Electronic Supplementary Material (ESI)

Lead-carboxylate/polyiodide hybrids constructing from halogen bonding and asymmetric viologen: structures, visible-light-driven photocatalytic properties and enchanced photocurrent responses

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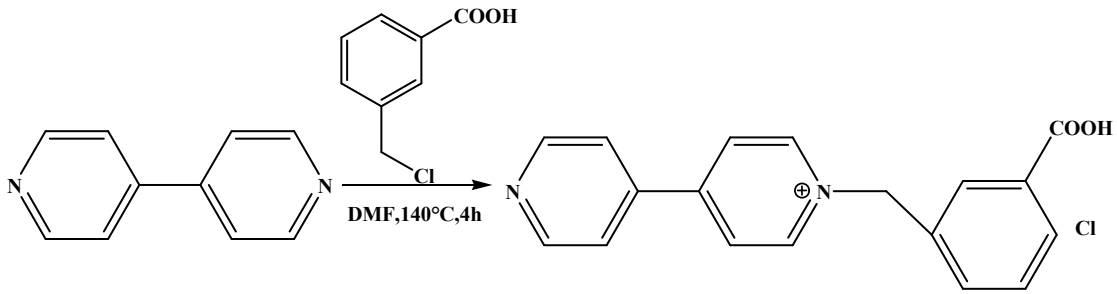
Experimental

Materials and Methods: All chemicals except cbpy·Cl (1-(3-carboxybenzyl)-4,4'-bipyridinium chloride) were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses for C, H and N were performed on a Vario MICRO elemental analyzer. IR spectra were recorded on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellet in the 4000~400cm^{-1} region. UV-Vis spectra were measured on a Perkin-Elmer lambda 900 UV/Vis spectrophotometer equipped with an integrating sphere at 293 K, and a $BaSO_4$ plates were used as reference. The absorption spectra were calculated from reflectance spectra using the Kubelka−Munk function: $\alpha/S = (1 - R)^2/(2R)$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.[1] Fluorescence spectra were carried out on a PW2424 spectrometer. Powder XRD patterns were obtained using a Philips X'Pert-MPD diffractometer with CuKα radiation (λ = 1.54056 Å). The photocurrent experiments were performed on a CHI650 electrochemistry workstation with three-electrode systems.

Synthesis of cbpy·Cl: cbpy·Cl was prepared according to literature method as shown in Scheme 1.[2] 7 mL DMF containing 4.6800 g (3 mol) 4,4'-bipyridine was heated to 140°C, and 3 mL DMF containing 1.7000 g (1 mmol) 3-(chloromethyl)-benzoic acid was dropped stepwise in 15 minutes. The mixture was kept reacting for 4 h. Afterwards, the resultant yellow precipitate was isolated by

filtration and washed with hot DMF solution to obtain product. Then the product was washed with ethyl acetate four times (25 mL) to removed residual 4,4'-bipyridine and dried at 60°C for 1 h (1.96 g , yield: 60%).



Scheme 1 Synthesis of cbpy·Cl

Synthesis of Hybrids

[(Pb(cbpy)I_3·I_3]$_n$ (1): cbpy·Cl (0.3270 g, 0.1 mmol), PbI_2 (0.3095 g, 0.67 mmol) and I_2 (0.1700g, 0.67 mmol) were dissolved in 15 mL H_2O. The mixture was stirred for 90 minutes and then removed into a 25 mL Teflon-lined autoclave. The autoclave was heated to 140 °C in 200 minutes and held at this temperature for 72 h. Then the autoclave was cooled to room temperature at a rate of 3°C/h. Black block single crystals were obtained and washed with ether (0.4440 g, yield 25.2 % based on Pb). Anal. Calcd. for $C_{18}H_{14}N_2O_2I_6Pb$ (1258.91): C, 17.17; H, 1.12; N, 2.22%. Found: C, 17.25; H, 1.29; N, 2.53%. IR (KBr, cm^{-1}): 3100(w), 3041(w), 1638(w), 1600(m), 1537(m), 1353(s), 800(s), 741(s), 460(m).

