Table S1 Selected bond lengths (Å) and angles (°) for **1**-**4**

Complex **1**			
Cd(1)-O(1)	2.248(5)	Cd(1)-N(2)	2.283(5)
Cd(1)-O(1)$^{\#1}$	2.248(5)	Cd(1)-O(2)	2.545(6)
Cd(1)-N(2)$^{\#1}$	2.283(5)	Cd(1)-O(2)$^{\#1}$	2.545(6)
O(1)-Cd(1)-O(1)$^{\#1}$	158.3(3)	O(1)-Cd(1)-N(2)$^{\#1}$	107.42(19)
O(1)$^{\#1}$-Cd(1)-N(2)$^{\#1}$	84.40(17)	O(1)-Cd(1)-N(2)	84.40(17)
O(1)$^{\#1}$-Cd(1)-N(2)	107.42(19)	N(2)$^{\#1}$-Cd(1)-N(2)	115.1(3)
O(1)-Cd(1)-O(2)	52.66(15)	O(1)$^{\#1}$-Cd(1)-O(2)	111.10(18)
N(2)$^{\#1}$-Cd(1)-O(2)	88.9(2)	N(2)-Cd(1)-O(2)	136.19(16)
O(1)-Cd(1)-O(2)$^{\#1}$	111.10(18)	O(1)$^{\#1}$-Cd(1)-O(2)$^{\#1}$	52.66(15)
N(2)$^{\#1}$-Cd(1)-O(2)$^{\#1}$	136.19(16)	N(2)-Cd(1)-O(2)$^{\#1}$	88.9(2)
O(2)-Cd(1)-O(2)$^{\#1}$	98.1(3)	O(1)-Cd(1)-C(1)$^{\#1}$	135.5(2)
O(1)$^{\#1}$-Cd(1)-C(1)$^{\#1}$	26.59(17)	N(2)$^{\#1}$-Cd(1)-C(1)$^{\#1}$	110.5(2)
N(2)-Cd(1)-C(1)$^{\#1}$	99.6(2)	O(2)-Cd(1)-C(1)$^{\#1}$	105.48(18)
O(2)$^{\#1}$-Cd(1)-C(1)$^{\#1}$	26.09(16)		
Symmetry codes: #1: -x+3/2,y,-z+1			
Complex **2**			
Cd(1)-N(4)$^{\#1}$	2.306(4)	Cd(1)-O(2)	2.320(3)
Cd(1)-N(2)	2.322(4)	Cd(1)-N(5)	2.326(4)
Cd(1)-O(4)	2.376(4)	Cd(1)-O(3)	2.527(4)
Cd(1)-O(1)	2.580(4)		
N(4)$^{\#1}$-Cd(1)-O(2)	139.11(16)	N(4)$^{\#1}$-Cd(1)-N(2)	93.72(14)
O(2)-Cd(1)-N(2)	89.72(13)	N(4)$^{\#1}$-Cd(1)-N(5)	87.88(15)
O(2)-Cd(1)-N(5)	86.67(14)	N(2)-Cd(1)-N(5)	175.99(14)
N(4)$^{\#1}$-Cd(1)-O(4)	134.16(14)	O(2)-Cd(1)-O(4)	86.04(14)
N(2)-Cd(1)-O(4)	93.91(15)	N(5)-Cd(1)-O(4)	87.59(15)
N(4)$^{\#1}$-Cd(1)-O(3)	82.66(17)	O(2)-Cd(1)-O(3)	138.17(17)
N(2)-Cd(1)-O(3)	89.24(16)	N(5)-Cd(1)-O(3)	94.61(16)
O(4)-Cd(1)-O(3)	52.34(15)	N(4)$^{\#1}$-Cd(1)-O(1)	87.04(15)
O(2)-Cd(1)-O(1)	52.23(13)	N(2)-Cd(1)-O(1)	89.40(14)
N(5)-Cd(1)-O(1)	87.01(14)	O(4)-Cd(1)-O(1)	138.15(14)
O(3)-Cd(1)-O(1)	169.50(15)		
Symmetry codes: #1: -x+1,-y+1,-z+2	#2: x,y-1,z	#3: x,y+1,z	
Complex **3**			
Zn(1)-O(1)	1.940(2)	Zn(1)-O(1)$^{\#1}$	1.940(2)
Zn(1)-N(2)	2.019(2)	Zn(1)-N(2)$^{\#1}$	2.019(2)
O(1)-Zn(1)-O(1)$^{\#1}$	112.25(14)	O(1)-Zn(1)-N(2)	119.38(9)
O(1)$^{\#1}$-Zn(1)-N(2)	103.61(9)	O(1)-Zn(1)-N(2)$^{\#1}$	103.61(9)
O(1)$^{\#1}$-Zn(1)-N(2)$^{\#1}$	119.38(9)	N(2)-Zn(1)-N(2)$^{\#1}$	98.74(14)
C(1)-N(2)-Zn(1)	134.2(2)	C(2)-N(2)-Zn(1)	121.0(2)
C(10)-O(1)-Zn(1)	118.1(2)		
Symmetry codes: #1: -x+1,y,-z+3/2	#2: -x+3/2,-y+5/2,-z+2		
Complex **4**			

