

A pyrrolo[3,2-b]pyrrole core containing covalent triazine-based framework (CTF) for photocatalytic H₂ production

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Experimental Section

Materials

4-cyano benzaldehyde, palladium acetate, eosin Y (EY), were purchased from TCI Ltd. (>99.998%). Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), trifluoromethane sulfonic acid (TFMS) and 2,3-butanedione, iron perchlorate $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ were obtained from Aldrich. Dichloro methane (CH_2Cl_2), dimethyl formamide (DMF), acetonitrile, glacial acetic acid, toluene, were procured from Merck India. NaBH_4 was purchased from SRL. Triethanolamine (TEOA) was bought from Spectrochem India. All of the chemicals were commercially available and used without further purification.

Characterizations

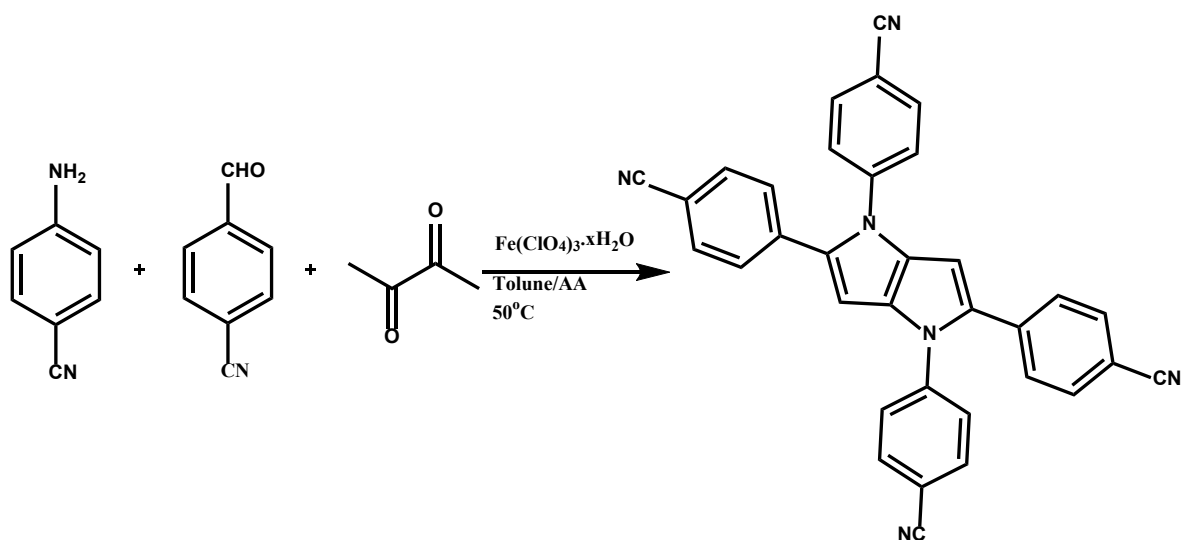
Fourier transform infrared (FT-IR) spectral measurements were performed using the PerkinElmer Spectrum Two FT-IR spectrometer in UATR mode within the range of 400 cm^{-1} to 4000 cm^{-1} . The powder X-ray diffraction (PXRD) data was performed with Bruker D8 Advance X-ray diffractometer (XRD) at room temperature using $\text{Cu K}\alpha$ radiation ($\lambda = 1.548\text{ \AA}$) in a 2θ range of $5\text{--}50^\circ$. Thermogravimetric analyses (TGA) were done at a ramp rate of 10°Cmin^{-1} under N_2 with PerkinElmer Pyris Diamond TG-DTA instruments. UV absorption spectra were recorded using a Cary 60 UV-vis (Agilent Technologies) with a 1 cm path-length quartz cell. Nitrogen gas adsorption-desorption of the samples was performed to obtain BET specific surface area (S_{BET}) using Quantachrome Autosorb iQ2 Instruments at liquid N_2 temperature (77 K). The samples were degassed under high vacuum (10^{-6} torr) at 120°C for 6h. After degassing, the sample tube was then transferred to the analysis port of the sorption analyser. Pore size distribution was calculated by non-local density functional theory (NLDFT) using the 'carbon slit pore' model. ^1H and ^{13}C NMR spectra were measured on Bruker-DRX 400 MHz instruments at room temperature in DMSO-d_6 . X-ray photoelectron spectroscopy (XPS) measurement was conducted by the Thermo Fisher

ESCALAB Xi+ microProbe instrument with a monochromatic Al-K α target, 1486.6 eV energy, and a maximum power of 15.0 KW. The high-resolution transmission electron microscopy (HR-TEM) images were collected from the JEOL, JEM-2100F instrument, operating at an accelerating voltage of 200 kV. Before the analysis, the 2-propanol solution of a small amount of sample was dispersed homogeneously in an ultrasonic cleaner for 2h to ensure maximum dispersion of the sample, and then 2 μ L of the solution was cast on a carbon coated Cu-grid (300 mesh size), put in an airtight desiccator, and dried at ambient temperature for two days. Electron paramagnetic resonance (EPR) experiments were conducted with a JEOL JESFA200 ESR Spectrometer instrument having an X-band Microwave unit. The amount of H₂ evolution was measured in GC (gas chromatography) using an Agilent 8860E (G2790A) instrument. Field emission scanning electron microscope (FE-SEM) images with elemental mapping were obtained using a Carl Zeiss SUPRA 55VP FESEM instrument. Energy dispersive X-ray spectroscopy (EDS) was performed by Oxford Instruments X-Max with INCA software coupled to the FE-SEM. Inductively coupled plasma optical emission spectrometry (ICP-OES) results were obtained from an Icap 7000 ICP-OES (Thermo Scientific).

Synthesis of 1,2,4,5-tetrakis(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (TPP)

1,2,4,5-tetrakis(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole was synthesized following a reported procedure.¹ In a typical method, 4-formylbenzotrile (8 mmol, 1.03g), and 4-aminobenzotrile (8 mmol, 0.85g) were dissolved in toluene (6 mL) in a round-bottom flask. Glacial acetic acid (6 mL) was then added to the reaction mixture, and the reaction mixture was stirred at 50 °C for 1h. Fe(ClO₄)₃·xH₂O (85 mg) was added, followed by the addition of diacetyl (0.35 mL, 4 mmol). The resulting mixture was stirred at 50 °C (oil bath) in an open flask under air overnight. The precipitate was filtered off, washed with cold methanol and dried under vacuum. Yield: 0.63 g (31%). ¹H NMR (400 MHz, DMSO-d₆), δ [ppm]: 7.95 (d, J = 8.56 Hz, 4H), 7.77 (d, J = 8.44 Hz, 4H), 7.48 (d, J = 8.56 Hz, 4H), 7.39 (d, J = 8.40 Hz, 4H), 6.93 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆), δ [ppm]: 142.90, 137.06, 134.40, 132.93, 128.64, 126.03, 99.59. HRMS (EI):

