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Six Co^{II} Coordination polymers Manifesting UV-light-driven Photocatalysis for the Degradation of Organic Dyes

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Materials and characterization

All purchased chemical reagents are analytically pure and not further purified when used. The 4-bmpnd ligand was synthesized according to the reported literature.[S1] IR spectra (KBr pellets) were measured using a Varian 640 FT-IR spectrometer at wavenumbers between 400 and 4000 cm^{-1}. Powder X-ray diffraction (PXRD) data were taken on a D/teX Ultra diffractometer equipped with Cu-Kα (λ = 1.5406 Å) radiation over the 2θ range of 5–50°; The solid-state diffuse-reflectance UV/vis spectra for powder samples were recorded with a Perkin-Elmer Lambda 750 UV/vis spectrometer equipped with an integrating sphere by using $BaSO_4$ as a white standard; UV-vis absorption spectra were obtained by using a SP-1901 UV-vis spectrophotometer.

X-Ray crystallography

The crystal data of CPs **1**−**6** were collected on a Bruker SMART APEX II diffractometer at 296K. In the collection process, a CCD area detector and graphite-monochromatic Cu-Kα (λ = 0.71073 Å) with the φ-ω scan technique was adopted. The structure was resolved by direct methods. The crystal data were refined by full-matrix least squares on F^2 by using the SHELXS-2014 programs.[S2] Crystallographic data and details of structural refinement for **1**−**6** are summarized in Table 1. Selected bond lengths and angles of the CPs **1**−**6** were listed in Table S1 in the Supporting Information and the crystallographic data in CIF format are available freely from the Cambridge Crystallography Data Centre (CCDC) via www.ccdc.cam.ac.uk/conts/retrieving.html. The CCDC numbers of CPs **1**−**6** are 1916792, 1916794, 1916797, 1916795, and 1943488−1943489, respectively.

Table S1 Selected bond distances (Å) and angles (°) for complexes **1–6**.

Complex **1**			
Co(1)–O(6)	2.0522(15)	Co(1)–O(6)#1	2.0522(15)
Co(1) –O(1W)	2.1266(15)	Co(1)–O(1W)#1	2.1266(15)
Co(1) –N(1)	2.1736(18)	Co(1)–N(1)#1	2.1736(19)
O(6)–Co(1)–O(6)#1	180.00(9)	O(6)–Co(1)–O(1W)	88.27(6)
O(6)#1–Co(1)–O(1W)	91.73(6)	O(6)–Co(1)–O(1W)#1	91.73(6)
O(6)#1–Co(1)–O(1W)#1	88.27(6)	O(1W)–Co(1)–O(1W)#1	180
O(6)–Co(1)–N(1)#1	89.83(6)	O(6)#1–Co(1)–N(1)#1	90.17(6)
O(1W)–Co(1)–N(1)#1	92.53(6)	O(1W)#1–Co(1)–N(1)#1	87.47(6)
O(6)–Co(1)–N(1)	90.17(6)	O(6)#1–Co(1)–N(1)	89.83(6)
O(1W)–Co(1)–N(1)	87.47 (6)	O(1W)#1–Co(1)–N(1)	92.53(6)
N(1)#1–Co(1)–N(1)	180		
Symmetry code for **1**: #1: $-x+1, -y+1, -z+1$			
Complex **2**			
Co(1)–O(6)#1	2.042(3)	Co(1)–O(3W)	2.124(4)
Co(1)–N(9)	2.128(4)	Co(1)–N(1)	2.145(4)
Co(1)–O(12)	2.214(4)	Co(1)–O(11)	2.277(4)
Co(2)–O(4)	1.950(4)	Co(2)–N(4)	2.061(4)
Co(2)–N(5)	2.066(4)	Co(2)–O(15)#2	2.097(4)
O(6)#1–Co(1)–O(1W)	90.24(15)	O(6)#1–Co(1)–N(9)	90.32(15)
O(1W)–Co(1)–N(9)	177.40(17)	O(6)#1–Co(1)–N(1)	102.23(16)
O(1W)–Co(1)–N(1)	87.14(16)	N(9)–Co(1)–N(1)	95.21(16)
O(6)#1–Co(1)–O(12)	112.09 (14)	O(1W)–Co(1)–O(12)	88.01(14)
N(9)–Co(1)–O(12)	89.42(15)	N(1)–Co(1)–O(12)	145.35(15)
O(6)#1–Co(1)–O(11)	170.44(14)	O(1W)–Co(1)–O(11)	88.85(15)
N(9)–Co(1)–O(11)	90.15(15)	N(1)–Co(1)–O(11)	87.23(14)
O(12)–Co(1)–O(11)	58.37(12)	O(4)–Co(2)–N(4)	111.40(17)
O(4)–Co(2)–N(5)	103.41(16)	N(4)–Co(2)–N(5)	102.48(17)
O(4)–Co(2)–O(15)#2	89.80(16)	N(4)–Co(2)–O(15)#2	150.96(18)
N(5)–Co(2)–O(15)#2	90.96(16)		
Symmetry code for **2**: #1: $-x+1, -y+1, -z-1$; #2: $-x, -y, -z-2$			
Complex **3**			
Co(1)–O(10)	1.938(2)	Co(1)–O(5)#1	2.000(2)
Co(1)–N(4)#2	2.050(3)	Co(1)–N(6)	2.063(3)
Co(2)–O(7)#3	1.974(2)	Co(2)–N(1)	2.089(3)
Co(2)–O(4)#4	2.103(2)	Co(2)–N(5)	2.214(3)
Co(2)–O(3)#4	2.247(3)	Co(2)–O(1W)	2.248(3)

