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Application of flexible bis-pyrazine-bis-amide ligands to construct various polyoxometalate-based metal–organic complexes

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

Compound **1**			
Cu(1)-O(2)	1.923(5)	O(3)-Cu(1)-N(1)	82.7(2)
Cu(1)-O(3)	1.931(5)	O(1W)-Cu(1)-N(1)	165.7(3)
Cu(1)-O(1W)	1.939(7)	O(2)-Cu(1)-O(1)	88.4(2)
Cu(1)-N(1)	1.977(6)	O(3)-Cu(1)-O(1)	95.7(2)
Cu(1)-O(1)	2.404(6)	O(1W)-Cu(1)-O(1)	100.0(3)
Cu(2)-N(3)	1.961(6)	N(1)-Cu(1)-O(1)	91.5(2)
Cu(2)-N(3)#1	1.961(6)	N(3)-Cu(2)-N(3)#1	179.998(1)
Cu(2)-O(4)#1	1.970(5)	N(3)-Cu(2)-O(4)#1	97.40(2)
Cu(2)-O(4)	1.970(5)	N(3)#1-Cu(2)-O(4)#1	82.60(2)
O(2)-Cu(1)-O(3)	175.5(2)	N(3)-Cu(2)-O(4)	82.60(2)
O(2)-Cu(1)-O(1W)	93.70(3)	N(3)#1-Cu(2)-O(4)	97.40(2)
O(3)-Cu(1)-O(1W)	87.60(3)	O(4)#1-Cu(2)-O(4)	179.999(2)
O(2)-Cu(1)-N(1)	95.2(2)		
Symmetry code for **1**: #1 –x–1, –y+2, –z+2			
Compound **2**			
Cu(1)-O(1)	1.962(2)	O(3)#1-Cu(1)-N(1)	93.06(10)
Cu(1)-O(3)#1	1.963(2)	O(1)-Cu(1)-N(5)#1	101.66(10)
Cu(1)-N(1)	1.969(2)	O(3)#1-Cu(1)-N(5)#1	82.63(10)
Cu(1)-N(5)#1	1.971(3)	N(1)-Cu(1)-N(5)#1	175.21(10)
Cu(1)-O(2)	2.322(2)	O(1)-Cu(1)-O(2)	85.22(9)
O(3)-Cu(1)#3	1.963(2)	O(3)#1-Cu(1)-O(2)	95.26(9)
N(5)-Cu(1)#3	1.971(3)	N(1)-Cu(1)-O(2)	87.41(9)
O(1)-Cu(1)-O(3)#1	175.64(9)	N(5)#1-Cu(1)-O(2)	95.04(9)
O(1)-Cu(1)-N(1)	82.63(10)		
Symmetry code for **2**: #1 –x–1/2, y+1/2, –z+1/2; #3 –x–1/, y–1/2, –z+1/2			
Compound **3**			
Cu(1)-O(1)#2	1.947(7)	O(1)#2-Cu(1)-O(1W)#2	94.2(3)

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Cu(1)-O(1)	1.948(7)	O(1)-Cu(1)-O(1W)#2	85.8(3)
Cu(1)-N(3)#2	1.957(7)	N(3)#2-Cu(1)-O(1W)#2	81.1(3)
Cu(1)-N(3)	1.957(7)	N(3)-Cu(1)-O(1W)#2	98.9(3)
Cu(1)-O(1W)#2	2.405(11)	O(1)#2-Cu(1)-O(1W)	85.8(3)
Cu(1)-O(1W)	2.405(11)	O(1)-Cu(1)-O(1W)	94.2(3)
N(1)-Cu(2)	2.002(13)	N(3)#2-Cu(1)-O(1W)	98.9(3)
Cu(2)-O(2)	1.950(9)	N(3)-Cu(1)-O(1W)	81.1(3)
Cu(2)-O(2)#3	1.950(9)	O(1W)#2-Cu(1)-O(1W)	180.0
Cu(2)-N(1)#3	2.002(13)	O(2)-Cu(2)-O(2)#3	179.999(1)
O(1)#2-Cu(1)-O(1)	180.0(4)	O(2)-Cu(2)-N(1)#3	96.8(4)
O(1)#2-Cu(1)-N(3)#2	97.0(3)	O(2)#3-Cu(2)-N(1)#3	83.2(4)
O(1)-Cu(1)-N(3)#2	83.0(3)	O(2)-Cu(2)-N(1)	83.2(4)
O(1)#2-Cu(1)-N(3)	83.0(3)	O(2)#3-Cu(2)-N(1)	96.8(4)
O(1)-Cu(1)-N(3)	97.0(3)	N(1)#3-Cu(2)-N(1)	179.999(1)
N(3)#2-Cu(1)-N(3)	180.000(1)		

Symmetry code for **3**: #2 –x–1, –y+1, –z –1 ; #3 –x, –y, –z

Compound **4**

Cu(1)-O(1)#2	1.969(11)	O(2)-Cu(2)-N(5)	82.8(4)
Cu(1)-O(1)	1.969(11)	O(2)#3-Cu(2)-N(5)	97.2(4)
Cu(1)-N(1)#2	2.011(16)	O(2)-Cu(2)-N(5)#3	97.2(4)
Cu(1)-N(1)	2.011(16)	O(2)#3-Cu(2)-N(5)#3	82.8(4)
Cu(2)-O(2)	1.950(8)	N(5)-Cu(2)-N(5)#3	179.998(1)
Cu(2)-O(2)#3	1.950(8)	O(2)#3-Cu(2)-N(5)#3	82.8(4)
Cu(2)-N(5)	1.973(9)	N(5)-Cu(2)-N(5)#3	179.998(1)
Cu(2)-N(5)#3	1.973(9)	N(5)-Cu(2)-O(1W)	100.72(3)
Cu(2)- O(1W)	2.446(10)	N(5)#3-Cu(2)- O(1W)	79.28(3)
Cu(2)- O(1W)#3	2.446(10)	N(5)-Cu(2)-O(1W)#3	79.28(3)
O(1)#2-Cu(1)-O(1)	179.998(1)	N(5)#3-Cu(2)-O(1W)#3	100.72(3)
O(1)#2-Cu(1)-N(1)#2	82.7(5)	O(2) -Cu(2)- O(1W)#3	86.73(3)
O(1)-Cu(1)-N(1)#2	97.3(5)	O(2)#3-Cu(2)- O(1W)	86.73(3)
O(1)#2-Cu(1)-N(1)	97.3(5)	O(1W)-Cu(2)- O(1W)#3	180.00(3)
O(1)-Cu(1)-N(1)	82.7(5)	O(2)-Cu(2)- O(1W)	93.27(3)
N(1)#2-Cu(1)-N(1)	180.0(5)	O(2)#3-Cu(2)- O(1W) #3	93.27(3)
O(2)-Cu(2)-O(2)#3	180.0		

