

Supporting Information

A metal-free covalent organic framework as photocatalyst for CO₂ reduction at low concentration of CO₂ in gas-solid system

Jin-Xian Cui,^a Lu-Jie Wang,^a Liu Feng,^b Bo Meng,^{*a} Zi-Yan Zhou,^{*a} Zhong-Min Su,^c

Kai Wang^d and Shao-Min Liu^{*d}

^a *College of Chemistry and Chemical Engineering, Shandong University of
Technology, Zibo, 255000 Shandong, China.*

E-mail: mb1963@126.com; zyzhou@sdut.edu.cn.

^b *Analytical Testing Center, Shandong University of Technology, Zibo, 255000
Shandong, China.*

^c *School of Chemistry and Environmental Engineering, Changchun University of
Science and Technology, Changchun, 130022 Jilin, China.*

^d *Department of Chemical Engineering, Curtin University, Perth 6102, Australia. E-
mail: shaomin.liu@curtin.edu.au.*

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1. Materials and methods

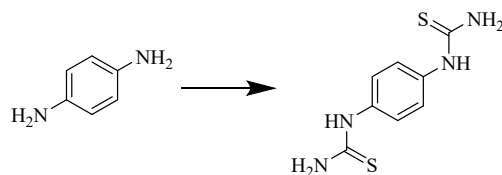
All chemicals with analytical purity were obtained commercially and used directly without further purification. Phloroglucinol and *p*-phenylenediamine were purchased from SAAN Chemical Technology (Shanghai) Co., Ltd. Trifluoroacetic acid and 1,4-dioxane were bought from Tianjin Guangfu Chemical Reagent Co., Ltd. Ammonium thiocyanate, methanol, dichloromethane, magnesium sulphate (MgSO₄), mesitylene and glacial acetic acid were obtained from Tianjin kemeo Chemical Reagent Co., Ltd. Trichloromethane was purchased from Sinopharm Chemical Reagent Co., Ltd.

Fourier Transform Infrared (FT-IR) spectra were carried out on a Thermo Nicolet 5700 using KBr pellet in the range of 4000-500 cm⁻¹. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advance diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) and the radiation was in the range of 2-35°. The simulation of COF was performed using Materials Studio software with spin-polarized DFT/GGA, where the PBE exchange-related functions were implemented in DMol3 (package). The simulation of X-ray diffraction pattern of COF was obtained with a reflect tools. Transmission electron microscope (TEM) images were recorded on a JEM-2010 at an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images were performed on XL-30 ESEM-FEG. The elemental mappings of the samples were determined by EDX equipped on SEM with the type of Genesis 2000. Nitrogen or carbon dioxide adsorption-desorption isotherms were detected using an automatic volumetric adsorption apparatus (ASIQM0G002-3) after the samples were

degassed at 393 K for 10 h. Brunauer-Emmett-Teller (BET) specific surface areas and DFT pore size distribution were obtained from the adsorption-desorption data. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 2500 thermal analyzer at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen flow. UV-vis absorption spectra were conducted using a UV-2550 spectrophotometer (Shimadzu, Japan). The photoluminescence (PL) spectra were measured by an F-380 spectrophotometer with an excitation wavelength at 380 nm. All calculations were performed using the Gaussian 16 package.

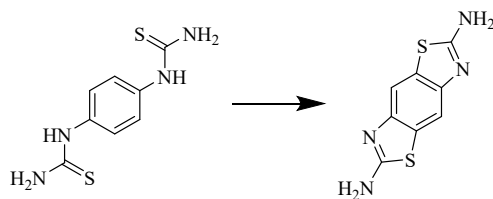
2. Synthetic procedures

2.1 Synthesis of 1,4-phenylenebis(thiourea)



p-phenylenediamine (1.7 g, 15.7 mmol), activated carbon (1 g) and 3 mol·L⁻¹ hydrochloric acid (12 mL, 36 mmol) were added in a 100 mL three-necked flask. After being refluxed for 20 min, the mixture was filtered and the filtrate was removed into another 100 mL three-necked flask with ammonium thiocyanate (4.84 g, 63.6 mmol). After being heating at 95°C for 24 h, the solid product was collected by filtration and dried at 30°C in vacuum overnight. Yield: 74.9%.

2.2 Synthesis of 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole (Bb-NH₂)



1,4-Phenylenebis(thiourea) (2 g, 8.9 mmol) and trichloromethane (10 mL) were added into a 100 mL three-necked flask. After ultrasonic mixing, trichloromethane solution (10 mL) containing liquid bromine (1.05 mL, 20.5 mmol) was slowly added into the mixture through a long neck funnel under stirring conditions, the temperature of the mixture was kept within 40°C. The suspension was stirred at room temperature for 12 h and refluxed for 24 h, then filtered and washed with trichloromethane (20 mL) for 4 times. The obtained solid and 20% sodium hydrogen sulfite solution (20 mL) were added into a 250 mL three-necked flask and stirred at 90°C. After filtration,

the solid and 4 mol·L⁻¹ hydrochloric acid (25 mL, 100 mmol) were mixed and heated for 30 min. After filtration, the filtrate was neutralized with aqueous ammonia to pH = 7. The suspension was filtered and washed twice with methanol (20 mL) and ether (10 mL) respectively. The obtained solid was dried in vacuum at 35°C. Yield: 71%. ¹H NMR (600 MHz, DMSO-d₆) δ (ppm): 7.604 (2H, s, Ar-H), 7.260 (4H, s, NH₂) (Figure S1).

