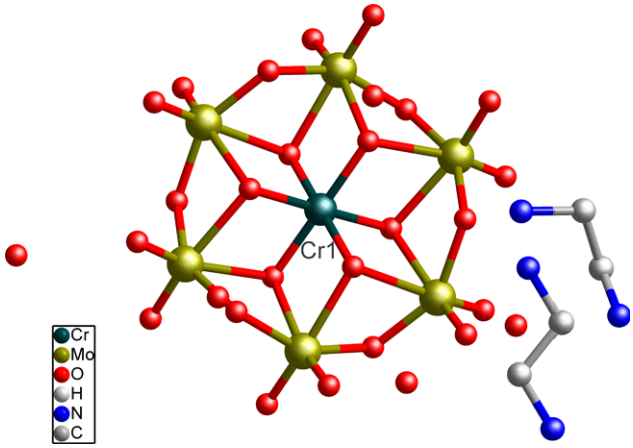


Figure S3. Ball-stick view of the asymmetric unit of **2**. Hydrogen atoms are omitted for clarity.

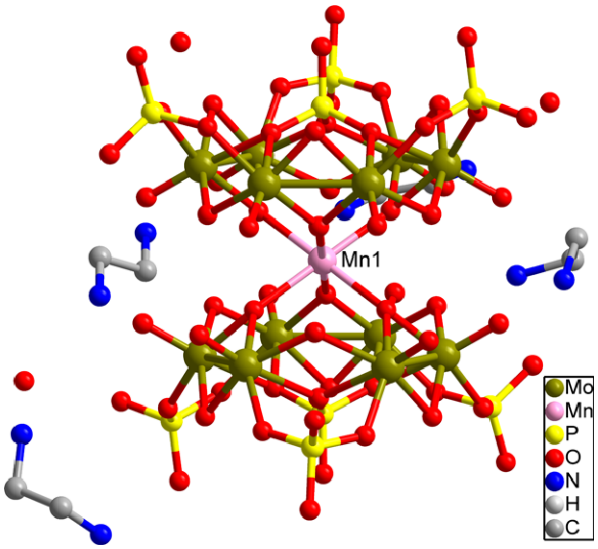


Figure S4. Ball-stick view of the asymmetric unit of **3**. Hydrogen atoms are omitted for clarity.

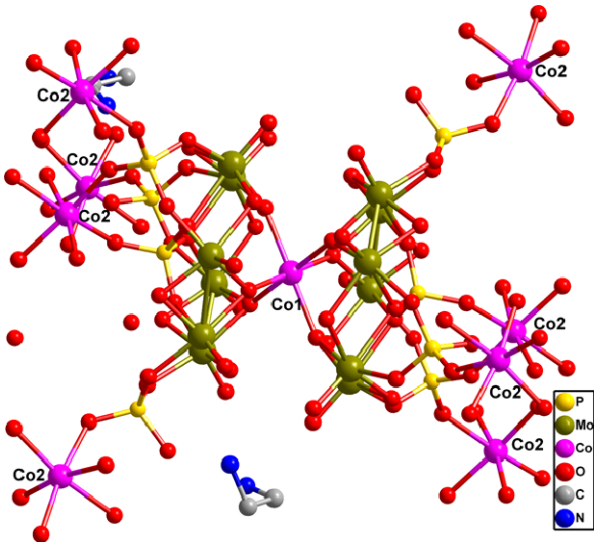


Figure S5. Ball-stick view of the asymmetric unit of **4**. Hydrogen atoms are omitted for clarity.

