

Tailoring pore microenvironments in scalable classic COFs boosts solar H₂O₂ production and antibiotic remediation

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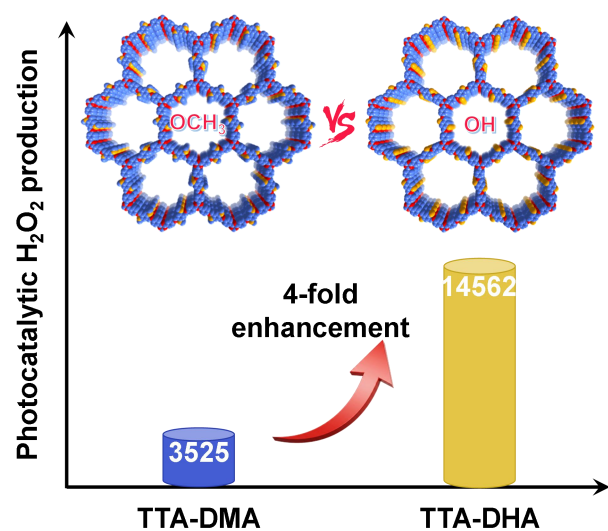
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Pore microenvironment engineering replaces methoxy groups with hydroxyl functionalization in scalable covalent organic frameworks, accelerating charge dissociation and lowering oxygen activation barriers to achieve a 4-fold performance enhancement in solar hydrogen peroxide photosynthesis while driving rapid antibiotic photodegradation.

Research Article

Tailoring pore microenvironments in scalable classic COFs boosts solar H₂O₂ production and antibiotic remediation

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ABSTRACT: Covalent organic frameworks (COFs) are promising for solar-driven chemical synthesis and environmental remediation, yet their practical application is constrained by the trade-off between structural sophistication and synthetic scalability. In this work, we develop a pore microenvironment engineering strategy on classic COF skeletons to boost photocatalytic performance without relying on intricate monomer design. Two isostructural hexagonal COFs (TTA-DMA and TTA-DHA) are synthesized via a facile, cost-effective autoclave solvothermal route using commercially available linkers, achieving gram-scale yield while preserving high crystallinity and uniform pore channels. Combined advanced transient spectroscopies and density functional theory calculations demonstrate that hydroxyl functionalization on pore walls rationally modulates localized electronic states, extending light harvesting, suppressing radiative charge recombination, accelerating charge separation, and lowering the O₂ activation energy barrier. The optimized TTA-DHA delivers an exceptional solar H₂O₂ production rate of 14,562 $\mu\text{mol g}^{-1} \text{h}^{-1}$ with an apparent quantum yield of 9.1% at 400 nm. The *in situ* generated H₂O₂ further drives a concurrent advanced oxidation cascade, achieving 85%-97% degradation of five representative recalcitrant antibiotics within 1 h under visible light. This work bridges scalable material fabrication with efficient solar energy conversion, providing a practical blueprint for functionalizing classic porous frameworks toward multipurpose applications.

KEYWORDS: Covalent organic frameworks; Scalable synthesis; H₂O₂ photosynthesis; Pore microenvironment engineering; Antibiotic degradation

1 Introduction

Solar-driven photosynthesis of hydrogen peroxide (H_2O_2) represents a premier frontier in green chemistry, offering a decentralized and zero-emission alternative to the energy-intensive industry [1-6]. By harnessing earth-abundant water and molecular oxygen, this sustainable approach yields an eco-friendly specialty chemical that can serve as a versatile reagent for a myriad of downstream platforms, spanning on-site chemical synthesis, green disinfection, and environmental purification [7-11]. Covalent organic frameworks (COFs) have emerged as compelling candidates for such solar-to-chemical conversions due to their atomic precision, highly ordered nanochannels, and programmable modularity [12-19]. To unlock their unique features for photocatalytic H_2O_2 production, tailored molecular engineering strategies for COFs—spanning donor-acceptor (D-A) construction, π -conjugation extension, topology/dimension regulation, heteroatom/heterocycle incorporation, and linkage engineering—have been widely adopted to optimize charge carrier dynamics and interfacial kinetics [12-18]. However, a persistent dilemma in current COF chemistry is the trade-off between structural sophistication and synthetic accessibility [20-22]. Unlocking specialized catalytic capabilities often relies on intricately tailored monomer designs that entail demanding multi-step synthesis and prohibitive costs. Consequently, such complexity severely impedes the practical implementation of these crystalline materials while obscuring clear insight into their intrinsic active sites [23-25].

To circumvent synthetic complexity, utilizing readily accessible classic COFs provides a practical starting point; yet these fundamental frameworks often exhibit inadequate functional specialization for challenging catalytic reactions [26-28]. Addressing this challenge requires establishing streamlined, scalable synthetic protocols while systematically investigating channel functional group effects. Subtle alterations of the functional groups decorating the inner walls of identical framework topologies can profoundly modify the macroscopic photocatalytic behavior by modulating localized electronic states and host-guest configurations [29-33]. While current microenvironment engineering primarily focuses on electronic property tuning, comprehensive investigations linking functional group modifications simultaneously to exciton dynamics, interfacial mass transport, and reaction energy barriers remain limited [29-33]. Driven by these considerations, we envisioned that implementing a protocol-simplified strategy on classic COFs would establish a controllable platform to systematically decipher these multifaceted group effects, thereby reconciling the gap between processing scalability and intrinsic catalytic performance [34-36].

In this work, we operationalized this design rationale by synthesizing two classic hexagonal networks—designated as TTA-DMA and TTA-DHA—via a protocol-simplified, autoclave-mediated condensation using cost-effective monomers [37, 38]. This streamlined synthetic route readily enables gram-scale synthesis without compromising structural integrity, high crystallinity, or pore uniformity, underscoring its practical viability. These isomorphic frameworks were subsequently evaluated for solar-driven H_2O_2 photosynthesis. Notably, the hydroxyl-functionalized TTA-DHA yields a superior production rate of $14,562 \mu\text{mol g}^{-1} \text{h}^{-1}$ with an apparent quantum yield of 9.1% at 400 nm, substantially outperforming its methoxy-bearing counterpart ($3525 \mu\text{mol g}^{-1} \text{h}^{-1}$). To understand the origin of this enhanced performance, a combined investigation using ultrafast optical spectroscopy and density functional theory calculations revealed that the channel-tailored hydroxyl groups enhance visible-light absorption, accelerate charge dynamics, and promote oxygen adsorption and activation by optimizing the energy barrier. As a practical application, the *in situ* generated H_2O_2 was integrated into a cascade purification process, enabling rapid degradation of recalcitrant antibiotic pollutants within 1 h under visible light. Overall, this study offers a practical strategy for optimizing COF photocatalysts by shifting the focus from complex monomer design to local microenvironment tuning of accessible frameworks, paving a cost-effective and scalable way for solar-to-chemical conversion.

2 Experimental

2.1 Synthesis of COFs

2.1.1 Synthesis of TTA-DMA

A 10 mL Schlenk tube was charged with TTA- NH_2 (56.6 mg, 0.16 mmol) and DMA (46.6 mg, 0.24 mmol), followed by the addition of 0.4 mL of 1,4- dioxane, 1.6 mL of mesitylene and 0.1 mL of acetic acid (HOAc). The reaction mixture was sonicated for 3 min, then heated at 120 °C for 3 days. The precipitated solid was collected by pipette extraction, and sequentially soaked in fresh THF with solvent renewal every 6 h over 24 h, followed by soaking in fresh acetone with solvent renewal every 6 h for 12 h. The resulting solid was dried under vacuum at 60 °C for 4 h to afford TTA-DMA as a yellow powder (80.4 mg, 85% yield).

2.1.2 Synthesis of TTA-DHA

A 10 mL Schlenk tube was charged with TTA- NH_2 (56.6 mg, 0.16 mmol) and DHA (39.8 mg, 0.24 mmol), followed by the addition of 0.4 mL of 1,4- dioxane, 1.6 mL of mesitylene and 0.1 mL of HOAc. The reaction mixture was sonicated for 3 min, then heated at 120 °C for 3 days. The precipitated solid was collected by pipette extraction, and sequentially soaked in fresh THF with solvent renewal every 6 h over 24 h, followed by soaking in fresh acetone with solvent renewal every 6 h for 12 h. The resulting solid was dried under vacuum at 60 °C for 4 h to afford TTA-DHA as a dark red powder (79.1 mg, 90% yield).

2.2 Photocatalytic H₂O₂ production

The photocatalytic production of H₂O₂ was carried out in a 100 mL reaction vessel. Briefly, 5 mg of the as-prepared COF photocatalyst was dispersed in a mixed solution consisting of 45 mL deionized water and 5 mL benzyl alcohol (BA). The reaction temperature was maintained at 20 °C via a circulating water bath. Before light irradiation, the suspension was ultrasonicated for 3 min to achieve homogeneous dispersion, followed by purging with pure oxygen for 30 min under dark conditions. The photocatalytic reaction was triggered by irradiation with a 300 W xenon lamp equipped with a 420 nm cutoff filter, with continuous magnetic stirring at 200 rpm throughout the reaction. The concentration of generated H₂O₂ in the suspension was determined using the cerium sulfate (Ce(SO₄)₂) titration method. In detail, 2 mL aliquots of the reaction mixture were withdrawn at predetermined time intervals and filtered through a 0.22 mm filter membrane. Subsequently, 0.5 mL of the filtrate was thoroughly mixed with an excess of cerium sulfate solution (0.25 mM, 20 mL). The absorbance of the mixed solution was recorded at 318 nm using a UV-vis spectrophotometer, and the H₂O₂ concentration was calculated accordingly.

For control experiments, oxygen was replaced with air or nitrogen; alternatively, 0.1 mmol of silver nitrate (AgNO₃) or *p*-benzoquinone (*p*-BQ) was added, with all other experimental parameters kept identical.

For long-term stability tests, the catalyst dosage was increased to 15 mg, and the concentration of cerium sulfate solution used for titration was correspondingly raised to 0.5 mM, while all other experimental conditions remained unchanged. At the end of each reaction cycle, the spent catalyst was thoroughly recovered by centrifugation, washed sequentially with water and EtOH to remove residual reactants, and subsequently dried under vacuum. The refreshed catalyst was then reintroduced into the subsequent run for the next catalytic cycle.

3 Results and discussion

3.1 Synthesis, Chemical Linkage, and Skeletal Identification

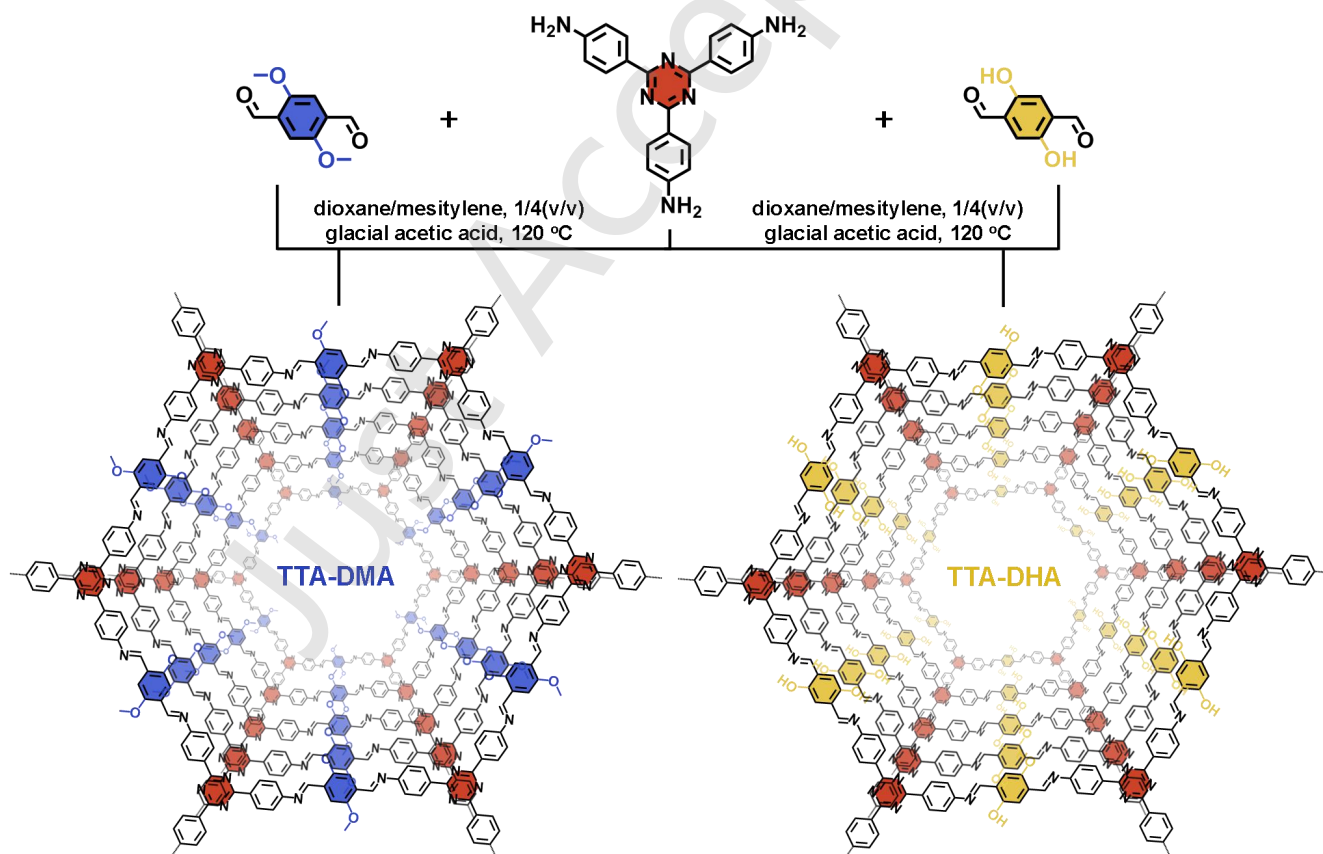


Figure 1. Synthesis and pore microenvironment modulation of TTA-based COFs. Synthetic routes toward TTA-DMA and TTA-DHA via solvothermal condensation at 120 °C in a dioxane/mesitylene mixture (1:4, v/v) with glacial acetic acid. The distinctive pore channel functionalities (methoxy groups in blue, hydroxyl groups in yellow) are highlighted within the extended hexagonal frameworks.

In an effort to operationalize our philosophy of utilizing structurally transparent platforms, we commenced our study by revisiting the synthesis of two well-established hexagonal topologies. Historically documented as COF-JLU5 and COF-JLU6 [37,

38], these specific frameworks traditionally demanded tedious operations based on vacuum-sealed glass ampoule techniques. Recognizing that such intricate operational barriers severely cloud the accessibility of these appealing networks, we implemented a protocol-simplified, autoclave-mediated condensation route to streamline the preparation while prioritizing economic feasibility [39-41]. Utilizing the identical sets of commercially available and cost-effective linker—namely, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA-NH₂) combined with either 2,5-dimethoxyterephthalaldehyde (DMA) or 2,5-dihydroxyterephthalaldehyde (DHA)—this straightforward synthetic protocol successfully delivers the highly crystalline, imine-linked frameworks with high quality. To explicitly highlight the structural composition and the channel-tailored microenvironments inside our customized system, these two isomorphous configurations are systematically designated as TTA-DMA and TTA-DHA hereafter (**Figure 1**).

Initial validation of the successful chemical condensation and the distinct functional environments was achieved via Fourier-transform infrared (FT-IR) spectroscopy (**Figure S1** and **S2**). For both TTA-DMA and TTA-DHA, the characteristic stretching vibration bands corresponding to the initial carbonyl groups (1670 cm⁻¹) of the aldehydes and the primary amine groups (3300-3400 cm⁻¹) of TTA-NH₂ completely vanished or significantly attenuated [42]. Concurrently, the emergence of a prominent newborn reflection at approximately 1620 cm⁻¹, which is unambiguously assigned to the stretching vibration of the typical C=N linkages, rigorously confirms the highly efficient imine condensation [43, 44]. Crucially, the spectrum of TTA-DHA was characterized by a highly diffuse and broadened absorption background spanning the region of 2500-3300 cm⁻¹ (**Figure S1**), a classic spectroscopic signature arising from the profound redshift of hydroxyl stretching vibrations governed by strong intramolecular hydrogen bonding [38]. In sharp contrast, the spectrum of TTA-DMA was highlighted by the distinctive methoxy features, explicitly manifested as the sharp C-H stretching spikes at 2830 cm⁻¹ alongside the intense, characteristic aryl ether asymmetric stretching vibration at 1210 cm⁻¹ (**Figure S2**) [37]. These spectroscopic fingerprints collectively validate the successful, unadulterated realization of the tailored pore microenvironments.

