Supporting information

Rational Design of Electron-Deficient COFs via Ketone and Sulfone Functionalization for Dramatically Enhanced Photocatalytic Hydrogen Peroxide Production

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1. Experimental Procedures

1.1 Materials

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. 1,3,5-Triformylphloroglucinol (Tp, 98%) was purchased from Shanghai Bide Pharmatech Ltd. The diamine monomers, including 4,4'-diaminodiphenylmethane (MDA, 97%), 4,4'-diaminodiphenyl sulfide (DADS, 98%), 4,4'-diaminobenzophenone (DABP, 98%), and 4,4'-diaminodiphenyl sulfone (DDS, 98%), were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. *N,N*-Dimethylformamide (DMF, anhydrous, 99.8%) and methanol (HPLC grade) were also supplied by Macklin. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO, 97%) was used as the spin trap for EPR measurements. Rhodamine B (RhB), methyl orange (MO), and tetracycline hydrochloride (TC, 96%) were used as model organic pollutants.

1.2 Characterization

The synthesized COFs were characterized using a suite of analytical techniques to confirm their structure, composition, and physicochemical properties. Powder X-ray Diffraction (PXRD): Patterns were recorded on a Rigaku SmartLab diffractometer (Japan) using Cu Kα radiation ($\lambda = 1.5406$ Å) generated at 40 kV and 40 mA. Data were collected in the 2θ range of 2° to 30° with a step size of 0.02°. Fourier-Transform Infrared Spectroscopy (FTIR): Spectra were obtained on a Thermo Fisher Scientific Nicolet iS20 spectrometer (USA) using the KBr pellet method, with measurements taken in the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. X-ray Photoelectron Spectroscopy (XPS): Measurements were performed on a Thermo Fisher Scientific ESCALAB Xi+ spectrometer (USA) with a monochromatic Al Kα X-ray source (1486.6 eV). All binding energies were calibrated using the C 1s peak at 284.8 eV as an internal reference. Solid-State UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS): Spectra were recorded on a Shimadzu UV-2700 spectrophotometer (Japan) equipped with an integrating sphere attachment. $BaSO_4$ was used as a 100% reflectance standard. Bandgap energies were derived from the corresponding Tauc plots. Electrochemical Measurements (Mott-Schottky, EIS, Photocurrent): These were carried out on a CHI 660F electrochemical workstation (CH Instruments Ins, shanghai, China) using a standard three-electrode system. A platinum wire and an Ag/AgCl (saturated KCl) electrode served as the counter and reference electrodes, respectively. The working electrode was prepared by coating a fluorine-doped tin oxide (FTO) glass with a catalyst slurry. Steady-State and Time-Resolved Photoluminescence (PL & TR-PL): Spectra and decay curves were acquired on an Edinburgh Instruments FLS1000 spectrofluorometer (UK). For steady-state PL, the excitation wavelength was set at 380 nm, and the emission was monitored around 630 nm. Time-resolved decays were measured using time-correlated single-photon counting (TCSPC) with the same excitation wavelength. Electron Paramagnetic Resonance (EPR) Spectroscopy: Signals of spin-trapped radicals were recorded on a Bruker A300 spectrometer at room temperature. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was used as the spin trap.

1.3 Synthesis of COFs (General Procedure)

The covalent organic frameworks Tp-MDA, Tp-DADS, Tp-DABP, and Tp-DDS were synthesized via a Schiff-base condensation reaction followed by tautomerization, using an analogous procedure with different diamine monomers.

Typically, 1,3,5-triformylphloroglucinol (Tp, 0.666 mmol) and the corresponding diamine monomer (MDA, DADS, DABP, or DDS, 0.999 mmol) were added to a 100 mL three-necked flask. Anhydrous N,N-dimethylformamide (DMF, 40 mL) was introduced as the solvent. The flask was then sealed, and the mixture was subjected to three cycles of vacuum evacuation and nitrogen purging to remove oxygen. Under a continuous nitrogen atmosphere, the reaction mixture was stirred and heated in an oil bath at 100 °C for 24 hours. After cooling to room temperature, the resulting precipitate was collected by filtration and washed thoroughly with ethanol to remove unreacted monomers and solvent residues. The final product was obtained as a colored powder after drying under vacuum at 60 °C for 12 hours.