Cd(1)-N(2)	2.231(7)	Cd(1)-N(3)	2.314(8)
Cd(1)-O(1)	2.316(6)	Cd(1)-O(3)	2.351(6)
Cd(1)-O(2)$^{\#1}$	2.390(6)	Cd(1)-O(4)	2.496(6)
Cd(1)-O(2)	2.622(6)	Cd(1)-C(8)	2.757(9)
N(2)-Cd(1)-N(3)	163.8(3)	N(2)-Cd(1)-O(1)	108.1(2)
N(3)-Cd(1)-O(1)	86.5(3)	N(2)-Cd(1)-O(3)	96.2(2)
N(3)-Cd(1)-O(3)	91.4(3)	O(1)-Cd(1)-O(3)	87.1(2)
N(2)-Cd(1)-O(2)$^{\#1}$	81.0(2)	N(3)-Cd(1)-O(2)$^{\#1}$	84.6(3)
O(1)-Cd(1)-O(2)$^{\#1}$	127.5(2)	O(3)-Cd(1)-O(2)$^{\#1}$	144.6(2)
N(2)-Cd(1)-O(4)	86.7(2)	N(3)-Cd(1)-O(4)	86.2(3)
O(1)-Cd(1)-O(4)	139.8(2)	O(3)-Cd(1)-O(4)	53.5(2)
O(2)$^{\#1}$-Cd(1)-O(4)	91.1(2)	N(2)-Cd(1)-O(2)	87.6(2)
N(3)-Cd(1)-O(2)	96.6(2)	O(1)-Cd(1)-O(2)	51.7(2)
O(3)-Cd(1)-O(2)	137.2(2)	O(2)$^{\#1}$-Cd(1)-O(2)	78.1(2)
O(4)-Cd(1)-O(2)	168.5(2)	N(2)-Cd(1)-C(8)	92.2(3)
N(3)-Cd(1)-C(8)	88.1(3)	O(1)-Cd(1)-C(8)	113.3(3)
O(3)-Cd(1)-C(8)	26.7(2)	O(2)$^{\#1}$-Cd(1)-C(8)	118.0(2)
O(4)-Cd(1)-C(8)	26.9(2)	O(2)-Cd(1)-C(8)	163.7(2)

Symmetry codes: #1: -x+1,y,-z+3/2 #2: x,y+1,z #3: x+1,y,z #4: x-1,y,z #5: -x,y,-z+1/2

Table S2 Specified hydrogen bond distances (Å) and angles (º) of complex **4**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<DHA
C28-H28···O3^{i}	0.93	2.41	3.287(11)	156.9
C21-H21···O3^{i}	0.93	2.43	3.341(11)	166.0

Symmetry code: (*i*) 1 - x, 1 - y, 1 - z.