O(10)–Co(1)–O(5)#1	101.42(11)	O(10)–Co(1)–N(4)#2	104.70(12)
O(5)#1–Co(1)–N(4)#2	123.97(12)	O(10)–Co(1)–N(6)	107.13(11)
O(5)#1–Co(1)–N(6)	105.63(11)	N(4)#2–Co(1)–N(6)	112.41(12)
O(7)#3–Co(2)–N(1)	103.31(12)	O(7)#3–Co(2)–O(4)#4	100.92(11)
N(1)–Co(2)–O(4)#4	153.17(11)	O(7)#3–Co(2)–N(5	94.56(11)
N(1)–Co(2)–N(5)	96.93(11)	O(4)#4–Co(2)–N(5)	92.46(11)
O(7)#3–Co(2)–O(3)#4	161.01(11)	N(1)–Co(2)–O(3)#4	95.36(11)
O(4)#4–Co(2)–O(3)#4	60.09(9)	N(5)–Co(2)–O(3)#4	86.52(11)
O(7)#3–Co(2)–O(1W)	82.12(12)	N(1)–Co(2)–O(1W)	90.66(13)
O(4)#4–Co(2)–O(1W)	81.36(12)	N(5)–Co(2)–O(1W)	172.25(12)
O(3)#4–Co(2)–O(1W)	94.35(11)		

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

Complex **4**

Co(1)–O(4)#1	2.0224(13)	Co(1)–O(3)#2	2.0227(13)
Co(1)–O(5)#3	2.0378(13)	Co(1)–N(1)	2.0617(15)
Co(1)–O(2)	2.0799(14)	Co(1)–Co(1)#2	2.7346(5)
O(4)#1–Co(1)–O(3)#2	91.73(6)	O(4)#1–Co(1)–O(5)#3	165.56(6)
O(3)#2–Co(1)–O(5)#3	88.43(7)	O(4)#1–Co(1)–N(1)	100.03(6)
O(3)#2–Co(1)–N(1)	105.83(6)	O(5)#3–Co(1)–N1	93.81(6)
O(4)#1–Co(1)–O(2)	89.81(6)	O(3)#2–Co(1)–O(2)	165.31(6)
O(5)#3–Co(1)–O(2)	86.48(7)	N(1)–Co(1)–O(2)	88.27(6)
O(4)#1–Co(1)–Co(1)#2	86.38(4)	O(3)#2–Co(1)–Co(1)#2	91.74(5)
O(5)#3–Co(1)–Co(1)#2	79.18(4)	N(1)–Co(1)–Co(1)#2	160.98(5)
O(2)–Co(1)–Co(1)#2	73.77(5)		

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

Complex **5**

Co(1)–O(1)	2.1050(19)	Co(1)–O(1)#1	2.1050(19)
Co(1)–O(1W)	2.0972(18)	Co(1)–O(1W) #1	2.0971(18)
Co(1)–N(1)	2.176(10)	Co(1)–N(1) #1	2.176(10)
Co(2)–O(4)	2.0941(18)	Co(2)–O(4)#2	2.0941(18)
Co(2)–N(2)	2.171(2)	Co(2)–N(2)#2	2.171(2)
Co(2)–O(2W)	2.0958(19)	Co(2)–O(2W)#2	2.096(2)
O(1W)#1–Co(1)–O(1W)	180.0	O(1W)–Co(1)–O(1)	89.92(8)
O(1W)#1–Co(1)–O(1)	90.8(8)	O(1W)–Co(1)–O(1)#1	90.08(8)
O(1W)#1–Co(1)–O(1)#1	89.92(8)	O(1W)#1–Co(1)–N(1)#1	86.7(3)
O(1W)–Co(1)–N(1)#1	93.9(3)	O(1W)–Co(1)–N(1)	86.7(3)
O(1W)#1–Co(1)–N(1)	93.3(3)	O(1)#1–Co(1)–O(1)	180.0
O(1)–Co(1)–N(1)	89.5(3)	O(1)#1–Co(1)–N(1)#1	89.5(3)
O(1)#1–Co(1)–N(1)	90.5(3)	O(1)–Co(1)–N(1)#1	90.5(3)

O(4)#2–Co(2)–N(2)#2	90.79(8)	O(4)–Co(2)–N(2)	90.79(8)
O(4)–Co(2)–N(2)#2	89.21(8)	O(4)#2–Co(2)–N(2)	89.21(8)
O(4)#2–Co(2)–O(2W)	90.25(8)	O(4)#2–Co(2)–O(2W)#2	89.75(8)
O(4)–Co(2)–O(2W)	89.75(8)	O(4)–Co(2)–O(2W)#2	90.25(8)
N(2)–Co(2)–N(2)#2	180.0	N(2)–Co(2)–O(2W)	92.15(9)
N(2)–Co(2)–O(2W)#2	87.85(9)	N(2)#2–Co(2)–O(2W)#2	92.15(9)
O(2W)–Co(2)–N(2)#2	87.85(9)	O(2W)–Co(2)–O(2W)#2	180.00(9)

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

Complex **6**

Co(1)–O(1)	2.158(5)	Co(1)–O(1W)	2.058(6)
Co(1)–O(3)#1	2.107(5)	Co(1)–O(4)	2.099(5)
Co(1)–N(1)#2	2.166(7)	Co(1)–N(4)	2.185(7)
O(1)–Co(1)–N(1)#1	90.3(2)	O(1)–Co(1)–N(4)	85.7(2)
O(1W)–Co(1)–O(1)	89.1(2)	O(1W)–Co(1)–O(3)#2	91.9(2)
O(1W)–Co(1)–O(4)	172.0(2)	O(1W)–Co(1)–N(1)#1	89.3(2)
O(1W)–Co(1)–N(4)	89.9(3)	O(3)#2–Co(1)–O(1)	170.8(2)
O(3)#2–Co(1)–N(1)#1	98.9(2)	O(3) #2–Co(1)–N(4)	85.1(2)
O(4)–Co(1)–O(1)	83.0(2)	O(4)–Co(1)–O(3)#2	96.0(2)
N(1)#1–Co(1)–N(4)	175.9(3)		