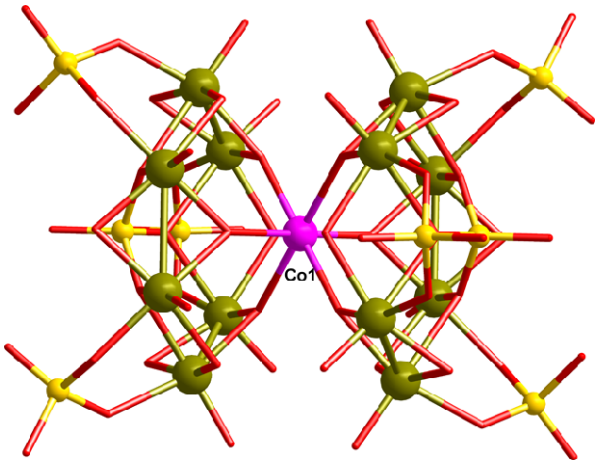


Figure S6. Structure of sandwich-type $Co[P_4Mo_6]_2$ cluster in **4**.

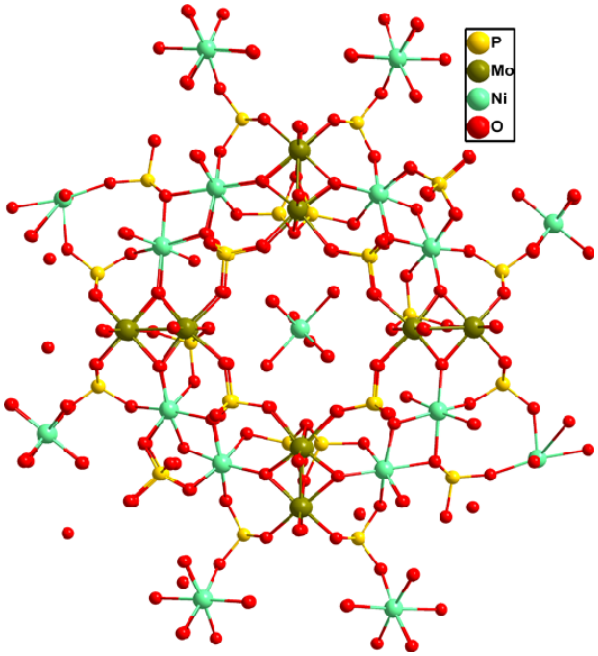


Figure S7. Ball-stick view of the asymmetric unit of **5**. Hydrogen atoms are omitted for clarity.

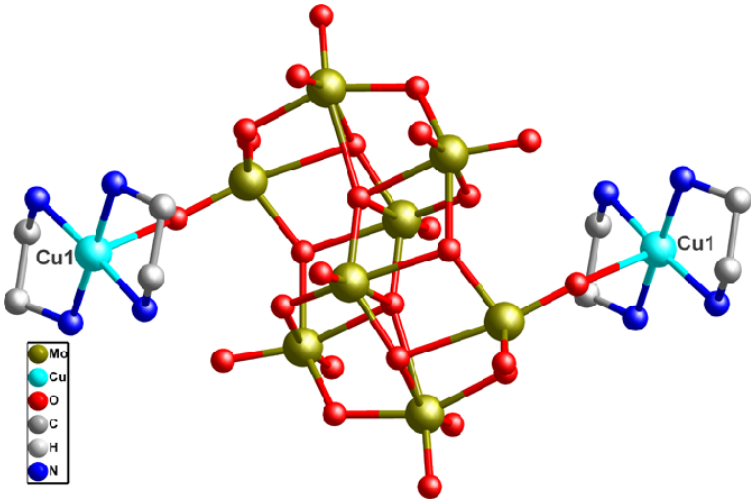


Figure S8. Ball-stick view of the asymmetric unit of **6**. Hdrogen atoms are omitted for clarity.

