

## Supplementary Information

### **Significant Improvement of Photocatalytic Hydrogen Evolution Performance in Covalent Organic Frameworks: Substituent Fine-Tuning**

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Text: 4

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## **Text S1. Regents and materials**

All reagents and solvents were purchased from commercial sources and used without further purification. 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde, 1,4-diamino-2,5-dicyanobenzene, 2,5-dichlorobenzene-1,4-diamine were purchased from Jilin Chinese Academy of Sciences - Yanshen Technology Co., Ltd. 2,5-dichlorobenzene-1,4-diamine, p-Phenylenediamine, Tetrahydrofuran (THF), 1,4-dioxane, mesitylene and Chloroplatinic acid hexahydrate were purchased from J&K Chemical Co. Ltd. Glacial acetic acid and 2,3,5,6-tetrafluorobenzene-1,4-diamine were purchased from Shanghai Macklin Biochemical Co., Ltd. Methanol, ascorbic acid and ethanol were obtained from Sinopharm Chemistry Reagent Co. Ltd. 2,5-Diaminotoluene was obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd.

## **Text S2. Characterization**

Powder X-ray diffraction (PXRD, Bruker D8 ADVANCE, Germany) using a Cu K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation ranging from  $2^\circ$  to  $40^\circ$  with a resolution of  $0.02^\circ$  was utilized to analysis the crystalline. Surface area and pore volume were measured by Brunauer-Emmette-Teller (BET) methods (ASAP2000 V3.01 A; Micromeritics, Norcross, GA).

All the electrochemical properties were investigated on a CHI760E electrochemical analyzer (Chenhua, Shanghai, China) in a standard Three-electrode system, using a platinum foil as counter electrode and Saturated Calomel Electrode (SCE) as the reference electrode. The electrolyte was a 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The working electrodes were prepared as follows: 5 mg of photocatalyst powder was dispersed in 0.15 ml of ethanol, and 0.05 ml Nafion was added as the adhesive, which was dip-coated on the surface of indium tin oxide (ITO) glass substrate and dried at room temperature. The light source was preheated for 10 min before each photocurrent test to maintain a stable light intensity. Mott-schottky curves were measured at a frequency of 1 kHz.

## **Text S3. Preparation of TpPa-X**

COF TpPa-1: Following is a modified procedure<sup>[1]</sup>, a quartz tube measuring 10 × 8 mm (o.d. × i.d.) was charged with 1,3,5-triformylphloroglucinol (Tp) (63 mg, 0.3 mmol), 1,4-phenylenediamine (Pa-1) (48 mg, 0.45 mmol), 1.5 ml of dioxane, 1.5 ml of mesitylene, and 0.3 ml of 6 M aqueous acetic acid (The exact amount to be added can be found in Table S1). The tube was flash frozen at 77 K in liquid N<sub>2</sub> bath, degassed by three freeze-pump-thaw cycles, and flame sealed. The reaction was heated at 120 °C for 5 d, yielding a red precipitate at the bottom of the tube. The powder was isolated by centrifugation and washed with THF (20 × 3) and MeOH (20 × 2), and dried at room temperature and evacuated under vacuum at 100 °C, 6h to afford a red powder.

## **Text S4. Photocatalytic hydrogen evolution**

50 mL of 0.1 M ascorbic acid aqueous solution was added into the photocatalytic hydrogen evolution vessel and 10 mg COF powder was dispersed into the system. A

certain amount of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (3% wt Pt relative to the amount of catalyst COF) was added as the precursor of co-catalyst Pt. The container containing the suspension is connected to the photocatalytic hydrogen evolution system (CEL-PAEM-D6, CEAULIGHT). Vacuum the reaction mixture for half an hour to ensure complete removal of air from the unit and check the air tightness of the system. It is then illuminated with a 300 W Xe light source with an optical cut-off filter ( $\lambda \geq 420$  nm). The temperature of the reaction solution is maintained at 5 °C by circulating the cooling water. After 1, 2, 3, and 4 hours of illumination, the volume of hydrogen precipitated was measured by a gas chromatographic analyzer equipped with a thermal conductivity detector (TCD), and the amount of hydrogen produced was determined by a standard curve.

