Supplementary Information

In situ synthesis of S-scheme COF-5@$CsPbBr_3$ heterojunction for efficient photocatalytic CO_2 reduction

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Experimental section

Materials

$PbBr_2$ (99.98%) and Cs_2CO_3 (99.99%) were obtained from Aladdin and used as the precursors for $CsPbBr_3$ QDs. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 1,4-phenylenediboronic acid (PBBA) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. as the precursors for COF-5. Acetonitrile (≥99.5%), mesitylene (98%), 1,4-dioxane (≥99.5%), 1-octadeceneand (≥90 %), oleylamine (80 %-90 %), cesium acetate (99.9%) and ethyl acetate (99.5%) were purchased from Aladdin. All reagents were of analytical grade and used without further purification.

Synthesis of COF-5

COF-5 was prepared by a simple solvothermal method with minor modifications. Briefly, HHTP (5 mM) and PBBA (7.5 mM) were dissolved in the mixture of acetonitrile/mesitylene/ 1,4-dioxane (20 mL) with the ratio of 15: 4 :1 and sonicated for 3 min. Then, the mixed solutions were filtered by 0.45 μm polytetrafluoroethylene (PTFE) to remove the insoluble particulates. Subsequently, the solution was heated to 90°C without stirring for 24 h under atmospheric pressure. Finally, colloids were washed several times to remove the excess monomer contamination and resuspended with the above solvent mixture to obtain the crystalline COF-5 colloidal suspension.

Synthesis of $CsPbBr_3$ QDs

$CsPbBr_3$ QDs was synthesized by hot injection method. 0. 1Mmol $PbBr_2$ was dispersed in 20 mL 1-octadeceneand (ODE), and then heated to 120 °C under the continuous Ar flow. Subsequently, 2.5 mL OA and 2.5 mL OLA were added into the mixture respectively. The solution was kept at 120 °C for at least 30 min. The mixture was then heated to 170°C. 0.75 mL cesium oleate and 1 mL ODE were uniformly mixed and added. After a short period of heat preservation, the solution was quickly cooled to room temperature under the protection of Ar flow, and the liquid contains $CsPbBr_3$ QD with obvious green fluorescence was then obtained. The liquid was washed with tertiary butanol and n-hexane for several times to obtain $CsPbBr_3$ QD solution in n-hexane with green fluorescence.

Synthesis of COF-5@$CsPbBr_3$ heterojunction

The COF-5@$CsPbBr_3$ heterojunction were synthesized by hot injection method to realize in-situ growth of $CsPbBr_3$ QDs on COF-5, and shown in the Scheme 1. 50 mg COF-5 was dispersed in 20 mL ODE, ultrasonic stirring 1 h. Then added 0. 1mM $PbBr_2$ and heated to 120°C under the continuous Ar flow. Subsequently, 2.5 mL OA and 2.5 mL OLA were added into the mixture respectively. The solution was kept at 120 °C for at least 30 min. The mixture was then heated to 170°C. 0.75 mL cesium oleate and 1 mL ODE were uniformly mixed and added. After a short period of heat preservation, the solution was quickly cooled to room temperature under the protection of Ar flow. The COF-5@$CsPbBr_3$ heterojunction was obtained after washed 3 times by n-hexane.

Synthesis of COF-5/$CsPbBr_3$

The COF-5/$CsPbBr_3$ QDs composites were obtained by a simple mechanical stirring method. 50 mg COF-5 was dispersed in 10 mL n-hexane solution, and fully dispersed by ultrasonic and shock. Then, 3 mL $CsPbBr_3$ QDs were added to the COF-5 mixture solution and stirred for 2 h. The COF-5/$CsPbBr_3$ composites were obtained by centrifuging the mixed solution and washing with n-hexane for 3 times and drying under vacuum for 12 h.