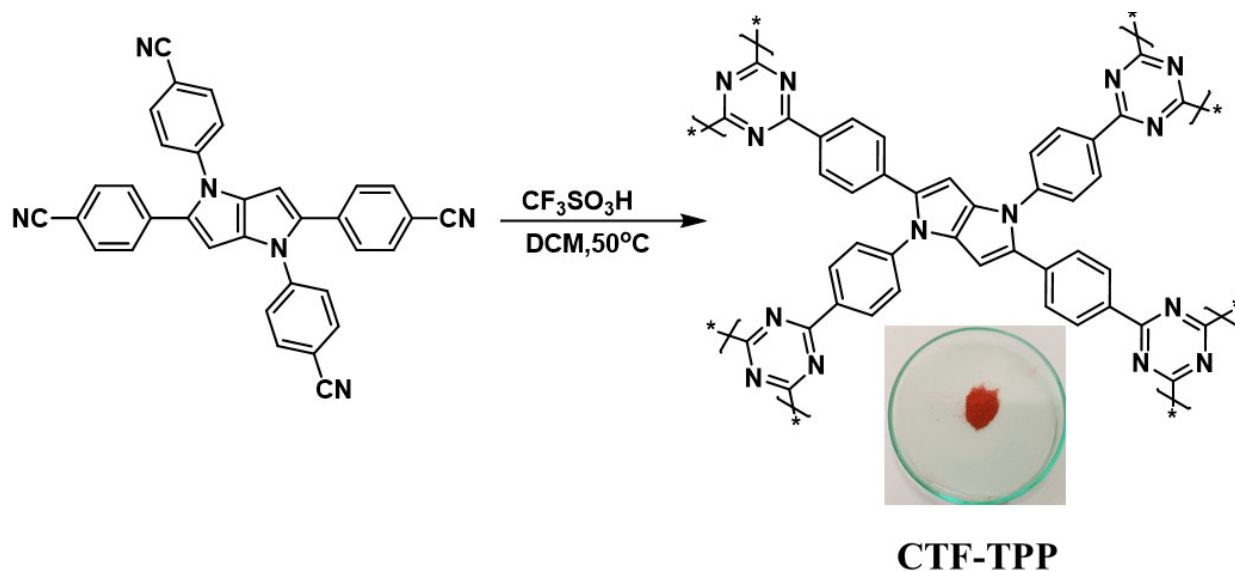
calculated for $C_{34}H_{18}N_6 [M^+]$: 510.1593, found: 510.1595. Figure S17 and S18 show the 1H NMR and ^{13}C NMR, respectively.



Scheme S1: Synthesis of the nitrile linker TPP.

Synthesis of CTF-TPP

The synthesis of CTF-TPP was carried out using a reported procedure.² First, 0.2 mmol (0.102g) of 1,2,4,5-tetrakis(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-b]-pyrrole (TPP) was added to a mixture of DCM/TFMS (1:0.2, v/v) in a 5 mL vial. The solution was shaken vigorously for a few minutes and then kept in a temperature-controlled oven at $50^\circ C$ for 24h. Then, it was quenched by adding a mixture of DCM/DMF (2:1, v/v) solution. The resulting red powder product was isolated by filtration and washed with water (2×30 mL), ethanol (2×30 mL), tetrahydrofuran (2×30 mL), acetone (30 mL). Final red product was collected by filtration and dried under vacuum at $80^\circ C$. Yield: 81.6 mg (80%).



Scheme S2: Synthesis of CTF-TPP.

Synthesis of CTF-TPP@Pt_n

20 mg of CTF-TPP powder was dispersed in 5 mL of aqueous solution containing H₂PtCl₆ (0.1 g/L). The mixture was stirred until it became uniform. Then, 2 mL of NaBH₄ aqueous solution (2 mg/mL) was added with vigorous stirring at room temperature. After 2 hours, another 2 mL of NaBH₄ aqueous solution (2 mg/mL) was added to the solution and stirred for 12h. The resulting precipitate was washed five times with deionized water and ethanol, respectively. Finally, the precipitate was dried under vacuum at 40°C and named as CTF-TPP@Pt_{0.5}.

Synthesis of CTF-TPP@Pt_{0.25}

The same procedure for CTF-TPP@Pt_{0.5} was followed by using CTF-TPP (20mg) and H₂PtCl₆ (0.05 g/L) aqueous solution.

Synthesis of CTF-TPP@Pt_{1.7}

The same procedure for CTF-TPP@Pt_{0.5} was followed by using CTF-TPP (20mg) and H₂PtCl₆ (0.2 g/L) aqueous solution.

Synthesis of CTF-TPP@Pd_{0.25}

The same procedure for CTF-TPP@Pt_{0.5} was followed by using CTF-TPP (20mg) and Pd(OAc)₂ (0.05 g/L) alcoholic solution.

Synthesis of CTF-TPP@Pd_{0.5}

The same procedure for CTF-TPP@Pt_{0.5} was followed by using CTF-TPP (20mg) and Pd(OAc)₂ (0.1 g/L) alcoholic solution.

Synthesis of CTF-TPP@Pd_{1.7}

The same procedure for CTF-TPP@Pt_{0.5} was followed by using CTF-TPP (20mg) and Pd(OAc)₂ (0.2 g/L) alcoholic solution.

Electrochemical characterization

The Mott-Schottky analysis and impedance measurement were conducted using CHI760E workstation (CHI Instruments, USA) through a conventional three-electrode system immersed in a 0.1 M Na₂SO₄ aqueous solution.

Preparation of working electrode for Mott-Schottky measurement

2.5 mg of respective CTF materials were dispersed in a solution of 250 μ L water, 250 μ L isopropyl alcohol (IPA), and 10 μ L of nafion to prepare a homogenous slurry. Subsequently, 12 μ L of slurry was coated on a glassy carbon electrode and then dried at room temperature. The Ag/AgCl electrode was employed as the reference electrode, and the platinum plate was used as the counter electrode, respectively. The measurements were carried out under frequencies of 0.5, 1, and 1.5 kHz.

Preparation of working electrode for impedance measurement

2.5 mg of respective CTF materials were dispersed in a solution of 250 μ L water, 250 μ L isopropyl alcohol (IPA), and 10 μ L of Nafion to prepare a homogenous slurry. Subsequently, 12 μ L of slurry was coated on a glassy carbon electrode and then dried at room temperature. The Ag/AgCl electrode was employed as the reference electrode, and the platinum plate was used as the counter electrode, respectively. A 0.1 M Na₂SO₄ solution was used as an electrolyte. The measurements

were carried out with a bias potential of -0.4 V with a frequency range from 10^{-2} to 10^5 Hz under a N_2 atmosphere.

Preparation of working electrode for transient photocurrent:

2.5 mg of respective CTF materials was dispersed in a solution of 250 μ L water, 250 μ L isopropyl alcohol (IPA), and 10 μ L of nafion to prepare a homogenous slurry. Subsequently, 300 μ L of slurry was coated on an FTO glass plate (1 cm \times 1 cm) and then dried at room temperature. The Ag/AgCl electrode was employed as the reference electrode, and the platinum plate was used as the counter electrode, respectively. The transient photocurrent responses were carried out under visible-light irradiation conditions (300 W Xenon arc lamp).

Photocatalytic H₂ evolution activity measurements

The photocatalytic hydrogen production experiments were carried out in a 17 mL optical reaction tube with stirring at ambient temperature using a 300 W Xe lamp equipped with a UV cut-off filter (> 420 nm). The 2 mg of the photocatalyst was dispersed in 5 mL deionized water with 1 mL triethanolamine (TEOA) as a sacrificial reagent, Eosin-Y as photosensitizer and then the suspension was stirred and purged with nitrogen for ~ 30 min to remove air. The reaction vessel with reacting solution were fixed, and irradiated by the Xe lamp. Hydrogen gas was measured by gas chromatography (nitrogen as a carrier gas) using a thermal conductivity detector (TCD). For each evaluation of hydrogen generation, 0.4 mL of the headspace was injected into the GC (Agilent Technologies, 7890A) and was quantified.

AQY measurement

The apparent quantum yield (AQY) for H₂ evolution was measured under the same reaction conditions using band-pass filter. Depending on the amounts of hydrogen gases produced by the photocatalytic reaction in an average of one hour, the AQY was calculated as follow:

$$\begin{aligned}
\eta_{AQY} &= \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100 \\
&= \frac{N_e}{N_p} \times 100 \\
&= \frac{2 \times M \times N_A}{\frac{E_{total}}{E_{photon}}} \times 100 \\
&= \frac{2 \times M \times N_A}{\frac{S \times P \times t}{\frac{hc}{\lambda}}} \times 100 \\
&= \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100
\end{aligned}$$

where M is the amount of H₂ molecules (mol), N_A is Avogadro constant (6.022 × 10²³/mol), h is the Planck constant (6.626 × 10⁻³⁴ Js), c is the speed of light (3 × 10⁸ m/s), S is the irradiation area (11.7cm²), P is the intensity of irradiation light (W/cm²), t is the photoreaction time (s), and λ is the wavelength of the monochromatic light (m), the AQY were calculated as 13.97% at 420 nm.

