

Regulating the Electronic Structure of Covalent Organic Frameworks via Heterocyclic Isomers for Highly Efficient Photocatalytic H₂O₂ Generation

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This study presents the fabrication of four COFs functionalized with thiophene and furan isomers and evaluates their performance in the photoproduction of H₂O₂. The authors propose a mechanism for precisely tuning electronic structures, offering valuable insights for the rational design of high-performance photocatalysts for H₂O₂ synthesis. The functionalized COFs and their activity in H₂O₂ photoproduction have been systematically investigated. This contribution would be valuable with the following discussion points being addressed.

1. Thiophene and furan isomers are famous electron-rich heterocyclic compounds which have been used as functionalized building blocks to modulate the electrical/optical properties and structures of COFs. The advantage of using DT2TA, DT3TA, DF2TA, and DF3TA to tune the electronic structure of COFs is suggested to be highlighted.
2. The experimental XRD patterns align with the simulated AA-stacking XRD pattern, as indicated by the sharp diffraction peaks corresponding to the (100), (110), and (210) facets. However, additional diffraction peaks observed in the experimental XRD patterns remain unresolved. Why does the experimental XRD pattern of DT2TA-TAPB (Fig. 2a) differ significantly from those of other samples (Figs. 2b-d)? While the authors propose an electronic structure mechanism, it is complicated by the ambiguity in the XRD analysis. It is crucial to elucidate these unidentified diffraction peaks, given that DT2TA-TAPB demonstrates the highest H₂O₂ photoproduction performance among the four functionalized COFs.
3. In the steady-state PL measurements (Supplementary Figure 6), the authors should provide discussions for the discrepancy observed in the PL baseline positions among the four COFs. In the TR-PL decay PL measurements (Supplementary Figure 7), the longer PL lifetime of DT2TA-TAPB was attributed to the retarded photogenerated charge recombination. It is recommended that the authors provide further discussions to support this attribution.
4. The experimental conditions used for obtaining the electrochemical data (e.g., EIS Nyquist, Tauc, and Mott-Schottky plots of COFs shown in Supplementary Figure 8, Figure 11, and Figure 12) are suggested to be given.
5. Temperature-dependent PL spectra, two-dimensional pseudo-color of fs-TA spectra, TA decay kinetic curves, and transient absorption spectra of DF2TA-TAPB and DF3TA-TAPB are recommended to be included as reference groups.
6. Please check Figs. 3b-g, Fig. 4f, and Fig. 4g. Number them according to the sequence they appear in the manuscript. Additionally, it may not be appropriate to compare the H₂O₂ photoproduction performance of the well-engineered DT2TA-TAPB with that of pristine carbon nitride.
7. The formation (kf) and decomposition (kd) kinetics of H₂O₂ on the surface of DT2TA-TAPB are suggested to be given. Long-term experiments should be performed to investigate the plateau of H₂O₂ photoproduction.
8. DT2TA-TAPB exhibited higher H₂O₂ photoproduction, whereas the intensity of DMPO-•O₂- adducts measured in the DT2TA-TAPB suspension was lower than that observed in the DT3TA-TAPB suspension (Fig. 5b and 5c). The signals of DMPO-•O₂- adducts obtained from prolonged experiments are recommended to be provided.
9. RRDE measurements are recommended to be performed as supplementary experiments for comparison with RDE measurements (Fig. 5f).

Reviewer #2

(Remarks to the Author)

The authors have designed and synthesized four thiophene- and furan-based COFs for photocatalytic H₂O₂ production under visible light illumination. They conducted detailed experimental and theoretical analyses, including investigations into the underlying mechanisms. While the study demonstrates significant potential, there are several critical concerns that need to be addressed before it can be considered suitable for publication in this high-impact journal:

- 1) The infrared spectra of DT2TA-TAPB and DF3TA-TAPB show obvious noise and need to be remeasured. Additionally, for DT2TA-TAPB, DT3TA-TAPB, and DF3TA-TAPB, the presence of C=O functional groups suggests that some unreacted starting materials remain in the products. Please give reasonable explanation.
- 2) The single-crystal data does not include the R1 and wR2 values, please provide the related information. It is necessary to provide details of the single-crystal testing instrument and methods.
- 3) To enable a comprehensive comparison, femtosecond time-resolved transient absorption spectra for DF2TA-TAPB and DF3TA-TAPB should be included and thoroughly discussed to provide insights into their photophysical processes.
- 4) To ensure accuracy and reproducibility of the performance data, error bars should be included in Fig. 4c-e.
- 5) The stability of the COF catalysts, particularly the best-performing sample (DT2TA-TAPB), needs further evaluation. Recyclability tests and post-experiment characterizations such as XRD, SEM, and IR should be conducted after long-term experiments or recycling tests.
- 6) Photocurrent response experiments should be carried out to assess the efficiency of photogenerated electron-hole separation in the COF samples.

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4

(Remarks to the Author)

The manuscript presented a COF-based photocatalyst that efficiently catalyzes O₂ reduction to generate H₂O₂ in the 10% EtOH/water solution. Comprehensive characterizations for the COF materials and systematic mechanistic investigations for the ORR reaction were conducted. The author found that 1) compared to furan, thiophene functional groups can enhance the charge carrier separation in the excited states and promote charge transfer; 2) a special pattern of sulfur and the adjacent carbon in the thiophene group can better adsorption of the reaction substrate, O₂, and stabilize the ORR intermediates. It is also impressive that the catalytic materials can produce H₂O₂ without the hole scavenger. The reviewer believes the argument of the manuscript can be strengthened after addressing the following points.

1) The data presented here suggested that COFs with thiophene, especially DT2TA-TAPB, possess an excited state (S1) with a charge-separated feature, as illustrated in Figure 1 and 3. It is plausible that this charge-separated S1 in DT2TA-TAPB favors electron transfer to O₂, which explains its better ORR performance. However, it is confusing that the authors are trying to characterize the "exciton dissociation" process within the COFs using temperature-dependent PL. The decrease of PL quantum yield with the increasing temperature occurs in most materials, including organic molecules, due to enhancing non-radiative pathways, such as internal conversion and intersystem crossing. There is no justification to attribute the decrease in PL intensity to exciton dissociation. If there is a further "exciton dissociation" process, what is the product state the author referred to? Is there a charge-separated electronic state lying below the S1? The method that the authors applied to estimate the dissociation barrier can be traced back to a work that employed temperature-dependent PL to analyze exciton dissociation in ZnO (Misra et al. Current Applied Physics, 2009), where both the conversion between bound and free excitons was observed in the PL spectra. The scenario is quite different since Frenkel excitons in organic systems generally have much greater exciton binding energy and remain localized.

2) The interpretation of transient absorption data made the mechanism even more confusing. In line 186, the authors attributed the two decay components in the ground state bleach signal kinetics monitored at 580 nm to the electron trapping (fast, τ_1) and the electron transfer processes (slow, τ_2) without rational justification. In fact, following this initial assignment, in line 189, the authors started to refer to the slower decay process (τ_2) as carrier recombination, a completely different process. Could the authors fix this assignment?

The reviewer attempted but eventually failed to interpret the TA data presented in the manuscript due to the lack of experimental details. It is essential to add the following information or supplementary information for clarification. 1) The pump irradiance. The validity of TA measurements requires correct choices of pump irradiance, especially for solid-state samples. Even without considering possible photodegradation caused by the high energy pump pulse, the kinetics can depend on the exciton density related to the photon flux. For instance, high irradiance above certain thresholds can cause biexciton annihilation, and the kinetics will be skewed. A pump power-dependence experiment will be helpful to justify whether the reported kinetics correctly reflected a single exciton decay process. 2) The atmosphere of the TA experiments. Based on the reaction mechanism proposed in the manuscript, if O₂ was present, TA would record the electron transfer

process from COFs to O₂, whereas intrinsic exciton decay would be the primary process observed in the inert atmosphere.

3) The solvent. Whether there are sacrificial hole scavengers (in this case, 10%v alcohol) in the system would also change the TA kinetics due to the hole transfer process. The reviewer suggests the authors think carefully about the abovementioned experimental parameters and provide them in an appropriate form in the revised manuscript. They should also reconsider what photochemical processes the TA data actually monitors.

3) The manuscript claimed a high yield of H₂O₂ for the photocatalyst in pure water without using a sacrificial electron donor. If there is no sacrificial reagent and the photocatalyst cannot oxidize water, as implied in the manuscript, I assume that the reaction will consume electrons in the photocatalyst, which will eventually cause the degradation of the photocatalyst. In the supplementary Figure 14, the yield of H₂O₂ increases linearly with the reaction time without a decline. Could the author explain where the electron comes from when no hole scavenger was presented.?

4) It is unclear how the authors defined electrons and the holes in the S₁ states of different COFs, as illustrated in Figures 1 and 3. Do the different color-shaded regions reflect the negative and positive charge distribution of the S₁ or the HOMO and LUMO of the ground state? The author should clarify how they interpreted the computational data. In fact, it was unclear if the DFT calculation was carried out for the ground state or if the authors conducted time-dependent DFT calculations to obtain the electronic structure of the excited state. More details about how the calculations were carried out must be provided in the supplemental information 1.11.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The revised manuscript addressed all the raised issues properly and is now ready for publication. I have no further comments.

Reviewer #2

(Remarks to the Author)

The authors have adequately addressed my previous concerns.

I have no additional comments, and I support the publication of the manuscript.

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4

(Remarks to the Author)

The authors addressed my concerns accurately. The manuscript is now suitable for publication.

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Point-to-Point Responses to the Reviewers' Comments (Manuscript ID: NCOMMS-24 80047)

As detailed below (black font: reviewers' comments; blue font: our responses; red font: revisions made in the manuscript).

Reviewer #1 (Remarks to the Author):

Overall comments: This study presents the fabrication of four COFs functionalized with thiophene and furan isomers and evaluates their performance in the photoproduction of H₂O₂. The authors propose a mechanism for precisely tuning electronic structures, offering valuable insights for the rational design of high-performance photocatalysts for H₂O₂ synthesis. The functionalized COFs and their activity in H₂O₂ photoproduction have been systematically investigated. This contribution would be valuable with the following discussion points being addressed.

Response: We sincerely appreciate the reviewer's positive comments and helpful suggestions, which have significantly improved the overall quality of the manuscript. We hope that the revised manuscript may be favorably considered for publication in *Nature Communications*.

Comments 1: Thiophene and furan isomers are famous electron-rich heterocyclic compounds which have been used as functionalized building blocks to modulate the electrical/optical properties and structures of COFs. The advantage of using DT₂TA, DT₃TA, DF₂TA, and DF₃TA to tune the electronic structure of COFs is suggested to be highlighted.

Response 1: Thank you for your feedback and suggestions. The advantages of using DT₂TA, DT₃TA, DF₂TA, and DF₃TA to tune the electronic structure of COFs are summarized as follows: (1) **Enhancing light absorption and charge transport:** The electron-rich nature of thiophene and furan influences the π -conjugated framework of COFs, thereby enhancing light-harvesting capabilities and facilitating carrier migration (*Nat Commun.* 2024, **15**, 4856; *Angew. Chem. Int. Ed.* 2023, **62**, e202216751); (2) **Regulating pore structure and surface chemistry:** The steric effects and connectivity orientations of thiophene and furan allow precise control over pore size and surface functionality, influencing electron transfer dynamics and pore structures (*Angew. Chem. Int. Ed.* 2024, **63**, e202320037); (3) **Enhancing chemical stability and reactivity:** The incorporation of sulfur in thiophene and oxygen in furan imparts distinct chemical stability and reactivity, improving both chemical stability and functional tunability of COFs (*J. Am. Chem. Soc.* 2020, **142**, 13316–13321).

Despite the substantial advantages of thiophene and furan isomers in optimizing the performance of COFs, their impact on photocatalytic H₂O₂ production remains unexplored. Notably, incorporating thiophene and furan isomers into COFs not only enables precise isomeric regulation but also offers deeper insights into the influence of elements from the same main group across different periods on the electronic structure. This dual-regulation strategy provides a unique approach to fine-tuning electronic structure, offering new perspectives for COF design and photocatalytic applications.

The additions in the manuscript are as follows:

“The incorporation of thiophene units effectively broadened the light absorption range and facilitated charge carrier separation^{1,2}. In addition, thiophene isomers modulated electron transfer direction in electrocatalysis³, while benzofuran improved COFs structural stability⁴. However, despite the promising potential of thiophene and furan in photocatalytic H₂O₂ generation, the simultaneous regulation of heterocyclic conformation and heteroatom type to precisely tune the electronic structure has yet to be explored.” (Page 3, Lines 73-78)

The cited references as follows:

1. Fang, Y. et al. Design and synthesis of broadband absorption covalent organic framework for efficient artificial photocatalytic amine coupling. *Nat. Commun.* **15**, 4856 (2024).
2. Bao, R. et al. Designing Thiophene-Enriched Fully Conjugated 3D Covalent Organic Framework as Metal-Free Oxygen Reduction Catalyst for Hydrogen Fuel Cells. *Angew. Chem. Int. Ed.* **62**, e202216751 (2023).
3. Wang, Q. et al. Positional Thiophene Isomerization: A Geometric Strategy for Precisely Regulating the Electronic State of Covalent Organic Frameworks to Boost Oxygen Reduction. *Angew. Chem. Int. Ed.* **63**, e202320037 (2024).
4. Su, Y. et al. Crystalline and Stable Benzofuran-Linked Covalent Organic Frameworks from Irreversible Cascade Reactions. *J. Am. Chem. Soc.* **142**, 13316–13321 (2020).

Comments 2: The experimental XRD patterns align with the simulated AA-stacking XRD pattern, as indicated by the sharp diffraction peaks corresponding to the (100), (110), and (210) facets. However, additional diffraction peaks observed in the experimental XRD patterns remain unresolved. Why does the experimental XRD pattern of DT₂TA-TAPB (Fig. 2a) differ significantly from those of other samples (Figs. 2b-d)? While the authors propose an electronic structure mechanism, it is complicated by the ambiguity in the XRD analysis. It is crucial to elucidate these unidentified diffraction peaks, given that DT₂TA-TAPB demonstrates the highest H₂O₂ photoproduction performance among the four functionalized COFs.

Response 2: Thank you for your constructive suggestions. In PXRD patterns, sharp diffraction peaks typically indicate well-ordered crystal structures, while broadened peaks reflect poor

crystallinity of the sample (*J. Am. Chem. Soc.* 2024, **146**, 16609–16618; *Chem. Mater.* 2011, **23**, 4094–4097). For samples with poor crystallinity, PXRD patterns generally exhibit weak, and unassignable diffraction peaks, which are commonly attributed to disorder or defects. The weak and unassigned diffraction peaks observed in DT₂TA-TAPB resulted from the incorporation of DT₂TA units with large steric bulk, disrupting the crystallization process and reducing the crystallinity (*Angew. Chem. Int. Ed.* 2023, **62**, e202315456; *J. Am. Chem. Soc.* 2023, **145**, 21798–21806; *J. Am. Chem. Soc.* 2024, **146**, 21025–21033).

Previous studies have shown that COFs crystallinity can be improved by adjusting reaction time (*Adv. Mater.* 2024, **36**, 2314056). Based on these findings, we optimized the PXRD patterns of DT₂TA-TAPB by varying the reaction time. As illustrated in **Figure R1**, upon extending the reaction time from 3 to 7 days, the unassigned and weak diffraction peaks observed in the PXRD pattern of DT₂TA-TAPB gradually disappeared, indicating a significant improvement in crystallinity. We also evaluated the catalytic performance of DT₂TA-TAPB synthesized with different reaction durations, and the results indicated no significant difference in H₂O₂ yield between samples synthesized for 3 and 7 days. These findings suggest that the improvement in crystallinity does not alter the conclusions drawn from our previous research.

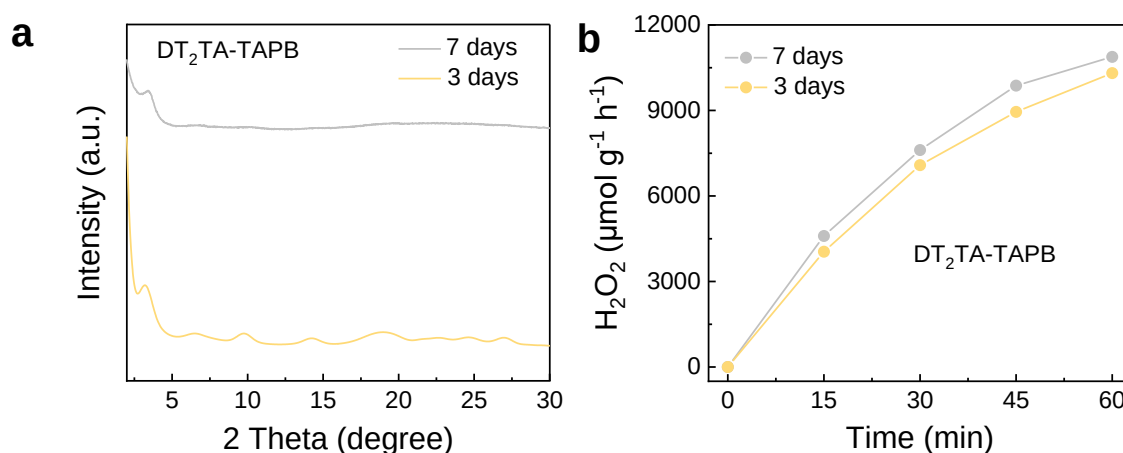


Figure R1 (a) PXRD patterns of DT₂TA-TAPB at different reaction different times. (b) Comparison of the performance of DT₂TA-TAPB at different reaction times.

