

## Electronic Supplementary Information

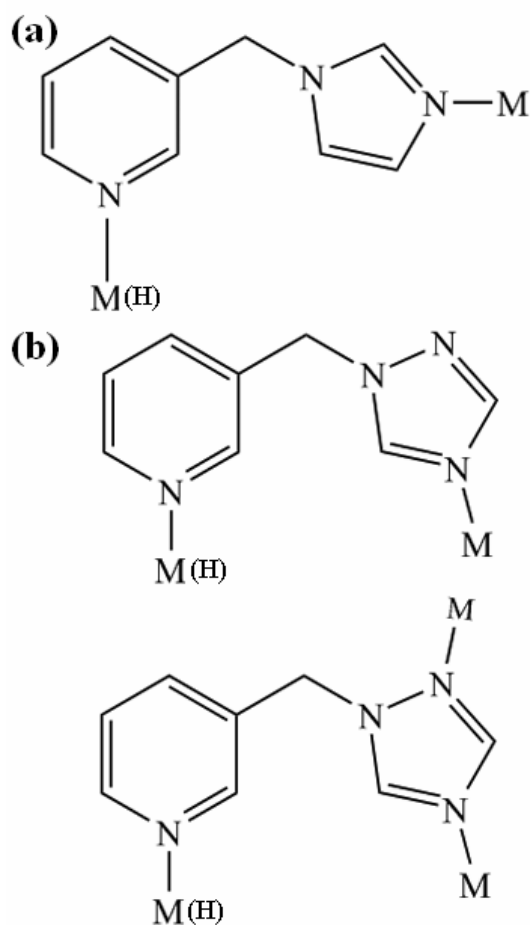
### Construction and property investigation of transition-metal-complexes modified octamolybdate hybrid materials based on V-shaped organic ligands

Hong-Ying Zang, Ya-Qian Lan, Guang-Sheng Yang, Xin-Long Wang, Kui-Zhan Shao,  
Guang-Juan Xu and Zhong-Min Su\*

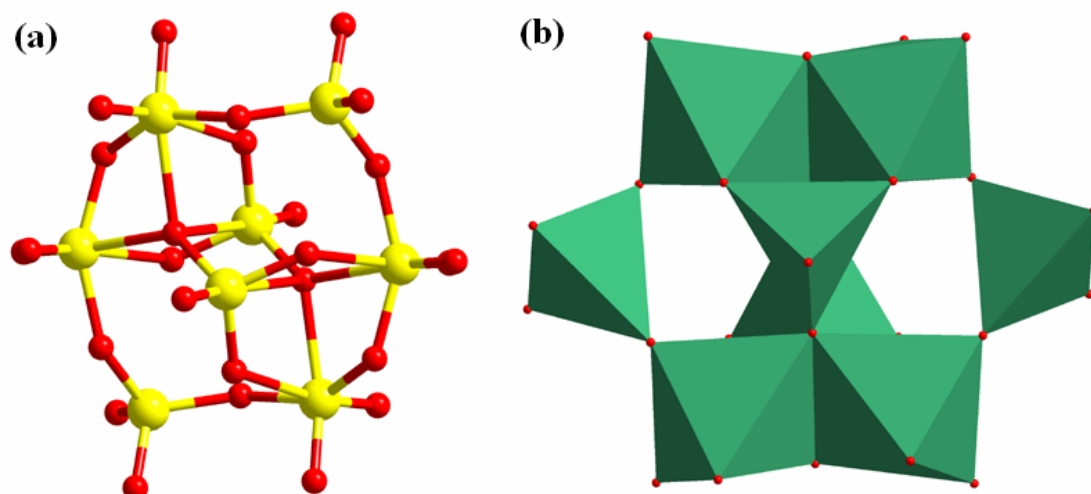
Institute of Functional Material Chemistry; Key Lab of Polyoxometalate Science of  
Ministry of Education, Faculty of Chemistry, Northeast Normal University,  
Changchun, 130024, Jilin, People's Republic of China.

\*Corresponding author.