**Table S1.** Amounts of monomers used to synthesize COFs. Where M is mesitylene and D is dioxane.

COF	Tp/mg	Pa-X/mg	Solvent (M :D)	Catalyst	Product/ mg	Yield (%)
TpPa-1	63	48	1: 1	0.3 ml 6 M AcOH	101	91
TpPa-CN <sub>2</sub>		60	3: 1		110	89
TpPa-Cl <sub>2</sub>		80	1: 3		124	87
TpPa-CH <sub>3</sub>		55	3: 1		109	92
TpPa-(CH <sub>3</sub> ) <sub>2</sub>		62	1: 1		112	90
TpPa-CN		60	1: 3		111	90

**Table S2.** Time-resolved fluorescence fit results.

Sample	$\tau_1$	$\tau_2$	B <sub>1</sub>	B <sub>2</sub>	$\tau$
TpPa-1	4.26*10 <sup>-9</sup>	4.25*10 <sup>-9</sup>	1.65	0.81	4.26*10 <sup>-9</sup>
TpPa-Cl <sub>2</sub>	1.98*10 <sup>-9</sup>	1.98*10 <sup>-9</sup>	0.53	1.98	1.98*10 <sup>-9</sup>
TpPa-CN <sub>2</sub>	2.53*10 <sup>-9</sup>	2.53*10 <sup>-9</sup>	1.29	0.85	2.53*10 <sup>-9</sup>
TpPa-CN	2.18*10 <sup>-9</sup>		54.24		2.18*10 <sup>-9</sup>
TpPa-CH <sub>3</sub>	2.28*10 <sup>-9</sup>		2.01		2.28*10 <sup>-9</sup>
TpPa-(CH <sub>3</sub> ) <sub>2</sub>	3.10*10 <sup>-9</sup>		2.10		3.10*10 <sup>-9</sup>

The data was fitted with using multiple exponential formulas (1). And the average decay time  $\tau$  was calculated by the formula (2).

$$R(t) = B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}} + B_3 e^{-\frac{t}{\tau_3}} \quad (1)$$

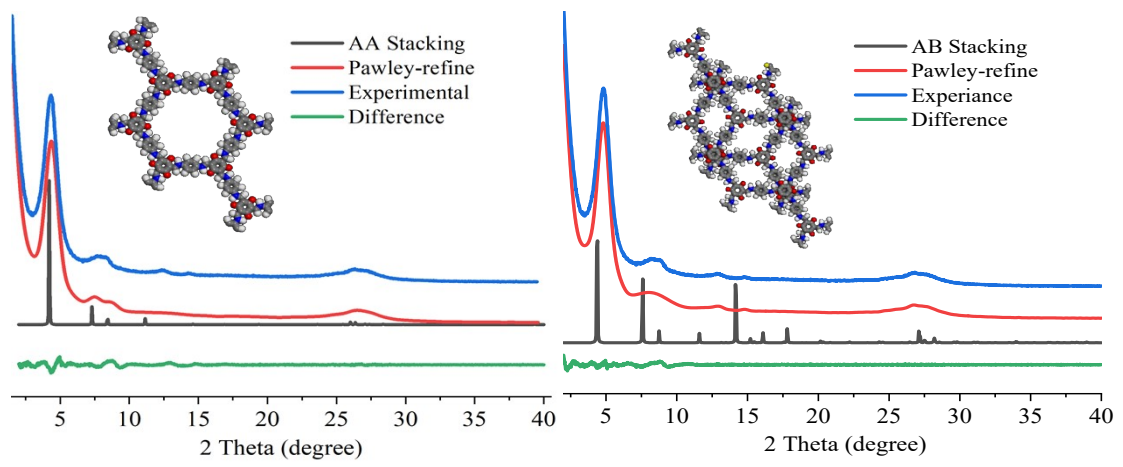
$$\tau = \frac{B_1 \times \tau_1^2 + B_2 \times \tau_2^2 + B_3 \times \tau_3^2}{B_1 \times \tau_1 + B_2 \times \tau_2 + B_3 \times \tau_3} \quad (2)$$

**Table S3.** Comparison of photocatalytic hydrogen evolution performances of TpPa-Cl<sub>2</sub> and TpPa-CN<sub>2</sub> with representative COFs and COF-based composites.

