Electronic Supplementary Material (ESI) for CrystEngComm.

Five compounds based on $[TeMo_6O_{24}]^{6-}$ and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions by using different symmetrical and asymmetric N-donor ligands

Jun Ying,* Chenxi Sun, Liang Jin, Aixiang Tian, Xiuli Wang*

Table S1. Selected bond lengths (Å) and angles (°) of compounds **1–5**.

Compound **1**

Cu(1)-N(2)	1.982(3)	Cu(1)-N(4) #3	1.997(3)
Cu(1)-O(6)	2.403(3)	Cu(1)-O(13)	1.903(2)
Cu(2)-N(1) #2	2.047(3)	Cu(2)-O(13)	1.909(2)
O(13)-Cu(1)-O(6)	95.53(11)	O(13)-Cu(1)-N(2)	88.48(11)
O(13)-Cu(1)-N(4) #3	93.65(11)	O(4)-Cu(1)-O(6)	88.55(9)
O(4)-Cu(1)-N(4) #3	89.46(11)	N(2)-Cu(1)-N(4) #3	175.30(12)
N(2)-Cu(1)-O(6)	89.58(11)	O(13) -Cu(2)-N(1)	87.37(10)

Symmetry codes for **1**: #1 1-X, 1-Y, 1-Z; #2 -X, 1-Y, 1-Z; #3 +X, 1-Y, -1/2+Z

Compound **2**

Cu(1)-O(12)	1.970(2)	Cu(1)-N(3)	2.032(3)
Cu(1)-N(2)	1.995(3)	Cu(1)-N(1)	2.000(3)
O(12)-Cu(1)-N(3)	174.58(11)	O(12)-Cu(1)-N(1)	94.48(11)
O(12)-Cu(1)-N(2)	93.67(11)	N(2)-Cu(1)-N(3)	85.76(11)
N(2)-Cu(1)-N(1)	168.41(13)	N(1)-Cu(1)-N(3)	85.35(12)

Symmetry codes for **2**: #1 1-X,1-Y,1-Z

Compound **3**

Cu(1)-N(1) #2	1.968(6)	Cu(1)-N(3) #3	2.027(7)
Cu(1)-N(2)	1.978(7)	N(1)-C(2)	1.331(9)
N(1)#2-Cu(1)-N(3) #3	118.9(3)	N(1) #2-Cu(1)-N(2)	129.7(3)
N(2)-Cu(1)-N(3) #3	108.9(3)	C(2)-N(1)-Cu(1) #4	120.7(6)
C(1)-N(1)-Cu(1) #4	119.8(5)	C(2)-N(1)-C(1)	117.2(6)

Symmetry codes for **3**: #1 5/2-X, 1/2-Y; #2 +X, 1-Y, -1/2+Z; #3 2-X, +Y, 1/2-Z

Compound **4**

Cu(1)-O1W	1.949(4)	Cu(1)-O2W	1.986(4)
Cu(1)-N(4) #2	1.944(4)	Cu(1)-N(1)	1.958(4)
O1W-Cu(1)-O2W	164.36(17)	O1W-Cu(1)-N(1)	89.82(16)
N(4) #2-Cu(1)-O2W	91.82(16)	N(4) #2-Cu(1)-O1W	88.92(16)
N(4) #2-Cu(1)-N(1)	173.55(18)	N(1)-Cu(1)-O2W	91.10(16)

Symmetry codes for **4**: #1 2-X,1-Y,1-Z; #2 +X,+Y,1+Z

Compound **5**

Cu(1)-O(25)	1.929(4)	Cu(1)-O(12)	2.201(4)
Cu(1)-N(1) #4	1.990(5)	Cu(1)-N(2)	2.078(5)
Cu(3)-O(22) #5	1.968(4)	Cu(3)-O(15) #6	2.303(4)
Cu(2)-O(25)	1.927(4)	Cu(2)-N(3)	1.966(4)
O(9) #3-Cu(1)-O(12)	98.54(16)	O(9) #3-Cu(1)-N(1) #4	87.86(17)
O(25)-Cu(1)-O(12)	97.23(17)	N(1) #4-Cu(1)-O(12)	93.39(18)
O(22)-Cu(3)-O3W	90.19(17)	O(22)-Cu(3)-O(15) #6	90.83(15)
O1W-Cu(2)-N(3)	174.72(19)	O(25)-Cu(2)-O1W	90.86(17)

Symmetry codes for **5**: #1 2-X, 1-Y, 1-Z; #2 1-X, 1-Y, 2-Z; #3 1-X, 1-Y, 1-Z; #4 1-X, 2-Y, 1-Z; #5 2-X, 1-Y, 2-Z; #6 1+X, +Y, +Z

