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Polycarboxylate-directed various Co(II) complexes based on a "V"-like bis-pyridyl-bis-amide derivative: Construction, electrochemical and photocatalytic properties

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Table S1. Selected bond distances (Å) and angles (°) for complex **1**

$C_{50}H_{36}CoN_{10}O_{14}$			
Co(1)–O(1)#1	2.0877(11)	Co(1)–O(1)	2.0877(11)
Co(1)–N(5)#1	2.1157(13)	Co(1)–N(5)	2.1157(13)
Co(1)–N(1)	2.1639(13)	Co(1)–N(1)#1	2.1639(13)
O(1)#1–Co(1)–O(1)	180.0	O(1)#1–Co(1)–N(5)#1	78.85(4)
O(1)–Co(1)–N(5)#1	101.15(4)	O(1)#1–Co(1)–N(5)	101.15(4)
O(1)–Co(1)–N(5)	78.85(4)	N(5)#1–Co(1)–N(5)	180.0
O(1)#1–Co(1)–N(1)	89.06(5)	O(1)–Co(1)–N(1)	90.94(5)
N(5)#1–Co(1)–N(1)	87.55(5)	N(5)–Co(1)–N(1	92.45(5)
O(1)#1–Co(1)–N(1)#1	90.94(5)	O(1)–Co(1)–N(1)#1	89.06(5)
N(5)#1–Co(1)–N(1)#1	92.45(5)	N(5)–Co(1)–N(1)#1	87.55(5)
N(1)–Co(1)–N(1)#1	180.0		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z$

Table S2. Selected bond distances (Å) and angles (°) for complex **2**

$C_{26}H_{25}CoN_5O_{13}$			
Co(1)–O(4)	2.072(2)	Co(1)–O(2W)	2.095(3)
Co(1)–O(1W)	2.088(2)	Co(1)–O(2)	2.132(2)
Co(1)–N(1)	2.165(3)	Co(1)–N(4)#1	2.197(3)
O(4)–Co(1)–O(1W)	177.09(10)	O(4)–Co(1)–O(2W)	93.32(11)
O(1W)–Co(1)–O(2W)	89.55(12)	O(4)–Co(1)–O(2)	88.17(10)

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O(1W)–Co(1)–O(2)	89.07(10)	O(2W)–Co(1)–O(2)	170.65(10)
O(4)–Co(1)–N(1)	88.24(10)	O(1W)–Co(1)–N(1)	91.39(11)
O(2W)–Co(1)–N(1)	88.36(11)	O(2)–Co(1)–N(1)	100.92(10)
O(4)–Co(1)–N(4)#1	89.14(10)	O(1W)–Co(1)–N(4)#1	91.69(11)
O(2W)–Co(1)–N(4)#1	82.30(10)	O(2)–Co(1)–N(4)#1	88.50(10)
N(1)–Co(1)–N(4)#1	170.14(11)		

Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2, -y + 1/2, z + 1/2$

Table S3. Selected bond distances (Å) and angles (°) for complex **3**

$C_{26}H_{26}CoN_4O_{11}$

Co(1)–O(1)	2.0045(15)	Co(1)–O(2)#1	2.0047(15)
Co(1)–O(3)#2	2.1167(15)	Co(1)–N(1)	2.1520(19)
Co(1)–N(4)#3	2.1850(19)	Co(1)–O(4)#2	2.4182(15)
O(1)–Co(1)–O(2)#1	117.17(7)	O(1)–Co(1)–O(3)#2	91.69(6)
O(2)#1–Co(1)–O(3)#2	150.49(6)	O(1)–Co(1)–N(1)	95.35(7)
O(2)#1–Co(1)–N(1)	90.22(7)	O(3)#2–Co(1)–N(1)	93.20(7)
O(1)–Co(1)–N(4)#3	91.73(7)	O(2)#1–Co(1)–N(4)#3	83.14(7)
O(3)#2–Co(1)–N(4)#3	90.39(7)	N(1)–Co(1)–N(4)#3	171.96(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 2$; #2 $-x + 1, -y + 1, -z + 2$; #3 $-x, -y + 1, -z + 1$

Table S4. Selected bond distances (Å) and angles (°) for complex **4**

$C_{26}H_{24}CoN_4O_{11}$

Co(1)–O(8)	2.00(2)	Co(1)–O(7)	2.034(19)
Co(1)–O(1)	2.15(2)	Co(1)–N(4)#1	2.16(3)
Co(1)–N(1)	2.19(3)	Co(1)–O(2)	2.25(2)
O(8)–Co(1)–O(7)	114.7(9)	O(8)–Co(1)–O(1)	96.7(9)
O(7)–Co(1)–O(1)	147.7(9)	O(8)–Co(1)–N(4)#1	91.8(10)
O(7)–Co(1)–N(4)#1	95.1(9)	O(1)–Co(1)–N(4)#1	91.1(10)
O(8)–Co(1)–N(1)	83.7(10)	O(7)–Co(1)–N(1)	88.2(9)
O(1)–Co(1)–N(1)	87.9(10)	N(4)#1–Co(1)–N(1)	175.3(10)
O(8)–Co(1)–O(2)	156.2(9)	O(7)–Co(1)–O(2)	89.1(8)
O(1)–Co(1)–O(2)	59.6(8)	N(4)#1–Co(1)–O(2)	86.7(10)
N(1)–Co(1)–O(2)	96.8(10)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z$

Table S5. Selected bond distances (Å) and angles (°) for complex **5**

$C_{27}H_{23}CoN_4O_9$

Co(1)–O(3)#1	2.0185(18)	Co(1)–O(2)	2.071(2)
Co(1)–N(1)	2.093(2)	Co(1)–N(4)#2	2.124(2)
Co(1)–O(1W)	2.161(2)		

O(3)#1–Co(1)–O(2)	143.03(8)	O(3)#1–Co(1)–N(1)	123.89(8)
O(2)–Co(1)–N(1)	91.29(9)	O(3)#1–Co(1)–N(4)#2	93.85(8)
O(2)–Co(1)–N(4)#2	94.45(9)	N(1)–Co(1)–N(4)#2	94.28(9)
O(3)#1–Co(1)–O(1W)	84.85(8)	O(2)–Co(1)–O(1W)	84.89(9)
N(1)–Co(1)–O(1W)	88.87(8)	N(4)#2–Co(1)–O(1W)	176.80(8)

Symmetry transformations used to generate equivalent atoms: #1 $x - 1$, y, z; #2 $-x + 1$, $y - 1/2$, $-z + 1/2$