The additions in the manuscript are as follows:

“Additionally, several weak and unassigned diffraction peaks were observed, likely attributable to the significant steric hindrance of DT₂TA molecules^{1,2}. This steric effect interfered with molecular arrangement, disrupted the crystallization process and ultimately led to reduced crystallinity³.” (Page 5, Lines 107-110)

The cited references as follows:

1. Hao, F. et al. Photo-Driven Quasi-Topological Transformation Exposing Highly Active Nitrogen Cation Sites for Enhanced Photocatalytic H₂O₂ Production. *Angew. Chem. Int. Ed.* **62**, e202315456 (2023).
2. Tong, L. et al. Atomically Precise Regulation of the N-Heterocyclic Microenvironment in Triazine Covalent Organic Frameworks for Coenzyme Photocatalytic Regeneration. *J. Am. Chem. Soc.* **146**, 21025–21033 (2024).
3. Pelkowski, C. E. et al. Tuning Crystallinity and Stacking of Two-Dimensional Covalent Organic Frameworks through Side-Chain Interactions. *J. Am. Chem. Soc.* **145**, 21798–21806 (2023).

Comments 3: In the steady-state PL measurements (Supplementary Figure 6), the authors should provide discussions for the discrepancy observed in the PL baseline positions among the four COFs. In the TR-PL decay PL measurements (Supplementary Figure 7), the longer PL lifetime of DT₂TA-TAPB was attributed to the retarded photogenerated charge recombination. It is recommended that the authors provide further discussions to support this attribution.

Response 3: We sincerely thank the reviewer for the valuable comments. The discrepancy in the PL baseline positions was attributed to variations in surface roughness among the COF samples, which likely affected the initial measurements. To ensure accuracy and reproducibility, we optimized the measurement conditions and repeated the experiments. As shown in **Figure R2**, the revised PL spectra exhibited consistent baseline positions. The manuscript has been updated accordingly to reflect the corrected data.

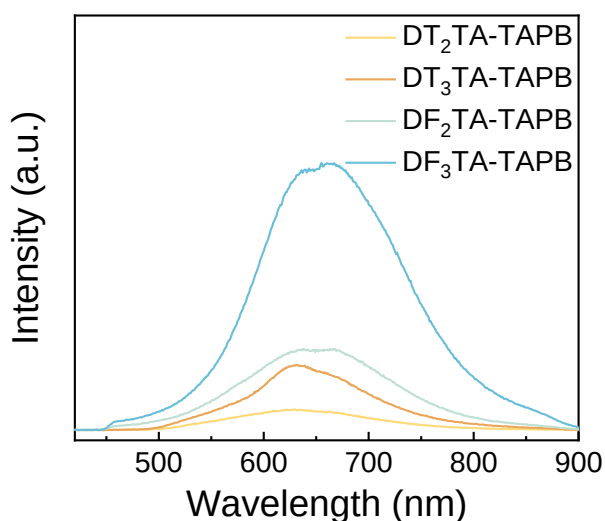


Figure R2 (Supplementary Fig. 6). Steady-state PL spectra of the COFs (excitation wavelength was 400 nm).

We are grateful to the reviewer for the insightful suggestion. Time-resolved photoluminescence (TR-PL) measurements revealed distinct differences in carrier lifetimes among the COFs. As depicted in **Figure R3**, DT₂TA-TAPB exhibited the longest PL lifetime (0.60 ns), surpassing DT₃TA-TAPB (0.45 ns), DF₂TA-TAPB (0.35 ns), and DF₃TA-TAPB (0.29 ns). This prolonged

lifetime was ascribed to the effective suppression of non-radiative recombination (*J. Am. Chem. Soc.* 2023, **145**, 18366-18381), which enhanced charge separation and promoted the migration of charge carriers to catalytic sites, thereby facilitating photocatalytic activity (*Nat. Commun.* 2023, **14**, 1106).

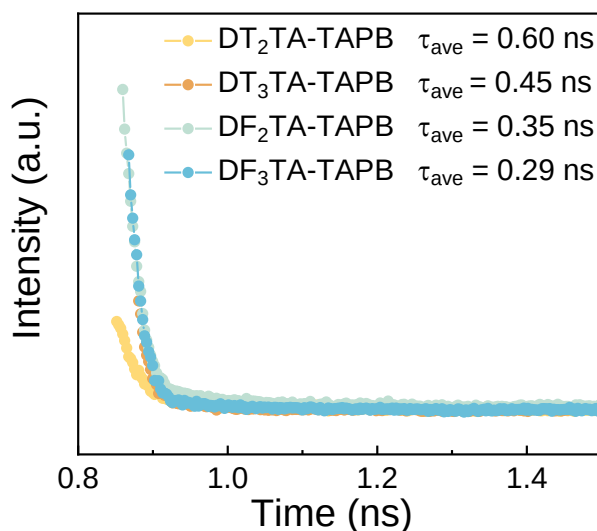


Figure R3 (Supplementary Fig. 7). TR-PL decay curves of the COFs.

The additions in the manuscript are as follows:

“As depicted in Supplementary Fig. 7, the PL lifetimes of DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB were 0.60, 0.45, 0.35, and 0.29 ns, respectively. Notably, the longest PL lifetime observed for DT₂TA-TAPB was attributed to its effective suppression of non-radiative recombination, which enhanced charge separation and facilitated the migration of photogenerated carriers to catalytic sites, thereby promoting photocatalytic activity^{1,2}.” (Page 7, Lines 151-155)

The cited references as follows:

1. Hojo, R. et al. Imidazophenothiazine-Based Thermally Activated Delayed Fluorescence Materials with Ultra-Long-Lived Excited States for Energy Transfer Photocatalysis. *J. Am. Chem. Soc.* **145**, 18366–18381 (2023).
2. Zhang, L. et al. Structurally Locked High-Crystalline Covalent Triazine Frameworks Enable Remarkable Overall Photosynthesis of Hydrogen Peroxide. *J. Am. Chem. Soc.* **146**, 29943–29954 (2024).

Comment 4: The experimental conditions used for obtaining the electrochemical data (e.g., EIS Nyquist, Tauc, and Mott-Schottky plots of COFs shown in Supplementary Figure 8, Figure 11, and Figure 12) are suggested to be given.

Response 4: We appreciate the reviewer’s valuable suggestion. The experimental conditions for electrochemical measurements have been added to the revised supplementary information.

The additions in the supplementary information are as follows:

Electrochemical impedance spectroscopy (EIS) measurement

“EIS measurements were performed using a Gamry electrochemical workstation (Interface 5000E, USA) equipped with a three-electrode cell system. The working electrode was prepared by dispersing 2 mg of catalyst in a mixed solution of 0.9 mL EtOH, 0.1 mL water, and 10 μ L Nafion, followed by sonication to ensure uniform dispersion. The resulting suspension was drop-cast onto a fluorine-doped tin oxide (FTO) substrate and allowed to dry at ambient conditions. A platinum wire served as the counter electrode, while an Ag/AgCl electrode functioned as the reference electrode. The electrolyte solution consisted of 0.5 mol·L⁻¹ Na₂SO₄ solution and 0.1 mol·L⁻¹ K₃[Fe(CN)₆]. EIS measurements were performed in the dark to evaluate the charge transfer resistance (R_{ct}) of the samples. The reference electrode was set to 0 V, and the frequency range was from 100000 Hz to 0.01 Hz.” (Page S11-12, Lines 180-190)

Tauc plot analysis

“The optical band gap energy of the photocatalyst was determined using the Tauc plot method based on the solid-state UV-vis spectrum. The band gap was calculated using the Tauc equation (4):

$$(\alpha h\nu)^{(1/n)} = A(h\nu - E_g) \quad (4)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the band gap energy, and A is a proportionality constant.

The band gap was estimated by plotting $(\alpha h\nu)^{1/n}$ against $h\nu$ and extrapolating the linear portion of the curve which intersected the horizontal axis.” (Page S-12, Lines 191-199)

Mott-Schottky measurement

“Mott-Schottky measurements were performed using a Gamry electrochemical workstation (Interface 5000E, USA) in a three-electrode cell system. The working electrode was prepared by dispersing 2 mg of catalyst in a solution of 0.9 mL ethanol, 0.1 mL water, and 10 μ L Nafion, followed by sonication to ensure uniform dispersion. The suspension was drop-cast onto an FTO substrate and dried at room temperature. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively, with 0.5 mol·L⁻¹ Na₂SO₄ solution as the electrolyte. Measurements were carried out at three different frequencies (1000 Hz, 2000 Hz, and 3000 Hz) over a potential range of -1 V to 1 V.” (Page S-12, Lines 200-208)

Comment 5. Temperature-dependent PL spectra, two-dimensional pseudo-color of fs-TA spectra, TA decay kinetic curves, and transient absorption spectra of DF₂TA-TAPB and DF₃TA-TAPB are recommended to be included as reference groups.

Response 5: We sincerely appreciate the reviewer for the valuable comments. In the revised manuscript, temperature-dependent PL spectra, two-dimensional pseudo-color of fs-TA spectra, TA decay kinetic curves, and the corresponding transient absorption spectra of DF₂TA-TAPB and DF₃TA-TAPB have been incorporated as reference groups (**Figure R4** and **Figure R5**). These data were further analyzed and discussed in detail in the main text to provide a more comprehensive comparison.

In accordance with Reviewer #4's suggestion to investigate the influence of pump irradiance, atmosphere, and solvent on the dynamics of photogenerated charge carriers, we re-measured the femtosecond transient absorption spectra of DT₂TA-TAPB and DT₃TA-TAPB to allow for more robust comparisons with DF₂TA-TAPB and DF₃TA-TAPB. To ensure data consistency and reliability, the original measurements for DT₂TA-TAPB and DT₃TA-TAPB were also updated alongside the newly acquired data for DF₂TA-TAPB and DF₃TA-TAPB.

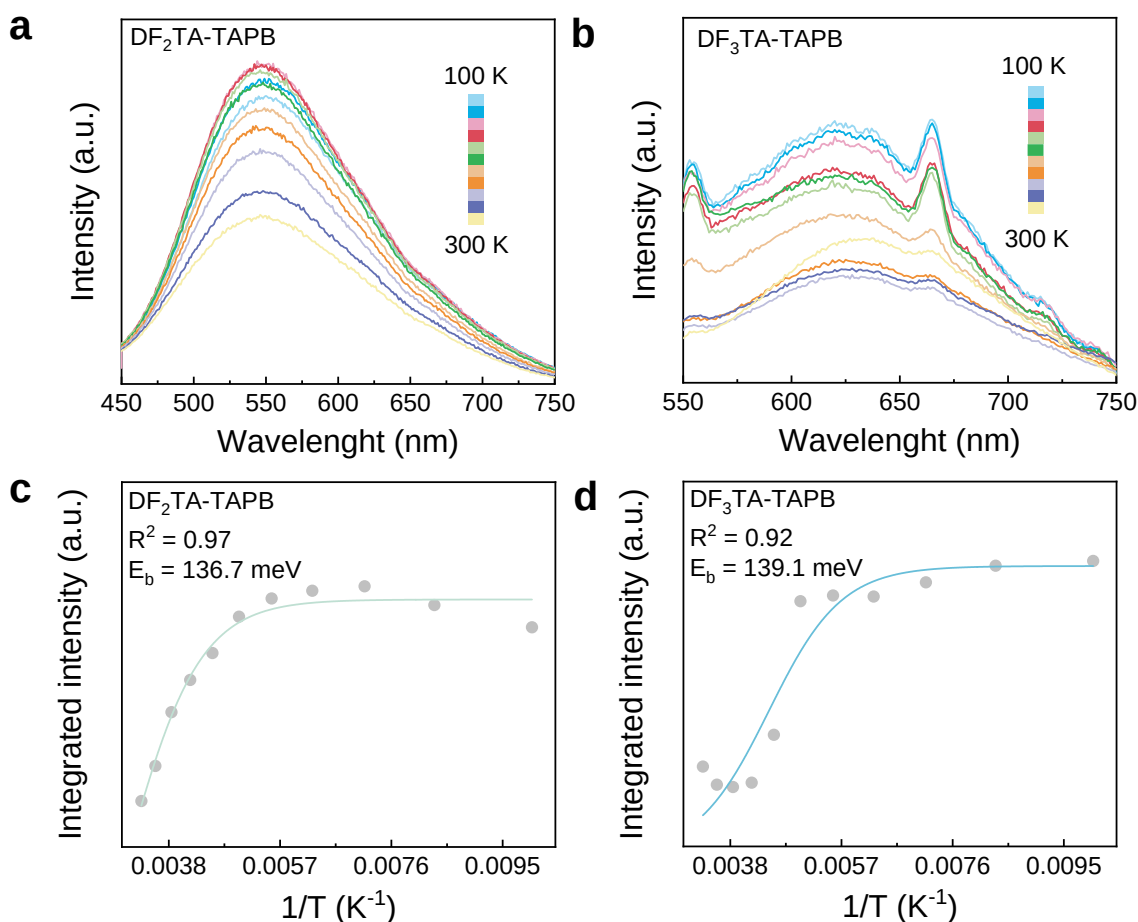


Figure R4 (Supplementary Fig. 11). Temperature-dependent PL spectra under 400 nm excitation for (a) DF₂TA-TAPB and (b) DF₃TA-TAPB. Arrhenius fitting curves for (c) DF₂TA-TAPB and (d) DF₃TA-TAPB.

The additions in the manuscript are as follows:

“Temperature-dependent PL spectroscopy of the COFs revealed that the integrated PL intensity decreased gradually as the temperature increased from 100 to 300 K. Fitting the experimental data using the Arrhenius equation yielded E_b values of 126.6, 137.8, 136.7, and 139.1 meV for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively (Fig. 3b, Fig. 3c, and Supplementary Fig. 11). These results suggested that the excitons in DT₂TA-TAPB dissociate more readily than those in other COFs, thereby increasing the proportion of free carriers¹.” (Page 9, Lines 189-194)

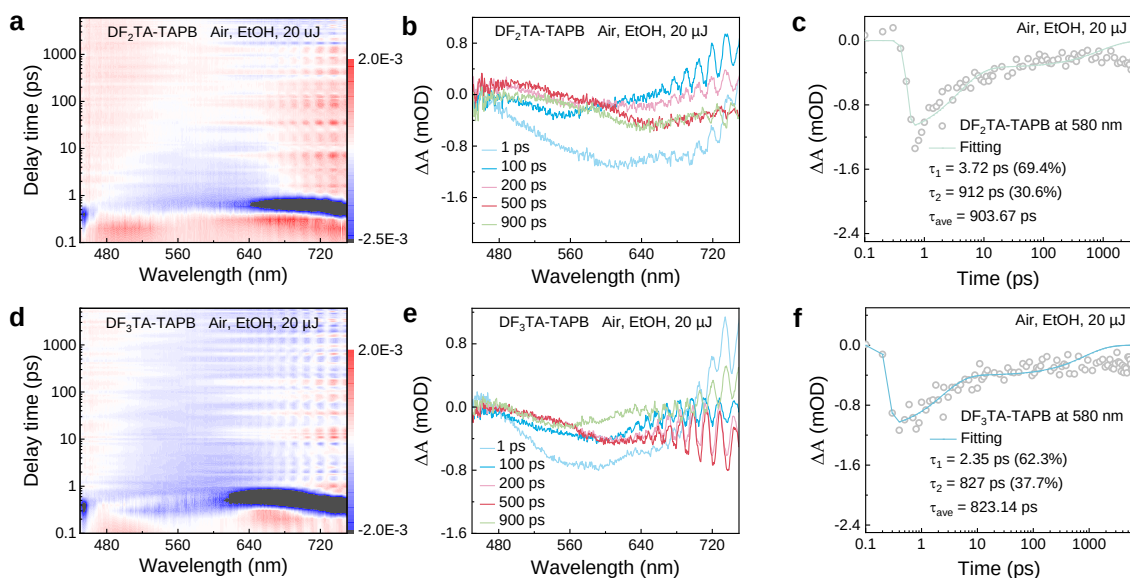


Figure R5 (Supplementary Fig. 15-16). Two-dimensional pseudo-color fs-TA spectra of (a) DF₂TA-TAPB and (d) DF₃TA-TAPB. TA spectra of (b) DF₂TA-TAPB and (e) DF₃TA-TAPB at various time delays. TA decay kinetic curves of (c) DF₂TA-TAPB and (f) DF₃TA-TAPB.