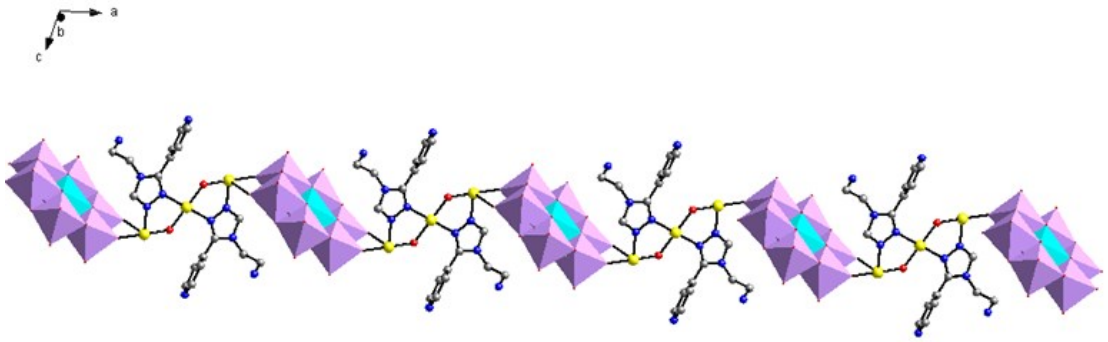

Fig. S1. The 1D chain of **1** with tri-nuclear Cu clusters linked by Anderson anions.

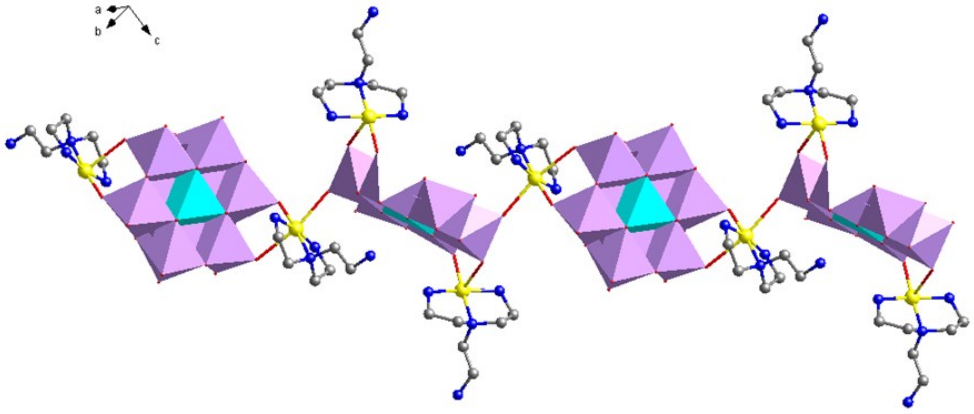

Fig. S2. The 1D chain of **2** with $[Cu(talm)]^{2+}$ subunits linked by Anderson anions.

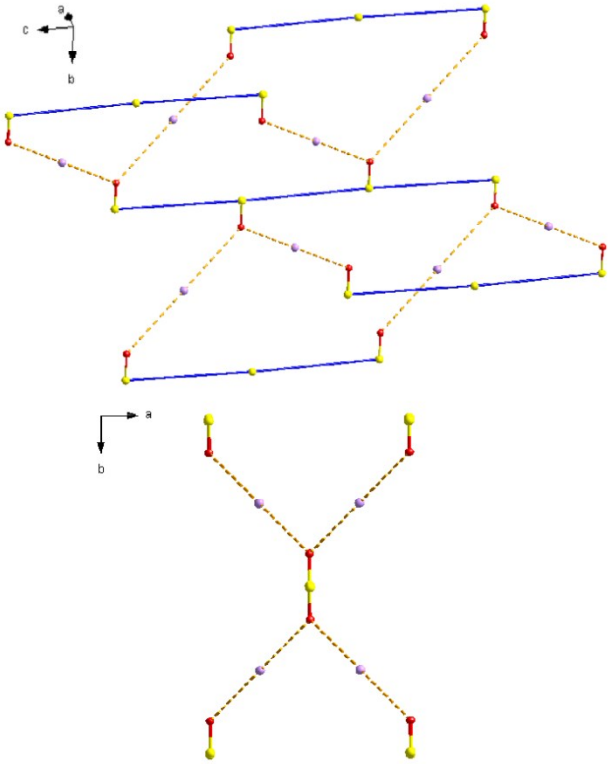

Fig. S3. The 2D topological structure connected by hydrogen bonds of compound **2** and the topology along *ab* plane. β-Mo_8 (purple), Ptep ligand (blue), Cu (yellow), O (red).

