

Supporting Information

Enhancement of covalent triazine framework containing S heteroatom for photocatalytic hydrogen evolution: The role of composite PEG

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Section 1. Material and Methods

All commercially available reagents and solvents were used as received without further purification. 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline and [2,2'-bithiophene]-5,5'-dicarbaldehyde were purchased from Shanghai Kylpharm Co., Ltd. Used all solvents and polyethylene glycol were purchased from Aladdin. Cobalt acetate, nickel acetate and zinc acetate were purchased from Sinopharm Chemical Reagent Co., Ltd.

Fourier transforms Infrared (FT-IR) spectra was recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, and the pressed product can be directly tested. The solid-state UV-visible analyzer was used for Jasco V-770 spectrometer Solid-state. ^{13}C crosspolarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using AVANCEIII/WB-400. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) measured on Jem-2100F spectroscopy: Oxford 64T. The operating voltage is 300 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 2.5^\circ$ up to 40° with 0.02° increment. Solid UV/Vis spectra was tested from 200 nm to 800 nm by using Shimadzu Corporation U-4100 Spectrophotometer. Liquid UV/Vis spectra was recorded on the Shimadzu Corporation UV-2700 Spectrophotometer within the wavelength range 200-800 nm. TGA analysis was carried out by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with Bel Japan Inc. Model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at 120°C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density

functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h. Fluorescence lifetime was measured on a Fluorolog-3 spectrofluorometer (Horiba JobinYvon) with a DeltaDiode (371 nm, DD-375L) as the excitation source and a picosecond photon detection module (PPD-850) or as the detector. Photoluminescence (PL) spectroscopy was recorded via the Fluorolog-3 spectrofluorometer (Horiba JobinYvon) at room temperature. PL dynamics were obtained by excitation with 200 ps laser pulses at 405 nm and measured by a time-correlated single-photon counting (TCSPC) system.

Photocatalytic hydrogen evolution: 10 mg TTBT-COF was well dispersed in 20 mL deionized water containing three sacrificial agents (1.0 mol L⁻¹ ascorbic acid (AA), 0.5 mol L⁻¹ triethanolamine (TEOA), and 1.0 mol L⁻¹ sodium ascorbate (Aa-Na)), respectively. Then 80 μL H₂PtCl₆ (2 wt% Pt) was introduced into the reaction system. The reaction solution was evacuated under vacuum over 30 min to completely discharge air and maintained at 6 °C with a cooling jacket in circulating cooling system. After that the reaction system was irradiated vertically under 300 W xenon lamp with 420 nm cut-off filter (160 mW cm⁻²). The average rate was obtained by photocatalysis for 4 h except in-situ photodeposition. In the next step, 10 mg TTBT-COF, was well dispersed in 20 mL deionized water containing the sacrificial agents AA at four different concentrations (1.5, 2.0, 2.5 mol L⁻¹), respectively, while in other conditions unchanged. Finally, 10 mg TTBT-COF, was well dispersed in 20 mL deionized water containing the sacrificial agents AA (2.0 mol L⁻¹), and introduced in the system with various amount of loading of Pt (1, 2, 3, and 4 wt%), respectively, while in other conditions unchanged. Based on the above tests, the optimal sacrificial agent for the photocatalytic hydrogen evolution reaction of TTBT-COF was AA (2 mol L⁻¹), and the optimal cocatalyst is H₂PtCl₆ (3 wt%). 10 mg TTBT-COF@PEG_x (x = 10, 20, 30) was well dispersed in 20 mL deionized water containing AA (2.0 mol L⁻¹), and H₂PtCl₆ (3 wt% Pt), while in other conditions unchanged. The average rate was obtained by photocatalysis for 4 h. For long-term experiments and recycled

