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A series of coordination polymers tuned terphenyl tetracarboxylates and bipyridyl ligands with different flexibilities manifesting fluorescence properties and photocatalytic activities

Bao Mu, Ru-Dan Huang*

Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, Beijing, 100081, P. R. China

ELECTRONIC SUPPLEMENTARY INFORMATION

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

Co(1)–O(5)#1	2.054(3)	Co(2)–O(2)	2.082(3)
Co(1)–O(5)	2.054(3)	Co(2)–O(2)#2	2.082(3)
Co(1)–O(1)	2.063(3)	Co(2)–O(6)#2	2.099(3)
Co(1)–O(1)#1	2.063(3)	Co(2)–O(6)	2.099(3)
Co(1)–N(1)#1	2.190(3)	Co(2)–N(3)#2	2.157(4)
Co(1)–N(1)	2.190(3)	Co(2)–N(3)	2.157(4)
O(5)#1–Co(1)–O(5)	180.00	O(2)–Co(2)–O(2)#2	180.00
O(5)#1–Co(1)–O(1)	90.32(11)	O(2)–Co(2)–O(6)#2	85.03(10)
O(5)–Co(1)–O(1)	89.68(10)	O(2)#2–Co(2)–O(6)#2	94.97(10)
O(5)#1–Co(1)–O(1)#1	89.68(10)	O(2)–Co(2)–O(6)	94.97(10)
O(5)–Co(1)–O(1)#1	90.32(10)	O(2)#2–Co(2)–O(6)	85.03(10)
O(1)–Co(1)–O(1)#1	180.00	O(6)#2–Co(2)–O(6)	180.00
O(5)#1–Co(1)–N(1)#1	91.91(12)	O(2)–Co(2)–N(3)#2	92.44(12)
O(5)–Co(1)–N(1)#1	88.09(12)	O(2)#2–Co(2)–N(3)#2	87.56(12)
O(1)–Co(1)–N(1)#1	88.55(12)	O(6)#2–Co(2)–N(3)#2	87.44(12)
O(1)#1–Co(1)–N(1)#1	91.45(12)	O(6)–Co(2)–N(3)#2	92.56(12)
O(5)#1–Co(1)–N(1)	88.09(12)	O(2)–Co(2)–N(3)	87.56(12)
O(5)–Co(1)–N(1)	91.91(12)	O(2)#2–Co(2)–N(3)	92.44(12)
O(1)–Co(1)–N(1)	91.45(12)	O(6)#2–Co(2)–N(3)	92.56(12)
O(1)#1–Co(1)–N(1)	88.55(12)	O(6)–Co(2)–N(3)	87.44(12)

* Corresponding author. *E-mail address:* huangrd@bit.edu.cn (R. D. Huang).

N(1)#1–Co(1)–N(1)	180.00	N(3)#2–Co(2)–N(3)	180.00

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

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

Co(1)–O(1)	1.985(2)	Co(2)–O(2)	2.030(2)
Co(1)–N(1)	2.058(4)	Co(2)–O(3)	2.033(3)
Co(1)–O(5)#1	2.000(2)	Co(2)–O(4)#1	2.002(2)
Co(1)–O(6)#4	2.136(3)	Co(2)–N(4)#2	2.100(3)
Co(1)–O(7)#4	2.200(3)	Co(2)–O(8)#3	2.206(3)
O(1)–Co(1)–N(1)	94.20(13)	O(5)#1–Co(1)–O(7)#4	91.30(12)
O(1)–Co(1)–O(5)#1	150.53(12)	O(4)#1–Co(2)–O(8)#3	86.50(12)
O(1)–Co(1)–O(6)#4	86.26(12)	O(2)–Co(2)–O(3)	101.43(13)
O(1)–Co(1)–O(7)#4	109.98(12)	O(2)–Co(2)–O(4)#1	151.02(12)
O(6)#4–Co(1)–O(7)#4	60.35(11)	O(2)–Co(2)–N(4)#2	96.43(13)
O(5)#1–Co(1)–N(1)	98.64(13)	O(2)–Co(2)–O(8)#3	81.45(12)
O(6)#4–Co(1)–N(1)	166.86(13)	O(3)–Co(2)–O(4)#1	104.48(13)
O(7)#4–Co(1)–N(1)	107.46(13)	O(3)–Co(2)–N(4)#2	90.75(14)
O(8)#3–Co2–N(4)#2	177.50(13)	O(3)–Co(2)–O(8)#3	88.39(12)
O(5)#1–Co(1)–O(6)#4	87.07(12)	O(4)#1–Co(2)–N(4)#2	95.99(13)

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

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

Co(1)–O(1)#1	2.095(2)	Co(1)–O(6)#1	2.097(2)
Co(1)–O(1)	2.095(2)	Co(1)–N(1)	2.159(3)
Co(1)–O(6)	2.097(2)	Co(1)–N(1)#1	2.159(3)
O(1)#1–Co(1)–O(1)	180.00	O(6)–Co(1)–N(1)	88.25(10)
O(1)#1–Co(1)–O(6)	88.03(9)	O(6)#1–Co(1)–N(1)	91.75(10)
O(1)–Co(1)–O(6)	91.97(9)	O(1)#1–Co(1)–N(1)#1	88.64(10)
O(1)#1–Co(1)–O(6)#1	91.97(9)	O(1)–Co(1)–N(1)#1	91.36(10)
O(1)–Co(1)–O(6)#1	88.03(9)	O(6)–Co(1)–N(1)#1	91.75(10)
O(6)–Co(1)–O(6)#1	180.00	O(6)#1–Co(1)–N(1)#1	88.25(10)
O(1)#1–Co(1)–N(1)	91.36(10)	N(1)–Co(1)–N(1)#1	180.00
O(1)–Co(1)–N(1)	88.64(10)		

Symmetry code for #1 –x+1, –y+1, –z+1

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

Ni(1)–O(1)	2.0623(19)	Ni(1)–O(5)#1	2.086(2)
Ni(1)–O(1)#1	2.0623(19)	Ni(1)–N(1)	2.122(3)
Ni(1)–O(5)	2.086(2)	Ni(1)–N(1)#1	2.122(3)
O(1)–Ni(1)–O(1)#1	180.00	O(5)–Ni(1)–N(1)	88.66(9)
O(1)–Ni(1)–O(5)	90.98(8)	O(5)#1–Ni(1)–N(1)	91.34(9)
O(1)#1–Ni(1)–O(5)	89.02(8)	O(1)–Ni(1)–N(1)#1	91.87(9)
O(1)–Ni(1)–O(5)#1	89.02 (8)	O(1)#1–Ni(1)–N(1)#1	88.13(9)
O(1)#1–Ni(1)–O(5)#1	90.98 (8)	O(5)–Ni(1)–N(1)#1	91.34(9)
O(5)–Ni(1)–O(5)#1	180.00	O(5)#1–Ni(1)–N(1)#1	88.66(9)
O(1)–Ni(1)–N(1)	88.13(9)	N(1)–Ni(1)–N(1)#1	180.00
O(1)#1–Ni(1)–N(1)	91.87(9)		

