Electronic supplementary information (ESI)

Two novel inorganic-organic hybrid materials constructed from two kinds of octamolybdate clusters and flexible tetradentate ligands

Hai-Yan Liu,[a,b] Liu Bo,[a] Jin Yang,*[a] Ying-Ying Liu,[a] Jian-Fang Ma,*[a] and Hua Wu[a]

[a] *Key Lab of Polyoxometalate Science*, *Department of Chemistry*, *Northeast Normal University*, *Changchun 130024*, *People's Republic of China*

[b]*Department of Chemistry and Pharmaceutical Engineering, Suihua University, Suihua 152061, People's Republic of China*

* Correspondence authors

E-mail: yangjinnenu@yahoo.com.cn (J. Yang)

E-mail: jianfangma@yahoo.com.cn (J.-F. Ma)

Fax: +86-431-85098620 (J.-F. Ma)

Table S1. Selected Bond Lengths [Å] and Angles [º] for **1** and **2**.

		Compound **1**	
Ag(1)-N(1)	2.242(14)	Ag(1)-O(17)	2.258(10)
Ag(1)-N(18)	2.290(14)	Ag(1)-O(4W)	2.769(10)
Ag(2)-O(1)#1	2.206(10)	Ag(2)-N(4)	2.217(14)
Ag(2)-N(19)	2.298(15)	Ag(3)-N(24)#2	2.134(16)
Ag(3)-N(3)	2.138(16)	Ag(3)-O(23)#1	2.697(16)
Ag(4)-N(13)	2.279(13)	Ag(4)-N(7)	2.283(14)
Ag(4)-O(2W)	2.340(13)	Ag(4)-O(50)#5	2.769(13)
Ag(5)-N(21)#3	2.115(17)	Ag(5)-N(9)	2.116(16)
Ag(5)-O(48)	2.741(16)	Ag(6)-O(1W)	2.182(15)
Ag(6)-N(11)	2.258(15)	Ag(6)-N(23)#4	2.305(16)
Ag(6)-O(34)#2	2.731(15)	Ag(7)-N(15)#2	2.150(17)
Ag(7)-N(12)	2.162(18)	Ag(7)-O(52)#5	2.635(17)
Ag(8)-N(17)	2.154(16)	Ag(8)-N(6)#2	2.160(15)
Ag(8)-O(15)	2.619(16)		
N(1)-Ag(1)-O(17)	119.8(5)	N(1)-Ag(1)-O(17)	119.8(5)
O(17)-Ag(1)-N(18)	128.4(4)	N(18)-Ag(1)-O(4W)	85.2(5)
O(17)-Ag(1)-O(4W)	75.8(4)	N(1)-Ag(1)-O(4W)	151.73(5)
O(1)#1-Ag(2)-N(4)	134.7(5)	O(1)#1-Ag(2)-N(19)	117.8(5)
N(4)-Ag(2)-N(19)	101.5(5)	N(24)#2-Ag(3)-N(3)	174.1(7)
N(24)-Ag(3)-O(23)#1	100.28(7)	N(3)-Ag(3)-O(23)#1	85.62(7)
N(13)-Ag(4)-N(7)	102.6(5)	N(13)-Ag(4)-O(2W)	141.5(5)
N(7)-Ag(4)-O(2W)	94.3(5)	N(7)-Ag(4)-O(50)#5	111.93(5)
O(2W)-Ag(4)-O(50)#5	87.28(5)	N(13)-Ag(4)-O(50)#5	116.85(5)
N(21)#3-Ag(5)-N(9)	168.3(7)	N(9)-Ag(5)-O(48)	92.82(7)
N(21)#3-Ag(5)-O(48)	98.6(7)	O(1W)-Ag(6)-N(11)	125.9(6)
O(1W)-Ag(6)-N(23)#4	109.2(6)	N(11)-Ag(6)-N(23)#4	105.7(6)
N(23)#4-Ag(6)-O(34)#2	112.67(6)	N(11)-Ag(6)-O(34)#2	119.51(6)
O(1W)-Ag(6)-O(34)#2	82.48(6)	N(15)#2-Ag(7)-N(12)	167.8(7)
N(15)#2-Ag(7)-O(52)#5	90.48(6)	N(12)-Ag(7)-O(52)#5	101.0(7)
N(17)-Ag(8)-N(6)#2	169.4(7)	N(17)-Ag(8)-O(15)	89.73(7)
N(6)#2-Ag(8)-O(15)	99.24(7)		
		Compound **2**	
Cu(1)-N(13)	1.858(6)	Cu(1)-N(11)	1.862(6)
Cu(1)-O(16)#4	2.603(6)	Cu(2)-N(2)	1.992(6)
Cu(2)-N(8)	2.014(6)	Cu(2)-N(12)	2.068(7)
Cu(2)-O(22)	2.178(5)	Cu(3)-N(1)	1.990(6)
Cu(3)-N(1)#1	1.990(6)	Cu(3)-O(9)	2.006(5)
Cu(3)-O(9)#1	2.006(5)	Cu(3)-O(6)	2.577(5)
Cu(3)-O(6)#1	2.577(5)	Cu(4)-N(9)#2	1.909(6)
Cu(4)-N(5)	1.909(7)	Cu(4)-O(13)#3	2.262(5)
Cu(4)-O(4)#2	2.273(5)	Cu(5)-N(6)	1.928(10)

