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Accelerated Exciton Dissociation and Charge Transfer via Third-Motif Engineered Conjugated Polymers for Photocatalytic Circulation-flow Synthesis of H₂O₂

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Abstract: Achieving effective exciton dissociation and charge transport in linear polymer photocatalysts for H₂O₂ photosynthesis remains a formidable challenge. Herein, we fabricated three-motif cross-linked polymers by rationally introducing a third functional component into a two-motif linear polymer, which were employed for circulation-flow photocatalytic H₂O₂ production. By strategically modulating the third component, we precisely tuned the electronic structure, significantly lowering exciton binding energy and enlarging molecular dipole moment. Compared to the original linear configuration, the resulting cross-linked structure creates multidirectional electron transport channels. Combined experimental and calculation investigations demonstrate that these synergistic effects collectively promote exciton dissociation and intramolecular electron transfer. PAQ-TABPB photocatalyst with optimized thirdmotif accelerates oxygen-to-superoxide radical transformation by lowering the *OOH binding energy, thereby facilitating the two-step single-electron oxygen reduction pathway, attaining an exceptional H₂O₂ production rate of 3351 µmol/g/h. Notably, we constructed a circulation-flow reactor for photocatalytic synthesis of H_2O_2 . Benefiting from improved gas-liquid mass transfer and efficient light irradiation, this flow-system achieved a 5.2-fold increase in H₂O₂ production compared to conventional batch reactor under the light intensity of 27 mW cm⁻², reaching an accumulated yield of 3125 µmol/g with stable recyclability. This work highlights the potential of multi-component polymeric photocatalysts and circulation-flow reactors for H₂O₂ photosynthesis.

Introduction

Hydrogen peroxide (H_2O_2) as an environmentally oxidant and a clean energy carrier, is widely utilized in various fields such as chemical engineering, healthcare, integrated circuits, fuel cells and environmental remediation^[1-2]. The global annual demand for H₂O₂ continues to grow due to its broad applications^[3]. The traditional industrial production of H₂O₂ mainly depends on the anthraquinone method-an energyconsuming process that poses environmental and safety issues^[4]. Artificial photosynthesis of H₂O₂ from pure water and oxygen system has emerged as an appealing alternative, offering a green and sustainable process for direct solar-tochemical energy conversion^[5-7]. Current artificial photosynthetic systems face several critical problems: (1) intrinsically high exciton dissociation energy of semiconductor materials^[8-9]; (2) low-efficiency charge separation and slow electron transport to active sites both within the bulk and on the surface of photocatalysts^[10-11]; (3) the lack of a seamless scale-up approach for photochemical processes from laboratory to industrial scale.^[12-13]. These issues severely hinder the advancement of photocatalytic technology for H₂O₂ production.

Linear conjugated polymers photocatalysts (LCPs) have emerged as a promising material platform for H₂O₂ production, owing to abundant building blocks, tunable electronic properties, precise redox sites, diverse linkage modes and facile synthetic route^[14-15]. Recently, various strategies have been explored to improve the efficiency of H₂O₂ photosynthesis in LCPs photocatalyst, including design of an appropriate donor-acceptor structure, development of novelty active sites, modification with functional groups, incorporation of redox moieties and optimization of linkage types^[16-19]. Despite these efforts, exploring LCPs based photocatalysts with a low exciton binding energy, efficient charge separation and enhanced electron transport for high efficiency overall photosynthesis of H₂O₂ is desirable. Generally, the reported LCPs photocatalysts are predominantly dual-component systems, with limited research on multi-component architecture. The quantity and type of additional components plays a significant role in determining its structure and electronic properties, which further influences

catalytic activity^[20-23]. Thus, modulating electron properties through controlled incorporation of additional components in LCPs photocatalysts is a key yet underexplored strategy.

Beyond photocatalysts design, another bottleneck in H₂O₂ production lies in scaling up of photochemical process. According to the Beer-Lambert law, light intensity decays significantly as it passes through a medium, meaning that light penetration is inherently limited. As a result, the conventional dimension-enlarging strategy used for batch reactors becomes ineffective^[24]. In contrast, flow reactors with narrow tubing channels substantially increases the irradiation surface area and also enhances mass and heat transfer during flowing^[25]. Particularly for gas-liquid reaction, the expanded gas-liquid interface, by forming slug flow with gas bubble and liquid drop, facilitates gas-liquid mass transfer and improved higher reaction efficiency^[26-27]. Conventional end-to-end continuous-flow reactors shows a poor scalability due to residence time constraints. Therefore, rationally designed scale-up strategies are critical for the production of H₂O₂. However, simultaneously resolving these objectives presents a significant challenge.

