Supplementary Material (ESI) for Dalton Transactions
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Novel Anderson-type $[TeMo_6O_{24}]^{6-}$-based metal-organic complexes tuned by different species and their coordination modes: Assembly, various architectures and properties

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Table. S1. Selected bond distances (Å) and angles (°) for the title complexes**.**

Complex **1**

Zn(1)–O(1W)	2.048(6)
Zn(1)–N(1)	2.088(7)
Zn(1)–O(8W)	2.129(6)
Zn(2)–O(1)	2.115(6)

Zn(2)–O(4W)	2.121(7)
Zn(2)–O(5W)	2.094(7)
O(1W)–Zn(1)–O(7W)	94.6(2)

O(7W)–Zn(1)–N(1)	172.4(3)
O(7W)–Zn(1)–O(2)	89.3(2)
O(1W)–Zn(1)–O(8W)	88.6(2)

N(1)–Zn(1)–O(8W)	92.9(3)
O(1W)–Zn(1)–O(3)	177.0(3)
N(1)–Zn(1)–O(3)	86.2(3)

O(8W)–Zn(1)–O(3)	88.7(2)	O(5W)–Zn(2)–O(3W)
O(2W)–Zn(2)–O(4W)	91.6(3)	O(2W)–Zn(2)–O(1)
O(4W)–Zn(2)–O(1)	178.0(3)	O(2W)–Zn(2)–O(6W)
O(4W)–Zn(2)–O(6W)	91.4(3)	O(1)–Zn(2)–O(6W)
O(2W)–Zn(2)–O(5W)	93.9(3)	O(4W)–Zn(2)–O(5W)

O(1)–Zn(2)–O(5W)	90.8(3)	O(6W)–Zn(2)–O(5W)
O(2W)–Zn(2)–O(3W)	174.4(3)	O(4W)–Zn(2)–O(3W)
O(1)–Zn(2)–O(3W)	87.7(2)	O(6W)–Zn(2)–O(3W)

Complex **2**

Zn(1)–O(1W)	2.060(4)	Zn(1)–O(2W)
Zn(1)–O(3W)	2.083(4)	Zn(1)–O(4W)
Zn(1)–O(1)	2.143(3)	Zn(1)–N(1)

Zn(2)–O(5W)	2.059(4)	Zn(2)–O(5W)#1
Zn(2)–N(2)	2.122(4)	Zn(2)–N(2)#1
Zn(2)–O(6W)#1	2.179(4)	Zn(2)–O(6W)
O(1W)–Zn(1)–O(2W)	92.44(15)	O(1W)–Zn(1)–O(1)
O(4W)–Zn(1)–O(3W)	174.07(16)	O(4W)–Zn(1)–O(1)

O(1W)–Zn(1)–O(4W)	96.35(17)	O(3W)–Zn(1)–O(1)
O(4W)–Zn(1)–O(2W)	86.78(14)	O(1W)–Zn(1)–O(4W)
O(1W)–Zn(1)–O(3W)	87.78(16)	O(5W)#1–Zn(2)–O(6W)
O(3W)–Zn(1)–O(2W)	88.80(15)	O(1W)–Zn(1)–O(2W)
O(2W)–Zn(1)–O(1)	89.48(14)	N(2)#1–Zn(2)–O(6W)

O(1W)–Zn(1)–N(1)	89.43(18)	N(2)–Zn(2)–O(6W)
O(4W)–Zn(1)–N(1)	89.75(16)	O(5W)–Zn(2)–O(5W)#1
O(3W)–Zn(1)–N(1)	94.96(16)	O(5W)–Zn(2)–N(2)
O(2W)–Zn(1)–N(1)	175.72(16)	O(5W)#1–Zn(2)–N(2)
O(1)–Zn(1)–N(1)	88.83(15)	O(5W)–Zn(2)–N(2)#1

N(2)#1–Zn(2)–O(6W)#1	90.94(16)	O(5W)#1–Zn(2)–N(2)#1
O(5W)–Zn(2)–O(6W)	89.39(18)	N(2)–Zn(2)–N(2)#1
O(5W)–Zn(2)–O(6W)#1	90.61(18)	O(6W)#1–Zn(2)–O(6W)
O(5W)#1–Zn(2)–O(6W)#1	89.39(18)	N(2)–Zn(2)–O(6W)#1