Turnover number

The turnover number (TON) was calculated after 4 hours photocatalysis by using the following

$$\text{formula: } \text{TON} = \frac{\text{moles of } H_2 \text{ molecules generated}}{\text{mole of active sites}}$$

(herein palladium amount on the surface of the photocatalyst is active sites)

Table S1: Comparison of H₂ evolution rate for 4h photocatalytic run by different wt% of Pd and Pt loaded photocatalysts

Catalyst	Pd/Pt NPs loading((ICP-OES) (wt%))	H ₂ Evolution ($\mu\text{mol g}^{-1} \text{h}^{-1}$)
CTF-TPP	-	153
CTF-TPP@Pd _{0.25}	0.25	286
CTF-TPP@Pt _{0.25}	0.25	209
CTF-TPP@Pd _{0.5}	0.5	1995
CTF-TPP@Pt _{0.5}	0.5	1152
CTF-TPP@Pd _{1.7}	1.7	560
CTF-TPP@Pt _{1.7}	1.7	495

Table S2 Photocatalytic H₂ production of synthesized photocatalyst with photosensitizer (PS) and without photosensitizer

H ₂ Production (μmolg^{-1}) of prepared photocatalyst for 2h					
CTF-TPP		CTF-TPP@Pd _{0.5}		CTF-TPP@Pt _{0.5}	
With PS	Without PS	With PS	Without PS	With PS	Without PS
220	14	2520	416	1216	180

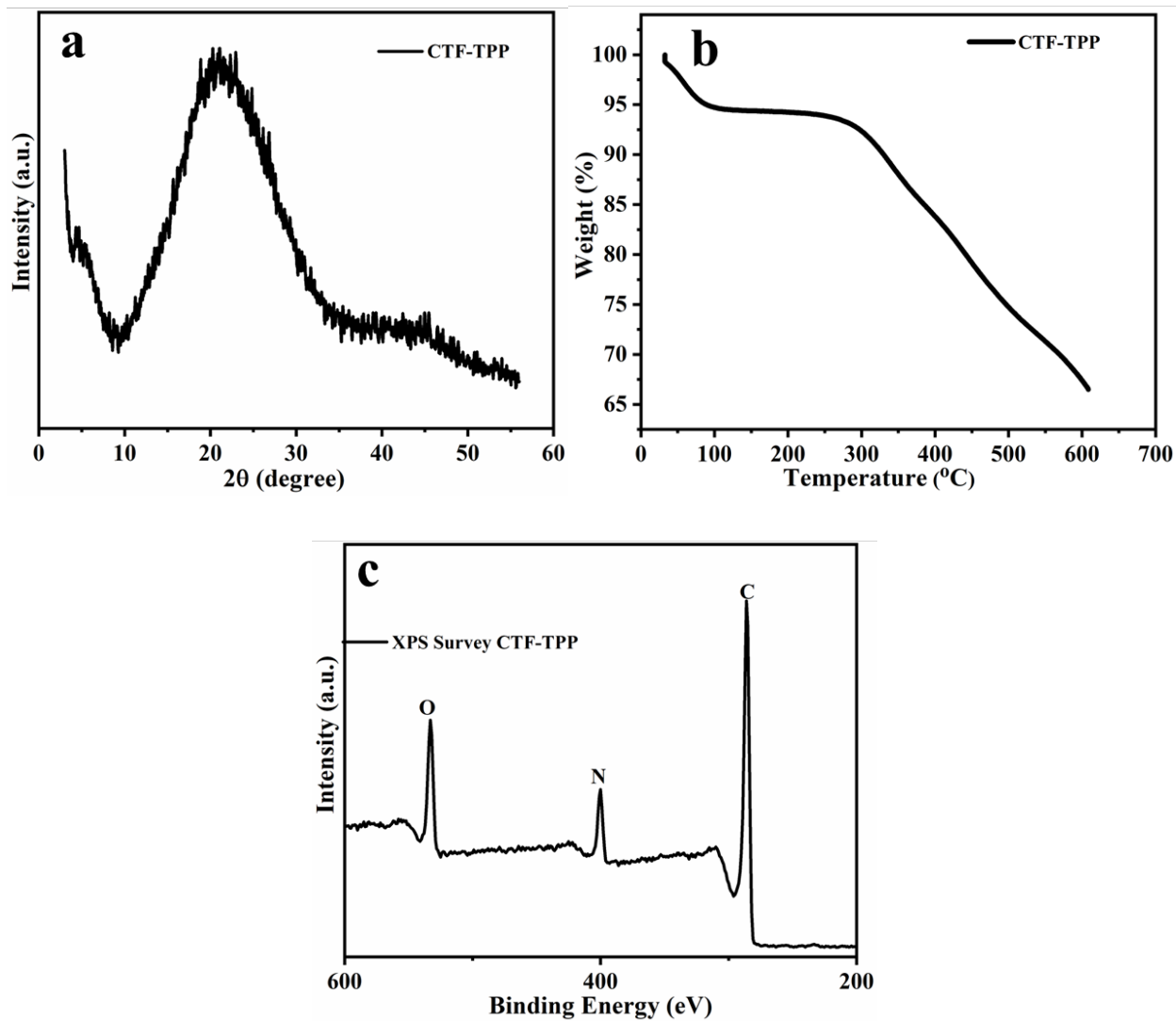


Fig. S1: (a) PXRD pattern, (b) TGA analysis in N_2 atmosphere, and (c) XPS survey spectra of CTF-TPP.

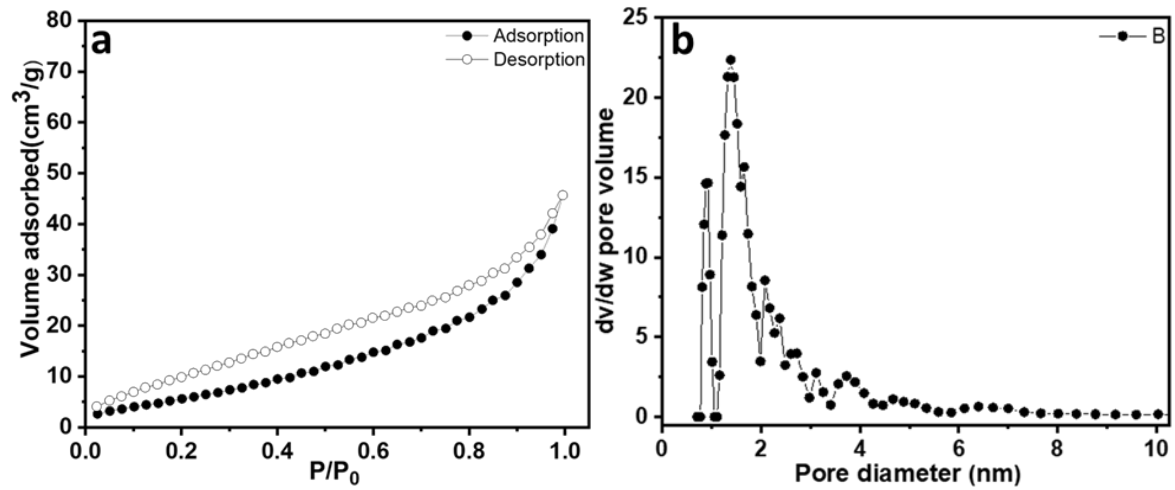


Fig. S2: (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of CTF-TPP.