Symmetry code for #1 –x+1, –y+1, –z+1

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

Ni(1)–O(4)#1	2.023(6)	Ni(1)–O(1)#3	2.103(6)
Ni(1)–O(3)#2	2.025(6)	Ni(1)–O(2)	2.117(5)
Ni(1)–N(1)	2.034(7)	Ni(1)–O(1)	2.143(5)
O(4)#1–Ni(1)–O(3)#2	165.5(2)	N(1)–Ni(1)–O(2)	108.6(2)
O(4)#1–Ni(1)–N(1)	96.4(3)	O(1)#3–Ni(1)–O(2)	158.9(2)
O(3)#2–Ni(1)–N(1)	93.9(3)	O(4)#1–Ni(1)–O(1)	85.6(2)
O(4)#1–Ni(1)–O(1)#3	83.9(2)	O(3)#2–Ni(1)–O(1)	86.0(2)
O(3)#2–Ni(1)–O(1)#3	85.7(2)	N(1)–Ni(1)–O(1)	170.4(3)
N(1)–Ni(1)–O(1)#3	91.6(2)	O(1)#3–Ni(1)–O(1)	97.99(19)
O(4)#1–Ni(1)–O(2)	87.6(2)	O(2)–Ni(1)–O(1)	62.0(2)
O(3)#2–Ni(1)–O(2)	98.8(2)		

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

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

Cd(1)–O(1)	2.427(8)	Cd(1)–O(9)	2.325(8)
Cd(1)–O(2)	2.350(7)	Cd(1)–O(10)	2.317(9)
Cd(1)–O(3)	2.411(8)	Cd(1)–N(1)	2.398(7)

Cd(1)–O(4)	2.361(7)	O(1)–Cd(1)–O(2)	54.5(3)
O(1)–Cd(1)–O(3)	85.7(3)	O(3)–Cd(1)–O(4)	54.1(2)
O(1)–Cd(1)–O(4)	139.3(2)	O(3)–Cd(1)–O(9)	87.1(3)
O(1)–Cd(1)–O(9)	95.1(3)	O(3)–Cd(1)–O(10)	94.4(3)
O(1)–Cd(1)–O10	86.8(3)	O(3)–Cd(1)–N(1)	136.7(3)
O(1)–Cd(1)–N(1)	137.6(3)	O(4)–Cd(1)–O(9)	89.5(3)
O(2)–Cd(1)–O(3)	139.4(3)	O(4)–Cd(1)–O(10)	89.9(3)
O(2)–Cd(1)–O(4)	166.2(2)	O(4)–Cd(1)–N(1)	82.8(3)
O(2)–Cd(1)–O(9)	88.9(3)	O(9)–Cd(1)–O(10)	177.7(3)
O(2)–Cd(1)–O(10)	91.1(3)	O(9)–Cd(1)–N(1)	88.3(3)
O(2)–Cd(1)–N(1)	83.4(3)	O(10)–Cd(1)–N(1)	89.3(3)

Table S7. Selected bond distances (Å) and angles (deg) for complex **7**.

Cd(1)–O(1)	2.198(10)	Cd(2)–O(2)	2.232(8)
Cd(1)–O(3)	2.390(9)	Cd(2)–N(1)#1	2.316(12)
Cd(1)–O(7)#2	2.203(12)	Cd(2)–O(4)#4	2.250(9)
Cd(1)–O(4)#3	2.326(7)	Cd(2)–O(8)#5	2.377(10)
Cd(1)–O(5)#3	2.486(9)	Cd(2)–O(9)#5	2.373(9)
Cd(1)–O(8)#5	2.243(8)	Cd(2)–O(6)#6	2.259(10)
O(1)–Cd(1)–O(3)	171.4(3)	O(5)#3–Cd(1)–	98.2(3)
O(1)–Cd(1)–O(7)#2	94.1(4)	O(9)#3–Cd(2)–N(1)#1	167.5(3)
O(1)–Cd(1)–O(4)#3	97.4(3)	O(2)–Cd(2)–N(1)#1	93.1(4)
O(1)–Cd(1)–O(5)#3	90.4(3)	O(6)#6–Cd(2)–N(1)#1	87.9(4)
O(4)#4–Cd(2)–O(8)#5	134.4(3)	O(2)–Cd(2)–O(4)#4	104.2(3)
O(1)–Cd(1)–O(8)#5	88.4(3)	O(4)#4–Cd(2)–	81.1(3)
O(3)–Cd(1)–O(7)#2	91.7(4)	O(2)–Cd(2)–O(8)#5	88.6(3)
O(3)–Cd(1)–O(4)#3	87.0(3)	O(4)#4–Cd(2)–	87.2(3)
O(3)–Cd(1)–O(5)#3	86.1(3)	O(8)#5–Cd(2)–	54.6(3)
O(3)–Cd(1)–O(8)#5	84.3(3)	O(6)#6–Cd(2)–	83.1(4)
O(4)#3–Cd(1)–O(7)#2	106.7(3)	O(2)–Cd(2)–O(9)#5	91.1(3)
O(5)#3–Cd(1)–O(7)#2	161.3(3)	O(6)#6–Cd(2)–	90.4(3)
O(7)#2–Cd(1)–O(8)#5	100.1(3)	O(2)–Cd(2)–O(6)#6	168.6(4)
O(4)#3–Cd(1)–O(5)#3	54.6(3)	O(4)#4–Cd(2)–N(1)#1	86.4(4)
O(4)#3–Cd(1)–O(8)#5	152.1(3)	O(8)#5–Cd(2)–N(1)#1	137.3(3)

Symmetry code for #1 –1+x, y, z; #2 1+x, y, z; #3 –1–x, –1/2+y, –3/2–z; #4 –1–x, –y, –1–z; #5 –x, –y, –1–z; #6 1+x, –1/2–y, 1/2+z

Table S8. Hydrogen-bonding geometry (Å, °) for complex **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O(4)–H(4)···N(2)[a]	0.82	1.82	2.6382	175
O(8)–H(8)···N(4)[b]	0.82	1.93	2.7427	169

Symmetry code for (a) 1–x, 1–y, 1–z (b) –1+x, y, –1+z

Table S9. Hydrogen-bonding geometry (Å, °) for complex **3**.

