A series of pyridyl-amide-based Zn^{II}/Cd^{II} coordination polymers and their polypyrrole-functionalized composite materials for tuning their photocatalytic properties

Xiu-Li Wang*, Xiao-Mei Wu, Guo-Cheng Liu, Hong-Yan Lin and Xiang Wang

Department of Chemistry, Bohai University, Liaoning Province Silicon Materials Engineering Technology Research Centre, Jinzhou 121000, P. R. China

Table S1 Selected bond distances (Å) and angles (°) for **CP1**–**CP6**.

CP1 $C_{32}H_{25}CdN_5O_{11}$			
Cd(1)-O(1)	2.200(8)	Cd(1)-O(1W)	2.314(8)
Cd(1)-N(4)#1	2.344(10)	Cd(1)-O(4)#2	2.345(8)
Cd(1)-N(1)	2.370(9)	Cd(1)-O(3)	2.442(9)
O(1)-Cd(1)-O(1W)	85.5(3)	O(1)-Cd(1)-N(4)#1	123.5(3)
O(1W)-Cd(1)-N(4)#1	80.1(3)	O(1)-Cd(1)-O(4)#2	95.5(3)
O(1W)-Cd(1)-O(4)#2	101.8(3)	N(4)#1-Cd(1)-O(4)#2	140.9(3)
O(1)-Cd(1)-N(1)	94.7(3)	O(1W)-Cd(1)-N(1)	168.2(4)
N(4)#1-Cd(1)-N(1)	90.1(3)	O(4)#2-Cd(1)-N(1)	90.0(3)
O(1)-Cd(1)-O(3)	150.2(3)	O(1W)-Cd(1)-O(3)	99.0(3)
N(4)#1-Cd(1)-O(3)	86.3(3)	O(4)#2-Cd(1)-O(3)	54.7(3)
N(1)-Cd(1)-O(3)	86.8(3)		
Symmetry code for **CP1**: #1 3/2 + x, 1/2 – y, 1/2 + z; #2 –1 + x, y, z			
CP2 $C_{34}H_{29}N_5O_8SCd$			
Cd(1)-O(1)	2.302(2)	Cd(1)-O(3)#1	2.306(2)
Cd(1)-N(1)	2.339(3)	Cd(1)-N(4)	2.388(3)
Cd(1)-O(7)#2	2.442(3)	Cd(1)-O(4)	2.484(3)
Cd(1)-O(2)	2.538(3)	O(1)-Cd(1)-O(3)#1	141.90(10)
O(1)-Cd(1)-N(1)	86.95(10)	O(3)#1-Cd(1)-N(1)	94.09(10)
O(1)-Cd(1)-N(4)	84.34(9)	O(3)#1-Cd(1)-N(4)	133.53(9)
N(1)-Cd(1)-N(4)	92.49(11)	O(1)-Cd(1)-O(7)#2	88.63(9)
O(3)#1-Cd(1)-O(7)#2	90.10(9)	N(1)-Cd(1)-O(7)#2	175.44(9)
N(4)-Cd(1)-O(7)#2	85.92(10)	O(1)-Cd(1)-O(4)	164.11(10)
O(3)#1-Cd(1)-O(4)	53.92(10)	N(1)-Cd(1)-O(4)	90.55(11)
N(4)-Cd(1)-O(4)	80.09(10)	O(7)#2-Cd(1)-O(4)	93.39(10)
O(1)-Cd(1)-O(2)	53.84(9)	O(3)#1-Cd(1)-O(2)	89.03(9)
N(1)-Cd(1)-O(2)	102.39(10)	N(4)-Cd(1)-O(2)	133.96(9)
O(7)#2-Cd(1)-O(2)	75.83(9)	O(4)-Cd(1)-O(2)	141.79(9)
Symmetry code for **CP2**: #1 1 + x, y, z; #2 2 – x, –y, 1 – z			

CP3 $C_{30}H_{24}N_4O_9SCd$

Cd(1)-O(4)	2.270(2)	Cd(1)-O(1)	2.325(2)
Cd(1)-N(1)	2.352(3)	Cd(1)-N(4)	2.371(2)
Cd(1)-O(7)#1	2.501(2)	Cd(1)-O(3)#2	2.535(2)
Cd(1)-O(2)	2.565(3)	O(4)-Cd(1)-O(1)	141.44(8)
O(4)-Cd(1)-N(1)	97.67(9)	O(1)-Cd(1)-N(1)	86.23(9)
O(4)-Cd(1)-N(4)	133.37(8)	O(1)-Cd(1)-N(4)	84.48(8)
N(1)-Cd(1)-N(4)	91.78(9)	O(4)-Cd(1)-O(7)#1	88.06(9)
O(1)-Cd(1)-O(7)#1	92.45(9)	N(1)-Cd(1)-O(7)#1	172.36(8)
N(4)-Cd(1)-O(7)#1	80.60(8)	O(4)-Cd(1)-O(3)#2	54.14(8)
O(1)-Cd(1)-O(3)#2	163.53(9)	N(1)-Cd(1)-O(3)#2	85.63(9)
N(4)-Cd(1)-O(3)#2	81.49(8)	O(7)#1-Cd(1)-O(3)#2	93.72(9)
O(4)-Cd(1)-O(2)	89.28(8)	O(1)-Cd(1)-O(2)	53.29(8)
N(1)-Cd(1)-O(2)	106.44(8)	N(4)-Cd(1)-O(2)	131.32(8)
O(7)#1-Cd(1)-O(2)	78.57(7)	O(3)#2-Cd(1)-O(2)	143.07(8)

Symmetry code for **CP3**: #1 2 – x, –y, 1 – z; #2 –1 + x, y, z

CP4 C_{30} H_{24} N_4 O_9 S Zn

Zn(1)-O(4)#1	1.945(2)	Zn(1)-O(1)	1.953(2)
Zn(1)-N(1)	2.088(3)	Zn(1)-N(4)#2	2.112(3)
O(4)#1-Zn(1)-O(1)	129.12(10)	O(4)#1-Zn(1)-N(1)	96.41(10)
O(1)-Zn(1)-N(1)	125.40(10)	O(4)#1-Zn(1)-N(4)#2	94.88(10)
O(1)-Zn(1)-N(4)#2	103.64(10)	N(1)-Zn(1)-N(4)#2	99.94(10)

Symmetry code for **CP4**: #1 1 + x, y, z; #2 –1 + x, y, –1 + z

CP5 C_{32} H_{24} N_4 O_8 Zn

Zn(1)-O(4)#1	1.898(5)	Zn(1)-O(1)	1.942(4)
Zn(1)-N(1)	2.072(6)	Zn(1)-N(4)#2	2.123(6)
O(4)#1-Zn(1)-O(1)	133.8(2)	O(4)#1-Zn(1)-N(1)	118.7(2)
O(1)-Zn(1)-N(1)	98.1(2)	O(4)#1-Zn(1)-N(4)#2	103.6(2)
O(1)-Zn(1)-N(4)#2	94.9(2)	N(1)-Zn(1)-N(4)#2	100.9(2)

Symmetry code for **CP5** #1 –1 + x, y, z; #2 –1 + x, y, –1 + z

CP6 $C_{40}H_{30}N_6O_{13}Zn_2$

Zn(1)-O(1)	1.940(2)	Zn(1)-O(4)#1	1.972(2)
Zn(1)-N(1)	2.024(3)	Zn(1)-N(3)#2	2.060(3)
O(1)-Zn(1)-O(4)#1	100.79(10)	O(1)-Zn(1)-N(1)	102.62(12)
O(4)#1-Zn(1)-N(1)	125.66(12)	O(1)-Zn(1)-N(3)#2	109.84(11)
O(4)#1-Zn(1)-N(3)#2	106.13(11)	N(1)-Zn(1)-N(3)#2	110.65(12)

Symmetry code for **CP6** #1 x, 2– y, –1/2 + z; #2 x, 1 – y, –1/2 + z

Table S2. The twist degrees of the **L** ligand in **CP1**–**CP6**.