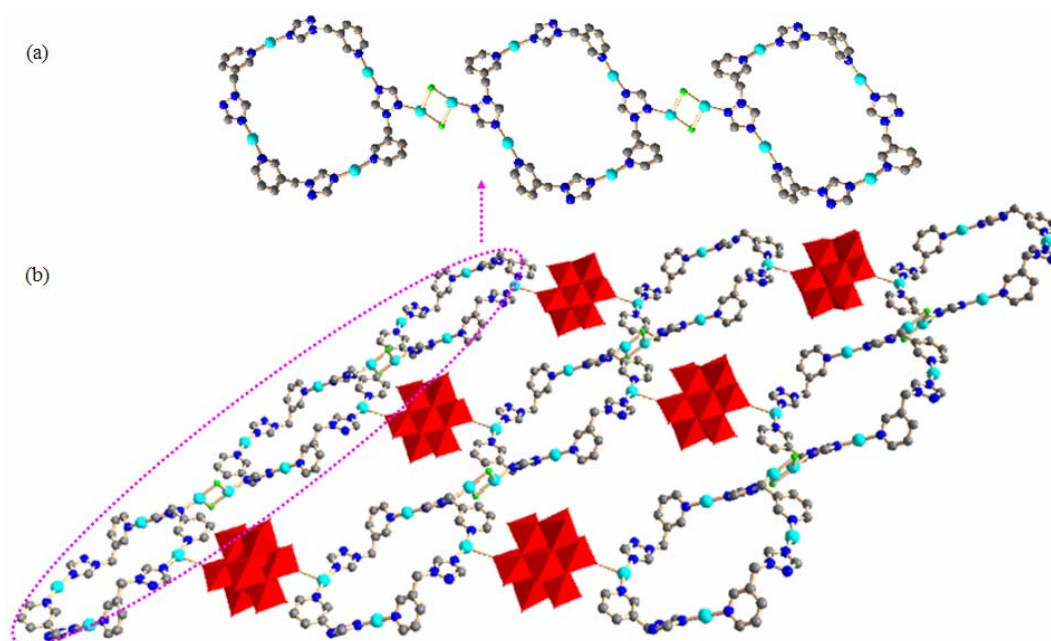
zmsu@nenu.edu.cn; Tel: +86 431 85099108



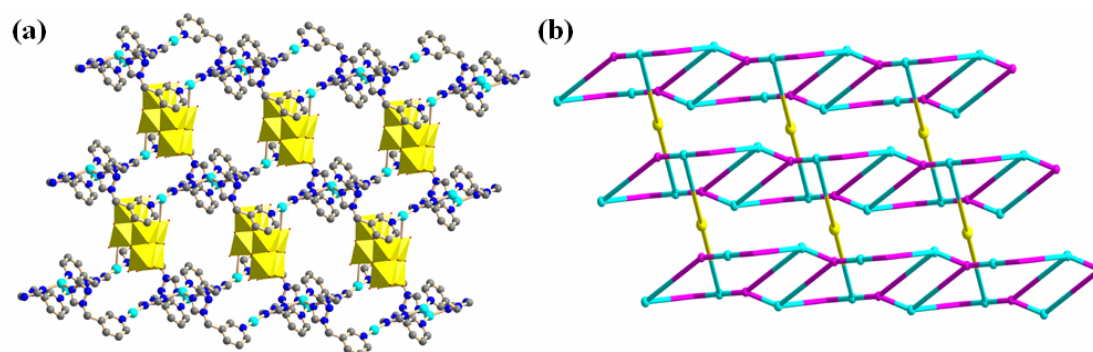
Scheme S1. Coordination numbers and Modes of  $L^1$ ,  $L^2$



**Fig. S1** (a) Ball-and-stick representation and (b) polyhedra representation of  $\theta$ -isomer of octamolybdate.



**Fig. S2.** (a) View of 1D metal-organic chain:  $\text{Cu}_2\text{Cl}_2$  bridges the adjacent closed loop into an infinite chain. (b) Every adjacent chains are linked by  $[\text{Mo}_8\text{O}_{26}]^{4-}$  anions into a 2D network in compound **5**.