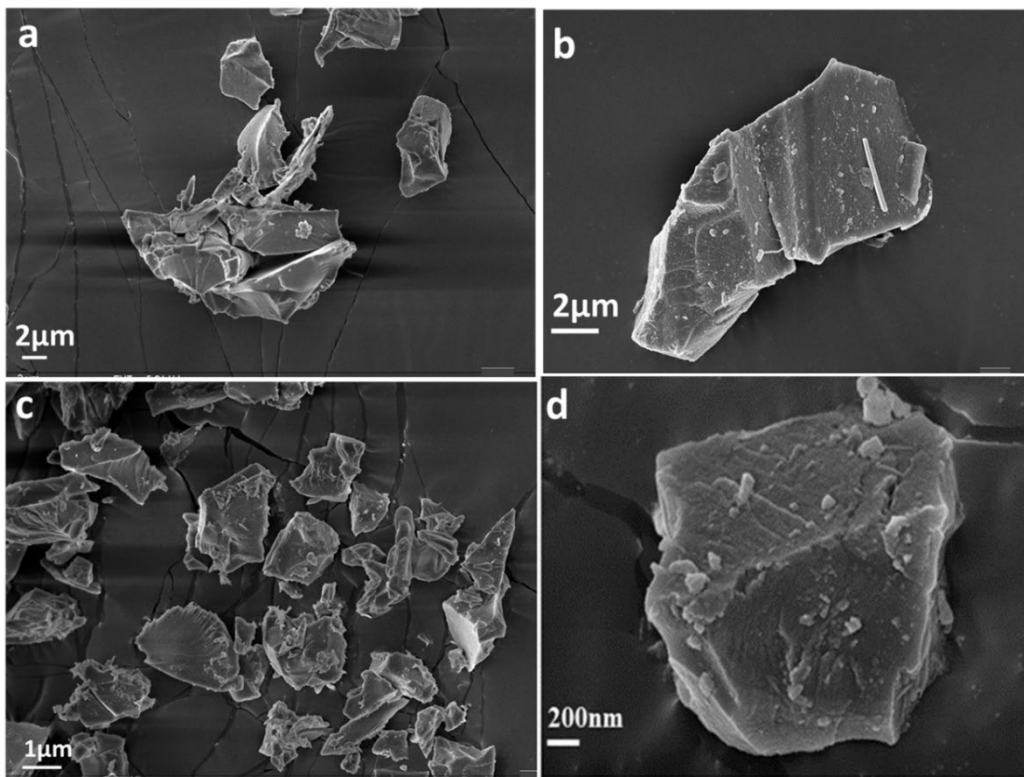


Fig. S3: FE-SEM images of (a-b) CTF-TPP@Pt_{0.5} and (c-d) CTF-TPP@Pd_{0.5}

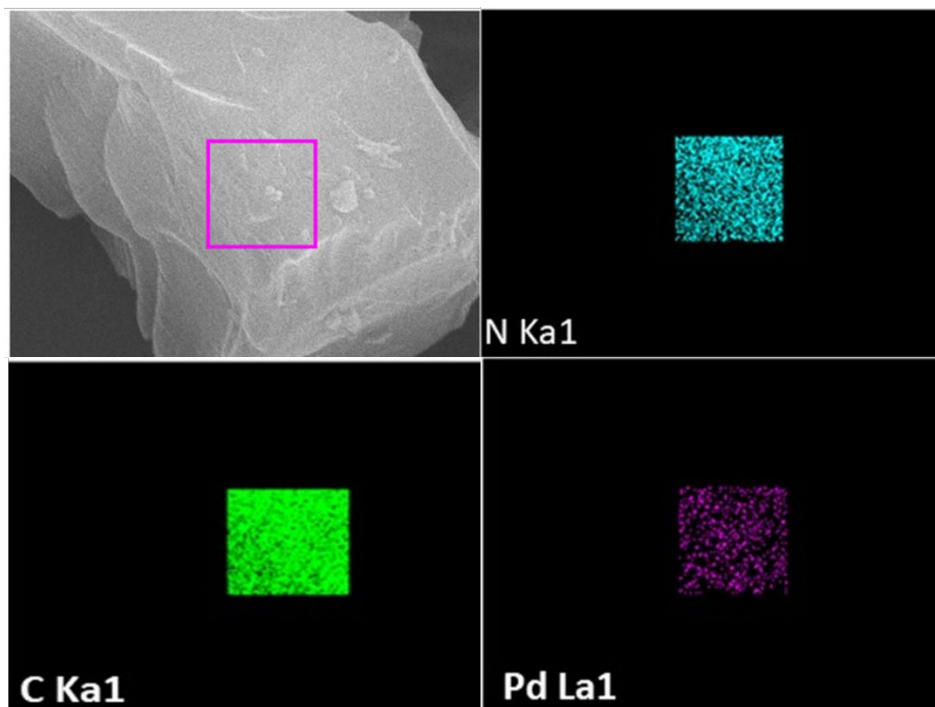


Fig. S4: FE-SEM images and dark-field EDX mapping of CTF-TPP@Pt_{0.5}.

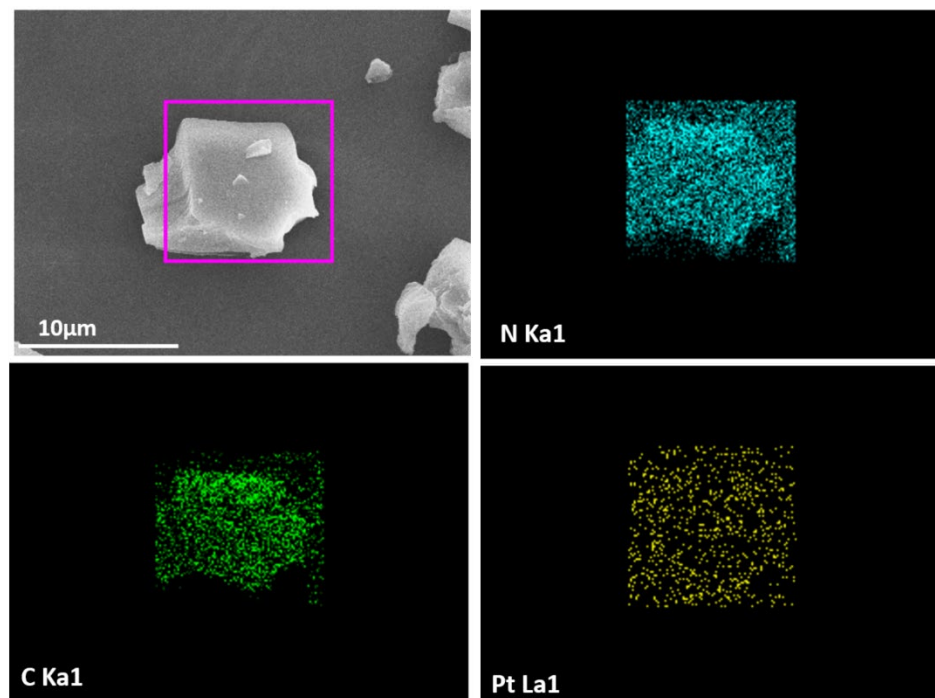


Fig. S5: FE-SEM images and dark-field EDX mapping of CTF-TPP@Pd_{0.5}.

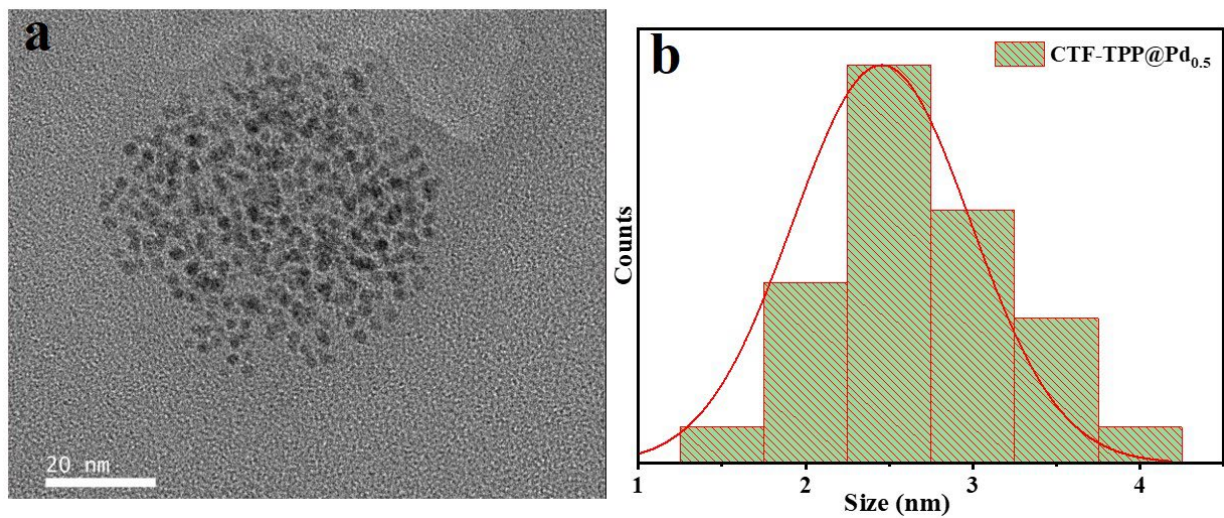


Fig. S6: (a) TEM image of CTF-TPP@Pd_{0.5}. (b) Size distribution of Pd nanoparticle on CTF-TPP@Pd_{0.5}.