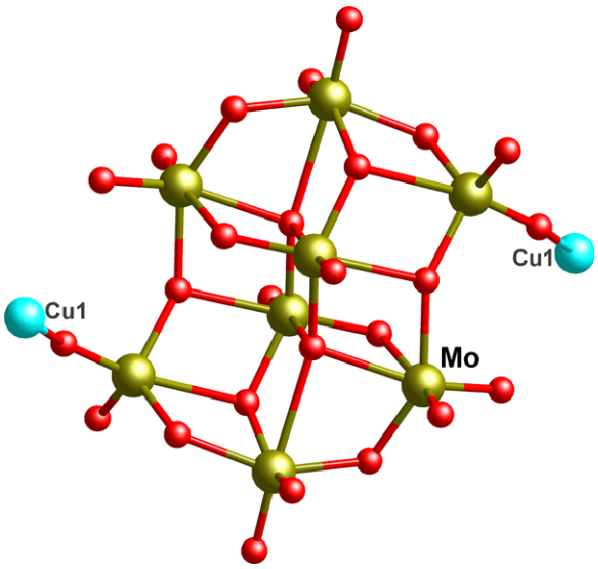


Figure S9. Structure of Mo_8 cluster in **6**.

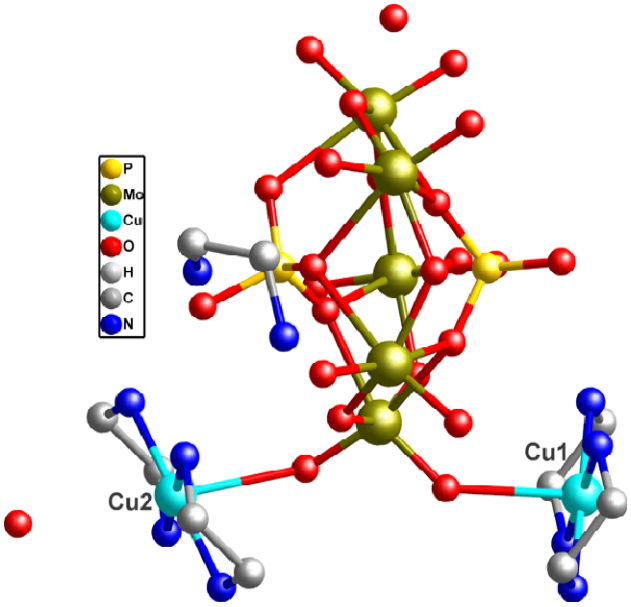


Figure S10. Ball-stick view of the asymmetric unit of **7**. Hydrogen atoms are omitted for clarity.

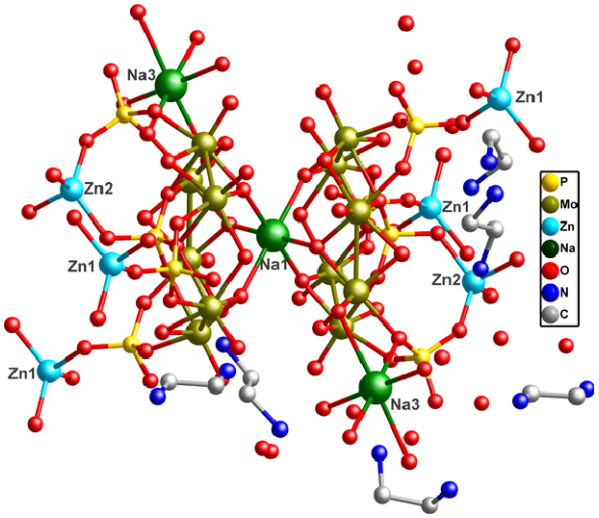


Figure S11. Ball-stick view of the asymmetric unit of **8**. Hydrogen atoms are omitted for clarity.