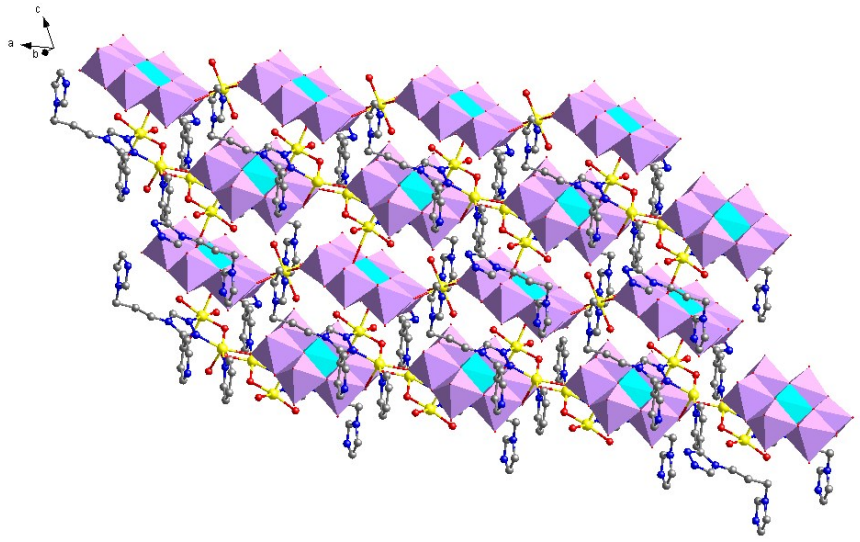

Fig. S4. The 2D sheet structure of **5**.

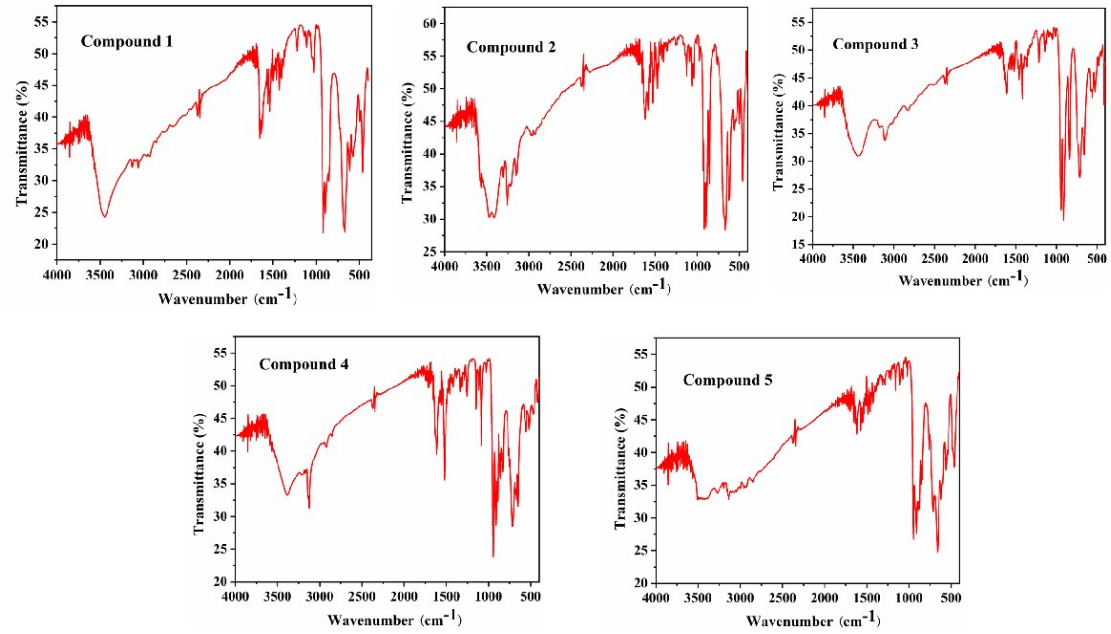

Fig. S5. The IR spectra of compounds **1**–**5**.