{[Pb(cbpy)$_2$]$_2$$I_2$·($I_3$)$_4$}$_n$ (2): The synthesis process of **2** is similar to that of **1** except that an addition solubilizer ethylhexadecyldimethylammonium bromide (0.0378 g, 0.1 mmol) was added. Red block crystals were collected by filtration and washed with ether (0.3087 g, yield: 27.2% based on Pb). Anal. Calcd. for $C_{36}H_{30}N_4O_5I_7Pb$ (1694.14): C, 25.52; H, 1.78; N, 3.31%. Found: C, 25.34; H, 1.59; N, 3.42%. IR (KBr, cm^{-1}): 3113(w), 3030(w), 1633(w), 1603(m), 1533(m), 1359(s), 800(s), 735(s), 460(m).

Single Crystal X-ray Diffraction Analyses

The intensity data of **1-2** were collected on a Bruker APEX II diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073Å) at room temperature, during which the *Lp* factor corrections and multi-scan absorption corrections were applied. The structures were solved by direct method and refined on F^2 with full-matrix least squares techniques using the SHELXTL-97 program.[3] For all non-hydrogen atoms, anisotropical refinements were carried out. Hydrogen

atoms of C–H were generated geometrically. Crystal data and refinement conditions are presented in below. Selected bond lengths and angles are listed in Table S1-S2, hydrogen bond details are given in Table S3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-1401578 (**1**), 1503953 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

***Crystal data for* 1**: $C_{18}H_{14}N_2O_2I_6Pb$, M_r=1258.91, black block crystal, Monoclinic, space group $P_{21/n}$, a=12.749(3), b=26.186(5), c=8.2336(16)Å, β=106.89°, V= 2630.2(10)Å^3, Z=4, density (calculated): 3.179 mg·cm^{-3}, μ=13.474mm^{-1}, F(000)= 2208, T=293(2) K, S= 1.092, final R indices: R_1=0.0358, wR_2= 0.0636 for 24525 reflections [I >2σ(I)]; R_1=0.0481, wR_2= 0.0672 for 5978 independent reflections (R(int) = 0.0515, all data,3.02≤θ ≤27.48°) and 262 parameters.

***Crystal data for* 2**: $C_{36}H_{30}N_4O_5I_7Pb$, M_r= 1694.14, red block crystal, Triclinic, Space group P-1, a=8.3858(17), b=15.738(3), c=18.332(4)Å, α=112.14(3), β=988.33(3), γ=96.94(3)°, V= 2176.4(10)Å^3, Z=2, density (calculated): 2.585 mg·cm^{-3}, μ= 8.885mm^{-1}, F(000)= 1534, T=293(2) K, S=0.993, final R indices: R_1=0.0581, wR_2=0.1187 for 21280 reflections [I >2σ(I)]; R_1=0.0929, wR_2= 0.1351 for 9720 independent reflections (R(int) = 0.0883, all data, 3.01≤θ ≤27.47°) and 487 parameters.

Photocatalytic testing

Photocatalytic degeneration measurements were also conducted according to classic method. 50 mg of catalyst powders were suspended in 80 mL RhB solution (10 ppm). Before irradiation, the suspension was magnetically stirred in the dark for 2 h to acheive adsorption-desorption equilibrium of the organic contaminants on the catalyst surface. The visible light source was a 300-W Xe arc lamp equipped with a λ≥420 nm cutoff filter and an IR filter. Three milliliters of sample solution were taken at given time intervals (3 0min) and separated through centrifugation. The residual concentration of pollutants in solution was analyzed by recording variations of the organics at the absorption band maximum in the UV–Vis spectra using a Lambda-800 UV-Vis spectrophotometer. The percentage of degradation is reported as C/C_0. C is the absorption of RhB at each irradiated time interval of the main peak of the absorption spectrum at 553nm. And C_0 is the absorption of the starting concentration when adsorption-desorption equilibrium is achieved.

