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Assembly of donor-acceptor hybrid heterostructures based on iodoplumbates and viologen coordination polymers

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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 MiniFlex-II X-Ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). TGA measurements were performed on a TG-209 system with a heating rate of 10 °C/min under an N_2-atmosphere. 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 *N*,*N*′-bis(carboxyethyl)-4,4'-bipyridinium (BCEbpy) was synthesized following the reported process.[S1]

Synthesis of compound 1. A solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.4 mmol, 99.5 mg in 5 mL of methanol) was carefully layered on a saturated KI solution (5 mL) containing PbI_2 (0.1 mmol, 46.1 mg) and BCEbpy (0.2 mmol, 54.4 mg) with MeOH/H_2O (1 mL/1 mL) placed between the two layers. Dark red platelike crystals of **1** formed in five days. The product was collected by filtration and dried in the vacuum oven. Yield: 18% based on PbI_2. 7679.95 Anal. Calcd for $C_{56}H_{84}I_{30}K_6N_8Ni_2O_{49.2}Pb_9$: C 8.75, H 1.09, N 1.46%. Found: C 8.77, H 1.08, N 1.49%. IR data (KBr, cm-1): 3509(m), 3103(w), 3049(m), 1611(s), 1543(s), 1437(s), 1374(s), 1284(s), 1194(m), 813(s), 719(s), 629(m).

Synthesis of compound 2. A solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (0.4 mmol, 100 mg in 5 mL of methanol) was carefully layered on a saturated KI solution (5 mL) containing PbI_2 (0.1 mmol, 46.1 mg) and BCEbpy (0.2 mmol, 54.4 mg) with MeOH/H_2O (1 mL/1 mL) placed between the two layers. Dark block crystals of **2** formed in one week. The product was collected by filtration and dried in the vacuum oven. Yield: 13% based on PbI_2. Anal. Calcd for $C_{14}H_{12}CoI_8N_2O_8Pb_3$: C 8.27, H 0.59, N 1.38%. Found: C 8.36, H 0.67, N 1.43%. IR data (KBr, cm-1): 3356(s), 3128(w), 2980(w), 2954(w), 1632(m),

1606(s), 1564(s), 1374(s), 1194(m), 1109(m), 1046(m), 840(m), 782(m).

Photocatalytic Activity Measurements

The photocatalytic activities of as-prepared samples **1** and **2** were 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 λ≥420 nm cut off filter and an IR filter. In the photo-degradation experiments of RhB, 50 mg of each sample of the compound was added to 50 mL of a 1×10^{-5} mol·L^{-1} solution of RhB. Before irradiation, the suspensions were magnetically stirred in the dark for 10 min to achieve adsorption-desorption equilibrium of the organic contaminants on the catalyst surfaces. 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 24 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.

Crystallographic data collection and refinement

Suitable single crystal of compounds **1-2** were mounted on glass fiber for the X-ray measurement. Diffraction data were collected on a Rigaku-AFC11 equipped with a Rigaku Saturn CCD area-detector system. The measurement was made by using graphic monochromatic Mo K*α* radiation (λ= 0.71073 Å) at 153 K under a cold nitrogen stream. The frame data were integrated and absorption correction using a Rigaku *CrysAlisPro* program package. All calculations were performed with the *SHELXTL* 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. For compound 1, 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 1545737 and 1545738 for **1** and **2**, respectively. 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** and **2**.

Complex	**1**	**2**
Empirical Formula	$C_{56}H_{84}I_{30}K_6N_8Ni_2O_{49.2}Pb_9$	$C_{14}H_{12}CoI_8N_2O_8Pb_3$
Formula weight	7679.95	2031.96
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*m*	$P\bar{1}$
a (Å)	23.839(5)	4.8932(10)
b (Å)	23.108(5)	11.453(2)
c (Å)	15.993(3)	16.896(3)
α (deg)	90	81.69(3)
β (deg)	99.99(3)	89.80(3)
γ (deg)	90	83.87(3)
V (Å^3)	8676(3)	931.5(3)
Z	2	1
T (K)	153(2)	153(2)
ρ_{calc}(g/cm^3)	2.802	3.622
μ (Mo Kα) (mm^{-1})	14.437	18.122
F(000)	6340	871
Collected reflections	33116	12807
Unique reflections	7867(0.0540)	3252(0.0558)
No. of observations	5884	2536
GOF	1.024	1.000
R_1[a],wR_2[b] (I>2σ(I))	0.0429, 0.1033	0.0704, 0.1847
R_1[a],wR_2[b](all data)	0.0668, 0.1125	0.0914, 0.2000

