Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Interlayer Polymerization Enables Cross-Plane Conjugation in COFs for Efficient Photocatalytic H_2O_2 Production

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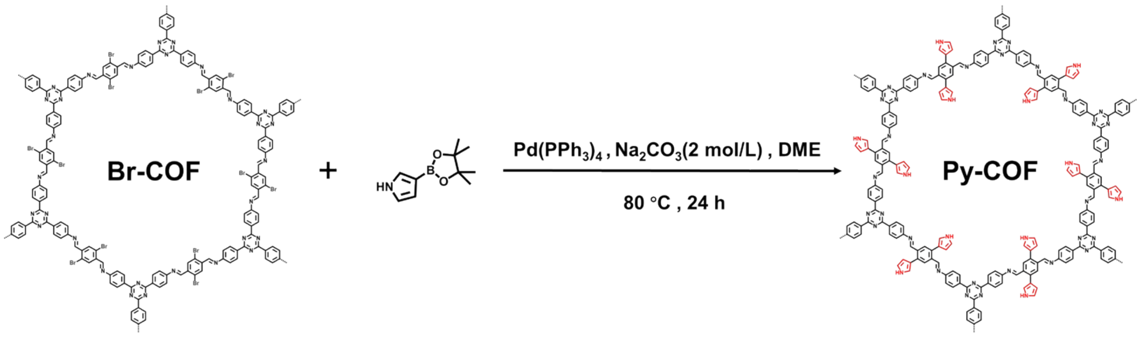
1. Materials and synthetic procedures

Materials

1,4-Phenylenedialdehyde, *N*-Bromosuccinimide (NBS), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1H-pyrrole (AR), Dimethyl sulfoxide-d6 (DMSO-d_6), Tetrakis (triphenylphosphine) palladium ($Pd(PPh_3)_4$), 4,4',4''-(1,3,5-triazine-2,4,6-triyI) trianiline (AR), Triethanolamine, sodium carbonate (Na_2CO_3), 1,2-dimethoxyethane (DME), 2,2,6,6-tetramethylpiperidine were purchased from Shanghai Haohong Biomedical Technology Co., Ltd. Hexadecyltrimethylammonium Bromide (CTAB, 99%), 4-Aminophenylboronic Acid Pinacetamide, Hydrogen Potassium Phthalate, 5,5-Dimethyl-1-Pyrrolin-*N*-Oxide (DMPO), L-tryptophan, KOH, 2-Chloro-1,1-Dibromo-4-Chlorobenzene, Acetonitrile, Petroleum Ether, Anhydrous Ethanol (EtOH) were purchased from Aladdin Reagents (Shanghai, China) Co., Ltd.

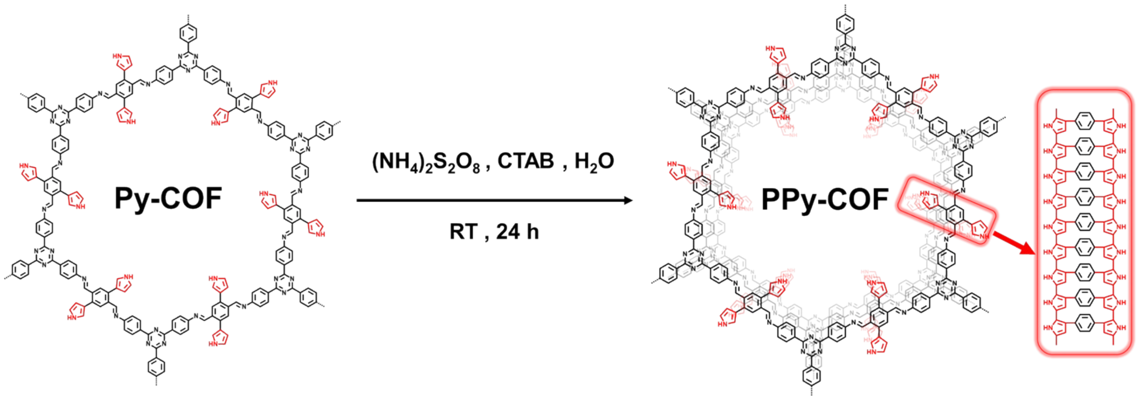
Synthesis of Py-COF

Br-COF (0.2460 g), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1H-pyrrole (1.00 mmol, 0.1930 g), and $Pd(PPh_3)_4$ (0.03 mmol, 0.0350 g) were mixed and then successively added with ethylene glycol dimethyl ether (DME, 2.5 mL), Na_2CO_3 solution (1.0 mL, 2.00 mol/L), and anhydrous methanol (1.0 mL). The mixture was heated and refluxed under a nitrogen atmosphere at 80 °C for 24 hours to obtain Py-COF. After cooling to room temperature, the product was thoroughly washed with acetone, THF, and dichloromethane, and then washed with a saturated cysteine solution to remove the palladium catalyst, then dried under vacuum at 60 °C overnight. The final product was obtained as a dark brown powder. The mass of Py-COF is approximately 0.1980 g with an isolated yield of 84.9%.



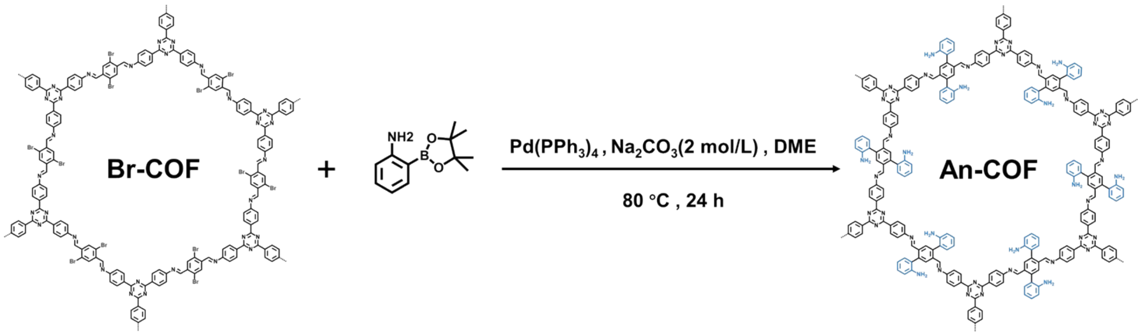
Synthesis of PPy-COF

Py-COF (0.2320 g), cetyltrimethylammonium bromide (CTAB) (0.16 mmol, 0.0590 g), triethanolamine (0.84 mmol, 0.1 mL) and deionized water (1.0 mL) were mixed together and then added to the ammonium persulfate solution (0.7 mL, 0.18 M). The mixture was stirred at room temperature for 24 hours. After the reaction was completed, the mixture was thoroughly washed with deionized water and methanol to obtain a light brown solid precipitate. The mass of PPy-COF is approximately 0.1670 g with an isolated yield of 72.0%.



