

*Supporting information*

**Z-Scheme heterojunction of porphyrin-based core-shell Zr-MOF@  
Pro-COF-Br hybrid materials for efficient visible-light-driven CO<sub>2</sub>  
reduction**

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## 1. Supporting experiment section

### 1.1 Materials and Measurements

2-Aminoterephthalic acid (NH<sub>2</sub>-BDC), Zirconium tetrachloride (ZrCl<sub>4</sub>), 4-Nitrobenzaldehyde, 2,5-dibromo-p-xylene, 1,4-Dimethoxybenzene, Propanoic Acid, pyrrole, pyridine, Stannous chloride (SnCl<sub>2</sub>), 1,4-Phthalaldehyde were purchased from Adamas-beta. Thieno[3,2-b]thiophene-2,5-dicarbaldehyde was purchased from Yanshen Technology Co. Ltd. (Jilin). Paraformaldehyde, CrO<sub>3</sub> and hexamethylenetetramine were purchased from Energy Chemical. 1,4-Dioxane and Boron tribromide were purchased from Aladdin Reagent Co. Ltd. (Shanghai). Dichloromethane (DCM), Acetic anhydride, N,N-Dimethylformamide (DMF), Tetrahydrofuran (THF), Acetone, Acetic acid, Hydrochloric acid, Methanol, Trichloromethane, Ammonia monohydrate, NaCl, acetic anhydride, sulfuric acid, ethanol, Formaldehyde solution and Magnesium sulfate were purchased from Xilong Chemicals. All the chemical reagents were in analytical grade and used without further purification.

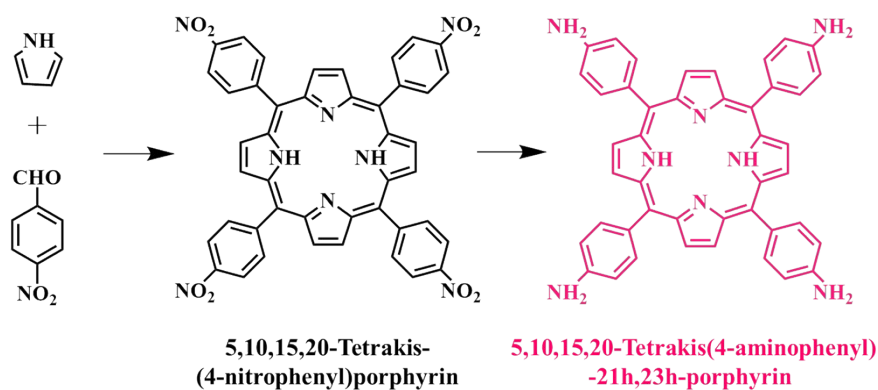
Scanning electron microscopy (SEM) measurements were performed on a JSM-7610FPlus microscope at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) images were recorded with a JEM-2100F instrument at an acceleration voltage of 120 kV. FT-IR spectra were obtained using Nicolet iN10 MX microscopic infrared spectrometer (Thermo Scientific Co., USA) in the range of 4000 to 400 cm<sup>-1</sup> under ambient condition. <sup>1</sup>H NMR spectra were recorded on a 400M NMR. Powder X-Ray Diffraction data were collected over the 2θ range 2–30° on an

Advance D8 equipped with Ni-filtered Cu K radiation (40 kV, 100 mA) at room temperature with a scan speed of  $6^{\circ}\cdot\text{min}^{-1}$ . The pore structure of the materials were measured by  $\text{N}_2$  adsorption-desorption isotherms at 77 K with Micromeritics ASAP 2460 surface area and porosity analyzer after desolvation at  $120^{\circ}\text{C}$  for 6 h under vacuum. The  $S_{\text{BET}}$  of the polymers were calculated using the BET model in the ranging of  $P/P_0 = 0.05\text{--}0.30$ , the total pore volume ( $V_{\text{total}}$ ) of the polymers was calculated from the isotherms at  $P/P_0 = 0.99$ , the pore size distribution (PSD), micropore area ( $S_{\text{micro}}$ ), and  $V_{\text{micro}}$  were all calculated by the non-local density functional theory (NLDFT) method. The X-ray photoelectron spectroscopy (XPS) characterization was detected via Thermo ESCALAB spectrometer with an Al K- $\alpha$  source.  $\text{CO}_2$  temperature programmed desorption ( $\text{CO}_2\text{--TPD}$ ) was studied by Chembet Pulsar TPR/TPD (QUANTACHROME). Electron paramagnetic resonance (EPR) was detected via Bruker A300. The ultraviolet photo-electron spectroscopy (UPS) characterization was detected via ThermoFisher Nexsa with a He I source. Thermogravimetric analysis (TGA) was performed on a thermal analysis instrument (METTLER TOLEDO Thermal Analysis) over the temperature range from room temperature to  $800^{\circ}\text{C}$  with a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  in nitrogen atmosphere. The light absorption properties of the catalysts were carried out by solid UV-vis diffuse reflectance spectra (UV-vis DRS, UV-2600, Shimadzu Instrument Co., Ltd.). Optoelectronic properties tested using electrochemical workstation (CHI660E). The photogenerated electron and hole separation properties were tested by photoluminescence (PL) emission spectra (F-2500, HITACHI, Japan). The

photocatalytic performance was carried out by gas chromatography (GC) analysis. (GC-2014C, Shimadzu Instrument Co., Ltd).  $^{13}\text{CO}_2$  isotope tracer experiment was performed by GC-MS (GC-MS0QP2020 NX). In situ FT-IR spectra were performed by Thermo scientific IS50. The Zeta potential was tested by Malvern particle size and Zeta potential analyzer (Malvern-ZS).

## 1.2 Synthesis of raw materials

### *Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)-21h,23h-porphine :*

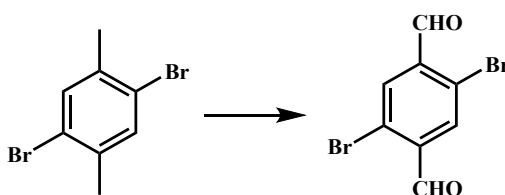


14.8 g 4-Nitrobenzaldehyde into a 250 mL round bottom flask, 16 mL acetic anhydride and 200 mL propanoic acid were added into round bottom flask, get a solution. And then 6.64 mL pyrrole was added into 20 mL of propionic acid to obtain b solution. Under  $\text{N}_2$  atmosphere, a solution was heated to reflux, then the pyrrole was slowly add into a solution, and continue to reflux for 3 h. After the reaction, the mixture was cooled to room temperature and left at room temperature for 24 h. The precipitate was filtrated, and washed with water, dried under  $60^\circ\text{C}$  for 24 h. After drying, the product was placed in a 250 mL round-bottom flask, 150 mL pyridine was added, heated and refluxed for 6 h, then cooled to room temperature. Subsequently, the mixture was placed at  $-5^\circ\text{C}$  for 12h, then filtrated and washed with acetone until

colorless. Finally, the product 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin was obtained.

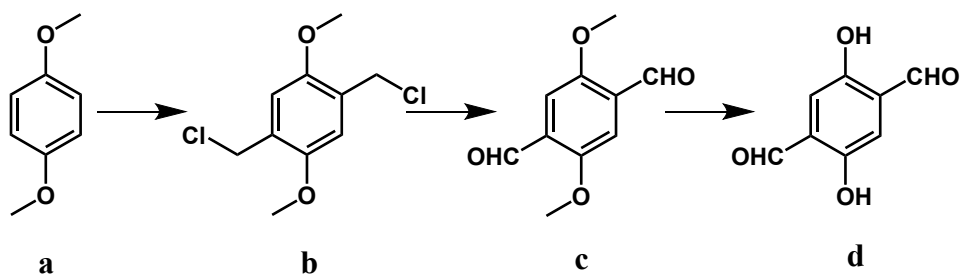
2.0 g 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin was dissolved in 100 mL concentrated hydrochloric acid to obtain the **c** solution. Then 9.0 g  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$  was dissolved in 40 mL concentrated hydrochloric acid, get **d** solution. Solution **d** was slowly dropped into solution **c**, and the reaction was heated to  $80^\circ\text{C}$  for 6 h. At the end of the reaction, the product was placed in ice water to cool, and then filtrated, and the product was dispersed in water. The pH was adjusted to 9 with ammonia, then filtrated and dried, and the crude product was obtained. The crude product was separated by column chromatography (methylene chloride: methanol: ammonia =10:1:0.3), the finally product 5,10,15,20-tetrakis(4-aminophenyl)-21h,23h-porphyrin was obtained.  $^1\text{H NMR}$  (400 MHz,  $\text{d}_6\text{-DMSO}$ , 298K, TMS): 8.88 (s, 8H), 7.85 (s, 8H), 7.01 (s, 8H), 5.61 (s, 8H), -2.75 (s, 2H) ppm.