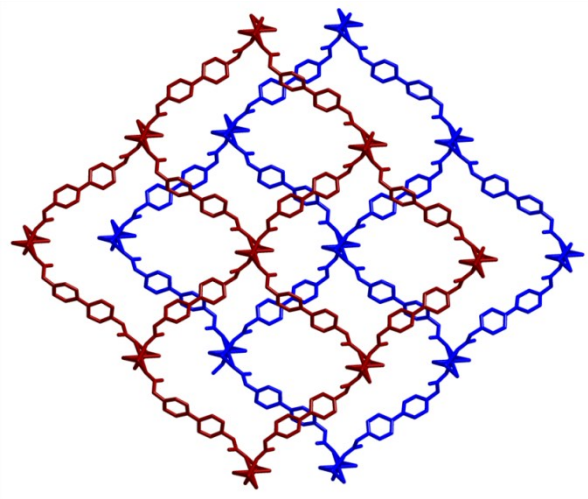

Figure S1. The two-dimensional coordination network in 1.

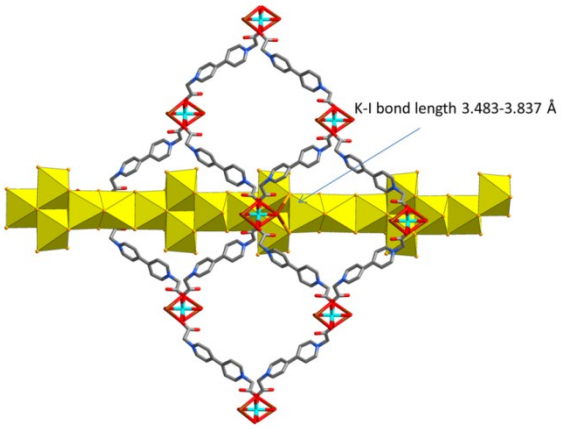

Figure S2. Iodoplumbate nanowire and 2D framework motif connected by K-I bond in **1**.

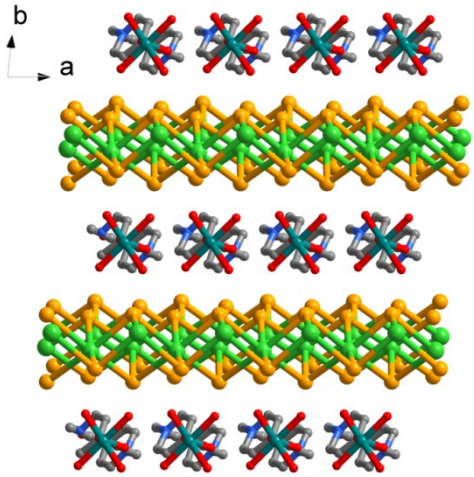

Figure S3. Packing diagram of **2** viewed along the *c* direction.

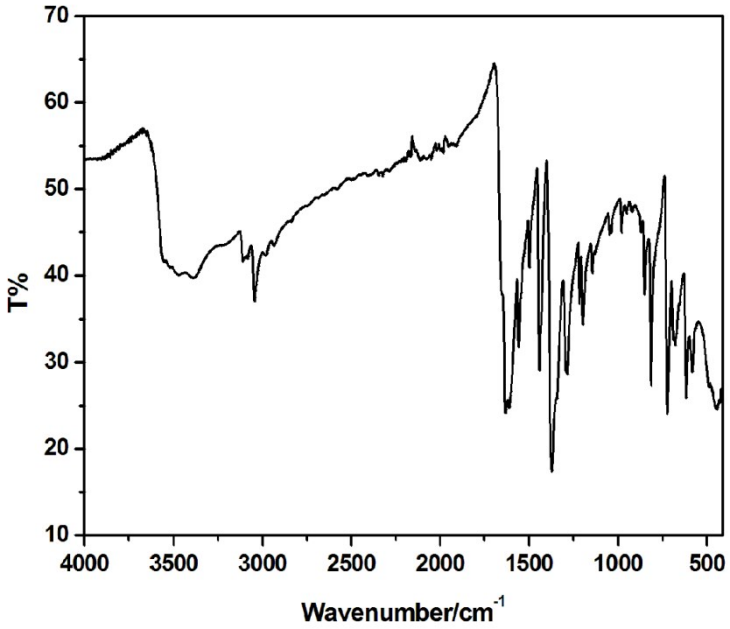

Figure S4. Infrared spectrum of **1**.