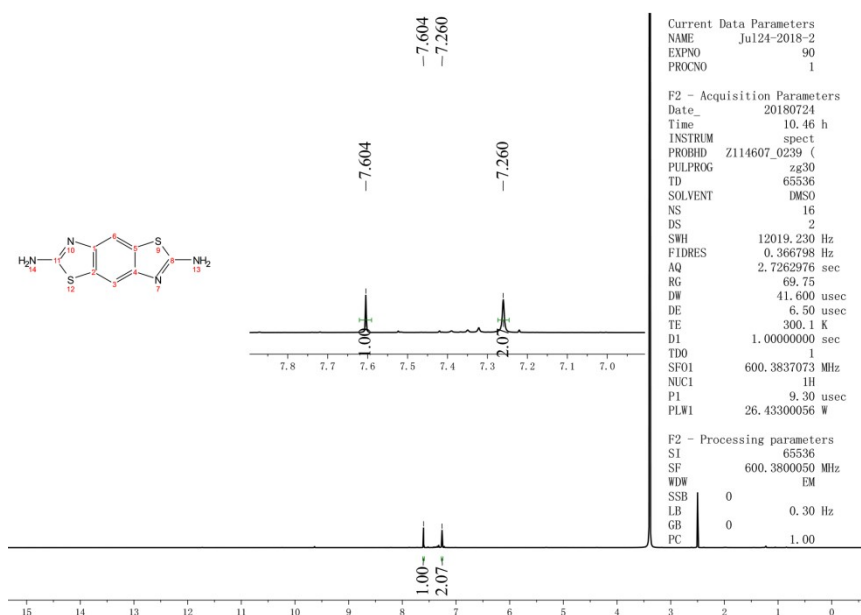
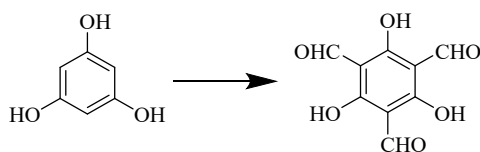


Fig. S1 ¹H NMR spectrum of Bb-NH₂.

2.3 Synthesis of 2,4,6-triformylphloroglucinol (Tp-CHO)



Phloroglucinol (2.03 g, 16.3 mmol), hexamethylenetetramine (5.03 g, 36 mmol) and trifluoroacetic acid (30 mL) were mixed in a 250 mL three-necked flask and refluxed for 3 h under N₂ atmosphere, and then 3 mol·L⁻¹ hydrochloric acid (50 mL) was added into the mixture and the reaction continued for 2 h. The reaction mixture was cooled to room temperature and filtrated, and then the filtrate was extracted with

dichloromethane (30 mL) for 5 times. The obtained organic phase was dried with anhydrous MgSO_4 and filtrated, then the filtrate was dried by rotary evaporator to obtain faint yellow solid. Yield: 14%. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 10.155 (s, 3H), 14.119 (s, 3H) (Figure S2).

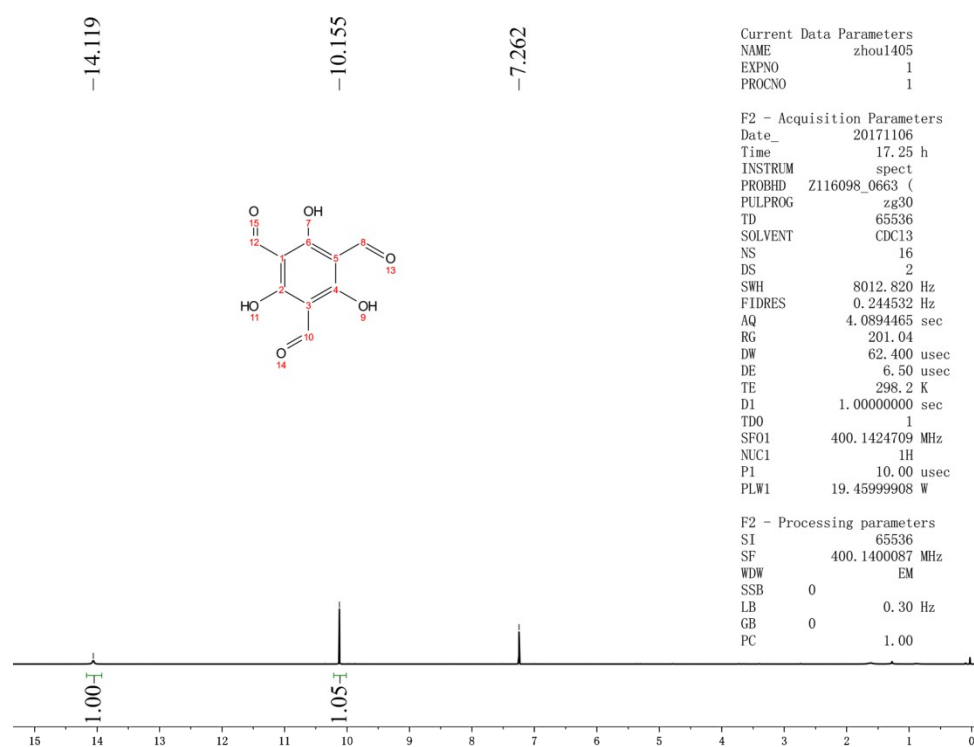


Fig. S2 ^1H NMR spectrum of Tp-CHO.