Symmetry codes for **2:** #**1** –x+1,–y–1,–z–2

Complex **3**

Cu(1)–O(3W)	1.942(2)	Cu(1)–O(1)
Cu(1)–N(1)	1.982(3)	Cu(1)–O(1W)
Cu(1)–O(2W)	2.400(3)	O(1)–Cu(1)–N(1)
O(3W)–Cu(1)–N(1)	172.80(12)	O(1)–Cu(1)–O(1W)
O(3W)–Cu(1)–O(1W)	91.32(11)	O(3W)–Cu(1)–O(2W)

	N(1)–Cu(1)–O(1W)	88.37(11)	N(1)–Cu(1)–O(2W)
	O(1)–Cu(1)–O(2W)	94.25(9)	O(3W)–Cu(1)–O(1)
	O(1W)–Cu(1)–O(2W)	88.18(9)	

Complex **4**

Cu(1)–N(1)	2.014(2)	Cu(1)–O(1)	2.316(2)
Cu(1)–O(2)	2.303(2)	Cu(1)–O(1W)	1.955(2)
Cu(1)–O(2W)	2.030(2)	Cu(1)–O(3W)	2.014(2)
Cu(2)–N(2)	1.995(2)	Cu(2)–N(2)#1	1.995(2)
Cu(2)–O(3)	2.242(2)	Cu(2)–O(3)#1	2.242(2)
Cu(2)–O(4W)	2.045(2)	Cu(2)–O(4W)#1	2.045(2)
O(1W)–Cu(1)–N(1)	177.27(12)	O(1W)–Cu(1)–O(3W)	86.09(11)
N(1)–Cu(1)–O(3W)	91.54(10)	O(1W)–Cu(1)–O(2W)	89.20(11)
N(1)–Cu(1)–O(2W)	93.29(10)	O(3W)–Cu(1)–O(2W)	172.54(9)
O(1W)–Cu(1)–O(2)	90.54(8)	N(1)–Cu(1)–O(2)	88.59(9)
O(3W)–Cu(1)–O(2)	100.99(8)	O(2W)–Cu(1)–O(2)	84.82(8)
O(1W)–Cu(1)–O(1)	92.92(8)	N(1)–Cu(1)–O(1)	88.30(9)
O(3W)–Cu(1)–O(1)	86.78(8)	O(2W)–Cu(1)– O(1)	87.70(8)
O(2)–Cu(1)–O(1)	171.71(7)	N(2)–Cu(2)–N(2)#1	179.999(2)
N(2)–Cu(2)–O(4W)	91.21(9)	N(2)#1–Cu(2)–O(4W)	88.79(9)
N(2)–Cu(2)–O(4W)#1	88.79(9)	N(2)#1–Cu(2)–O(4W)#1	91.21(9)
O(4W)–Cu(2)–O(4W)#1	179.999(1)	N(2)–Cu(2)–O(3)#1	91.62(8)
N(2)#1–Cu(2)–O(3)#1	88.38(8)	O(4W)–Cu(2)–O(3)#1	96.37(8)
O(4W)#1–Cu(2)–O(3)#1	83.63(8)	N(2)–Cu(2)–O(3)	88.38(8)
N(2)#1–Cu(2)–O(3)	91.62(8)	O(4W)–Cu(2)–O(3)	83.63(8)
O(4W)#1–Cu(2)–O(3)	96.37(8)	O(3)#1–Cu(2)–O(3)	179.999(1)

Symmetry codes for **4**: #1-x+2,-y-1,-z

Table S2a. Selected hydrogen–bonding geometry (Å, º) for complex **1**

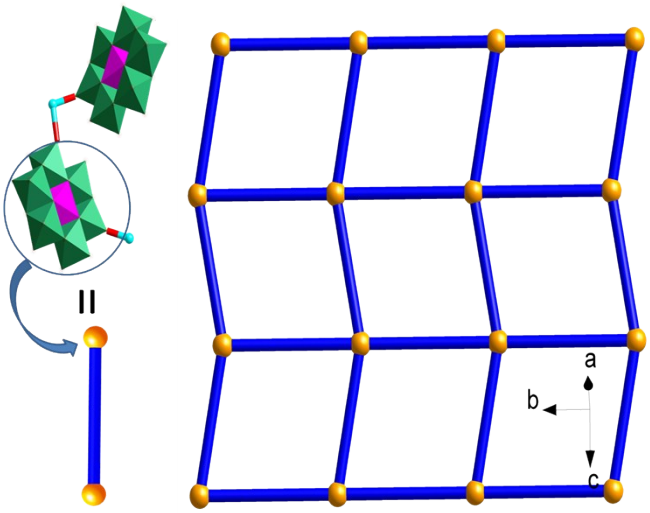
D–H···A	D–H	H···A	D···A	D–H···A
C(4)–H(4A)···O(24)	0.93	2.35	3.246	161
C(13)–H(13A)···O(18)	0.93	2.51	3.322	146