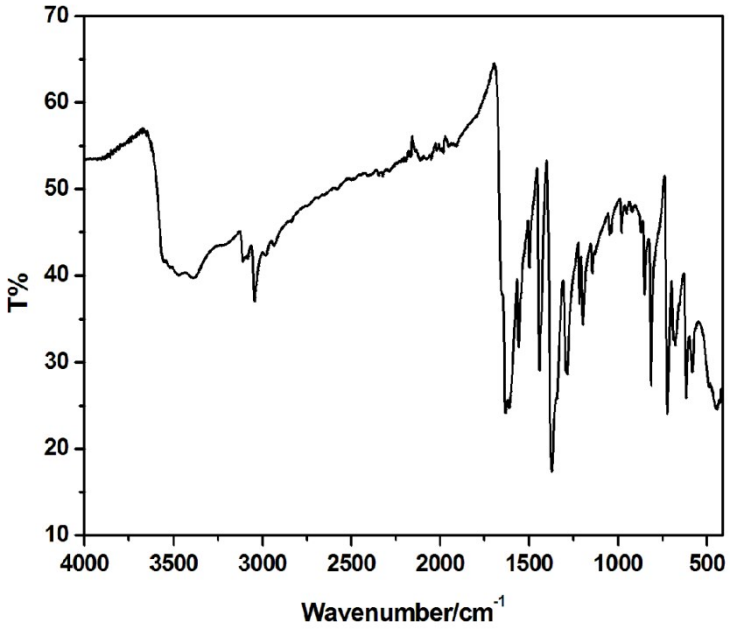

Figure S5. Infrared spectrum of **2**.

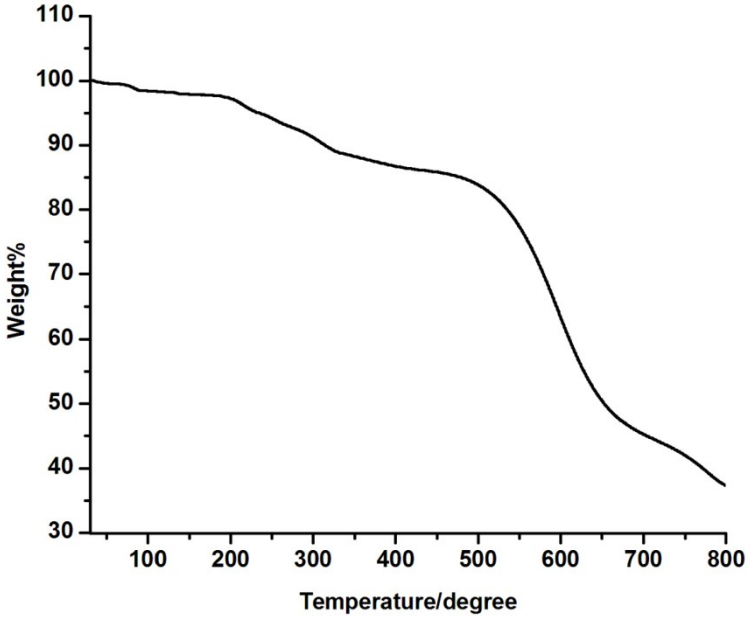

Figure S6. TGA curve of **1** under N_2 atmosphere with a heating rate of 10 °C/min.

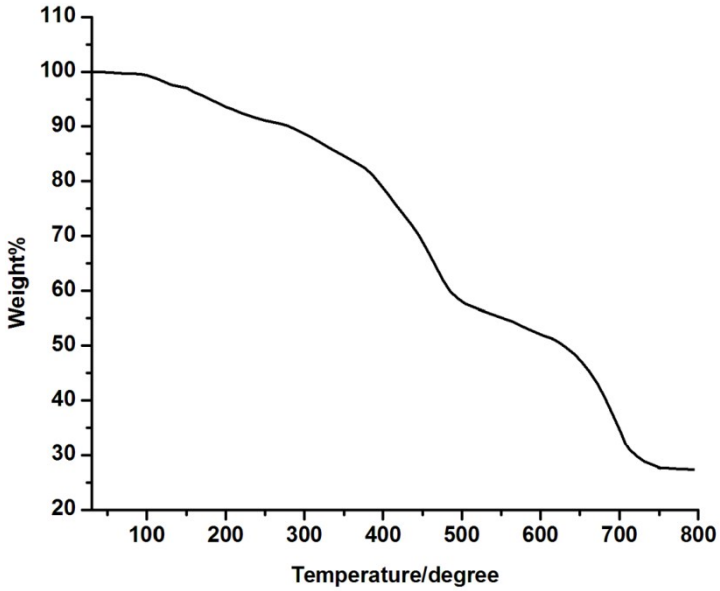

Figure S7. TGA curve of **2** under N_2 atmosphere with a heating rate of 10 °C/min.