Table S3 The coordination modes of H_2dpb ligand and the roles of ancillary ligands in complexes **1**-**4**

Complex	Coord. modes	Ancillary ligands/role	Dihedral angles (°) of H_2dpb	Structure and topology
1	Mode I	Bimb/bridging	42.04(7)/59.69(9)/32.43(7)	2D + 2D → 3D (2,2,4)-connected $(12^5\cdot16)(12)^2$ unprecedented 2-fold interpenetrated network
2	Mode I	Tib/bridging	32.85(2)/31.12(2)/31.85(1)	2D → 3D (2,3,5)-connected $(4^2\cdot6\cdot8^6\cdot12)(4^2\cdot6)(8)$ unprecedented 3D supramolecular network
3	Mode II	4,4′-Bibp/bridging	18.78(4)/34.31(3)/47.91(4)	1D chain → 3D supramolecular structure
4	Mode III	1,3-Bitl/bridging	35.78(2)/27.96(3)/19.18(3)	2D → 3D 4-connected 3D supramolecular network

Table S4 Wavelengths of the emissionmaxima and excitation (nm) of **1-4** and free organic ligands at room temperature

Complex/ligand	λ_{ex}/nm	λ_{em}/nm
1	275	375
2	270	369
3	265	376
4	255	383
H_2dpb	275	405
Tib	275	371
4,4′-bibp	270	378
Bimb	220	380
1,3-bitl	280	385

Table S5 The degradation ratio of MB in Cd(II)/Zn(II) CPs

Coordination Polymer	MB Degradation Ratio (%)	Time (min)
$[Cd_3(3,4'\text{-tmbpt})_2(L)_2(H_2O)]\cdot 1.5H_2O$	50	90
$[NaCd_3(4,4'\text{-tmbpt})(L)_2(OH)]\cdot H_2O$	60	90
$\{[Zn(4\text{-bpah})(1,3\text{-BDC})(H_2O)]\}_n$	31	160
$\{[Cd(4\text{-bpah})(1,3\text{-BDC})]\}_n$	33	160
$\{[Cd(3\text{-bpah})(1,3\text{-BDC})]\cdot H_2O\}_n$	35	160

Fig. S1

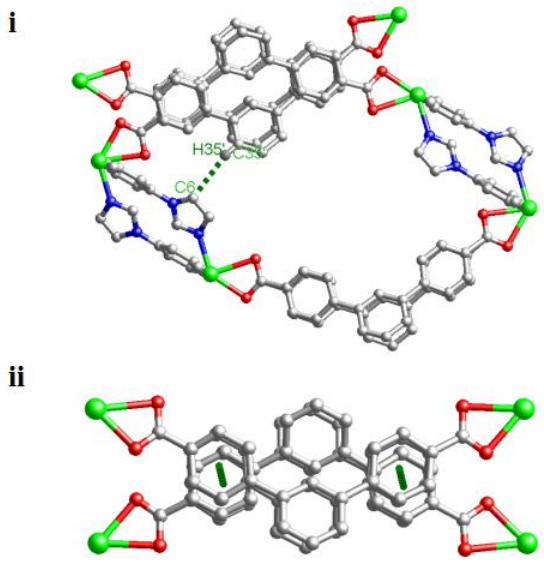


Fig. S1 The C-H···C and π-π interactions.