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

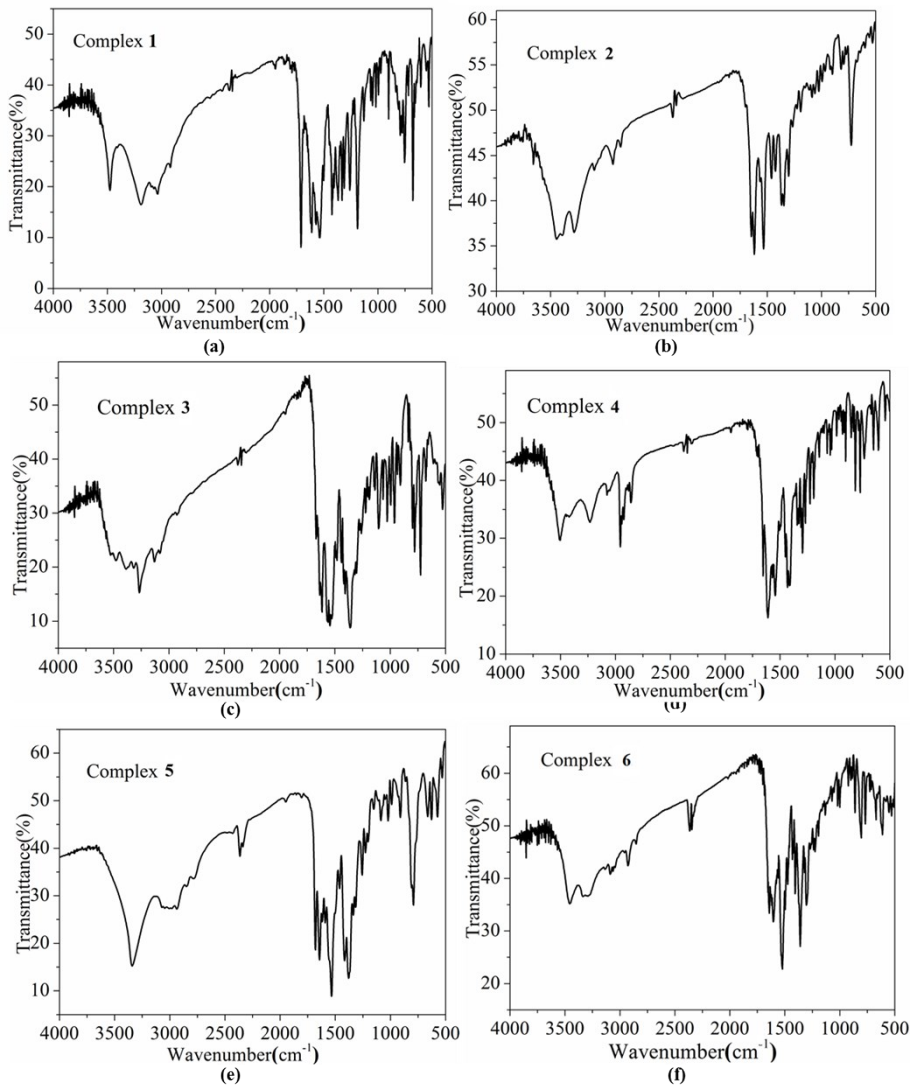


Fig. S1 The IR spectra of complexes **1**–**6**.

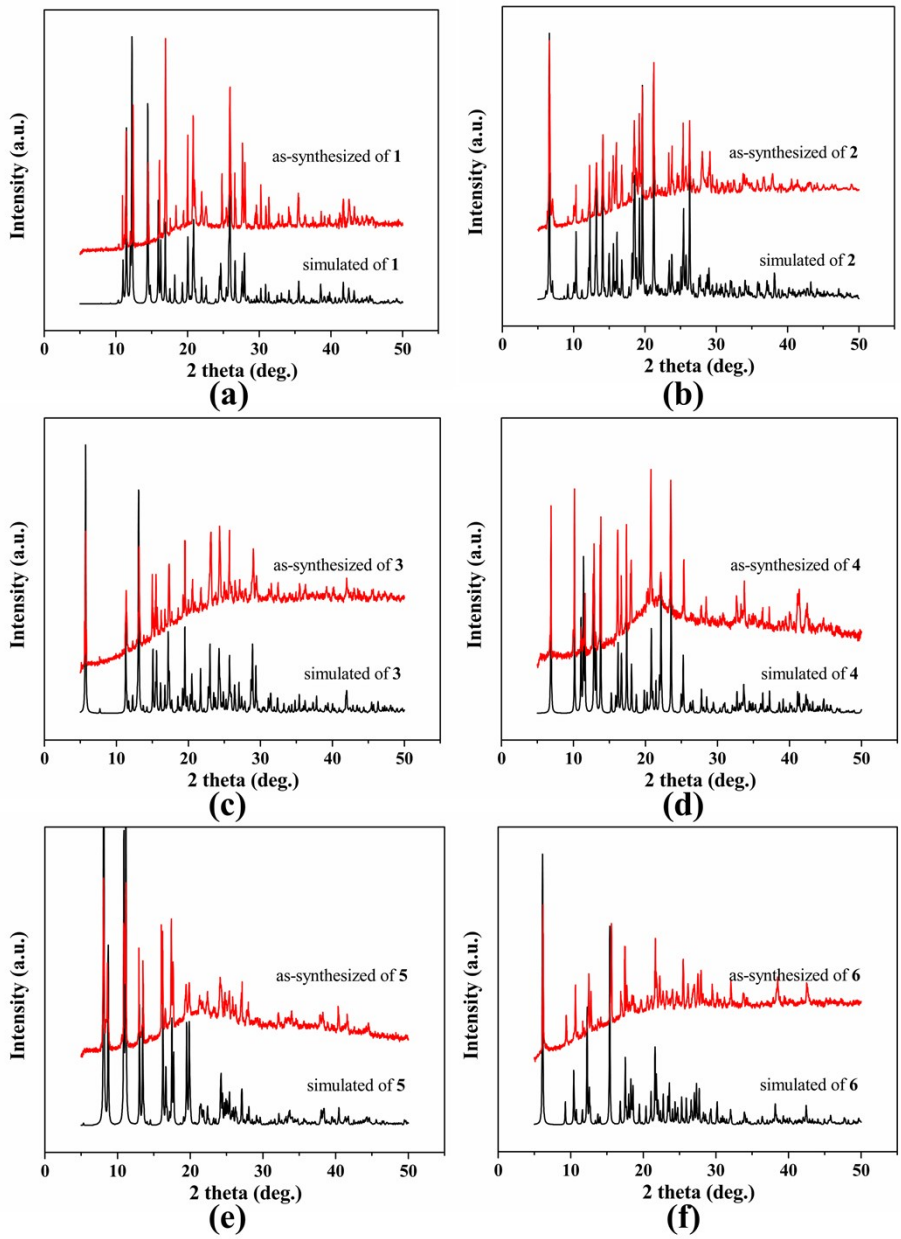


Fig. S2 The PXRD patterns of complexes **1**–**6**.