***Synthesis of 2,5-dibromo-1,4-diformylbenzene :***



The 2,5-dibromo-1,4-diformylbenzene was synthesized according to our previous works.<sup>1</sup>

***Synthesis of 2,5-Dimethoxyterephthalaldehyde (c) and 2,5-Dihydroxyterephthalaldehyde (d) :***



(1) 20.0 g 1,4-Dimethoxybenzene (**a**) was dissolved in 60 mL 1,4-Dioxane, then added 10 mL 37wt% Formaldehyde solution and 6.0 g Paraformaldehyde in above solution. The mixture was heated to 90°C at stirring, and then 20 mL of concentrated hydrochloric acid was added. After 1 h, added 60 mL hydrochloric acid again and continue stirred about 0.5 h. And then the reaction was cooled to room temperature, obtained the white precipitate. The white precipitate was filtrated, and washed with water, dried under 60°C for 24 h to gate the crude product. The crude product was further recrystallization with acetone to obtain the product **b**. And the product **b** was obtained by dried under vacuum at 60°C for 24 h. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 298K, TMS): 6.93 (s, 2H), 4.64 (s, 4H), 3.86 (s, 6H) ppm.

(2) 10.0 g **b** and 12.0 g hexamethylenetetramine were dissolved in 100 mL Trichloromethane, the mixture was heated to 90°C for 24 h at stirred. After being cooled to room temperature, the light yellow solid was filtered, washed with trichloromethane, and dried under vacuum at 60°C. The solid power was added in a small amount of water, and subsequently added 30 mL acetic acid to acidify. The mixture was heated to 90°C for 24 h at stirred, after being cooled to room temperature. The mixture solution was extracted with dichloromethane, the organic phase was washed with water several times, then water was removed with magnesium sulfate, and then the solvent was also removed to obtain a crude product. The crude product

was recrystallization with ethanol to obtain the yellow-green product **c**. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 298K, TMS): 10.4 (s, 2H), 7.44 (s, 2H), 3.94 (s, 6H) ppm.

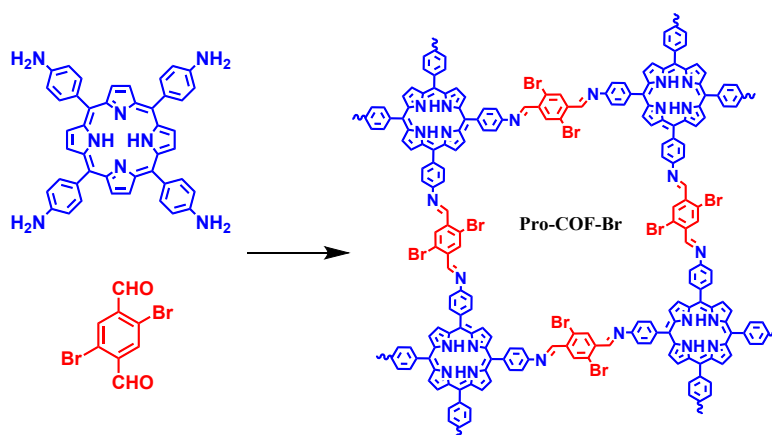
(3) 0.4 g **c** was dissolved in 20 ml dichloromethane at 0°C. And the 11.3 mL Boron tribromide was added dropwise in above solution under N<sub>2</sub> atmosphere. The reaction was reacted for 0.5 h at 0°C, after being removed to room temperature continue reacted 3 h. Then 50.0 mL water was added in mixture, and the mixture extracted with dichloromethane, the organic phase was washed with water several times, then water was removed with magnesium sulfate, and then the solvent was also removed to obtain an orange crude product **d**. The crude product was recrystallization with acetone to obtain the final product **d**. Yield: 0.35 g (87%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 298K, TMS): 10.31 (s, 4H), 7.22 (s, 2H) ppm.

### **1.3 Preparation of MOF, COF and MOFs@COFs**

#### ***Preparation of NH<sub>2</sub>-UiO-66 (Zr-MOF):***

0.4 mmol ZrCl<sub>4</sub> and 0.4 mmol NH<sub>2</sub>-BDC were dissolved in 40.84 mL DMF, and continued sonicated about 30 min until the solution was cleared. 9.16 mL of acetic acid was added slowly in above mixture with stirring. Then the mixture was transferred into a 100 mL Teflon-lined autoclave and heated at 120°C for 24 h. After cooling to room temperature, the precipitates were separated from the reaction mixture by centrifugation, and washed thoroughly with DMF and ethanol to remove any unreacted starting materials. Finally, the obtained solid was dried under vacuum at 60°C for 24 h.

#### ***Preparation of Pro-COF-Br:***



Pro-COF-Br was synthesized by a solvothermal method. Weight 0.04 mmol (27.00 mg) 5,10,15,20-tetrakis(4-aminophenyl)-21h,23h-porphyrin and 0.08 mmol (23.26 mg) 2,5-dibromo-1,4-diformylbenzene into a 5 mL ampoule, and added 3.0 mL mixed solvent of 1,2-dichlorobenzene and 1-Butanol (v/v = 1:1), thereafter sonicated about 15 min until the solution was uniformly. And then 0.3 ml 6.0 M acetic acid was added dropwise, which the precipitation was appeared. The resultant mixture was sonicated for 2 min for getting a homogeneous dispersion, and then frozen under liquid N<sub>2</sub> bath and degassed by three freeze-pump-thaw cycles. Thereafter, the tube was sealed off and left undisturbed at 120°C for 3 days. The precipitate was gained by filtration, washed with DCM, THF, acetone and methanol. The product was further purified in a Soxhlet extractor with THF and methanol for 24 h. Then the product was collected after drying under vacuum at 60°C for 24 h.

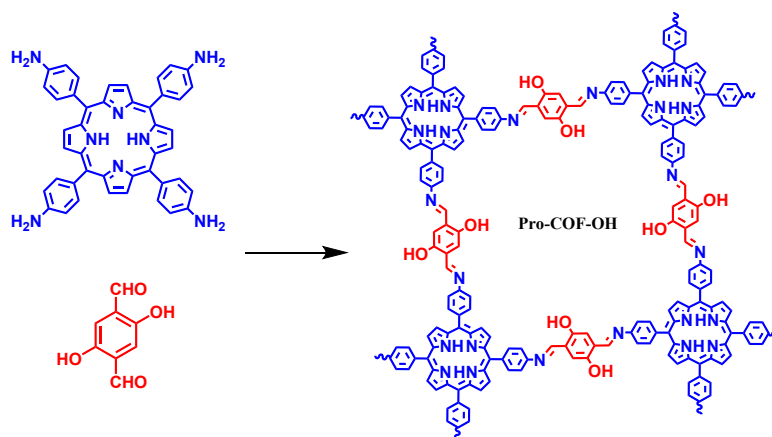
***Preparation of NH<sub>2</sub>-UiO-66@Pro-COF-Br (M@C-Br) :***

A series of M@C-Br hybrid materials were synthesized by solvothermal method. 10 mg NH<sub>2</sub>-UiO-66 and 0.08 mmol (23.26 mg) 2,5-dibromo-1,4-diformylbenzene were added into 1.5 mL mixed solvent of 1.5 mL 1,2-dichlorobenzene and 1-Butanol (v/v = 1:1), thereafter, the mixture sonicated about 15 min to make the mixture into a uniform suspension. Then added 1.5 mL mixed solvent of 1,2-dichlorobenzene and 1-Butanol (v/v = 1:1) containing 0.04 mmol (14.18 mg) TAPP to the above suspension



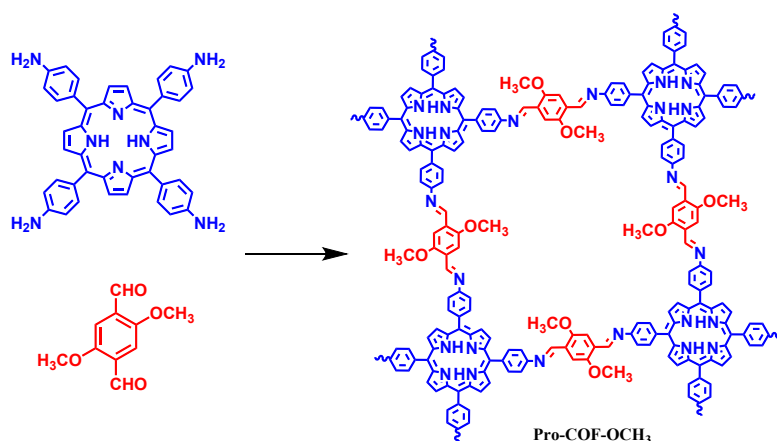
and continue sonication for 0.5 h. 0.3 ml 6.0 M acetic acid was added dropwise, the resultant mixture was sonicated for 2 min for getting a homogeneous dispersion, and then frozen under liquid N<sub>2</sub> bath and degassed by three freeze-pump-thaw cycles. Thereafter, the tube was sealed off and left undisturbed at 120°C for 3 days. A dark brown precipitate was gained by filtration, washed with DCM, THF, acetone and methanol. The product was further purified in a Soxhlet extractor with THF and methanol for 24 h. Then the product was collected after drying under vacuum at 60°C for 24 h, named M@C-Br-1. The M@C-Brs with different shell thickness was prepared by changing the different feeding amounts of NH<sub>2</sub>-UiO-66. When the amounts of NH<sub>2</sub>-UiO-66 were 20 mg, 30 mg, and 40 mg, the prepared M@C-Brs were named M@C-Br-2, M@C-Br-3 and M@C-Br-4, respectively.

