

Supporting Information

Constructing conjugate bridge for efficient electron transport on the interface of inorganic-organic hetero-junction

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S1. Materials and measurements.

Materials.

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted.

Measurements.

Powder X-ray diffraction (XRD) measurements were performed on a Smartlab instrument with Cu K α ($\lambda=1.5418$ Å) radiation and X-Ray 40 kV/30 mA over the angular range 2θ 3°–40° at a scan rate of 10° min⁻¹.

FT-IR measurements were performed on the Nicolet Impact 410 Fourier transforms infrared spectrometer.

N₂ adsorption isotherms and pore size distribution were obtained on the Micromeritics ASAP 2010M analyzer.

Thermogravimetric analysis (TGA) was carried out on a METTLER-TOLEDO TGA/DSC 3+ analyser with a heating rate of 10 °C min⁻¹ under air flow.

X-ray photoelectron spectrum (XPS) was measured by a VG ESCALAB MKIIX-ray photoelectron spectrometer using Mg-K α as the exciting source (1253.6 eV) and binding energy calibration was based on C_{1s}, N_{1s} and O_{1s}.

We dispersed the sample (1 mg) in 2 mL ethanol by ultrasound and placed the dispersed droplets on a clean silicon wafer. After the ethanol volatilized, the silicon wafer supporting sample was kept at 60 °C for 12 h and then tested by SEM. SEM was acquired by using Hitachi SU8010 scanning electron microscopes at 3 kV and 5 μ A.

We dispersed the sample (1 mg) in 5 mL ethanol by ultrasound and placed the dispersed droplets on a clean microgrid. After the ethanol volatilized, the microgrid supporting sample was kept at 60 °C for 12 h and for TEM imagery. TEM was performed on the JEOL 2100F at 2000 kV.

Photoluminescence (PL) and time-resolved fluorescence spectra were obtained using a FLSP920 Edinburgh fluorescence spectrometer.

All hydrogen production experiments were measured using by Labsolar-IIIAG and PLS-SXE300 Xe lamp (Beijing Perfect Light Technology Co., Ltd.).

UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded at room temperature on a Cary7000 Spectrophotometer.

S2. Experimental procedures

Synthesis of amino-CD. *p*-Phenylene diamine (10 mg) was dissolved in 10 mL ethanol, and then the solution was transferred into a poly(tetrafluoroethylene)-lined autoclave. After heating at 160 °C in oven for 6 h and cooling down to room temperature, dark-red suspensions were obtained. After extraction and purification by dichloromethane, CD powder was obtained in 10-20 wt% yields.¹

Synthesis of N₃-COF and CD-N₃-COF. N₃-Ald (25 mg, 0.065 mmol) in 0.5 mL mesitylene, 0.5 mL 1,4-dioxane, and 50 μL 6 M acetic acid aqueous solution were suspended in a 10 mL high temperature and pressure bottle. After adding amino-CD (0.1-1.0 mg) and hydrazine hydrate (5 μL, 50-60% solution, Sigma-Aldrich) to the suspension, the vial was then sealed and heated in an oil bath at 120 °C under autogenous pressure for 3 days. The precipitate was washed with respective chloroform (25 mL), acetone (25 mL), and tetrahydrofuran (25 mL). The resulting solid was dried in an oven at 60 °C to obtain light yellow powder of N₃-COF as well as CD-N₃-COF.²

Synthesis of CD@N₃-COF. N₃-COF (20 mg) were dispersed in the mixture of dioxane (0.5 mL) and mesitylene (0.5 mL). The amino-CD (0.1-1.0 mg) was poured into the system; after stirred overnight at room temperature, the solid was filtered and washed with ethanol (15 mL) for three times to obtain the physical doped solid, CD@N₃-COF.

Synthesis of CD/N₃-COF.

CD (10 mg), *p*-nitrobenzaldehyde (5 mg), and anhydrous magnesium sulfate (50 mg) were reacted in 5 mL tetrahydrofuran and stirred at 25 °C for 24 h before filtration. The filtrate was concentrated via a rotary evaporation. The crude products were then purified with a silica column chromatography using a

mixture of methylene chloride and methanol as eluent to get product **1**.³ 200 mg of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 10 mL of ethanol and added to product **1** (10 mg) in a 25 mL round bottomed flask. After heated under reflux for 3 hours, the solution was added to 70 mL of 1 M hydrochloric acid and stirred for 1 h to get product **2**.⁴ Product **2** (10 mg) was dissolved in 5 mL methanol and cooled to $-10\text{ }^\circ\text{C}$, and then sodium borohydride (5 mg) was gradually added in a small portion. The reaction was kept at $10\text{ }^\circ\text{C}$ overnight, then extracted with dichloromethane for 3 times. The organic phase was concentrated via rotary evaporation got **amino-CD-r**.³

