Step-wise Synthesis of Inorganic-organic Hybrid Based on γ-Octamolybdate-based Tectons

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Table S1. Selected bond lengths [Å] and angles [deg] for **1**.

Mo(1)-O(1)	1.698(4)	Mo(3)-O(5)	1.702(4)
Mo(1)-O(3)	1.754(4)	Mo(3)-O(6)	1.715(4)
Mo(1)-O(4)	1.890(4)	Mo(3)-O(7)	1.880(4)
Mo(1)-O(11)#1	1.938(4)	Mo(3)-O(2)	2.121(4)
Mo(1)-O(2)	2.146(4)	Mo(3)-N(1)	2.211(5)
Mo(1)-O(11)	2.381(3)	Mo(3)-O(4)	2.244(4)
Mo(2)-O(9)	1.699(4)	Mo(4)-O(13)	1.693(4)
Mo(2)-O(8)	1.707(4)	Mo(4)-O(12)	1.719(4)
Mo(2)-O(2)#1	1.923(4)	Mo(4)-O(10)	1.917(4)
Mo(2)-O(10)	1.939(4)	Mo(4)-O(7)	1.965(4)
Mo(2)-O(11)	2.280(4)	Mo(4)-O(11)	2.261(4)
Mo(2)-O(3)	2.333(4)	Mo(4)-O(4)	2.292(4)
O(1)-Mo(1)-O(3)	103.15(18)	O(5)-Mo(3)-O(6)	106.5(2)
O(1)-Mo(1)-O(4)	104.50(18)	O(5)-Mo(3)-O(7)	103.71(19)
O(3)-Mo(1)-O(4)	100.25(16)	O(6)-Mo(3)-O(7)	101.66(19)
O(1)-Mo(1)-O(11)#1	100.64(17)	O(5)-Mo(3)-O(2)	91.46(18)
O(3)-Mo(1)-O(11)#1	98.85(16)	O(6)-Mo(3)-O(2)	155.32(19)
O(4)-Mo(1)-O(11)#1	143.83(16)	O(7)-Mo(3)-O(2)	89.98(16)
O(1)-Mo(1)-O(2)	98.25(17)	O(5)-Mo(3)-N(1)	91.4(2)
O(3)-Mo(1)-O(2)	158.45(15)	O(6)-Mo(3)-N(1)	86.02(19)
O(4)-Mo(1)-O(2)	76.49(15)	O(7)-Mo(3)-N(1)	160.05(18)
O(11)#1-Mo(1)-O(2)	74.50(14)	O(2)-Mo(3)-N(1)	76.54(16)
O(1)-Mo(1)-O(11)	177.72(16)	O(5)-Mo(3)-O(4)	161.48(18)
O(3)-Mo(1)-O(11)	78.23(14)	O(6)-Mo(3)-O(4)	91.32(18)
O(4)-Mo(1)-O(11)	76.92(14)	O(7)-Mo(3)-O(4)	76.81(15)
O(11)#1-Mo(1)-O(11)	77.30(14)	O(2)-Mo(3)-O(4)	70.03(14)
O(2)-Mo(1)-O(11)	80.30(13)	N(1)-Mo(3)-O(4)	84.70(16)
O(9)-Mo(2)-O(8)	104.3(2)	O(13)-Mo(4)-O(12)	104.23(19)
O(9)-Mo(2)-O(2)#1	98.60(18)	O(13)-Mo(4)-O(10)	98.07(19)

O(8)-Mo(2)-O(2)#1	104.47(18)	O(12)-Mo(4)-O(10)	101.32(18)
O(9)-Mo(2)-O(10)	96.98(17)	O(13)-Mo(4)-O(7)	99.74(19)
O(8)-Mo(2)-O(10)	103.50(19)	O(12)-Mo(4)-O(7)	93.64(18)
O(2)#1-Mo(2)-O(10)	143.34(16)	O(10)-Mo(4)-O(7)	153.11(16)
O(9)-Mo(2)-O(11)	99.42(17)	O(13)-Mo(4)-O(11)	163.45(17)
O(8)-Mo(2)-O(11)	156.32(17)	O(12)-Mo(4)-O(11)	91.70(16)
O(2)#1-Mo(2)-O(11)	71.67(14)	O(10)-Mo(4)-O(11)	73.98(14)
O(10)-Mo(2)-O(11)	73.16(14)	O(7)-Mo(4)-O(11)	83.44(15)
O(9)-Mo(2)-O(3)	169.56(17)	O(13)-Mo(4)-O(4)	92.89(17)
O(8)-Mo(2)-O(3)	86.11(17)	O(12)-Mo(4)-O(4)	160.53(17)
O(2)#1-Mo(2)-O(3)	79.66(14)	O(10)-Mo(4)-O(4)	85.07(14)
O(10)-Mo(2)-O(3)	79.08(14)	O(7)-Mo(4)-O(4)	74.09(14)
O(11)-Mo(2)-O(3)	70.22(13)	O(11)-Mo(4)-O(4)	72.23(13)

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

Table S2. Selected bond lengths [Å] and angles [deg] for **2**.