Table S2b. Selected hydrogen–bonding geometry (Å, º) for complex **2**

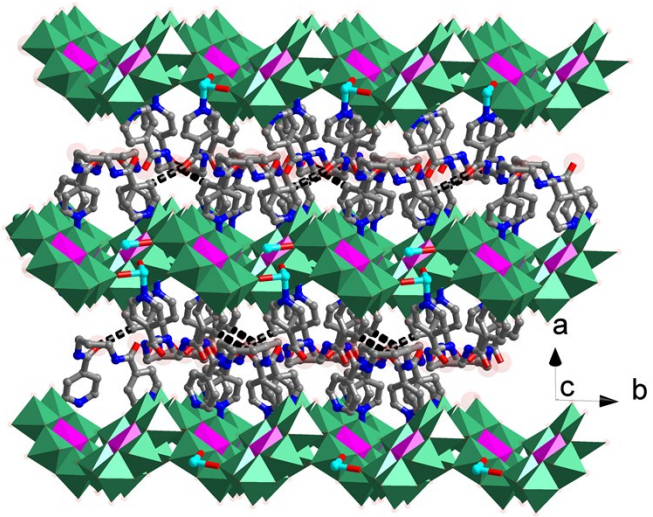
D–H···A	D–H	H···A	D···A	D–H···A
C(13)–H(13A)···O(12)	0.93	2.57	3.261	131

Table S2c. Selected hydrogen–bonding geometry (Å, º) for complex **3**

D–H···A	D–H	H···A	D···A	D–H···A
C(12)–H(12A)···O(13)	0.93	2.45	3.079(5)	125



(a)



(b)

Fig. S1. (a) Schematic view of the 2D net in **3.** All 4-dpyp molecules and coordinated water molecules are omitted for clarity**; (b)** Representation of the 3D supramolecular framework of **3.**

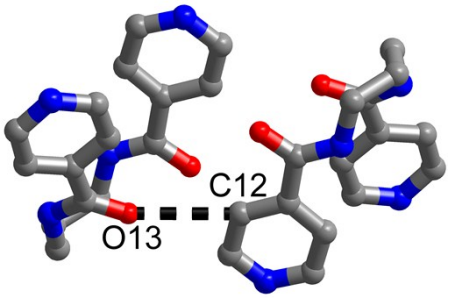


Fig. S2. Selected hydrogen bond C(12)–H(12A)···O(13) for complex **3**

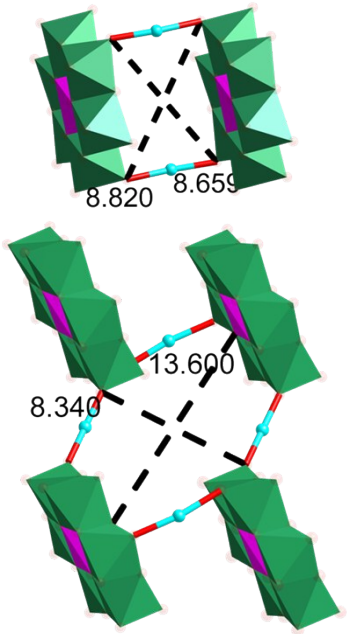


Fig. S3. Two types of the $Cu_n(TeMo_6)_n$ loops in complex **4**.

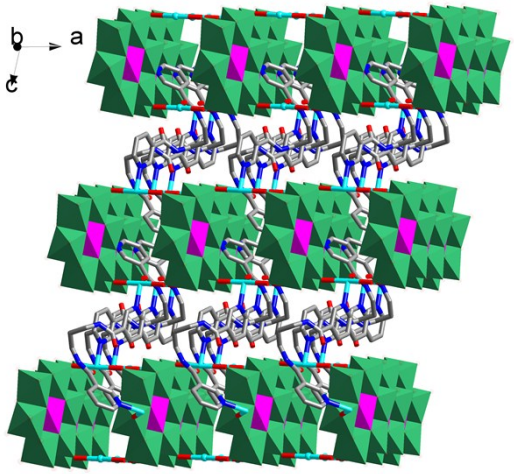


Fig. S4. The 3D framework of complex **4**.

