

## *Supporting Information*

### **Application of fully conjugated covalent organic frameworks containing alkyne groups to the performance of photocatalytic CO<sub>2</sub> reduction**

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## 1. Materials and general procedures

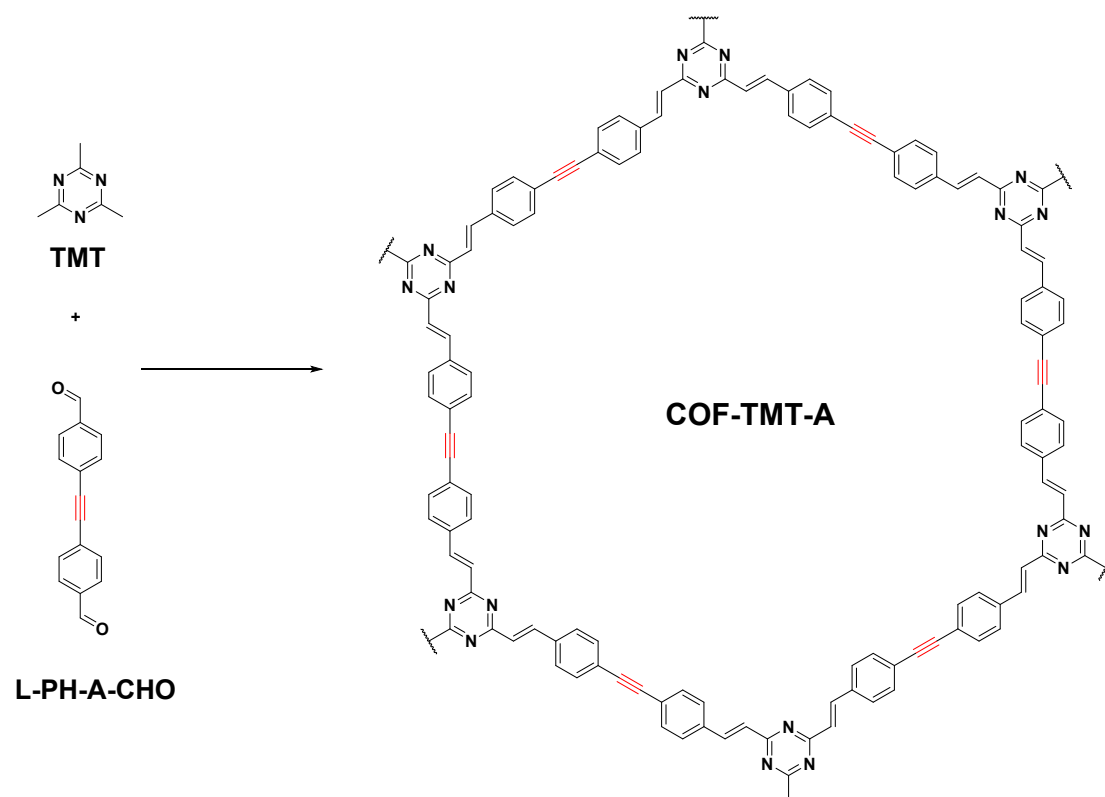
All reagents and starting materials were obtained from commercial sources and no further purification was required.

## 2. Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded using a RIGAKU D/MAX 2550/PC with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), at a scan speed of  $1^\circ \text{ min}^{-1}$  and a step size of  $0.02^\circ$  in  $2\theta$ . Fourier infrared (FT-IR) spectra were measured using a Fourier infrared (FT-IR) spectrometer model Bruker-Tensor 27 from Bruker, Germany. The UV absorption spectra were measured by a model UV2600 from Shimadzu Corporation, Japan. Thermogravimetric analysis (TGA) was performed in an air atmosphere using US-PE STA6000 with a heating rate of  $10 \text{ K}\cdot\text{min}^{-1}$ .  $\text{N}_2$  isotherms and specific surface areas were determined at  $77 \text{ K}$  using a microcrystalline ASAP 2460 automated system with a Brunauer-Emmett-Taylor (BET) model, and samples were degassed in vacuum ( $<1 \times 10^{-5} \text{ bar}$ ) at  $100 \text{ }^\circ\text{C}$  for 8 h, followed by  $\text{N}_2$  physisorption. The  $^{13}\text{C}$  solid-state NMR was measured by a Bruker AVANCE III 600 NMR instrument (TMS as internal standard). Steady-state photoluminescence (PL) spectra were measured using an Edinburgh FL/FS900 spectrophotometer. Scanning electron microscopy was measured by Hitachi model S4800. Electrochemical impedance spectroscopy (EIS), photocurrent ( $i\sim t$ ), Mott-Schottky curves (M-S) and other electrochemical tests were performed on an electrochemical workstation (CHI660E, Shanghai, China).

