Supporting Information

Unprecedented cyclic $[Mo_6O_{19}]^{2-}$ cluster and five organic-inorganic hybrid complexes based on polyoxomolybdates and 4-amino-3,5-bis(pyridyl)-1,2,4-triazole

Ming-Xing Li[a,c,*], Hui-Ling Chen[a], Jin-Peng Geng[a], Xiang He[a], Min Shao[b], Shou-Rong Zhu[a], Zhao-Xi Wang[a,*]

[a] *Department of Chemistry, College of Science, Shanghai University, Shanghai 200444 , China*

[b] *Instrumental Analysis and Research Center, Shanghai University, Shanghai 200444, China*

[c] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

* Corresponding author. E-mail: mx_li@mail.shu.edu.cn, zxwang@shu.edu.cn

Table S1. Crystallographic data and structural refinements for **1**–**5**

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{12}H_{14}CuMo_4N_6O_{15}$	$C_{24}H_{24}Mo_8N_{12}O_{26}$	$C_{12}H_{12}CuMo_4N_6O_{14}$	$C_{12}H_{12}CuMoN_6O_5$	$C_{24}H_{28}CoMo_6N_{12}O_{23}$
Formula weight	929.59	1664.07	911.58	479.76	1487.15
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	9.689(2)	10.626(1)	7.6630(4)	10.9052(6)	9.5193(8)
b (Å)	9.847(2)	15.821(1)	29.474(2)	17.603(1)	10.9534(9)
c (Å)	13.533(2)	12.852(1)	9.7421(6)	7.8921(4)	11.4935(9)
α (º)	99.395(2)	90	90	90	91.786(1)
β (º)	109.368(2)	100.703(1)	101.823(1)	92.640(2)	113.800(1)
γ (º)	101.945(2)	90	90	90	105.469(1)
V (Å^3)	1153.6(3)	2123.1(2)	2153.7(2)	1513.39(14)	1043.60(15)
Z	2	2	4	4	1
D_c (g cm^{-3})	2.676	2.603	2.811	2.106	2.366
F(000)	890	1592	1740	948	719
μ (mm^{-1})	3.109	2.390	3.324	2.275	2.231
Reflections collected	5993	10770	11121	8029	5378
Unique reflections	4012	3753	3804	2670	3617
R_{int}	0.0193	0.0190	0.0177	0.0640	0.0147
GOF	1.061	1.079	1.099	1.054	1.103
R_1, wR_2 [$I>2\sigma(I)$]	0.0350, 0.0996	0.0240, 0.0592	0.0210, 0.0482	0.0448, 0.0912	0.0264, 0.0702
R_1, wR_2 (all data)	0.0387, 0.1040	0.0270, 0.0608	0.0231, 0.0490	0.0713, 0.1045	0.0277, 0.0710

Table S2. Selected bond distances (Å) and angles (°) for **1**–**5**

		1 [a]	
Cu(1)-N(1)	1.964(4)	Cu(1)-N(2)#2	2.029(4)
Cu(1)-N(3)#1	1.959(4)	Cu-O(12)	2.507 (4)
Mo(1)-O(2)	2.009(4)	Mo(2)-O(2)#3	1.805(4)
N(3)#1-Cu(1)-N(1)	127.61(17)	N(1)-Cu(1)-N(2)#2	115.78(17)
N(3)#1-Cu(1)-N(2)#2	115.57(16)	N(1)-Cu(1)-O(12)	99.68(2)
		2 [b]	
Mo(1)-O(1)	1.695(3)	Mo(3)-O(7)	1.696(3)
Mo(1)-O(2)	1.956(2)	Mo(3)-O(6)	1.698(3)
Mo(1)-O(3)	1.736(3)	Mo(3)-O(5)	1.885(3)
Mo(1)-O(4)	1.953(2)	Mo(3)-O(2)#1	1.999(2)
Mo(1)-O(11)	2.171(2)	Mo(3)-O(4)	2.336(2)
Mo(1)-O(11)#1	2.359(2)	Mo(3)-O(11)#1	2.361(2)
Mo(2)-O(8)	1.691(3)	Mo(4)-O(12)	1.696(3)
Mo(2)-O(9)	1.705(3)	Mo(4)-O(13)	1.704(3)
Mo(2)-O(10)	1.904(3)	Mo(4)-O(10)	1.902(3)
Mo(2)-O(4)	1.985(2)	Mo(4)-O(5)#1	1.927(3)
Mo(2)-O(11)	2.312(2)	Mo(4)-O(3)#1	2.327(3)
Mo(2)-O(2)#1	2.341(2)	Mo(4)-O(11)	2.394(2)
		3 [c]	
Cu(1)-N(1)	1.982(3)	Cu(1)-O(10)	1.981(2)
Cu(1)-N(6)#2	2.004(3)	Cu(1)-O(14)	1.924(2)
Cu(1)-O(12)	2.519(2)		
O(10)-Cu(1)-N(1)	84.39(11)	O(14)-Cu(1)-N(6)#2	91.25(11)
O(14)-Cu(1)-O(4)	92.21(10)	N(1)-Cu(1)-N(6)#2	93.83(12)
O(14)-Cu(1)-N(1)	171.00(12)	O(10)-Cu(1)-N(6)#2	167.52(11)
		4 [d]	
Cu(1)-O(1)	1.964(5)	Mo(1)-O(2)	1.738(4)
Cu(1)-O(2)	2.163(4)	Mo(1)-O(3)	1.746(4)
Cu(1)-O(4)#1	1.920(4)	Mo(1)-O(4)	1.785(4)
Cu(1)-N(1)#2	2.017(5)	Mo(1)-O(5)	1.761(5)

Cu(1)-N(6)	2.024(5)	N(6)-Cu(1)-O(2)	96.35(19)
O(4)#1-Cu(1)-O(1)	171.63(19)	N(1)#2-Cu(1)-N(6)	162.2(2)

5 [e]

Mo(1)-N(2)	2.359(3)	Mo(3)-O(3)	1.993(3)
Mo(1)-O(1)	1.690(3)	Mo(3)-O(7)	2.203(3)
Mo(1)-O(2)	1.993(3)	Mo(3)-O(8)	1.717(3)
Mo(1)-O(3)	1.862(3)	Mo(3)-O(9)	1.8878(4)
Mo(1)-O(4)	1.754(3)	Mo(3)-O(10)	2.324(3)
Mo(1)-O(7)	2.230(3)	Mo(3)-O(11)	1.695(3)
Mo(2)-N(1)	2.582	Mo(2)-O(7)	1.879(3)
Mo(2)-O(5)	1.708(3)	Mo(2)-O(2)	2.224(3)
Mo(2)-O(6)	1.708(3)	Mo(2)-O(2)#4	1.987(3)
Co(1)-N(6)#2	2.159(3)	Co(1)-O(4)	2.083(3)
Co(1)-N(5)#4	2.200(3)		

Symmetry codes: [a] #1 x, y-1, z; #2 -x+1, -y+1, -z; #3 -x+1, -y+1, -z+1. [b] #1 -x+1, -y, -z+2. [c] #2 x-1, -y+3/2, z-1/2. [d] #1 x, -y+1/2, z-1/2; #2 x+1, -y+1/2, z+1/2. [e] #2 x+1, y, z; #4 -x+1, -y+1, -z.

