

Supplementary Information

Influence of Structural Isomerism in Multicomponent Covalent Organic Frameworks on Their Photocatalytic H₂O₂ Production

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Materials

Tris(4-formylphenyl)amine (TFPA), 1,3,5-Tris(4-aminophenyl)triazine (TAPT), Tris(4-aminophenyl)amine (TFPT), 1,3,5-Tris(4-formylphenyl)triazine (>98%) (TAPA), were purchased from bide pharm. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (>98%), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (>98%), purchased from Aladdin of Shanghai. n-BuOH (n-Butanol) (>98%), purchased from Energy Chemical. Acetic acid (>99.8%), Methanol (MeOH), Isopropanol (IPA), Ethanol (EtOH), 5,5-dimethylpyrroline N-oxide (DMPO), Tetrahydrofuran, o-DCB (1,2-Dichlorobenzene, 99%), styrene were purchased from JK chemical of Beijing. All the reagents and solvents used for the synthesis were commercially available and used without further purification.

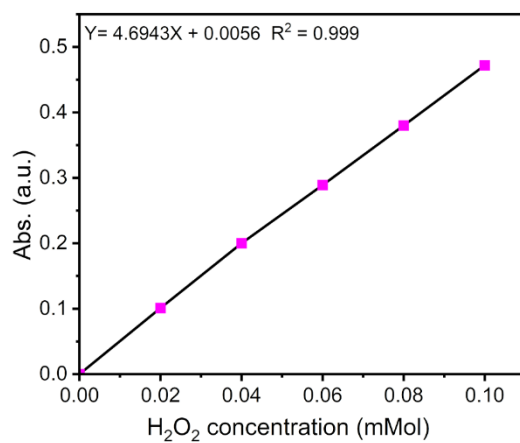
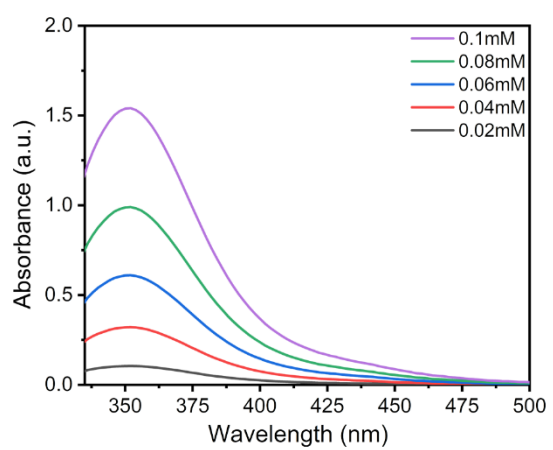
Characterization

The synthesized COFs were characterized using a range of techniques: Powder X-ray diffraction (PXRD) pattern of samples was recorded on an X-ray diffractometer with Cu-K α radiation, $\lambda=1.5406$ Å (XRD, SmartLab, Rigaku, Japan). The morphologies of as-synthesized samples were observed by transmission electron microscopy (TEM) under an accelerated voltage of 200 kV (FEI Tecnai F20, American). Scanning electron microscopy (SEM) images were captured using field emission scanning electron microscopy (Hitachi S4800). Nitrogen sorption measurements were carried out on a Quantachrome Quadrasorb SI instrument. All samples were degassed at 120 °C for 12 h before the actual measurement. The surface area was calculated by using Brunauer-Emmett-Teller (BET) calculations and pore size distributions were calculated using the nonlocal density functional theory (NLDFT) method on the N₂ adsorption branch. Fourier transform infrared spectroscopy (FTIR) spectra were collected on an ALPHA II spectrometer (Bruker Ltd., Germany). Ultraviolet-Visible Spectroscopy (UV-Vis-DRS) was performed by ultraviolet spectrophotometer (UH5700). The free radicals of O₂^{•-}/OOH were recorded on Electron paramagnetic resonance (EPR, Bruker JES-FA300) using 60.0 mM of DMPO as the spin-trapper agent. Solid EPR measurements in X-band (Microwave power: 1 microwatt-100 milliwatts) were performed at 293 K by a Freiberg Instruments Germany MS5000 micro. ¹³C NMR experiments were performed on Bruker Avance III 400 WB spectrometer. The temperature-dependent photoluminescence (PL) spectra were recorded using a FLS1000 spectrometer in the solid state. The measurements were

conducted at different temperatures 75 K, 100 K, 125 K, 150 K, 175 K, 200 K, 225 K and 250 K. The Photoluminescence spectra (PL) of the sample was obtained at room temperature through fluorescence spectroscopy (FSL980, Edinburgh, UK). X-ray photoelectron spectroscopy (XPS) and valence band X-ray photoelectron spectroscopy (VB-XPS) were conducted on a ESCALAB QXi XPS (Thermo Scientific). Ultraviolet photoelectron spectroscopy (UPS) measurements were performed on Thermo ESCALAB XI+ instrument. A -5.0 V bias was applied to the samples to get the secondary-electron cutoff, which accelerated all the photoelectrons with higher kinetic energy to overcome the work function of the analyzer. The work function (Φ) is calculated as the energetic difference between the Fermi level and the vacuum level, as defined by the secondary-electron edge of UPS spectra ($\Phi = h\nu - (E_{cutoff} - E_F)$). Binding energies were calibrated by measuring the Fermi edge of a clean Au film, which was found to be -4.9 eV. The valence band maximums were calculated using the equation potential of normal hydrogen electrode; Φ : the electron work function of the analyzer).[1, 2]

Photocatalytic H₂O₂ production

10 mg photocatalysts and water-isopropanol (9/1 v/v) were put in a hermetic device composed of a quartz tube. The suspension was well dispersed by ultrasonication for 30 min and O₂ was bubbled into the suspension for 30 min in the dark. Prior to the photocatalytic tests, the suspension was stirred for 30 min in dark to reach the absorption and desorption equilibrium. A 300 W Xe lamp (Perfect Light PLS-SEX 300D) was used as the light source. A cutoff filter was used to achieve visible-light irradiation ($\lambda > 420$ nm). The light radiation intensity was measured using a light power meter (PL-MW2000 PerfectLight) before each photocatalysis, to ensure the repeatability and accuracy of experiments with stable light intensity. The concentration of H₂O₂ was determined by UV-vis spectrophotometer. For example, 1mL liquid was sampled filtrated with a 0.22 μ M filter to further remove the photocatalysts. The amount of H₂O₂ was analyzed by iodometry. The sample was mixed with pre-prepared 2 mL of 0.1 mol L⁻¹ potassium hydrogen phthalate (C₈H₅KO₄) aqueous solution and 2 mL of 0.4 mol L⁻¹ potassium iodide (KI) aqueous solution, which was then kept for 30 min. H₂O₂ molecules react with iodine ions (I⁻) under acidic conditions to generate triiodide ions (I₃⁻), which have strong absorption near 350 nm.[3, 4] The absorbance of I₃⁻ at 350 nm is measured by ultraviolet spectrophotometer (UH 5700), and then the amount of H₂O₂ generated by each reaction can be calculated according to the standard curve.



Electrochemical and photoelectrochemical tests

Rotating disk electrode (RDE) measurement was carried out on an electrochemical workstation (Gamry Reference 600 Potentiostat) with a conventional three-electrode system. A platinum plate and Hg/HgO (saturated KOH) electrodes were used as counter electrode and reference electrodes, respectively. The linear sweep voltammograms (LSV) were obtained in an O₂ saturated 0.1 M phosphate buffer solution (PBS, pH = 7) solution at room temperature with a scan rate 10 mV s⁻¹ and different rotation speeds. The average number of electrons (n) was calculated by Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

where J is the current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the rotating speed (rpm), n is transferred electron number, F is Faraday constant (96485 C mol⁻¹), C₀ is the bulk concentration of O₂ (1.26 ×10⁻³ mol cm⁻³), D₀ is the diffusion coefficient of O₂ (2.7 ×10⁻⁵ cm² s⁻¹), and ν is kinetic viscosity of the electrolyte (0.01 cm² s⁻¹), respectively.[5, 6]

Photocurrent responses and electrochemical impedance spectroscopy (EIS) measurements were conducted with a standard three-electrode system in Na₂SO₄ solution (0.5M) on the Gamry Reference 600 Potentiostat. A 300 W xenon lamp was used as the light source, and the transient photocurrent with a bias of -0.1 V was tested over time during the on/off light cycle. The electrochemical impedance spectrum is measured over a frequency range of 1000 kHz to 0.01 Hz.

Evaluating the photocatalytic decomposition rate of H₂O₂

In the N₂ saturated environment, 10 mg of photocatalyst was uniformly dispersed in 50 mL of a 0.2 mM H₂O₂ solution, followed by agitation for 30 min to reach adsorption-desorption equilibrium. Illumination was then initiated, and 1 mL aliquots of the solution were extracted every 15 min to measure the residual concentration of H₂O₂ using UV-vis spectrophotometry.

AQY measurements

AQY was measured under the illumination of a 300 WXe lamp (PLS-SXE300, Beijing Perfect light) with different bandpass of 420, 500, 520, 550 and 600 nm. The light intensity at 420, 500, 520, 550 and 600 nm was 31, 66.2, 74, 78 and 121 W m⁻², respectively. The reaction system temperature was maintained at 25 °C by a flow of cooling water. The active area of the reactor was approximately 7.06 cm². The final AQY at a certain light irradiation wavelength was calculated according to equation:

$$\text{AQY} = \frac{(\text{number of H}_2\text{O}_2 \text{ production}) \times 2}{\text{number of incident photons}} \times 100\%$$

The number of incident photons is:

$$N_{\text{incident}} = \frac{Pt}{h\nu} = \frac{Pt\lambda}{hc} = \frac{ISt\lambda}{hc}$$

Where I is the light power intensity (W m⁻²), S is the irradiation area (m²), t is the reaction time (s), λ is the wavelength length (m) of the monochromatic light, h is Planck's constant (6.63×10⁻³⁴ m² kg s⁻¹), and c is the speed of light in free space (3.0×10⁸ m s⁻¹).[7, 8]

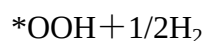
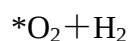
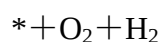
In situ DRIFTS measurements

In-situ diffuse reflectance infrared Fourier transform spectroscopy (In situ DRIFTS) was performed on INVENIO-S, Bruker equipped with a liquid N₂ cooled MCT detector and a high temperature reaction chamber (Praying Mantis, Harrick). The sample was filled into an in-situ IR cell, and O₂ and H₂O vapors were introduced into the cell and fiber source 300 W Xe lamp (PLS-SXE300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) through the CaF₂ window of the cell. Before the measurement, the samples were degassed at 393 K for 1 h. The baseline was obtained before the sample reached O₂ adsorption equilibrium within 30 min.

Theoretical-calculation details

All calculations were performed using the CP2K software package.[9] Geometry optimization and frequency calculation were carried out using the PBE functional with D3 dispersion corrections (PBE-D3) to account for van der Waals interactions.[10, 11] The DZVP-MOLOPT-SR-GTH basis set and GTH pseudopotentials were employed for the optimization. A cutoff energy of 400 eV was used to define the auxiliary plane-wave grid for the electronic density. To ensure the accuracy of the computed energies, the self-consistent field (SCF) procedure was considered converged when the total energy change between iterations was below 10⁻⁶.