Table S6. Selected bond distances (Å) and angles (°) for complex **6**

$C_{54}H_{42}Co_3N_8O_{22}$

Co(1)–O(5)#2	2.013(5)	Co(1)–O(5)#3	2.013(5)
Co(1)–O(3)#4	2.020(5)	Co(1)–O(3)	2.020(5)
Co(2)–O(1W)	2.086(6)	Co(2)–O(2W)	2.088(6)
Co(2)–N(4)#5	2.105(7)	Co(2)–N(1)	2.128(7)
Co(2)–O(1)	2.130(5)	Co(2)–O(2)	2.206(6)
O(5)#2–Co(1)–O(5)#3	96.4(3)	O(5)#2–Co(1)–O(3)#4	114.0(2)
O(5)#3–Co(1)–O(3)#4	116.7(2)	O(5)#2–Co(1)–O(3)	116.7(2)
O(5)#3–Co(1)–O(3)	114.0(2)	O(1W)–Co(2)–O(2W)	84.3(2)
O(3)#4–Co(1)–O(3)	100.1(3)	O(1W)–Co(2)–N(4)#5	96.0(3)
O(2W)–Co(2)–N(4)#5	92.0(3)	O(1W)–Co(2)–N(1)	90.9(2)
O(2W)–Co(2)–N(1)	174.3(3)	N(4)#5–Co(2)–N(1)	91.5(3)
O(1W)–Co(2)–O(1)	168.2(2)	O(2W)–Co(2)–O(1)	90.8(2)
N(4)#5–Co(2)–O(1)	94.9(2)	N(1)–Co(2)–O(1)	93.3(2)
O(1W)–Co(2)–O(2)	108.4(2)	O(2W)–Co(2)–O(2)	86.8(3)
N(4)#5–Co(2)–O(2)	155.3(2)	N(1)–Co(2)–O(2)	91.8(2)
O(1)–Co(2)–O(2)	60.4(2)	O(1W)–Co(2)–C(1)	138.5(3)
O(2W)–Co(2)–C(1)	86.6(3)	N(4)#5–Co(2)–C(1)	124.8(3)
N(1)–Co(2)–C(1)	95.1(3)	O(1)–Co(2)–C(1)	30.1(2)
O(2)–Co(2)–C(1)	30.5(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2$, $-y + 1/2$, $z + 1/2$; #2 $x + 1/2$, $-y + 3/2$, $-z$; #3 $-x + 3/2$, $-y + 3/2$, $z - 1/2$; #4 $-x + 2$, y, $-z - 1/2$; #5 $-x + 3/2$, $-y + 1/2$, $z - 1/2$

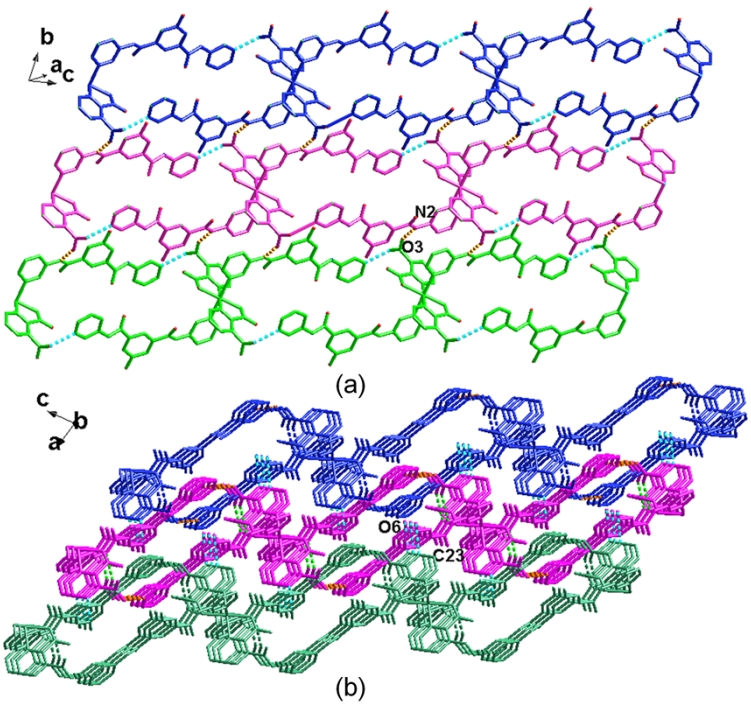


Fig. S1. (a) The 2D network of complex **1** extended by hydrogen bonding interactions; (b) The 3D supramolecular framework derived from 2D layers bridged by hydrogen bonding interactions.

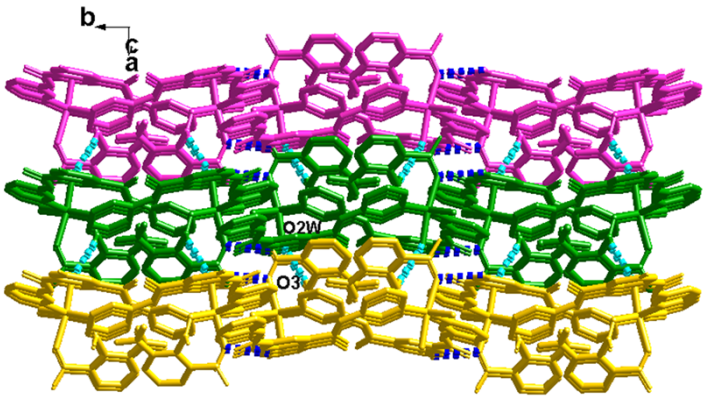


Fig. S2. The 3D supramolecular framework of **2** extended by hydrogen bonding interactions.