3.2 Crystalline Lattices, Porous Textures, and Gram-Scale Scalability

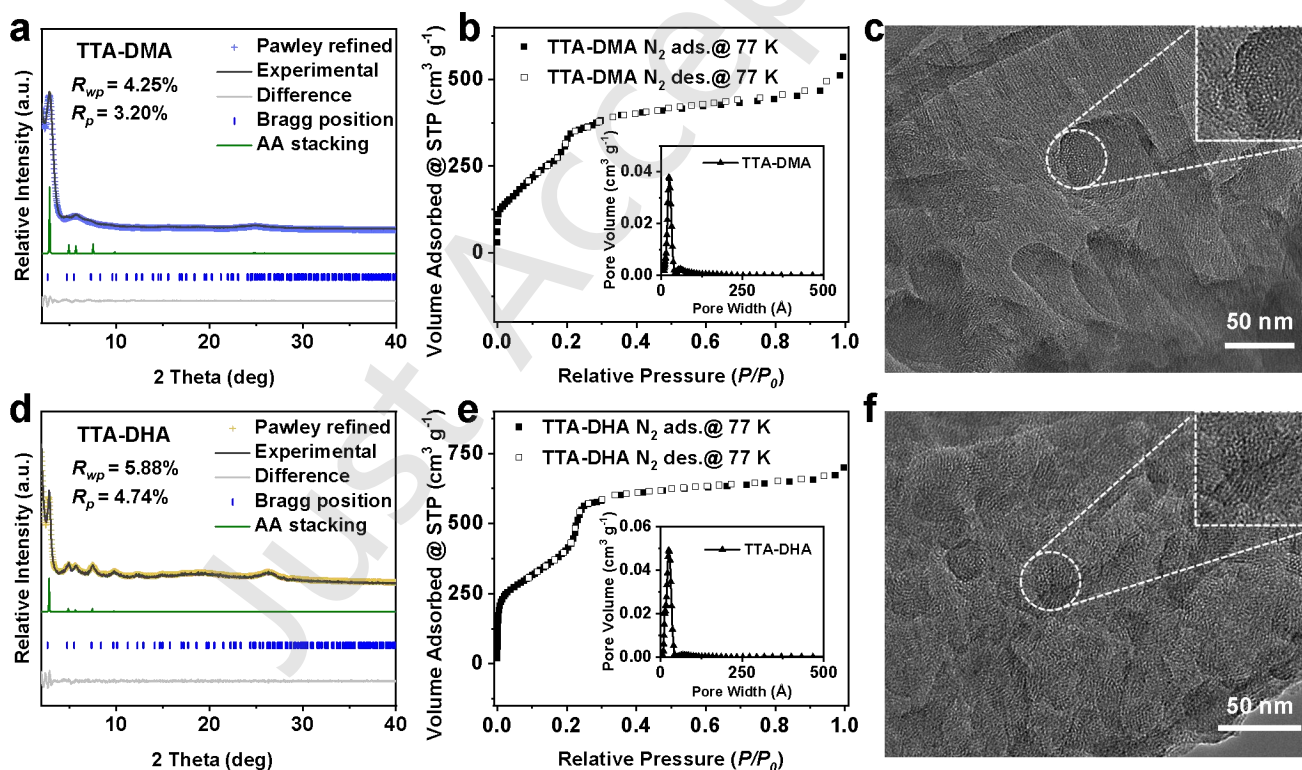


Figure 2. Crystalline structures and porous properties. Experimental and Pawley-refined PXRd patterns of (a) TTA-DMA and (d) TTA-DHA with corresponding refinement residuals and simulated AA-stacking profiles. N_2 sorption isotherms profiles at 77 K and the derived pore size distributions (insets) of (b) TTA-DMA and (e) TTA-DHA. HR-TEM images of (c) TTA-DMA and (f) TTA-DHA displaying the porous frameworks (insets: expanded lattice views). Scale bars = 50 nm.

Definitive evidence regarding the crystalline lattice integrity of these structurally transparent platforms was gathered through powder X-ray diffraction (PXRd) analysis (**Figure 2a** and **2d**). Both TTA-DMA and TTA-DHA exhibit well-defined, highly intense primary diffraction reflections at 2 theta angle of $\sim 2.8^\circ$, matching well with the simulated AA-stacking hexagonal models (**Figure S3** and **S4**). When compared with the historically reported benchmarks synthesized via the traditional vacuum-sealed ampoule route (COF-JLU5 and COF-JLU6), our autoclave-derived samples reproduce the identical

structural periodicities and manifest sharper peak profiles and comparable, if not superior, diffraction intensities [37, 38]. This preservation of reflection positioning and structural coherence confirms that such a straightforward and user-friendly synthetic protocol is highly capable of driving long-range crystalline ordering with high fidelity, ensuring a reliable material platform for exploring localized channel chemistry.

The permanent porosity and distinct textural traits of these isomorphous configurations were further investigated via nitrogen adsorption-desorption measurements at 77 K (**Figure 2b** and **2e**). Both frameworks display reversible Type-IV isotherms characterized by an abrupt, inflection-like structural step in the relative pressure range of $P/P_0 = 0.1$ - 0.3 , indicative of an ordered mesoporous framework [45]. The derived Brunauer-Emmett-Teller (BET) specific surface area of TTA-DMA was calculated to be $1400 \text{ m}^2 \text{ g}^{-1}$, which closely approaches that of the pristine ampoule-synthesized literature benchmark (COF-JLU5, $1632 \text{ m}^2 \text{ g}^{-1}$). And the BET surface area of the hydroxyl-functionalized TTA-DHA reached $2100 \text{ m}^2 \text{ g}^{-1}$, substantially outperforming the previously reported counterpart (COF-JLU6, $1450 \text{ m}^2 \text{ g}^{-1}$). Analysis of the nonlocal density functional theory (NLDFT) pore size distributions reveals a uniform, singular pore channel alignment (**Figure 2b** and **2e inset**), with experimental pore diameters estimated at 2.5 nm for TTA-DMA and 2.6 nm for TTA-DHA, closely matching the theoretical predictions. Concurrently, the total pore volumes ($0.92 \text{ cm}^3 \text{ g}^{-1}$ for TTA-DMA and $1.13 \text{ cm}^3 \text{ g}^{-1}$ for TTA-DHA) remain highly prominent, with TTA-DHA also exhibiting an enhanced pore capacity over COF-JLU6 ($0.96 \text{ cm}^3 \text{ g}^{-1}$). This variation in pore parameters likely stems from the distinct spatial demands of the channel-exposed functional groups, wherein the sterically less hindered $-\text{OH}$ groups in TTA-DHA afford a more open and accessible pore space compared to the bulkier $-\text{OCH}_3$ groups in TTA-DMA. Such well-defined pore environments help minimize structural ambiguities, ensuring that subsequent variances in photocatalytic behavior can be reasonably correlated to the tailored channel microenvironments [35, 46]. Direct visual evidence of this crystalline perfection and open-channel morphology was obtained via high-resolution transmission electron microscopy (HR-TEM). The HR-TEM snapshots clearly resolve highly oriented, long-range hexagonal domain alignments and well-defined honeycomb-like lattice fringes (**Figure 2c** and **2f**) [47].

To demonstrate the high practicality and operational scalability of these channel-tailored networks, gram-scale fabrications were executed across three independent batches utilizing the same straightforward autoclave scheme. Simply scaling up the precursor inputs yielded over 1.0 g of pristine TTA-DMA and TTA-DHA products per run. Structural, morphological, and chemical evaluations via PXRD, SEM, and FT-IR confirmed the exceptional robustness and batch-to-batch reproducibility of this route (**Figures S5-S7**). The gram-scale powders across all three batches retained sharp crystallographic reflections, uniform particle morphology, and identical imine-linkage vibrational signatures consistent with their milligram-level counterparts, thereby securing a steady material foundation for subsequent photophysical and catalytic inquiries [21].

3.3 Photophysical Traits, Band Structures, and Charge Dynamics

Insight into how the tailored channel microenvironments modulate electronic profiles and exciton dynamics was initially gained through a systematic photophysical and photoelectrochemical screening (**Figure 3**). As presented in the UV-vis diffuse reflectance spectra (DRS, **Figure 3a**), TTA-DMA displays a sharp absorption edge at approximately 500 nm, corresponding to its bright yellow powder appearance. Upon replacing the methoxy groups with hydroxyl functions, TTA-DHA exhibits a profound absorption redshift, extending its light-harvesting boundary deep into the region up to 650 nm (macroscopically manifested as a red powder) [48]. This pronounced bathochromic shift is primarily ascribed to the intramolecular hydrogen bonding ($\text{O}-\text{H}\cdots\text{N}=\text{C}$) within TTA-DHA, which reinforces molecular planarity, elevates intra-skeletal electronic conjugation, and promotes potential keto-enol tautomerism [31].

The absolute energy levels were subsequently executed via Mott-Schottky measurements. The positive slopes extracted from the linear alignments confirm the intrinsic n-type semiconductor nature for both frameworks (**Figure 3b** and **S8**) [49]. Extrapolation of the linear plots at multiple frequencies reveals a flat-band potential of -1.11 V (vs. Ag/AgCl) for TTA-DMA (**Figure S8**), which translates to a conduction band minimum (CBM) level of approximately -0.91 V (vs. NHE). Meanwhile, the CBM for TTA-DHA was pinpointed at -0.70 V (vs. NHE, **Figure 3b**). The optical bandgaps were evaluated from Tauc plots, yielding 2.44 eV for TTA-DMA and a narrowed 1.67 eV for TTA-DHA (**Figures S9** and **S10**). By integrating these values with the Mott-Schottky results, the detailed electronic band structures were established (**Figure 3c**) [50]. Crucially, the valence band maximum (VBM) position of TTA-DHA is located at 0.97 V (vs. NHE), which is markedly elevated compared to that of TTA-DMA (1.53 V vs. NHE). This electronic configuration underscores that while both platforms possess a sufficiently negative CBM to drive the single-electron reduction of oxygen ($\text{O}_2/\bullet\text{O}_2^-$, -0.33 V vs. NHE) or the two-electron pathway to hydrogen peroxide ($\text{O}_2/\text{H}_2\text{O}_2$, 0.68 V vs. NHE) [51].

Looking beyond thermodynamic alignment, the localized channel chemistry exerts an exceptional influence on the kinetic charge separation and trafficking across the crystalline networks. Electrochemical impedance spectroscopy (EIS, **Figure 3d**) reveals a remarkably compressed Nyquist semicircle diameter for TTA-DHA relative to TTA-DMA, demonstrating a significantly minimized charge transfer resistance at the solid-liquid boundary [52]. This kinetic acceleration is further corroborated by the transient photocurrent responses (**Figure 3e**), where TTA-DHA delivers a boosted and reproducible

photocurrent density over multiple on-off solar illumination cycles, indicating optimized photogenerated carrier separation [39, 53]. Steady-state and time-resolved photoluminescence (TR-PL) spectroscopies were cooperatively employed to track the microscopic exciton fates. Under identical photo-excitation, TTA-DMA displays an intense, broad radiative emission centered at ~550 nm (**Figure 3f**), which decays with an average lifetime of 1.66 ns (**Figure S11**). In contrast, the steady-state PL emission of TTA-DHA is almost completely quenched, whereas its transient lifetime is prolonged to 1.94 ns. This profound combination of intensive steady-state fluorescence suppression and an elongated exciton life expectancy provides an unambiguous mechanistic fingerprint. It substantiates that the customized hydroxylated channels within TTA-DHA act as an elite electronic conduit that effectively deactivates unavailing, immediate radiative recombination pathways [54], successfully shifting the light-induced excitons into a long-lived, highly productive charge-separated state available for interfacial catalytic cascades. Temperature-dependent PL (TD-PL) measurements were performed to quantitatively evaluate the energetic barrier for exciton dissociation (**Figure S12**) [55-57]. By fitting the temperature-dependent integrated PL intensity with the Arrhenius equation, the exciton binding energy (E_b) of TTA-DHA was determined to be 40.3 meV, noticeably lower than that of TTA-DMA (52.0 meV, **Figure S12**). This reduced E_b confirms that channel hydroxylation effectively weakens the Coulombic attraction within electron-hole pairs, thereby facilitating thermal exciton dissociation into free charge carriers.

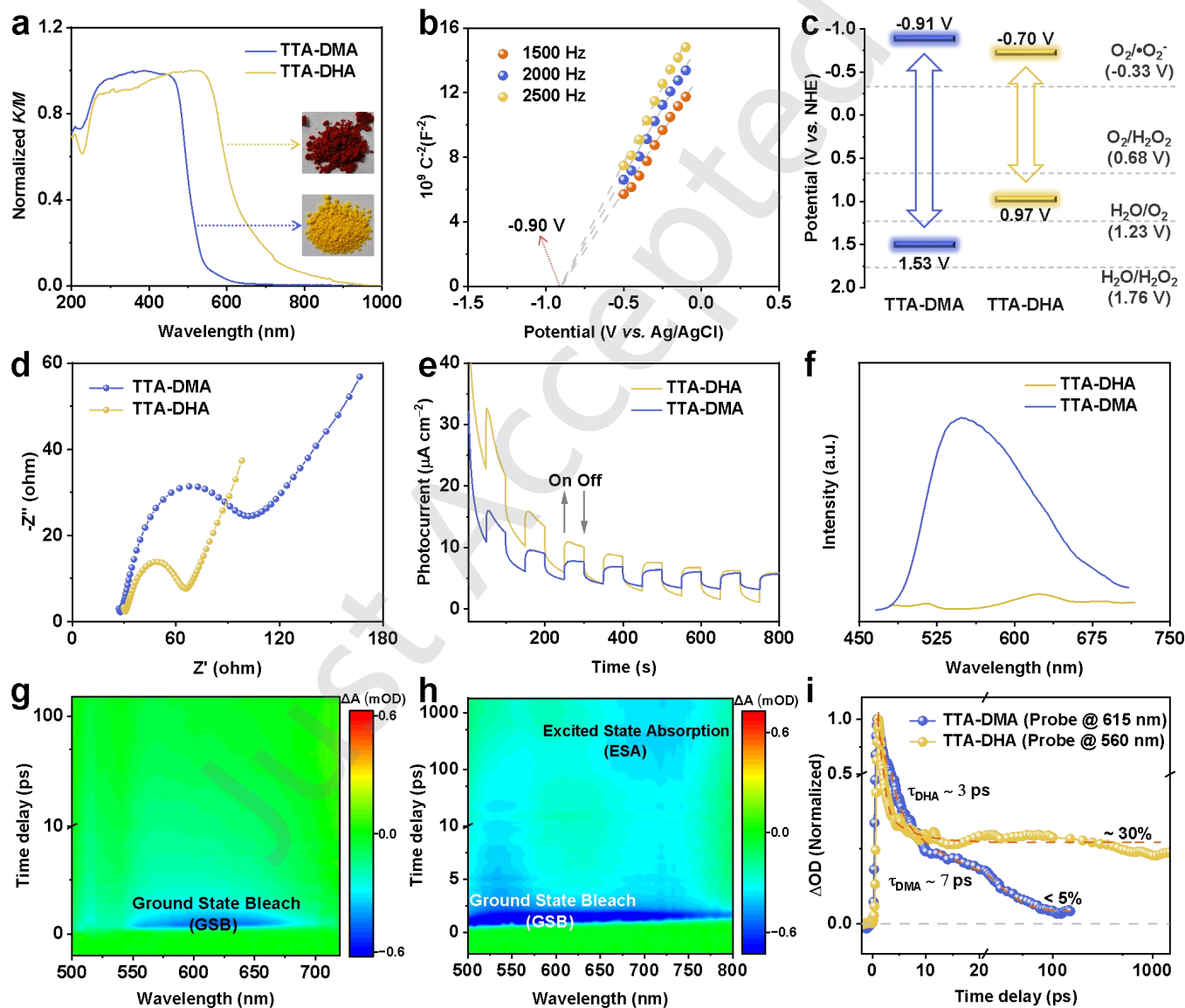


Figure 3. Optoelectronic landscapes and tailored charge-trafficking dynamics within the channel-functionalized frameworks. (a) UV-vis diffuse reflectance spectra of TTA-DMA and TTA-DHA (Insets: digital photographs of the corresponding sample powders). (b) Mott-Schottky plots of TTA-DHA measured at frequencies of 1500, 2000, and 2500 Hz. (c) Experimentally determined band structures of TTA-DMA and TTA-DHA relative to the NHE scale, along with the relevant redox potentials for H_2O_2 production. (d) Electrochemical impedance spectroscopy Nyquist plots. (e) Transient photocurrent responses over several on-off light irradiation cycles at an applied potential. (f) Steady-state photoluminescence spectra recorded at an excitation wavelength of 400 nm. 2D pseudocolor transient-absorption map of TTA-DMA (g) and TTA-DHA (h). (i) Time-resolved decay curves of the transient absorption signal. The curves show the decay of the excited state absorption (ESA) and ground state bleach (GSB) for TTA-DMA (Probe @ 615 nm, blue circles) and TTA-DHA (Probe @ 560 nm, yellow circles). The decay constants are $\tau_{DHA} \sim 3$ ps and $\tau_{DMA} \sim 7$ ps. The residual signal is $\sim 30\%$ for TTA-DHA and $< 5\%$ for TTA-DMA.

(h). (i) Normalized transient- absorption kinetic traces extracted at the characteristic probe wavelengths for TTA- DMA (615 nm) and TTA- DHA (560 nm).