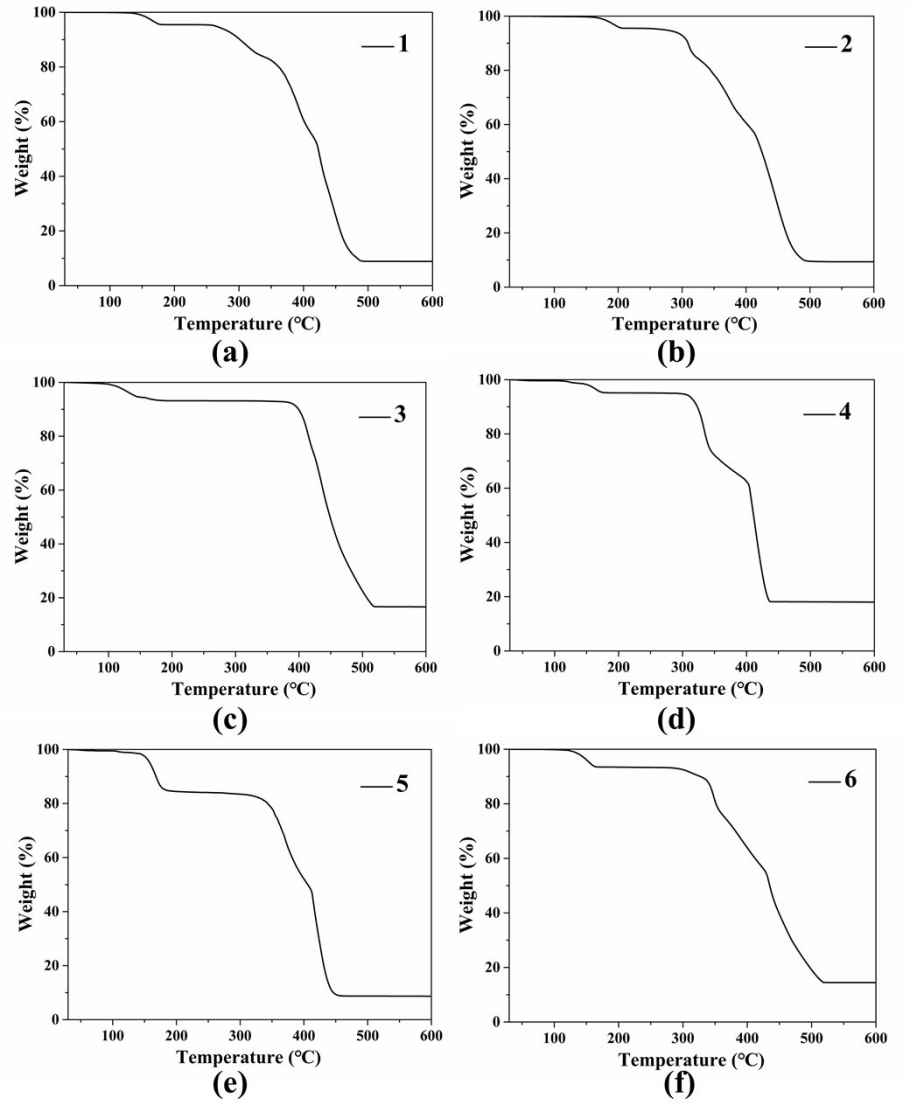
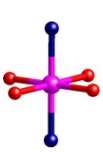
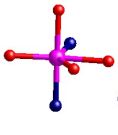
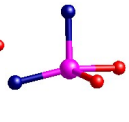
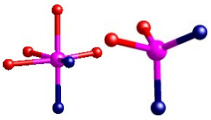
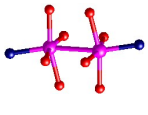
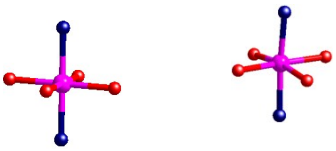
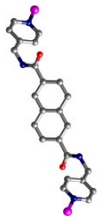
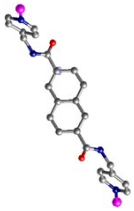
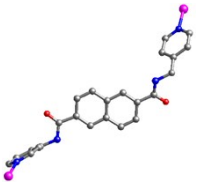
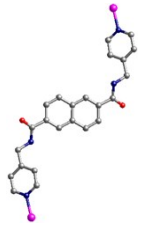
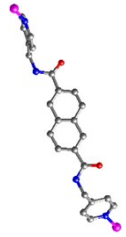
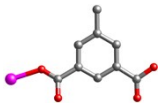
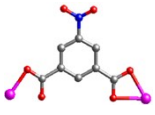
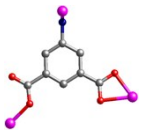
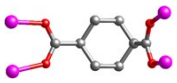
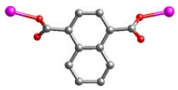
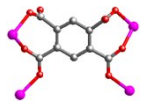
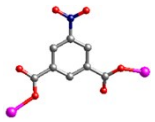
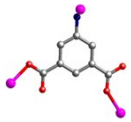


Fig. S3 The TG curves of complexes **1**–**6**.

Table S2 The coordination modes of Co^{II} ions, 4-bmpnd and polycarboxylates in complexes **1–6**.