Cu(5)-N(6)#3	1.928(10)		
N(13)-Cu(1)-N(11)	164.6(3)	N(13)-Cu(1)-O(16)#4	103.99(3)
N(11)-Cu(1)-O(16)#4	90.98(3)	N(2)-Cu(2)-N(8)	128.7(3)
N(2)-Cu(2)-N(12)	119.2(3)	N(8)-Cu(2)-N(12)	111.6(3)
N(2)-Cu(2)-O(22)	89.7(2)	N(8)-Cu(2)-O(22)	92.7(2)
N(12)-Cu(2)-O(22)	95.4(2)	N(1)-Cu(3)-N(1)#1	180
N(1)-Cu(3)-O(9)	88.6(2)	N(1)#1-Cu(3)-O(9)	91.4(2)
N(1)-Cu(3)-O(9)#1	91.4(2)	N(1)#1-Cu(3)-O(9)#1	88.6(2)
O(9)-Cu(3)-O(9)#1	180	N(1)-Cu(3)-O(6)	94.87(2)
N(1)-Cu(3)-O(6)#1	85.14(2)	O(6)-Cu(3)-O(6)#1	180
N(9)#2-Cu(4)-N(5)	152.5(3)	N(9)#2-Cu(4)-O(13)#3	94.8(2)
N(5)-Cu(4)-O(13)#3	106.1(2)	N(9)#2-Cu(4)-O(4)#2	99.6(2)
N(5)-Cu(4)-O(4)#2	99.5(3)	O(13)#3-Cu(4)-O(4)#2	86.09(18)
N(6)-Cu(5)-N(6)#3	180		

Symmetry codes For **1:** #1 -x+1,y+1/2,-z+1; #2 x+1,y,z ;#3 x,y,z-1; #4 x+1,y,z-1; #5 –x+1,-y+2,-z. For **2**: #1 -x,-y,-z+2; #2 x,y+1,z; #3 -x-1,-y+1,-z+2; #4 -x,-y,-z+1.

Table S2: Crystal Data and Structure Refinements for L^1 and L^2**.**

	L^1	**L^2**
Empirical formula	$C_{54}H_{54}N_{12}O_5$	$C_{28}H_{24}N_6$
Fw	951.09	444.53
Crystal size [mm]	0.28×0.20×0.12	0.32×0.24×0.20
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	15.487(5)	6.6930(4)
b [Å]	18.635(5)	9.4581(4)
c [Å]	9.233(5)	9.7729(6)
α [°]	90	71.507(4)
β [°]	101.196(5)	71.631(5)
γ [°]	90	87.487(4)
Volume [$Å^3$]	2613.9(18)	555.73(5)
Z	2	1
D_c(g/cm^3)	1.208	1.328
GOF	0.871	1.010
Reflns collected/unique	10633 / 4690	9896 / 2912
R_{int}	0.0273	0.0268
R_1 [I>2σ(I)]	0.0657	0.0403

wR_2 (all data)	0.1878	0.1034

Structure of L^1 ligand. As shown in Fig. S1, the asymmetric unit of L^1 consists of one L^1 molecule and two and a half lattice water molecules. The L^1 ligand adopts a distorted *tran*-conformation. The three methylene groups arrange in a zigzag shape.