To gain deeper spectroscopic insights into the ultrafast exciton relaxation dynamics, femtosecond transient absorption (fs-TA) spectroscopy was performed (**Figures 3g-3i**) [58]. As presented in the 2D pseudocolor TA maps, TTA-DMA displays a dominant ground-state bleach (GSB) feature in the 550-700 nm region (**Figure 3g**). The kinetic decay trace of TTA-DMA probed at 615 nm yields a rapid decay time constant of $\tau = 7$ ps (**Figure 3i**). The signal decays almost completely back to the baseline within 10 ps with a negligible residual component ($< 5\%$), indicating that photogenerated excitons in TTA-DMA predominantly undergo rapid geminate recombination back to the ground state without forming abundant free charge carriers [59]. In sharp contrast, TTA-DHA exhibits a distinct spectral profile featuring a broad excited-state absorption (ESA) band across the 550-800 nm region (**Figure 3h**). When probed at 560 nm (within the ESA region), the kinetic trace reveals an ultrafast initial decay phase with a time constant of $\tau = 3$ ps (**Figure 3i**). Rather than representing energy dissipation to the ground state, this 3-ps process corresponds to the highly efficient dissociation of photogenerated excitons into a charge-separated (CS) state. Following this rapid charge-splitting event, a long-lived ESA signal plateau with $\sim 30\%$ of the initial amplitude persists beyond the 1000-ps delay time window. This persistent $\sim 30\%$ long-lived ESA signal evidences that a significant fraction of photogenerated excitons in TTA-DHA successfully converts into long-lived free charge carriers instead of undergoing geminate recombination [60]. This dominant non-radiative charge-dissociation channel is consistent with the lowered E_b and the severely quenched photoluminescence intensity of TTA-DHA (**Figure 3f**), confirming that the incorporation of DHA units substantially accelerates exciton dissociation and stabilizes long-lived charges for subsequent redox process [61].

3.4 Photocatalytic Performance and Interfacial Molecular Mechanisms

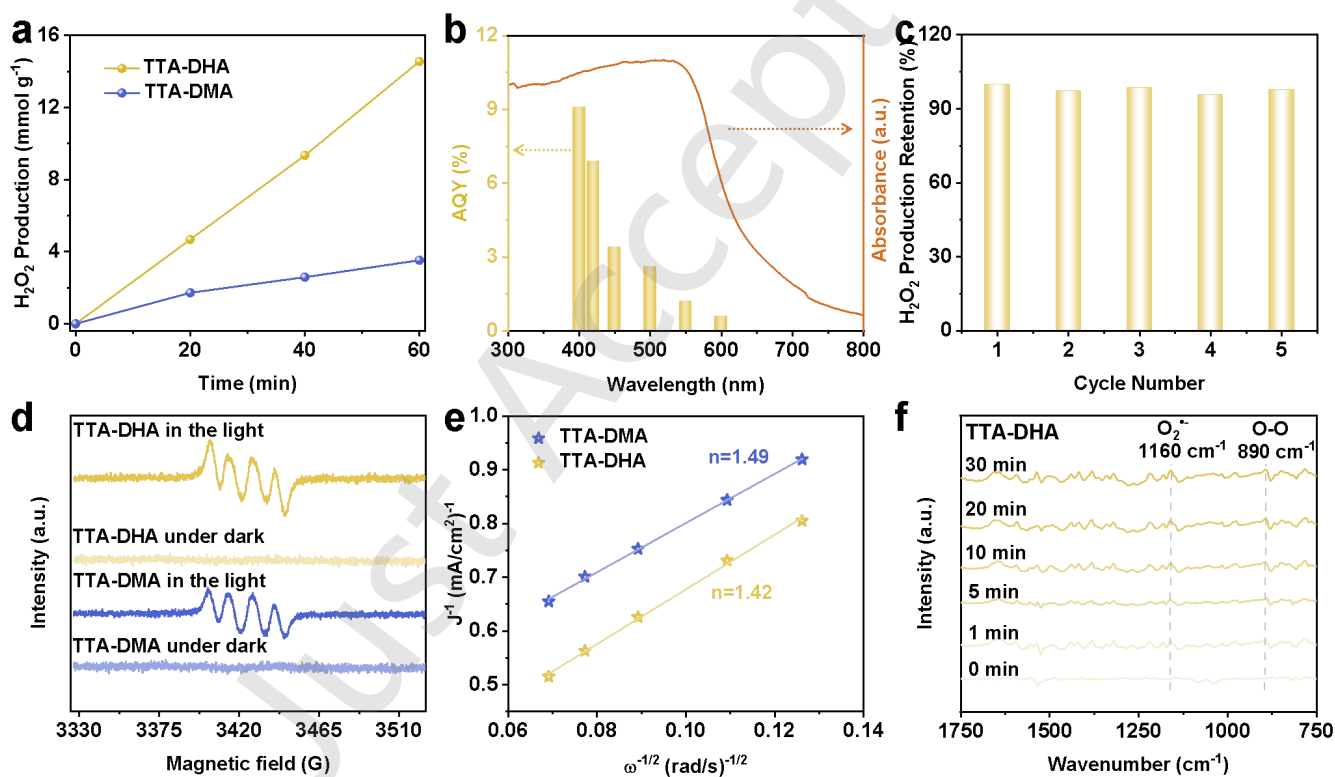


Figure 4. Visible-light-driven H_2O_2 photosynthetic performance and molecular-level mechanistic pathways over the channel-tailored configurations. (a) Photocatalytic H_2O_2 production rates as a function of light irradiation time. (b) Wavelength-dependent apparent quantum yield of TTA-DHA plotted against its UV-vis absorption spectrum. (c) Photocatalytic stability and recycling tests of TTA-DHA over five consecutive cycles. (d) Electron paramagnetic resonance spectra for DMPO- $\bullet O_2^-$ adducts obtained over TTA-DMA and TTA-DHA under dark and light irradiation. (e) Koutecky-Levich plots derived from rotating disk electrode measurements, with calculated electron transfer numbers (n). (f) *In situ* diffuse reflectance infrared Fourier transform spectra captured over TTA-DHA during the photocatalytic H_2O_2 evolution process.

Evaluation of the visible-light-driven photocatalytic activity was initiated under ambient conditions with the assistance of benzyl alcohol (BA) as a sacrificial electron donor (**Figure 4**) [62]. Under continuous illumination, TTA-DHA exhibits a linear and steady H_2O_2 evolution profile, delivering a total yield of $14,562\ \mu mol\ g^{-1}\ h^{-1}$ (**Figure 4a**). This production rate substantially outpaces that of its methoxy-functionalized counterpart (TTA-DMA, $3525\ \mu mol\ g^{-1}\ h^{-1}$), demonstrating that the localized hydroxyl engineering within the channels brings about a nearly 4-fold enhancement in catalytic output. This significant

divergence can be attributed to the extended spectral response and enhanced charge separation intrinsic to the hydroxylated framework. Additionally, control tests show negligible H_2O_2 decomposition over both frameworks across 90 min under dark and light conditions (**Figure S13**), confirming that secondary decomposition does not affect the net accumulation yield. To confirm the correlation between macro-photoactivity and the optical absorption edge, the wavelength-dependent apparent quantum yields (AQY) were systematically profiled (**Figure 4b**). The calculated AQY values for TTA-DHA closely trace its diffuse reflectance spectrum, yielding a peak efficiency of 9.1% at 400 nm, which scales to 6.9% at 420 nm, 3.4% at 450 nm, and 2.6% at 500 nm. Benefiting from the proton-transfer-induced absorption redshift, measurable quantum efficiencies of 1.2% at 550 nm and 0.6% at 600 nm are successfully sustained well into the long-wavelength regime [63].

Control experiments were conducted to clarify the boundary requirements and establish the nature of this catalytic pathway (**Figure S14**) [63]. The exclusion of either light or the catalyst results in negligible product evolution, confirming a strict photocatalytic process. Purging the reaction medium with nitrogen induces an almost absolute shutdown of chemical evolution, identifying dissolved oxygen as the irreplaceable precursor for H_2O_2 generation [10]. Moreover, a decrease in efficiency from pure oxygen to air ($3168 \mu\text{mol g}^{-1} \text{h}^{-1}$) underscores the importance of oxygen availability within the pore channels. The absence of BA leads to a noticeable decline in performance, indicating its vital role as a hole scavenger to maintain charge balance. Taken together, these oxygen-dependent behaviors and control trends demonstrate that the observed H_2O_2 evolution operates via an oxygen reduction reaction (ORR) pathway. Crucially, introducing the electron capturer AgNO_3 dampens the reaction kinetics, while adding the superoxide scavenger *p*-benzoquinone leads to a complete stop in H_2O_2 formation, unveiling photogenerated electrons and transient superoxide intermediates ($\bullet\text{O}_2^-$) as the key drivers of this interfacial ORR process [63].

Beyond initial catalytic output, long-term framework robustness represents a critical criterion for practical applicability. As illustrated in **Figure 4c**, TTA-DHA sustains its catalytic performance with negligible degradation across five sequential cycles, keeping over 95% of its primary capability. To validate this macroscopic endurance, post-catalysis structural and morphological cross-examinations were implemented (**Figure S15**) [32]. The PXRD profiles of TTA-DHA recorded after long-term catalytic runs exhibit highly intense reflections identical to the pristine baseline, illustrating that the long-range crystalline lattice stays uncompromised (**Figure S15a**). Concurrently, field-emission scanning electron microscopy (FE-SEM) imaging demonstrates a preservation of the original interlaced nanofibrous architecture (**Figure S15b** and **S15d**). This structural stability is further supported by FT-IR spectroscopy (**Figure S15c**), where the characteristic stretching peaks stay almost unadulterated. Together, these experimental findings indicate good chemical stability and frame preservation for TTA-DHA during ongoing catalysis [31].

To clarify the reduction pathway and kinetics enabled by the tailored pore environments, spin-trapping electron paramagnetic resonance (EPR) and rotating disk electrode (RDE) measurements were conducted [30]. Upon transitioning from dark environments to visible light, both configurations prompt the appearance of the classic characteristic signals indexed to the $\text{DMPO} \cdot \bullet\text{O}_2^-$ adducts (5,5-Dimethyl-1-pyrroline N-oxide, DMPO) (**Figure 4d**), identifying superoxide radicals as a key transient radical intermediate during the ORR process [30]. Tracking the time-resolved evolution profiles reveals that for both TTA-DMA and TTA-DHA, the peak intensities of these characteristic signals expand with prolonged photo-irradiation time, demonstrating a continuous, light-driven accumulation of $\bullet\text{O}_2^-$ radical species (**Figure S16** and **S17**). Crucially, a horizontal comparison at given irradiation interval demonstrates that TTA-DHA delivers a much higher peak-to-peak intensity relative to TTA-DMA (**Figure 4d** and **S16-S17**). This kinetic acceleration is a direct consequence of the optimized carrier dynamics within the framework; the suppressed interfacial charge resistance and the prolonged exciton lifetime collaboratively ensure a continuous delivery of reactive electrons to the channel-exposed oxygen molecules [52]. To quantify the definitive electron transfer kinetics at the catalyst-electrolyte boundary, Koutecky-Levich plots (**Figure 4e**) were mathematically derived from the rotating disk electrode polarization trajectories (**Figure S18** and **S19**). The electron transfer numbers (*n*) were calculated to be 1.42 for TTA-DHA and 1.49 for TTA-DMA. These fractional profiles indicate a dominant selective two-electron ($2e^-$) ORR mechanism toward H_2O_2 [29]. Direct real-time evidence tracking the dynamic binding configuration of active oxygen intermediates throughout the catalytic progression was captured via *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*In situ* DRIFTS, **Figure 4f**). Upon prolonged photo-excitation over the TTA-DHA, two synchronized infrared absorption responses gradually intensify. A distinctive vibrational signal materializes at 890 cm^{-1} , which is assigned to the O–O stretching vibration of adsorbed oxygen molecules, signifying successful geometric confinement and chemical activation within the optimized framework pore spaces [64]. Concurrently, another characteristic signal emerges prominently at 1160 cm^{-1} , an index that matches with the asymmetric stretching vibrations of surface-confined superoxide species ($\bullet\text{O}_2^-$). This time-dependent enhancement of both the O–O stretching and the downstream $\bullet\text{O}_2^-$ vibrational modes provides a molecular-level validation of the structural design [36].

3.5 Electronic Structures and Theoretical Reaction Mechanisms

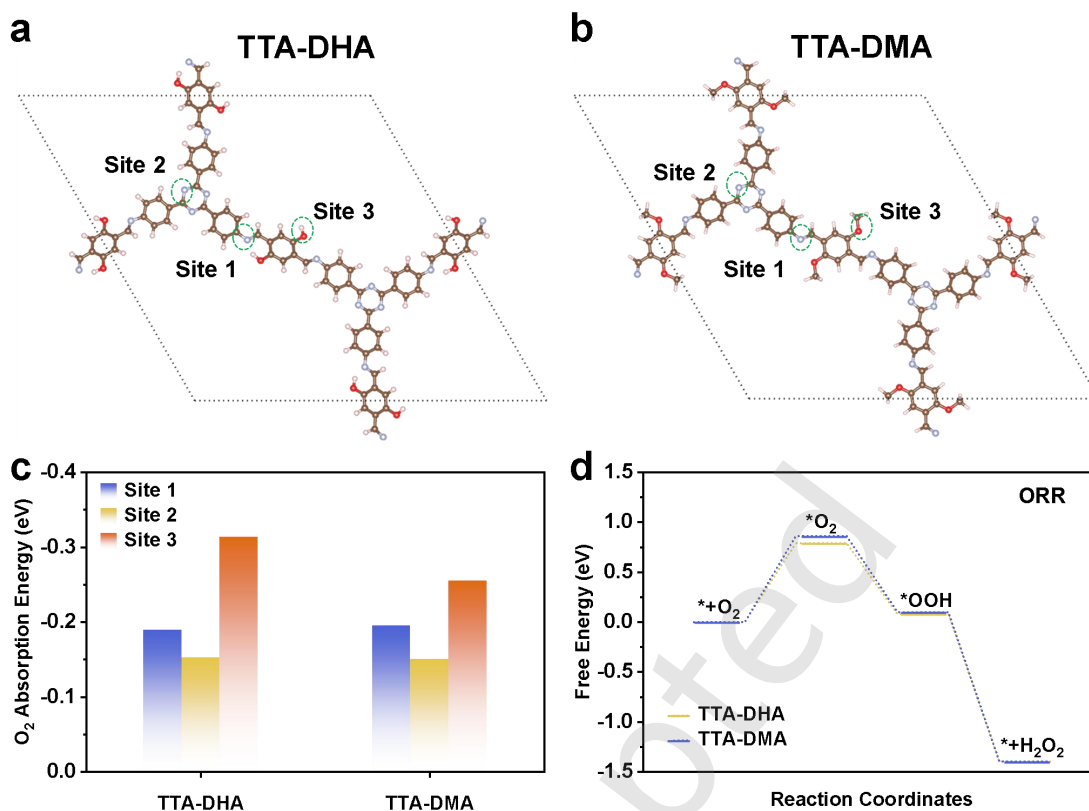


Figure 5. Density functional theory calculation studies for photocatalytic H₂O₂ production. Optimized structural models and designated active centers within the crystalline unit cells of (a) TTA-DHA and (b) TTA-DMA for O₂ adsorption. (c) Calculated O₂ adsorption energies at different active sites of TTA-DHA and TTA-DMA. (d) Calculated Gibbs free energy profiles for the two-electron oxygen reduction reaction pathway toward H₂O₂ photosynthesis over the optimal active sites of TTA-DHA and TTA-DMA.

Density functional theory (DFT) calculations reveal the energetic landscapes and electronic configurations [65]. The spatial topologies of the frontier molecular orbitals were first examined (**Figure S20** and **S21**), revealing that the highest occupied molecular orbitals (HOMO) are predominantly localized on the electron-donating DHA and DMA segments, whereas the lowest unoccupied molecular orbitals (LUMO) are inherently confined within the electron-deficient TTA cores. This spatial separation creates a favorable environment to suppress charge recombination [66]. Complementing this, the electronic band structures and projected density of states (PDOS) profiles (**Figure S22** and **S23**) demonstrate that TTA-DHA possesses a more contracted bandgap than TTA-DMA, which is thermodynamically favorable for visible-light harvesting. Crucially, the HOMO edge of TTA-DHA exhibits an intensified degree of orbital hybridization stemming from the mixing of channel-exposed oxygen lone pairs with the framework π -network. This enhanced hybridization elevates the intrinsic electron donor capability, translating directly into augmented interfacial photochemical reactivity [67].

To establish the precise atomic localization of these reaction boundaries, geometric optimization and oxygen adsorption energy (E_{ads}) evaluations were conducted across three prospective coordination centers: the carbon of the imine linkage (Site 1), nitrogen atoms within the triazine ring (Site 2), and the oxygen atoms of the functionalized DHA/DMA ligands (Site 3) (**Figure 5a** and **5b**; with detailed structural models compiled in **Figure S24** and **S25**) [68]. As quantitatively illustrated in **Figure 5c**, Site 3 yields the most prominent exothermicity for both porous frameworks, registering E_{ads} of -0.314 eV for TTA-DHA and -0.255 eV for TTA-DMA. These calculations confirm that the oxygen sites serve as the primary binding and reaction centers [68], where the hydroxyl functionalization in TTA-DHA provides a higher oxygen affinity to facilitate $^*\text{O}_2$ enrichment within the pore microenvironment. The thermodynamic free-energy landscapes of the stepwise ORR proceeding at these optimized functional sites were subsequently traced (**Figure 5d**). For both polymeric architectures, the initial single-electron capture transition exhibits positive free-energy changes, identifying this activation step as the rate-determining step (RDS) for the entire cascade [69]. TTA-DHA delivers a lowered activation barrier (0.790 eV) for this RDS compared to TTA-DMA (0.861 eV). Once this endothermic obstacle is overcome, the subsequent proton-coupled single-electron reduction steps transform into downhill (**Figure 5d**) [64]. Collectively, these theoretical calculations show that optimized band alignment, enhanced orbital hybridization, and a lower activation barrier together drive the superior H₂O₂ photosynthesis in the hydroxyl-engineered framework.