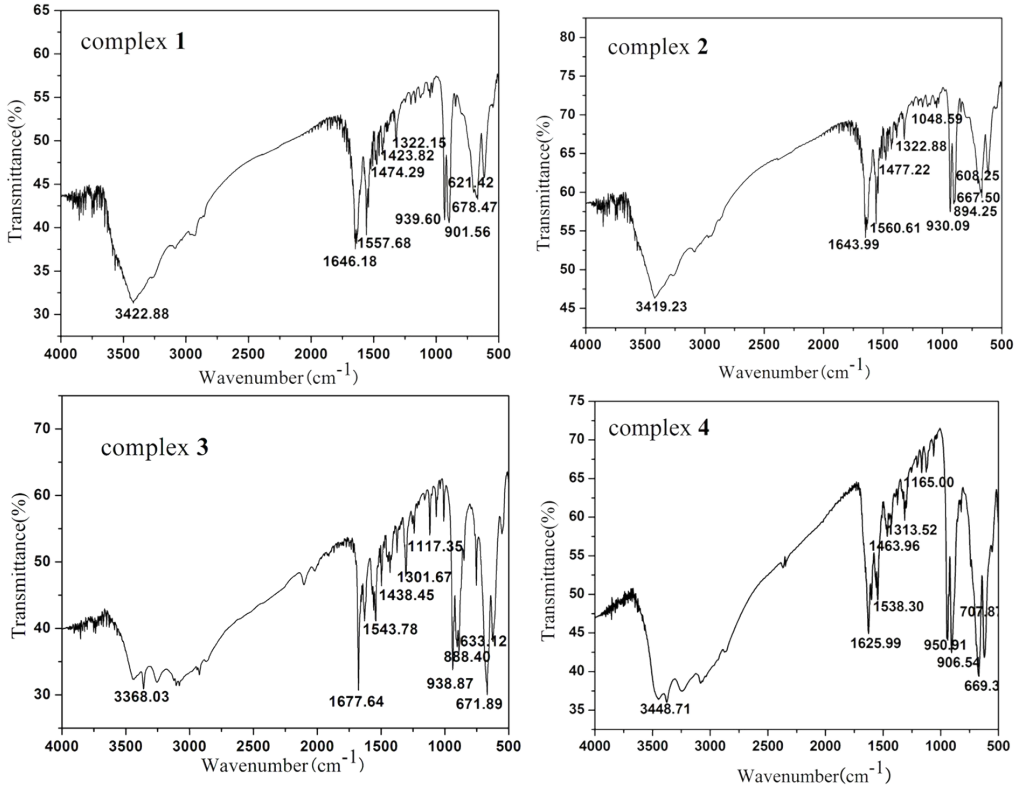


Fig. S5. The IR spectra of the title complexes**.**

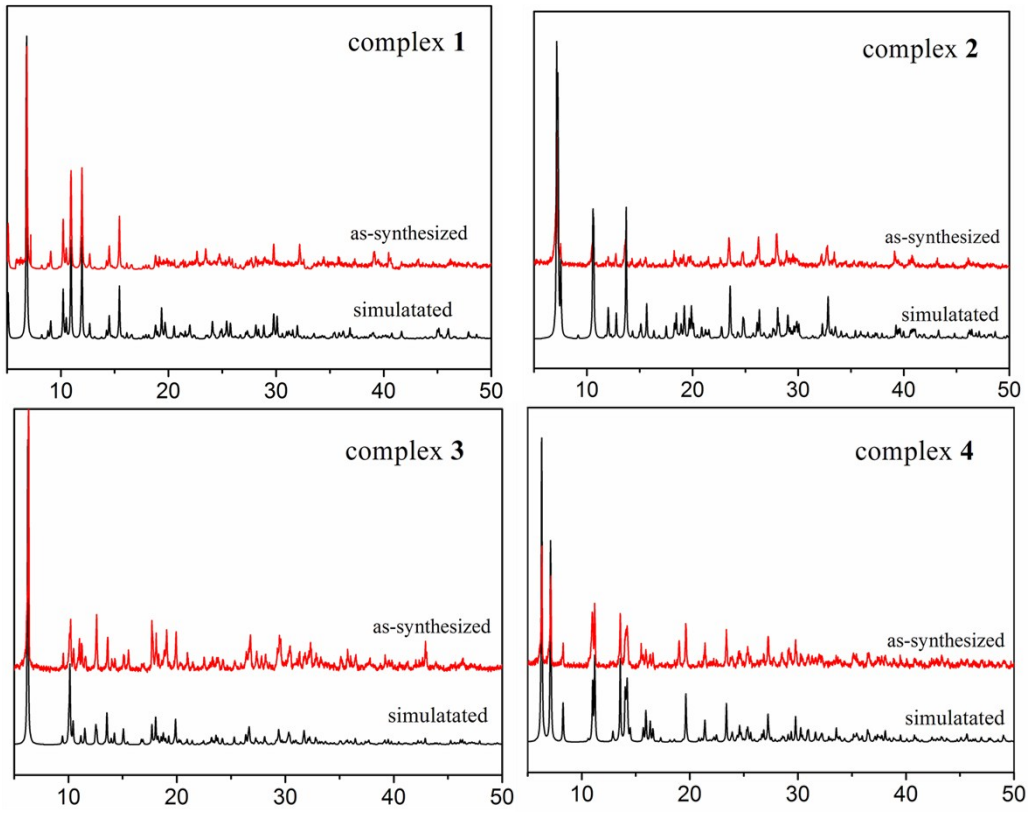