Electrode Preparation and Photocurrent Measurement

Typical solution coating method is adopted to prepare the photocurrent measurement electrodes of compounds **1** and **2**. The new prepared powder (5 mg) was dissolved in 0.3 mL of DMF, and the suspension was dispersed evenly to obtain a slurry. The slurry was spread onto precleaned ITO glass (1 × 1 cm, 14 Ω per square cm), whose side part was previously protected using Scotch tape. The working electrode was dried overnight under ambient conditions. A copper wire was connected to the side part of the working electrode using conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. A 150 W high-pressure xenon lamp, located 15 cm away from the surface of the ITO electrode, was employed as a full-wavelength light source. The photocurrent experiments were performed on a CHI660 electrochemistry workstation in a three-electrode system, with the sample-coated ITO glass as the working electrode mounted on the window with an area of 0.25 cm^2, a Pt wire as auxiliary electrode, and a Ag/AgCl electrode as reference electrode. The supporting electrolyte solution was a 0.2 $mol \cdot L^{-1}$ sodium sulfate aqueous solution. The applied potential was 0.5 V for all measurements. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated at intervals of 20 s.

Computational Details The cif files of **1** and **2** were used to construct the calculated models. The electronic structure calculations were carried out using density functional theory (DFT) with the three non-local gradient-corrected exchange–correlation functions (GGA-PBE) and using CASTEP code,[4] which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 550 eV. The parameters used in the calculations and convergence criteria were according to the default values of the CASTEP program in Materials Studio 8.0.

Table S1 selected bond distances (in Å) and angles (in °) for 1 and 2

1			
Pb(1)-O(1)	2.447(5)	Pb(1)-O(2)#1	2.689(4)
Pb(1)-O(2)	2.821(33)	Pb(1)-N(2)	2.586(5)
Pb(1)-I(1)	3.2093(7)	Pb(1)-I(1) #1	3.452(4)
Pb(1)-I(4)	3.524(7)	Pb(1)-I(4) #1	3.514(2)
I(1)-I(2)	3.1291(8)	I(2)-I(3)	2.7631(9)
I(4)-I(5)	3.0427(9)	I(5)-I(6)	2.8510(9)
O(1)-Pb(1)-N(2)	87.73(18)	O(1)-Pb(1)-O(2)#1	50.42(14)

N(2)-Pb(1)-O(2)#1	81.81(16)	O(1)-Pb(1)-I(1)	83.51(11)
N(2)-Pb(1)-I(1)	77.60(13)	O(2)#1-Pb(1)-I(1)	130.01(10)
I(3)-I(2)-I(1)	177.58(3)	I(6)-I(5)-I(4)	175.73(3)
Symmetry code: #1 x,-y+3/2,z-1/2			
2			
Pb(1)-O(1)	2.448(6)	Pb(1)-O(1)#2	2.679(6)
Pb(1)-O(3)	2.726(7)	Pb(1)-O(2)	2.734(7)
Pb(1)-O(4)	2.444(5)	Pb(1)-N(4)#1	2.598(7)
Pb(1)-I(4)#1	3.672(44)	I(7)-I(7)#3	2.748(2)
I(1)-I(2)	2.8902(15)	I(2)-I(3)	2.9612(15)
I(4)-I(5)	2.9972(13)	I(5)-I(6)	2.8363(13)
I(7)-I(7) #3	2.7463(3)		
O(4)-Pb(1)-O(1)	76.4(2)	O(4)-Pb(1)-N(4)#1	81.3(2)
O(1)-Pb(1)-N(4)#1	85.9(2)	O(4)-Pb(1)-O(1)#2	77.65(19)
O(1)-Pb(1)-O(1)#2	77.2(2)	N(4)#1-Pb(1)-O(1)#2	155.6(2)
O(4)-Pb(1)-O(3)	49.9(2)	O(1)-Pb(1)-O(3)	126.21(18)
N(4)#1-Pb(1)-O(3)	89.2(2)	O(1)#2-Pb(1)-O(3)	86.8(2)
O(4)-Pb(1)-O(2)	123.10(19)	O(1)-Pb(1)-O(2)	50.34(18)
N(4)#1-Pb(1)-O(2)	76.9(2)	O(1)#2-Pb(1)-O(2)	104.44(19)
O(3)-Pb(1)-O(2)	165.7(2)	I(1)-I(2)-I(3)	178.59(3)
I(6)-I(5)-I(4)	177.71(4)		
Symmetry code: #1 -x+3,-y+1,-z+1; #2 -x+2,-y,-z+1; #3 -x+4,-y+1,-z			

