

Supporting Information for

**Organic Small Molecular Heterostructures for Enhanced Photocatalytic
Hydrogen Evolution via Isomer Engineering**

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1. Structural and morphology characterization

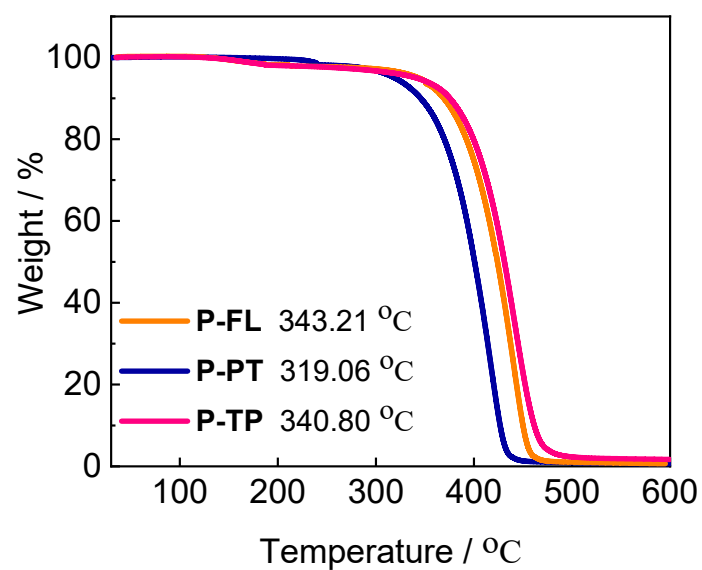


Fig. S1 TGA curves of **P-FL**, **P-PT**, and **P-TP**.

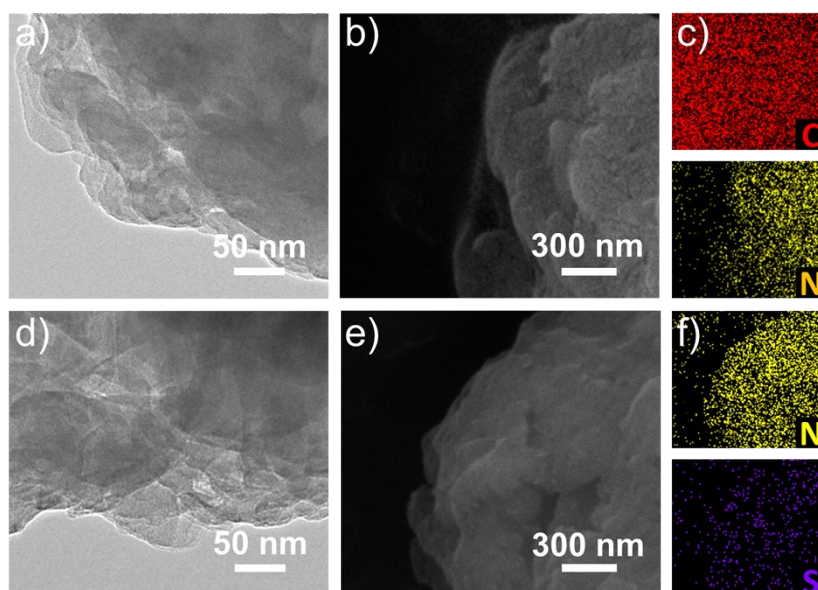


Fig. S2 (a) TEM image, (b) SEM image, and (c) EDS elements mapping of **P-FL/g-CN**. (d) TEM image, (e) SEM image, and (f) EDS elements mapping of **P-PT/g-CN**.

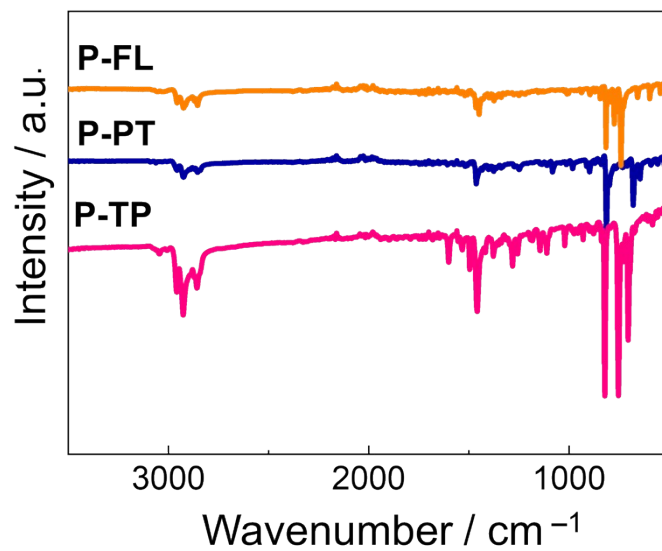


Fig. S3 FT-IR spectra of P-FL, P-PT, and P-TP.