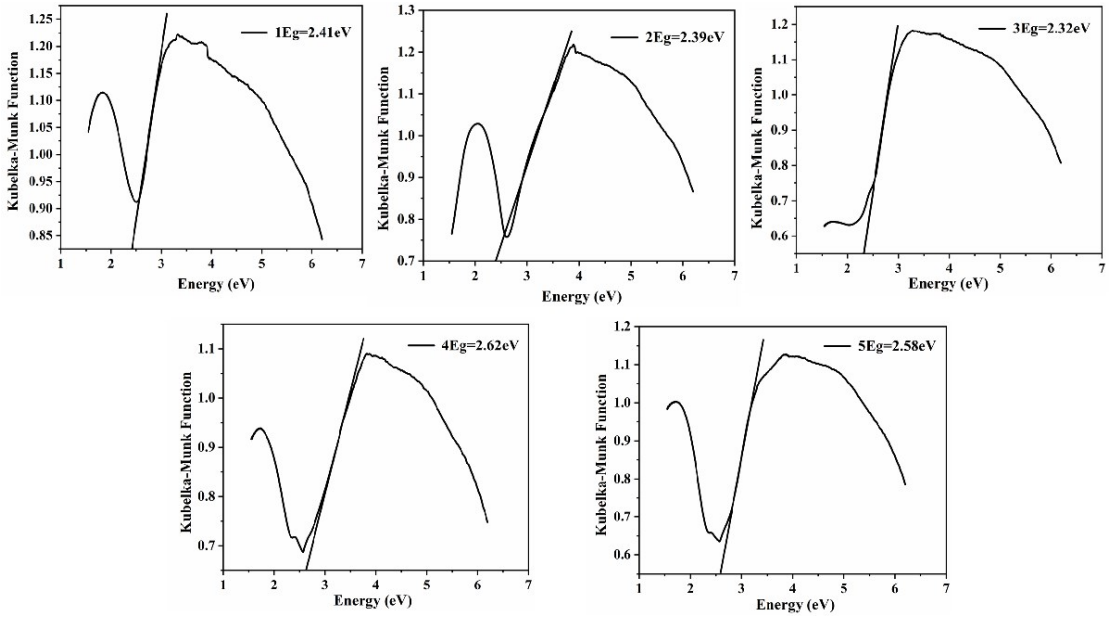

Fig. S6. The solid-state optical diffuse-reflectance spectra of compounds **1–5**.

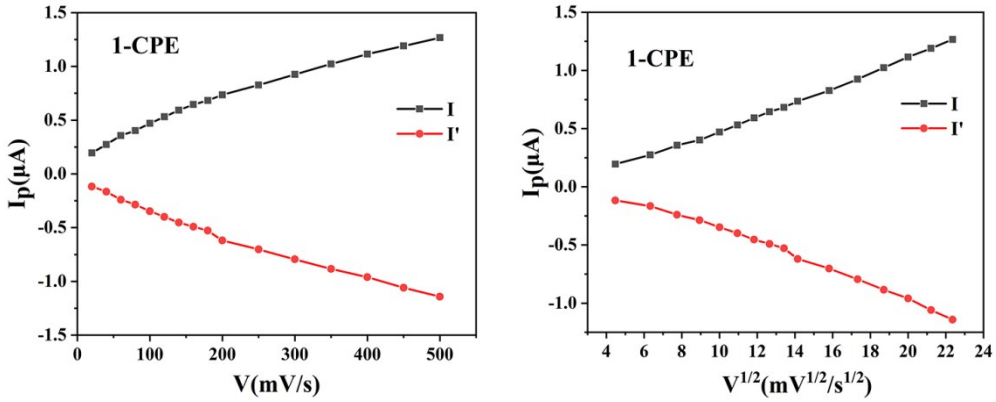

Fig. S7. The dependence of anodic peak and cathodic peak currents of **1**–CPE on scan rates.

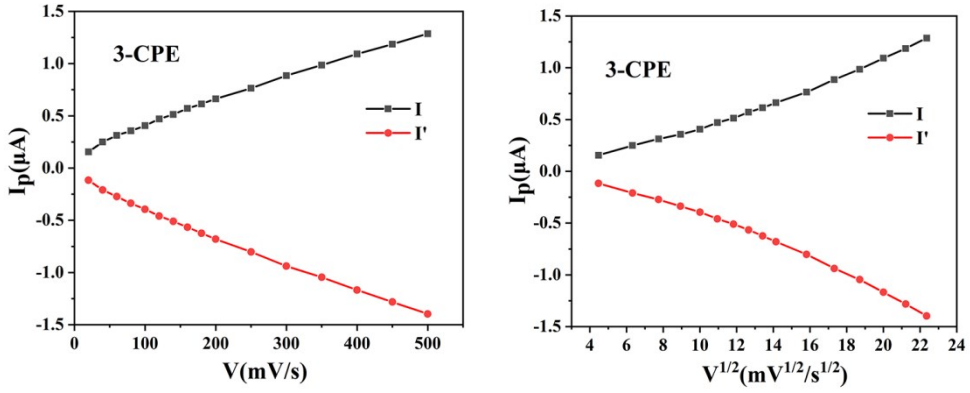

Fig. S8. The dependence of anodic peak and cathodic peak currents of **3**–CPE on scan

rates.