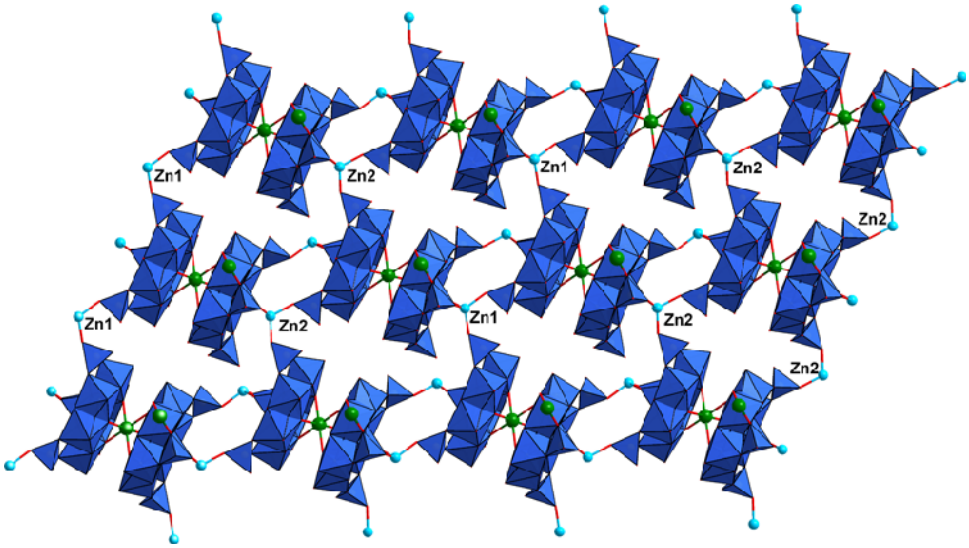


Figure S12. View of the 2D layered network in **8**.

unit species / SMCs	Mo-Mo Bond	MoO_5	MoO_6	corner-sharing	edge-sharing
Mo_2V	0	0	2	3	2
Mo_4	2	0	4	5	2
Mo_5	0	0	5	9	4
Mo_6^1	0	0	6	12	6
Mo_6^2	3	0	6	12	6
Mo_8	0	2	6	12	13

Figure S13. Detailed comparison of unit species found in different SMCs.