Complex	1	2	3	4	5	6
Metal ions						
N-donors						
Carboxylates						
						

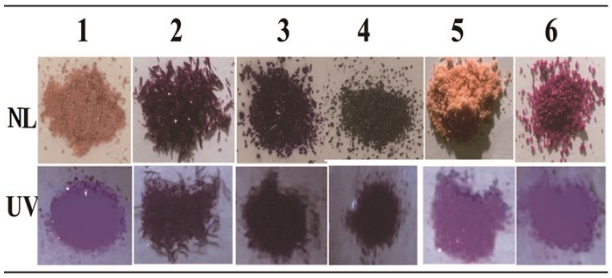
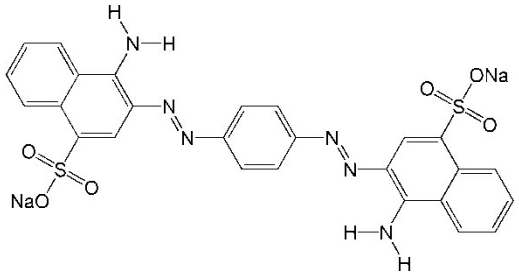
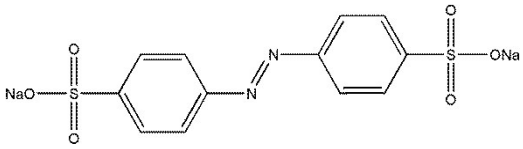
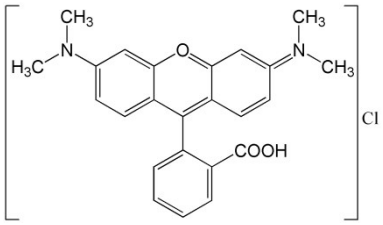
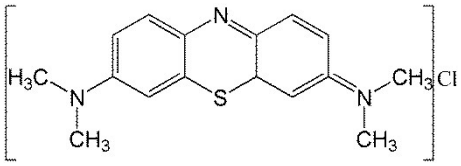
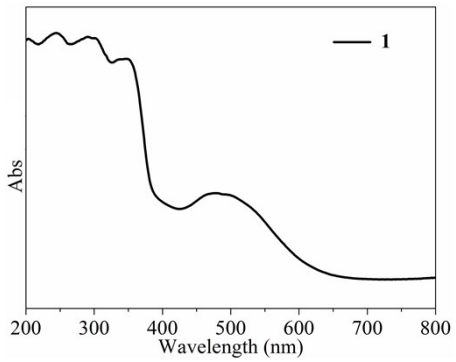


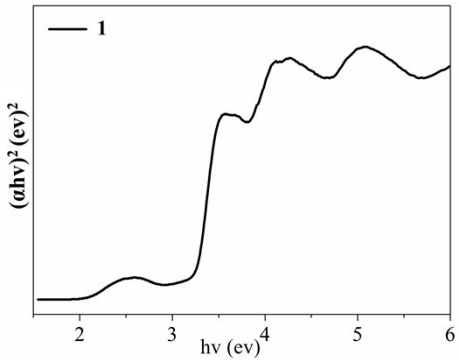
Fig. S4 The photographs of solid-state sample of complexes **1–6** at room temperature. (NL= normal light, UV=ultraviolet)

Table S3 The structures and nature of organic dyes

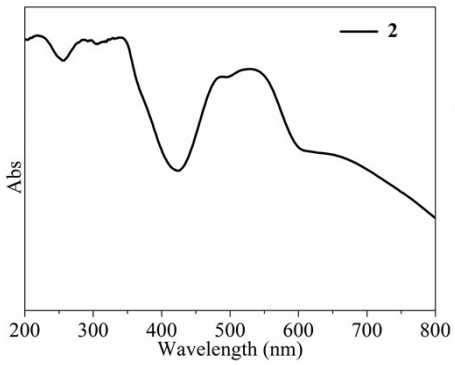
Dye name	Chemical structures	Ionicity	Size (nm^3)	Absorption l max (nm)
Congo Red (CR)		**Anionic**	**2.61*0.86*0.39**	**493**
Methyl Orange (MO)		**Anionic**	**1.54*0.48*0.28**	**467**
Rhodamine B (RhB)		**Cationic**	**1.56*1.35*0.42**	**552**
Methylene Blue (MB)		**Cationic**	**1.38*0.64*0.21**	**672**


1
Abs
200 300 400 500 600 700 800
Wavelength (nm)

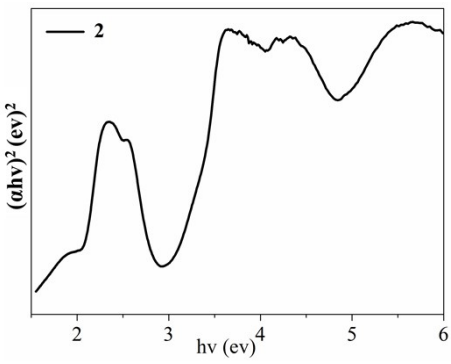
(a)


1
(αhv)² (ev)²
2 3 4 5 6
hv (ev)

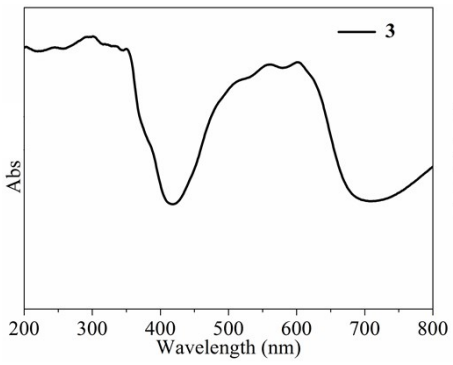
(b)


2
Abs
200 300 400 500 600 700 800
Wavelength (nm)

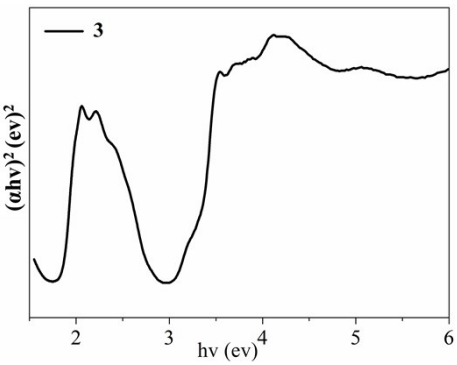
(c)


2
(αhv)² (ev)²
2 3 4 5 6
hv (ev)

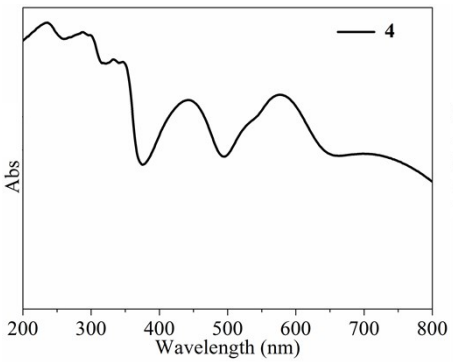
(d)