Zn(1)-N(8)#1	2.008(5)	Mo(2)-O(3)	2.201(4)
Zn(1)-N(3)	2.028(5)	Mo(2)-O(2)	2.335(4)
Zn(1)-N(1)	2.029(5)	Mo(3)-O(12)	1.685(4)
Zn(1)-O(5)#2	2.143(4)	Mo(3)-O(13)	1.738(4)
Zn(1)-O(13)	2.222(4)	Mo(3)-O(11)	1.921(4)
Mo(1)-O(1)	1.692(4)	Mo(3)-O(4)#3	1.942(4)
Mo(1)-O(2)	1.751(4)	Mo(3)-O(3)#3	2.189(4)
Mo(1)-O(10)#3	1.874(4)	Mo(3)-O(10)	2.374(4)
Mo(1)-O(3)#3	1.950(4)	Mo(4)-O(8)	1.693(5)
Mo(1)-O(7)#3	2.202(4)	Mo(4)-O(9)	1.717(5)
Mo(1)-O(3)	2.444(4)	Mo(4)-O(11)	1.912(4)
Mo(2)-O(6)	1.697(4)	Mo(4)-O(7)	2.120(4)
Mo(2)-O(5)	1.738(4)	Mo(4)-O(10)	2.197(4)
Mo(2)-O(4)	1.919(4)	Mo(4)-N(5)	2.214(5)
Mo(2)-O(7)	1.932(4)		
N(8)#1-Zn(1)-N(3)	119.5(2)	O(6)-Mo(2)-O(2)	174.91(19)
N(8)#1-Zn(1)-N(1)	126.4(2)	O(5)-Mo(2)-O(2)	81.59(17)
N(3)-Zn(1)-N(1)	113.9(2)	O(4)-Mo(2)-O(2)	83.01(16)
N(8)#1-Zn(1)-O(5)#2	91.34(19)	O(7)-Mo(2)-O(2)	82.38(15)
N(3)-Zn(1)-O(5)#2	90.35(19)	O(3)-Mo(2)-O(2)	71.72(14)
N(1)-Zn(1)-O(5)#2	91.9(2)	O(12)-Mo(3)-O(13)	103.2(2)
N(8)#1-Zn(1)-O(13)	89.02(19)	O(12)-Mo(3)-O(11)	100.4(2)
N(3)-Zn(1)-O(13)	85.59(19)	O(13)-Mo(3)-O(11)	98.69(19)
N(1)-Zn(1)-O(13)	91.48(19)	O(12)-Mo(3)-O(4)#3	101.8(2)
O(5)#2-Zn(1)-O(13)	175.52(16)	O(13)-Mo(3)-O(4)#3	95.36(19)
O(1)-Mo(1)-O(2)	103.76(19)	O(11)-Mo(3)-O(4)#3	150.20(17)
O(1)-Mo(1)-O(10)#3	105.76(18)	O(12)-Mo(3)-O(3)#3	90.22(18)

