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A heterometallic D-A hybrid heterostructural framework with enhanced visible-light photocatalytic properties

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Materials and Methods: All chemicals and reagents were used as received unless otherwise stated. IR spectra were recorded in the range 4000-400 cm^{-1} on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku Ultima IV diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range of 5−50° at a rate of 10°/min. Thermal stability studies were performed on a Mettler-Toledo TGA 2 thermoanalyzer with a heating rate of 10°C/min under an N_2 atmosphere in the range of 30-800°C. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere. The organic ligand 1-(4-carboxybenzyl)-4,4'-bipyridinium chloride (Hcpb·Cl) was synthesized following the reported process.[S1]

Synthesis of neutral cpb ligand

Due to the Cl$^-$ anion in Hcpb·Cl ligand that can influence the synthesis of complex, we firstly obtained crystals of its neutral salt to remove the Cl$^-$ anion through added the NaOH solution. Hcpb·Cl (2.76 g, 10 mmol) was dissolved in water/DMSO (100 mL, 9:1) and the pH value was adjusted to 7 with 0.20 mol L^{-1} NaOH solution. Then the solution stood in a dark room for several days to give crystals of neutral cpb ligand.

Synthesis of compound 1. An acetonitrile solution (5mL) of CuI (0.20 mmol, 38.1 mg) was carefully layered on a solution (5 mL) containing $Ce(NO_3)_2·6H_2O$ (0.10 mmol, 43.1 mg) and cpb (0.05mmol, 13.8 mg) with $MeCN/H_2O$ (1 mL/1 mL) placed between the two layers. Dark platelike crystals of **1** formed in several days. The product was collected by filtration and dried in the vacuum oven. Yield: 23% based on cpb ligand. Combined with TGA and volume/count electrons analysis, the result we calculated is that there are approximately four acetonitrile, two water molecules in the formula. Anal. Calcd for $C_{68}H_{56}CeCu_6I_9N_{12}O_{14}$: C 28.72, H 1.97, N 3.94%. Found: C 28.45, H 1.75, N 4.06%. IR data (KBr, cm^{-1}): 3407(br), 3108(w), 3046(w), 1637(s), 1597(s), 1530(s), 1456(s), 1388(s), 1288(m), 1207(s), 1003 (m), 851(m), 808(s), 780(s), 652(s).

Photocatalytic Activity Measurements

The photocatalytic activity of as-prepared compound 1 was evaluated by the degradation of RhB as model dye pollutant. In a typical process, the visible light source was a 300 W Xe lamp equipped with a $\lambda \geq 420$ nm cut off filter and an IR filter. In the photo-degradation experiments of RhB, 50 mg of powder compound 1 was added to 50 mL of a 1×10^{-5} $mol·L^{-1}$ solution of RhB. The distance between the light source and the reaction cell containing the reaction mixture was fixed at 15.0 cm. Before irradiation, the suspensions were magnetically stirred in the dark for 60 min to achieve adsorption-desorption equilibrium of the organic contaminants on the catalyst surfaces. During the photodegradation reaction, stirring was continued to keep the mixture in suspension. Every 5 min, 3 mL of the suspensions were continually taken from the reaction cell and the catalyst was separated from the suspension by centrifugation. The residual concentrations of RhB in solution were analyzed by recording variations of the organics at the absorption band maximum in the UV–Vis spectra using a UV-Vis spectrophotometer. For collecting an adequate sample in the recycling experiment, two or even more of the photocatalytic processes were carried out under the same conditions, and then the samples were separated through centrifugation. All of the precipitates from the different processes were collected, combined, and dried in an oven at 60 °C for 12 h. After that, 50 mg of dried sample was used to perform the second photocatalytic experiment according to the same method as that of the first study. The third recycling experiment was also carried out with the same method. The percentage of degradation is reported as C/C_0. Here, C is the absorption of RhB at each irradiated time interval of the main peak of the absorption spectrum at 554 nm. And C_0 is the absorption of the starting concentration when adsorption-desorption equilibrium is achieved.