To overcome these limitations, we prepared two three-motif crosslinked polymer photocatalysts through pre-polymerization and post-modification route for the circulation-flow photocatalytic H₂O₂ production (Scheme 1). Compared to a two-component linear polymer, the addition of aromatic triamine as the third component directed the linear precursors to undergo multidirectional polymerization, ultimately forming an asymmetric cross-linked network. Engineering the third additive component enables significantly reduces exciton binding energy, enhances the molecular dipole moment and provides multi-directional electron channels, collectively enabling effective charge separation. This transformation in electron properties facilitates the conversion of oxygen into superoxide radicals, thereby boosting the efficiency of H2O2 production via an indirect twoelectron ORR pathway. The optimized three-motif PAQ-TABPB displayed an exceptional H₂O₂ generation rate of 3351 µmol/g/h, approximately 10.3-fold and 3.8-fold higher than that of the twomotif PAQ and three-motif PAQ-TBZ, respectively. Meanwhile, we constructed a circulation-flow reactor with intensified light irradiation and improved gas-liquid mass transfer for the scalable photocatalytic synthesis of H₂O₂. Under a light intensity of only 27 mW cm⁻², the advanced circulation-flow reactor achieves a 5.2-fold enhancement in H2O2 production compared to conventional batch reactor, showcasing great potential for industrial-scale H₂O₂ manufacturing.



Scheme 1. Illustration of rational design of three-motif cross-linked polymers introducing a third functional component into a two-motif linear polymer.

Results and Discussion

Synthesis and Characterization of Three-motif Crosslinked Polymer Photocatalysts Typically, the linear conjugated polymers PAQ were synthesized by imide condensation of pyromellitic dianhydride (PMDA) and 2,6diaminoanthracene-9,10-dione (AQ) ligands (Figure S1). For the synthesis of multicomponent PAQ-TBZ and PAQ-TABPB crosslinked conjugated polymers, we first obtained the polyamic acid (PAA) oligomers end-capped by carboxyl through a prepolymerization method, and then added of different triamine molecule of aromatic triamines 1,3,5-Tris [4 aminophenyl]benzene (TBZ) or 1,3,5-tris [4-amino(1,1-biphenyl-4-yl)]benzene (TABPB) (Figure S2) and formed stoichiometrically the cross-linked structure framework by the solvothermal reaction (Figure 1a). Gel permeation chromatography (GPC) was used to determine the molecular weights of the PAA oligomeric acceptors^[28]. The average molecular weights (Mw) was measured to be 2.052 kDa, with corresponding polydispersity index (PDI, PDI= Mw / Mn, Mn= 1.853 kDa) of 1.107 (Figure S3-4). The Fourier transform infrared (FTIR) spectrum showed characteristic amide (-CONH-) peaks of PAA oligomers, including N-H stretching around 3036 cm⁻¹ and C=O stretching band near 1651 cm^{-1[29]}. Additionally, the appearance of the peaks for carboxyl groups at 1715 cm⁻¹ (C=O vibrating in -COOH) and 3375 cm⁻¹ (O-H vibrating in -COOH) confirmed the PAA structure (Figure S5).

Chemical structure changes induced by thermal imidization monitored using FTIR spectroscopy, ¹³C crosswere polarization/magic angle spinning solid-state nuclear magnetic resonance (¹³C CP-MAS NMR) spectrum and X-ray photoelectron spectroscopy (XPS). Compared to the PMDA, AQ, TBZ and TABPB monomers, three photocatalysts both exhibited characteristic bands at near 1783 and 1721 cm⁻¹, which were assigned to the asymmetric and symmetric vibrations of carbonyl groups, respectively^[30]. The appearance of a new absorption band at ~1365 cm⁻¹, assigned to C-N-C stretching vibrations in five-membered imide rings, verified successful imidization reaction (Figure S6 and Figure 1b). The ¹³C CP-MAS NMR spectrum was also used to check the chemical structure (Figure 1c). The presence of imide carbonyl groups was evidenced by ¹³C CP-MAS NMR signals: 165.3 ppm in PAQ, 165.2 ppm in PAQ-TBZ, and 165.5 ppm in PAQ-TABPB^[31]. The remaining signals in the 100-150 ppm region were ascribed to both C-N moieties and aromatic carbons. None of three polymers exhibited any signals of NH₂ groups around 150 ppm. Meanwhile, XPS and EA analysis of PAQ-TBZ and PAQ-TABPB confirmed its elemental composition of carbon, nitrogen, oxygen and hydrogen (Figure S7-8 and Table S1). High-resolution C1s, N1s and O1s spectra further revealed specific bonding environments. The C1s spectrum was deconvoluted into peaks for aromatic carbon (C-C/C=C) at 284.8 eV, imide C-N bonds at 286.0 eV and carbonyl carbons (from AQ and imide structures) at 288.5 eV^[32]. The N1s spectrum showed a single peak characteristic of imide nitrogen (O=C-N-C=O) centered at 400.3 eV and the O1s spectrum exhibited a major peak attributed to carbonyl oxygen at 532.8 eV.

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Figure 1. a) Schematic for the synthesis of three-motif conjugated polymers with a cross-linked network through imide condensation reaction; b) FT-IR spectra of PAQ, PAQ-TBZ and PAQ-TABPB; c) Solid state ¹³C CP-MAS NMR spectra of PAQ, PAQ-TBZ and PAQ-TABPB; d) N₂ sorption isotherms at 77 K calculated by NLDFT of PAQ, PAQ-TBZ and PAQ-TABPB; e) Isothermal titration calorimetry profiles of PAQ, PAQ-TBZ and PAQ-TABPB in O₂-saturated water; f) Water vapor adsorption and desorption isotherms of PAQ, PAQ-TBZ and PAQ-TABPB measured at 298.15 K; g) Schematic illustration of the electronic band structure of PAQ, PAQ-TBZ and PAQ-TABPB.

