Supplementary Information

# Regulating Pt-covalent triazine framework Schottky junctions by using tailor-made nitrogen sites towards efficient photocatalysis

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#### 1. Materials

All the chemical reagents and solvents were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. or Sinopharm Chemical Reagent Co., Ltd.. Unless otherwise stated, the commercially available reagents and solvents were used without further purification.

# 2. Characterization Methods

The Monomer structures were checked with <sup>1</sup>H NMR on a JEOL (JNM-ECZ400S/L1) 400 MHz spectrometer. <sup>13</sup>C CP/MAS NMR measurement was recorded using a JNM-ECZ600R spectrometer. The Powder X-ray diffraction (PXRD) measurements were performed using X-ray diffraction (D8 Advance, Bruker). Fourier-transform infrared (FT-IR) spectra were recorded on a Mattson Alpha-Centauri spectrometer (Nicolet iS50, Thermo Scientific). Elemental analysis was measured by a VarioMicrocube Elemental Analyser (Elementar). Thermogravimetric analysis (TGA) (STA 449F5, Perkin Elmer Instruments) with a temperature interval between 35 and 800 °C. Scanning electron microscopy (SEM) images were obtained with an MAIA3 LMH. Transmission electron microscopy (TEM) images of the samples were characterized by transmission electron microscope (Talos F200X). UV-vis absorption spectra were obtained in the solid state on a Lambda 950, PerkinElmer. The fluorescence properties were measured with an Edinburgh FLS9 spectrofluorometer. Time-correlated single photon counting (TCSPC) measurements were recorded on instruments Edinburgh FLS9 fluorescence spectrometer.

### 3. DFT Calculation

The density-functional theory calculations were performed with the Quantum Espresso software package<sup>1</sup>. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization of the exchange-correlation energy functional with ultrasoft pseudo potentials were employed. Brillouin zone integration was done using a uniform Monkhorst-Pack with a k-point grid of  $2 \times 1 \times 8$  for geometry optimization and electronic structure calculations. Grimme's DFT-D3 approach for the treatment of London dispersion correction was applied.

#### 4. Synthesis of Monomers

4.1 Synthesis of monomers of CTF-Py-1



Synthesis process of CTF-Py-1 monomer

6-Bromo-3-pyridinecarboxaldehyde (4 mmol, 744 mg), 4-formylphenylboronic acid (5.6 mmol, 839.7 mg) and potassium carbonate (20 mmol, 2764.2 mg) were added to a 100 mL flask. Then 1,4-dioxane (32 mL) and water (7.2 mL) were added as the solvent mixture. The above system was purged using a nitrogen bubble for 20 min. Then add tetrakis (triphenylphosphine) palladium (0.2 mmol, 231.1 mg) and continue to be purged using nitrogen for 30 min. The reaction system was heated at 105 °C for 48 h under nitrogen atmosphere. After the reaction system was cooled to room temperature, add water and filter to get the solid. The solid was dissolved in DCM and filtered. The crude product was purified by column chromatography to afford a yellow solid (Yield, 58.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.17 (s, 1H), 10.11 (s, 1H), 9.18 (d, J = 2.1 Hz, 1H), 8.27 (dd, J = 10.8, 8.4 Hz, 3H), 8.01 (dd, J = 16.0, 8.2 Hz, 3H).

## 4.2 Synthesis of monomers of CTF-Py-2



Synthesis process of CTF-Py-2 monomer

5-Bromopyridine-2-carboxaldehyde (4 mmol, 744 mg), 4-formylphenylboronic acid (5.6 mmol, 839.7 mg), and potassium carbonate (20 mmol, 2764.2 mg) were added to a 100 mL flask. Then 1,4-dioxane (32 mL) and water (7.2 mL) were added as the solvent mixture. The above system was purged using a nitrogen bubble for 20 min. Then add tetrakis (triphenylphosphine) palladium (0.2 mmol, 231.1 mg) and continue to be purged using nitrogen for 30 min. The reaction system was heated at 105 °C for 48 h under nitrogen atmosphere. After the reaction system was cooled to room temperature, add water and filter to get the solid. The solid was dissolved in DCM and filtered. The crude product was purified by column chromatography to afford a yellow solid (Yield, 48.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.14 (s, 1H), 10.10 (s, 1H), 9.05 (s, 1H), 8.07 (dd, J = 23.9, 8.7 Hz, 3H), 7.82 (d, J = 8.2 Hz, 2H).

#### 5. Synthesis of CTFs

5.1 Synthesis of CTF-Py-1



Synthesis process of CTF-Py-1

CTF-Py-1 monomer (0.25 mmol, 52.8 mg), terephthalimidamide hydrochloride (0.5 mmol, 117.6 mg), and sodium carbonate (1.2 mmol, 127.2 mg) were added to a 25 mL round-bottomed flask. And dimethylsulfoxide (15 mL) was added as the solvent. The round bottom flask was heated at 100 °C, 120 °C, and 140 °C for 24 h under air atmosphere with a gradient heating method. After the reaction was stopped, the crude product was obtained by filtration of the reaction system, which was washed with DMF, anhydrous alcohol, dilute hydrochloric acid (1 M), deionized water and freeze-dried to obtain a yellow powder with 94.5% yield.

