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## RESEARCH ARTICLE

# Photocatalytic Solar Hydrogen Peroxide Production on Donor+Acceptor Linear Polymer Semiconductor Powders Reconfigurable by H-Bonding and $\pi$ -Stacking Interactions

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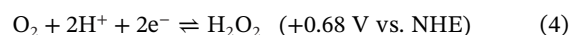
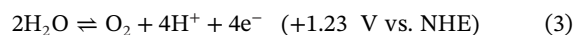
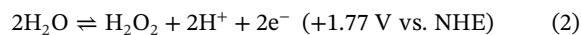
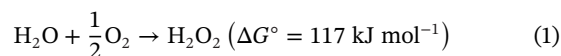
## ABSTRACT

Developing an artificial photosynthesis technology that converts earth-abundant resources into fuels using metal-free photocatalysts with water as an electron donor is challenging. A few active organic semiconductors require harsh synthesis conditions and expensive reagents. Here, we report that a 1,4-conjugated linear polymer, poly(2,3-dihydroxynaphthalene) [poly23DHN], synthesized by the polymerization of inexpensive 23DHN at room temperature, behaves as a heterogeneous catalyst for artificial photosynthesis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in water with  $\text{O}_2$ . The polymer is soluble in polar organic solvents but insoluble in water. The insolubilization of the polymer leads to self-assembly of a hydroquinone–quinone donor+acceptor semiconducting architecture via H-bonding and  $\pi$ -stacking interactions. The formed powders catalyze water oxidation and  $\text{O}_2$  reduction under visible light up to  $\sim 700$  nm. Photocatalyst sheets easily prepared by dropping a polymer-dissolved solution onto a substrate stably generate  $\text{H}_2\text{O}_2$ . This polymer design that creates semiconducting structure through spontaneous H-bonding and  $\pi$ -stacking offers a scalable, easy-to-handle, cost-effective approach for solar fuel generation.

## 1 | Introduction

Artificial photosynthesis, which directly converts solar energy into chemical energy, is essential for a sustainable-energy society [1]. The design of active, easy-to-handle powder photocatalysts that efficiently promote uphill reactions, such as  $\text{H}_2$  generation [2, 3],  $\text{N}_2$  reduction [4], and  $\text{CO}_2$  reduction [5], has been studied extensively over the past decade. Recently, the production of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) from water and  $\text{O}_2$  (Equation (1)) has received increasing attention because  $\text{H}_2\text{O}_2$  is an indispensable oxidant and a potential liquid energy carrier alternative to  $\text{H}_2$  [6]. Photocatalysis in water with  $\text{O}_2$  usually involves  $2\text{e}^-$  (Equation (2)) and  $4\text{e}^-$  (Equation (3)) water oxidation reactions

(WOR) by valence band holes ( $\text{VB } h^+$ ), and  $2\text{e}^-$  (Equation (4)) and  $4\text{e}^-$  (reverse reaction of Equation (3))  $\text{O}_2$  reduction reactions (ORR) by conduction band electrons ( $\text{CB } e^-$ ) [7].



Several inorganic semiconductor photocatalysts have been investigated for this purpose [8, 9]. However, many of these catalysts

suffer from three major problems: they require rare and/or expensive metals, readily decompose the produced  $\text{H}_2\text{O}_2$  via disproportionation on their surface, and exhibit low selectivity for the  $2\text{e}^-$  ORR (Equation (4)). Recently, organic semiconductor photocatalysts have attracted increasing attention owing to their metal-free nature, low  $\text{H}_2\text{O}_2$ -decomposition activity, and high  $2\text{e}^-$  ORR selectivity [10, 11]. Although several semiconductors have been proposed, many are ineffective for  $\text{H}_2\text{O}_2$  production because they are inherently inactive in the WOR (Equations (2) and (3)) [12–14].