The XPS results for PAQ-TABPB were similar to PAQ-TBZ. Therefore, these findings collectively affirm that the PAQ-TBZ and PAQ-TABPB photocatalysts exhibited a complete imide structure.

The X-ray diffraction (XRD) patterns of as-synthesized PAQ, PAQ-TBZ and PAQ-TABPB exhibited characteristic diffraction peaks that were markedly different from the starting materials, providing additional evidence for successful imide ring formation (**Figure S9**). The Brunaue-Emmet-Teller (BET) surface area of PAQ, PAQ-TBZ and PAQ-TABPB was calculated to be 82, 169 and 203 m² g⁻¹ by collecting the Nitrogen adsorption/desorption isotherms at 77 K (Figure 1d), respectively. This phenomenon indicates a transition from linear polymers to cross-linked polymers, resulting in a significant increase in specific surface area, which provides abundant active sites. The morphology of three polymers were investigated using scanning electron microscopy (SEM) (Figure S12) and transmission electron microscopy (TEM) (Figure S13). PAQ showed a block-like morphology, while PAQ-TBZ displayed a stacked sheet-like morphology. The PAQ-TABPB photocatalyst exhibited a nanoflower-like morphology composed of nanosheets with a length of approximately 100 nm. Thermal gravimetric analysis

(TGA) of three polymers were measured in nitrogen from room temperature to 800 °C. In nitrogen, little weight loss occurred until the onset of decomposition at 550 °C, indicating that three polymers had a high thermal stability (**Figure S14**). The ζ potentials of PAQ, PAQ-TBZ and PAQ-TABPB photocatalysts were -27.8, -26.7 and -28.7 mV in H₂O aqueous solution, indicating the negative charged feature on the surface of catalysts (**Figure S15**). The three photocatalysts displayed hydrophilic characteristics, as demonstrated by their contact angles: PAQ (45°), PAQ-TBZ (41°) and PAQ-TABPB (35°) (**Figure S16**). This hydrophilic property is highly advantageous for photocatalytic reactions.

We investigated the interaction between the photocatalyst surface and oxygen molecules using isothermal titration calorimetry (ITC)^[33] (Figure 1e). The heat changes were measured by titrating saturated oxygen deionized water into argon-saturated aqueous solutions of PAQ, PAQ-TBZ and PAQ-TABPB. The heat changes observed in the PAQ-TABPB and PAQ-TBZ solutions were significantly greater than those in the PAQ solution, indicating that the O₂ adsorption capacity of the three-motif polymers are superior to a two-motif linear polymer. In addition, water vapor adsorption-desorption experiments were conducted on PAQ, PAQ-TBZ and PAQ-TABPB polymers (Figure 1f). The water adsorption isotherms revealed that PAQ had a water uptake of 63.9 mg/g. PAQ-TBZ displayed an enhanced water adsorption capacity of 94.3 mg/g, while PAQ-TAPBP exhibited the most substantial water uptake at 198.7 mg/g. A higher water concentration within the polymer matrix enable facilitate the mass transport of water, thereby potentially enhancing the reaction efficiency of H₂O₂ generation^[10,11]. Collectively, these results indicate that incorporating a third component into the linear polymer backbone improves the adsorption ability for O₂ and the H₂O adsorption capacity, which is favorable for the photocatalytic production of H2O2 without sacrificial reagents.

The optical band gap and band positions are essential for photocatalytic H_2O_2 production. To elucidate the electronic properties of the prepared photocatalysts, we conducted UV-vis absorption measurements (Figure S17 and 18) and Mott-Schottky tests (Figure S19)^[34]. The optical bandgaps were determined using Tauc's plots $(\alpha h \upsilon)^{1/2}$, yielding values of 2.47 eV (PAQ), 2.56 eV (PAQ-TBZ), and 2.63 eV (PAQ-TABPB). Frequency-dependent Mott-Schottky measurements (1.2, 1.8 and 2.4 kHz) showed characteristic positive slopes, confirming n-type semiconductor behavior in all materials. A flat band potential of -0.45, -0.49 and -0.67 V (vs. Ag/AgCI) was obtained for PAQ, PAQ-TBZ and PAQ-TABPB, namely -0.24, -0.28 and -0.46 V (vs. NHE), respectively. A typical 3-electrodeconfiguration was used for the measurements. E_{CB} (V vs. NHE) and E_{VB} are calculated according to the formula E_{CB} (V vs. NHE) = E_{fb} (V vs. Ag/AgCl) + 0.21 - X, and E_{VB} = E_{CB} + E_g), where X is from 0.1-0.2 V (the conduction bands of n-type semiconductors are normally 0.1-0.2 eV deeper than the flat-band potential). We used 0.1 V, so E_{CB} is calculated to be -0.34 -0.38 and -0.56 V (vs. NHE), and E_{VB} is calculated to be 2.13, 2.18 and 2.07 V (vs. NHE) (Figure 1g). The band positions of the three polymer photocatalysts are thermodynamically suitable for H₂O₂ photosynthesis, involving a two-step single-electron oxygen reduction reaction (ORR) coupled with a direct two-electron water oxidation reaction (WOR).