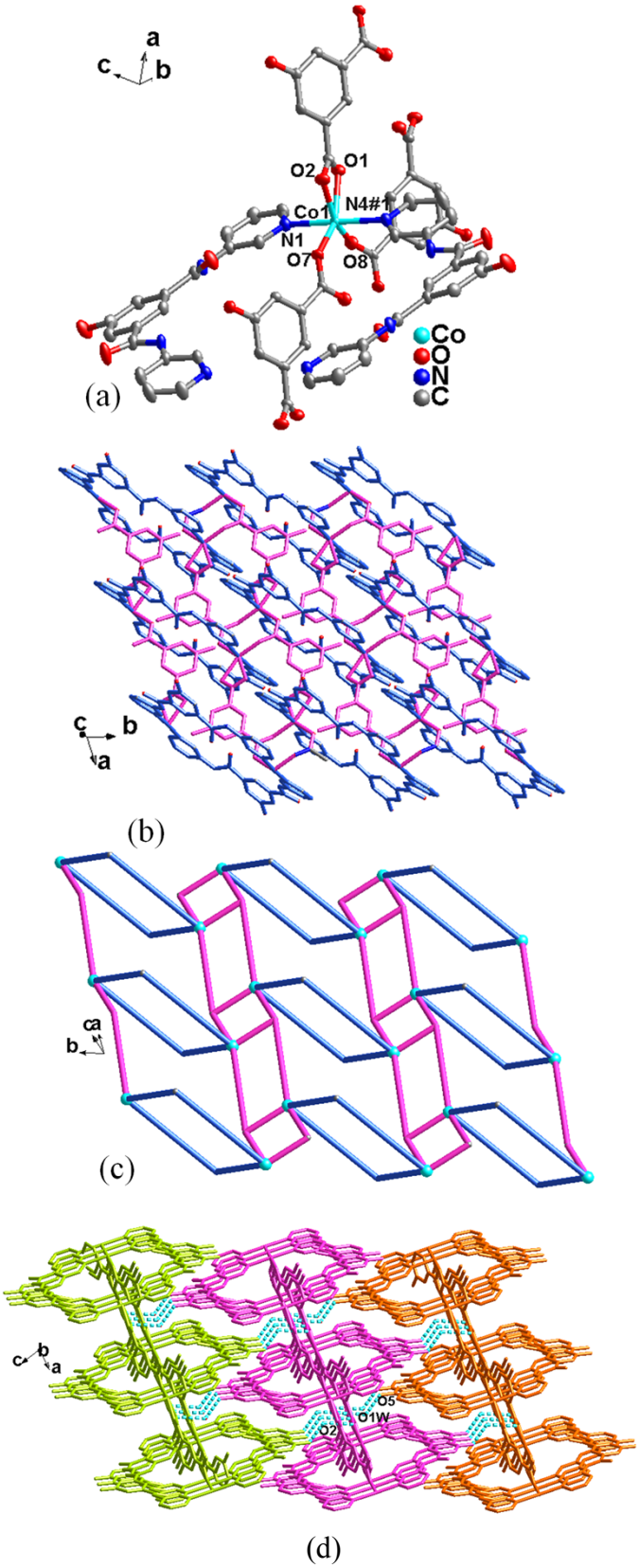


Fig. S3. (a) Coordination environment of the Co^{II} ion in **4** (#1 $-x + 1, -y, -z$); (b) The 2D networkof **4**; (c) The 2D topology with $(4^2 \cdot 6)(4^3 \cdot 6 \cdot 8^4 \cdot 10^2)(4)$; (d) The 3D supramolecular framework of **4** extended by hydrogen bonding interactions. The hydrogen atoms are omitted for clarity.

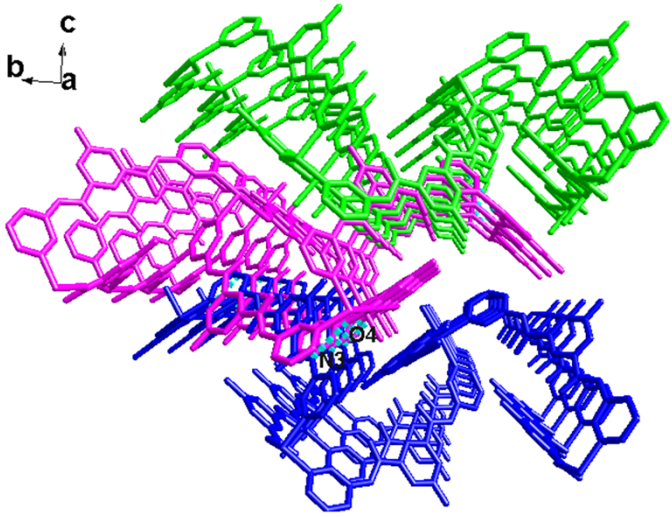


Fig. S4. The 3D supramolecular framework of **5** extended by hydrogen bonding interactions.

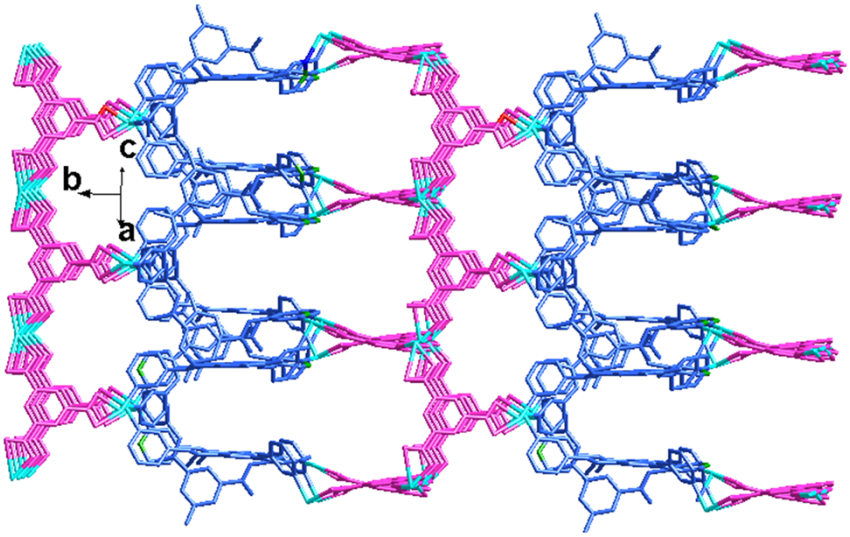
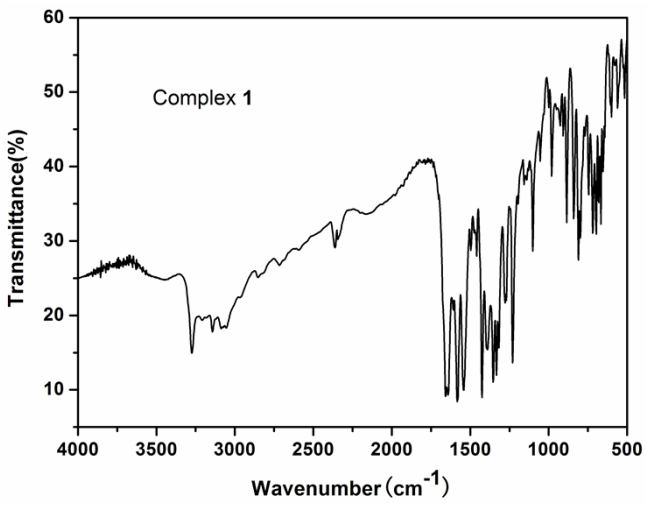
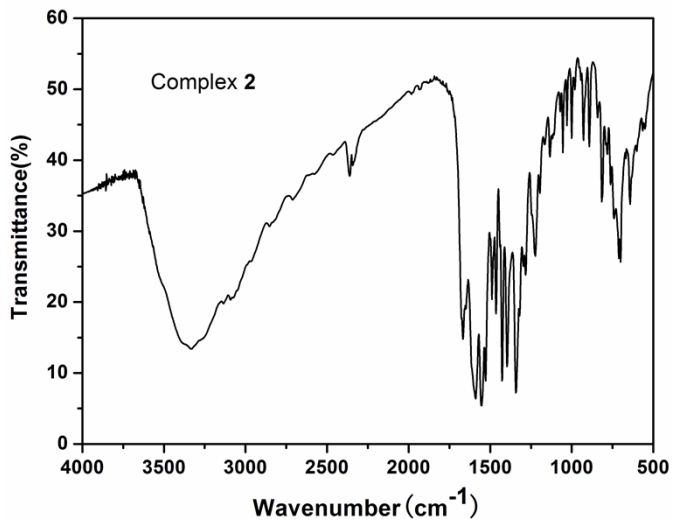


Fig. S5. The 3D framework of **6**.



