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A Series of Anderson-type Polyoxometalate-based Metal–organic Complexes: pH-dependent electrochemical behaviours and as Electrocatalysts and Photocatalysts

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

		Complex **1**	
O(1)-Cu(1)	1.990(4)	N(1)-Cu(2)	2.002(5)
O(1W)-Cu(1)	2.173(5)	Cu(1)-O(3)	1.953(4)
Cu(1)-O(2W)	1.963(4)	Cu(1)-N(3)	1.981(5)
N(2)-Cu(2)	1.975(4)	Cu(2)-O(4)	1.920(4)
Cu(2)-O(7)#1	1.936(4)	O(7)-Cu(2)#1	1.936(4)
Mo(1)-O(1)-Cu(1)	140.6(2)	C(10)-N(1)-Cu(2)	129.4(4)
C(6)-N(1)-Cu(2)	111.5(4)	O(3)-Cu(1)-O(2W)	172.16(19)
O(3)-Cu(1)-N(3)	88.03(18)	O(2W)-Cu(1)-N(3)	97.67(19)
O(3)-Cu(1)-O(1)	87.43(17)	O(2W)-Cu(1)-O(1)	85.57(18)
N(3)-Cu(1)-O(1)	162.84(18)	O(3)-Cu(1)-O(1W)	93.48(19)
O(2W)-Cu(1)-O(1W)	91.0(2)	N(3)-Cu(1)-O(1W)	98.3(2)
O(1)-Cu(1)-O(1W)	98.5(2)	O(4)-Cu(2)-O(7)#1	87.94(17)
O(4)-Cu(2)-N(2)	175.08(19)	O(7)#1-Cu(2)-N(2)	95.36(18)
O(4)-Cu(2)-N(1)	95.51(18)	O(7)#1-Cu(2)-N(1)	164.42(18)
N(2)-Cu(2)-N(1)	82.28(18)		
Symmetry codes for **1:** #1 -x,-y-1,-z+1			
		Complex **2**	
Cu(1)-O(1W)	1.985(6)	Cu(1)-O(4W)	1.970(6)
Cu(1)-N(1)	2.017(7)	Cu(1)-O(3W)	2.026(6)
Cu(1)-O(2W)	2.185(6)	O(1W)-Cu(1)-O(4W)	172.6(3)
O(1W)-Cu(1)-N(1)	90.9(3)	O(4W)-Cu(1)-N(1)	89.2(3)
O(1W)-Cu(1)-O(3W)	89.6(3)	O(4W)-Cu(1)-O(3W)	89.7(3)
N(1)-Cu(1)-O(3W)	174.6(3)	O(1W)-Cu(1)-O(2W)	87.8(3)
O(4W)-Cu(1)-O(2W)	99.6(2)	N(1)-Cu(1)-O(2W)	94.2(3)
O(3W)-Cu(1)-O(2W)	91.2(3)		
		Complex **3**	
Cu(1)-N(1)	1.990(3)	Cu(1)-O(1W)	1.997(3)
Cu(1)-N(1)#1	1.990(3)	Cu(1)-O(1W)#1	1.997(3)
Cu(1)-O(1)	2.393(2)	Cu(1)-O(1)#1	2.393(2)
N(1)-Cu(1)-N(1)#1	180.0(15)	N(1)-Cu(1)-O(1W)	89.17(11)
N(1)#1-Cu(1)-O(1W)	90.83(11)	N(1)-Cu(1)-O(1W)#1	90.83(11)

N(1)#1-Cu(1)-O(1W)#1	89.17(11)	O(1W)-Cu(1)-O(1W)#1	180.000(2)
N(1)-Cu(1)-O(1)	87.72(9)	N(1)#1-Cu(1)-O(1)	92.28(9)
O(1W)-Cu(1)-O(1)	93.73(9)	O(1W)#1-Cu(1)-O(1)	86.27(9)
N(1)-Cu(1)-O(1)#1	92.28(9)	N(1)#1-Cu(1)-O(1)#1	87.72(9)
O(1W)-Cu(1)-O(1)#1	86.27(9)	O(1W)#1-Cu(1)-O(1)#1	93.73(9)
O(1)-Cu(1)-O(1)#1	180.000(1)		