O(2)-Mo(1)-O(10)#3	101.59(18)	O(13)-Mo(3)-O(3)#3	163.93(18)
O(1)-Mo(1)-O(3)#3	103.43(19)	O(11)-Mo(3)-O(3)#3	87.39(16)
O(2)-Mo(1)-O(3)#3	98.25(18)	O(4)#3-Mo(3)-O(3)#3	72.93(16)
O(10)#3-Mo(1)-O(3)#	139.33(17)	O(12)-Mo(3)-O(10)	160.57(18)
O(1)-Mo(1)-O(7)#3	96.61(17)	O(13)-Mo(3)-O(10)	95.84(17)
O(2)-Mo(1)-O(7)#3	159.18(16)	O(11)-Mo(3)-O(10)	72.53(15)
O(10)#3-Mo(1)-O(7)#	76.57(16)	O(4)#3-Mo(3)-O(10)	80.02(15)
O(3)#3-Mo(1)-O(7)#3	72.47(15)	O(3)#3-Mo(3)-O(10)	71.68(14)
O(1)-Mo(1)-O(3)	178.68(18)	O(8)-Mo(4)-O(9)	104.7(2)
O(2)-Mo(1)-O(3)	76.72(15)	O(8)-Mo(4)-O(11)	100.6(2)
O(10)#3-Mo(1)-O(3)	75.29(15)	O(9)-Mo(4)-O(11)	102.2(2)
O(3)#3-Mo(1)-O(3)	75.27(16)	O(8)-Mo(4)-O(7)	94.3(2)
O(7)#3-Mo(1)-O(3)	82.82(13)	O(9)-Mo(4)-O(7)	155.75(19)
O(6)-Mo(2)-O(5)	103.5(2)	O(11)-Mo(4)-O(7)	88.55(16)
O(6)-Mo(2)-O(4)	96.46(19)	O(8)-Mo(4)-O(10)	166.1(2)
O(5)-Mo(2)-O(4)	102.3(2)	O(9)-Mo(4)-O(10)	89.11(19)
O(6)-Mo(2)-O(7)	95.40(19)	O(11)-Mo(4)-O(10)	76.98(16)
O(5)-Mo(2)-O(7)	106.14(19)	O(7)-Mo(4)-O(10)	72.02(15)
O(4)-Mo(2)-O(7)	145.60(17)	O(8)-Mo(4)-N(5)	96.2(2)
O(6)-Mo(2)-O(3)	103.27(19)	O(9)-Mo(4)-N(5)	83.8(2)
O(5)-Mo(2)-O(3)	153.23(17)	O(11)-Mo(4)-N(5)	159.97(18)
O(4)-Mo(2)-O(3)	73.07(16)	O(7)-Mo(4)-N(5)	79.35(17)
O(7)-Mo(2)-O(3)	72.81(16)	O(10)-Mo(4)-N(5)	84.09(17)

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

Table S3. Selected bond lengths [Å] and angles [deg] for **3**.

Ni(1)-N(1)	2.065(5)	Mo(2)-O(3)	2.237(4)
Ni(1)-O(4)#2	2.101(4)	Mo(3)-O(8)	1.702(5)
Ni(1)-N(5)	2.122(5)	Mo(3)-O(7)	1.717(4)
Mo(1)-O(1)	1.689(4)	Mo(3)-O(9)	1.924(4)
Mo(1)-O(2)	1.743(4)	Mo(3)-O(6)	1.938(4)
Mo(1)-O(3)	1.892(4)	Mo(3)-O(10)	2.255(4)
Mo(1)-O(10)	1.949(4)	Mo(3)-O(2)#2	2.346(4)
Mo(1)-O(6)	2.172(4)	Mo(4)-O(11)	1.699(5)
Mo(1)-O(10)#2	2.421(4)	Mo(4)-O(13)	1.716(5)
Mo(2)-O(5)	1.689(4)	Mo(4)-O(9)	1.918(4)
Mo(2)-O(4)	1.741(4)	Mo(4)-O(12)	2.023(4)
Mo(2)-O(12)#2	1.882(4)	Mo(4)-O(10)	2.246(4)
Mo(2)-O(6)	2.071(4)	Mo(4)-O(3)#2	2.261(4)
Mo(2)-N(7)	2.228(5)		
N(1)#1-Ni(1)-O(4)#2	91.43(18)	O(6)-Mo(2)-N(7)	78.47(18)
N(1)-Ni(1)-O(4)#2	88.57(19)	O(5)-Mo(2)-O(3)	162.8(2)
N(1)#1-Ni(1)-O(4)#3	88.57(18)	O(4)-Mo(2)-O(3)	93.01(18)