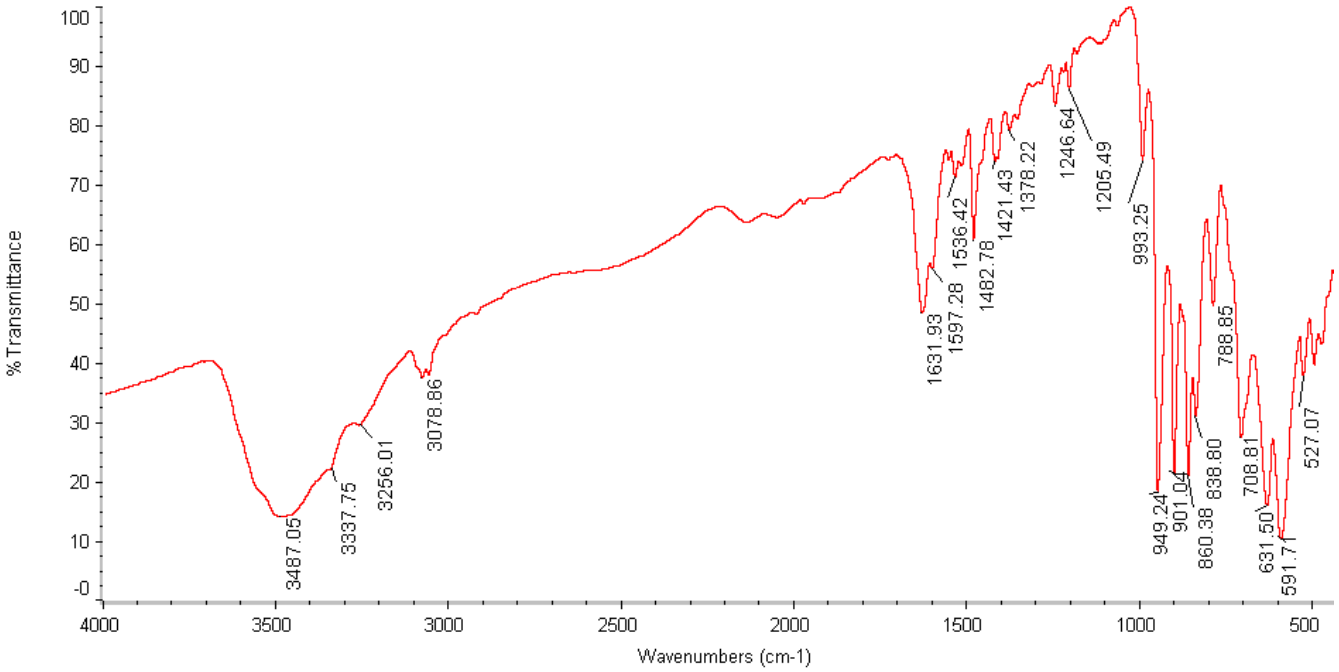


Figure S1a. IR spectrum of $[Mo_8O_{26}Cu_2(4\text{-abpt})_2]_n \cdot 4nH_2O$ (**1**)

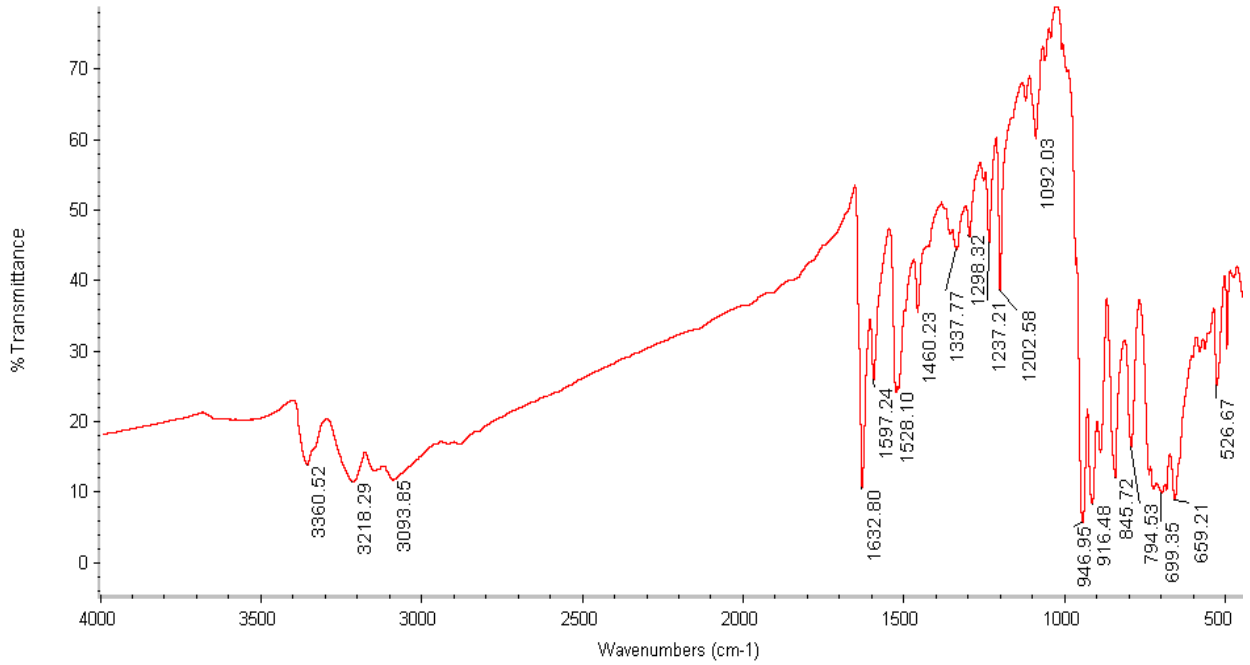


Figure S1b. IR spectrum of (4-H_2abpt)$_2$·[Mo_8O_{26}] (**2**)