***Preparation of Pro-COF-OH and NH<sub>2</sub>-UiO-66@Pro-COF-OH (M@C-OH):***



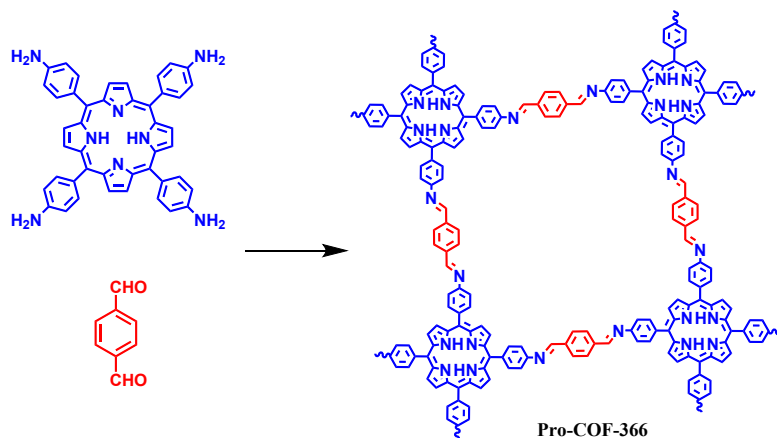
The synthesis method was the same as that of the Pro-COF-Br. The Pro-COF-OH was prepared by replacing 2,5-dibromo-1,4-diformylbenzene with 0.08 mmol (13.30 mg) 2,5-dihydroxyterephthalaldehyde. Corresponding, the synthesis method of M@C-OH hybrid material was the same as that of the M@C-Br hybrid material.

***Preparation of Pro-COF-OCH<sub>3</sub> and NH<sub>2</sub>-UiO-66@Pro-COF-OCH<sub>3</sub> (M@C-OCH<sub>3</sub>):***



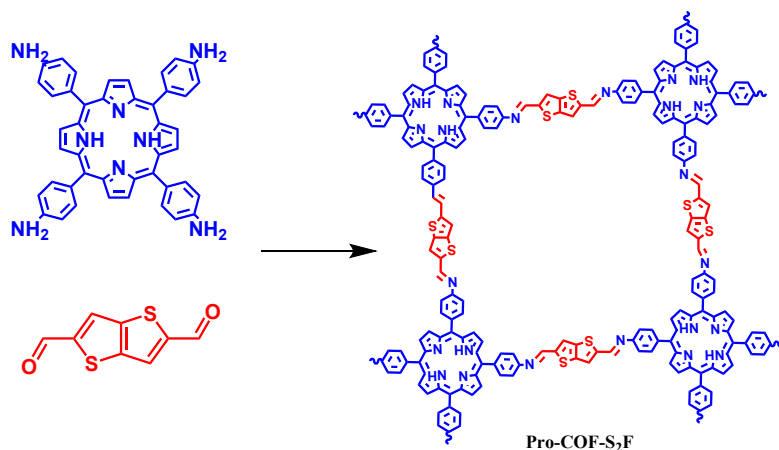
The synthesis method was the same as that of the Pro-COF-Br. The Pro-COF-OCH<sub>3</sub> was prepared by replacing 2,5-dibromo-1,4-diformylbenzene with 0.08 mmol (12.98 mg) 2,5-dimethoxyterephthalaldehyde. Corresponding, the synthesis method of M@C-OCH<sub>3</sub> hybrid material was the same as that of the M@C-Br hybrid material.

***Preparation of Pro-COF-366 and NH<sub>2</sub>-UiO-66@Pro-COF-366 (M@C-366):***



The synthesis method was the same as that of the Pro-COF-Br. The Pro-COF-366 was prepared by replacing 2,5-dibromo-1,4-diformylbenzene with 0.08 mmol (10.73 mg) 1,4-phthalaldehyde. Corresponding, the synthesis method of M@C-366 hybrid material was the same as that of the M@C-Br hybrid material.

***Preparation of Pro-COF-S<sub>2</sub>F and NH<sub>2</sub>-UiO-66@Pro-COF-S<sub>2</sub>F (M@C-S<sub>2</sub>F):***



The synthesis method was the same as that of the Pro-COF-Br. The Pro-COF-S<sub>2</sub>F was prepared by replacing 2,5-dibromo-1,4-diformylbenzene with 0.08 mmol (15.70 mg) thieno[3,2-b]thiophene-2,5-dicarbaldehyde. Corresponding, the synthesis method of M@C-S<sub>2</sub>F hybrid material was the same as that of the M@C-S<sub>2</sub>F hybrid material. In contrast, the mixed solvent was changed to benzyl alcohol and o-dichlorobenzene (v/v = 3:1).

#### 1.4 Photocatalytic CO<sub>2</sub> reduction experiments

The performance of the photocatalytic reduction of CO<sub>2</sub> was tested in a reactor with a volume of 100 mL. The process enables the simulation of the sunlight with a PLS-SXE300 300 W Xenon lamp source. The specific operation steps are as follows: the 10 mg sample was dispersed in a small amount of deionized water by ultrasound, and then transferred to a small evaporation dish and placed in a vacuum drying oven to remove water, so as to obtain a film of catalytic agent. 0.084g NaHCO<sub>3</sub> was placed at the bottom of the reactor, and then the prepared sample was placed in it. Ar gas was pumped for 20 min, and then 0.3 mL 2 M H<sub>2</sub>SO<sub>4</sub> was gently injected into the reactor to fully react with NaHCO<sub>3</sub> to produce CO<sub>2</sub>. Finally, the Xenon lamp was turned on to shine light on the reactor at a distance of about 20 cm from the sample. The

photocatalytic reaction was performed at room temperature. Sample the gas products every 1 h, and then collect by gas chromatography.

### **1.5 Photoelectric performance**

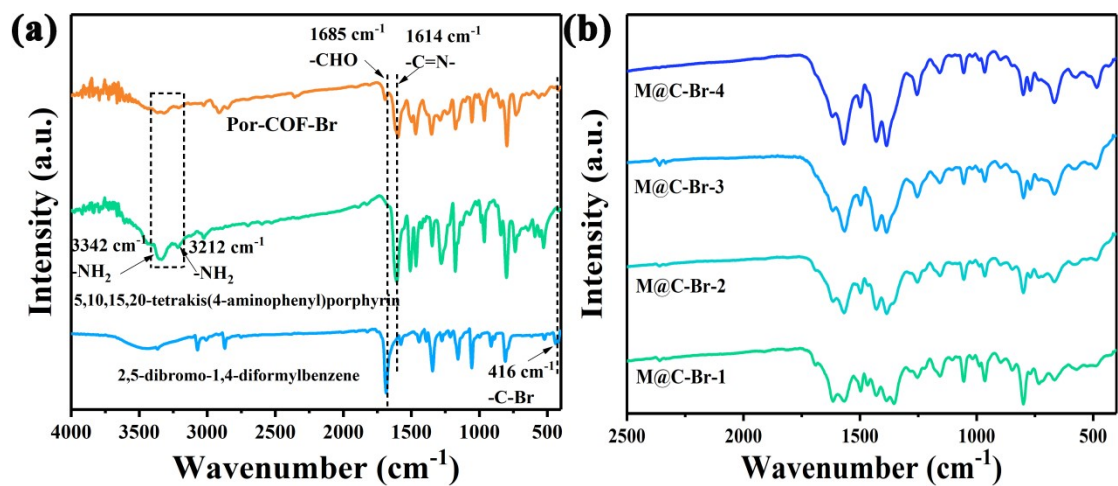
The photoelectric chemical test of the samples was carried out on the CHI660e electrochemical workstation. The process adopted a three-electrode system, namely Ag/AgCl as the reference electrode, Pt sheet as the counter electrode, and the sample coated on the FTO slide as the working electrode. The preparation method of working electrode was as follows: Disperse 10 mg sample in 475 uL ethanol, ultrasound for 40 min to make it evenly dispersed, and then add 25 uL Nafion membrane solution for another ultrasound for 5 min, then drop 100 uL from the obtained mixture onto FTO wave plate, and then dry it. Electrochemical stations can be used to measure photocurrent response, chemical impedance spectroscopy and Mott-Schottky equation. During the test, the source was 300 W PLS-SXE300 Xenon lamps.