CPs	**CP1**	**CP2**	**CP3**	**CP4**	**CP5**	**CP6**
θ_1	49.44	48.93	14.97	34.92	30.71	60.28
θ_2	63.24	33.88	49.13	88.31	87.40	44.90
θ_3	43.94	61.73	87.52	42.39	40.14	60.28
θ_4	24.71	45.89	31.77	16.56	16.57	44.90

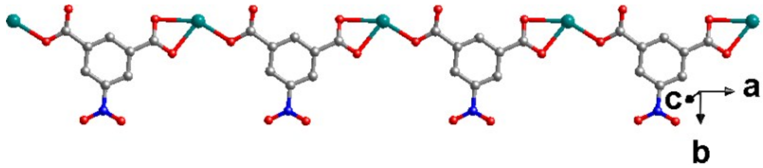


Fig. S1 The 1D linear [Cd(5-NIP)]$_n$ chain in **CP1**.

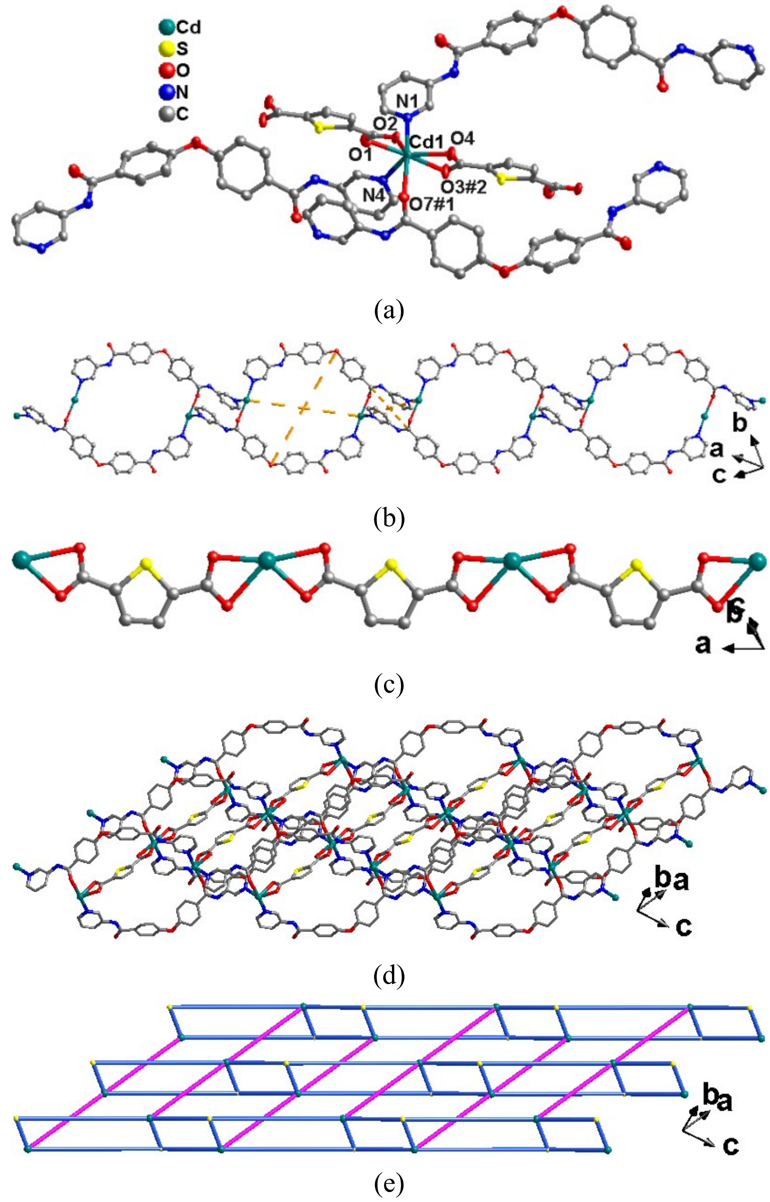


Fig.S2 (a) Coordination environment of Cd^{II} ion in **CP3**. All H atoms and lattice water molecules are omitted for clarity (#1 2 – x, –y, 1 – z; #2 –1 + x, y, z). (b) The 1D [Cd$_2$(**L**)$_2$]$_n$ ladder-like chain of **CP3**. (c) The 1D linear [Cd(2,5-TPD)]$_n$ chain. (d) 2D layer of **CP3**; (e) Simplification of the 3,5-connected network.

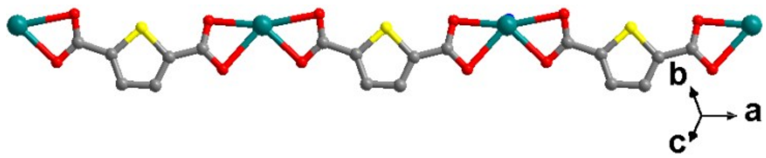


Fig. S3 The 1D [Cd(2,5-TPD)]$_n$ linear chain of **CP2**.