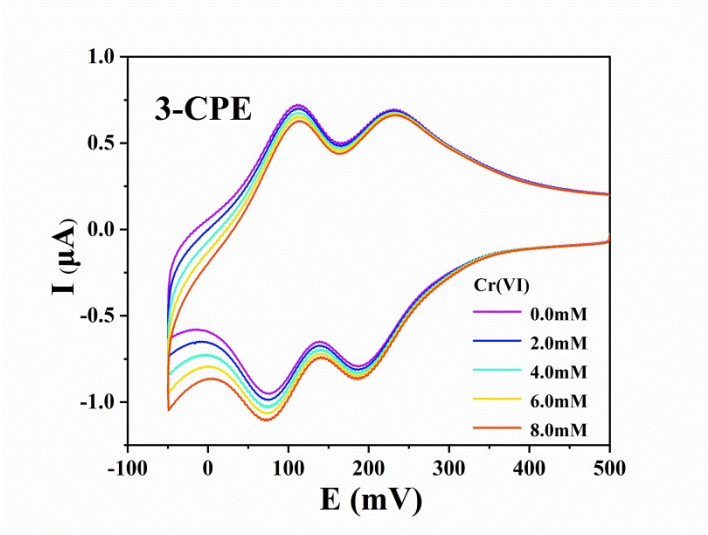

Fig. S9. Cyclic voltammograms of the **3**–CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution containing 0–8 mM Cr(Ⅵ). Scan rate: 200 $mV \cdot s^{-1}$.

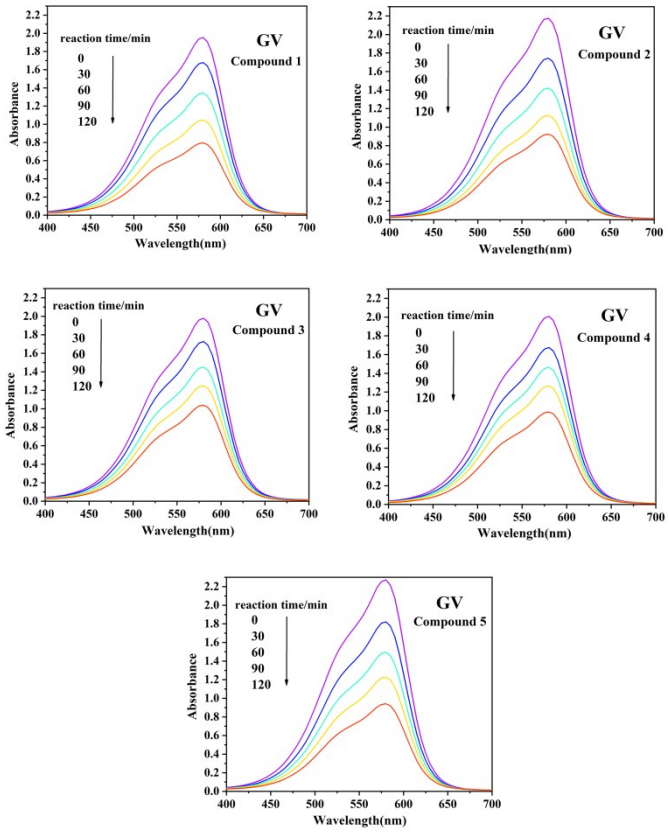

Fig. S10. The absorption spectra of GV solution during the decomposition reaction under UV irradiation with compounds **1**–**5** as the catalyst.