### **1.6 Fluorescence spectrometry test**

During the fluorescence spectrum test, the sample was not pretreated. The fluorescence curve was obtained when the excitation wavelength was 365 nm. The sample scanning speed is  $1200 \text{ nm} \cdot \text{min}^{-1}$ , and the voltage and slit width are adjusted according to the sample conditions.

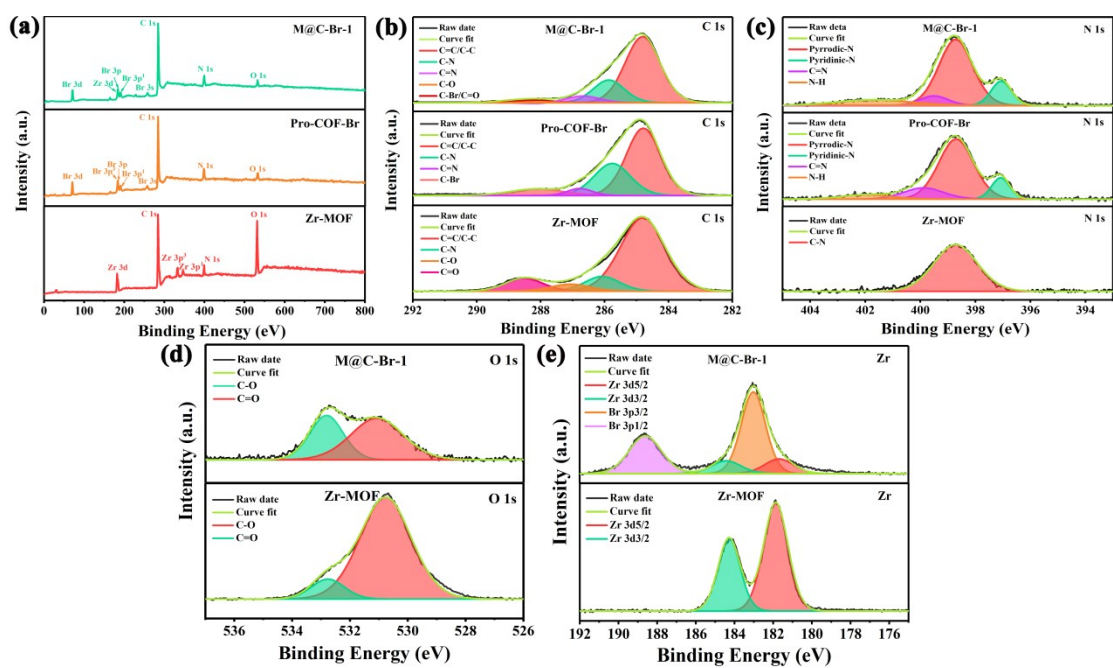
## **2. Supplemental figures and tables**

### **2.1 Figure S1**



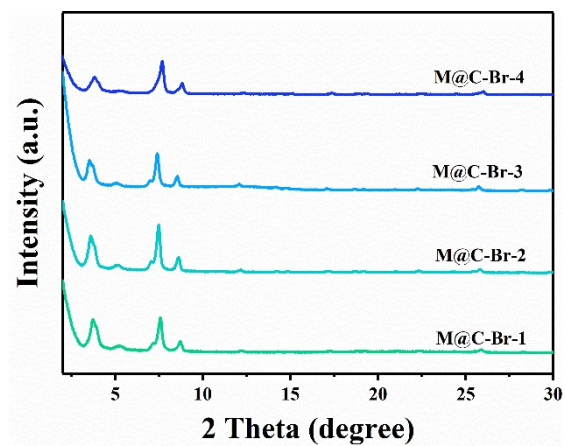
**Fig. S1** The FT-IR patterns of (a) raw materials and Pro-COF-Br, (b) the M@C-Br-(1~4) samples.

## 2.2 Figure S2



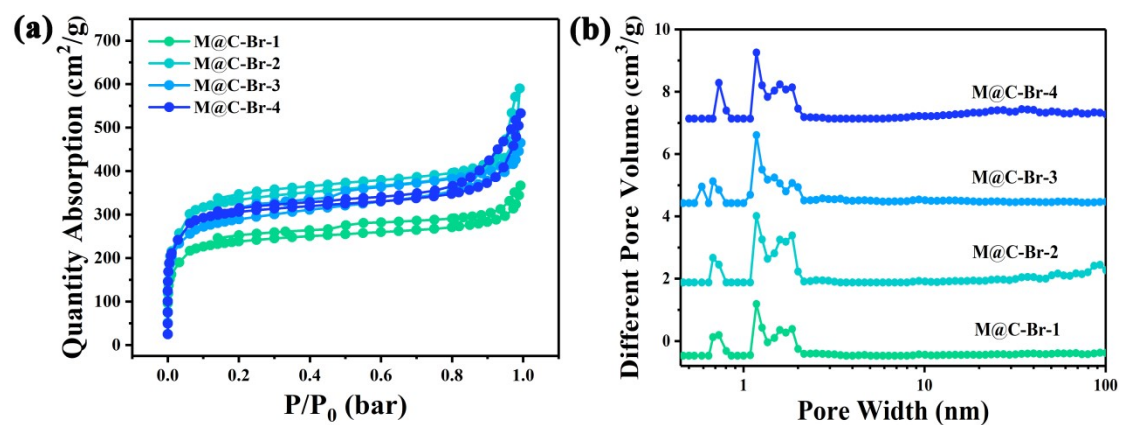
**Fig. S2** (a) The XPS survey of Zr-MOF, Pro-COF-Br, and M@C-Br-1, (b) C 1s, (c) N 1s, (d) O 1s, (e) Zr 3d.

### 2.3 Figure S3



**Fig. S3** The PXRD patterns of M@C-Br-(1~4) samples.

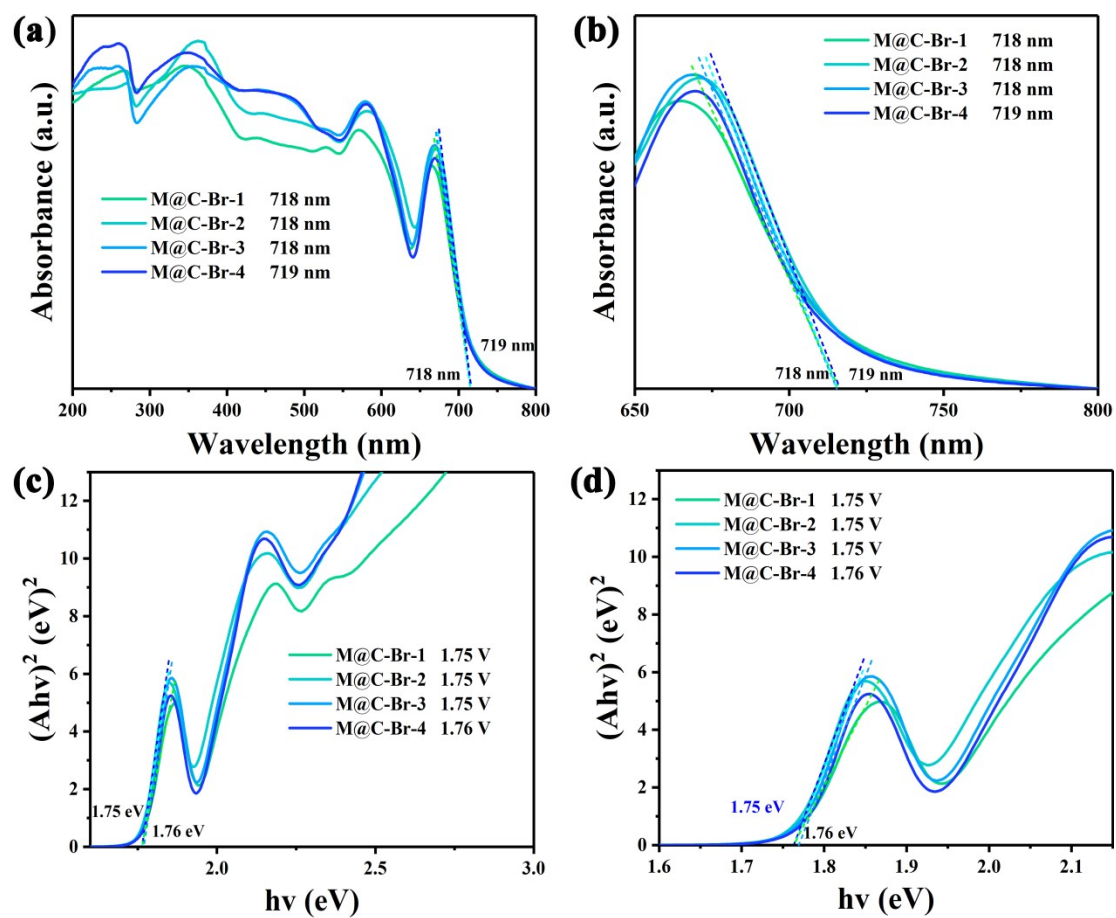
## 2.4 Figure S4



**Fig. S4** (a)  $\text{N}_2$  adsorption-desorption curves and (b) The pore size distribution (PSD) of the M@C-Br-(1~4) samples.

