Supporting Information

Molecularly Engineered Covalent Organic Frameworks for Hydrogen Peroxide Photosynthesis

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Supporting Information for

Molecularly engineered covalent organic frameworks for hydrogen peroxide photosynthesis

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Part 1 Experimental Section

Materials. 2,2′-bipyridine-5,5′-diamine (Bpy, >97%) and 1,3,5-triformylphloroglucinol (Tp, >97%) were from Shanghai Tensus Biotech Co., Ltd. N, N-dimethylacetamide (DMAC, 99.8%, Extra Day, with molecular sieves, water ≤50 ppm) was provided by Energy Chemical. o-dichlorobenzene (o-DCB, 99%), acetic acid (AcOH, ≥99.8%) and 2,6-Diaminoanthraquinone (Daaq) were purchased from Aladdin.

Synthesis of COF-TfpBpy. 1,3,5-Triformylphloroglucinol (Tfp) and 2,2′-bipyridine-5,5′-diamine (Bpy) were put into a 10 mL glass ampoule. Then a mixed solvent of N,N-dimethylacetamide (DMAC) and dichlorobenzene (3:1) were also added, and ultrasonically make it uniformly dispersed. Then quickly added 0.6 mL of 6 M acetic acid (AcOH) aqueous solution and sonicate again. After degassing, the reaction was conducted at 120 °C for 3 days. Th e solid was then washed away with a large amount of DMAC, acetone and dichloromethane and dried under vacuum.[1]

Protonation of COF-TfpBpy. 20mg COF-TfpBpy was dispersed in 2 mL 1M HCl, stirred vigorously for 12 h, washed with pure water to neutrality, and freeze-dried for 12 h.

Synthesis of AP-TfpBpy. 1,3,5-Triformylphloroglucinol (Tfp) and 2,2′-bipyridine-5,5′-diamine (Bpy) were put into a 10 mL glass ampoule. Then added dioxane solvent and sonicate to make it evenly dispersed. Then quickly added 0.6 mL of 6 M acetic acid (AcOH) aqueous solution and sonicate again. After degassing, the reaction was conducted at 120 °C for 3 days. The solid was then washed away with a large amount of DMAC, acetone and dichloromethane and dried under vacuum.

Synthesis of COF-TfpDaaq. 1,3,5-Triformylphloroglucinol (Tfp) and 2,6-Diaminoanthraquinone (Daaq) were put into a 10 mL glass ampoule. Then a mixed solvent of N,N-dimethylacetamide (DMAC) and mesitylene (3:1) were also added, and ultrasonically make it uniformly dispersed. Then quickly added 0.05 mL of 6 M aqueous acetic acid (AcOH) and sonicate again. After degassing, the reaction was conducted at 120 °C for 3 days. The catalyst was cleaned several times with 1,4-dioxane, tetrahydrofuran and acetone, and dried under vacuum at 80 °C for 12 h.[2]

Synthesis of COF-TfpBd. 1,3,5-Triformylphloroglucinol (Tfp) and Benzidine (BD) were put into a 10 mL glass ampoule. Then add a mixed solvent of mesitylene and dioxane (1:1), and ultrasonic treatment to make it evenly dispersed. Then quickly add
0.5 mL of 3 M acetic acid (AcOH) in water and sonicate again. After degassing, react at 120°C for 3 days. Then a large amount of acetone was used to wash off the solid and dried under vacuum.\(^3\)

**Synthesis of COF-TfpBpy-Mo.** COF-TfpBpy (20 mg) and Mo(CO)\(_6\) (11 mg) were dispersed in 20 ml toluene solution and reacted at 110 °C for 6 h under the protection of N\(_2\) atmosphere. After cooling to room temperature, it was washed with methanol and water, and vacuum dried at 80 °C for 12 h.

**Synthesis of AP-TfbBpy.** 1,3,5-Triformylbenzene (Tfb) and 2,2'-bipyridine-5,5'-diamine (BPY) were put into a 10 mL glass ampoule. Then added dioxane solvent and sonicate to make it evenly dispersed. Then quickly added 0.6 mL of 6 M acetic acid (AcOH) aqueous solution and sonicate again. After degassing, reacting at 120°C for 3 days. The solid was then washed away with a large amount of DMAC, acetone and dichloromethane and dried under vacuum.

**Synthesis of COF-TfpPa.** 1,3,5-triformylphloroglucinol (Tfp) and p-phenylenediamine (Pa) were put into a 10 mL glass ampoule. Then added a mixed solvent of mesitylene and dioxane (1:1), and ultrasonic treatment to make it evenly dispersed. Then quickly added 0.25 mL of 6 M acetic acid (AcOH) in water and sonicate again. After degassing, reacting at 120 °C for 3 days. Then a large amount of acetone was used to wash off the solid and dried under vacuum.\(^4\)

**Synthesis of linear bipyridine non-porous polymer.** In a single neck round-bottom flask, 16.2 mg (0.15 mmoL) of p-phenylenedialdehyde, 31.8 mg (0.15mmoL) of 2, 2'-bipyridine-5, 5'-diamine (Bpy) was added in 20 ml of anhydrous ethanol. 3ml of glacial acetic acid was subsequently added to the above mixture as the catalyst. Then the mixture was heated to 75 °C and was stirred magnetically. The reaction lasted for 4 h, after which the mixture was cooled down to room temperature. Finally, the insoluble matter is filtered out and washed with a large amount of DMF followed by washing with water, ethanol and acetone. The filtered solid powder was vacuum dried at 70 °C for 12 h.