**Fig. S3.** (a) View of the 2D network of compound **6**. (b) Topological representation of the 3-connected 2D network.<sup>16</sup>

**Table S1.** Hydrogen-Bonding Geometry for **3** (in Å and deg)

D-H...A	d(D-H)	d(D...A)	<(DHA)
N(4)-H(1N)...O(1W)	0.857(10)	2.754(5)	145(5)
O(1W)-H(1B)...N(2)#5	0.850(10)	2.968(5)	148(3)
O(1W)-H(1A)...O(9)#6	0.849(10)	2.819(4)	150(4)

Symmetry codes: #1 -x+1, -y, -z+1; #3 x, y-1, z-1; #4 x-1, y+1, z; #5 x, y+1, z; #6 x-1/2, -y+1/2, z+1/2.

**Table S2.** Selected Bond Lengths (Å) and Angles (deg) for compound **1**

Compound 1			
Cu(1)-N(3)	1.971(7)	Cu(1)-O(1W)	2.108(7)
Cu(1)-O(13)	2.231(5)		
N(3)-Cu(1)-O(1W)#1	91.2(3)	N(3)-Cu(1)-O(13)#1	89.4(3)
N(3)-Cu(1)-O(13)	90.6(2)	O(1W)-Cu(1)-O(13)#1	96.1(2)
N(3)-Cu(1)-O(1W)	88.8(3)	O(1W)-Cu(1)-O(13)	83.9(2)

Symmetry codes: #1 -x+1, -y+2, -z+2.

**Table S3.** Selected Bond Lengths (Å) and Angles (deg) for compound **2**

Compound 2			
Cu(1)-N(3)	1.982(5)	Cu(1)-N(4)#1	2.041(5)
Cu(1)-N(6)	2.002(5)	Cu(1)-O(6)	2.430(4)
Cu(1)-N(1)#1	2.019(5)	Cu(1)-O(10)#4	2.474(4)
N(3)-Cu(1)-N(6)	93.1(2)	N(1)#1-Cu(1)-N(4)#1	88.8(2)

N(3)-Cu(1)-N(1)#1	178.2(2)	N(3)-Cu(1)-O(6)	89.98(17)
N(6)-Cu(1)-N(1)#1	88.7(2)	N(6)-Cu(1)-O(6)	95.47(18)
N(3)-Cu(1)-N(4)#1	89.5(2)	N(1)#1-Cu(1)-O(6)	89.41(18)
N(6)-Cu(1)-N(4)#1	174.7(2)	N(4)#1-Cu(1)-O(6)	89.14(17)
N(6)-Cu(1)-O(10)#4	87.643(2)	N(3)-Cu(1)-O(10)#4	89.530(2)

Symmetry codes: #1  $-x+3/2, y-1/2, -z+3/2$ ; #4  $x+1/2, -y+1/2, z+1/2$ .

**Table S4.** Selected Bond Lengths (Å) and Angles (deg) for compound **3**

<b>Compound 3</b>			
Cu(1)-N(3)	1.972(3)	Cu(1)-O(13)	1.983(2)
Cu(1)-O(7)#1	2.374(2)		
N(3)-Cu(1)-O(13)#2	89.03(11)	N(3)-Cu(1)-O(13)	90.97(11)
N(3)-Cu(1)-O(7)#1	87.73(11)	N(3)#2-Cu(1)-O(7)#1	92.27(11)
O(13)#2-Cu(1)-O(7)#1	96.03(9)	O(13)-Cu(1)-O(7)#1	83.97(9)

Symmetry codes: #1  $-x+1/2, -y+1/2, -z$ ; #2  $-x, -y, -z$ .