$\text{N}_3\text{-Ald}$ (25 mg, 0.065 mmol) in 0.5 mL mesitylene, 0.5 mL 1,4-dioxane, and 50 μL 6 M acetic acid were suspended in a 10 mL high temperature and pressure bottle. After adding amino-CD-r (0.1 mg) and hydrazine hydrate (5 μL , 50-60% solution, Sigma-Aldrich) to the suspension, the vial was then sealed and heated in an oil bath at $120\text{ }^\circ\text{C}$ under autogenous pressure for 3 days. The precipitate was washed with respective chloroform (25 mL), acetone (25 mL), and tetrahydrofuran (25 mL). The resulting solid was dried in an oven at $60\text{ }^\circ\text{C}$ to obtain single bond linked CD/ N_3 -COF (light yellow powder).

Electrochemical Studies. Electrochemical experiments were performed according to reported methods using a conventional three-electrode battery with platinum as the counter electrode and Ag/AgCl as the reference electrode (0.1 M Na_2SO_4 electrolyte).⁵ In the preparation of working electrode, indium tin oxide (ITO) glass was divided into $1\text{cm} \times 1\text{cm}$ after ultrasonic treatment in ethanol for 30 minutes; and then the electrode was dried under nitrogen flow. 5 mg COF powder, 50 μL Nafion, and 1 mL ethanol were mixed and treated by ultrasound for 30 minutes to obtain the slurry. Spread 40 μL of slurry onto ITO glass. The working electrodes were immersed in the electrolyte for 60 s before any measurements were taken. For Mott-Schottky experiments, the perturbation signal was 5 mV with the frequency of 600, 800 and 1000 Hz. For EIS

measurement, the applied sine wave potential amplitude was 5 mV with AC amplitude in the frequencies range of 0.01 Hz to 10⁵ Hz. The photocurrent response was tested under 300 W xenon lamp (PerfectLight, PLS-SXE300D). The applied potentials vs. Ag/AgCl were converted to RHE potentials using the following Equation:

$$E_{\text{RHE}} = 0.059\text{pH} + E_{\text{Ag/AgCl}} + E^{\theta}_{\text{Ag/AgCl}} \quad (E^{\theta}_{\text{Ag/AgCl}} = 0.199 \text{ V})$$

Photocatalytic. The hydrogen production experiments were proceeded on Labsolar-IIIAG (Beijing Perfect Light Technology Co., Ltd.). All photocatalysis experiments were performed in a double-walled glass reactor, where the outer compartment is circulated with water kept at a constant temperature (25 °C) through a thermostat. The reactor was top irradiated through a quartz window with a 300W Xe lamp (PLS-SXE300) as the source of simulated sunlight. For each experiment, the photocatalyst (COF; 20 mg) was suspended in 0.1M PBS (40 ml, pH=7) containing TEoA (400 μL; 2.95 mmol). Hexachloroplatinic acid (20 μL, 8 wt% aqueous solution, Sigma-Aldrich) was added for the in-situ formation of platinum as the co-catalyst. The head space was subjected to several cycles of evacuation and argon backfill before the experiment. In the course of the experiment, the head space of the reactor was periodically sampled and the components were quantified by GC 7900 gas chromatograph (Techcomp, 5 Å molecular sieve stainless steel packed column, Ar as carrier gas and TCD detector). After the photocatalysis experiment, the COFs were recovered by filtration, washed with water, and then dried at 100 °C.²

S3. Supplementary characterization

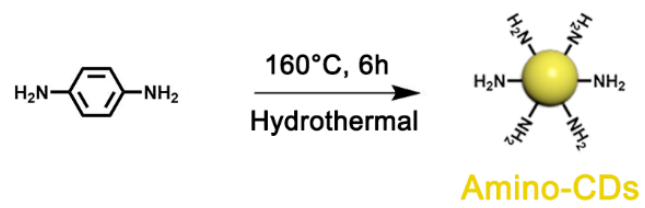


Figure S1. Preparation procedure of amino group-grafted CD nano-particles.

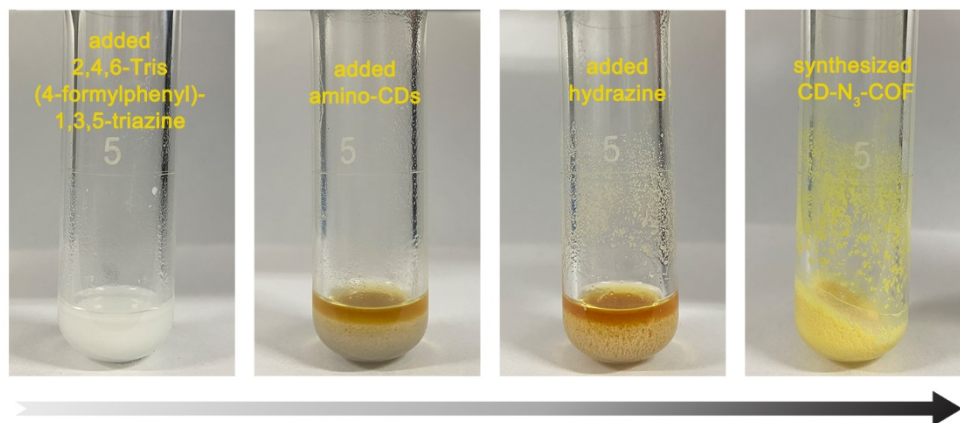


Figure S2. Synthetic process of CD-N₃-COFs.