### 3.Synthesis

#### 3.1 Synthesis of COF-TMT-A



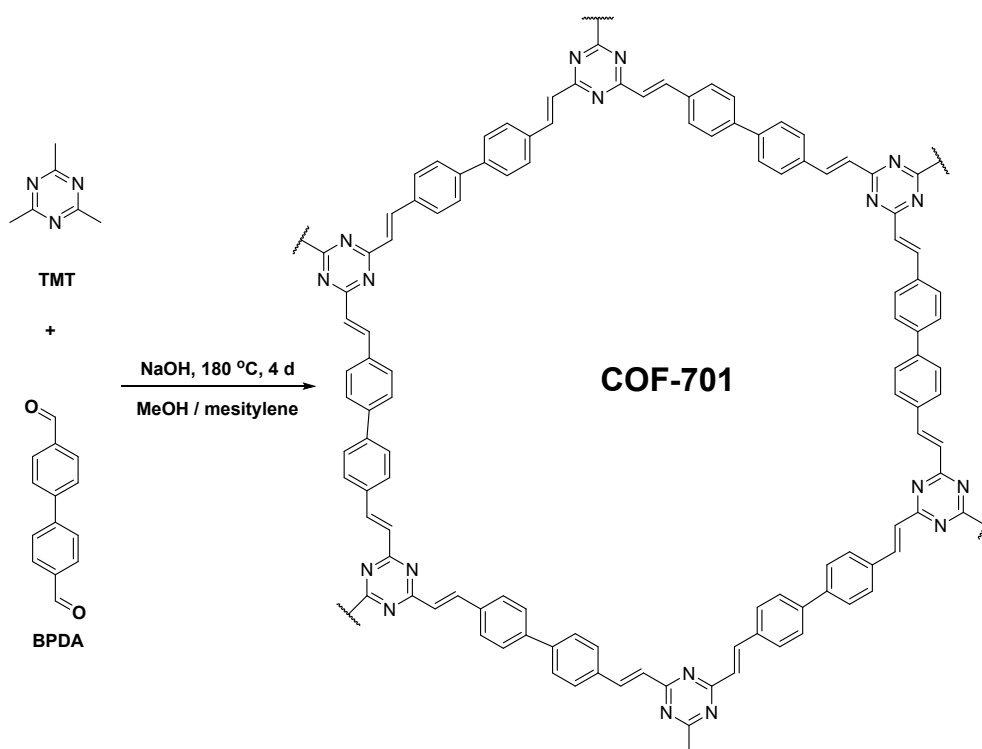
**Fig.S1.** Synthesis of COF-TMT-A

Base catalysis: 2,4,6-trimethyl-1,3,5-triazine (TMT, 24.6 mg, 0.2 mmol), 1,2-di(4'-formylphenyl)acetylene (L-PH-A-CHO, 70 mg, 0.3 mmol), sodium hydroxide (35 mg), methanol (2 mL), and trimethylbenzene (14 mL) were added to a Teflon-lined autoclave (23 mL). toluene (14 mL). The autoclave was sealed and placed in a preheated 180 °C oven for 4 days. After the reaction was completed, the autoclave was cooled and the precipitate formed was collected by filtration and washed three times with water, methanol and acetone in turn, and dried under vacuum at 100 °C to obtain 70 mg of fluffy yellow solid powder as COF-TMT-A in 74% yield.

Acid catalysis: 2,4,6-trimethyl-1,3,5-triazine (TMT, 6 mg, 0.049 mmol), 1,2-di(4'-formylphenyl)acetylene (L-PH-A-CHO, 34 mg, 0.147 mmol), 0.45 mL of 1,4-dioxane, 0.45 mL of trimethylbenzene, 0.2 mL of trifluoroacetic acid (TFA) and 0.025 mL of anhydrous acetonitrile were weighed into 10 mL ampoules. Add 0.025 mL anhydrous acetonitrile to 10 mL ampoule, sonicate for 15 minutes, then freeze the ampoule under liquid nitrogen and pump it with oil. After the ampoule returned to room temperature, it was placed in an oven and heated to 150 °C for 72 h. After the reaction was completed, the precipitate was removed from the solution, filtered and washed with diluted ammonia, water, methanol and acetone in turn, and then dried in an oven under vacuum at 120 °C for 24 h to obtain 15 mg of yellow powder in 50%

yield.

### 3.2 Synthesis of COF-701



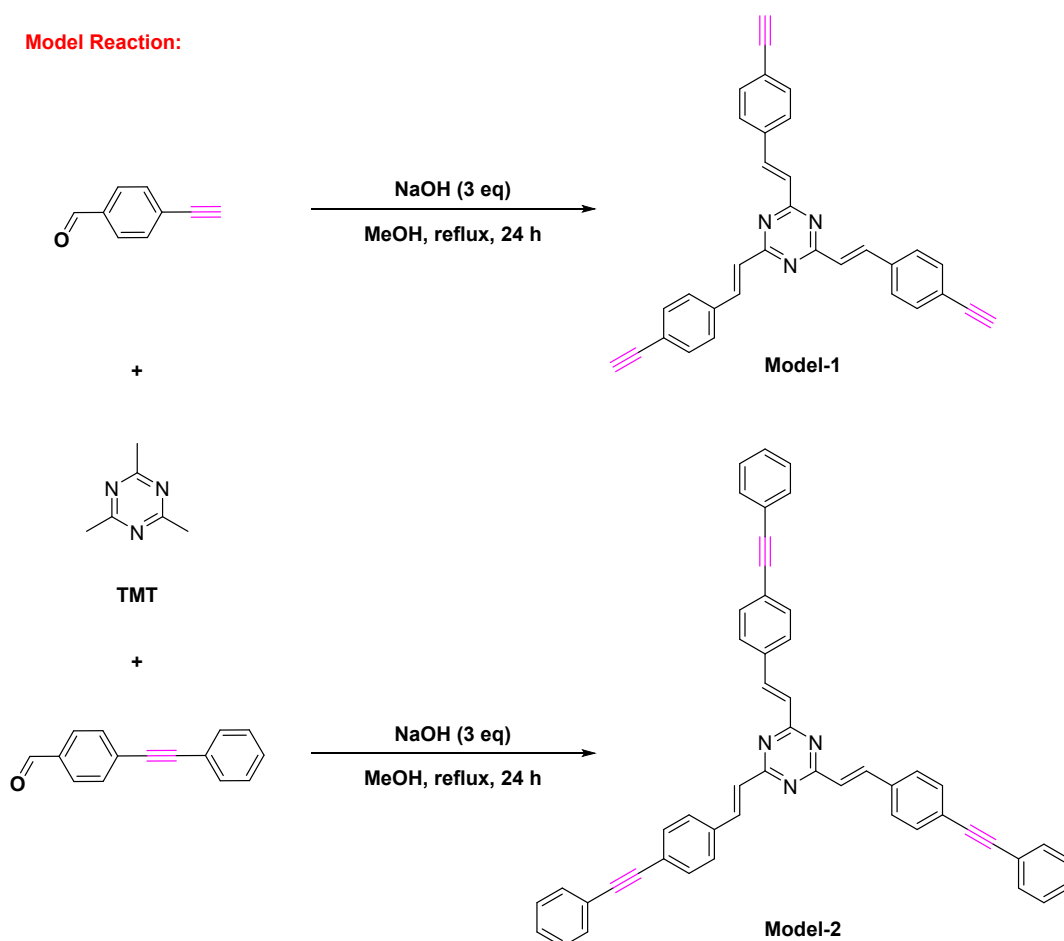
**Fig.S2.** Synthesis of COF-701

Base catalysis: 2,4,6-trimethyl-1,3,5-triazine (TMT, 24.6 mg, 0.2 mmol), 4,4'-Biphenyldicarboxaldehyde (BPDA, 63.1 mg, 0.3 mmol), sodium hydroxide (35 mg), methanol (2 mL), and trimethylbenzene (14 mL) were added to a Teflon-lined autoclave (23 mL). toluene (14 mL). The autoclave was sealed and placed in a preheated 180 ° C oven for 4 days. After the reaction was completed, the autoclave was cooled and the precipitate formed was collected by filtration and washed three times with water, methanol and acetone in turn, and dried under vacuum at 100 ° C to obtain 70 mg of fluffy yellow solid powder as COF-701 in 70% yield.