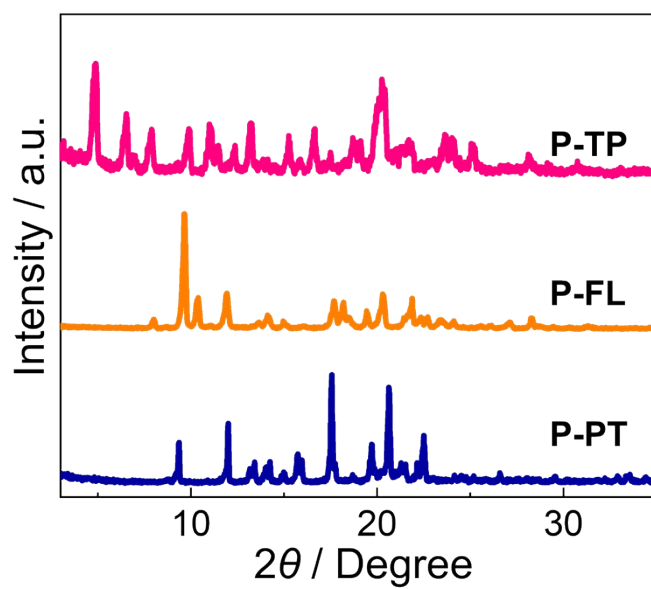


Fig. S4 XRD spectra of P-FL, P-PT, and P-TP.

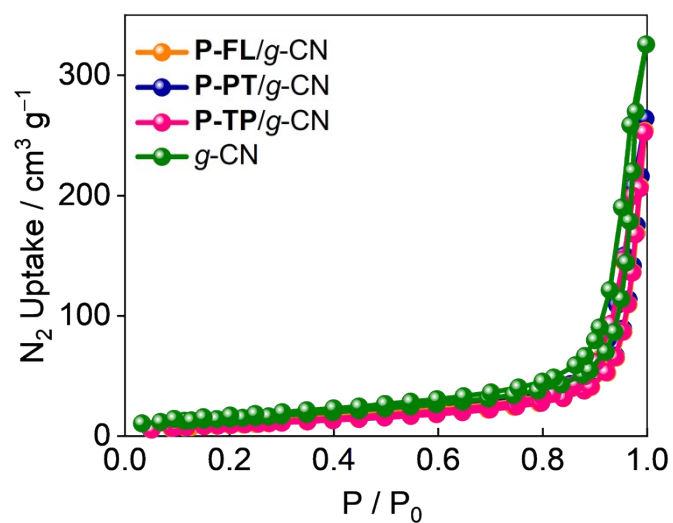


Fig. S5 N_2 adsorption isotherms of **P-FL/g-CN**, **P-PT/g-CN**, **P-TP/g-CN**, and **g-CN**.

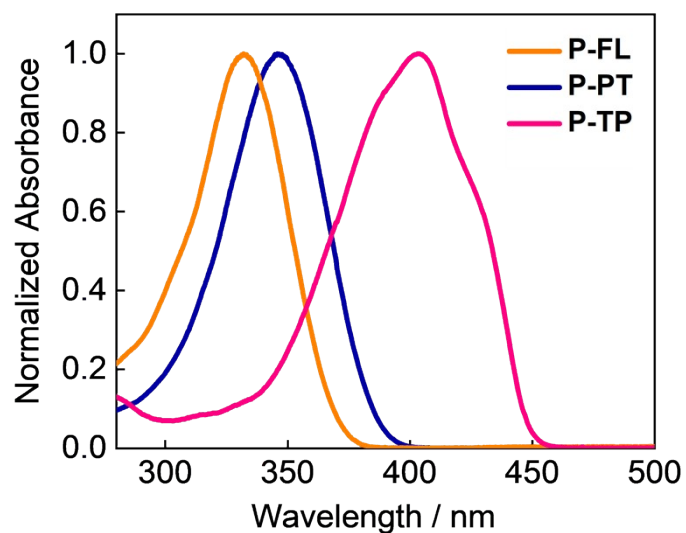


Fig. S6 UV-vis absorption spectra of **P-FL**, **P-PT**, and **P-TP** in CH_2Cl_2 solution.