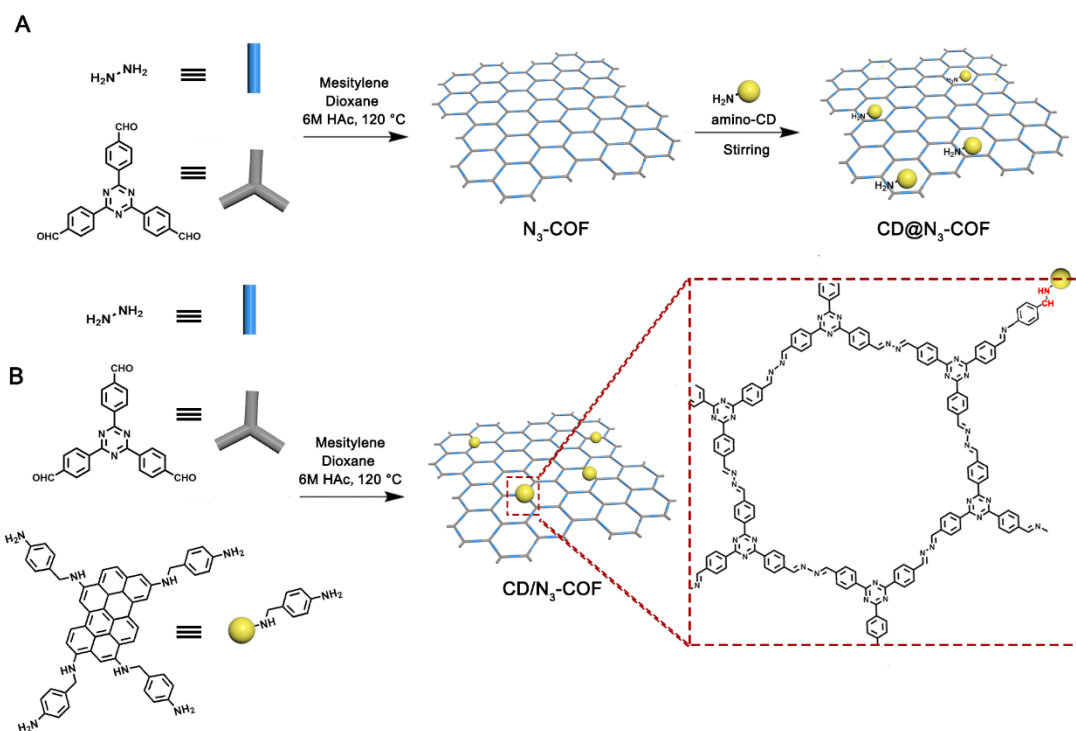
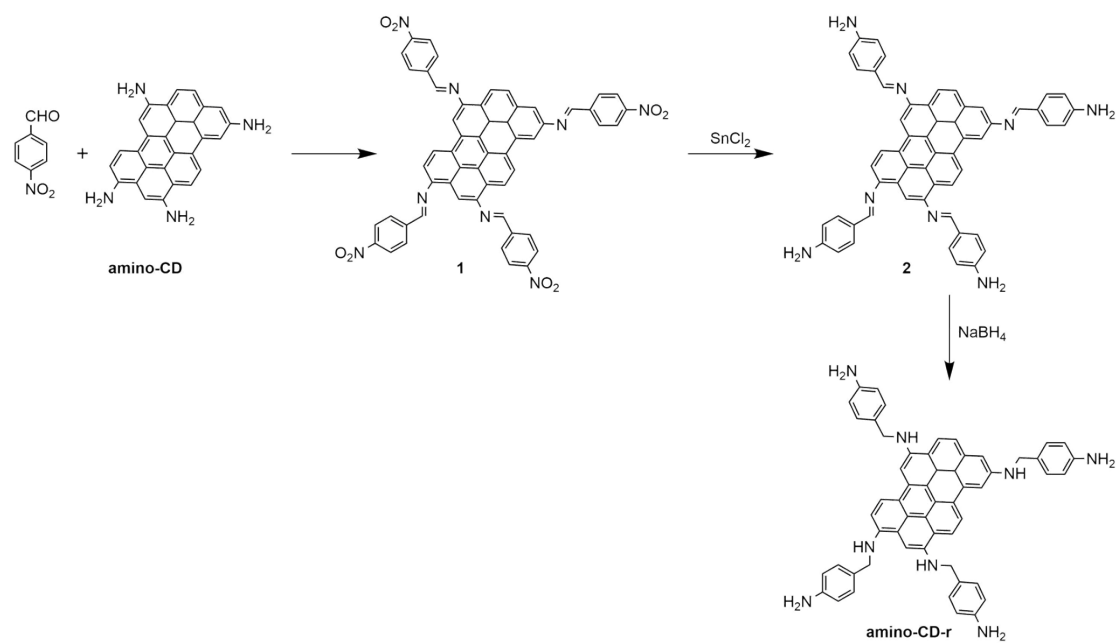