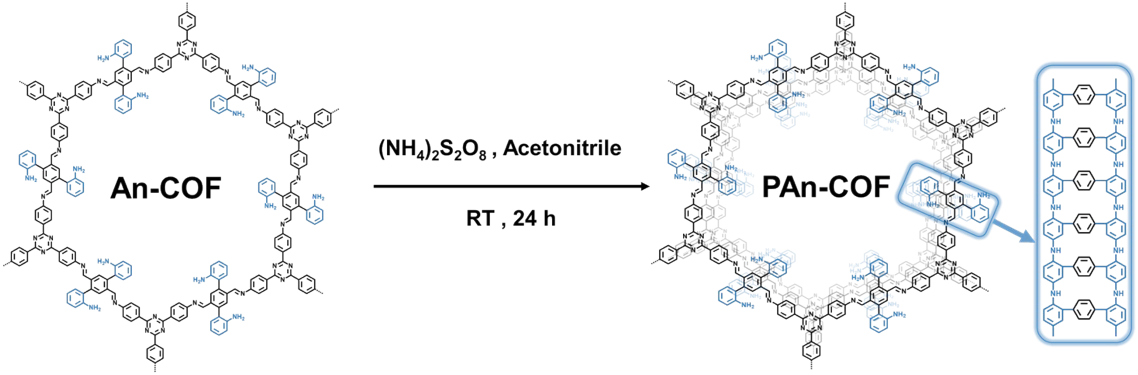
Synthesis of An-COF

Br-COF (0.2460 g), 2-aminophenylboronic acid pinacol ester (1.00 mmol, 0.2190 g) and $Pd(PPh_3)_4$ (0.03 mmol, 0.0350 g) were mixed and then successively added with ethylene glycol dimethyl ether (DME, 2.5 mL), Na_2CO_3 solution (1.0 mL, 2.00 mol/L), and anhydrous methanol (1.0 mL). The mixture was heated and refluxed under a nitrogen atmosphere at 80 °C for 24 hours to obtain An-COF. After the reaction was completed, the product was thoroughly washed with acetone, THF and dichloromethane, and then washed with a saturated cysteine solution to remove the palladium catalyst, then dried under vacuum at 60 °C overnight. The final product was obtained as a dark green powder. The mass of An-COF is approximately 0.2210 g with an isolated yield of 85.2%.



Synthesis of PAn-COF

The mixture was prepared by slowly adding the aqueous solution of ammonium persulfate (0.4564 g, 0.02 M) to the acetonitrile solution of An-COF (0.2590 g, 0.10 M), and then stirring at room temperature for 24 hours. After the reaction was completed, the mixture was thoroughly washed with deionized water and methanol to obtain a light green solid precipitate. The mass of PAn-COF is approximately 0.1740 g with an isolated yield of 67.1%.



2. Instruments and methods

The X-ray powder diffraction experiment was conducted using the German Bruker D8 Advance diffractometer with Cu–Kα1 radiation (λ = 1.5406 Å, sweep speed of $6^{o}\cdot\mathrm{min}^{-1}$). The Fourier Transform Infrared Spectroscopy (FT-IR) was tested using the German Bruker VERTEX 70 + HYPERION 2000. Nitrogen adsorption isotherms were performed on the BEL sorp-max at 77 K, and the Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The TGA 4000 thermogravimetric analyzer was used for thermogravimetric analysis (TGA) under a nitrogen atmosphere from 30 °C to 800 °C at a heating rate of 10°C min^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out using the XPS-7000 spectrometer with a Mg Kα X-ray source. UV-vis diffuse-reflectance spectroscopy was tested using the UV3600 ultraviolet-visible spectrophotometer, with the wavelength range being 200-800 nm. Specifically, the spectrometer undergoes an automatic light-source/filter changeover at approximately 393 nm. The steady-state photoluminescence (PL) spectra were tested using a FLS920 steady-state fluorescence spectrophotometer. Electron spin resonance (ESR) was tested at room temperature using the spectrometer of the Japanese company JEOL model JES-X320, with a magnetic field strength of 321-331 mT. All electrochemical tests were conducted using the electrochemical station (CHI 660E, Chenhua). The light exposure experiments were performed using the BBZM-III type 300 W xenon light source equipped with an extinction filter with $\lambda > 420$ nm.

The transient photocurrent measurements

5 mg of the photocatalyst was added to 1 mL of ethanol and 20 μL of 5% Nafion solution, and then ultrasonicated to prepare a uniformly dispersed ink. The obtained ink (80 μL) was dropped onto ITO glass and dried in the air. All the tests were conducted on the CHI660E electrochemical workstation using a three-electrode system. The transient photocurrent measurement was carried out under the illumination of a 300 W xenon lamp (with a 420 nm cut-off filter). The ITO conductive glass loaded with the material (1×2 cm^2) served as the working electrode, the platinum sheet electrode was used as the counter electrode, and the Ag/AgCl electrode was used as the reference electrode. The electrolyte was a 0.1 M Na_2SO_4 solution.

Mott-Schottky measurements

The electrolyte and electrodes used in the above transient photocurrent test are the same. It is also measured in a three-electrode system, with measurement frequencies of 1000 Hz, 1500 Hz and 2000 Hz.

Electrochemical impedance spectroscopy (EIS) measurements

The device used for the electrochemical impedance spectroscopy (EIS) test is the same as described above. The electrochemical impedance spectroscopy (EIS) was collected on an open-circuit voltage of 0 V with an amplitude of 5 mV over a frequency between 1 and 10^5 Hz.

Electron Spin Resonance (ESR) measurements

The electron spin resonance test was conducted using the Electron Spin Resonance Spectrometer (JES-X320). The test conditions were as follows: the magnetic field range was 321-331 mT, power was 0.988 mW, frequency was 9250.455 MHz, central field: 326.0 G, modulation width: 0.3 mT. 5,5-Dimethyl-1-pyrrolin-*N*-oxide (DMPO) and 2,2,6,6-Tetramethylpiperidone (TEMP) were respectively used as spin trapping agents for capturing $\cdot O_2^-$, $\cdot OH$ and $^1O_2$ superoxide free radicals.

Photocatalytic H_2O_2 production

The photocatalytic experiments were always conducted in a reaction bottle containing 2 mg of catalyst and 8 mL of deionized water. Then, the light experiments were carried out under a 300 W xenon lamp (equipped with a 420 nm cut-off filter). During the light exposure process in the oxygen system, oxygen was continuously introduced. During the reaction, the temperature remained at room temperature.

Hydrogen peroxide detection methods (iodometric method)[S1-S4]

The reaction solution was sampled every 15 minutes. The obtained solution was filtered through a 0.22 μm filter. The volume of the filtered solution was measured as 0.2 mL and mixed evenly with 1 mL of 0.4 M potassium iodide solution and 1 mL of 0.1 M potassium hydrogen phthalate solution. Then the ultraviolet absorption spectrum of the mixed solution was measured after 30 minutes of reaction in the dark condition. In an acidic condition, hydrogen peroxide reacts with I^- to form I_3^- ($H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$), which has a strong absorption peak at 350 nm. We use a UV spectrophotometer to detect the absorbance of the reaction system at 350 nm and compare it with the standard curve to obtain the concentration of hydrogen peroxide.