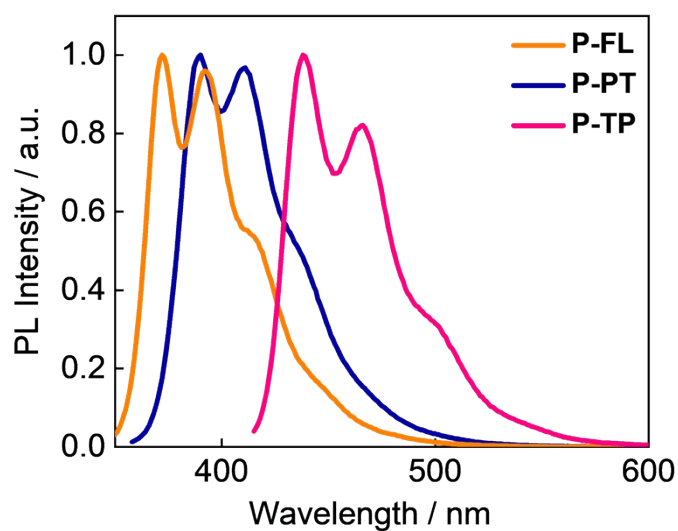


Fig. S7. PL spectra of **P-FL**, **P-PT**, and **P-TP** in CH₂Cl₂ solution.

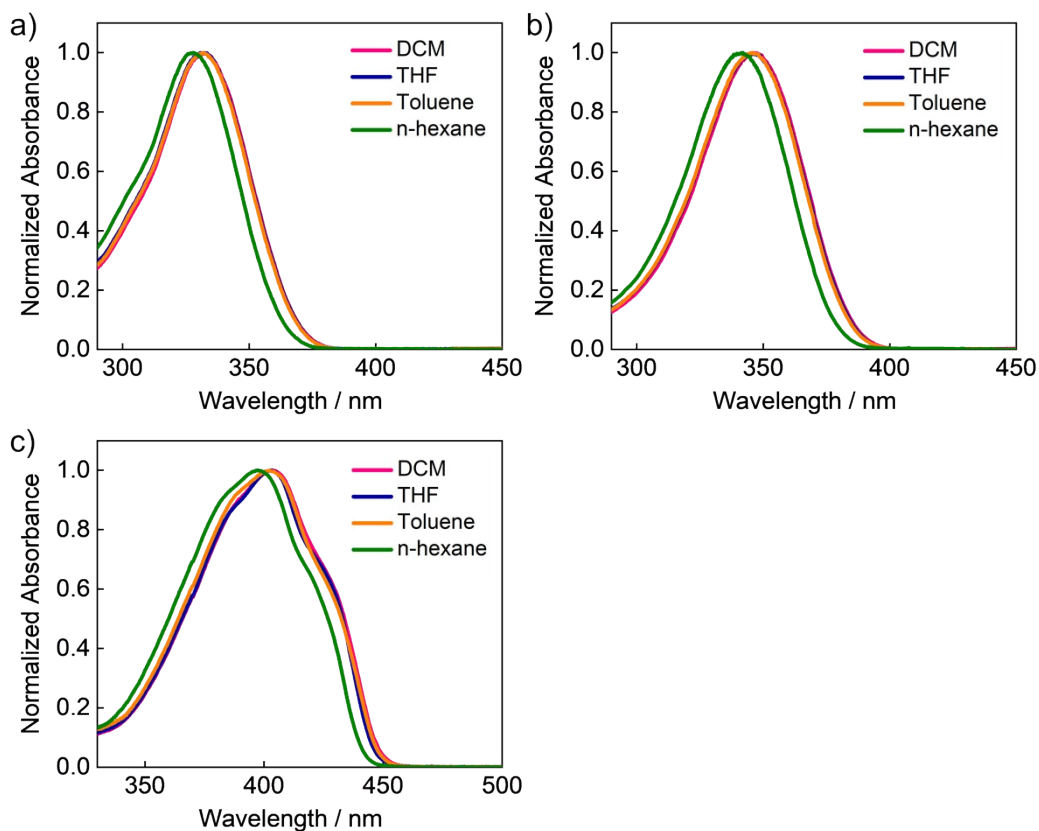


Fig. S8 UV-vis absorption spectra of (a)**P-FL**, (b) **P-PT**, and (c) **P-TP** in different solutions.