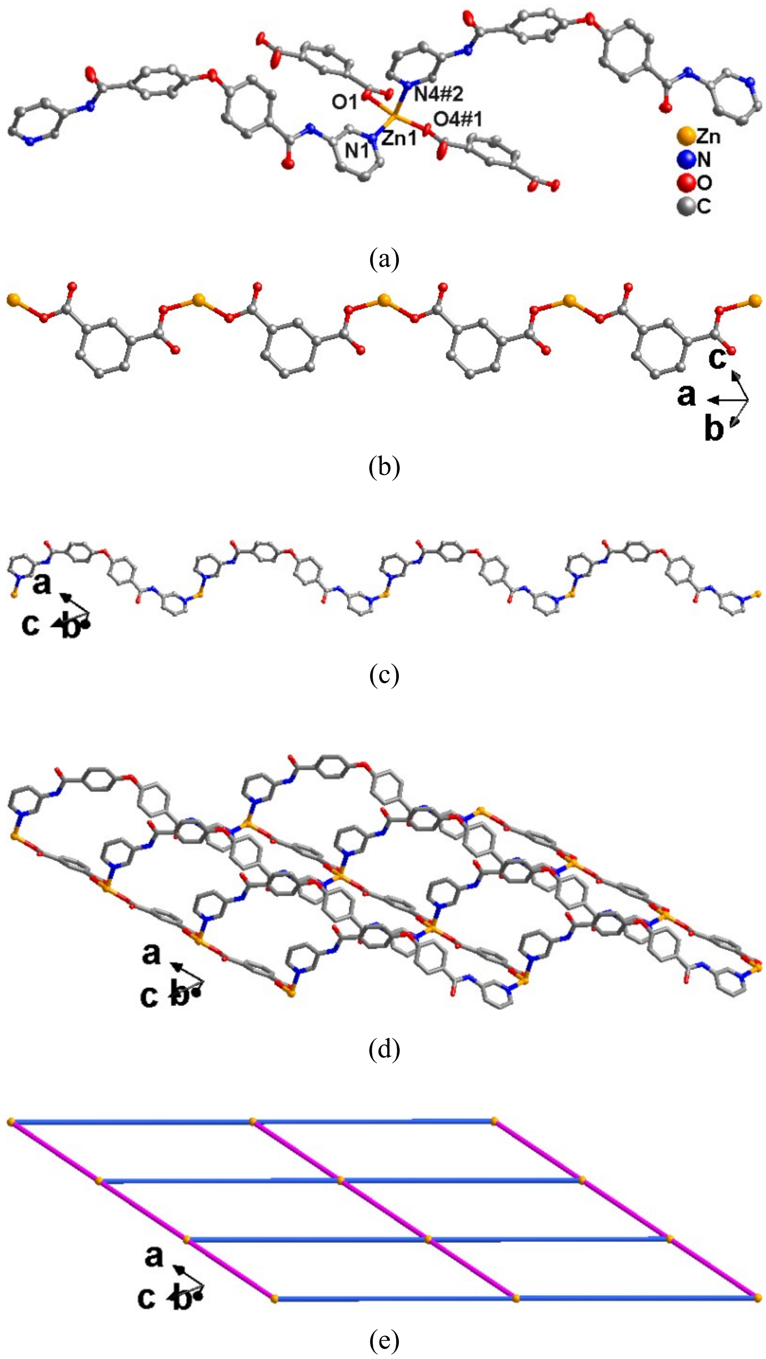


Fig. S4 (a) The coordination environment of Zn^{II} ion in **CP5**. All H atoms and lattice water molecules are omitted for clarity (#1 –1 + x, y, z; #2 –1 + x, y, –1 + z). (b) View of the 1D [Zn(1,3-BDC)]$_n$ linear chain. (c) The 1D [Zn(**L**)]$_n$ wave-like chain. (d) 2D layer of **CP5**; (e) Simplification of the 4-connected network.

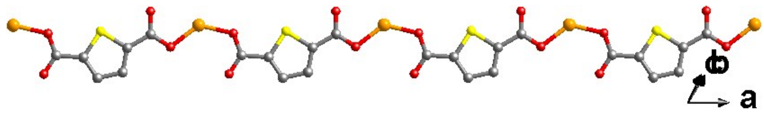


Fig. S5 The 1D [Zn(2,5-TPD)]$_n$ infinite linear chain in **CP4**.

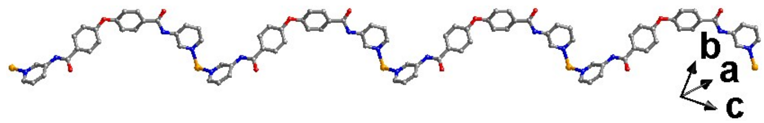
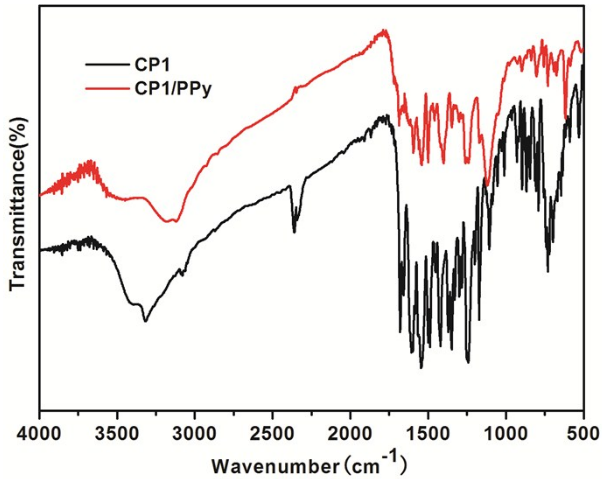
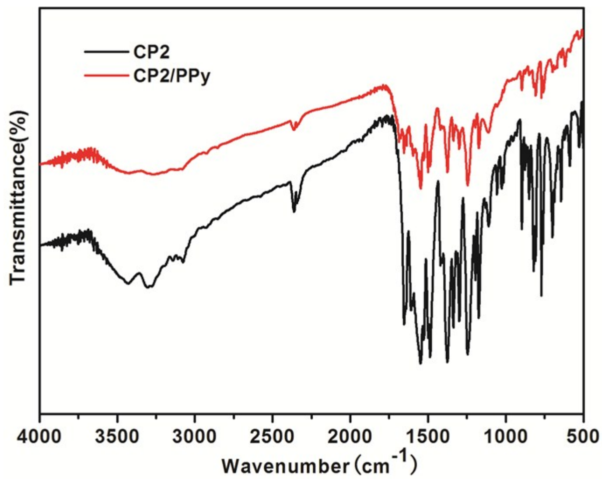


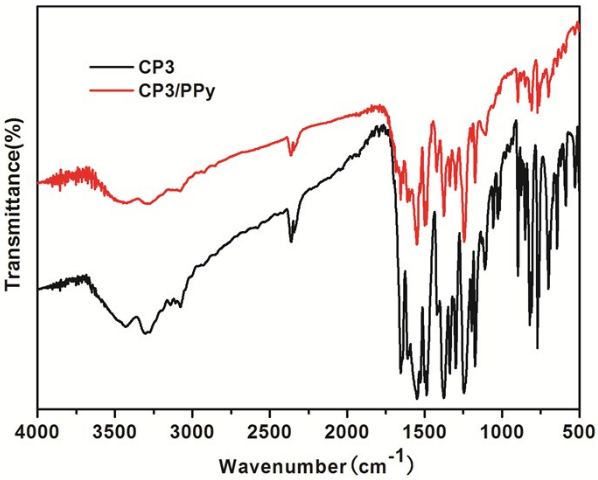
Fig. S6 View of the 1D [Zn(**L**)]$_n$ wave-like chain in **CP4**.