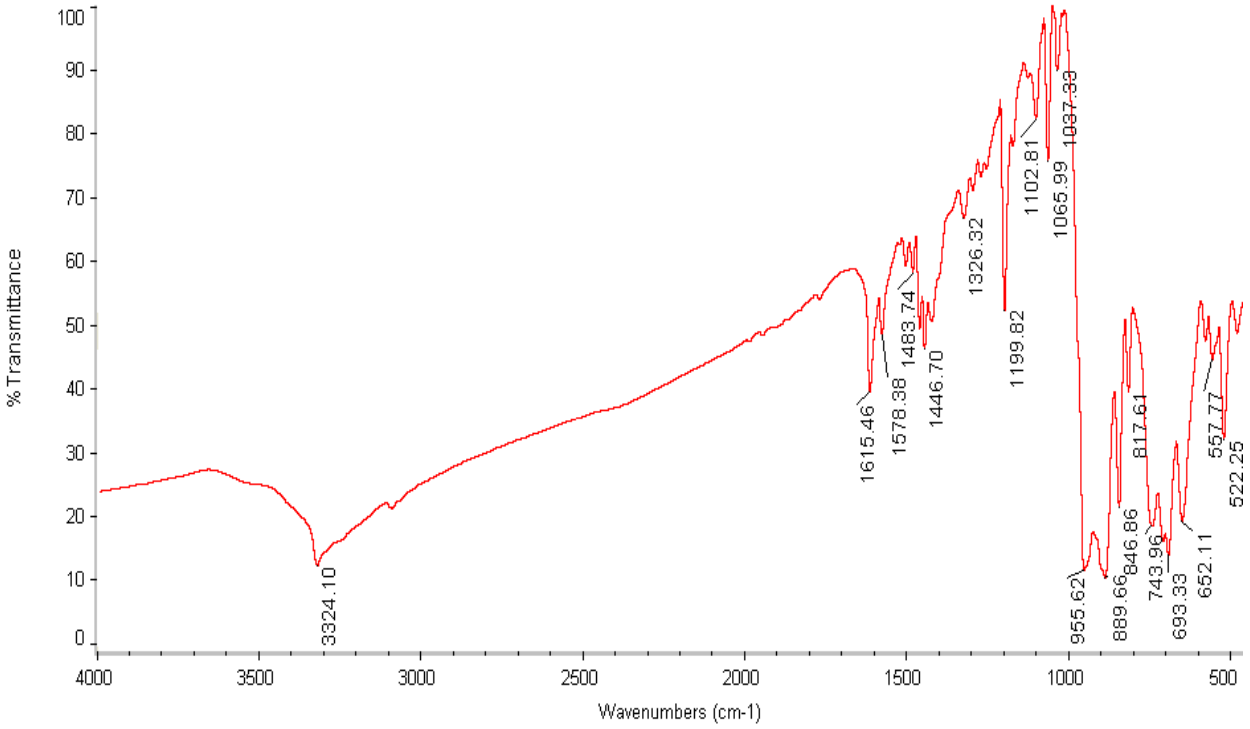


Figure S1c. IR spectrum of [$Mo_8O_{26}Cu_2$(3-abpt)$_2$(H_2O)$_2$]$_n$ (**3**)

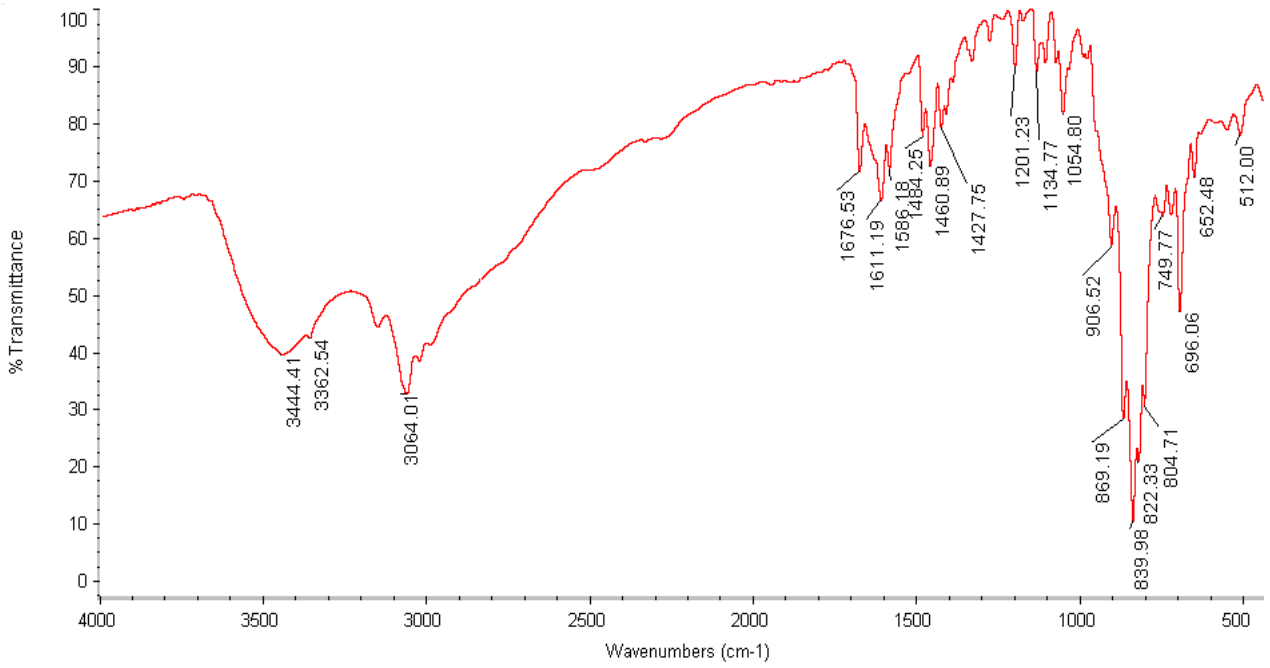


Figure S1d. IR spectrum of $[MoO_4Cu(3\text{-abpt})(H_2O)]_n$ (**4**)