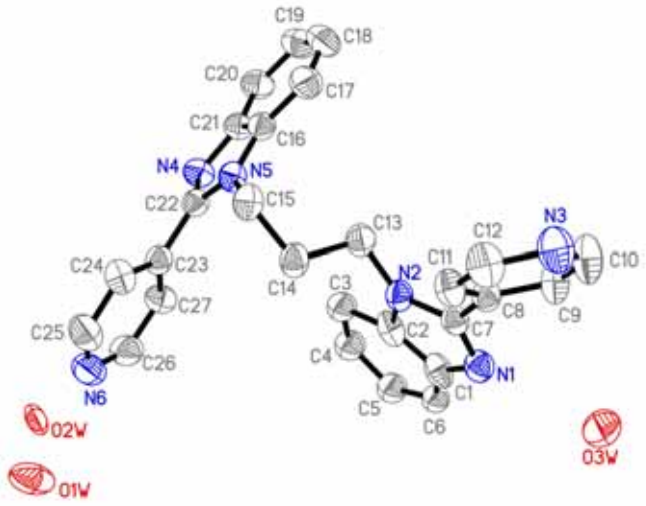


Fig. S1 Crystal structure of L^1 ligand (30% probability displacement ellipsoids).

Structure of L^2 ligand. Single-crystal X-ray diffraction analysis reveals that there is half a L^2 molecule lying about an inversion center (Fig. S2). The L^2 ligand adopts a *tran*-conformation.

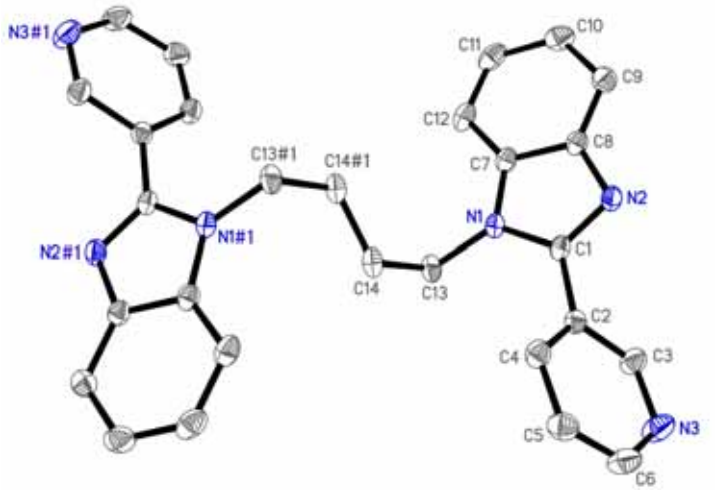
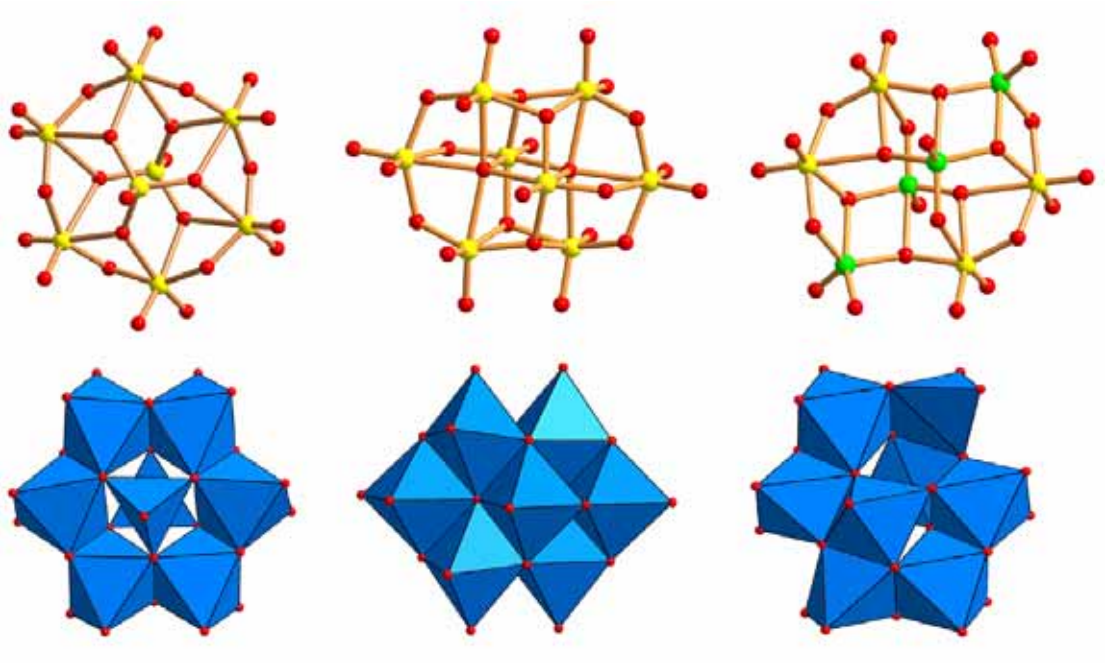


Fig. S2. Crystal structure of L^1 ligand (30% probability displacement ellipsoids). Symmetry codes for the generated atoms: #1 -x+2, -y, -z+2.