Acid catalysis: 2,4,6-trimethyl-1,3,5-triazine (TMT, 6 mg, 0.049 mmol), 4,4'-Biphenyldicarboxaldehyde (BPDA, 31 mg, 0.147 mmol), 0.45 mL of 1,4-dioxane, 0.45 mL of trimethylbenzene, 0.2 mL of trifluoroacetic acid (TFA) and 0.025 mL of anhydrous acetonitrile were weighed into 10 mL ampoules. Add 0.025 mL anhydrous acetonitrile to 10 mL ampoule, sonicate for 15 minutes, then freeze the ampoule under liquid nitrogen and pump it with oil. After the ampoule returned to room temperature, it was placed in an oven and heated to 150 ° C for 72 h. After the reaction was

completed, the precipitate was removed from the solution, filtered and washed with diluted ammonia, water, methanol and acetone in turn, and then dried in an oven under vacuum at 120 °C for 24 h to obtain 15 mg of yellow powder in 54% yield.

### 3.3 Model Reaction



**Fig.S3.** Model reaction

Synthesis of compound Model-1: 0.123 g of TMT (1 mmol) and 0.429 g of 4-ethynylbenzaldehyde (3.3 mmol) were added to 10 mL of anhydrous methanol solution. The reaction was heated and refluxed for 24 h under stirring conditions. After the completion of the reaction monitored by TLC, the product was filtered, washed with methanol, and dried to obtain a beige solid powder, which was compound Model-1, 0.380 g, and the yield was 83%. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.20 (m, 3H), 7.61 (m, 6H), 7.56-7.49 (m, 6H), 7.11 (m, 3H), 3.20 (d, J = 3.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.92, 140.81, 135.76, 132.64, 127.98, 126.99, 123.54, 83.35, 79.16.

Synthesis of compound Model-2: 0.123 g of TMT (1 mmol) and 0.680 g of 4-phenylethynylbenzaldehyde (3.3 mmol) were added to 10 mL of anhydrous methanol solution, and the reaction was heated and refluxed for 24 h under stirring

conditions. After the reaction was monitored by TLC, filtered, washed with methanol, and dried to obtain a yellow solid powder, which was compound Model-2, 0.450 g, yield 66%. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.21 (d, J = 15.9 Hz, 3H), 7.63 (d, J = 8.3 Hz, 6H), 7.59 -7.52 (m, 12H), 7.38 -7.33 (m, 9H), 7.11 (d, J= 15.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.00, 140.99, 135.16, 132.11, 131.70, 128.55, 128.43, 128.07, 126.67, 124.83, 123.04, 91.57, 89.25.

## 4. Photocatalytic Reactions

Photocatalytic reduction of CO<sub>2</sub>: Typically, the photocatalyst (50 mg) was homogeneously dispersed in 50 mL of a mixture of acetonitrile/TEOA (30:1) by magnetic stirring. During the reaction, the temperature was maintained at 15°C, CO<sub>2</sub> gas was continuously introduced and the solution was irradiated using a 300 W xenon lamp (Ceralux 300BF) equipped with a 400 nm cut-off filter lamp. The amount of possible products CO, CH<sub>4</sub>, HCOO<sup>-</sup> evaporated was measured every 2 hours using a chromatograph equipped with a thermal conductivity detector (SPSIC, GC-112AT, argon carrier). Control experiments were also carried out under the same experimental method under dark conditions, N<sub>2</sub> gas conditions, etc.

Photocatalysis Hydrogen decomposition of water: 10 mg of photocatalyst was dispersed in 34 mL of water and 4 mL of (10% V) TEOA and 0.0026 ml of H<sub>2</sub>PtCl<sub>6</sub> (3 wt% Pt) in a quartz reactor. 0.0026 ml H<sub>2</sub>PtCl<sub>6</sub> (3wt%Pt) was added as a precursor for the in situ generation of the platinum co-catalyst. Pt was used as a co-catalyst and triethanolamine (TEOA) as an electron donor (Fig. S14,15). The quartz reactor was degassed with a vacuum pump and then backfilled with N<sub>2</sub>. This process was repeated three times. After the last cycle, the flask was backfilled with N<sub>2</sub> (1.0 atm). The temperature of the reaction solution was kept at 25°C and the reaction mixture was irradiated using a 300 W xenon lamp with a filter (800 >  $\lambda$  > 420 nm). After the reaction, the generated gases were analyzed by FID gas chromatography. After collecting the samples and washing them with water, cyclic photocatalytic tests were performed using the same procedure.

## 5. Electrochemical Measurements

Electrochemical measurements were performed on a three-electrode electrochemical cell equipped with an electrochemical station. First, to prepare the working electrode, 6 mg of fully ground sample photocatalyst was dispersed in 3 mL of 0.2 wt% Nafion and 2 mL of ethanol using an ultrasonic instrument. The sample was then dropped onto a piece of fluoride tin oxide (FTO) glass substrate covering an area of 1 cm<sup>2</sup>. The uncovered part of the electrode was coated with epoxy resin. The working electrode was dried naturally in air. The photocurrent was recorded by an electrochemical workstation equipped with a conventional three-electrode cell. A platinum plate electrode and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrodes were immersed in 0.2 M aqueous sodium sulfate solution. The working electrode was illuminated by a 300 W Xe lamp (PLS-SXE300C) with a 420 nm cut-off filter on the back to reduce the effect of semiconductor layer thickness. Each measurement was repeated three times under

ambient conditions.