3
Abs
200 300 400 500 600 700 800
Wavelength (nm)

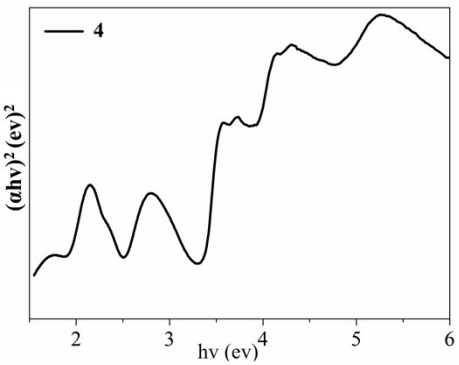
(e)


3
(αhv)² (ev)²
2 3 4 5 6
hv (ev)

(f)


4
Abs
200 300 400 500 600 700 800
Wavelength (nm)

(g)


4
(αhv)² (ev)²
2 3 4 5 6
hv (ev)

(h)

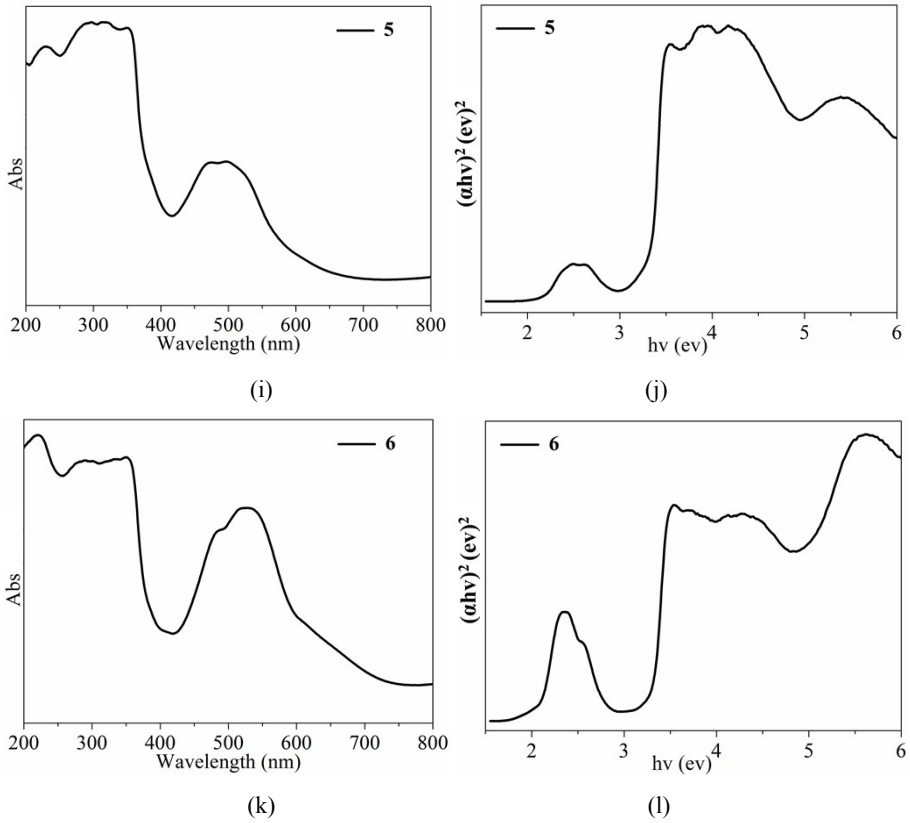


Fig. S5 UV-vis solid state diffuse-reflectance spectra and optical absorption spectra of complexes **1**–**6**.

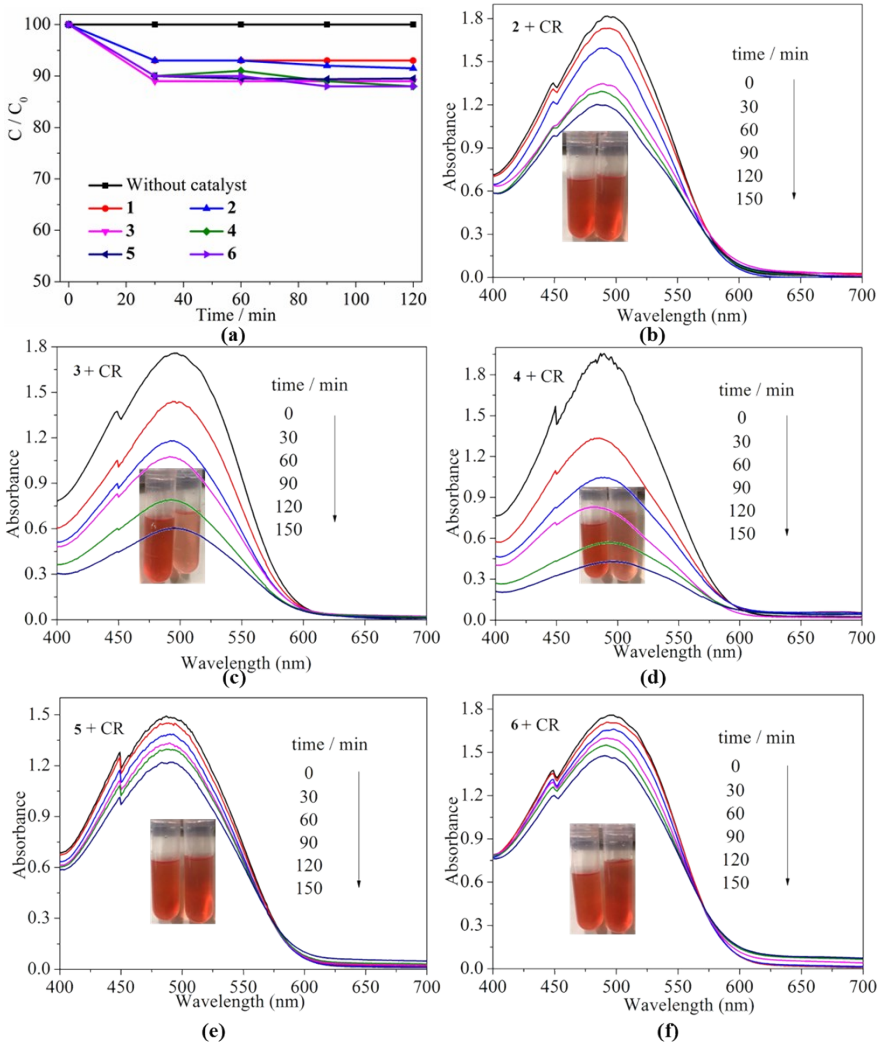


Fig. S6 The absorption spectra of the CR solution during the decomposition reaction with the presence of complexes **1**−**6** under dark (a) and complexes **2**−**6** under UV irradiation (b−f).