N(1)-Ni(1)-O(4)#3	91.43(18)	O(12)#2-Mo(2)-O(3)	76.36(17)
N(1)#1-Ni(1)-N(5)	90.6(2)	O(6)-Mo(2)-O(3)	70.55(16)
N(1)-Ni(1)-N(5)	89.4(2)	N(7)-Mo(2)-O(3)	84.38(17)
O(4)#2-Ni(1)-N(5)	89.41(18)	O(8)-Mo(3)-O(7)	104.2(2)
O(4)#3-Ni(1)-N(5)	90.59(18)	O(8)-Mo(3)-O(9)	96.6(2)
N(1)#1-Ni(1)-N(5)#1	89.4(2)	O(7)-Mo(3)-O(9)	103.0(2)
N(1)-Ni(1)-N(5)#1	90.6(2)	O(8)-Mo(3)-O(6)	98.0(2)
O(4)#2-Ni(1)-N(5)#1	90.59(18)	O(7)-Mo(3)-O(6)	103.6(2)
O(4)#3-Ni(1)-N(5)#1	89.41(19)	O(9)-Mo(3)-O(6)	145.36(18)
O(1)-Mo(1)-O(2)	104.6(2)	O(8)-Mo(3)-O(10)	99.57(19)
O(1)-Mo(1)-O(3)	103.9(2)	O(7)-Mo(3)-O(10)	156.22(19)
O(2)-Mo(1)-O(3)	101.74(18)	O(9)-Mo(3)-O(10)	74.23(16)
O(1)-Mo(1)-O(10)	102.7(2)	O(6)-Mo(3)-O(10)	72.44(16)
O(2)-Mo(1)-O(10)	98.08(18)	O(8)-Mo(3)-O(2)#2	170.09(18)
O(3)-Mo(1)-O(10)	141.40(18)	O(7)-Mo(3)-O(2)#2	85.57(18)
O(1)-Mo(1)-O(6)	96.89(19)	O(9)-Mo(3)-O(2)#2	79.36(17)
O(2)-Mo(1)-O(6)	158.33(18)	O(6)-Mo(3)-O(2)#2	80.99(16)
O(3)-Mo(1)-O(6)	75.27(16)	O(10)-Mo(3)-O(2)#2	70.67(14)
O(10)-Mo(1)-O(6)	74.15(16)	O(11)-Mo(4)-O(13)	105.6(2)
O(1)-Mo(1)-O(10)#2	177.62(19)	O(11)-Mo(4)-O(9)	102.2(2)
O(2)-Mo(1)-O(10)#2	77.57(17)	O(13)-Mo(4)-O(9)	96.6(2)
O(3)-Mo(1)-O(10)#2	76.47(16)	O(11)-Mo(4)-O(12)	93.4(2)
O(10)-Mo(1)-O(10)#2	75.94(16)	O(13)-Mo(4)-O(12)	98.34(19)
O(6)-Mo(1)-O(10)#2	80.90(15)	O(9)-Mo(4)-O(12)	154.66(18)
O(5)-Mo(2)-O(4)	103.9(2)	O(11)-Mo(4)-O(10)	91.29(19)
O(5)-Mo(2)-O(12)#2	102.9(2)	O(13)-Mo(4)-O(10)	162.4(2)
O(4)-Mo(2)-O(12)#2	99.78(19)	O(9)-Mo(4)-O(10)	74.56(16)
O(5)-Mo(2)-O(6)	92.4(2)	O(12)-Mo(4)-O(10)	85.35(16)
O(4)-Mo(2)-O(6)	157.55(19)	O(11)-Mo(4)-O(3)#2	160.3(2)
O(12)#2-Mo(2)-O(6)	91.28(17)	O(13)-Mo(4)-O(3)#2	90.79(19)
O(5)-Mo(2)-N(7)	94.3(2)	O(9)-Mo(4)-O(3)#2	86.23(17)
O(4)-Mo(2)-N(7)	84.9(2)	O(12)-Mo(4)-O(3)#2	73.21(16)
O(12)#2-Mo(2)-N(7)	160.35(18)	O(10)-Mo(4)-O(3)#2	73.68(15)

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

Table S4. Selected bond lengths [Å] and angles [deg] for **4**.

Ni(1)-N(5)	2.045(6)	Mo(2)-O(4)	1.947(4)
Ni(1)-N(4)	2.067(5)	Mo(2)-O(3)	2.250(4)
Ni(1)-N(7)	2.086(5)	Mo(2)-O(5)	2.321(4)
Ni(1)-O(3W)	2.115(5)	Mo(3)-O(9)	1.704(4)
Ni(1)-O(1)#1	2.125(4)	Mo(3)-O(5)#2	1.738(4)
Ni(1)-O(2W)	2.135(5)	Mo(3)-O(10)	1.891(4)
Mo(1)-O(2)	1.720(4)	Mo(3)-O(3)	1.939(4)