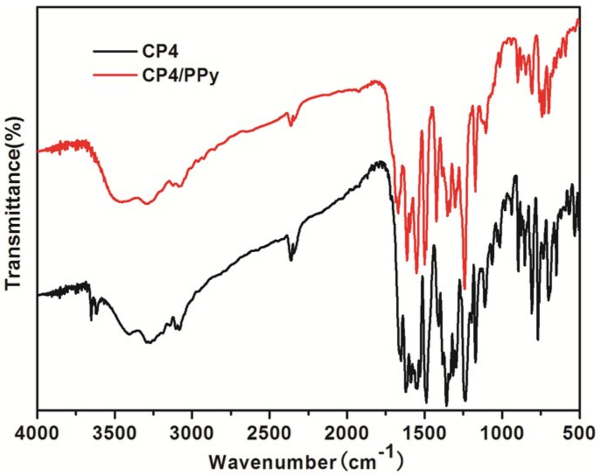
(a)



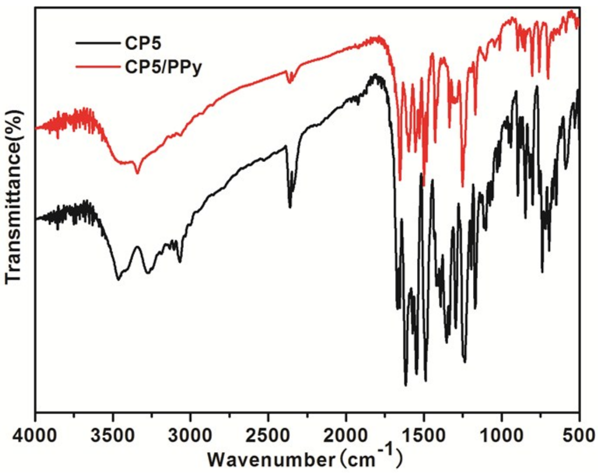
(b)


CP3
CP3/PPy
Transmittance(%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)

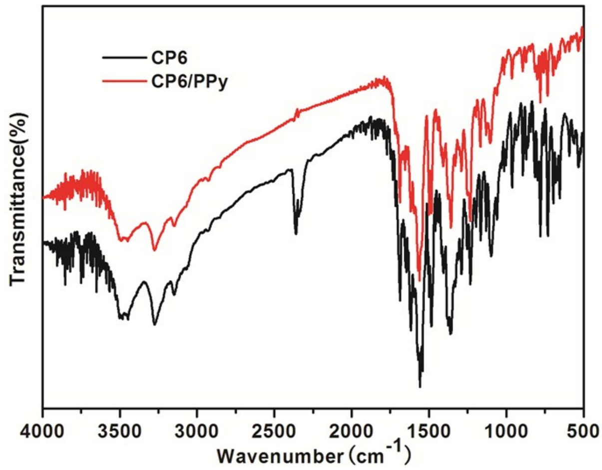
(c)


CP4
CP4/PPy
Transmittance(%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)

(d)

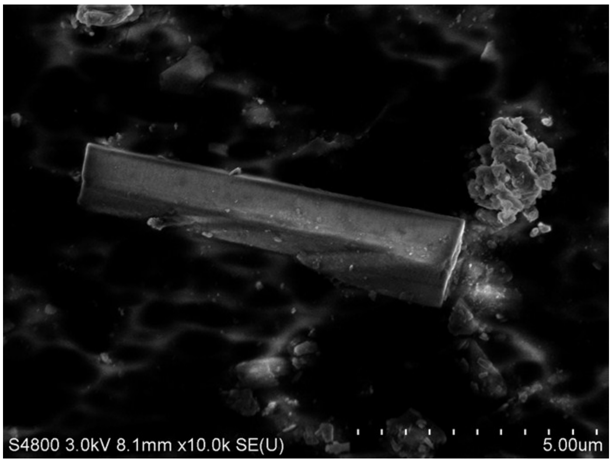

CP5
CP5/PPy
Transmittance(%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)

(e)

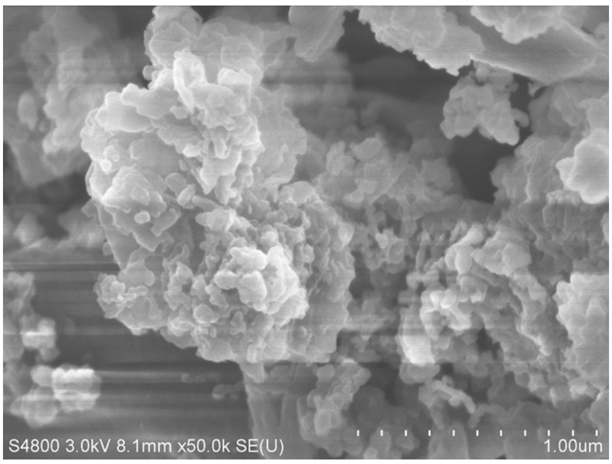


(f)

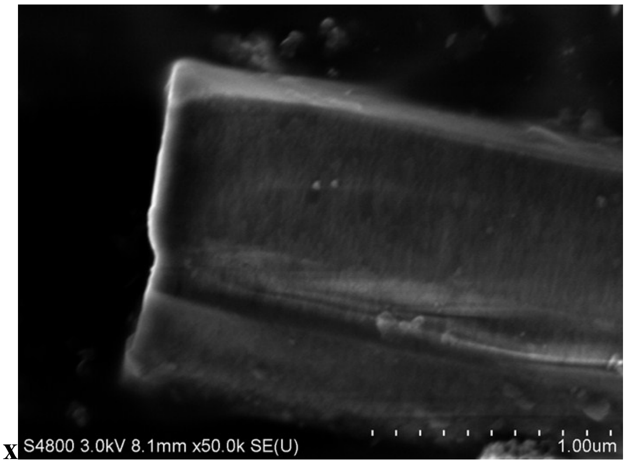
Fig. S7 The IR spectra of **CP1**–**CP6** and their **PPy/CP1–PPy/CP6** composite materials.



(a)

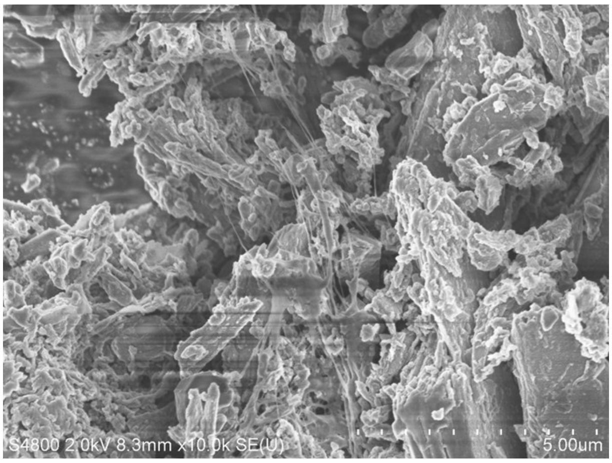


(b)



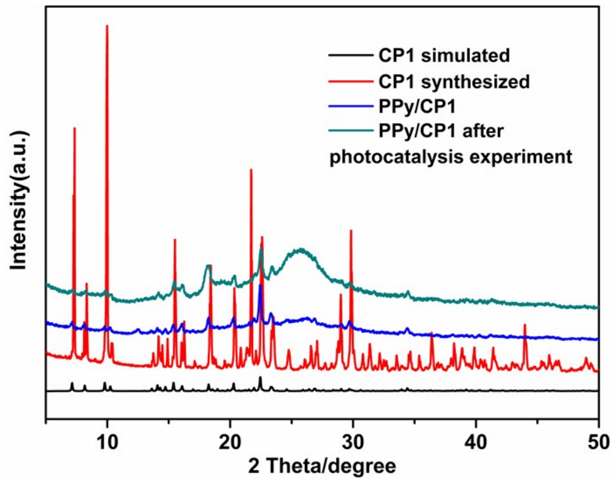
x

(c)