experiment, 10 mg TTBT-COF@PEG₃₀ was adopted with 20 mL deionized water containing 2.0 mol L⁻¹ AA (3 wt% Pt) and radiated under 300W xenon lamp with 420 nm cut-off filter (160 mW cm⁻²). The evolved gases were analyzed by gas chromatography equipped with Ar as the carrier gas (GC7920, TDX01 chromatographic column, CEAULIGHT). The evolved hydrogen was detected with a thermal conductivity detector (TCD) referencing against high-purity hydrogen with a known volume. The catalyst and solution sprayed on the reactor wall are neglected, hydrogen dissolved in the reaction solution was not detected and measured. In addition, the effect of changed pressure by generated hydrogen on photocatalysis was ignored. The hydrogen evolution rates were calculated on the basis of a linear regression fitting curve (R² = 0.9996), the value of the rate curve excludes the Pt photodeposition period. As a comparison, TTBT-COF and TTBT-COF@PEG_x were carried out H₂ evolution performance under the same conditions.

The test of apparent quantum yield (AQY) for hydrogen evolution was similar to photocatalytic hydrogen evolution measurement but a 300 W Xe lamp with different bandpass filters (central wavelength: 450, 500, 550nm) was used as the source of light. Universally, 10 mg TTBT-COF and TTBT-COF@PEG_x was employed accompanying with 20 mL deionized water containing 2.0 mol L⁻¹ AA (3 wt% Pt). The intensities of incident light were measured by CEL-NP2000 optical power meter respectively, while the average intensity of irradiation was determined to be 10.45 mW cm⁻² at 450 nm. So the AQY was calculated can be calculated by using the following equation:

$$\begin{aligned}
 AQY(\%) &= \frac{\text{number of product obtained}}{\text{number of incident photon}} \times 100\% \\
 &= \frac{n_p \times N_A}{\frac{P \times S \times t \times \lambda}{h \times c}} \times 100\% \\
 &= \frac{n_p \times N_A \times h \times c}{P \times S \times t \times \lambda}
 \end{aligned}$$

where n_p is the mole number of product obtained (mol), N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), P is the optical density (W cm^{-2}), S is the light irradiation area (18.1 cm^2), t is the light irradiation time (s), λ is the monochromatic light wavelength (m), h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}$), and c is the speed of light ($3 \times 10^8 \text{ m s}^{-1}$)

Electrochemical impedance spectroscopy (EIS) and cycling stability All the photoelectrochemical measurements of samples were recorded on the electrochemical workstation (CHI760E, CH Instrument Corp, Shanghai) using a standard three-electrode cell at room temperature, the glass carbon electrode (GCE) were used as working electrode, a platinum wire electrode, and a saturated calomel electrode (SCE) as counter and reference electrode, respectively.

Section 2. Synthesis Procedures

Synthesis of TTBT-COF

The monomers 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TAPT) (50 mg, 0.15 mmol) and [2,2'-bithiophene]-5,5-dicarbaldehyde (BTDA) (45 mg, 0.22 mmol) were placed in a 5 mL of Pyrex tube containing mesitylene (0.5 mL), dioxane (1.0 mL), and acetic acid aqueous solution (0.2 mL 6 mol L⁻¹). The mixture was treated under ultrasound for 3 minutes to obtain a uniform dispersion. The tube was frozen at 77 K using liquid N₂ and degassed by three freeze-pump-thaw cycles, sealed under vacuum, and then heated at 120 °C for 3 days. A deep red solid powder was formed, which was collected by centrifugation and washed with tetrahydrofuran to remove unreacted monomers. Finally, the product TTBT-COF was dried at 80 °C for 10 hours under vacuum with a yield of 75.53%.

Synthesis of TTBT-COF@PEG_x (x = 10, 20, 30)

20 mg of TTBT-COF was placed in a Pyrex tube containing PEG acetonitrile solution with x wt% (x = 10, 20, 30). Then the acetonitrile mixture was evacuated gradually. The reaction continued at 100 °C for 12 hours. After cooling to room temperature, the red solid product was washed with acetonitrile and water, and separated by centrifugation. Finally, the red solid powder TTBT-COF@PEG_x was dried at 80 °C under vacuum for 12 hours.