Figure S3. Synthetic route for single bond linked CD particles. $\text{CD@N}_3\text{-COF}$ (A) and $\text{CD/N}_3\text{-COF}$ (B).

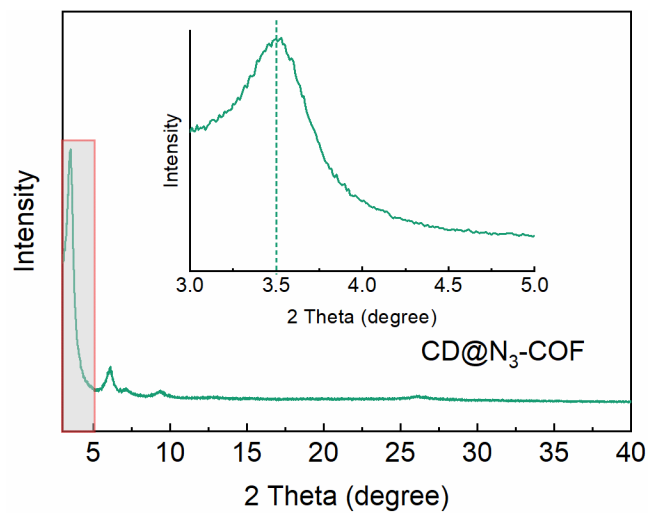


Figure S4. PXRD patterns for CD@N₃-COF.

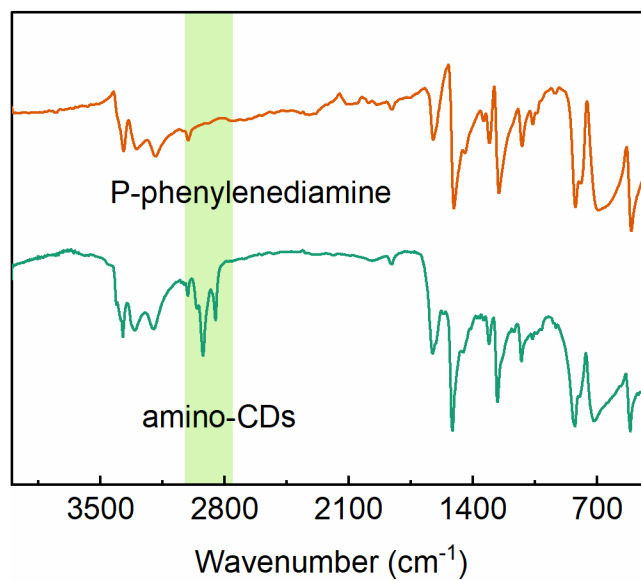


Figure S5. FT-IR spectra for *p*-phenylenediamine and amino-CDs.

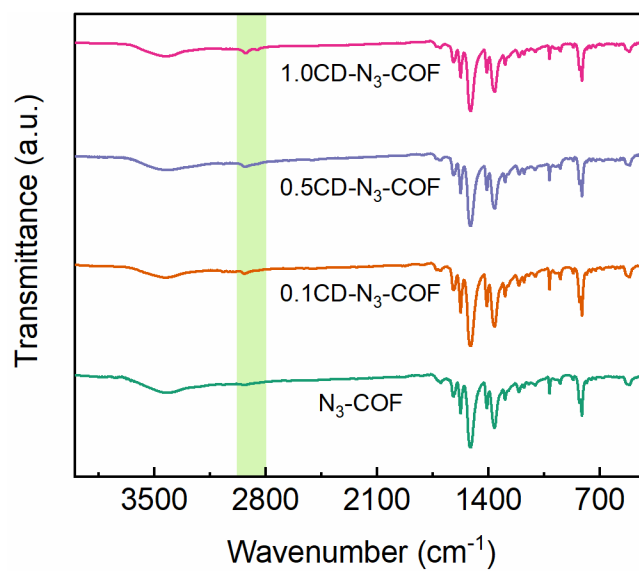


Figure S6. FT-IR spectra for N₃-COF and CD-N₃-COFs.