The additions in the manuscript are as follows:

“The fs-TA spectra of COFs exhibited a broad ground-state bleach signal at 450-680 nm, attributed to the combined contributions of ground-state bleaching and stimulated emission (Fig. 3d-g and Supplementary Fig. 12-16). Furthermore, a positive absorption signal was observed at the wavelengths > 700 nm, which stemmed from excited-state absorption resulting from photogenerated electrons. Fitting the decay curves at a probe wavelength of 580 nm with a bi-exponential model revealed two distinct relaxation pathways for the photogenerated electrons: a short-lived component (τ₁) corresponding to electron trapping and a long-lived component (τ₂) associated with electron-hole recombination^{2,3}. The τ₁ values for the four COFs

were similar, probably because of their structural similarity. In contrast, DT₂TA-TAPB exhibited a significantly longer τ_2 (2677 ps) than the other COFs, indicating an extended carrier lifetime. The average carrier lifetimes (τ_{ave}) were determined to be 2677.65, 1618.55, 903.67, and 823.14 ps for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively. These findings revealed that DT₂TA-TAPB effectively suppressed charge recombination, thereby substantially enhancing photocatalytic H₂O₂ generation.” (Page 9, Lines 196-209)

The cited references as follows:

1. Huang, Y. et al. Achieving a solar-to-chemical efficiency of 3.6% in ambient conditions by inhibiting interlayer charges transport. *Nat. Commun.* **15**, 5406 (2024).
2. Qiu, J. et al. COF/In₂S₃ S-Scheme Photocatalyst with Enhanced Light Absorption and H₂O₂-Production Activity and fs-TA Investigation. *Advanced Materials*. **36**, 2400288 (2024).
3. Cheng, C. et al. Verifying the Charge-Transfer Mechanism in S-Scheme Heterojunctions Using Femtosecond Transient Absorption Spectroscopy. *Angew. Chem. Int. Ed.* **62**, e202218688 (2023).

Comment 6: Please check Figs. 3b-g, Fig. 4f, and Fig. 4g. Number them according to the sequence they appear in the manuscript. Additionally, it may not be appropriate to compare the H₂O₂ photoproduction performance of the well-engineered DT₂TA-TAPB with that of pristine carbon nitride.

Response 6: We sincerely appreciate the reviewer’s meticulous and constructive feedback. In the revised manuscript, we have carefully reviewed and corrected the sequential numbering of Fig. 3b-g, 4f, and 4g to maintain consistency.

Given the variability in reaction conditions—such as light intensity, radiation wavelength, sacrificial agent, and reaction time—across different laboratories, we synthesized g-C₃N₄, a benchmark photocatalyst, following a previously reported method (*CCS Chem.* 2022, **4**, 3751–3761), and compared its photocatalytic performance with that of DT₂TA-TAPB. As suggested, we have moved the comparison of H₂O₂ production rates between DT₂TA-TAPB and g-C₃N₄ to the supplementary information.

Additionally, to comprehensively assess the photocatalytic performance of DT₂TA-TAPB, we compared it with recently reported COF-based photocatalysts. As depicted in **Figure R6**, DT₂TA-TAPB exhibited a markedly higher H₂O₂ yield under both 10% EtOH and pure water conditions compared to most COF-based photocatalysts reported to date, underscoring its exceptional performance in photocatalytic H₂O₂ production.

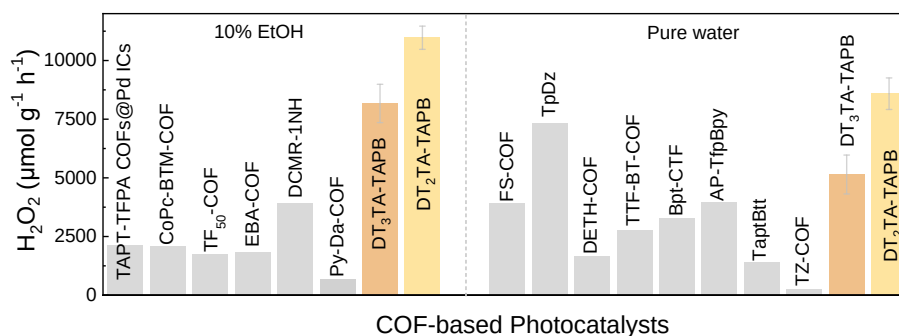


Figure R6 (Fig. 4g). Performance comparison of DT₂TA-TAPB with other recently reported COF-based photocatalysts in 10% EtOH or pure water.

The additions in the manuscript are as follows:

“Furthermore, we synthesized a benchmark sample, g-C₃N₄ (Supplementary Fig. 25)¹, and compared its H₂O₂ production performance with that of DT₂TA-TAPB. The results indicated that the H₂O₂ production rate of DT₂TA-TAPB was approximately 23- and 41-times higher than that of g-C₃N₄ in 10% EtOH and pure water, respectively (Supplementary Fig. 26). Meanwhile, the H₂O₂ yield of DT₂TA-TAPB was far superior to that of the majority of reported COF-based photocatalysts without adding a sacrificial agent or in pure water (**Fig. 4g** and Supplementary Table 1), highlighting its remarkable performance of photocatalytic H₂O₂ production.” (Page 12-13, Lines 278-285)

The cited references as follows:

1. Tan, F. et al. Aqueous Synthesis of Covalent Organic Frameworks as Photocatalysts for Hydrogen Peroxide Production. *CCS Chem.* **4**, 3751–3761 (2022).

Comment 7: The formation (k_f) and decomposition (k_d) kinetics of H₂O₂ on the surface of DT₂TA-TAPB are suggested to be given. Long-term experiments should be performed to investigate the plateau of H₂O₂ photoproduction.

Response 7: We sincerely thank the reviewer for the constructive comments. Long-term photocatalytic experiments with DT₂TA-TAPB revealed a steady increase in H₂O₂ concentration over the initial 24 h, followed by a plateau that remained stable up to 28 h (**Figure R7**), indicating the establishment of a dynamic equilibrium between H₂O₂ formation and decomposition. To further elucidate the reaction mechanism, the kinetics of H₂O₂ formation and decomposition were systematically investigated. H₂O₂ generation followed zero-order kinetics, while its decomposition adhered to first-order kinetics, consistent with previous reports (*Nat Commun.* 2025, **16**, 503; *Adv. Funct. Mater.* 2021, **31**, 2106120). The kinetic constants were derived by fitting the H₂O₂ formation curve, yielding a formation rate constant

(k_f) of $186.3 \mu\text{M}\cdot\text{h}^{-1}$ and a decomposition rate constant (k_d) of 0.131 h^{-1} (**Figure R8**). These results indicated that, in the initial stage of H_2O_2 formation, the rate constant for formation was significantly higher than that for decomposition. As the reaction progressed, the two rate constants gradually approached equilibrium, leading to a stabilized concentration of H_2O_2 .

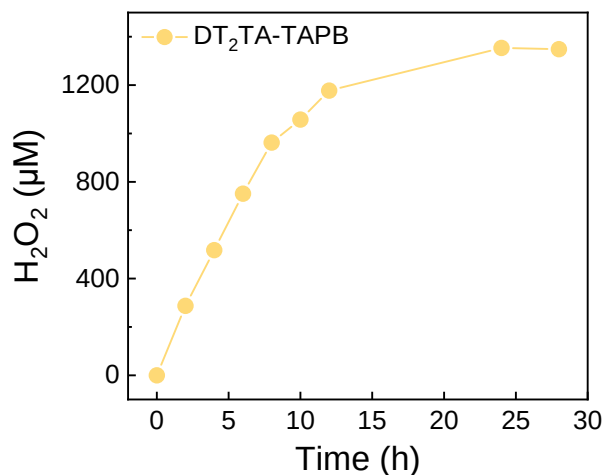


Figure R7 (Fig. 4h). Long-term photocatalytic H_2O_2 production by $\text{DT}_2\text{TA-TAPB}$ (Reaction conditions: 10 mg catalyst in 40 mL pure water, under air atmosphere, irradiated by a 300 W Xenon lamp (light intensity: 100 mW cm^{-2})).

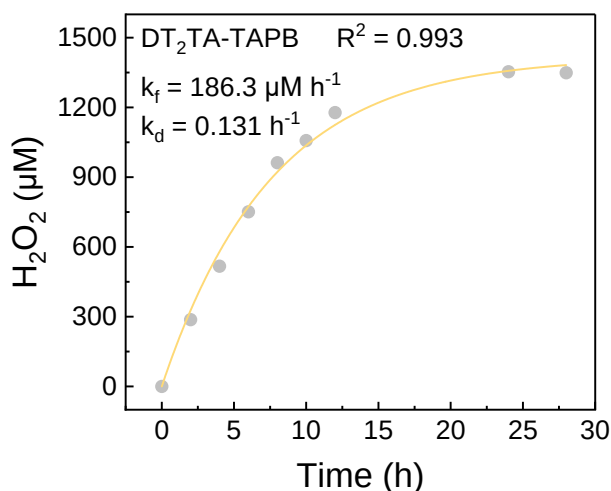


Figure R8 (Supplementary Fig. 30). H_2O_2 formation and decomposition rate constant.

The additions in the manuscript are as follows:

“To assess the practical application of $\text{DT}_2\text{TA-TAPB}$, long-term photocatalytic H_2O_2 production experiments were conducted under simulated natural conditions. The results revealed that $\text{DT}_2\text{TA-TAPB}$ continuously and stably produced H_2O_2 over the initial 24 h, followed by a plateau that remained stable up to 28 h, indicating the establishment of a dynamic equilibrium between H_2O_2 formation and decomposition (**Fig. 4h**)” (Page 13, Lines 285-289)

“To elucidate the underlying mechanism, the kinetics of H₂O₂ formation and decomposition were systematically studied. H₂O₂ formation followed zero-order kinetics, whereas its decomposition adhered to first-order kinetics^{1,2}. Accordingly, the overall H₂O₂ generation process could be described as follows:

$$[\text{H}_2\text{O}_2] = \frac{k_f}{k_d} (1 - e^{-k_d t}) \quad (1)$$

where *t* denotes the reaction time, [H₂O₂] represents the concentration of generated H₂O₂, and *k_f* and *k_d* correspond to the rate constants for its formation and decomposition, respectively. The kinetic constants were derived by fitting the H₂O₂ formation curve, yielding a formation rate constant (*k_f*) of 186.3 μM·h⁻¹ and a decomposition rate constant (*k_d*) of 0.131 h⁻¹ (Supplementary Fig. 30). These findings indicated that, in the initial stage, H₂O₂ formation rate constant significantly exceeded its decomposition. As the reaction progressed, the two rate constants gradually approached equilibrium, resulting in a stabilized concentration of H₂O₂.”
(Page 13-14, Lines 295-307)

The cited references are as follows:

1. Chakraborty, A. et al. Enhancing photocatalytic hydrogen peroxide generation by tuning hydrazone linkage density in covalent organic frameworks. *Nat. Commun.* **16**, 503 (2025).
2. Zhang, X. et al. Keto-anthraquinone covalent organic framework for H₂O₂ photosynthesis with oxygen and alkaline water. *Nat. Commun.* **15**, 2649 (2024).

Comment 8: DT₂TA-TAPB exhibited higher H₂O₂ photoproduction, whereas the intensity of DMPO-•O₂⁻ adducts measured in the DT₂TA-TAPB suspension was lower than that observed in the DT₃TA-TAPB suspension (Fig. 5b and 5c). The signals of DMPO-•O₂⁻ adducts obtained from prolonged experiments are recommended to be provided.

Response 8: Thanks to the reviewer for the insightful comment. DT₂TA-TAPB exhibited a higher H₂O₂ yield; however, the intensity of DMPO-•O₂⁻ adducts in its suspension was lower than that observed for DT₃TA-TAPB. This discrepancy suggested that DT₂TA-TAPB predominantly forms an endoperoxide intermediate via a one-step, two-electron pathway, thereby directly generating H₂O₂ (*Angew. Chem. Int. Ed.* 2023, **62**, e202305355). This conclusion was further supported by quantitative detection of the superoxide radicals using the nitro blue tetrazolium (NBT) method. Meanwhile, ring-disk electrode experiments also confirmed DT₂TA-TAPB primarily follows one-step, two-electron oxygen reduction pathway, whereas DT₃TA-TAPB undergoes a two-step, single-electron process.

To further substantiate this mechanism, the long-term evolution of $\text{DMPO}\cdot\text{O}_2^-$ adducts was monitored. This signal initially increased and then gradually declined. Additionally, a slight shift in the $\text{DMPO}\cdot\text{O}_2^-$ peaks were observed in the $\text{DT}_3\text{TA-TAPB}$ system, potentially indicating the conversion of $\text{DMPO}\cdot\text{O}_2^-$ to $\text{DMPO}\cdot\text{OOH}$ (*Angew. Chem. Int. Ed.* 2024, **63**, e202410381). Notably, the signal intensity of $\text{DMPO}\cdot\text{O}_2^-$ in $\text{DT}_2\text{TA-TAPB}$ was consistently lower than that in $\text{DT}_3\text{TA-TAPB}$ (**Figure R9**), while the H_2O_2 production in $\text{DT}_2\text{TA-TAPB}$ was superior to that in $\text{DT}_3\text{TA-TAPB}$, providing evidence that H_2O_2 formation in $\text{DT}_2\text{TA-TAPB}$ occurs via the endoperoxide pathway. However, since endoperoxides feature a closed-shell structure without unpaired electrons, they do not generate EPR signals.

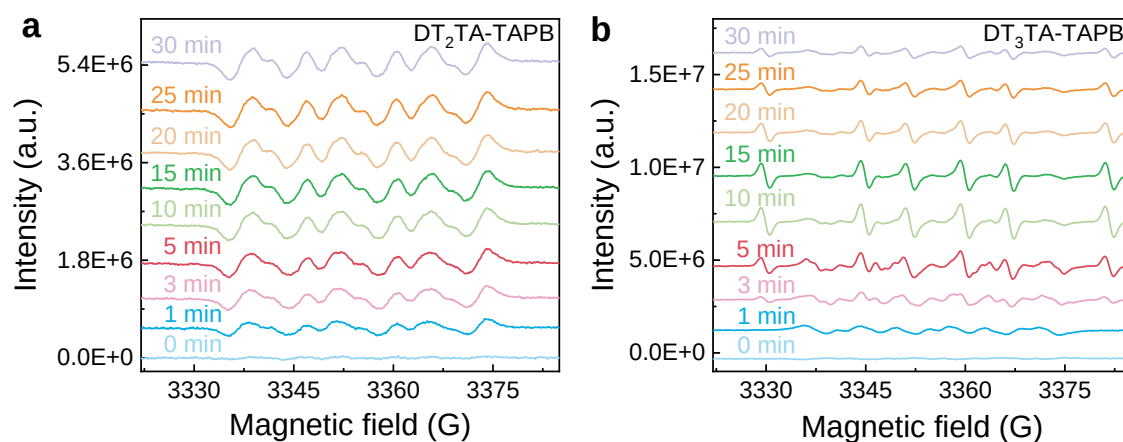


Figure R9 (Fig. 5b and 5c). Time-dependent in situ EPR spectra of (a) $\text{DT}_2\text{TA-TAPB}$ and (b) $\text{DT}_3\text{TA-TAPB}$.

The additions in the manuscript are as follows:

“The in situ EPR spectra of $\text{DT}_2\text{TA-TAPB}$ and $\text{DT}_3\text{TA-TAPB}$ exhibited a typical sixfold characteristic peak for $\text{DMPO}\cdot\text{O}_2^-$, the intensity of which increased and then decreased over time (**Fig. 5b** and **Fig. 5c**)¹. A slight shift in the $\text{DMPO}\cdot\text{O}_2^-$ peaks was observed in the $\text{DT}_3\text{TA-TAPB}$, suggesting a potential conversion of $\text{DMPO}\cdot\text{O}_2^-$ to $\text{DMPO}\cdot\text{OOH}$ ². Notably, the weaker $\text{DMPO}\cdot\text{O}_2^-$ signal in the $\text{DT}_2\text{TA-TAPB}$ suspension was likely owing to the predominant formation of an endoperoxide in $\text{DT}_2\text{TA-TAPB}$ via a one-step, two-electron pathway, directly promoting H_2O_2 generation³.” (Page 15, Lines 334-340)

The cited references as follows:

1. Liu, Y. et al. Fluorination of Covalent Organic Framework Reinforcing the Confinement of Pd Nanoclusters Enhances Hydrogen Peroxide Photosynthesis. *J. Am. Chem. Soc.* **145**, 19877–19884 (2023).
2. He, J. et al. Piezo-catalysis Mechanism Elucidation by Tracking Oxygen Reduction to Hydrogen Peroxide with In situ EPR Spectroscopy. *Angew. Chem. Int. Ed.* **63**, e202410381 (2024).
3. Luo, Y. et al. Sulfone-Modified Covalent Organic Frameworks Enabling Efficient Photocatalytic Hydrogen Peroxide Generation via One-Step Two-Electron O_2 Reduction. *Angew. Chem. Int. Ed.* **62**, e202305355 (2023).