## 6.Surface area of COF-TMT-A

N<sub>2</sub> isotherms and specific surface areas were determined at 77 K using a microcrystalline ASAP 2460 automated system with a Brunauer-Emmett-Taylor (BET) model, and samples were degassed in vacuum ( $<1 \times 10^{-5}$  bar) at 100 ° C for 8 h, followed by N<sub>2</sub> physisorption.

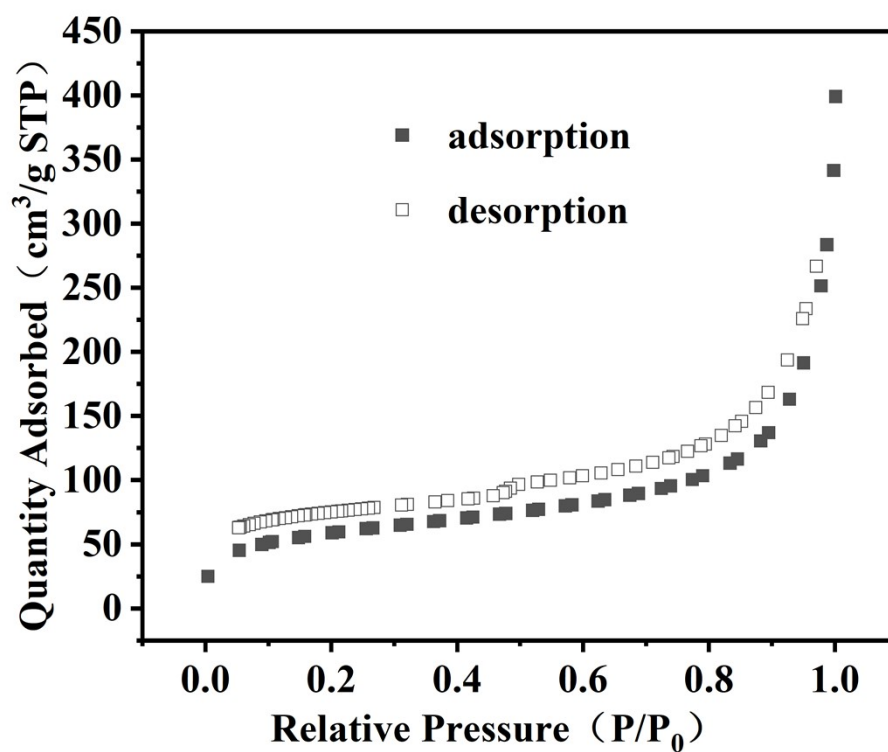


Fig.S4. The specific surface area of COF-TMT-A



## 7. Pore size of COF-TMT-A

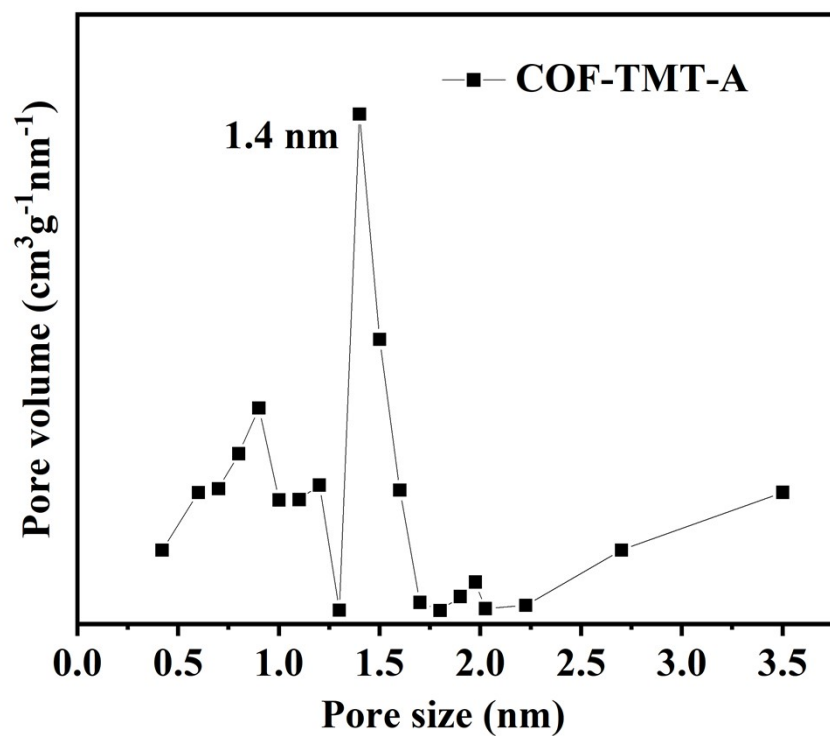
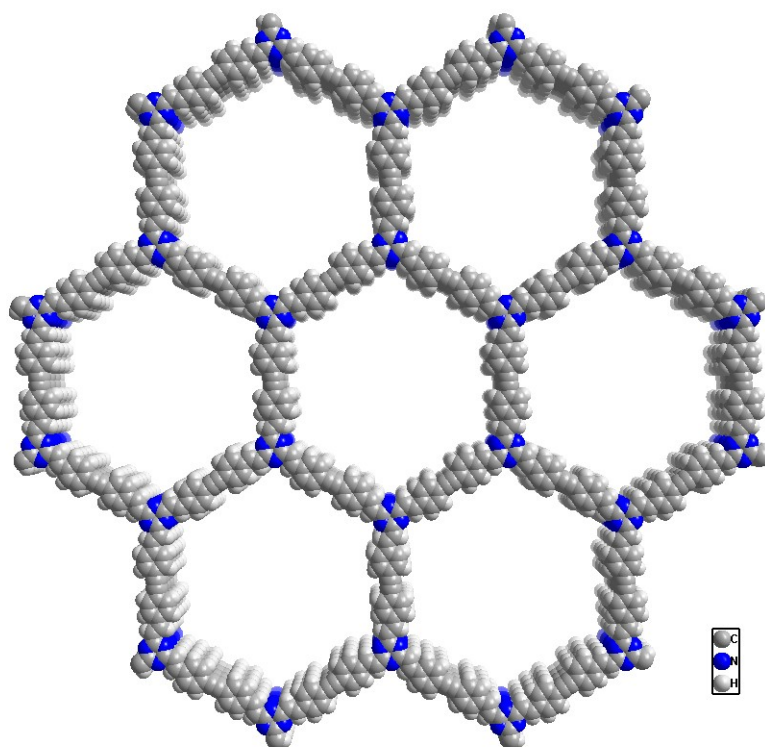
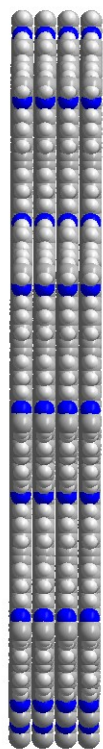