Photocatalytic Performance and Circulation-Flow **Photosynthesis.** The photosynthesis of H_2O_2 by the synthetic polymer based photocatalysts was evaluated in O2-saturated pure water under simulated solar irradiation. As evidenced in Figure 2a, PAQ-TABPB exhibited remarkable photocatalytic activity with a H₂O₂ production rate reaching 3351 µmol g⁻¹ h⁻¹, significantly outperforming both (1236 µmol g⁻¹ ⁻h¹) and PAQ (324 µmol g⁻¹ h⁻¹) under identical catalyst dosages. Figure 2b showed that the cumulative amount of H₂O₂ production of PAQ, PAQ-TBZ and PAQ-TABPB reached 0.86 mM, 2.01 mM and 6.62 mM, respectively. Both the three-motif polymeric photocatalysts displayed excellent photocatalytic cycling performance, retaining their activity after 8 cycles (Figure S21). The photocatalyst powder after cumulative reactions was subjected to SEM and FTIR analyses, revealing almost no changes in its morphology and chemical structure, confirming the good stability of the imide bond-linked framework (Figure S22 and S23). PAQ-TABPB achieved a solar-to-H₂O₂ conversion efficiency of 0.36%, exceeding the typical plant photosynthetic efficiency of 0.10% (Figure S24). The apparent quantum yield (AQY) for both polymeric photocatalysts were determined using monochromatic light across different wavelengths (Figure S25). PAQ-TABPB obtained the AQY of 6.36%, %, 6.25%, 4.65%, 3.12%, 2.31% and 1.29% at 400, 420, 450, 530, 600 and 650 nm, respectively (Figure 2c). Moreover, all three photocatalysts displayed weak H₂O₂ decomposition capability after continuous 8h irradiation, which favors the accumulation of H₂O₂ (Figure S26). The H₂O₂ production performance of PAQ-TBZ and PAQ-TAPBP photocatalysts was also assessed in tap water and lake water. As demonstrated in Figure S28, both PAQ-TBZ and PAQ-TAPBP photocatalysts exhibited commendable H₂O₂ production capabilities even when using different water guality. Notably, a three-motif photocatalyst with optimized composition (PAQ-TABPB) represents an advanced polymer photocatalyst with high-efficiency H₂O₂ synthesis performance (Table S2). These results highlight the potential of the multi-motif polymeric photocatalysts developed for H₂O₂ photosynthesis.

The development of an efficient photocatalytic flow synthesis system is pivotal for the scalable H₂O₂ production and practical implementation of advanced photocatalysts. When we utilized a traditional batch reactor for the large-scale photocatalytic production of H₂O₂, the performance of PAQ-TABPB significantly declined. This deterioration is attributed to inefficient gas-liquid mass transfer and inadequate light penetration. Therefore, we employed a circulation-flow strategy to achieve seamless scale-up of photocatalytic synthesis of H₂O₂ (Figure 2d). After PAQ-TABPB and water were mixed in the reservoir and formed a uniform suspension under 02 atmosphere, the reaction mixture was pumped out via a peristaltic pump at an optimized flow rate of 300 mL/min, then went through the coil tubing reactor under efficient light irradiation and return to the reservoir (Figure 2e). Under such a high-speed flow situation, 1/8-inch tubing reactor (I.D. 1.58 mm, O.D. 3.17 mm) ensured efficient light irradiation meanwhile



Figure 2. a) Typical time course of PAQ, PAQ-TBZ and PAQ-TABPB for H_2O_2 production with O_2 -saturated water under simulated sunlight irradiation; b) Photocatalytic H_2O_2 accumulation of PAQ, PAQ-TBZ and PAQ-TABPB photocatalyst in 6 hours; c) The wavelength-dependent apparent quantum yield (AQY) of PAQ-TABPB in the photocatalytic H_2O_2 production; d) Schematic illustration and comparison of the conventional bath reaction system and circulation-flow synthesis system for photocatalytic H_2O_2 production; e) Photographs of the circulation-flow synthesis system of PAQ-TABPB for H_2O_2 production; f) H_2O_2 activity and cycling stability curves of the bath reaction system and circulation-flow synthesis system.

mitigated solid settling. Another peristaltic pump was used to deliver O₂ at 99 cc/min from the reservoir to mix with reaction suspension at the T-mixer and form uniform gas-liquid slug flow (Figure S29). The alternating O₂ bubbles and suspension droplets facilitated mass transfer compared with batch reactor, in which gas-liquid interface is restricted to the reactor shape. The H₂O₂ photosynthesis efficiency of the circulation-flow reactor was evaluated in O₂-saturated pure water solution (120 mL) under a light irradiation intensity of only 27 mW cm⁻². As depicted in Figure 2f, the circulation-flow system enabled PAQ-TABPB to achieve exceptional photocatalytic activity, producing 3125 µmol/g of H₂O₂ within 6 hours while demonstrating excellent stability and practicability over three consecutive cycles. Remarkably, the circulation-flow reactor achieved a 5.2-fold enhancement in H₂O₂ production efficiency relative to conventional batch reactor under the same conditions. The significant improvement is attributed to enhanced gas-liquid mass transfer and optimized light utilization efficiency. Besides, we readily separated PAQ-TABPB from the heterogeneous reaction suspension via facile vacuum filtration. (Figure S32).