Photocatalytic activity test

10 mg of the as-prepared sample was dispersed in a solution of acetonitrile, TEOA (50 mL, 4:1) and 100 μL H_2O in a 100 mL quartz reactor and subjected to ultrasonication for 10 min. The quartz reactor was degassed with a vacuum pump and then backfilled with CO_2 (99.999%) to a pressure of 50-60 kPa. The temperature of the reaction solution was maintained at 298 K, and the reaction mixture was irradiated under a 300 W Xe lamp (PLSFX300HU, Beijing Perfectlight Technology Co., Ltd, China) with a $\lambda \geq 420$ nm cutoff filter while being vigorously stirred and kept 5 cm away from the Xe lamp. A 4A gas chromatograph (Fuli instruments, GC9790II(PLF-01)) equipped with TCD and FID detectors was connected to the quartz reactor for the analysis of H_2, CO and CH_4.

Recyclable stability test

After the photocatalytic reaction was carried out under visible light illumination ($\lambda \geq 420$ nm) for 5 h, the catalyst was collected by centrifugation and washed with acetonitrile. The supernatant was reconstituted in fresh acetonitrile, TEOA and H_2O. The mixture was ultrasonicated for 5 min. Then, the sample was backfilled with CO_2 after being vacuumed. The resultant mixture was directly used for the next photocatalytic cycle. The above steps were repeated 5 times, with each illumination lasting 5 h.

Characterization Methods

The N_2 adsorption-desorption isotherms were collected at 77K by ASAP 2460 system, and the sample were pretreatment at 80 ℃ for 24 h. Powder X-ray diffraction (PXRD) patterns were recorded on a desktop X-ray diffractometer (MiniFlex600/600C) with Cu Kα radiation ($\lambda = 1.5418$ Å) in the range of 2θ from 2° to 80°. Fourier transformation infrared (FT IR) spectra were acquired using a Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was measured by Thermo ESCALAB 250 spectrometer and all elements binding energies were calibrated with the C 1s line at 284.8 eV of surface adventitious carbon. Transmission electron microscopy (TEM) and field emission scanning electron microscope (FESEM) images were recorded by JEM-2100F (JEOL, Japan) and JSM7500F, respectively. The elemental composition was evaluated using an Energy Dispersive Spectrometer (EDS). The ultraviolet-visible diffuse reflectance (UV-vis DRS) spectra were performed UV-vis spectrophotometer (Shimadzu, UV-2700i, Japan). Photoluminescence (PL) spectra were performed on Fluorescence Spectrophotometer (LabRam HR, HORIBA Jobin Yvon, France). Time-resolved photoluminescence (TRPL) spectra were examined by a fluorescence lifetime spectrophotometer (Spirit 1040-8-SHG, Newport, US) with a 490 nm laser excitation source. The energy band structure was determined by measuring ultraviolet photoelectron spectra (UPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA). Electrochemical impedance spectroscopy (EIS) and photocurrent measurements were performed on a CHI-660e workstation (Shanghai Chenhua Instruments Co.), with Pt wire, Ag/AgCl (saturated KCl), and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6)/ethyl acetate solution functioning as the counter electrode, reference electrode, and electrolyte, respectively. gas chromatographic analysis was determined by GC9790II (PLF-01, Fuli instruments) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) column.