1.4 Photocatalytic activity tests

In a typical reaction setup, 10 mg of photocatalyst was dispersed in a mixture solution of ultrapure water (100 mL). The photoreaction was irradiated with a 300 W xenon lamp after bubbling with O_2 for 15 minutes under continuous stirring. At given time intervals, a certain suspension was collected and filtered with a Millipore filter (0.45 μm) to remove the photocatalyst. The H_2O_2 concentration was determined by iodometry. Typically, 0.5mL of the reaction solution was added to a 1 mL mixture solution of 2.5 mmol of N,N-Diethyl-p-phenylenediamine sulfate (98%) in 10 mL of a 5 mM sulfuric acid (H_2SO_4) solution.1.25 mmol of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 10 mL of water, and the reaction was allowed to proceed for 2 min. Under acidic conditions, the H_2O_2 molecules will react with Fe^{2+} to generate Fe^{3+}, The colorless DPD was oxidized by Fe^{3+} to generate the red DPD radical cation (DPD^{+}•). The absorbance of this product was measured at 551 nm, which is its established absorption maximum in aqueous solution, to ensure precise and sensitive quantification, which was further used to quantify the generated H_2O_2. The production rate was calculated by the following equation:

$$R = \frac{Y}{(V \times M \times T)} \# \ (1)$$

Where R is the H_2O_2 production rate, Y is the H_2O_2 yield, V is the volume of the reaction solution, M is the mass of the catalyst, and T is the photocatalysis reaction time.

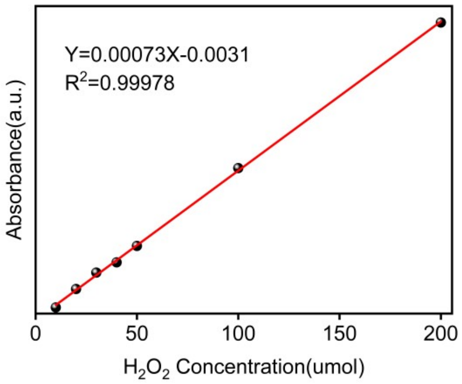

Fig. S1 Standard calibration curve for the spectrophotometric quantification of H_2O_2.

1.5 Electrochemical tests

The electrochemical measurements were performed on a CHI660F electrochemical workstation (Chinstruments, Shanghai) using a standard three-electrode system with Ag/AgCl electrode as the reference electrode and platinum foil as the counter electrode, respectively, while the working electrode was prepared by depositing the as-synthesized samples on FTO glass. A 0.5 M Na2SO4 aqueous solution was used as the electrolyte. The sample was prepared by first dispersing 5 mg of the powder in 300 μL of Isopropanol, followed by ultrasonication for 30 minutes. Subsequently, 30 μL of naphthol was added to the mixture, which was then thoroughly homogenized using a vortex mixer. Finally, the resulting mixture was drop-cast onto an FTO substrate placed on a hot plate set at 60°C.

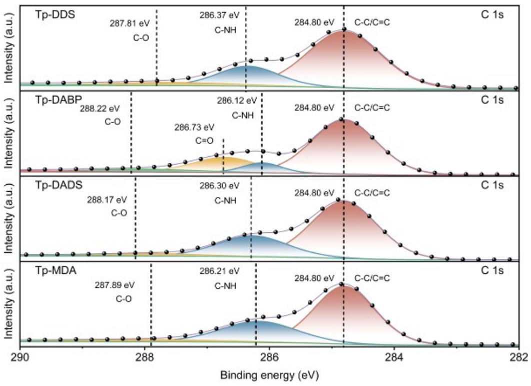

Fig. S2. XPS high-resolution spectra of the COFs. C 1s spectra of Tp-MDA, Tp-DADS, Tp-DABP, and Tp-DDS, respectively.