Section 3. Characterization

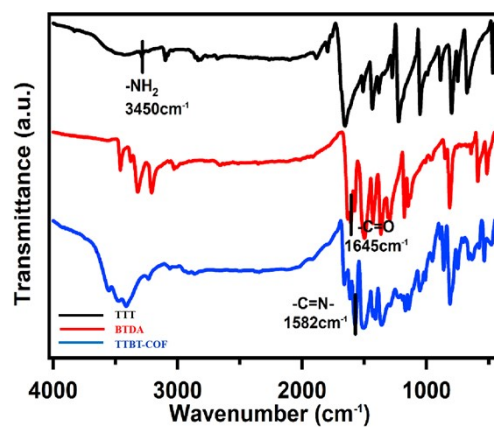


Fig. S1 The FT-IR spectra of TTT, BTDA, and TTBT-COF.

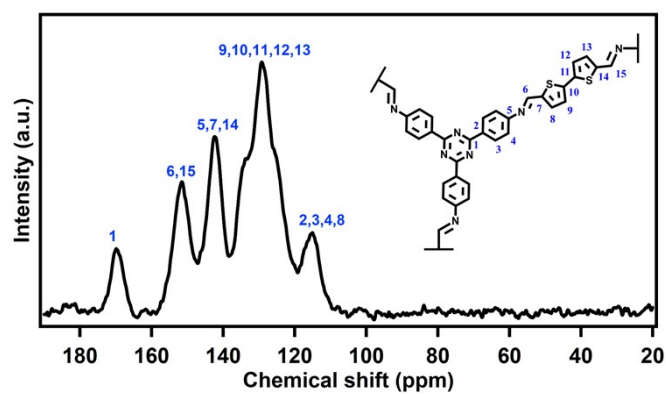


Fig. S2 The ^{13}C CP-MAS NMR spectra of TTBT-COF.

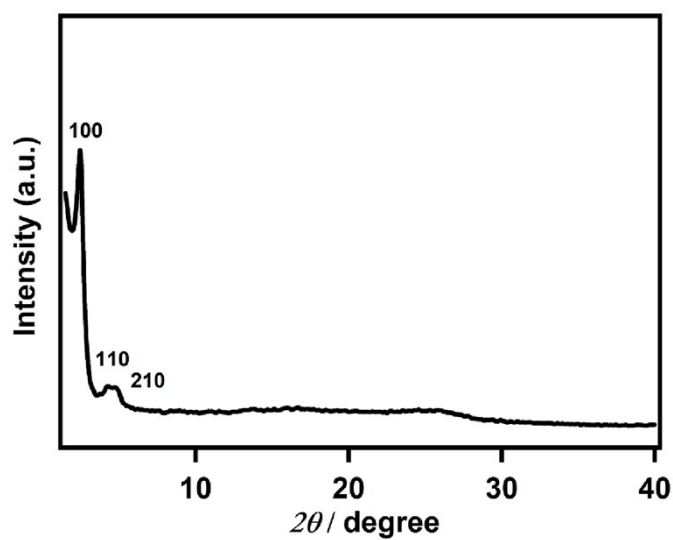


Fig. S3 The PXRD pattern of TTBT-COF.

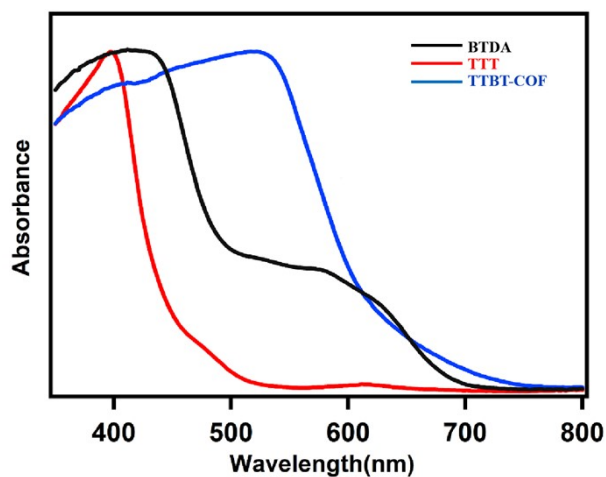


Fig. S4 The UV-vis spectra of TTT, BTDA, and TTBT-COF.