The five states of the reaction process are as follows:



*H₂O₂

*+H₂O₂

The exchange-correlation functional was treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) formulation. The plane-wave basis set was truncated at an energy cutoff of 500 eV. The Brillouin zone was sampled using a Monkhorst–Pack k-point grid with a spacing of 0.04 Å⁻¹. Both geometry optimization and subsequent electronic structure calculations, including charge density difference and electron localization function (ELF) analyses, were carried out with a convergence criterion of 1.0×10^{-5} eV/atom for energy, 0.03 eV/Å for maximum force, 0.001 Å for maximum displacement, and 0.05 GPa for maximum stress, corresponding to the Fine quality setting in CASTEP.

Supplemental Figs. S1-S37

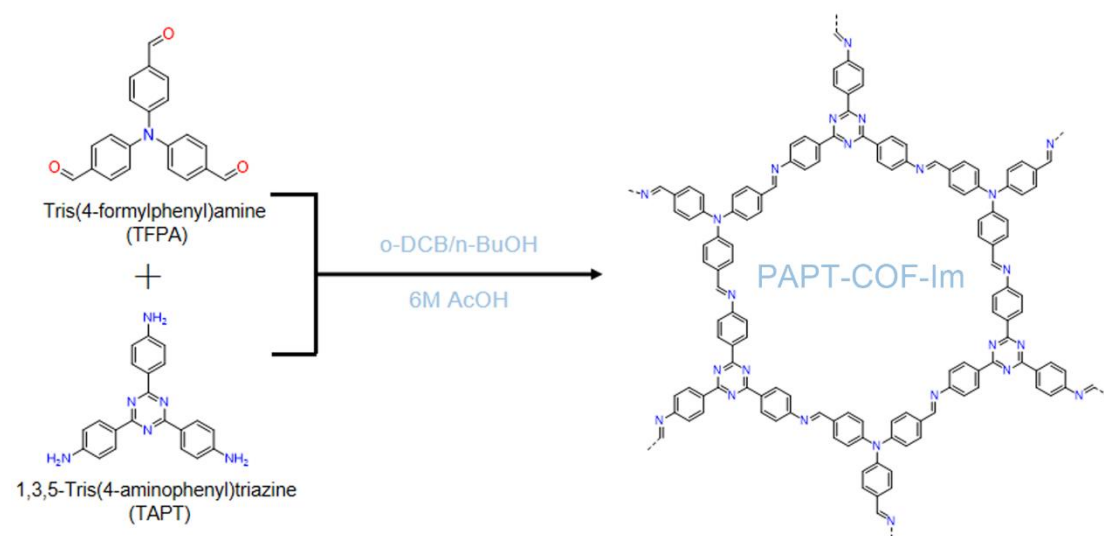


Fig. S1. Schematic illustration of the synthetic route of PAPT-COF-Im.

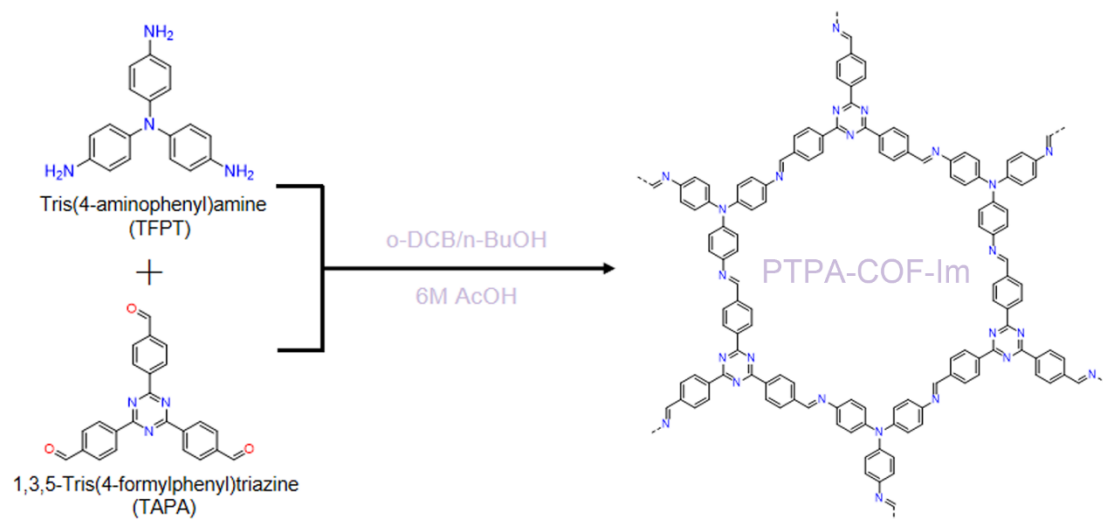


Fig. S2. Schematic illustration of the synthetic route of PTPA-COF-Im.

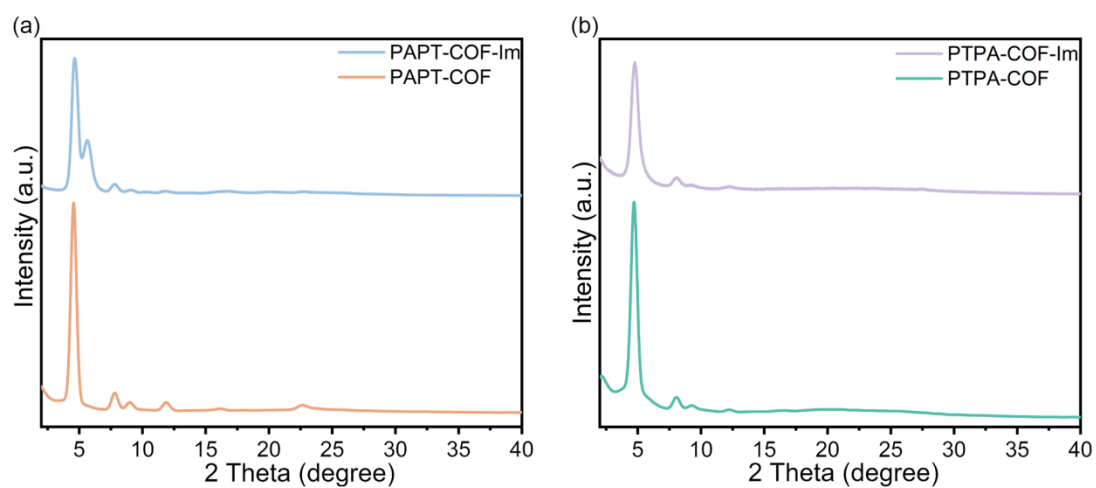


Fig. S3. PXRD patterns of (a) PAPT-COF-Im and PAPT-COF, and (b) PTPA-COF-Im and PTPA-COF.

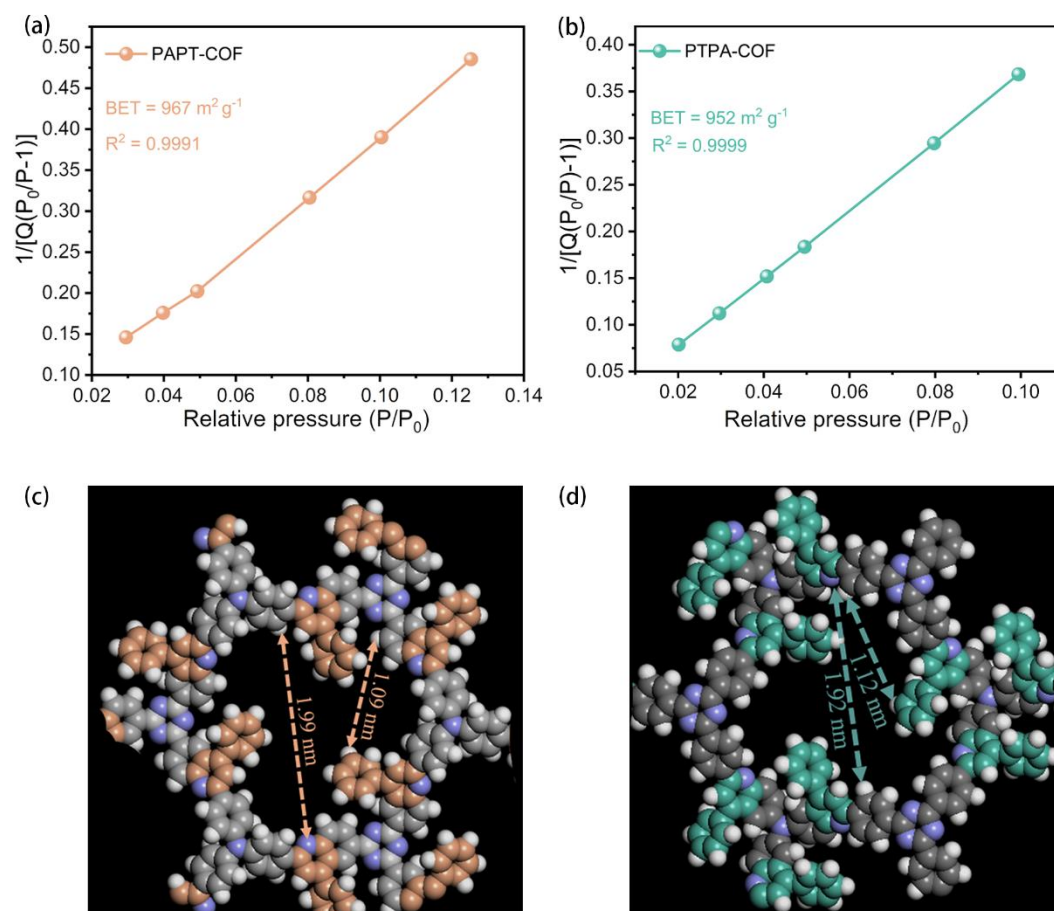


Fig. S4. BET plots of (a) PAPT-COF and (b) PTPA-COF. Theoretically calculated pore width of (c) PAPT-COF and (d) PTPA-COF.