**Table S5.** Selected Bond Lengths (Å) and Angles (deg) for compound **4**

<b>Compound 4</b>			
Cu(1)-N(1)	1.994(3)	Cu(1)-N(8)	2.019(3)
Cu(1)-N(5)	2.003(3)	Cu(1)-O(12)	2.437(3)
Cu(1)-N(4)	2.014(3)		
N(1)-Cu(1)-N(5)	90.17(14)	N(4)-Cu(1)-N(8)	88.12(14)
N(1)-Cu(1)-N(4)	179.50(15)	N(1)-Cu(1)-O(12)	84.61(12)
N(5)-Cu(1)-N(4)	89.45(14)	N(5)-Cu(1)-O(12)	91.23(12)
N(1)-Cu(1)-N(8)	92.27(14)	N(4)-Cu(1)-O(12)	95.08(12)
N(5)-Cu(1)-N(8)	177.06(14)	N(8)-Cu(1)-O(12)	90.63(12)

**Table S6.** Selected Bond Lengths (Å) and Angles (deg) for compound **5**

<b>Compound 5</b>			
Cu(1)-N(5)	1.873(10)	Cu(2)-Cl(1)#2	2.559(6)
Cu(1)-N(4)#1	1.870(10)	Cu(3)-N(1)	1.878(9)
Cu(2)-N(6)	1.987(10)	Cu(3)-N(8)	1.913(9)
Cu(2)-Cl(1)	2.151(6)	Cu(3)-O(13)	2.303(7)
N(5)-Cu(1)-N(4)#1	173.9(5)	N(1)-Cu(3)-N(8)	163.5(4)

N(6)-Cu(2)-Cl(1)	158.1(4)	N(1)-Cu(3)-O(13)	96.0(3)
N(6)-Cu(2)-Cl(1)#2	100.3(3)	N(8)-Cu(3)-O(13)	100.5(3)
Cl(1)-Cu(2)-Cl(1)#2	101.50(19)	Cu(2)-Cl(1)-Cu(2)#2	78.50(19)

Symmetry codes: #1 -x, -y+2, -z+3; #2 -x-1, -y+3, -z+2.

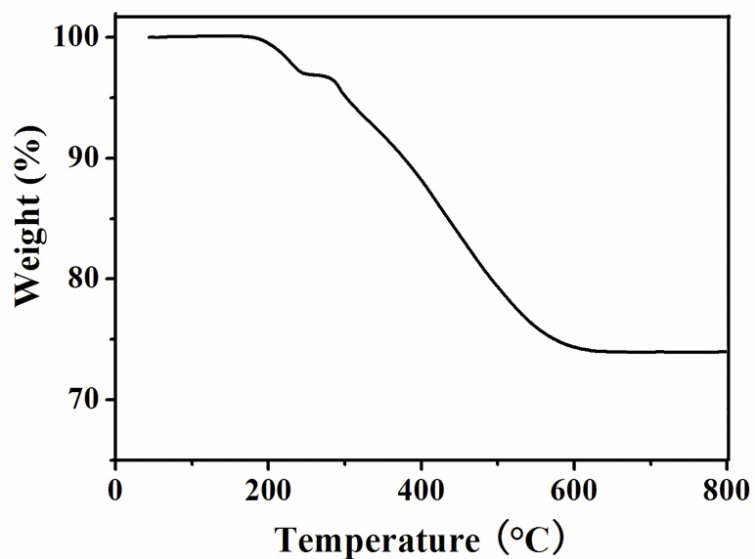


Fig. S4. The TG curve for compound 1.