D–H···A	D–H	H···A	D···A	D–H···A
O(6)–H(6C)···O(2)[a]	0.85	2.14	2.8565	142

Symmetry code for (a) 1–x, 1–y, 1–z

Table S10. Hydrogen-bonding geometry (Å, °) for complex **4**.

D–H···A	D–H	H···A	D···A	D–H···A
O(3)–H(3)···O(6)[a] --H(3)	0.82	1.77	2.5775	166
O(5)–H(5B)···O(4)[b]	0.85	2.02	2.8645	175
O(6)–H(6A)···O(1)	0.85	1.92	2.7637	171
O(6)–H(6B)···O(4)[c]	0.85	2.02	2.8654	171

Symmetry code for (a) 1+x, y, z (b) –1+x, y, 1+z (c) 2–x, 1–y, –z

Table S11. Hydrogen-bonding geometry (Å, °) for complex **6**.

D–H···A	D–H	H···A	D···A	D–H···A
O(10)–H(10A)···N(2)[a]	0.85	2.14	2.9899	175
O(10)–H(10B)···O(1)[b]	0.85	1.82	2.6724	175

Symmetry code for (a) –1+x, y, z (b) –x, 1–y, 1–z

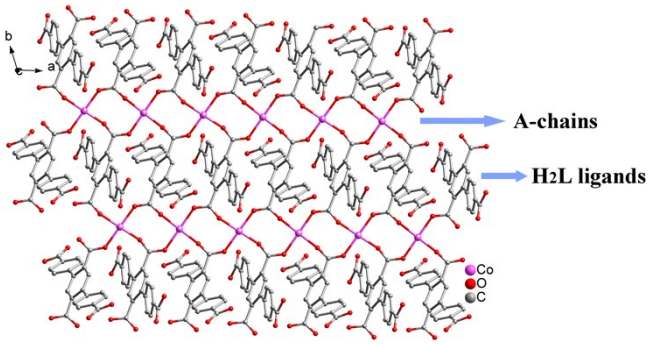


Fig. S1. The 2D coordination layer based on the Co-O A-chains and **H_2L** ligands in **1**.

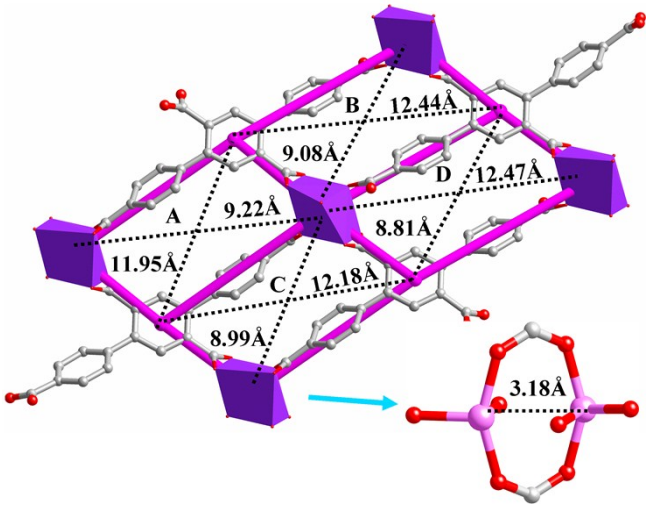


Fig. S2. The quadrilaterals with different sizes and the dinuclear Co^{II} unit in complex **2**.

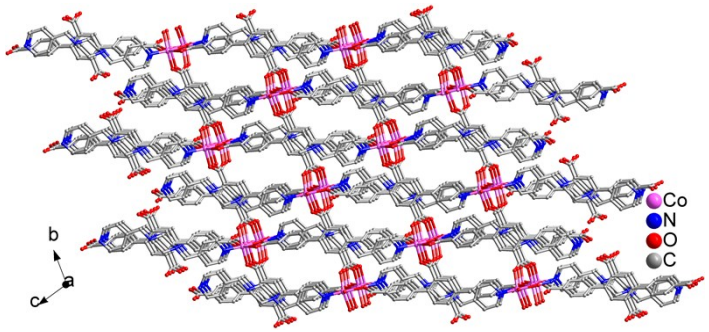


Fig. S3. The 3D framework of complex **2**.

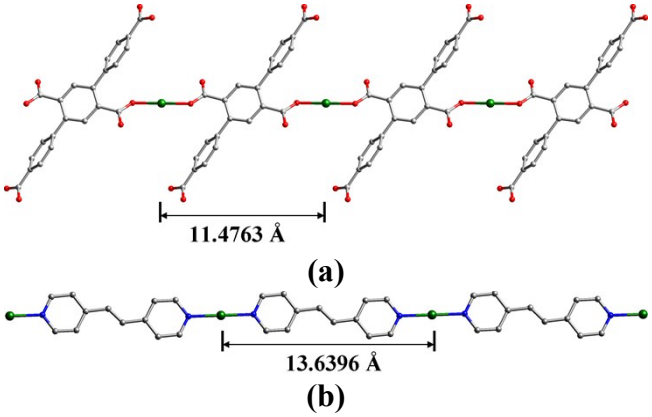


Fig. S4. (a) The "H"-type 1D Ni-**H_2L** chain in complex **4**. (b) The 1D straight chain based on Ni^{II} ions and **bpe**.

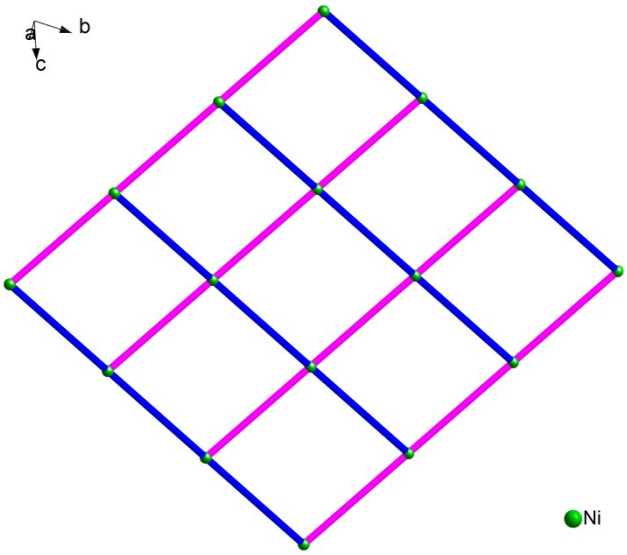


Fig. S5. The 4-connected 2D grid in **4**.