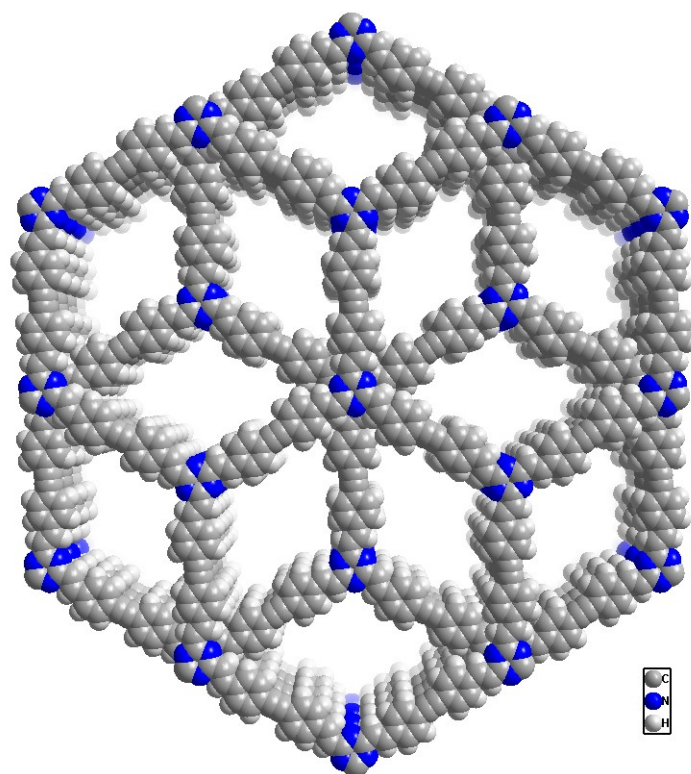
Fig.S5. Pore size of COF-TMT-A

## 8. Stacking plot





**Fig.S6.** AA stacking plot of COF-TMT-A



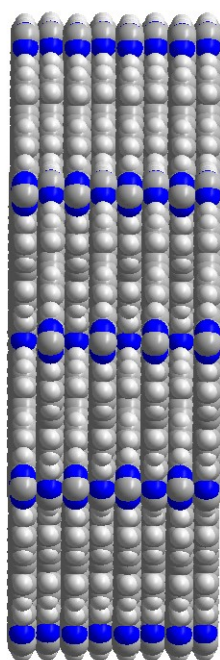


Fig.S7. AB stacking plot of COF-TMT-A

## 9. Refined XRD of COF-TMT-A

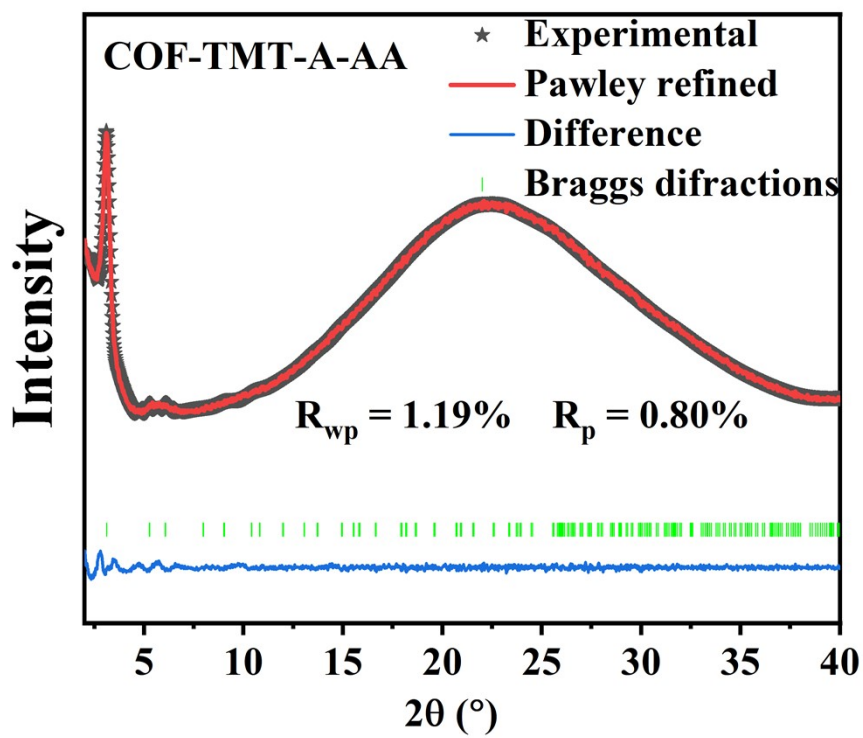


Fig.S8. Refined XRD of AA-stacked COF-TMT-A

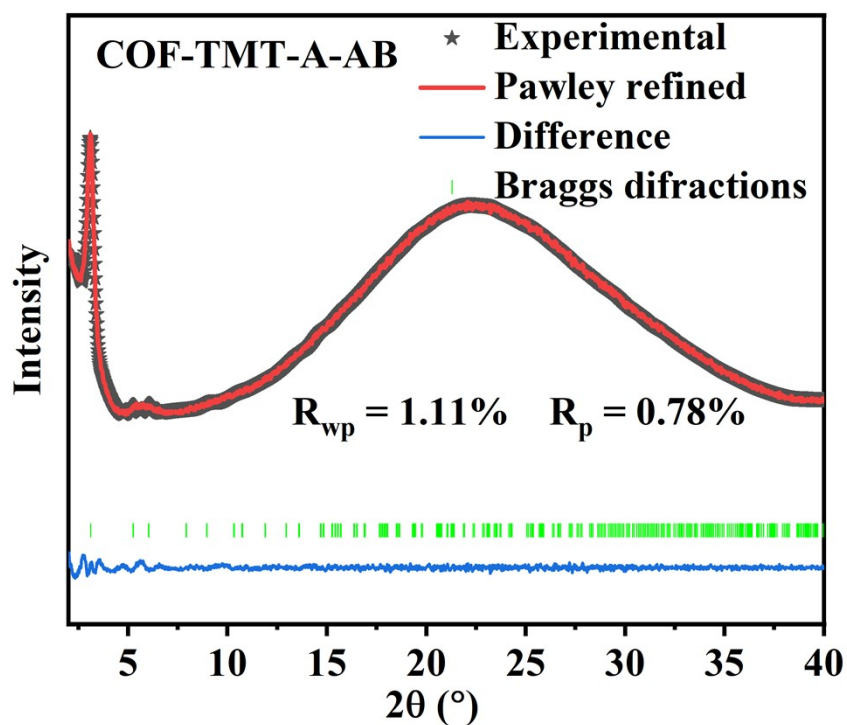