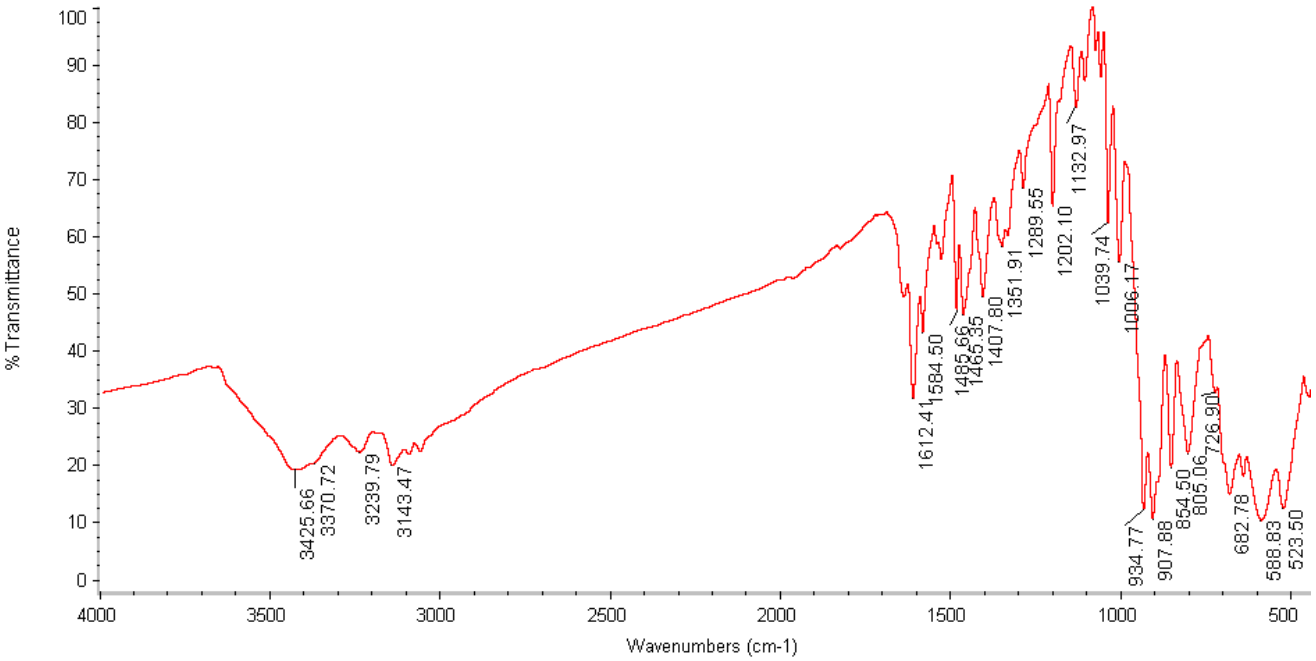


Figure S1e. IR spectrum of $[Mo_6O_{19}Co(3\text{-abpt})_2]_n{\cdot}4nH_2O$ (**5**)

Figure S1. Infrared spectra of complexes **1**-**5**

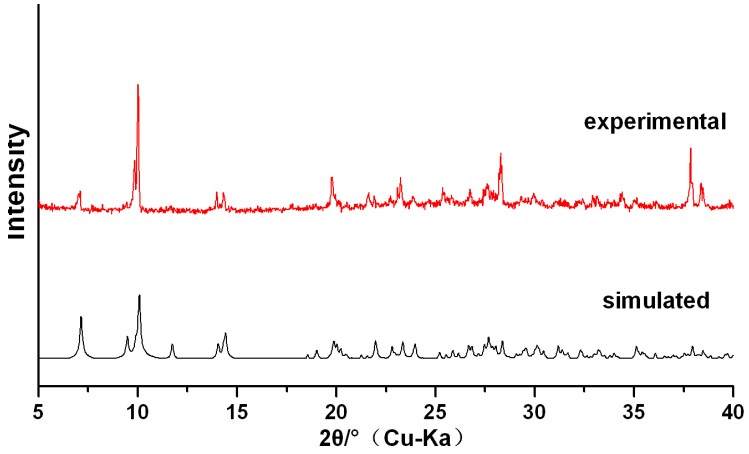


Figure S2a. The PXRD pattern of **1**.

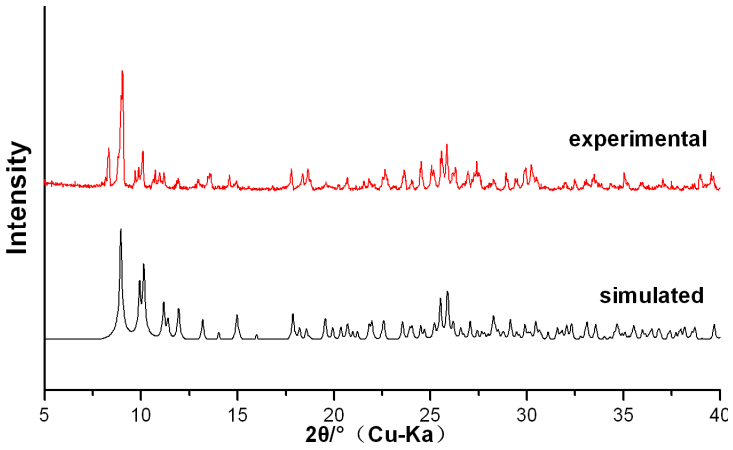


Figure S2b. The PXRD pattern of **2**.

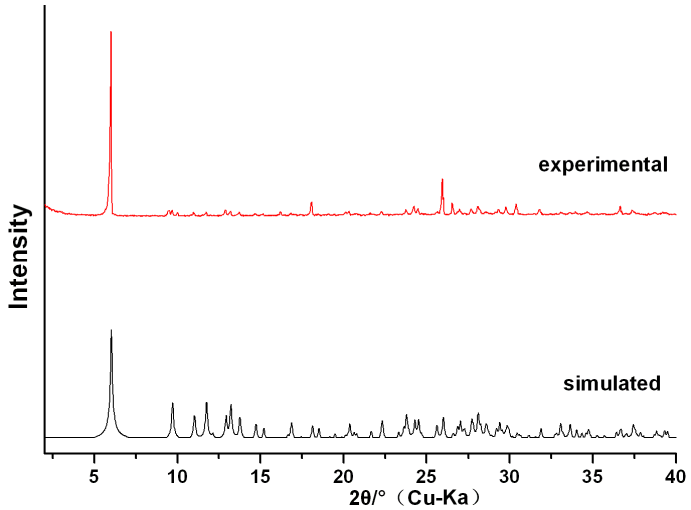


Figure S2c. The PXRD pattern of **3**.