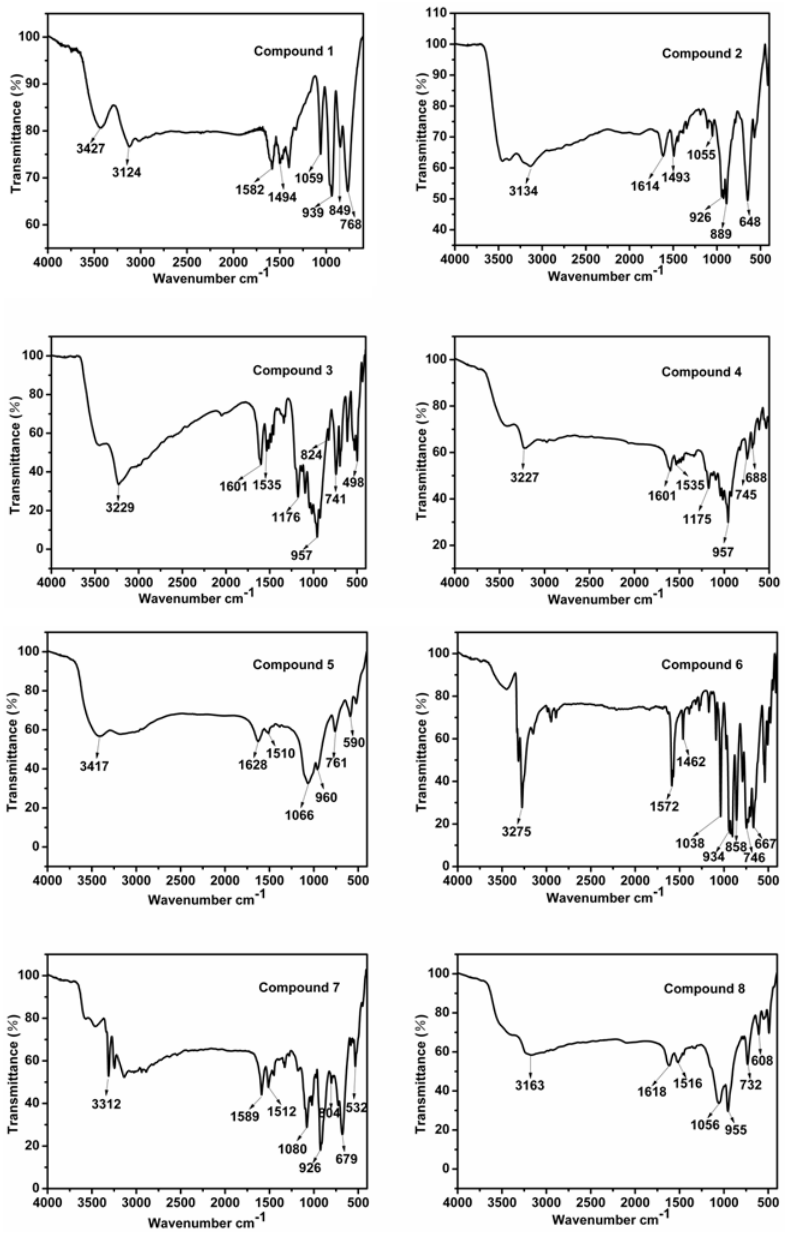


Figure S14. IR spectra of compounds **1**-**8**. In the spectra of 1-8, the characteristic bands at 1059, 939, 849 and 768 cm^{-1} for **1**, 1055, 926, 889 and 648 cm^{-1} for **2**, 957, 824 and 741 cm-^{1} for **3**, 957, 745 and 688 cm^{-1} for **4**, 1066, 960 and 761 cm^{-1} for **5**, 934, 858, 746 and 667 cm^{-1} for **6**, 1080, 926, 804 and 679 cm^{-1} for **7**, 1056, 955 and 732 cm^{-1} for **8** are attributed to the ν(Mo-Ot) and ν(Mo-O-Mo) vibrations, respectively.[1-3] The bands at 1582 and 1494 cm^{-1} for **1**, 1614 and 1493 cm^{-1} for **2**, 1601 and 1535 cm-^{1} for **3**, 1601 and 1535 cm^{-1} for **4**, 1572 and 1462 cm^{-1} for **6**, 1589 and 1512 cm^{-1} for **7**, 1618 and 1516 cm^{-1} for **8** are characteristic for the en molecule.[4-5]