## 5.2 Synthesis of CTF-Py-2



Synthesis process of CTF-Py-2

CTF-Py-2 monomer (0.25 mmol, 52.8 mg), terephthalimidamide hydrochloride (0.5 mmol, 117.6 mg), and sodium carbonate (1.2 mmol, 127.2 mg) were added to a 25 mL round-bottomed flask. And dimethylsulfoxide (15 mL) was added as the solvent. The round bottom flask was heated at 100 °C, 120 °C, and 140 °C for 24 h under air atmosphere with a gradient heating method. After the reaction was stopped, the crude product was obtained by filtration of the

reaction system, which was washed with DMF, anhydrous alcohol, dilute hydrochloric acid (1 M), deionized water and freeze-dried to obtain a yellow powder with 95.0% yield.

#### 5.3 Synthesis of CTF-BPy



Synthesis process of CTF-BPy

2,2'-bipyridine-5,5'-dicarbaldehyde (0.25 mmol, 53.1 mg), terephthalimidamide hydrochloride (0.5 mmol, 117.6 mg), and sodium carbonate (1.2 mmol, 127.2 mg) were added to a 25 mL round-bottomed flask. And dimethylsulfoxide (15 mL) was added as the solvent. The round bottom flask was heated at 100 °C, 120 °C, and 140 °C for 24 h under air atmosphere with a gradient heating method. After the reaction was stopped, the crude product was obtained by filtration of the reaction system, which was washed with DMF, anhydrous alcohol, dilute hydrochloric acid (1 M), deionized water and freeze-dried to obtain a yellow powder with 93.0% yield.

### 6. Experimental procedure for photocatalysis

6.1 Preparation of platinum-loaded photocatalysts

Pt nanoparticles were loaded on CTFs by a chemical reduction method via NaBH<sub>4</sub> reductant before photocatalytic hydrogen production performance testing. CTFs (25 mg) were dispersed in water (15 mL) and sonicated for 30 min to make the dispersion homogeneous. Chloroplatinic acid was added. And after stirring for 2 h, the newly prepared aqueous NaBH<sub>4</sub> solution was added drop by drop, and the stirring was continued for 1 h. It was left to stand overnight, filtered, and vacuum-dried at 100 °C for 10 h to get the Pt@CTFs photocatalysts.

#### 6.2 Photocatalytic hydrogen production performance test

The photocatalytic hydrogen evolution performance from water splitting was tested under simulated sunlight (AM 1.5 G, 100 mW·cm<sup>-2</sup>) in a 180 mL photoreactor. The photocatalyst (10

mg) was dispersed in 36 mL of water. TEA (4 mL) was used as an electron sacrificial agent. The entire photocatalytic testing process was conducted at 25°C. Determination of the amount of hydrogen produced in the photocatalytic process by gas chromatography (GC7890, Agilent).

# 6.3 The calculations of apparent quantum yield (AQY)

Firstly, the photocatalytic hydrogen evolution was tested under simulated sunlight (AM 1.5 G,  $100 \text{ mW} \cdot \text{cm}^{-2}$ ) in a 180 mL photoreactor. The photocatalyst (50 mg) was dispersed in 36 mL of water. TEA (4 mL) was used as an electron sacrificial agent. The entire photocatalytic testing process was conducted at 25°C. Determination of the amount of hydrogen produced in the photocatalytic process by gas chromatography (GC7890, Agilent). When the photocatalytic hydrogen production rate was stable, the Xenon lamp filter was changed to DT 420 nm to test the apparent quantum efficiency.

The AQY was calculated as the following equation:

$$AQY = \frac{2CN_A}{PSt\lambda/hc} \times 100\%$$

Where C is the amount of H<sub>2</sub> (mol); N<sub>A</sub> is the Avogadro constant ( $6.02 \times 10^{23}$  mol<sup>-1</sup>); P is the incident light intensity (W cm<sup>-2</sup>); S is the light area (cm<sup>2</sup>); t is the light irradiation time (s);  $\lambda$  is the irradiation light wavelength (420 nm); h is the Plank constant ( $6.626 \times 10^{-34}$  J·s); c is light speed ( $3 \times 10^8$  m s<sup>-1</sup>).

Additional experimental results



Figure S1. FT-IR spectrum of CTFs.



Figure S2. Solid-state <sup>13</sup>C NMR spectrum of (a) CTF-Py-1, (b) CTF-Py-2 and (c) CTF-BPy.



Figure S3. PXRD pattern for (a) CTF-Py-1, (b) CTF-Py-2 and (c) CTF-BPy.



Figure S4. SEM image of CTFs.



Figure S5. Nitrogen sorption isotherm curve of (a) CTF-Py-1, (b) CTF-Py-2 and (c) CTF-BPy.



Figure S6. TGA curve of (a) CTF-Py-1, (b) CTF-Py-2 and (c) CTF-BPy.



