

Fully conjugated sp^2 carbon-linked cyano-containing D–A–A covalent organic frameworks for overall hydrogen peroxide photosynthesis

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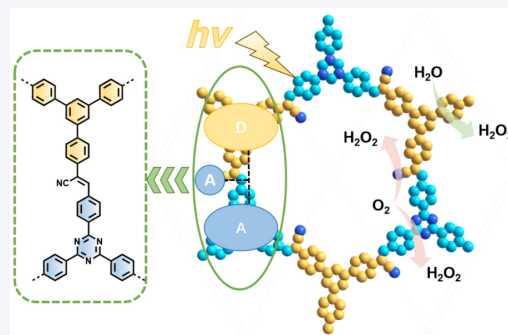
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ABSTRACT: Covalent organic frameworks (COFs) have emerged as promising photocatalysts for hydrogen peroxide (H_2O_2) production, yet their performance is often limited by inefficient photogenerated charge separation and transport. Herein, a sp^2 carbon-conjugated donor–acceptor–acceptor (D–A–A) COF (TFPT-TCPB-COF) (TFPT = 2,4,6-tris(4-formylphenyl)-1,3,5-triazine, and TCPB = 2,2'-(5'-(4-(cyanomethyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)diacetonitrile) incorporating a strong electron-withdrawing cyano group was rationally designed and synthesized via an optimized solvothermal method. The unique D–A–A architecture, together with abundant reductive active sites (triazine and cyano groups) for two-electron oxygen reduction and oxidative sites (benzene rings) for two-electron water oxidation, enables efficient H_2O_2 generation in pure water without sacrificial agents. As a result, TFPT-TCPB-COF achieves a high H_2O_2 production rate of $4.43 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is 1.72 times greater than that of its imine-linked analogue (TFPT-TAPB-COF). Additionally, it exhibits an apparent quantum yield of 12.4% at 420 nm, outperforming most reported COF-based photocatalysts. Experimental and theoretical analyses reveal that the enhanced activity originates from improved charge separation and transport, as well as a modulated electronic structure that lowers the energy barriers for key $^{\bullet}\text{OOH}$ and $^{\bullet}\text{OH}$ intermediates during the photocatalytic process. This work provides important molecular insights into the design of advanced COF photocatalysts with donor–acceptor architectures for efficient solar energy conversion.

KEYWORDS: covalent organic frameworks, sp^2 carbon linkage, cyano group, charge transfer channels, H_2O_2 photosynthesis



A D–A–A type COF for overall hydrogen peroxide photosynthesis

1 Introduction

Hydrogen peroxide (H_2O_2) is widely recognized as a versatile oxidant and a promising energy carrier owing to its high energy

density, environmental benignity, and excellent water solubility, which facilitate storage and transportation [1–4]. Moreover, its strong oxidative capability underpins broad applications in industrial manufacturing, sterilization, disinfection, and chemical synthesis, driving steadily increasing global demand [5, 6]. Currently, industrial-scale H_2O_2 production is dominated by the anthraquinone process; however, this method suffers from significant limitations, including high energy consumption, reliance on high-pressure hydrogen and costly noble metal catalysts, and the generation of hazardous byproducts [7, 8]. These drawbacks underscore the urgent need for sustainable and efficient alternative production strategies [9]. In this context, artificial photosynthesis of

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H₂O₂ from O₂ and H₂O, which utilizes solar energy to drive the oxygen reduction reaction (ORR) and water oxidation reaction (WOR), represents a green and sustainable approach for H₂O₂ generation [10–13]. Therefore, the development of efficient photocatalysts capable of achieving high solar energy utilization efficiency in H₂O₂ photosynthesis has become a critical research priority.

As one kind of effective photocatalysts, metal-free organic polymer semiconductors have attracted considerable attention for green, cost-effective, and safe H₂O₂ photosynthesis recently, owing to their low toxicity, earth-abundant elemental composition, and recyclability [14–16]. Among them, covalent organic frameworks (COFs), a class of crystalline porous polymers, have emerged as promising photocatalysts for H₂O₂ production. Their advantages include tunable molecular structures for precise band engineering, high porosity for efficient mass transport, large specific surface areas for enhanced exposure of active sites, and excellent chemical and thermal stability for sustained photocatalytic performance [17–21]. However, COFs constructed with conventional imine linkages often suffer from inefficient separation and transport of photogenerated charge carriers (e[−]–h⁺ pairs), primarily due to limited π -electron delocalization arising from the polarized nature of the imine bond, which significantly constrains H₂O₂ photosynthesis [22–27]. To overcome this limitation, the development of fully π -conjugated COFs has been proposed as an effective strategy, as their extended conjugation facilitates charge delocalization and enhances carrier mobility [28–30]. In addition, the construction of donor–acceptor (D–A) architectures via rational molecular design has been demonstrated to suppress charge recombination through intrinsic electron push–pull effects between donor and acceptor units [31–33]. Nevertheless, conventional binary D–A systems often suffer from rapid exciton recombination along lateral pathways [34]. Therefore, the design of more sophisticated D–A architectures with multiple charge transfer channels has become an important strategy to promote efficient charge separation and significantly enhance photocatalytic H₂O₂ production [35].

As a response, herein, a sp² carbon-conjugated and cyano-functionalized donor–acceptor–acceptor (D–A–A) covalent organic framework (TFPT–TCPB–COF) was synthesized via a solvothermal Knoevenagel condensation between 2,2'-(5'-(4-(cyanomethyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)diacetonitrile (TCPB) and 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TFPT), and its photocatalytic H₂O₂ production performance was systematically investigated. In this architecture, the triazine units of TFPT act as electron-accepting centers, while the cyano groups of TCPB function as additional electron-withdrawing units and the benzene moieties serve as electron donors, collectively forming a D–A–A system with dual charge-transfer pathways that promote efficient charge separation and transport. For comparison, an imine-linked analogue (TFPT–TAPB–COF) featuring a conventional D–A configuration was constructed via a Schiff-base reaction. Both COFs exhibit high crystallinity and ordered mesoporous structures, facilitating mass transport and active site accessibility. Notably, the robust sp² carbon linkages and fully conjugated framework of TFPT–TCPB–COF endow superior electrical conductivity and structural stability. In addition, compared with TFPT–TAPB–COF with only one kind of reductive active sites (triazine) for 2 e[−] ORR and oxidative sites (benzene rings) for 2e[−] WOR, the TFPT–TCPB–COF contains two kinds of reductive active sites (triazine and cyano groups) for 2e[−] ORR and oxidative sites (benzene rings) 2e[−] WOR.