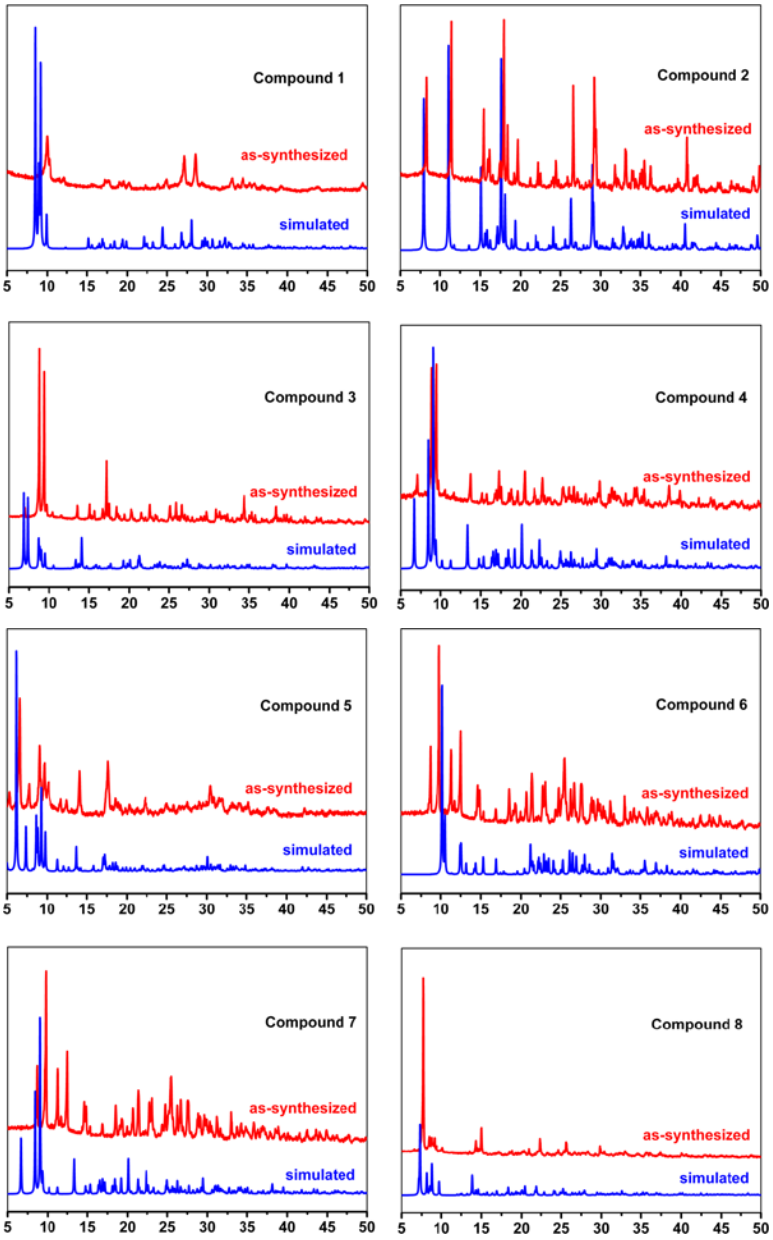


Figure S15. The simulative (blue line) and experimental (red line) powder X-ray diffraction patterns for compounds **1**-**8**. The diffraction peaks of both simulated and experimental patterns mach well in positions, thus indicating that the phase purities of the compounds **1**-**8** are well.