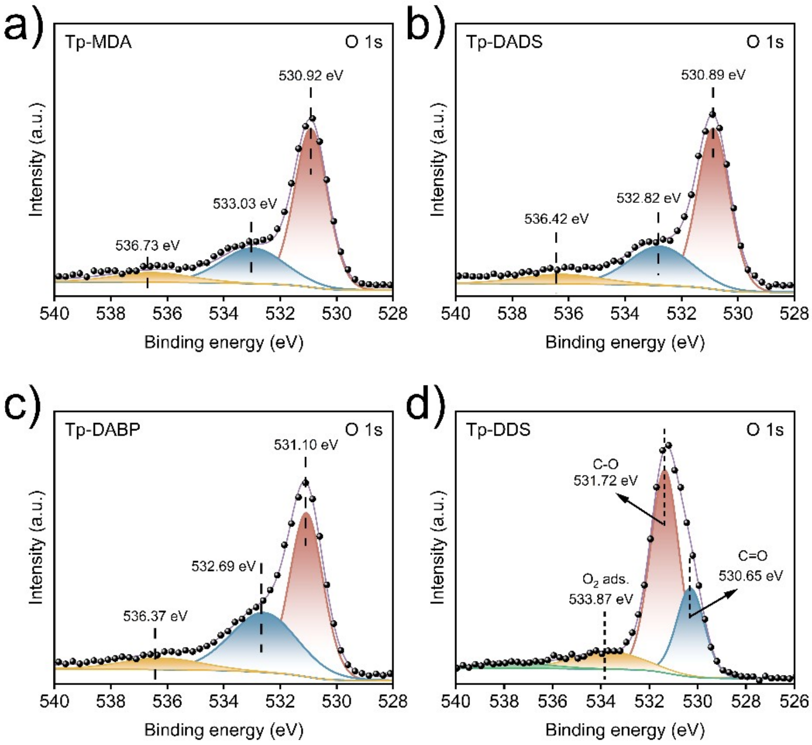

Fig. S3. XPS high-resolution spectra of the COFs. O 1s spectra of Tp-MDA, Tp-DADS, Tp-DABP, and Tp-DDS, respectively.

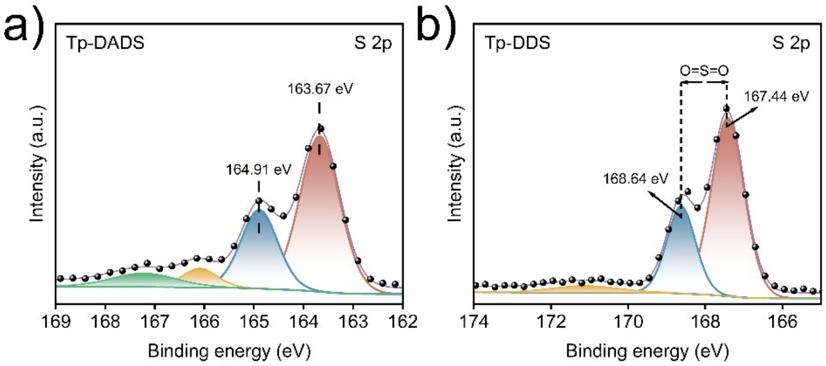

Fig. S4. XPS high-resolution spectra of the COFs. S 2p spectra for the sulfur-containing COFs, The distinct peak at ~167.44 eV in Tp-DDS confirms the presence of the sulfone group (+VI oxidation state), while the doublet at ~163.67 eV in Tp-DADS is characteristic of the thioether sulfur (-II oxidation state).