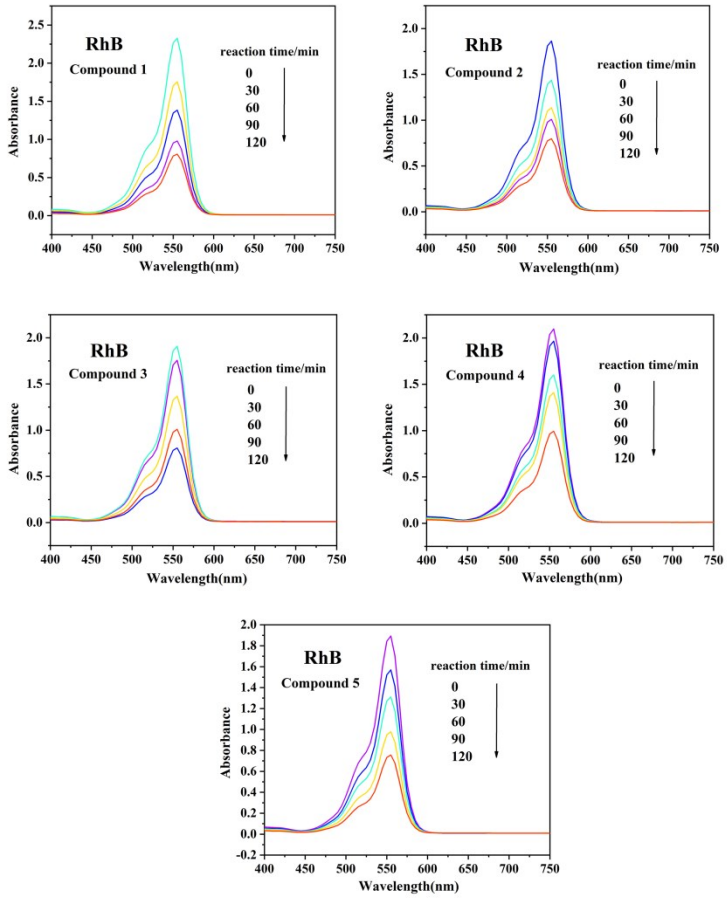

Fig. S11. The absorption spectra of RhB solution during the decomposition reaction under UV irradiation with compounds **1–5** as the catalyst.

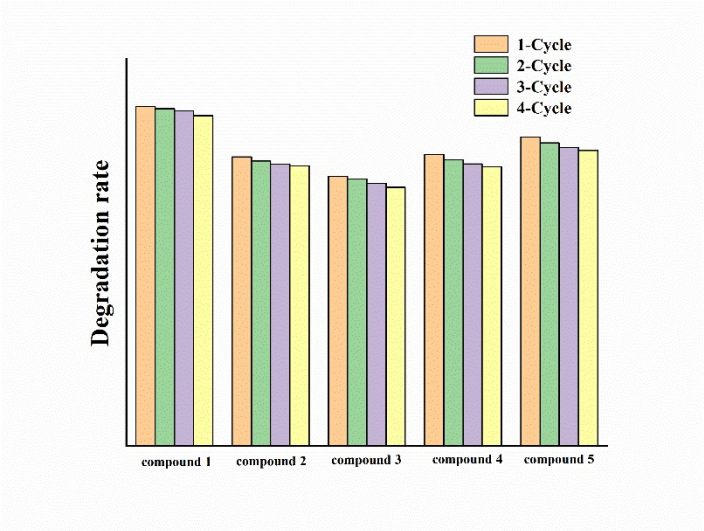

Fig. S12. Four cycles of photocatalytic degradation of compounds **1–5**.