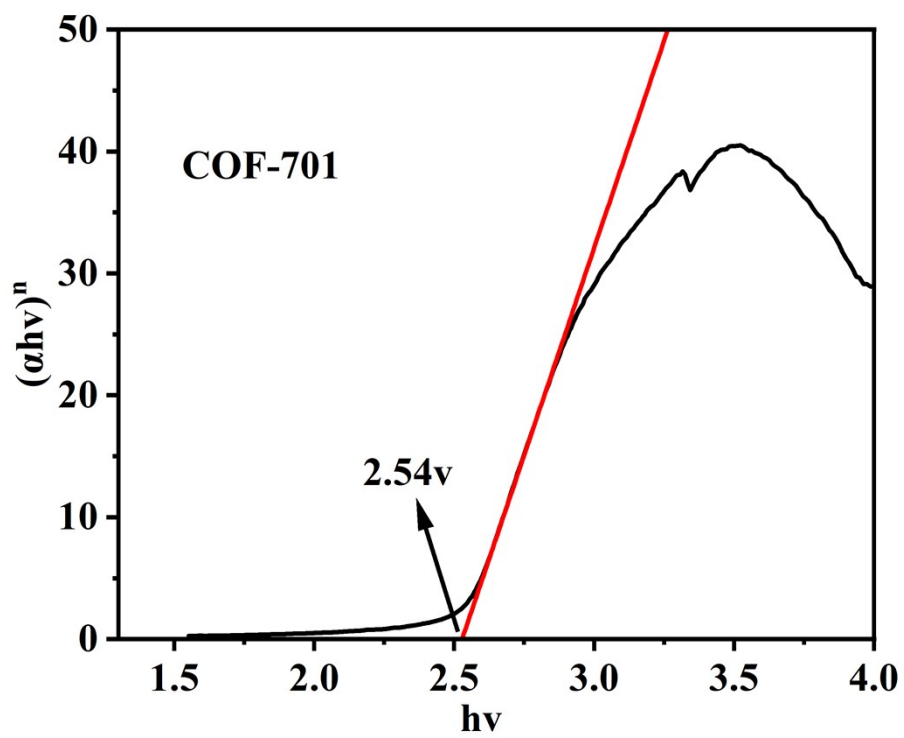


Fig.S9. Refined XRD of AB-stacked COF-TMT-A

## 10. The optical bandgap is estimated by Tauc plot

The UV absorption spectrum shows a broadening of the absorption range, from the general UV absorption to the visible range. The optical bandgap of COF-TMT-A is estimated by Tauc plot to be 2.24 eV, which is much smaller than that of COF-701 at 2.54 eV.