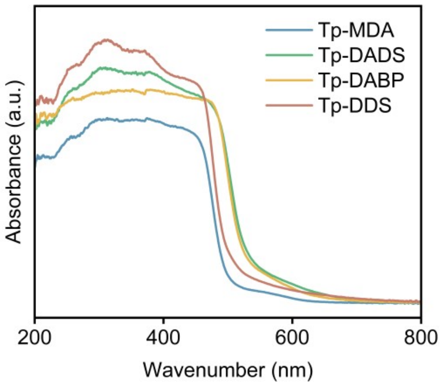

Fig. S5. Solid-state UV-Vis diffuse reflectance spectra of Tp-MDA, Tp-DADS, Tp-DABP, and Tp-DDS, revealing their visible-light absorption capabilities for photocatalytic applications.

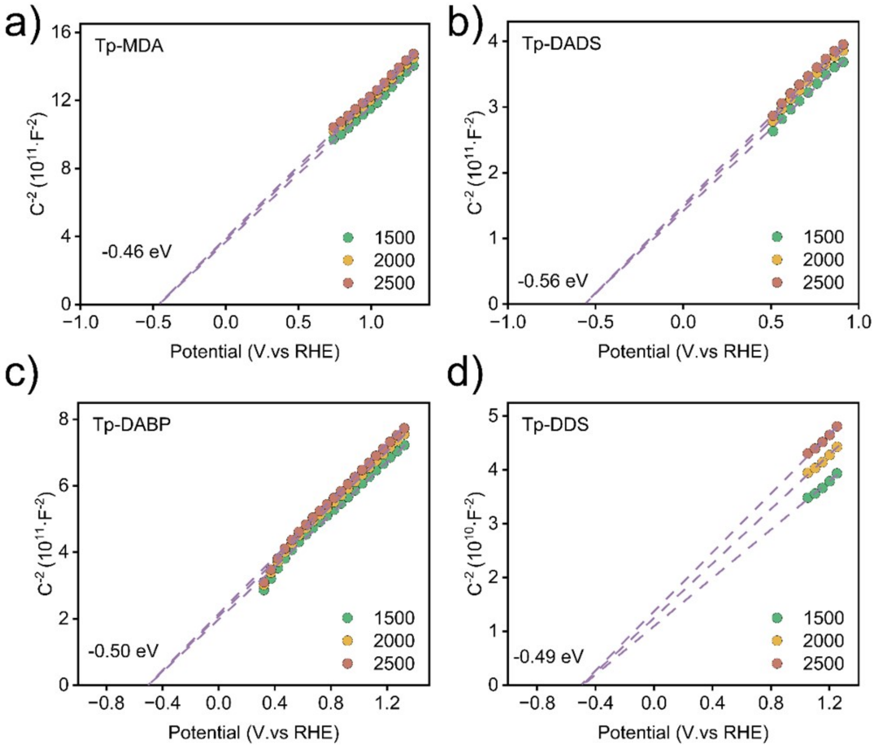

Fig. S6. Determination of lowest unoccupied molecular orbital (LUMO) minimum potentials. (a-d) Mott-Schottky plots for Tp-MDA, Tp-DADS, Tp-DABP, and Tp-DDS, respectively, measured at a frequency of 1500, 2000, 2500 Hz in 0.5 M Na_2SO_4 aqueous solution (pH ~7).

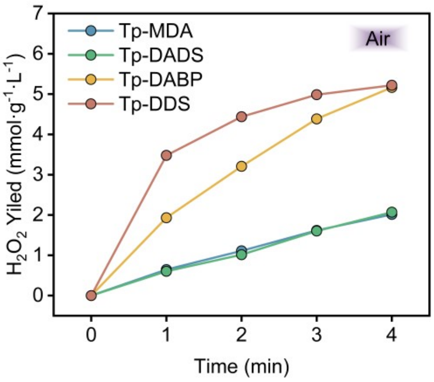

Fig. S7. Photocatalytic stability and H_2O_2 quantification method. Long-term (4 h) photocatalytic H_2O_2 production stability test in air-saturated water under visible light irradiation.