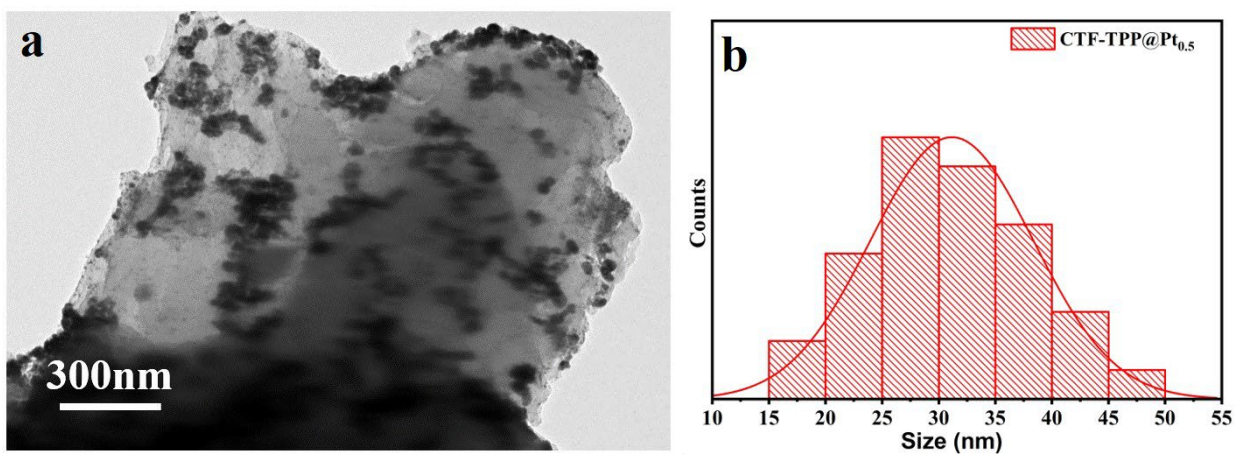


Fig. S7: (a) TEM image of CTF-TPP@Pt_{0.5}. (b) size distribution of Pt nanoparticles on CTF-TPP@Pt_{0.5}.

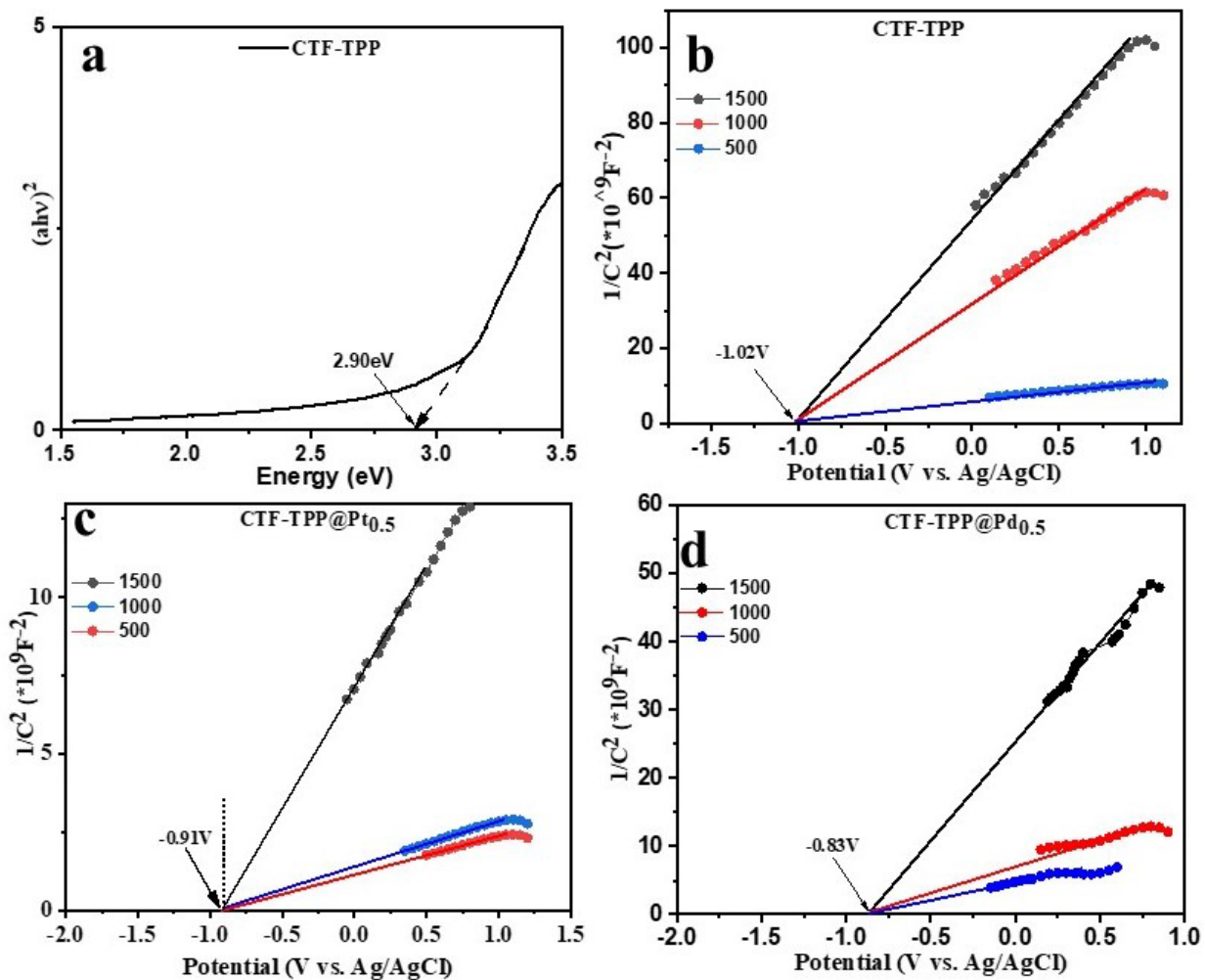


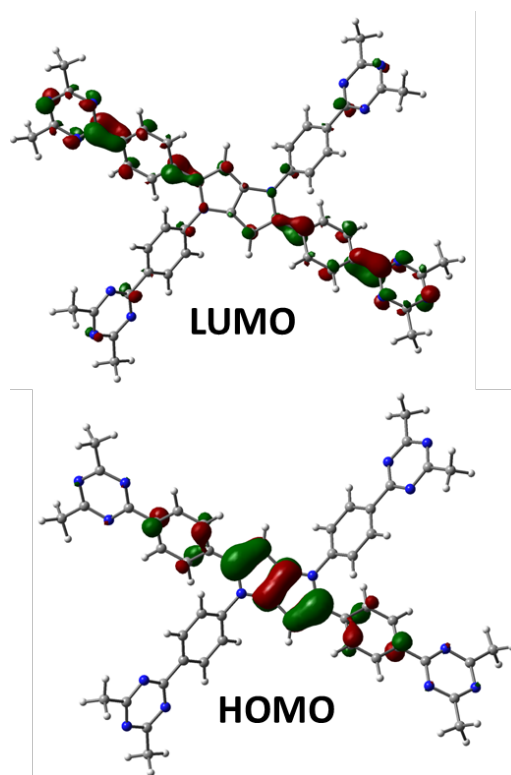
Fig. S8: (a) Tauc plot of CTF-TPP. (b-d) Mott-Schottky plots of CTF-TPP, CTF-TPP@Pt_{0.5}, and CTF-TPP@Pd_{0.5}.