In addition, the sp²-carbon linkage not only enhances the chemical stability and conjugation degree but also facilitates more efficient charge transfer between donor and acceptor units. On the other hand, the cyano group as the second acceptor further deepens the lowest unoccupied molecular orbital (LUMO) level, which further promotes electron–hole separation [36, 37]. Importantly, these two factors synergistically ensure a rigid and highly conjugated backbone that allows the cyano groups to effectively participate in photoinduced charge transfer.

Attributing to these merits, TFPT–TCPB–COF achieves an H₂O₂ production rate of 4.43 mmol·g^{−1}·h^{−1} in pure water without sacrificial agents, 1.72 times higher than that of TFPT–TAPB–COF. Experimental and theoretical studies reveal that the D–A–A architecture enhances exciton dissociation and charge mobility, while lowering the energy barriers for the formation of key [•]OOH and [•]OH intermediates, thereby accelerating H₂O₂ photogeneration.

2 Experimental

2.1 Synthesis of TFPT–TAPB–COF

TFPT–TAPB–COF was synthesized via a solvothermal Schiff-base condensation. Briefly, TAPB (10.5 mg, 0.03 mmol) and TFPT (11.8 mg, 0.03 mmol) were dispersed in a mixed solvent of 1,2-dichlorobenzene (o-DCB, 0.5 mL) and 1-butanol (n-BuOH, 0.5 mL). The suspension was sonicated for 20 min to achieve a homogeneous mixture, followed by the addition of 6 M aqueous acetic acid (0.1 mL) and brief sonication (30 s). The reaction mixture was then subjected to three freeze–pump–thaw cycles for degassing, flame-sealed under vacuum, and heated at 120 °C for 72 h. After cooling to room temperature, the resulting yellow precipitate was collected by filtration, thoroughly washed with dichloromethane (CH₂Cl₂) five times, and further purified by Soxhlet extraction using tetrahydrofuran (THF). The final product was obtained after vacuum drying for 12 h.

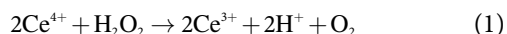
2.2 Synthesis of TFPT–TCPB–COF

TFPT–TCPB–COF was synthesized via a solvothermal Knoevenagel condensation. Specifically, TCPB (8.5 mg, 0.02 mmol) and TFPT (7.9 mg, 0.02 mmol) were dispersed in a mixed solvent of o-DCB (0.4 mL) and n-BuOH (0.6 mL). The suspension was sonicated for 20 min to ensure homogeneous dispersion, followed by the addition of 0.2 M tetrabutylammonium hydroxide (TBAH, 0.1 mL) and brief sonication (30 s). The resulting mixture was subjected to three freeze–pump–thaw cycles for degassing, flame-sealed under vacuum, and heated at 120 °C for 5 days. After naturally cooling to room temperature, the resulting solid was collected by filtration, thoroughly washed with CH₂Cl₂ five times, and further purified by Soxhlet extraction using THF. The final product was obtained after drying under vacuum for 12 h.

2.3 H₂O₂ photosynthesis test

For the photocatalytic evaluation, 5 mg of catalyst was dispersed in 50 mL of pure water by ultrasonication for 30 min. The resulting suspension was transferred into a quartz reactor and saturated with O₂ for 20 min under continuous stirring. Photocatalytic reactions were carried out under irradiation from a 300 W Xe lamp, while the reactor temperature was maintained at 25 °C using a circulating water system. The concentration of H₂O₂ produced was quantified using a ultraviolet–visible (UV–vis) spectrophotometric method.

Specifically, 2 mL of the reaction solution was withdrawn at designated intervals and filtered through a 0.22 μm membrane to remove suspended catalysts. The filtrate was then mixed with a pre-prepared $\text{Ce}(\text{SO}_4)_2$ solution, and the H_2O_2 concentration was determined by monitoring the absorbance change using a UV-vis spectrophotometer. This method was based on the redox reaction in which yellow Ce^{4+} was reduced by H_2O_2 to colorless Ce^{3+} , as described in Eq. (1)



The concentration of produced H_2O_2 could be calculated by Eq. (2)

$$c(\text{H}_2\text{O}_2) = 0.5 \times c(\text{Ce}^{4+}) \quad (2)$$

The yellow and transparent $\text{Ce}(\text{SO}_4)_2$ solution (4.0 mM) was prepared by dissolving 66.40 mg of $\text{Ce}(\text{SO}_4)_2$ in 50 mL of 0.5 M H_2SO_4 . For calibration, a series of standard H_2O_2 solutions with known concentrations were added to the $\text{Ce}(\text{SO}_4)_2$ solution, and their absorbance was recorded using a UV-vis spectrophotometer. A calibration curve was established based on the linear relationship between absorbance intensity and H_2O_2 concentration, which was subsequently used to determine the H_2O_2 concentrations in the collected samples.

3 Results and discussion

TFPT-TAPB-COF featuring a D-A architecture was synthesized

via Schiff-base condensation between the electron-deficient TFPT acceptor and the electron-rich TAPB donor. To further enhance H_2O_2 photosynthesis, a D-A-A COF, TFPT-TCPB-COF, was constructed through Knoevenagel condensation between TFPT and a cyanomethyl-functionalized TCPB donor, introducing multiple charge-transfer pathways (Fig. 1).

To elucidate the crystalline structures of the as-synthesized COFs, powder X-ray diffraction (PXRD) analysis, combined with theoretical simulations, was employed. As shown in Figs. 2(a) and 2(d), both TFPT-TAPB-COF and TFPT-TCPB-COF display prominent diffraction peaks at $2\theta = 4.07^\circ$ and 3.95° , respectively, which can be indexed to the (100) plane. Notably, the experimental PXRD patterns are in good agreement with the simulated AA-stacking models, conforming their *hcb* topology. Pawley refinement further confirms this structural assignment, yielding low residual values (TFPT-TAPB-COF: $R_p = 3.60\%$ and $R_{wp} = 4.51\%$; and TFPT-TCPB-COF: $R_p = 3.44\%$ and $R_{wp} = 4.44\%$), indicative of a high degree of consistency between the experimental data and the eclipsed AA-stacking structures (Fig. S1 in the Electronic Supplementary Material (ESM)). Both COFs crystallize in the $P\bar{6}$ space group. The refined unit cell parameters are $a = b = 25.15 \text{ \AA}$, $c = 3.44 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ for TFPT-TAPB-COF, and $a = b = 25.43 \text{ \AA}$, $c = 3.44 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ for TFPT-TCPB-COF. Furthermore, transmission electron microscopy (TEM) images reveal that both COFs exhibit a spherical particle morphology (Fig. S2 in the ESM).