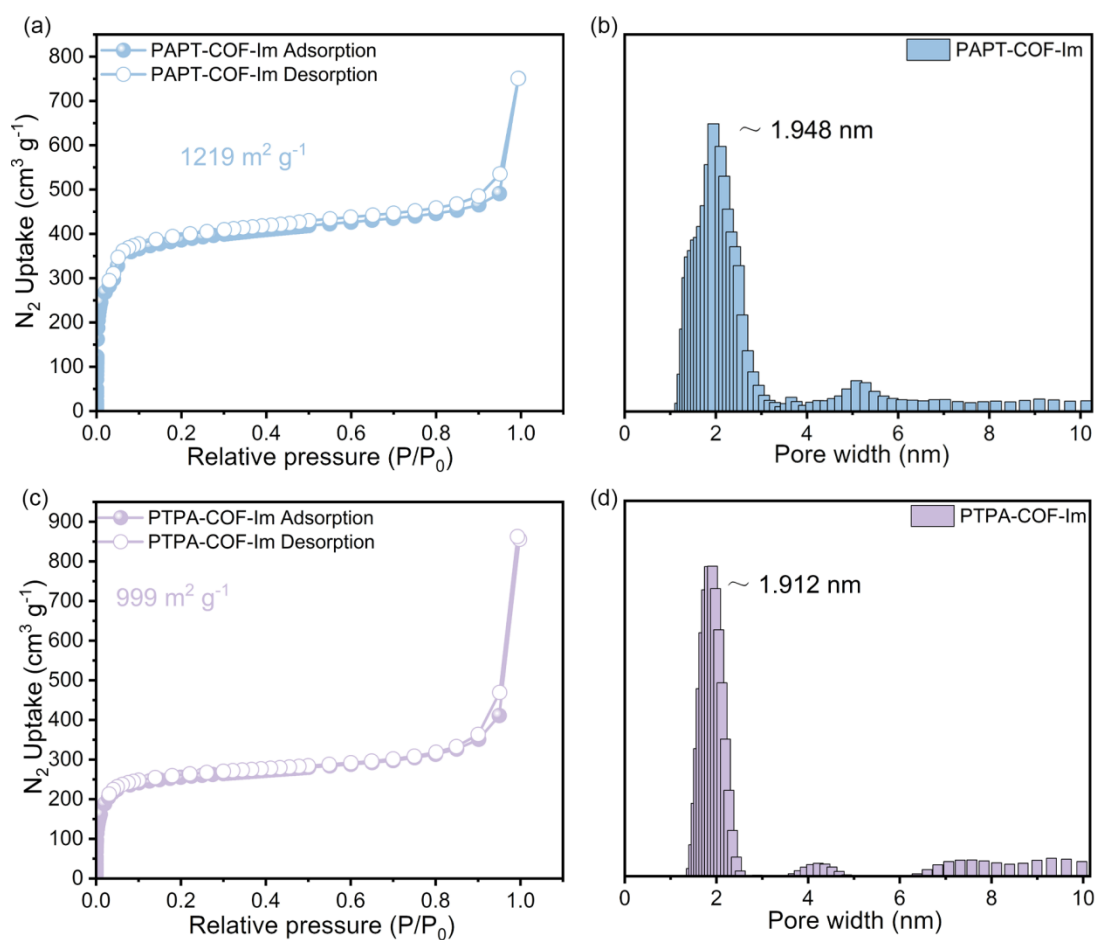


Fig. S5. Nitrogen adsorption-desorption isotherms of (a) PAPT-COF-Im and (c) PTPA-COF-Im. Pore size distributions of (b) PAPT-COF-Im and (d) PTPA-COF-Im.

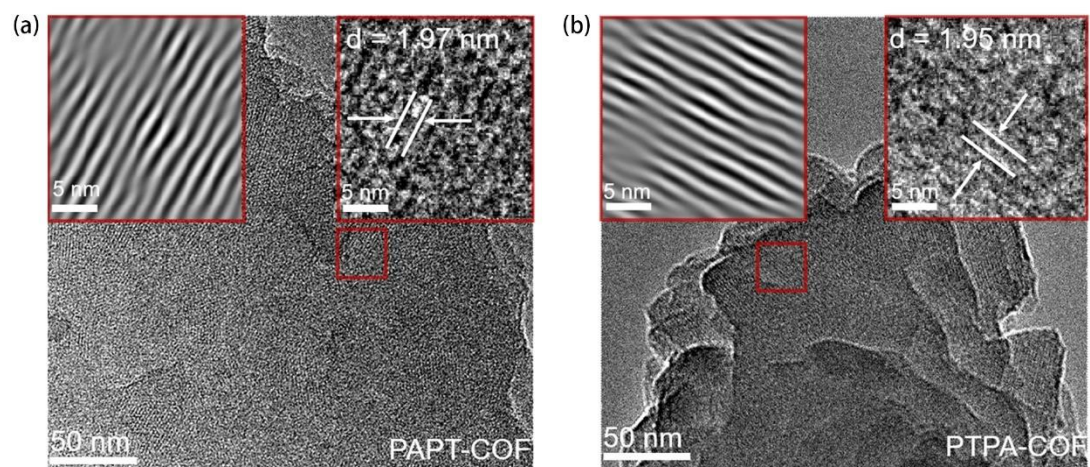


Fig. S6. HR-TEM image of (a) PAPT-COF and (b) PTPA-COF. Inset: the magnified image and corresponding Fourier-filtered image of selected red area.

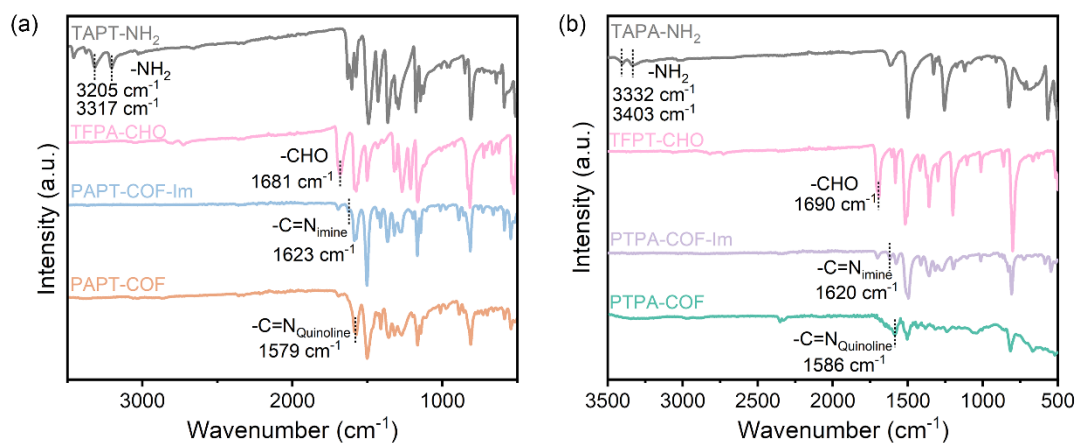


Fig. S7. FT-IR spectra of (a) PAPT-COF and PAPT-COF-Im, and (b) PTPA-COF and PTPA-COF-Im, along with their corresponding monomers.

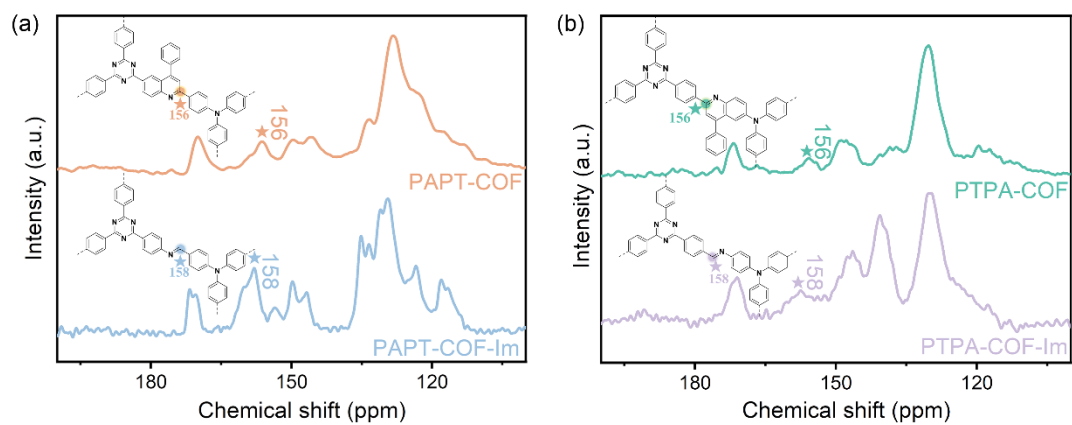


Fig. S8. ^{13}C solid-state NMR spectra of the synthesized COFs and the corresponding Im-COFs of (a) PAPT-COF and (b) PTPA-COF.

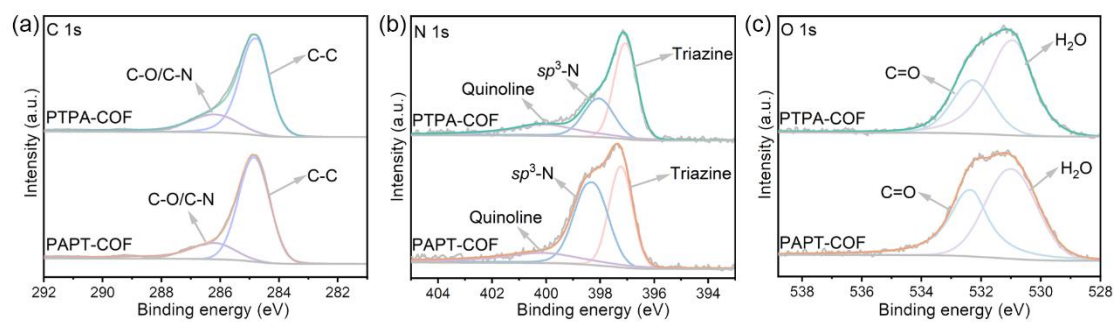


Fig. S9. (a) C 1s, (b) N 1s, and (c) O 1s XPS spectra of PAPT-COF and PTPA-COF.

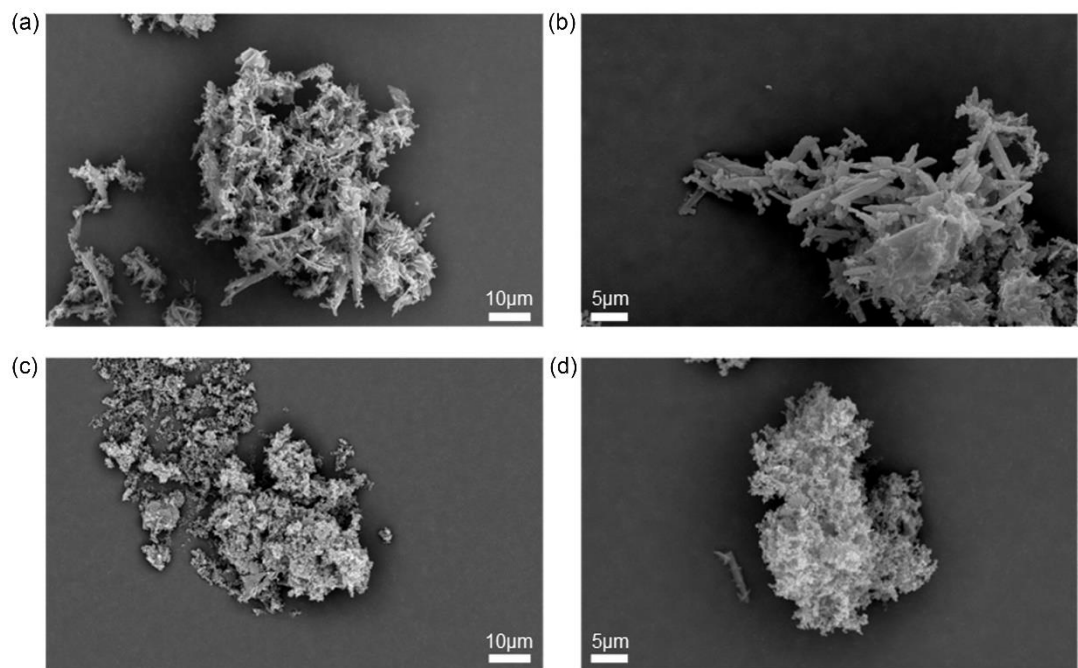


Fig. S10. SEM images of (a, b) PAPT-COF and (c, d) PTPA-COF.

