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Effect of polyoxoanions and amide groups coordination modes on the assembly of polyoxometalate–based metal–organic complexes constructed from a semi–rigid bis–pyridyl–bis–amide ligand

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Table. S1. Selected bond distances (Å) and angles (°) for complexes **1**–**4.**

		Complex **1**	
Cu(1)–N(1)	1.995(12)	Cu(1)–N(4)	1.974(12)
Cu(1)–O(1)	2.027(9)	Cu(1)–O(1W)	2.054(10)
Cu(1)–O(2)	2.274(9)	O(1)–Cu(1)–O(1W)	159.9(4)
N(4) –Cu(1)–N(1)	173.5(5)	N(4) –Cu(1)–O(2)	97.6(4)
N(4) –Cu(1)–O(1)	85.8(4)	N(1)–Cu(1)–O(2)	88.6(4)
N(1)–Cu(1)–O(1)	94.5(4)	O(1)–Cu(1)–O(2)	102.7(4)
N(4) –Cu(1)–O(1W)	85.1(5)	O(1W)–Cu(1)–O(2)	96.2(4)
N(1)–Cu(1)–O(1W)	92.6(5)		
		Complex **2**	
Cu(1)–O(1)	2.507(11)	Cu(1)–N(1)	1.994(13)
Cu(1)–O(1W)	2.028(12)	Cu(1)–O(2W)	2.234(12)
Cu(1)–N(2)	2.003(15)	Cu(1)–O(3W)	1.983(11)
O(1)–Cu(1)–N(1)	94.91(5)	O(1)–Cu(1)–N(2)	88.83(5)
O(1)–Cu(1)–O(1W)	84.89(6)	O(1)–Cu(1)–O(2W)	174.64(5)
O(3W)–Cu(1)–O(1)	92.51(5)	O(3W)–Cu(1)–N(1)	88.9(5)
O(3W)–Cu(1)–N(2)	91.8(5)	O(3W)–Cu(1)–O(2W)	92.8(5)
N(1)–Cu(1)–N(2)	173.2(6)	N(1)–Cu(1)–O(2W)	95.7(6)
O(1W)–Cu(1)–N(1)	87.53(6)	O(1W)–Cu(1)–N(2)	91.41(5)
O(1W)–Cu(1)–O(2W)	89.83(5)	O(1W)–Cu(1)–O(3W)	175.79(5)
N(2)–Cu(1)–O(2W)	90.93(6)		
		Complex **3**	
Cu(1)–O(1)	2.529(12)	Cu(1)–O(1W)	2.001(15)
Cu(1)–O(2W)	2.264(15)	Cu(1)–O(3W)	1.976(14)
Cu(1)–N(1)	2.005(16)	Cu(1)–N(2)	1.978(19)
O(3W)–Cu(1)–N(2)	91.8(7)	N(2)–Cu(1)–O(2W)	91.5(8)
O(3W)–Cu(1)–N(1)	87.5(6)	N(1)–Cu(1)–O(2W)	95.3(7)
N(2)–Cu(1)–N(1)	173.1(7)	O(2W)–Cu(1)–O(1W)	89.6(7)
O(1W)–Cu(1)–O(3W)	175.4(7)	N(1)–Cu(1)–O(1W)	88.4(7)
N(2)–Cu(1)–O(1W)	91.9(7)	O(2W)–Cu(1)–O(3W)	92.9(7)

O(1) –Cu(1)–O(1W)	92.5(7)	O(1)–Cu(1)–O(2W)	85.1(7)
O(1)–Cu(1)–O(3W)	174.7(7)	O(1)–Cu(1)–N(1)	85.2(7)
O(1)–Cu(1)–N(4)	88.0(6)		