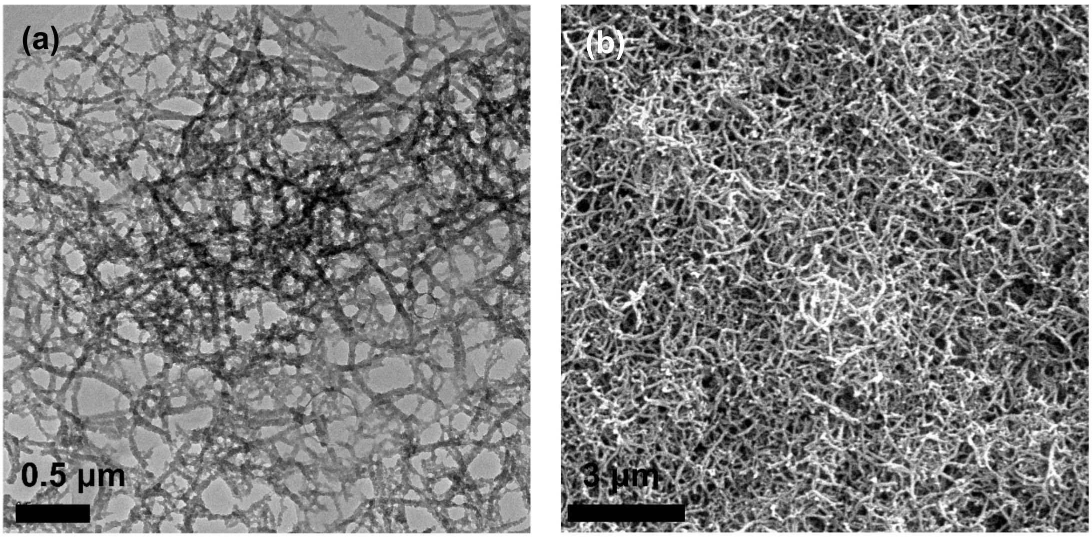

Fig. S1 (**a**) TEM and (**b**) SEM images of COF-5.

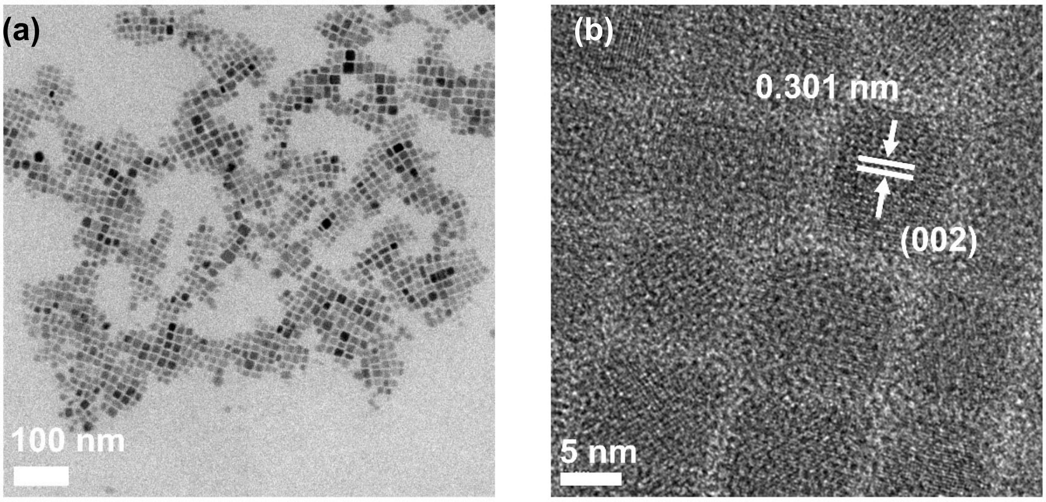

Fig. S2 (**a**) TEM and (**b**) HRTEM images of $CsPbBr_3$ QDs.

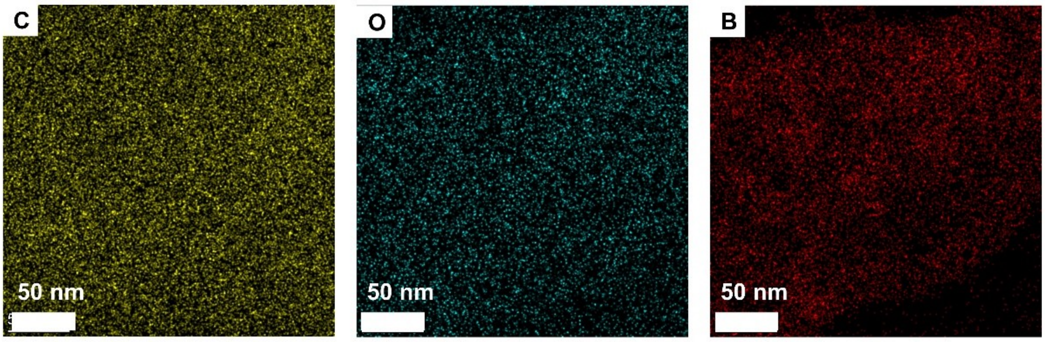

Fig. S3 TEM elemental mapping images of COF-5@$CsPbBr_3$ heterojunction.