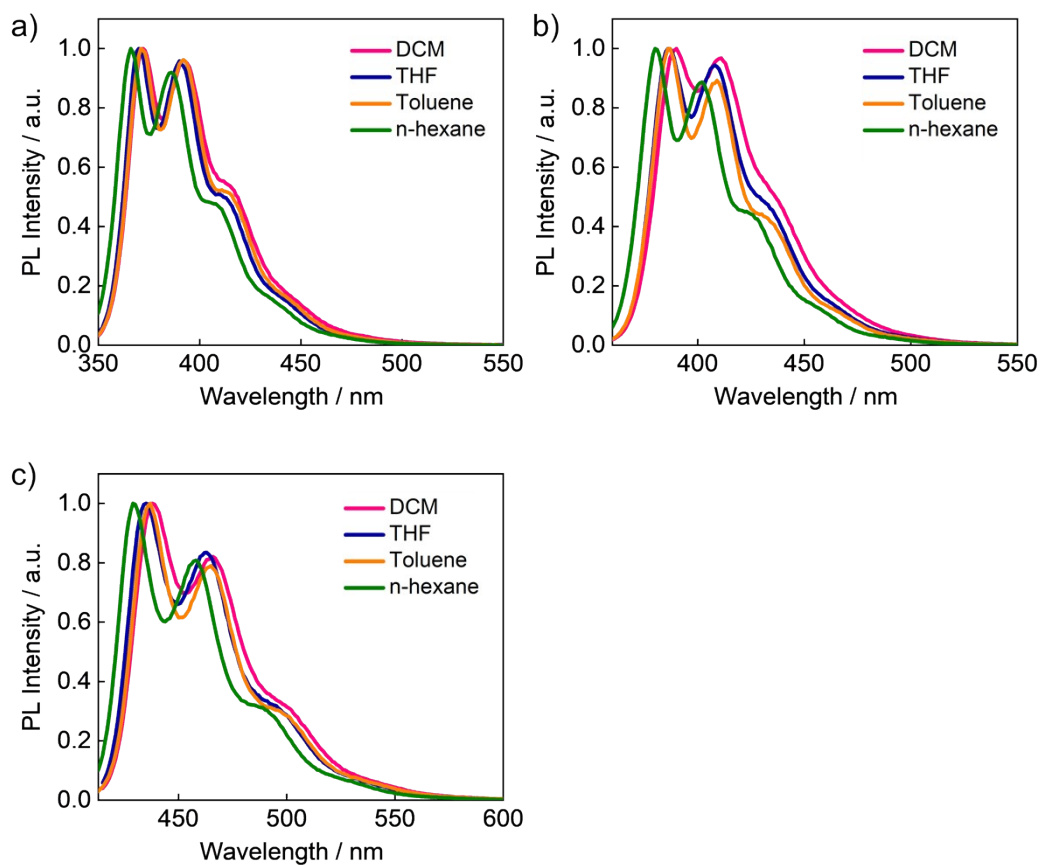


Fig. S9 PL spectra of (a)P-FL, (b) P-PT, and (c) P-TP in different solutions.

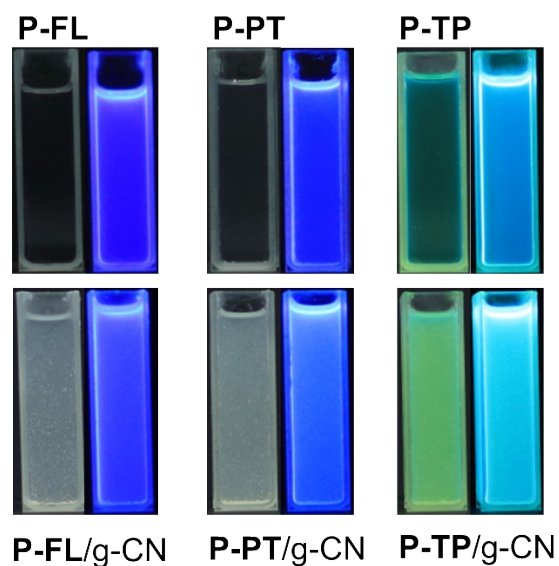


Fig. S10. Color change of g-CN before and after adding it to the CH_2Cl_2 solution of three materials.

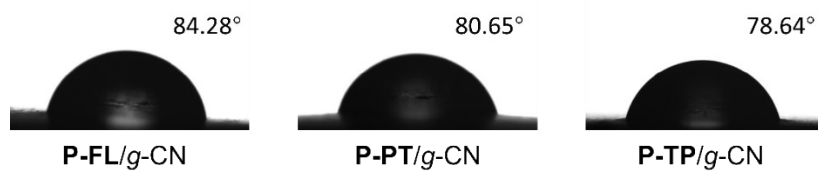


Fig. S11 Images of contact angle measurement of **P-FL/g-CN**, **P-PT/g-CN**, **P-TP/g-CN**