**Fig.S10.** The optical bandgap of COF-701 is estimated by Tauc plot

## 11.The thermal stability of COF-TMT-A

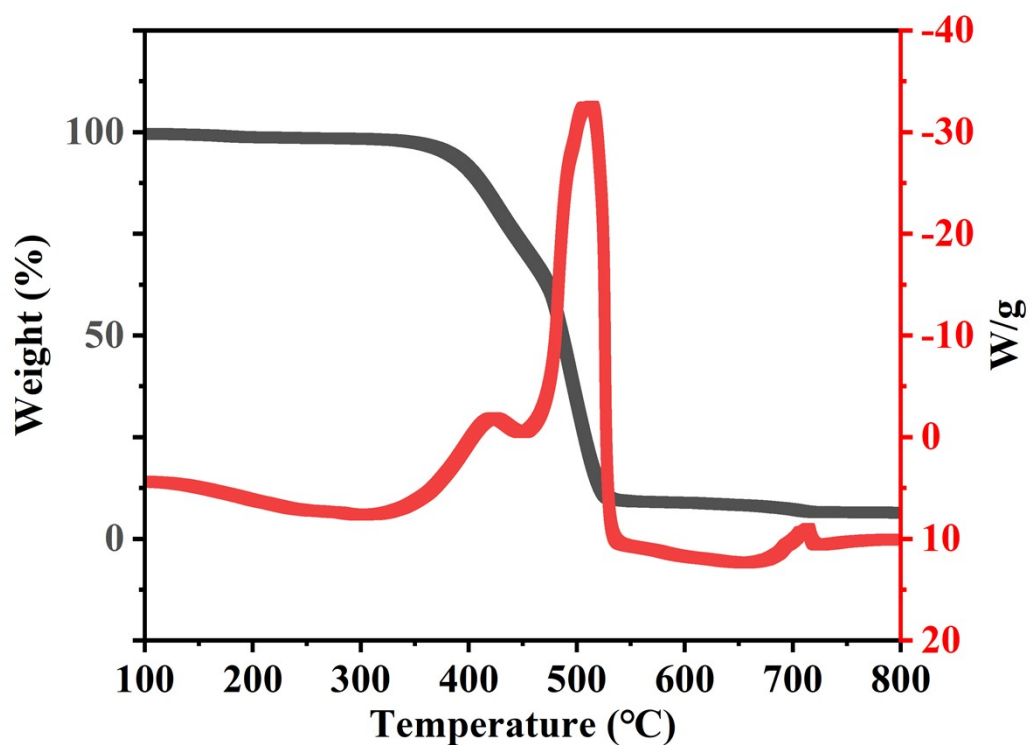
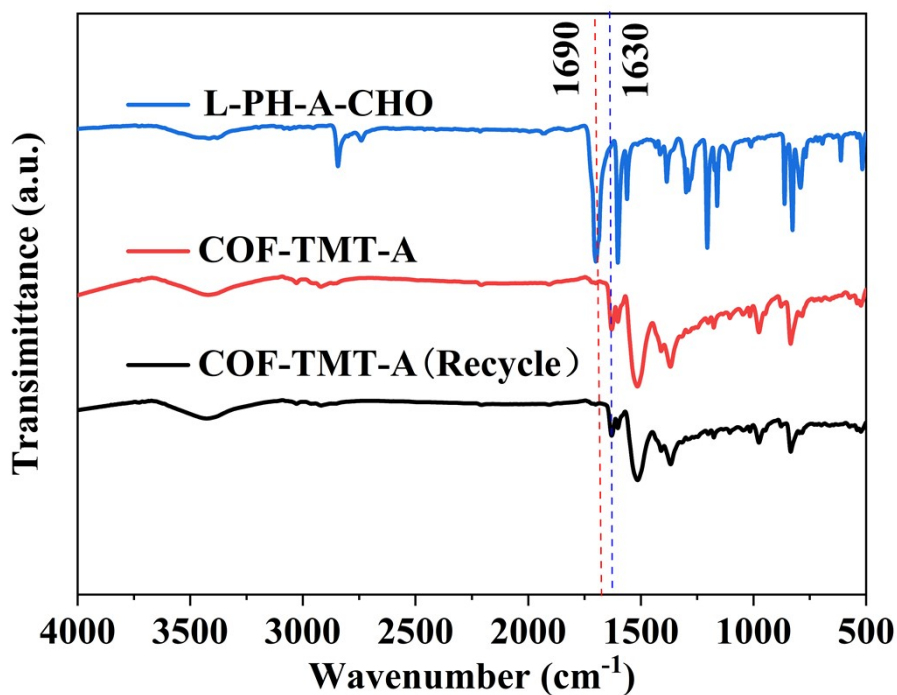


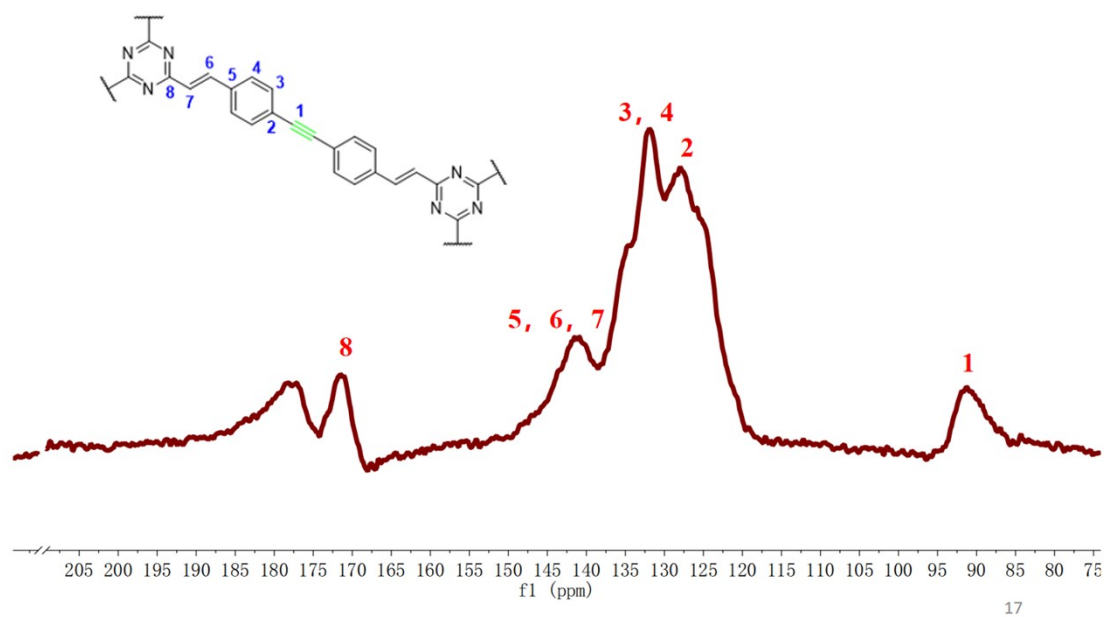
Fig.S11. The thermal stability of COF-TMT-A