**Characterization.** The morphologies and microstructures of Catalytic materials were characterized by JEOL JEM-2100F (URH) Field Emission Electron Microscope (TEM) and JSM-7500F Emission Electron Microscope (SEM). XRD patterns were obtained by a Bruker AXS D8 Advance powder diffractometer using Ni filtered Cu K\(\alpha\) radiation (3 °/min). The BEL SORP-MAX volume adsorption analyzer and
analyzer (Novatouch, Quantachrome) were used to carry out N\textsubscript{2} (77K) adsorption-desorption measurement and BET analysis. X-ray photoelectron spectrum (XPS) of samples (AlKa, 150 W, C1s 284.6 eV) were determined by X-ray photoelectron spectrometer (Thermos Scientific ESCALAB 250XI). The UV-Vis absorption spectra were recorded using UH4150 (HITACHI) was used to determine the DRS in the range of 200-800 nm. Time-resolved PL spectra was recorded by a FLS980 multifunction steady state and transient state fluorescence spectrometer. The electrochemical impedance and photocurrent Response of the catalysts were measured on electrochemical workstation (CHI660D, CHI Instruments, Shanghai, China). The Fourier transform infrared (FTIR) spectrum of the samples was acquired from a Nicolet iS-50 instrument at the scan range of 400-4000 cm\textsuperscript{-1}. The solid phase 13C NMR spectra were obtained on an Agilent 600 M solid state NMR spectrometer.

**H\textsubscript{2}O\textsubscript{2} photocatalysis.** 5 mg catalyst and 10 ml water were evenly dispersed in a quartz bottle with a volume of 50 ml and passed into dry air, stirred for 30 min under dark conditions to reach adsorption-desorption equilibrium, and then irradiated with a xenon lamp source (PLS-SXE300D, Beijing Perfectlight). After sampling every 10 minutes, filter with a 0.22 μm filter to detect the content of H\textsubscript{2}O\textsubscript{2} in the solution.

**H\textsubscript{2}O\textsubscript{2} detection methods.** A phosphate buffer was prepared by dissolving 2.8756 g K\textsubscript{2}HPO\textsubscript{4}·3H\textsubscript{2}O and 11.935 g KH\textsubscript{2}PO\textsubscript{4} in 200 ml deionized water. Then prepared N, N-diethyl-1,4-phenylenediamine sulfate (DPD, 97%, Aldrich) and peroxidase (POD, horseradish, Aldrich) stock solutions. (Dissolve 0.1 g DPD in 10 ml 0.05 M H\textsubscript{2}SO\textsubscript{4} solution and 10 mg POD in 10 ml deionized water.) During the experiment, take 2.5ml sample solution into a quartz tube each time, added 0.4 ml phosphate buffer and 50 μL POD solution in sequence. Liter and 50 microliters of DPD solution, mix well. Useing UV-2600 (Shanghai Tianmei Scientific Instrument Co., Ltd.) to measure absorbance at 552 nm. Calibrate the H\textsubscript{2}O\textsubscript{2} concentration by diluting a 30% H\textsubscript{2}O\textsubscript{2} stock solution.\textsuperscript{[5]}

**RhB degradation.** 10 mg Rhodamine B (RhB) and 278 mg FeSO\textsubscript{4} · 7H\textsubscript{2}O were dissolved in a 1 L volumetric flask. Taking out 3.5 ml RhB solution and put it in a 10 ml centrifuge tube, and then 0.5 ml photocatalytic H\textsubscript{2}O\textsubscript{2} solution was gradually added. The color change of RhB was recorded by video.

**Sterilization of \textit{E. coli}.** Escherichia coli (\textit{E. coli}) was cultured in LB broth for 16 h in a shaking incubator. Then, the bacterial liquid was centrifuged (10,000 rpm, 1 min) with 0.85% physiological saline and washed twice. 3 mL Bacterial liquid, 0.5 ml
photocatalytic H$_2$O$_2$ solution and 0.1 mL FeSO$_4$ ·7H$_2$O (0.1 mM) were added a 10 ml centrifuge tube, the concentration of the bacterial in the system was about 10$^5$ cfu/ mL. Took 100 μL bacterial solution every 15 min. The obtained samples were diluted to an appropriate concentration, and then 100 μL of bacterial solution was applied to the agar plate. At least, the agar plates were incubated for 12 h at 37 °C in a biochemical tank.