Symmetry codes for **3**: #1 -x+2,-y+1,-z+2

Complex **4**

Cu(1)-O(4)	1.953(19)	Cu(1)-N(1)	1.987(3)
Cu(1)-O(7)#2	2.018(2)	Cu(1)-O(2)	2.128(2)
Cu(1)-O(1)	2.161(2)	Cu(1)-O(3)	2.307(3)
Cu(2)-O(5)	1.926(2)	Cu(2)-O(6)	1.934(2)
Cu(2)-O(4)#4	1.967(2)	Cu(2)-O(4)	1.975(2)
Cu(2)-O(3)#4	2.358(2)	Cu(2)-Cu(2)#4	2.9880(7)
O(3)-Cu(2)#4	2.358(2)	O(4)-Cu(2)#4	1.967(2)
O(7)-Cu(1)#2	2.018(2)	O(4)-Cu(1)-N(1)	176.80(10)
O(4)-Cu(1)-O(7)#2	89.94(8)	N(1)-Cu(1)-O(7)#2	89.98(10)
O(4)-Cu(1)-O(2)	86.24(9)	N(1)-Cu(1)-O(2)	93.35(10)
O(7)#2-Cu(1)-O(2)	170.28(9)	O(4)-Cu(1)-O(1)	92.42(8)
N(1)-Cu(1)-O(1)	90.78(10)	O(7)#2-Cu(1)-O(1)	93.28(9)
O(2)-Cu(1)-O(1)	95.80(9)	O(4)-Cu(1)-O(3)	83.58(8)
N(1)-Cu(1)-O(3)	93.22(10)	O(7)#2-Cu(1)-O(3)	89.42(9)
O(2)-Cu(1)-O(3)	81.29(9)	O(1)-Cu(1)-O(3)	175.19(9)
O(5)-Cu(2)-O(6)	90.31(9)	O(5)-Cu(2)-O(4)#4	168.51(9)
O(6)-Cu(2)-O(4)#4	97.05(9)	O(5)-Cu(2)-O(4)	94.33(9)
O(6)-Cu(2)-O(4)	161.62(9)	O(4)#4-Cu(2)-O(4)	81.43(8)
O(5)-Cu(2)-O(3)#4	88.56(9)	O(6)-Cu(2)-O(3)#4	95.17(9)
O(4)#4-Cu(2)-O(3)#4	81.95(8)	O(4)-Cu(2)-O(3)#4	102.13(9)
O(5)-Cu(2)-Cu(2)#4	134.02(7)	O(6)-Cu(2)-Cu(2)#4	135.09(7)
O(4)#4-Cu(2)-Cu(2)#4	40.82(6)	O(4)-Cu(2)-Cu(2)#4	40.60(6)
O(3)#4-Cu(2)-Cu(2)#4	92.68(7)		

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

Complex **5**

Cu(1)-O(3W)	1.953(2)	Cu(1)-O(2W)	1.988(3)
Cu(1)-N(1)	2.003(3)	Cu(1)-O(1)	2.004(3)
Cu(1)-O(1W)	2.274(3)	Cu(1)-O(3)#1	2.355(3)
O(3W)-Cu(1)-O(2W)	90.59(11)	O(3W)-Cu(1)-N(1)	174.67(12)
O(2W)-Cu(1)-N(1)	93.10(11)	O(3W)-Cu(1)-O(1)	87.07(11)
O(2W)-Cu(1)-O(1)	177.66(10)	N(1)-Cu(1)-O(1)	89.23(11)
O(3W)-Cu(1)-O(1W)	92.97(11)	O(2W)-Cu(1)-O(1W)	87.28(11)
N(1)-Cu(1)-O(1W)	91.04(11)	O(1)-Cu(1)-O(1W)	92.89(10)
O(3W)-Cu(1)-O(3)#1	91.22(11)	O(2W)-Cu(1)-O(3)#1	90.85(10)
N(1)-Cu(1)-O(3)#1	84.90(11)	O(1)-Cu(1)-O(3)#1	89.15(10)
O(1W)-Cu(1)-O(3)#1	175.43(10)		