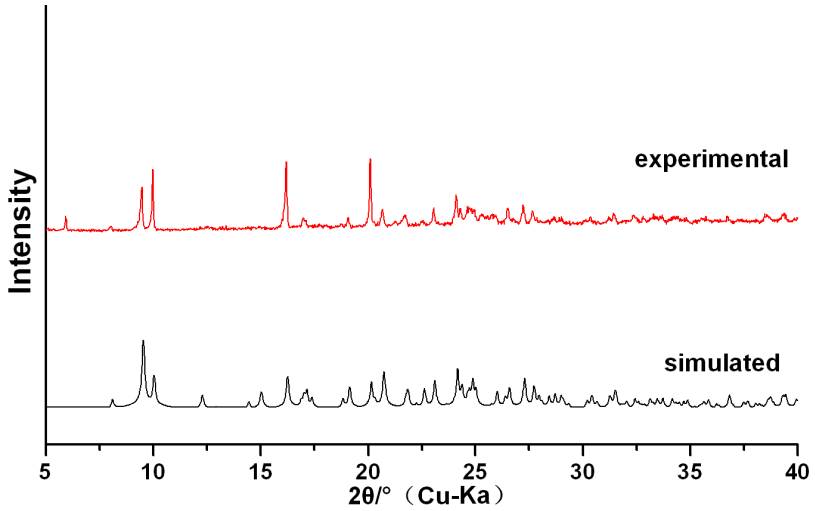


Figure S2d. The PXRD pattern of **4**.

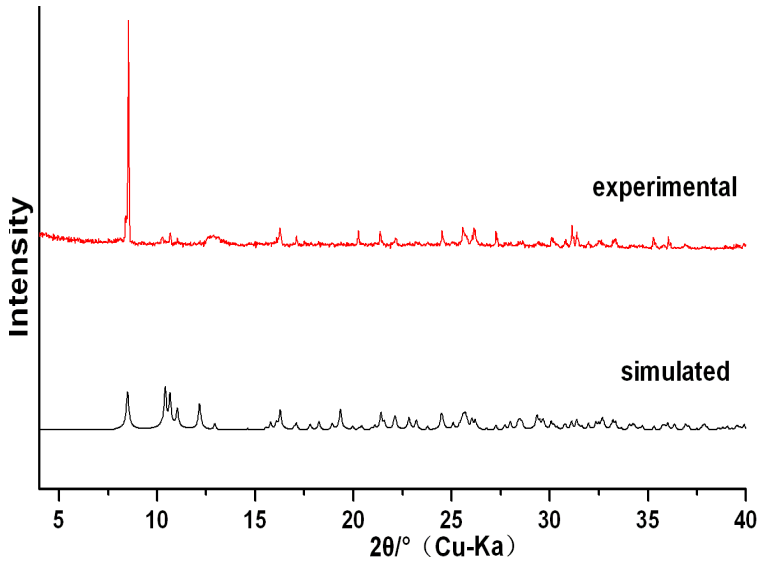
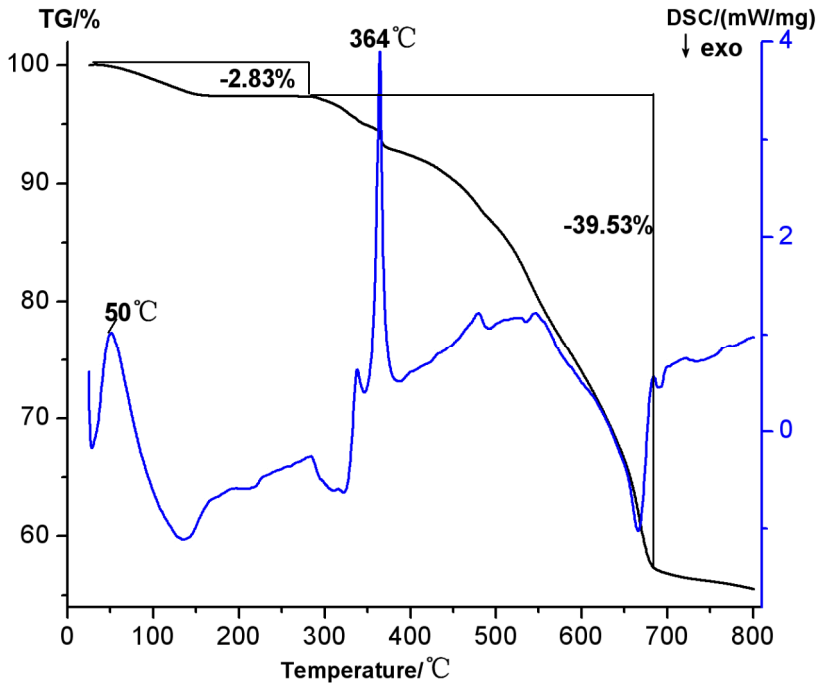


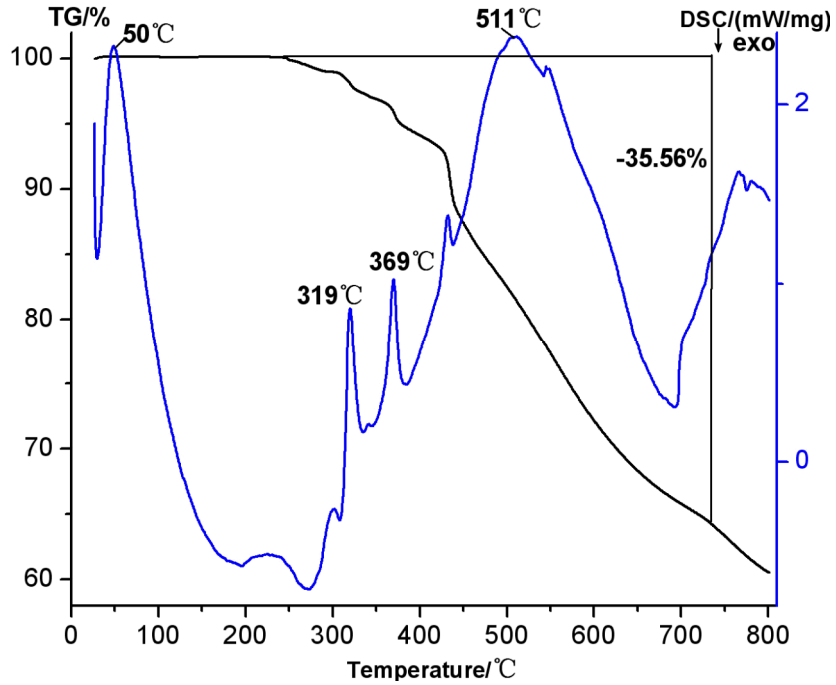
Figure S2e. The PXRD pattern of **5**.