The Rubost Driving Force and Reduced Exciton Binding Energy. To fundamentally understand the electronic properties of the three-component photocatalyst system, we performed comprehensive density functional theory (DFT) simulations. The representative molecular fragments of PAQ. PAQ-TBZ and PAQ-TABPB were modeled to elucidate their electronic structure (Figure S33). For PAQ, the lowest unoccupied molecular orbital (LUMO) was distributed on PMDA mojety, and the highest occupied molecular orbital (HOMO) was localized on PMDA and AQ units. The partial overlap between the LUMO and HOMO orbitals in PAQ hinders charge carrier separation, and results in a high electron-hole recombination rate^[35]. Conversely, the molecular orbital distribution of PAQ-TBZ was similar to PAQ-TABPB, the LUMO was concentrated on the PMDA mojety, while the HOMO dispersed around the whole TBZ or TABPB fragment (Figure S34). This suggests that electrons are transferred from TABPB or TBZ units to PMDA moiety. Obviously, the introduction of the third component induces pronounced formation of the typical donor-acceptor (D-A) properties in conjugated skeleton, which is beneficial for charge separation.

The ground-state charge distribution was assessed through molecular electrostatic potential (MESP) analysis. As shown in **Figure 3a**, carbonyl functional groups from both AQ and PMDA units exhibit electron-withdrawing feature, suggesting their role as reductive active sites. Notably, TBZ or TABPB connects to PMDA-AQ framework via imide bonds, inducing a significant

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Figure 3. a) The molecular electrostatic potential and ground-state dipole moment of PAQ, PAQ-TBZ and PAQ-TABPB; b) Real-space hole (blue regions) and electron (green regions) distributions of AQ-PMDA-AQ unit on PAQ, AQ-PMDA-TBZ unit on PAQ-TBZ and AQ-PMDA-TABPB unit on PAQ-TABPB in the excited state; The intensity of photoluminescence emission as a function of temperature for c) PAQ, d) PAQ-TBZ, e) PAQ-TABPB and inset: temperature-dependent photoluminescence spectra from 90 K to 270 K.

increase in molecular dipole moment from 0.266 D to 0.682 D and 0.724 D, respectively. The strategically optimized threecomponent PAQ-TABPB system possesses a larger dipole moment, establishing a robust built-in electric field that accelerates exciton dissociation, thereby significantly boosting photocatalytic activity^[36]. To highlight the significance of crosslinked architectures, we selected anthracene-2,6-diamine (DA) as an advantageous electron-donor unit to replace AQ moiety in the synthesis of PDA linear polymer (Figure S35). Theoretical calculations revealed that this rational donor substitution enable achieve spatially separated HOMO and LUMO orbitals while amplifying the dipole moment by 4.14-fold (Figure S36). However, the photocatalytic H₂O₂ production efficiency only improved by 2.69-fold. This performance limitation is attributed to the limited intramolecular charge transport channels within linear polymers. Tetraamino aromatic linker also as a third component in linear polymer enlarged dipole moment and established multidirectional charge transport, boosting H₂O₂ production to 1852 µmol g⁻¹ h⁻¹ (Figure S37-38).

The excited-state charge distribution characteristics of the three polymeric systems were elucidated through timedependent DFT (TD-DFT) simulations^[37] (Figure S39 and Figure 3b). Under photoexcitation, electrons (green region) localize predominantly on the carbonyl groups of PMDA, while holes (bule region) distribute across the benzene rings of both PMDA and AQ units. The spatial overlap between electron and hole regions leads to a high charge recombination rate of 92.49%, which impedes surface catalytic reactions. Remarkably, upon incorporating the third component TBZ, electrons become uniformly concentrated on PMDA, while holes are localized on TBZ. This spatially segregated electron-hole distribution dramatically suppresses charge recombination, yielding a lower overlap rate of 0.63%. The PAQ-TABPB incorporated with optimal third-component exhibits photoinduced electron transfer from TABPB to both PMDA and AQ segment, achieving a strongly delocalized electron state. The electron-enriched carbonyl groups on PMDA and AQ as abundant reaction active sites improved the ORR efficiency.