The chemical structures of TFPT-TAPB-COF and TFPT-TCPB-COF were characterized by Fourier transform infrared (FT-IR)

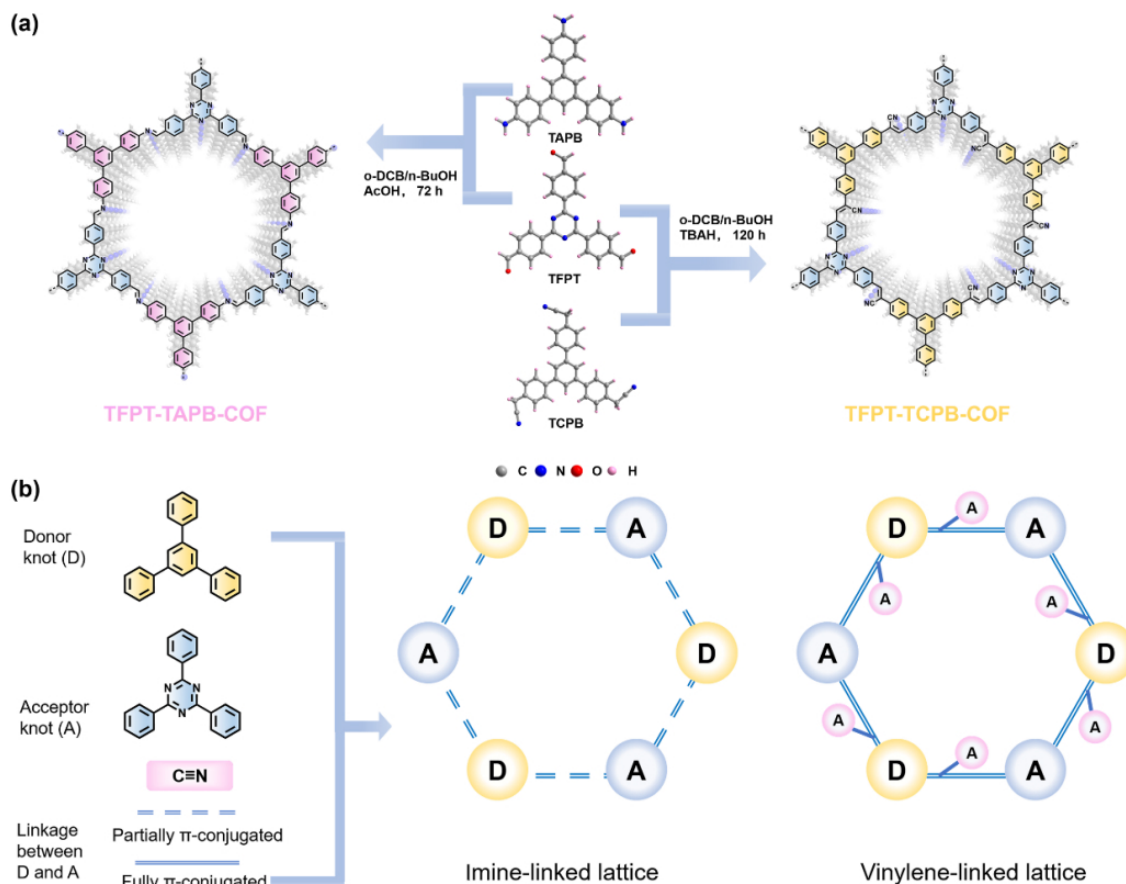


Figure 1 (a) Schematic representation of TFPT-TAPB-COF and TFPT-TCPB-COF. (b) Schematics of electron donor knot (D), acceptor knot (A), and linkages between D and A.