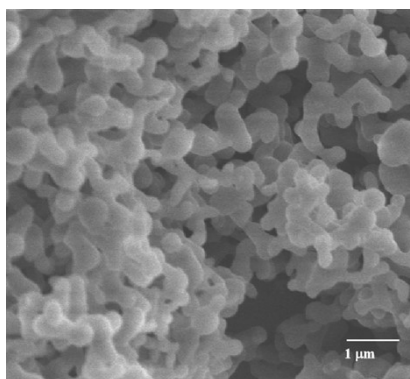


Fig. S5 The SEM image of TTBT-COF.

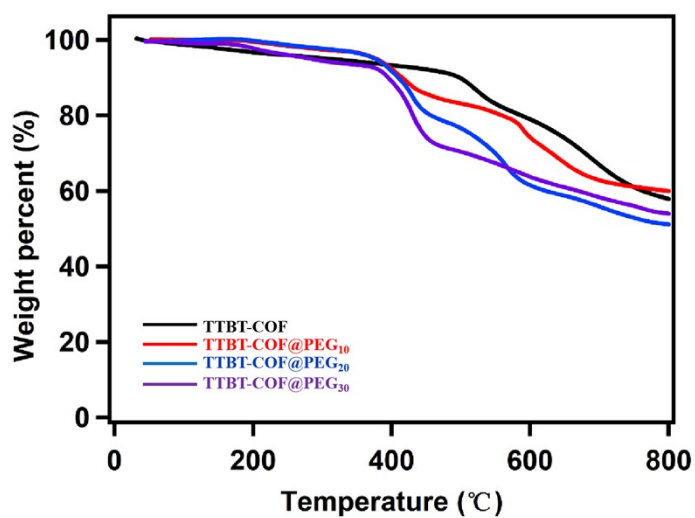


Fig. S6 The TGA curves of TTBT-COF and TTBT-COF@PEG_x (x = 10, 20, 30) under nitrogen atmosphere.

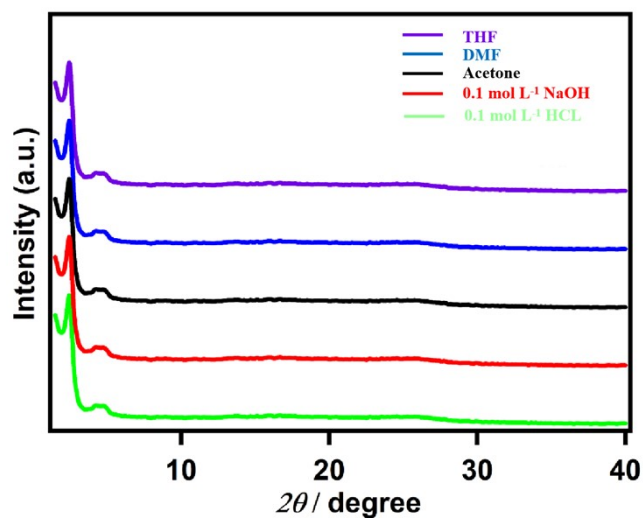


Fig. S7 The PXRD patterns of TTBT-COF after treatment in different solvents for 12 hours.

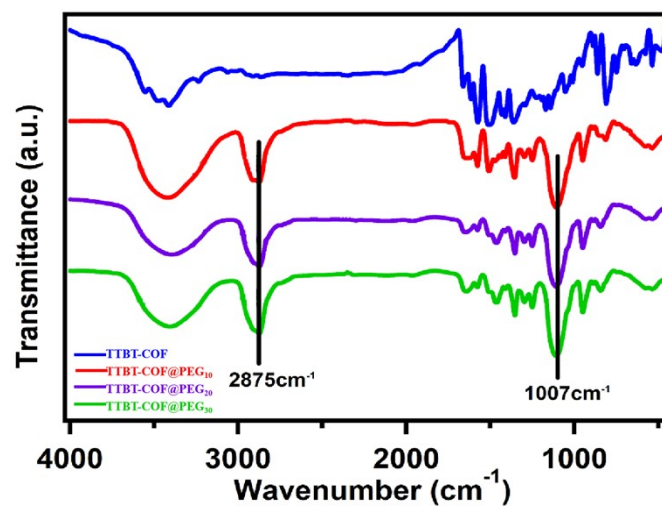


Fig. S8 The FT-IR spectra of TTBT-COF and TTBT-COF@PEG_x (x = 10, 20, 30).