2.4 Synthesis of TpBb-COF

TpBb-COF was synthesized by the previously reported method with modification.¹ A glass tube of 25 mL measuring 10×300 mm (o.d \times length) was charged with Bb- NH_2 (66 mg, 0.3 mmol), Tp-CHO (42 mg, 0.2 mmol), 1,4-dioxane (3 mL), mesitylene (1 mL) and 6 M glacial acetic acid (0.4 mL). The mixture was sonicated for 30 min and then flash frozen in a liquid nitrogen bath at 77 K. After three freeze-pump-thaw cycles, the tube was sealed under vacuum and heated at 120°C for 72 h under stationary condition. The precipitate at the bottom of the tube

obtained from the reaction was collected by filtration, and then washed with dichloromethane and acetone, respectively. Finally, the product was dried at 100°C under vacuum for 24 h to obtain a red solid as activated TpBb-COF.

2.5 Synthesis of COF-TpPa-1

The synthesis of COF-TpPa-1 was carried out using a previously reported method with slight modification.² A 25 mL glass tube measuring 10 × 300 mm (o.d. × length) was charged with p-phenylenediamine (32 mg, 0.3 mmol), Tp-CHO (42 mg, 0.2 mmol), 1,4-dioxane (1.5 mL), mesitylene (1.5 mL) and 6 M glacial acetic acid (0.4 mL). The mixture was sonicated for 30 min, and then the tube was flash frozen at 77 K (liquid N₂ bath). After three freeze-pump-thaw cycles, the system evacuated to vacuum and sealed. The mixture was warmed to room temperature then heated at 120°C and left undisturbed for 72 h. The precipitate was collected by filtration and subsequently washed by dichloromethane and acetone. Finally, the product was dried at 100°C under vacuum for 24 h to obtain a red powder as activated COF-TpPa-1.

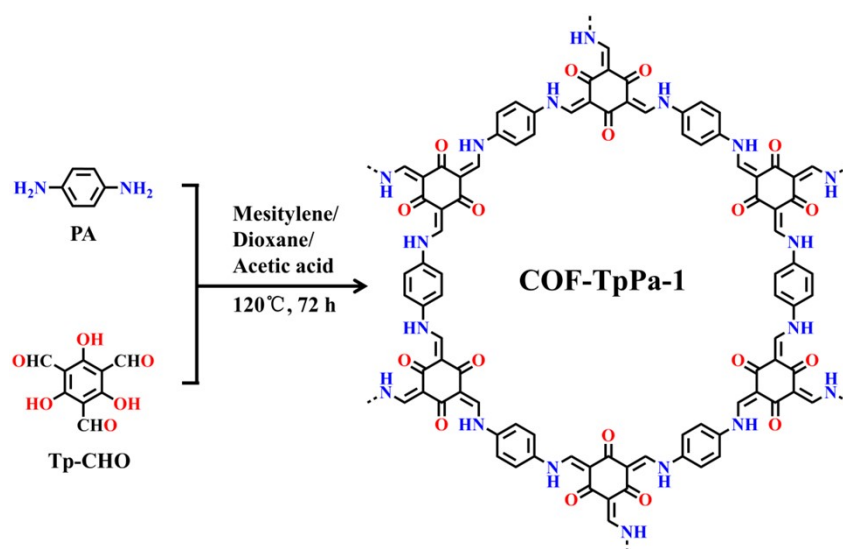


Fig. S3 Synthesis of COF-TpPa-1.

2.6 Synthesis of g-C₃N₄

The synthesis of g-C₃N₄ was carried out using a previously reported method with slight modification.^{3,4} The urea powder (10 g) was placed in a covered alumina crucible and heated to 550°C at a heating rate of 2.5°C·min⁻¹ in a muffle furnace. The temperature was maintained for 4 h and then cooled to 25°C to obtain pure g-C₃N₄.

3. Electrochemical measurements

Electrochemical measurements were performed in 0.2 M sodium sulfate solution on an electrochemical workstation (CHI 760e, China) using a three-electrode system. A platinum electrode and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The preparation of the working electrodes were as follows: A mixture of 1 mL of photocatalyst (2 mg), 5% Nafion suspension (10 μ L) and ethanol (1 mL) was sonicated for 1 h, and then dropped onto a piece of indium tin oxide (ITO) conductive glass measuring 1 \times 3 cm². The photocurrent measurements were conducted with a 40 W LED as a light source.

4. Photocatalytic measurements

The catalyst (1 mg) was uniformly dispersed in 2 mL of ethanol through sonication, and then dropped evenly onto a piece of glass measuring $1 \times 3 \text{ cm}^2$. The prepared sample was dried in vacuum at 100°C for 12 h and then placed in a reactor containing $200 \mu\text{L}$ deionized water. The reactor was thoroughly degassed and then backfilled with certain gas (pure CO_2 or diluted CO_2). CO_2 was diluted by injecting a certain volume of high-purity N_2 and CO_2 into a gas sampling bag by a high-capacity syringe for thorough mixing. Water vapor was introduced into the reactor through bubbling in the process of gas charging, the system was filled with saturated water vapor. In order to prevent the shortage of saturated water vapor, the additional $200 \mu\text{L}$ deionized water was added in advance. The light source was a PAR30 white LED with power of 40 W and color temperature of 6000 K with a cutoff filter ($\lambda \geq 420 \text{ nm}$). The constant temperature water circulation device was used to control the reaction temperature. After light irradiation, the gas products were detected by gas chromatography (GC-1120). CO was quantified with FID detector using TDX-01 column; H_2 and O_2 were quantified with TCD detector using 5 \AA molecular sieve column. The data were obtained through repeated experiments.