Fig. S6. Powder X–ray diffraction patterns of the title complexes.

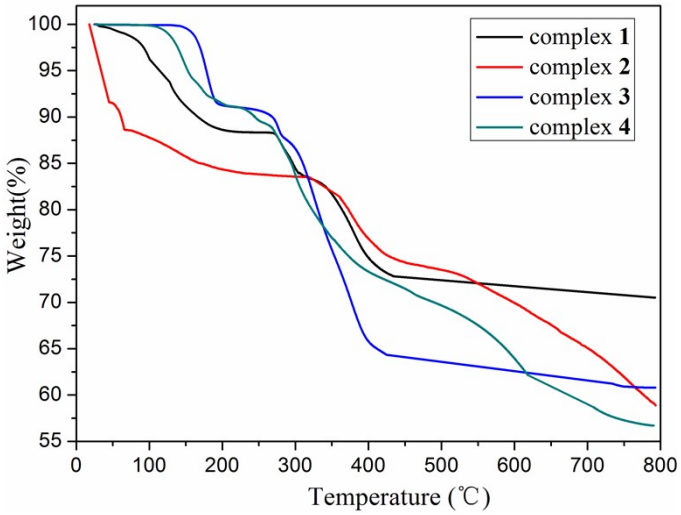


Fig. S7. The TGA curves of the title complexes.