Calculation details

The crystallographic data of complex **1** were used to calculate the electronic band structure by using density functional theory (DFT) with the CASTEP code based on gradient corrected exchange-correlation functionals (GGA-PBE), which uses the 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 cut-off energy E_c of 350 eV. Pseudoatomic calculations were performed for Ce-$4f^1 5d^1 6s^2$, Cu-$3d^{10} 4s^1$, I-$4d^{10} 5s^2 5p^5$, O-$2s^2 2p^4$, C-$2s^2 2p^2$, N-$2s^2 2p^3$ and H-$1s^1$. The other calculating parameters and convergence criteria were set using the default values of the CASTEP code.

Crystallographic data collection and refinement

Suitable single crystal of compound **1** was mounted on glass fiber for the X-ray measurement. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD areadetector system. The measurement was made by using graphic monochromatic Mo Kα radiation (λ= 0.71073 Å) at 153 K under a cold nitrogen stream. The frame data were integrated and absorption correction using a Rigaku *CrystalClear* program package. All calculations were performed with the *SHELXTL-97* program package [S2], and structures were solved by direct methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON to remove diffuse electron density associated with these badly disordered solvent molecules.[S3] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication number CCDC 1888166 for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinements for **1**.

Complex	**1**
Empirical Formula	$C_{68}H_{48}CeCu_6I_9N_8O_{12}$
Formula weight	2832.60
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	27.453(6)
b (Å)	16.474(3)
c (Å)	20.208(4)
α (deg)	90
β (deg)	104.43(3)
γ (deg)	90
V (Å^3)	8851(3)
Z	4
T (K)	153(2)

ρ_{calc}(g/cm^3)	2.126
μ (Mo Kα) (mm^{-1})	5.112
F(000)	5268
Collected reflections	78675
Unique reflections	20060
No. of observations	10646
GOF	1.056
R_1^a,wR_2^b (I>2σ(I))	0.0703, 0.1639
R_1^a,wR_2^b(all data)	0.1421, 0.1951

Table S2. Photocatalytic Degradation of Aqueous RhB by various materials under Visible or UV Light.