Currently, three types of WOR-active organic semiconductors have been investigated for  $\text{H}_2\text{O}_2$  production: graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) [15–17], resorcinol-formaldehyde (RF) resins [18–20], and covalent organic frameworks (COFs) [21–23]. These semiconductors are composed of multibranched covalent-bonded networks that are synthesized under harsh reaction conditions or using expensive reagents.  $\text{g-C}_3\text{N}_4$  and RF resins can be synthesized using inexpensive precursors such as melamine and resorcinol but require high-temperature pyrolysis (>823 K) [15] and hydrothermal treatment under high-temperature (523 K) and high-pressure (4 MPa) conditions, respectively [18–20]. In contrast, COFs can be synthesized under milder conditions (~393 K) but require expensive donor (D) and acceptor (A) monomers [21–23]. The construction of multibranched covalent networks has been essential for WOR-active semiconductors. However, these robust networks significantly reduce the flexibility and solubility in solvents that are characteristic of organic polymers, making post-processing, such as immobilization and shaping, difficult. Thus, it is necessary to design easy-to-handle, easy-to-process, WOR-active organic semiconductors that can be synthesized under ambient conditions using inexpensive reagents.

Polycatechols (polyCCs) are naturally occurring multibranched polymers that can be synthesized via the oxidative polymerization of CC monomers under ambient conditions (Figure 1A) [24]. Owing to their high biocompatibility and high adsorption capabilities originating from the  $-\text{OH}$  groups [24, 25], they have been widely used as adhesives and surface modifiers in the biomedical and environmental fields [24, 26, 27]. Recently, the application of polyCCs in photothermal conversion has been studied because their  $\pi$ -extended structures absorb broad-wavelength light in the visible to near-infrared (NIR) region [28, 29]. Their structural feature is that, as shown in Figure 1A, the *o*-quinone unit (A), which is the oxidized form of inherent *o*-hydroquinone unit (D), is spontaneously formed during the polymerization. This creates H-bonding interactions between the hydroquinone  $-\text{OH}$  and quinone  $\text{C}=\text{O}$  units, resulting in  $\pi$ -extended low-gap electronic band structures [30, 31]. We hypothesized that controlling the hydroquinone–quinone interaction may create donor+acceptor (D+A) semiconducting structures that are active for photocatalytic WOR and ORR under visible light.

Herein, we report that poly(2,3-dihydroxynaphthalene) [poly23DHN], synthesized via the oxidative polymerization of inexpensive 23DHN at room temperature (Figure 1B), behaves as a D+A semiconductor that is active for  $\text{H}_2\text{O}_2$  production under visible light. Poly23DHN is a 1,4-conjugated linear polymer comprising hydroquinone and quinone units. The polymer was soluble in polar organic solvents (Figure 1Ba)