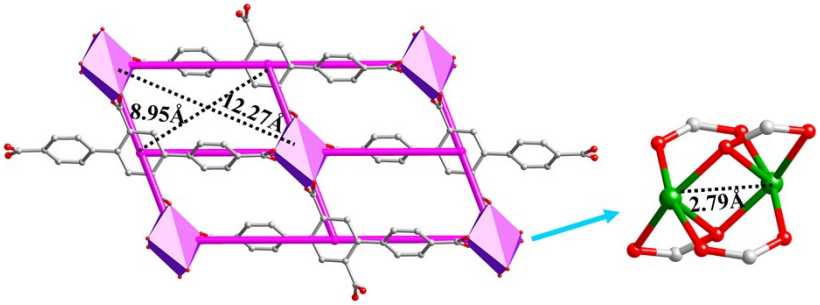
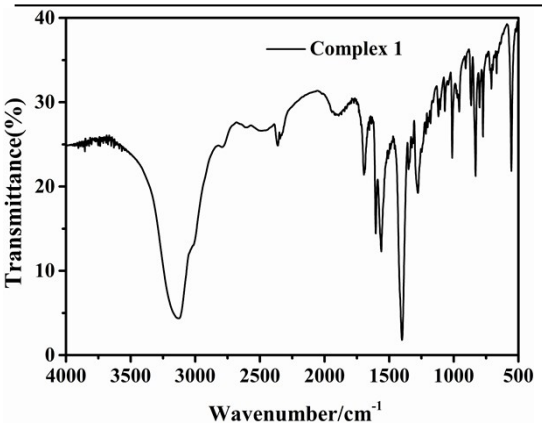
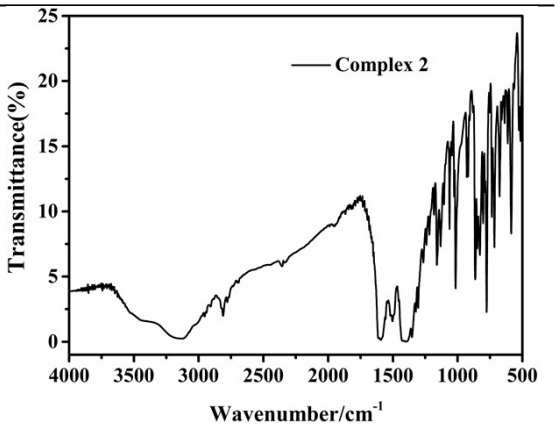


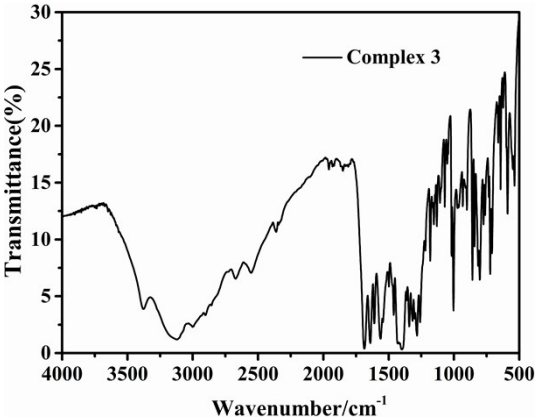
Fig. S6. The quadrilaterals with the same size and dinuclear Ni^{II} unit in **5**.


Complex 1
Transmittance(%)
Wavenumber/cm-1

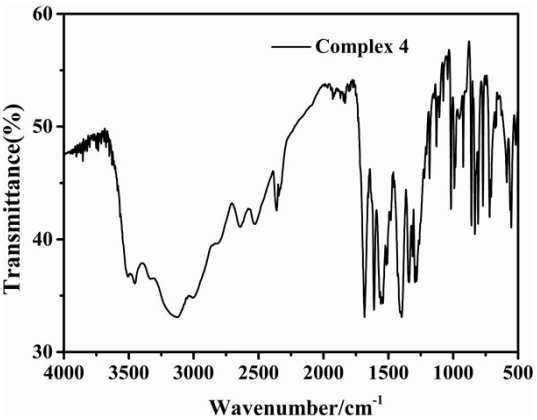
(a)


Complex 2
Transmittance(%)
Wavenumber/cm-1

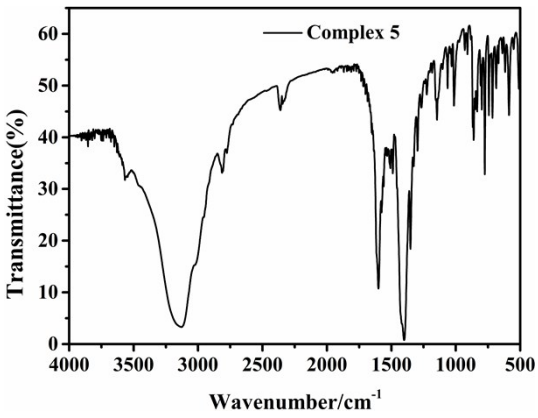
(b)


Complex 3
Transmittance(%)
Wavenumber/cm-1

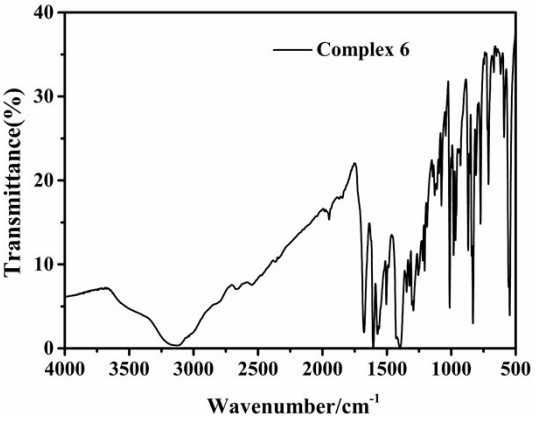
(c)


Complex 4
Transmittance(%)
Wavenumber/cm-1

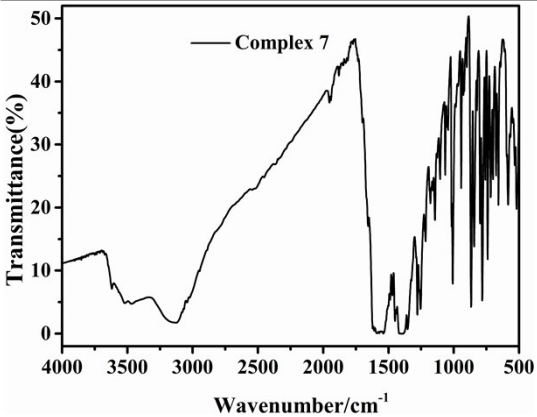
(d)


Complex 5
Transmittance(%)
Wavenumber/cm-1

(e)