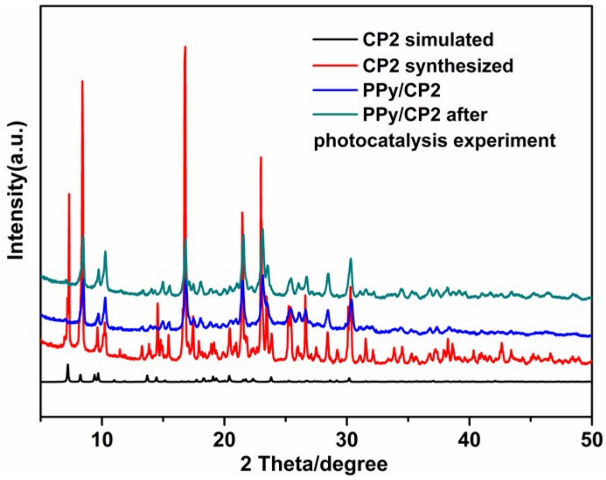


(d)

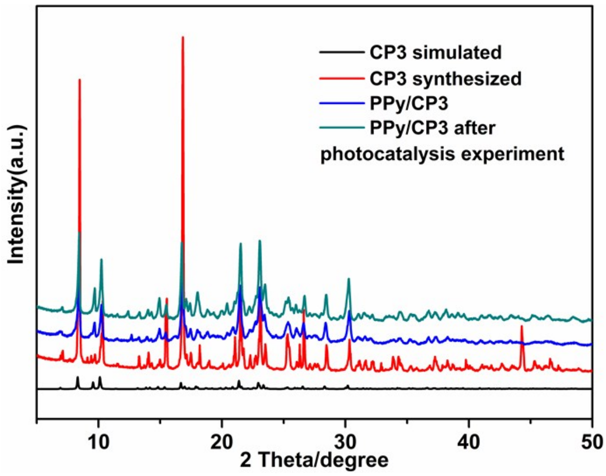
Fig. S8 SEM pictures of micro-size particles of **CP1** (a), **PPy/CP1** (b), **CP6** (c), **PPy/CP6** (d).



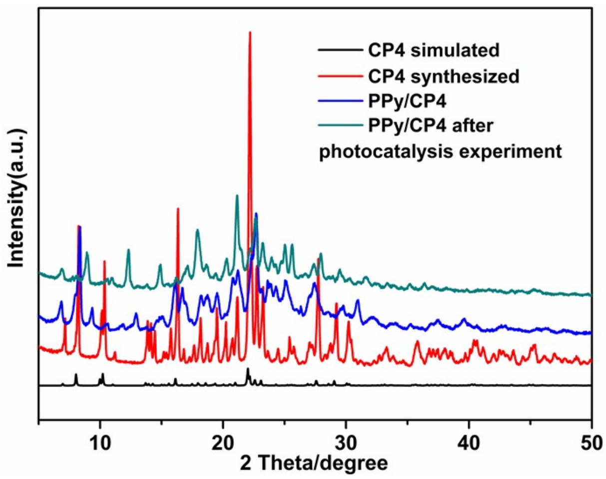
(a)


CP2 simulated
CP2 synthesized
PPy/CP2
PPy/CP2 after
photocatalysis experiment
Intensity(a.u.)
10
20
30
40
50
2 Theta/degree

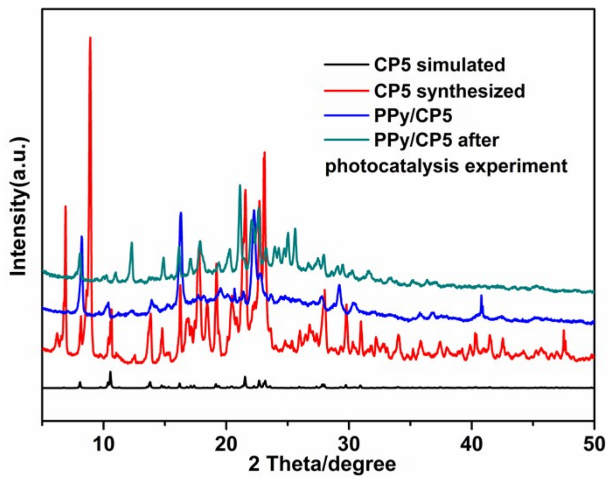
(b)


CP3 simulated
CP3 synthesized
PPy/CP3
PPy/CP3 after
photocatalysis experiment
Intensity(a.u.)
10
20
30
40
50
2 Theta/degree

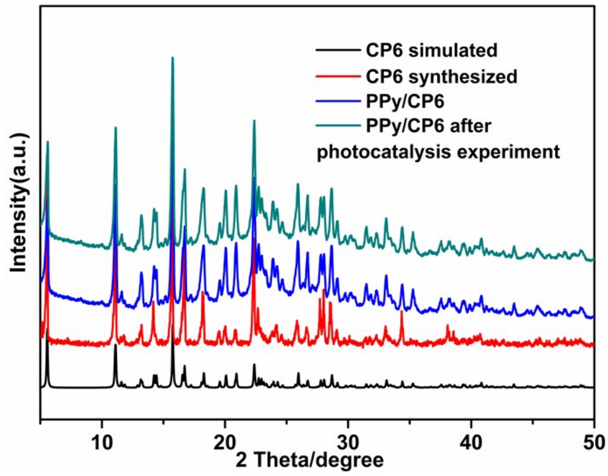
(c)


CP4 simulated
CP4 synthesized
PPy/CP4
PPy/CP4 after
photocatalysis experiment
Intensity(a.u.)
10
20
30
40
50
2 Theta/degree

(d)



(e)



(f)

Fig. S9 The PXRD patterns of **CP1**–**CP6** and **PPy/CP1–PPy/CP6** composite materials and the PXRD patterns of **PPy/CP1–PPy/CP6** after photocatalytic processes.