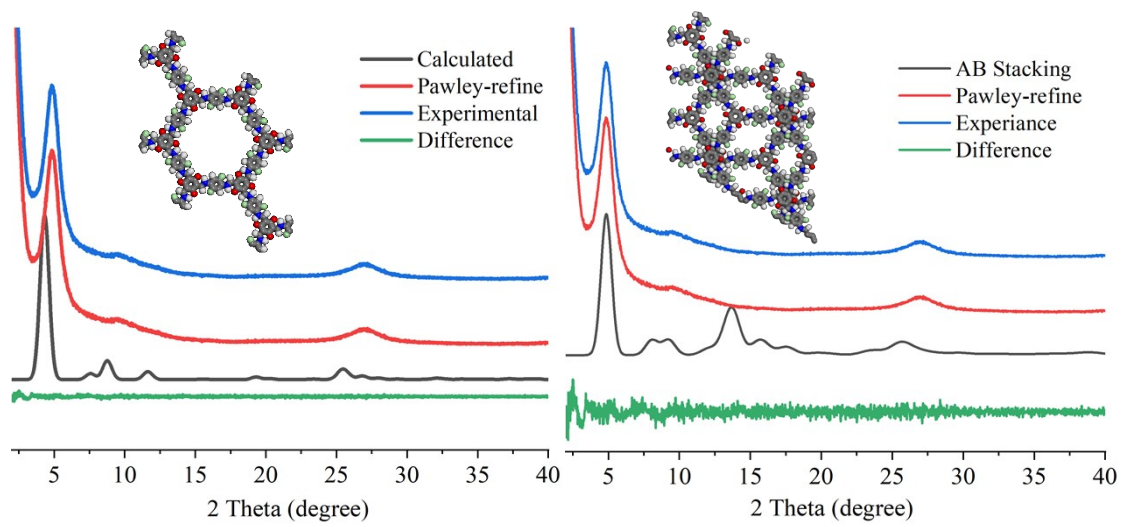
Photocatalyst	$\lambda$ (nm)	Sacrificial reagent	HER ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Ref
TpPa-Cl <sub>2</sub>	> 420	AA	99230	This work
TpPa-CN <sub>2</sub>	> 420	AA	76930	
CYANO-COF	> 420	AA	60850	Nat. Commun., 2022, 13, 2357
CYANO-CON	> 420	AA	134200	
Cu-sulphen-HDCOF-NS	> 420	Triethanolamine	36900	J. Mater. Chem. A, 2020, 8, 25094
TtaTfa_AC	> 420	AA	20700	Angew. Chem. Int. Ed., 2021, 60, 19797
TpaTfa_AC	> 420	AA	14900	
TtaTpa_AC	> 420	AA	10800	
NKCOF-113 M	> 420	TEOA	13100	Adv. Sci., 2022, 2203832
COF-JLU100	> 420	TEOA	107380	Angew. Chem. Int. Ed., 2022, 61, e202208919

COF-JLU35	> 420	AA	70800	J. Am. Chem. Soc., 2023, 145, 8364 8374
COF-JLU36	> 420	AA	23600	
PY-DHBD-COF	> 420	AA	71160	Nat. Comm., 2022, 13, 1355
Ni-Py-COF	> 420	AA	13231	Angew. Chem. Int. Ed., 2022, 61, e202204326
[Mo <sub>3</sub> S <sub>13</sub> ] @ZnP- Pz-PEO-COF	> 420	Lactic acid	11000	Nat. Commun., 2023, 14, 329
Tp-2C/BPy <sup>2-</sup> - COF	> 420	AA	34600	Angew. Chem. Int. Ed., 2021, 60, 9642 9649
Tz-COF-3	> 420	AA	43200	ACS Catal., 2022, 12, 9494 9502
Pt@TpBpy-NS	> 420	Sodium ascorbate	22666	Nat. Commun., 2023, 14, 593
FOO-COF	> 420	AA	119100	Appl. Catal., B., 2023, 330, 122581
BTT-BPy- PCOF(AC)	> 420	AA	21200	Angew. Chem. Int. Ed., 2023, 62, e202300224