Symmetry code for **4**: #2 –x+1, –y+1, –z; #3 –x+2, –y, –z

Compound **5**

Cu(2)-O(1)	1.928(7)	N(1)-Cu(1)-N(2)#2	91.6(4)
Cu(1)-N(1)	1.990(10)	N(1)#2-Cu(1)-N(2)#2	88.4(4)
Cu(1)-O(2)#2	1.963(8)	O(2)#2-Cu(1)-N(2)	89.4(3)
Cu(1)-O(2)	1.963(8)	O(2)-Cu(1)-N(2)	90.6(3)
Cu(1)-N(1)#2	1.990(10)	N(1)-Cu(1)-N(2)	88.4(4)
Cu(1)-N(2)#2	2.430(9)	N(1)#2-Cu(1)-N(2)	91.6(4)
Cu(1)-N(2)	2.430(9)	N(2)#2-Cu(1)-N(2)	179.999(1)
Cu(2)-O(1)#3	1.928(7)	N(1)-Cu(1)-N(1)#2	179.999(1)

Cu(2)-N(4)	1.946(9)	O(1)#3-Cu(2)-N(4)	96.6(3)
Cu(2)-N(4)#3	1.946(9)	O(1)-Cu(2)-N(4)	83.4(3)
O(2)#2-Cu(1)-O(2)	179.999(1)	O(1)#3-Cu(2)-N(4)#3	83.4(3)
O(2)#2-Cu(1)-N(1)	97.2(4)	O(1)-Cu(2)-N(4)#3	96.6(3)
O(2)-Cu(1)-N(1)	82.8(4)	N(4)-Cu(2)-N(4)#3	179.999(2)
O(2)#2-Cu(1)-N(1)#2	82.8(4)	O(1)#3-Cu(2)-O(1)	179.999(1)

Symmetry code for **5** #2 –x–1, –y, –z; #3 –x–2, –y–1, –z–1

Table S2. Selected hydrogen–bonding geometry (Å, º) for compound **3** and **5**

	D–H···A	D–H	H···A	D···A	D–H···A
Compound **3**	N(5)–H(5B)···O(22)	0.86	2.23	3.0478	159
Compound **5**	C(7)–H(7A···O(10)	0.93	2.45	3.3506	162

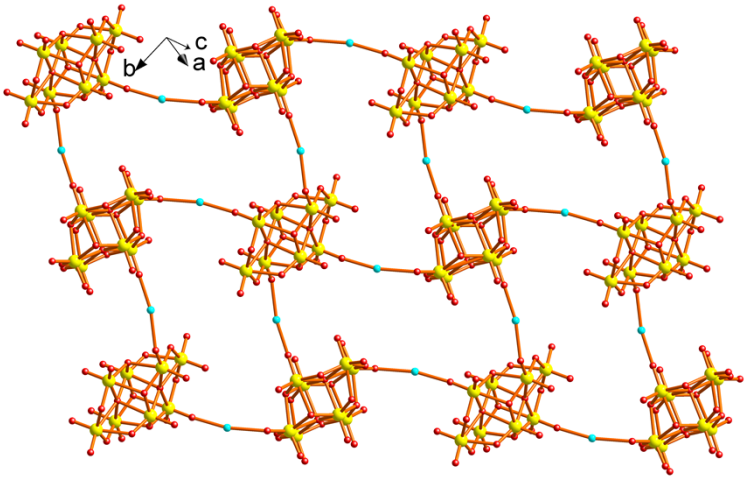


Fig. S1 The 2D inorganic layer structure in **2** (The L^1 ligands are omitted for clarity.).