The detection of $\cdot O_2^-$ by Nitroblue tetrazolium (NBT)

The detection of $\cdot O_2^-$ is carried out using Nitroblue tetrazolium (NBT) (absorption maximum at 259 nm). Specifically, the detection of $\cdot O_2^-$ is conducted by adding 0.5 mM Nitroblue tetrazolium (NBT) solution and 5 mg of catalyst to the reactor and conducting a light exposure experiment, removing 1 mL of the sample at a specific time, and detecting the concentration of Nitroblue tetrazolium (NBT) by UV-visible spectrophotometry after filtration through a 0.22 μm filter.

The apparent quantum yield (AQY) calculation

The wavelength-dependent photosynthesis experiments were conducted using 450, 550 and 650 nm bandpass glass filters under the illumination of a 300 W xenon lamp. The AQY[S5-S6] is calculated by the following equation:

$$\mathrm{AQY}(\%) = \frac{hc \times n_{\mathrm{H_2O_2}} \times N_{\mathrm{A}} \times 2}{ISt\lambda} \times 100\% \qquad \text{(S1)}$$

where $n_{\mathrm{H_2O_2}}$ is the number of evolved H_2O_2 molecules; N_{A} is Avogadro number (6.02×10^{23}); I is light power intensity (1000 W $\mathrm{cm^{-2}}$); S is the irradiation area ($\mathrm{cm^2}$); t is the reaction time (s); λ is the wavelength (m); h is Planck's constant (6.63×10^{-34} $\mathrm{m^2\ kg\ s^{-1}}$); c is the speed of light (3×10^8 $\mathrm{m\ s^{-1}}$).

Density functional theory (DFT) calculation

All density functional theory (DFT) calculations were performed using the CASTEP module implemented in the Materials Studio software package. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange-correlation interaction. The van der Waals interactions were accounted for by the DFT-D2 correction scheme of Grimme. The core–electron interactions were described by on-the-fly generated ultrasoft pseudopotentials. A plane-wave kinetic energy cutoff of 450 eV was set for all calculations. The Brillouin zone was sampled using a k-point grid of 2 × 2 × 1, which was tested to be sufficient for energy convergence. The self-consistent field (SCF) convergence tolerance was set to 1.0×10^{-6} eV atom^{-1}. Geometry optimizations were performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm, with convergence criteria set to 1.0×10^{-5} eV atom^{-1} for total energy, 0.03 eV Å^{-1} for maximum ionic force, 0.05 GPa for maximum stress, and 0.001 Å for maximum atomic displacement.

3. Results

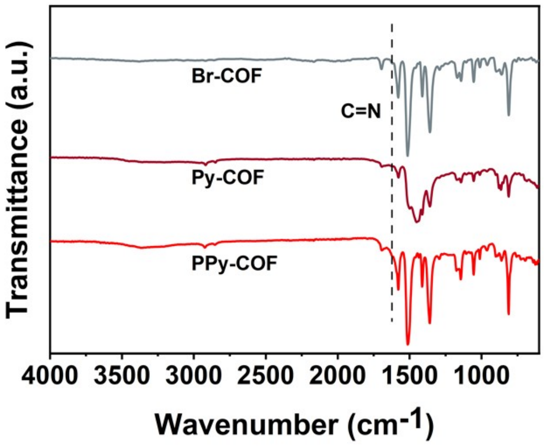


Figure S1. FT-IR spectra of Br-COF, Py-COF and PPy-COF.

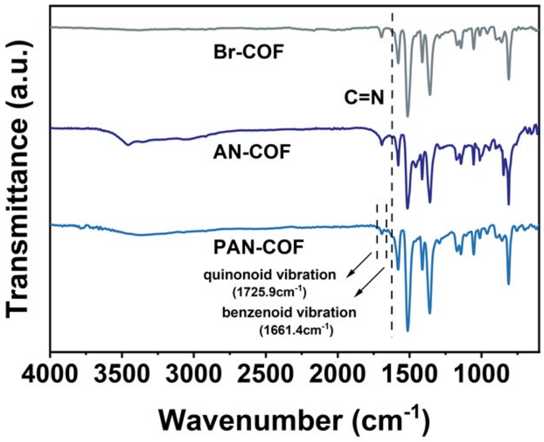


Figure S2. FT-IR spectra of Br-COF, An-COF and PAn-COF.

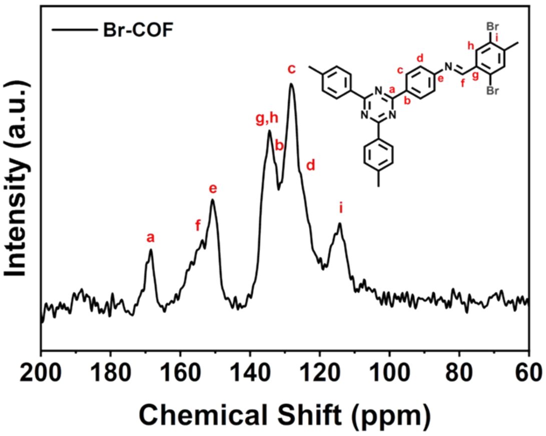


Figure S3. ^{13}C NMR spectrum of Br-COF.

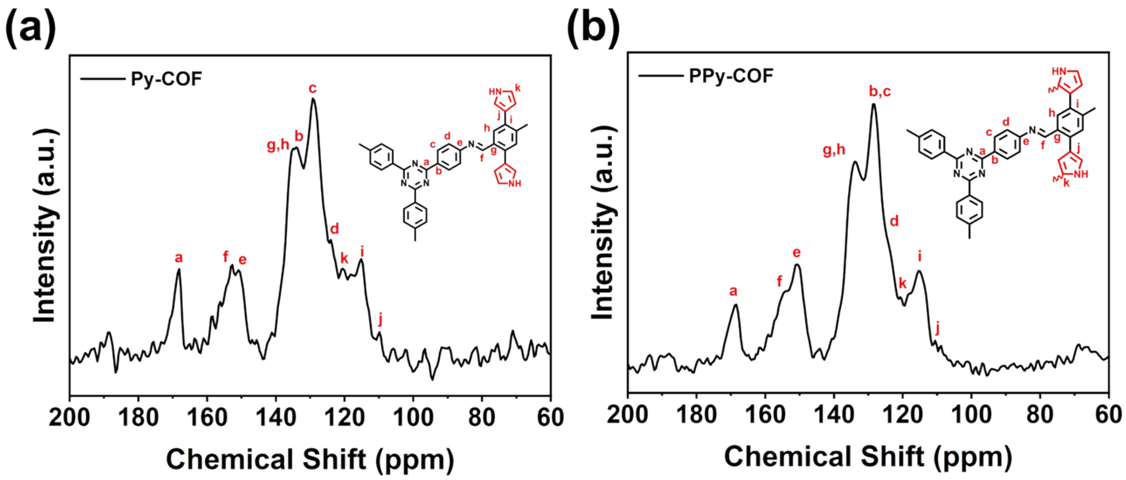


Figure S4. ^{13}C NMR spectra of (a) Py-COF and (b) PPy-COF.