5. Determination of apparent quantum efficiency (AQE)

TpBb-COF (10 mg) was uniformly dispersed in 2 mL of ethanol through sonication, and then dropped evenly onto a piece of ITO conductive glass measuring $1 \times 3 \text{ cm}^2$. The light source was a PAR30 white LED with power of 40 W and color temperature of 6000 K with a cutoff filter ($\lambda^0 = 420 \text{ nm}$). The FZ-A radiometer was used to measure the average intensity of incident illumination ($10.85 \text{ mW}\cdot\text{cm}^{-2}$). The number of incident photons (N) is 2.48×10^{20} calculated by equation (1).

$$N = \frac{E\lambda}{hc} = \frac{10.85 \times 3 \times 3600 \times 1 \times 420 \times 10^{-12}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 2.48 \times 10^{20} \quad (1)$$

Where, h is the Planck constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), c is the speed of light ($3 \times 10^8 \text{ m}\cdot\text{s}^{-1}$), λ is the wavelength of light (m).

In pure CO_2 , the amount of CO molecules generated in 1 h was $3.97 \times 10^{-2} \mu\text{mol}$.

The apparent quantum efficiency is 0.01927% calculated by equation (2).

$$\begin{aligned} \text{AQE}_1 &= \frac{2 \times \text{the number of evolved syngas molecules}}{\text{the number of incident photons}} \\ &= \frac{2 \times 3.97 \times 10^{-8} \times 6.02 \times 10^{23}}{2.48 \times 10^{20}} \times 100\% \\ &= 0.01927\% \end{aligned} \quad (2)$$

In 30% CO_2 , the amount of CO molecules generated in 1 h was $6.35 \times 10^{-2} \mu\text{mol}$.

The apparent quantum efficiency is 0.03083% calculated by equation (3).

$$\begin{aligned} \text{AQE}_2 &= \frac{2 \times \text{the number of evolved syngas molecules}}{\text{the number of incident photons}} \\ &= \frac{2 \times 6.35 \times 10^{-8} \times 6.02 \times 10^{23}}{2.48 \times 10^{20}} \times 100\% \\ &= 0.03083\% \end{aligned} \quad (3)$$

6. Supplementary figures

6.1 Structural modeling

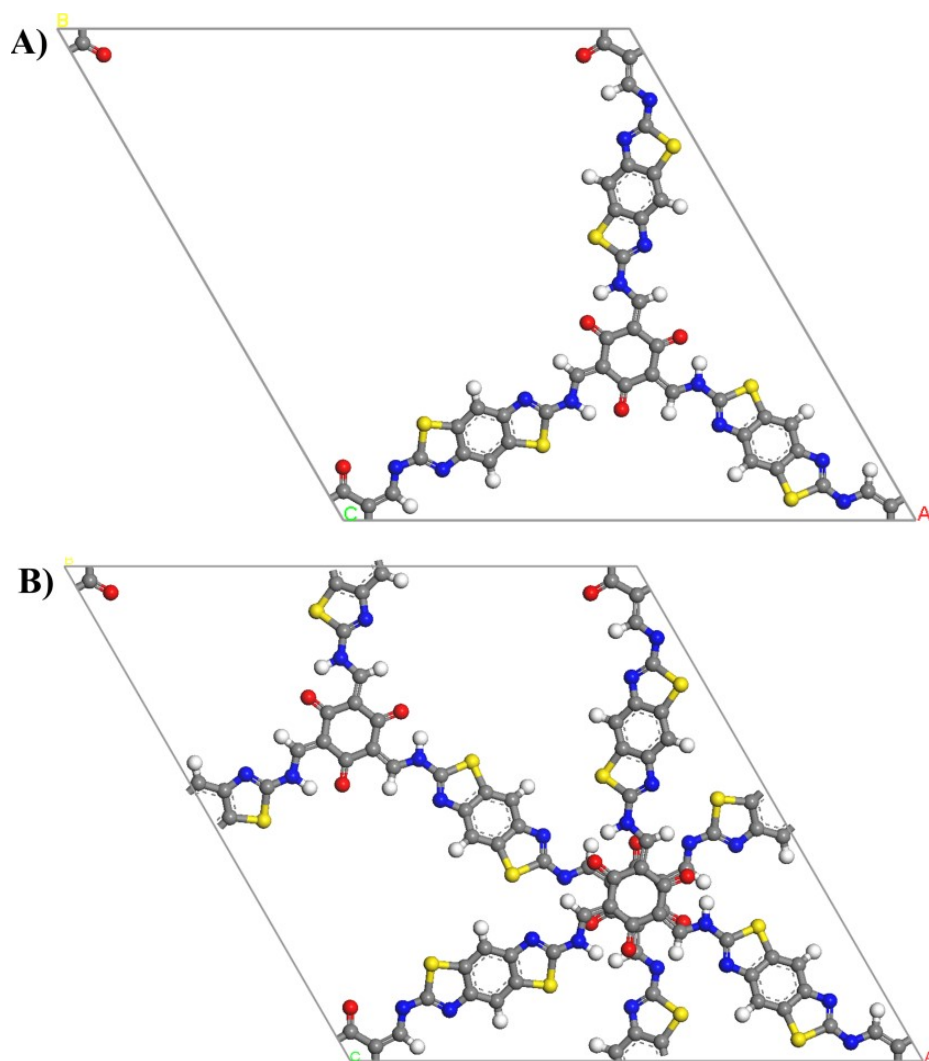


Fig. S4 Crystal structure models of TpBb-COF (a) AA-stacking model (space group P3, $a = b = 28.971 \text{ \AA}$, $c = 3.500 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$); (b) AB-stacking model (space group P3, $a = b = 28.971 \text{ \AA}$, $c = 10.500 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$).