Comment 9: RRDE measurements are recommended to be performed as supplementary experiments for comparison with RDE measurements (Fig. 5f).

Response 9: We sincerely appreciate the reviewer's insightful comments. Rotating ring-disk electrode (RRDE) measurements were performed to assess H_2O_2 selectivity and compared with the RDE results. As illustrated in **Figure R10** and **Figure R11**, $\text{DT}_2\text{TA-TAPB}$ exhibited significantly higher selectivity for photocatalytic H_2O_2 production than $\text{DT}_3\text{TA-TAPB}$. RDE measurements further revealed that electron transfer numbers of 1.92 and 1.34 for $\text{DT}_2\text{TA-TAPB}$ and $\text{DT}_3\text{TA-TAPB}$, respectively, with the former approaching 2. These findings collectively suggested that $\text{DT}_2\text{TA-TAPB}$ predominantly facilitated O_2 reduction via the direct two-electron pathway, whereas $\text{DT}_3\text{TA-TAPB}$ favored a stepwise single-electron process in H_2O_2 production.

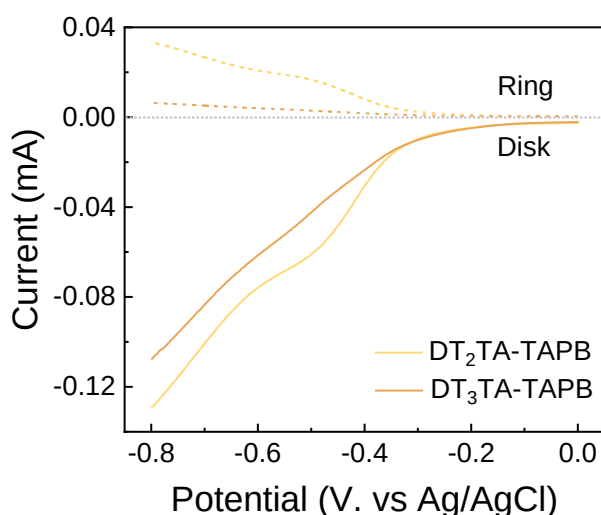


Figure R10 (Supplementary Fig. 35). RRDE curves of $\text{DT}_2\text{TA-TAPB}$ and $\text{DT}_3\text{TA-TAPB}$ measured at 1600 rpm in O_2 -saturated 0.1 M phosphate buffer (pH = 7) electrolyte.

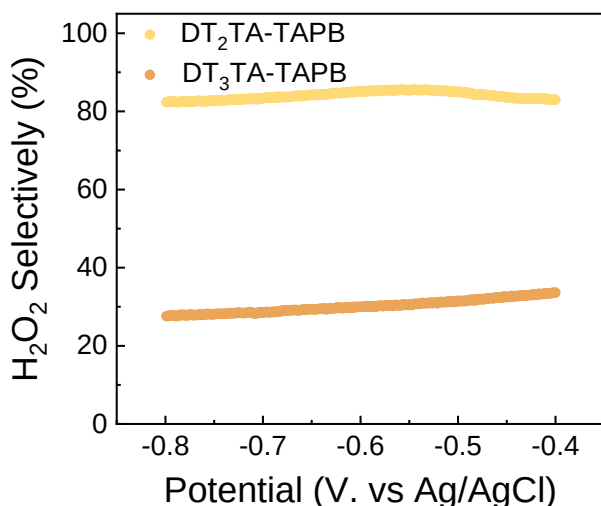


Figure R11 (Supplementary Fig. 36). Calculated H₂O₂ selectivity of DT₂TA-TAPB and DT₃TA-TAPB based on RRDE measurements.

The additions in the manuscript are as follows:

“Rotating ring-disk electrode (RRDE) measurements further revealed that DT₂TA-TAPB exhibited significantly higher selectivity for H₂O₂ production than DT₃TA-TAPB (Supplementary Fig. 35 and 36). These findings provided compelling evidence that DT₂TA-TAPB facilitated efficient H₂O₂ generation under visible light through a direct one-step, two-electron ORR pathway, whereas the step-wise one-electron pathway played a more dominant role in the DT₃TA-TAPB system.” (Page 16, Lines 350-355)

The additions in the supplementary information are as follows:

Rotating ring-disk electrode (RRDE) measurements

“The oxygen reduction reaction (ORR) activity was evaluated using a rotating ring-disk electrode (RRDE) as the working electrode, which was prepared following the ring-disk electrode (RDE) methodology. The measurements were conducted in a 0.1 M phosphate buffer solution (pH = 7) at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. To ensure sufficient dissolved O₂, the electrolyte solution was purged with oxygen for 1 h prior measurements. The potential of the ring electrode was set to 0.6 V (vs. Ag/AgCl reference electrode) to detect the generated H₂O₂. The selectivity of H₂O₂ was calculated using equation (7):

$$\text{H}_2\text{O}_2 (\%) = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad (7)$$

Where I_r is the ring current, I_d is the disk current, and N is the collection efficiency (0.37)”.
(Page S14-15, Lines 248-257)

Reviewer #2 (Remarks to the Author):

Overall comments: The authors have designed and synthesized four thiophene- and furan-based COFs for photocatalytic H₂O₂ production under visible light illumination. They conducted detailed experimental and theoretical analyses, including investigations into the underlying mechanisms. While the study demonstrates significant potential, there are several critical concerns that need to be addressed before it can be considered suitable for publication in this high-impact journal:

Response: We sincerely appreciate the reviewer's positive evaluation of our work and their valuable suggestions for improving our manuscript. In response, we have carefully revised the manuscript, addressing each concern in detail and incorporating necessary modifications to enhance the overall quality and rigor of our study. We hope that our revisions have satisfactorily addressed all concerns and that the manuscript now meets the publication standards of *Nature Communications*.

Comment 1: The infrared spectra of DT₂TA-TAPB and DF₃TA-TAPB show obvious noise and need to be remeasured. Additionally, for DT₂TA-TAPB, DT₃TA-TAPB, and DF₃TA-TAPB, the presence of C=O functional groups suggests that some unreacted starting materials remain in the products. Please give reasonable explanation.

Response 1: We sincerely appreciate the reviewer's thorough examination and valuable suggestions. To address the noise observed in the FT-IR spectra of DT₂TA-TAPB and DF₃TA-TAPB, we further purified the samples and remeasured all the spectra using an upgraded instrument to enhance signal quality. The revised spectra exhibit significantly reduced noise and more clearly reflect the molecular features of the materials (**Figure R12**).

Regarding the presence of C=O functional groups in DT₂TA-TAPB, DT₃TA-TAPB, and DF₃TA-TAPB, the remeasured FT-IR spectra of DT₃TA-TAPB and DF₃TA-TAPB no longer exhibited the characteristic C=O stretching vibrations, suggesting that the previously observed signals likely originated from trace amounts of adsorbed precursors. However, a weak C=O stretching vibrations peak observed in DT₂TA-TAPB was likely a consequence of the significant steric from the 2-position thiophene units, which hindered the complete extension of framework, leading to the retention of a small fraction of aldehyde groups at the terminal positions of the COFs.

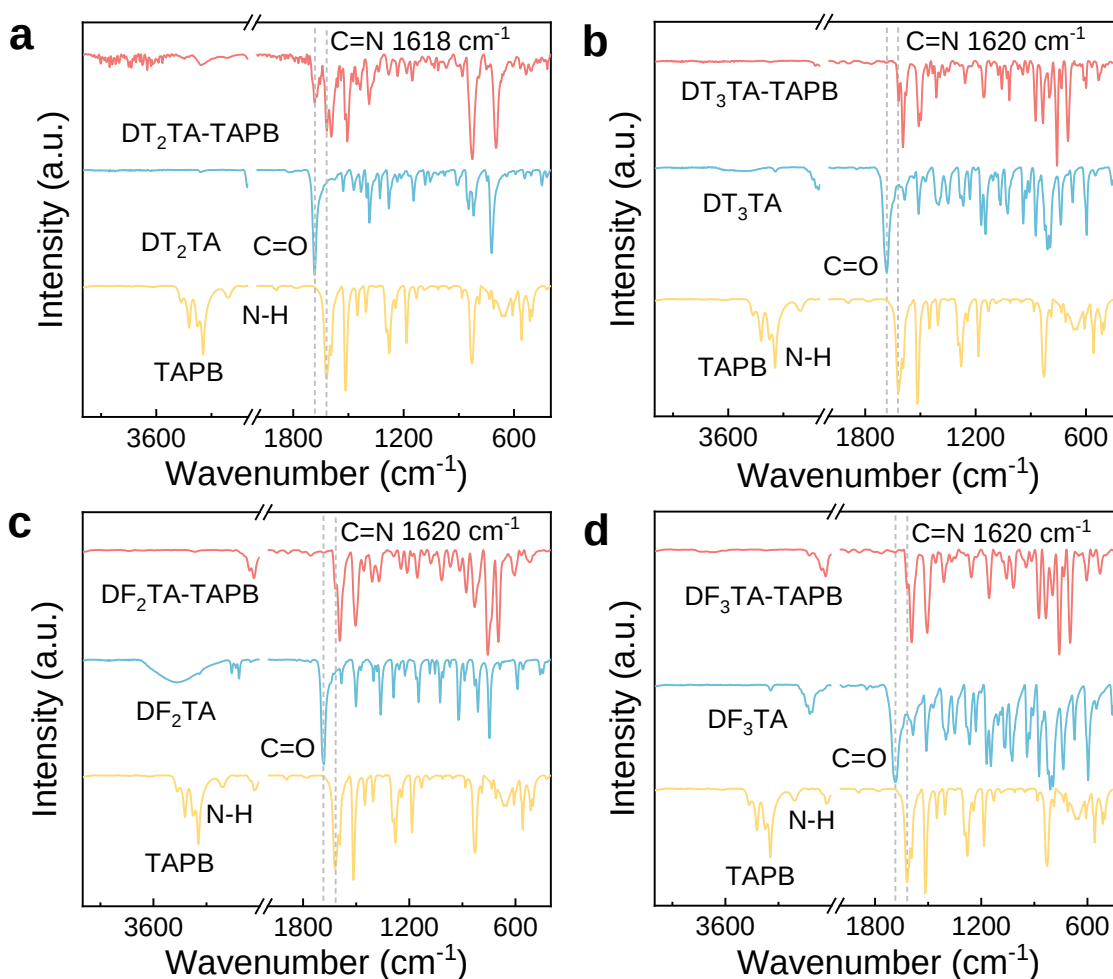


Figure R12 (Supplementary Fig. 2). (a-d) FT-IR spectra of DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, and corresponding organic building blocks.

The additions in the manuscript are as follows:

“The FT-IR spectra of the COFs exhibited the disappearance of C=O stretching bands at 1685 cm⁻¹ and appearance of C=N stretching vibrations at approximately 1620 cm⁻¹, confirming successful formation of C=N bonds (Fig. 2f and Supplementary Fig. 2). However, a weak C=O stretching vibrations peak observed in DT₂TA-TAPB was likely a consequence of the significant steric from the 2-position thiophene units, which hindered the complete extension of framework, leading to the retention of a small fraction of aldehyde groups at the terminal positions of the COFs.” (Page 6, Lines 126-132)

The additions in the supplementary information are as follows:

“Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Tensor 27 (TENSOR27, Germany) Fourier transformation infrared spectrometer using KBr pellets.” (Page S-3, Lines 36-38)

Comment 2: The single-crystal data does not include the R_1 and wR_2 values, please provide the related information. It is necessary to provide details of the single-crystal testing instrument and methods.

Response 2: Thank you for your valuable comment. As suggested, we have added the R_1 and wR_2 values of the single-crystal data for the four aldehyde monomers in the revised supplementary information (**Table R1 and Table R2**). Furthermore, detailed descriptions of the instruments and methodologies employed for single-crystal analysis have been added.

Table R1 (Supplementary Table 2). Single crystal data of DT₂TA and DT₃TA.

Name	DT ₂ TA	DT ₃ TA
Formula	C ₁₆ H ₁₀ O ₂ S ₂	C ₃₂ H ₂₀ O ₄ S ₄
CCDC Deposition Number	2323749	2323748
Formula weight	298.36	596.72
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁
Temperature/K	302.49(10)	150.00(10)
a/Å	10.53950(10)	8.91610(10)
b/Å	7.62970(10)	16.69800(10)
c/Å	17.2813(2)	9.02220(10)
$\alpha/^\circ$	90	90
$\beta/^\circ$	102.6980(10)	91.9050(10)
$\gamma/^\circ$	90	90
F (000)	616.0	272.0
ρ_{calc} , g/cm ³	1.462	1.476
Volume/Å ³	1355.66(3)	1342.49(2)
Z	4	2
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0463$	$R_1 = 0.0411$
	$wR_2 = 0.1349$	$wR_2 = 0.1214$
Final R indexes [all data]	$R_1 = 0.0478$	$R_1 = 0.0414$
	$wR_2 = 0.1366$	$wR_2 = 0.1217$

Table R1 (Supplementary Table 3). Single crystal data of DF₂TA and DF₃TA.

Name	DF ₂ TA	DF ₃ TA
Formula	C ₈ H ₅ O ₂	C ₁₆ H ₁₀ O ₄
CCDC Deposition Number	2339826	2323750
Formula weight	133.12	264.22
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n
Temperature/K	291.9(7)	300.56(10)
a/Å	3.86971(18)	12.2699(2)
b/Å	17.5555(8)	3.93519(8)
c/Å	9.1719(4)	12.9934(2)
α /°	90	90
β /°	101.218(5)	95.9334(18)
γ /°	90	90
F(000)	276.0	272.0
ρ_{calc} , g/cm ³	1.447	1.406
Volume/Å ³	611.19(5)	624.01(2)
Z	4	2
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0469$	$R_1 = 0.0727$
	$wR_2 = 0.1357$	$wR_2 = 0.2274$
Final R indexes [all data]	$R_1 = 0.0526$	$R_1 = 0.0779$
	$wR_2 = 0.1410$	$wR_2 = 0.2348$

The additions in the supplementary information are as follows:

Single-crystal measurement

“Single-crystal X-ray diffraction (SXR) measurements were performed on a Rigaku XtaLAB Synergy-DW diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5418$ Å). Data acquisition, processing, and reduction were carried out using the CrysAlisPro software suite. The structure was solved using the SHELXT program with intrinsic phasing in Olex2, and refined by least-squares minimisation using the SHELXL package. Detailed crystallographic data for the aldehyde monomers were provided in Supplementary Table 2 and 3.” (Page S16, Lines 290-296)

Comment 3: To enable a comprehensive comparison, femtosecond time-resolved transient absorption spectra for DF₂TA-TAPB and DF₃TA-TAPB should be included and thoroughly discussed to provide insights into their photophysical processes.

Response 3: Thank you for your valuable feedback. In response, we have included the femtosecond time-resolved transient absorption spectra of DF₂TA-TAPB and DF₃TA-TAPB (**Figure R13**) and have provided a detailed discussion of their photophysical processes in the revised manuscript.

In response to Reviewer #4's comments regarding the influence of pump irradiance, atmosphere, and solvent on photogenerated carrier dynamics, we re-measured the femtosecond data for DT₂TA-TAPB and DT₃TA-TAPB to facilitate a more precise comparison with DF₂TA-TAPB and DF₃TA-TAPB. To ensure data consistency and reliability, the original measurements for DT₂TA-TAPB and DT₃TA-TAPB were also updated alongside the newly acquired data for DF₂TA-TAPB and DF₃TA-TAPB.