Complex **4**

Cu(1)–O(1)	1.986(9)	Cu(1)–N(4)#2	2.009(10)
Cu(1)–O(1W)	1.991(10)	Cu(1)–O(2)	2.364(9)
Cu(1)–N(1)	2.001(10)	Cu(1)–O(3)#2	2.425(8)
K(1)–O(13)	1.739(11)	Mo(1)–O(9)	1.694(9)
K(1)–O(4)	1.926(12)	Mo(1)–O(7)	1.707(9)
K(1)–O(8)	2.115(12)	Mo(1)–O(10)	1.935(8)
K(1)–O(12)	2.280(14)	Mo(1)–O(5)	1.949(8)
K(1)–O(9)	2.446(10)	Mo(1)–O(6)	2.246(8)
K(1)–O(6)	2.450(8)	Mo(1)–O(6)#1	2.322(8)
Mo(2)–O(16)	1.657(9)	Mo(3)–O(3)	1.695(8)
Mo(2)–O(12)	1.768(10)	Mo(3)–O(8)	1.723(10)
Mo(2)–O(11)	1.828(9)	Mo(3)–O(14)	1.827(9)
Mo(2)–O(5)	2.065(8)	Mo(3)–O(10)	2.097(9)
Mo(2)–O(10)#1	2.254(8)	Mo(3)–O(5)#1	2.295(8)
Mo(2)–O(6)	2.351(8)	Mo(3)–O(6)	2.306(8)
Mo(4)–O(1)	1.706(9)	Mo(4)–O(4)	1.769(11)
Mo(4)–O(11)	1.973(9)	Mo(4)–O(6)	2.348(8)
Mo(4)–O(14)	1.990(10)	Mo(4)–O(7)#1	2.378(10)
O(1)–Cu(1)–O(1W)	176.0(4)	O(2) –Cu(1)–O(3)#2	167.3(3)
O(1)–Cu(1)–N(1)	87.0(4)	O(9)–Mo(1)–O(7)	105.2(5)
O(1W)–Cu(1)–N(1)	91.3(4)	O(9)–Mo(1)–O(10)	99.9(4)
O(1)–Cu(1)–N(4)#2	91.4(4)	O(7)–Mo(1)–O(10)	98.1(4)
O(1W)–Cu(1)–N(4)#2	90.6(4)	O(9)–Mo(1)–O(5)	100.5(4)
N(1)–Cu(1)–N(4)#2	175.6(4)	O(7)–Mo(1)–O(5)	98.3(4)
O(1)–Cu(1)–O(2)	84.8(4)	O(10)–Mo(1)–O(5)	149.4(3)
O(1W)–Cu(1)–O(2)	91.6(4)	O(9)–Mo(1)–O(6)	92.7(4)
N(1)–Cu(1)–O(2)	90.7(4)	O(7)–Mo(1)–O(6)	162.1(4)
N(4)#2–Cu(1)–O(2)	93.2(4)	O(10)–Mo(1)–O(6)	78.2(3)
O(1)–Cu(1)–O(3)#2	83.0(3)	O(5)–Mo(1)–O(6)	78.2(3)
O(1W)–Cu(1)–O(3)#2	100.7(4)	O(9)–Mo(1)–O(6)#1	169.3(4)
N(1)–Cu(1)–O(3)#2	92.2(4)	O(7)–Mo(1)–O(6)#1	85.5(4)
N(4)#2–Cu(1)–O(3)#2	83.5(4)	O(10)–Mo(1)–O(6)#1	77.7(3)
O(11)–Mo(2)–O(6)	79.2(4)	O(5)–Mo(1)–O(6)#1	78.1(3)
O(5)–Mo(2)–O(6)	73.6(3)	O(6)–Mo(1)–O(6)#1	76.6(3)
O(10)#1–Mo(2)–O(6)	71.3(3)	O(13)–K(1)–O(4)	104.6(6)
O(3)–Mo(3)–O(8)	104.0(5)	O(13)–K(1)–O(8)	101.2(6)
O(3)–Mo(3)–O(14)	103.9(5)	O(4)–K(1)–O(8)	99.6(4)
O(8)–Mo(3)–O(14)	101.6(5)	O(13)–K(1)–O(12)	98.8(5)
O(3)–Mo(3)–O(10)	97.2(4)	O(4)–K(1)–O(12)	94.3(4)
O(8)–Mo(3)–O(10)	94.9(4)	O(8)–K(1)–O(12)	151.8(4)

O(13)–K(1)–O(9)	95.4(5)	O(4)–K(1)–O(9)	159.6(4)
O(8)–K(1)–O(9)	79.8(4)	O(12)–K(1)–O(9)	78.7(4)
O(13)–K(1)–O(6)	167.3(5)	O(4)–K(1)–O(6)	87.8(4)
O(8)–K(1)–O(6)	78.4(3)	O(12)–K(1)–O(6)	77.8(3)
O(9)–K(1)–O(6)	72.0(3)	O(11)–Mo(2)–O(5)	149.5(4)
O(14)–Mo(3)–O(10)	149.1(4)	O(16)–Mo(2)–O(12)	104.3(6)
O(3)–Mo(3)–O(5)#1	92.1(3)	O(16)–Mo(2)–O(11)	103.7(5)
O(8)–Mo(3)–O(5)#1	160.0(4)	O(12)–Mo(2)–O(11)	100.7(4)
O(14)–Mo(3)–O(5)#1	85.5(4)	O(16)–Mo(2)–O(5)	98.6(4)
O(10)–Mo(3)–O(5)#1	71.1(3)	O(12)–Mo(2)–O(5)	93.5(4)
O(3)–Mo(3)–O(6)	163.5(4)	O(12)–Mo(2)–O(6)	91.2(5)
O(8)–Mo(3)–O(6)	90.7(4)	O(16)–Mo(2)–O(10)#1	92.2(4)
O(14)–Mo(3)–O(6)	80.0(4)	O(12)–Mo(2)–O(10)#1	159.9(5)
O(10)–Mo(3)–O(6)	73.8(3)	O(11)–Mo(2)–O(10)#1	86.0(4)
O(5)#1–Mo(3)–O(6)	72.0(3)	O(5)–Mo(2)–O(10)#1	72.5(3)
O(1)–Mo(4)–O(4)	106.8(5)	O(16)–Mo(2)–O(6)	163.2(4)
O(1)–Mo(4)–O(11)	100.1(4)	O(6)–Mo(4)–O(7)#1	71.8(3)
O(4)–Mo(4)–O(11)	96.8(4)	O(1)–Mo(4)–O(7)#1	86.5(4)
O(1)–Mo(4)–O(14)	100.3(4)	O(4)–Mo(4)–O(7)#1	166.7(4)
O(4)–Mo(4)–O(14)	99.4(5)	O(11)–Mo(4)–O(7)#1	79.8(3)
O(11)–Mo(4)–O(14)	149.0(4)	O(14)–Mo(4)–O(7)#1	78.4(4)
O(1)–Mo(4)–O(6)	158.3(4)	O(11)–Mo(4)–O(7)#1	79.8(3)
O(4)–Mo(4)–O(6)	94.9(4)	O(14)–Mo(4)–O(6)	75.9(3)
O(11)–Mo(4)–O(6)	76.6(3)		