Figure S2. The measured and simulated powder X-ray diffraction patterns of **1**–**5**

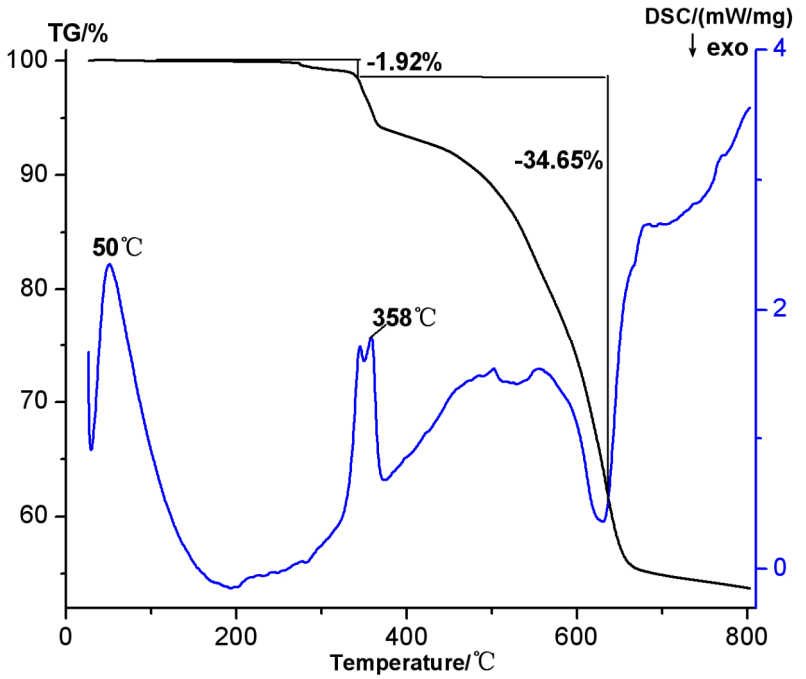
(The compound **2** and **4** seem to contain a crystalline impurity. We have not obtained more satisfying PXRD)



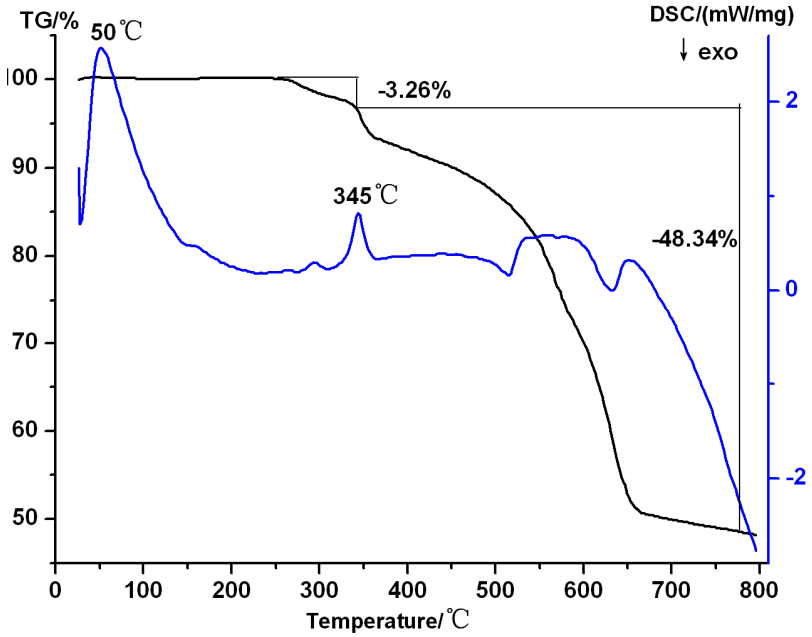
$[Mo_8O_{26}Cu_2(4\text{-abpt})_2]_n{\cdot}4nH_2O$ (**1**)



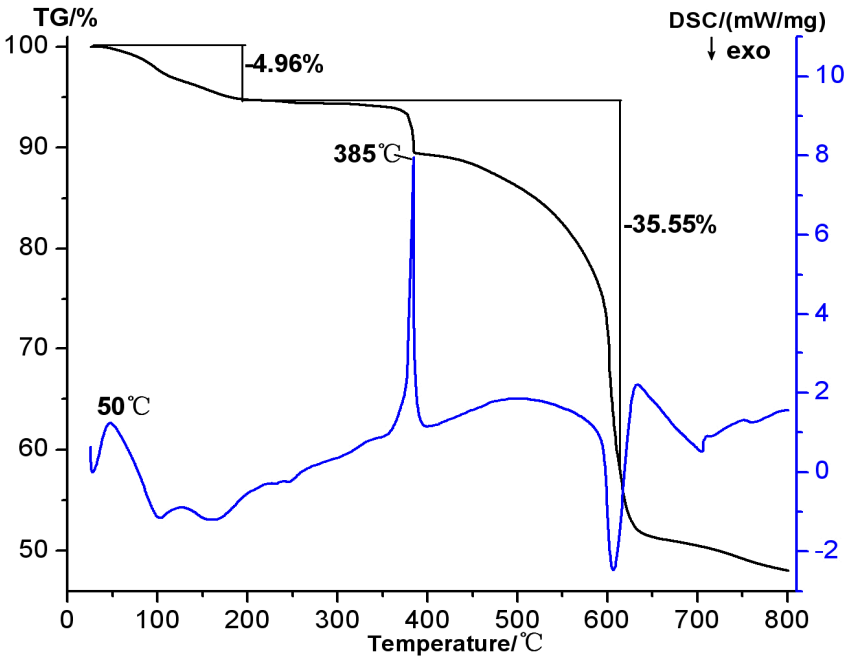
$(4\text{-}H_2abpt)_2{\cdot}[Mo_8O_{26}]$ (**2**)



$[Mo_8O_{26}Cu_2(3\text{-abpt})_2(H_2O)_2]_n$ (**3**)



$[MoO_4Cu(3\text{-abpt})(H_2O)]_n$ (**4**)



$[Mo_6O_{19}Co(3\text{-abpt})_2]_n{\cdot}4nH_2O$ (**5**)