Symmetry codes for **5:** #1 -x,-y+4,-z-1

Complex **6**

Cu(1)-N(1)#2	1.994(4)	Cu(1)-N(1)	1.994(4)
Cu(1)-O(1W)#2	2.007(3)	Cu(1)-O(1W)	2.007(3)
Cu(1)-O(1)#2	2.293(3)	Cu(1)-O(1)	2.293(3)
Cu(2)-O(4W)	1.949(4)	Cu(2)-O(2W)	2.002(4)
Cu(2)-N(2)	2.011(4)	Cu(2)-O(3W)	2.024(4)
Cu(2)-O(2)	2.317(3)	Cu(2)-O(3)	2.350(3)
N(1)#2-Cu(1)-N(1)	180.0(3)	N(1)#2-Cu(1)-O(1W)#2	89.23(15)
N(1)-Cu(1)-O(1W)#2	90.77(15)	N(1)#2-Cu(1)-O(1W)	90.77(15)
N(1)-Cu(1)-O(1W)	89.23(15)	O(1W)#2-Cu(1)-O(1W)	180.0(1)
N(1)#2-Cu(1)-O(1)#2	91.56(14)	N(1)-Cu(1)-O(1)#2	88.44(14)
O(1W)#2-Cu(1)-O(1)#2	84.01(13)	O(1W)-Cu(1)-O(1)#2	95.98(13)
N(1)#2-Cu(1)-O(1)	88.44(14)	N(1)-Cu(1)-O(1)	91.56(14)
O(1W)#2-Cu(1)-O(1)	95.98(13)	O(1W)-Cu(1)-O(1)	84.01(13)
O(1)#2-Cu(1)-O(1)	180.0(13)	O(4W)-Cu(2)-O(2W)	86.84(18)
O(4W)-Cu(2)-N(2)	175.94(18)	O(2W)-Cu(2)-N(2)	91.44(17)
O(4W)-Cu(2)-O(3W)	88.51(18)	O(2W)-Cu(2)-O(3W)	172.11(14)
N(2)-Cu(2)-O(3W)	93.60(17)	O(4W)-Cu(2)-O(2)	90.60(14)
O(2W)-Cu(2)-O(2)	102.47(13)	N(2)-Cu(2)-O(2)	86.17(14)
O(3W)-Cu(2)-O(2)	83.94(13)	O(4W)-Cu(2)-O(3)	93.50(14)
O(2W)-Cu(2)-O(3)	86.07(13)	N(2)-Cu(2)-O(3)	90.05(14)
O(3W)-Cu(2)-O(3)	87.86(13)	O(2)-Cu(2)-O(3)	170.73(12)

Symmetry codes for **6**: #2 -x,-y+1,-z

Complex **7**

Cu(1)-O(3W)	1.963(4)	Cu(1)-O(2)	1.984(4)
Cu(1)-O(2W)	1.985(4)	Cu(1)-N(1)	2.012(4)
Cu(1)-O(1W)	2.278(4)	Cu(1)-O(1)	2.370(5)
O(3W)-Cu(1)-O(2)	176.99(17)	O(3W)-Cu(1)-O(2W	90.85(19)
O(2)-Cu(1)-O(2W)	86.13(19)	O(3W)-Cu(1)-N(1)	93.86(18)
O(2)-Cu(1)-N(1)	89.13(18)	O(2W)-Cu(1)-N(1)	172.0(2)
O(3W)-Cu(1)-O(1W)	90.65(18)	O(2)-Cu(1)-O(1W)	89.55(16)
O(2W)-Cu(1)-O(1W)	93.4(2)	N(1)-Cu(1)-O(1W)	93.01(18)
O(3W)-Cu(1)-O(1)	89.69(16)	O(2)-Cu(1)-O(1)	90.15(16)
O(2W)-Cu(1)-O(1)	87.4(2)	N(1)-Cu(1)-O(1)	86.21(17)
O(1W)-Cu(1)-O(1)	179.17(16)		