Fig. S2

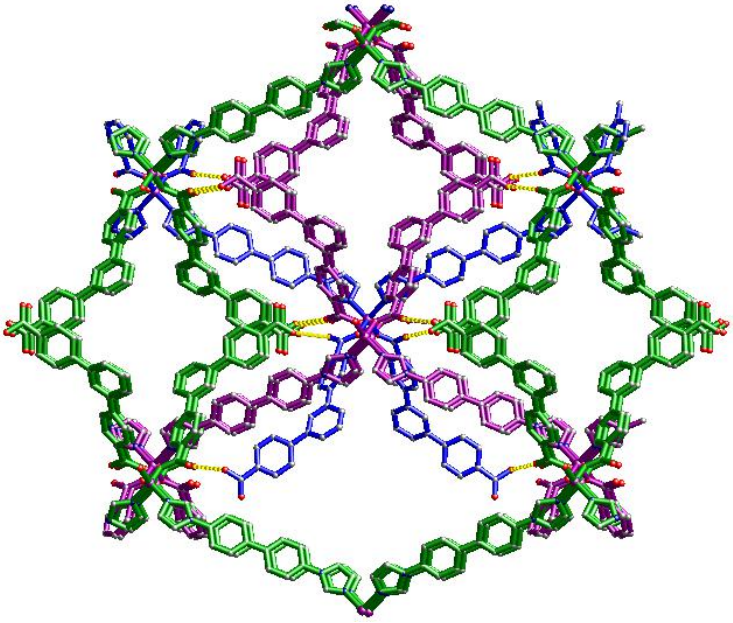


Fig. S2 The O-H···O hydrogen bonds along [1,1,0] orientation.

Fig. S3

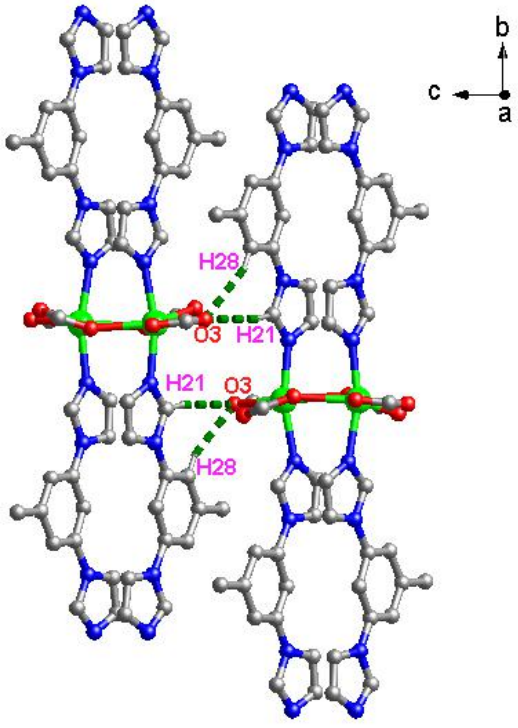


Fig. S3 The C-H···O bonds along [0,1,1] orientation.

Fig. S4

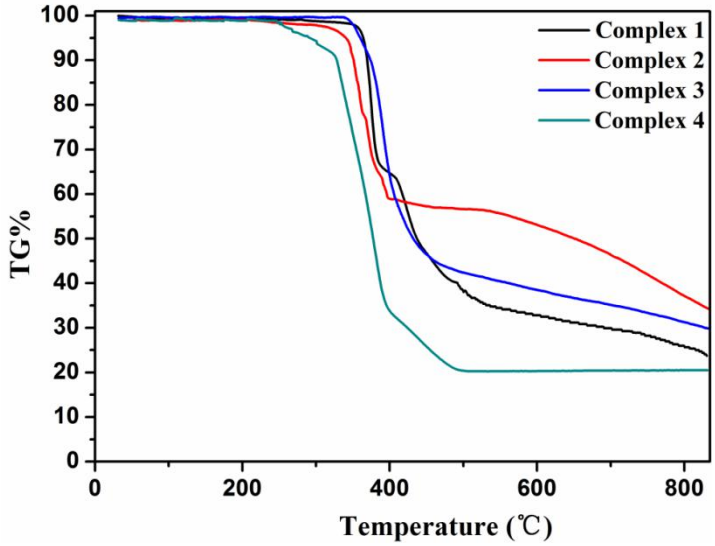
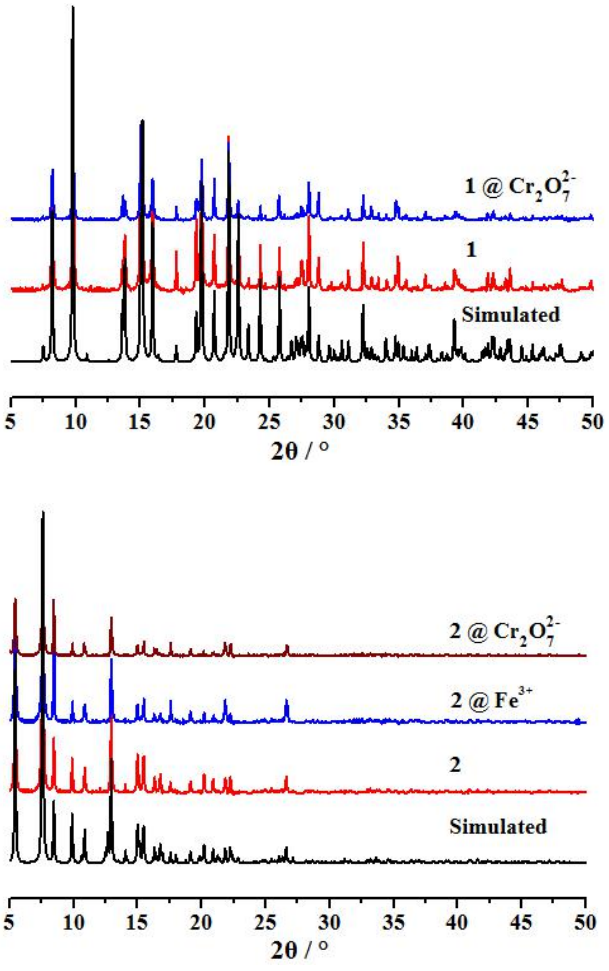