**Photoelectrochemical measurements:** The Mott–Schottky plots, photocurrent response and electrochemical impedance of the catalysts were measured on an electrochemical workstation (CHI660E, CHI Instruments, Shanghai, China). A 300 W Xe lamp was utilized as the light source and Na$_2$SO$_4$ (0.5 M, pH=6.5) aqueous solution was used as the supporting electrolyte throughout the photocurrent measurements. A platinum wire and Ag/AgCl electrode were used as, counter electrode and reference electrode, respectively. 0.003 g ethyl cellulose was dissolved in about 10 mL ethanol with 0.03 g catalyst. Then, a glass stick was applied to FTO with a layer of high-temperature adhesive tape on the edge, followed by drying in air and activation at 120 °C for 3 h.

\[
E \text{ (VS. RHE)} = E \text{ (VS. Ag/AgCl)} + 0.197 V + 0.0591*pH
\]

**In-situ Fourier transform infrared spectrometer (FT-IR) analysis:** In-situ Fourier transform infrared spectrometry was performed on a Nicolet iS-50 instrument. The sample was filled into an in-situ IR cell, and O$_2$ and H$_2$O vapors were introduced into the cell and fiber source (FX300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) through the CaF$_2$ window of the cell. Before the measurement, the samples were degassed at 423 K for 4 h. The baseline was obtained before the sample reached O$_2$ adsorption equilibrium within 1 h.

**Mass spectrometry method:** The $^{18}$O$_2$ isotope was measured on the mass spectrometer (Shimadzu GCMS-QP2010 Plus). Adding 5 ml of $^{18}$O$_2$, 3 ml of H$_2$O, and 7.5 mg of catalyst COF-TfpBpy to the reactor (5 ml) connected to the mass spectrometer, and the mixture was evenly mixed and irradiated with a 300 w xenon lamp (λ > 420 nm) for 5 h. After injecting N$_2$ to rule out O$_2$ in a new reactor (5 ml) with 2 mL above photocatalytic H$_2$O$_2$ solution, an appropriate amount of MnO$_2$ was adding to generate O$_2$. At end, the O$_2$ was detected by mass spectrometry.

**Computational details:** The calculations were carried out using density functional theory (DFT) implemented via the Vienna Ab-initio Simulation Package (VASP). The
generalized gradient approximation (GGA) functional and Perdew–Burke–Ernzerhof (PBE) functional were used for the electronic exchange and correlation effects. Modifying Gaussian path and smearing width is 0.2 eV.

Geometries were optimized until the energy and the force were converged to 1.0×10^{-5} eV/atom and 0.05 eV/Å, respectively. An energy cutoff was set as 400 eV for the plane-wave expansion of the electronic wave function. A vacuum region of 15 Å was introduced to avoid the interactions between the periodic slabs. Besides, k-point grid is set to 3 * 2 * 1.

The adsorption energy \( E_{\text{ads}} \) of \( \text{O}_2 \) or \( \text{H}_2\text{O} \) molecule on the surface is calculated as follow:

\[
E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{O}_2} \ (E_{\text{H}_2\text{O}})
\]

where \( E_{\text{total}} \) represents the energy of surface with adsorbed \( \text{O}_2 \) or \( \text{H}_2\text{O} \) molecule, \( E_{\text{surface}} \) and \( E_{\text{O}_2} \) or \( E_{\text{H}_2\text{O}} \) represent the energies of isolated surface and \( \text{O}_2 \) or \( \text{H}_2\text{O} \), respectively.
Part 2 Characterizations of COF-TfpBpy and AP-TfpBpy

Figure S1 The XRD (a), IR (b) and solid state $^{13}$C NMR (c, d) spectra of COF-TfpBpy and AP-TfpBpy.

Figure S2 The XPS spectrum of COF-TfpBpy and AP-TfpBpy. Survey scan XPS profile (a), C 1s (b), N 1s (c) and O 1s (d) XPS spectrum of COF-TfpBpy and AP-TfpBpy.
Figure S3 SEM and TEM images of AP-TfpBpy (a,c) and (b,d).COF-TfpBpy.

Figure S4 Adsorption and desorption curve (a) and porosity data (b) of COF-TfpBpy and AP-TfpBpy.

Note S1:
The powder X-ray diffraction (PXRD) pattern of COF-TfpBby (red line) shows that a strong peak corresponding to the (100) plane reflection is displayed at 2θ=3.68°,
indicating that there is an open channel. The broad peak at 2θ=26° is mainly due to the π-π accumulation between the COF layers corresponding to the (002) plane. The relatively broad peaks can be attributed to strain defects and grain size effects in the crystal lattice. However, AP-TfpBpy (green line) has no obvious diffraction peak at 2θ=3.68°, indicating that its structure has no crystal form (Figure S1a). Based on the experimental and simulated XRD pattern, COF-TfpBpy should be a COF materials with AA stacking mode rather than conjugated porous polymer.

According to FT-IR (Figure S1b), strong peaks corresponding to the stretching frequency of the ketone form are observed at 1608 cm⁻¹ (C=O) and 1579 cm⁻¹ (C=C) (Figure S1b). It is the same as the COF-TfpBpy reported in the previous literature. AP-TfpBpy also has two corresponding strong peaks at 1607 cm⁻¹ and 1579 cm⁻¹, indicating that C=O and C=C also exist, and the other parts may be different in infrared due to crystallinity.

As shown in Figure S1c, the ¹³C CP-MAS solid state NMR of COF-TfpBpy shows carbonyl (C=O), imine bond (C=N) and carbon at δ182.8, 148.9 ppm and 106.0 ppm respectively. Carbon double bond (C=C) carbon signal. The ¹³C CP-MAS solid-state NMR of AP-TfpBpy also has a corresponding peak at the same position. The solution ¹³C NMR (Figure S1c, d) spectra of the two structures are not significantly different, indicating that they belong to the same substance in structure.