6.2 Elemental mapping images

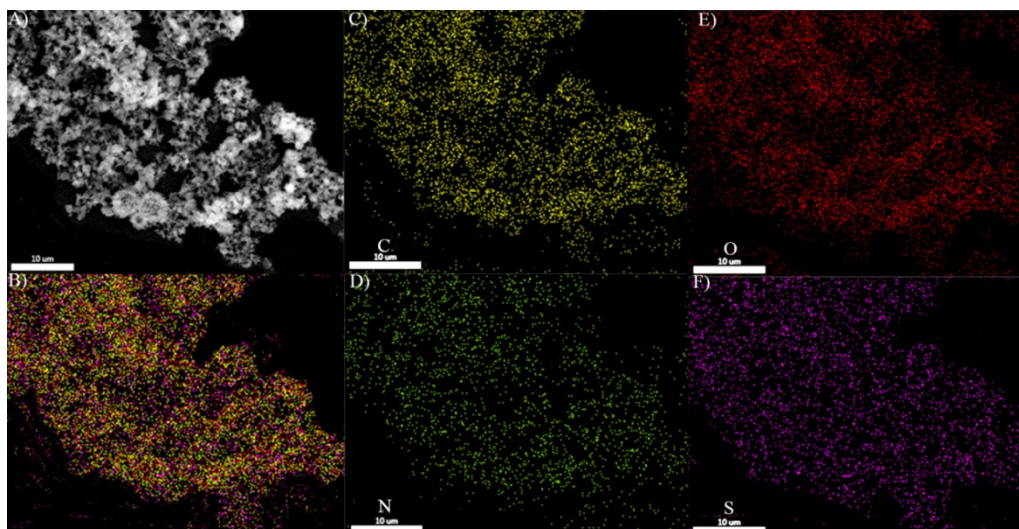


Fig. S5 Elemental mapping images of TpBb-COF.

6.3 Thermogravimetric analysis

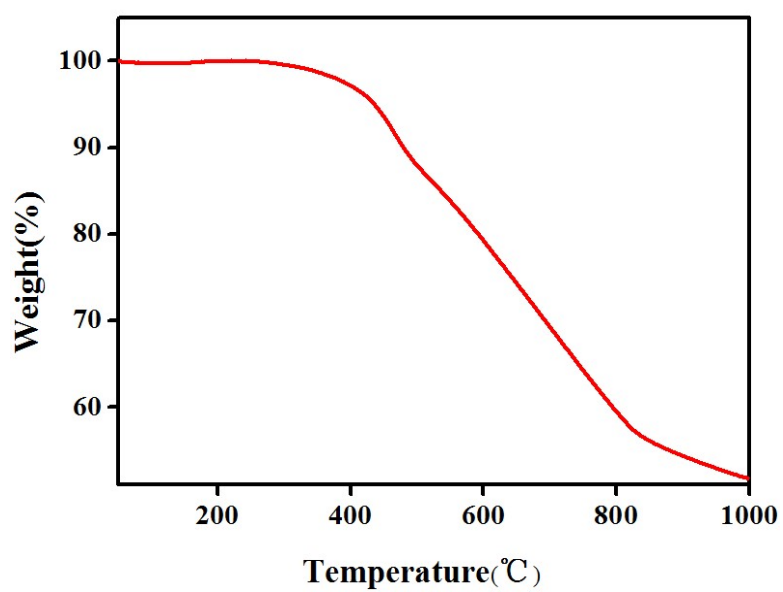


Fig. S6 TGA for TpBb-COF.

6.4 Porosity and specific surface area analysis

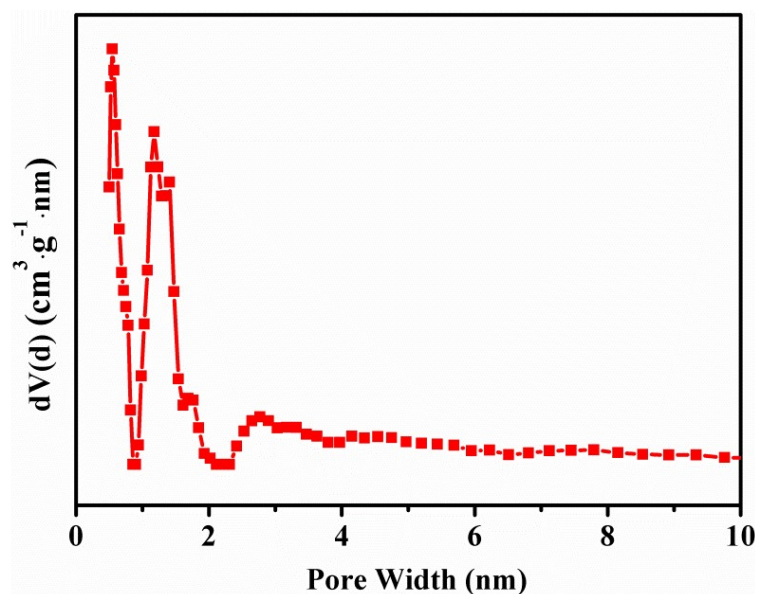


Fig. S7 Pore size distribution plot of TpBb-COF.