(a)


Complex 2
Transmittance(%)
Wavenumber (cm-1)
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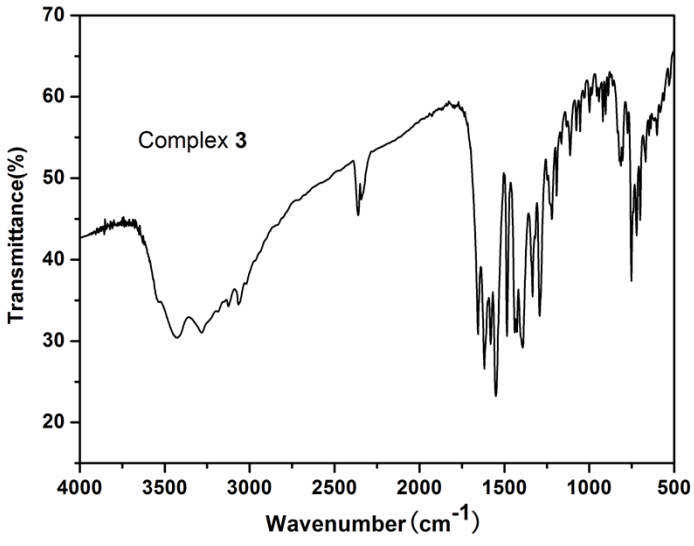
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500

(b)


Complex 3
Transmittance(%)
Wavenumber (cm-1)
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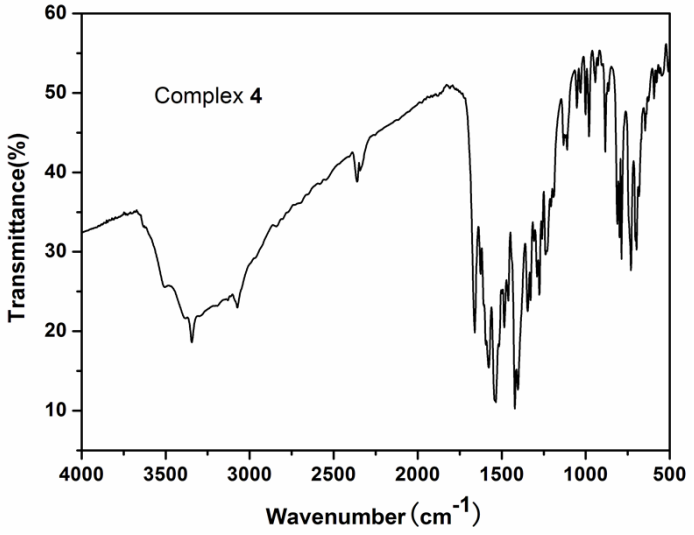
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500

(c)


Complex 4
Transmittance(%)
Wavenumber (cm-1)
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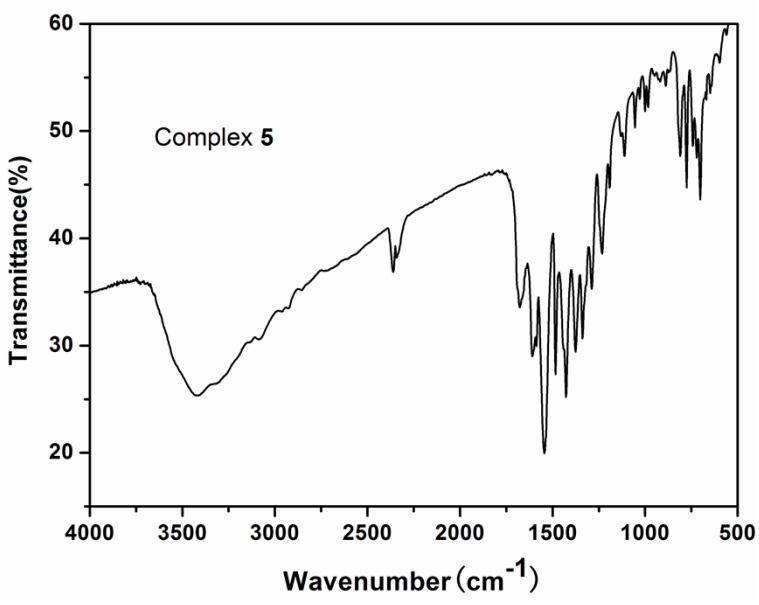
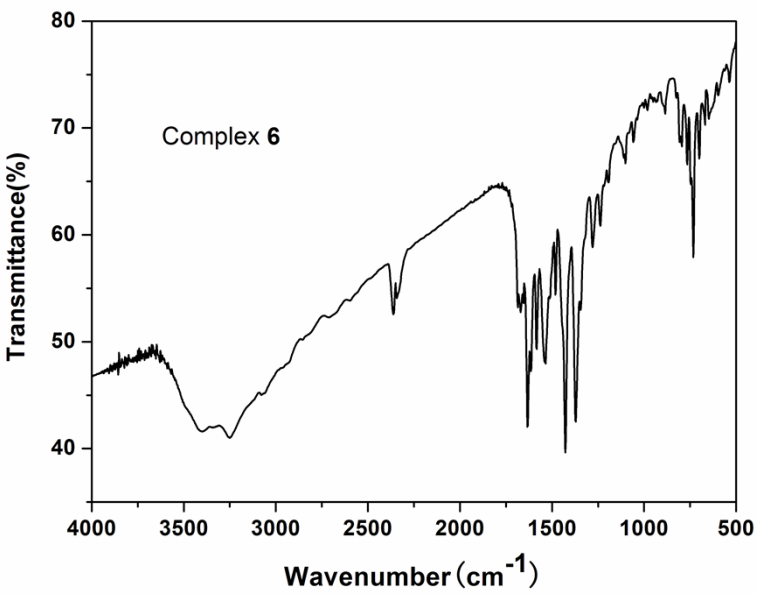
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500

(d)

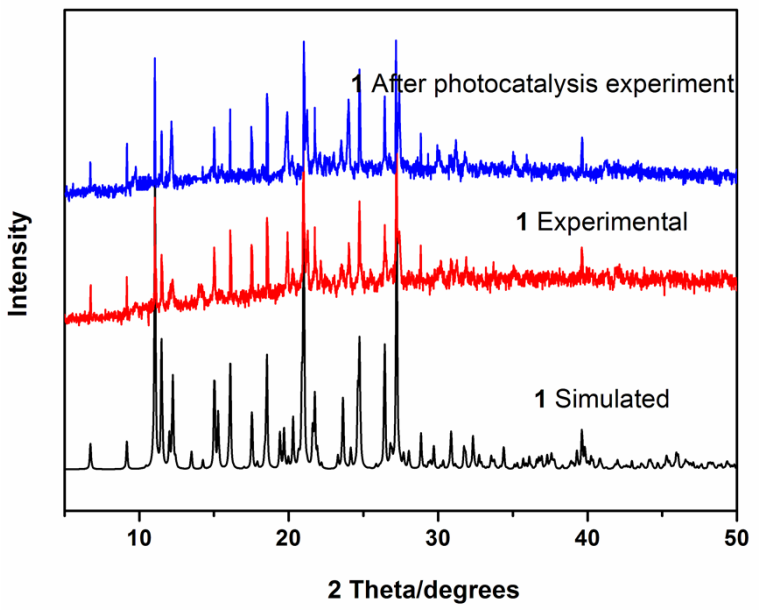


(e)