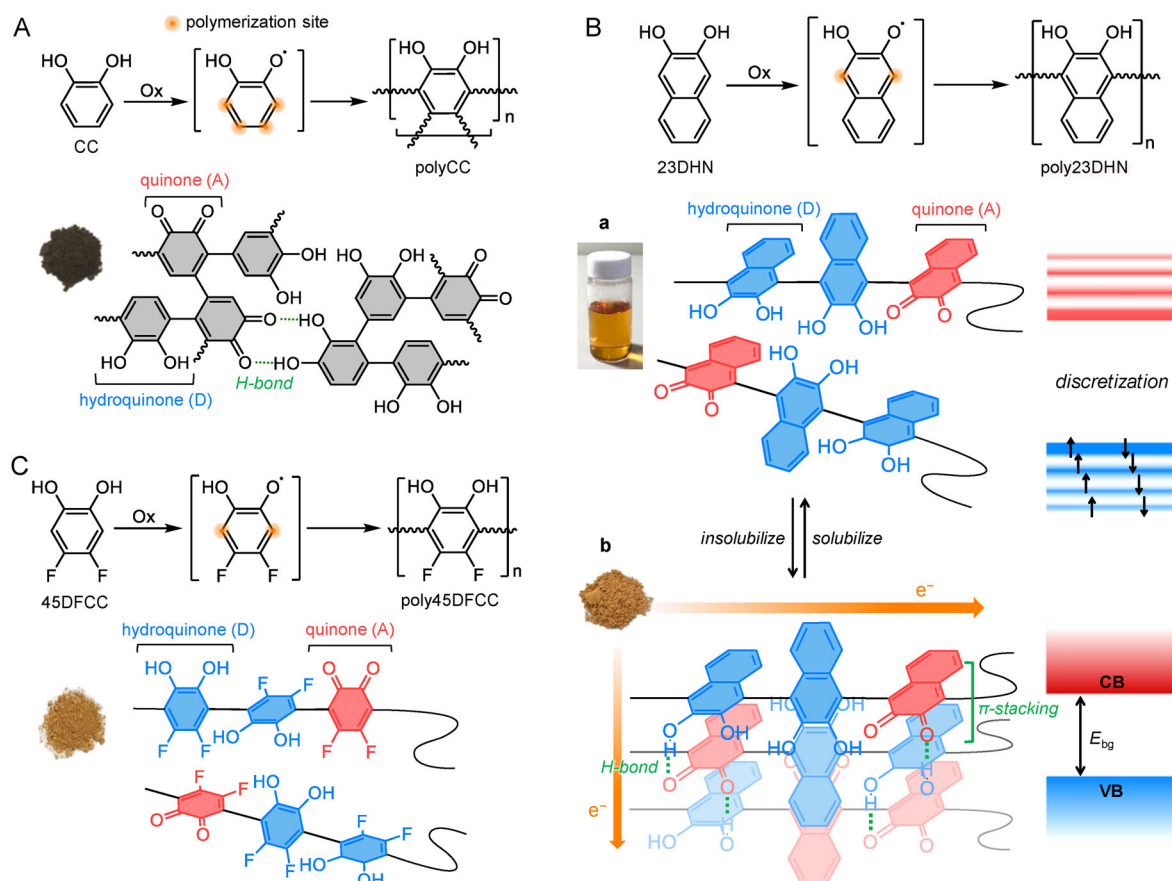
but insoluble in water (Figure 1Bb). The insolubilization spontaneously induces H-bonding and  $\pi$ -stacking between the hydroquinone and quinone units, creating a hydroquinone–quinone D+A semiconducting architecture that catalyzes WOR and ORR. Furthermore, poly23DHN can be easily immobilized onto several substrates by dropping a polymer-dissolved solution followed by drying. The soluble linear polymer that reconfigures semiconducting architecture via H-bonding and  $\pi$ -stacking may represent a new class of heterogeneous photocatalyst for artificial photosynthesis.

## 2 | Results and Discussions

### 2.1 | Synthesis of Polymers

The polymers were synthesized by the oxidative polymerization of several monomers listed in Figure 2A, including 23DHN, CC, dopamine (DPM), and 4,5-difluoroCC (45DFCC). An ethanol solution containing each respective monomer (3 mmol) was added dropwise to a  $\text{KIO}_3$  solution (4.5 mmol), and the mixture was stirred at 298 K for 24 h. The resulting solids were recovered by centrifugation and washed with water. Subsequent drying afforded a yellow-to-black powder. X-ray photoelectron spectroscopy (XPS) of the obtained poly23DHN powder (Figure S1) showed no iodide (I) component in the I 3d region, suggesting that I components were removed completely. The diffuse reflectance (DR) UV–vis spectrum of poly23DHN (Figure 2B, red) shows a broad absorption band extending to ~700 nm. Scanning electron microscopy (SEM; Figure 3A) and transmission electron microscopy (TEM; Figure 3B) observations of poly23DHN showed randomly shaped particles with diameters of 1–5  $\mu\text{m}$ , similar to those of the other polymers (Figure S2). The observed sizes were consistent with the average diameters ( $2.3 \pm 0.6 \mu\text{m}$ ) determined by dynamic light scattering analysis (Figure S3).  $\text{N}_2$  adsorption/desorption analysis of the poly23DHN powder showed a type-II isotherm with a low specific surface area (5.1  $\text{m}^2 \text{g}^{-1}$ ), similar to the other polymers (Figure S4), indicative of nonporous solids.