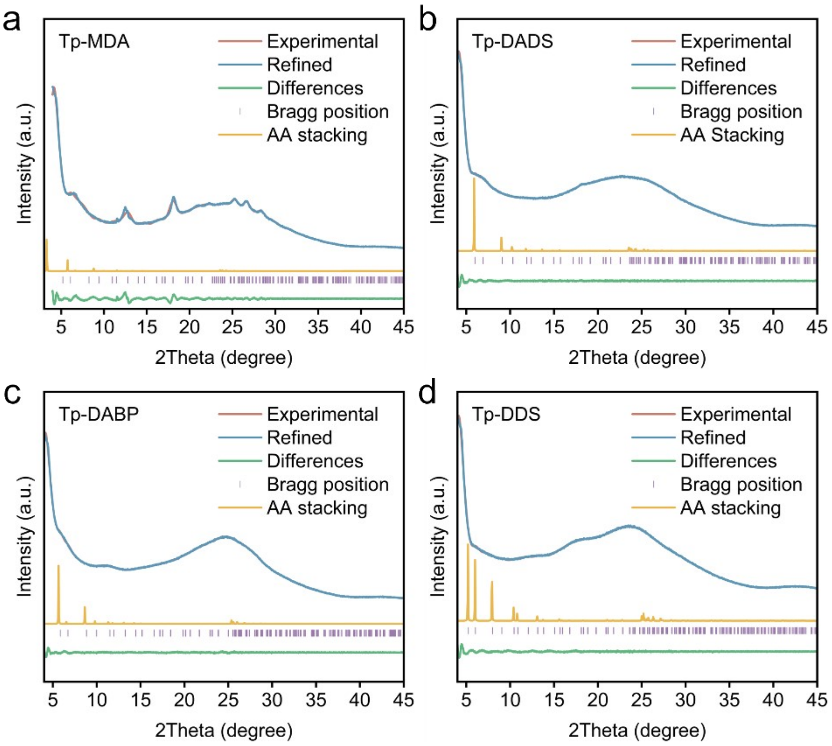

Figure S8. Experimental, simulated, and Pawley-refined XRD patterns of Tp-MDA, Tp-DADS, Tp-DABP, Tp-DDS, including the difference plot.

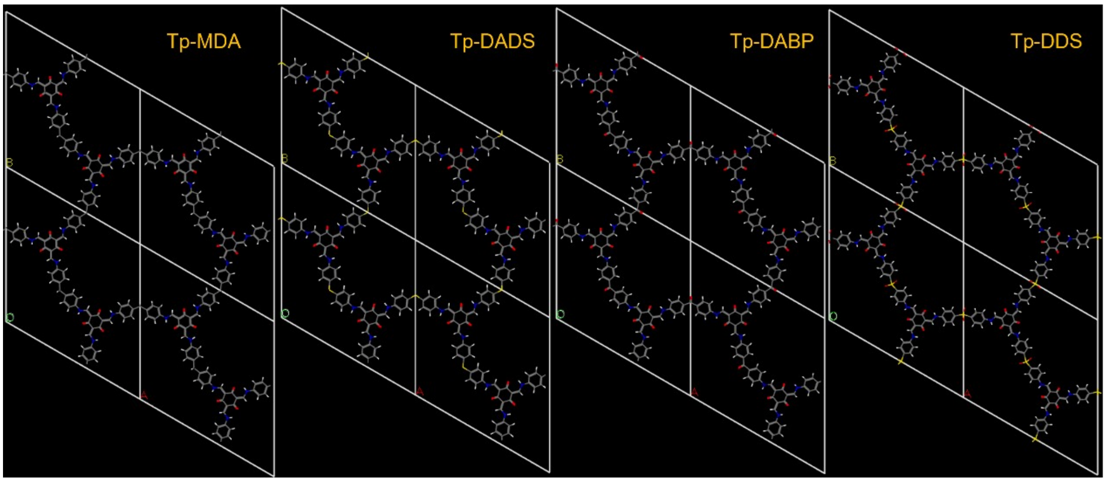

Figure S9. Structural models of the four synthesized COFs, Tp-MDA, Tp-DADS, Tp-DABP, Tp-DDS.