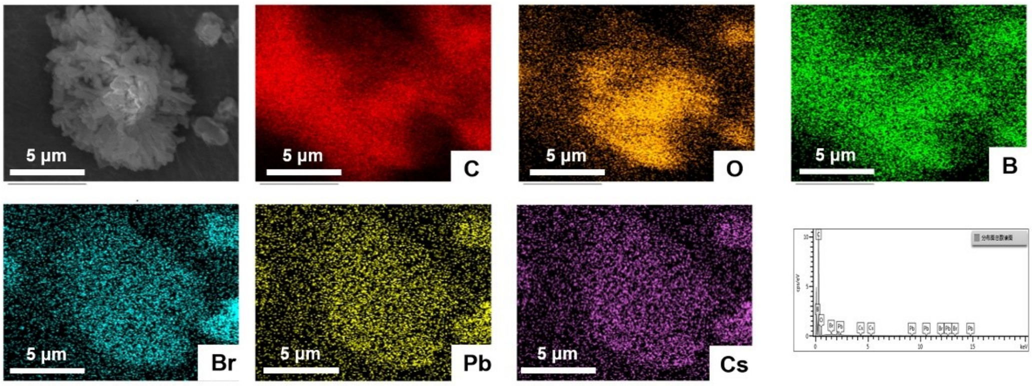

Fig. S4 SEM elemental mapping images of COF-5@$CsPbBr_3$ heterojunction.

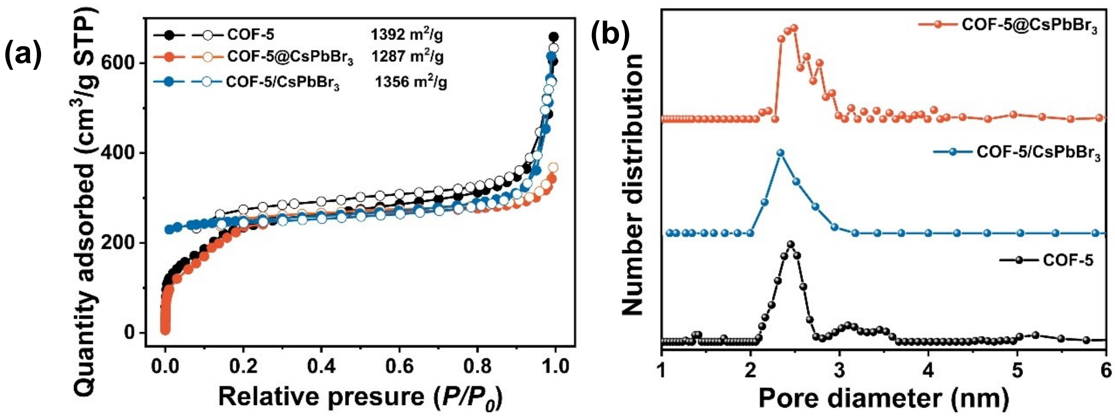

Fig. S5 (**a**) N_2 sorption isotherms and (**b**) pore size distributions of COF-5 and COF-5@$CsPbBr_3$ heterojunction.

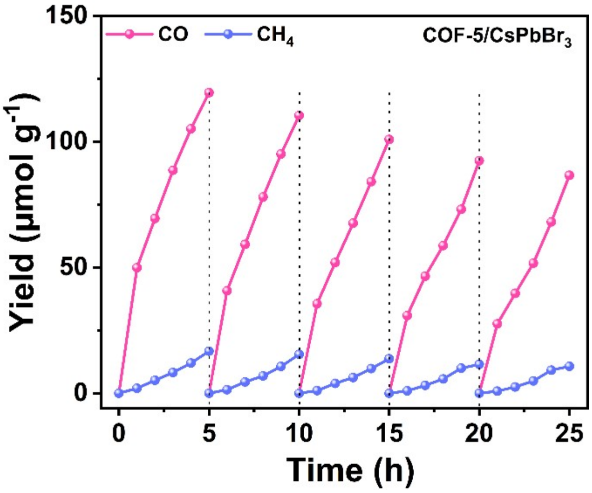

Fig. S6 Cycling curves of the photocatalytic production of CO for COF-5/CsPbBr.