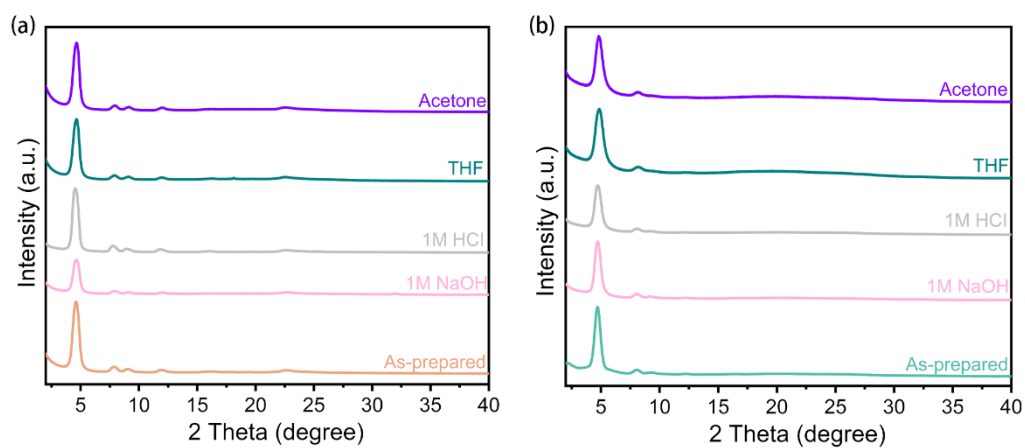


Fig. S11. PXRD patterns of (a) PAPT-COF and (b) PTPA-COF before and after treatments in acetone, THF, 1M HCl and 1M NaOH aqueous solutions.

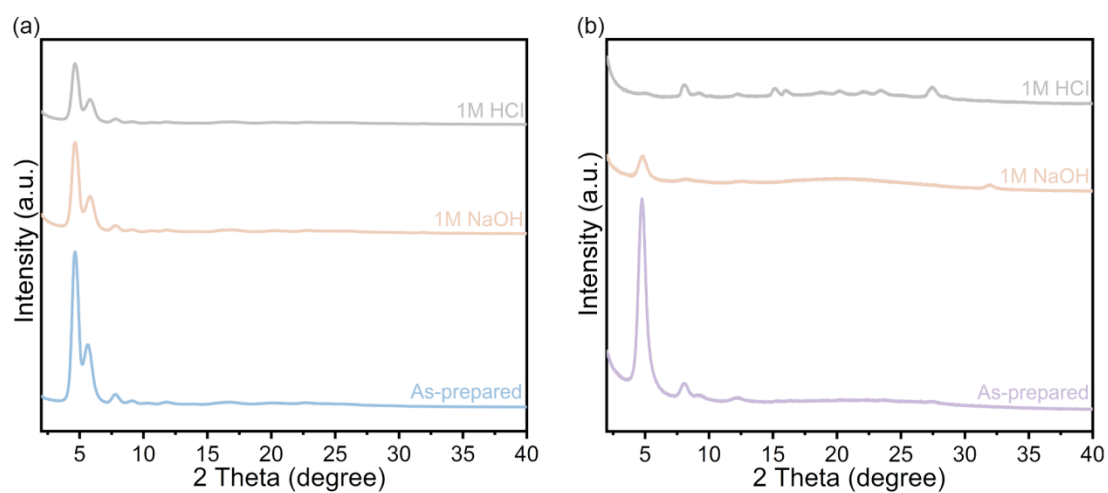


Fig. S12. PXRD patterns of (a) PAPT-COF-Im and (b) PTPA-COF-Im before and after treatments in 1M NaOH and 1M HCl aqueous solutions.

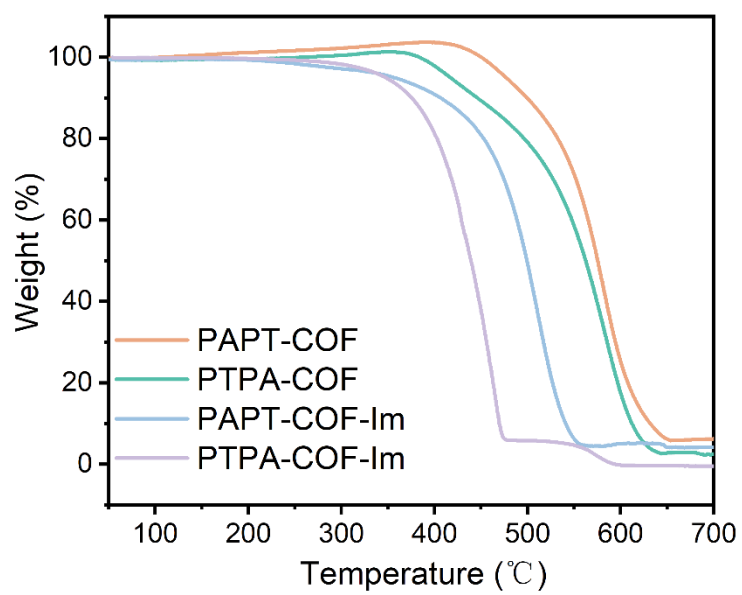


Fig. S13. TGA curves of PAPT-COF, PTPA-COF, PAPT-COF-Im, and PTPA-COF-Im.

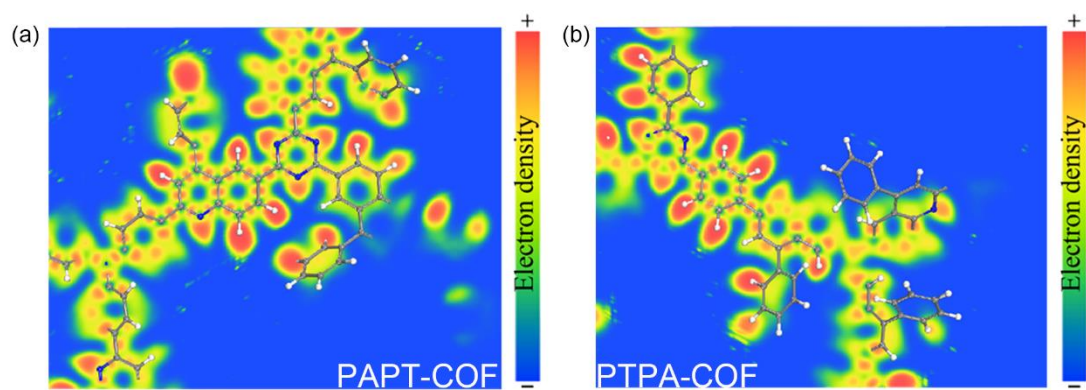


Fig. S14. Electron localization function of (a) PAPT-COF and (b) PTPA-COF.

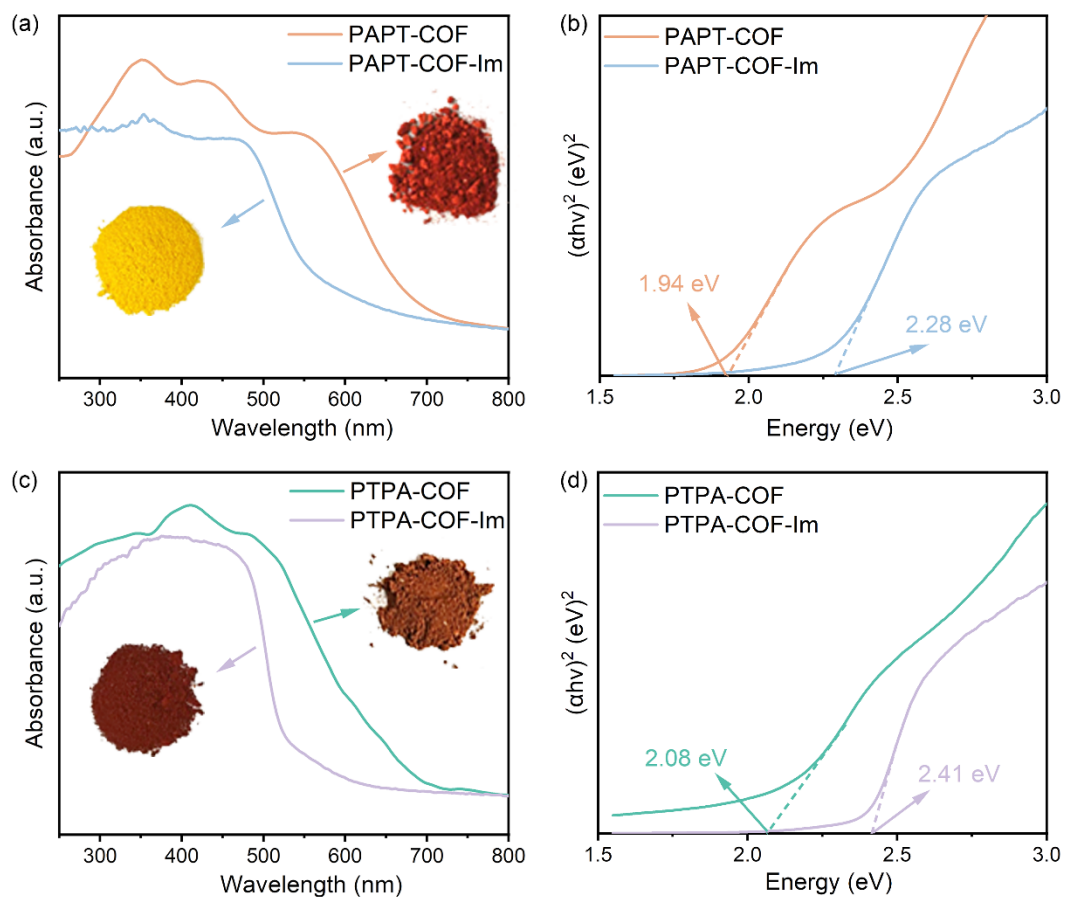


Fig. S15. (a, c) UV-vis DRS and (b, d) Tauc plots of PAPT-COF, PTPA-COF and corresponding Im-COFs.

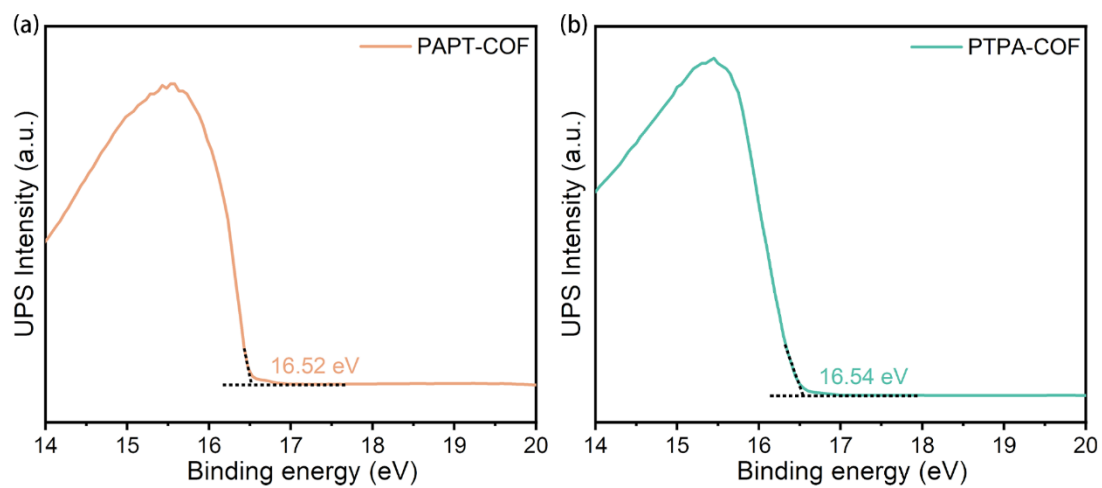


Fig. S16. UPS spectra of (a) PAPT-COF and (b) PTPA-COF.