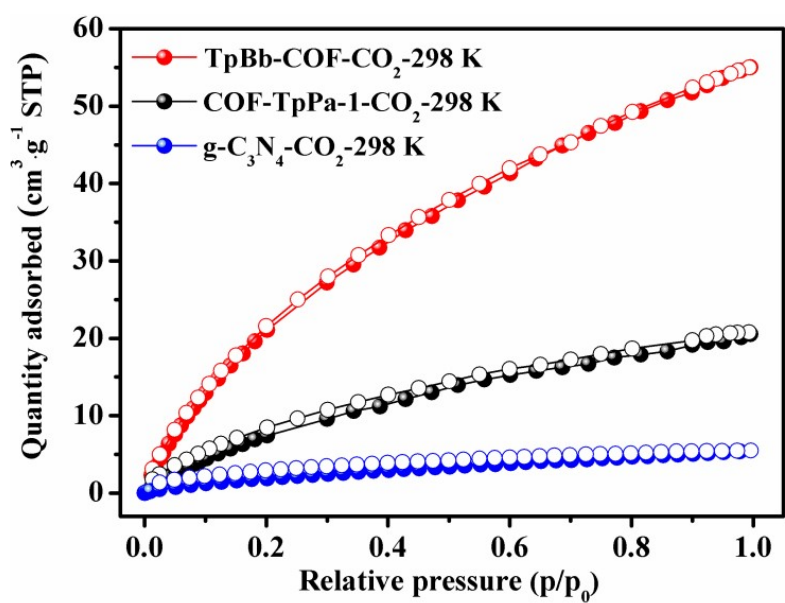


Fig. S8 CO₂ adsorption-desorption isotherms of TpBb-COF, COF-TpPa-1 and g-C₃N₄ at 298K.

6.5 Mott-Schottky plots

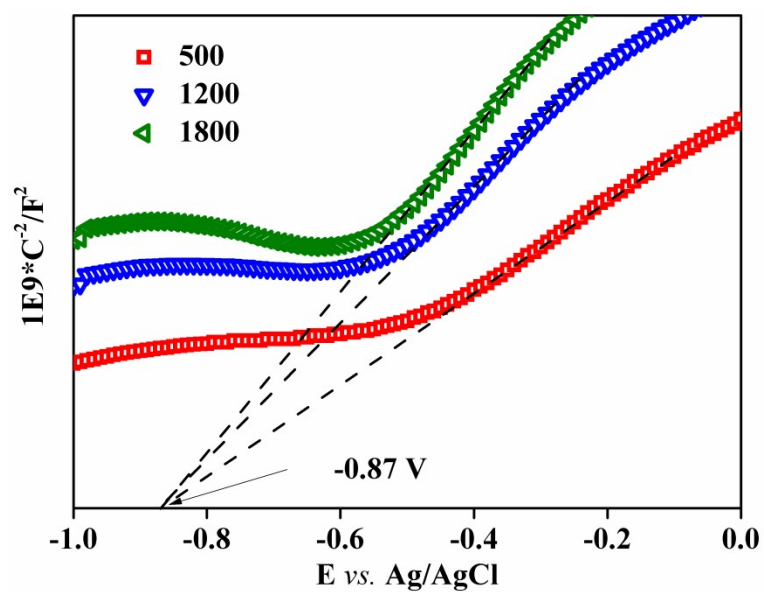


Fig. S9 Mott-Schottky plots of COF-TpPa-1.

6.6 Stability test

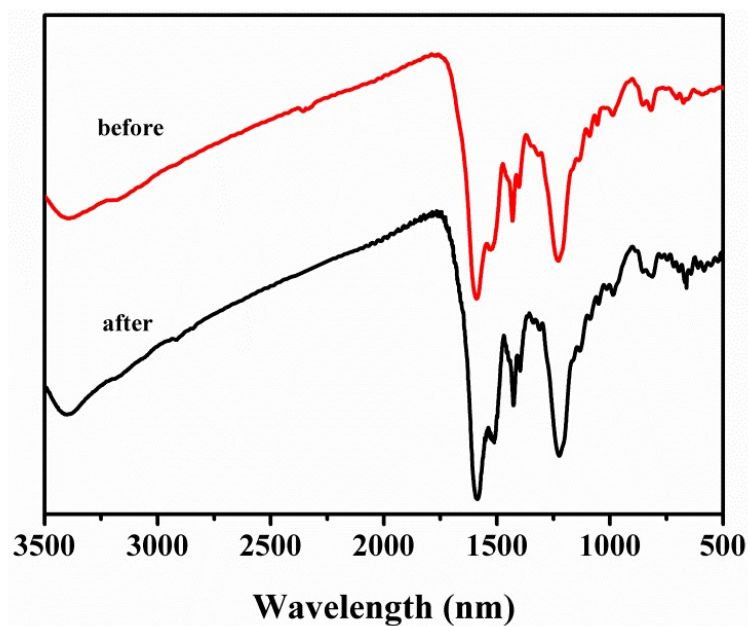


Fig. S10 FT-IR spectra of TpBb-COF after 36 h of continuous reaction.

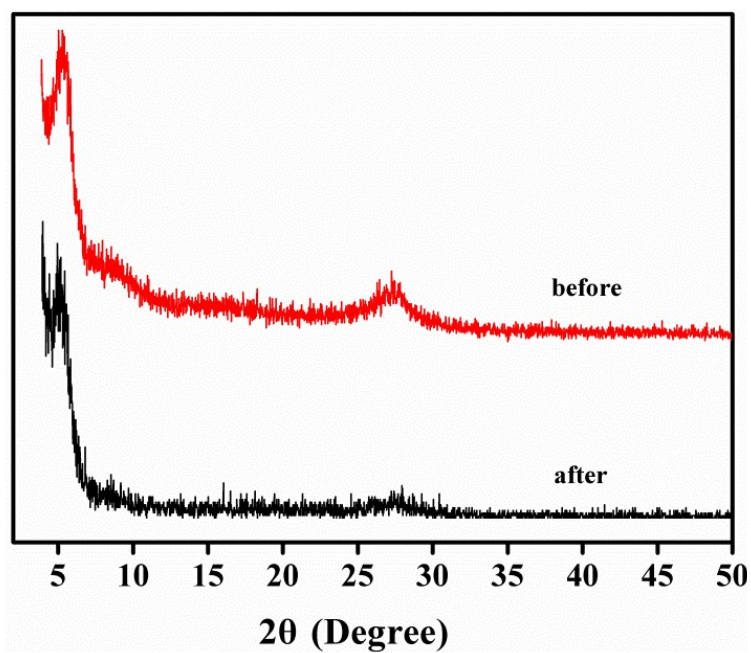


Fig. S11 PXRD of TpBb-COF after 36 h of continuous reaction.