The N1 s deconvolution of COF-TfpBpy and AP-TfpBpy showed two peaks at 398.35 eV and 399.59 eV, corresponding to the N atoms of pyridine N and secondary N (Figure S2c); their C1 s deconvolution are 285.6 and 284.3 eV, corresponding to the hydroxyl and carbonyl groups on the benzene ring, respectively (Figure S2b). Their O1 deconvolutions are 532.1 and 530.5 eV, respectively, corresponding to C-OH and C=O on the benzene ring, which may be caused by the existence of tautomerism(Figure S2d).

The SEM and TEM images (Figure S3) show that the crystals of COF-TfpBpy and AP-TfpBpy are both interlaced linear morphology, and there are a large number of individual crystallites aggregated; and they seem to be only a few layers thick. However, it can be seen from the SEM image that COF-TfpBpy has a tendency to form a spherical structure, but AP-TfpBpy does not.

The adsorption and desorption curves and BET of COF-TfpBby and AP-TfpBpy under N₂ are shown in Figure S4. It is known that the specific surface areas of COF-TfpBby and AP-TfpBpy are 939.44 m² g⁻¹ and 865.45 m² g⁻¹, respectively.
AP-TfpBpy's Brunauer-Emmett-Teller (BET) is significantly reduced, indicating that the crystallinity of COFs directly affects the size of its active contact surface. The pore size distribution graph of COF-TfpBpy and AP-TfpBpy prepared by solvothermal method has a peak at 1.89 nm, indicating that the material is a mesoporous material.
Part 3 Characterizations of g-C3N4

Figure S5 Structural characterization of g-C3N4. (a) XRD pattern of g-C3N4; (b) IR spectra of g-C3N4; (c and d) adsorption and desorption curve and porosity data of g-C3N4.

Figure S6 The XPS spectrum of g-C3N4. Survey scan XPS profile (a), N 1s (b), and C 1s (c) XPS spectrum of g-C3N4.
Figure S7 SEM (a) and TEM (b) images of g-C₃N₄.

Note S2:

Figure S5a shows that the XRD spectrum of g-C₃N₄ has two peaks at 12.7° and 28°, which are consistent with the typical graphite phase carbon nitride diffraction peaks, corresponding to the (100) peak of the in-plane repeating unit and stacked between the aromatic ring layer (002) peak, which means that g-C₃N₄ is obtained.

The FTIR spectrum of g-C₃N₄ is shown in Figure S5b. The characteristic peak at 2900-3400 cm⁻¹ corresponds to the stretching vibration absorption peak of -NH₂ or -OH, the peak in the range of 1200-1650 cm⁻¹ corresponds to the stretching vibration of the CN heterocyclic ring, and the peak at 810 cm⁻¹ is the characteristic peak of the triazine ring structure.⁷

The g-C₃N₄ prepared by thermal polymerization has a small specific surface area, low catalytic efficiency, and lack of active sites. As shown in Figure S5, the Brunauer-Emmett-Teller (BET) specific surface area of traditional synthetic g-C₃N₄ is 10.17 m² g⁻¹.

XPS spectroscopy confirms that there are only three elements of C, O and N in the material, and there are three different bonding environments for C and four different bonding environments for N, which further confirms the successful preparation of g-C₃N₄ (Figure S6a).
The N 1s spectrum of g-C$_3$N$_4$ (Figure S6b) can be divided into 4 characteristic peaks. The binding energies are 398.5 eV, 400.0 eV, 401.3 eV and 404.3 eV, which correspond to the sp$^2$ hybrid N in triazine (N-C=N), Tertiary N in (N-(C)$_3$), N in C-NH$_2$ structure, and charge effects, respectively.

The C 1s spectrum of g-C$_3$N$_4$ (Figure S6c) can be divided into 3 characteristic peaks. The characteristic peaks with binding energies of 284.6 eV and 288.1 eV are attributed to sp$^2$ C=C bond and sp$^2$ bonded carbon (N-C=N), respectively; The weak peak at 293.4 eV may be due to the O-C=O bond or C=O bond generated by g-C$_3$N$_4$ heating in air.$^{[8]}$

As shown in Figure S7, it can be seen from the scanning electron microscope (SEM) that g-C$_3$N$_4$ is a large layered structure, and the transmission electron microscope (TEM) image shows that its thickness is relatively thin.
Part 4 Standard curve of H$_2$O$_2$

![Absorption spectra of H$_2$O$_2$](image)

**Figure S8** (a) The absorption spectra of H$_2$O$_2$ at different concentrations (0 µM, 2.5 µM, 5 µM, 10 µM, 15 µM, 25 µM, 50 µM) at wavelengths of 400-700 nm; (b) and a standard curve of H$_2$O$_2$ concentration-absorbance was drawn.

![Standard curve of H$_2$O$_2$](image)

**Figure S9** The effect of different electron sacrificial reagents on DPD-POD method to measure H$_2$O$_2$ concentration.

**Note S3:**

30% H$_2$O$_2$ standard solution is used to prepare H$_2$O$_2$ solutions of different concentrations. The absorbance is measured under an ultraviolet-visible
spectrophotometer (Figure S8).