Table S2 hydrogen bond details in 1 and 2

Compounds	D-H⋯A	d(D-H)	d(H⋯A)	∠DHA	d(D⋯A)	Symmetry Code
1	C(13)-H(13)⋯O(1)	0.93	2.34	150	3.185(9)	x,y,1+z
2	O(5)-H(5B)⋯O(5)	0.85	2.52	121	3.052(12)	-1-x,-y,1-z
	C(8)-H(8A)⋯O(5)	0.97	2.47	166	3.417(13)	1+x,y,z
	C(31)-H(31)⋯O(3)	0.93	2.27	143	3..068(16)	1+x,y,z
	C(9)-H(9)⋯I(4)	0.93	3.03	144	3.819(11)	1+x,y,z

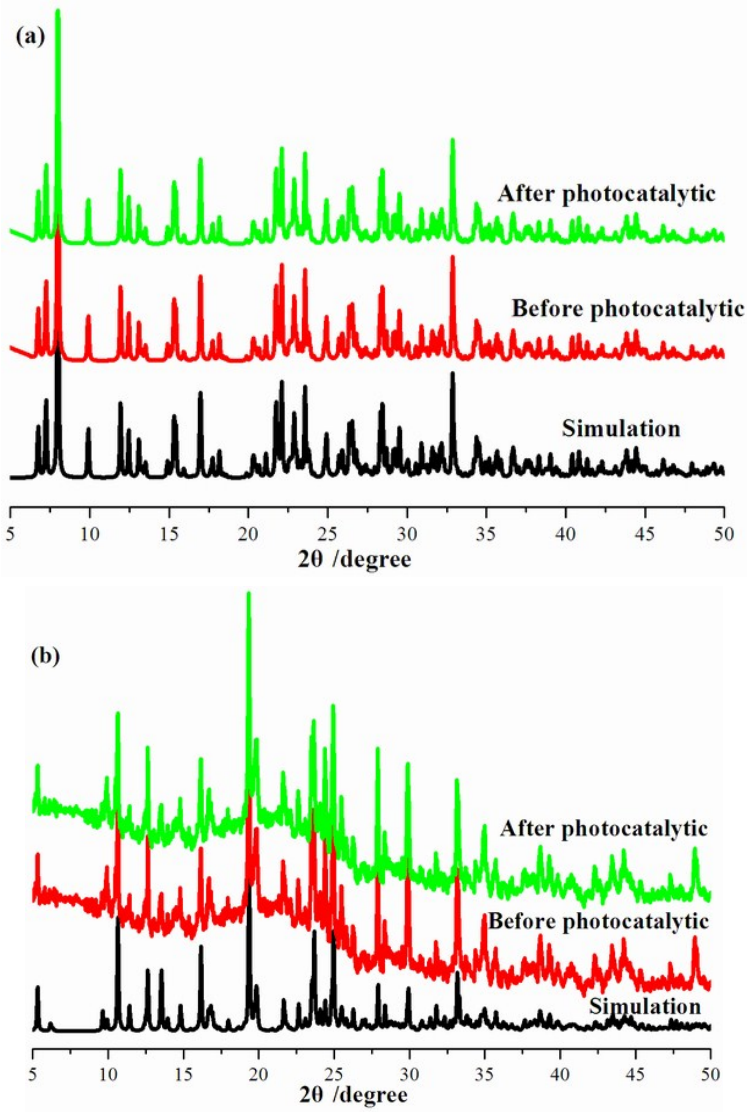
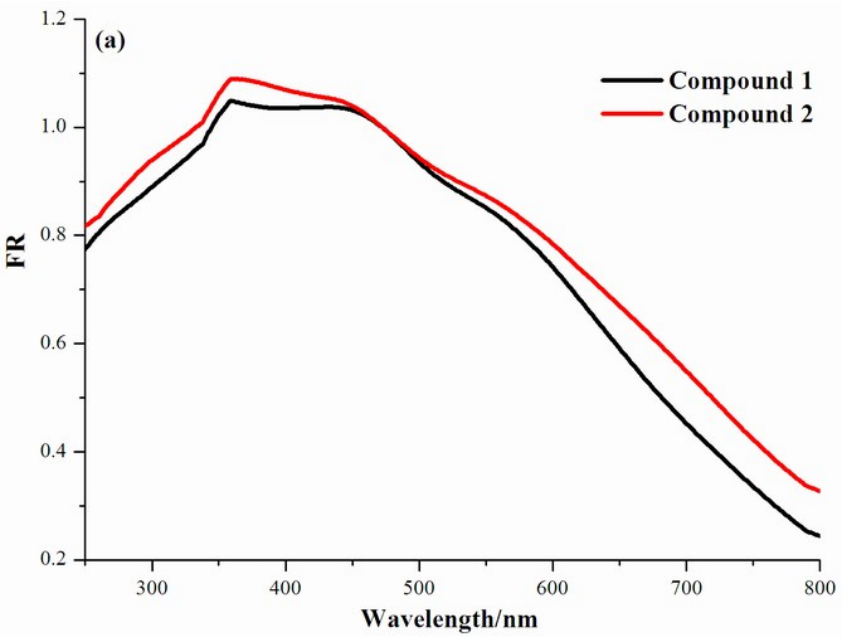


Fig. S1 Powder X-ray diffraction (PXRD) patterns under different conditions for compounds 1 (a) and 2 (b)