Fig. S4 The TGA curves for complexes **1-4**.

Fig. S5



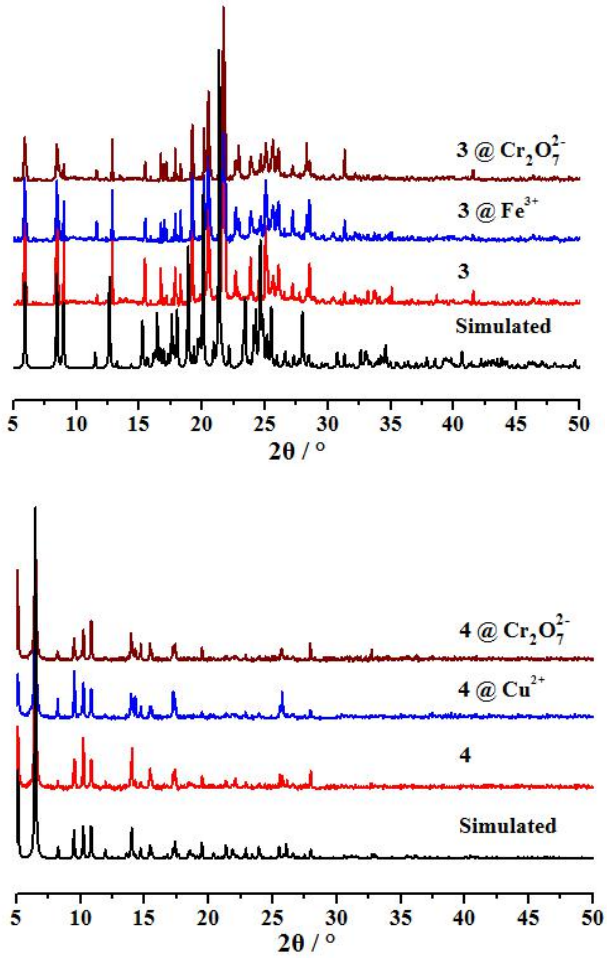


Fig. S5 PXRD patterns of simulated , **2-4** @ Fe^{3+}/ Cu^{2+} and **1-4** @ $Cr_2O_7^{2-}$.