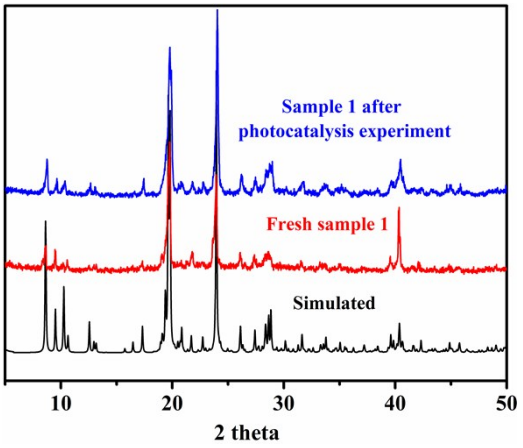

Complex 6
Transmittance(%)
Wavenumber/cm-1

(f)

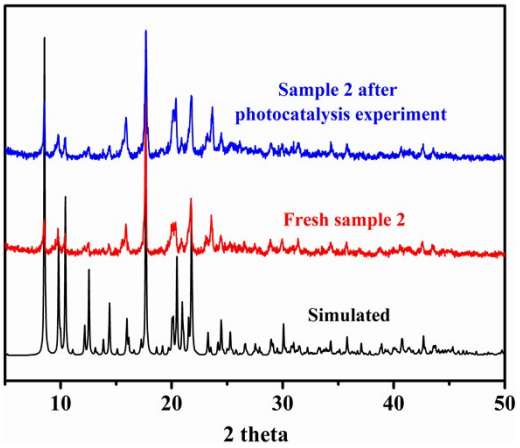


(g)

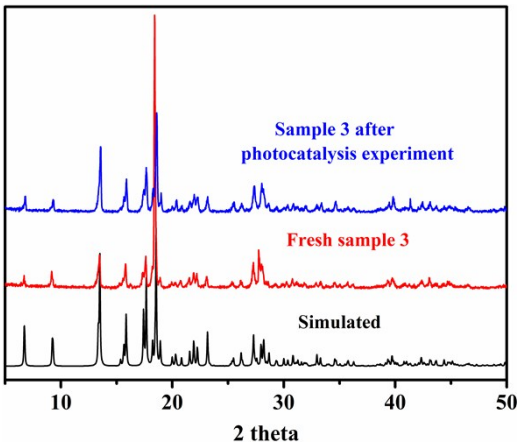
Fig. S7. The IR spectra of complexes **1**–**7**.



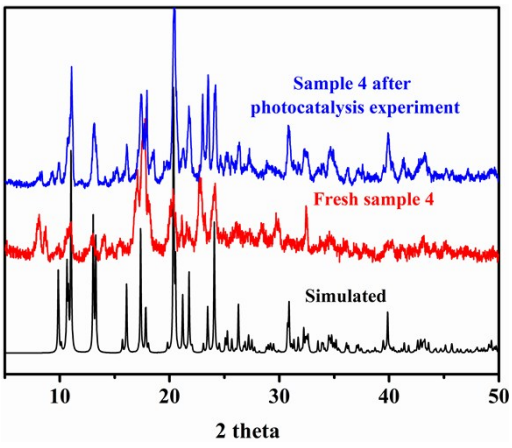
(a)



(b)



(c)



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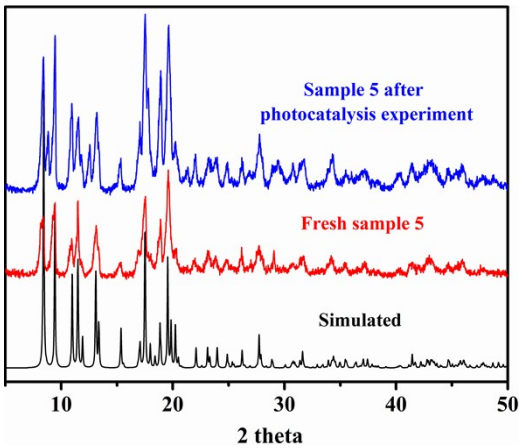

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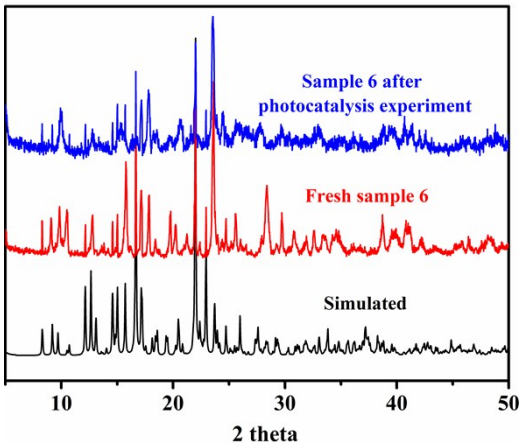

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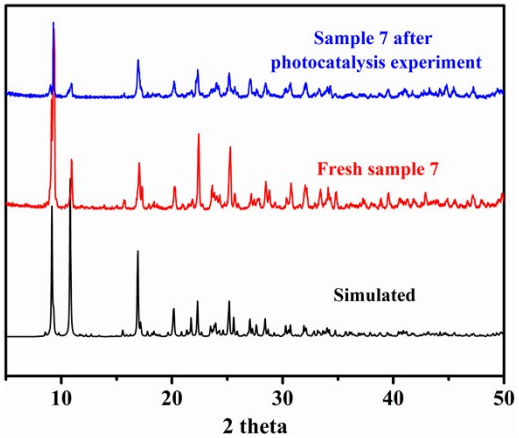


(g)

Fig. S8. The simulated (black line), fresh samples (red line) and samples after photocatalytic experiments (MB) (blue line) powder X–ray diffraction patterns for complexes **1**–**7**.

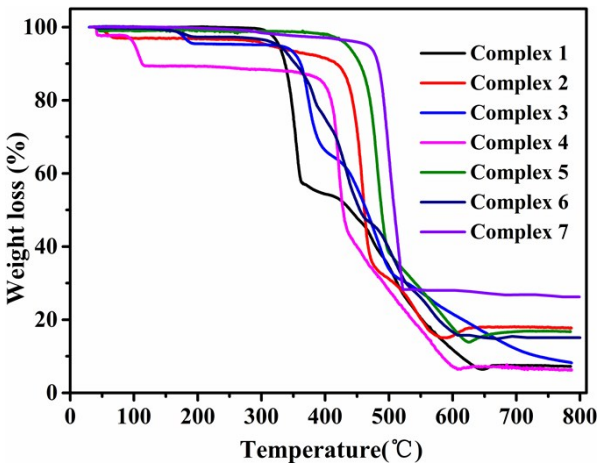


Fig. S9. The TG curves of complexes **1**–**7**.