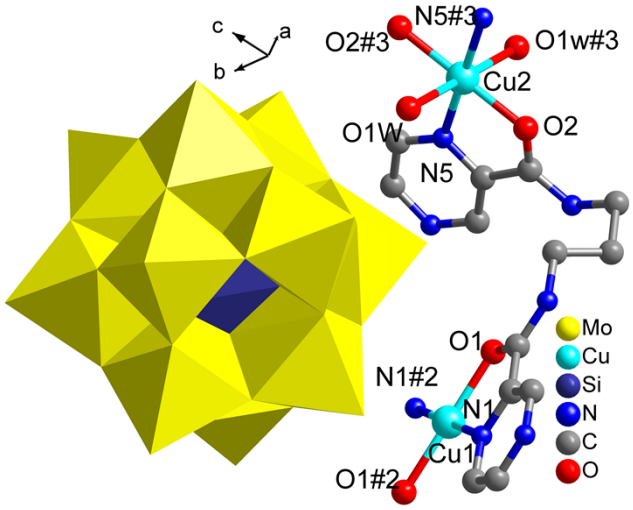
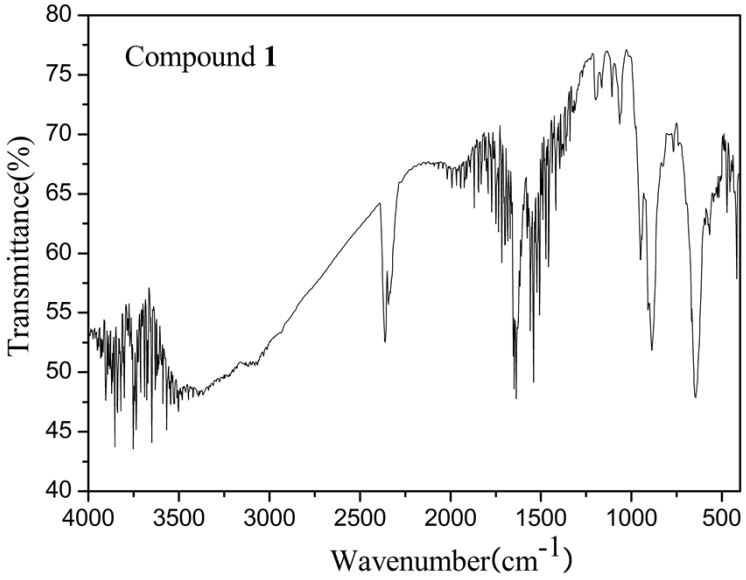
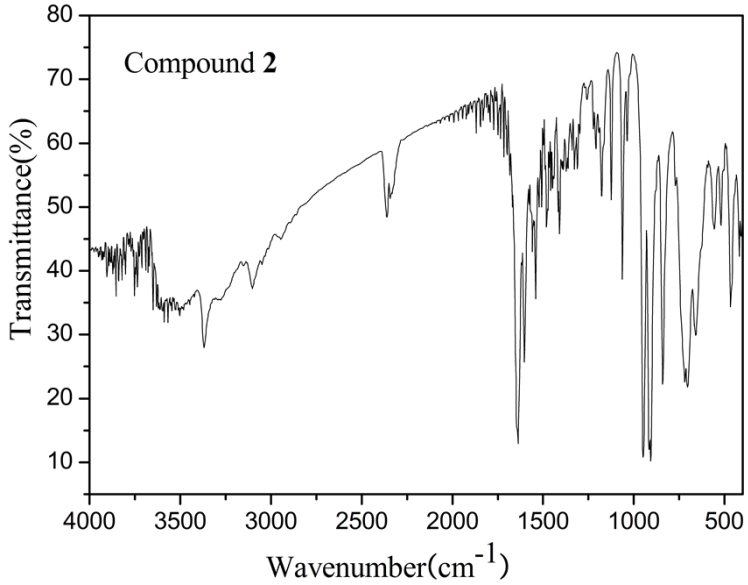
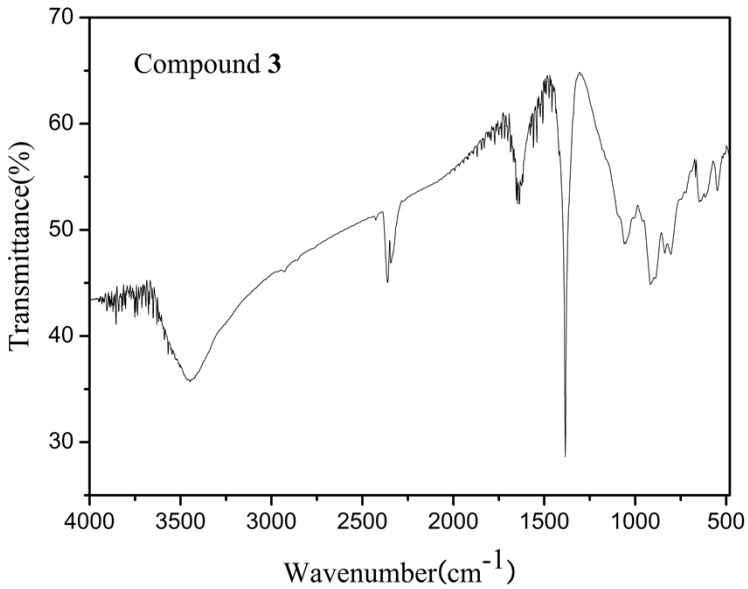


Fig.S2 The coordination environment of the Cu^{II} ion in **4**. All H atoms and lattice water molecules are omitted for clarity. Symmetry codes: #2 –x+1, –y+1, –z; #3 –x+2, –y, –z.


Compound 1
Transmittance(%)
Wavenumber(cm-1)
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
500


Compound 2
Transmittance(%)
Wavenumber(cm-1)
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500


Compound 3
Transmittance(%)
Wavenumber(cm-1)
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
500