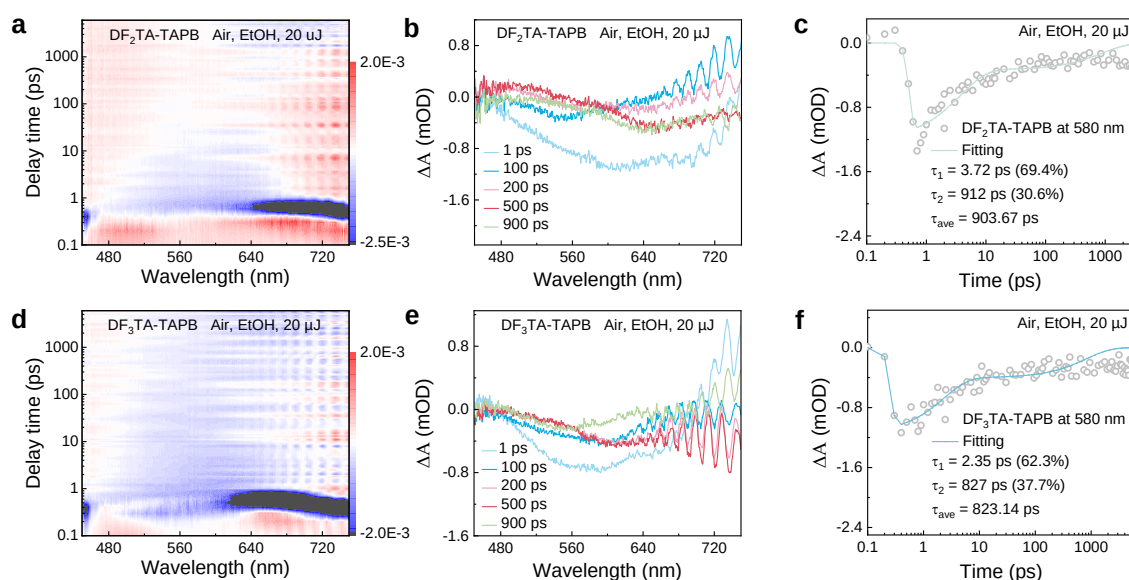


Figure R13 (Supplementary Fig. 15-16). Two-dimensional pseudo-color fs-TA spectra of (a) DF₂TA-TAPB and (d) DF₃TA-TAPB. TA spectra of (b) DF₂TA-TAPB and (e) DF₃TA-TAPB at various time delays. TA decay kinetic curves of (c) DF₂TA-TAPB and (f) DF₃TA-TAPB.

The additions in the manuscript are as follows:

“The fs-TA spectra of COFs exhibited a broad ground-state bleach signal at 450-680 nm, attributed to the combined contributions of ground-state bleaching and stimulated emission (**Fig. 3d-g** and Supplementary Fig. 12-16). Furthermore, a positive absorption signal was observed at the wavelengths > 700 nm, which stemmed from excited-state absorption resulting from photogenerated electrons. Fitting the decay curves at a probe wavelength of 580 nm with a bi-exponential model revealed two distinct relaxation pathways for the photogenerated

electrons: a short-lived component (τ_1) corresponding to electron trapping and a long-lived component (τ_2) associated with electron–hole recombination^{1,2}. The τ_1 values for the four COFs were similar, probably because of their structural similarity. In contrast, DT₂TA-TAPB exhibited a significantly longer τ_2 (2677 ps) than the other COFs, indicating an extended carrier lifetime. The average carrier lifetimes (τ_{ave}) were determined to be 2677.65, 1618.55, 903.67, and 823.14 ps for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively. These findings revealed that DT₂TA-TAPB effectively suppressed charge recombination, thereby substantially enhancing photocatalytic H₂O₂ generation.” (Page 9, Lines 196-209)

The cited references as follows:

1. Qiu, J. et al. COF/In₂S₃ S-Scheme Photocatalyst with Enhanced Light Absorption and H₂O₂-Production Activity and fs-TA Investigation. *Advanced Materials*. **36**, 2400288 (2024).
2. Cheng, C. et al. Verifying the Charge-Transfer Mechanism in S-Scheme Heterojunctions Using Femtosecond Transient Absorption Spectroscopy. *Angew. Chem. Int. Ed.* **62**, e202218688 (2023).

Comment 4: To ensure accuracy and reproducibility of the performance data, error bars should be included in Fig. 4c-e.

Response 4: Thank you for your valuable suggestions. As depicted in **Figure R14-R17**, we have added error bars to the revised manuscript to enhance the accuracy and reproducibility of the performance data. Building upon our initial data, we conducted three additional experimental sets, totaling four replicates. In addition, we have included line plots corresponding to the bar charts in Fig 4c-e to illustrate the time-dependent H₂O₂ production curves. These additions enable a clearer visualization of the trends in H₂O₂ yield over time during the photocatalytic process.

In response to the reviewer’s suggestion to include error bars, we have repeated the relevant measurements to ensure statistical reliability. Consequently, some values were slightly adjusted compared to those in the original manuscript. However, the updated performance data do not alter the original conclusions, as the observed trends remain consistent.

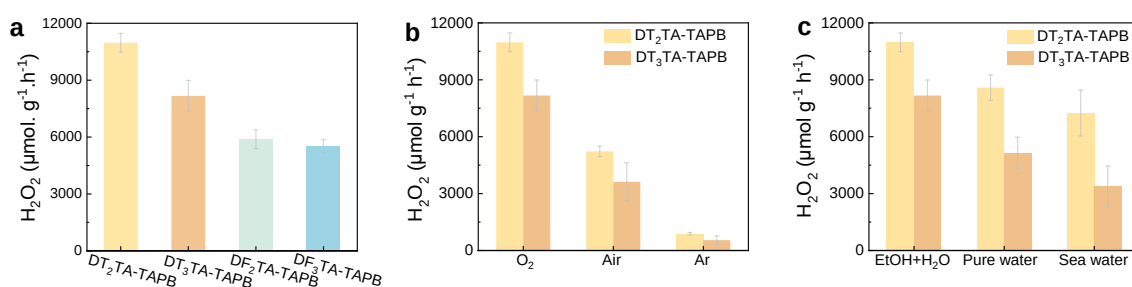


Figure R14 (Fig. 4c-e). (a) Photocatalytic H_2O_2 yield of the COFs. Reaction condition: 300 W Xenon lamp $\lambda > 420$ nm, 10% EtOH solution. (b) H_2O_2 yields of $\text{DT}_2\text{TA-TAPB}$ and $\text{DT}_3\text{TA-TAPB}$ under different atmospheres. (c) Photocatalytic H_2O_2 production rates of $\text{DT}_2\text{TA-TAPB}$ and $\text{DT}_3\text{TA-TAPB}$ in pure water, 10% EtOH, and seawater. Error bars indicate the standard deviations of four replicate measurements.

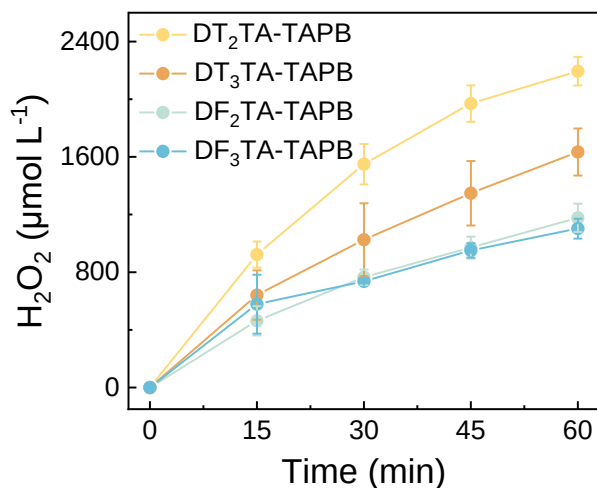


Figure R15 (Supplementary Fig. 20). Time-dependent H_2O_2 production curves for different photocatalysts under visible light irradiation. Reaction condition: 300 W Xenon lamp ($\lambda > 420$ nm), 10% EtOH solution. Error bars indicate the standard deviations of four replicate measurements.

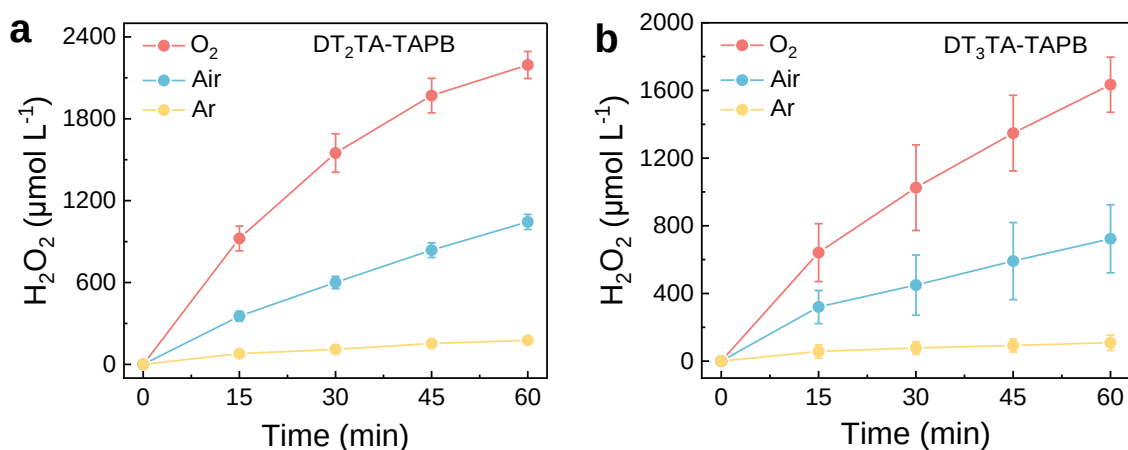


Figure R16 (Supplementary Fig. 21). Time-dependent H_2O_2 production curves for (a) $\text{DT}_2\text{TA-TAPB}$ and (b) $\text{DT}_3\text{TA-TAPB}$ under various atmosphere. Error bars represent the standard deviations of four replicate measurements.

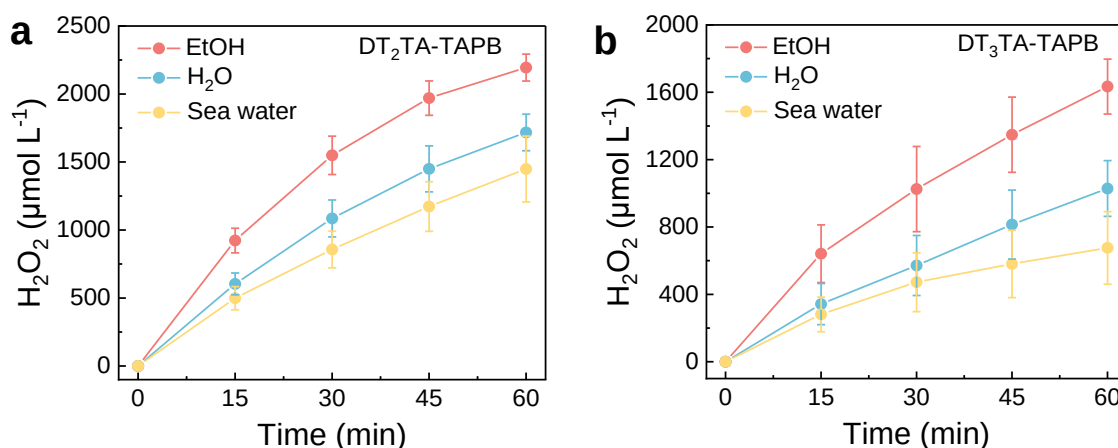


Figure R17 (Supplementary Fig. 22). Time-dependent H₂O₂ production curves for (a) DT₂TA-TAPB and (b) DT₃TA-TAPB in 10% EtOH, pure water, and seawater. Error bars represent the standard deviations of four replicate measurements. Error bars indicate the standard deviations of four replicate measurements.

The additions in the manuscript are as follows:

“As presented in **Fig. 4c** and Supplementary Fig. 20, the developed COFs exhibited excellent photocatalytic H₂O₂ production, with yields of 10972, 8171, 5886, and 5514 μmol h⁻¹ g⁻¹ for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively.” (Page 11, Lines 244-247)

“As depicted in **Fig. 4d** and Supplementary Fig. 21, the H₂O₂ yield of DT₂TA-TAPB and DT₃TA-TAPB under an O₂ atmosphere were obviously higher than that obtained under air (DT₂TA-TAPB: 5223 μmol h⁻¹ g⁻¹, DT₃TA-TAPB: 3617 μmol h⁻¹ g⁻¹) and Ar (DT₂TA-TAPB: 885 μmol h⁻¹ g⁻¹, DT₃TA-TAPB: 544 μmol h⁻¹ g⁻¹) atmosphere, and almost no H₂O₂ was detected under the Ar atmosphere, indicating that O₂ was an indispensable reactant in H₂O₂ generation.” (Page 12, Lines 254-259)

“As illustrated in **Fig. 4e** and Supplementary Fig. 22, DT₂TA-TAPB and DT₃TA-TAPB generated 8587 and 5143 μmol g⁻¹ h⁻¹ H₂O₂ in pure water and 7245 and 3381 μmol g⁻¹ h⁻¹ H₂O₂ in seawater.” (Page 12, Lines 261-263)

Comment 5: The stability of the COF catalysts, particularly the best-performing sample (DT₂TA-TAPB), needs further evaluation. Recyclability tests and post-experiment characterizations such as XRD, SEM, and IR should be conducted after long-term experiments or recycling tests.

Respond 5: We appreciate the reviewer’s valuable comments. In response, long-term stability experiments were conducted to evaluate photocatalytic H₂O₂ production of DT₂TA-TAPB. The results demonstrated that a steady increase in H₂O₂ concentration over the initial 24 h, followed by a plateau that remained stable up to 28 h (**Figure R18**), indicating the establishment of a dynamic equilibrium between H₂O₂ formation and decomposition. Additionally, cycling stability was assessed. After five consecutive cycles (each lasting 1 h), the H₂O₂ production rate remained stable with negligible variation (**Figure R19**). To further assess the structural integrity of DT₂TA-TAPB after cycling, PXRD, FT-IR, and SEM analyses were conducted (**Figure R20** and **Figure R21**). RXRD revealed a slight decrease in peak intensity, likely owing to catalyst delamination, while minor changes in the FT-IR spectra suggested partial oxidation. SEM analysis showed negligible morphological changes. These results indicate that, despite minor structural changes, the catalyst retained its overall stability throughout the cycling process.

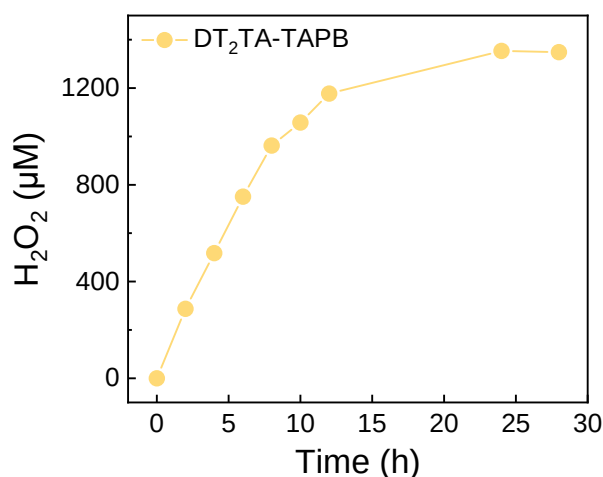


Figure R18 (Fig. 4h). Long-term photocatalytic H₂O₂ production by DT₂TA-TAPB (Reaction conditions: 10 mg catalyst in 40 mL pure water, under air atmosphere, irradiated by a 300 W Xenon lamp (light intensity: 100 mW cm⁻²)).

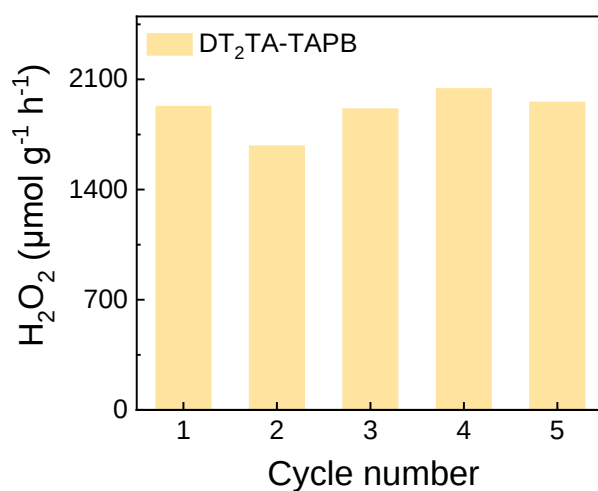


Figure R19 (Supplementary Fig. 27). Cyclic stability experiment of $\text{DT}_2\text{TA-TAPB}$ photocatalytic H_2O_2 production. Reaction conditions: air atmosphere, pure water, 300 W Xenon lamp (light intensity: 100 mW cm^{-2}).