Figure S3. Thermal analysis curves of **1**–**5**

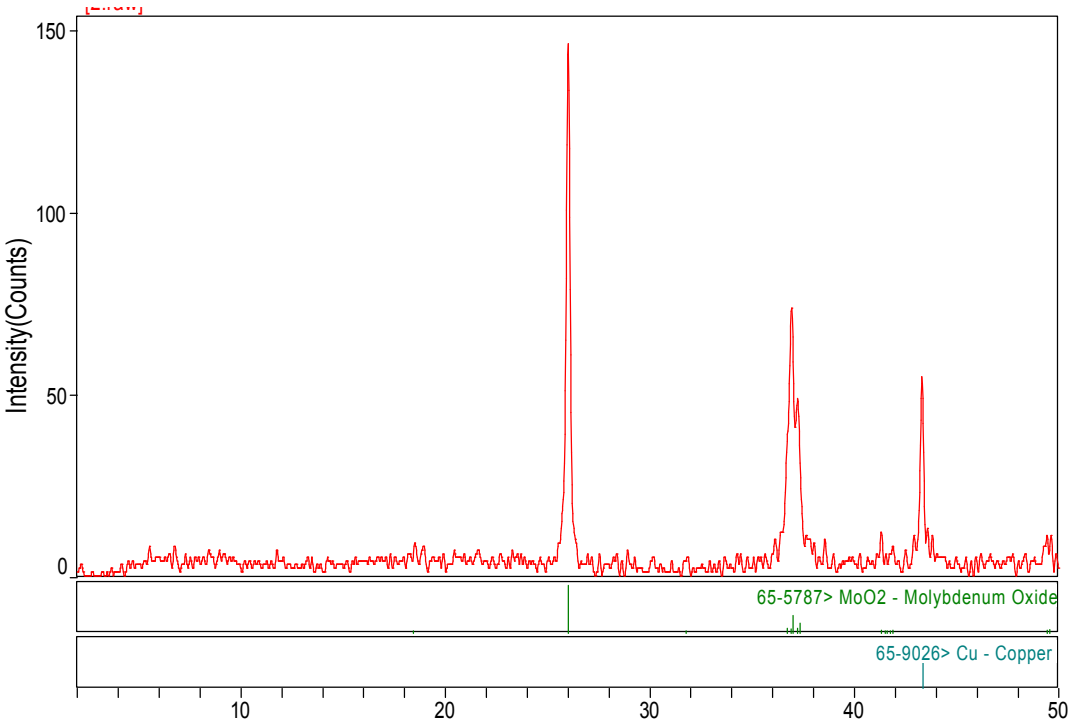


Figure S4a. The residue PXRD pattern of **1** (a mixture of MoO_2 and Cu)