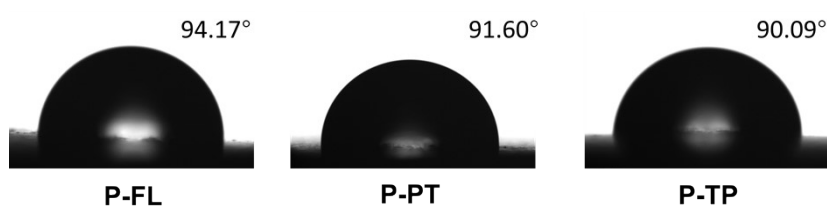


Fig. S12 Images of contact angle measurement of **P-FL**, **P-PT**, **P-TP**

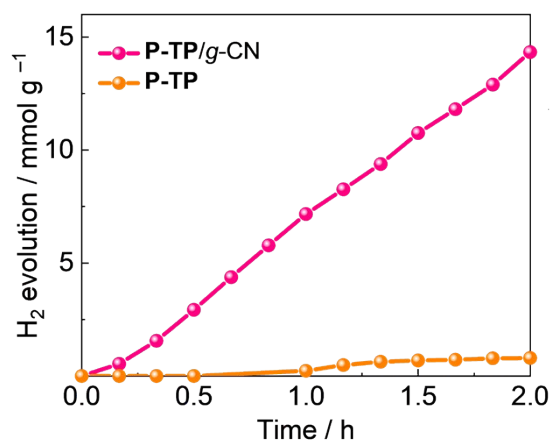


Fig. S13 Photocatalytic H₂ evolution rates of **P-TP**, **P-TP/g-CN**

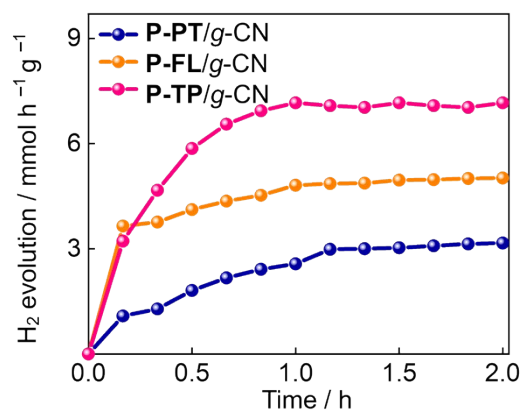


Figure S14. Time-dependent photocatalytic hydrogen evolution of **P-FL/g-CN**, **P-PT/g-CN**, and **P-TP/g-CN**.

Table S1 Relative ratios of two carbon species determined by C 1s spectra for samples

Sample	C=C/C-C			N-C=N		
	Binding Energy (eV)	area	%	Binding Energy (eV)	area	%
g-CN	284.80	16859.68	14	288.44	103050.00	86
P-FL/g-CN	284.80	55491.72	39	288.43	85805.55	61
P-PT/g-CN	284.80	43976.33	34	288.44	85535.40	66
P-TP/g-CN	284.80	63067.53	40	288.25	94800.29	60

Table S2 Relative ratios of two carbon species determined by N 1s spectra for samples

Sample	C-N=C			N-(C) ₃			N-H		
	Binding	area	%	Binding	area	%	Binding	area	%
	Energy (eV)			Energy (eV)			Energy (eV)		
g-CN	398.68	147829.1	69.1	399.86	39318.55	18.4	401.00	26641.82	12.5
P-FL/g-CN	398.43	102606.8	63.2	399.29	45914.87	28.3	400.83	13838.84	8.5
P-PT/g-CN	398.3	93113.55	59.4	399.2	45497.79	29.0	400.76	18206.55	11.6
P-TP/g-CN	398.16	115149.8	67.3	399.2	38127.16	22.3	400.63	17808.56	10.4

Table S3 Optical, electrochemical and DFT calculation data for **P-FL**, **P-PT** and **P-TP**.

Compound	λ^{\max} / nm	E_g (eV) ^a	$E_{\text{onset}}^{\text{ox1}}$ (V) ^b	LUMO (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^e	HOMO (eV) ^e	E_g (eV) ^e
P-FL	340	3.15	0.92	-2.57	-5.72	-1.32	-5.34	4.02
P-PT	349	3.13	0.29	-1.96	-5.09	-1.38	-5.14	3.76
P-TP	371	2.82	0.50	-2.48	-5.30	-1.71	-4.93	3.22

^aEstimated from the onset absorption; ^bOnset potential; ^cCalculated from $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{Opt}}$;

^dCalculated from $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox1}} + 4.8)$; ^eEstimated from DFT calculations

Table S4 Comparison of photocatalytic hydrogen evolution performances under ambient conditions of recently-reported g-CN-based photocatalysts.