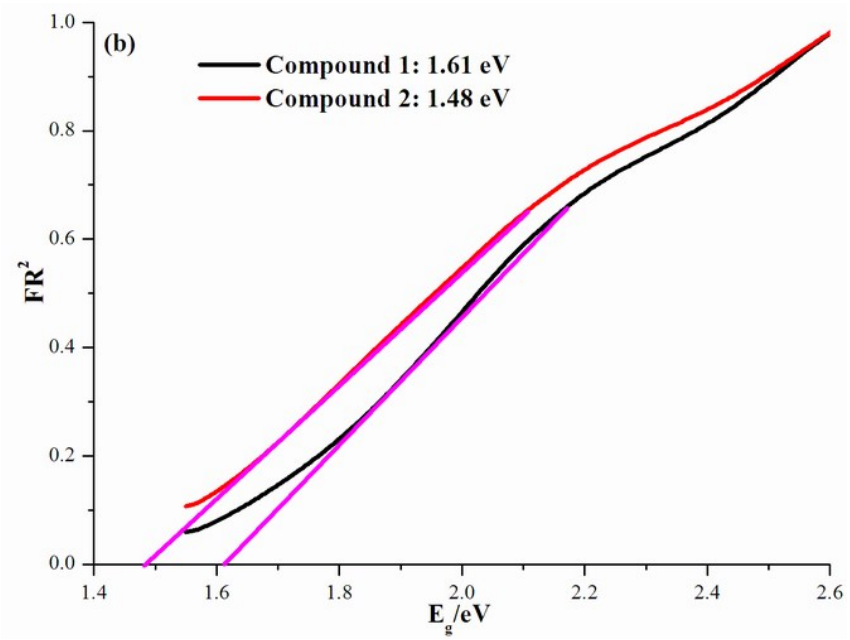
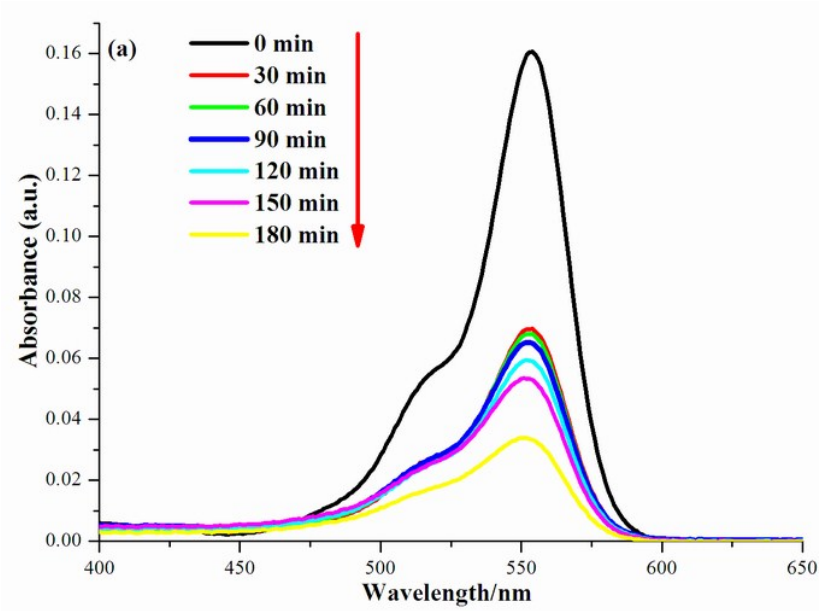


Fig. S2 Solid state electronic spectra (a) and optical diffuse-reflection spectra of 1 and 2