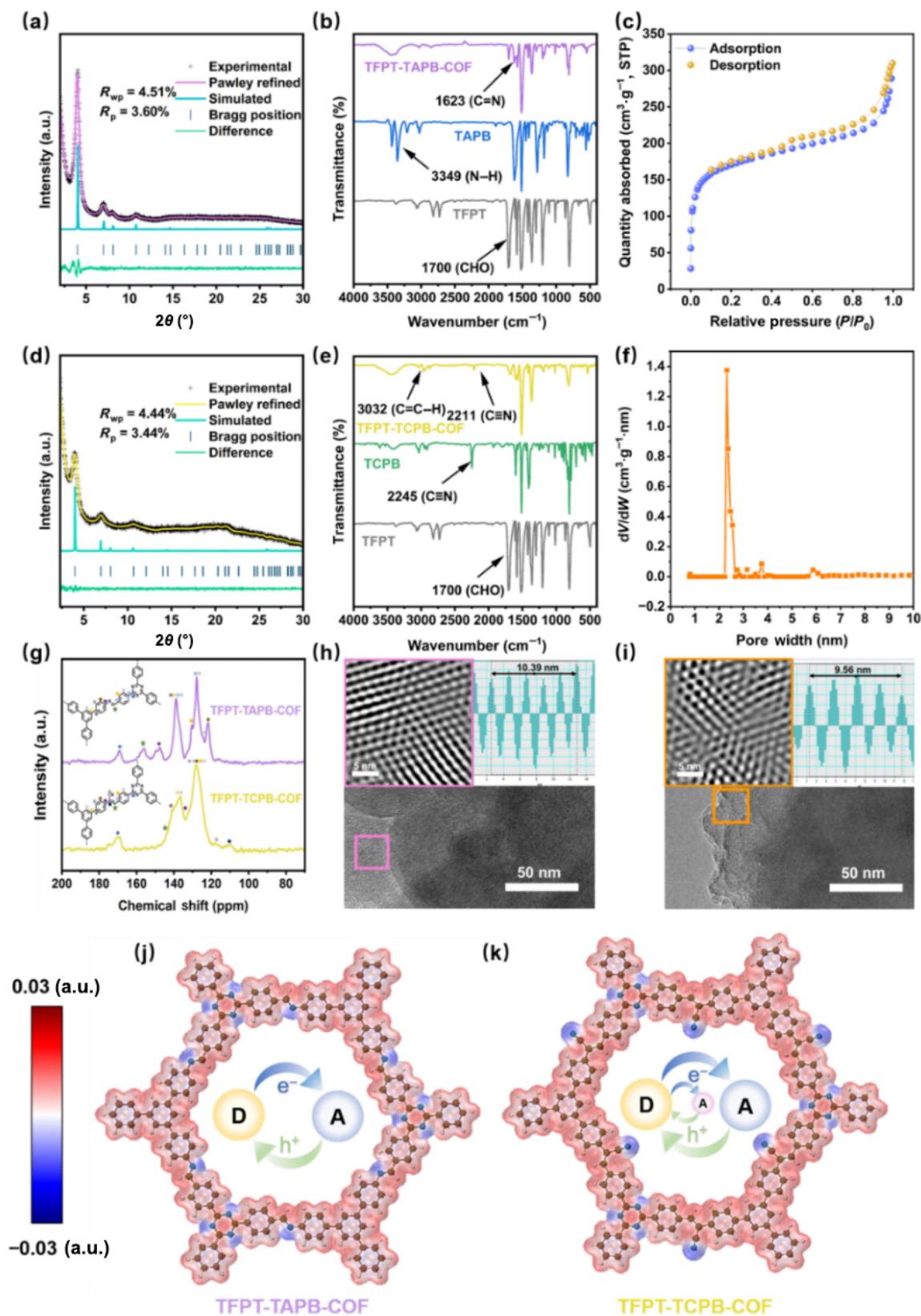


Figure 2 ((a) and (d)) Experimental and Pawley refined and simulated PXRD patterns of (a) TFPT-TAPB-COF and (d) TFPT-TCPB-COF. ((b) and (e)) FT-IR spectra of (b) TFPT-TAPB-COF and (e) TFPT-TCPB-COF and materials. (c) N_2 adsorption and desorption isotherm at 77 K and (f) pore-size distribution of TFPT-TCPB-COF. (g) Solid-state ^{13}C CP/MAS NMR spectra of TFPT-TAPB-COF (pink) and TFPT-TCPB-COF (yellow). ((h) and (i)) HRTEM images of (h) TFPT-TAPB-COF and (i) TFPT-TCPB-COF. ((j) and (k)) Electrostatic potential surface of (j) TFPT-TAPB-COF and (k) TFPT-TCPB-COF, the insets show the corresponding charge transfer channels where the yellow sphere (denoted by yellow D), blue sphere (denoted by blue A), and pink sphere (denoted by pink A) represent triphenyl benzene, triphenyl triazine, and cyano group, respectively.

spectroscopy and solid-state ^{13}C cross-polarization magic-angle-spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) spectroscopy (Figs. 2(b), 2(e), and 2(g)). In the FT-IR spectrum of TFPT-TAPB-COF, the disappearance of the C=O stretching vibration of TFPT (1700 cm^{-1}) and the N-H stretching of TAPB (3349 cm^{-1}), together with the emergence of a characteristic C=N stretching band at 1623 cm^{-1} , confirms the successful formation of imine linkages. For TFPT-TCPB-COF, the presence of C=C-H and C $\equiv$ N stretching vibrations at approximately 3032 and 2211 cm^{-1} , respectively, verifies the formation of acrylonitrile-type linkages [38, 39]. The ^{13}C CP/MAS NMR spectra of both COFs display a signal at ~ 169 ppm, corresponding to the triazine carbon atoms. In TFPT-TAPB-COF, an additional peak at ~ 156 ppm is assigned to the imine carbon, whereas in TFPT-TCPB-COF, a peak at ~ 110 ppm is attributed to cyano-substituted carbon atoms within the vinylenes linkages [23]. X-ray photoelectron spectroscopy (XPS) further confirms the presence of C and N elements in both materials. The high-resolution C 1s spectrum of TFPT-TCPB-COF exhibits peaks at 286.7, 285.6, and 284.8 eV, corresponding to C=N (triazine), C $\equiv$ N, and C=C species, respectively (Fig. S3 in the ESM), while the imine linkage in TFPT-TAPB-COF is evidenced by a characteristic peak at 286.1 eV. The N 1s spectrum of TFPT-TCPB-COF shows peaks at 398.9 and 400.1 eV, assigned to triazine C=N and cyano nitrogen, respectively [40], whereas a weak peak at 400.2 eV in TFPT-TAPB-COF indicates residual amine groups from incomplete condensation (Fig. S4 in the ESM). Furthermore, both COFs retain their crystallinity after immersion in acetone, N,N-dimethylformamide (DMF), and 6 M HCl for 72 h (Figs. S5 and S6 in the ESM), demonstrating excellent chemical stability. However, TFPT-TAPB-COF undergoes structural degradation in 6 M NaOH due to the hydrolysis of imine bonds, whereas TFPT-TCPB-COF maintains its crystallinity under the same conditions, attributable to the robust and irreversible sp^2 C=C linkages [18].

In addition, the permanent porosity of these two COFs was explored via N_2 sorption measurements. As shown in Figs. 2(c) and 2(f), and Fig. S7 in the ESM, both TFPT-TCPB-COF and TFPT-TAPB-COF exhibit typical mesoporous characteristics. N_2 adsorption-desorption isotherms were measured at 77 K after vacuum degassing. Brunauer-Emmett-Teller (BET) analysis reveals a specific surface area of $635\text{ m}^2\text{ g}^{-1}$ for TFPT-TCPB-COF, whereas TFPT-TAPB-COF displays a significantly higher surface area of $1738\text{ m}^2\text{ g}^{-1}$. Pore size distribution analysis indicates dominant pore diameters centered at 2.37 nm for TFPT-TCPB-COF and 2.15 nm for TFPT-TAPB-COF, which are in good agreement with the simulated values of 2.35 and 2.33 nm, respectively. Furthermore, high-resolution TEM (HR-TEM) images reveal well-defined and periodically ordered lattice fringes with spacings of 2.39 nm for TFPT-TCPB-COF and 2.07 nm for TFPT-TAPB-COF, corresponding to their (100) planes. These observations further confirm the high crystallinity and ordered porous structures of both COFs (Figs. 2(h) and 2(i)).

As illustrated in Figs. 2(j) and 2(k), electrostatic potential (ESP) mapping reveals that the negative electrostatic potential in both TFPT-TAPB-COF and TFPT-TCPB-COF is primarily localized on the triazine rings and cyano groups [41]. In both structures, the triazine units of TFPT act as the main electron-accepting centers, whereas TFPT-TCPB-COF further incorporates cyano groups as additional acceptor sites, thereby introducing an extra charge-transfer pathway. Consequently, TFPT-TAPB-COF and TFPT-TCPB-COF exhibit one and two charge-transfer channels,

respectively, leading to distinct electron migration pathways. In TFPT-TAPB-COF, electrons are transferred from the benzene donor units to the triazine acceptor units along the framework backbone. In contrast, TFPT-TCPB-COF enables electron transfer not only from benzene units to triazine units but also to the cyano groups located on the side chains. This dual charge-transfer pathway endows TFPT-TCPB-COF with enhanced donor-acceptor interactions (insets of Figs. 2(j) and 2(k)). As a result, the presence of multiple charge-transfer channels significantly promotes exciton dissociation and charge carrier mobility, thereby contributing to improved photocatalytic performance [42].