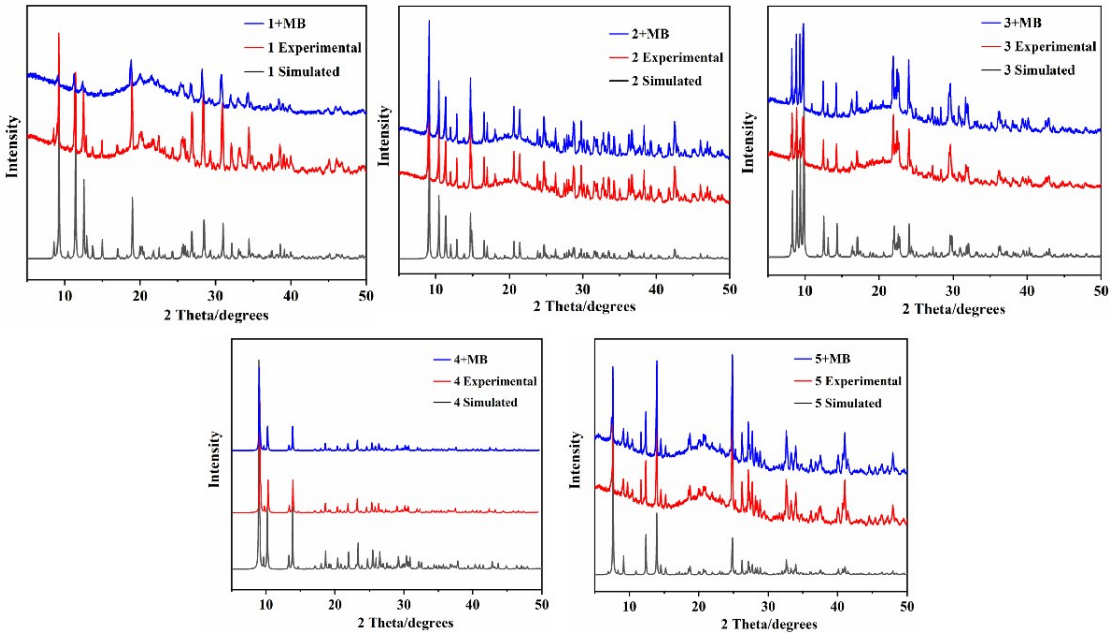

Fig. S13. The PXRD spectra of compounds **1–5**.

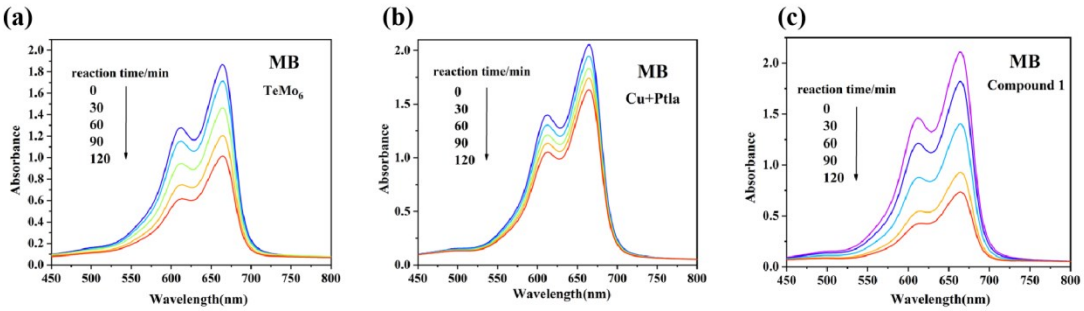

Fig. S14. Under UV irradiation, the absorption spectrum of MB solution after adding $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$(a), metal organic unit(b), and compound **1**(c).

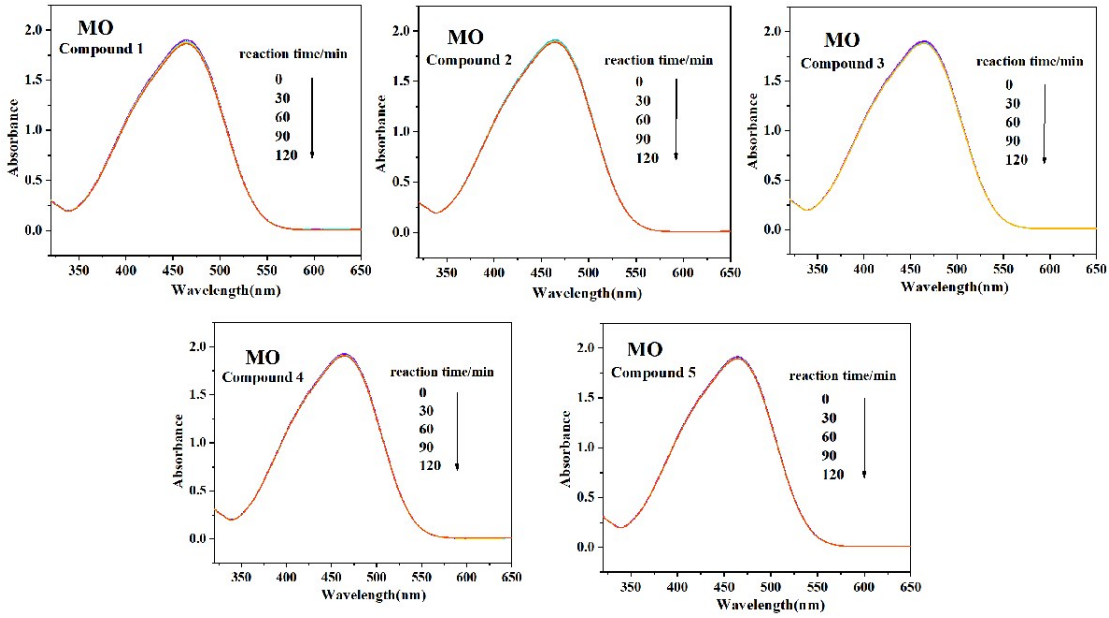

Fig. S15. The absorption spectra of the MO solution with the compounds **1–5** as the catalyst.