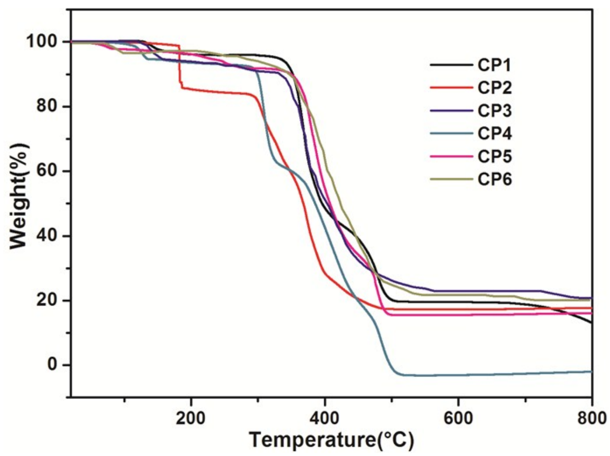
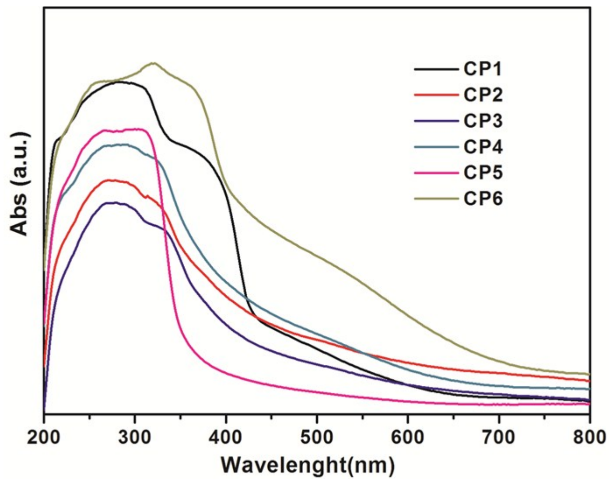
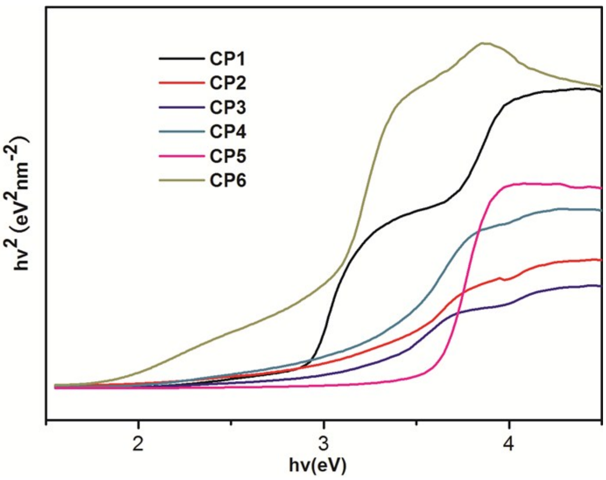


Fig. S10 The TG curves of compounds **CP1**–**CP6**.

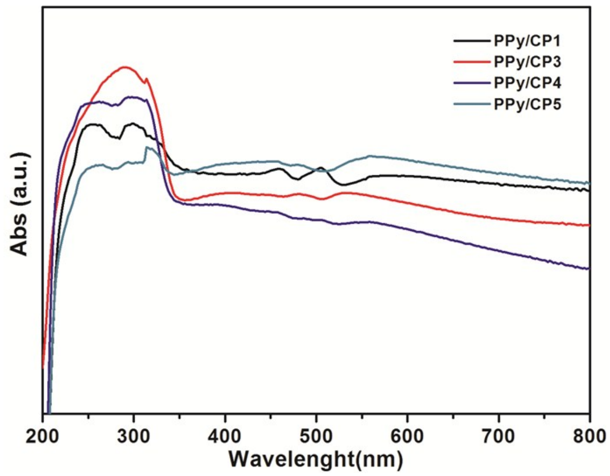


(a)

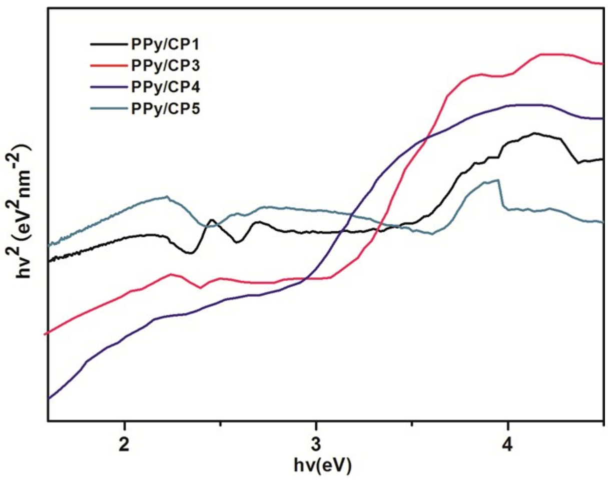


(b)

Fig. S11 (a) UV−vis diffuse-reflectance spectra of **CP1–CP6** with $BaSO_4$ as background; (b) Tauc plots of **CP1**–**CP6**.

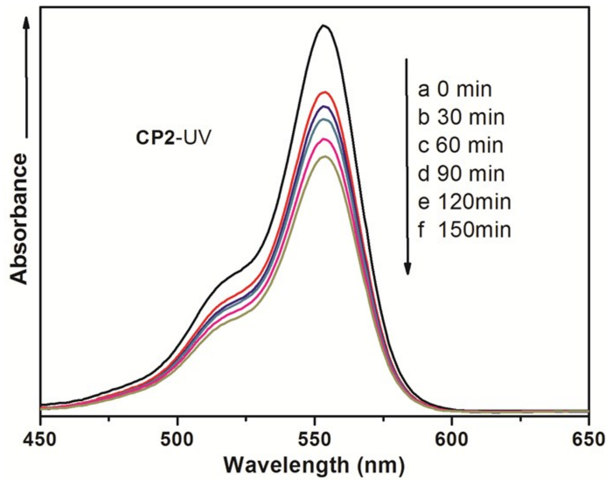


(a)

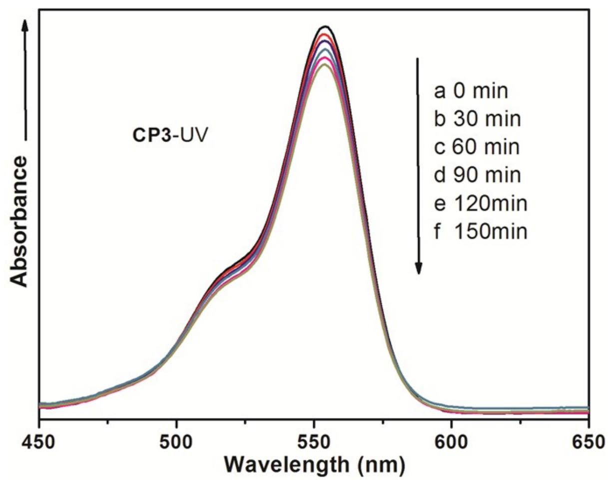


(b)

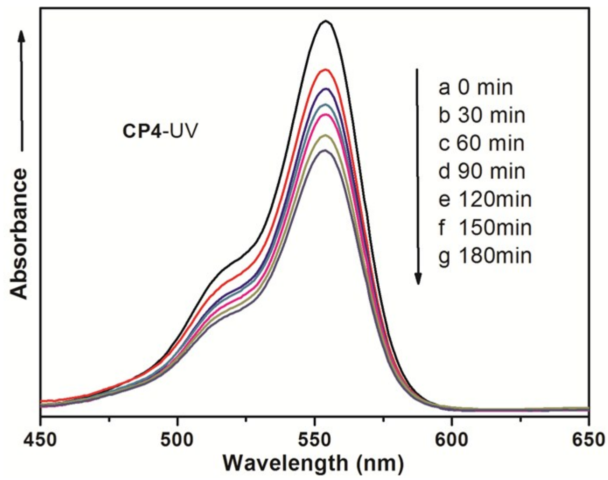
Fig. S12 (a) UV−vis diffuse-reflectance spectra of **PPy/CP1**, **PPy/CP3**, **PPy/CP4** and **PPy/CP5** with $BaSO_4$ as background; (b) Tauc plots of corresponding composite materials **PPy/CPn**.