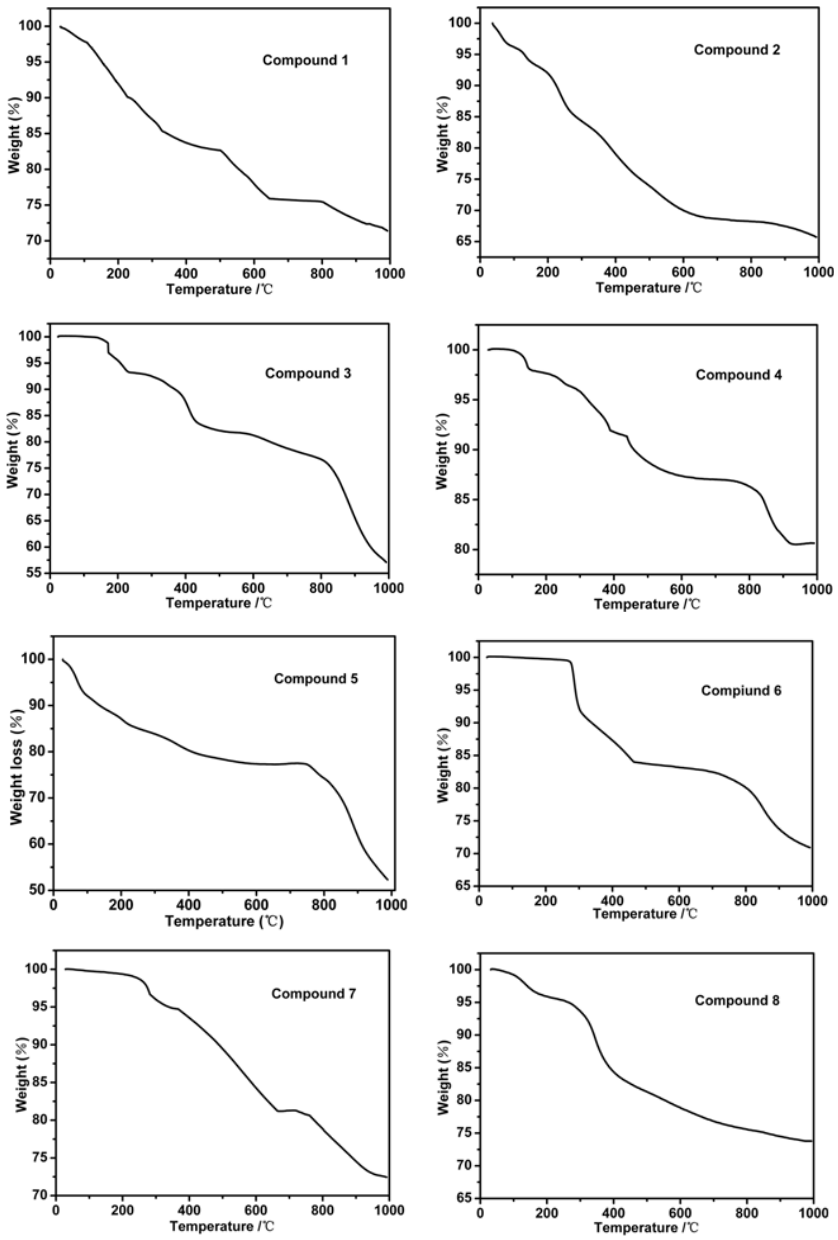
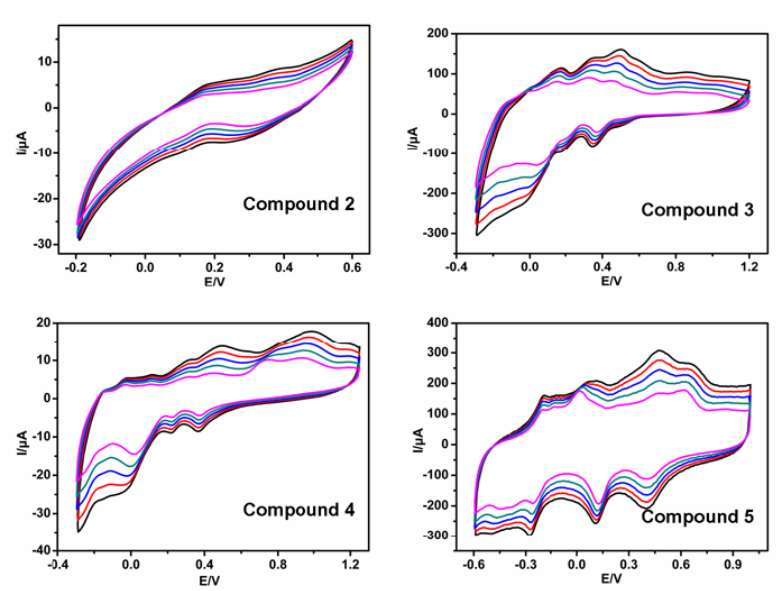


Figure S16. The TG spectras of compounds **1**-**8**. TG analyses curve of compound **2** has three weight loss processes. The one (7.05%) from room temperature to 174 °C is attributed to the loss of five free water molecules (calcd 7.49%). The second weight loss (7.96%) from 180 to 300 °C corresponds to the removal of en molecules (calcd, 7.74%). The remaining structure begins to decompose at 325 °C. The curve of compound **3** reveals an initial weight loss (3.06%) in the 25-170 °C range and a second weight loss (13.52%) in the 170-430 °C. These two losses correspond to the release of water molecules (calcd. 3.61%) and the en molecules (calcd. 14.79%), respectively. Compound **4** lost its water molecules (exp. 1.61%; calcd. 1.56%) from 25 to 150 °C, and the en molecules (exp. 6.34%; calcd. 6.26%) from 150 to 400 °C.