Materilas	**Irrigation**	**Time (min)**	**Degradation efficiency (%)**	**Ref.**

NTU-9	Vis	80	100	S4
$[Cu^{II}(salimcy)](Cu^{I}I)_2\cdot DMF$	Vis	50	95	S5
$Cu_2(hfipbb)_2(4,4'\text{-}bpy)(H_2O)$	Vis	360	70	S6
$(Me_4N)_6[Cu_{12}(OH)6(pz)_6(btc)_6]\cdot 21H_2O$	UV	320	51	S7
$Cu_4(dcpcpb)_2(\mu_3\text{-}OH)_2(CH_3OH)_2(H_2O)$	UV	90	19	S8
$Cu_6(\mu_3\text{-}O)(\ \mu_3\text{-}OH)(pz)_6(btc)$	UV	105	98	S9
$[Co_2(tkcomm)(tkiymm)]\cdot 4.25H_2O$	UV	600	66	S10
Cu(ptz)(I)	Vis	35	70	S11
Cu(dm-bim)	Vis	34	100	S12
MIL-53(Fe)	Vis	50	62.1	S13
$[Co_2(1,4\text{-}bdc)(ncp)_2]\cdot 4H_2O$	Vis	300	67.52	S14
$Fe_2(bhbdh)$	Vis	15	90	S15
$(UO_2)_8(1,4\text{-}ndc)_{12}(4,4'\text{-}bpyH_2)_3(4,4'\text{-}bpyH)_3$	Vis	600	100	S16
$Ag(2,2'\text{-}bpy)(UO_2)(1,4\text{-}bdc)_{1.5}$	Vis	240	90	S17
$[(UO2)_2(bta)(\ \mu_3\text{-}OH_2)]\cdot 2(HN(CH_3)_2)\cdot H_2O$	Vis	130	50	S18
$UO_2(1,4\text{-}ndc)((CH_3)_2SO))_2$	Vis	180	100	S19
$[La(H_2O)_4(2,6\text{-}pdc)]_4\ (PMo_{12}O_{40})F$	UV	240	85	S20
$[Cu^{I}bbi]_4(SiW_{12}O_{40})\cdot H_2O$	UV	420	100	S21
$[CoCl_{0.5}(H_2O)_{0.5}(Hdppzc)_2](PW_{12}O_{40})_{0.5}\cdot 3.5H_2O$	Vis	80	90	S22
$[(H_2bix)_2(NaHP_2Mo_5O_{23})]\cdot 2H_2O$	UV	150	35	S23
$[Co(bix)_2](VW_{12}O_{40})\cdot(H_2bix)\cdot 2H_2O$	UV	420	91.2	S24
$K_2[Ag_6(5\text{-}pytz)_4](PW_{12}O_{40})$	UV	360	72	S25
ZFC-1	Vis	140	85	S26
Ag_2S–ZnS@AZCE	Vis	120	98	S27
Fe-CN	Vis	150	96	S28
$CeO_2\text{-}TiO_2$	UV-Vis	480	99.89	S29
NNU-15(Ce)	Vis	12	99	S30
$Co_3(BPT)2(bpp)$	Vis	120	90	S31
$\{[Cd_4(BPTC)_2(DMA)_4(H_2O)_2](DMA)\}_n$	UV	600	72	S32
$[Ce(cpb)_4(H_2O)_4][Cu_6I_9]$	**Vis**	**60**	**100**	**This work**

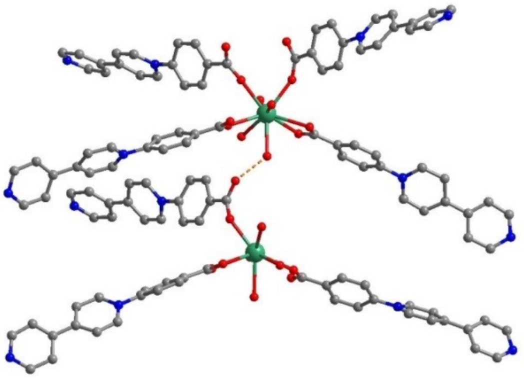

Figure S1. The hydrogen bond interactions between the carboxyl group and water in **1**.

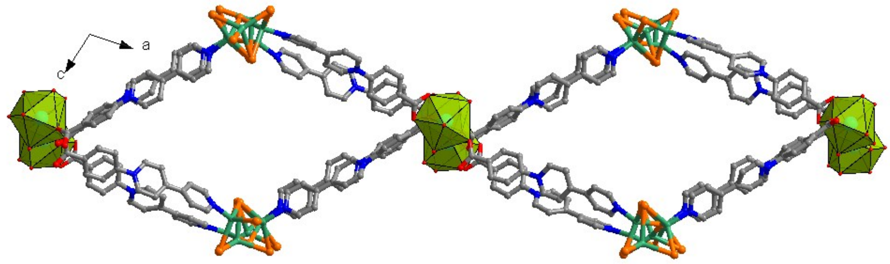

Figure S2. View of the 2D structure in **1** along the *b* axis.