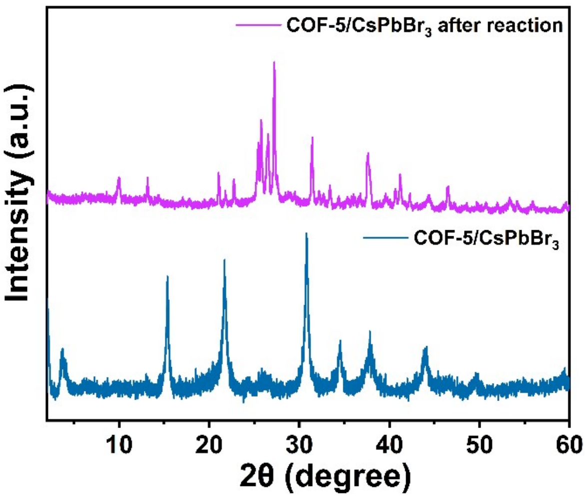

Fig. S7 PXRD patterns of COF-5/$CsPbBr_3$ before and after CO_2RR reaction

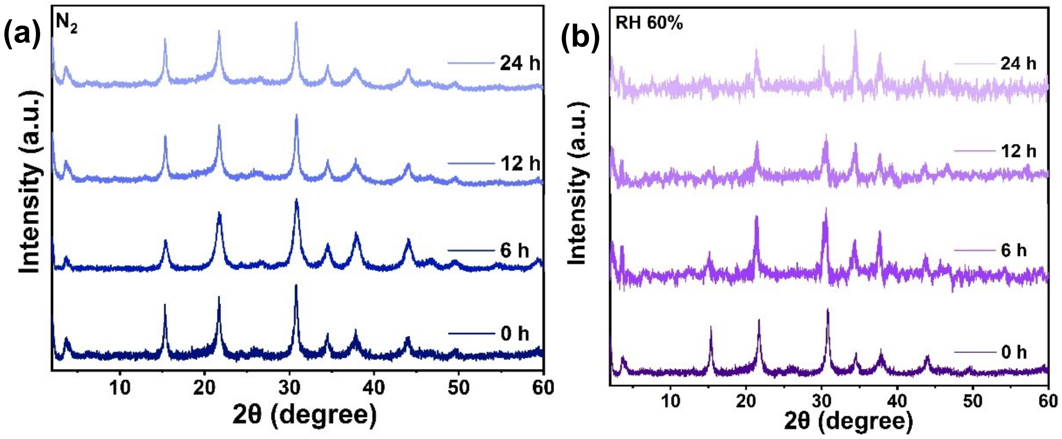

Fig. S8 XRD patterns of COF-5@$CsPbBr_3$ heterojunction treated at different time in the N_2 atmosphere (a) and 60% RH (b).

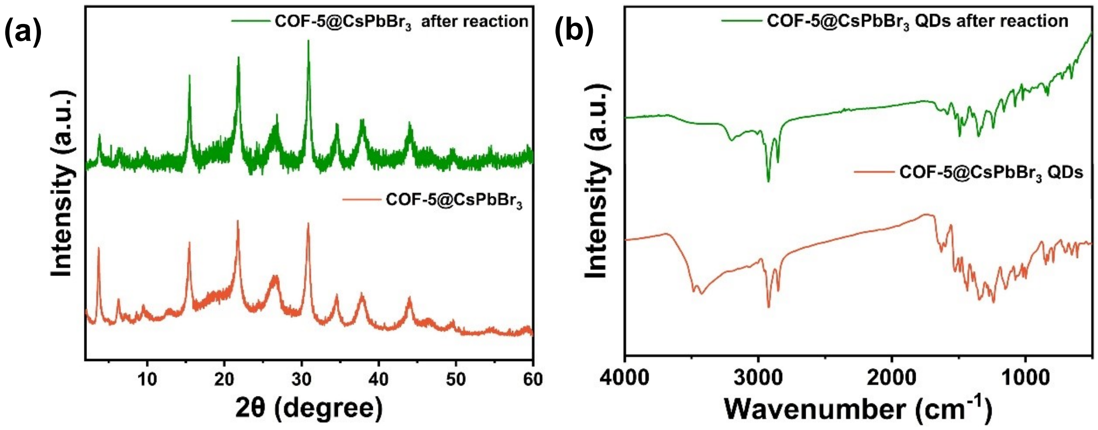

Fig. S9 (**a**) PXRD patterns and (**b**) FTIR spectra of COF-5@CsPbBr$_3$ heterojunction before and after CO$_2$RR reaction