Symmetry code: #1 –x, y+1, –z/2; #2 x+1/2, –y+1/2, z+1/2.

Table S2. Selected hydrogen–bonding geometry (Å, º) for complex **1**

D–H···A	D–H	H···A	D···A	D–H···A
C(10)–H(10B)···O(13),	0.97	2.44	3.32	151

Table S3. Selected hydrogen–bonding geometry (Å, º) for complex **2**

D–H···A	D–H	H···A	D···A	D–H···A
C(14)–H(14B)···O(11)	0.97	2.45	3.2294	137

Table S4. Selected hydrogen–bonding geometry (Å, º) for complex **3**

D–H···A	D–H	H···A	D···A	D–H···A
C(15)–H(15B)···O(23)	0.97	2.47	3.2465	137

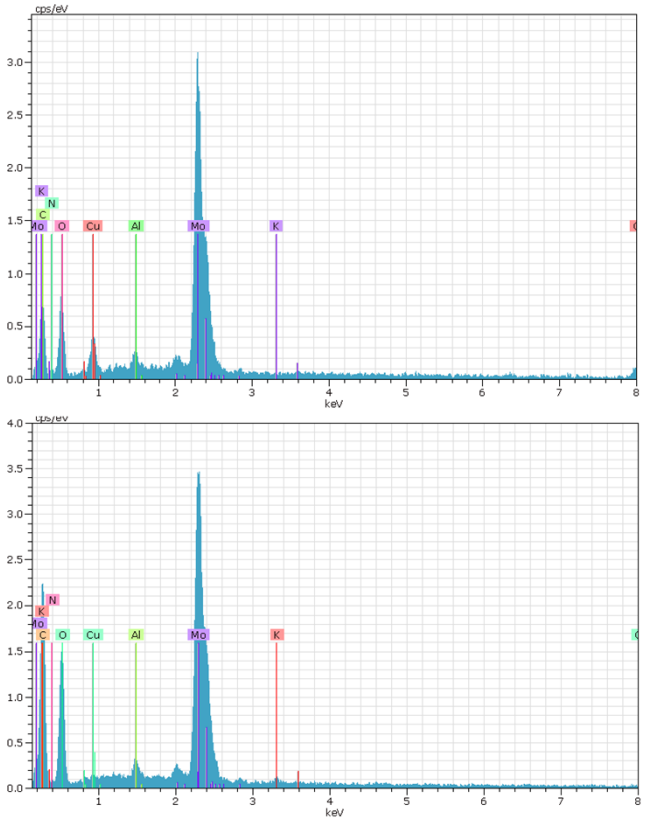

Fig. S1 The EDS spectra of single crystal of **4.**

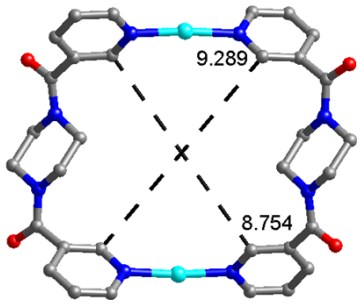

Fig. S2 The $[Cu_2L_2]$ metal–organic loop in **1**.