3.6 Photocatalytic Remediation of Antibiotic Contaminants

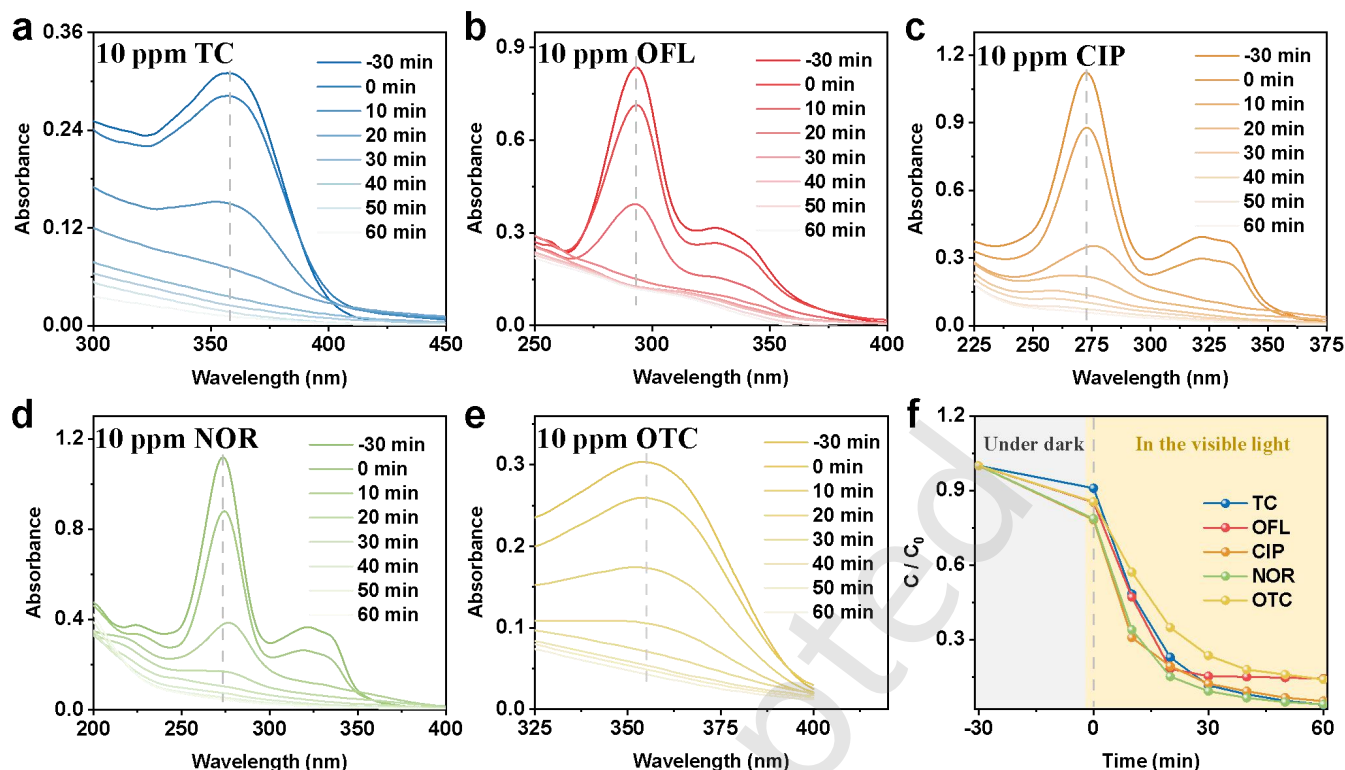


Figure 6. Broad-spectrum photocatalytic antibiotic degradation performance of TTA-DHA. (a-e) Time-dependent UV-vis absorption spectra tracking the photocatalytic degradation of various antibiotics (10 ppm) over TTA-DHA under visible light irradiation: (a) tetracycline (TC), (b) ofloxacin (OFL), (c) ciprofloxacin (CIP), (d) norfloxacin (NOR), and (e) oxytetracycline (OTC). The periods from -30 to 0 min represent the adsorption-desorption equilibrium established in the dark. (f) Photocatalytic degradation efficiency profiles (C/C_0) of the five target antibiotic pollutants as a function of irradiation time.

To evaluate the environmental applicability of the tailored framework and leverage its efficient oxygen reduction kinetics [11, 70], the optimized TTA-DHA was implemented for the deconstruction of emerging antibiotic pollutants under visible-light irradiation (Figure 6). Five recalcitrant antibiotic targets—tetracycline (TC, Figure 6a), ofloxacin (OFL, Figure 6b), ciprofloxacin (CIP, Figure 6c), norfloxacin (NOR, Figure 6d), and oxytetracycline (OTC, Figure 6e)—were systematically profiled. Prior to light exposure, a 30-min dark experiment was conducted to establish the adsorption-desorption equilibrium. Benefiting from ordered hydrophilic pore channels, all antibiotic molecules undergo efficient pore diffusion and localized pre-concentration, as reflected by the steady attenuation in baseline absorbance during the dark period (Figure 6a-6e). Under visible-light irradiation, the primary absorption bands for TC (358 nm), OFL (293 nm), CIP (273 nm), NOR (274 nm), and OTC (355 nm) decreased rapidly within 60 min (Figure 6a-6e). The subtle hypsochromic or bathochromic shifts in peak maxima reflect the transient evolution of intermediates during structural degradation [71]. The kinetic curves (C/C_0) further illustrate the broad degradation capability of the system (Figure 6f) [47]. Within 60 min, TTA-DHA achieved over 95% removal for TC, NOR, and CIP, while eliminating more than 85% of OFL and OTC. This efficiency stems from accelerated charge separation and suppressed recombination in the hydroxylated channels, promoting continuous reactive species generation [11]. Radical quenching measurements (Figure S26) reveal that $\bullet\text{O}_2^-$ and *in situ* generated H_2O_2 serve as the predominant active species, with other reactive species also contributing to the cooperative photodegradation process [72]. For comparison, the control framework TTA-DMA displays weaker dark adsorption ($\sim 3\%$ - 10%) and lower total degradation ($\sim 80\%$ - 90%) under identical conditions (Figure S27), highlighting the key role of intra-pore hydroxyl groups in boosting local substrate enrichment and interfacial charge transfer.

4 Conclusions

In summary, this work realizes efficient photocatalytic H_2O_2 production and antibiotic remediation through precise pore microenvironment engineering on classic, readily accessible COF skeletons. We confirm that atomic-level variations in pore wall functionalities can significantly modulate macroscopic catalytic performance, without relying on intricate monomer design or complex synthetic procedures. The superior activity of hydroxyl-functionalized TTA-DHA originates from multiple synergistic effects: expanded light absorption, suppressed radiative charge recombination, accelerated interfacial charge transfer, and lowered activation energy barrier for the rate-determining step of oxygen reduction. The optimized TTA-DHA

also features excellent cycling stability and gram-scale scalability. This study shifts the optimization paradigm of COF photocatalysis from elaborate monomer engineering to localized microenvironment tuning of classic porous frameworks, offering a feasible, cost-effective path to high-performance photocatalytic porous materials.

Electronic Supplementary Material: Supplementary material (Figures S1–S27 and Tables S1–S2) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909298>.

Data availability

All data supporting the conclusions of this paper are provided in the manuscript and the Electronic Supplementary Material. Any additional data related to this work are available from the corresponding author upon reasonable request.

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Declaration of competing interest

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

Author contribution statement

S.M. W.Z. and B.Z. conceived the project. S.M. and X.W. synthesized and characterized target COFs. X.W. and X.F. performed the photocatalytic H₂O₂ production experiments and antibiotic-related performance tests. G.Z. conducted theoretical calculations. X.F. and D.M. assisted with characterization measurements and data analysis. S.M. W.Z. and B.Z. drafted the manuscript, and all authors revised the manuscript and approved the final submitted version.

Use of AI statement

None.

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Electronic Supplementary Material

Tailoring pore microenvironments in scalable classic COFs boosts solar H₂O₂ production and antibiotic remediation

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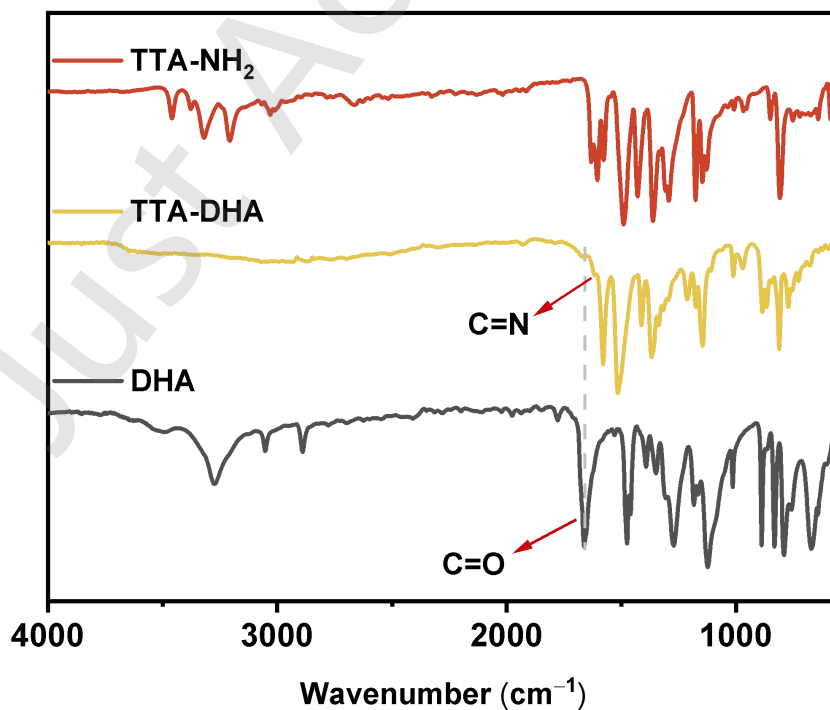


Figure S1. FT-IR spectra of TTA-NH₂ (top, red), TTA-DHA (middle, yellow), and DHA monomer (bottom, grey).

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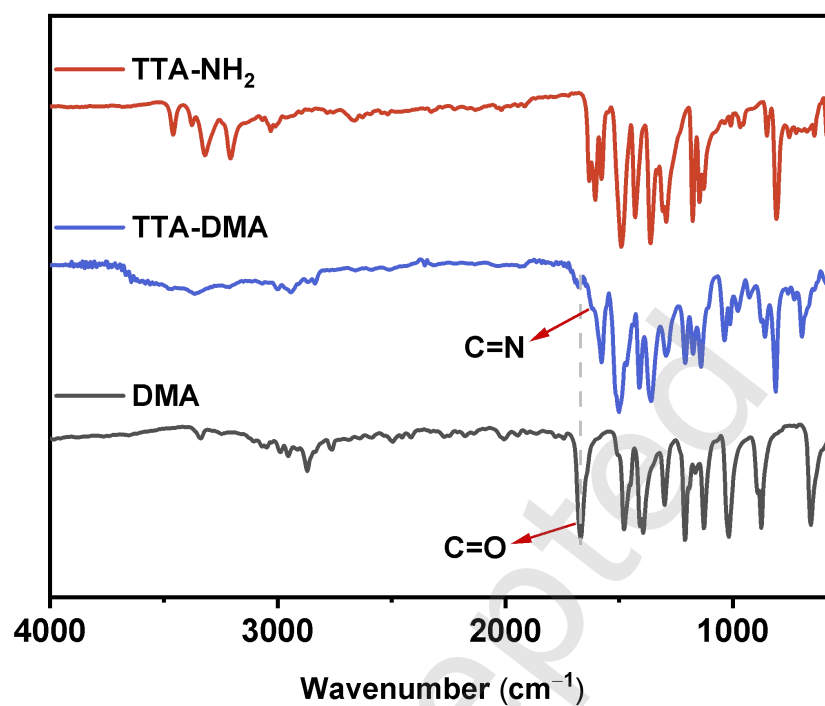


Figure S2. FT-IR spectra of TTA-NH₂ (top, red), TTA-DMA (middle, blue), and DMA monomer (bottom, grey).

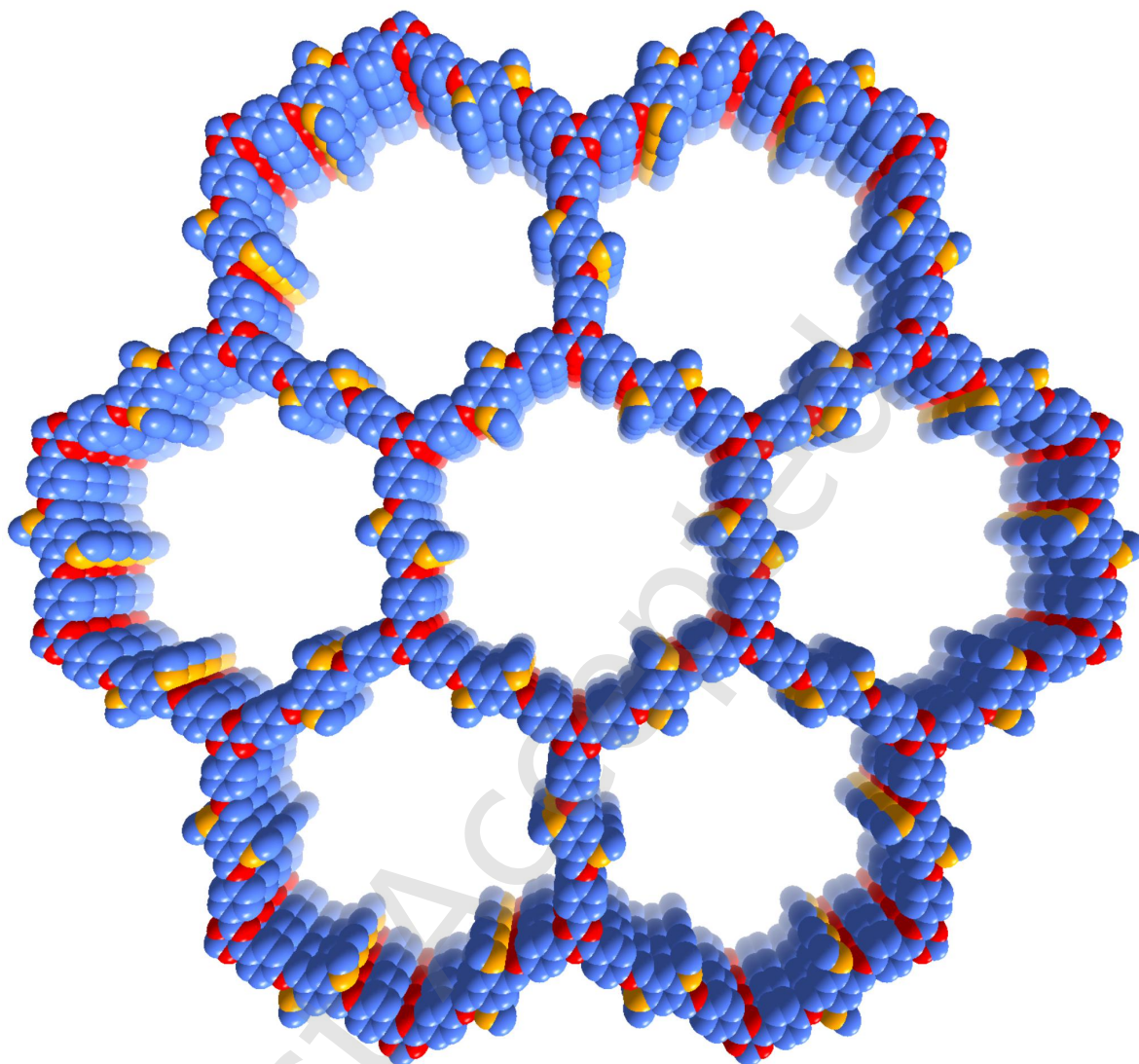


Figure S3. Graphic view of the modeled crystal structure for TTA-DMA featuring AA-stacking mode along the c -axis, illustrating the periodic arrangement of the ordered hexagonal nanochannels (carbon atoms are shown in blue, nitrogen atoms in red, oxygen atoms in yellow, and hydrogen atoms are omitted for clarity).