PolyCC and polyDPM are insoluble in any solvent because oxidation of these monomers creates multiple high-electron-density sites and produces multibranched polymers (Figure 1A) [32, 33]. In contrast, poly23DHN and poly45DFCC are linear polymers because the *para* positions of the monomers are protected by fused rings (Figure 1B) or substituents (Figure 1C) [32, 34]. Therefore, they are soluble in common polar organic solvents such as acetone, ethanol, MeCN, DMSO, THF, and ethyl acetate, but insoluble in water and nonpolar solvents such as toluene and *n*-hexane (Figure S5). The solubility of poly23DHN in acetone, ethanol, and MeCN at 298 K was 8.1, 17.3, and 7.6 g/L, respectively. Static light scattering analysis of poly23DHN dissolved in MeCN (Figure S6) determined its weight-average molecular weight ( $M_w$ ) to be ~140 000, with a polymerization degree of ~900, similar to that of poly45DFCC. This  $M_w$  is moderate compared with common linear polymers such as polystyrene used for packaging (100 000–400 000) [35], poly(acrylic acid), and polyacrylamide used for textile finishing and papermaking (100 000–1 000 000) [36]. These findings indicate that poly23DHN is soluble in polar organic solvents but insoluble in water, enabling its use for photocatalytic reactions in aqueous media.



**FIGURE 1** | Structures of polycatechols in solution and the solid state. (A) polyCC, (B) poly23DHN, and (C) poly45DFCC.