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Figure 4. a) EIS spectra of PAQ, PAQ-TBZ and PAQ-TABPB; b) Photocurrent spectra of PAQ, PAQ-TBZ and PAQ-TABPB; c) The open circuit voltage decay of PAQ, PAQ-TBZ and PAQ-TABPB; d) The surface photovoltage spectra of PAQ, PAQ-TBZ and PAQ-TABPB under illumination; e) Time-resolved photoluminescence spectra of PAQ, PAQ-TBZ and PAQ-TABPB; f) Electron paramagnetic resonance for conduction band electrons spectra of PAQ, PAQ-TBZ and PAQ-TABPB; f) Electron paramagnetic resonance for conduction band electrons spectra of PAQ, PAQ-TBZ and PAQ-TABPB after irradiation; g), h) and i) Surface potentials of PAQ, PAQ-TBZ and PAQ-TABPB detected via atomic force microscope equipped with Kelvin probe.

The exciton binding energy (E_b) governs electron-hole Coulombic interactions and determines exciton dissociation efficiency in photocatalysts^[38]. Minimizing E_b through rational design of polymer semiconductors is crucial for enhancing photocatalytic performance. We performed Temperaturedependent photoluminescence (TD-PL) measurements to investigate the exciton dissociation. The Eb can be experimentally determined by analyzing the photoluminescence intensity at different temperatures using the Arrhenius equation: $I(T)=I_0/[1+Aexp(-E_b/k_BT)]$. As illustrated in **Figure 3c-3e**, the fluorescence intensity of PAQ, PAQ-TBZ and PAQ-TABPB gradually increases with decreasing temperature from 270 K to 90 K. Based on the fitting results, three-motif polymer photocatalyst dispalved a significantly lower exciton binding energy compared to its two-motif polymer photocatalyst. Specifically, the exciton binding energy of PAQ-TABPB with the optimized third component (50.81 meV) and PAQ-TBZ (54.93 meV) is significantly lower than that of PAQ (65.86 meV). This experimental finding shows excellent agreement with DFT computational predictions. The incorporation of a third component in linear conjugated polymer induces spatial separation of LUMO and HOMO orbitals, a larger molecular dipole and a higher electron delocalization. Moreover, the optimization of a third component serves as an effective strategy to reduce exciton binding energy (E_b) in organic polymers, which promotes exciton dissociation into free electrons and holes.

Enhanced Charge Separation and Rapid Electron Transport. Subsequently, we performed a series of photoelectrochemical characterization to investigate the excitonic dissociation behavior within the prepared photocatalyst. The electrochemical impedance spectroscopy (EIS) measurements were first carried out. In contrast to PAQ and PAQ-TBZ, PAQ-TABPB exhibits the smallest semicircular arc radius in the Nyquist plot, indicating its lower electron transfer resistance (Figure 4a). PAQ-TABPB with optimized third component facilitates more efficient exciton dissociation, producing more charge carriers, as evidenced by transient photocurrent and open circuit voltage decay (OCVD) measurements^[39]. Photocurrent tests showed PAQ-TABPB achieved the strongest transient photocurrent response under light irradiation,

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Figure 5. a) Photocatalytic controlled experiment under different reaction conditions for PAQ, PAQ-TBZ and PAQ-TABPB; b) EPR signals for capturing hydroxyl radicals of PAQ, PAQ-TBZ and PAQ-TABPB under 300 W Xe lamp; c) EPR signals for capturing superoxide radicals of PAQ, PAQ-TBZ and PAQ-TABPB under 300 W Xe lamp; d) The Koutecky-Levich plots obtained by rotating disk electrode measurements; e) ${}^{18}O_2$ lsotopic labeling experiments. The produced H₂ ${}^{18}O_2$ was converted to H₂ ${}^{18}O_2$; f) *In situ* FTIR spectrum of PAQ-TABPB for photosynthetic H₂O₂ production with increasing illumination time; g) Gibbs free energy diagram of the C=O group of PAQ-TBZ and PAQ-TABPB by an indirect 2e⁻ ORR pathway; h) Schematic illustration revealing photocatalytic H₂O₂ production mechanism of PAQ-TABPB.

confirming superior charge separation in its molecular skeleton (**Figure 4b**). Moreover, PAQ-TABPB also displayed an enhanced open-circuit voltage than both PAQ and PAQ-TBZ, indicating enhanced production of charge carriers with higher concentration (**Figure 4c**). In addition, **Figure 4d** reveals that PAQ-TABPB had a remarkable surface photovoltage of $8.34 \,\mu$ V under illumination, representing a 1.84-fold and 6.31-fold enhancement compared with PAQ-TBZ and PAQ, respectively. This significant improvement unambiguously confirms the superior charge separation and transfer efficiency of PAQ-TABPB.

At the same time, time-resolved photoluminescence spectroscopy (TR-PL) revealed that the average lifetimes of PAQ, PAQ-TBZ and PAQ-TABPB were 1.63, 2.87 and 3.79 ns, respectively (**Figure 4e**). This confirms that PAQ-TABPB exhibits sufficiently prolonged charge carrier lifetime compared to both PAQ and PAQ-TBZ, showing that the photogenerated

electrons from PAQ-TABPB effectively drive surface reaction^[40]. Furthermore, solid-state electron paramagnetic resonance spectroscopy unequivocally demonstrated that PAQ-TABPB generated the most intense unpaired electron signal when exposed to light (Figure 4f). This phenomenon is attributed to the combined effects of its large molecular dipole moment and low exciton binding energy, which synergistically promote exciton dissociation to generate a higher concentration of free electrons. The charge density distributions of three polymerbased photocatalysts were analyzed using Kelvin probe force microscopy (KPFM)^[41] (Figure 4g-4i). PAQ-TABPB displayed a significantly enhanced surface contact potential difference of 128 mV, representing 1.25-fold and 2.97-fold increases than PAQ-TBZ (102 mV) and PAQ (43 mV), respectively. These results collectively demonstrated that embedding a third component into linear conjugated polymer significantly improves intramolecular

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charge separation and accelerates electron transfer, which offering optimal conditions for promoted photocatalytic efficiency.