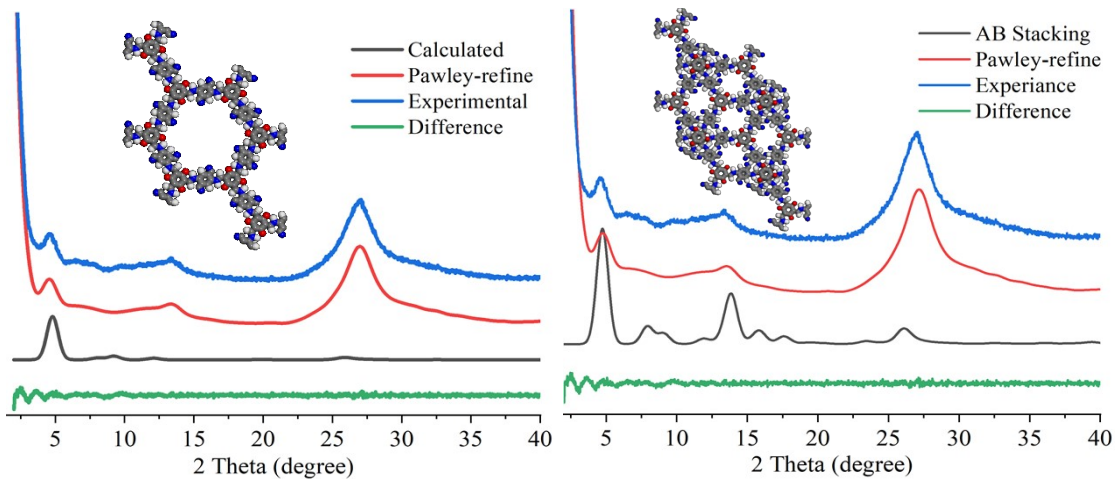
TpPa-1



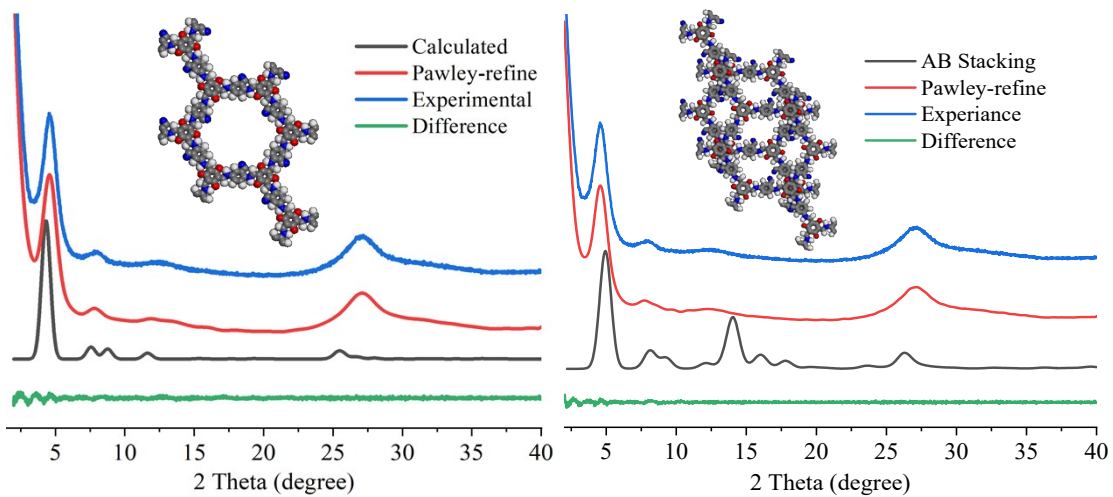
TpPa-Cl<sub>2</sub>



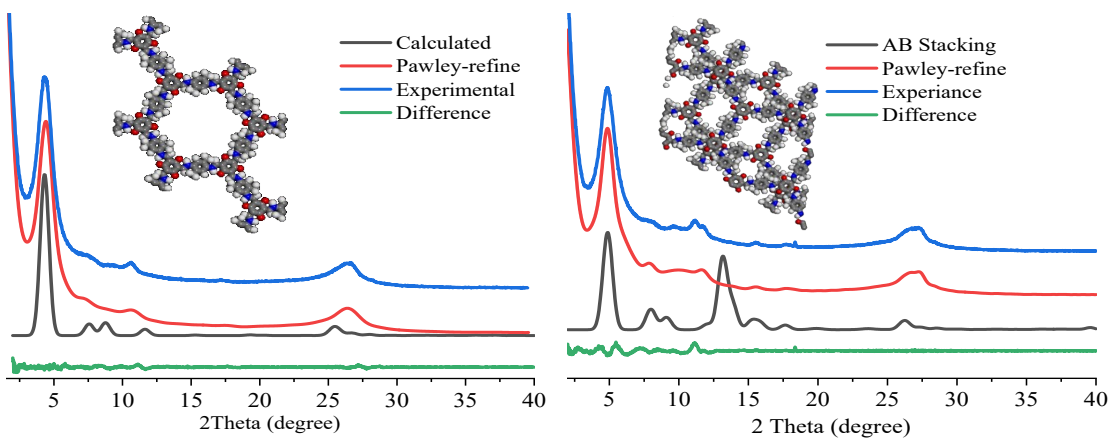
TpPa-CN<sub>2</sub>



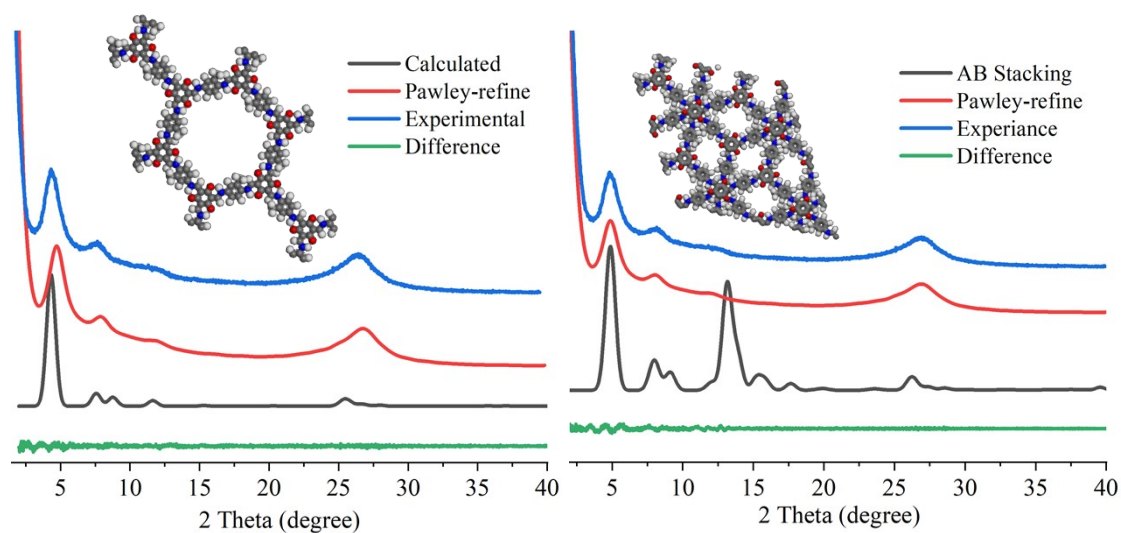
TpPa-CN