Material structure	Co-catalyst	Light source	H ₂ evolution	Ref
MWCNT/g-CN	None	300 W Xenon arc lamp ($\lambda > 395$ nm)	44 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[1]
TiO ₂ /g-CN	None	LEDs (3 W, 420 nm)	112 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[2]
rGO/g-CN	Pt (1.0 wt%)	LEDs (3 W, 420 nm)	874 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[3]
CdS/g-C ₃ N ₄ /CuS	None	350 W Xenon arc lamp ($\lambda > 420$ nm)	1151.2 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[4]
Carbon fiber/g-C ₃ N ₄	Pt (1.0 wt%)	350 W Xenon arc lamp ($\lambda > 420$ nm)	1081 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[5]
PCN/TBT	Pt (3.0 wt%)	300 W Xenon arc lamp (AM 1.5G)	4630 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[6]
MoS ₂ /g-C ₃ N ₄	None	300 W Xe lamp ($\lambda > 420$ nm)	12 mmol h ⁻¹ g ⁻¹	[7]
P3/g-C ₃ N ₄	Pt (1.0 wt%)	300 W Xe lamp ($\lambda > 420$ nm)	13 mmol h ⁻¹ g ⁻¹	[8]
P-TP/g-CN	Pt (3.0 wt%)	300 W Xe lamp ($\lambda > 420$ nm)	7.1 mmol h ⁻¹ g ⁻¹	This work

2. Stability of P-TP/g-CN before and after HER reaction.

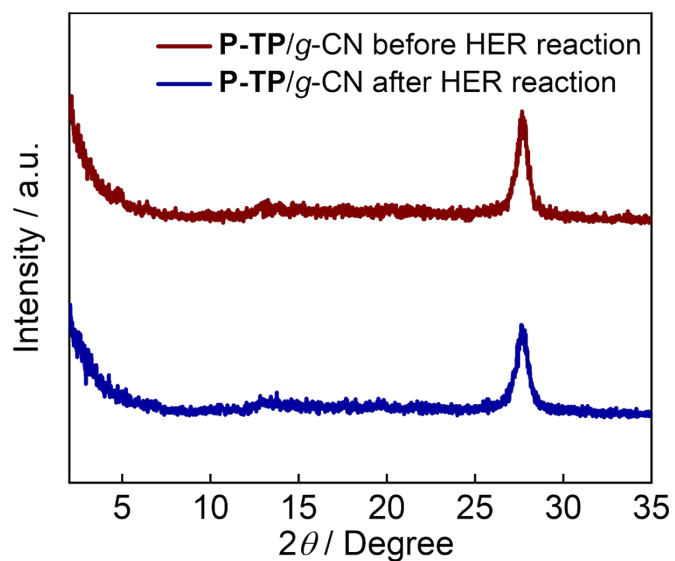


Fig. S15 XRD patterns of P-TP/g-CN before and after HER reaction.

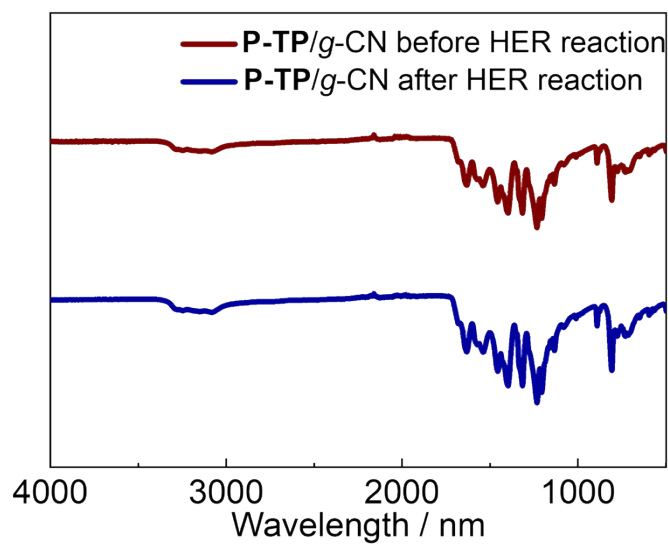


Fig. S16 FT-IR spectra of P-TP/g-CN before and after HER reaction.

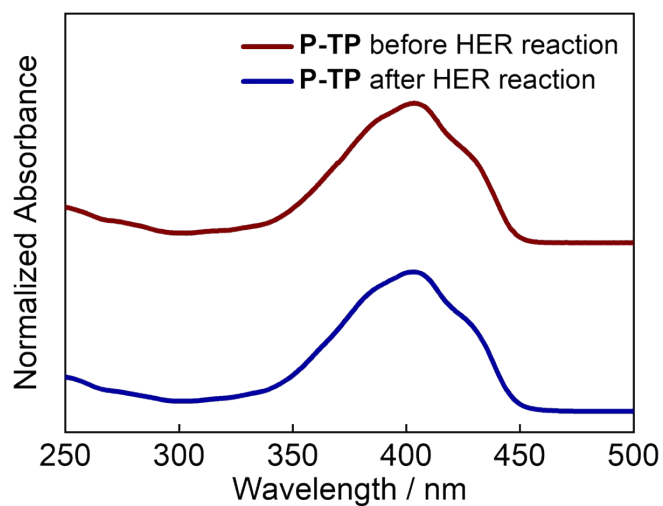


Fig. S17 UV-Vis spectra of **P-TP** before and after HER reaction.