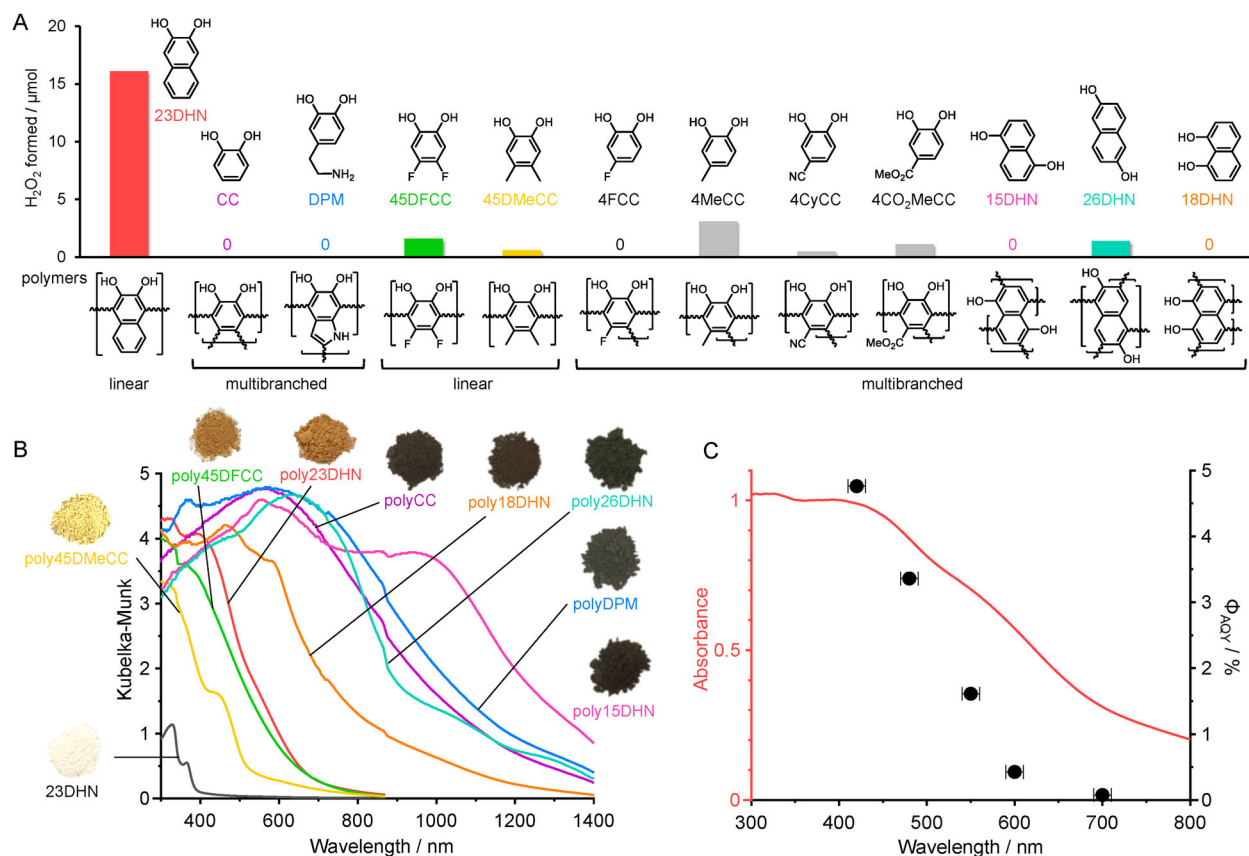
## 2.2 | Photocatalytic Activity

Photoreactions were carried out by visible-light irradiation ( $\lambda > 420$  nm) of polymer powder (50 mg) suspended in water (30 mL) under an  $O_2$  atmosphere (1 bar) at 298 K using a Xe lamp with magnetic stirring. Figure 2A summarizes the amount of  $H_2O_2$  generated during 6 h of photoirradiation of the respective polymers. Although most polymers generated almost no  $H_2O_2$ , poly23DHN showed high activity for  $H_2O_2$  generation. As shown in Figure S7, poly23DHN stably generated  $H_2O_2$  even after 40 h of photoirradiation. In addition, the polymer, when reused for subsequent photoreactions, showed activity comparable to that of the fresh polymer, without a loss of activity after four reuse cycles (Figure S8). Figure 2C shows the action spectrum for  $H_2O_2$  generation on poly23DHN, determined by monochromatic light irradiation. This spectrum agrees with the absorption spectrum of poly23DHN, suggesting that photoexcitation of poly23DHN leads to  $H_2O_2$  generation.

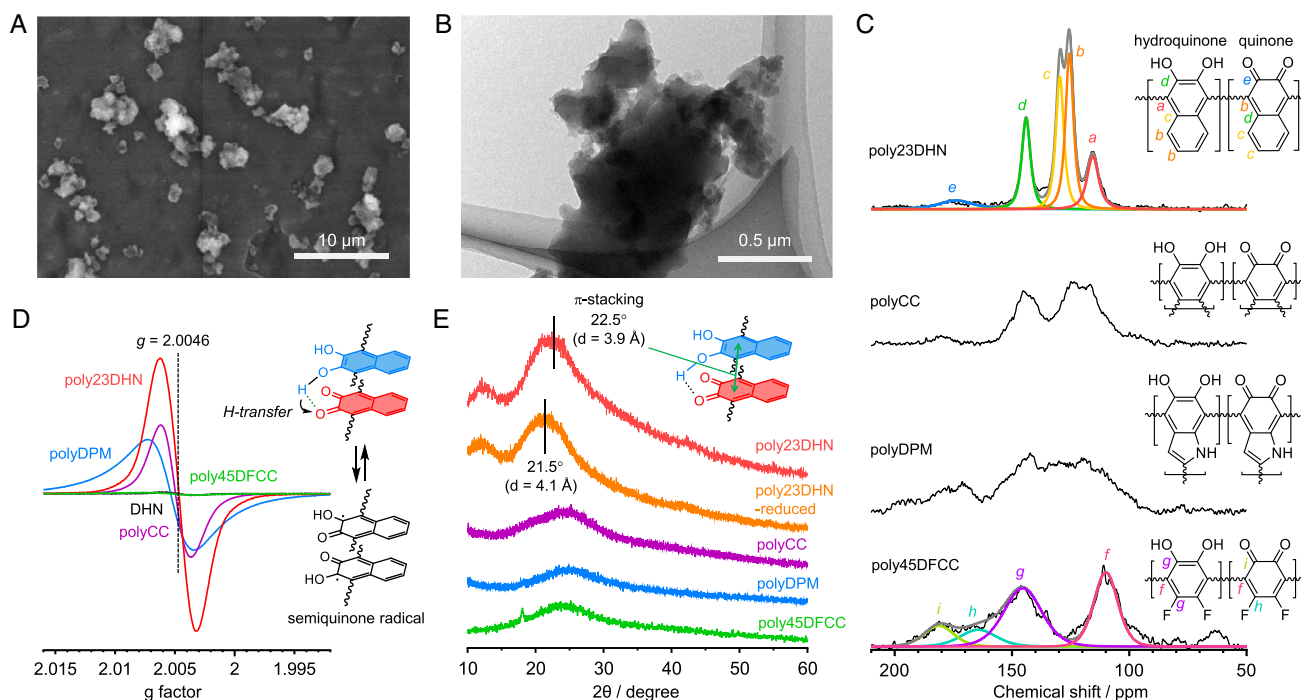
Photoexcited poly23DHN catalyzes both WOR and ORR, generating  $H_2O_2$ . Electrochemical analysis confirmed the WOR (Figure S9); linear sweep voltammetry (LSV) measured using a poly23DHN-loaded fluorine-doped tin oxide (FTO) electrode under an  $N_2$  atmosphere showed an oxidation current at  $>1.9$  V (vs. reversible hydrogen electrode (RHE)) assigned to WOR. The half-photoreaction further confirmed this behavior (Figure S10); photoirradiation of poly23DHN in water with  $AgNO_3$  as an electron acceptor under an Ar atmosphere produced both  $O_2$