Mo(1)-O(1)	1.724(4)	Mo(3)-O(7)	2.174(5)
Mo(1)-O(4)	1.907(5)	Mo(3)-O(3)#2	2.383(4)
Mo(1)-O(13)#2	1.952(5)	Mo(4)-O(12)	1.697(5)
Mo(1)-O(10)#2	2.234(4)	Mo(4)-O(11)	1.708(5)
Mo(1)-O(3)	2.266(4)	Mo(4)-O(13)	1.894(4)
Mo(2)-O(8)	1.695(5)	Mo(4)-O(7)	2.116(4)
Mo(2)-O(6)	1.717(4)	Mo(4)-N(1)	2.206(6)
Mo(2)-O(7)	1.928(4)	Mo(4)-O(10)	2.238(5)
N(5)-Ni(1)-N(4)	93.6(2)	O(7)-Mo(2)-O(3)	72.98(17)
N(5)-Ni(1)-N(7)	88.9(2)	O(4)-Mo(2)-O(3)	73.73(16)
N(4)-Ni(1)-N(7)	99.7(2)	O(8)-Mo(2)-O(5)	88.1(2)
N(5)-Ni(1)-O(3W)	90.9(2)	O(6)-Mo(2)-O(5)	168.0(2)
N(4)-Ni(1)-O(3W)	90.5(2)	O(7)-Mo(2)-O(5)	81.47(16)
N(7)-Ni(1)-O(3W)	169.84(19)	O(4)-Mo(2)-O(5)	79.34(16)
N(5)-Ni(1)-O(1)#1	92.4(2)	O(3)-Mo(2)-O(5)	70.88(15)
N(4)-Ni(1)-O(1)#1	171.8(2)	O(9)-Mo(3)-O(5)#2	104.0(2)
N(7)-Ni(1)-O(1)#1	85.92(19)	O(9)-Mo(3)-O(10)	105.22(19)
O(3W)-Ni(1)-O(1)#1	83.93(18)	O(5)#2-Mo(3)-O(10)	101.2(2)
N(5)-Ni(1)-O(2W)	177.6(2)	O(9)-Mo(3)-O(3)	101.47(19)
N(4)-Ni(1)-O(2W)	87.3(2)	O(5)#2-Mo(3)-O(3)	98.5(2)
N(7)-Ni(1)-O(2W)	93.1(2)	O(10)-Mo(3)-O(3)	141.57(18)
O(3W)-Ni(1)-O(2W)	86.8(2)	O(9)-Mo(3)-O(7)	96.1(2)
O(1)#1-Ni(1)-O(2W)	86.43(18)	O(5)#2-Mo(3)-O(7)	159.72(17)
O(2)-Mo(1)-O(1)	103.9(2)	O(10)-Mo(3)-O(7)	75.56(17)
O(2)-Mo(1)-O(4)	96.7(2)	O(3)-Mo(3)-O(7)	74.54(17)
O(1)-Mo(1)-O(4)	100.3(2)	O(9)-Mo(3)-O(3)#2	177.23(19)
O(2)-Mo(1)-O(13)#2	100.4(2)	O(5)#2-Mo(3)-O(3)#2	78.36(17)
O(1)-Mo(1)-O(13)#2	94.4(2)	O(10)-Mo(3)-O(3)#2	75.54(15)
O(4)-Mo(1)-O(13)#2	154.05(17)	O(3)-Mo(3)-O(3)#2	76.63(17)
O(2)-Mo(1)-O(10)#2	94.91(18)	O(7)-Mo(3)-O(3)#2	81.47(15)
O(1)-Mo(1)-O(10)#2	159.80(18)	O(12)-Mo(4)-O(11)	105.2(3)
O(4)-Mo(1)-O(10)#2	84.41(17)	O(12)-Mo(4)-O(13)	103.8(2)
O(13)#2-Mo(1)-O(10)#2	74.85(17)	O(11)-Mo(4)-O(13)	100.5(2)
O(2)-Mo(1)-O(3)	164.40(19)	O(12)-Mo(4)-O(7)	93.4(2)
O(1)-Mo(1)-O(3)	90.24(18)	O(11)-Mo(4)-O(7)	154.3(2)
O(4)-Mo(1)-O(3)	74.05(17)	O(13)-Mo(4)-O(7)	91.78(17)
O(13)#2-Mo(1)-O(3)	84.68(17)	O(12)-Mo(4)-N(1)	94.3(2)
O(10)#2-Mo(1)-O(3)	72.04(15)	O(11)-Mo(4)-N(1)	81.9(2)
O(8)-Mo(2)-O(6)	103.7(2)	O(13)-Mo(4)-N(1)	160.3(2)
O(8)-Mo(2)-O(7)	105.0(2)	O(7)-Mo(4)-N(1)	79.21(18)
O(6)-Mo(2)-O(7)	97.41(19)	O(12)-Mo(4)-O(10)	163.3(2)
O(8)-Mo(2)-O(4)	102.7(2)	O(11)-Mo(4)-O(10)	91.1(2)
O(6)-Mo(2)-O(4)	95.6(2)	O(13)-Mo(4)-O(10)	75.84(17)
O(7)-Mo(2)-O(4)	145.49(19)	O(7)-Mo(4)-O(10)	70.05(16)