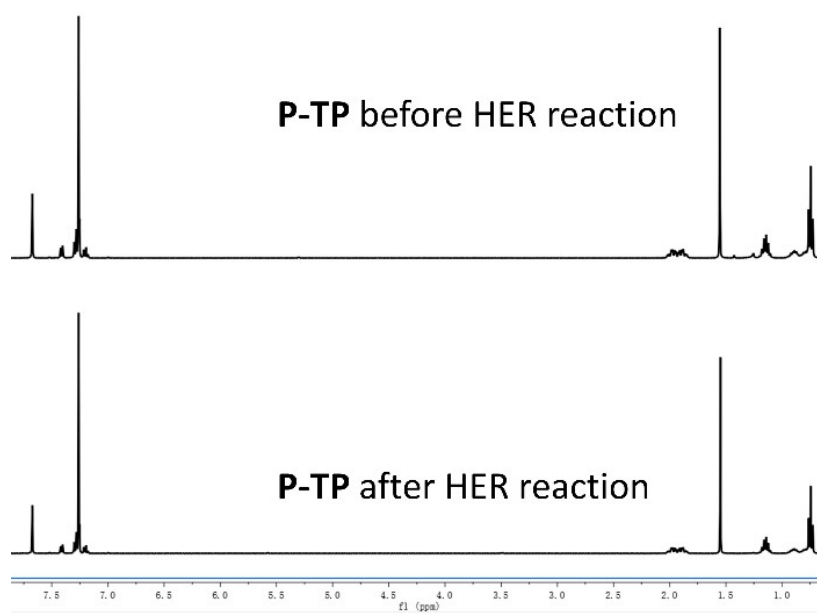


Fig. S18 ¹H NMR spectra of **P-TP** before and after HER reaction.

3. NMR spectra

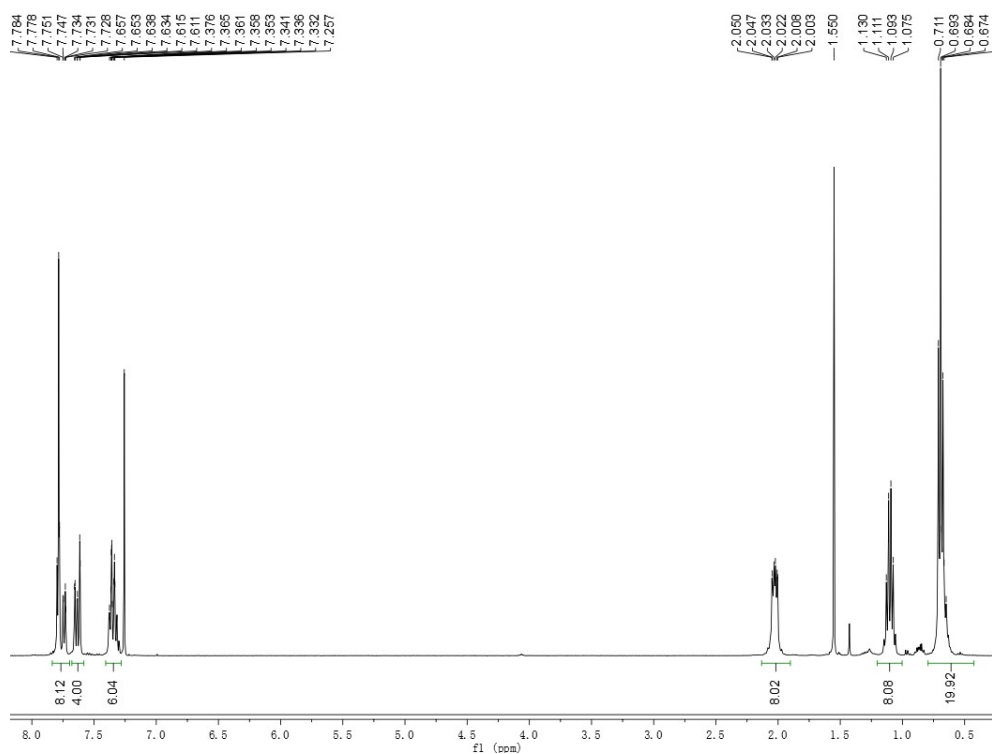


Fig. S19 ¹H NMR spectrum of P-FL.