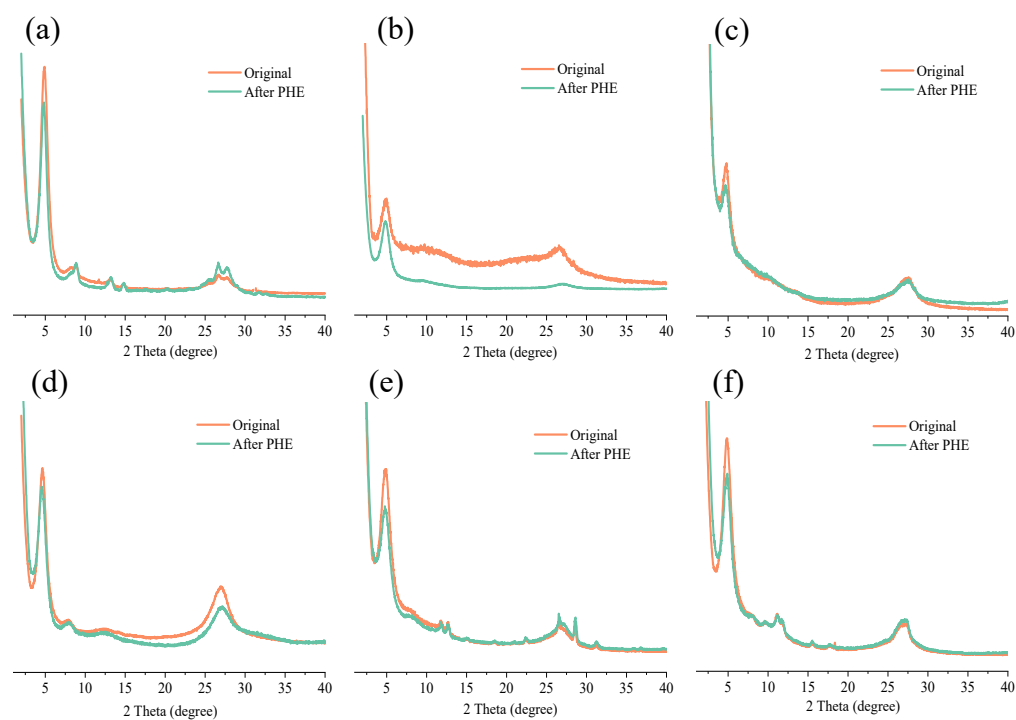
TpPa-(CH<sub>3</sub>)<sub>2</sub>



TpPa-CH<sub>3</sub>



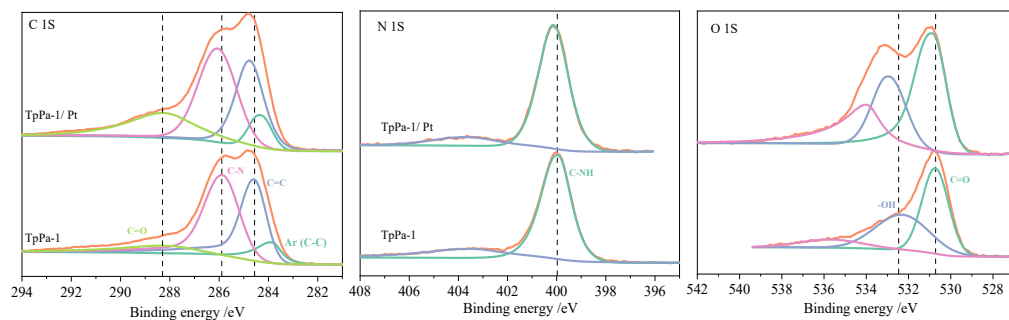
**Figure S1.** Synchrotron PXRD patterns of six COFs.



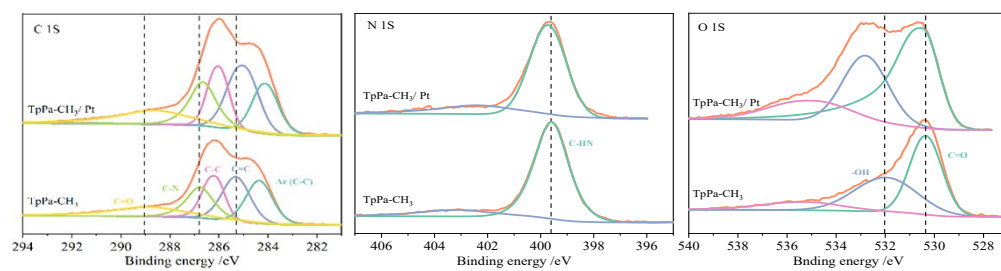
**Figure S2.** Synchrotron PXRD patterns of TpPa-1 (a), TpPa-Cl<sub>2</sub> (b), TpPa-CN<sub>2</sub> (c), TpPa-CN (d) and TpPa-CH<sub>3</sub> (e), TpPa-(CH<sub>3</sub>)<sub>2</sub> (f) before and after photocatalytic hydrogenolysis treatment.