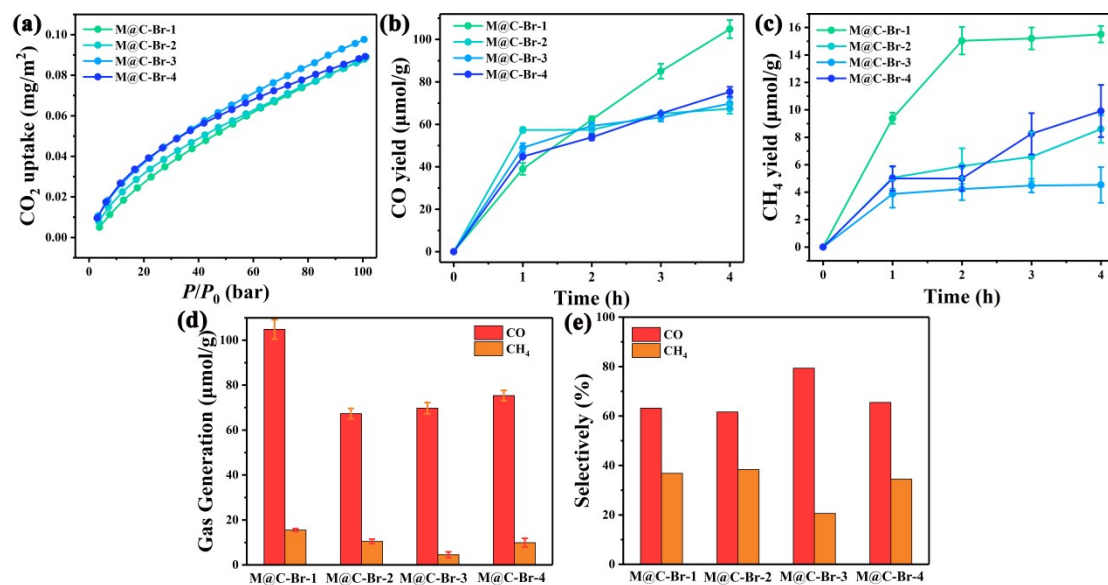


## 2.5 Figure S5



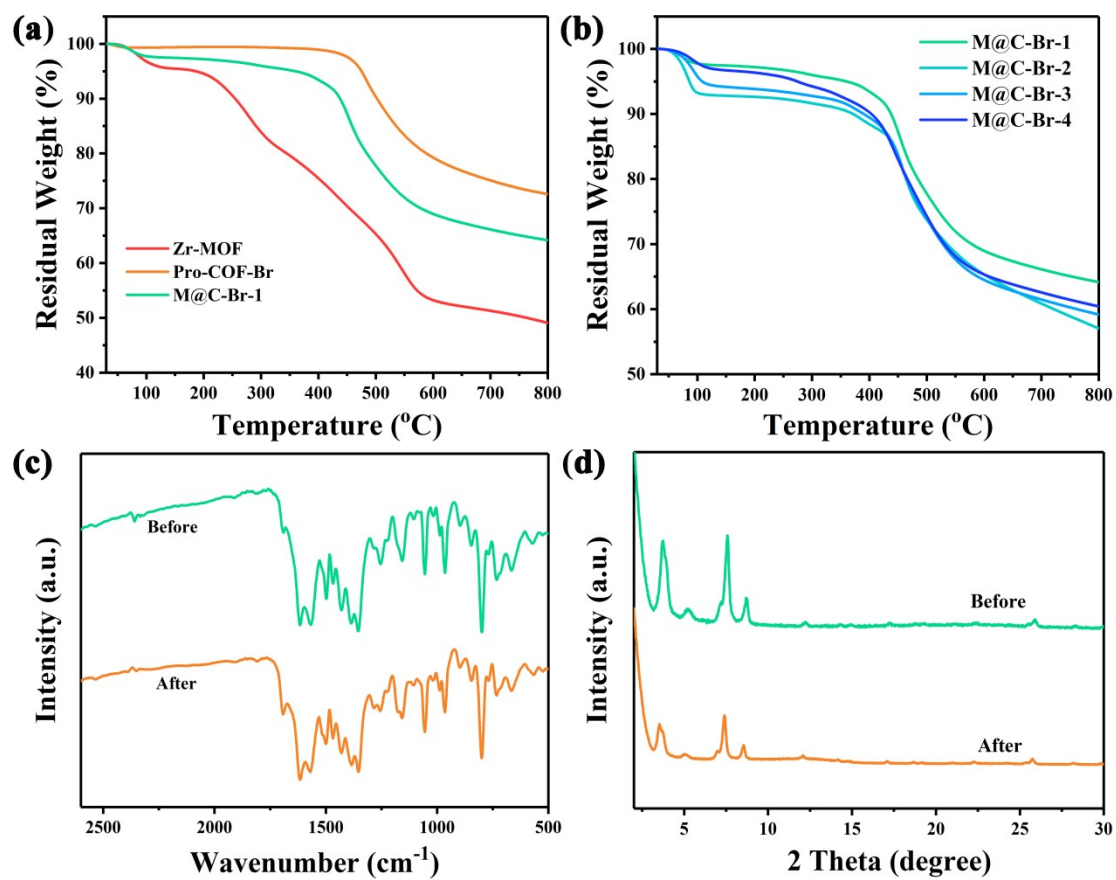
**Fig. S5** (a, b) UV-vis DRS of M@C-Br-(1~4) and (c, d)  $(A*hv)^2$  with photon energy ( $h\nu$ ) graph of the relationship of change of M@C-Br-(1~4).

## 2.6 Figure S6



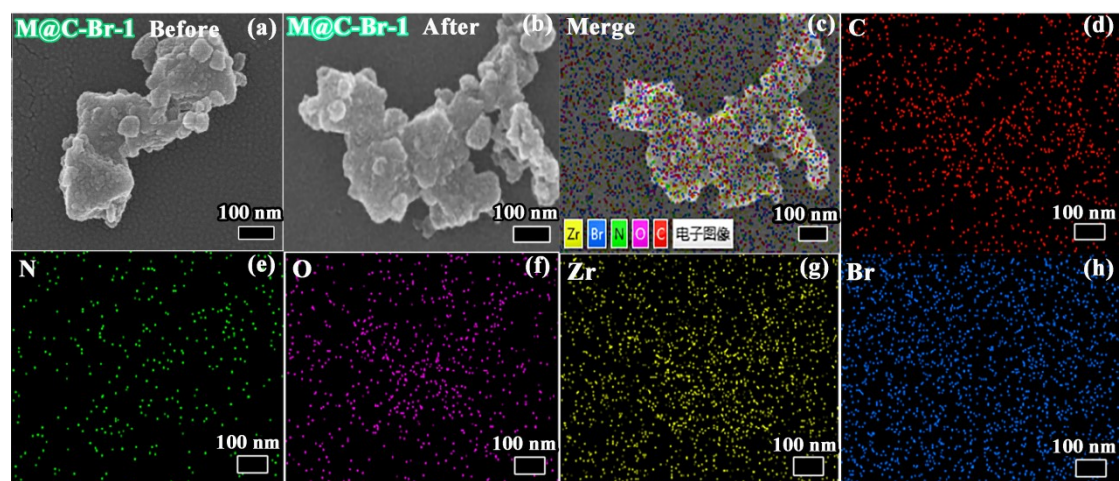
**Fig. S6** (a) CO<sub>2</sub> adsorption isotherms, (b) CO<sub>2</sub> to CO conversion curves with time, (c) CO<sub>2</sub> to CH<sub>4</sub> conversion curves with time, (d) CO<sub>2</sub> photocatalytic reduction performance of M@C-Br-(1~4), (e) Product selectivity.