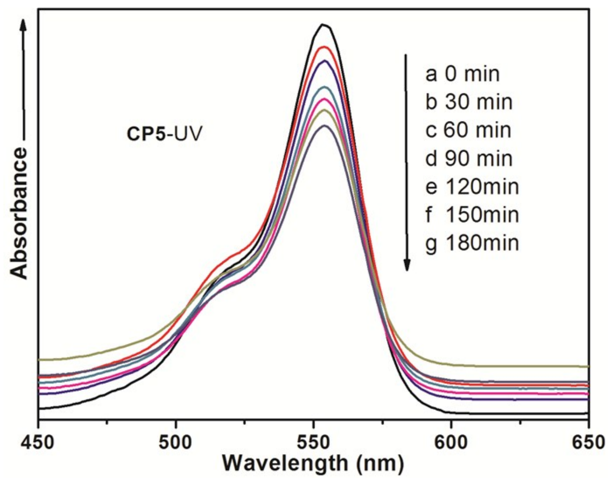
(a)



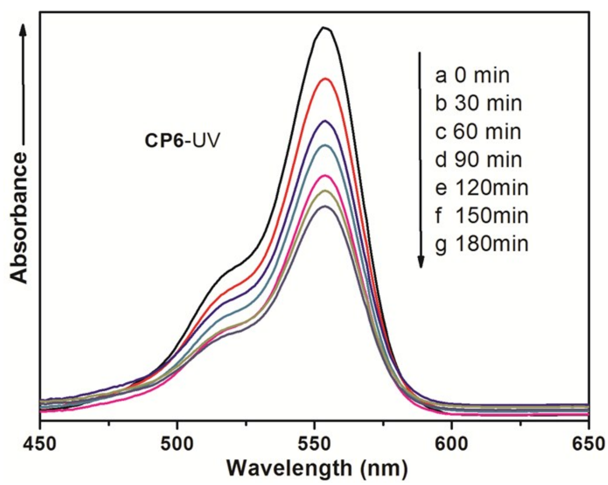
(b)



(c)



(d)



(e)

Fig. S13 Absorption spectra of the RhB solution during the decomposition reaction under UV irradiation in the presence of **CP2**–**CP6**.

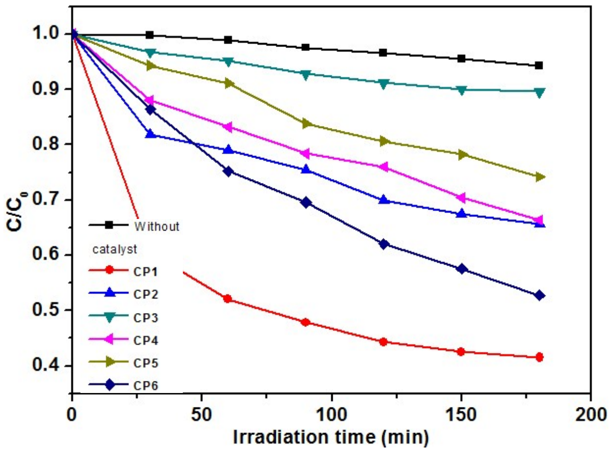
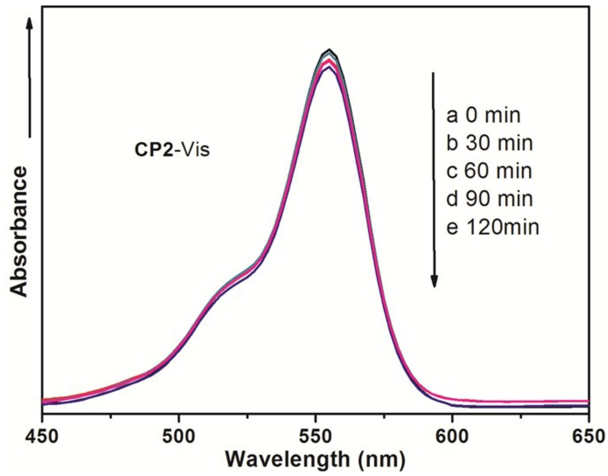
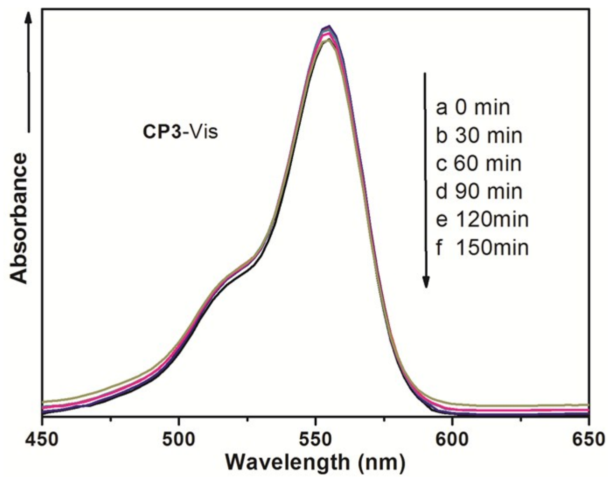


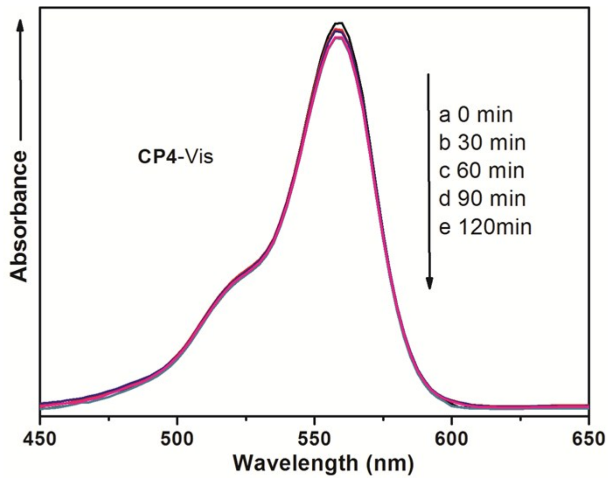
Fig. S14 The degradation ratio of RhB for **CP1**–**CP6** under UV light irradiation.



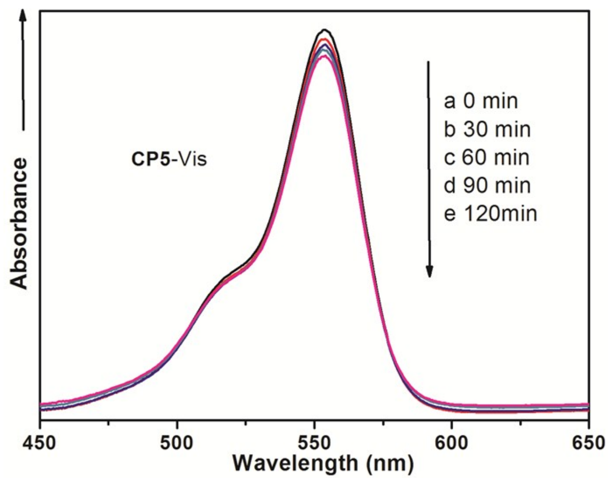
(a)



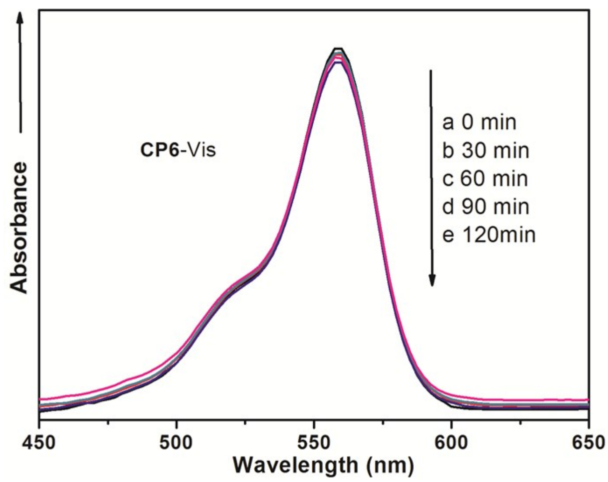
(b)



(c)



(d)



(f)

Fig. S15 Absorption spectra of the RhB solution during the decomposition reaction under visible light irradiation in the presence of **CP2**–**CP6**.