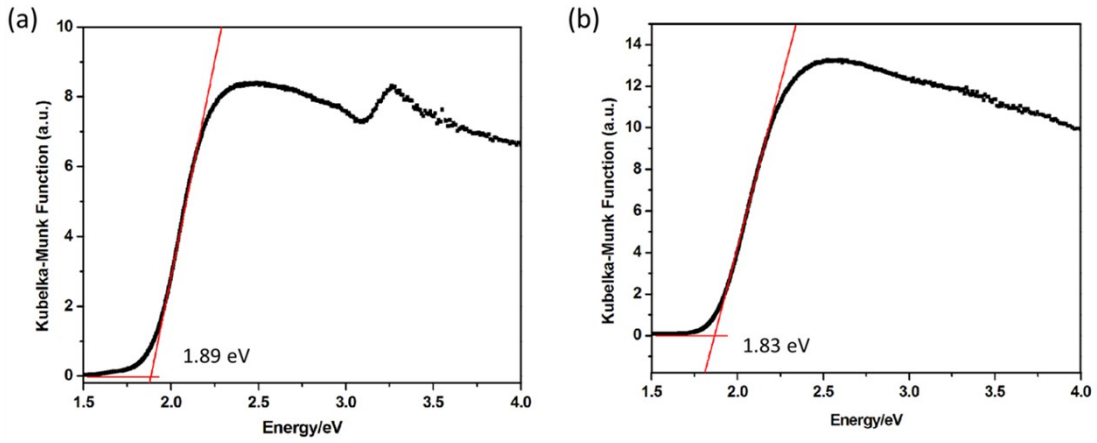

Figure S8. Room-temperature optical absorption spectra for solid samples of **1** and **2**.

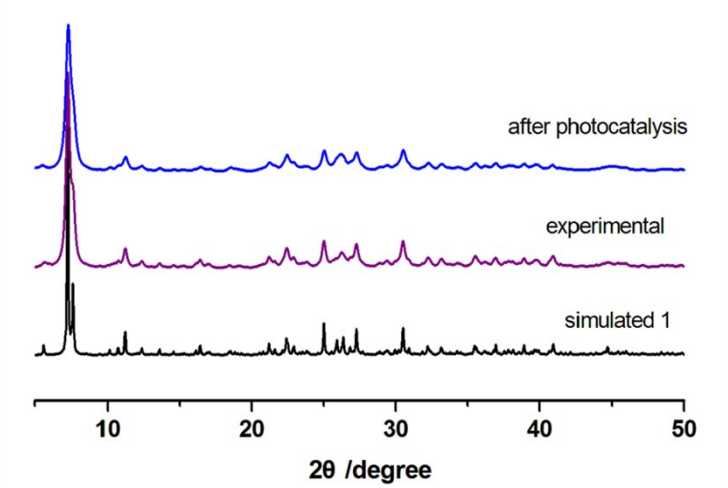

Figure S9. Experimental and simulated XRD powder patterns for **1** before and after the photocatalysis.

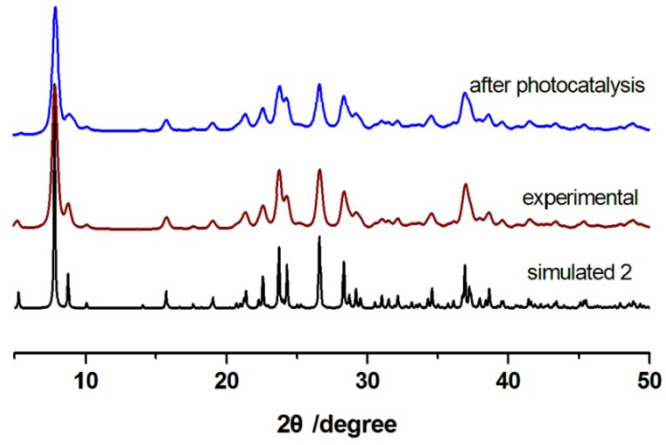

Figure S10. Experimental and simulated XRD powder patterns for **2** before and after the photocatalysis.