## 2.7 Figure S7



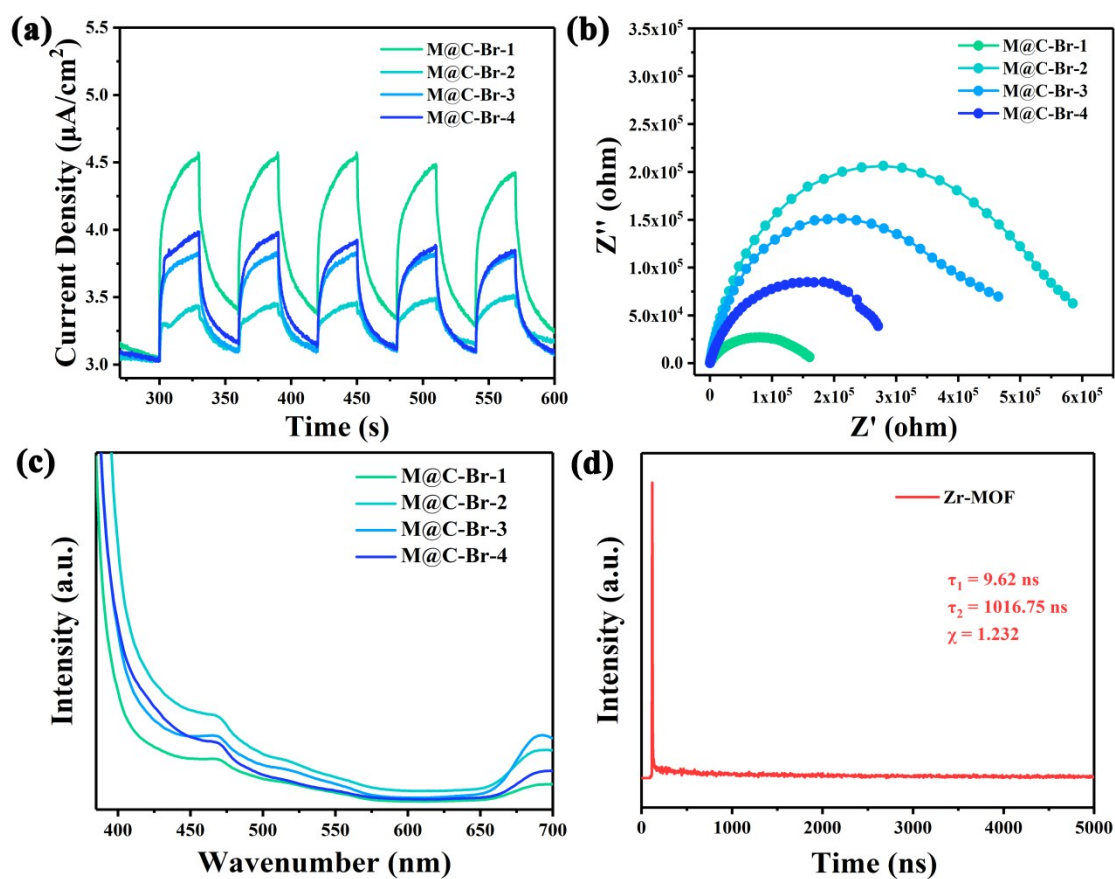
**Fig. S7** (a, b) The TGA of Zr-MOF, Pro-COF-Br, and M@C-Br-(1~4), (c) FT-IR spectra and (d) PXRD patterns of M@C-Br-1 before and after photocatalytic.

## 2.8 Figure S8



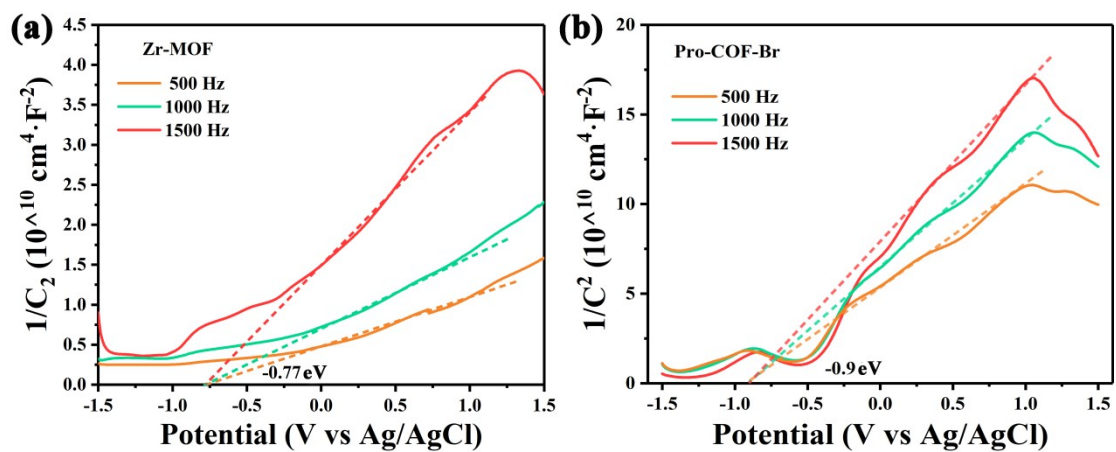
**Fig. S8** SEM patterns of M@C-Br-1 (a) before and (b) after photocatalytic and (c-h) EDS of M@C-Br-1 after photocatalytic.

## 2.9 Figure S9



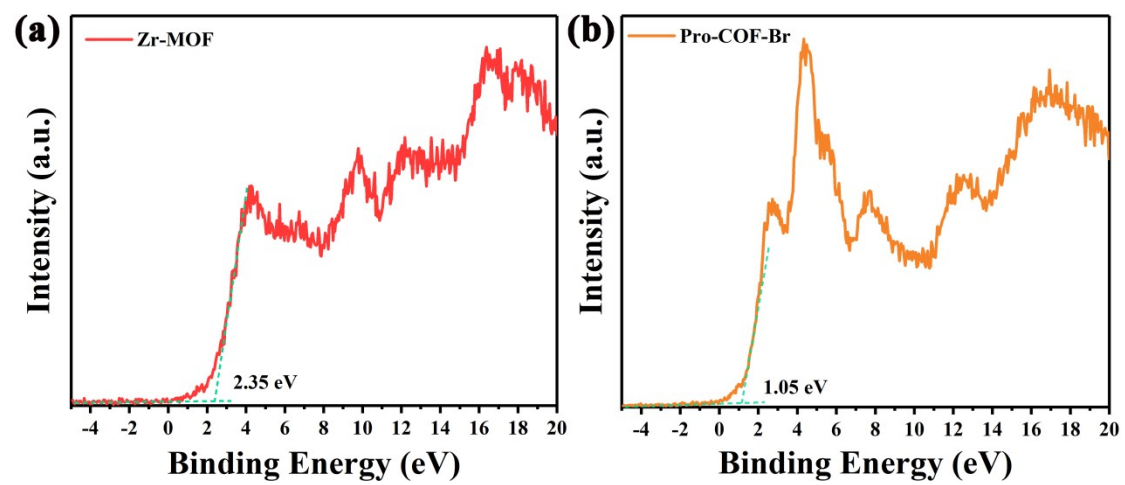
**Fig. S9** (a) Photocurrent response diagram, (b) Electrochemical impedance Nyquist diagram, (c) The photoluminescence spectrum of M@C-Br-(1~4), (d) Transient photoluminescence of Zr-MOF.

## 2.10 Figure S10



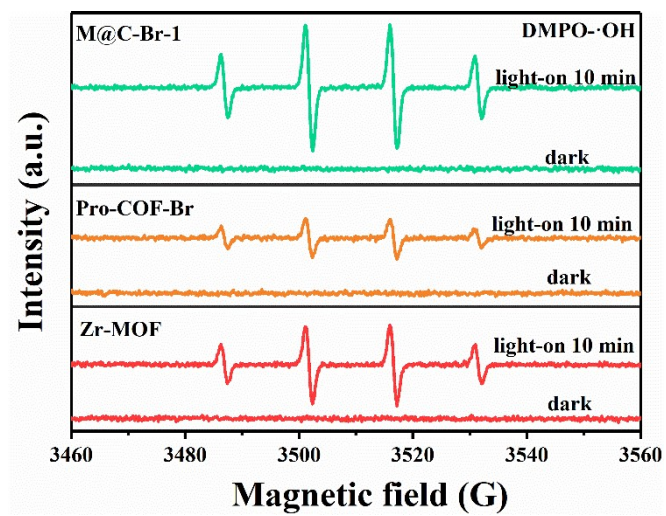
**Fig. S10** Mott-Schottky plots of (a) Zr-MOF and (b) Pro-COF-Br.