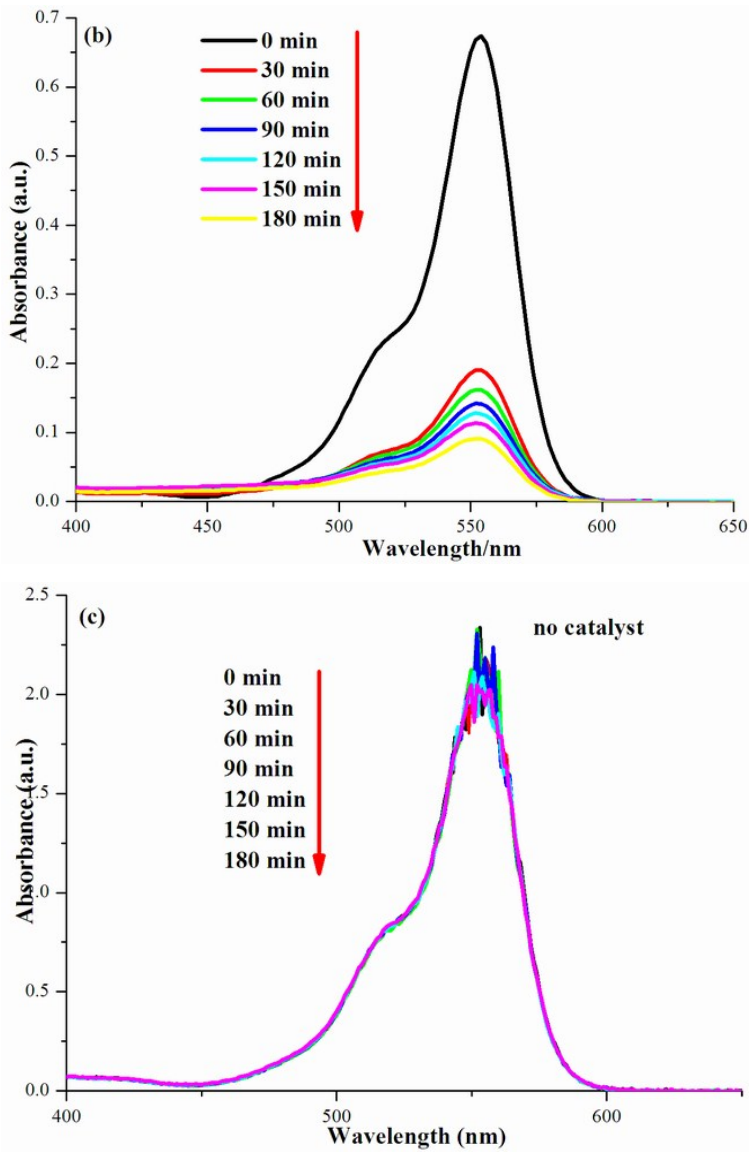


Fig. S3 Time-dependent UV−Vis spectra of RhB with the presence of 1 (a), 2 (b) and without