Bader proposed the DPD (N,N-diethylphenylenediamine)/POD (horseradish peroxidase) method to measure low-concentration hydrogen peroxide in water in 1988. The experimental method is: adjust the pH of the sample, and then add DPD and POD solutions. If there is hydrogen peroxide in the water, the hydrogen peroxide will oxidize POD, and the oxidation product of POD will then oxidize DPD into positive ion radical DPD $^\cdot{\ddot{\cdot}}$. DPD $^\cdot{\ddot{\cdot}}$ is a pink compound, it has two absorption peaks, 510 mm and 551 mm. Because this method can only detect low-concentration hydrogen peroxide in water, and our photocatalytic production of hydrogen peroxide has a higher concentration, it must be diluted before testing.$^{[9]}

In order to detect the influence of different electronic sacrificial reagents on the detection method, as shown in Figure S9, we set it under dark conditions, use the same concentration of hydrogen peroxide, and add the same concentration of electronic sacrificial reagents (KBrO$_3$, NaIO$_3$, AgNO$_3$) to Judge their influence on the concentration of H$_2$O$_2$ measured by the DPD-POD method. It can be clearly seen from the figure that KBrO$_3$ has the least impact on the detection method, while AgNO$_3$ has the opposite effect. In summary, we chose KBrO$_3$ as the electronic sacrificial reagent.
Part 5 Catalytic activity and stability

Figure S10 (a) Five cycles of COF-TfpBpy after 8 h irradiation for photocatalytic H$_2$O$_2$ production. (b and c) long time photocatalytic synthesis of H$_2$O$_2$. (d) XRD of COF-TfpBpy before and after photocatalytic reaction. (e) IR spectra of COF-TfpBpy before and after photocatalytic reaction. Conditions: $\lambda > 420$ nm; at 298 K under one sun light illumination (100 mW cm$^{-2}$); 400 mL H$_2$O; 600 mg COF-TfpBpy.
Part 6 AYQ and SCC

The photocatalytic reaction was carried out in pure deionized water (400 ml) with photocatalyst (600 mg) in a foil reflective light-concentrating reactor. After ultrasonication and Air bubbling, the bottle was irradiated by an Xe lamp (light intensity at 420-700 nm: 40.8 mW cm\(^{-2}\)). The optical power was determined by a PL-MW 2000 photoradiometer (Beijing Perfect Light Technology Co., Ltd., Beijing, China).

For Calculation of the apparent quantum yield (AQY), the incident light was monochromated by band-pass glass filters.

For solar-to-chemical conversion (SCC), a UV cut filter (\(\lambda > 420\) nm) was used to avoid decomposition of the formed H\(_2\)O\(_2\) by absorbing UV light.

Calculation of the apparent quantum yield (AQY):

\[
AQY = \frac{N_{H,O_2}}{N_P} = \frac{2 \times \text{the number of evolved } H_2O_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%
\]

\[
= \frac{2N_e \times M_{H,O_2}}{PS \lambda \frac{hc}{PSS}} = \frac{2 \times 6.02 \times 10^{23} \times M_{H,O_2}}{PS \times 40 \times 60 \times 420 \times 10^{-9}} \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{PSS}
\]

SCC efficiency (%): \[
\text{SCC efficiency} = \left( \frac{\Delta G \text{ for } H_2O_2 \text{ generation (J mol}^{-1}\text{))} \left( H_2O_2 \text{ formed (mol)} \right) \right) \frac{\text{[total input power (W)] [reaction time (s)]}}{100%}
\]

where \(\Delta G = 117 \text{ kJ mol}^{-1}\). For example, when using COF-TpBpy as the catalyst, the irradiated sample areas are 16 cm\(^2\) during 60 min of on sun illumination. Therefore, the calculated total input energy is 5760 J. During the 60 min photocatalytic reaction, \(x \mu\text{mol H}_2\text{O}_2\) is generated and the energy generated by H\(_2\)O\(_2\) formed is 0.117x J.

SCC Efficiency=0.117x/5760
**Table S1.** Comparison of H$_2$O$_2$ production of polymer photocatalytic material under one sun light when non-sacrificial/stabilizer-free. Light intensity: AM 1.5 100 mW cm$^{-2}$

| Photocatalysts | Light source | H$_2$O$_2$ (μM h$^{-1}$) | AQY (%)@420 nm | SCC (%) | Temperature (K) | Refs. |
|----------------|--------------|--------------------------|----------------|---------|-----------------|-------|
| g-$\text{C}_3\text{N}_4$/PDI | λ>420 nm | ~190 | 2.5 | ~0.1 | 298 | 10 |
| g-$\text{C}_3\text{N}_4$/BDI | λ>420 nm | ~250 | 4.6% | 0.13 | 298 | 11 |
| g-$\text{C}_3\text{N}_4$/PDI/rGO | λ>420 nm | ~380 | 6.1 | 0.2 | 298 | 12 |
| g-$\text{C}_3\text{N}_4$/MTI | λ>420 nm | ~330 | 6.1 | 0.18 | 298 | 13 |
| g-$\text{C}_3\text{N}_4$/PDI-BN-rGO | λ>420 nm | 530 | 7.3 | 0.28 | 298 | 14 |
| CTF | λ>420 nm | 58.4 | 0.14 | 298 | 15 |
| RF resins$^a$ | λ>420 nm | ~1080 | 7.5$^d$ | 0.5 | 333 | 16 |
| RF resins$^b$ | λ>420 nm | ~1350 | 8.4 | ~0.75 | 333 | 17 |
| RF resins$^c$ | λ>300 nm | ~1480 | 1.07 | 323 | 18 |
| RF/P3HT | λ>300 nm | ~1840 | 10 | 1.0 | 333 | 19 |
| COF-TfpBpy | λ>300 nm | 1042 | 8.1 | 0.57 | 298 | This work |
| COF-TfpBpy | λ>300 nm | 1970 | 13.5 | 1.08 | 333 |  |