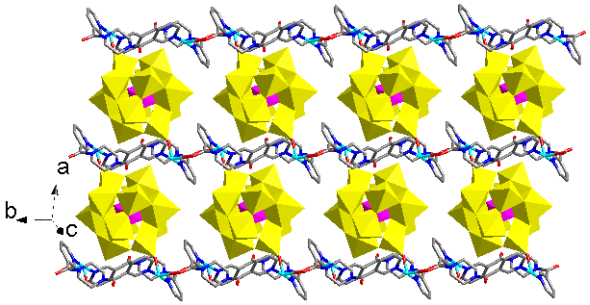

Fig. S3 The 2D layer in **1.**

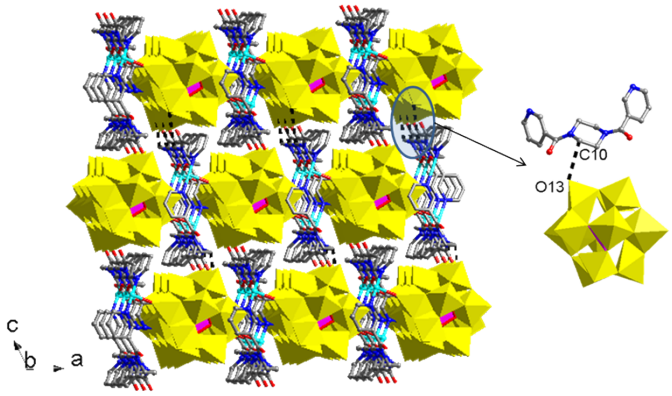

Fig. S4 The 3D supramolecular framework of **1.**

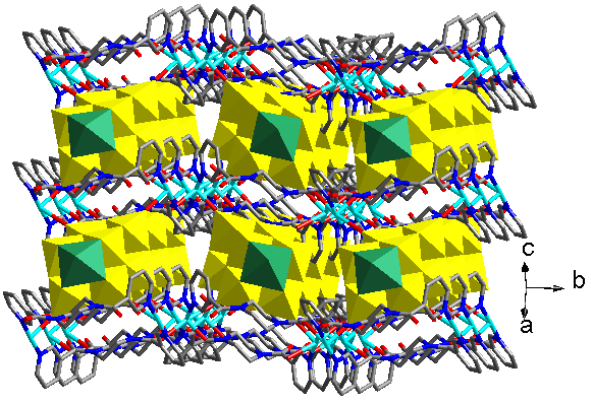

Fig. S5 The 3D framework of **4**.

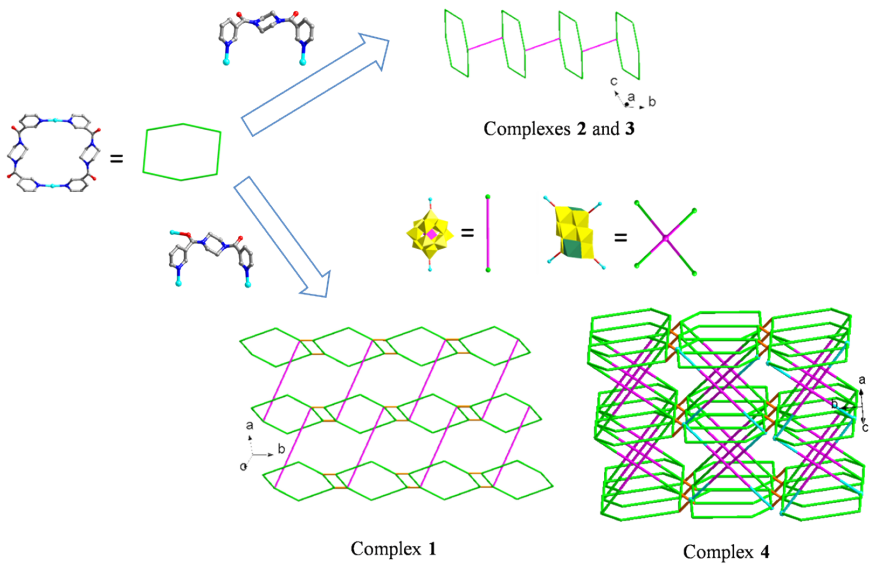

Fig. S6 View of the scheme of complexes **1**–**4** showing the influence of the coordination modes of L ligand and polyoxoanions on the structures

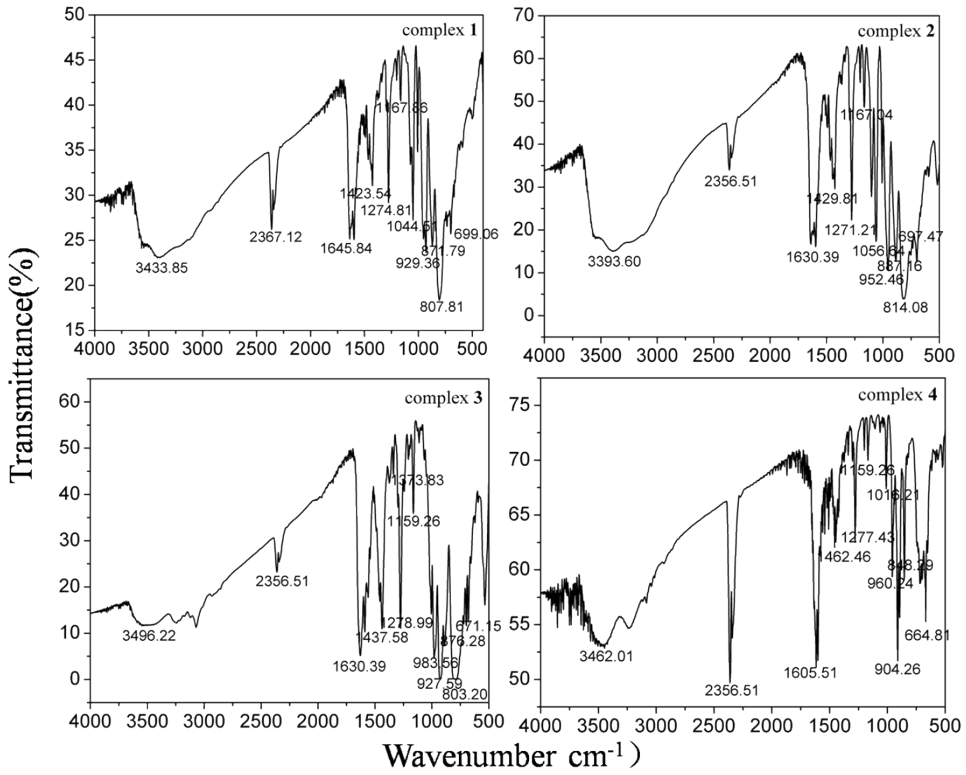

Fig. S7 The IR spectra of the title complexes.