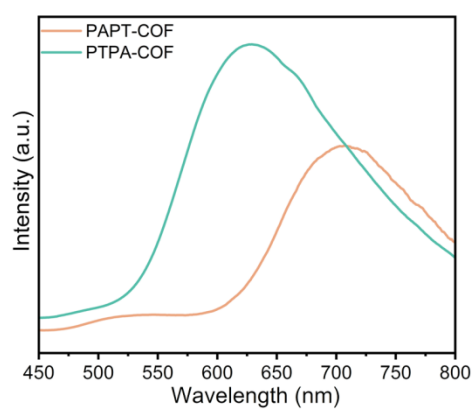


Fig. S17. PL spectra of PAPT-COF and PTPA-COF. (Excitation wavelength of 427 nm)

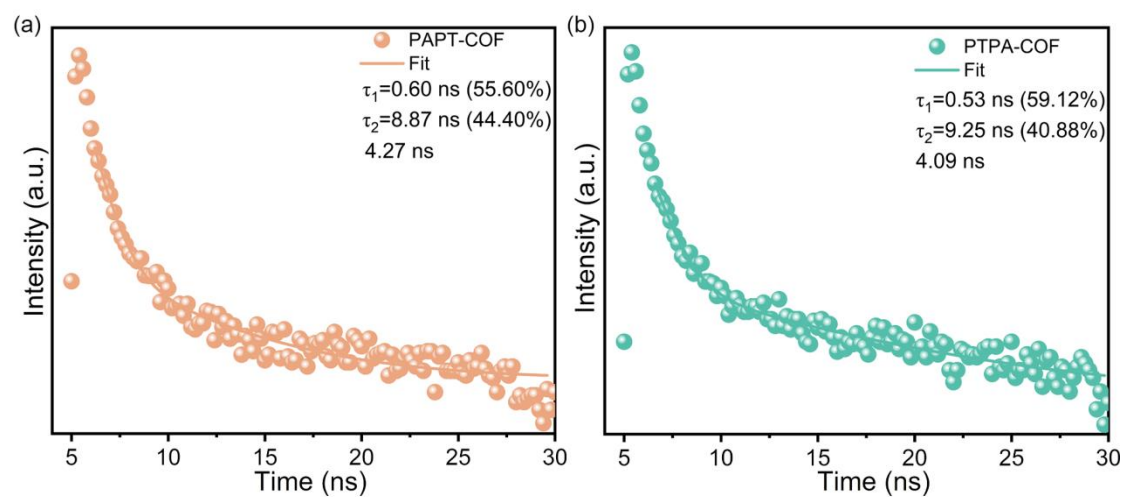


Fig. S18. PL lifetime of PAPT-COF and PTPA-COF. (Excitation wavelength of 444 nm)

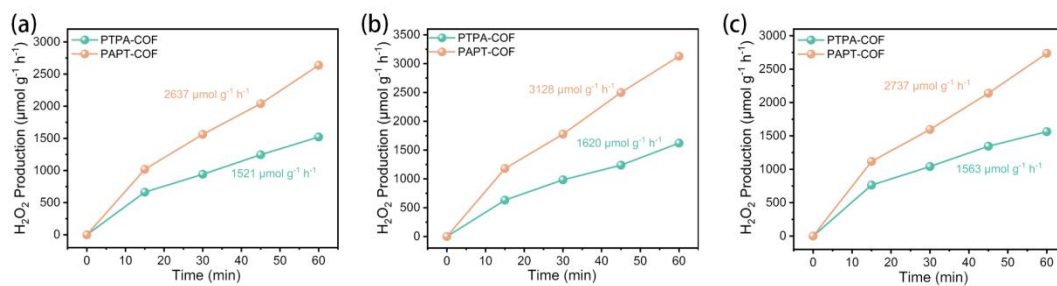


Fig. S19. H_2O_2 production of PAPT-COF and PTPA-COF with different sacrificial reagents over 1h (a) pure water, (b) water: isopropanol = 9:1 and (c) water: ethanol = 9:1 (10 mg catalyst in 45 mL water and 5 mL sacrificial agent, $\lambda > 420 \text{ nm}$ Xe lamp).

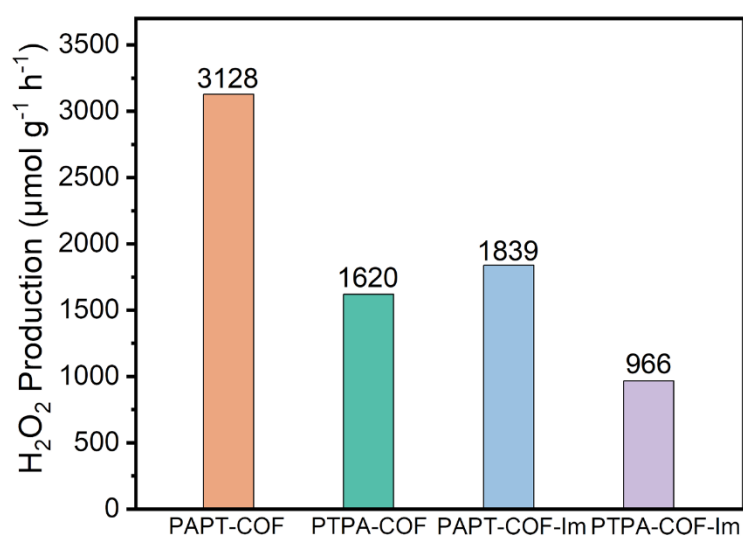


Fig. S20. Comparison of photocatalytic H₂O₂ production for PAPT-COF, PTPA-COF, PAPT-COF-Im and PTPA-COF-Im (10 mg catalyst in 45 mL water and 5 mL isopropanol, $\lambda > 420$ nm Xe lamp).

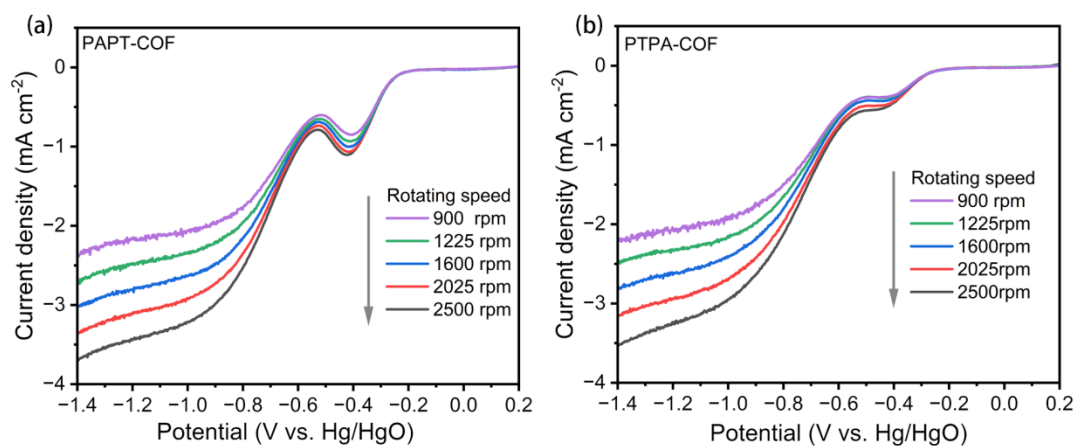


Fig. S21. The LSV curves were measured on RDE with different rotating rates for (a) PAPT-COF and (b) PTPA-COF.

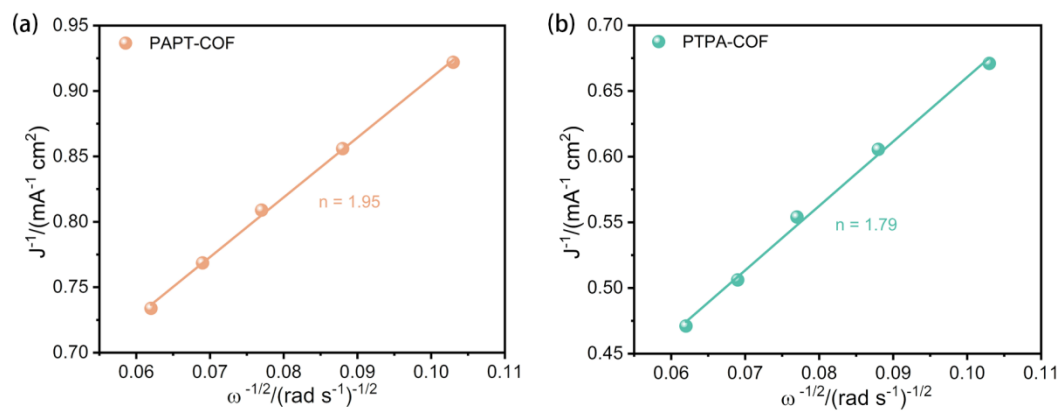


Fig. S22. The Koutechy-Levich plots of (a) PAPT-COF and (b) PTPA-COF.

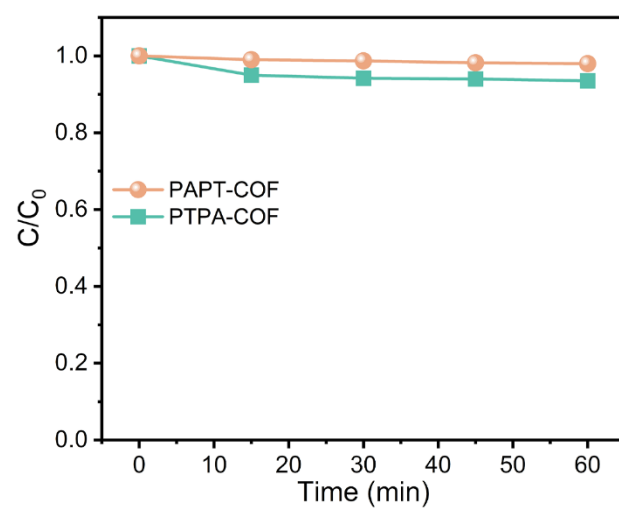


Fig. S23. H_2O_2 decomposition experiments of PAPT-COF and PTPA-COF.