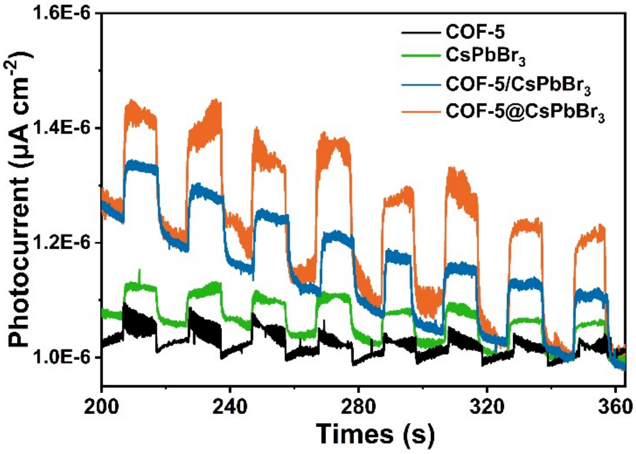

Fig. S10 Photocurrent-time profile of COF-5, $CsPbBr_3$ QDs, COF-5/$CsPbBr_3$, and COF-5@$CsPbBr_3$ heterojunction

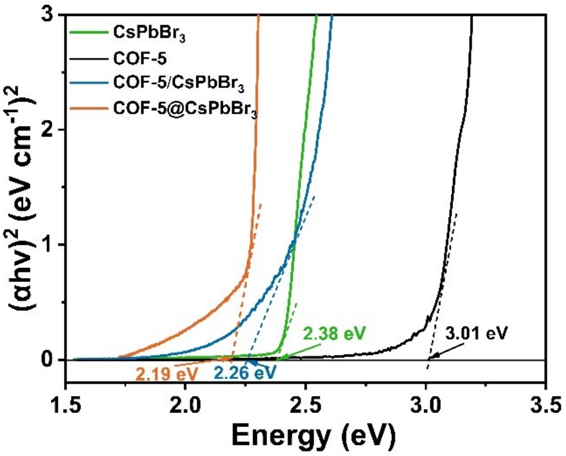

Fig. S11 Tauc plots of COF-5, CsPbBr$_3$ QDs, COF-5/CsPbBr$_3$, and COF-5@CsPbBr$_3$ heterojunction.

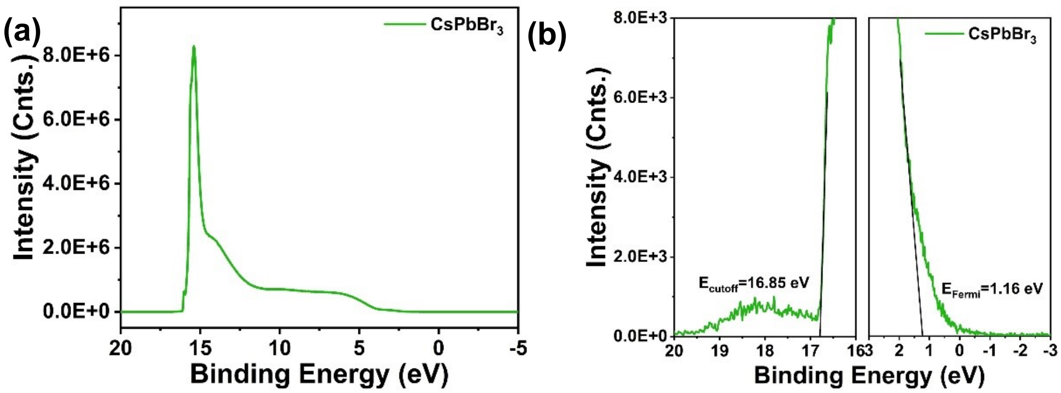

Fig. S12 (**a**) Full scan UPS spectra and (**b**) Cutoff edge (left) and Fermi edge (right) spectra of $CsPbBr_3$ QDs.