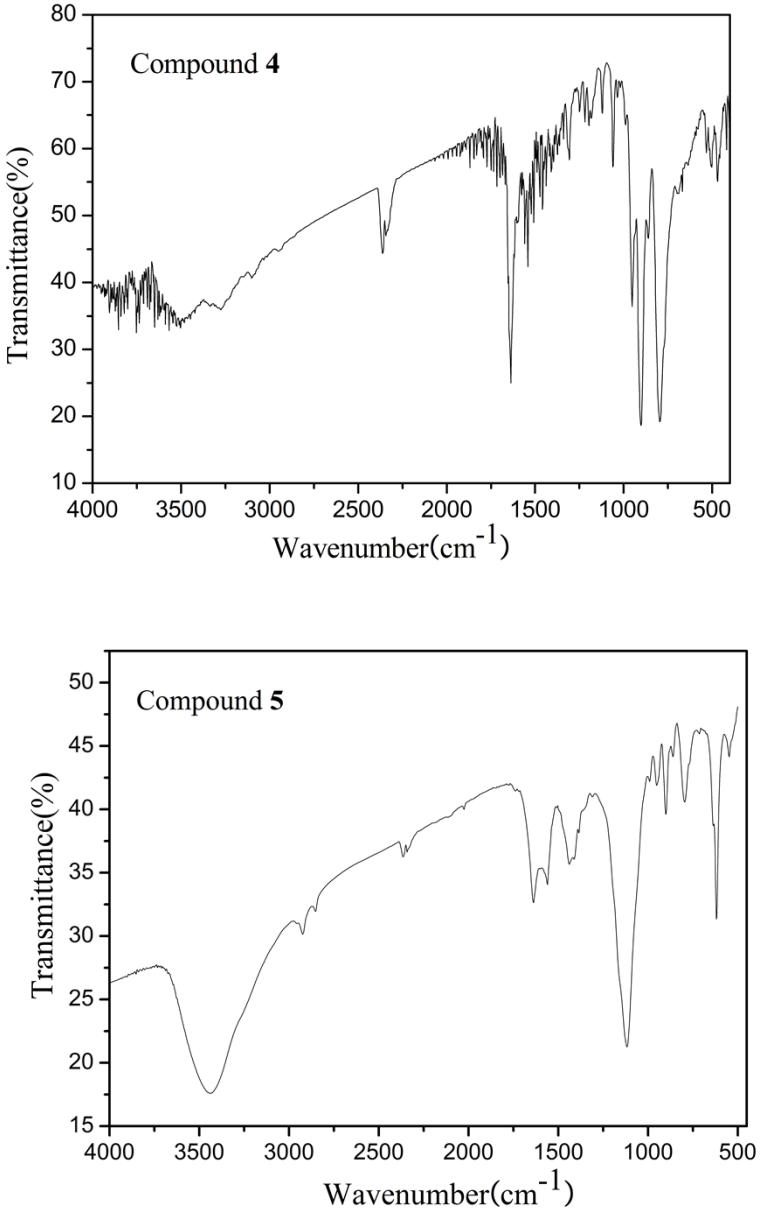
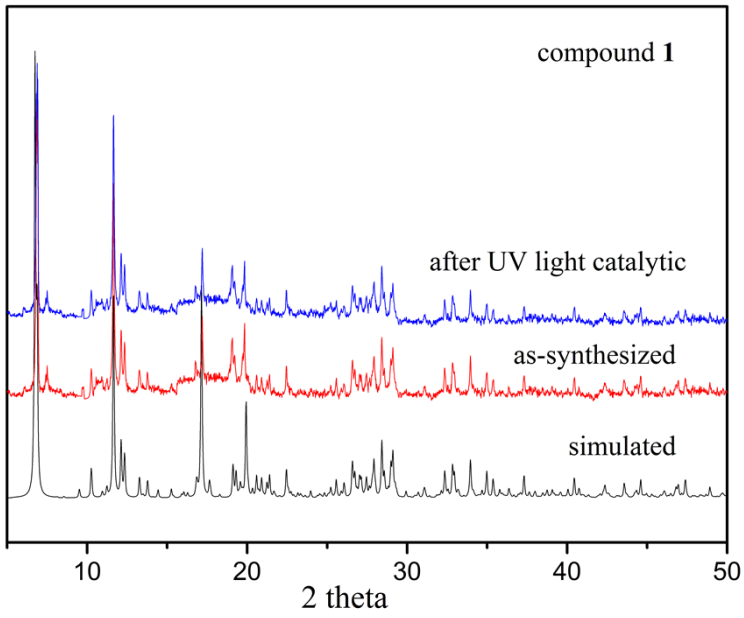
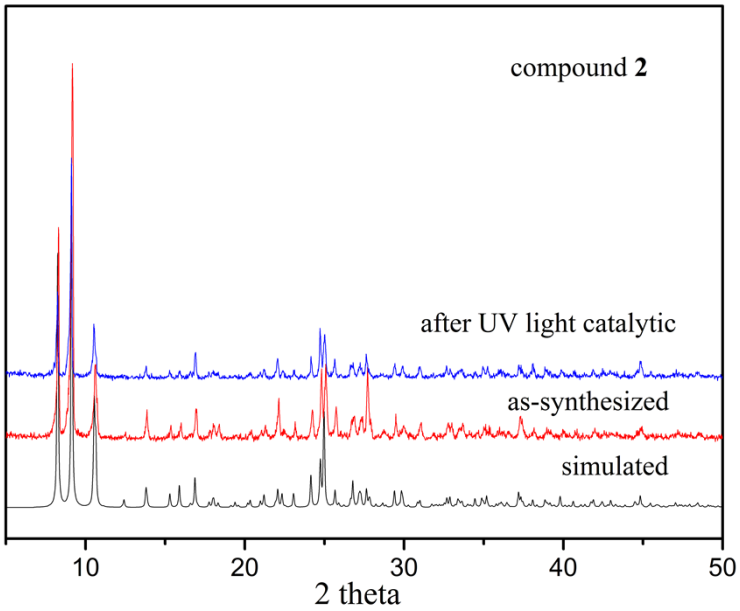
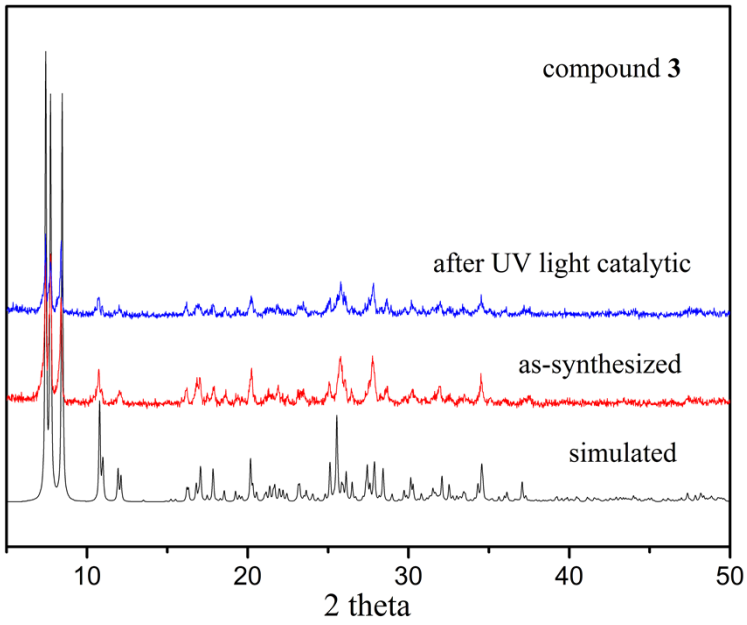
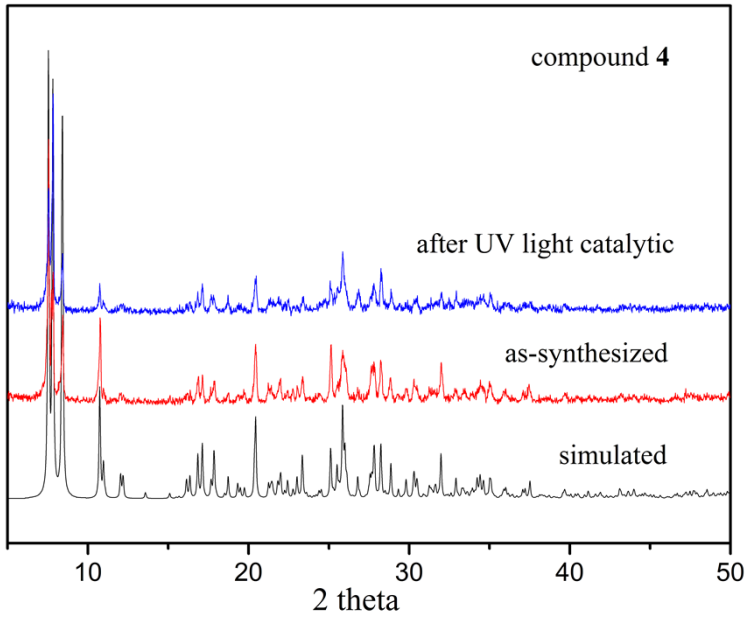


Fig. S3. The IR spectra of compounds **1**-**5.**


compound 1
after UV light catalytic
as-synthesized
simulated
10
20
30
40
50
2 theta


compound 2
after UV light catalytic
as-synthesized
simulated
10
20
30
40
50
2 theta


compound 3
after UV light catalytic
as-synthesized
simulated
10
20
30
40
50
2 theta


compound 4
after UV light catalytic
as-synthesized
simulated
10
20
30
40
50
2 theta