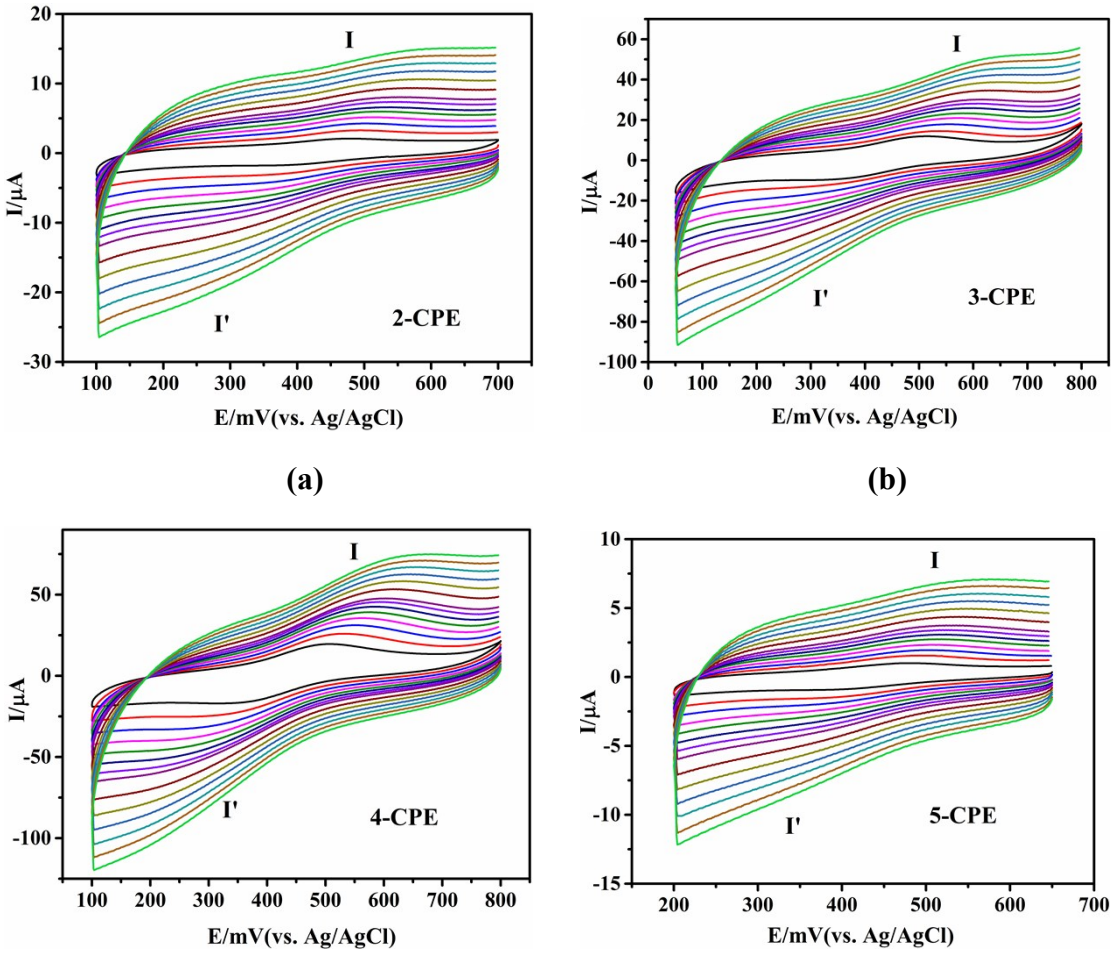
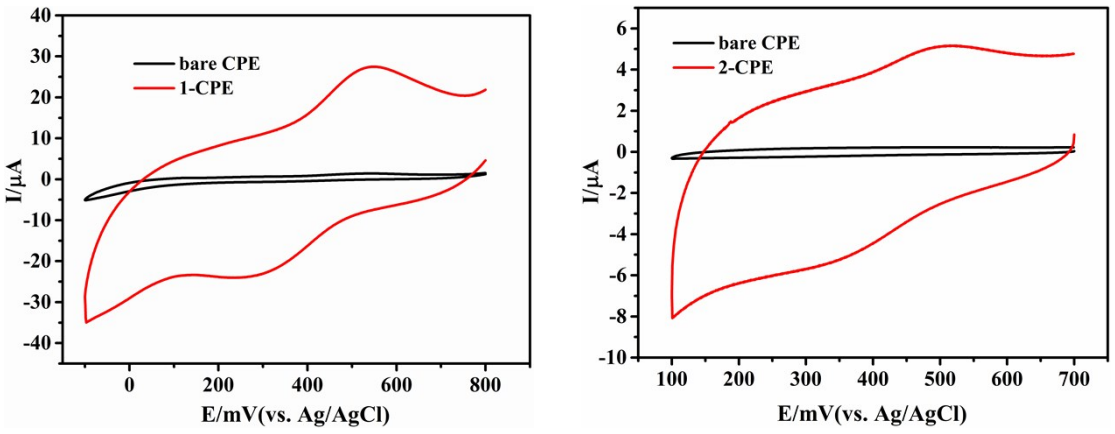
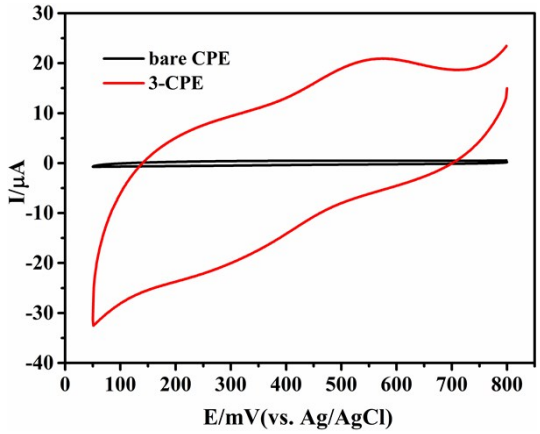


Fig. S10. Cyclic voltammograms of the **2–**, **3–**, **4–**, **5–**CPE in 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 25, 50, 75, 100, 125, 150, 175, 200, 250, 300, 350, 400, 450, 500 $mV \cdot s^{-1}$).