For compound **5**, there are two distinct weight loss procedures in the range of 25–220 °C, corresponding to the loss of thirty-three lattice water and twenty-two coordinated water molecules per formula unit (exp. 16.68%; calcd. 16.75%). And then the remaining structure began to decompose. The TGA curve of compound **6** shows a one-step weight loss process from 262 to 460 °C, corresponding to the loss of free water molecules (exp. 16.03%; calcd. 15.99%). Then the framework begins to decompose. In the TG curve of compound **7** there are three continuous weight loss steps. The first weight loss of 3.33% in the temperature range of 25–280 °C corresponds to the release of two lattice water molecules, in accordance with the calculated value of 3.02%. The second weight loss steps of 15.30% in the temperature range of 280–660 °C correspond to the loss of three organic en ligands, which are in accordance with the calculated value of 15.59%. The remaining structure is broken down above 730 °C, and decomposition does not end until heating to 900 °C. For compound **8**, there are two distinct weight loss procedures in the range of 25–1000 °C, corresponding to the loss of eleven lattice water and two coordinated water molecules per formula unit (exp. 6.82%; calcd. 7.50%), and five en molecules (exp. 9.10%; calcd. 9.93%).



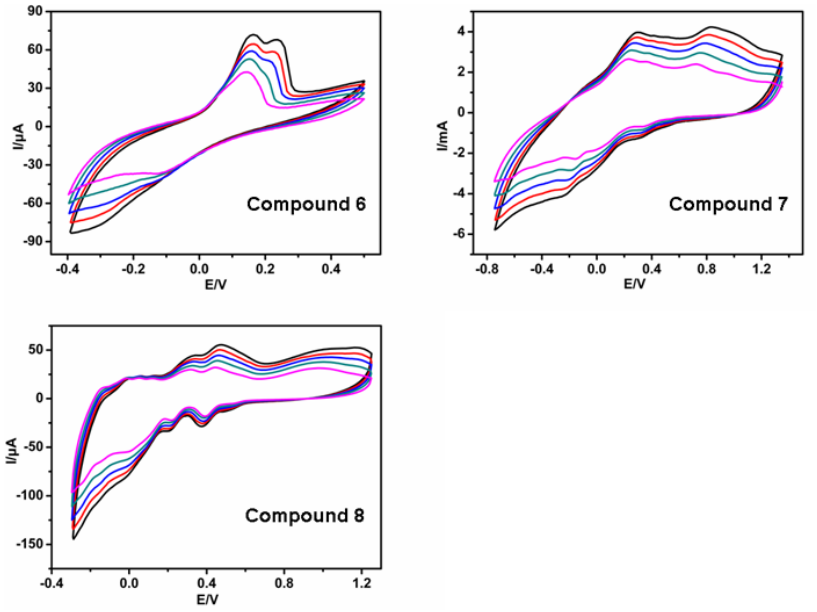


Figure S17. Cyclic voltammograms of the eight CPEs in 1 M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 100, 150, 200, 250, 300 mVs^{-1}). There exist three reversible redox peaks I-I', II-II' and III-III' with the half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at 425 (I-I'), 262 (II-II'), and 68 (III-III') mV for **3**, 428 (I-I'), 264 (II-II'), and 38 (III-III') mV for **4**, and 445 (I-I'), 100 (II-II'), and 36(III-III') mV for **5**, 368 (I-I'), 117 (II-II'), and -152 (III-III') mV for **7**, and 424 (I-I'), 269 (II-II'), and 22 (III-III') mV for **8**, respectively. The redox peaks I-I', II-II' and III-III' ascribed to three consecutive two-electron processes of Mo. The potential shifts of the three reversible redox peaks in compounds **3**-**5** and **7**-**8** comparing reported may relate to the effect of polyanions and the different linkers.[6-8] For compound **2**, we recorded the electrochemical signal. Such a phenomenon has never been observed and discussed in reported in Ref.[9-10] For compound **6**, it can be seen that in the range +300 to -300 mV, two redox peaks appear which can be ascribed to the Mo electronic transition.[11]

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