O(8)-Mo(2)-O(3)	159.0(2)	N(1)-Mo(4)-O(10)	84.58(19)
O(6)-Mo(2)-O(3)	97.30(19)		

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

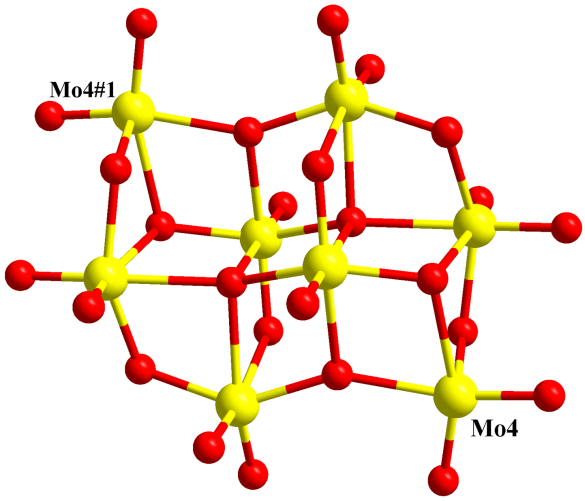

Fig. S1 Ball-and-stick representation of γ-$[Mo_8O_{26}]^{4-}$.

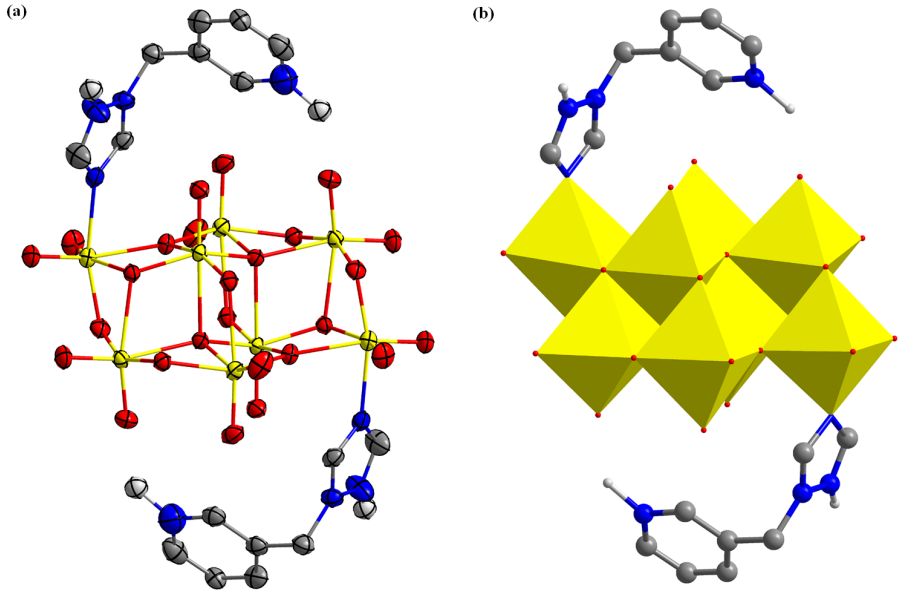

Fig. S2 (a) Crystal structure of the discrete molecule **1** in which octamolybdate is derived by L^1 ligands. (b) Polyhedral representation of discrete molecule **1**.

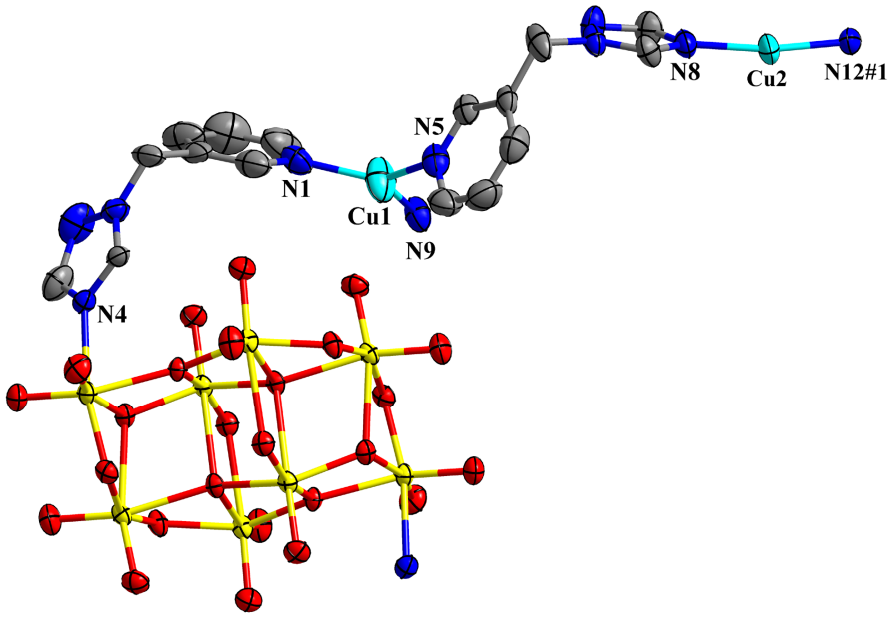

Fig. S3 Coordination mode of Cu^{I} in compound **2** with 50% thermal ellipsoids. All hydrogen atoms were omitted for clarity.