(α-Mo_8O_{26})$^{4-}$ (β-Mo_8O_{26})$^{4-}$ (ζ-Mo_8O_{26})$^{5-}$

Fig. S3 Ball-stick and polyhedral representations of the structures of α-, β-, and ζ-clusters of $(Mo_8O_{26})^{4-}$.

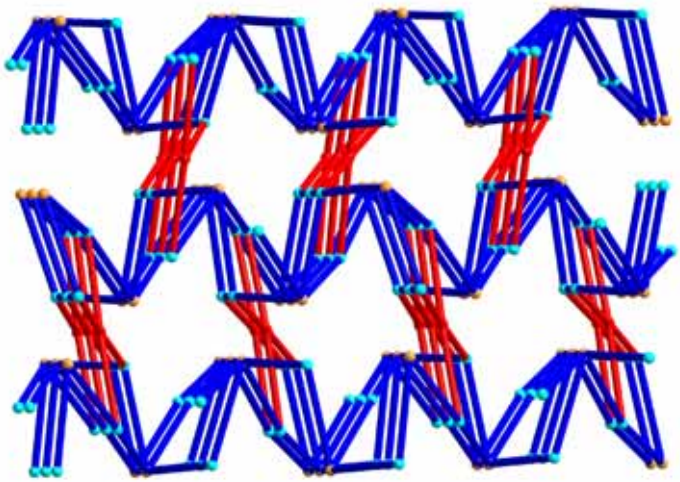


Fig. S4 Schematic view of the (3,4)-connected framework with $(4\cdot8\cdot12)(4\cdot8^3\cdot10^2)(4^2\cdot8^2\cdot10^2)$ topology in **1**.

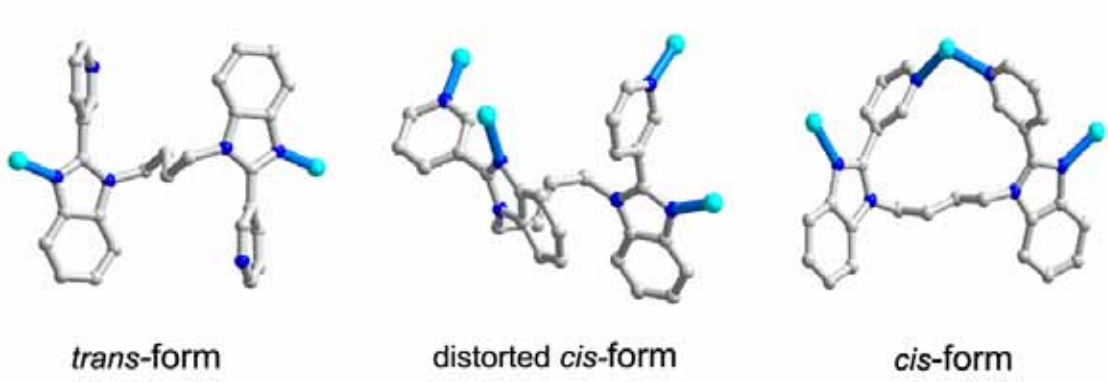


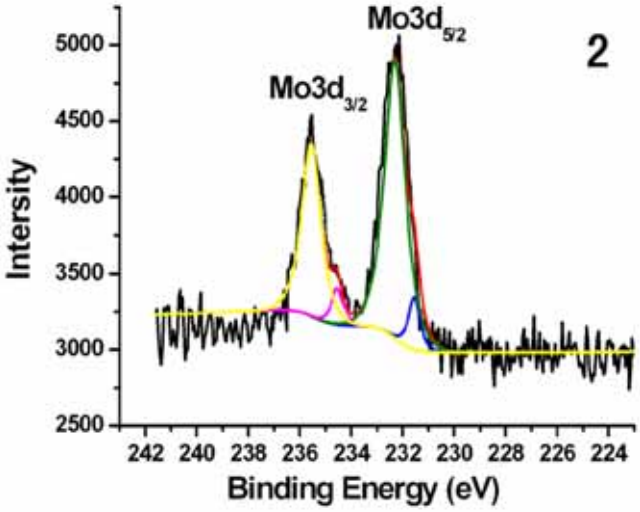
Fig. S5 The configurations of L2 ligand in **2**.