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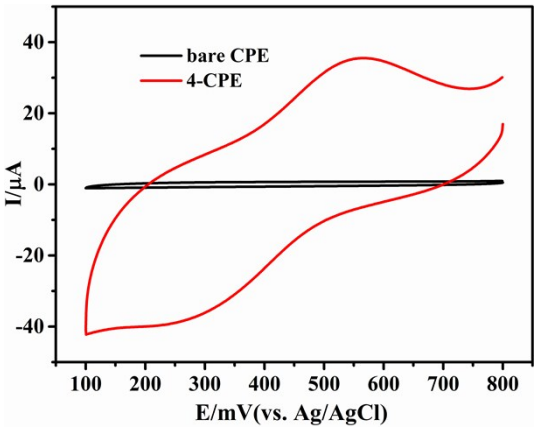

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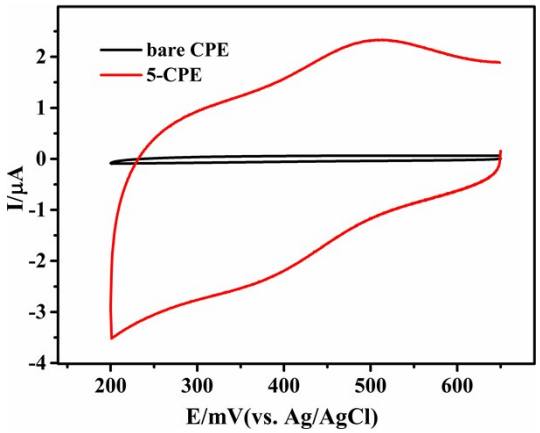
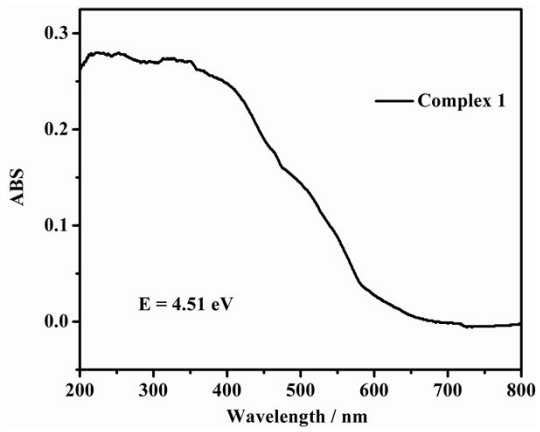
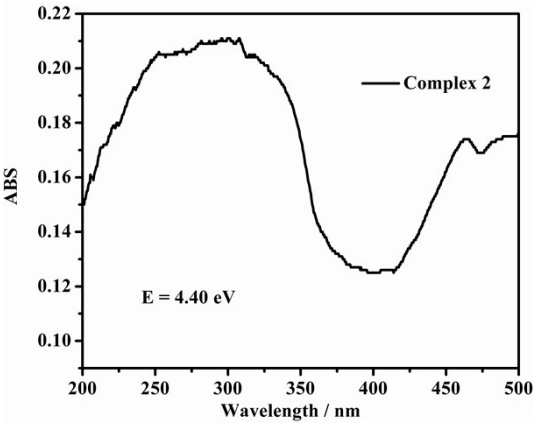


(e)

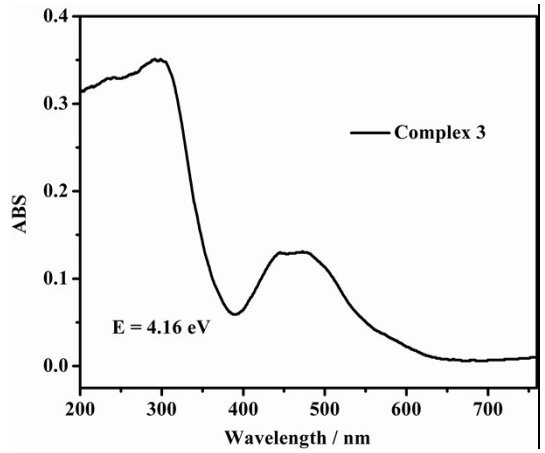
Fig. S11. Cyclic voltammogram of **1–**, **2–**, **3–**, **4–**, **5–**CPE (–100 to 900 mV for **1–**CPE, 100 to 700 mV for **2–**CPE, 50 to 800 mV for **3–**CPE, 100 to 800 mV for **4–**CPE and 200 to 650 mV for **5–**CPE) in 0.01 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution for complexes **1**–**5**. Scan rate: 100 mVs^{-1}.



(a)



(b)



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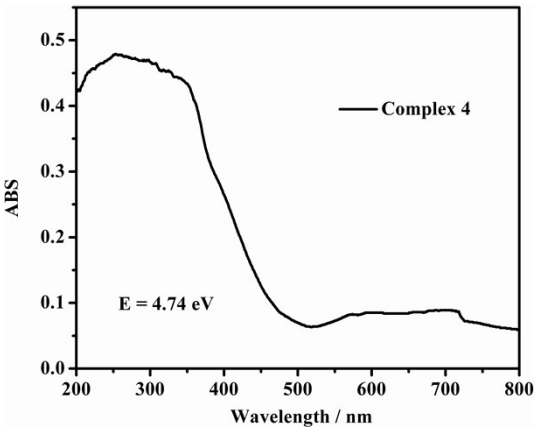

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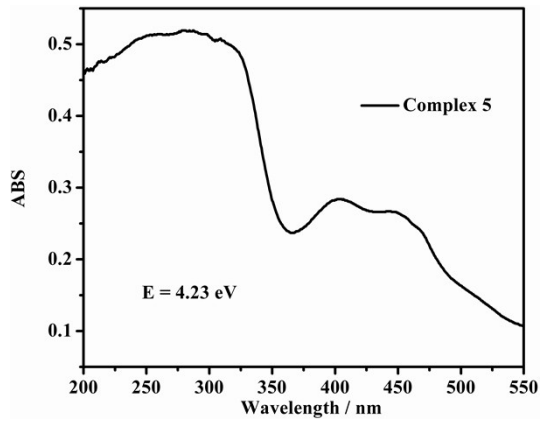

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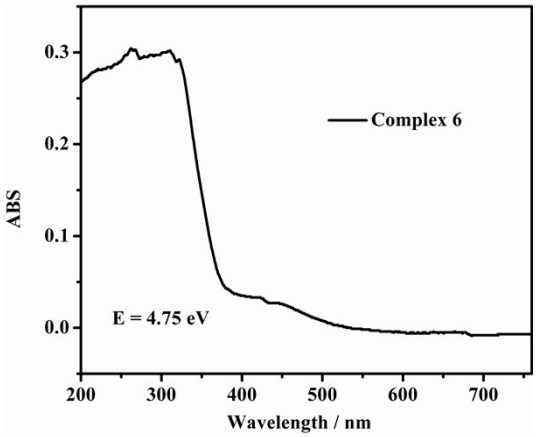