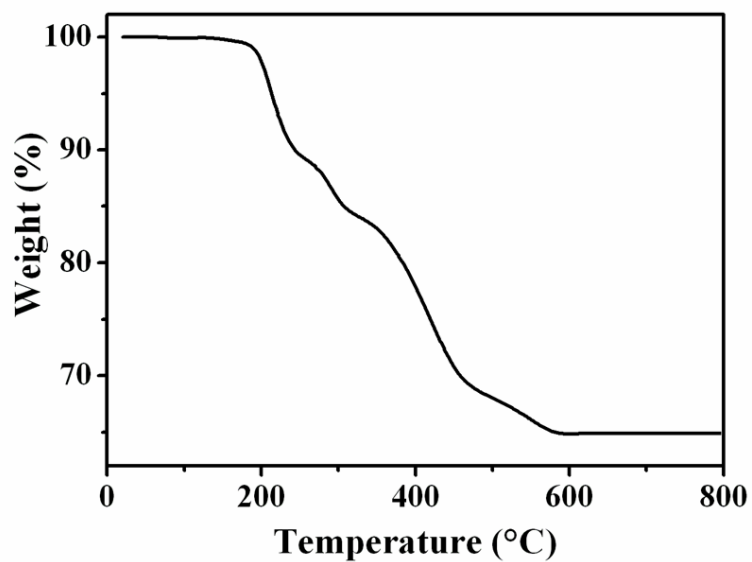
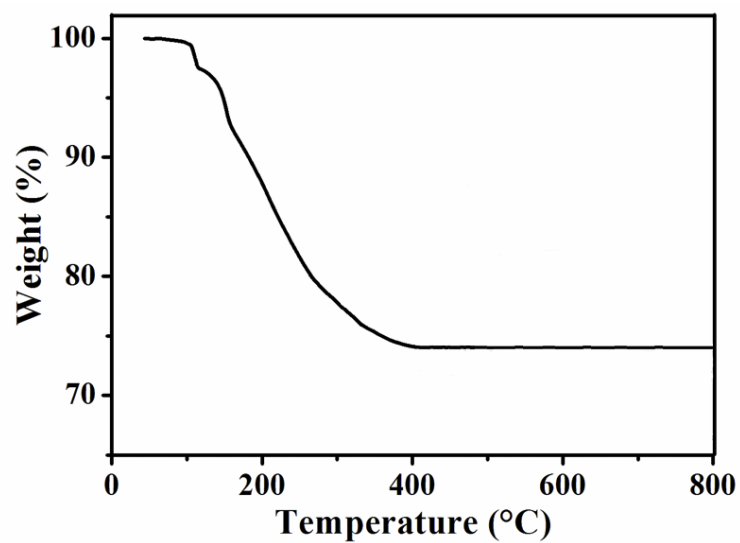
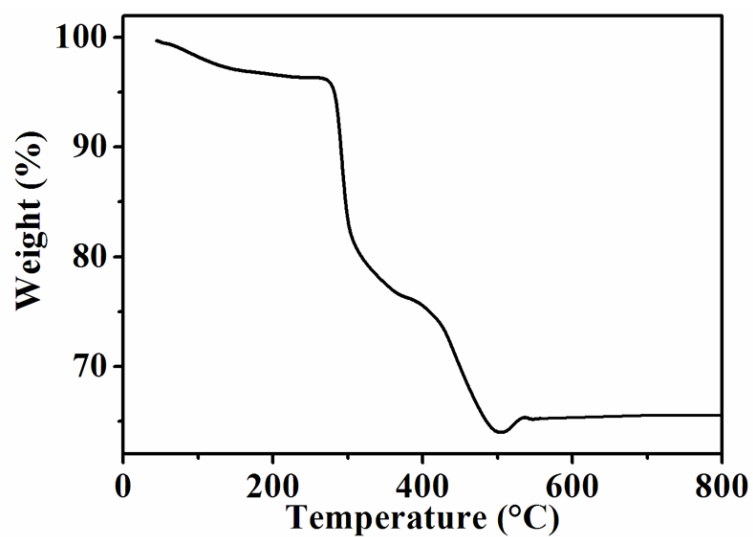


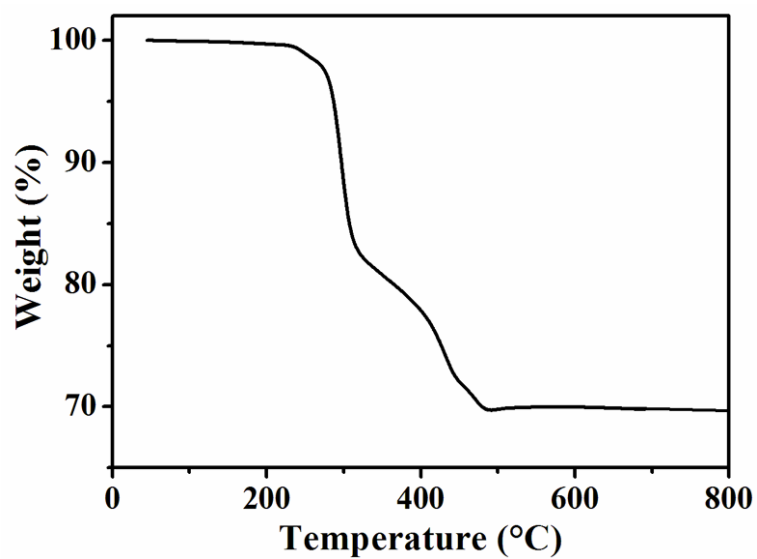
Fig. S5. The TG curve for compound 2.