$^a$ Prepared by Stöber method  
$^b$ Prepared by acid-catalysed polycondensation  
$^c$ Mesoporous resorcinol-formaldehyde spheres (MRFS)  
$^d$ @450 nm
Part 7 Band structure of g-C₃N₄, COF-TfpBpy and AP-TfpBpy

Figure S11 Kubelka-Munk-transformed reflectance spectra of COF-TfpBpy, AP-TfpBpy (a) and g-C₃N₄ (b).

Figure S12 Mott-Schottky plots of COF-TfpBpy (a), AP-TfpBpy (b) and g-C₃N₄ (c) of film electrodes at frequency of 500 Hz, 1000 Hz, and 2000 Hz in an aqueous solution of Na₂SO₄ (0.1 M; pH 6.6).
Figure S13 Schematic band structure diagram of COF-TfpBpy, AP-TfpBpy and g-C₃N₄.

Note S4:

Kubelka-Munk equation: \( F(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \)

K- Absorption coefficient, S- Scattering coefficient

R- The limit value of the reflection coefficient \( R_\infty \) of an infinitely thick sample

F(\( R_\infty \))- Reduction function or Kubelka-Munk function

The actual measured \( R_\infty ' \) is not the absolute reflectance \( R_\infty \), that is, the relative reflectance relative to a standard sample.

The optical bandgaps estimated from the corresponding Kubelka–Munk-transformed reflectance spectra are 2.37 eV, 2.32 eV, and 2.86 eV for COF-TfpBpy, AP-TfpBpy and g-C₃N₄, respectively (Figure S11). Mott-Schottky plots showed the CB values of COF-TfpBpy, AP-TfpBpy and g-C₃N₄ are 0.21, 0.23 and -0.67 V (Figure S12). According to the energy band structure diagram, the VB values of COF-TfpBpy, AP-TfpBpy and g-C₃N₄ are 2.58, 2.55 and 2.20 V (Figure S13). The band structure of COF-TfpBpy and AP-TfpBpy is sufficient for the synthesis of H₂O₂ from H₂O (\( E_{H₂O₂/H₂O} = +1.78 \text{ V vs NHE} \)) and O₂ (\( E_{O₂/H₂O₂} = +0.68 \text{ V vs NHE} \))
Part 8 Wettability of the COF-TfpBpy

Figure S14 Contact angle of COF-TfpBpy and g-C₃N₄.
Part 9 Characterizations of COF-TfpDaaq

**Figure S15** The XRD (a), IR (b) and Solution $^{13}$C NMR (c, d) spectra of COF-TfpDaaq.

**Figure S16** The XPS spectrum of COF-TfpDaaq. Survey scan XPS profile (a), C 1s (b), N 1s (c) and O 1s (d) XPS spectrum of COF-TfpDaaq.
Figure S17 SEM (a) and TEM (b) images of COF-TfpDaaq.

Figure S18 Adsorption and desorption curve (a) of porosity data (b) of COF-TfpDaaq.
Figure S19 UV-vis DRS spectra (a), Kubelka-Munk-transformed reflectance spectra (b), Mott-Schottky plots (c) and schematic band structure diagram (d) of COF-TfpDaaq.

Note S5:

COF-TfpDaaq shows a strong diffraction peak of 3.5° and a broad peak of 27°, corresponding to the (100), and (001) reflection surfaces of the structure, respectively (Figure S15a). Fourier transform infrared (Figure S15b) and $^{13}$C crosspolarization magic angle spinning (CP-MAS) solid-state NMR spectroscopy (Figure S15c, d) further confirms COF-TfpDaaq structures. The appearance of a new C-N stretching vibration peak at 1250 cm$^{-1}$ is characteristic of β-ketoenamine C-N bond in COF-TfpDaaq.$^{[20]}$ The preferential formation of the keto form rather than the enol tautomer is further confirmed by the C=O stretching vibration at 1615 cm$^{-1}$ and the absence of O-H bond resonance in its FT-IR spectrum. As the spectra of COF-TfpDaaq exhibit resonances at 145 ppm that are assigned to the enamine carbon (=CNH) and α-enamine carbon at 115 ppm. In addition, the resonance at ~180 ppm corresponds to the ketone resonance. XPS spectra show the presence of C, N, and O in COF-TfpDaaq (Figure S16). High-resolution X-ray photoelectron spectroscopy also differentiates between C, N and O atoms in the different bonding environments.$^{[21]}$ The morphology of as-prepared catalysts was characterized by Scanning Electron Microscope (SEM) and Transmission electron microscopy (TEM)
(Figure S17). According to SEM, it can be seen that COF-TfpDaaq is an interconnected porous network structure, and it also shows a structure similar to folds or wrinkles.