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

D–H···A	D–H	H···A	D···A	D–H···A
C(9)–H(9A) ···O(26)	0.93	2.56	3.262	133

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

D–H···A	D–H	H···A	D···A	D–H···A
C(7)–H(7A) ···O(2)	0.93	2.55	3.3355	142

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

D–H···A	D–H	H···A	D···A	D–H···A
C(12)–H(12A) ···O(8),	0.93	2.37	3.167(5)	143

Table S2d. Selected hydrogen–bonding geometry (Å, °) for complex **5**

D–H···A	D–H	H···A	D···A	D–H···A
N(4)–H(4C) ···O(12),	0.86	1.78	2.639(4)	177
O3W–H3WB ···O(7)	0.85	2.48	2.922(4)	113

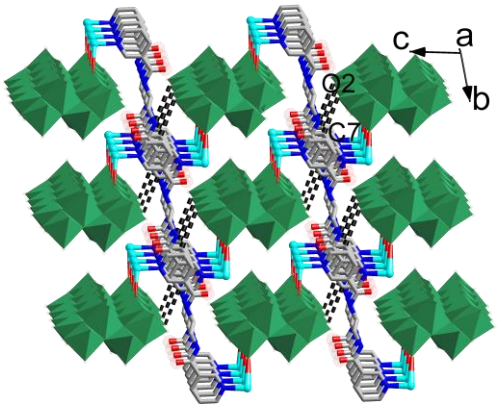

Fig. S1. The **3**D supramolecular framework in **2**

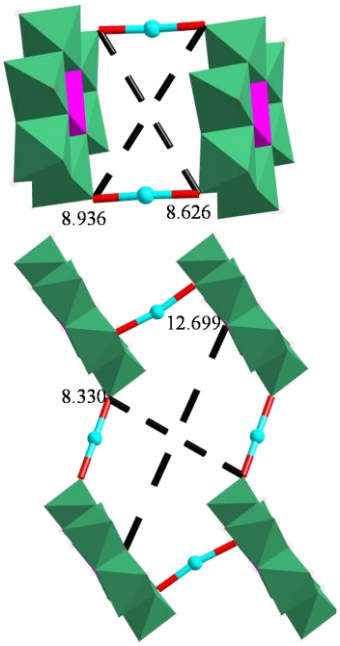

Fig. S2. Two kinds of the $Cu_2(TeMo_6)_2$ and $Cu_4(TeMo_6)_4$ loops in complex **6**

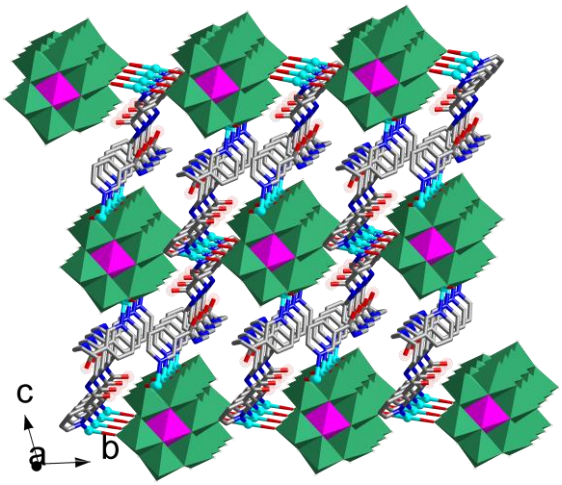

Fig. S3. The 3D framework of complex **6**.