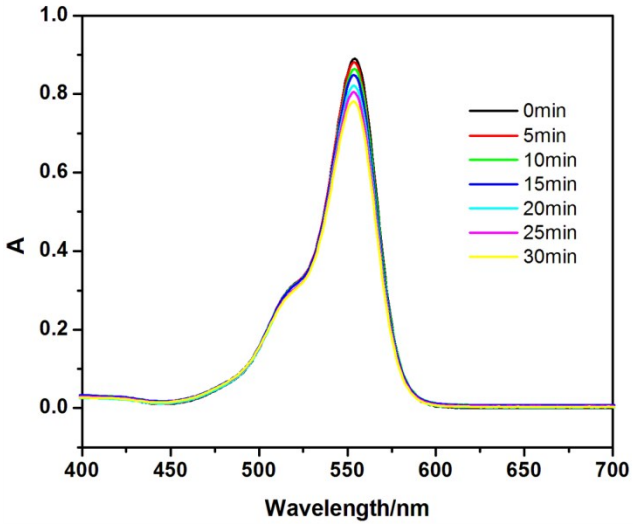

Figure S11. The absorption spectra of the RhB solution without presence of catalyst.

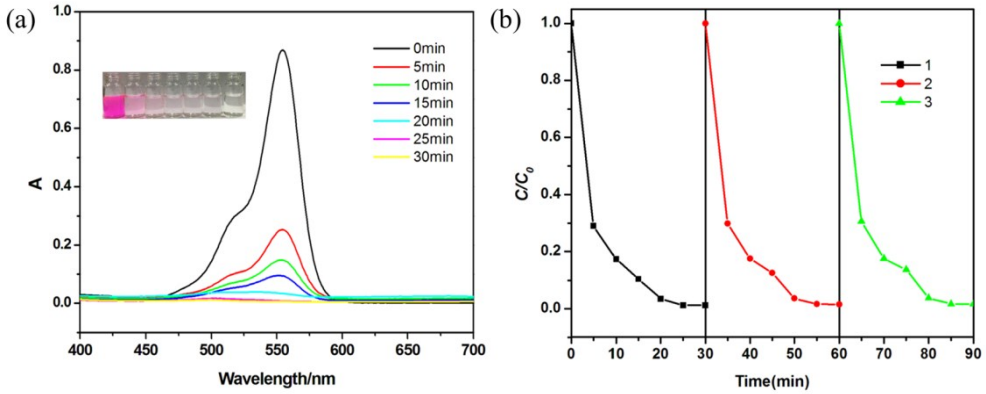

Figure S12. (a) The absorption spectra of the RhB solution in the presence of **1** under exposure to visible light. (b) The irradiation-time dependences of the relative concentration C/C_0 of the RhB over **1** during cycling photocatalytic experiments under visible light.

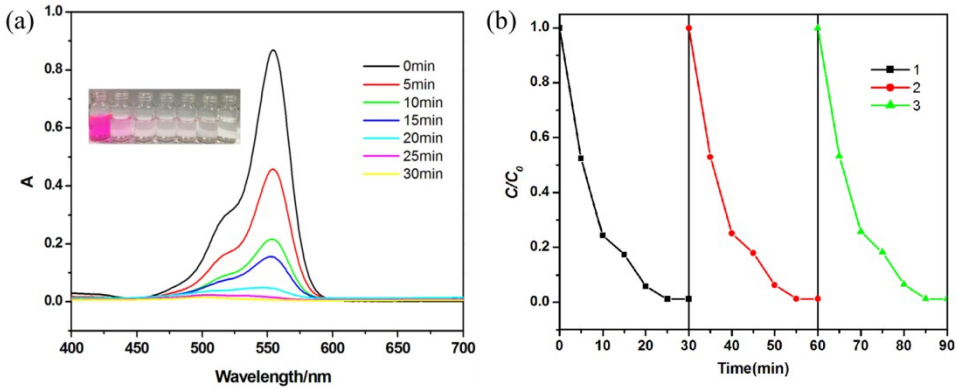

Figure S13. (a) The absorption spectra of the RhB solution in the presence of **2** under exposure to visible light. (b) The irradiation-time dependences of the relative concentration C/C_0 of the RhB over **2** during cycling photocatalytic experiments under visible light.

References

[S1] A. D. Phillips, Z. Fei, W. H. Ang, R. Scopelliti, P. J. Dyson, A crystallographic story of snakes and ladders: encapsulated water polymers and rigid metal complexes based on mono-N-substituted carboxylate 4, 4′ -bipyridine. *Cryst. Growth Des.* **2009**, *9*, 1966.

[S2] G. Sheldrick, A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112.

[S3] A. L. Spek, Single-crystal structure validation with the program PLATON. J. Appl. Cryst., **2003**, *36*, 7.