According to the COF-TfpBby N₂ adsorption and desorption curve and BET (Figure S18), it is known that its specific surface area is 653.39 m² g⁻¹. and the pore size distribution of COF-DAAQ has a peak at 2.14 nm, indicating that the material is a mesoporous material.

In addition, the energy band structure of COF-TfpDaaq and the positions of CB and VB are calculated by DRS spectra, Kubelka-Munk converted reflectance spectra and Mott-Schottky diagrams. It is found that the values of VB, CB and optical band gap correspond to 2.34, 0.32, 2.02 V (Figure S19).
**Part 10 Characterizations of COF-TfpBd**

**Figure S20** The XRD (a) and IR (b) spectra of COF-TfpBd.

**Figure S21** Adsorption and desorption curve (a) and porosity data (b) of COF-TfpBd.
Figure S22 UV-vis DRS spectra (a), Kubelka-Munk-transformed reflectance spectra (b), Mott-Schottky plots (c) and schematic band structure diagram (d) of COF-TfpBd.

**Note S6:**

COF-TfpBD shows a strong diffraction peak of 3.4°, corresponding to the (100), reflection surfaces of the structure (**Figure S20a**). The FT-IR spectrum of COF-TfpBD (**Figure S20b**) shows a typical broad and strong band, which corresponds to the characteristic C=C stretch of aromatic hydrocarbons in the 1596 cm\(^{-1}\) region and the CN stretch of amines close to 1257 cm\(^{-1}\). There is also a weak band close to 1618 cm\(^{-1}\), which corresponds to the C=O bond of the ketone form in the tautomeric keto-enamine form.\(^{[22]}\)

\(\text{N}_2\) adsorption isotherm at 77 K to check the structural stiffness and permanent porosity of COF-TfpBD (**Figure S21**). The BET surface area of COF-TfpBD is 596.6 m\(^2\) g\(^{-1}\). The pore size distribution of COF-TfpBD was found to be between 2.15 nm.

In addition, the energy band structure of COF-TfpDaq and the positions of CB and VB are calculated by DRS spectra, Kubelka-Munk converted reflectance spectra and Mott-Schottky diagrams. It is found that the values of VB, CB and optical band gap correspond to 2.13, -0.07, 2.20 V (**Figure S22**).
Part 11 Characterizations of COF-TfpPa

Figure S23 The XRD (a) and IR (b) spectra of COF-TfpPa.

Figure S24 Adsorption and desorption curve (a) and porosity data (b) of COF-TfpPa.
Figure S25 UV-vis DRS spectra (a), Kubelka-Munk-transformed reflectance spectra (b), Mott-Schottky plots (c) and schematic band structure diagram (d) of COF-TfpPa.

Note S7:

The powder X-ray diffraction (PXRD) pattern of COF-TfpPa shows a strong peak at 4.5°, corresponding to the reflection from the (100) plane (Figure S23a). There are also small peaks at 2θ=8.3°, 11.9° and 26.8° of COF-TfpPa, which are attributed to the (200), (210) and (001) reflection planes.\textsuperscript{[23]}

Interestingly, the FT-IR spectrum does not show the characteristic stretch bands of hydroxyl (-OH) or imine (C=N) functional groups (Figure S23b). If the compound exists in the form of enol, it should be there. On the contrary, they present a strong peak under the peak at 1578 cm\(^{-1}\) in the ketone form, indicating that it exists in the ketone form. However, because of the peak broadening in the extended structure, the C=O peaks of COF-TfpPa at 1616 cm\(^{-1}\) are merged with the C-C stretching band at 1578 cm\(^{-1}\) and appeared as a shoulder. And the BET surface area of COF-TfpPa is 614.74 m\(^2\) g\(^{-1}\). The pore size distribution of COF-TfpBD was found to be between 2.14 nm (Figure S24).

In addition, the energy band structure of COF-TfpPa and the positions of CB and VB are calculated by DRS spectra, Kubelka-Munk converted reflectance spectra and Mott-Schottky diagrams. It is found that the values of VB, CB and optical band gap correspond to 2.63, 0.20, 2.43 V (Figure S25).
Part 12 Characterizations of COF-TfpBpy-Mo

Figure S26 The XRD (a), and IR (b) spectra of COF- TfpBpy-Mo.

Figure S27 TEM (a) and HAAD-STEM (b) images of COF- TfpBpy-Mo.
**Figure S28** UV-vis DRS spectra (a), Kubelka-Munk-transformed reflectance spectra (b), Mott-Schottky plots (c) and schematic band structure diagram (d) of COF-TfpBpy-Mo.

**Figure S29** H₂O₂ degradation study by COF-TfpBpy-Mo. Conditions: λ > 420 nm (298K; xenon lamp, light intensity at 420-700 nm: 40.8 mW cm⁻²), water (10 ml), catalyst (15 mg), Ar atmosphere.

**Note S8:**

According to the XRD patterns of COF-TfpBpy and COF-TfpBpy-Mo (Figure S1a and Figure S26a), it can be seen that there are no extra peaks, indicating that the
solid COF frame structure is still retained after the cobalt modification.