Table S3. Decay Parameters of synthesized photocatalyst

Systems	Lifetime, τ (ns)	Pre-exponential factors (A)	Relative amplitude (B)	Average lifetime, τ_{avg} (ns)	χ^2
CTF-TPP	$\tau_1=1.26$ $\tau_2=3.27$	0.815	$B_1=89.56$ $B_2=10.44$	1.71	1.00056
CTF-TPP@Pd	$\tau_1=1.37$ $\tau_2=5.57$	0.247	$B_1=91.52$ $B_2=8.48$	2.51	0.99534
CTF-TPP@Pt	$\tau_1=1.35$ $\tau_2=3.6$	0.795	$B_1=91.06$ $B_2=8.94$	1.82	1.01575

$$\tau_{\text{avg}} = \frac{\tau_1^2 A_1 + \tau_2^2 A_2}{\tau_1 A_1 + \tau_2 A_2}$$

$$A_2 = \frac{B_2}{B_1 + B_2} \quad A_1 = \frac{B_1}{B_1 + B_2}$$

**Fig. S9:** Optimized HOMO–LUMO structures of CTF-TPP.

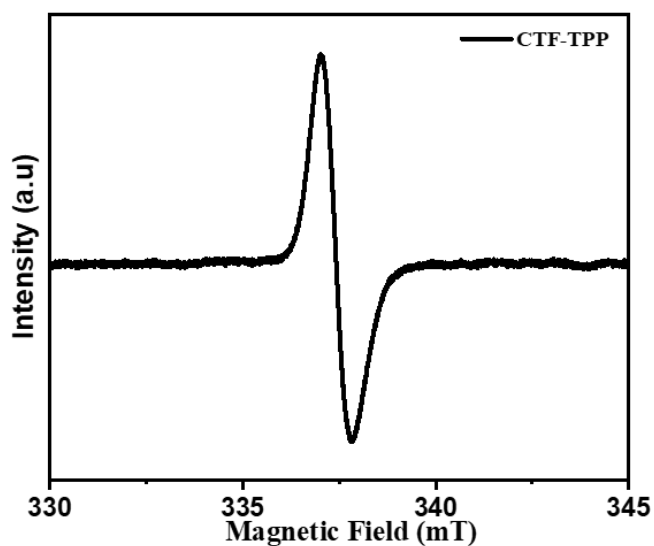


Fig. S10: EPR spectra of CTF-TPP.

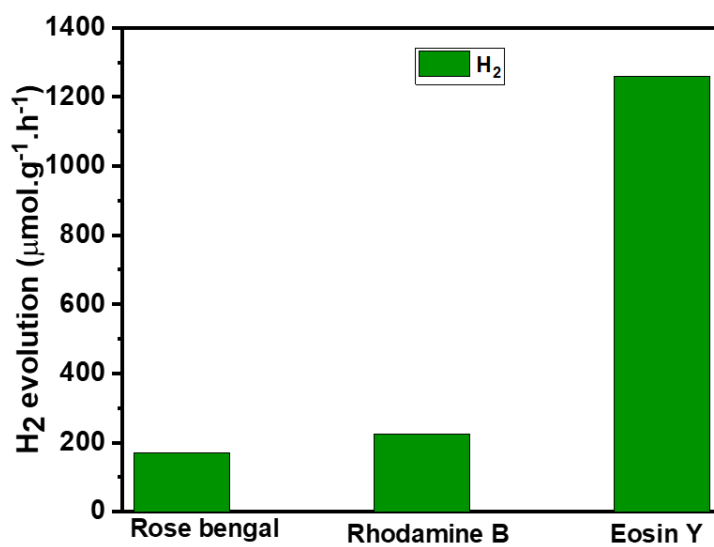


Fig. S11: Photocatalytic H₂ evolution using different dye of CTF-TPP@Pd_{0.5}.

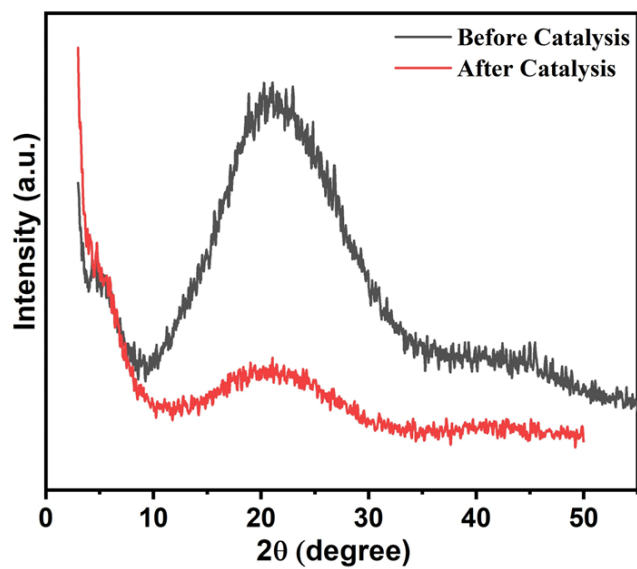


Fig. S12: PXRD pattern before and after catalysis of CTF-TPP@Pd_{0.5}.

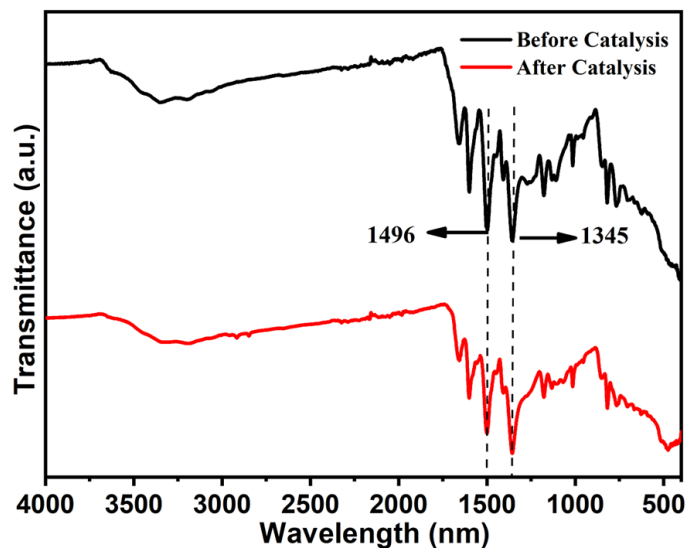


Fig. S13: FT-IR spectra before and after catalysis of CTF-TPP@Pd_{0.5}.