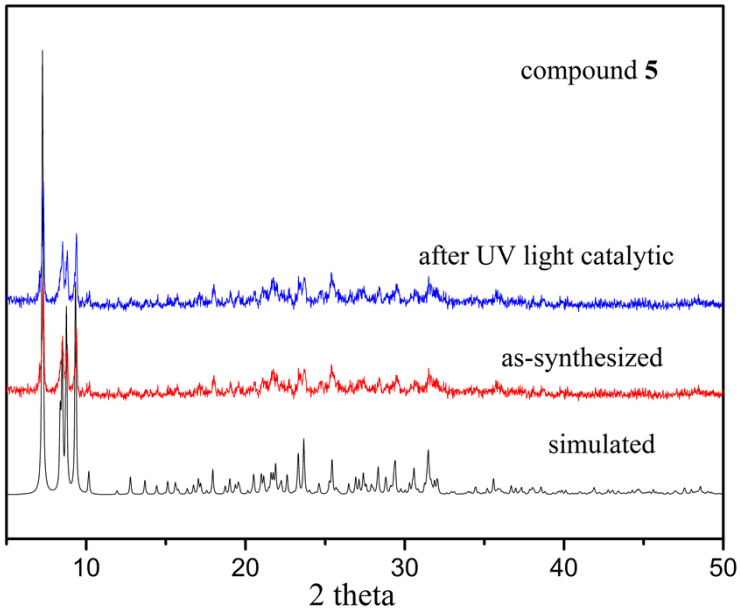


Fig. S4. The PXRD patterns of compounds **1- 5**.

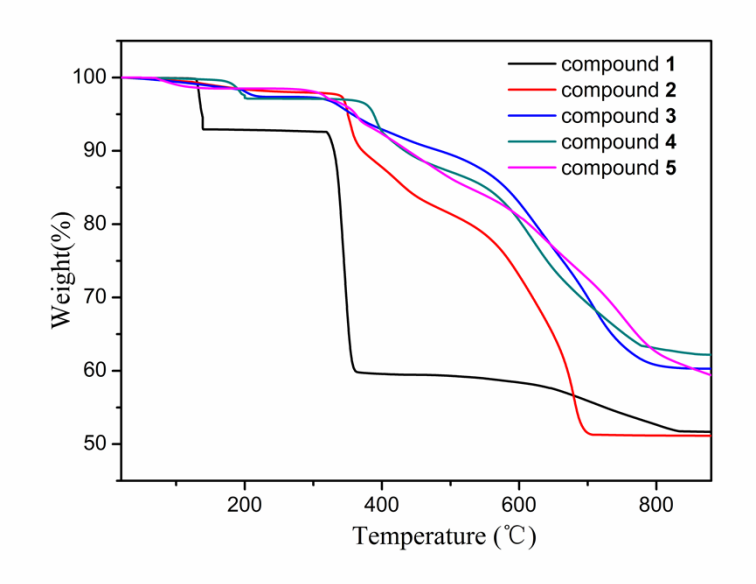


Fig. S5. The TG curves of compounds **1–5**.

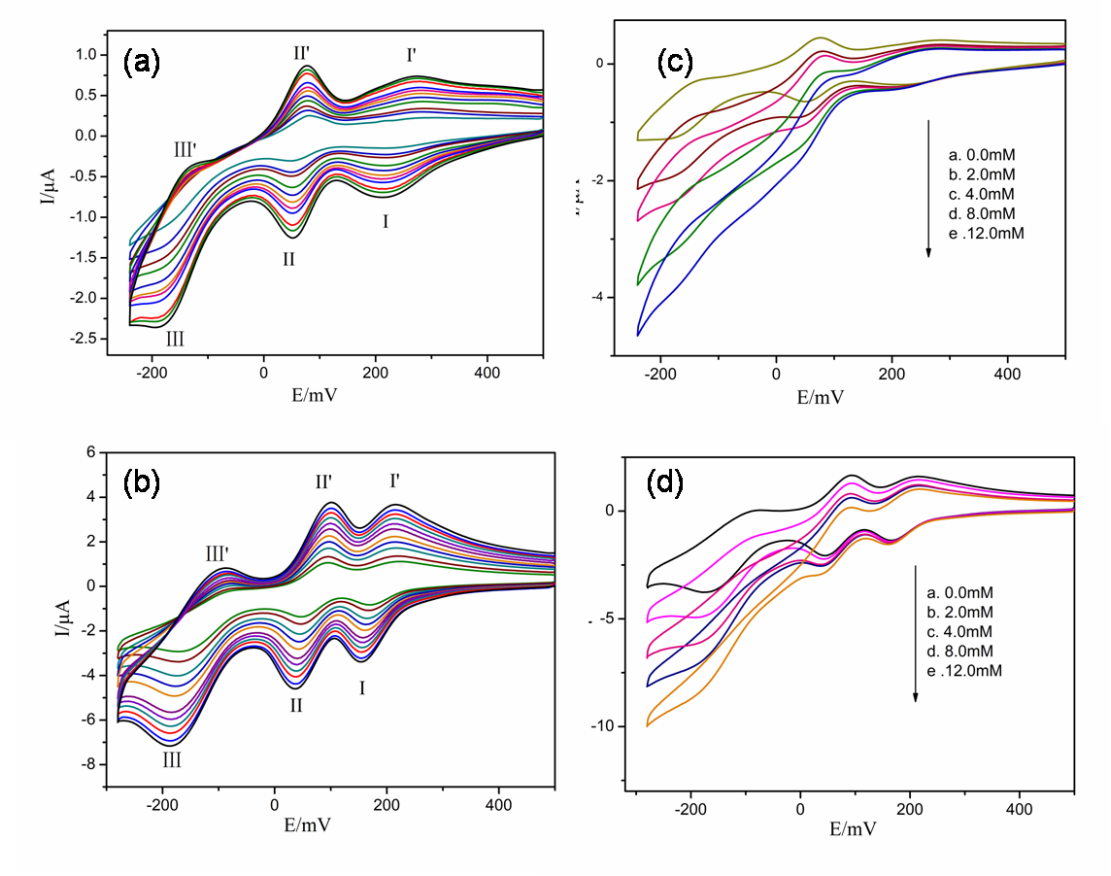


Fig. S6. Cyclic voltammograms of the **3**–CPE (a) and **5**–CPE (b) in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 80, 120, 160, 200, 250, 300, 350, 400, 450, 500 mV·s^{-1} for **3**–CPE and 40, 120, 160, 200, 250, 300, 350, 400, 450, 500 mV·s^{-1} for **5**–CPE). Cyclic voltammograms of **3**-CPE (c) and **5**-CPE (d) in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 solution containing 0.0–12.0 mM H_2O_2.