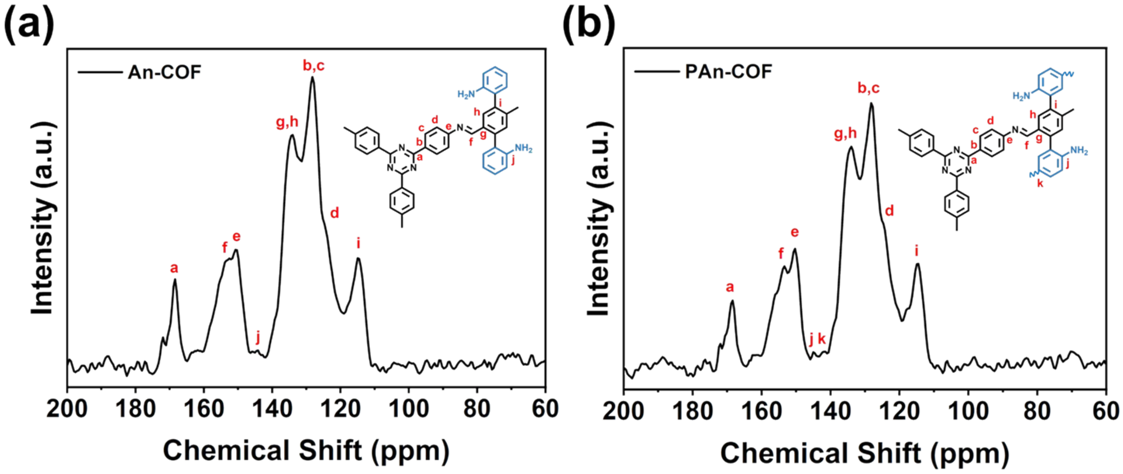


Figure S5. ^{13}C NMR spectra of (a) An-COF and (b) PAn-COF.

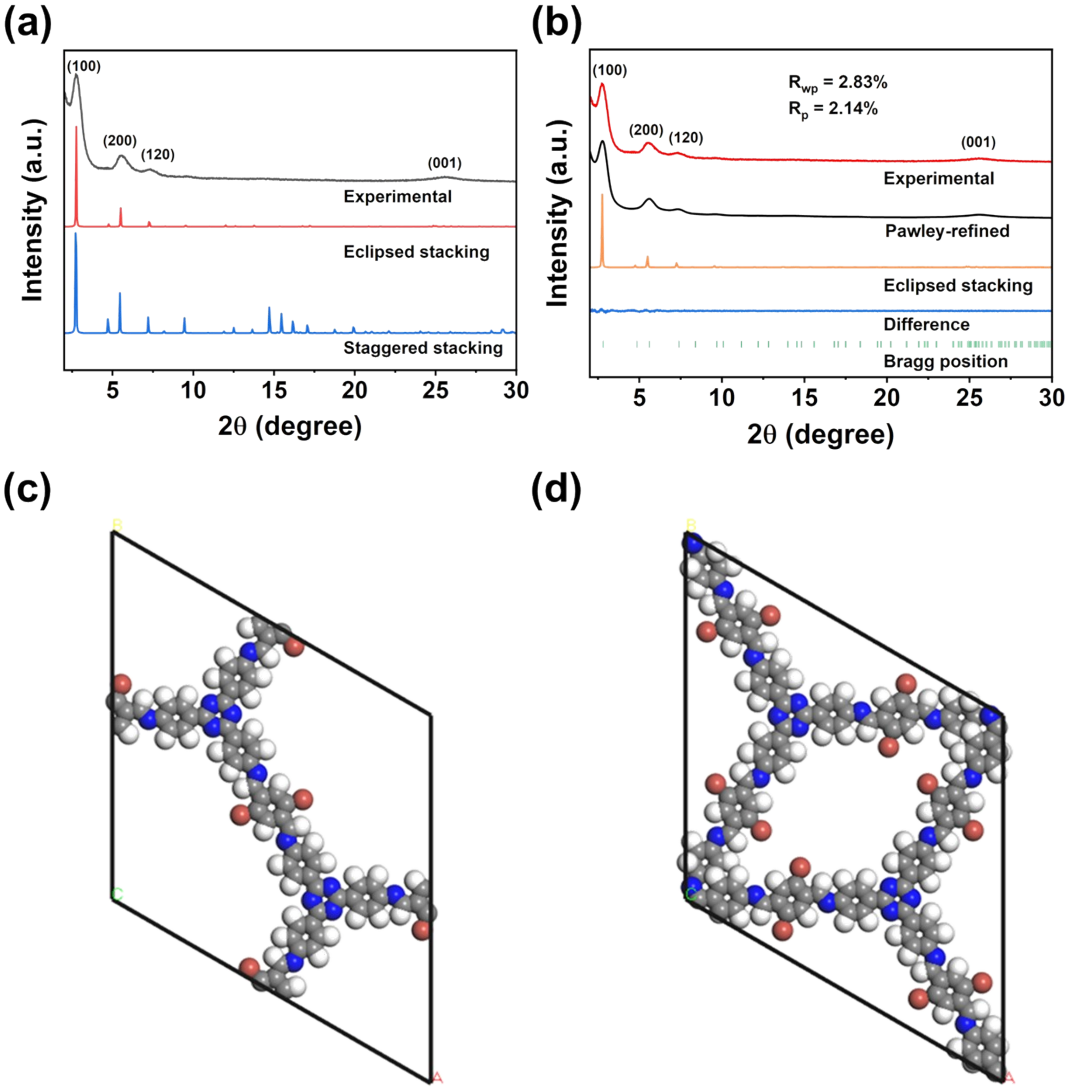


Figure S6. (a) Experimental and Simulated PXRD patterns of Br-COF; (b) Experimental, Pawley-refined and Simulated PXRD patterns of Br-COF; The proposed unit cells of Br-COF with (c) the eclipsed (AA) stacking mode and (d) the staggered (AB) stacking mode.