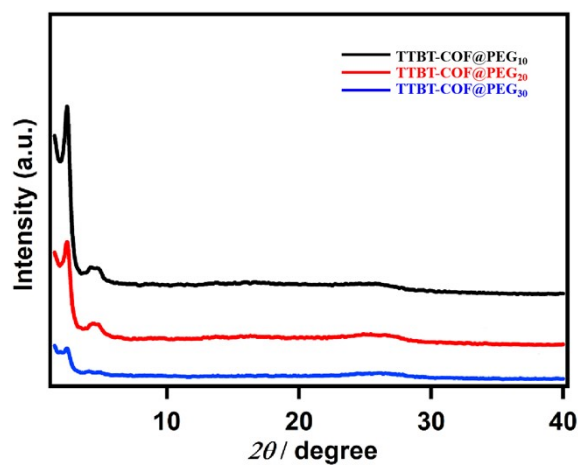


Fig. S9 The PXRD patterns of TTBT-COF@PEG_x (x = 10, 20, 30).

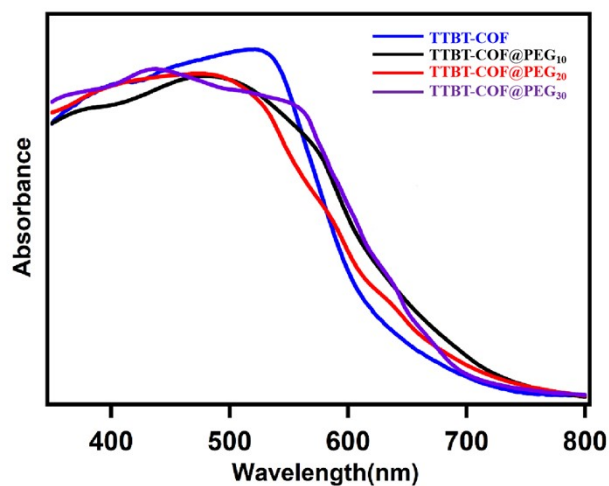


Fig. S10 The UV-vis spectra of TTBT-COF, and TTBT-COF@PEG_x (x = 10, 20, 30).

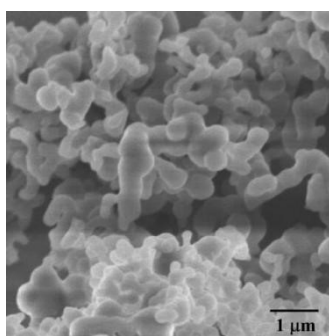


Fig. S11 The SEM image of TTBT-COF@PEG₃₀.

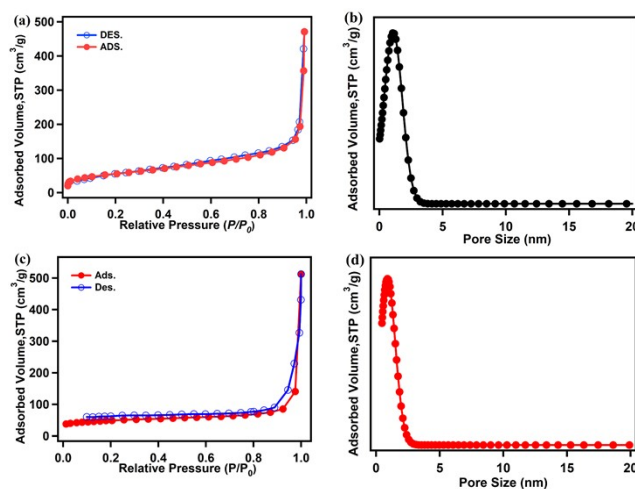


Fig. S12 (a) Nitrogen adsorption-desorption isotherm curves of TTBT-COF. (b) Nitrogen adsorption-desorption isotherm curves of TTBT-COF@PEG₃₀. (c) Pore size distributions of TTBT-COF. (d) Pore size distributions of TTBT-COF@PEG₃₀.