any catalyst (c) under the irradiation of xenon-lamp

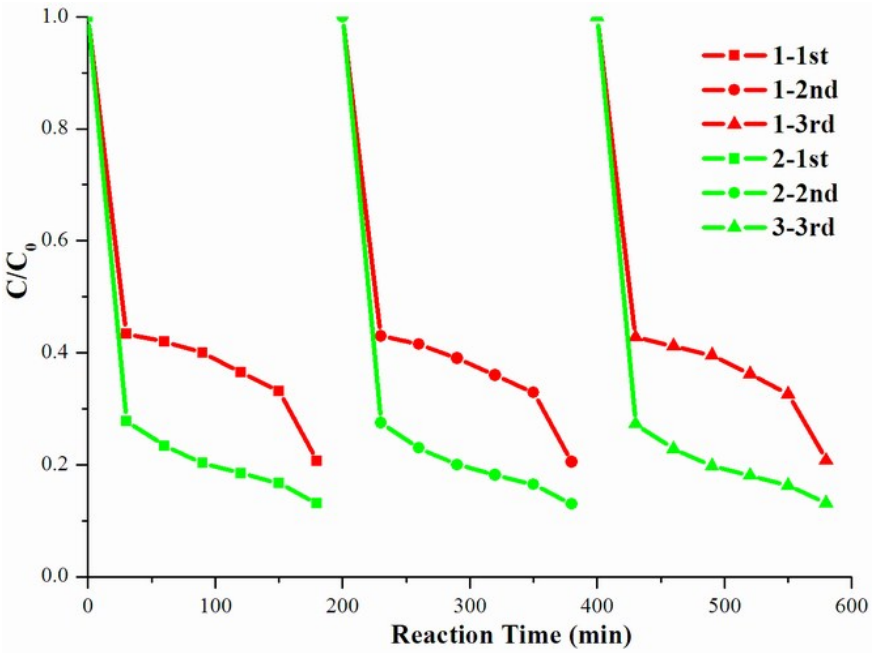
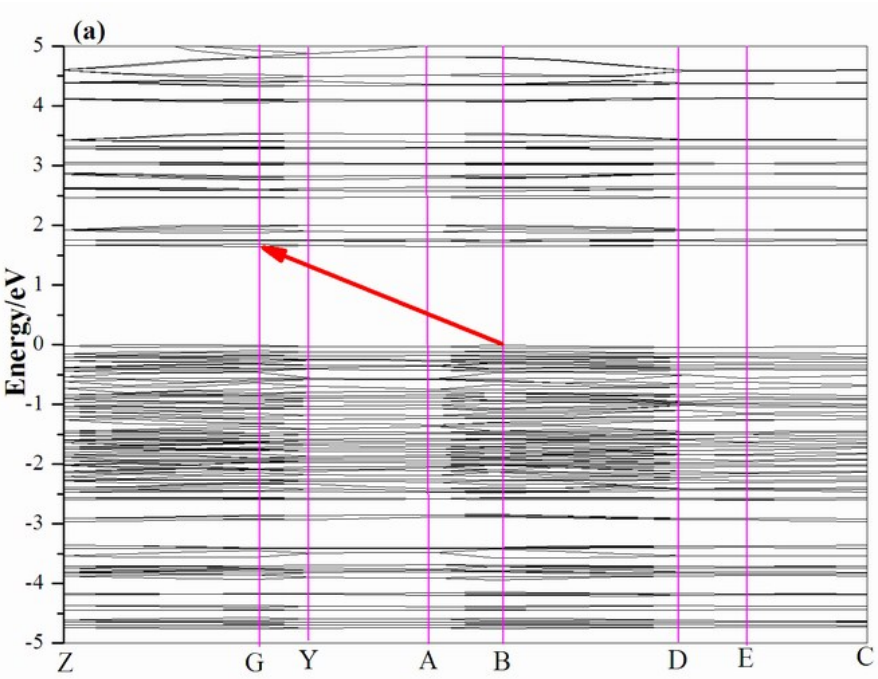