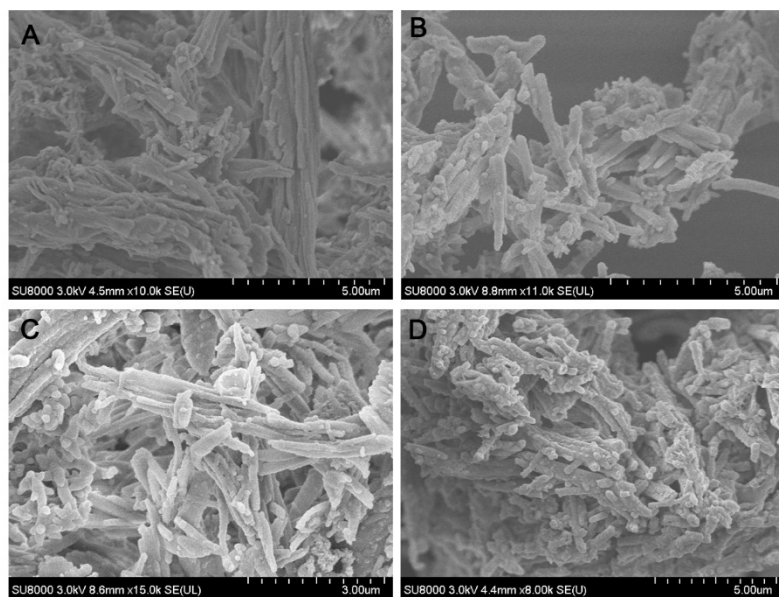


Figure S7. SEM images for N₃-COF (A), 0.1CD-N₃-COF (B), 0.5CD-N₃-COF (C), and 1.0CD-N₃-COF (D).

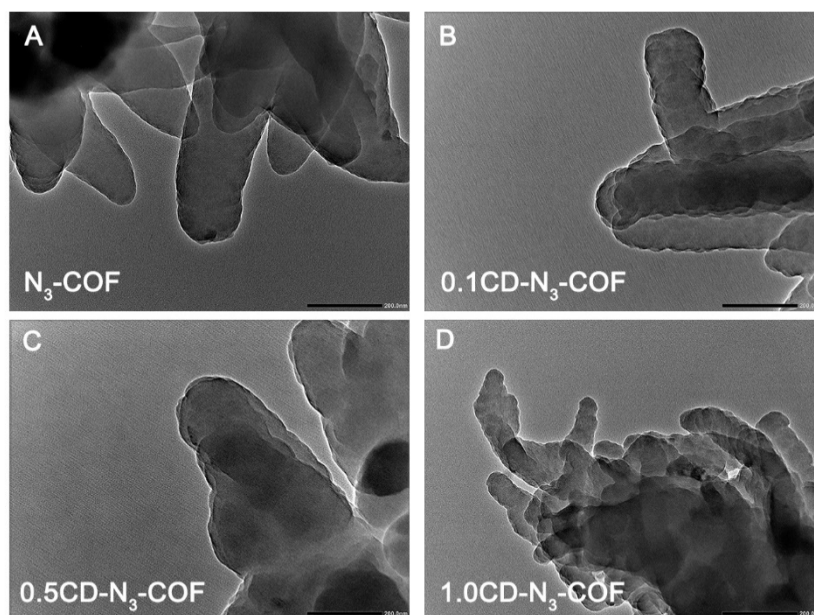


Figure S8. TEM images for N_3 -COF and CD- N_3 -COFs.