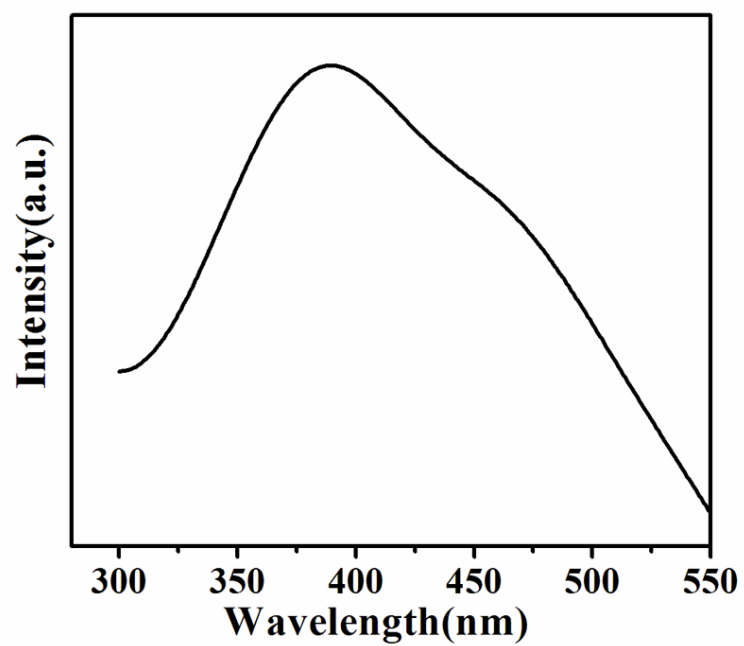
**Fig. S6.** The TG curve for compound 3.



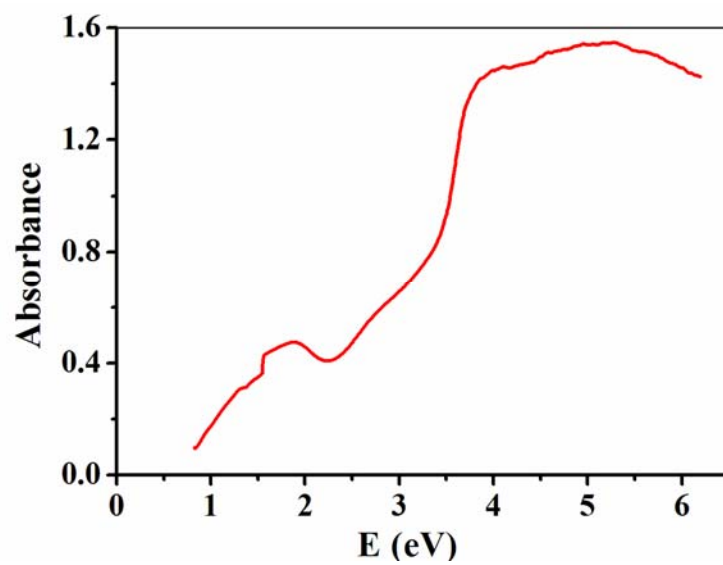
**Fig. S7.** The TG curve for compound 4.



**Figure S8.** The TG curve for compound **5**.



**Fig. S9.** Fluorescent emission spectrum of **5** in the solid state at room temperature ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ).



**Fig. S10.** The UV/Visible-NIR spectrum of **5**.