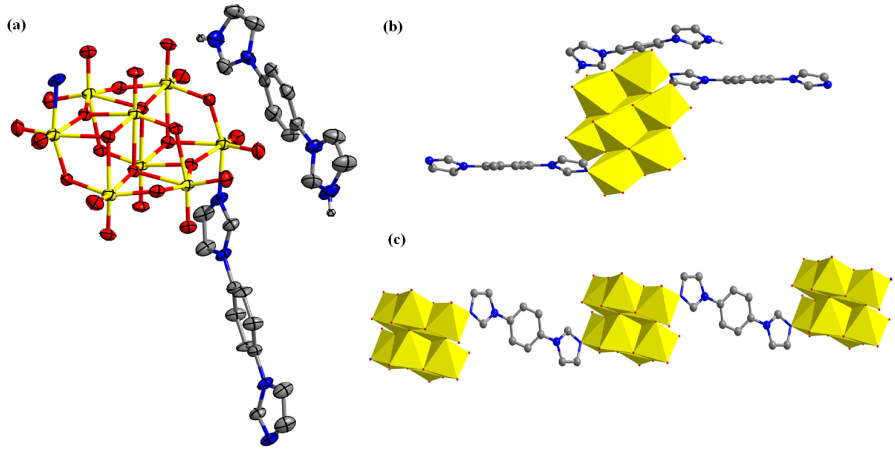

Fig. S4 (a) Molecular structure of compound **3** with 50% thermal ellipsoids. All hydrogen atoms were omitted for clarity except protonated hydrogen atoms. (b) The polyhedron representation of the molecular unit. (c) The L^2 ligands connect octamolybate anions to propagate into a 1D chain.