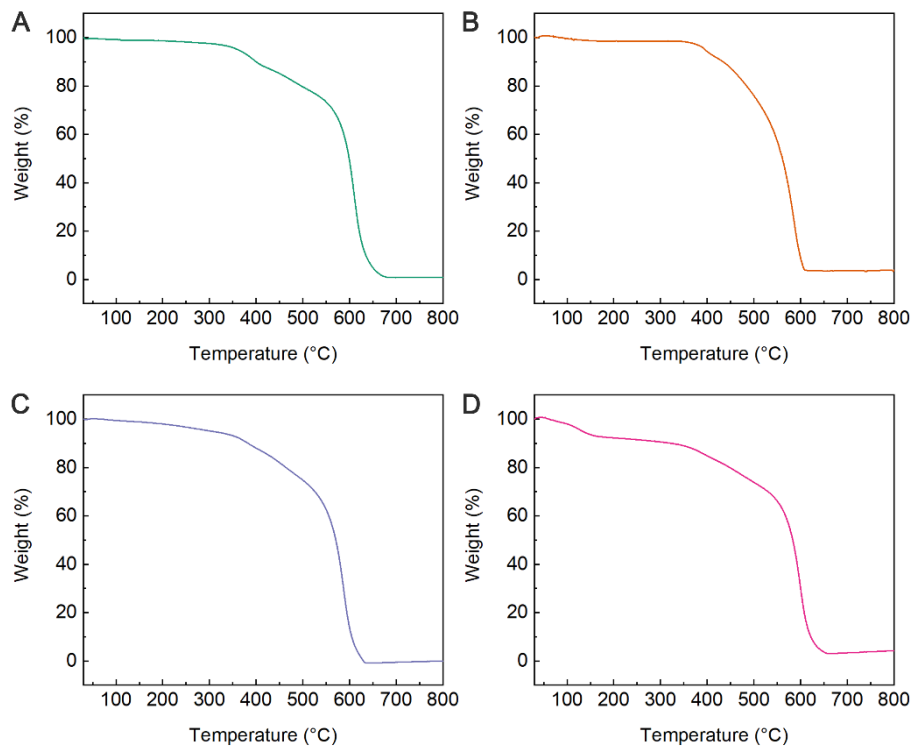


Figure S9. TGA curves for N₃-COF (A), 0.1CD-N₃-COF (B), 0.5CD-N₃-COF (C), and 1.0CD-N₃-COF (D).

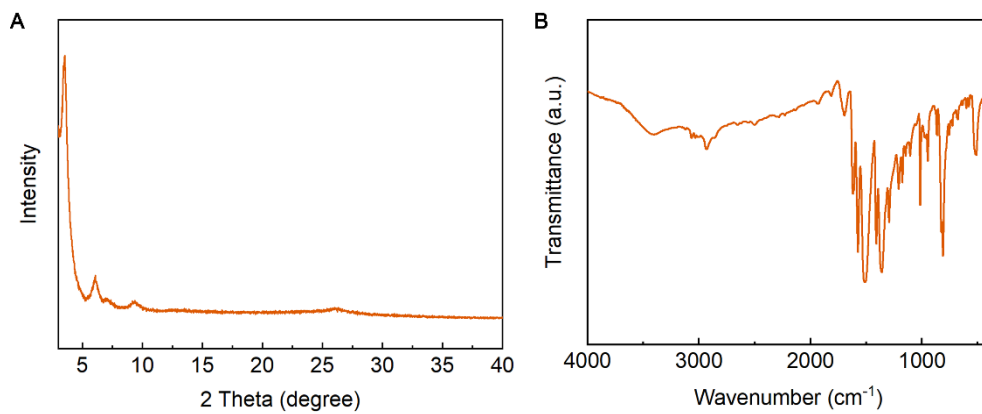


Figure S10. PXRD pattern and FT-IR spectrum for 0.1CD-N₃-COF after soaked in water for 24 h.

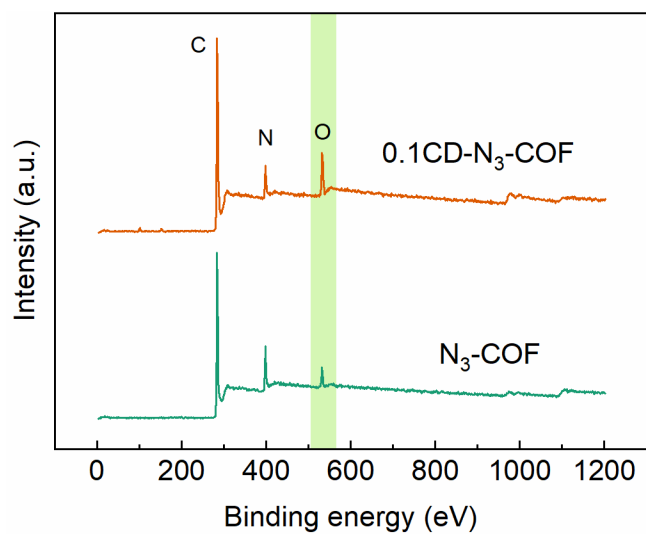


Figure S11. XPS full spectra for 0.1CD-N₃-COF and N₃-COF.