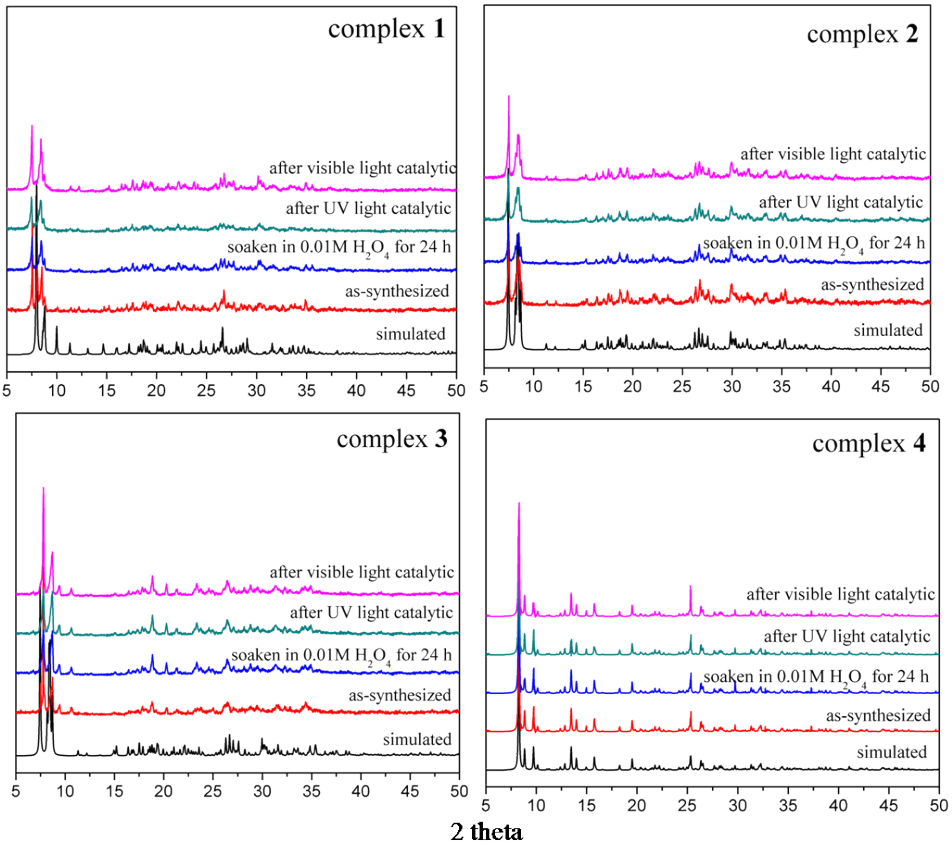

Fig. S8 Powder X–ray diffraction patterns of the title complexes.