TpPa-1

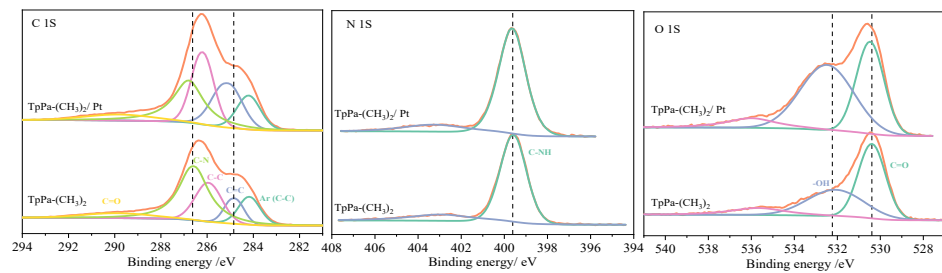




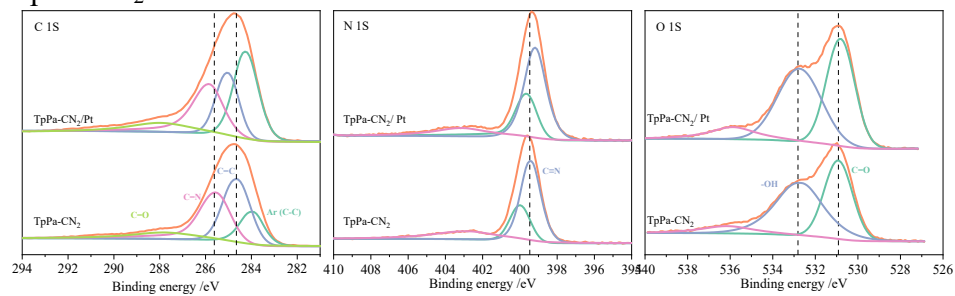
### TpPa-CH<sub>3</sub>



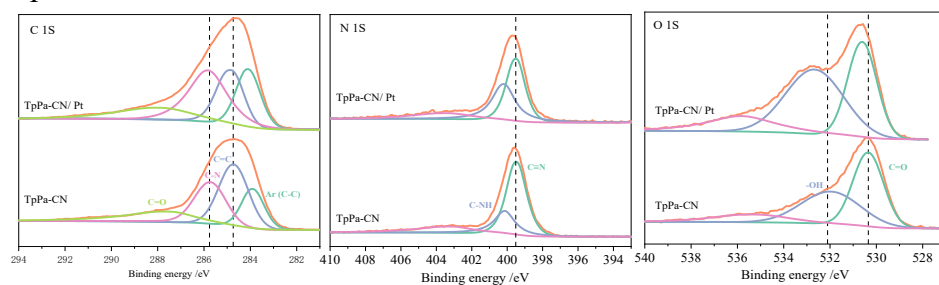
### TpPa-(CH<sub>3</sub>)<sub>2</sub>



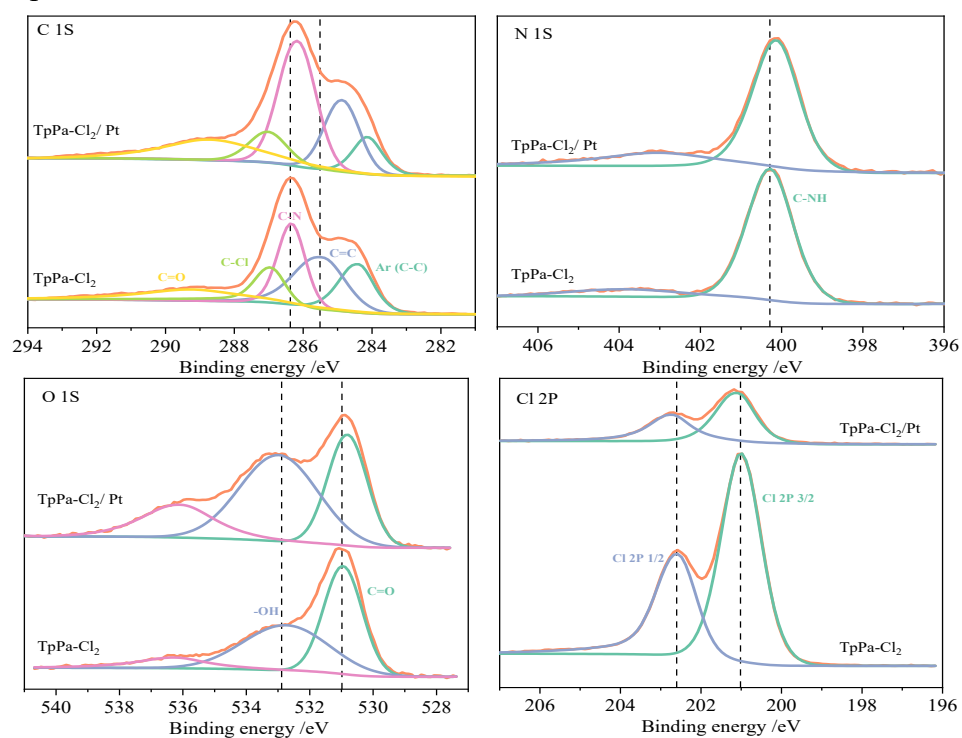
### TpPa-CN<sub>2</sub>



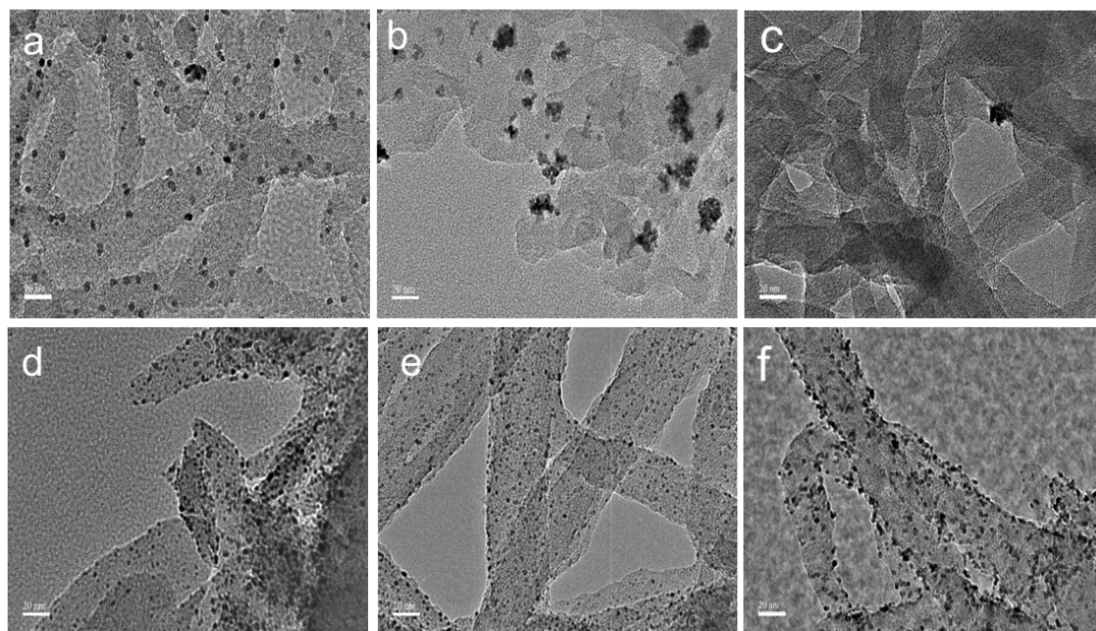
### TpPa-CN



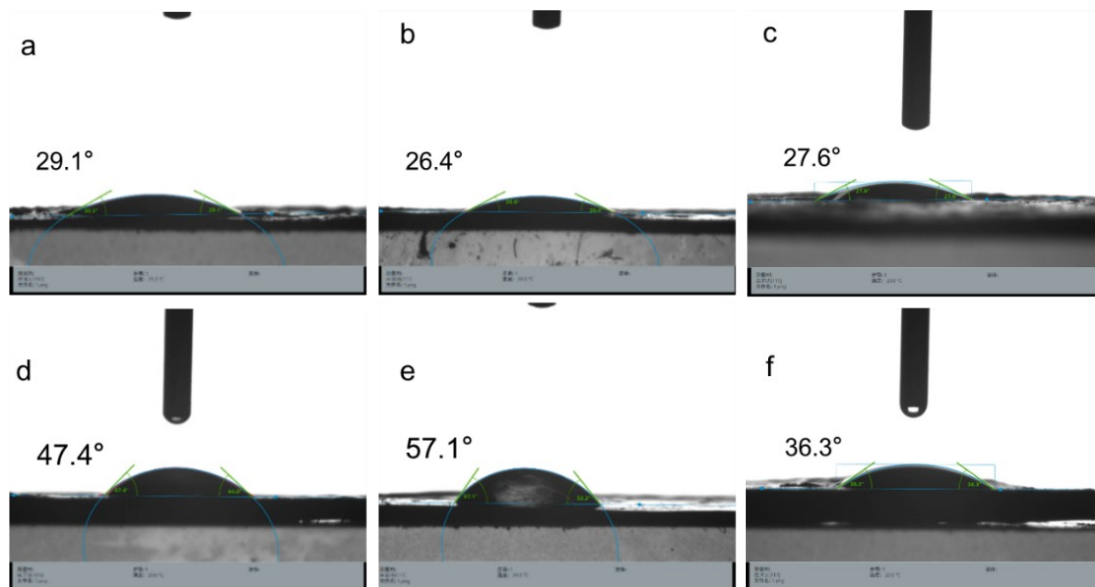
## TpPa-Cl<sub>2</sub>



**Figure S3.** XPS changes before and after six COF platinum loads.



**Figure S4.** a-f is the HR-TEM of TpPa-Cl<sub>2</sub>, TpPa-CN<sub>2</sub>, TpPa-CN, TpPa-1 and TpPa-(CH<sub>3</sub>)<sub>2</sub>, TpPa-CH<sub>3</sub>, respectively.



**Figure S5.** a-f is the contact angle of TpPa-Cl<sub>2</sub>, TpPa-CN<sub>2</sub>, TpPa-CN, TpPa-1 and TpPa-(CH<sub>3</sub>)<sub>2</sub>, TpPa-CH<sub>3</sub>, respectively.

## Reference

- [1] Kandambeth S, Mallick A, Lukose B, et al. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route[J]. Journal of the American Chemical Society, 2012, 134(48): 19524-19527.