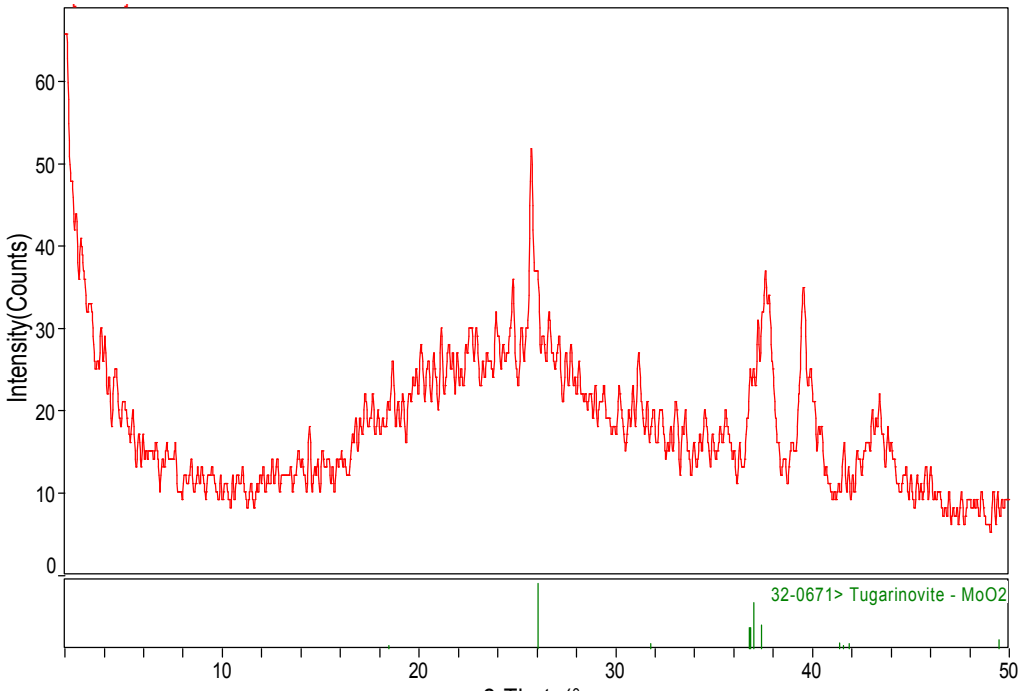


Figure S4b. The residue PXRD pattern of **2**（MoO_2）

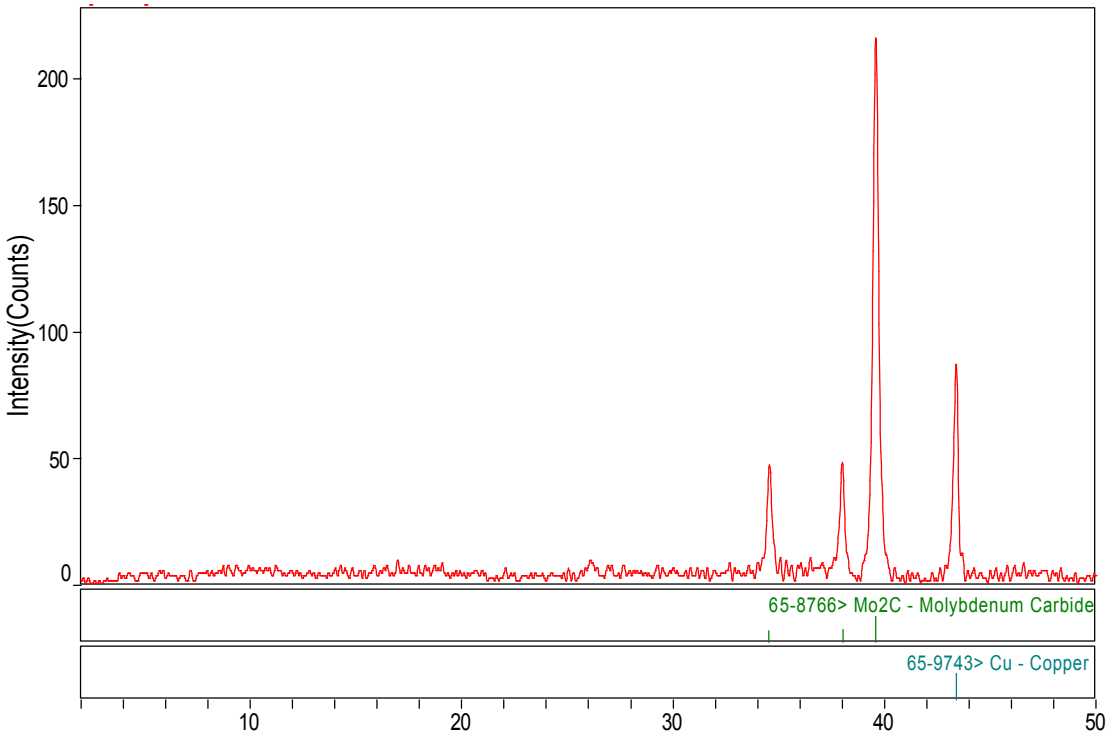


Figure S4c. The residue PXRD pattern of **3**（a mixture of Mo_2C and Cu）

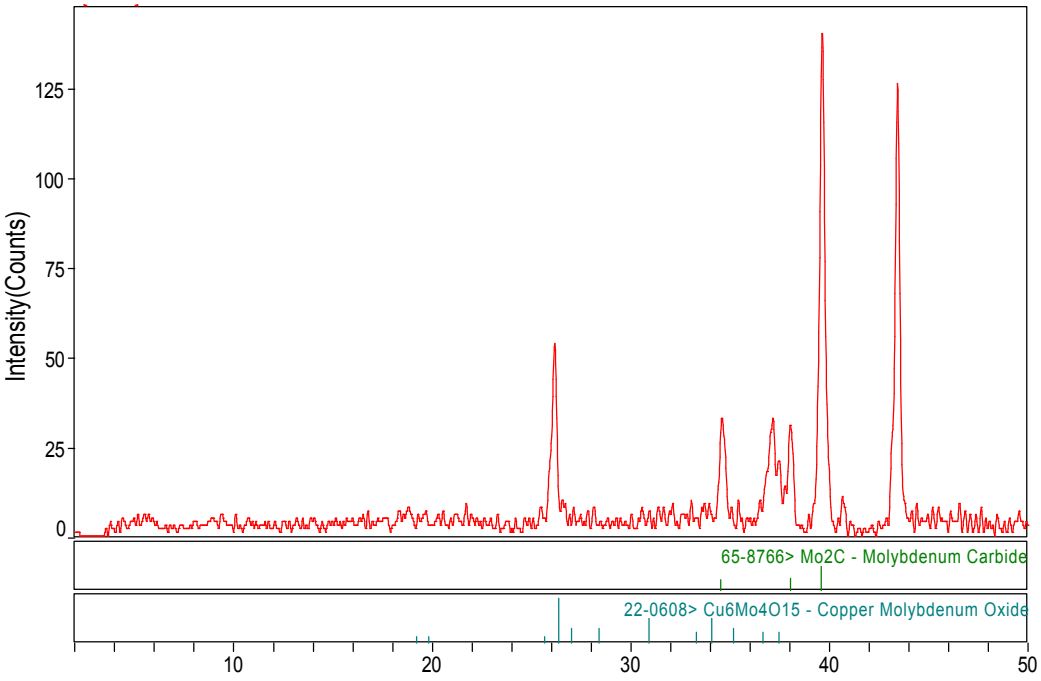


Figure S4d. The residue PXRD pattern of **4**（new compound $CuMoO_4$）

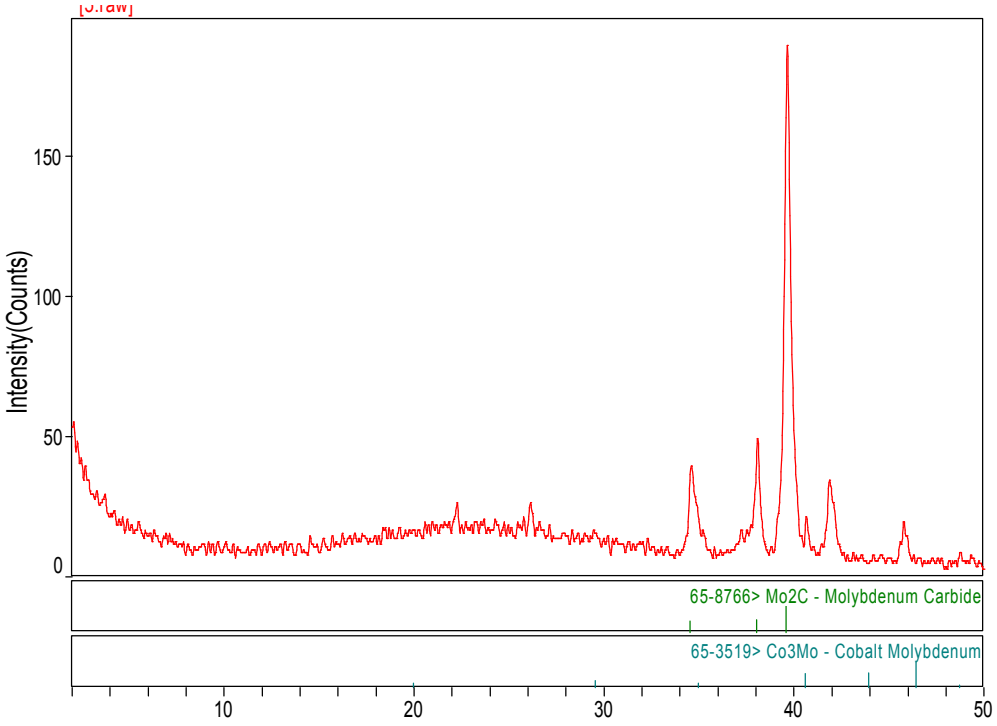


Figure S4e. The residue PXRD pattern of **5**（a mixture of Mo_2C and Co_3Mo）

Figure S4. The powder X-ray diffraction patterns of TG residues for **1**–**5**