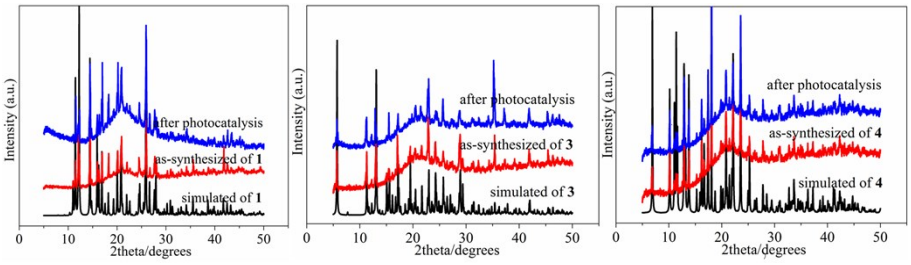


Fig. S7 The PXRD of complexes **1, 3** and **4** after photocatalytic degradation of CR.

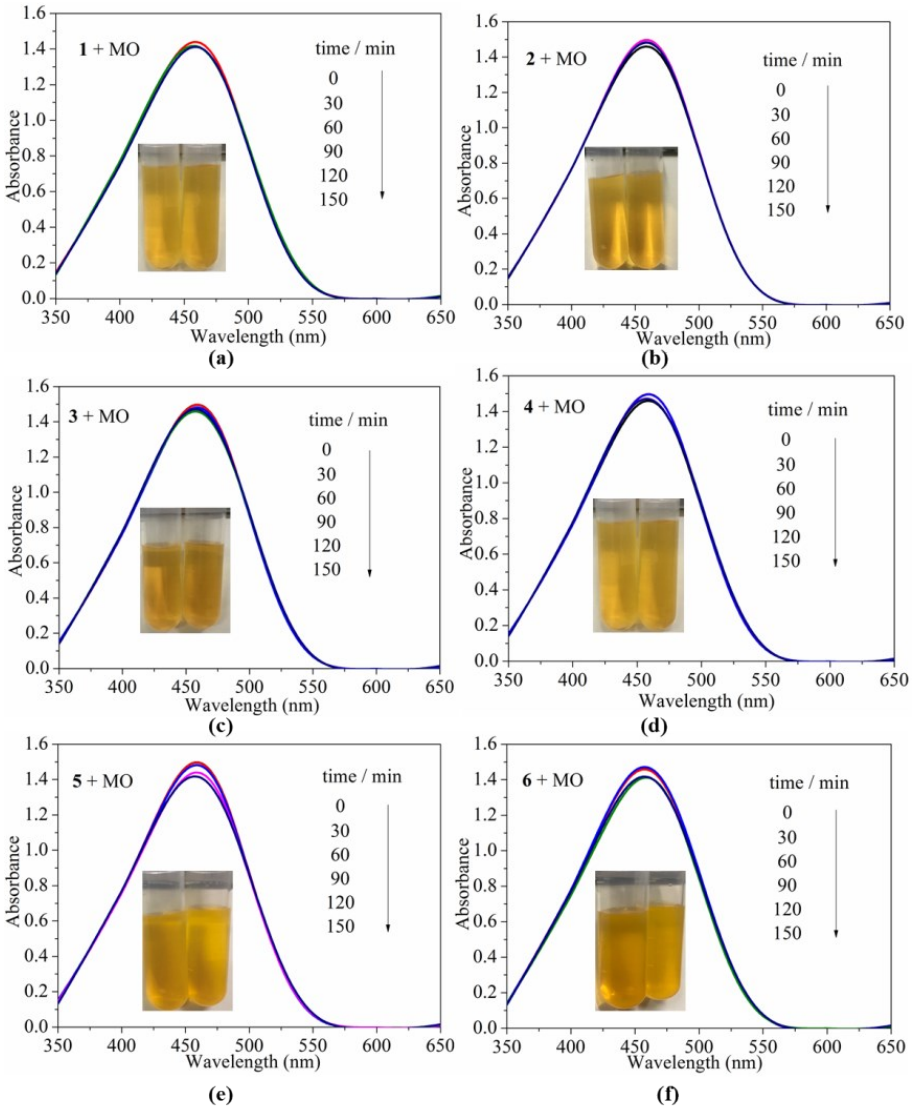


Fig. S8 The absorption spectra of the MO solution during the decomposition reaction with the presence of complexes **1**−**6** (a−f) under UV irradiation.