(f)

Fig. S6. The IR spectra of complexes **1**–**6**.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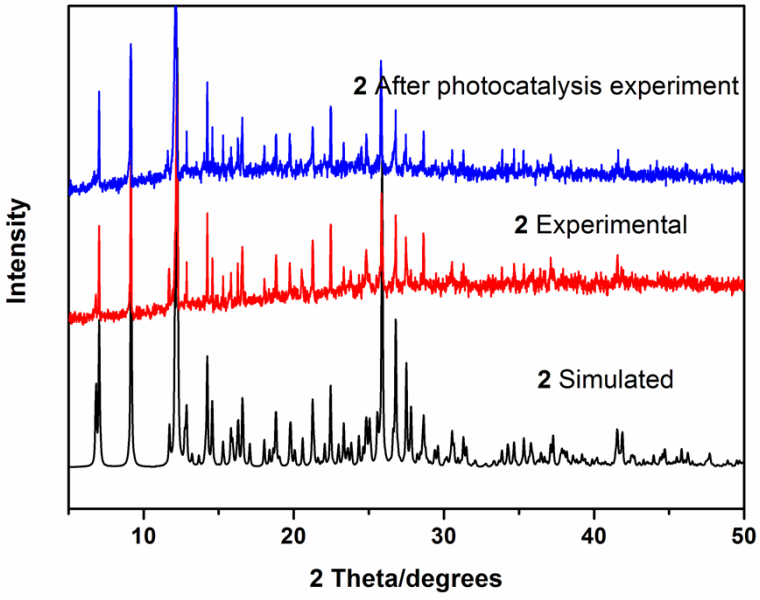
1 Experimental
1 Simulated
Intensity
10
20
30
40
50
2 Theta/degrees

(a)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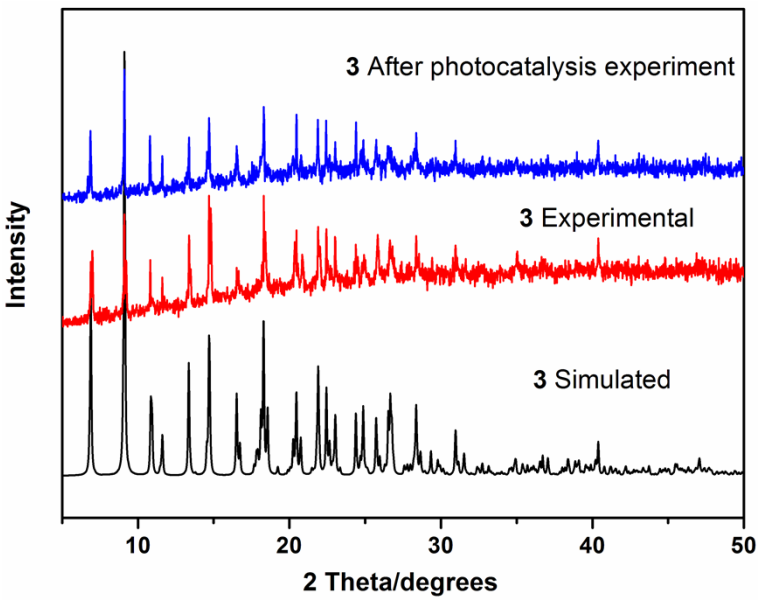
2 Experimental
2 Simulated
Intensity
10
20
30
40
50
2 Theta/degrees

(b)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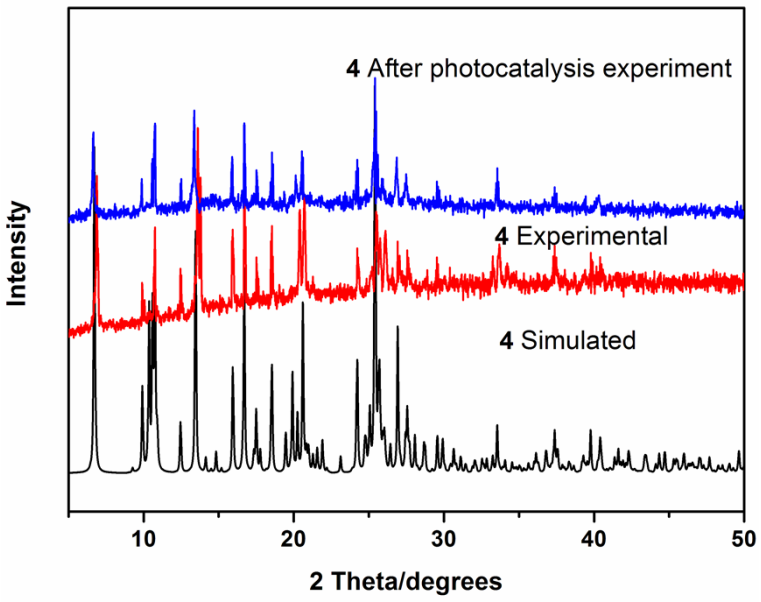
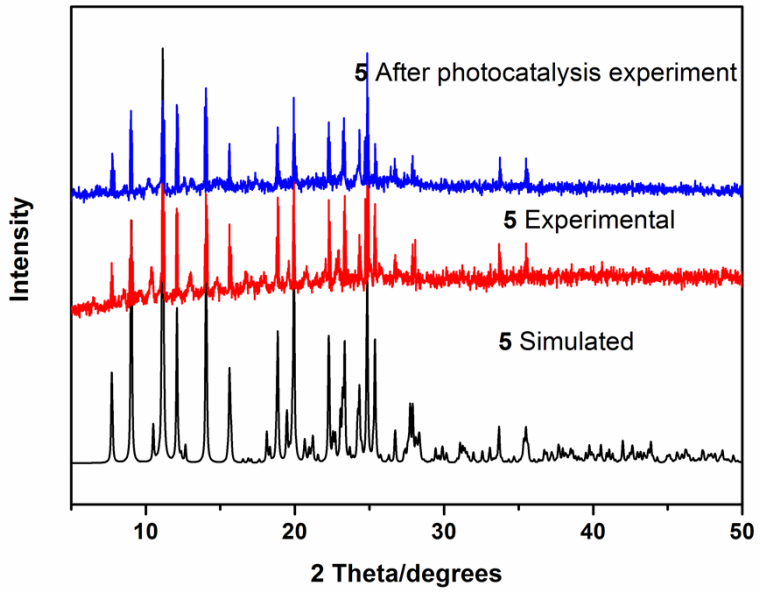
3 Experimental
3 Simulated
Intensity
10
20
30
40
50
2 Theta/degrees