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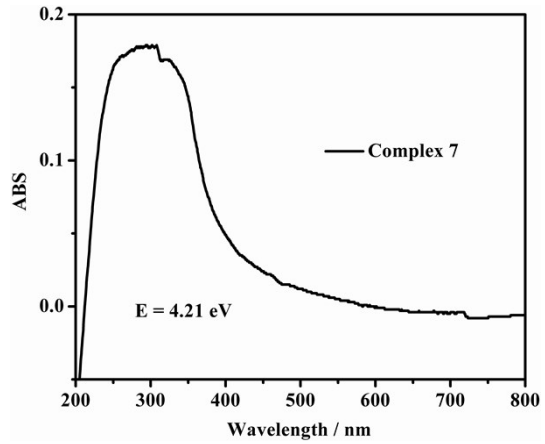
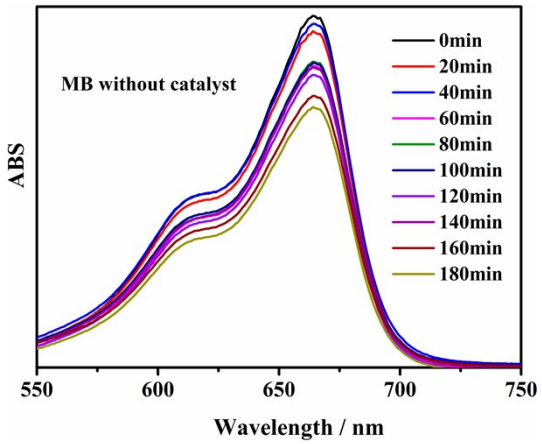
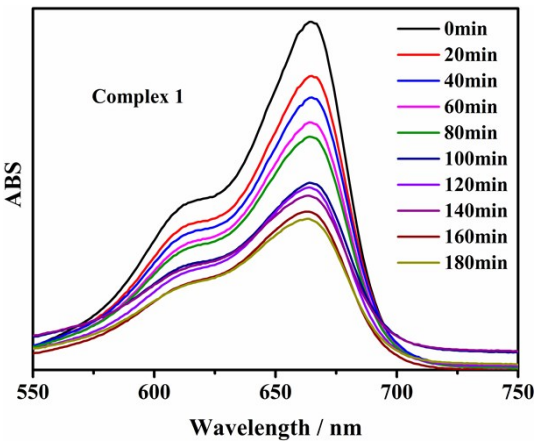


(g)

Fig. S12. The solid UV-vis spetra of the title complexes and the calculative bandgaps.


MB without catalyst
0min
20min
40min
60min
80min
100min
120min
140min
160min
180min
ABS
550
600
650
700
750
Wavelength / nm

(a)


Complex 1
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100min
120min
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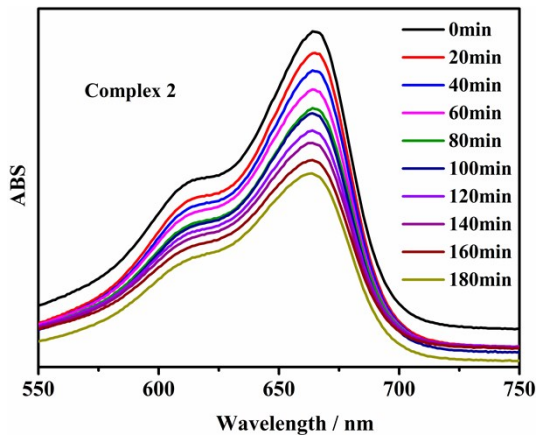
160min
180min
ABS
550
600
650
700
750
Wavelength / nm

(b)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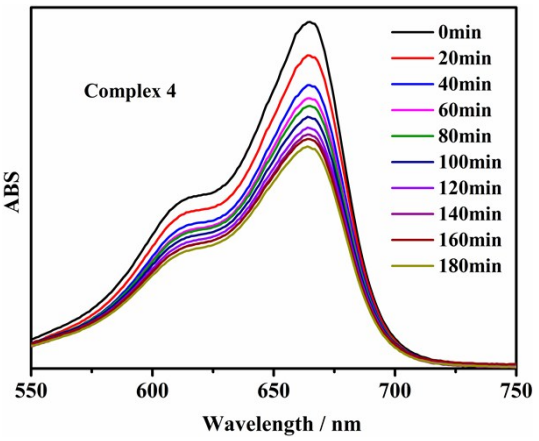
100min
120min
140min
160min
180min
ABS
550
600
650
700
750
Wavelength / nm

(c)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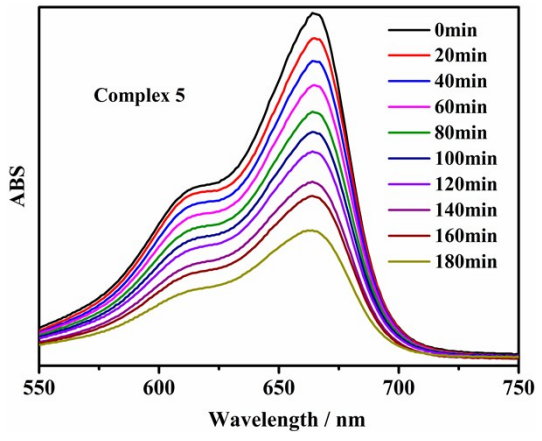
750
Wavelength / nm

(d)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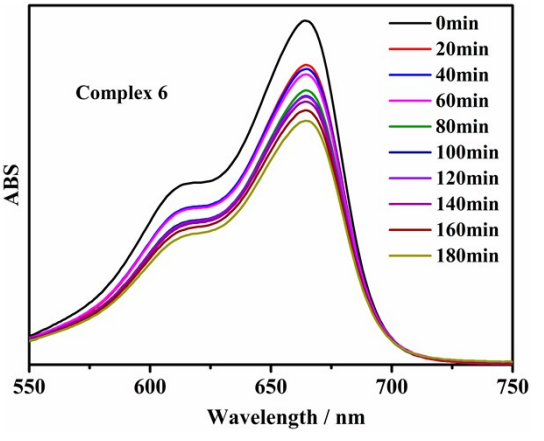
Wavelength / nm

(e)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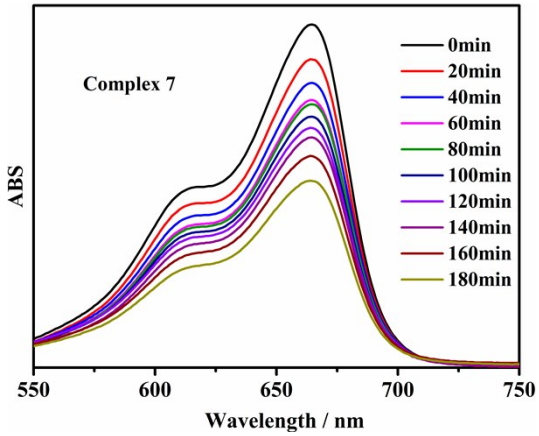
750
Wavelength / nm

(f)



(g)

Fig. S13. Absorption spectra of the MB solution during the decomposition reaction under the visible light irradiation with the presences of complexes **1**–**2**, **4**–**7**, and no crystal in the same conditions.