The FTIR spectrum shows that strong peaks corresponding to the stretching frequency of the ketone form are observed at 1608 cm⁻¹ (C=O) and 1579 cm⁻¹ (C=C) (Figure S26b). COF-TfpBpy-Mo still has the same characteristic functional groups as COF-TfpBpy, but some red shifts and obvious broadening of the C-N peak have occurred, which means that Mo and the bipyridine N atom are coordinated in the COF skeleton.

According to the transmission electron microscope (TEM) image (Figure S27a), COF-TfpBpy-Mo appears to be only a few layers thick. In the HAAD-STEM image (Figure S27b), it can be observed that Mo metal particles are present on the original COF-TfpBpy. TEM images showed that the morphology of COF was intact after loading Mo.

In addition, the energy band structure of COF-TfpBpy-Mo and the positions of CB and VB are calculated by DRS spectra, Kubelka-Munk converted reflectance spectra and Mott-Schottky diagrams. It is found that the values of VB, CB and optical band gap correspond to 2.13, 0.18, 1.95 V (Figure S28).
Part 13 Characterizations of AP-TfbBpy

Figure S30 The XRD (a), and IR (b) spectra of AP-TfbBpy.

Figure S31 UV-vis DRS spectra (a) Kubelka-Munk-transformed reflectance spectra (b) Mott-Schottky plots (c) and schematic band structure diagram (d) of AP-TfbBpy.
Note S9:

The XRD pattern of AP-TfbBpy has a main diffraction peak at 2θ=24.5°, corresponding to the (001) plane; AP-TfbBpy has no obvious diffraction peak at 2θ=3.7°, indicating that its structure has no crystal form (Figure S30a).

The FT-IR spectrum of AP-TpbBpy shows a strong C=N stretch at 1618 cm\(^{-1}\) (Figure S30b), indicating the formation of an imine bond. The characteristic peak at 1271 cm\(^{-1}\) is attributed to the strong stretching of C-N. The new peak formed at 1584 cm\(^{-1}\) is designated as the C=C stretch, but the peak of AP-TfbBpy at this point is weakened to be negligible, indicating that TfbBpy does not exist in the ketone form.

In addition, the energy band structure of COF-TfbBpy and the positions of CB and VB are calculated by DRS spectra, Kubelka-Munk converted reflectance spectra and Mott-Schottky diagrams. It is found that the values of VB, CB and optical band gap correspond to 2.18, 0.13, 2.05 V (Figure S31).
Part 14 The influence of specific surface area and porosity

**Figure S32** The amount of H$_2$O$_2$ generated per unit surface area of COF-TfpBpy, AP-TfpBpy, COF-TfpBd, COF-TfpPa and COF-TfpDaq.

**Figure S33** Linear bipyridine non-porous polymer: (a) structure and IR spectra, (b) BET, (c) porosity data, (d) photocatalytic activity for H$_2$O$_2$ production in pure water.
Part 15 Average electron transfer number of ORR

Figure S34 Linear-sweep RDE voltammograms of (a) COF-TfpBpy and (b) COF-TfpDaaq measured at different rotating speeds.
Part 16 ESR and Capture experiment of active species

Figure S35 Under dark and visible light, the DMPO spin trapping EPR spectra of COF-TfpBpy and COF-TfpDaaq measured ·OH (a) and ·OOH (b).

Figure S36 The influence of benzoquinone (BQ, ·O₂⁻ scavenger) and tert Butanol (·OH scavenger) for the H₂O₂ generation on bipyridine based COF-TfpBpy, AP-TfbBpy and AP-TfpBpy, and non-bipyridine based COF-TfpDaaq, COF-TfpBd and COF-TfpPa.
Part 17 In-situ Fourier transform infrared (in situ IR)

**Figure S37** C=N functional group change graph over time.

**Figure S38** In-situ FT-IR spectrum of (a) COF-TfpBpy (b) COF-TfpDaaq for photosynthetic H$_2$O$_2$ production at 3500-4000 cm$^{-1}$. 

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Part 18 The importance of protonation for \( \text{H}_2\text{O}_2 \) Photosynthesis.

Figure S39 (a) The absorption spectra of \( \text{H}_2\text{O}_2 \) photosynthesis in nonaqueous solvents; (b) protonation of COF-TfpBpy for \( \text{H}_2\text{O}_2 \) photosynthesis. Conditions: \( \lambda > 420 \) nm (298K; xenon lamp, light intensity at 420-700 nm: 40.8 mW cm\(^{-2}\)), water (10 ml), catalyst (15 mg).
Part 19 Theoretical calculation

**Figure S40** Adsorption energies of H\textsubscript{2}O and O\textsubscript{2} on different N sites of COF-TfpBpy. (a) one H\textsubscript{2}O molecular on imine nitrogen atom, (b) O\textsubscript{2} molecular on bipyridine on C=NH\textsuperscript{+} via O\textsuperscript{2}\textsuperscript{-} intermediate species, (c) one H\textsubscript{2}O molecular on bipyridine nitrogen atoms, (d) O\textsubscript{2} molecular on bipyridine via O\textsuperscript{2}\textsuperscript{-} intermediate species, (e) two H\textsubscript{2}O molecular on bipyridine nitrogen atoms, (f) O\textsubscript{2} molecular on bipyridine via endoperoxide intermediate specie.
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