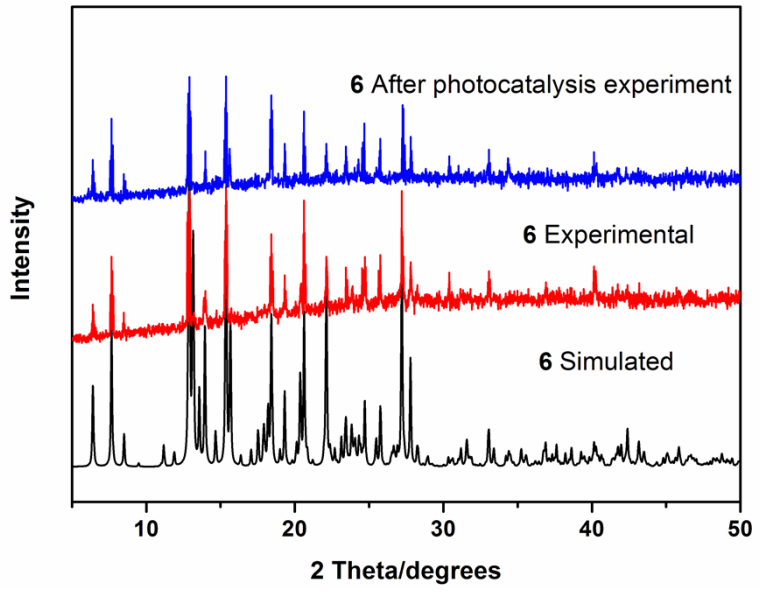
(c)


4 After photocatalysis experiment
4 Experimental
4 Simulated
Intensity
10
20
30
40
50
2 Theta/degrees

(d)



(e)



(f)

Fig. S7. The PXRD patterns of complexes **1**–**6**.

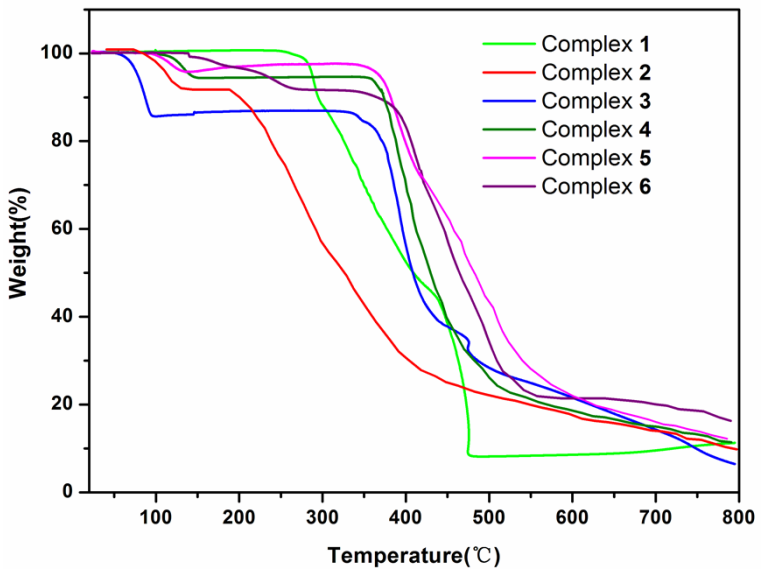
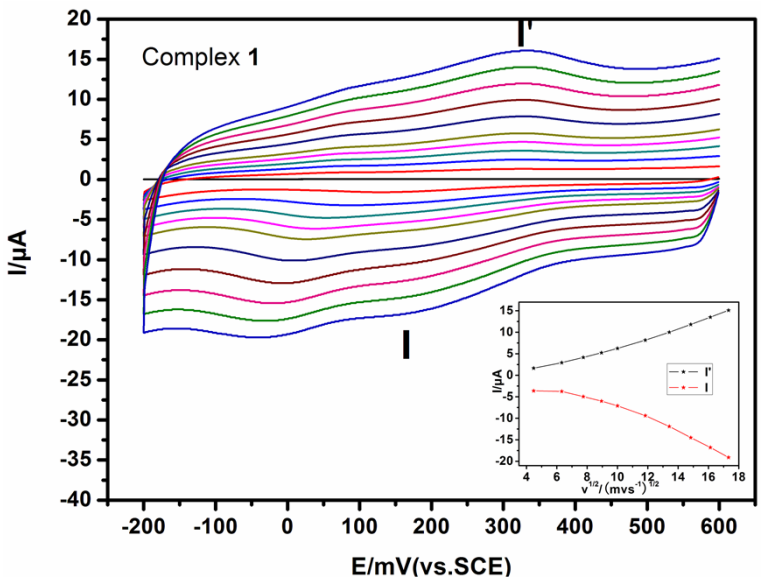
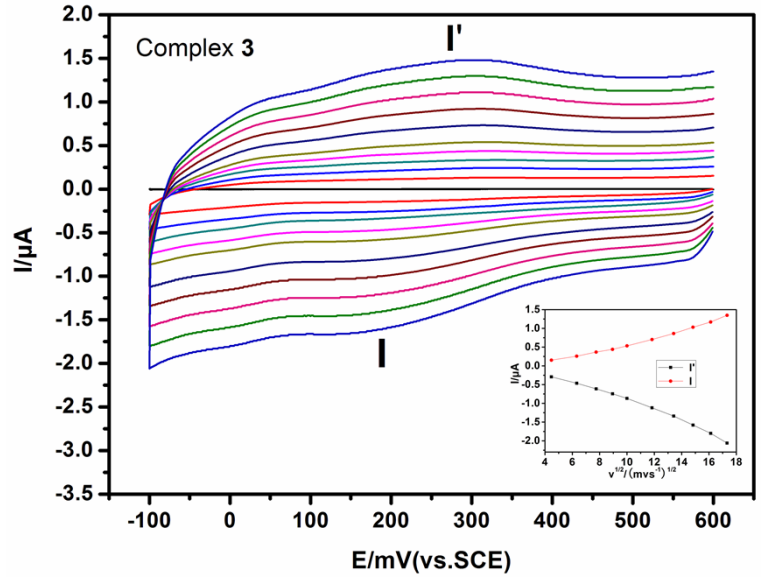


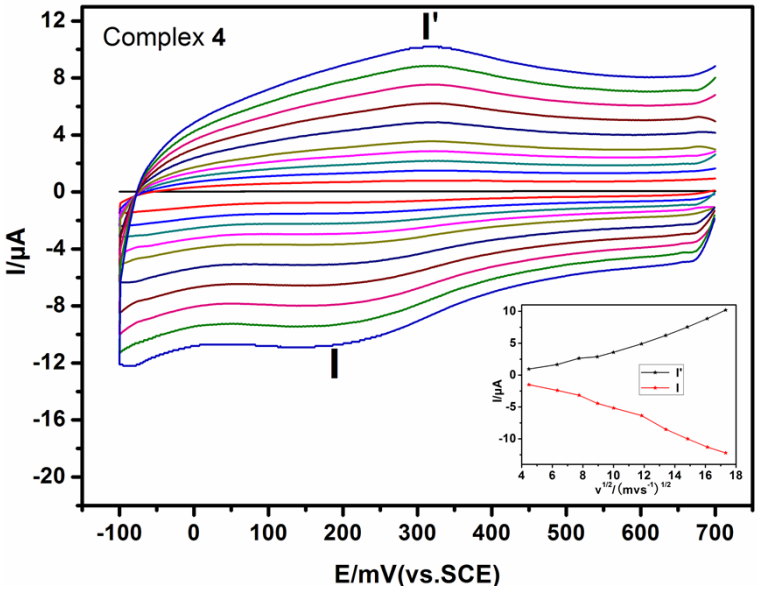
Fig. S8. The TG curves of complexes **1**–**6**.