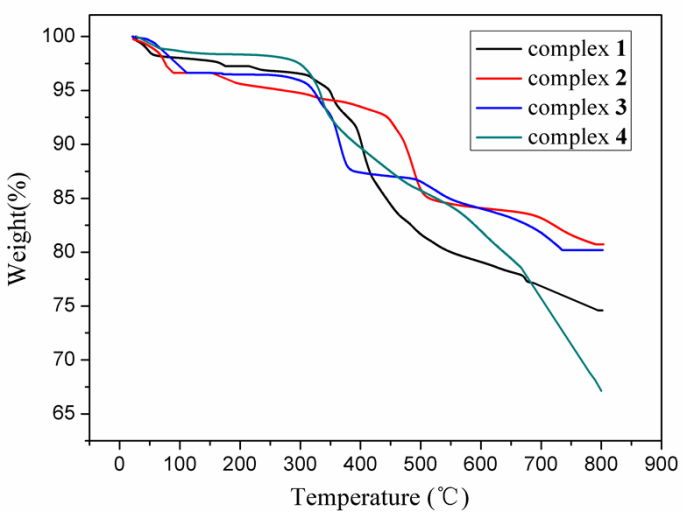

Fig. S9 The TGA curves of the title complexes**.**

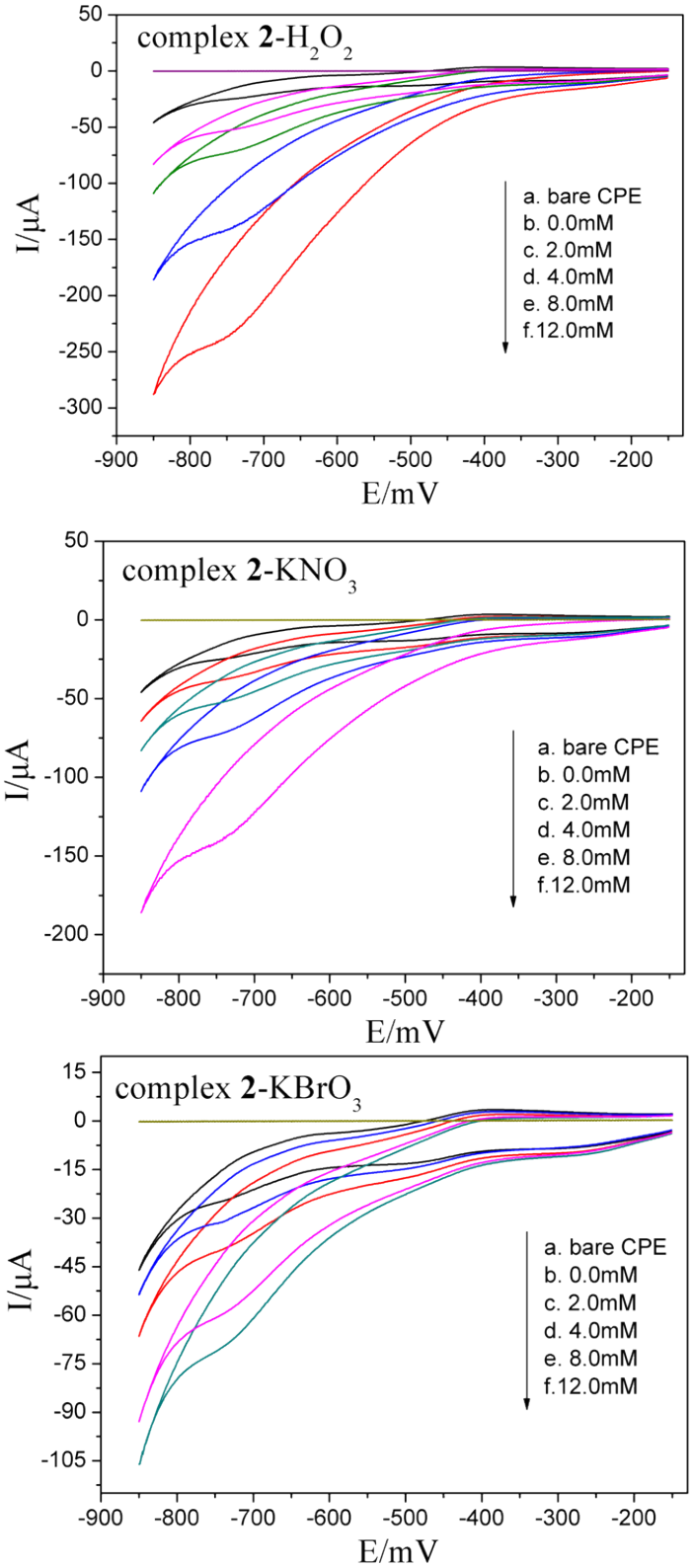

Fig. S10 Cyclic voltammograms of **2**–CPE in 0.01 M H_2SO_4 aqueous solution containing 0.0 – 12.0 mM H_2O_2/KNO_2/$KBrO_3$. Scan rate: 200 mV·s $^{-1}$.