## 2.11 Figure S11



**Fig. S11** The XPS valence band spectra of (a) Zr-MOF and (b) Pro-COF-Br.

## 2.12 Figure S12



**Fig. S12** Electron paramagnetic resonance (EPR) spectra of DMPO-•OH adducts.



## 2.13 Figure S13

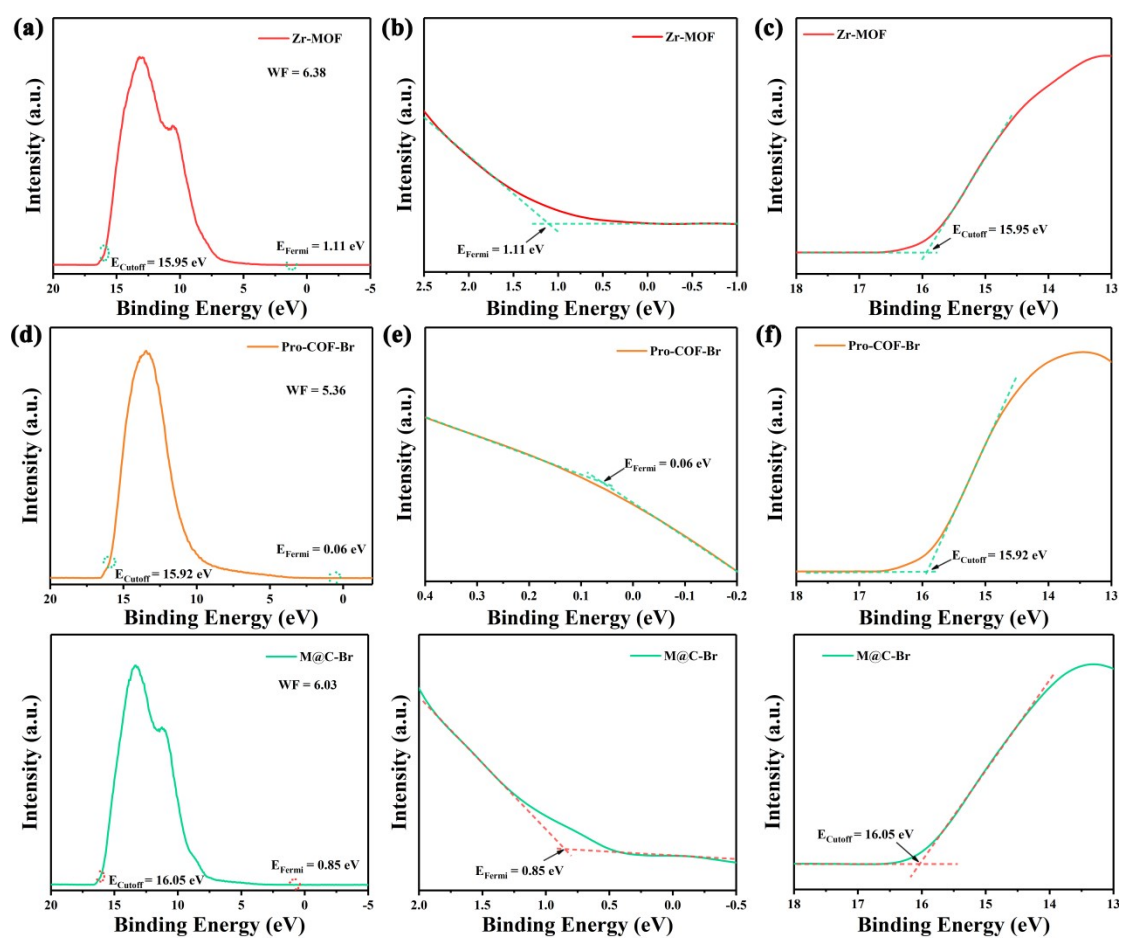
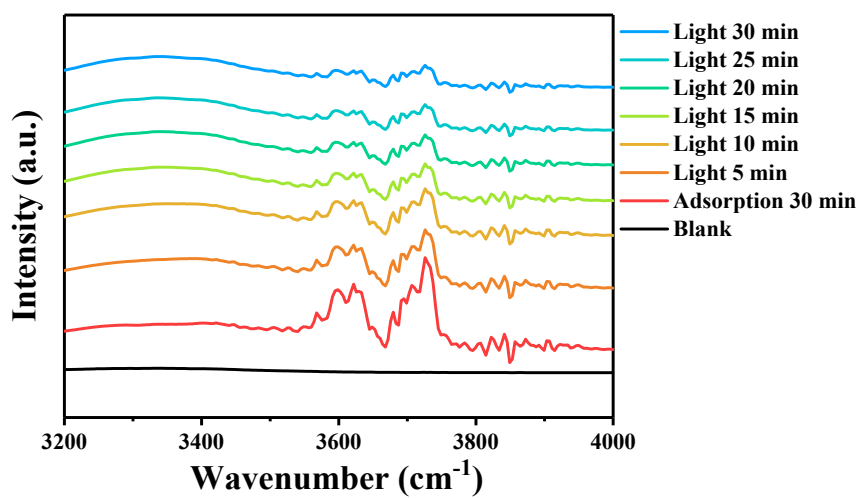


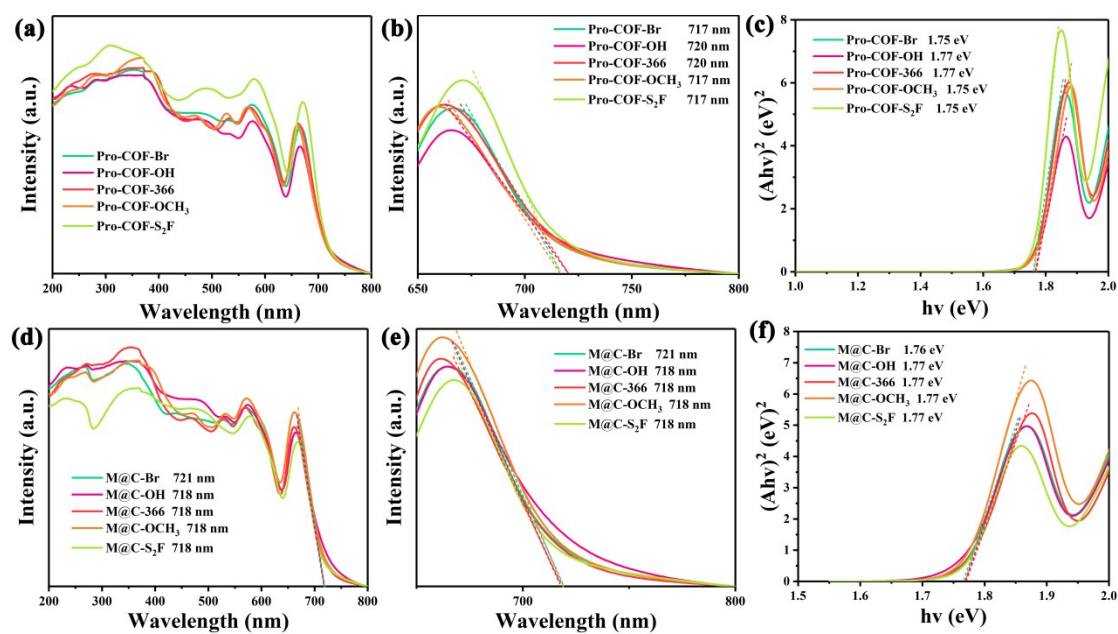
Fig. S13 UPS plots of Zr-MOF, Pro-COF-Br, and M@C-Br-1.