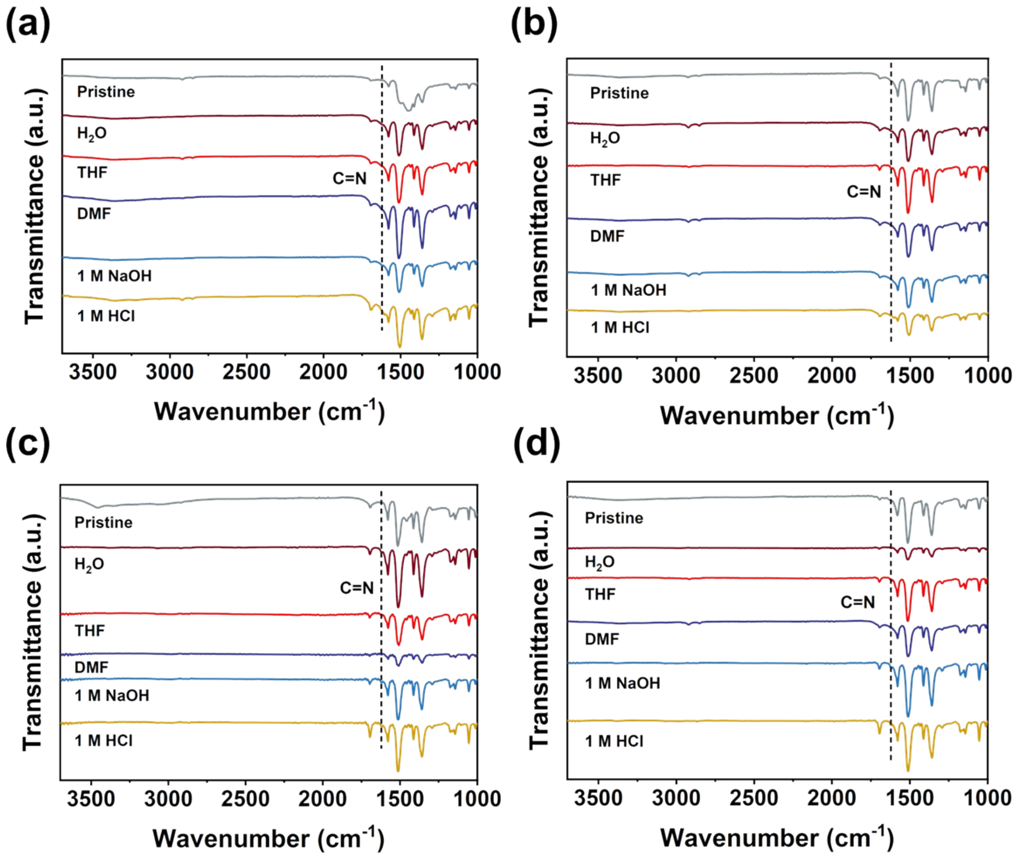


Figure S7. FT-IR spectra of (a) Py-COF; (b) PPy-COF; (c) An-COF and (d) PAn-COF after immersing in H_2O, THF, DMF, aqueous 1 M NaOH and 1 M HCl solutions at room temperature for 24 hours.

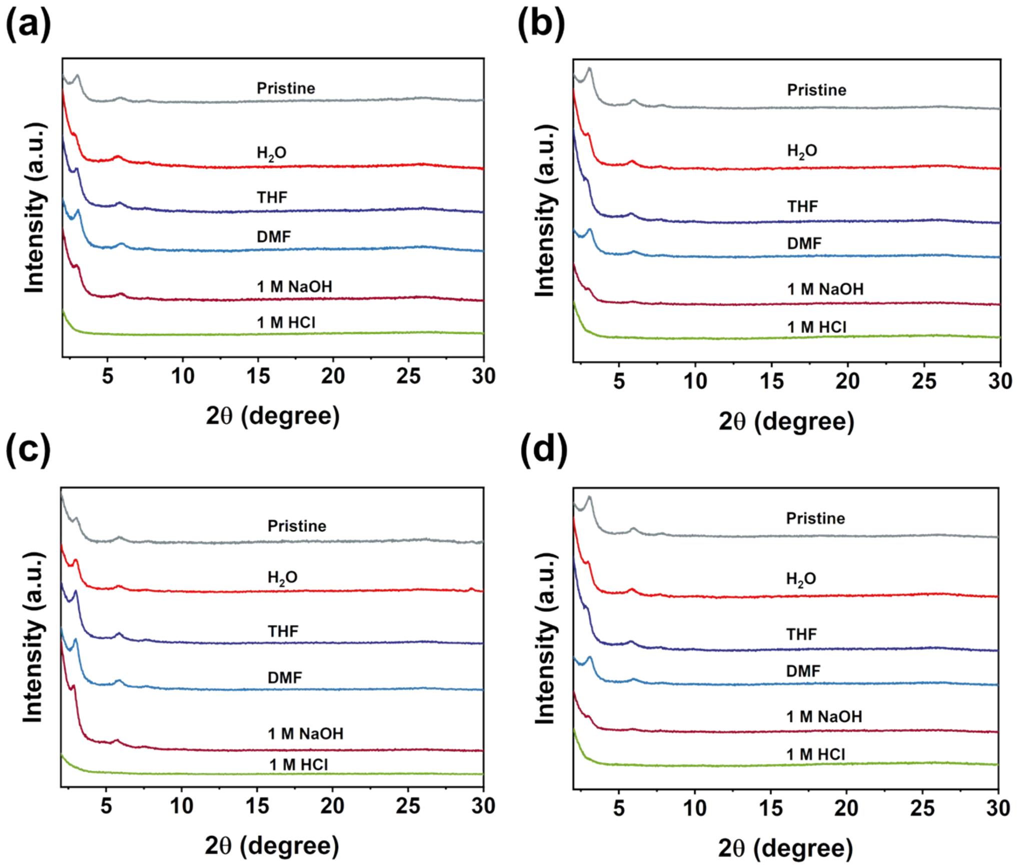


Figure S8. PXRD patterns of (a) Py-COF; (b) PPy-COF; (c) An-COF and (d) PAn-COF after immersing in H_2O, THF, DMF, aqueous 1M NaOH and 1M HCl solutions at room temperature for 24 hours.

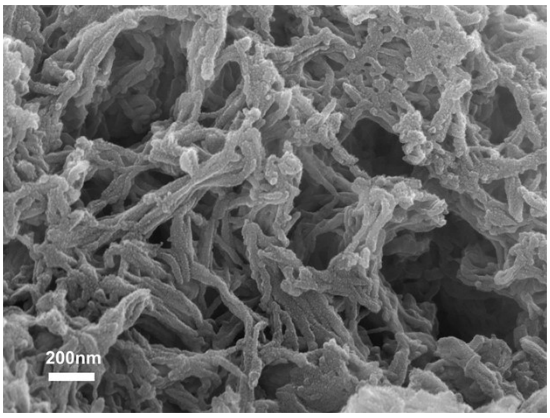


Figure S9. SEM image of An-COF.

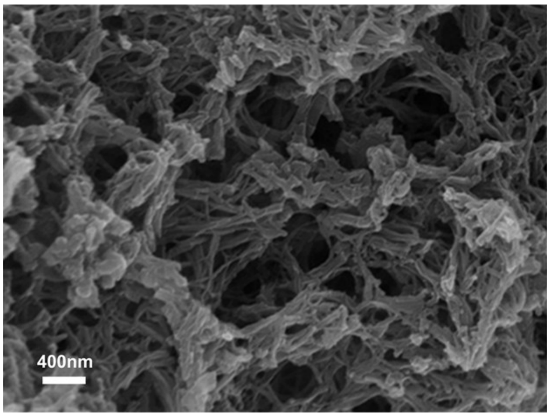


Figure S10. SEM image of PAn-COF.