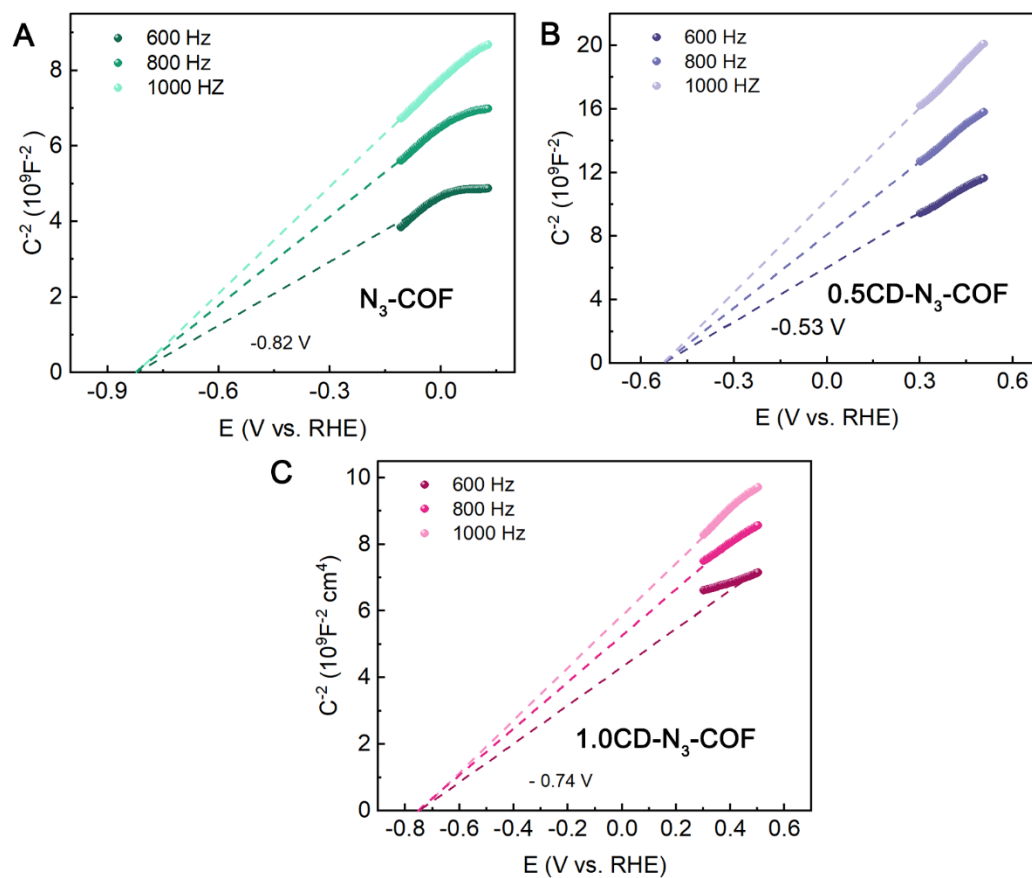


Figure S12. Mott-Schottky plots for N_3 -COF, 0.5CD- N_3 -COF, and 1.0CD- N_3 -COF.

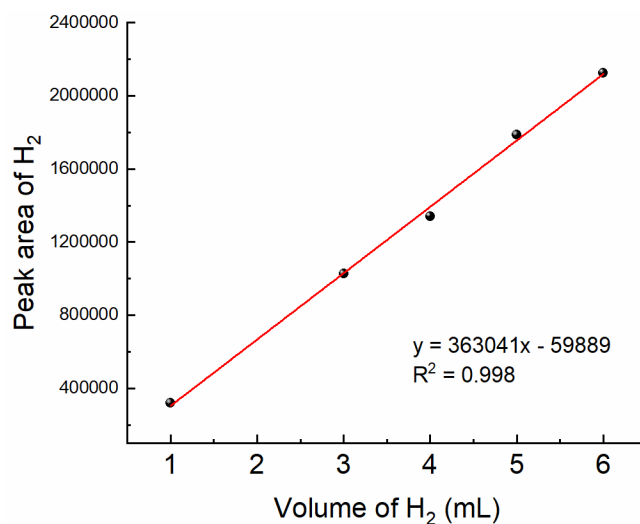


Figure S13. Standard curve of H₂ production.

The generated amount of H₂ evolved was analyzed by chromatography with a known concentration of H₂ as standard gas. According to the fitted standard curve, the relationship between the peak area and the volume of H₂ evolved can be expressed as Equation:

$$y = 363041x - 59889$$

Where y is the peak area corresponded to H₂ in the chromatography, and x is the volume of H₂ evolved (mL).

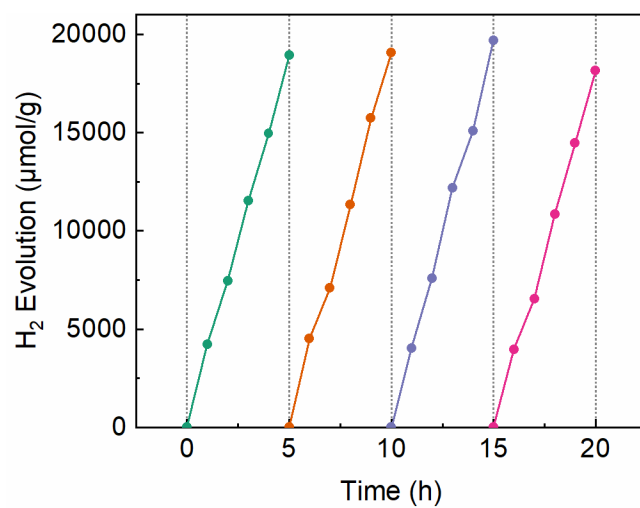
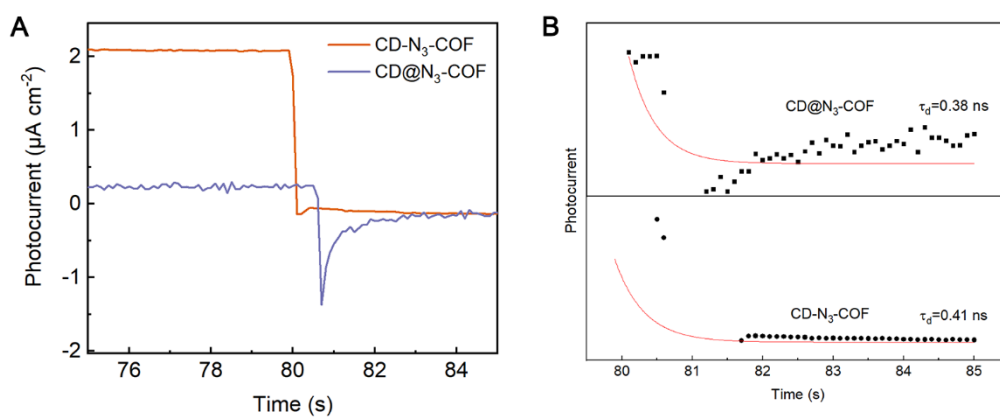