6.7 Isotopic labeling experiment

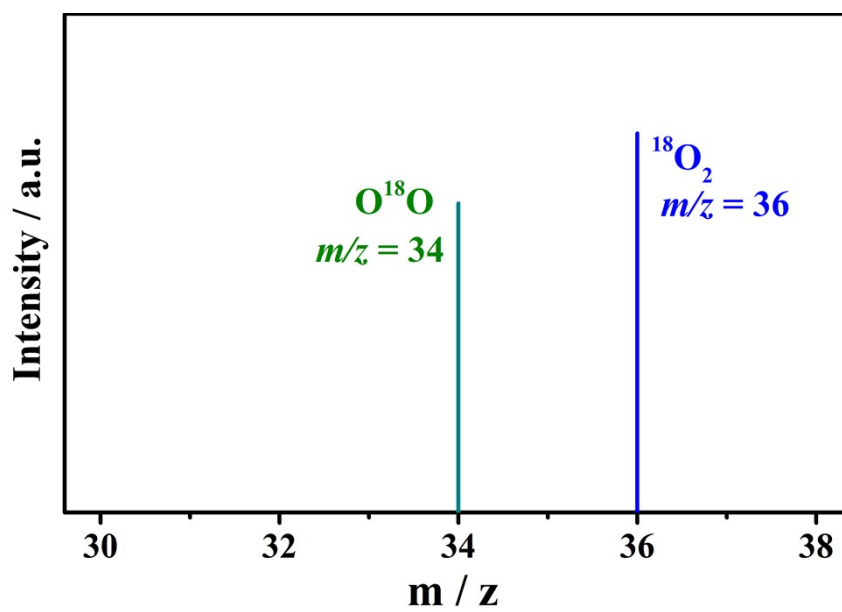


Fig. S12 Mass spectroscopy of $O^{18}O$ ($m/z = 34$) and $^{18}O_2$ ($m/z = 36$) produced from the photocatalytic reaction.

7. Density functional theory (DFT) calculations

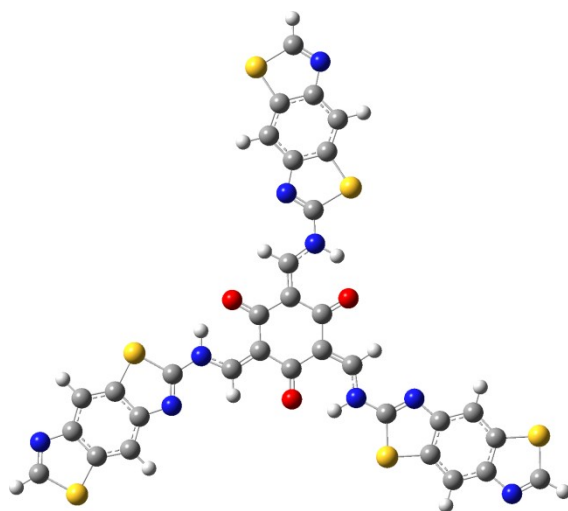


Fig. S13 Computational model for TpBb-COF. Carbon (grey), Nitrogen (blue), Hydrogen (white), Oxygen (red) and Sulfur (yellow).

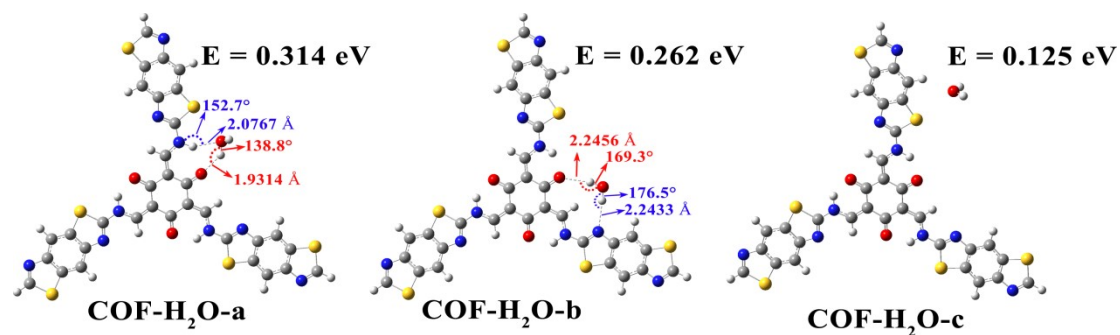


Fig. S14 Adsorption schematic diagrams of H₂O at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