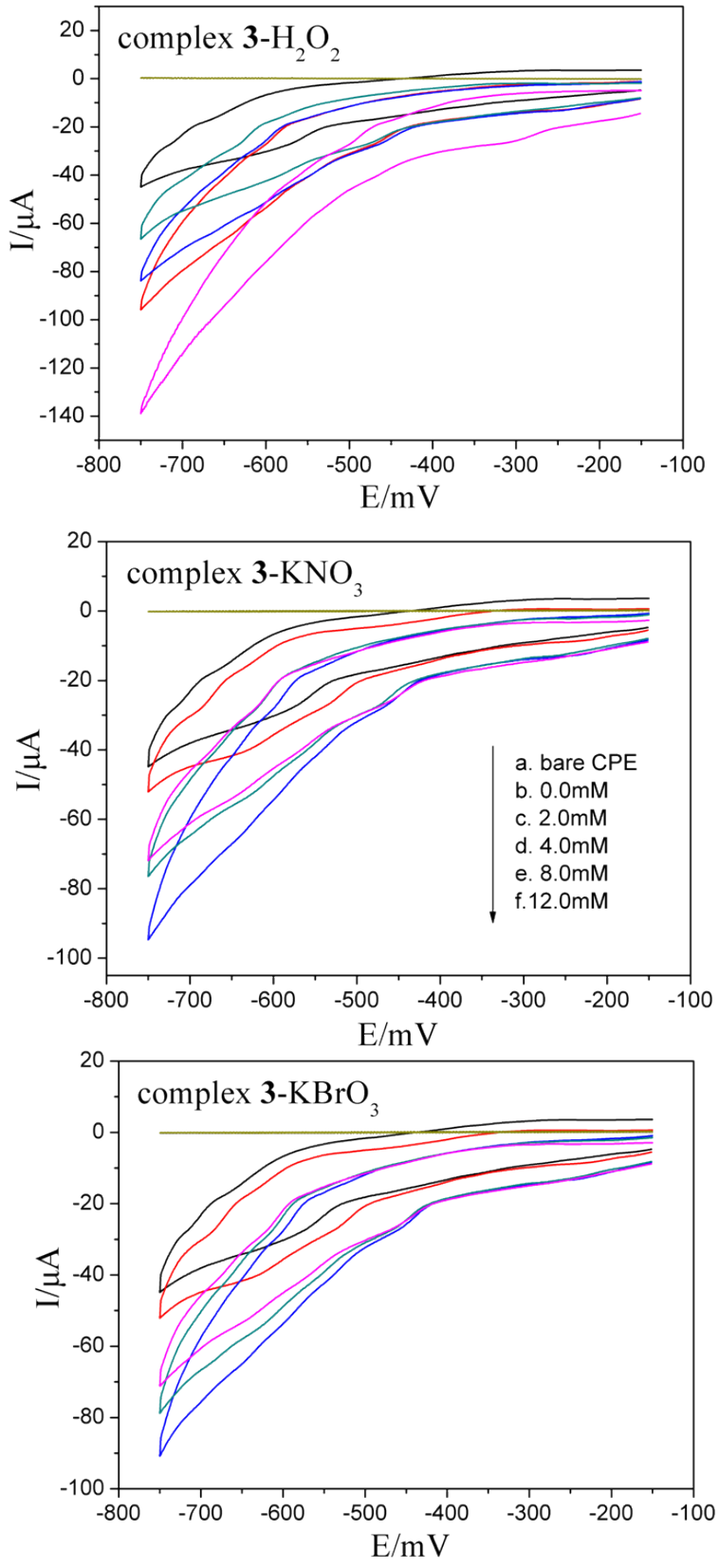

Fig. S11 Cyclic voltammograms of **3**–CPE in 0.01 M H_2SO_4 aqueous solution containing 0.0 − 12.0 mM H_2O_2/KNO_2/$KBrO_3$. Scan rate: 200 $mV \cdot s^{-1}$

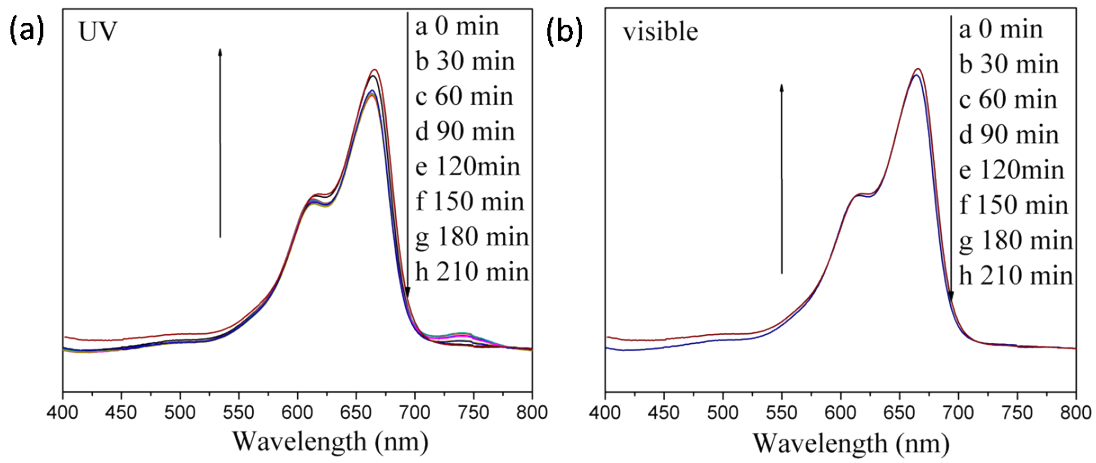

Fig. S12 Absorption spectra of the MB solution during the decomposition reaction under UV and visible irradiation without complex