and  $H_2O_2$ . This indicates that  $4e^-$  WOR (Equation (3)) and  $2e^-$  WOR (Equation (2)) occurred simultaneously, with a selectivity for  $2e^-$  WOR of  $\sim 30\%$  based on the electron transfer number per  $O_2$  molecule. The ORR on poly23DHN was confirmed by rotating ring-disk electrode (RRDE) measurements under  $O_2$  (Figure S11). The LSV measured on a poly23DHN-loaded disk electrode showed a reduction current at  $<0.5$  V (vs. RHE) attributable to ORR. A simultaneous increase in the ring current indicates that poly23DHN produces  $H_2O_2$  via  $2e^-$  ORR (Equation (4)) as well as water via  $4e^-$  ORR (the reverse reaction of Equation (3)), with a  $2e^-$  ORR selectivity of  $\sim 60\%$ . The results indicate that photoexcited poly23DHN produces  $H_2O_2$  through  $2e^-$  WOR and  $2e^-$  ORR.

To confirm the simultaneous production of  $H_2O_2$  by  $2e^-$  WOR and  $2e^-$  ORR, isotopic photoreactions were performed in  $H_2^{16}O$  containing poly23DHN under  $^{16}O_2$  or  $^{18}O_2$  atmosphere (1 bar). After the photoirradiation, the gas phase was replaced with a He gas. The  $H_2O_2$  generated in solution was decomposed with  $MnO_2$ , and the evolved  $O_2$  gas was analyzed by a gas chromatography-mass spectrometry (Figure S12). After the  $^{16}O_2$  photoreaction,  $^{16}O_2$  was detected with almost 100% selectivity. In contrast, after the  $^{18}O_2$  photoreaction, 44%  $^{16}O_2$  and 55%  $^{18}O_2$  were detected, indicating that the  $H_2O_2$  formed consisted of  $H_2^{16}O_2$  generated via  $2e^-$  WOR of  $H_2^{16}O$  and  $H_2^{18}O_2$  generated via  $2e^-$  ORR of  $^{18}O_2$ . The  $H_2^{16}O_2$  (44%) and  $H_2^{18}O_2$  (55%) compositions were consistent with the  $2e^-$  WOR selectivity ( $\sim 30\%$ ) determined by the half photoreaction (Figure S10) and the  $2e^-$  ORR selectivity ( $\sim 60\%$ )



**FIGURE 2** | Photocatalytic activity and optical properties of the polymers. (A) Amount of  $\text{H}_2\text{O}_2$  generated on the respective polymers during 6 h of photoirradiation (water (30 mL), polymer (50 mg),  $\text{O}_2$  (1 bar),  $\lambda > 420$  nm (Xe lamp), 298 K). (B) DR UV-vis spectra of the polymer powders. (C) Absorption spectrum of poly23DHN and action spectrum for  $\text{H}_2\text{O}_2$  generation.