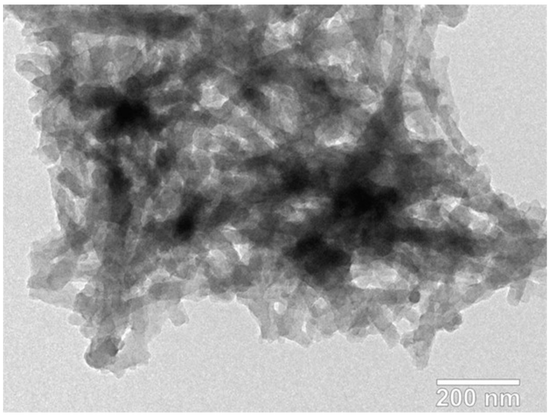


Figure S11. TEM image of Py-COF.

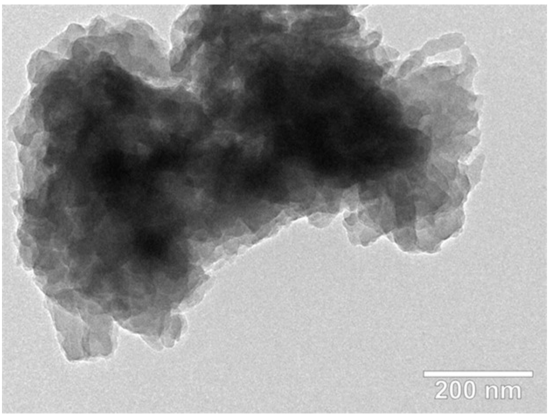


Figure S12. TEM image of PPy-COF.

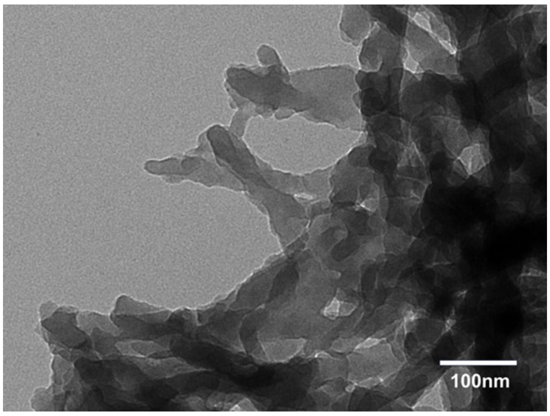


Figure S13. TEM image of An-COF.

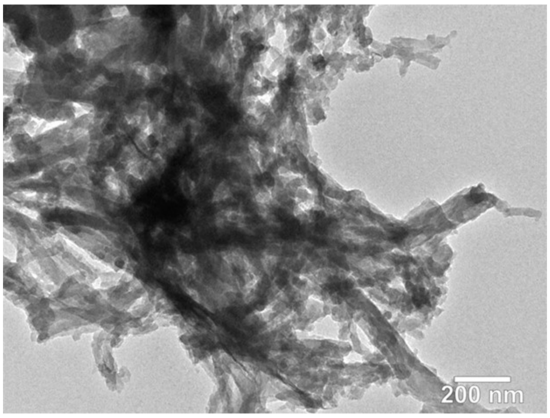


Figure S14. TEM image of PAn-COF.

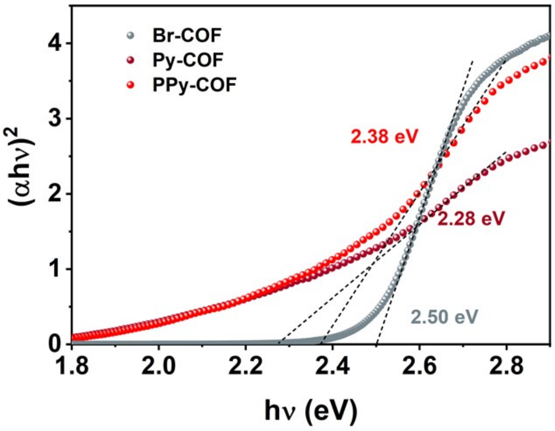


Figure S15. Band gaps of Br-COF, Py-COF and PPy-COF.

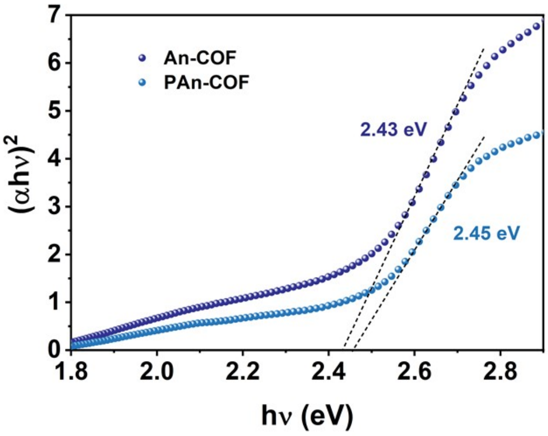


Figure S16. Band gaps of An-COF and PAn-COF.

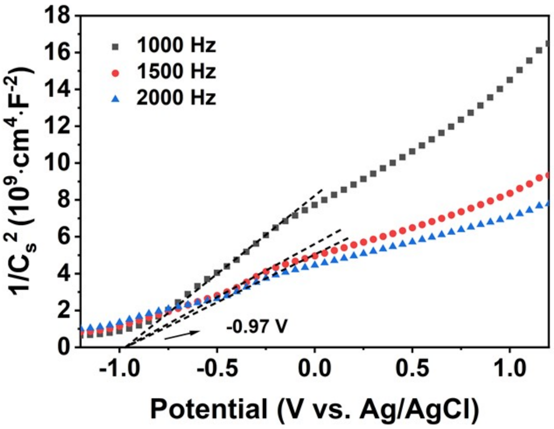


Figure S17. Mott-Schottky plot of Br-COF.

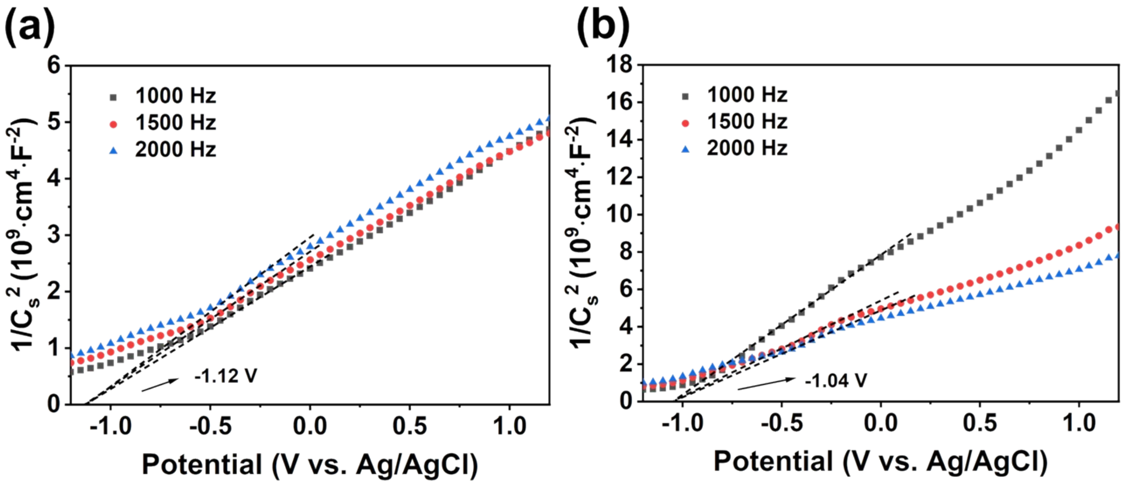


Figure S18. Mott-Schottky plots of (a) Py-COF and (b) PPy-COF.