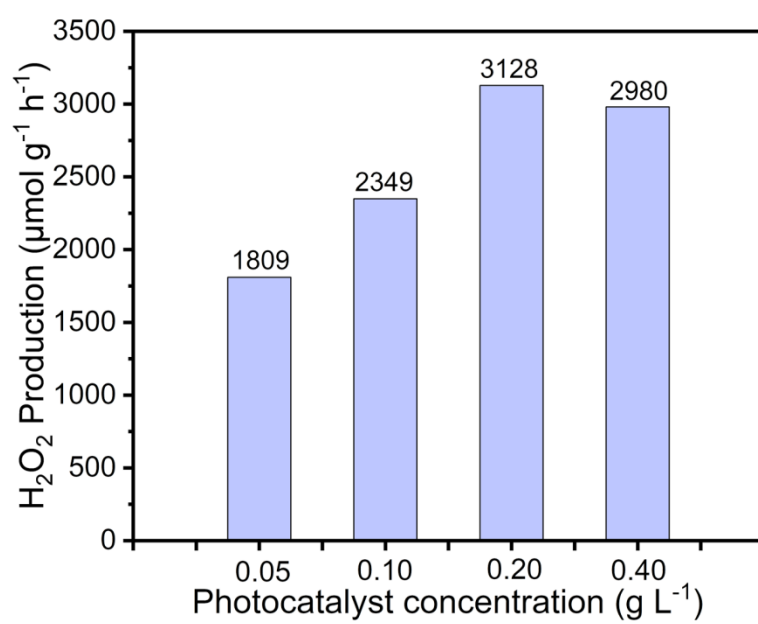


Fig. S24. H₂O₂ photogeneration of PAPT-COF with different concentrations.

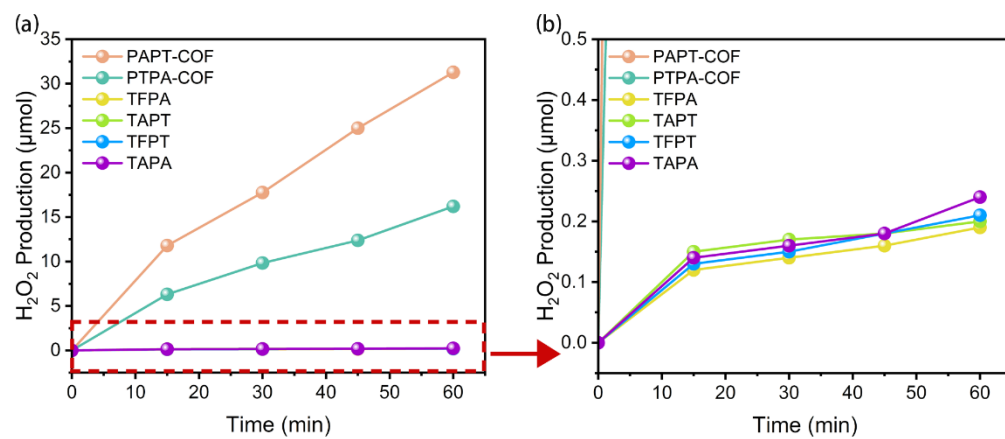


Fig. S25. Comparison of H_2O_2 photogeneration for (a) COFs and (b) the corresponding monomers.

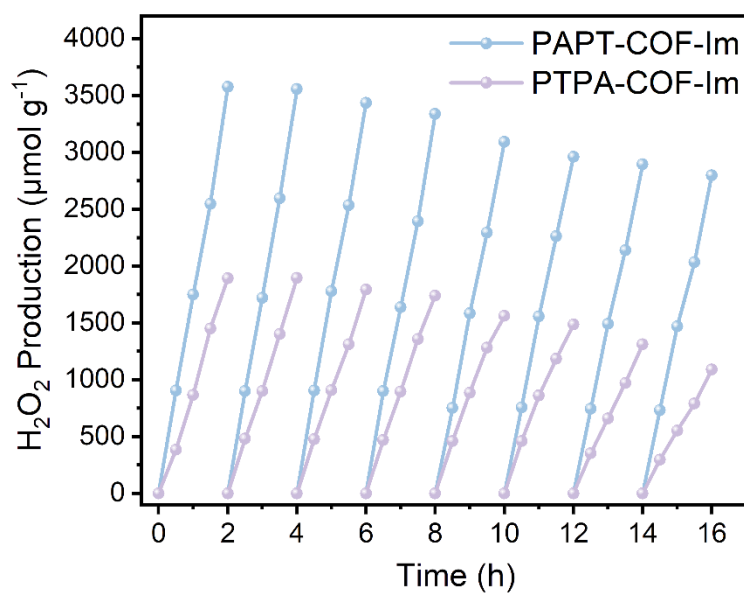


Fig. S26. Recycling H₂O₂ production on PAPT-COF-Im and PTPA-COF-Im (10 mg catalyst in 45 mL water and 5 mL isopropanol, $\lambda > 420$ nm Xe lamp).

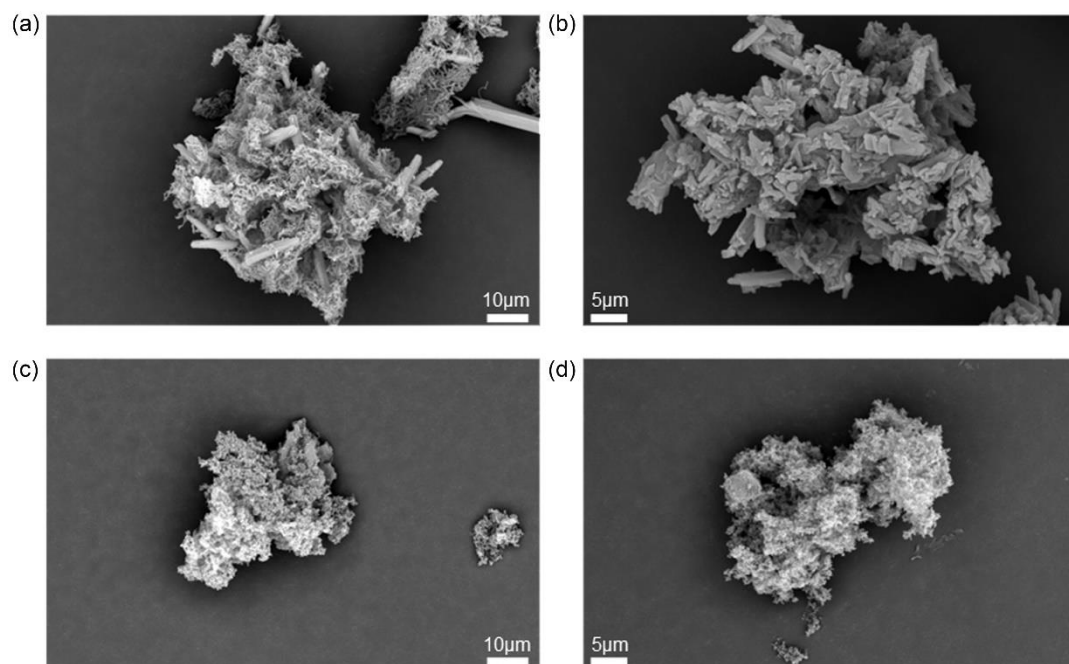


Fig. S27. SEM images of (a, b) PAPT-COF and (c, d) PTPA-COF after photocatalysis.

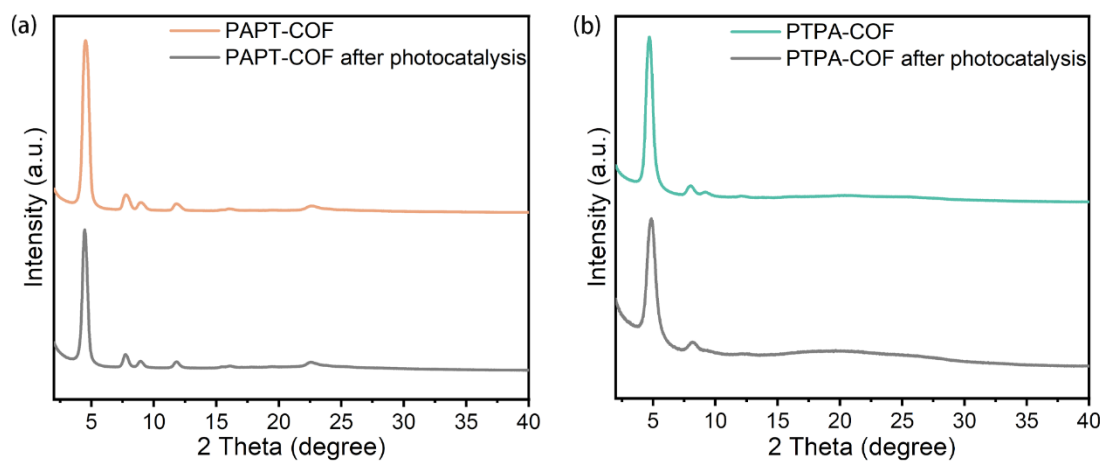


Fig. S28. PXRD patterns of (a) PAPT-COF and (b) PTPA-COF before and after photocatalysis.

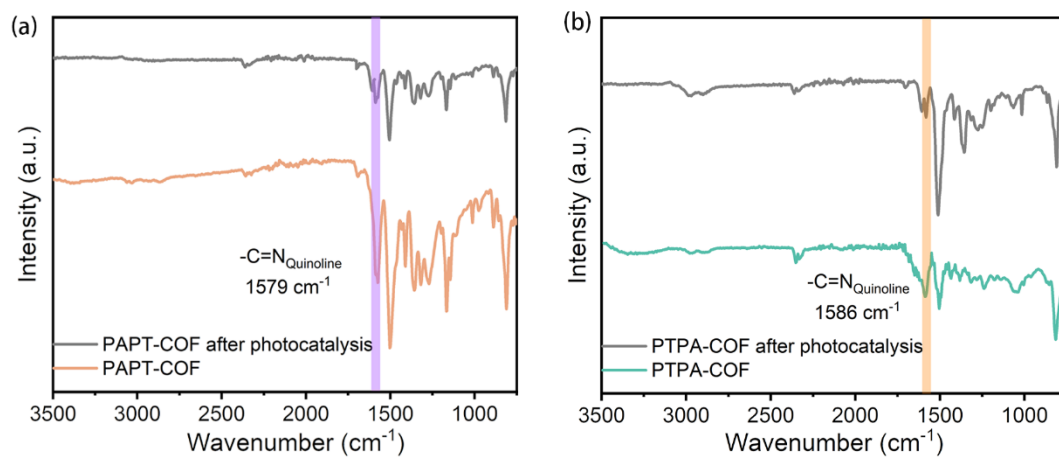


Fig. S29. FT-IR spectra of (a) PAPT-COF and (b) PTPA-COF before and after photocatalysis.

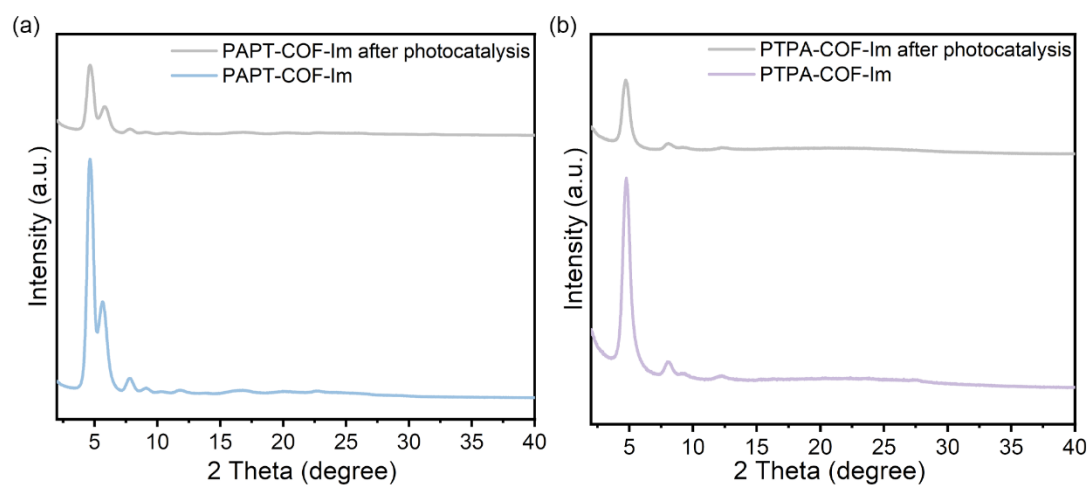


Fig. S30. PXRD patterns of (a) PAPT-COF-Im and (b) PTPA-COF-Im before and after photocatalysis.