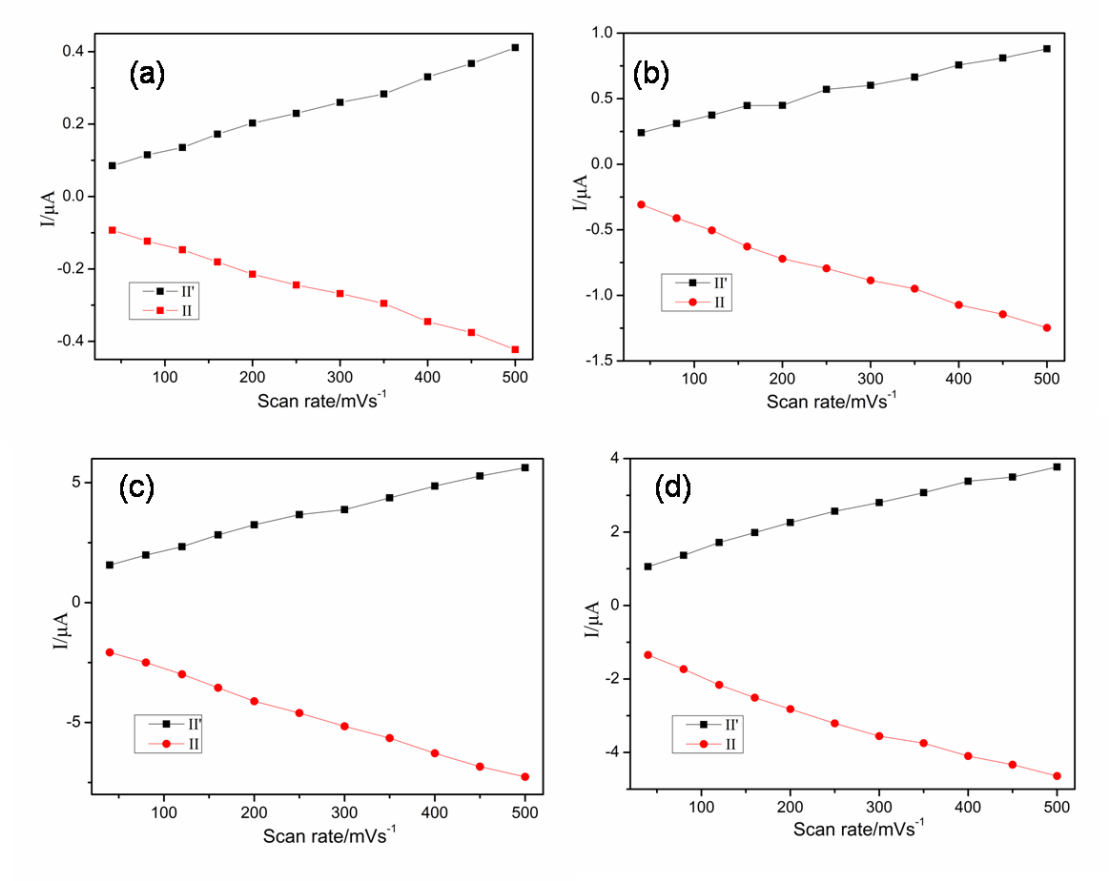


Fig. S7. The dependence of anodic peak (II) and cathodic peak (II') currents for **2**–CPE(a), **3**–CPE(b), **4**–CPE(c), **5**–CPE(d).

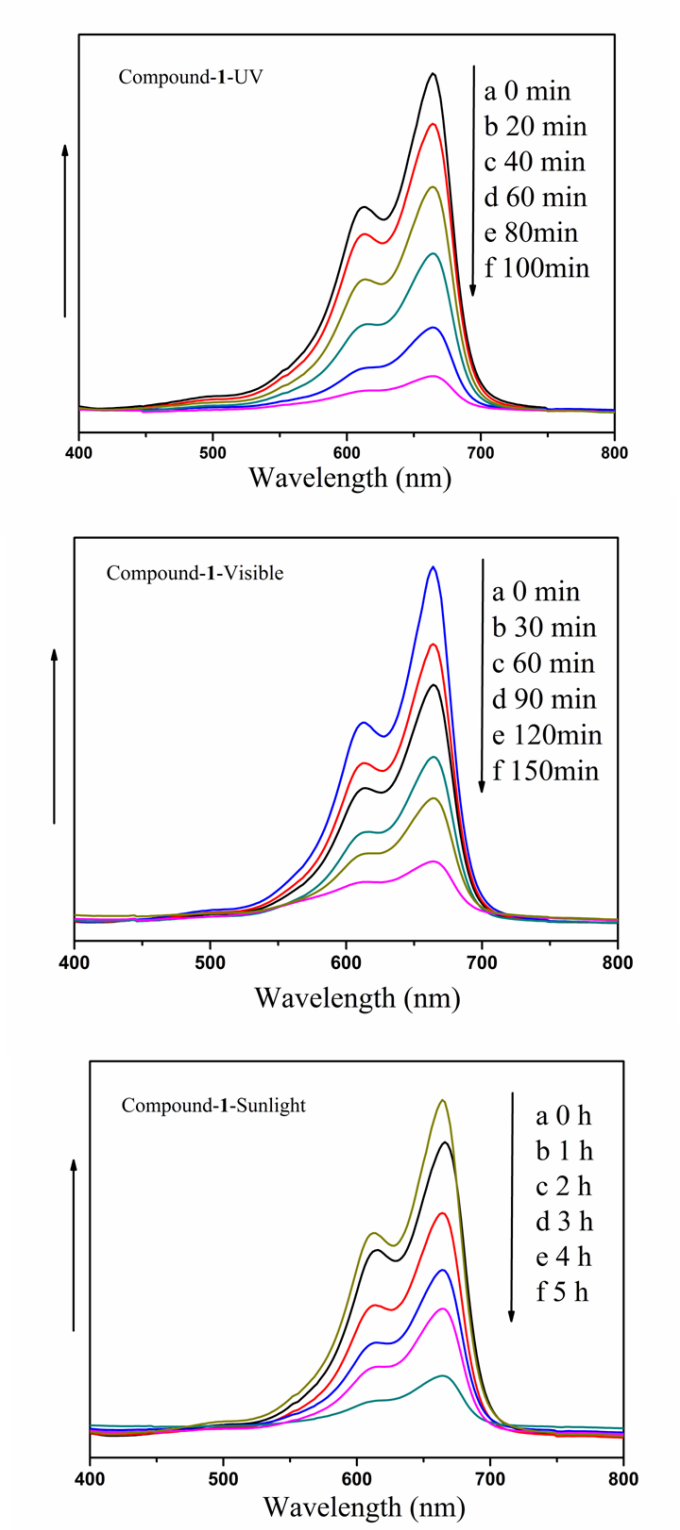


Fig. S8. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **1**.