UV-vis diffuse reflectance spectroscopy (DRS) demonstrates that both COFs exhibit strong visible-light absorption (Fig. 3(a)). Tauc plot analysis reveals bandgaps of 2.62 eV for TFPT-TAPB-COF and 2.49 eV for TFPT-TCPB-COF. Notably, TFPT-TCPB-COF shows a slight red shift in the absorption edge, indicating enhanced light-harvesting capability, which can be attributed to its conjugated sp^2 carbon linkage [23]. To further elucidate the electronic structures, Mott-Schottky (MS) measurements were conducted at multiple frequencies (Fig. S8 in the ESM). The flat-band potentials (E_f) of TFPT-TAPB-COF and TFPT-TCPB-COF were determined to be -0.61 and -0.75 V (vs. Ag/AgCl), corresponding to conduction band potentials (E_c) of -0.41 and -0.55 V (vs. normal hydrogen electrode (NHE), pH = 7), respectively. Accordingly, the valence band potentials (E_v) were calculated to be 2.21 and 1.94 V, based on the relationship $E_g = E_v - E_c$. These band structures (Fig. 3(b)) indicate that both COFs are thermodynamically capable of driving H_2O_2 production via two-electron oxygen reduction (2e^- ORR) and water oxidation (2e^- WOR) pathways.

Beyond light absorption, charge separation and transport play critical roles in determining photocatalytic performance [43, 44]. The photoluminescence (PL) spectrum of TFPT-TCPB-COF exhibits a markedly lower emission intensity than that of TFPT-TAPB-COF (Fig. 3(c)), indicating suppressed electron-hole recombination and enhanced charge separation [45]. Consistently, TFPT-TCPB-COF displays a higher photocurrent density (Fig. 3(d)), reflecting improved charge separation efficiency and increased availability of surface charge carriers for photocatalytic reactions [46]. Electrochemical impedance spectroscopy further shows a smaller semicircle diameter in the Nyquist plot for TFPT-TCPB-COF, suggesting faster interfacial charge transfer (Fig. 3(e)) [47]. Moreover, time-resolved PL analysis reveals a longer average carrier lifetime for TFPT-TCPB-COF (8.18 ns) compared to TFPT-TAPB-COF (2.42 ns), confirming that the multiple charge-transfer pathways effectively promote charge separation and transport (Fig. 3(f)) [48].

Femtosecond time-resolved transient absorption (fs-TA) spectroscopy was employed to further investigate the photoexcited carrier dynamics of the two COFs (Figs. 3(g)–3(l)) [49]. Both TFPT-TAPB-COF and TFPT-TCPB-COF exhibit a negative transient absorption signal centered at $\sim 525\text{ nm}$, corresponding to ground-state bleaching (GSB), consistent with their steady-state absorption spectra. In addition, a positive excited-state absorption (ESA) band appears at $\sim 700\text{ nm}$ for both samples (Figs. 3(g) and 3(j)). The GSB signals spanning 400–650 nm are more intense for TFPT-TCPB-COF than for TFPT-TAPB-COF, indicating a higher photoexcitation efficiency in the former (Figs. 3(h) and 3(k)). The fitted kinetic analysis reveals that both TFPT-TCPB-COF and TFPT-TAPB-COF have two exponential decay processes, including