Figure S9. Nitrogen sorption isotherm curve of (a) Pt@CTF-Py-1, (b) Pt@CTF-Py-2 and (c) Pt@CTF-BPy.



Figure S10. (a) TEM image of Pt@CTF-Py-1; (b) EDS elemental mappings of Pt@CTF-Py-1.



Figure S11. (a) TEM image of Pt@CTF-Py-2; (b) EDS elemental mappings of Pt@CTF-Py-2.



Figure S12. (a) TEM image of Pt@CTF-BPy; (b) EDS elemental mappings of Pt@CTF-BPy.



Figure S13. Hydrogen evolution rates of Pt@CTF-Py-1 with different sacrificial agents.



# Wavenumber (cm<sup>-1</sup>)

Figure S14. FT-IR spectra of corresponding Pt@CTF-Py-1 before and after 5 cycles photocatalytic process.



Figure S15. PXRD spectra of corresponding Pt@CTF-Py-1 (a) before and (b) after 5 cycles photocatalytic process.



Figure S16. UV-vis absorption spectroscopy of corresponding Pt@CTF-Py-1 before and after 5 cycles photocatalytic process.



Figure S17. (a) UV-vis absorption spectroscopy of the CTF-Py-1, CTF-Py-2 and CTF-Bpy. (b) the Tauc plots of CTFs.



Figure S18. Calculated band structures and corresponding PDOS for (a) CTF-Py-1, (b) CTF-Py-2 and (c) CTF-BPy.



Figure S19. C 1s XPS spectra of CTF-Py-1, CTF-Py-2, CTF-BPy, Pt@CTF-Py-1, Pt@CTF-Py-2 and Pt@CTF-BPy, respectively.



Figure S20. N 1s XPS spectra of CTF-Py-1, CTF-Py-2, CTF-BPy, Pt@CTF-Py-1, Pt@CTF-Py-2 and Pt@CTF-BPy, respectively.



Figure S21. Steady-state photoluminescence (PL) spectra for CTFs excited at 375 nm.

Sample	C (%)		N (%)		H (%)		S (%)		C/N
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Ratio
CTF-Py-1	74.84	65.02	21.08	17.95	4.09	4.70	0	0.24	3.62
CTF-Py-2	74.84	66.13	21.08	17.56	4.09	4.46	0	0.30	3.77
CTF-BPy	72.10	62.98	24.03	19.73	3.86	4.60	0	0.20	3.19

 Table S1. Elemental analysis results of the CTFs.

	a		Hydrogen		
Catalyst	Sacrificial	Filter cut	evolution rate	References	
	reagent		(µmol g <sup>-1</sup> h <sup>-1</sup> )		
				Angew. Chem. Int.	
CTF-HUST-1	TEOA	$\lambda > 420 \text{ nm}$	1460	Ed. 2017, 56,	
				14149-14153.	
CTE ULICT		$\lambda > 420 \text{ nm}$	5100	Angew. Chem. Int.	
C1F-HUS1-	TEOA			Ed. 2018, <b>57</b> ,	
Cl				11968-11972.	
T2N CTE	TEOA	1 > 120	6495 05	ChemSusChem	
I SN-CIF	TEOA	$\lambda \ge 420 \text{ nm}$	6483.03	2022, <b>15</b> , e2022008.	
				ACS Appl. Mater.	
Dav	TEOA	$\lambda > 395 \text{ nm}$	7240	Interfaces 2022, 14,	
Бру <sub>0.66</sub>				14182-14192.	
DTT Day	TEOA	$\lambda > 420 \text{ nm}$	15800	Angew. Chem. Int.	
BII-Bpy-				<i>Ed.</i> 2023,	
PCOF(AC)				e202300224.	
N3-COF	TEOA	$\lambda > 420 \text{ nm}$	1703	Nat. Commun. 2015,	
				<b>6,</b> 8508.	
CTF-N	TEOA	$\lambda > 420 \text{ nm}$	10760	J. Mater. Chem. A,	
				2018, <b>6,</b> 19775-	
				19781.	
				Angew. Chem. Int.	
CTF-BT/Th-1	TEOA	$\lambda > 420 \text{ nm}$	6600	Ed. 2019, <b>58,</b> 8676-	
				8680.	
ter-CTF-0.7	TEOA	$\lambda > 420 \text{ nm}$	007	ACS Catal. 2019, 9,	
			996	9438-9445.	
				Angew. Chem. Int.	
PyTz-COF	AA	AM 1.5G	2072.4	<i>Ed.</i> 2021, <b>60,</b> 1869-	
				1874.	
PCP-10	TEA	$\lambda > 420 \text{ nm}$	31.7	Macromolecules.	

**Table S2.** Comparison of the photocatalytic hydrogen evolution performance with other conjugated porous polymers.

				2016, <b>49</b> , 6903- 6909.
Pt@CTF-Py-1	TEA	AM 1.5G	14960	This work
Pt@CTF-Py-2	TEA	AM 1.5G	5403	This work