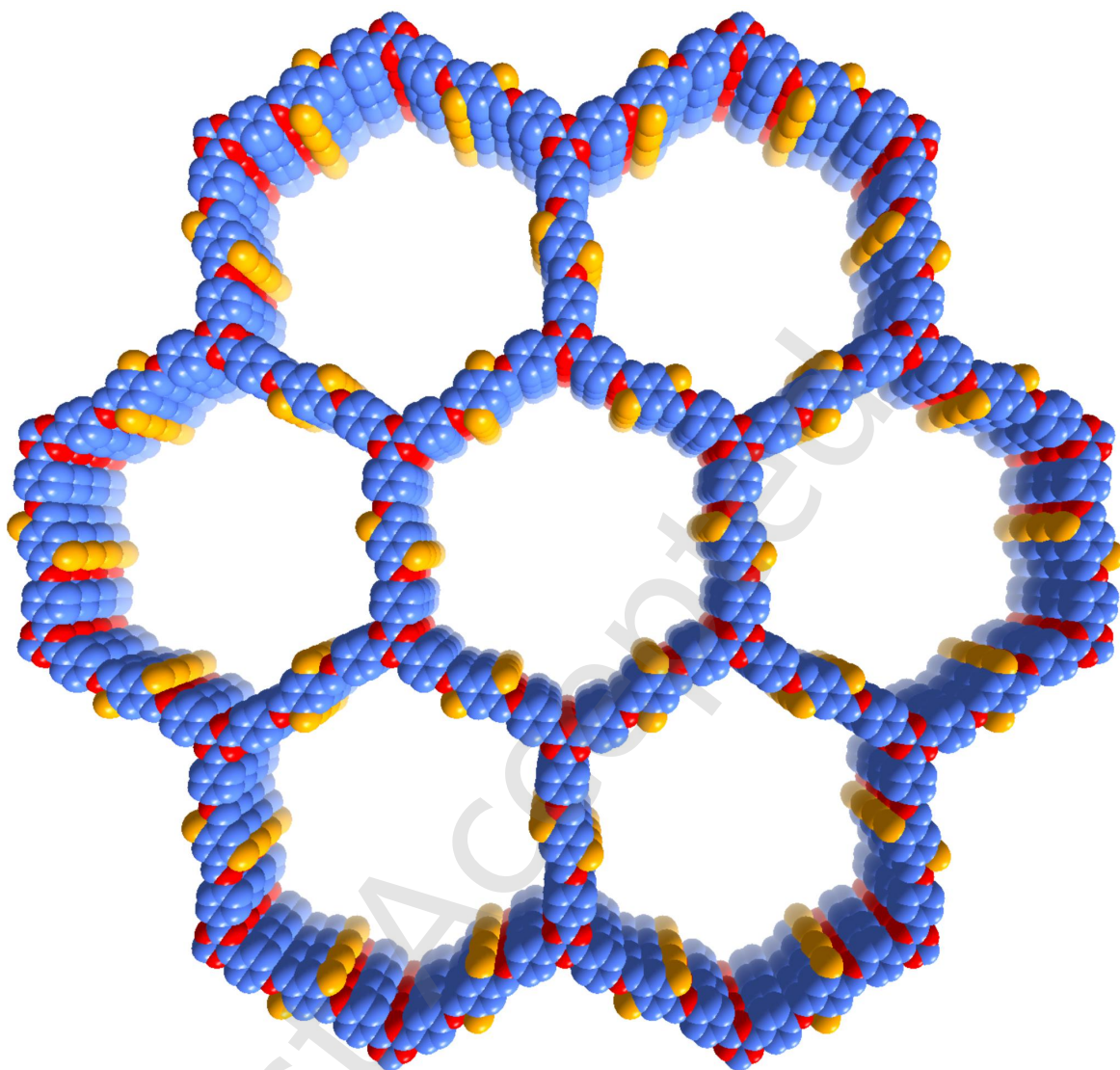


Figure S4. Graphic view of the modeled crystal structure for TTA-DHA featuring AA-stacking mode along the c -axis, illustrating the periodic arrangement of the ordered hexagonal nanochannels (carbon atoms are shown in blue, nitrogen atoms in red, oxygen atoms in yellow, and hydrogen atoms are omitted for clarity).

Table S1. Unit cell parameters, space group, and atomic positions of the AA-stacking structural model for TTA-DMA, H atoms omitted for clarity.

Space group: P6/M			
$a = b = 36.0101 \text{ \AA}, c = 3.6004 \text{ \AA}$			
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$			
Atom	x (Å)	y (Å)	z (Å)
C1	0.34484	0.57226	0.5
C2	0.3628	0.54708	0.5
C3	0.45611	0.48043	0.5
C4	0.41312	0.63339	0.5
C5	0.4311	0.60823	0.5
N6	0.42336	0.53816	0.5
C7	0.52368	0.54298	0.5
C8	0.35087	0.64213	0.5
C9	0.40595	0.56483	0.5
C10	0.36984	0.6156	0.5
C11	0.46295	0.55189	0.5
C12	0.48049	0.52413	0.5
N13	0.30893	0.62482	0.5
C14	0.60964	0.58282	0.5
O15	0.58746	0.53863	0.5

Table S2. Unit cell parameters, space group, and atomic positions of the AA-stacking structural model for TTA-DHA, H atoms omitted for clarity.

Space group: P6/M			
$a = b = 36.3015 \text{ \AA}, c = 3.4136 \text{ \AA}$			
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$			
Atom	x (Å)	y (Å)	z (Å)
C1	0.34511	0.5724	0.5
C2	0.36317	0.54729	0.5
C3	0.45659	0.48095	0.5
C4	0.41333	0.63364	0.5
C5	0.43141	0.60855	0.5
N6	0.42386	0.53854	0.5
C7	0.52423	0.54313	0.5
C8	0.35097	0.64221	0.5
C9	0.40634	0.56513	0.5
C10	0.37004	0.61575	0.5
C11	0.46348	0.55238	0.5
C12	0.48102	0.52462	0.5
N13	0.30901	0.6248	0.5
O14	0.58584	0.53866	0.5

6. Additional characterization

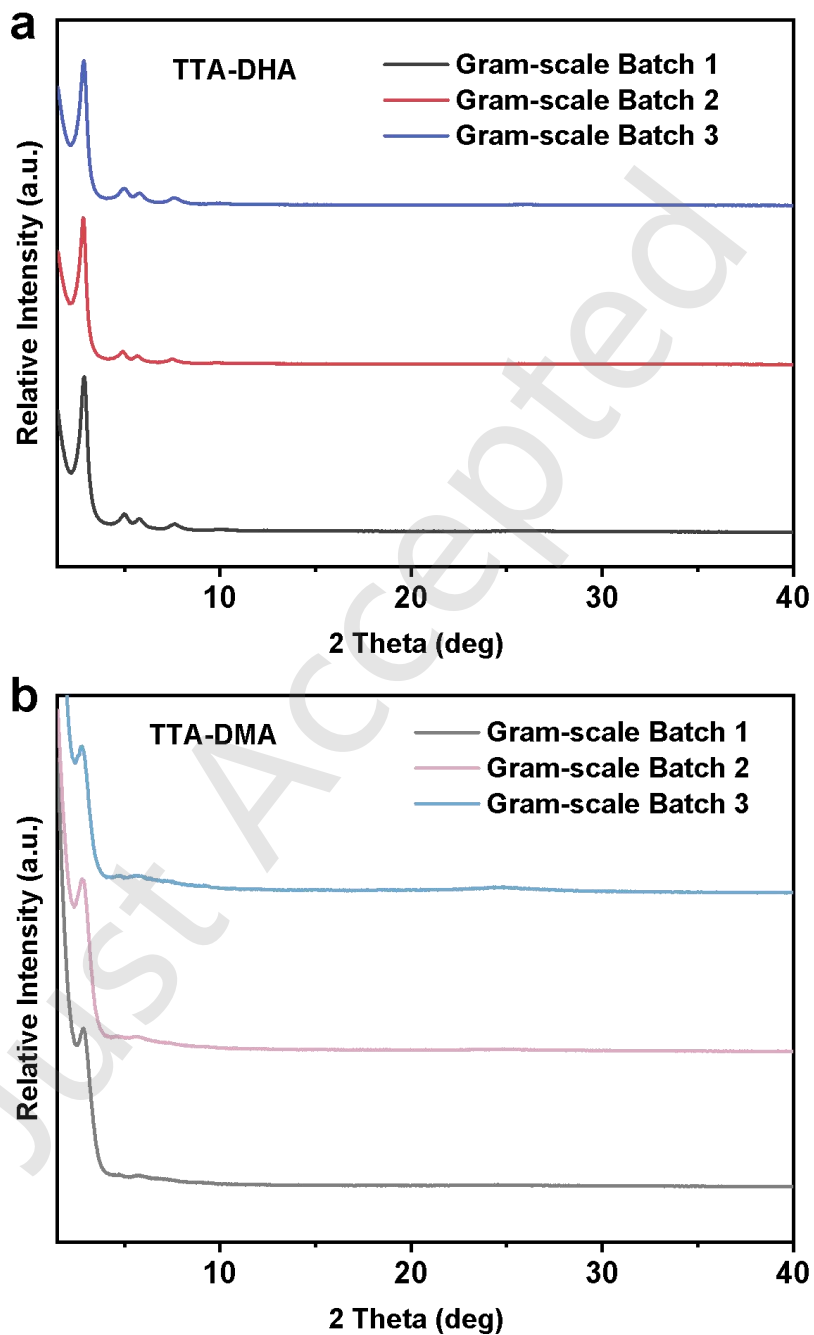


Figure S5. Experimental PXRD patterns of three independent gram-scale synthesis batches for (a) TTA-DHA and (b) TTA-DMA.

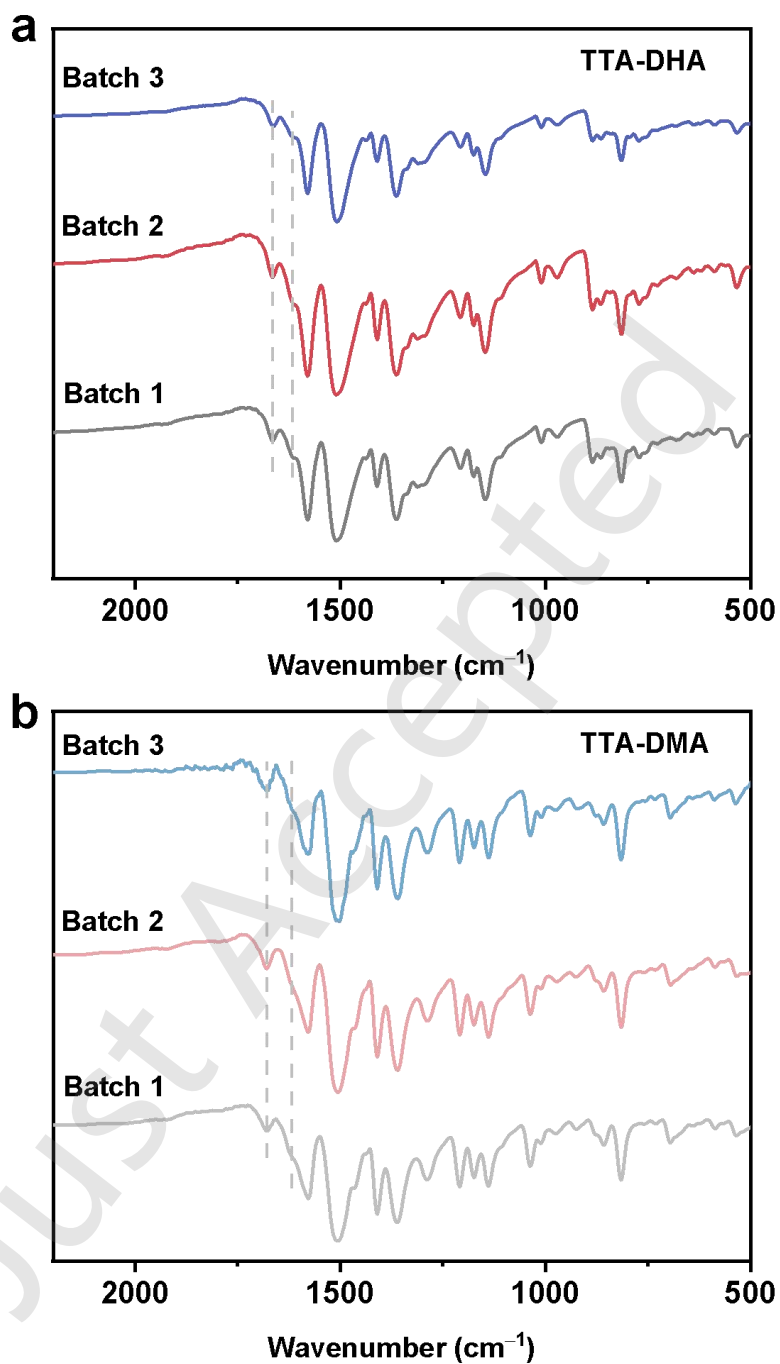


Figure S6. FT-IR spectra of three independent gram-scale synthesis batches for (a) TTA-DHA and (b) TTA-DMA.

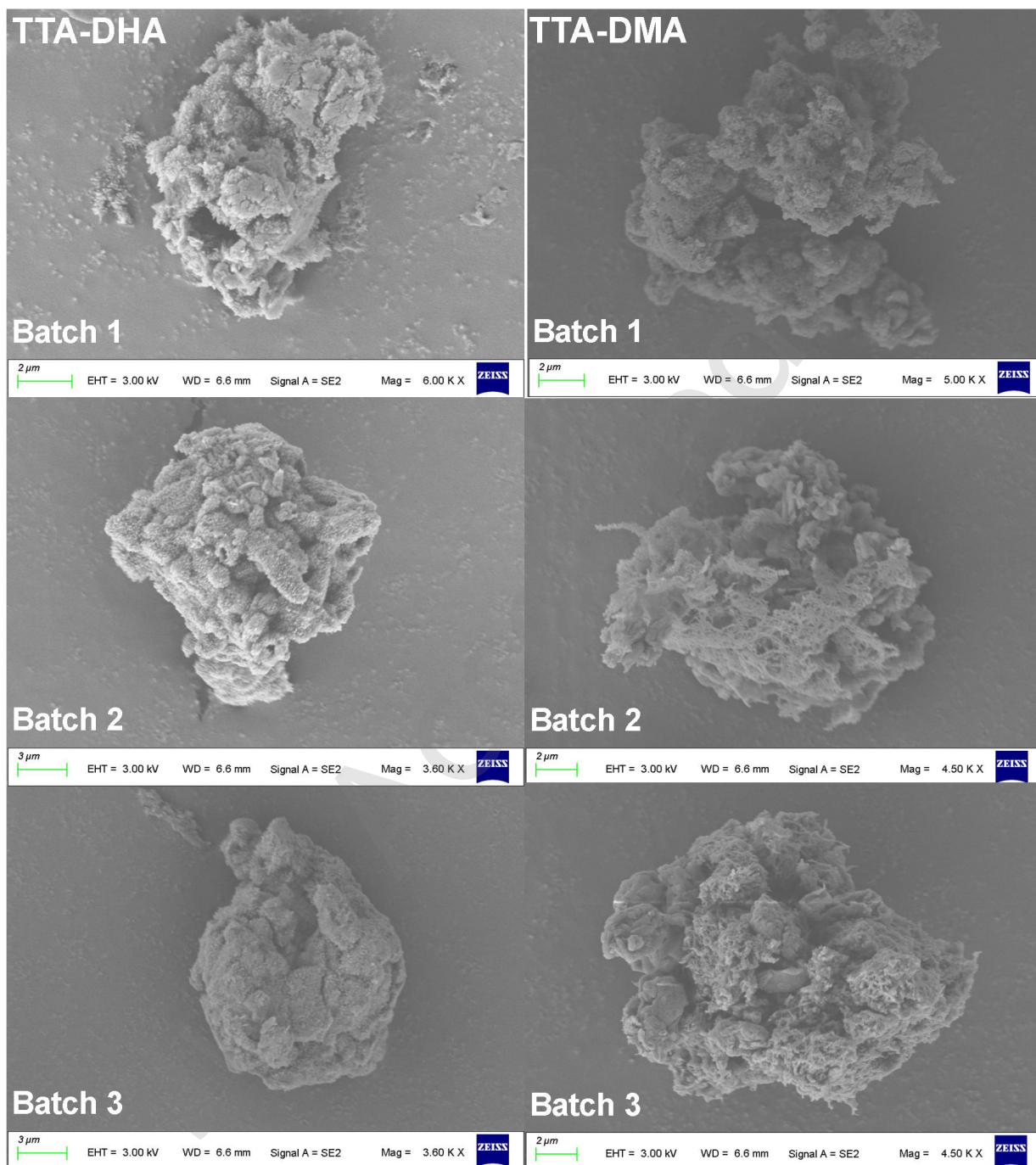


Figure S7. SEM images of TTA-DHA (left) and TTA-DMA (right) obtained from three independent gram-scale synthesis batches.

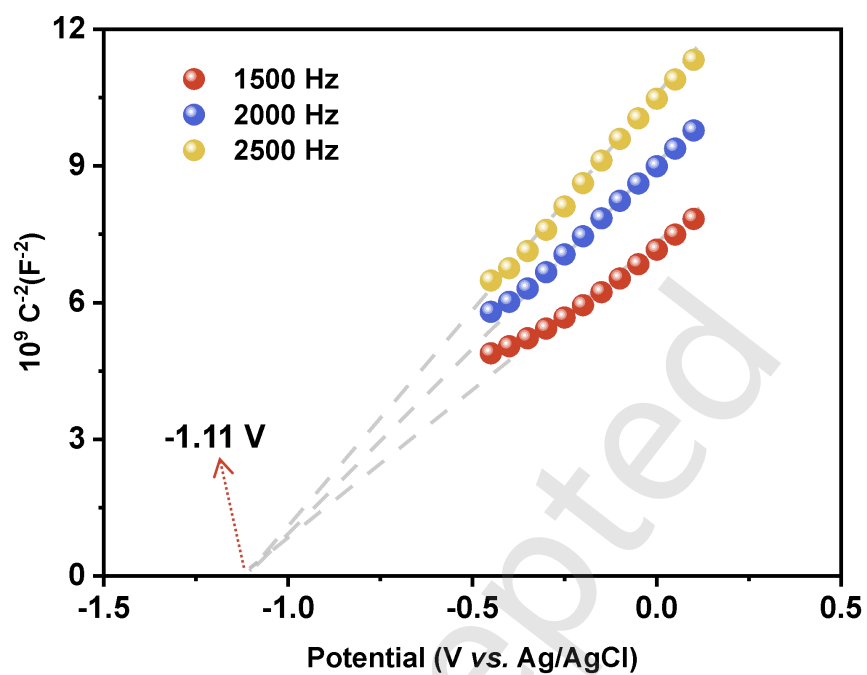


Figure S8. Mott-Schottky plots of TTA-DMA collected at diverse frequencies of 1500, 2000, and 2500 Hz (vs. Ag/AgCl).