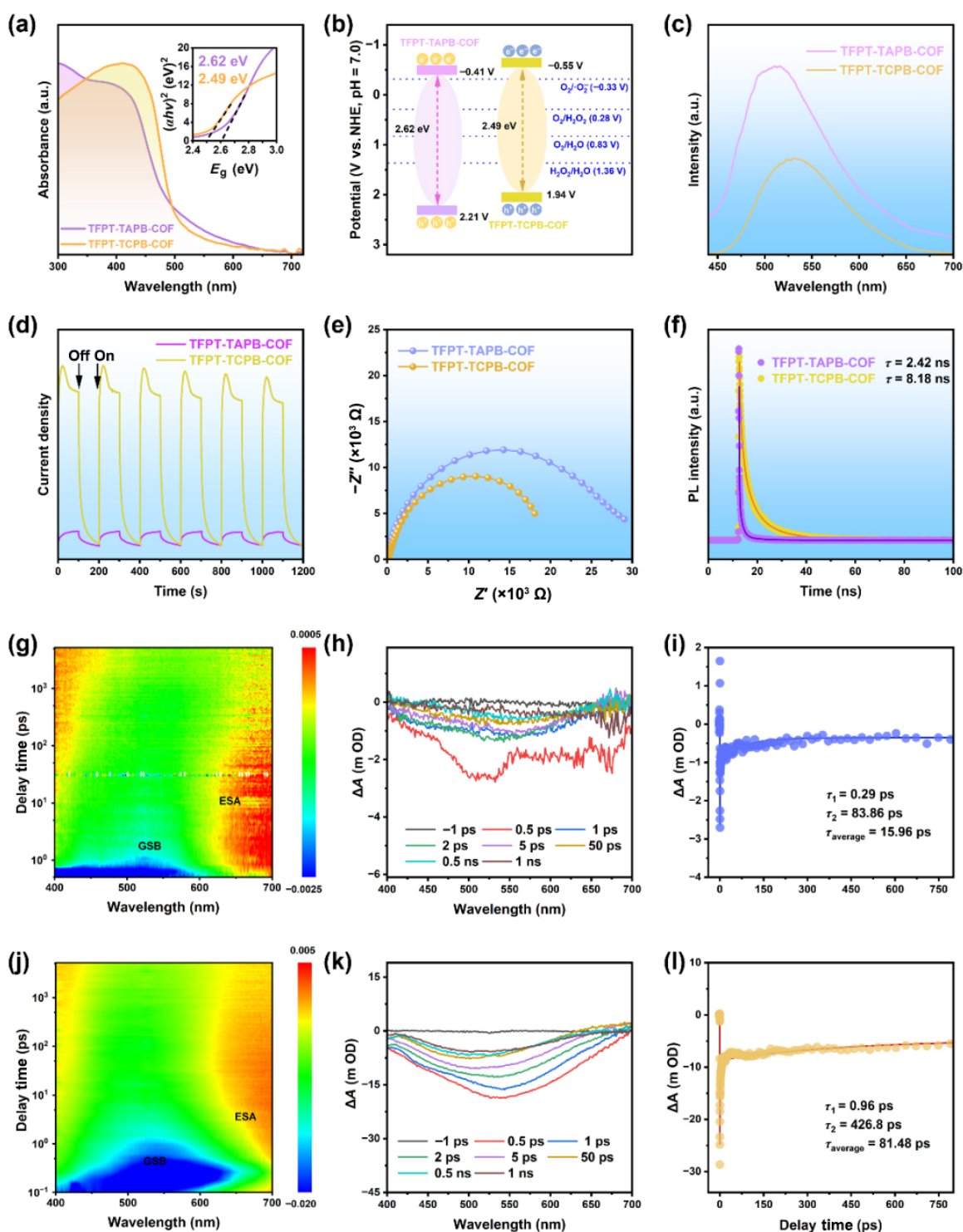


Figure 3 (a) UV-vis DRS spectra of TFPT-TAPB-COF and TFPT-TCPB-COF (inset: calculated Tauc plots). (b) Illustration of electronic band structures of TFPT-TAPB-COF and TFPT-TCPB-COF. (c) PL spectra of TFPT-TAPB-COF and TFPT-TCPB-COF. (d) Transient photocurrents of TFPT-TAPB-COF and TFPT-TCPB-COF. (e) Nyquist plots of TFPT-TAPB-COF and TFPT-TCPB-COF. (f) TRPL spectra of TFPT-TAPB-COF and TFPT-TCPB-COF. ((g) and (j)) Pseudocolor TA plots of (g) TFPT-TAPB-COF and (j) TFPT-TCPB-COF. ((h) and (k)) Transient TA spectra at different probe delays of (h) TFPT-TAPB-COF and (k) TFPT-TCPB-COF. ((i) and (l)) Decay kinetic curves of (i) TFPT-TAPB-COF and (l) TFPT-TCPB-COF.

the short lifetime (τ_1 , 0.29 ps for TFPT-TAPB-COF and 0.96 ps for TFPT-TCPB-COF) for electron trap and long lifetime (τ_2 , 83.86 ps for TFPT-TAPB-COF and 426.8 ps for TFPT-TCPB-COF) for the exciton recombination. In addition, TFPT-TCPB-COF possesses a significantly prolonged average excited-state lifetime (81.48 ps)

compared to TFPT-TAPB-COF (15.96 ps) that was obtained based on their τ_1 and τ_2 values (Figs. 3(i) and 3(l)). These results suggest more efficient exciton dissociation and reduced recombination of TFPT-TCPB-COF [50]. This improvement can be attributed to the presence of multiple charge-transfer pathways in TFPT-TCPB-

COF, arising from interactions among benzene donor units, triazine acceptors, and cyano groups. In contrast to the single-channel charge-transfer system in TFPT-TAPB-COF, the D-A-A architecture in TFPT-TCPB-COF enhances intramolecular charge transfer (ICT) efficiency [51]. Consequently, the improved ICT facilitates effective exciton separation and charge carrier migration, enabling the generation of a higher density of reactive charges for photocatalytic H_2O_2 production and ultimately leading to superior catalytic performance.

Inspired by the favorable photoelectric performance of TFPT-TCPB-COF, the photocatalytic H_2O_2 production performance of TFPT-TCPB-COF and reference TFPT-TAPB-COF sample was evaluated under full-spectrum irradiation, with H_2O_2 concentrations quantified using a cerium sulfate method (Fig. S9 in the ESM). Experimental details are provided in the ESM. As shown in Fig. 4(a), both COFs exhibit photocatalytic activity in pure water; however, TFPT-TCPB-COF demonstrates a significantly enhanced performance. The H_2O_2 concentration increases steadily with reaction time, reaching a production rate of $4.43 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is approximately 1.72 times higher than that of TFPT-TAPB-COF ($2.58 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and surpasses most reported COF-based systems under comparable conditions (Fig. 4(e)). In addition to its high activity, TFPT-TCPB-COF exhibits excellent stability, maintaining nearly unchanged photocatalytic performance over five consecutive cycles (Fig. 4(b)). The apparent quantum yield (AQY) of TFPT-TCPB-COF was further evaluated at different wavelengths (420–700 nm), reaching a maximum of 12.4% at 420 nm, which exceeds that of TFPT-TAPB-COF (11.8% at 420 nm) (Figs. 4(c) and 4(f)). Structural stability was also confirmed by PXRD and FT-IR analyses, which show negligible changes after photocatalysis (Figs. S11 and S12 in the ESM). Moreover, TEM observations indicate that the morphology of TFPT-TCPB-COF remains

essentially intact after the reaction (Fig. S13 in the ESM), highlighting its robust structural integrity for sustained H_2O_2 production. Based on above results, the sp^2 carbon-linked D-A-A system with rich effective reductive active units (triazine ring and cyano moiety) rather than the BET surface area plays the key role in improving the photocatalytic H_2O_2 production activity.

To elucidate the photocatalytic mechanism of H_2O_2 production over TFPT-TCPB-COF, a series of control experiments were performed. As shown in Fig. 4(d), photocatalytic activity was evaluated under air, N_2 , and dark conditions [52–54]. Under air ($\text{O}_2:\text{N}_2 = 21:79$), TFPT-TAPB-COF and TFPT-TCPB-COF exhibit H_2O_2 production rates of 1.12 and $4.23 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, with the superior performance of TFPT-TCPB-COF further highlighting its enhanced photocatalytic efficiency. In contrast, only a negligible amount of H_2O_2 is detected under a N_2 atmosphere, indicating that O_2 is the primary reactant and that H_2O_2 formation predominantly proceeds via the ORR pathway. Moreover, no detectable H_2O_2 is produced in the absence of light, confirming that photoexcitation is essential for the reaction. To further probe the reaction pathway, potassium iodate (KIO_3) and p-benzoquinone (p-BQ) were employed as scavengers for electrons (e^-) and superoxide radicals ($\cdot\text{O}_2^-$), respectively [55]. The addition of KIO_3 markedly suppresses H_2O_2 production, demonstrating the critical role of photogenerated electrons in driving the ORR process. More importantly, the presence of p-BQ scavenger for $\cdot\text{O}_2^-$ completely inhibits H_2O_2 formation, indicating that $\cdot\text{O}_2^-$ serves as a key intermediate during the $2e^-$ ORR process. These results suggest that the ORR proceeds predominantly via a stepwise single-electron pathway ($\text{O}_2 \rightarrow \cdot\text{O}_2^- \rightarrow \text{H}_2\text{O}_2$).