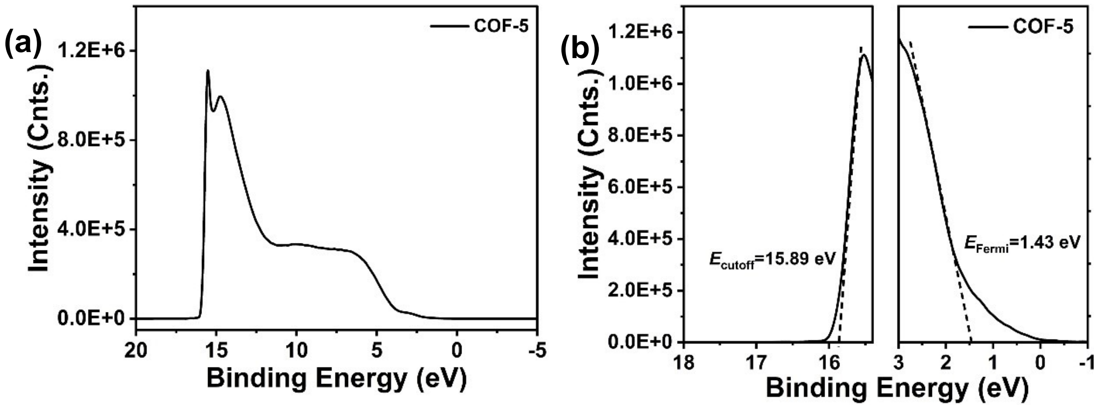

Fig. S13 (**a**) Full scan UPS spectra and (**b**) Cutoff edge (left) and Fermi edge (right) spectra of COF-5.

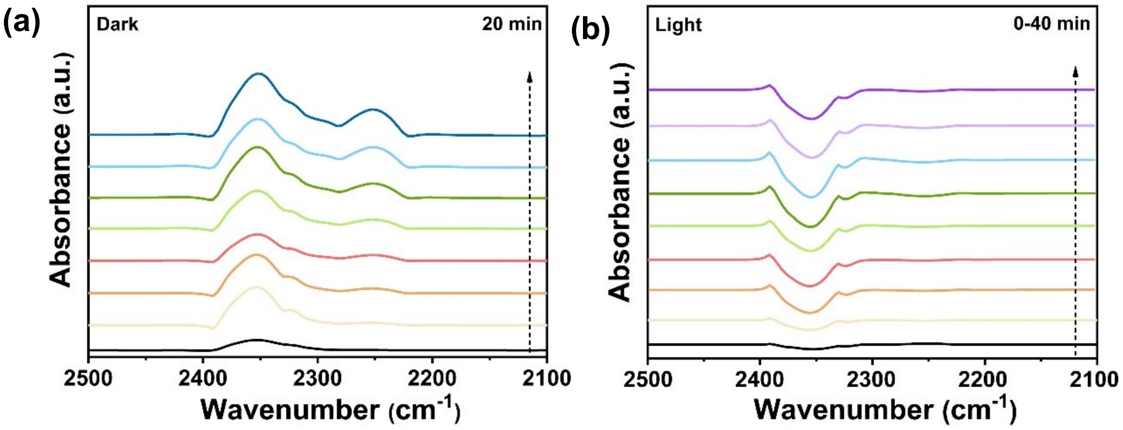

Fig. S14 In-situ DRIFTS spectra of CO_2 interaction with COF-5@$CsPbBr_3$ heterojunction (**a**) in the dark and (**b**) under visible light irradiation.

Table S1 Fitted TRPL parameters of COF-5, $CsPbBr_3$ QDs, COF-5/$CsPbBr_3$, and COF-5@$CsPbBr_3$ heterojunction.

Sample	**A_1**	**τ_1**	**A_2**	**τ_2**	**τ_{av}**
COF-5	0.14	2.44	0.83	1.01	0.73
$CsPbBr_3$ QDs	0.36	0.56	0.64	19.69	12.40
COF-5/$CsPbBr_3$	0.80	0.50	0.20	2.95	0.51
COF-5@$CsPbBr_3$ heterojunction	0.74	0.42	0.26	2.03	0.44