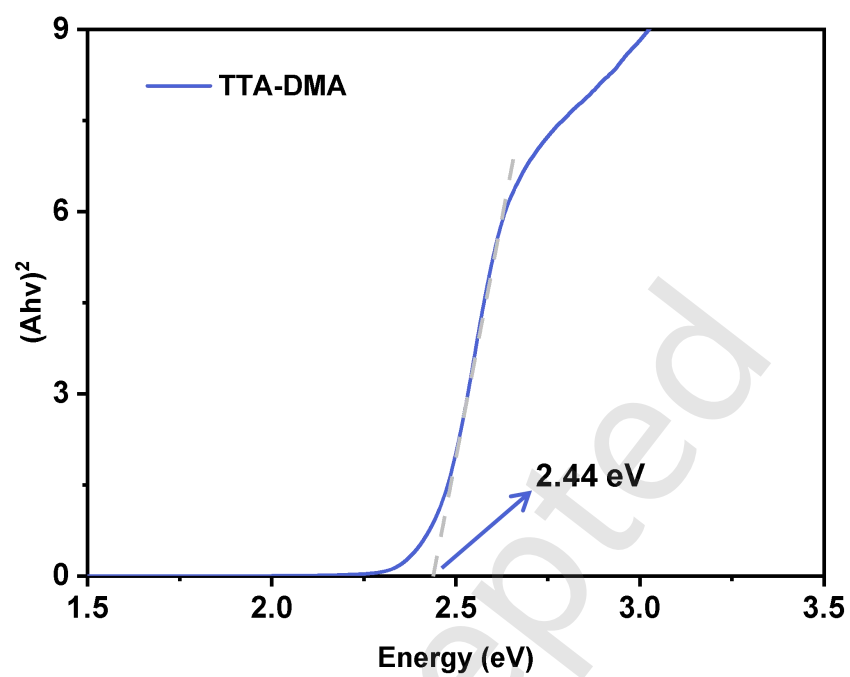


Figure S9. Tauc plot of TTA-DMA.

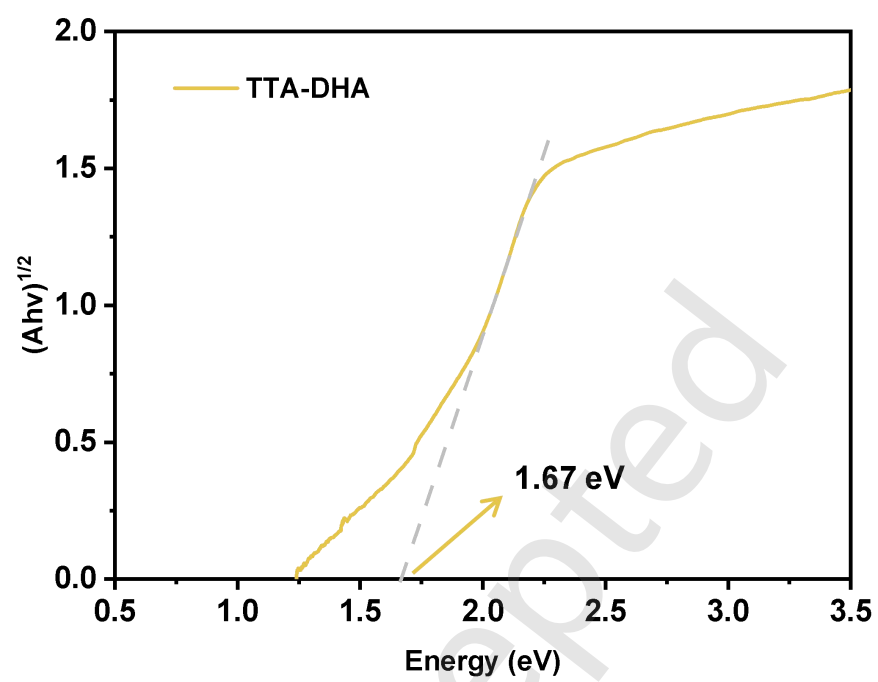


Figure S10. Tauc plot of TTA-DHA.

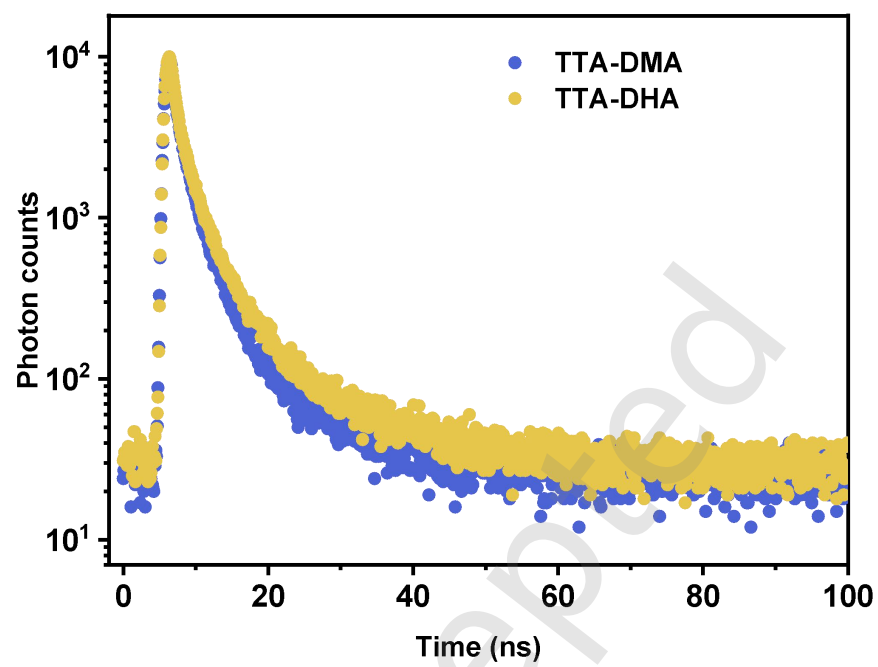


Figure S11. Time-resolved photoluminescence decay profiles tracking the exciton lifetimes.

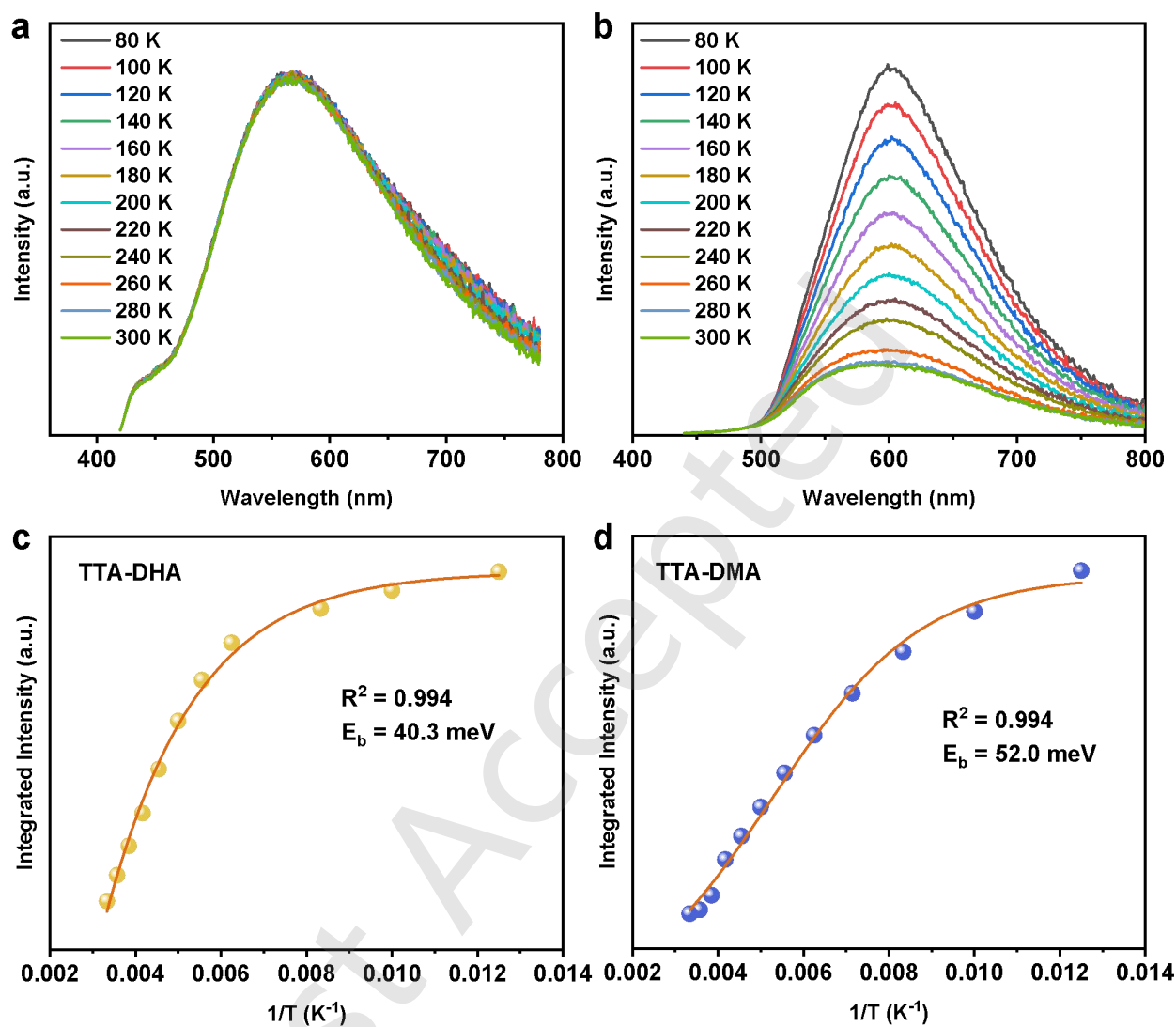


Figure S12. Temperature-dependent photoluminescence (TD-PL) spectra of (a) TTA-DHA and (b) TTA-DMA measured from 80 K to 300 K. Integrated PL intensity as a function of reciprocal temperature ($1/T$) and the corresponding fitting curves for (c) TTA-DHA ($E_b = 40.3$ meV) and (d) TTA-DMA ($E_b = 52.0$ meV).

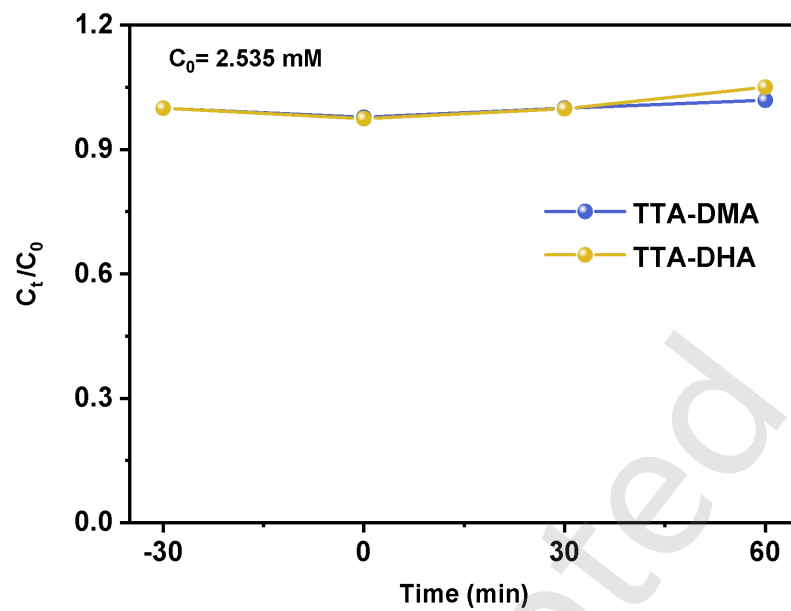


Figure S13. Decomposition curves (C_t/C_0) of 2.535 mM H_2O_2 in the presence of TTA-DMA and TTA-DHA under dark and visible-light conditions.

7. Additional photocatalytic results

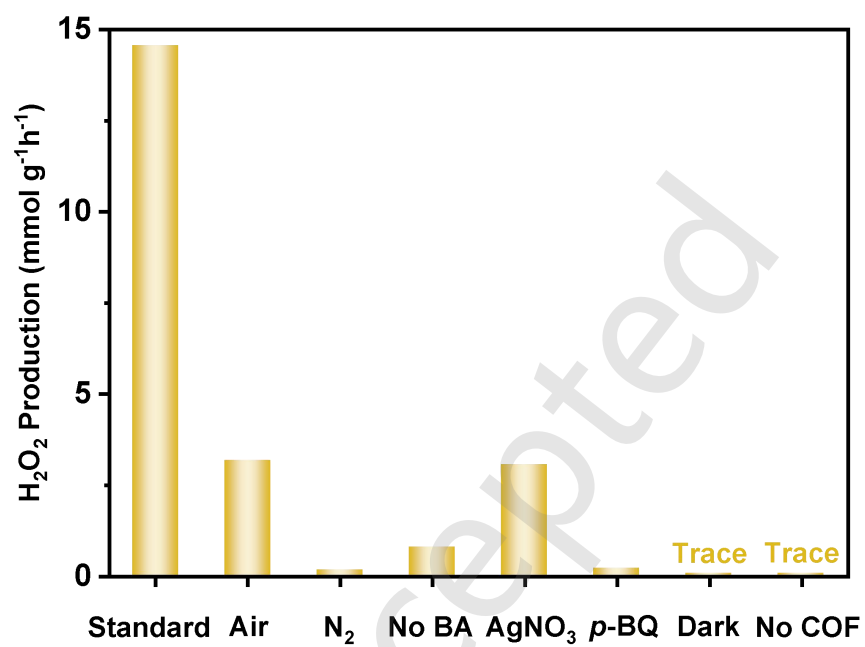


Figure S14. Photocatalytic H₂O₂ production rates of TTA-DHA under control conditions.

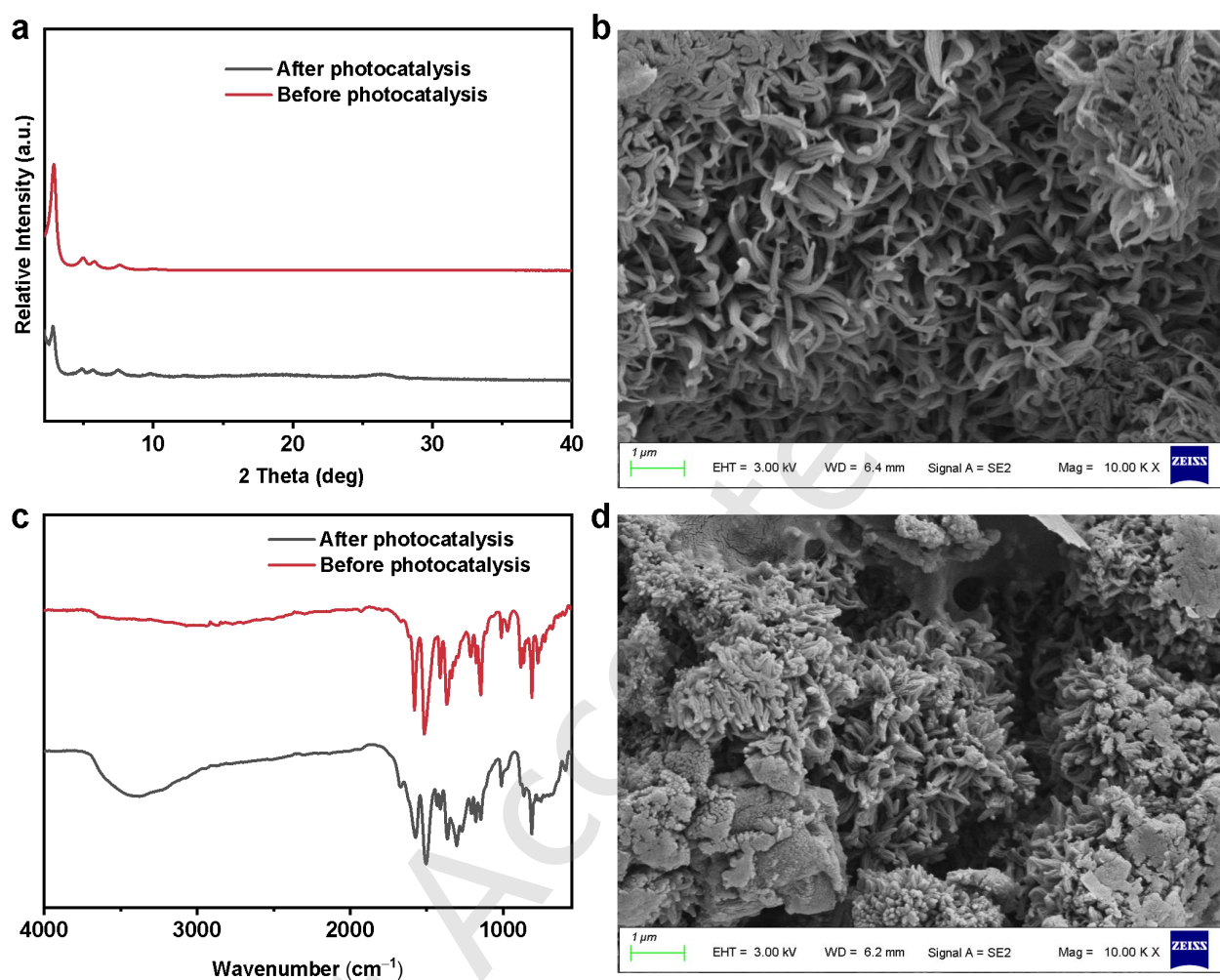


Figure S15. Structural and morphological stability evaluation of TTA-DHA before and after long-term photocatalytic reaction: (a) PXRD patterns; (b, d) FE- SEM images; (c) FT- IR spectra.