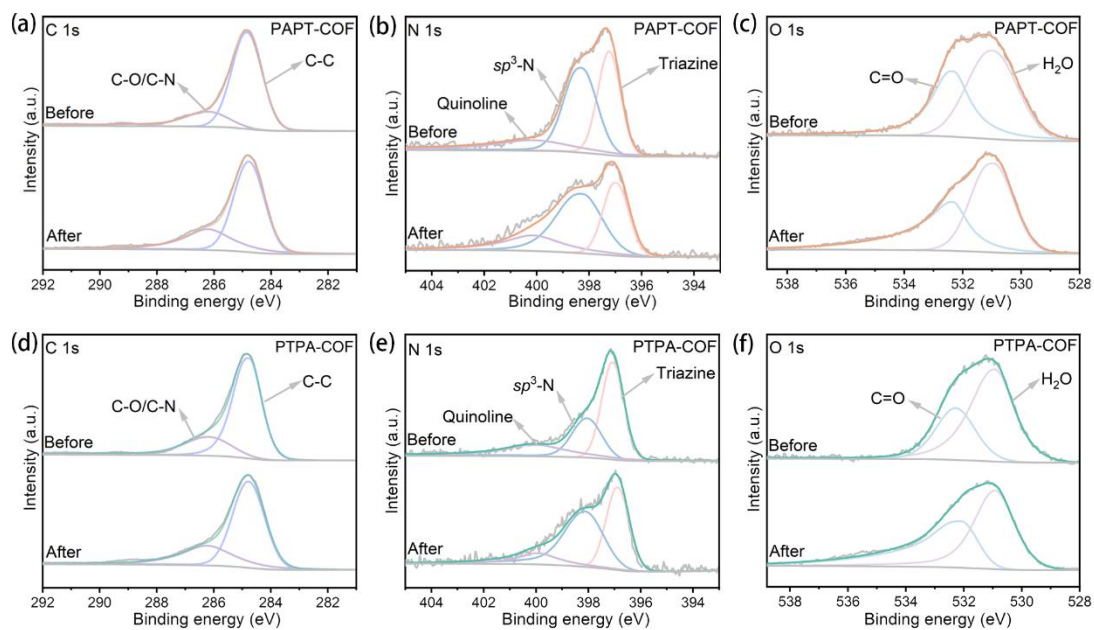


Fig. S31. XPS patterns of (a-c) PAPT-COF and (d-f) PTPA-COF before and after photocatalysis.

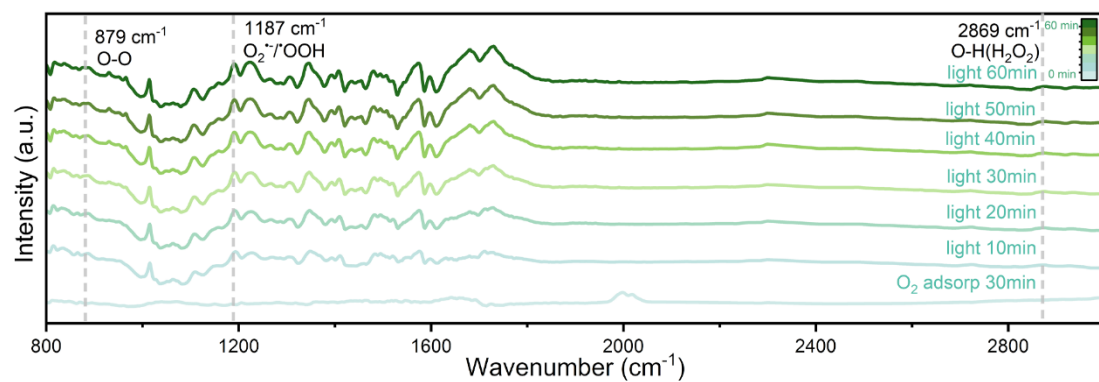


Fig. S32. In situ DRIFTS spectra of PTPA-COF for H_2O_2 production at 800-3000 cm^{-1} .

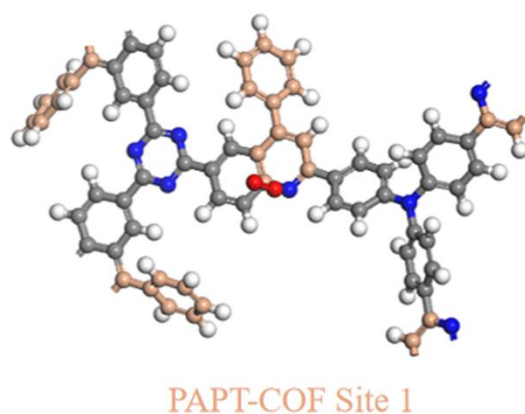


Fig. S33. The O₂ adsorption site and configuration at site 1 on PAPT-COF.

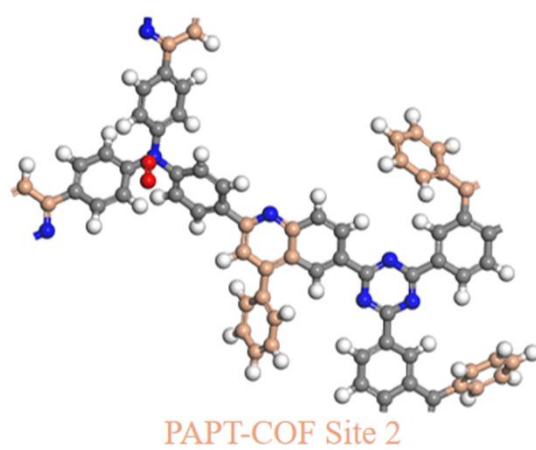
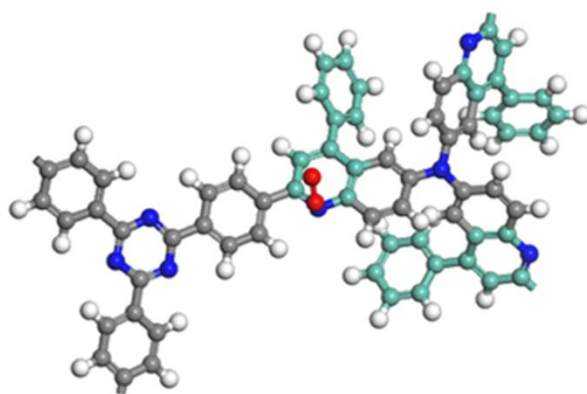
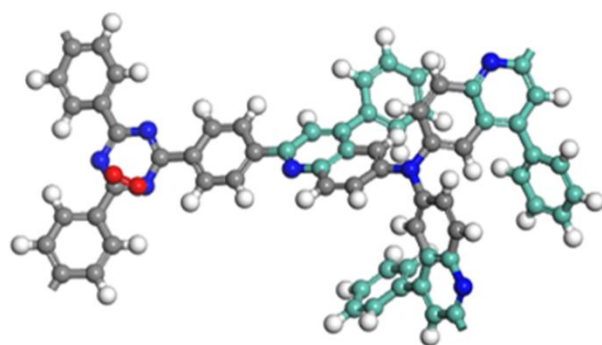


Fig. S34. The O₂ adsorption site and configuration at site 2 on PAPT-COF.



PTPA-COF Site 1

Fig. S35. The O₂ adsorption site and configuration at site 1 on PTPA-COF.



PTPA-COF Site 3

Fig. S36. The O₂ adsorption site and configuration at site 3 on PTPA-COF.

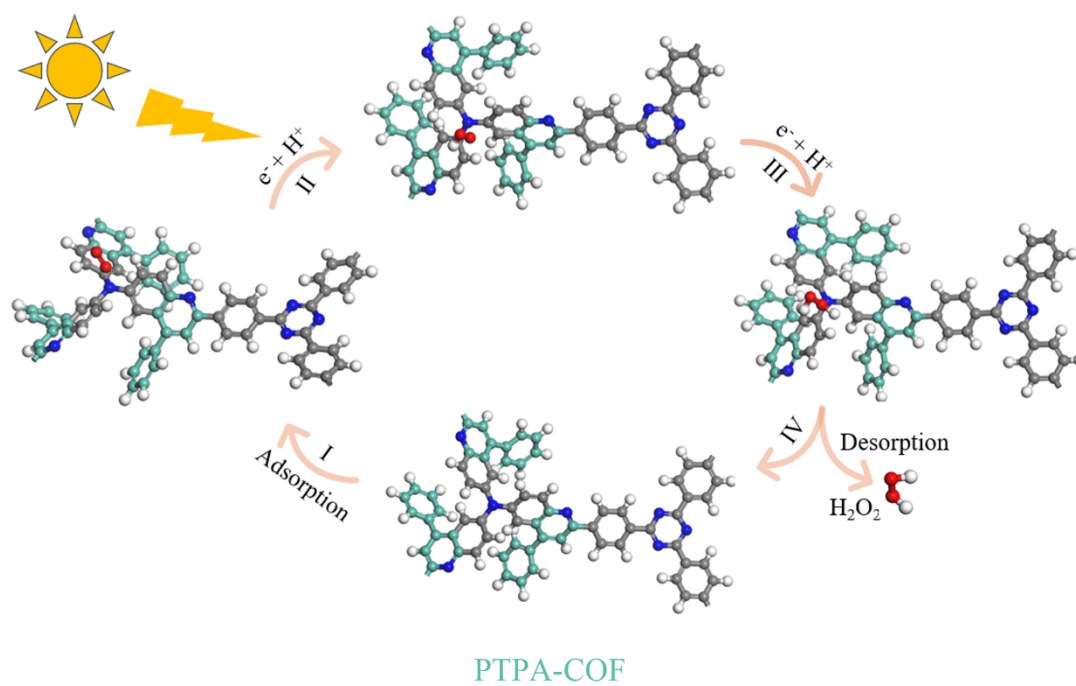


Fig. S37. The proposed mechanism of H_2O_2 generation via 2e^- ORR pathway on PTPA-COF.