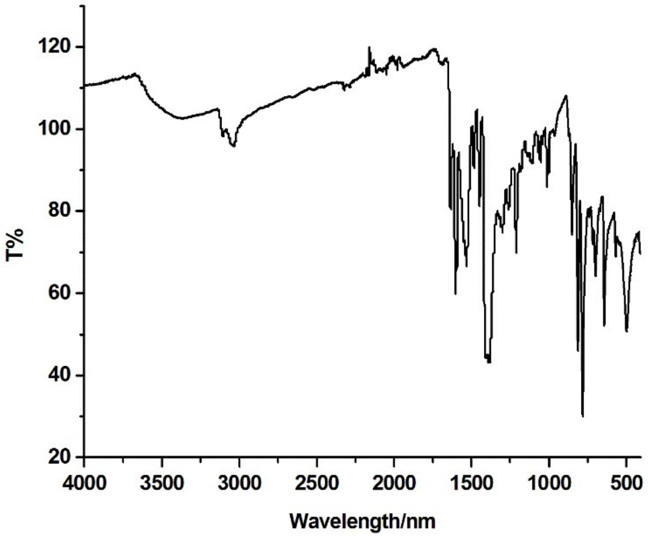

Figure S3. Infrared spectrum of **1**.

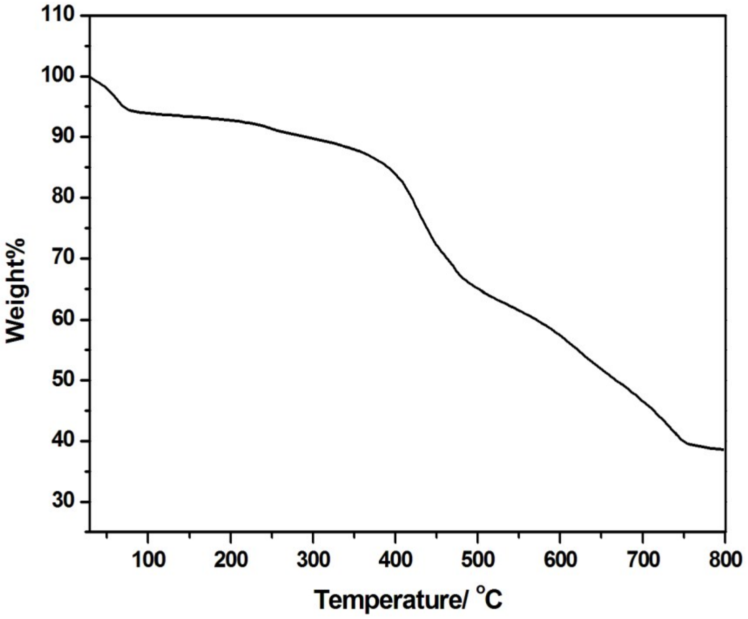

Figure S4. TGA curve of **1** under N_2 atmosphere with a heating rate of 10 °C/min.

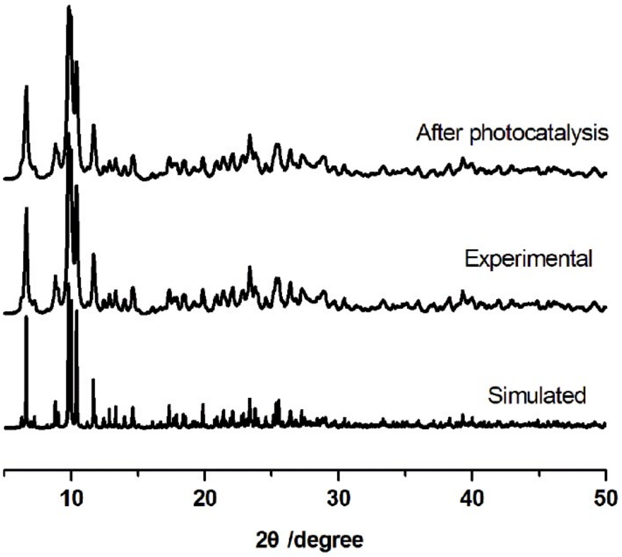

Figure S5. PXRD patterns of **1** before and after the photocatalysis.

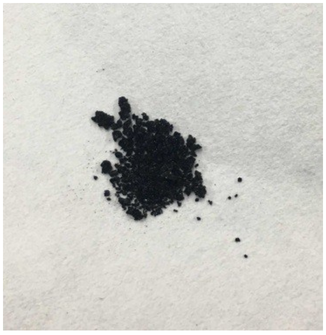

Figure S6. Photograph of compound **1**.