Fig. S6 (a-c)

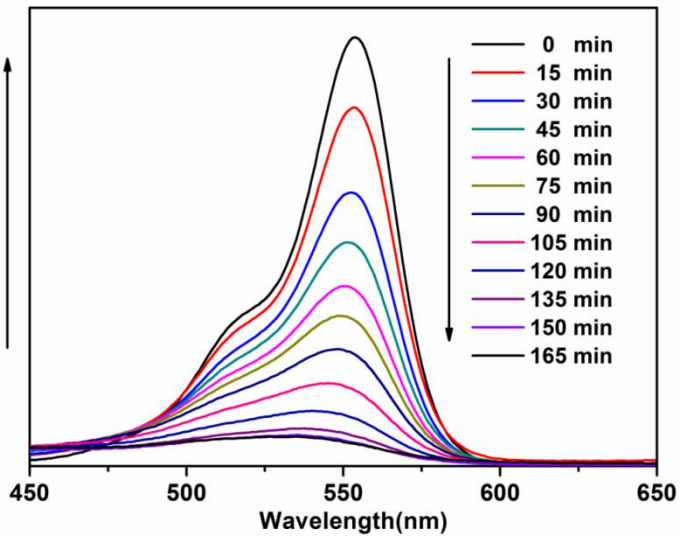


Fig. S6 (a) Absorption spectra of the RhB solution in the presence of complex **1**.

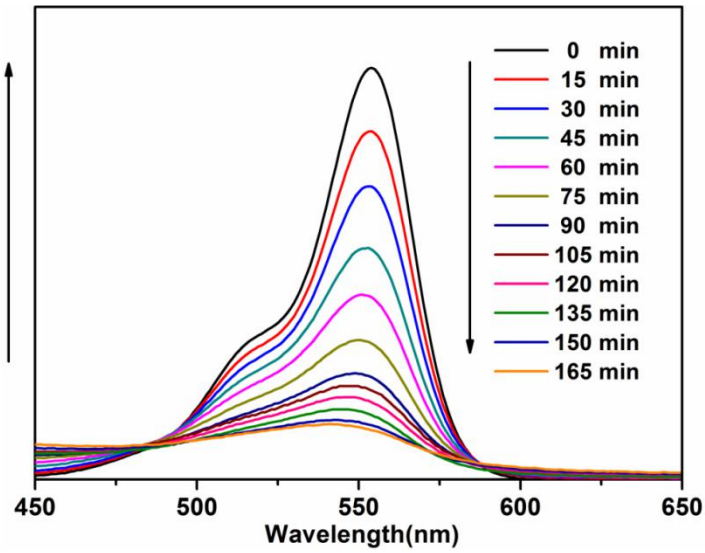


Fig. S6 (b) Absorption spectra of the RhB solution in the presence of complex **2**.

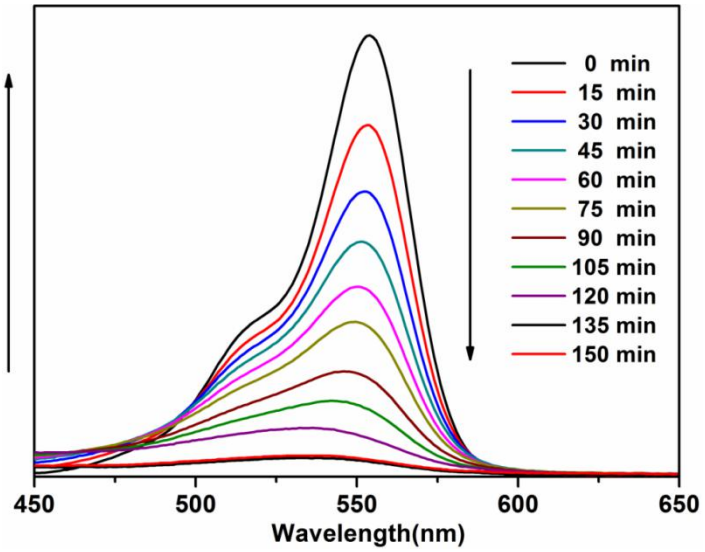


Fig. S6 (c) Absorption spectra of the RhB solution in the presence of complex **4**.