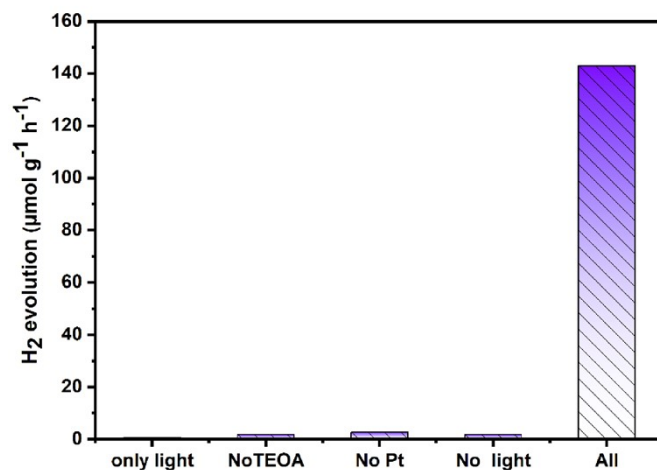


Fig. S13 Photocatalytic H₂ evolution reaction condition testing of TTBT-COF.

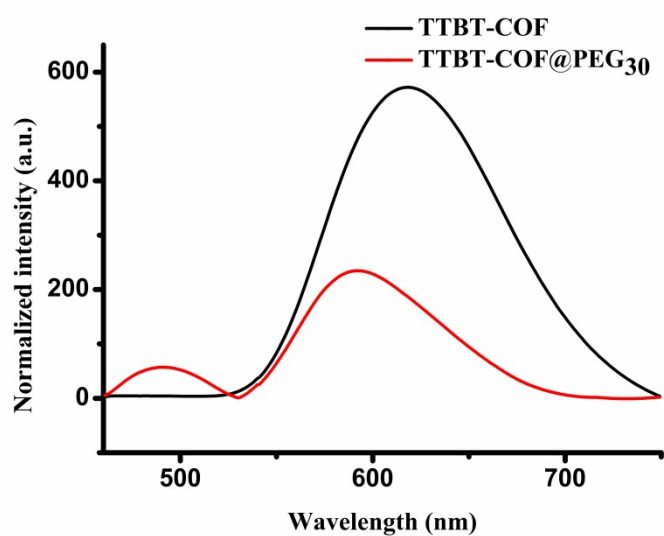


Fig. S14 Photoluminescence spectroscopy of TTBT-COF and TTBT-COF@PEG₃₀.

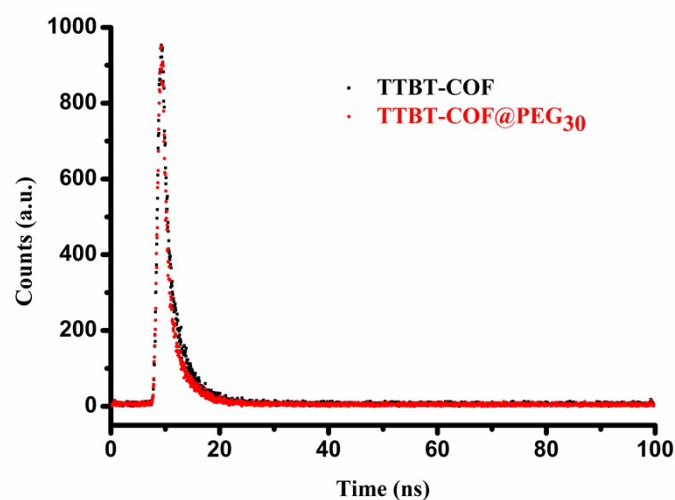


Fig. S15 Time-resolved photoluminescence spectra of TTBT-COF and TTBT-COF@PEG₃₀.

Table S1 Summary of COFs based photocatalytic H₂ evolution systems.