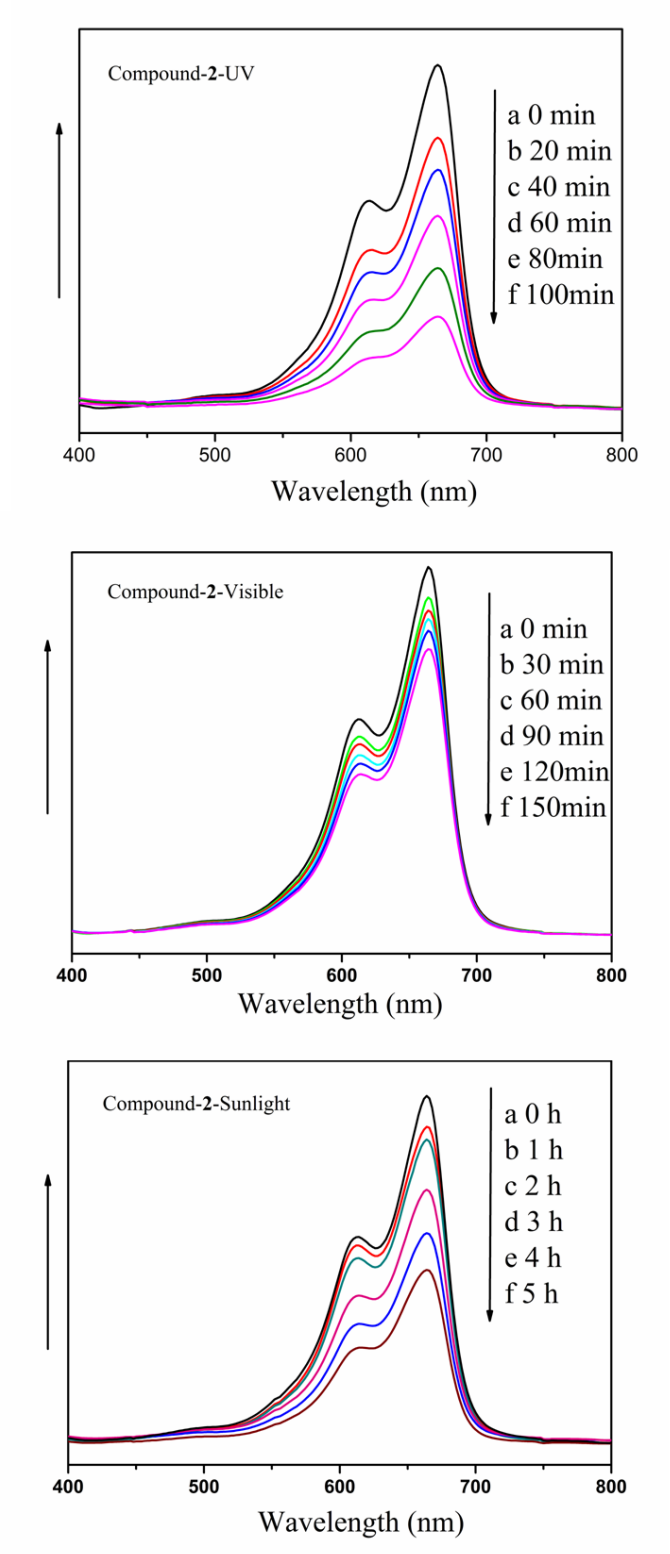


Fig. S9. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **2**.

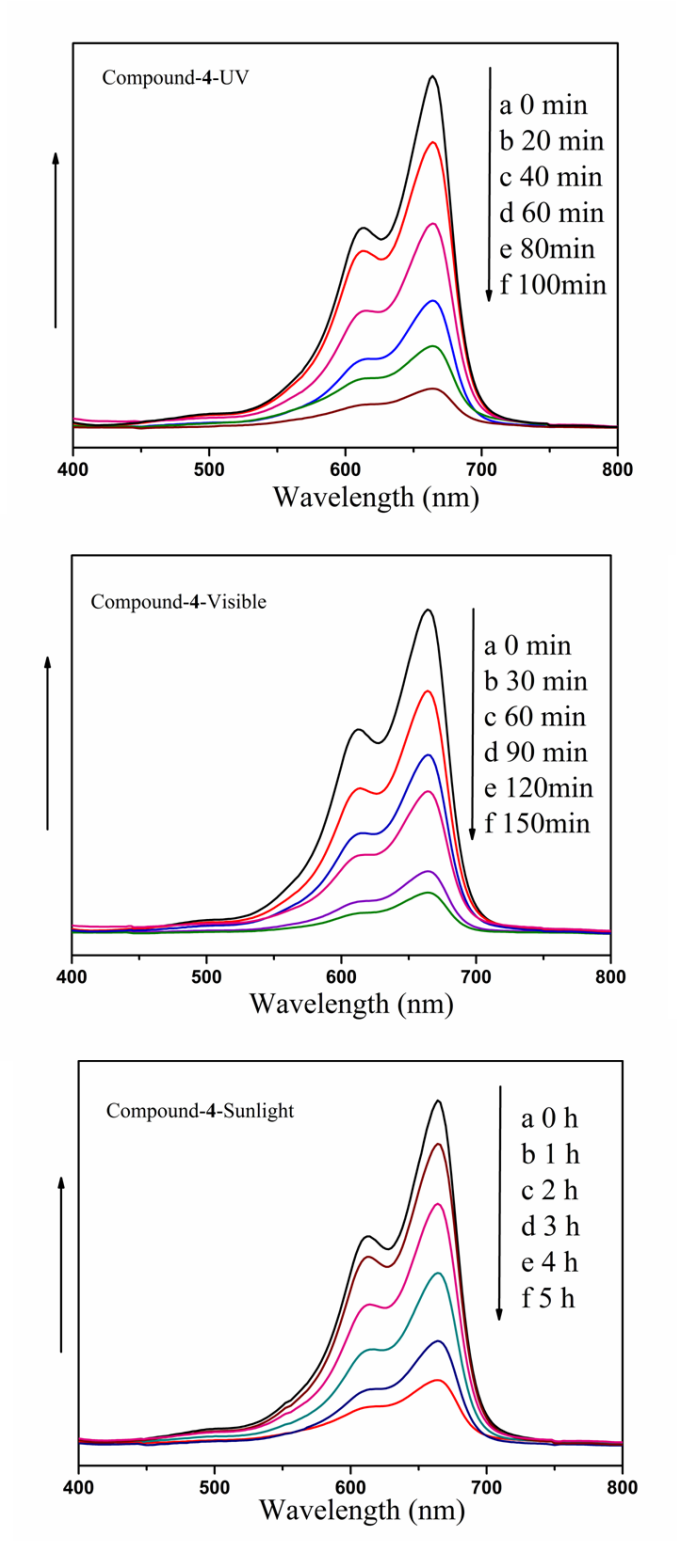


Fig. S10. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **4**.