8. Photocatalytic mechanism study

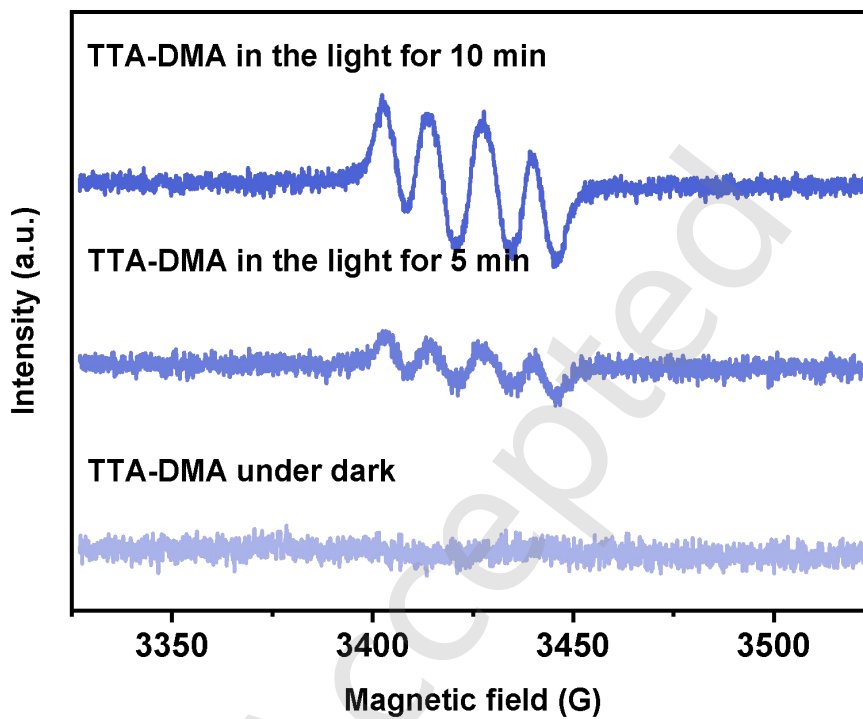


Figure S16. EPR spectra of TTA-DMA under dark conditions and upon visible- light irradiation for 5 and 10 min.

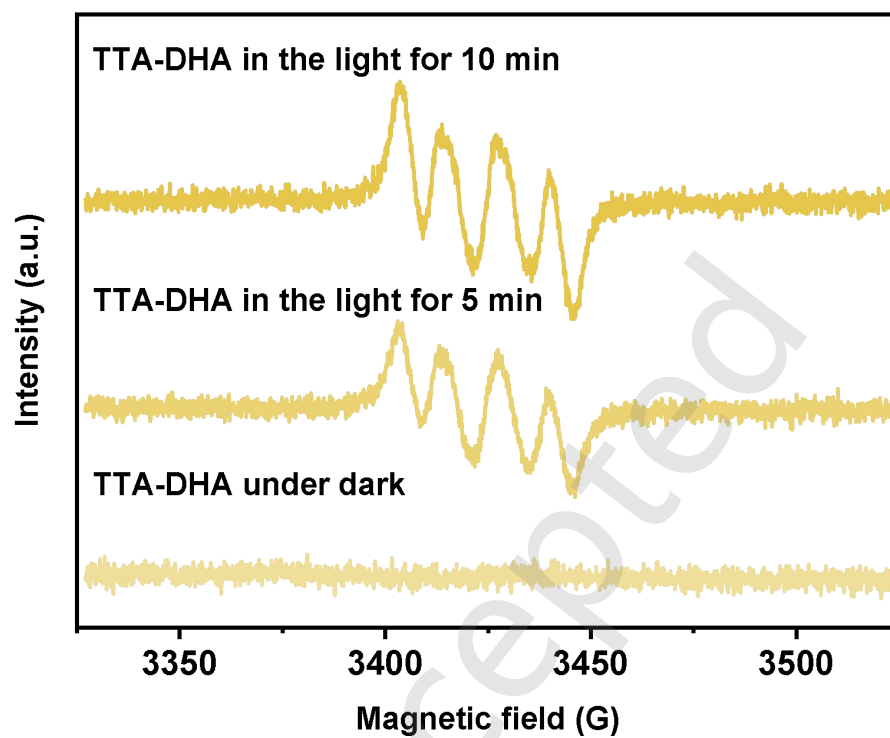


Figure S17. EPR spectra of TTA- DHA under dark conditions and upon visible- light irradiation for 5 and 10 min.

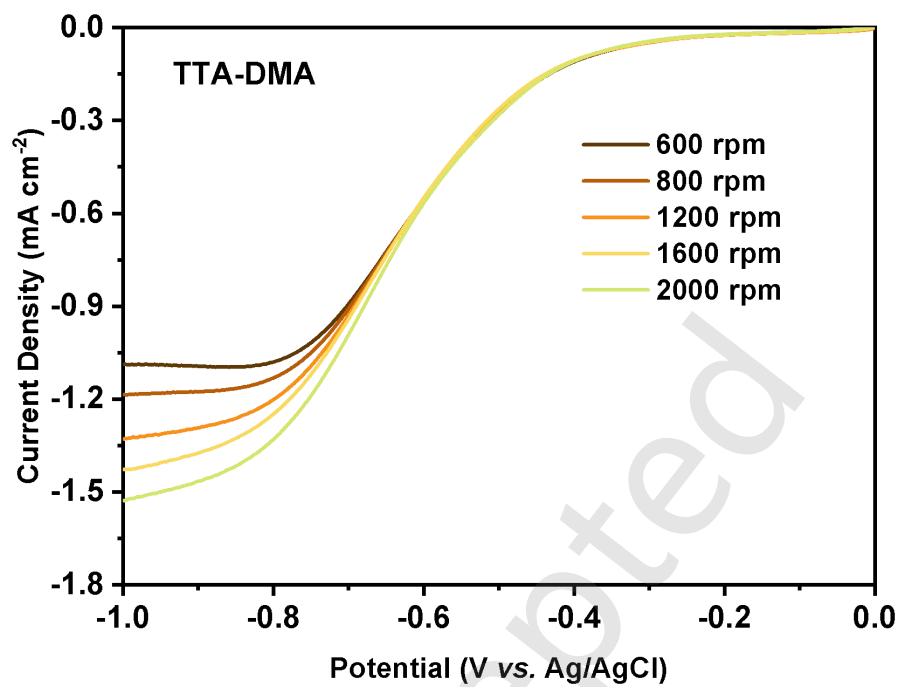


Figure S18. Linear-sweep RDE voltammograms of TTA-DMA at different rotating speeds.

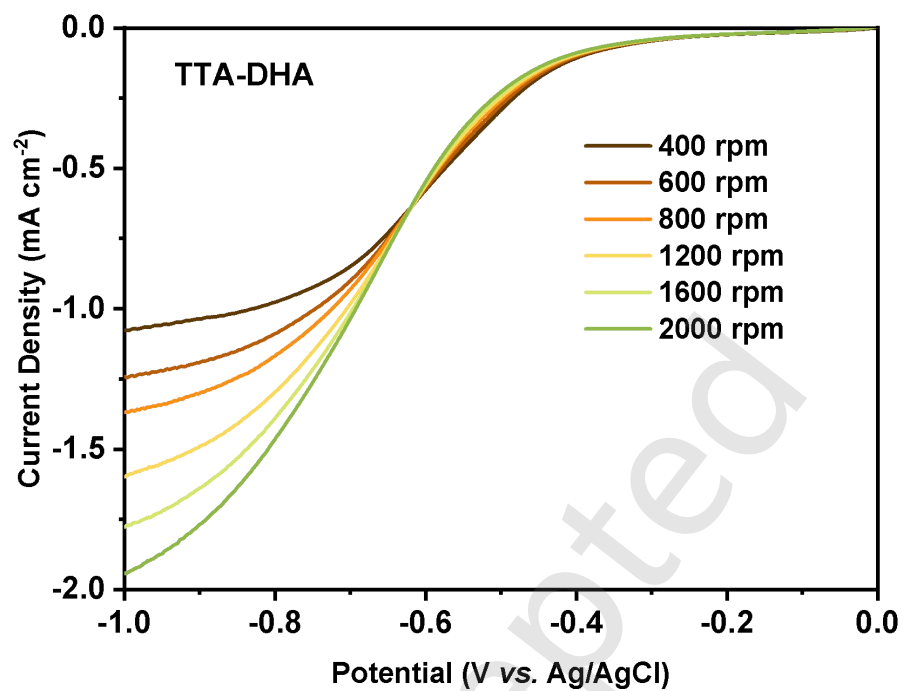


Figure S19. Linear-sweep RDE voltammograms of TTA-DHA at different rotating speeds.

9. Additional calculation results

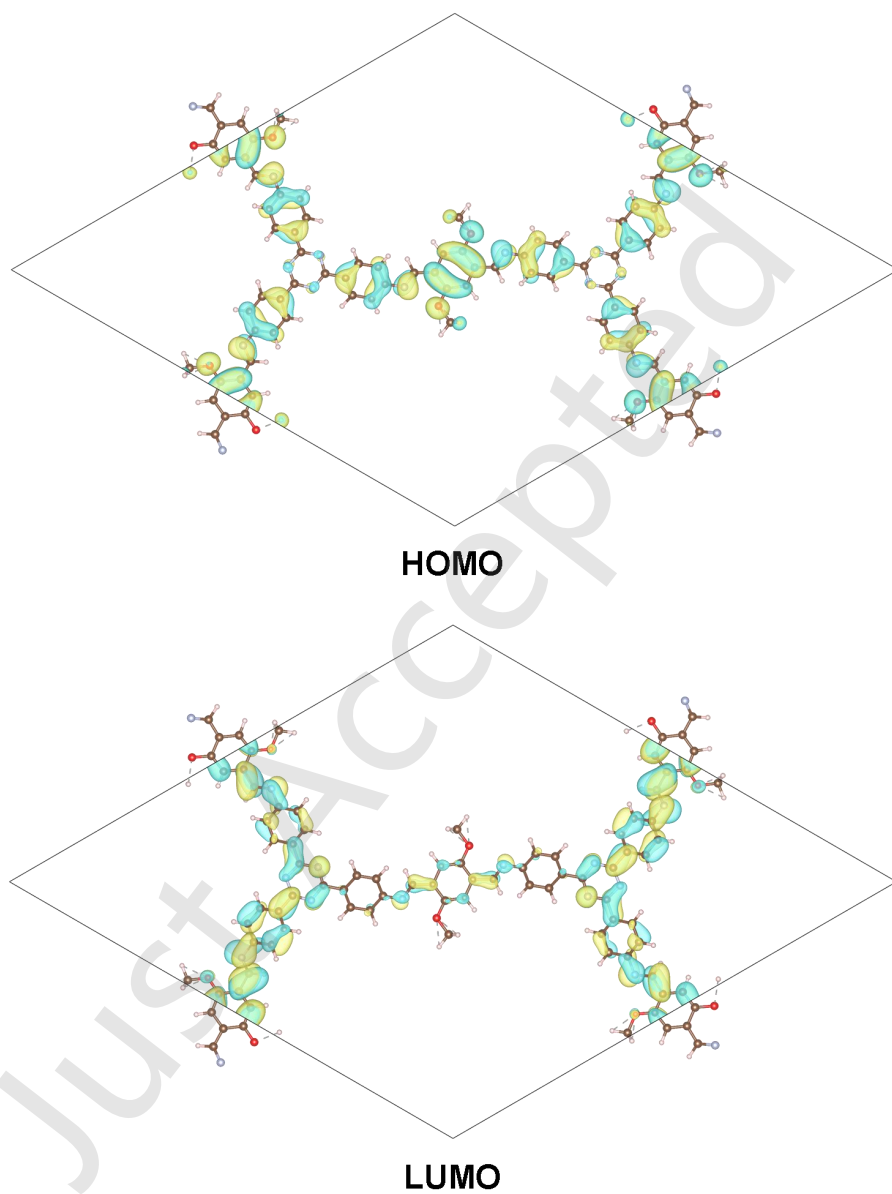


Figure S20. Top-view models of HOMO (top) and LUMO (bottom) distributions for TTA-DMA.

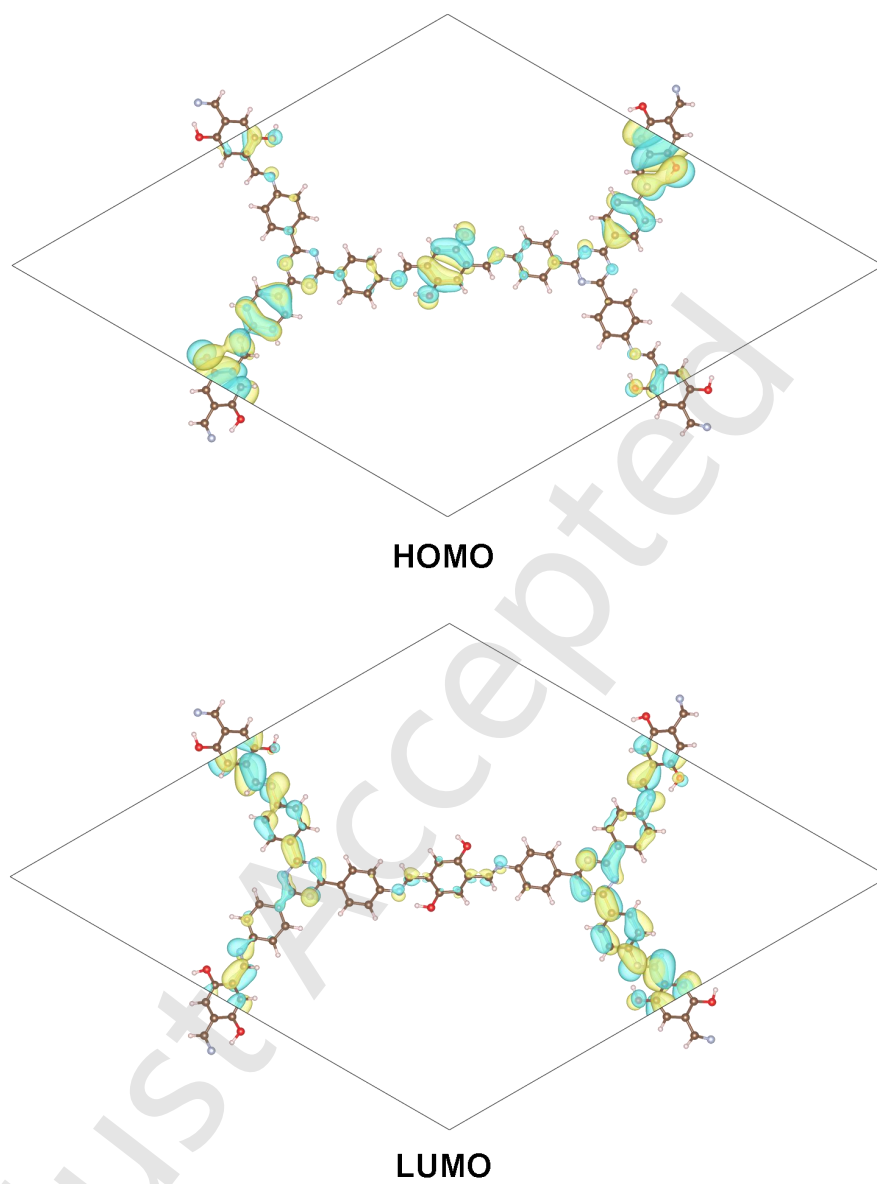


Figure S21. Top-view models of HOMO (top) and LUMO (bottom) distributions for TTA-DHA.