COFs	Light source	Sacrificial reagent	Pt loading	HER rate	Reference
TFPT-COF	300 W Xe lamp (cut off 420 nm)	10% V TEOA	4 mg COF catalyst, 2.4 μ L (8 wt% H ₂ PtCl ₆)	1.9 mmol h ⁻¹ g ⁻¹ (5 h)	<i>Chem. Sci.</i> 2014 , 5, 2789
N3-COF	300 W Xe lamp (cut off 420 nm)	1% V TEOA	5 mg COF catalyst, 5 μ L (8 wt% H ₂ PtCl ₆)	1.7 mmol h ⁻¹ g ⁻¹ (5 h)	<i>Nat. Commun.</i> 2015 , 6, 8508
TP-BDDA	300 W Xe lamp (cut off 395 nm)	10% V TEOA	3 wt% H ₂ PtCl ₆	324 \pm 10 μ mol h ⁻¹ g ⁻¹ (10 h)	<i>J. Am. Chem. Soc.</i> 2018 , 140, 1423.
A-TEBPY-COF	300 W Xe lamp (cut off 420 nm)	10% V TEOA	10 mg COF catalyst, 6 μ L (8 wt% H ₂ PtCl ₆)	98 μ mol h ⁻¹ g ⁻¹ (22 h)	<i>Adv. Energy Mater.</i> 2018 , 8, 1703278
g-C18N3-COF	300 W Xe lamp (cut off 420 nm)	1 M ascorbic acid	3 wt%	14.6 μ mol h ⁻¹ g ⁻¹ (16 h)	<i>J. Am. Chem. Soc.</i> 2019 , 141, 14272.
FS-COF	300 W Xe lamp (cut off 420 nm)	0.1 M ascorbic acid	5 mg COF catalyst, 5 μ L (8 wt% H ₂ PtCl ₆)	10.1 \pm 0.3 mmol h ⁻¹ g ⁻¹ (5 h)	<i>Nat. Chem.</i> 2018 , 10, 1180
sp ² c-COF	300 W Xe lamp (cut off 420 nm)	10% V TEOA	3 wt% H ₂ PtCl ₆	1360 μ mol h ⁻¹ g ⁻¹ (5 h)	<i>Chem</i> 2019 , 5, 1632
ZnPor-DETH-COF	300 W Xe lamp (cut off 400 nm)	1% V TEOA	2.5 mg COF catalyst, 2.5 μ L (8 wt% H ₂ PtCl ₆)	413 μ mol h ⁻¹ g ⁻¹ (10 h)	<i>Nat. Commun.</i> 2021 , 12, 1354.
CTF NSs	300 W Xe lamp (cut off 400 nm)	10 mL TEOA	50 mg COF catalyst, (3 wt% H ₂ PtCl ₆)	512.3 μ mol h ⁻¹ g ⁻¹ (5 h)	<i>Angew. Chem. Int. Ed.</i> , 2021 , 60, 25381.
COF-JLU100	300 W Xe lamp (cut off 400 nm)	50 mL TEoA 50 mL ascorbic acid	12 wt% H ₂ PtCl ₆ 1 wt% H ₂ PtCl ₆	107.4 mmol h ⁻¹ g ⁻¹ 84.6 mmol h ⁻¹ g ⁻¹ (4 h)	<i>Angew. Chem. Int. Ed.</i> , 2022 , 61, e202208919.
CTFS CTFSe	visible light irradiation (\geq 420 nm)	10 mL TEOA	50 mg COF catalyst, (3 wt% H ₂ PtCl ₆)	499.23 μ mol h ⁻¹ g ⁻¹ 5792.8 μ mol h ⁻¹ g ⁻¹ (9 h)	<i>Sci. China Chem.</i> , 2023 , 66, 2363.

Table S2. Apparent quantum efficiency (AQY) of TTBT-COF and TTBT-COF@PEG₃₀ under monochromatic irradiation of different wavelength.

Wavelength (nm)	Light power density (mW·cm ²)	Hydrogen production rate (μ mol·h ⁻¹ ·g ⁻¹)		AQY	
		TTBT-COF	TTBT-COF@PEG ₃₀	TTBT-COF	TTBT-COF@PEG ₃₀
450	10.45	290	340	0.12%	0.13%
500	12.52	450	480	0.13%	0.14%
550	12.43	380	410	0.10%	0.11%