**FIGURE 3** | Morphological and structural properties of the polymers. (A) SEM and (B) TEM images of the poly23DHN powder. (C) Solid-state DD/MAS/ $^{13}\text{C}$  NMR spectra of the polymer powders. (D) ESR spectra of the polymer powders measured after photoirradiation at 298 K. (E) XRD patterns of the polymer powders and the poly23DHN powder reduced with  $\text{NaBH}_4$ .

determined by the RRDE measurements (Figure S11). The results support the simultaneous production of  $\text{H}_2\text{O}_2$  through  $2\text{e}^-$  WOR and  $2\text{e}^-$  ORR on the photoexcited poly23DHN.

### 2.3 | Structure in the Solid State

Poly23DHN is a 1,4-conjugated linear polymer composed of hydroquinone and quinone units (Figure 1B). The C and O compositions were determined by XPS (Figure S13). The C 1s spectrum was deconvoluted into three components: C—C (284.6 eV), C—O (286.1 eV), and C=O (288.6 eV) [37, 38]. The O 1s spectrum consisted of C—O (533.2 eV) and C=O (531.9 eV) components with a C—O/C=O ratio of 71%/29%, indicating that poly23DHN contains quinone units. Solid-state dipolar-decoupling magic-angle spinning  $^{13}\text{C}$  nuclear magnetic resonance (DD/MAS/ $^{13}\text{C}$  NMR) spectroscopy was used to determine the polymer structure. Based on density functional theory (DFT) calculations of a hydroquinone–quinone conjugate model (Figure S14), the poly23DHN spectrum (Figure 3C) was deconvoluted into five components (a–e) [39]. The ratio of the peak areas (a/e) determined a hydroquinone/quinone ratio of 73%/27%, consistent with the ratio (71%/29%) determined by XPS. These results confirm that poly23DHN is a 1,4-conjugated linear polymer consisting of ~70% hydroquinone and ~30% quinone units.

The poly23DHN powder has a three-dimensional structure (Figure 1Bb) featuring H-bonding between hydroquinone and quinone moieties, as well as  $\pi$ -stacking between these units. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirmed the H-bonding (Figure S15). The poly23DHN powder showed peaks at  $\sim 1700\text{ cm}^{-1}$ , assigned to  $\nu_{\text{C=O}}$  stretching vibration of quinone [40], and at  $\sim 3300\text{ cm}^{-1}$  assigned to  $\nu_{\text{O—H}}$  vibration of hydroquinone, which is H-bonded to quinone C=O [41]. Chemical reduction of the powder with  $\text{NaBH}_4$  weakened both peaks due to reduction of the quinone C=O, confirming the presence of H-bonding. The electron spin resonance (ESR) spectrum of the poly23DHN powder (Figure 3D) showed a strong signal ( $g = 2.0046$ ), which was assigned to a semiquinone radical formed via H-transfer from hydroquinone —OH to quinone C=O, as observed in hydroquinone–quinone systems such as eumelanin [42] and ubiquinone [43]. This supports the hydroquinone–quinone H-bonding interactions. The hydroquinone–quinone  $\pi$ -stacking was confirmed by the x-ray diffraction (XRD) analysis (Figure 3E). The poly23DHN powder exhibited a peak at  $2\theta = \sim 22.5^\circ$  ( $d = \sim 3.9\text{ \AA}$ ), assigned to the (002) plane of  $\pi$ -stacked aromatics [44, 45]. In contrast, the  $\text{NaBH}_4$ -reduced powder showed this peak at a lower angle ( $2\theta = \sim 21.5^\circ$ ;  $d = \sim 4.1\text{ \AA}$ ), indicating an increased stacking distance. The results indicate that, as shown in Figure 1Bb, the poly23DHN powder possesses a hydroquinone–quinone D+A  $\pi$ -stacked architecture stabilized by H-bonding between hydroquinone and quinone units.