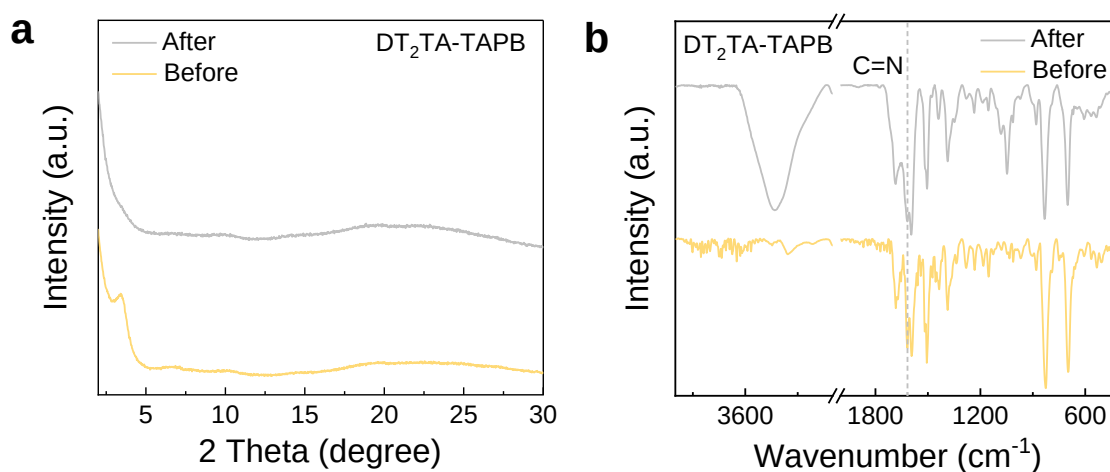


Figure R20 (Supplementary Fig. 28). (a) PXRD patterns and (b) FT-IR spectra of $\text{DT}_2\text{TA-TAPB}$ before and after the photocatalytic reaction.

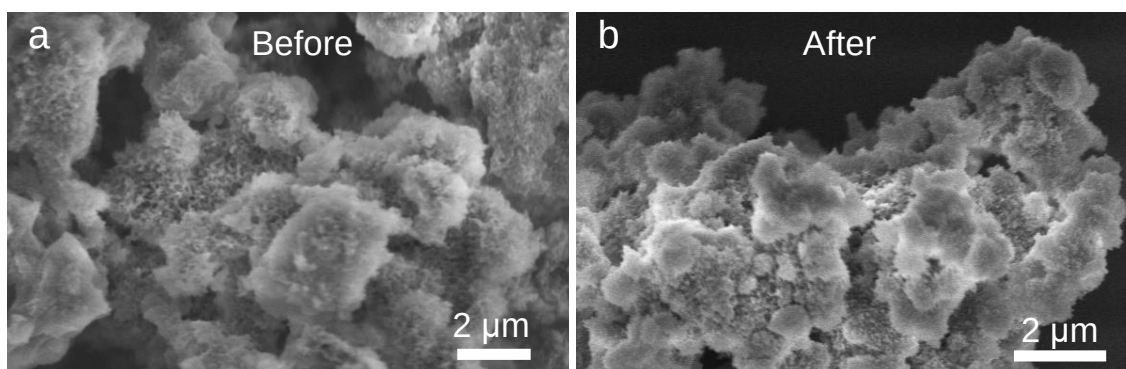


Figure R21 (Supplementary Fig. 29). (a-b) SEM images of $\text{DT}_2\text{TA-TAPB}$ before and after the photocatalytic reaction.

The additions in the manuscript are as follows:

“To assess the practical application of DT₂TA-TAPB, long-term photocatalytic H₂O₂ production experiments were conducted under simulated nature conditions. The results revealed that DT₂TA-TAPB continuously and stably produced H₂O₂ over the initial 24 h, followed by a plateau that remained stable up to 28 h, indicating the establishment of a dynamic equilibrium between H₂O₂ formation and decomposition (**Fig. 4h**). The performance of DT₂TA-TAPB remained stable over five successive cycles (Supplementary Fig. 27), highlighting its sustained photocatalytic activity. Additionally, the recovered DT₂TA-TAPB exhibited minor variations in RXRD and FT-IR spectra, with PXRD exhibited a slight decline in peak intensity, presumably owing to catalyst delamination, while minor changes in the FT-IR spectra suggested partial oxidation (Supplementary Fig. 28). In contrast, SEM morphology remained largely unchanged (Supplementary Fig. 29). These findings imply that the catalyst preserved its structural stability despite minor changes induced during cycling.” (Page 13, Lines 285-295)

The additions in the supplementary information are as follows:

Cycling Stability Experiment

“5 mg of the DT₂TA-TAPB catalyst was dispersed in 25 mL of pure water and irradiated with a 300 W Xenon lamp (light intensity: 100 mW cm⁻²) under an air atmosphere for 1 h. After the reaction, the catalyst was centrifuged, washed, and dried. The recovered sample was then weighed and reused for the subsequent photocatalytic reaction. This process was repeated five times, with each cycle lasting 1 h, using the recycled photocatalyst.” (Page S-10, Lines 152-157)

Comment 6: Photocurrent response experiments should be carried out to assess the efficiency of photogenerated electron–hole separation in the COF samples.

Response 6: Thank you very much for your insightful comment. In response to your suggestion, we have incorporated photocurrent response measurements and the corresponding experimental details into the revised manuscript. As presented in **Figure R22**, the transient photocurrent response results revealed that DT₂TA-TAPB exhibited a significantly higher photocurrent density than the other COFs, underscoring its superior charge separation efficiency.

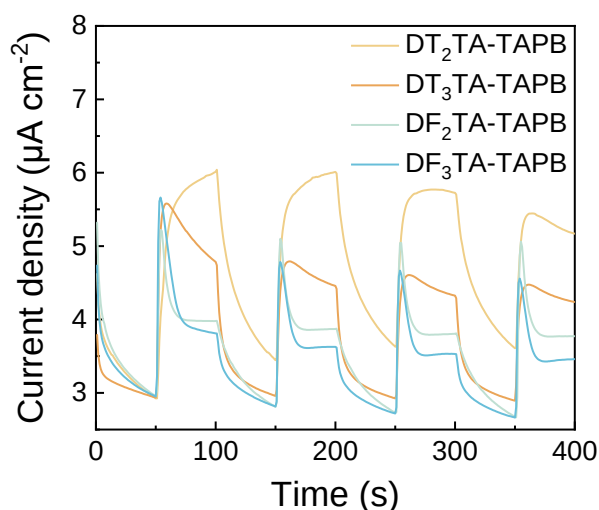


Figure R22 (Supplementary Fig. 8). Transient photocurrent responses of the COFs under illumination.

The additions in the manuscript are as follows:

“Moreover, DT₂TA-TAPB exhibited a markedly higher photocurrent density than the other COFs, highlighting its superior capability in facilitating the transport of photogenerated charge carriers (Supplementary Fig. 8).” (Page 7, Lines 156-158)

The additions in the supplementary information are as follows:

Photocurrent measurement

“The experiments were conducted using a CHI660 electrochemical workstation (Shanghai Chenhua Instruments) equipped with a three-electrode system. The working electrode was prepared by dispersing 2 mg of the catalyst in a mixed solution of 0.9 mL ethanol, 0.1 mL deionized water, and 10 μL of Nafion, followed by sonication to achieve a homogeneous suspension. The resulting suspension was drop-cast onto a fluorine-doped tin oxide (FTO) substrate and naturally dried at room temperature. A platinum wire served as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode, and a 0.5 mol·L⁻¹ Na₂SO₄ aqueous solution as the electrolyte. A 300W Xenon lamp (CEL-HXF300-T3, Beijing Zhongjiao Jinyuan Technology Co., Ltd) with a wavelength of $\lambda > 420$ nm, was used as the light source to illuminate the working electrode. Photocurrent responses were recorded during four continuous "on/off" cycles, each lasting 50-second. During the measurements, the initial voltage was set at 0 V, with a sampling interval of 0.1 second and a sensitivity of 1×10^{-5} A V⁻¹.” (Page S12-13, Lines 209-221)

Reviewer #3 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4 (Remarks to the Author):

Overall comments: The manuscript presented a COF-based photocatalyst that efficiently catalyzes O_2 reduction to generate H_2O_2 in the 10% EtOH/water solution. Comprehensive characterizations for the COF materials and systematic mechanistic investigations for the ORR reaction were conducted. The author found that 1) compared to furan, thiophene functional groups can enhance the charge carrier separation in the excited states and promote charge transfer; 2) a special pattern of sulfur and the adjacent carbon in the thiophene group can better adsorption of the reaction substrate, O_2 , and stabilize the ORR intermediates. It is also impressive that the catalytic materials can produce H_2O_2 without the hole scavenger. The reviewer believes the argument of the manuscript can be strengthened after addressing the following points.

Response: We sincerely appreciate the reviewer's insightful and constructive comments, which have been invaluable in improving the quality and clarity of our manuscript. In response, we have meticulously revised the manuscript and thoroughly addressed all points raised. We hope that the modifications made in accordance with the reviewer's suggestions will meet the standards of *Nature Communications* and render the manuscript suitable for publication. Please find our detailed point-by-point responses below.

Comment 1: The data presented here suggested that COFs with thiophene, especially DT₂TA-TAPB, possess an excited state (S_1) with a charge-separated feature, as illustrated in Figure 1 and 3. It is plausible that this charge-separated S_1 in DT₂TA-TAPB favors electron transfer to O_2 , which explains its better ORR performance. However, it is confusing that the authors are trying to characterize the "exciton dissociation" process within the COFs using temperature-dependent PL. The decrease of PL quantum yield with the increasing temperature occurs in most materials, including organic molecules, due to enhancing non-radiative pathways, such as internal conversion and intersystem crossing. There is no justification to attribute the decrease in PL intensity to exciton dissociation. If there is a further "exciton dissociation"

process, what is the product state the author referred to? Is there a charge-separated electronic state lying below the S_1 ? The method that the authors applied to estimate the dissociation barrier can be traced back to a work that employed temperature-dependent PL to analyze exciton dissociation in ZnO (Misra et al. *Current Applied Physics*, 2009), where both the conversion between bound and free excitons was observed in the PL spectra. The scenario is quite different since Frenkel excitons in organic systems generally have much greater exciton binding energy and remain localized.

Response 1: We sincerely appreciate the reviewer's insightful comments. Regarding the use of temperature-dependent photoluminescence (PL) measurements to characterize the exciton dissociation process, we conducted a thorough analysis and revised our discussion as follows: Excitons, defined as electron-hole pairs generated upon photoexcitation, formed a bound state due to Coulomb interactions. The energy required to overcome this Coulomb attraction and achieve complete separation, referred to as the exciton binding energy, was significantly influenced by temperature (*Proc. Natl. Acad. Sci.* 2024, **121**, e2403434121; *Adv. Mater.* 2019, **31**, 1806671; *J. Am. Chem. Soc.* 2012, **134**, 18189–18192). As temperature increased, thermal excitation enhanced the kinetic energy of charge carriers, weakening the Coulomb interaction between the electron and hole. This reduction in binding strength increased the probability of exciton dissociation (*Nat. Mater.* 2013, **12**, 29–33). Moreover, elevated temperatures induced stronger lattice vibrations (phonon interactions), promoting non-radiative relaxation pathways and further facilitating exciton dissociation. Consequently, higher temperatures generally resulted in reduced fluorescence intensity, accompanied by spectral redshifts or peak broadening. These temperature-dependent PL variations provided valuable insights into exciton's stability and binding energy (*Nat. Commun.* 2022, **13**, 2357; *J. Am. Chem. Soc.* 2024, **146**, 1318–1325).

By systematically measuring fluorescence spectra at varying temperatures, we can estimate the exciton binding energy either quantitatively or semi-quantitatively. At low temperature, fluorescence emission predominantly originated from the radiative recombination of bound excitons, whereas at higher temperatures, a fraction of excitons acquired sufficient thermal energy to dissociate into free charge carriers, resulting in reduced PL intensity (*ACS Nano*. 2014, **8**, 12814–12825). This behavior was analyzed using the Arrhenius equation, which enabled the determination of the exciton binding energy. Notably, this methodology has been extensively validated in both organic semiconductors (*Angew. Chem. Int. Ed.* 2019, **58**, 10236; *Angew. Chem. Int. Ed.* 2025, **64**, e202417712) and covalent organic frameworks (COFs) (*J. Am. Chem. Soc.* 2024, **146**, 1318–1325; *Nat. Commun.* 2022, **13**, 2357). The widespread

application of temperature-dependent PL in these studies highlighted its importance and reliability in probing exciton binding energy.

The additions in the manuscript are as follows:

“As the temperature increased, thermal excitation weakened the Coulombic attraction between electrons and holes, thereby facilitating exciton dissociation and reducing PL intensity^{1,2,3,4}. This phenomenon was analyzed using the Arrhenius equation, which was employed to estimate the exciton binding energy (E_b) from temperature-dependent PL variations^{5,6,7}. Temperature-dependent PL spectroscopy of the COFs revealed that the integrated PL intensity decreased gradually as the temperature increased from 100 to 300 K. Fitting the experimental data using the Arrhenius equation yielded E_b values of 126.6, 137.8, 136.7, and 139.1 meV for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively (**Fig. 3b**, **Fig. 3c**, and Supplementary Fig. 11). These results suggested that the excitons in DT₂TA-TAPB dissociate more readily than those in other COFs, thereby increasing the proportion of free carriers⁸.”

(Page 8-9, Lines 185-194)

The cited references as follows:

1. Alvertis, A. M. et al. Phonon screening and dissociation of excitons at finite temperatures from first principles. *Proc. Natl. Acad. Sci.* **121**, e2403434121 (2024).
2. Jiang, Y., Wang, X., Pan, A. Properties of Excitons and Photogenerated Charge Carriers in Metal Halide Perovskites. *Adv. Mater.* **31**, 1806671 (2019).
3. Grancini, G. et al. Hot exciton dissociation in polymer solar cells. *Nat. Mater.* **12**, 29–33 (2012).
4. Dimitrov, S. D. et al. On the Energetic Dependence of Charge Separation in Low-Band-Gap Polymer/Fullerene Blends. *J. Am. Chem. Soc.* **134**, 18189–18192 (2012).
5. Ru, C. et al. Regulation of Exciton Effects in Functionalized Conjugated Polymers by B-N Lewis Pairs for Visible-Light Photocatalysis. *Angew. Chem. Int. Ed.* **64**, e202417712 (2025).
6. Fu, G. et al. Construction of Thiadiazole-Bridged sp²-Carbon-Conjugated Covalent Organic Frameworks with Diminished Excitation Binding Energy Toward Superior Photocatalysis. *J. Am. Chem. Soc.* **146**, 1318–1325 (2024).
7. Li, C. et al. Covalent organic frameworks with high quantum efficiency in sacrificial photocatalytic hydrogen evolution. *Nat. Commun.* **13**, 2357 (2022).
8. Huang, Y. et al. Achieving a solar-to-chemical efficiency of 3.6% in ambient conditions by inhibiting interlayer charges transport. *Nat. Commun.* **15**, 5406 (2024).

Comment 2: The interpretation of transient absorption data made the mechanism even more confusing. In line 186, the authors attributed the two decay components in the ground state bleach signal kinetics monitored at 580 nm to the electron trapping (fast, τ_1) and the electron transfer processes (slow, τ_2) without rational justification. In fact, following this initial assignment, in line 189, the authors started to refer to the slower decay process (τ_2) as carrier recombination, a completely different process. Could the authors fix this assignment? The reviewer attempted but eventually failed to interpret the TA data presented in the manuscript

due to the lack of experimental details. It is essential to add the following information or supplementary information for clarification. 1) The pump irradiance. The validity of TA measurements requires correct choices of pump irradiance, especially for solid-state samples. Even without considering possible photodegradation caused by the high energy pump pulse, the kinetics can depend on the exciton density related to the photon flux. For instance, high irradiance above certain thresholds can cause biexciton annihilation, and the kinetics will be skewed. A pump power-dependence experiment will be helpful to justify whether the reported kinetics correctly reflected a single exciton decay process. 2) The atmosphere of the TA experiments. Based on the reaction mechanism proposed in the manuscript, if O₂ was present, TA would record the electron transfer process from COFs to O₂, whereas intrinsic exciton decay would be the primary process observed in the inert atmosphere. 3) The solvent. Whether there are sacrificial hole scavengers (in this case, 10%v alcohol) in the system would also change the TA kinetics due to the hole transfer process. The reviewer suggests the authors think carefully about the abovementioned experimental parameters and provide them in an appropriate form in the revised manuscript. They should also reconsider what photochemical processes the TA data actually monitors.

Respond 2: We thank the reviewer for the detailed and insightful comments. We acknowledge the confusion caused by our initial interpretation of the transient absorption (TA) data and have thoroughly revised this section in the manuscript to ensure conceptual consistency and clarity. Specifically, in the revised manuscript, τ_1 is assigned to electron trapping, while τ_2 is attributed to charge carrier recombination rather than electron transfer (*Adv. Mater.* 2024, **36**, 2400288; *Angew. Chem. Int. Ed.* 2023, **62**, e202218688).