Photocatalytic Mechanism of H2O2 Production. To elucidate the H₂O₂ generation mechanism and identify the relevant intermediates, we performed comprehensive experiments and characterizations. Upon transitioning from O₂ atmosphere to air atmosphere, all prepared catalysts presented a significant decrease in hydrogen peroxide yield, highlighting the crucial role of oxygen photocatalysis in H₂O₂ generation. To ascertain the active species involved in H₂O₂ generation, controlled experiments were carried out using potassium iodate (KIO₃), methanol (MeOH) and isopropanol (IPA) as the corresponding sacrificial agent for electrons (e⁻), holes (h⁺) and hydroxyl radicals (•OH), respectively (Figure 5a). MeOH addition boosted H₂O₂ production, while the presence of KIO₃ inhibited it. supporting the electron-driven oxygen reduction pathway for H_2O_2 production. The persistent detection of H_2O_2 formation in Ar-purged KIO₃ solution, coupled with the absence of measurable O2, indicates that photogenerated holes enable mediate water oxidation to form H₂O₂ (Figure S40). The water oxidation half-reaction of PAQ, PAQ-TBZ, and PAQ-TABPB were investigated using rotating ring-disk electrode (RRDE) measurements^[42]. At a fixed potential of 0.6 V, distinct reduction currents were detected at the Pt ring electrode, confirming the generation of H₂O₂ through water oxidation. By contrast, when the potential was held at -0.23 V, no oxidation current was observed, illustrating the absence of O2 evolution via water oxidation in these systems (Figure S41).

Electron spin resonance (ESR) technique was used to study the radical intermediates in H₂O₂ synthesis process. The hydroxyl radicals (•OH) were captured by 5,5-dimethyl-1pyrroline N-oxide (DMPO) in water, whereas the superoxide radicals (•O2⁻) were trapped by DMPO in Methanol. As shown in Figure 5b, no •OH signal was detected in any of the polymeric photocatalysts after light irradiation. IPA addition has minimal effect on the H₂O₂ yields from PAQ, PAQ-TBZ and PAQ-TABPB, demonstrating that the H₂O₂ generation pathway is independent of •OH radical participation. Both ESR and trapping experiments jointly verified the occurrence of a direct two-electron WOR pathway. Six distinct peaks assigned to DMPO-•O2- adducts were detected in all three systems, showing intensity trends of PAQ < PAQ-TBZ < PAQ-TABPB (Figure 5c). These results confirm a two-electron ORR pathway for H₂O₂ production through •O2⁻ intermediates, where PAQ-TABPB shows superior •O2⁻ production ability owing to enhanced charge separation. The photocatalytic production of superoxide radicals was quantified by monitoring the characteristic absorbance decay of nitro blue tetrazolium (NBT) at 259 nm^[43]. All polymeric photocatalysts exhibited a gradual decrease in NBT absorbance after light irradiation, indicating •O2⁻ generation, and the declining tendency correlated well with ESR measurements (Figure S42). These observations conclusively exhibited that photocatalytic H₂O₂ generation in our system occured via both an indirect ORR process and a direct WOR pathway.

The oxygen reduction reaction (ORR) electron transfer number (n) was quantified through rotating disk electrode (RDE) measurements^[44] (**Figure S43**). Koutecky-Levich analysis revealed the n of 1.57, 1.92 and 2.18 for PAQ, PAQ-TBZ and PAQ-TABPB, respectively (Figure 5d). PAQ-TABPB possessed a higher 2e⁻ ORR selectivity, suggesting its superior photocatalytic preference for H₂O₂ production. Therefore, we verified that tailoring the constituent motifs in polymer-based photocatalysts was an effective approach to promote rapid $\cdot O_2^{-1}$ generation through improved charge separation and transfer. ¹⁸O isotope-labeling experiments combined with parallel controls were used to identify the O sources in the production process of H₂O₂^[45]. We investigated PAQ-TABPB's photocatalytic H₂O₂ generation in H₂¹⁶O under ¹⁸O₂ atmosphere, using a control system containing only H₂¹⁶O and ¹⁸O₂ without any photocatalyst (Figure S44). Compared to the control sample, PAQ-TABPB exhibited a strong ¹⁸O signal after 8-hour illumination, providing a direct evidence that the oxygen source in the oxygen reduction half-reaction originates from molecular oxygen (Figure 5e). To detect the O element in H₂O₂ produced from H₂O oxidation reaction, we employed the system of H₂¹⁸O and ¹⁶O₂ atmosphere (Figure S45). Isotopic analysis results showed that ¹⁸O signals were observed in the produced H₂O₂, and was approximately 4.9 times higher than that control sample, confirming H₂O₂ production from H_2O oxidation (Figure 5e). Photocatalytic H_2O_2 generation was observed exclusively in the H₂O /acetonitrile mixed solution (50%) or H_2O (100%), while no significant H_2O_2 was observed in pure acetonitrile (0%)^[46] (Figure S46-47). This result identifies water as the sole proton source for photocatalytic H₂O₂ formation.