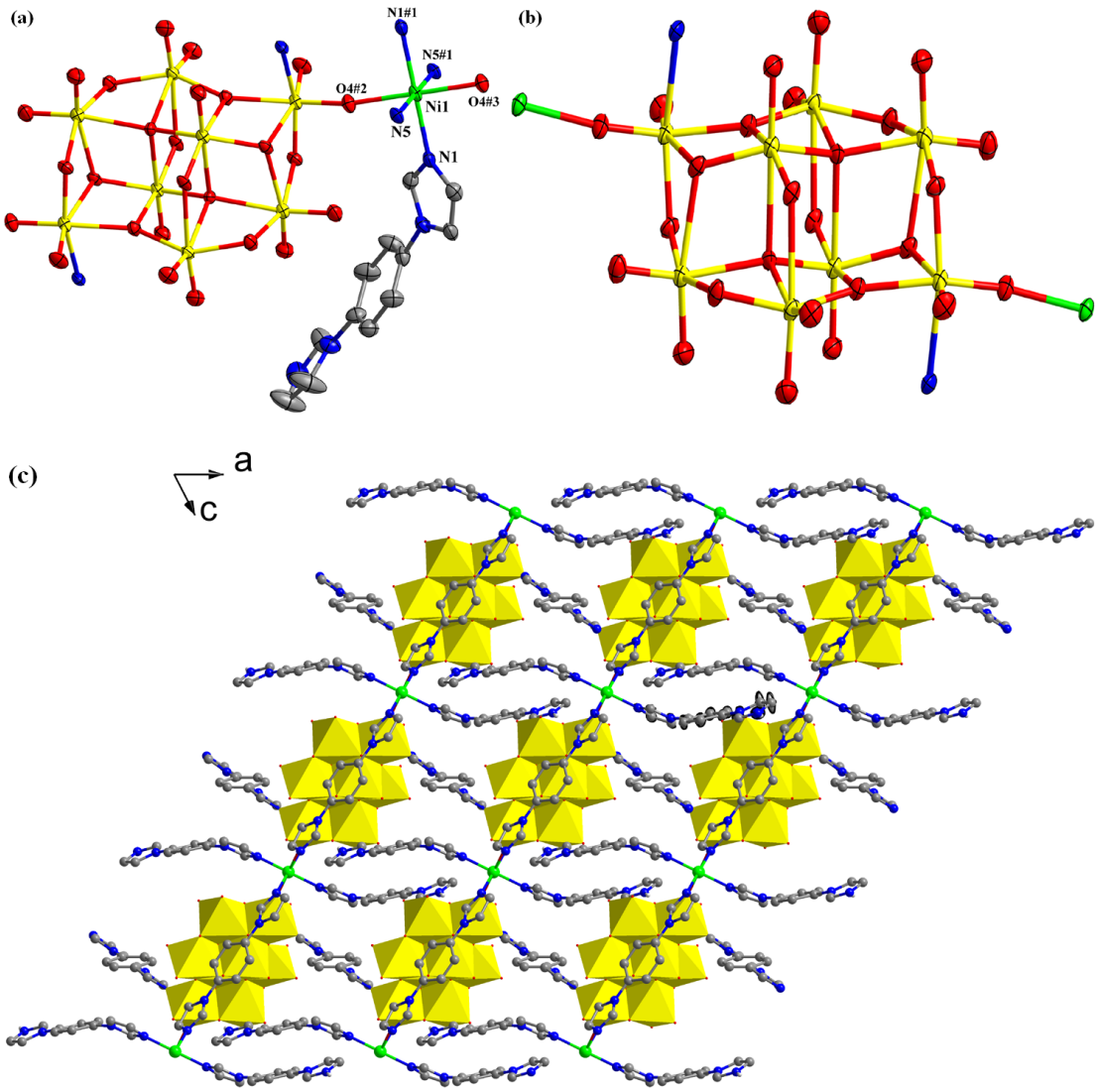

Fig. S5 (a) Coordination mode of Ni^{II} in compound **4** with 50% thermal ellipsoids. All hydrogen atoms were omitted for clarity. (b) Coordination mode of γ-octamolybdate isomer. (c) Perspective view of packing of the framework in **4** along *b* axis.

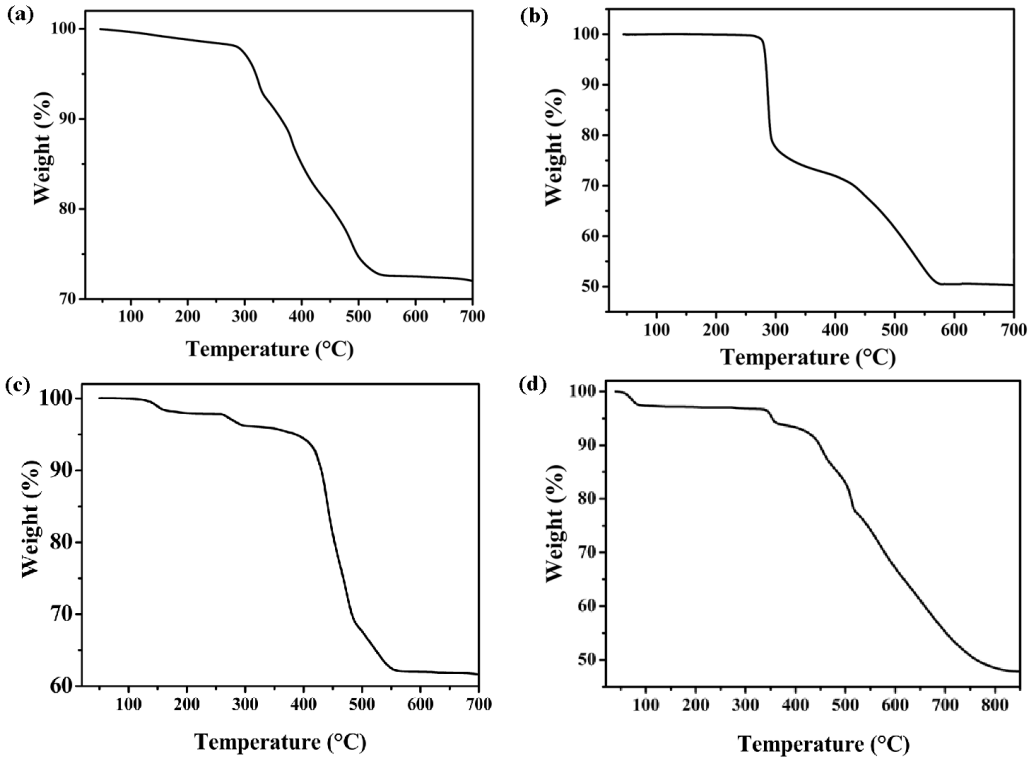

Fig. S6 The TG curves of compounds **1-4.**