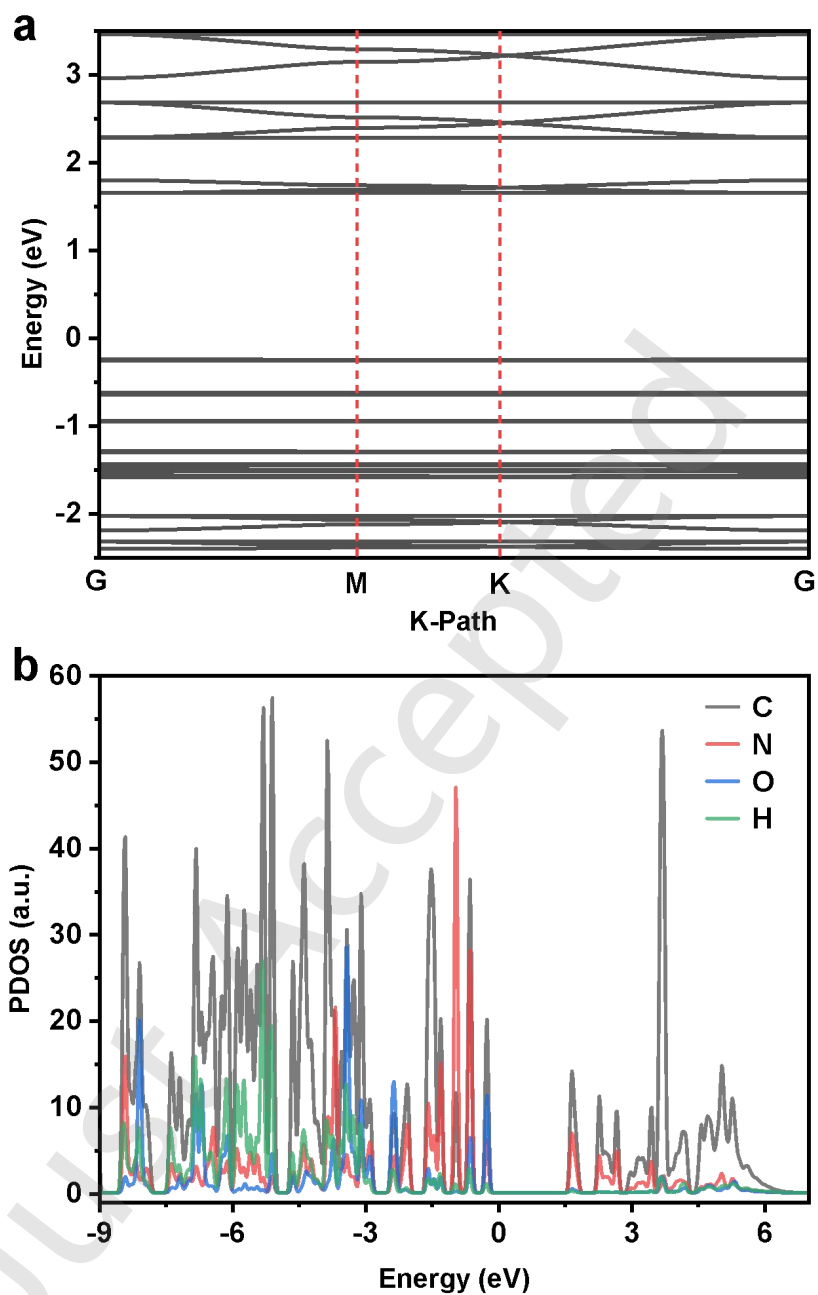


Figure S22. Electronic structure calculations for TTA-DMA: (a) calculated band structure; (b) total and partial density of states.

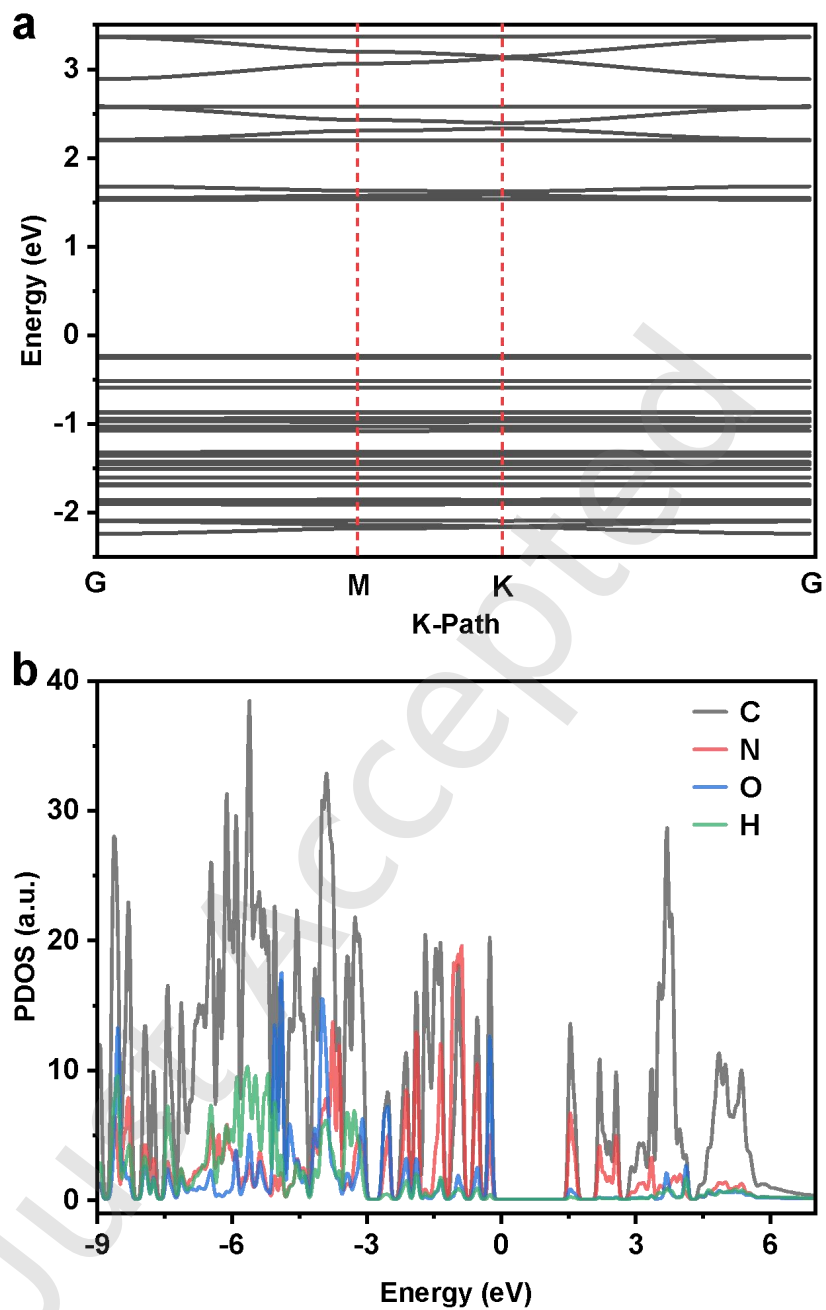


Figure S23. Electronic structure calculations for TTA- DHA: (a) calculated band structure; (b) total and partial density of states.

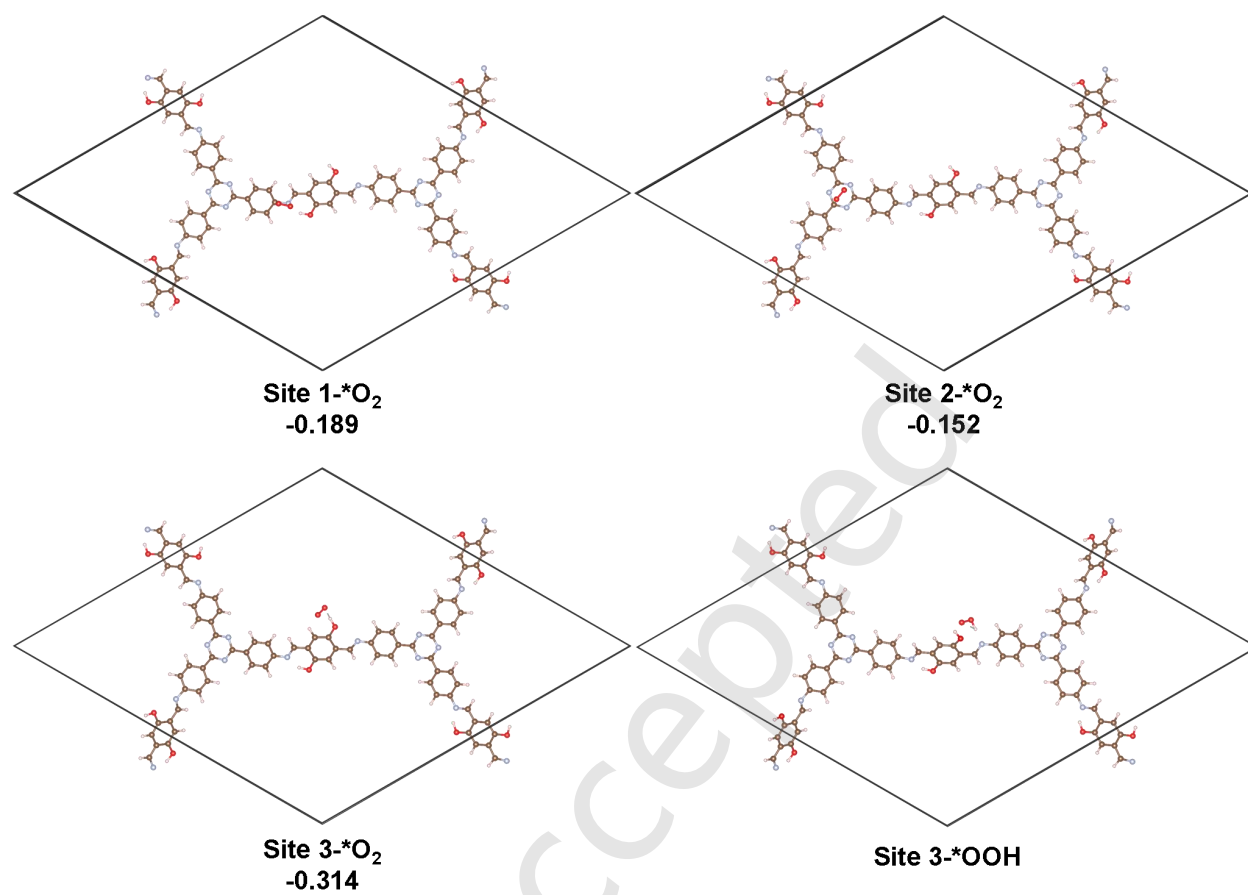


Figure S24. Optimized adsorption configurations of *O_2 and *OOH intermediates at diverse active sites on the TTA-DHA framework (the values denote the corresponding adsorption energies in eV).

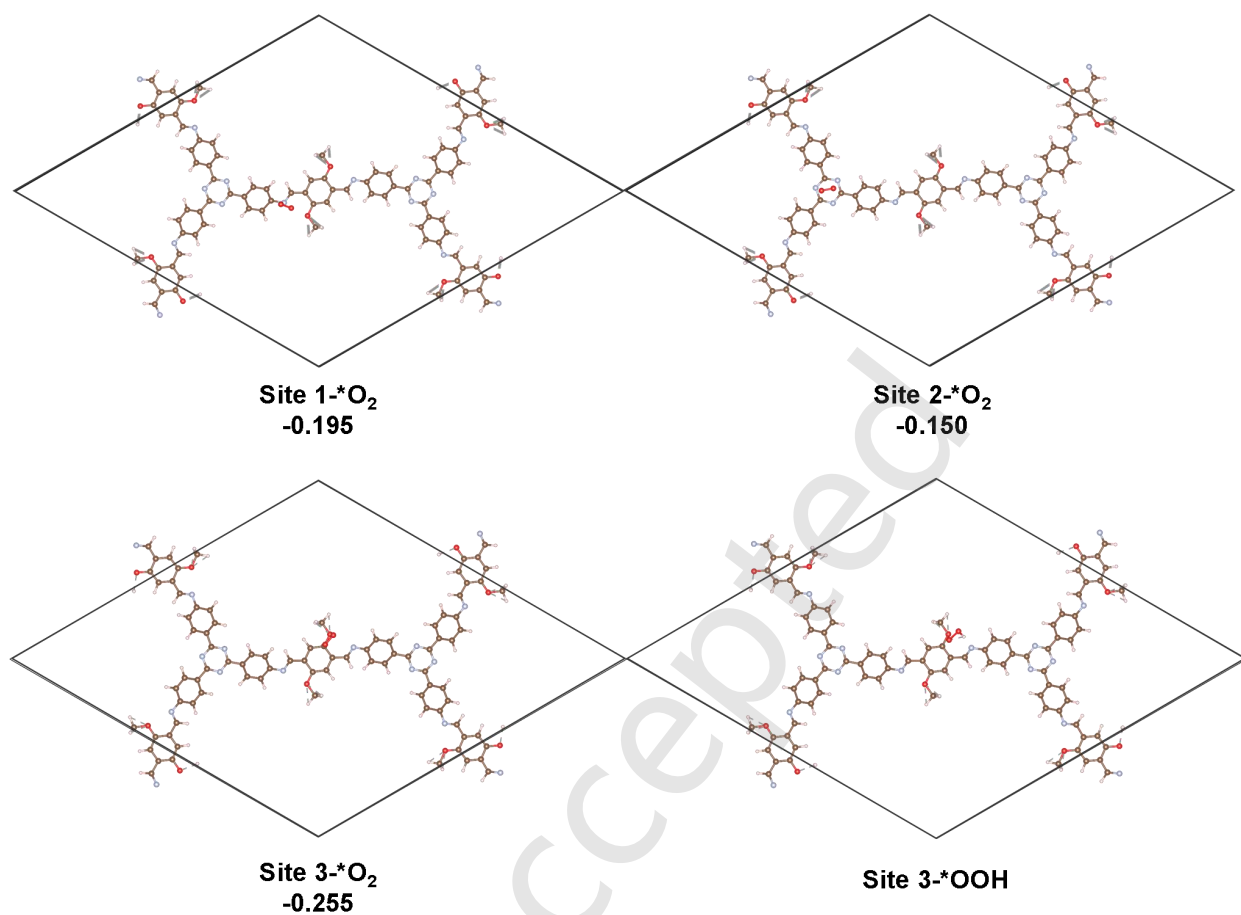


Figure S25. Optimized adsorption configurations of *O_2 and *OOH intermediates at diverse active sites on the TTA-DMA framework (the values denote the corresponding adsorption energies in eV).

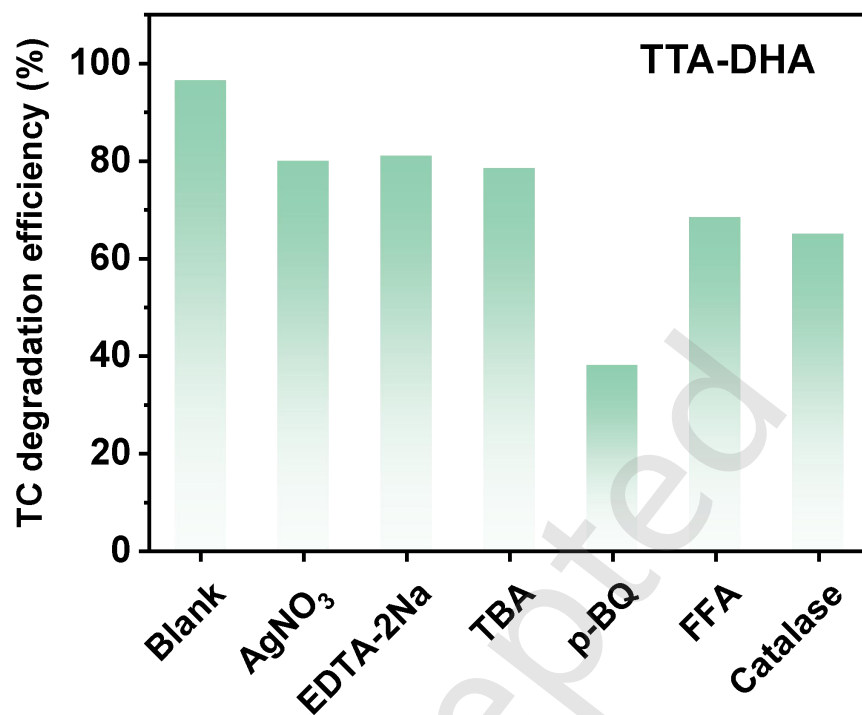


Figure S26. Control experiments of tetracycline (TC) photodegradation over TTA-DHA with various scavengers and suppressors (AgNO₃ for e⁻, EDTA-2Na for h⁺, TBA for •OH, *p*-BQ for •O₂⁻, FFA for ¹O₂, and catalase for H₂O₂) under visible-light irradiation.

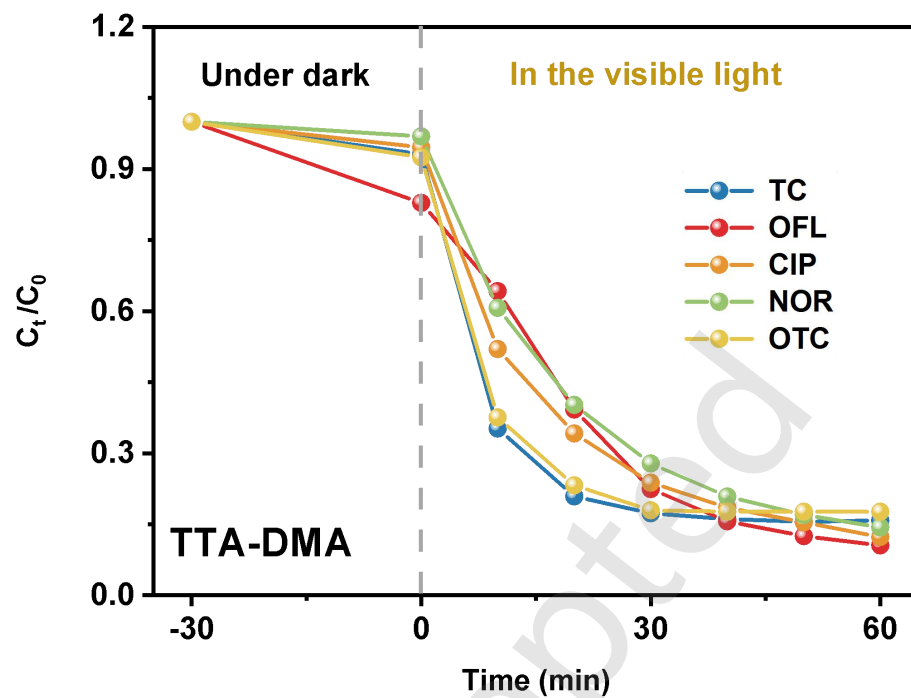


Figure S27. Dark adsorption and photocatalytic degradation performance of the control framework TTA-DMA toward five representative antibiotics (TC, OFL, CIP, NOR, and OTC) under visible-light irradiation.