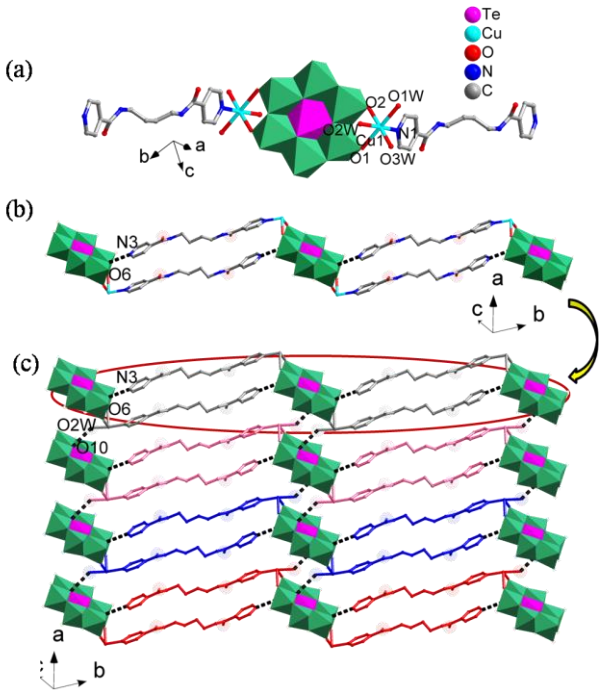

Fig. S4. (a) The coordination environment of the Cu^{II} ion in **7**. All H atoms and lattice water molecules are omitted for clarity. (b) The 1D supramolecular chain linked by hydrogen bonding interaction [N(3)–H(3B)···O(6)]. (c) The 2D supramolecular network of **7** formed by hydrogen bonding interaction [O2W–H2WB···O(10)].