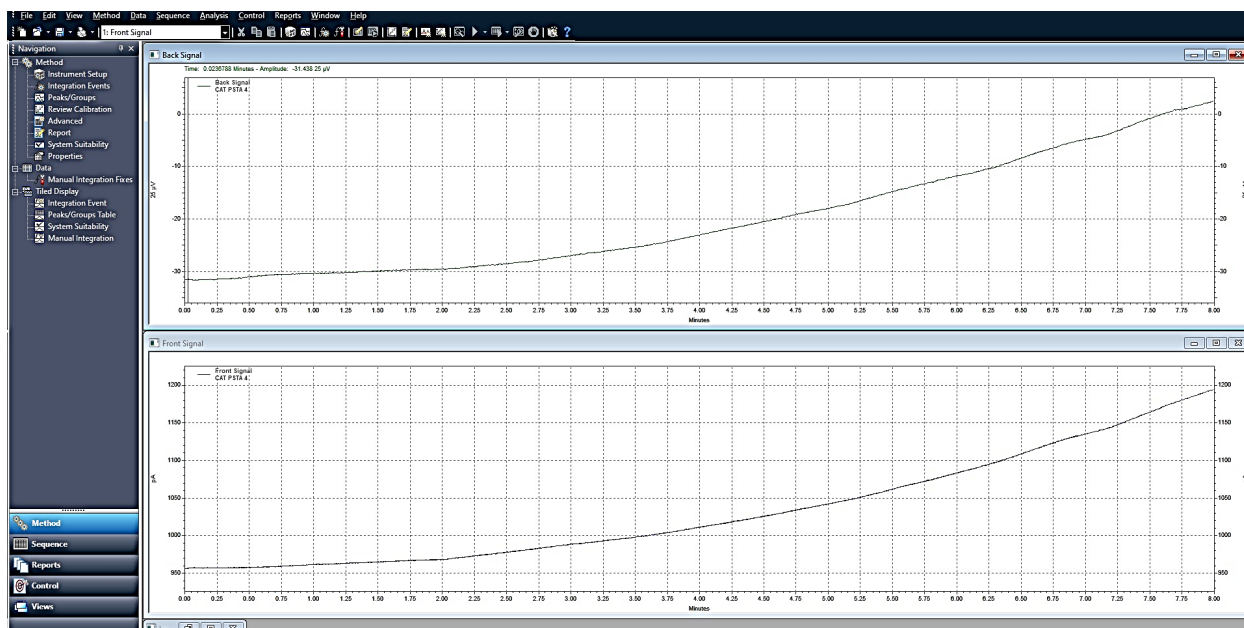


Fig. S14 (a) Gas chromatogram for H_2 (2 mg CTF-TPP@Pd_{0.5}, 3 mL TEOA and 4 mg EY).

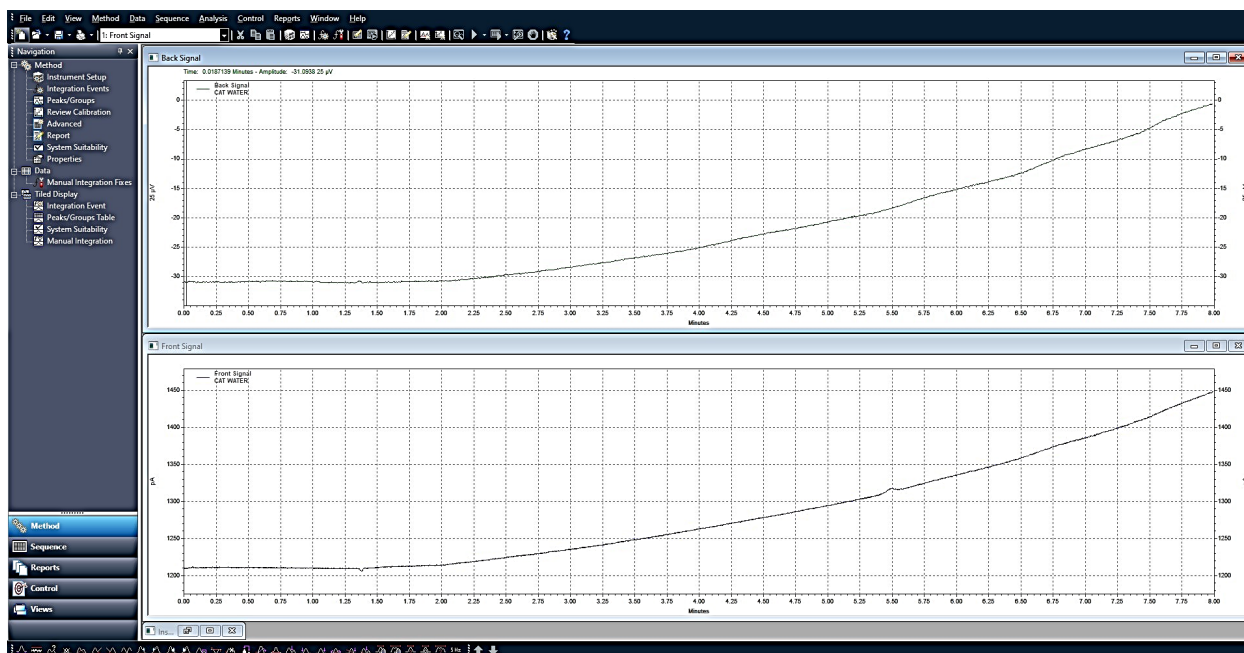


Fig. S14 (b) Gas chromatogram for H_2 (2 mg CTF-TPP@Pd_{0.5}, 5mL H₂O and 4 mg EY).

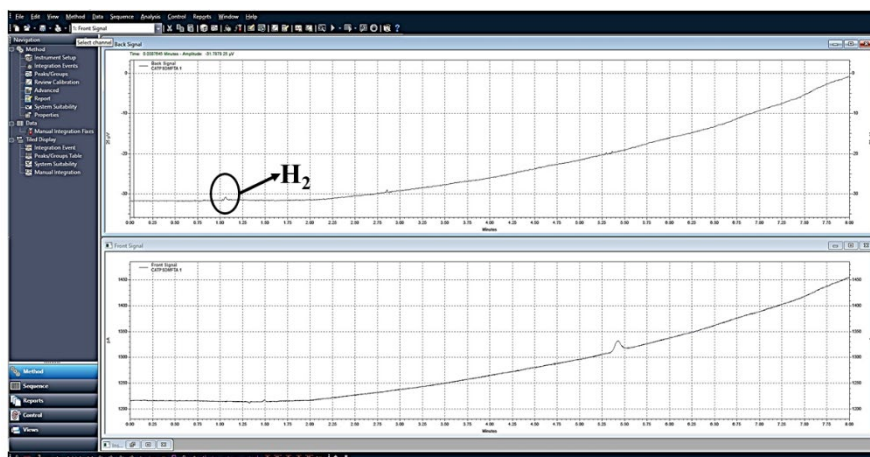


Fig. S14 (c) 2 mg photocatalyst (CTF-TPP@Pd_{0.5}), 1 mL triethanolamine and 4 mg eosin-Y were dispersed in 4 mL DMF. Negligible amount of H₂ observed, and it is due to may be small amount of water is present in DMF.



Fig. S15: Gas chromatograms: The peak of hydrogen evolution for CTF-TPP@Pd_{0.5} applying 2 mg photocatalyst, 5 mL water, 1 mL TEOA and 4 mg EY.



Fig. S16: Experimental set up of photocatalytic H₂ evolution.

Table S4. The photocatalytic efficacy of CTFs documented in the literature

Catalyst	Co catalyst	Condition	Amount of Catalyst	H₂ evolution	Reference
CTF-1 CTF-2 CTF-3	3 wt% Pt	>420 nm, TEOA	25 mg	35 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 296 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 45 $\mu\text{mol g}^{-1} \text{h}^{-1}$	3
CTF-S ₁₀	1 wt% Pt	>420 nm, TEOA	20 mg	2000 $\mu\text{mol g}^{-1} \text{h}^{-1}$	4
CTF-1-100W	2.01 wt% Pt	>420 nm, TEOA	50 mg	5500 $\mu\text{mol g}^{-1} \text{h}^{-1}$	5
PCP-10	2 wt% Pt	>420 nm, TEA	12 mg	2642 $\mu\text{mol g}^{-1} \text{h}^{-1}$	6
CTF-N	~2 wt%Pt	>420 nm TEOA	50 mg	538 $\mu\text{mol g}^{-1} \text{h}^{-1}$	7
CTF-HUST-C1	3 wt% Pt	>420 nm, TEOA	50 mg	5100 $\mu\text{mol g}^{-1} \text{h}^{-1}$	8
CTF-1	8wt% Pt	>420 nm, TEOA	25mg	1082 $\mu\text{mol g}^{-1} \text{h}^{-1}$	9
N ₃ -COF	8 wt% Pt	>420 nm TEOA	5 mg	1703 $\mu\text{mol g}^{-1} \text{h}^{-1}$	10
TFPT-COF	8 wt% Pt	>420 nm; TEOA	10 mg	1970 $\mu\text{mol g}^{-1} \text{h}^{-1}$	11
PCTF-8	2.3 wt% Pt	>420 nm; TEOA	10mg	119 $\mu\text{mol g}^{-1} \text{h}^{-1}$	12
CTF-HUST-3 CTF-HUST-1 CTF-HUST-2 CTF-HUST-4	3 wt% Pt	>420 nm TEOA	50mg	1238 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 1460 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 2647 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 1582 $\mu\text{mol g}^{-1} \text{h}^{-1}$	13
CTF-TPP@Pd _{0.5}	0.5wt% Pd	>420 nm; TEOA Dye	2 mg	1995 $\mu\text{mol g}^{-1} \text{h}^{-1}$	This work