To identify the reactive oxygen species involved in the ORR process, electron paramagnetic resonance (EPR) spectroscopy was conducted using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a

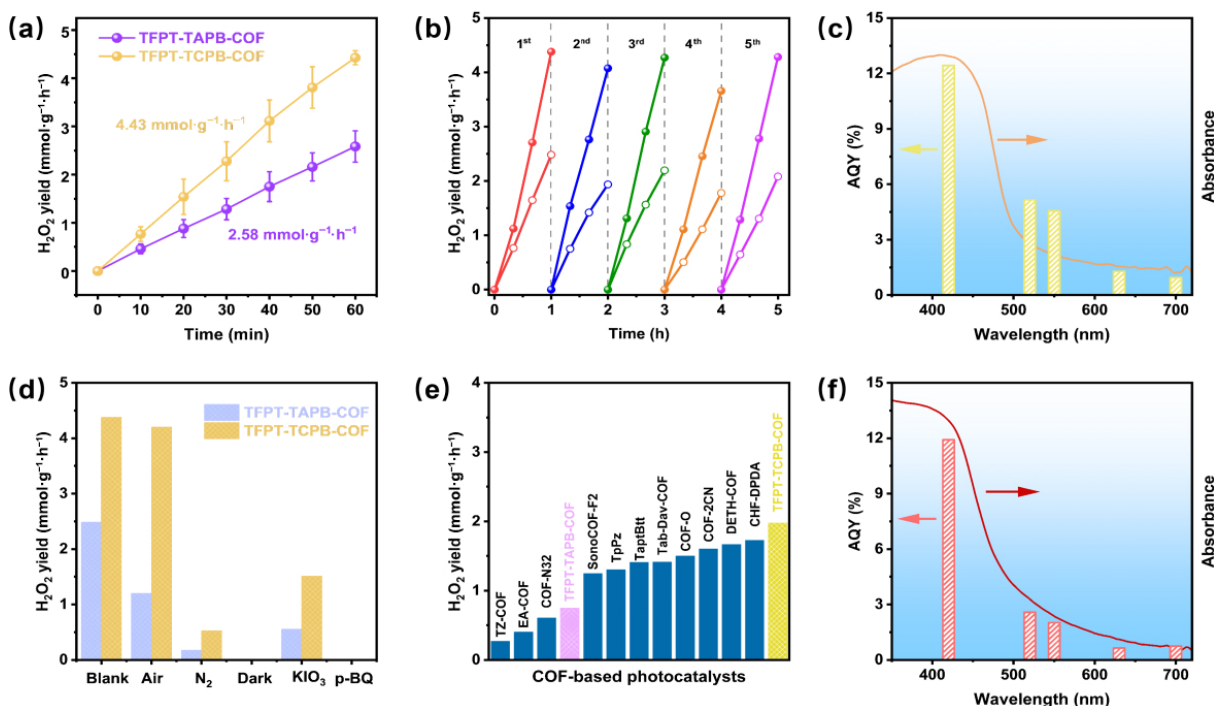


Figure 4 (a) The photocatalytic performance of H_2O_2 production using full-spectrum illumination for TFPT-TAPB-COF and TFPT-TCPB-COF. (b) Photocatalytic H_2O_2 synthesis cycles stability of TFPT-TAPB-COF and TFPT-TCPB-COF. (c) and (f) AQY of (c) TFPT-TCPB-COF and (f) TFPT-TAPB-COF. (d) The photocatalytic performance of H_2O_2 production under different conditions. (e) The comparison of H_2O_2 photosynthesis rates of TFPT-TAPB-COF and TFPT-TCPB-COF with other reported photocatalysts under visible light.

spin-trapping agent [55]. As shown in Fig. 5(a), characteristic DMPO- $\cdot\text{O}_2^-$ signals are observed for both TFPT-TAPB-COF and TFPT-TCPB-COF, confirming the formation of superoxide radicals. Quantitative analysis based on the nitroblue tetrazolium (NBT) method further reveals that TFPT-TCPB-COF generates a higher concentration of $\cdot\text{O}_2^-$ compared to TFPT-TAPB-COF (Fig. S15 in the ESM), indicating more efficient electron transfer for superoxide formation. To further elucidate the photocatalytic mechanism, *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed under visible-light irradiation in the presence of O_2 and H_2O [32, 49]. As shown in the DRIFT image in Fig. 5(b), the intensity of the vibration band at 1028 cm^{-1} , assigned to $\cdot\text{OH}$ intermediates, increases progressively with irradiation time, suggesting the involvement of water oxidation. Additionally, characteristic bands corresponding to O-O (978 cm^{-1}) and $\cdot\text{O}_2^-$ (1180 cm^{-1}) are observed, confirming the stepwise reduction of adsorbed O_2 to superoxide species. As a result, the p-BQ quenching combined with DRIFT test synergistically demonstrates the photocatalytic ability of TFPT-TCPB-COF for both ORR and WOR, promoting efficient H_2O_2 photosynthesis. Rotating ring-disk electrode (RRDE) measurements were conducted to evaluate the $2e^-$ WOR pathway and its selectivity. When the Pt ring electrode was held at $+0.6\text{ V}$ vs. Ag/AgCl, pronounced oxidation currents were detected within the potential range of $1.3\text{--}2.4\text{ V}$ vs. reversible hydrogen electrode (RHE) (Fig. S16 in the ESM), indicating H_2O_2 generation via the $2e^-$ WOR pathway. In contrast, only a weak reduction current was observed at -0.23 V vs. Ag/AgCl, confirming the suppression of the competing $4e^-$ pathway. Furthermore, RRDE analysis of the ORR process shows an average H_2O_2 selectivity of $\sim 70\%$ within $0.10\text{--}0.35\text{ V}$ vs. RHE, with a corresponding electron transfer

number (n) of 2.59 (Fig. S17 in the ESM), demonstrating the preferential $2e^-$ ORR pathway on TFPT-TCPB-COF. The inadequate H_2O_2 selectivity of 70% could be attributed to different $2e^-$ selectivity among triazine, cyano, and benzene ring active sites with distinct electronic structures and intermediate binding affinities. Specifically, triazine and cyano groups are electron-withdrawing, which typically stabilize the key $\cdot\text{O}_2^-$ intermediate and favor the $2e^-$ ORR pathway. In contrast, benzene rings are electron-rich and may facilitate O-O bond cleavage, leading to partial $4e^-$ reduction.