Fig. S4 Rcycling tests of 1 and 2 for RhB photodegradation under light irradiation



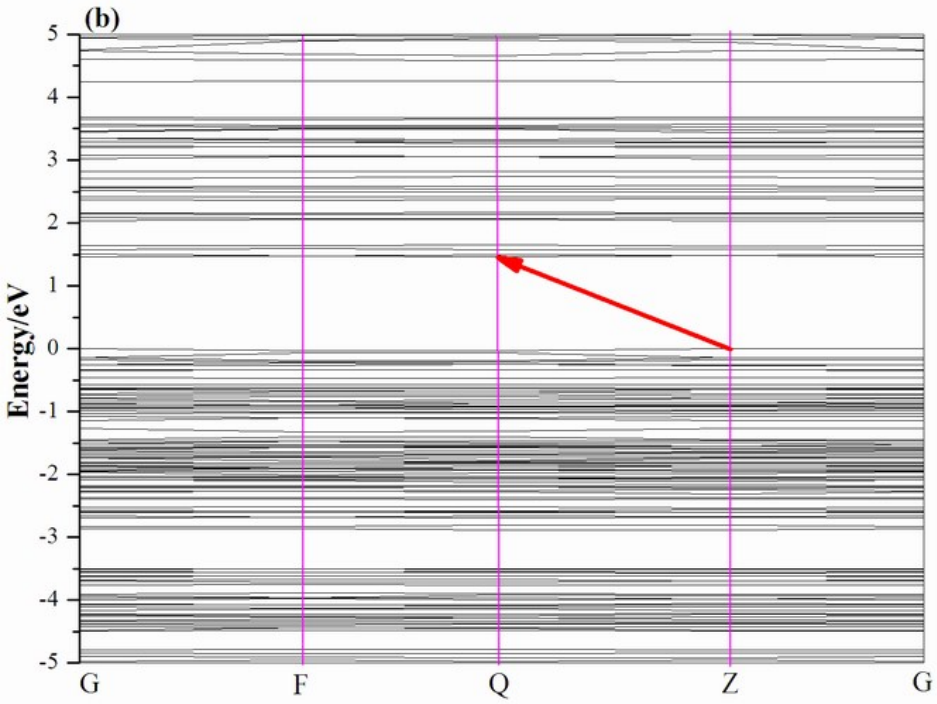


Fig. S5 Band structures of 1 (a), 2 (b), the Fermi level is set at 0 eV

References

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