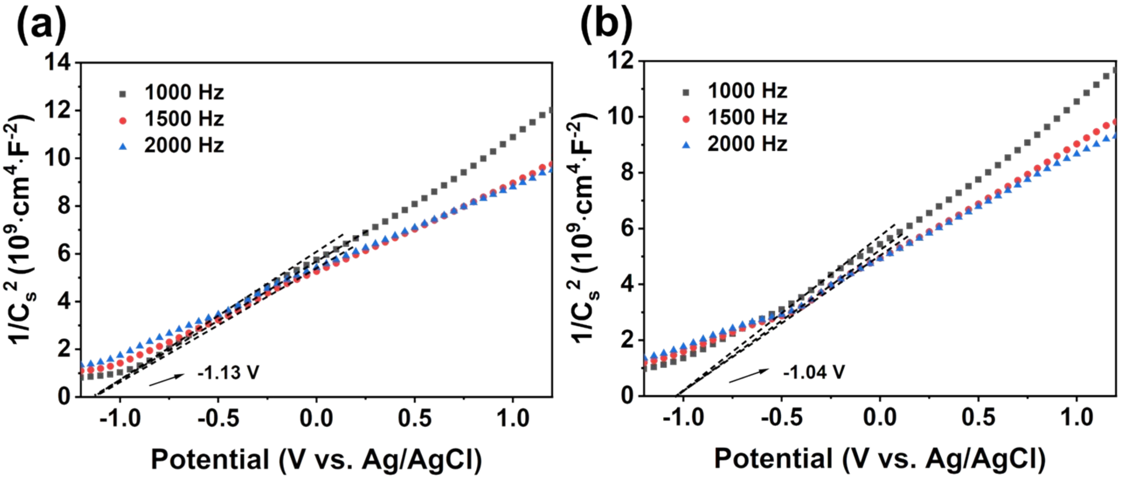


Figure S19. Mott-Schottky plots of (a) An-COF and (b) PAn-COF.

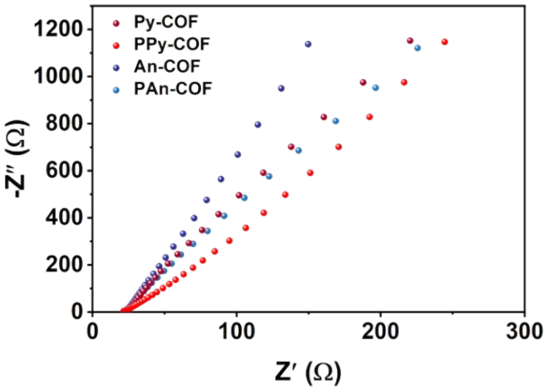


Figure S20. EIS plots of Py-COF, PPy-COF, An-COF and PAn-COF.

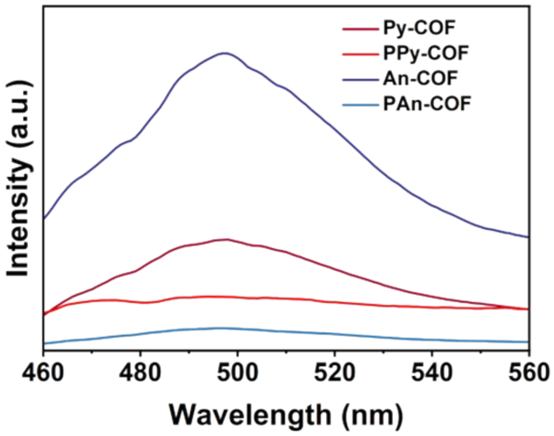
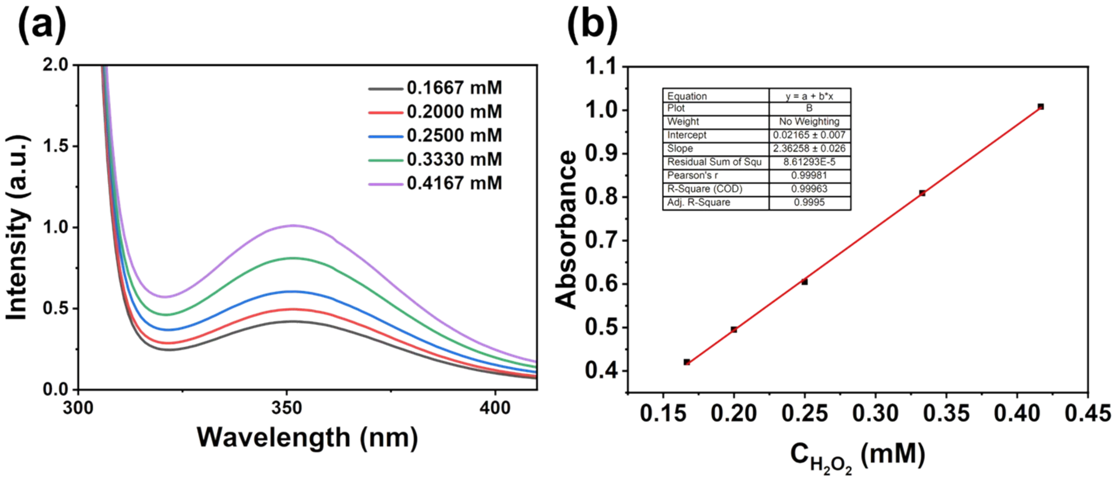


Figure S21. PL fluorescence intensity of Py-COF, PPy-COF, An-COF and PAn-COF.



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0.02165 ± 0.007
Slope	2.36258 ± 0.026
Residual Sum of Squ	8.61293E-5
Pearson's r	0.99981
R-Square (COD)	0.99963
Adj. R-Square	0.9995

Figure S22. (a) The UV-vis absorption spectra of I_3^- solutions with different concentrations and (b) standard curve of H_2O_2 concentration-absorbance.