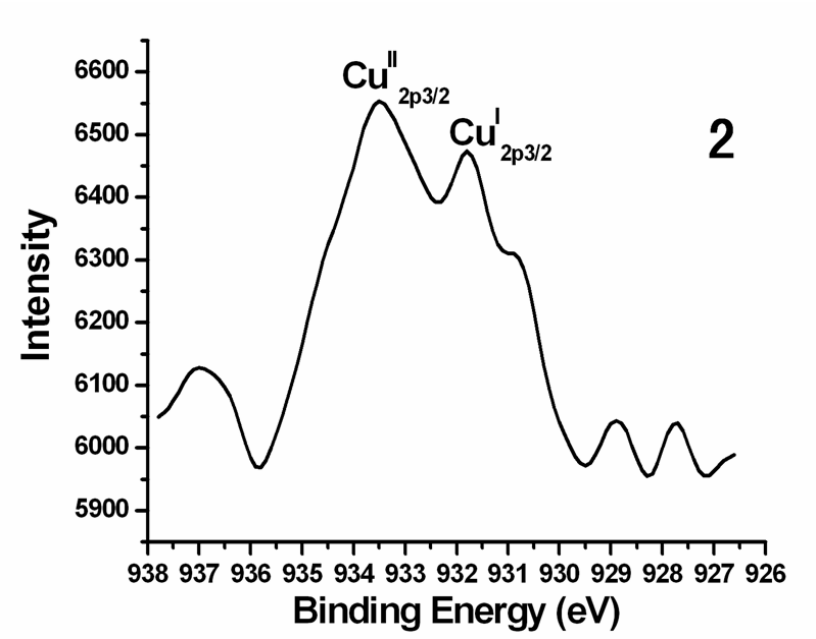
XPS Spectrum

The oxidation states of Mo and Cu in **2** are further confirmed by XPS measurements. In the XPS spectrum (Fig. S6), two overlapped pecks at 232.4 and 231.5 eV are attributed to Mo^{6+} ($3d_{5/2}$) and Mo^{5+} ($3d_{5/2}$), respectively.[1] Two peaks at 933.5 and 931.7 eV are ascribed to Cu^{2+} ($2p_{3/2}$) and Cu^{+} ($2p_{3/2}$), respectively. Two peaks at 954.3 and 951.3 eV are attributed to Cu^{2+} ($2p_{1/2}$) and Cu^{+} ($2p_{1/2}$), respectively.[2]

(1) T. A. Patterson, J. C. Carver, D. E. Leyden and D. M. Hercules, *J. Phys. Chem.*, 1976, **80**, 1700.

(2) (*a*) J.-Q. Sha, J. Peng, H.-S. Liu, J. Chen, B.-X. Dong, A.-X. Tian and Z.-M. Su, *Eur. J. Inorg. Chem.*, 2007, 1268; (*b*) J. Chen, J.-Q. Sha, J. Peng, Z.-Y. Shi, B.-X. Dong and A.-X. Tian, *J. Mol. Struct.*, 2007, **846**, 128.





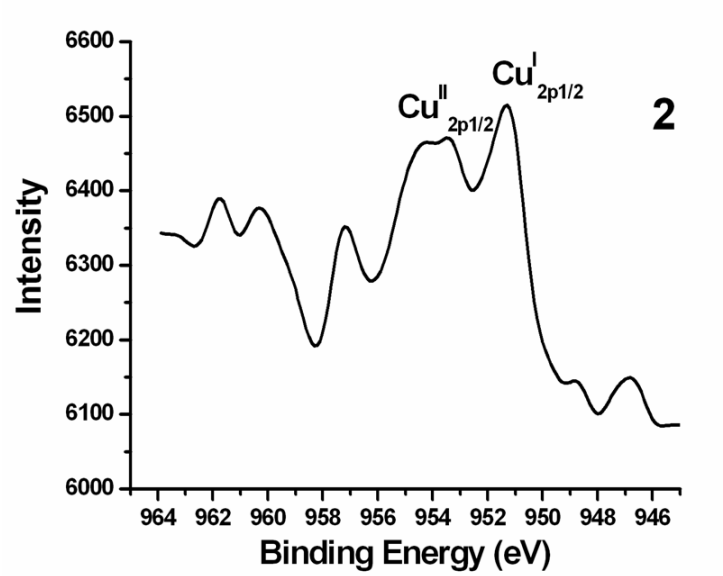


Fig. S6 XPS of compound **2**.