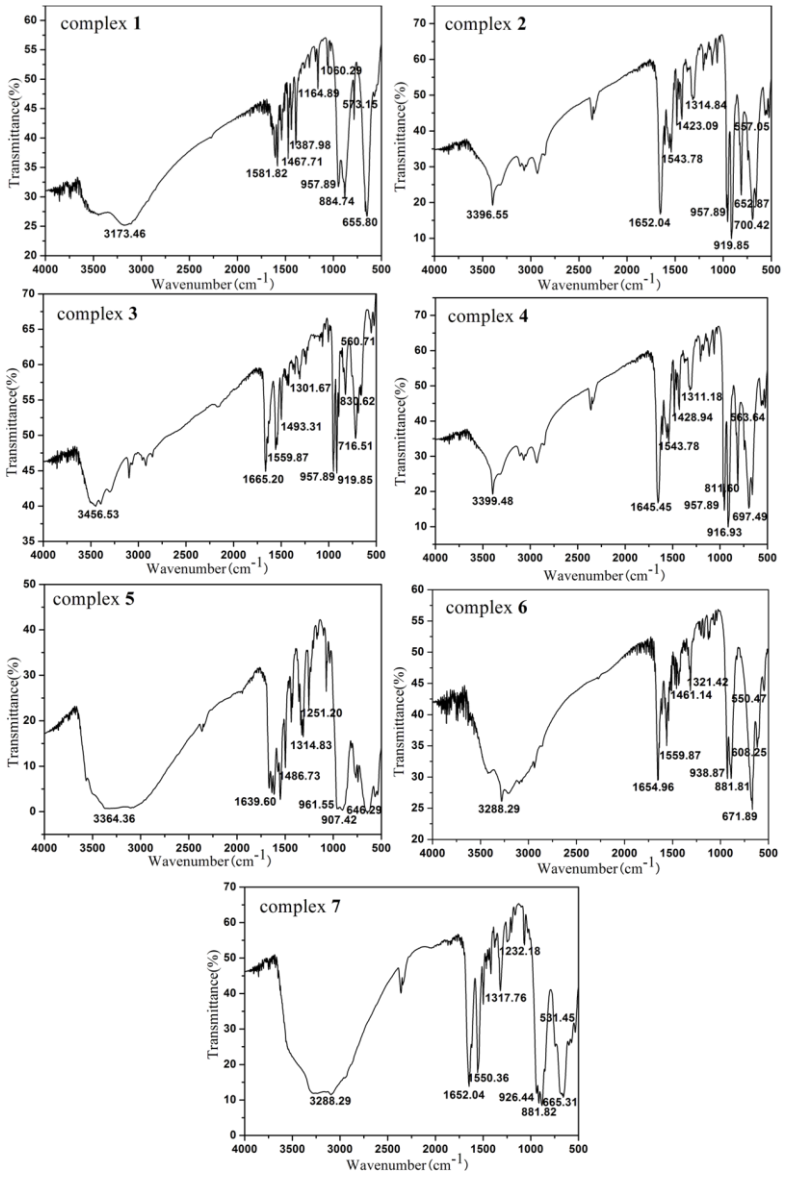

Fig. S5. The IR spectra of the title complexes**.**

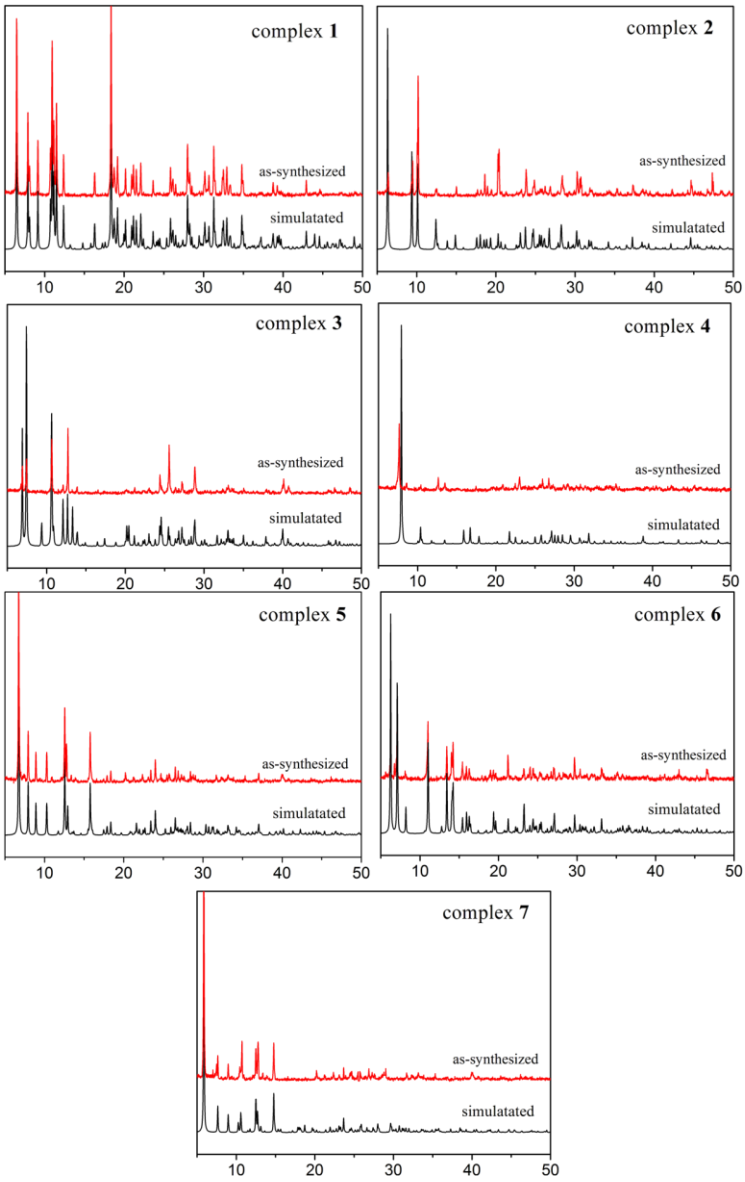

Fig. S6. Powder X–ray diffraction patterns of the title complexes.