(a)



(b)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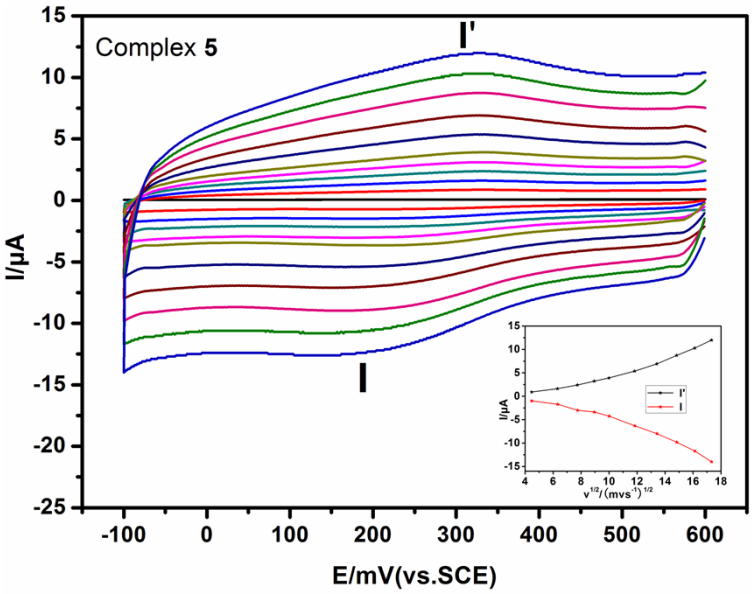
I'
I
I/μA
E/mV(vs.SCE)
I/μA
I'
I
v^1/2/(mvs^-1)^1/2

(c)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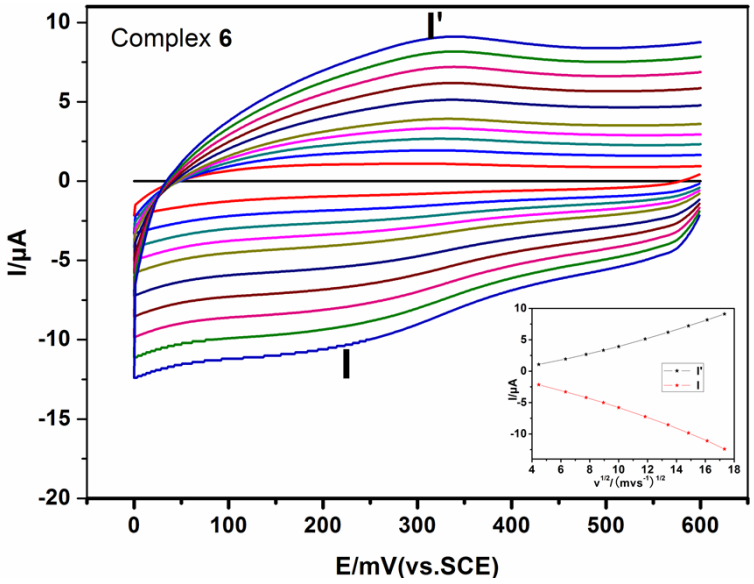
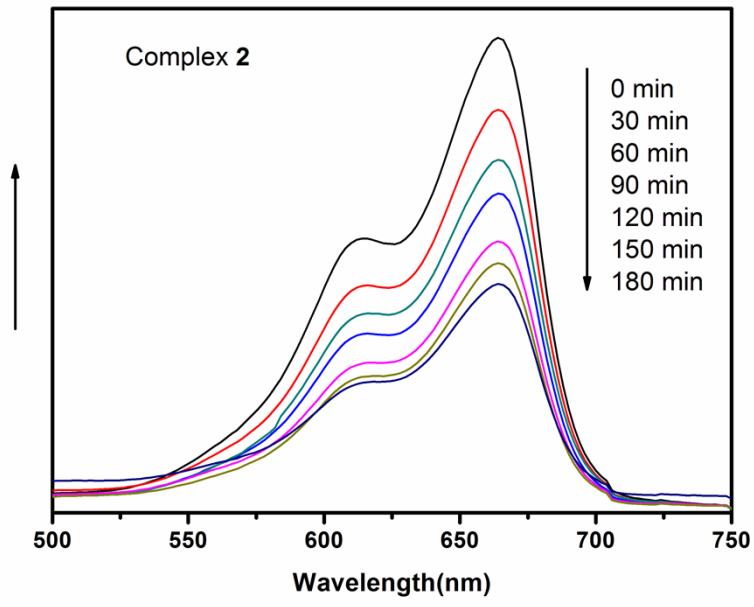
I/μA
E/mV(vs.SCE)
I/μA
I'
I
v^1/2/(mvs^-1)^1/2

(d)

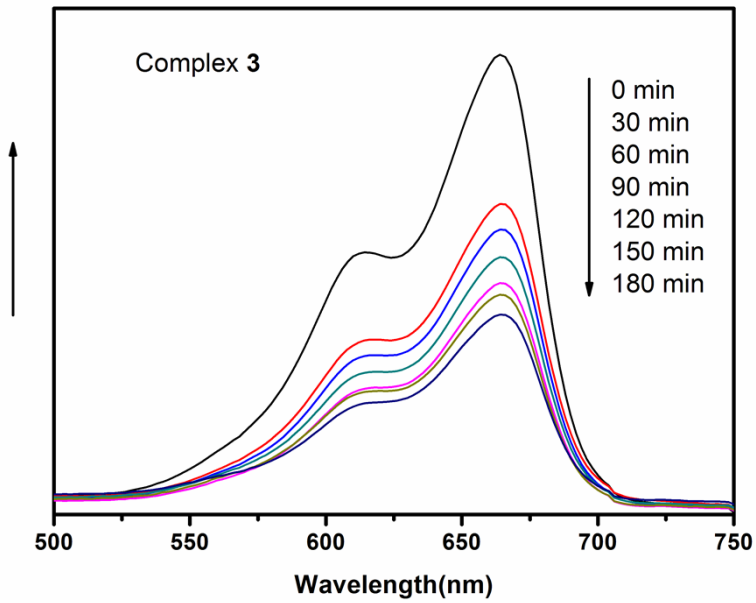


(e)

Fig. S9. Cyclic voltammograms of the **1**-CPE and **3**–**6**-CPEs in 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 140, 180, 220, 260, 300 mV s^{-1}). The inset shows the plots of the anodic and cathodic peak currents against the square-root of the scan rates.