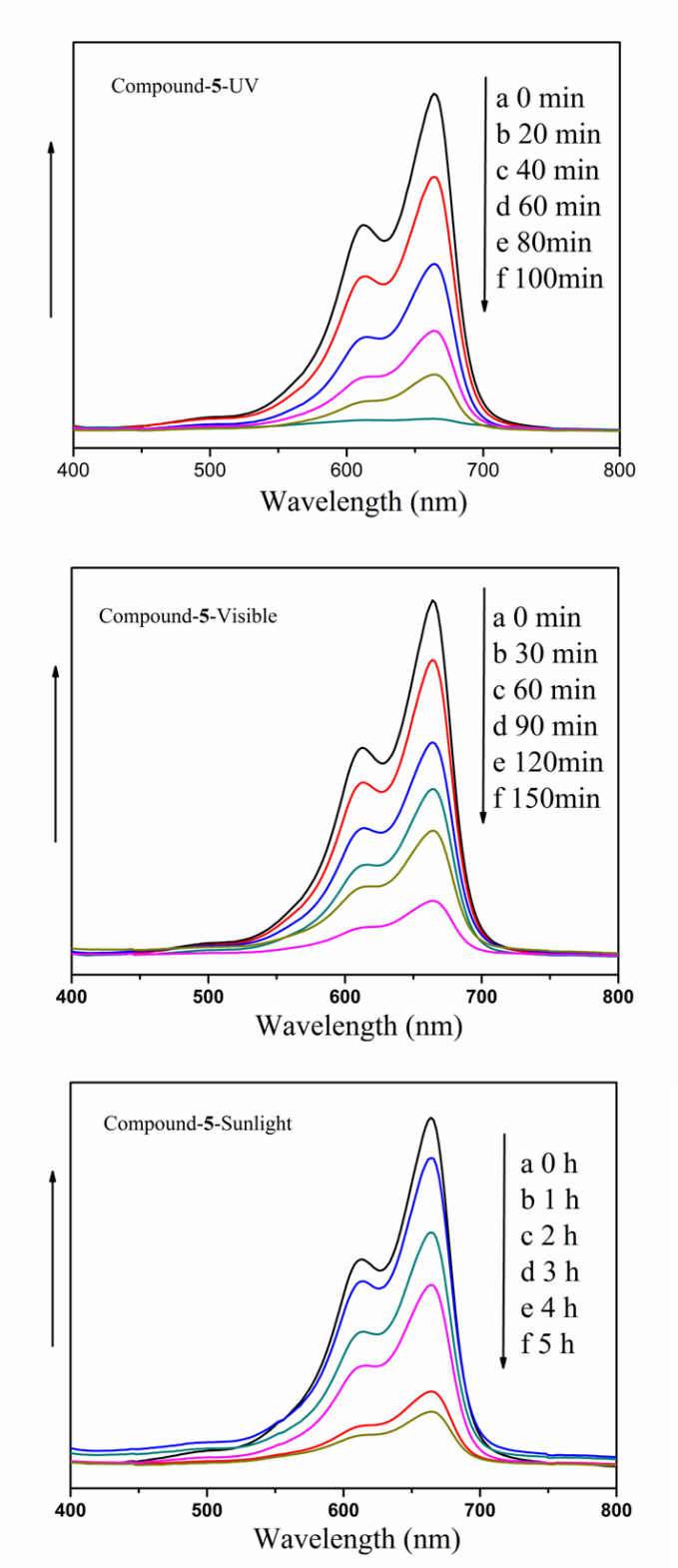


Fig. S11. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **5**.

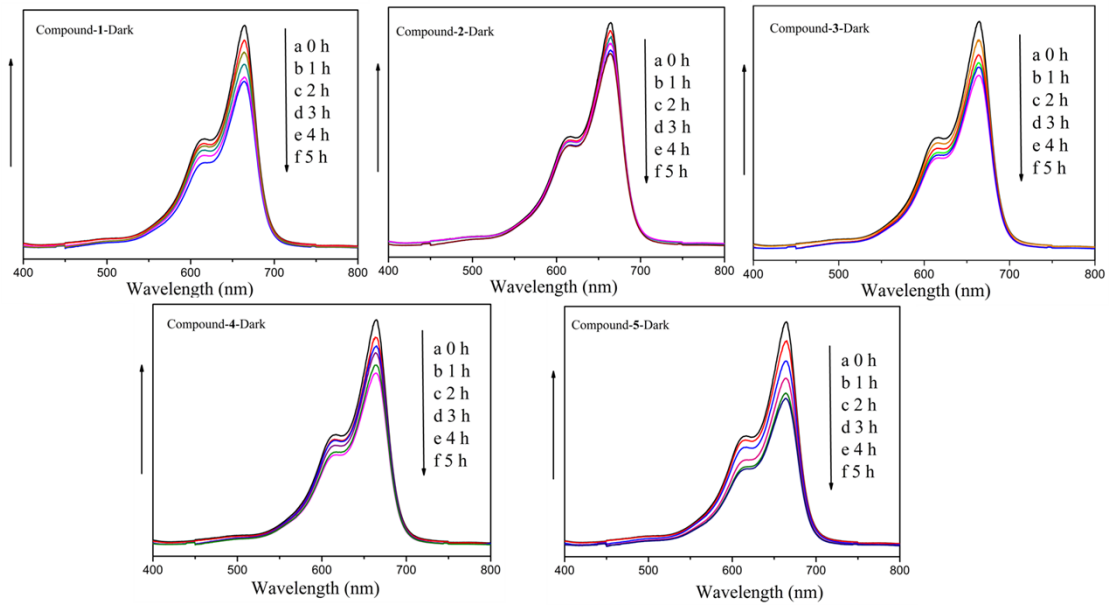


Fig. S12. Absorption spectra of the MB solution during the decomposition reaction in the presence of the compounds **1-5** under the dark environment.