In situ DRIFTS analysis was employed to monitor the evolution of active sites and reaction intermediates for PAQ, PAQ-TBZ and PAQ-TABPB in oxygen-saturated aqueous solution (Figure S48-50). The absorbance intensities at O-O (949 cm⁻¹), •O₂⁻ (1105 cm⁻¹) and * OOH (1283 cm⁻¹) exhibited time-dependent enhancement with prolonged light exposure^[47] (Figure 5f). Simultaneously, the growing absorption at 1631 cm⁻ ¹ assigned to -C=O group vibrations confirmed carbonyl groups as the reductive active center for a two-step single-electron O₂ reduction route^[48]. To investigate the reaction pathways of the catalytic process on the PAQ-TABPB photocatalyst from a thermodynamic standpoint, DFT calculation were performed. A suitable O₂ adsorption energy is critical for an efficient ORR process^[34]. Compared to other sites, site 1 exhibited an optimal oxygen adsorption energy (Figure S51). This suggests that the carbonyl group serves as the active site for oxygen reduction reaction, the finding that is consistent with in-situ DRIFTS and excited-state computational results.

Since carbonyl groups are the reductive site for the ORR, we performed calculations on the same site in the PAQ-TBZ and PAQ-TABPB (**Figure 5g**). In particular, *OOH is the ratedetermining step of ORR for H_2O_2 production^[49]. The incorporation of the TABPB ligand into PAQ linear polymer significantly lowered the energy for the formation of crucial intermediates *OOH compared to PAQ-TBZ. Meanwhile, the overall Gibbs free energy change for the reduction of O_2 to H_2O_2 was more thermodynamically favorable on PAQ-TABPB than PAQ-TBZ. Moreover, the water oxidation sites in PAQ-TABPB also were investigated. Results from excited-state calculations indicated that the TABPB unit was a hole-accumulation region,

showing that the active sites for water oxidation were located on the TABPB moiety. The formation of the key *OH intermediate is widely considered the rate-determining step in water oxidation for H₂O₂ production^[50]. Consistent with this, our calculated results revealed that site 2 at the carbon atoms in benzene from TABPB exhibited the lowest Gibbs free energy for *OH formation ($\Delta G^*_{OH} = 2.02 \text{ eV}$), positioning it as the optimal active site for water oxidation (**Figure S54**).

By combining experimental and computational results, we summarize the photocatalytic mechanism of the superior PAQ-TABPB (Figure 5h). Under photoexcitation, a three-motif PAQ-TABPB polymeric photocatalyst with a larger dipole moment and lower exciton binding energy achieves highly efficient charge separation, where electrons migrate from the electron-donating TABPB unit to the electron-accepting carbonyl moiety of PMDA and AQ. Concurrently, hole accumulation on the TABPB benzene rings drives direct water oxidation for H₂O₂ formation. The oxygen molecule is adsorbed on the -C=O reductive active site to generate the $\cdot O_2^-$ intermediate species, and $\cdot O_2^-$ is transformed into *OOH via a single-electron reduction. Subsequently, the *OOH undergoes other one-electron reduction to yield the final H₂O₂ product. However, conventional two-motif photocatalyst exhibited inefficient charge separation, resulting in sluggish superoxide radical generation that ultimately limits the overall H₂O₂ production efficiency (Figure S55).

Conclusion

In summary, this study contributes an innovative strategy to significantly improve electronic properties in linear conjugated polymers through the modulation of a functional third component. The integration of a third component induces a structural transition from a linear to a cross-linked network architecture, effectively establishing multi-directional electron transport channels. Experimental and theoretical studies demonstrated that the rational incorporation of a third component into linear polymers enable enlarge molecular dipole moments, reduce exciton binding energy and lower the Gibbs free energy for *OOH formation, with these synergistic effects collectively boosting photocatalytic H_2O_2 production activity. Simultaneously, the circulation-flow reactor we constructed provides a valuable reference for the practical large-scale application of advanced polymeric photocatalyst.

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Conflict of Interest

There is no conflict to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Three-motif cross-linked polymer photocatalyst • multi-component modulation • circulation-flow synthesis • exciton dissociation • photocatalytic H_2O_2 production

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Three-motif cross-linked conjugated polymer

A novel strategy for improved electronic properties in linear conjugated polymers was presented through the modulation of engineered a third component. Optimization of the third component significantly lowers exciton binding energy, enlarges molecular dipole moment and creates multidirectional electron transport channels, collectively boosting the solar-to- H_2O_2 conversion efficiency.