(a)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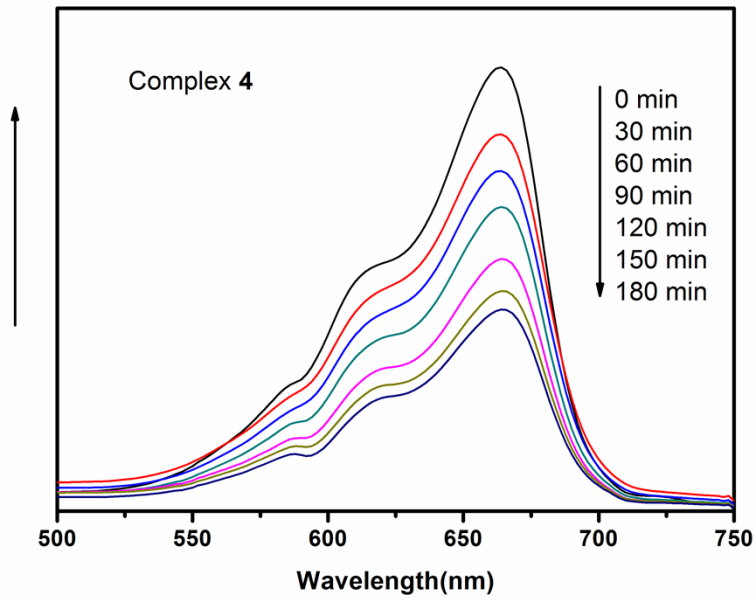
0 min
30 min
60 min
90 min
120 min
150 min
180 min
500
550
600
650
700
750
Wavelength(nm)

(b)


Complex 4
0 min
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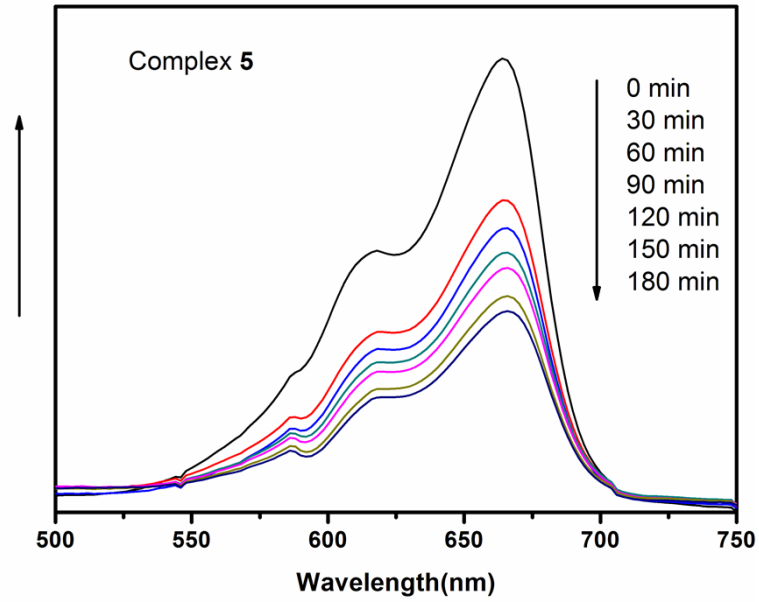
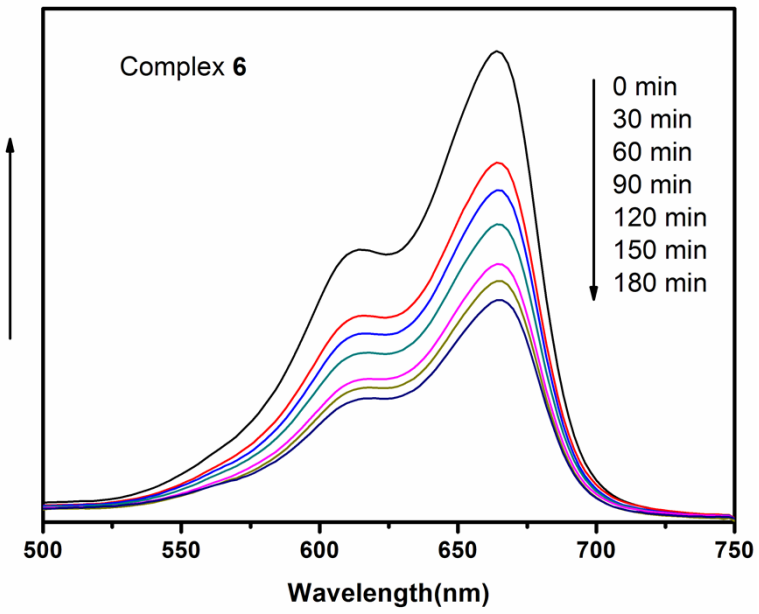
60 min
90 min
120 min
150 min
180 min
500
550
600
650
700
750
Wavelength(nm)

(c)

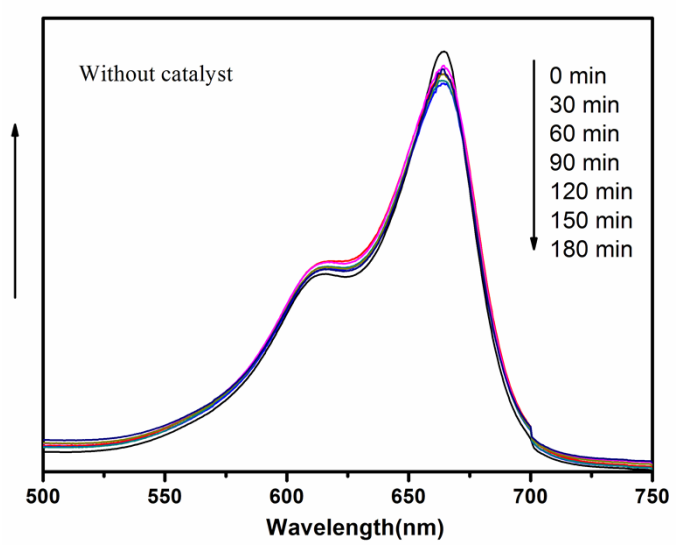


(d)

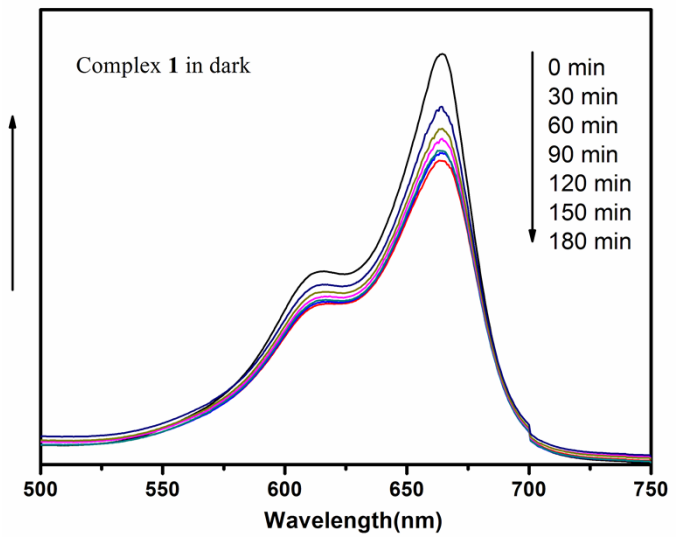


(e)

Fig. S10. Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of complexes **2**–**6**.



(a)



(b)

Fig. S11. Absorption spectra of the MB solution during the decomposition reaction under UV irradiation without catalyst and complex **1** in the dark.