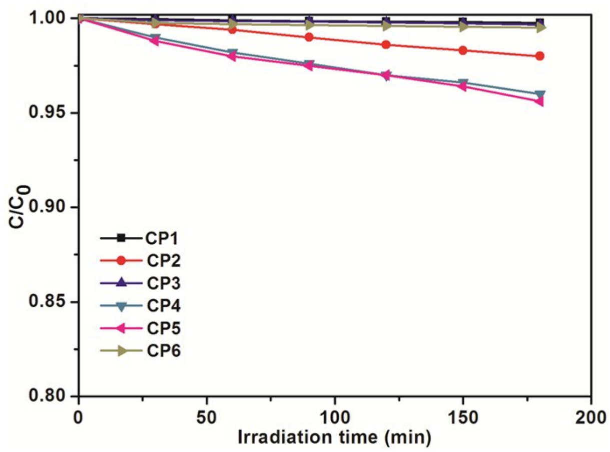
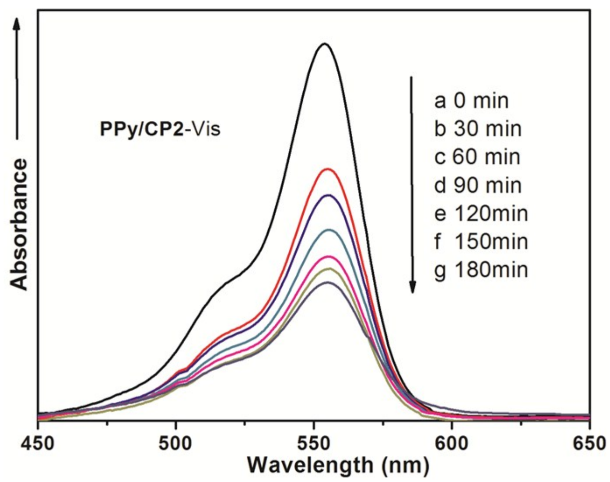
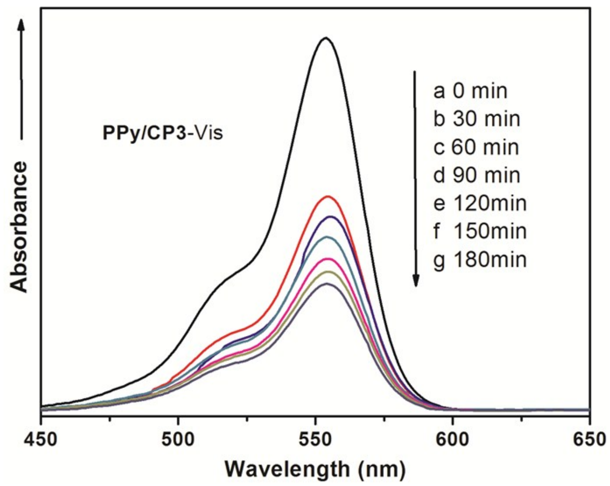


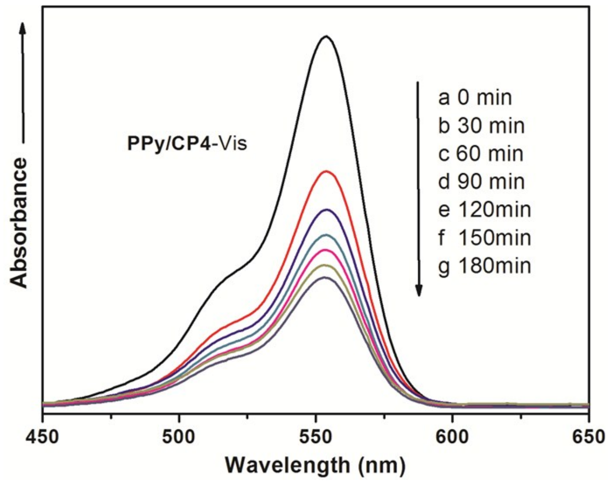
Fig. S16 The degradation ratio of RhB for **CP1**–**CP6** under visible light irradiation.



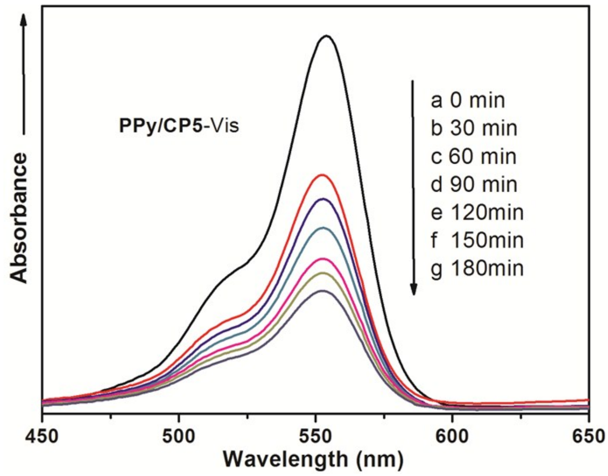
(a)



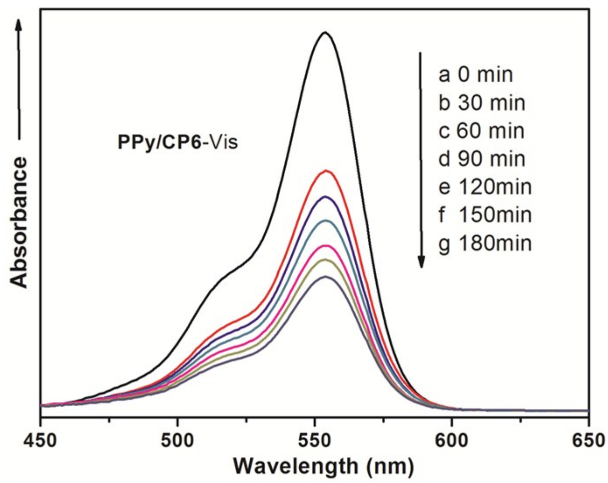
(b)



(c)



(d)



(e)

Fig. S17 Absorption spectra of the RhB solution during the decomposition reaction under visible irradiation in the presence of **PPy/CP2**–**PPy/CP6** composite materials.