Fig. S7 (a-c)

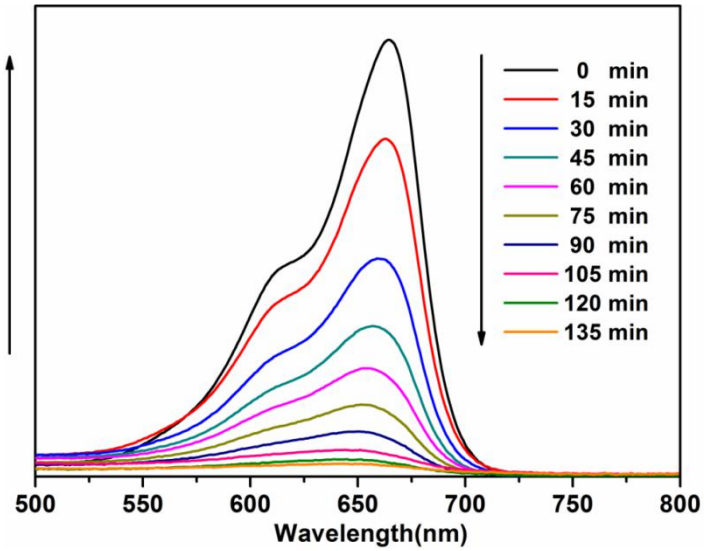


Fig. S7 (a) Absorption spectra of the MB solution in the presence of complex **1**.

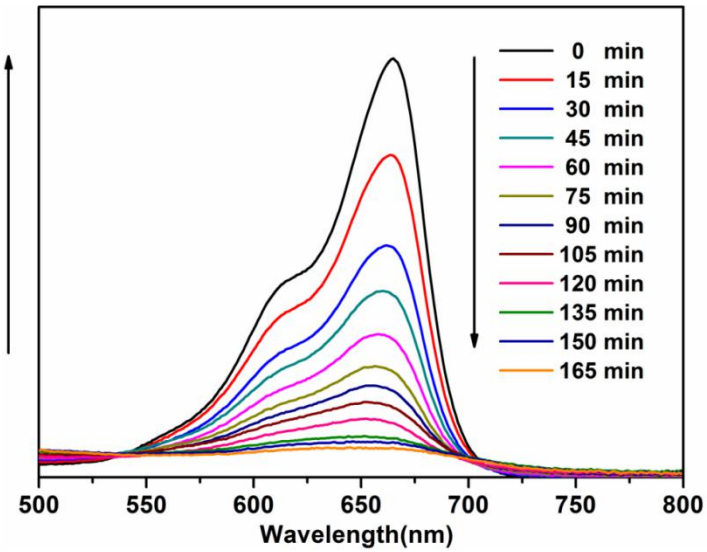


Fig. S7 (b) Absorption spectra of the MB solution in the presence of complex **2**.