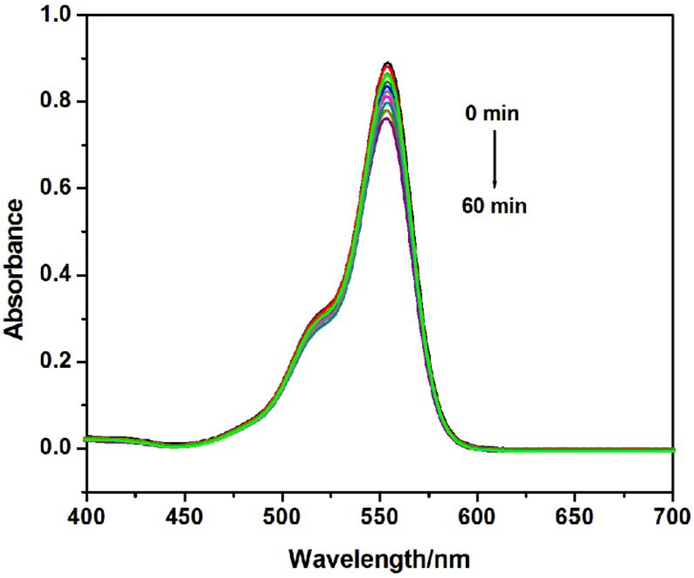

Figure S7. The absorption spectra of the RhB solution presence of $Ce(NO_3)_3$.

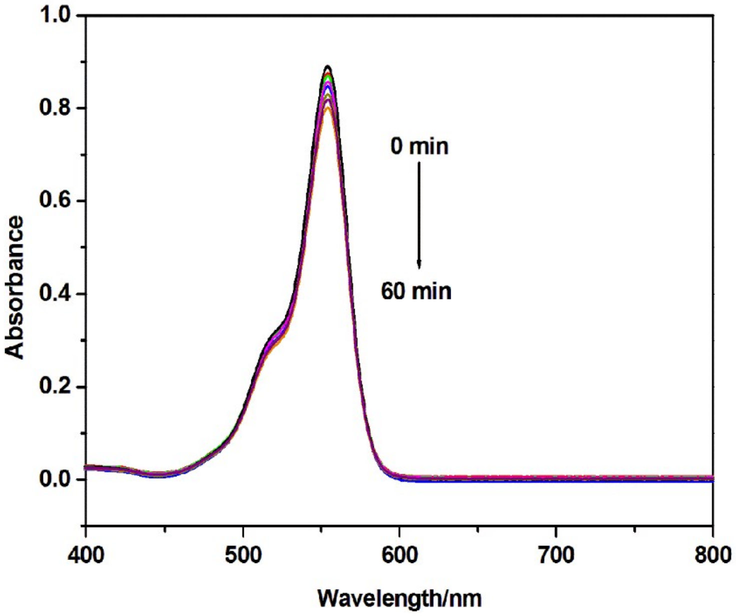

Figure S8. The absorption spectra of the RhB solution without presence of catalyst.