Supplemental Tables S1-S3

Table S1. Fractional atomic coordinates for the unit cell of PAPT-COF with AA stacking.

a=b= 23.169928 Å, c= 20.000000 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$							
C1	0.59238	0.19447	0.50987	C57	0.86762	0.69887	0.47574
C2	0.62447	0.15793	0.50081	H58	0.81601	0.65233	0.56743
C3	0.52201	0.16072	0.51818	H59	0.92612	0.73615	0.38561
C4	0.58856	0.08755	0.50034	H60	0.84601	0.73099	0.47168
H5	0.67803	0.18480	0.49315	C61	0.12364	0.58709	0.49366
C6	0.48572	0.09217	0.51751	C62	0.16598	0.64557	0.45794
C7	0.61892	0.04732	0.49057	C63	0.15284	0.55561	0.52904
H8	0.43185	0.06528	0.52331	C64	0.23466	0.67136	0.45703
C9	0.57752	0.97895	0.48667	H65	0.14499	0.67016	0.42852
N10	0.47833	0.98609	0.50649	C66	0.22143	0.58200	0.52993
C11	0.50740	0.94969	0.49500	H67	0.12021	0.51044	0.55671
H12	0.59937	0.94720	0.48086	C68	0.26338	0.64018	0.49354
H13	0.81033	0.30765	0.52463	H69	0.26657	0.71567	0.42788
C14	0.94678	0.46397	0.50832	H70	0.24328	0.55797	0.55885
C15	0.69211	0.07680	0.48565	N71	0.70374	0.40217	0.51029
C16	0.73491	0.12163	0.53432	C72	0.63671	0.36884	0.51010
C17	0.71998	0.05916	0.43254	C73	0.60246	0.40813	0.50983
C18	0.80375	0.14822	0.52971	C74	0.53385	0.37592	0.50081
H19	0.71380	0.13467	0.57630	C75	0.63896	0.47854	0.51806
C20	0.78887	0.08600	0.42789	C76	0.49924	0.41170	0.50037
C21	0.83097	0.13069	0.47638	H77	0.50730	0.32235	0.49316
H22	0.83613	0.18249	0.56798	C78	0.60656	0.51471	0.51740
H23	0.80968	0.07228	0.38617	C79	0.42866	0.38119	0.49064
H24	0.88463	0.15169	0.47268	H80	0.63340	0.56860	0.52311
C25	0.46340	0.87657	0.49388	C81	0.40155	0.42250	0.48679
C26	0.47952	0.83424	0.45806	N82	0.50776	0.52186	0.50644
C27	0.40286	0.84733	0.52943	C83	0.44229	0.49266	0.49501
C28	0.43670	0.76554	0.45711	H84	0.34796	0.40062	0.48108
H29	0.52505	0.85527	0.42860	H85	0.49785	0.19030	0.52460
C30	0.36070	0.7787	0.53025	C86	0.51740	0.05361	0.50828
H31	0.39035	0.87991	0.55729	C87	0.38520	0.30795	0.48559
C32	0.37687	0.73680	0.49367	C88	0.38734	0.26511	0.53416
H33	0.44911	0.73367	0.42787	C89	0.33989	0.28005	0.43235
H34	0.31490	0.75678	0.55926	C90	0.34547	0.19622	0.52932
N35	0.69879	0.29670	0.51029	H91	0.42131	0.28623	0.57628
C36	0.73247	0.36375	0.51018	C92	0.29819	0.21111	0.42746

C37	0.80597	0.39795	0.50999	H93	0.33843	0.31282	0.39424
C38	0.84237	0.46657	0.50096	C94	0.30094	0.16897	0.47583
C39	0.83983	0.36139	0.51824	H95	0.34744	0.16382	0.56753
C40	0.91273	0.50112	0.50051	H96	0.26380	0.19027	0.38564
H41	0.81541	0.49318	0.49328	H97	0.26855	0.11527	0.47195
C42	0.90837	0.39371	0.51750	C98	0.41310	0.53662	0.49380
C43	0.95278	0.57171	0.49082	C99	0.35468	0.52053	0.45797
H44	0.93538	0.36681	0.52318	C100	0.44445	0.59721	0.52930
C45	0.02115	0.59880	0.48682	C101	0.32889	0.56345	0.45699
N46	0.01427	0.49250	0.50640	H102	0.33011	0.47496	0.42855
C47	0.05053	0.55798	0.49494	C103	0.41807	0.63945	0.53011
H48	0.05283	0.65240	0.48106	H104	0.48951	0.60966	0.55716
H49	0.69270	0.50282	0.52438	C105	0.35999	0.62328	0.49358
C50	0.53632	0.48288	0.50827	H106	0.28467	0.55112	0.42771
C51	0.92295	0.61514	0.48583	H107	0.44202	0.68530	0.55905
C52	0.87788	0.61287	0.53435	N108	0.59834	0.30170	0.51024
C53	0.94023	0.66039	0.43254	C109	0.63168	0.26799	0.51012
C54	0.85053	0.65446	0.52932	N110	0.33340	0.66675	0.49370
H55	0.86517	0.57899	0.57653	H111	0.68723	0.02507	0.39435
C56	0.91269	0.70183	0.42749	H112	0.97456	0.66196	0.39450

Table S2. Fractional atomic coordinates for the unit cell of PTPA-COF with AA stacking.

a=b= 23.003474 Å, c= 20.000000 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$							
C1	0.63107	0.26218	0.24607	C57	0.82399	0.64037	0.40093
C2	0.65538	0.23030	0.28681	H58	0.89574	0.64439	0.32868
C3	0.56970	0.22372	0.21088	C59	0.77377	0.60051	0.44662
C4	0.61978	0.15974	0.29426	H60	0.71846	0.50265	0.49210
H5	0.70254	0.25985	0.31304	H61	0.83712	0.69228	0.39313
C6	0.53395	0.15518	0.21766	H62	0.74780	0.62128	0.47459
C7	0.64252	0.12378	0.33493	C63	0.05311	0.55325	0.30333
H8	0.48730	0.12487	0.19066	C64	0.08301	0.51362	0.29197
C9	0.60393	0.05450	0.33639	C65	0.09497	0.62198	0.31673
N10	0.51983	0.05315	0.26315	C66	0.15223	0.54151	0.29462
C11	0.54271	0.02047	0.30013	H67	0.05046	0.46071	0.28106
H12	0.61948	0.02628	0.36808	C68	0.16443	0.65034	0.31801
H13	0.75042	0.30139	0.17943	H69	0.07313	0.65384	0.32468
C14	0.87868	0.43592	0.25963	C70	0.19393	0.61038	0.30731
C15	0.70546	0.15887	0.37424	H71	0.17541	0.51090	0.28654
C16	0.71613	0.20935	0.42041	H72	0.19692	0.70362	0.32714
C17	0.75571	0.14171	0.36598	N73	0.30540	0.70769	0.30849
C18	0.77571	0.24207	0.45695	C74	0.26761	0.64025	0.30843
H19	0.67702	0.22216	0.42802	C75	0.63128	0.36855	0.24601
C20	0.81542	0.17470	0.40236	C76	0.57492	0.34413	0.28646
H21	0.74802	0.10309	0.32995	C77	0.65436	0.43008	0.21111
C22	0.82567	0.22505	0.44785	C78	0.54007	0.37991	0.29403
H23	0.78314	0.28082	0.49267	H79	0.55717	0.29684	0.31247
H24	0.85413	0.16134	0.39487	C80	0.62155	0.46592	0.21790
H25	0.87227	0.25092	0.47597	C81	0.48146	0.35726	0.33475
C26	0.50000	0.94658	0.30317	H82	0.63803	0.51271	0.19113
C27	0.43057	0.91698	0.29158	C83	0.45088	0.39605	0.33647
C28	0.52669	0.90450	0.31674	N84	0.53356	0.48012	0.26330
C29	0.38911	0.84785	0.29426	C85	0.47807	0.45731	0.30032
H30	0.41042	0.94974	0.28045	H86	0.40727	0.38066	0.36831
C31	0.48547	0.83514	0.31805	H87	0.55189	0.24945	0.17843
H32	0.58032	0.92607	0.32478	C88	0.55744	0.12102	0.25934
C33	0.41609	0.80594	0.30720	C89	0.45376	0.29432	0.37400
H34	0.33540	0.82492	0.28599	C90	0.49361	0.28378	0.42029
H35	0.50608	0.80244	0.32725	C91	0.38653	0.24397	0.36559
N36	0.40198	0.69450	0.30858	C92	0.46693	0.22425	0.45685
C37	0.37230	0.73235	0.30837	H93	0.54540	0.32294	0.42795
C38	0.73743	0.36823	0.24627	C94	0.36000	0.18429	0.40197

C39	0.76918	0.42463	0.28666	H95	0.35557	0.25156	0.32946
C40	0.77605	0.34513	0.21157	C96	0.40013	0.17420	0.44761
C41	0.83977	0.45964	0.29416	H97	0.49824	0.21694	0.49272
H42	0.73953	0.44239	0.31256	H98	0.30807	0.14550	0.39437
C43	0.84464	0.37802	0.21839	H99	0.37955	0.12765	0.47577
C44	0.87558	0.51848	0.33455	C100	0.44685	0.50008	0.30353
H45	0.87508	0.36156	0.19175	C101	0.48652	0.56949	0.29209
C46	0.94491	0.54917	0.33617	C102	0.37813	0.47341	0.31712
N47	0.94662	0.46629	0.26343	C103	0.45867	0.61089	0.29478
C48	0.97914	0.52194	0.30021	H104	0.53944	0.58970	0.28111
H49	0.97298	0.59296	0.36777	C105	0.34980	0.51456	0.31842
H50	0.69807	0.44796	0.17891	H106	0.34625	0.41982	0.32521
C51	0.56379	0.44239	0.25936	C107	0.38979	0.58389	0.30758
C52	0.84030	0.54641	0.37351	H108	0.48930	0.66458	0.28662
C53	0.78993	0.50684	0.41986	H109	0.29652	0.49393	0.32765
C54	0.85717	0.61362	0.36481	N110	0.29237	0.59807	0.30863
C55	0.75706	0.53375	0.45618	C111	0.35985	0.62766	0.30856
H56	0.77734	0.45509	0.42779	N112	0.66662	0.33299	0.23855

Table S3. Comparison of photocatalytic H₂O₂ generation for COF-based catalysts

Catalysts	Light (nm)	Solvent	H ₂ O ₂ (μmol h ⁻¹ g ⁻¹)	AQY	References
PAPT-COF	λ > 420 nm	H ₂ O:isopropanol = 9:1	3128	2.13%	This work
PTPA-COF			1620		
TAPT-HAT-COF	λ > 420 nm	10 vol% isopropanol	44.5	5.4%	[12]
TAPD-(Me) ₂ COF	λ = 420-700 nm	H ₂ O: EtOH = 9:1	97	--	[13]
TPB-DMTP-COF	λ > 420 nm	H ₂ O	2900	--	[14]
BD-COF	λ > 420 nm	H ₂ O	670	--	[15]
COF-TTA-TTA	LED (λ = 420nm)	H ₂ O	2406	--	[16]
COF-TfpBpy	λ > 420 nm	H ₂ O	695	8%	[17]
DMCR-1NH	λ > 420 nm	H ₂ O	2264	10.2%	[18]
COF-TAPB-BPDA	λ = 420 nm	H ₂ O: BA = 4:1	1240	--	[19]
CoPc-BTM-COF	λ = 400 nm	H ₂ O: EtOH = 9:1	2096	8.6% at 630 nm	[20]
TpPz	λ > 420 nm	H ₂ O	1418	--	[21]
EBA-COF	LED (λ = 420 nm)	H ₂ O: EtOH = 9:1	1830	4.4%	[22]
1H-COF	λ > 420 nm	H ₂ O	1483	5.4%	[12]
FS-COFs	λ > 420 nm	H ₂ O	3904.2	6.21%	[23]
Bpy-TAPT	λ > 420 nm	H ₂ O	4038	8.6%	[24]

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