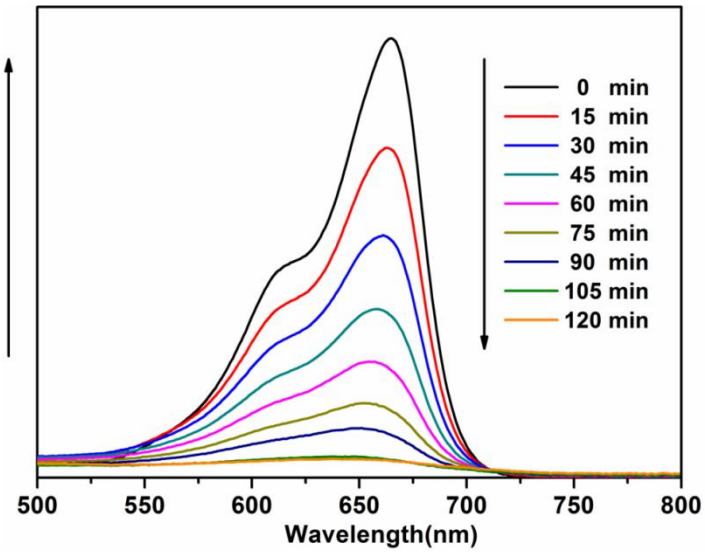
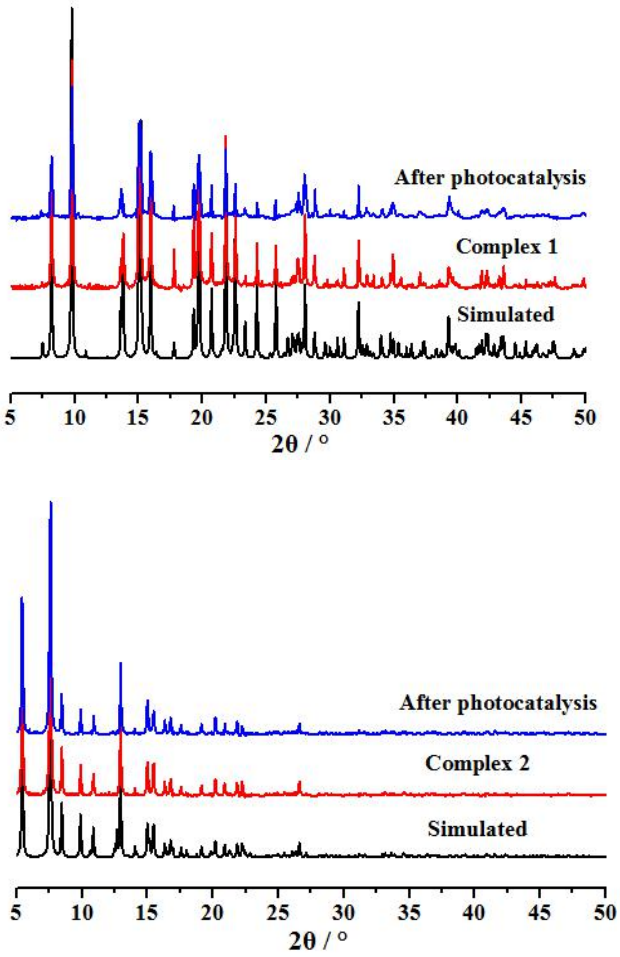


Fig. S7 (c) Absorption spectra of the MB solution in the presence of complex **4**.

Fig. S8



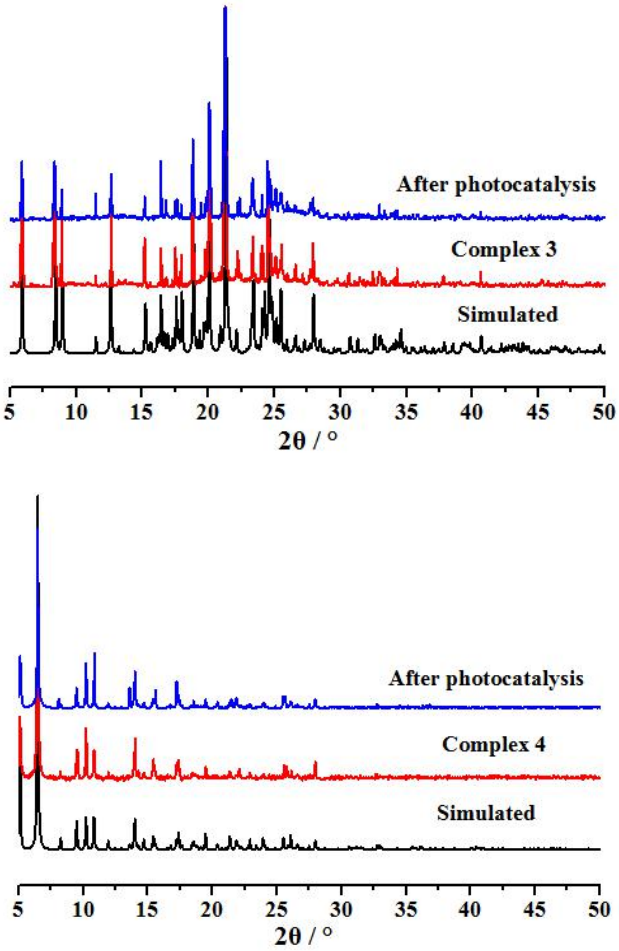


Fig. S8 PXRD patterns of complexes **1**-**4** before and after photocatalysis process.