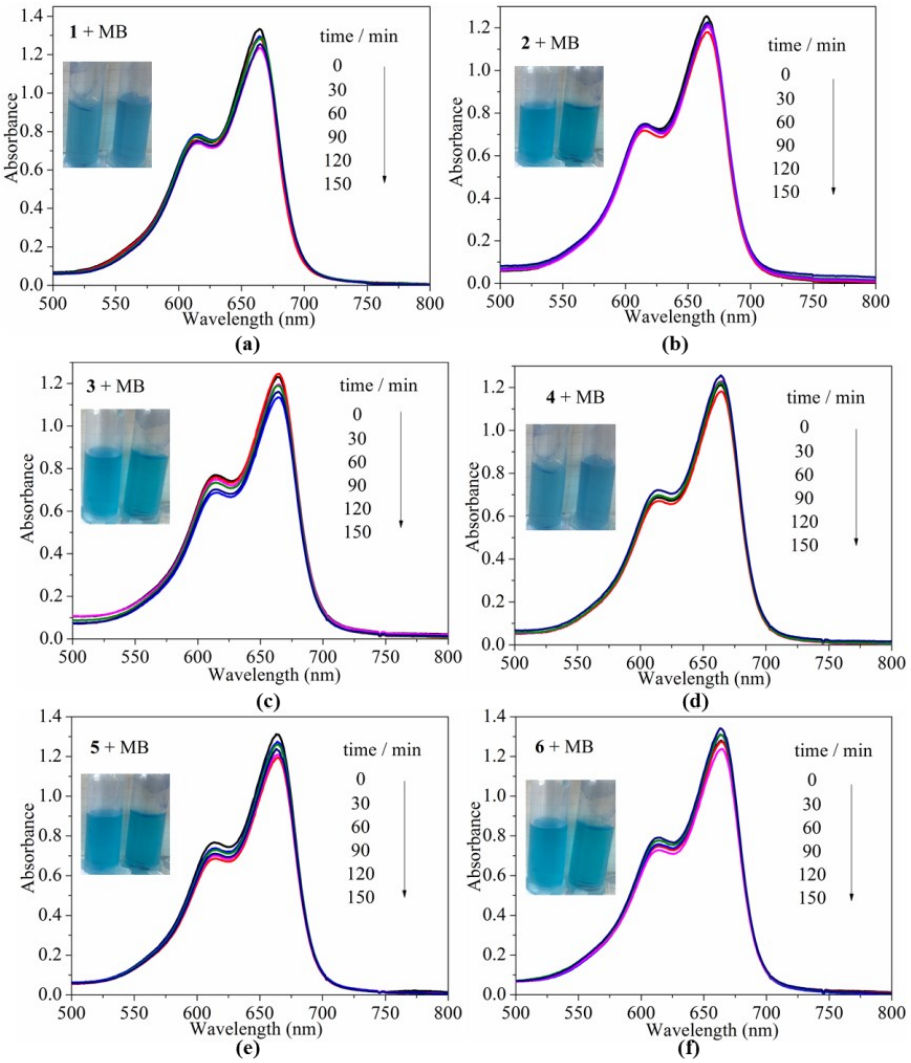


Fig. S9 The absorption spectra of the MB solution during the decomposition reaction with the presence of complexes **1**−**6** (a−f) under UV irradiation.

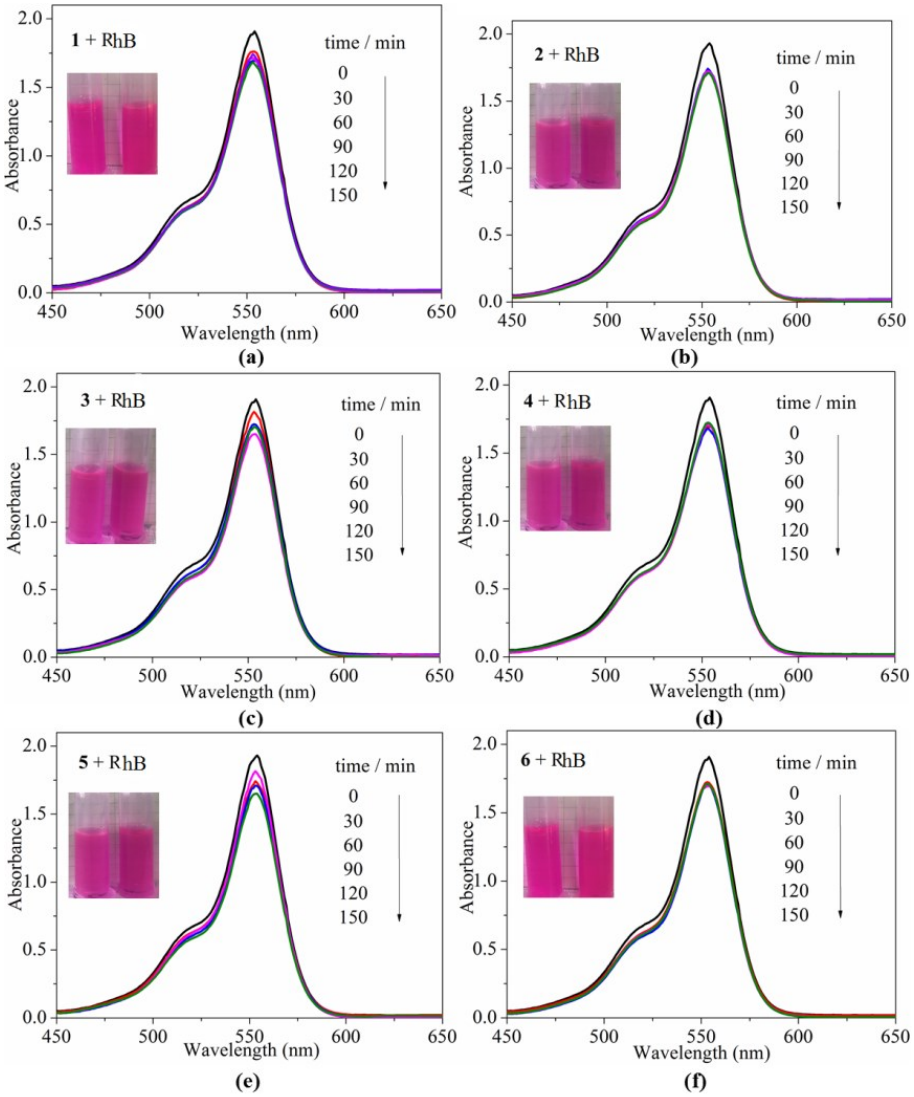


Fig. S10 The absorption spectra of the RhB solution during the decomposition reaction with the presence of complexes **1**−**6** (a−f) under UV irradiation.

References

S1. X. L. Wang, J. Luan, F. F. Sui, H. Y. Lin, G. C. Liu and C. Xu, *Cryst. Growth Des*., 2013, **13**, 3561−3576.

S2. M. Sarka and K. Biradha, *Cryst. Growth Des*., 2006, **61**, 202−208.