Figure S14. Cycle tests of H₂ evolution for 0.1CD-N₃-COF.



Sample	CD@N ₃ -COF	CD-N ₃ -COF
t_n /ns	0.52	1.71
t_d /s	0.38	0.41
L_n/L	3.75×10^{-5}	6.46×10^{-5}

Figure S15. (A) Photocurrent decay and (B) electron transport length of CD-N₃-COF and CD@N₃-COF.

The electron diffusion length (L_n) was obtained according to the calculation formula of $L_n = L (\tau_n/\tau_d)^{1/2}$. τ_n is fluorescence lifetime and τ_d (electron transfer time) is obtained by fitting the decay curve of the photocurrent transient to the function of $\exp(-t/\tau_d)$.⁶

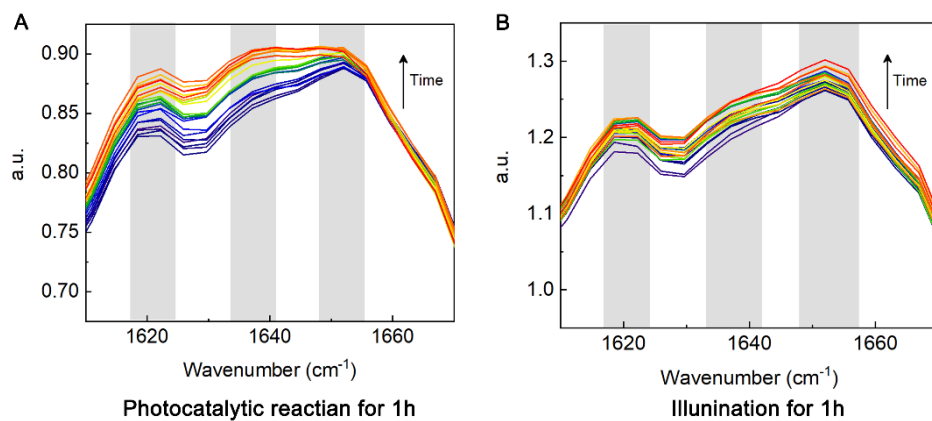


Figure S16. In situ FT-IR spectra of 0.1CD-N₃-COF under illumination for 1h.

Table S1. Comparison of photocatalytic hydrogen evolution rates for COF-based photocatalysts

Photocatalyst (amount)	Light source	Cocatalyst	Sacrificial reagent	HER ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	References
CD-N ₃ -COF	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	8 wt% H ₂ PtCl ₆	TEOA	3787	<i>This work</i>
N ₃ -COF (5 mg)	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	Pt	TEOA	1704	<i>Nat. Commun.</i> 2015 , 6, 8508-8516.
N ₂ -COF (5 mg)	AM 1.5	Co-1	TEOA	782	<i>J. Am. Chem. Soc.</i> 2017 , 139, 16228-16234
TP-BDDA-COF (10 mg)	300 W Xe-lamp ($\lambda > 395 \text{ nm}$)	3 wt% Pt	TEOA	3240	<i>J. Am. Chem. Soc.</i> 2018 , 140, 1423-1427.
TPDTz-COF (5 mg)	AM 1.5	NiME	TEOA	941	<i>J. Am. Chem. Soc.</i> 2019 , 141, 11082-11092
g-C ₄₀ N ₃ -COF (50 mg)	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	Pt	TEOA	4120	<i>Nat. Commun.</i> 2019 , 10, 2467-2476
Porphyrin-based COF (2.5 mg)	300 W Xe-lamp ($\lambda > 400 \text{ nm}$)	8 wt% H ₂ PtCl ₆	TEOA	413	<i>Nat. Commun.</i> 2021 , 12, 1-9.

S4. References

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