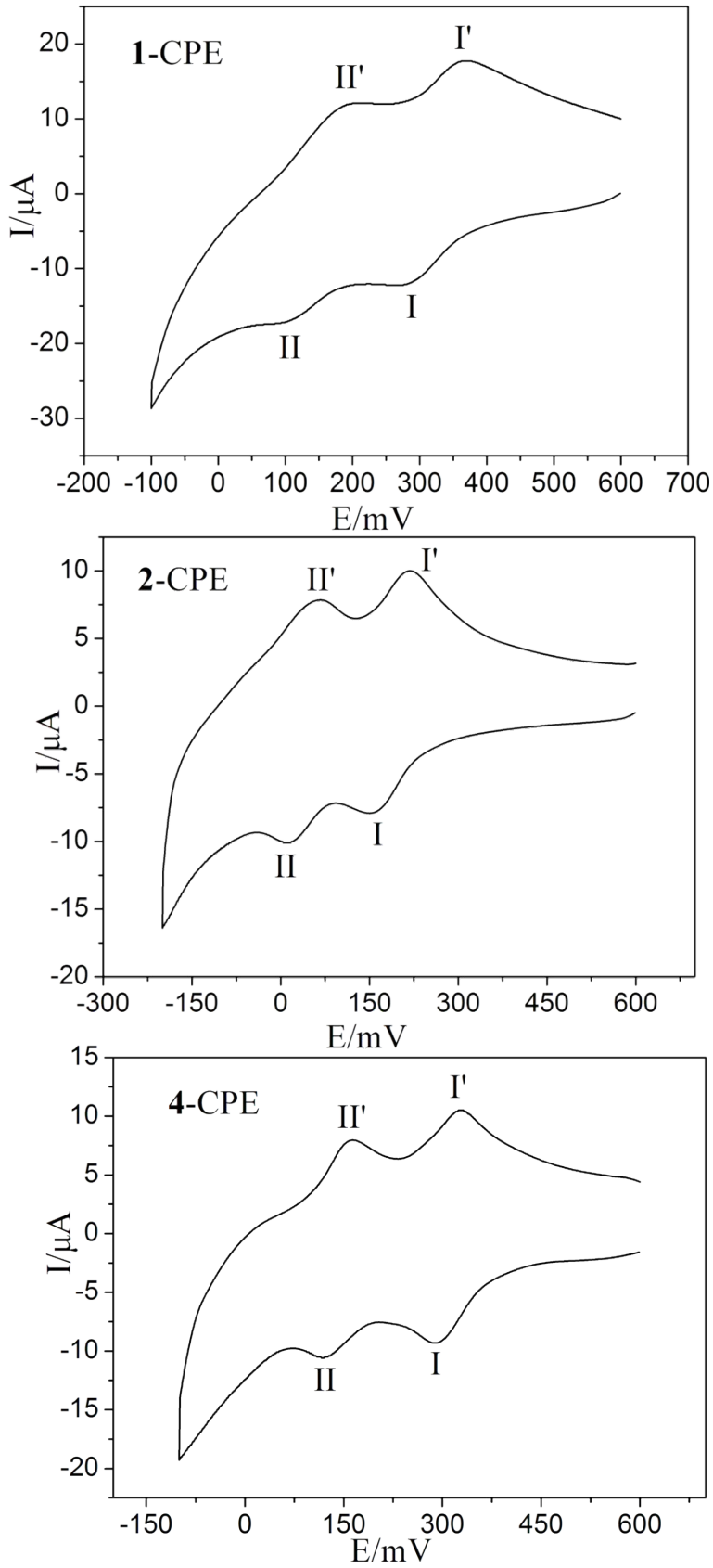


Fig. S8 The Cyclic voltammograms of the **1-, 2-** and **4**–CPEs in 0.01 M H_2SO_4 aqueous solution. Scan rate: 40 $mV \cdot s^{-1}$

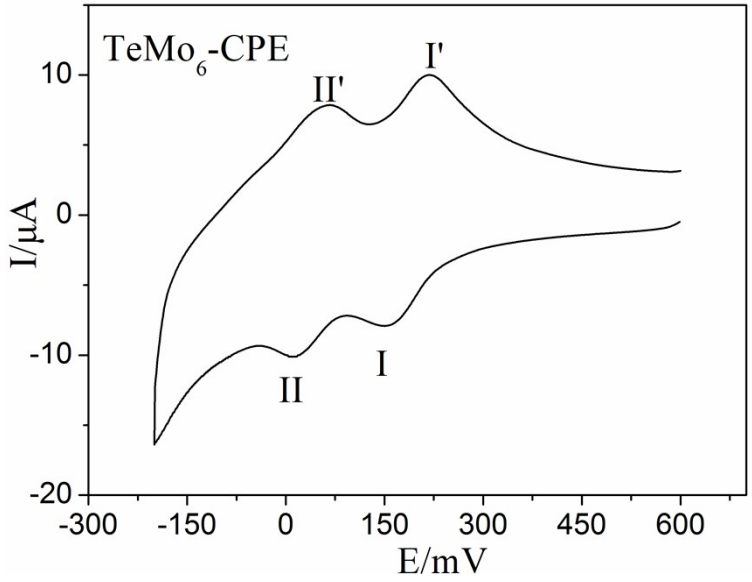


Fig. S9. The Cyclic voltammograms of the $TeMo_6$–CPE in 0.01 M H_2SO_4 aqueous solution. Scan rates: 200 $mV \cdot s^{-1}$