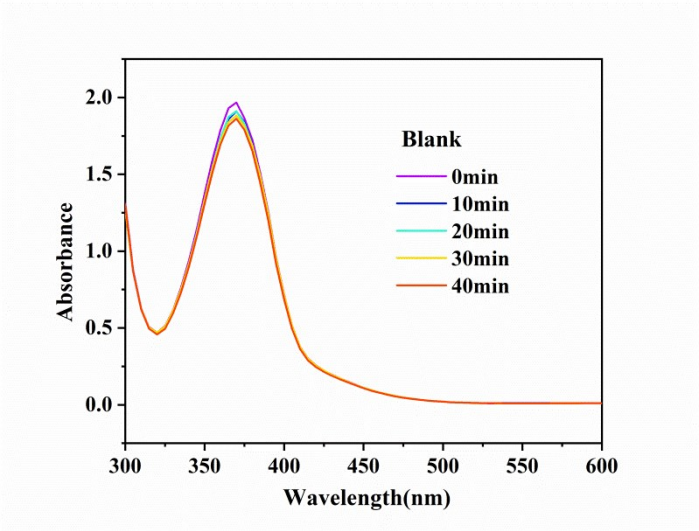

Fig. S16. UV spectra of the Cr(VI) solution without compounds used as the photoreduction catalysts.

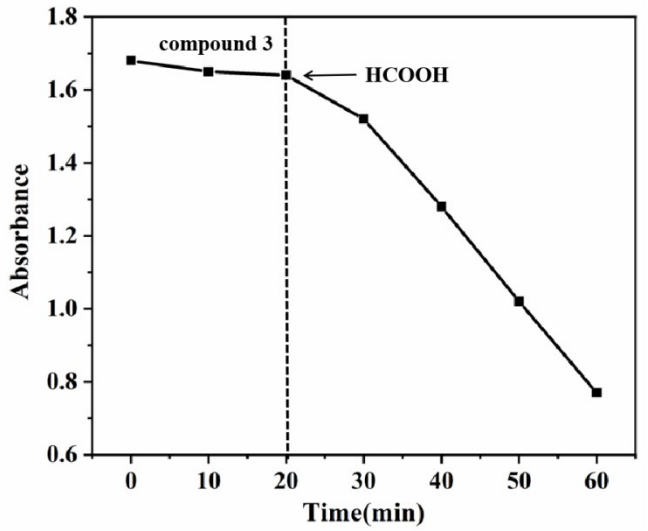

Fig. S17. Comparative experiment of compound **3** catalytic reduction Cr(VI): no formic acid was added in the first 20 minutes, and formic acid was added after 20 minutes.

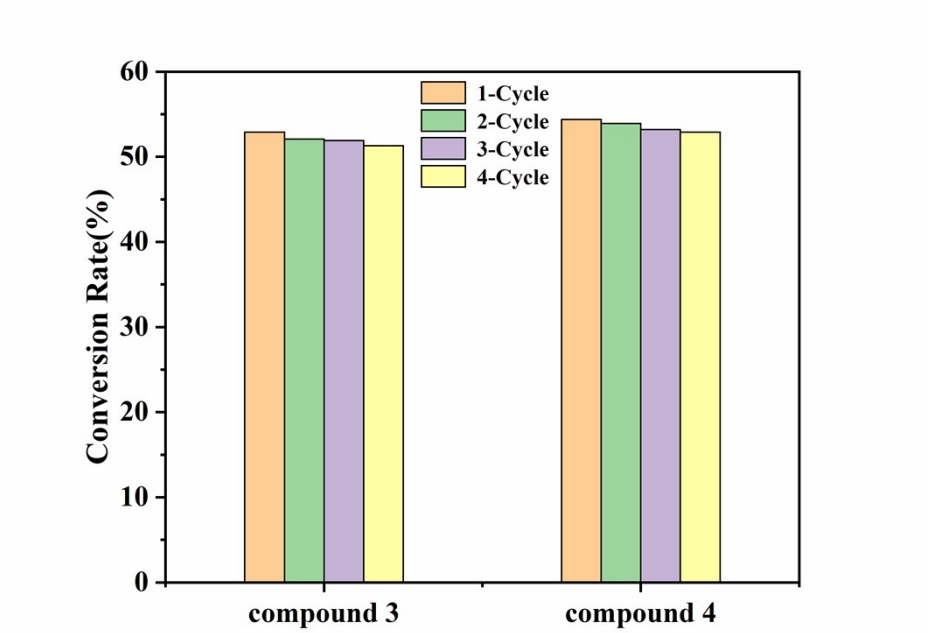

Fig. S18. Four cycles of photocatalytic reduction of compounds **3** and **4**.