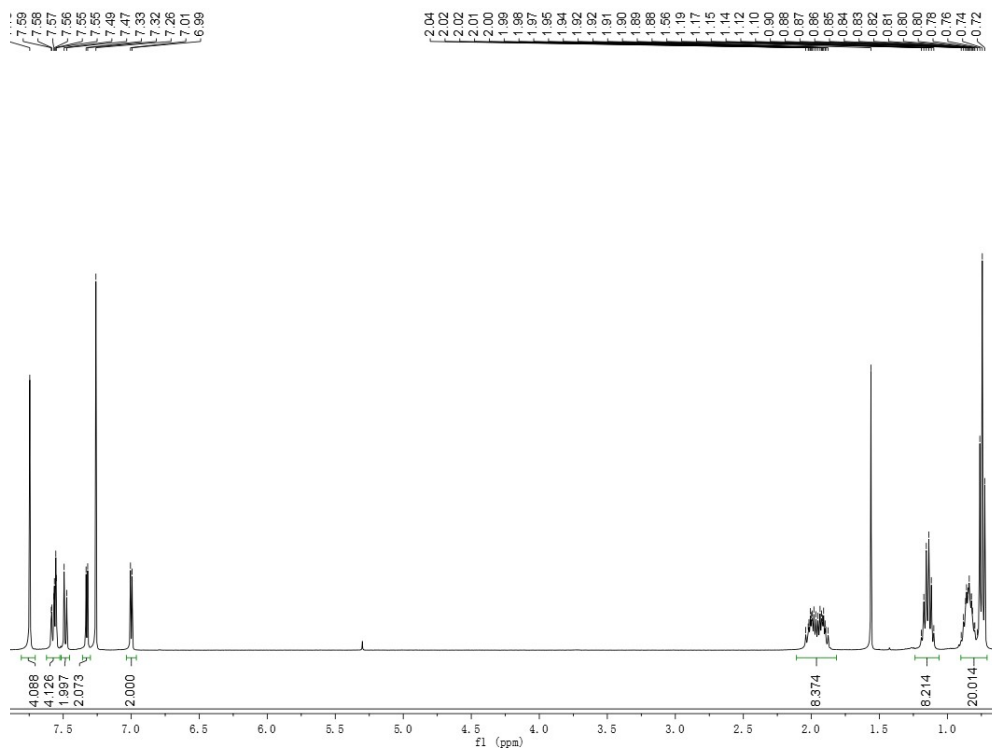


Fig. S20 ¹H NMR spectrum of P-PT.

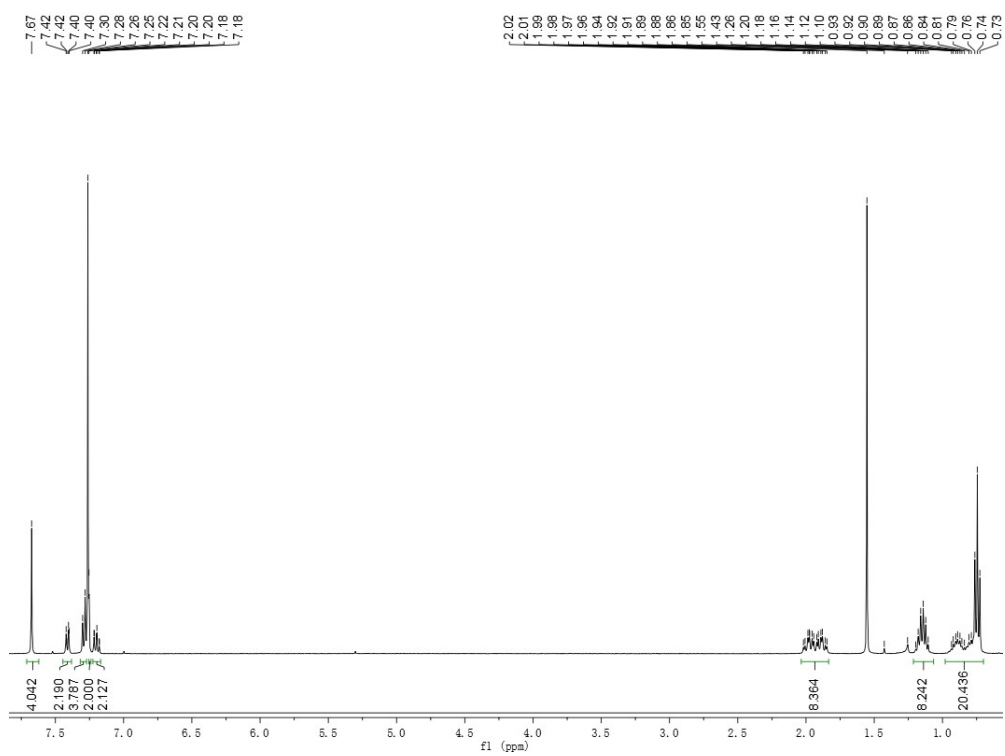


Fig. S21 ¹H NMR spectrum of P-TP.

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