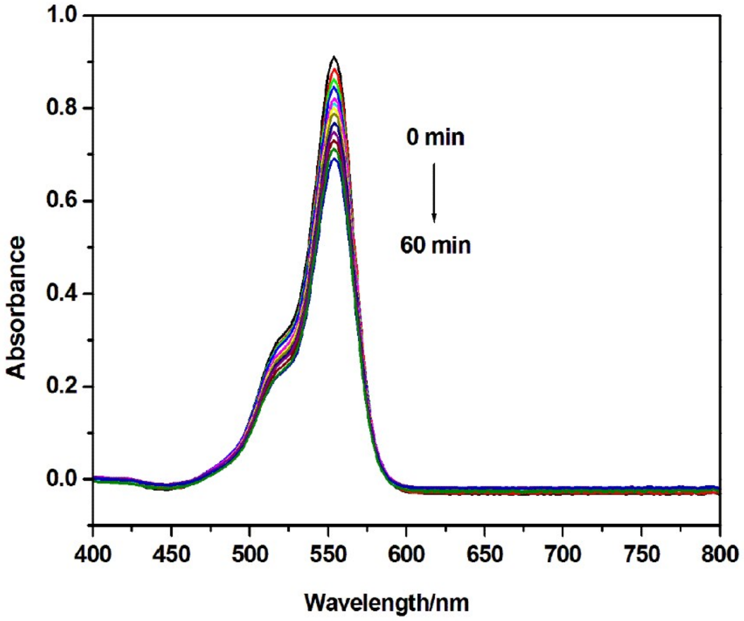

Figure S9. The absorption spectra of the RhB solution presence of CuI.

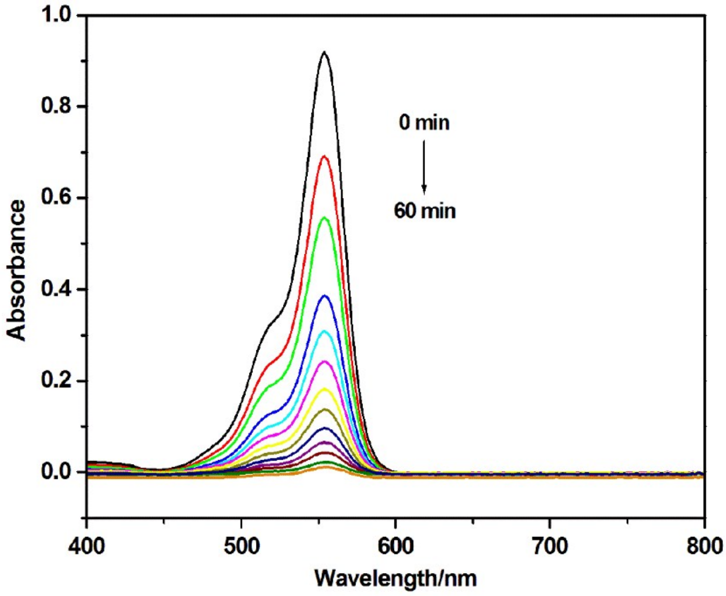

Figure S10. The absorption spectra of the RhB solution in the presence of **1** under exposure to visible light.

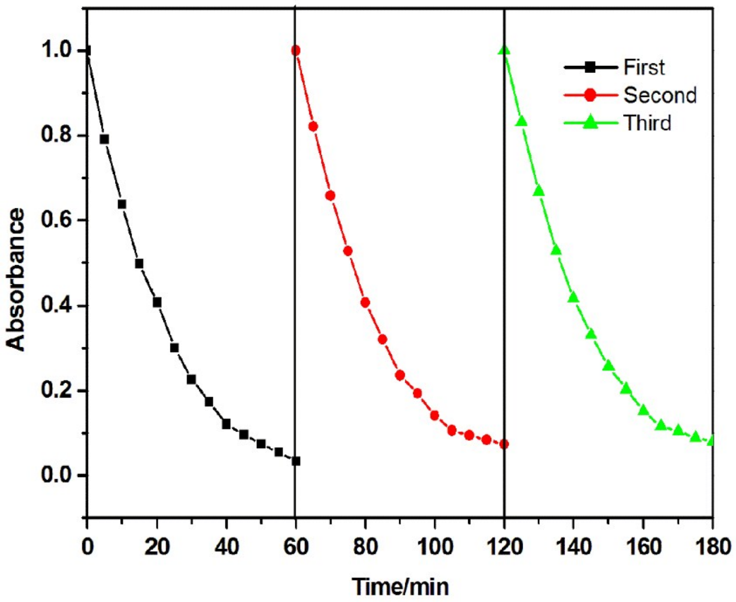

Figure S11. The irradiation-time dependences of the relative concentration C/C_0 of the RhB over **1** during cycling photocatalytic experiments under visible light.

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