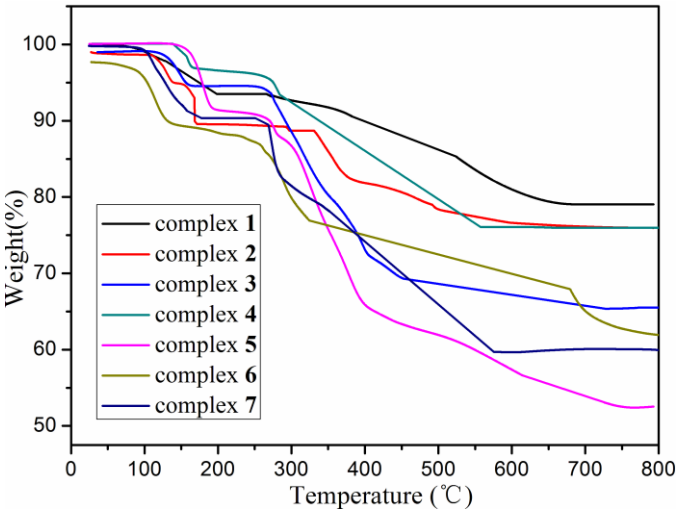

Fig. S7. The TGA curves of the title complexes**.**

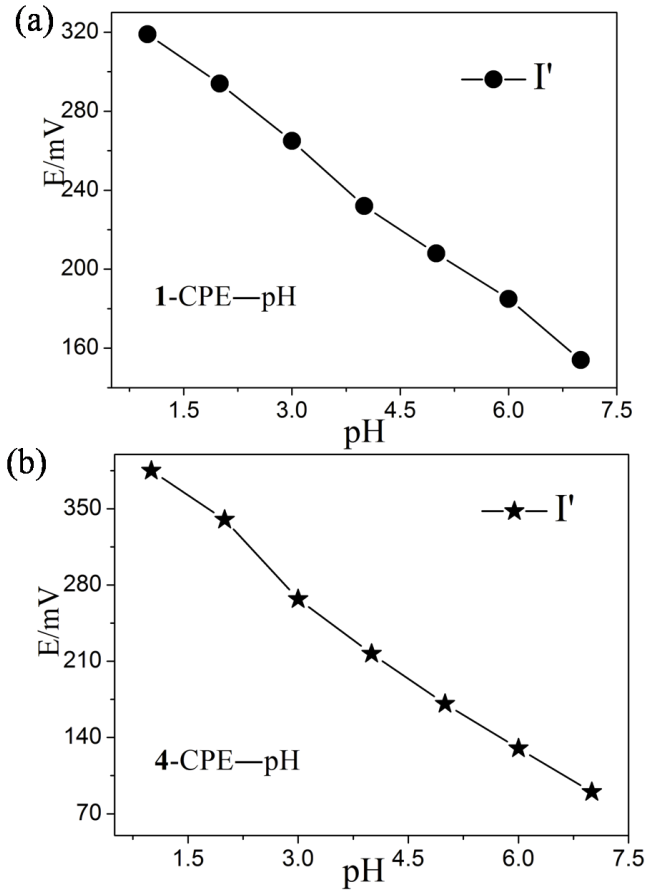

Fig. S8. The dependence of anodic peak potentials on the pH values of medium for **1**–(a) and **4**–(b)CPE.

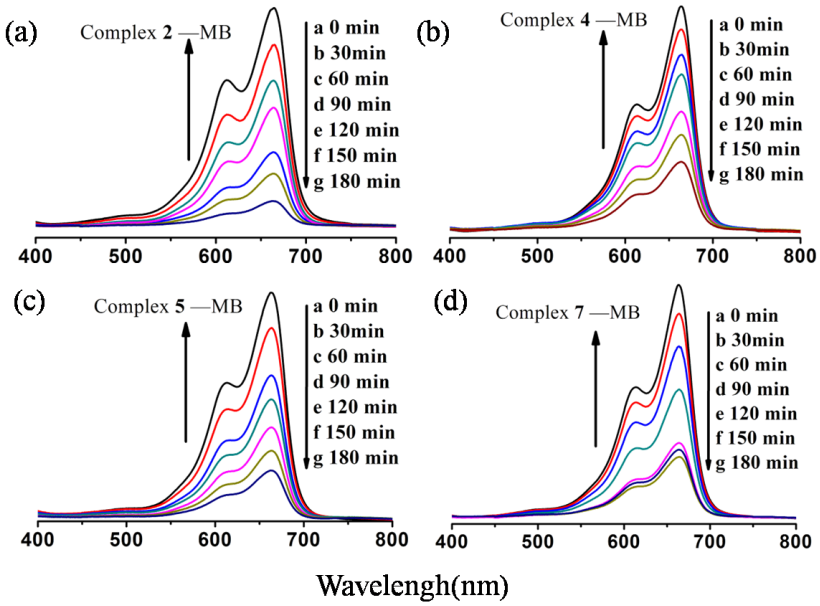

Fig. S9. Absorption spectra of the MB solution during the decomposition reaction under UV irradiation at the presence of complexes **2**, **4**, **5** and **7.**