¹H NMR:

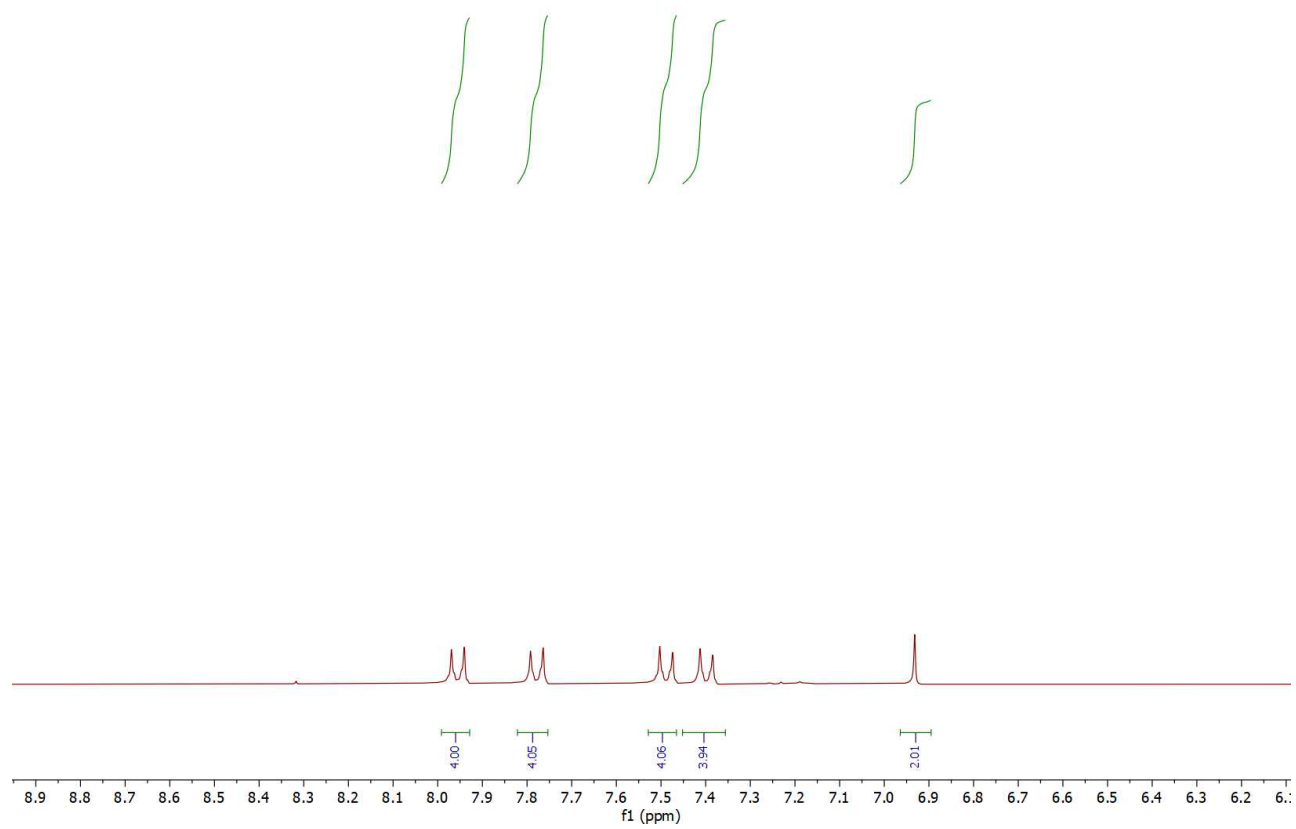


Fig. S17: ¹H NMR of synthesized TPP ligand

¹³C NMR:

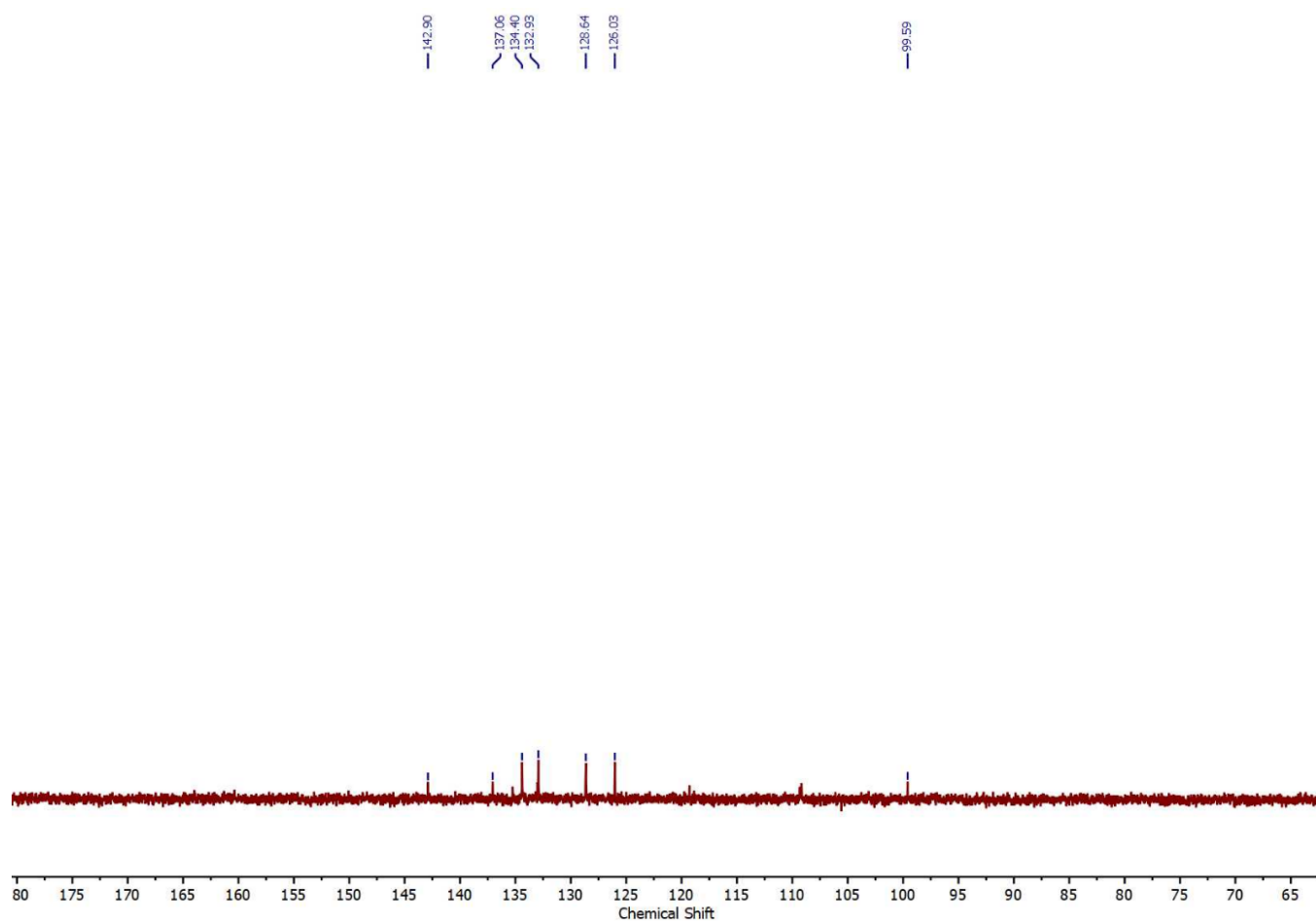


Fig. S18: ¹³C NMR of synthesized TPP ligand.

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