In response to the reviewer's request, we have added the following experiments and clarified the influence of pump irradiance, atmospheric conditions, and solvent on the electron transfer dynamics (**Figure R23-R26**).

Influence of pump irradiance on electron transfer dynamics

The influence of pump fluence (2 μ J, 10 μ J, and 20 μ J) on the dynamics of photogenerated charge carriers was systematically investigated (*J. Am. Chem. Soc.* 2017, **139**, 5216–5224). The results indicated that at 20 μ J, the carrier lifetime was significantly prolonged, whereas at 2 μ J, the transient signal was extremely weak (*Chem. Mater.* 2020, **32**, 224–233). This phenomenon was likely due to reduced Coulomb interaction between charge carriers at higher pump irradiance, which promoted exciton dissociation and enhanced the generation of free charge carriers, ultimately improving electron transfer dynamics.

Influence of atmospheric conditions on electron transfer dynamics

The effect of atmospheric conditions on the dynamics of photogenerated charge carriers was investigated (*J. Am. Chem. Soc.* 2023, **145**, 18141–18147). The results revealed that the excited-state lifetime in air was significantly longer than that under a nitrogen atmosphere. The prolongation of lifetime was attributed to the presence of oxygen, which acted as an electron acceptor and facilitated efficient photoinduced charge transfer between the COFs and O₂ molecules (*Angew. Chem. Int. Ed.* 2025, **64**, e202421356). In contrast, measurements under nitrogen atmosphere more accurately reflected the intrinsic exciton decay dynamics of the photocatalyst.

Influence of solvent on the electron transfer dynamics

The influence of the solvent on the dynamics of photogenerated charge carriers was explored. The results demonstrated that the excited-state lifetime in ethanol was longer than in pure water, likely owing to ethanol acting as a hole scavenger, which facilitated hole extraction and effectively suppressed charge recombination (*J. Am. Chem. Soc.* 2017, **139**, 7904–7912; *Nat Commun.* 2025, **16**, 258; *Acc. Chem. Res.* 2021, **54**, 4383–4394). These findings further emphasized the crucial role of the solvent environment in regulating the dynamics of photogenerated charge carriers.

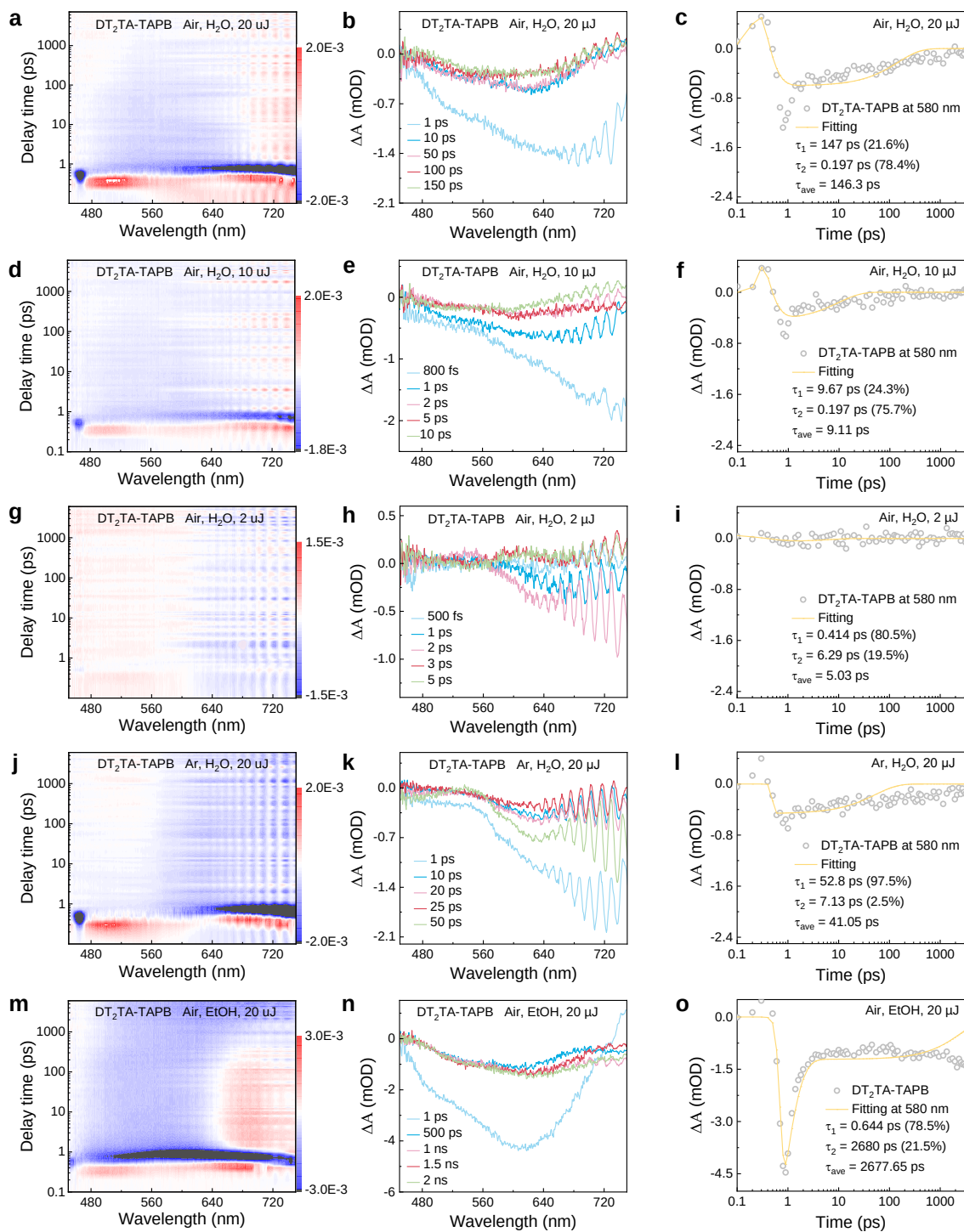


Figure R23 (Supplementary Fig. 13). Femtosecond transient absorption spectra of DT₂TA-TAPB under various experimental conditions, including pseudo-color plots, fs-TA spectra, and decay curves. (a-c) Measurements conducted in air-saturated pure water with a pump pulse of 20 μJ. (d-f) Measurements conducted in air-saturated pure water with a pump pulse of 10 μJ. (g-i) Measurements conducted in air-saturated pure water with a pump pulse of 2 μJ. (j-l) Measurements conducted in Ar-saturated pure water with a pump pulse of 20 μJ. (m-o) Measurements conducted in air-saturated ethanol with a pump pulse of 20 μJ.

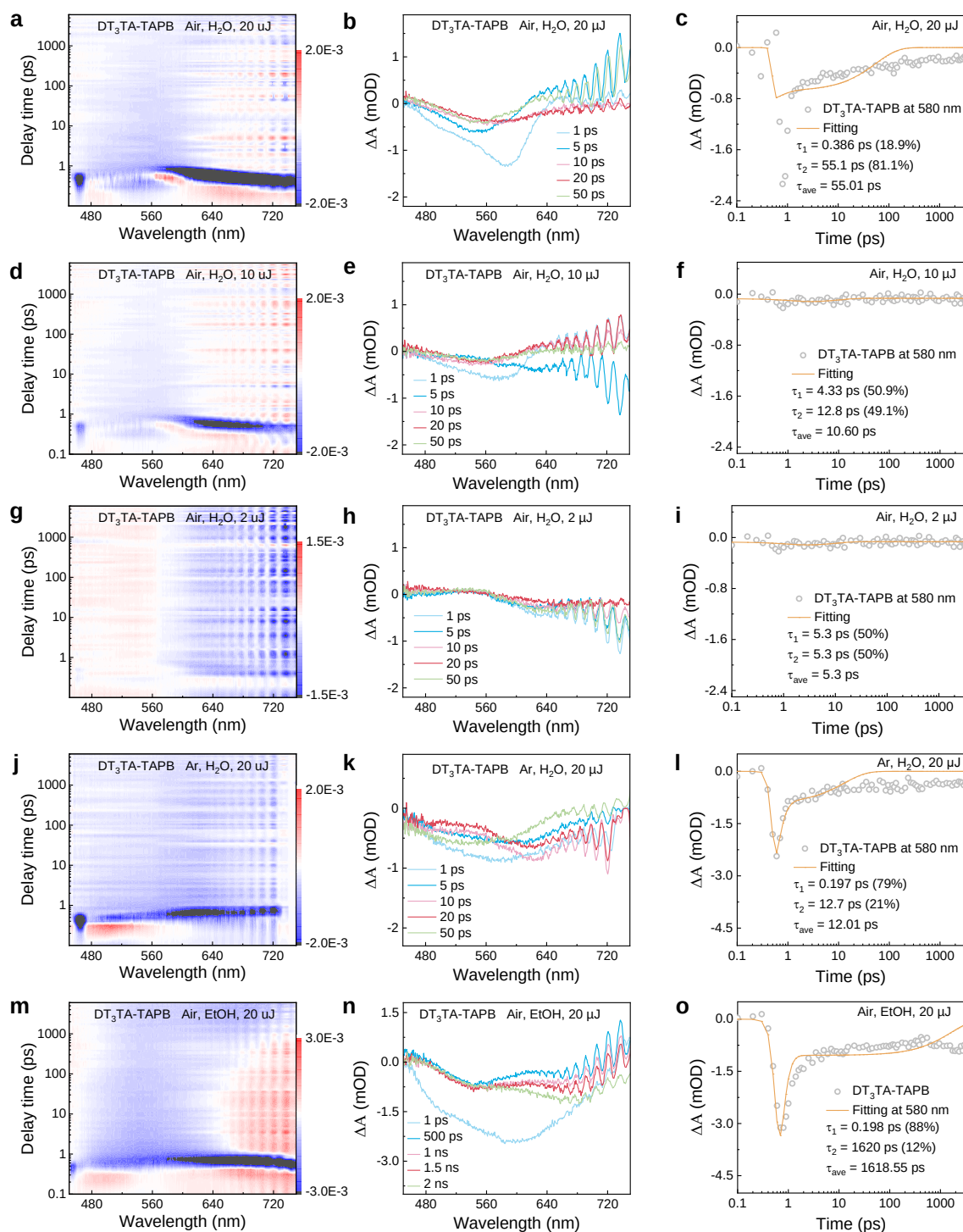


Figure R24 (Supplementary Fig. 14). Femtosecond transient absorption spectra of DT₃TA-TAPB under various experimental conditions, including pseudo-color plots, fs-TA spectra, and decay curves. (a-c) Measurements conducted in air-saturated pure water with a pump pulse of 20 μJ. (d-f) Measurements conducted in air-saturated pure water with a pump pulse of 10 μJ. (g-i) Measurements conducted in air-saturated pure water with a pump pulse of 2 μJ. (j-l) Measurements conducted in Ar-saturated pure water with a pump pulse of 20 μJ. (m-o) Measurements conducted in air-saturated ethanol with a pump pulse of 20 μJ.

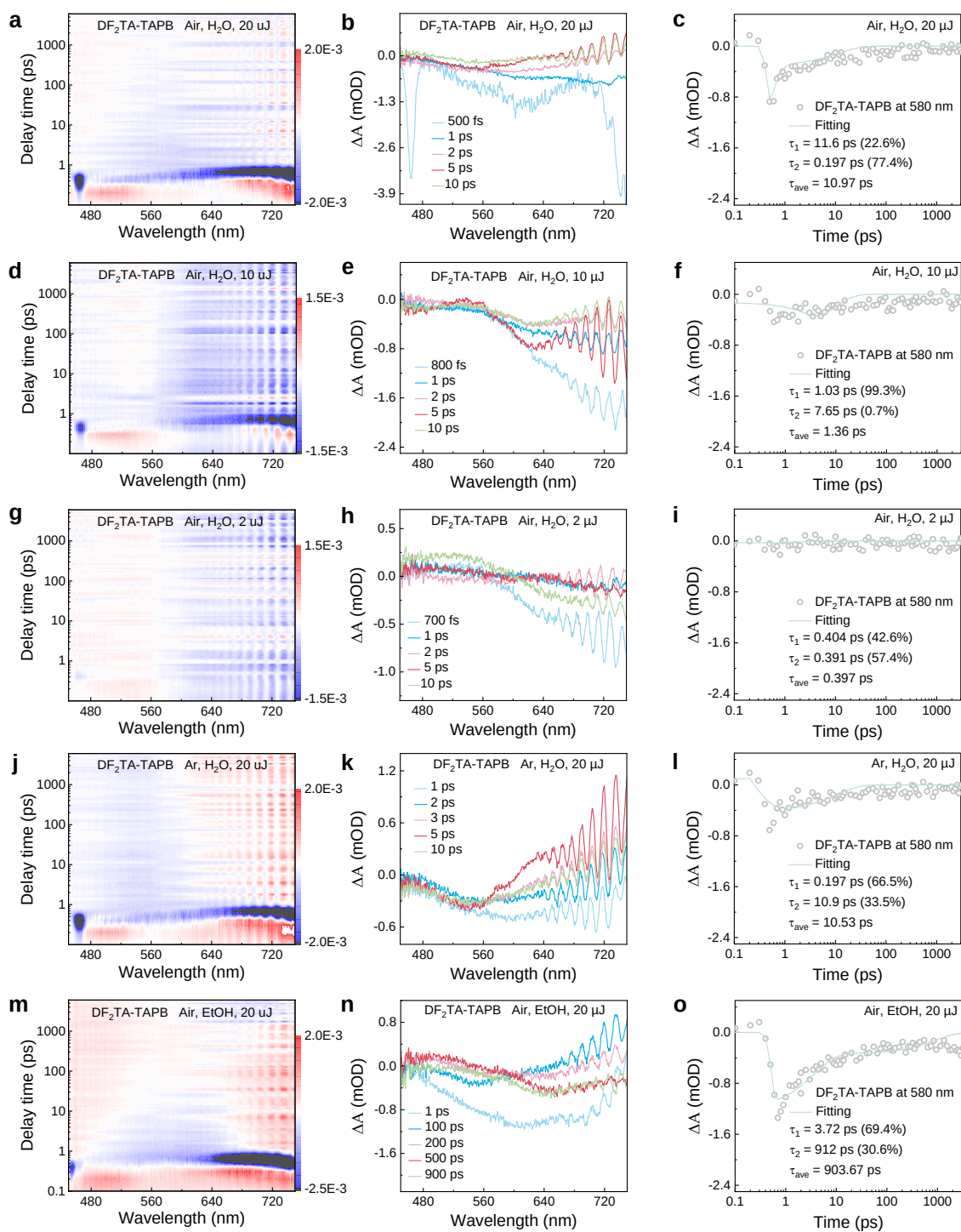


Figure R25 (Supplementary Fig. 15). Femtosecond transient absorption spectra of DF₂TA-TAPB under various experimental conditions, including pseudo-color plots, fs-TA spectra, and decay curves. (a-c) Measurements conducted in air-saturated pure water with a pump pulse of 20 μJ. (d-f) Measurements conducted in air-saturated pure water with a pump pulse of 10 μJ. (g-i) Measurements conducted in air-saturated pure water with a pump pulse of 2 μJ. (j-l) Measurements conducted in Ar-saturated pure water with a pump pulse of 20 μJ. (m-o) Measurements conducted in air-saturated ethanol with a pump pulse of 20 μJ.