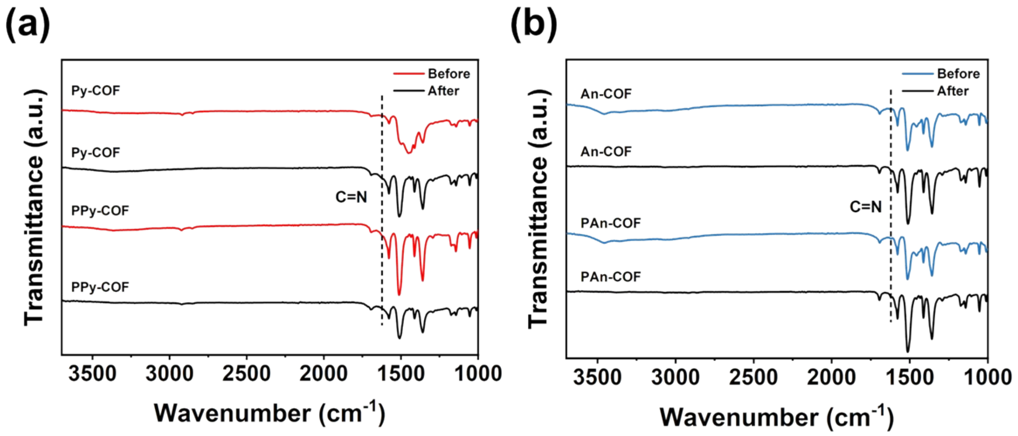


Figure S23. FT-IR spectra of (a) Py-COF, PPy-COF and (b) An-COF and PAn-COF before and after light irradiation.

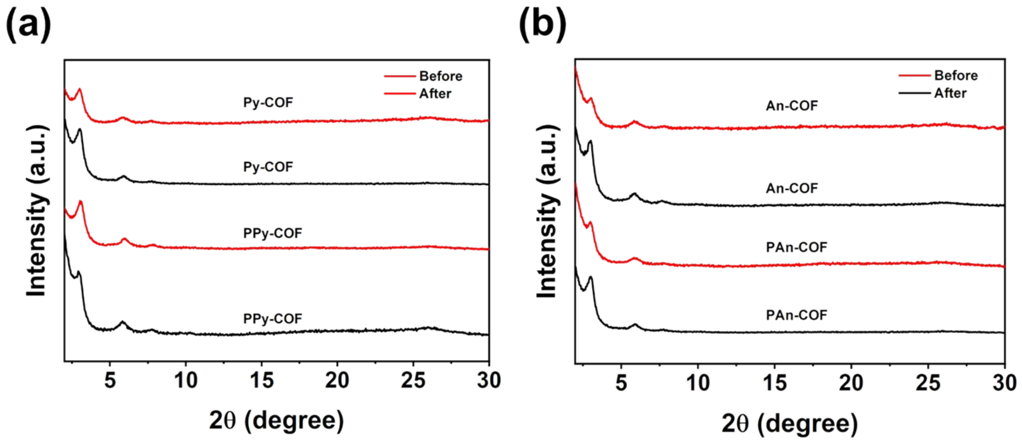


Figure S24. PXRD patterns of (a) Py-COF, PPy-COF and (b) An-COF and PAn-COF before and after light irradiation.

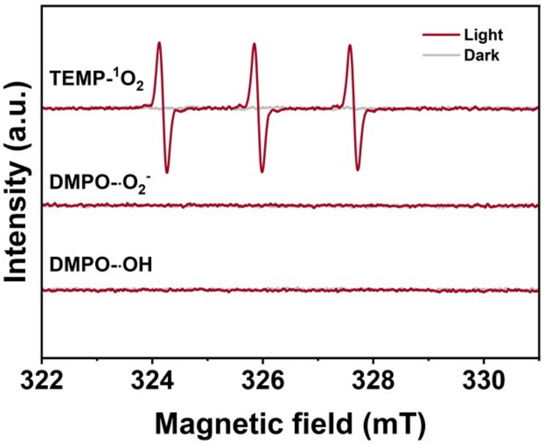


Figure S25. ESR spectra of Py-COF.

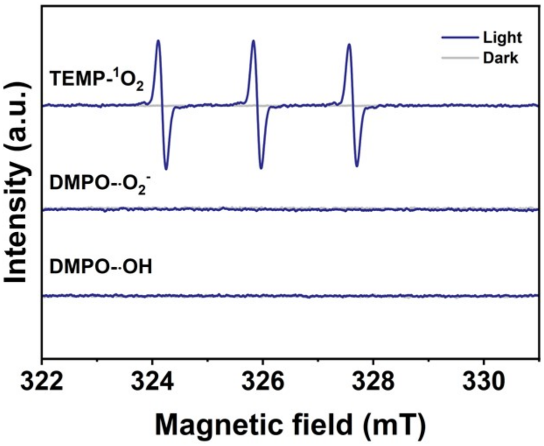


Figure S26. ESR spectra of An-COF.

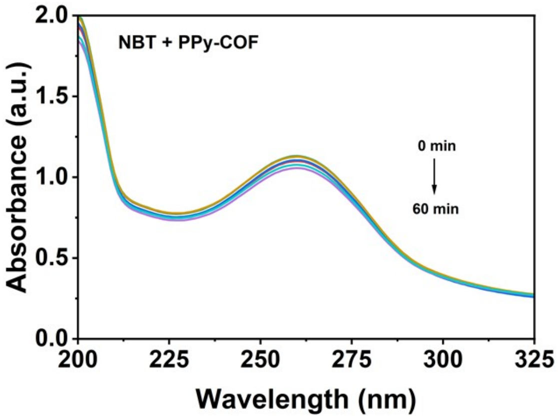


Figure S27. The ultraviolet absorption of Nitroblue tetrazolium (NBT) after adding PPy-COF within 60 minutes.

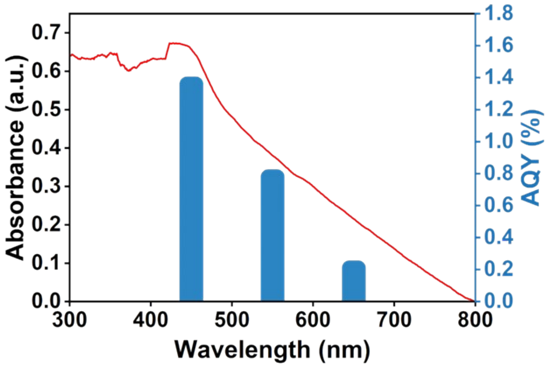


Figure S28. The AQY for photocatalytic H_2O_2 generation of PPy-COF.

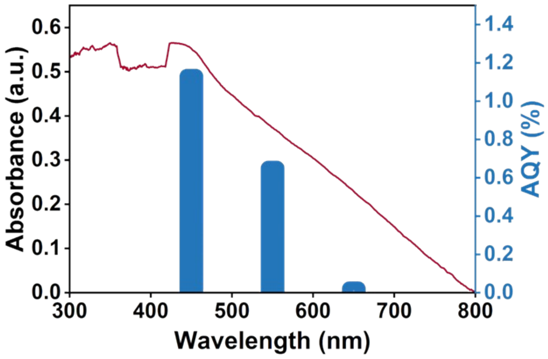


Figure S29. The AQY for photocatalytic H_2O_2 generation of Py-COF.

Supporting references

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S6 L. Li, X. Lv, Y. Xue, H. Shao, G. Zheng, Q. Han, *Angewandte Chemie International Edition* 2024, **63**, e202320218.