## 2.14 Figure S14



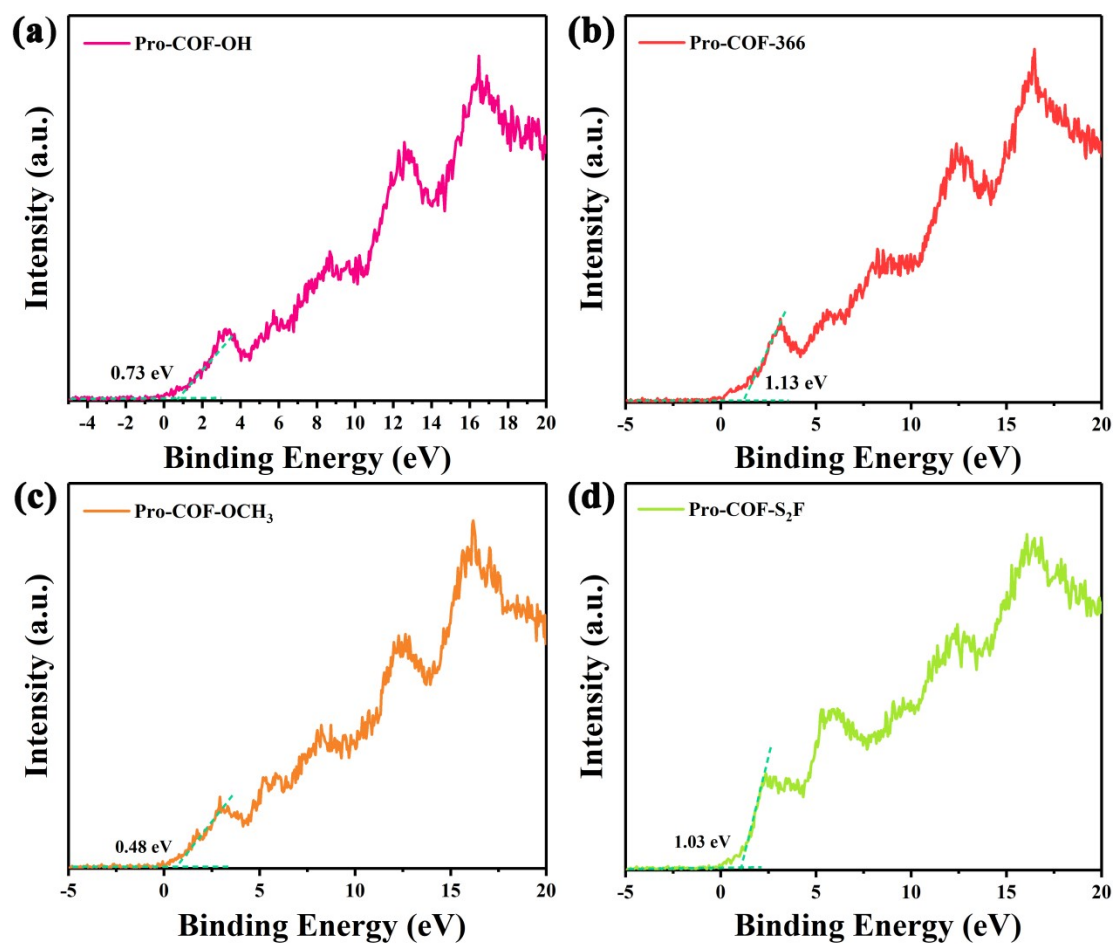
**Fig. S14** In situ FT-IR spectra of M@C-Br-1 at different time in the region of 3200-4000  $\text{cm}^{-1}$ .

## 2.15 Figure S15



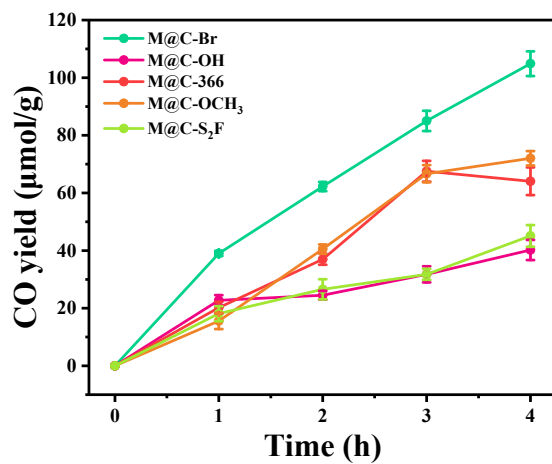
**Fig. S15** UV-vis DRS of (a, b) different COFs and (d, e) different hybrid materials,  $(Ah\nu)^2$  with photon energy ( $h\nu$ ) graph of the relationship of change of (c) different COFs and (f) different hybrid materials.

## 2.16 Figure S16



**Fig. S16** The XPS valence band spectrum of (a) Pro-COF-OH, (b) Pro-COF-366, (c) Pro-COF-OCH<sub>3</sub>, and (d) Pro-COF-S<sub>2</sub>F.

## 2.17 Figure S17



**Fig. S17** Conversion of CO<sub>2</sub> to CO as a function of the time of the five different hybrid materials.

## 2.18 Table S1

**Table S1** Porous parameters of Zr-MOF, Pro-COF-Br, and M@C-Br-(1~4).

Samples	$S_{\text{BET}}^a$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$S_{\text{micro}}^b$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_{\text{total}}^c$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$V_{\text{micro}}^d$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Pore size (nm)
Zr-MOF	667	532	0.54	0.21	0.59/0.68/1.27
Pro-COF-Br	1174	719	1.03	0.28	1.18/1.86
M@C-Br-1	922	663	0.57	0.26	0.73/1.18/1.86
M@C-Br-2	1294	924	0.91	0.35	0.73/1.18/1.86
M@C-Br-3	1091	709	0.72	0.28	0.73/1.18/1.86
M@C-Br-4	1181	884	0.83	0.34	0.73/1.18/1.86

<sup>a</sup> The  $S_{\text{BET}}$  was calculated by using the BET model. <sup>b</sup> The  $S_{\text{micro}}$  ( $d < 2$  nm) was calculated by using the NLDFT method. <sup>c</sup> The  $V_{\text{total}}$  was calculated at  $P/P_0 = 0.99$ . <sup>d</sup> The  $V_{\text{micro}}$  ( $d < 2$  nm) was calculated by using NLDFT model.

## 2.19 Table S2

**Table S2** Summary of COFs and MOFs-based photocatalysts for CO<sub>2</sub> reduction.

Samples	Light	Condition	Products ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	Ref.
M@C-Br-1	300 W Xe lamp With (320-780 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (106.35) CH <sub>4</sub> (15.51)	This work
Zr-MOF	300 W Xe lamp With (320-780 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (40.65) CH <sub>4</sub> (12.62)	This work
COF-OH	300 W Xe lamp With (320-780 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (33.21) CH <sub>4</sub> (6.49)	This work
MTCN-H (ys)	300 W Xe lamp With (300-1200 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (67.48)	2
TAPBB-COF	Xe lamp With (200-1000 nm)	CO <sub>2</sub> /H <sub>2</sub> O 12 h	CO (295.2)	3
Mo-COF	300 W Xenon lamp With $\lambda \geq 420$ nm	CO <sub>2</sub> /H <sub>2</sub> O, 2 h	CO (6.19) CH <sub>4</sub> (1.08) C <sub>2</sub> H <sub>4</sub> (3.57)	4
COF-318-TiO <sub>2</sub>	300 W Xenon lamp With (380-800 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (278.67)	5
TiO <sub>2</sub> -INA@CuP-Ph COF	300W Xe Lamp With (350-780 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 1 h	CO (50.50)	6
Mn-TCPP	300W Xe Lamp With (350-780 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 4 h	CO (84.00) CH <sub>4</sub> (212.00)	7
PCN-601	300W Xe Lamp With $\lambda \geq 410$ nm	CO <sub>2</sub> /H <sub>2</sub> O, 10 h	CH <sub>4</sub> (100.1)	8
CsPbBr <sub>3</sub> QDs/UiO-66(NH <sub>2</sub> )	300 W Xe lamp With (420-800 nm)	CO <sub>2</sub> /H <sub>2</sub> O, 12 h	CO (3.12) CH <sub>4</sub> (98.52)	9
Bi <sub>2</sub> S <sub>3</sub> /UiO-66	The PLS-SXE300 Xe lamp	CO <sub>2</sub> /H <sub>2</sub> O, 3 h	CO (76.8)	10

## 2.20 Table S3

**Table S3** Parameters related to the carrier lifetime of the Zr-MOF, Pro-COF-Br, and M@C-Br-1.

Samples	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_{\text{average}}$ (ns)	$\chi_2$
Zr-MOF	9.62	1016.75	941.52	1.232
Pro-COF-Br	0.42	2.36	53.70	1.272
M@C-Br-1	0.53	1.92	64.76	1.152



## 2.21 Table S4

**Table S4** The values of Zeta-potential of polymers.

Sample	Zeta-potential (mV)
Zr-MOF	-13.02
Por-COF-Br	-31.35
Pro-COF-OH	-28.64
Pro-COF-366	-20.85
Pro-COF-OCH <sub>3</sub>	-16.85
Pro-COF-S <sub>2</sub> F	-22.99
M@C-Br	-25.62
M@C-OH	-16.10
M@C-OCH <sub>3</sub>	-19.69
M@C-366	-13.52
M@C-S <sub>2</sub> F	-18.77

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