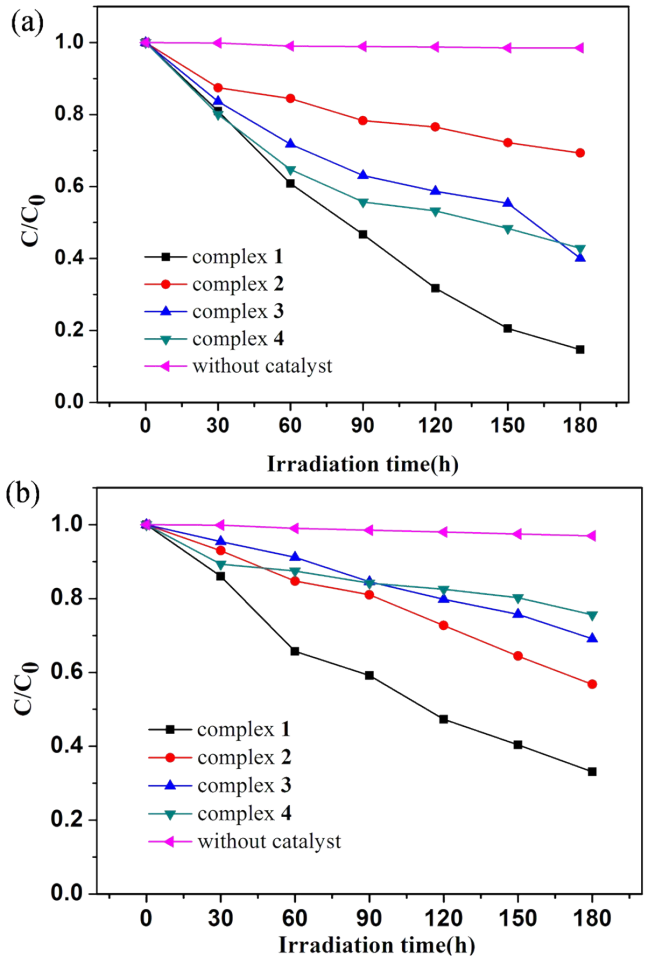


Fig. S10 Photocatalytic decomposition rate of MB (a) and RhB (b) solution under UV irradiation with the use of title complexes.

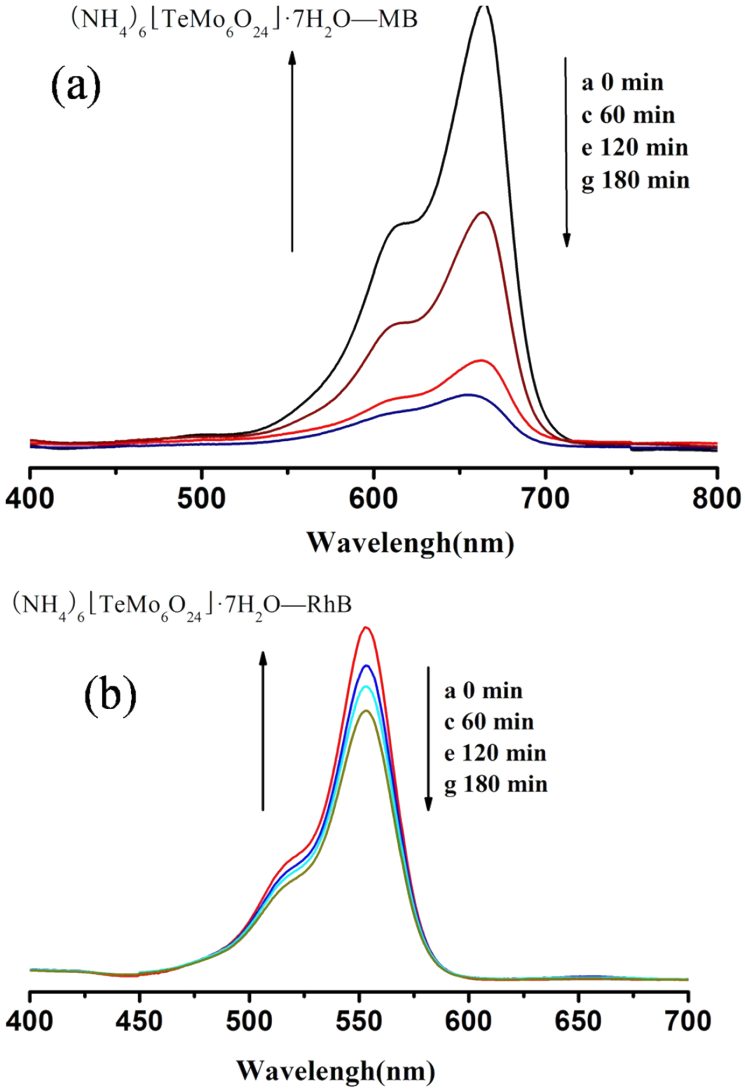


Fig. S11. Absorption spectra of the MB/RhB solution during the decomposition reaction under UV irradiation at the presence of $[TeMo_6O_{24}]^{6-}$ polyoxometalate alone**.**