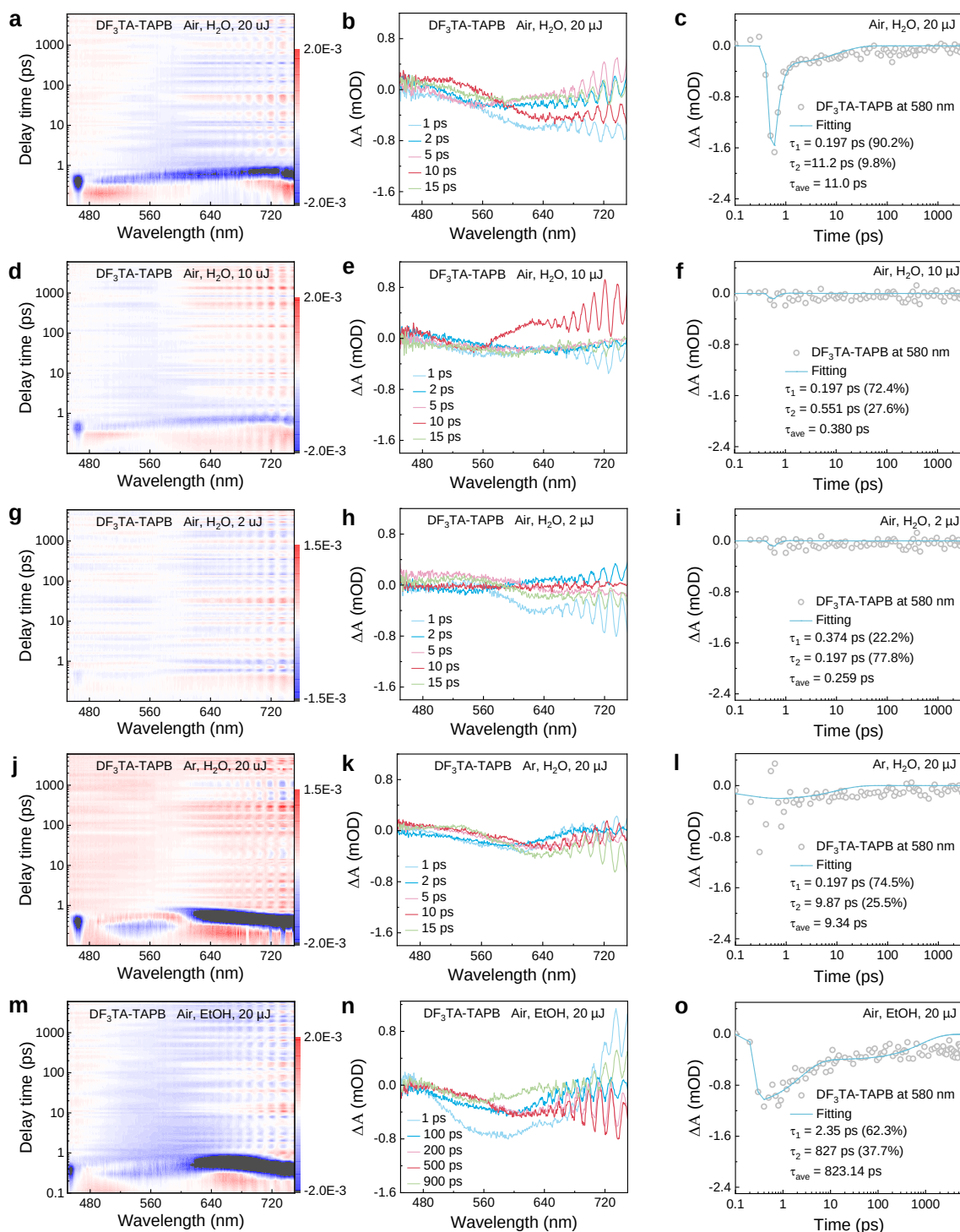


Figure R26 (Supplementary Fig. 16). Femtosecond transient absorption spectra of DF₃TA-TAPB under various experimental conditions, including pseudo-color plots, fs-TA spectra, and decay curves. (a-c) Measurements conducted in air-saturated pure water with a pump pulse of 20 μJ. (d-f) Measurements conducted in air-saturated pure water with a pump pulse of 10 μJ. (g-i) Measurements conducted in air-saturated pure water with a pump pulse of 2 μJ.

2 μ J. (j–l) Measurements conducted in Ar-saturated pure water with a pump pulse of 20 μ J.
(m–o) Measurements conducted in air-saturated ethanol with a pump pulse of 20 μ J.

The additions in the manuscript are as follows:

“Fitting the decay curves at a probe wavelength of 580 nm with a bi-exponential model revealed two distinct relaxation pathways for the photogenerated electrons: a short-lived component (τ_1) corresponding to electron trapping and a long-lived component (τ_2) associated with electron–hole recombination^{1,2}. The τ_1 values for the four COFs were similar, probably because of their structural similarity. In contrast, DT₂TA-TAPB exhibited a significantly longer τ_2 (2677 ps) than the other COFs, indicating an extended carrier lifetime. The average carrier lifetimes (τ_{ave}) were determined to be 2677.65, 1618.55, 903.67, and 823.14 ps for DT₂TA-TAPB, DT₃TA-TAPB, DF₂TA-TAPB, and DF₃TA-TAPB, respectively. These findings revealed that DT₂TA-TAPB effectively suppressed charge recombination, thereby substantially enhancing photocatalytic H₂O₂ generation.” (Page 9, Lines 200-209)

“The influence of external environmental factors—including pump irradiance³, atmospheric conditions⁴, and solvent effect^{5,6,7}—on charge transfer dynamics was systematically studied. At a pump irradiance of 20 μ J, the carrier lifetimes were significantly prolonged, whereas at 2 μ J, the transient signal was considerably weaker⁸. This behavior was likely attributed to the weakening of Coulomb interactions between charge carriers at higher pump intensities, which facilitated exciton dissociation and enhanced the generation of free charge carriers. Additionally, increased pump fluence improved carrier concentration, fostering stimulated emission and partially suppressing non-radiative recombination, which enhanced electron-hole separation. Moreover, the excited-state lifetime of photogenerated charge carriers was notably longer in air than in a nitrogen atmosphere, likely because oxygen acted as an electron acceptor, captured photogenerated electrons and prolonged their lifetime⁹. Similarly, the excited-state lifetime in ethanol exceeded that in pure water, due to ethanol served as a sacrificial hole scavenger, thus suppressing charge recombination. These findings highlighted the critical role of environmental factors in exploring the dynamics of photogenerated charge carriers.” (Page 9-10, Lines 209-221)

The cited references as follows:

1. Qiu, J. et al. COF/In₂S₃ S-Scheme Photocatalyst with Enhanced Light Absorption and H₂O₂-Production Activity and fs-TA Investigation. *Advanced Materials*. **36**, 2400288 (2024).
2. Cheng, C. et al. Verifying the Charge-Transfer Mechanism in S-Scheme Heterojunctions Using Femtosecond Transient Absorption Spectroscopy. *Angew. Chem. Int. Ed.* **62**, e202218688 (2023).
3. Godin, R. et al. Time-Resolved Spectroscopic Investigation of Charge Trapping in Carbon Nitrides Photocatalysts for Hydrogen Generation. *J. Am. Chem. Soc.* **139**, 5216–5224 (2017).

4. Lin, W. et al. Decoupled Artificial Photosynthesis via a Catalysis-Redox Coupled COF||BiVO₄ Photoelectrochemical Device. *J. Am. Chem. Soc.* **145**, 18141–18147 (2023).
5. Venkatraman, R. K., Orr-Ewing, A. J. Solvent Effects on Ultrafast Photochemical Pathways. *Acc. Chem. Res.* **54**, 4383–4394 (2021).
6. Corp, K. L., Schlenker, C. W. Ultrafast Spectroscopy Reveals Electron-Transfer Cascade That Improves Hydrogen Evolution with Carbon Nitride Photocatalysts. *J. Am. Chem. Soc.* **139**, 7904–7912 (2017).
7. Deng, Z. et al. Revealing the excited-state mechanisms of the polymorphs of a hot exciton material. *Nat. Commun.* **16**, 258 (2025).
8. Liu, Y. et al. Tuning Intermediate-Band Cu₃VS₄ Nanocrystals from Plasmonic-like to Excitonic via Shell-Coating. *Chem. Mater.* **32**, 224–233 (2020).
9. Li, W. et al. Unsymmetric Protonation Driven Highly Efficient H₂O₂ Photosynthesis in Supramolecular Photocatalysts via One-Step Two-Electron Oxygen Reduction. *Angew. Chem. Int. Ed.* **64**, e202421356 (2025).

Comment 3: The manuscript claimed a high yield of H₂O₂ for the photocatalyst in pure water without using a sacrificial electron donor. If there is no sacrificial reagent and the photocatalyst cannot oxidize water, as implied in the manuscript, I assume that the reaction will consume electrons in the photocatalyst, which will eventually cause the degradation of the photocatalyst. In the supplementary Figure 14, the yield of H₂O₂ increases linearly with the reaction time without a decline. Could the author explain where the electron comes from when no hole scavenger was presented.?

Respond 3: We sincerely appreciate the reviewers' insightful comments. As illustrated in **Figure R27** and **Figure R28**, isotope labeling experiments confirmed that H₂O₂ was generated through both oxygen reduction and water oxidation pathways. Specifically, water was oxidized by holes to produce O₂, which was subsequently reduced to H₂O₂. Under a nitrogen atmosphere, continuous N₂ purging resulted in negligible H₂O₂ generation, while four-electron water oxidation to O₂ remained detectable. These results suggested that, in the absence of a sacrificial reagent, water acted as both the electron and oxygen source. This dual-pathway mechanism accounts for the observed linear increase in H₂O₂ yield over time and highlighted the remarkable photostability of DT₂TA-TAPB. The efficient consumption of holes via water oxidation enhanced charge utilization and mitigated photocatalyst degradation caused by hole accumulation. In the revised manuscript, we have refined and elaborated on this mechanism to strengthen the scientific rigor and clarity of our discussion.

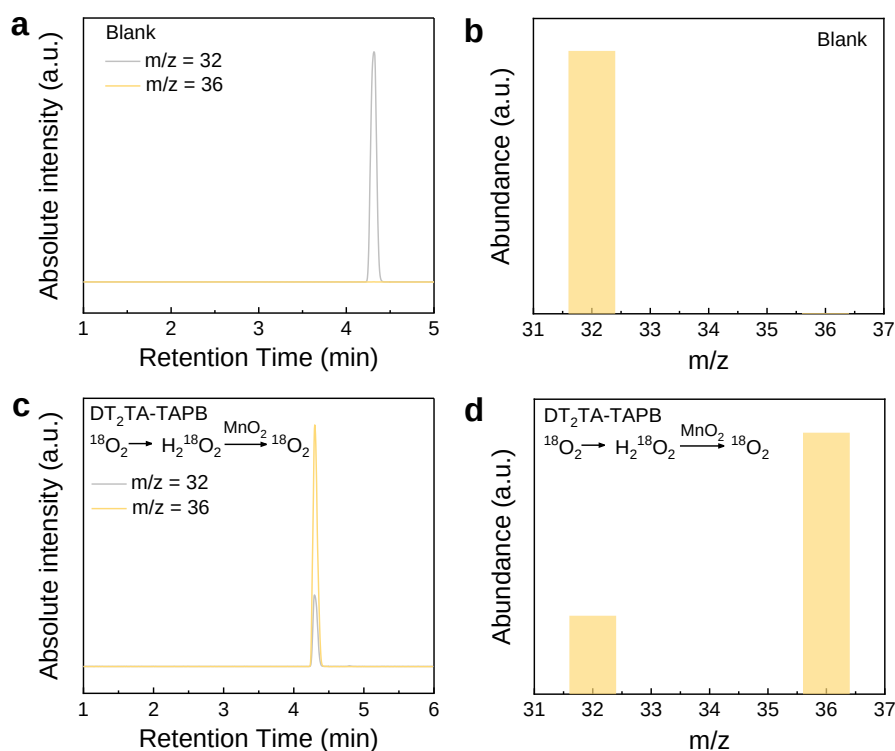


Figure R27 (Supplementary Fig. 38). (a-b) Chromatograms and mass spectra of the blank sample. (c-d) Chromatograms and mass spectra of ^{18}O -labeled oxygen molecules used to probe the source of H_2O_2 generation over $\text{DT}_2\text{TA-TAPB}$.

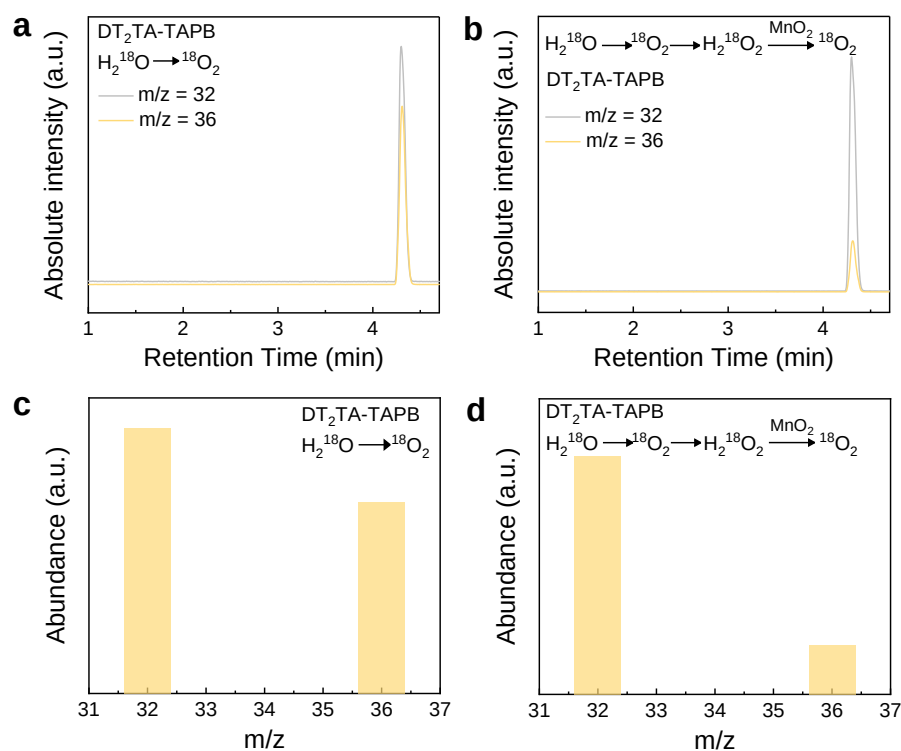


Figure R28 (Supplementary Fig. 39) (a-b) Chromatograms of ^{18}O -labeled H_2O used to probe the origin of H_2O_2 generation over $\text{DT}_2\text{TA-TAPB}$. (c-d) Mass spectra of ^{18}O -labeled H_2O tracing the source of H_2O_2 formation over $\text{DT}_2\text{TA-TAPB}$.

The additions in the manuscript are as follows:

“These results demonstrated that H₂O₂ was generated via a synergistic mechanism involving both water oxidation and oxygen reduction during the photocatalysis over DT₂TA-TAPB, with water simultaneously acting as the electron and oxygen source in the absence of a sacrificial reagent. This dual-pathway mechanism not only improved the utilization efficiency of photogenerated charge carriers but also effectively mitigated catalyst degradation associated with hole accumulation.” (Page 16-17, Lines 372-376)

Comment 4: It is unclear how the authors defined electrons and the holes in the S₁ states of different COFs, as illustrated in Figures 1 and 3. Do the different color-shaded regions reflect the negative and positive charge distribution of the S₁ or the HOMO and LUMO of the ground state? The author should clarify how they interpreted the computational data. In fact, it was unclear if the DFT calculation was carried out for the ground state or if the authors conducted time-dependent DFT calculations to obtain the electronic structure of the excited state. More details about how the calculations were carried out must be provided in the supplemental information 1.11.

Respond 4: We sincerely appreciate the reviewer’s valuable comments. To address the ambiguity in the computational methodology, we provided the following clarification. Time-dependent density functional theory (TDDFT) was employed to investigate the excited-state characteristics of the COFs. As shown in Figure 1 and 3, the color-mapped regions represented the electron and hole distributions in the S₁ excited state, rather than the ground-state charge distribution or the spatial profiles of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Specifically, the blue regions represented electron distribution, while the green regions correspond to hole distribution. To elucidate the spatial separation of charge carriers in the excited state, hole-electron analysis was performed based on the S₁ excited state, including the calculation of the spatial overlap integral (Sr index) and mapping of electron-hole distribution in the S₁ excited state. These analyses were performed using Multiwfn (*J. Chem. Phys.* 2024, **161**, 082503; *J. Comput. Chem.* 2012, **33**, 580-592) and VMD (*J. Mol. Graph.* 1993, **14**, 33-38). This computational approach enabled a precise evaluation of charge separation and spatial distribution in the excited state.

The additions in the supplementary information are as follows:

“Density functional theory (DFT) calculations were performed using the CP2K/Quickstep package. Cell parameters were optimized via a hybrid Gaussian and plane-wave approach, employing the Orbital Transformation method for wavefunction optimization. The 1s electrons

of H, 2s and 2p electrons of N, C, and O, 3s and 3p electrons of S were explicitly considered as valence electrons. Goedecker–Teter–Hutter (GTH) pseudopotentials and double- ζ valence polarized (DZVP–GTH) basis sets were applied to all elements, with a plane-wave cutoff energy of 400 Ry. The Perdew-Burke-Ernzerhof (PBE) functional was used to describe exchange correlation effects, and all calculations were corrected by Grimme D3 method. The convergence criterion for the maximum force was set to 0.02 eV Å⁻¹. For excited-state calculation, Time-dependent density functional theory (TDDFT) was utilized for static analyses. Hole and electron distribution, including spatial overlap integral (Sr index) calculations and electron-hole spatial separation in the S₁ state, were further analyzed using Multiwfn program^{1,2} and visualized with the VMD software³.” (Page S15-16, Lines 276-289)

The cited references as follows:

1. Lu, T. A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. *J. Chem. Phys.* **161**, 082503 (2024).
2. Lu, T., Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580–592 (2012).
3. Humphrey William, Andrew Dalke, Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graph.* **14**, 33–38 (1993).