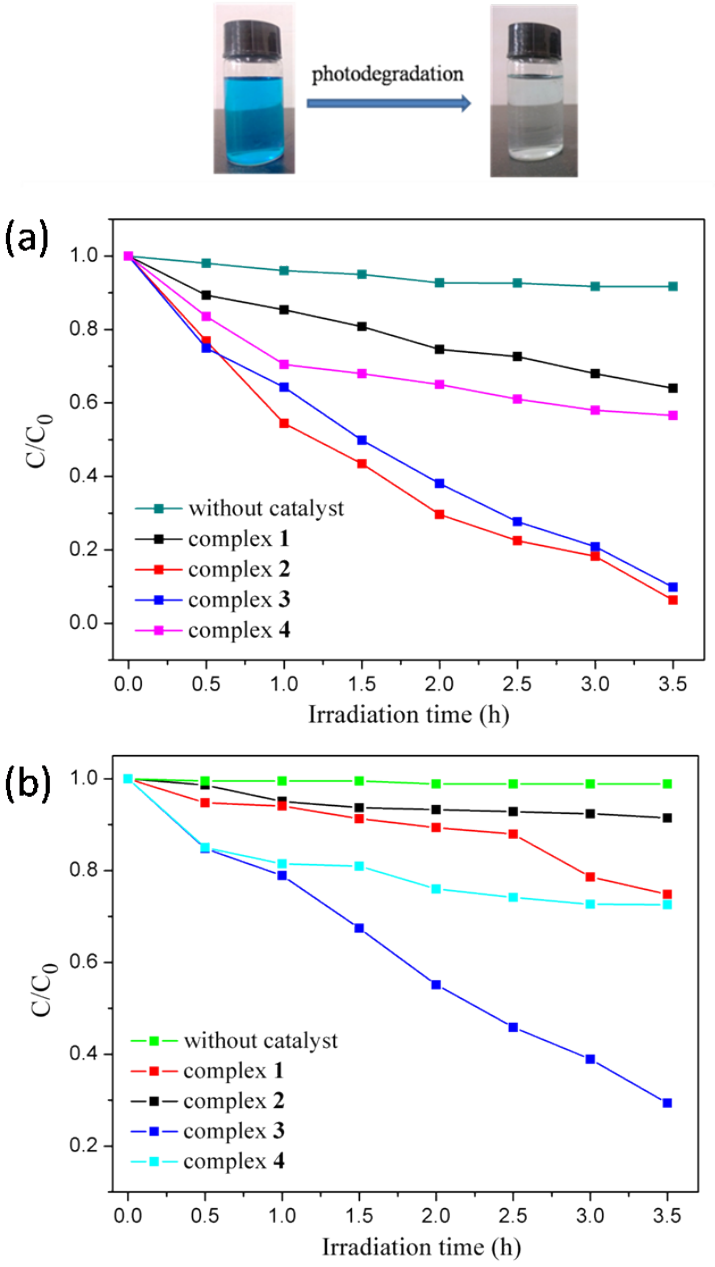

Fig. S13 Photocatalytic decomposition rate of MB solution under UV (a), and visible (b) irradiation with the use of title complexes.

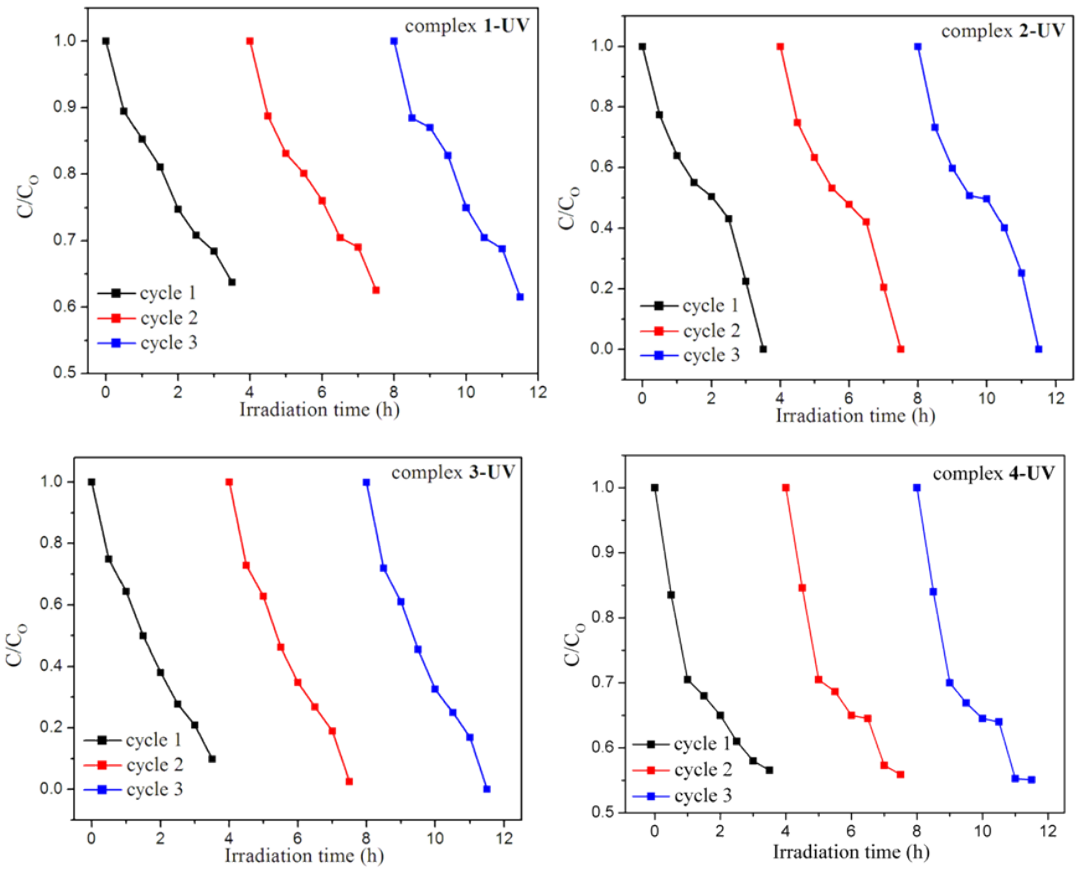

Fig. S14. Three times of MB degradation test under UV irradiation by the title complexes.