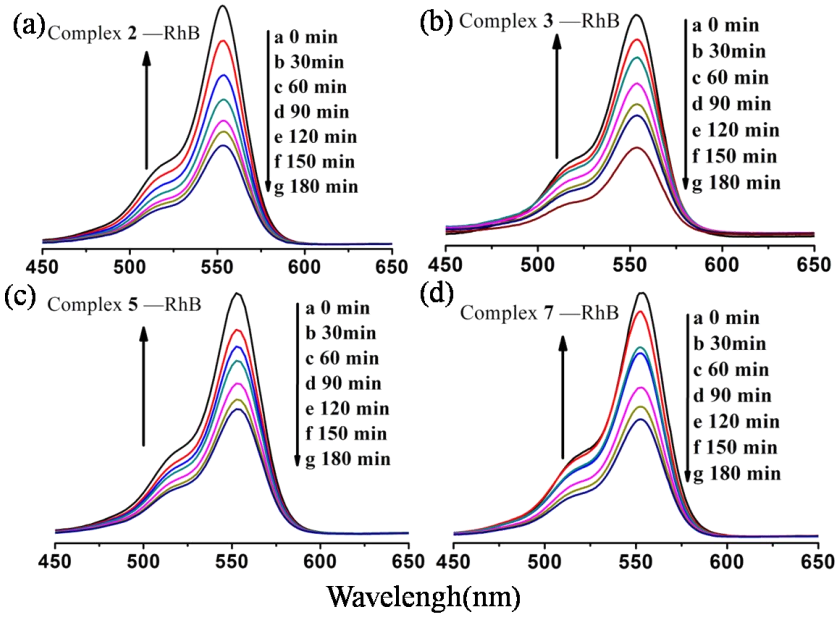

Fig. S10. Absorption spectra of the RhB solution during the decomposition reaction under UV irradiation at the presence of complexes **2**, **3**, **5** and **7.**

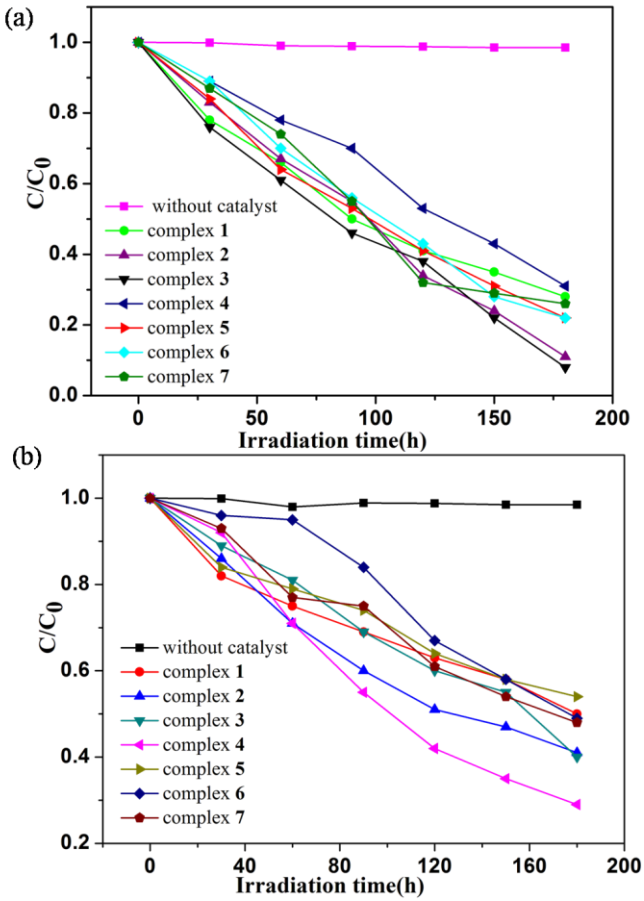

Fig. S11 Photocatalytic decomposition rate of MB solution (a), and RhB (b) under UV irradiation with the use of title complexes.