## 12.Fourier Transform Infrared (FTIR) Spectral Characterization



**Fig.S12.** Fourier Transform Infrared (FTIR) Spectral Characterization of Recovered COF-TMT-A

### 13. $^{13}\text{C}$ solid-state NMR of Recovered COF-TMT-A



**Fig.S13.**  $^{13}\text{C}$  solid-state NMR of Recovered COF-TMT-A

## 14. The specific surface area

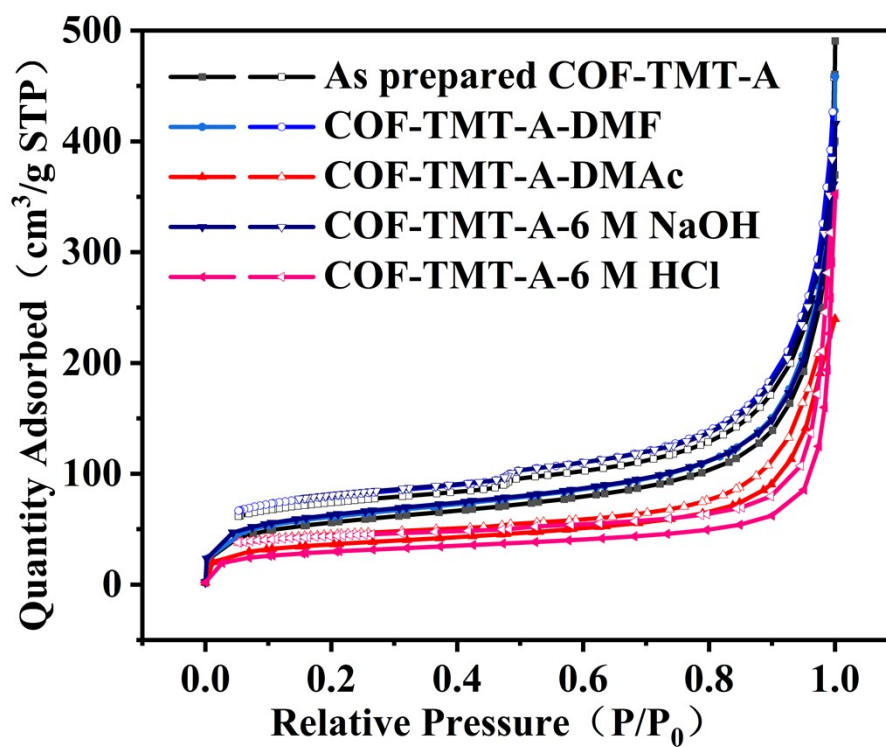


Fig.S14. The specific surface area of Recovered COF-TMT-A



## 15. Photocatalysis Hydrogen decomposition of water

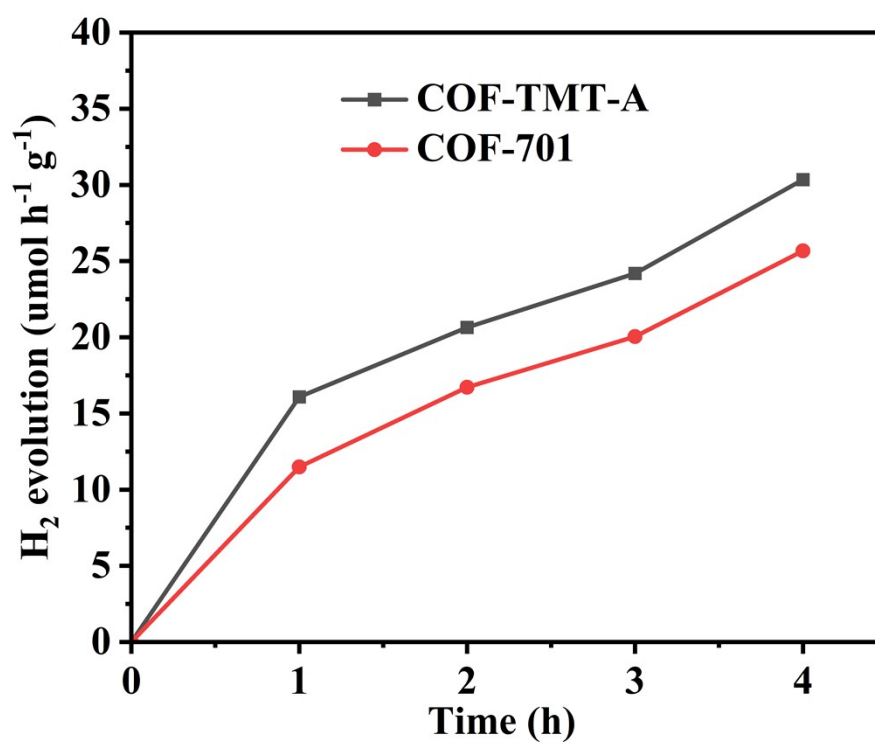
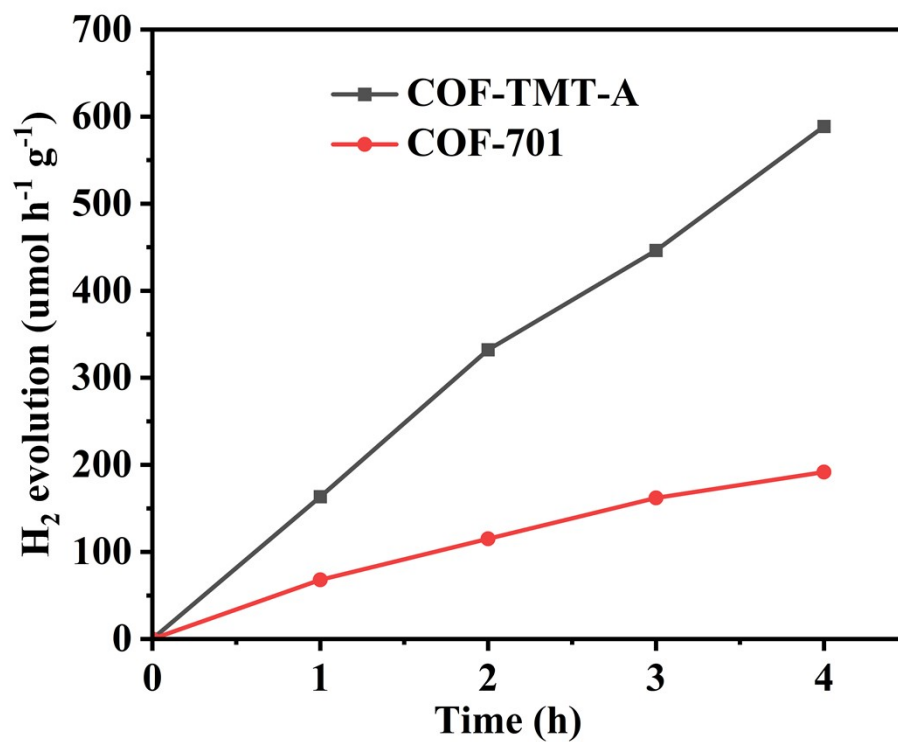


Fig.S15. Photocatalysis Hydrogen decomposition of water  
Solvent:  $\text{H}_2\text{O}$ : TEOA=9: 1



**Fig.S16.** Photocatalysis Hydrogen decomposition of water  
solvent: H<sub>2</sub>O: TEOA=9: 1, 3wt%Pt