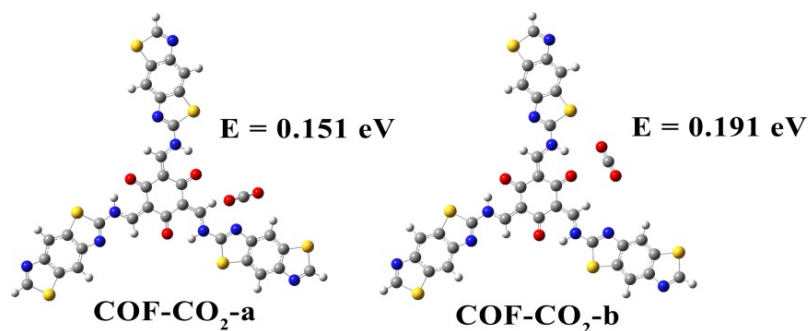


Fig. S15 Adsorption schematic diagrams of CO₂ at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

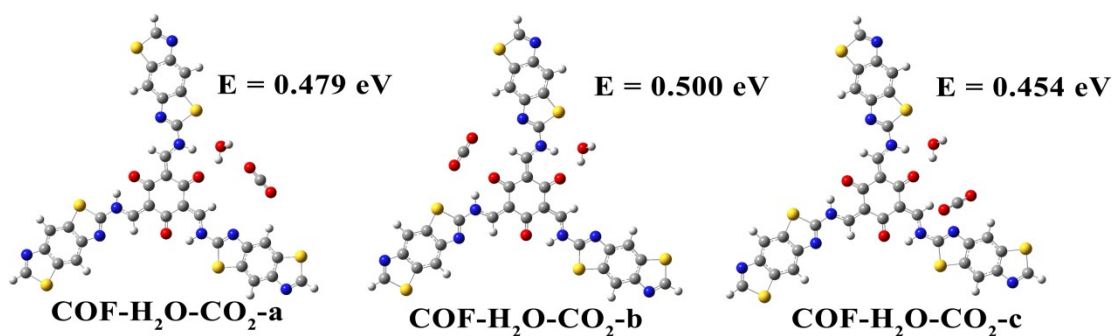


Fig. S16 Adsorption schematic diagrams of H₂O-CO₂ at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

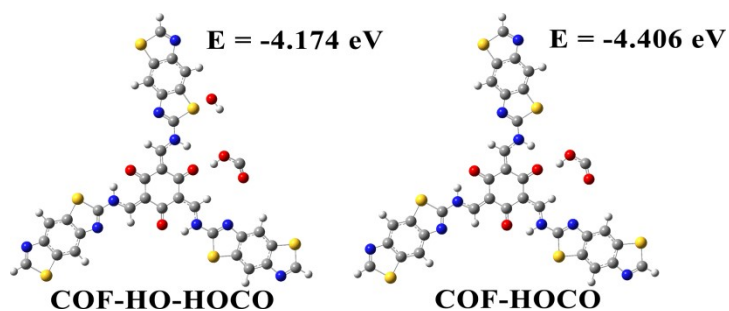


Fig. S17 Adsorption schematic diagrams of HO-HOCO and HOCO at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

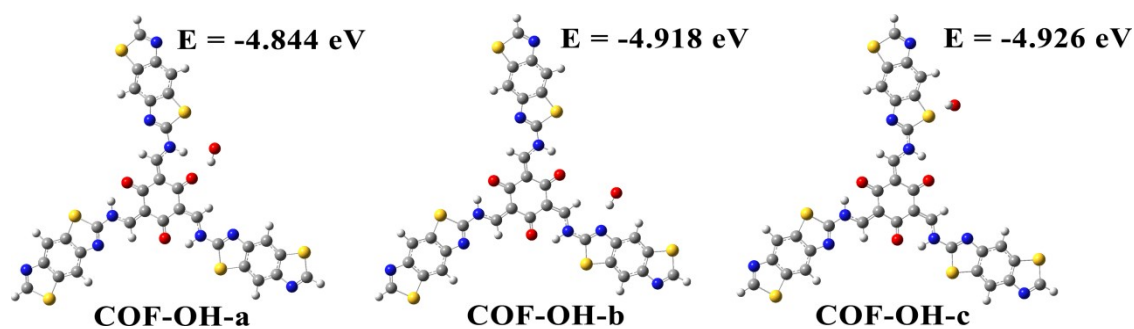


Fig. S18 Adsorption schematic diagrams of OH at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

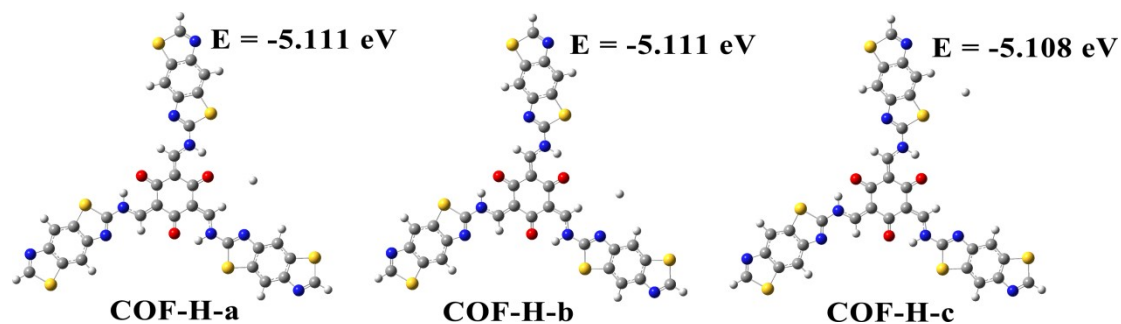


Fig. S19 Adsorption schematic diagrams of H at different sites on TpBb-COF. Carbon (grey), Nitrogen (blue), Oxygen (red) and Sulfur (yellow).

8. References

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