Theoretical calculations based on partial density of states (PDOS) analysis indicate that the valence band maximum (VBM) and conduction band minimum (CBM) of both COFs are predominantly composed of C 2p orbitals, reflecting strong π -electron delocalization within their frameworks (Fig. S18 in the ESM). Notably, TFPT-TCPB-COF exhibits a higher contribution of N 2p and C 2p orbitals near the CBM ($1\text{--}2\text{ eV}$) compared to TFPT-TAPB-COF, suggesting enhanced electron-accepting capability and more efficient charge transfer, which is beneficial for the photocatalytic ORR process [42, 56]. Density functional theory (DFT) calculations were further conducted to elucidate the electronic structures and reaction mechanisms [57–59]. The highest occupied molecular orbital (HOMO) of TFPT-TCPB-COF is mainly localized on the benzene and triazine units, whereas LUMO is primarily distributed over the triazine and cyano groups (Fig. S19 in the ESM), indicating electron transfer from benzene donors to both triazine and cyano acceptors. In contrast, TFPT-TAPB-COF exhibits electron transfer from benzene donors to imine and triazine acceptors. Based on these charge distributions, the free energy profiles for H_2O_2 production via the two-electron ORR and WOR pathways were calculated [4, 60]. As can be observed in Figs. 5(c) and 5(f), for both TFPT-TAPB-COF and TFPT-TCPB-

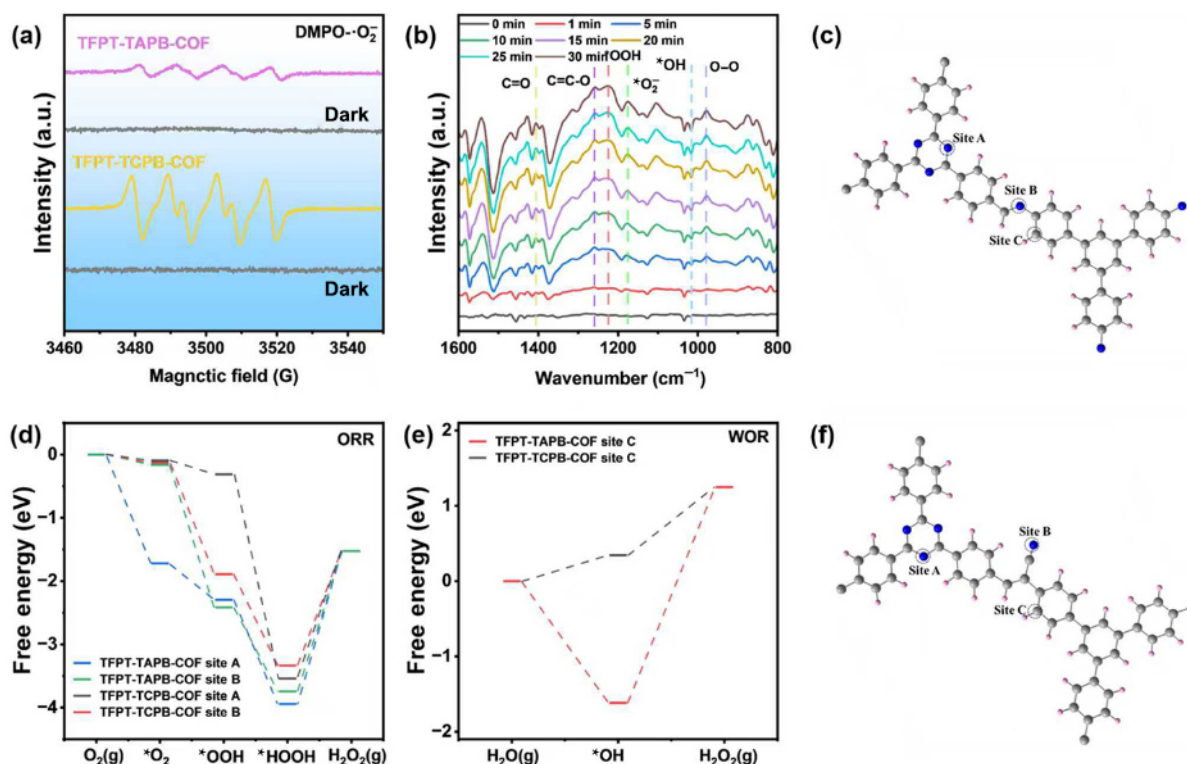


Figure 5 (a) EPR spectra of DMPO- $\cdot\text{O}_2^-$ of TFPT-TAPB-COF and TFPT-TCPB-COF under visible-light irradiation ($\lambda > 420\text{ nm}$) and dark conditions. (b) *In situ* DRIFT spectra of TFPT-TCPB-COF with a certain amount of H_2O and O_2 . ((c) and (f)) The O_2 and H_2O adsorption site of (c) TFPT-TAPB-COF and (f) TFPT-TCPB-COF. ((d) and (e)) Calculated energy profile for (d) oxidation of water into H_2O_2 and (e) reduction of oxygen into H_2O_2 on COFs at $U = 0\text{ V}$ vs. NHE at pH = 7.

COF, sites A and B act as the role for adsorbing H_2O receives and site C acts as the role for adsorbing O_2 . As shown in Fig. 5(d), H_2O_2 desorption is identified as the rate-determining step (RDS) for the ORR pathway in both COFs. Importantly, TFPT-TCPB-COF exhibits lower energy barriers for this step at both active sites compared to TFPT-TAPB-COF, with the lowest barrier observed at the cyano N site (site B), consistent with its superior catalytic performance. For the WOR pathway (Fig. 5(e)), the conversion of $^*\text{OH}$ to H_2O_2 is the RDS, and TFPT-TCPB-COF again shows a reduced energy barrier relative to TFPT-TAPB-COF, further confirming its enhanced catalytic efficiency.

4 Conclusions

In summary, two triazine-based 2D COFs, namely imine-linked TFPT-TAPB-COF and sp^2 carbon-linked TFPT-TCPB-COF, were successfully constructed with high crystallinity and porosity for photocatalytic H_2O_2 production. The integration of robust sp^2 carbon linkages with a D–A–A architecture in TFPT-TCPB-COF not only enhances electrical conductivity but also facilitates exciton separation and charge transport, thereby significantly improving charge transfer dynamics, as confirmed by comprehensive optoelectronic characterizations. Compared with TFPT-TAPB-COF, TFPT-TCPB-COF exhibits superior optoelectronic properties and markedly enhanced photocatalytic performance for H_2O_2 production from O_2 and H_2O . Moreover, the enhanced chemical stability imparted by the irreversible sp^2 carbon framework further supports its practical applicability. DFT calculations reveal that the rationally designed sp^2 -conjugated D–A–A framework plays a critical role in promoting both the two-electron oxygen reduction and water oxidation pathways. Overall, this work provides valuable insights into the rational design of high-performance COF-based photocatalysts for sustainable chemical synthesis.

Electronic Supplementary Material: Supplementary materials (experimental details, supplementary Figures S1–S19, and Tables S1–S3) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908941>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the supplementary materials. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Z. P. W. and J. F.: Data curation, validation, writing manuscript,

experimental design. G. X. Z., Z. W., and S. L. Z.: Data curation, validation, writing manuscript. Z. P. L. and T. T. S.: Project administration, writing manuscript, experimental design, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

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