### 2.4 | Semiconducting Properties

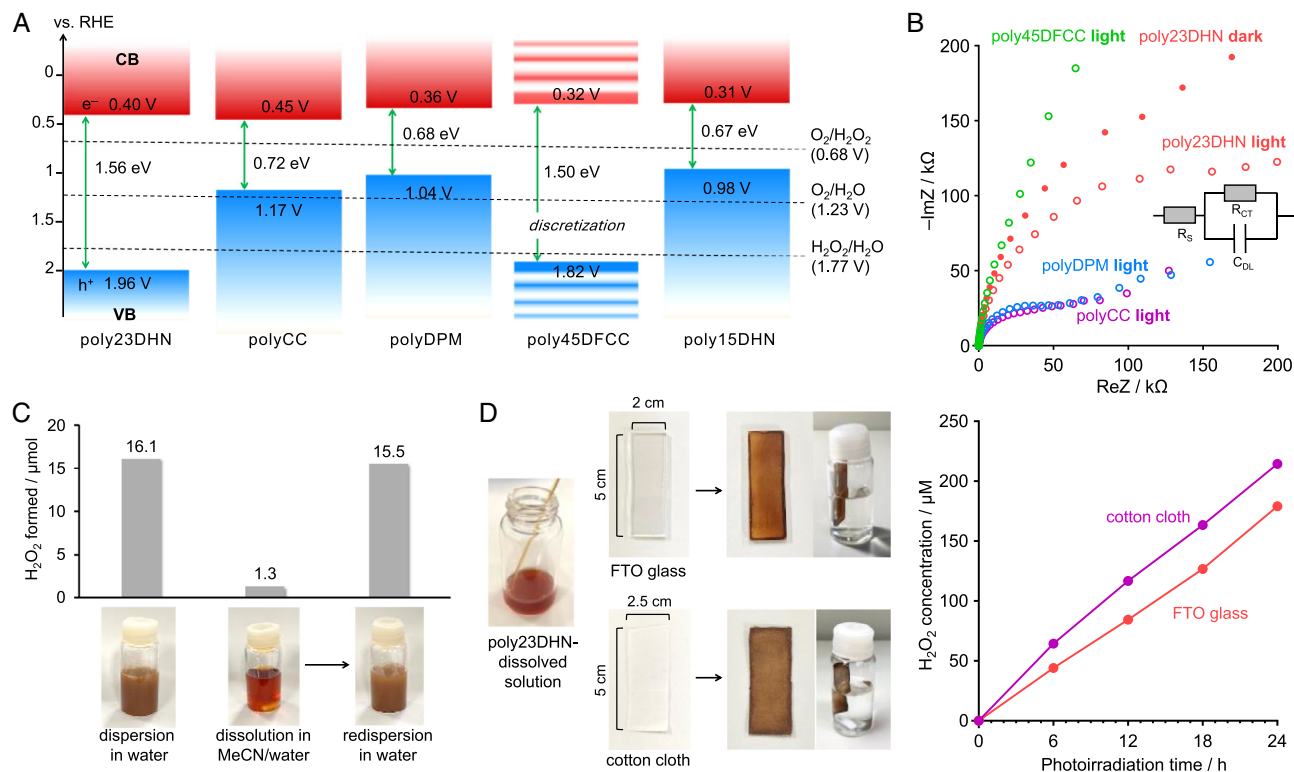
The D+A interactions in the poly23DHN powder through H-bonding and  $\pi$ -stacking (Figure 1Bb) create a low-bandgap semiconductor. The Tauc plot derived from the absorption data (Figure S16) yielded a bandgap energy ( $E_{\text{bg}}$ ) of 1.56 eV (795 nm).

The Mott–Schottky plot of the powder (Figure S17) exhibited a positive slope, characteristic of an n-type semiconductor. These data determined its CB and VB levels of 0.40 and 1.96 V (vs. RHE), respectively (Figure 4A). The CB lies above the potential for  $2\text{e}^-$  ORR (0.68 V, Equation (4)), while the VB lies below the potentials for both  $4\text{e}^-$  WOR (1.23 V, Equation (3)) and  $2\text{e}^-$  WOR (1.77 V, Equation (2)). Therefore, poly23DHN possesses a band structure suitable for  $\text{H}_2\text{O}_2$  production under visible light. Electrochemical impedance spectroscopy (EIS) Nyquist plots (Figure 4B) of poly23DHN-loaded FTO in  $\text{Na}_2\text{SO}_4$  solution showed a large charge-transfer resistance ( $R_{\text{CT}}$ ) in the dark, whereas photoirradiation significantly reduced  $R_{\text{CT}}$ . In addition, ESR spectra of poly23DHN (Figure S18) indicated that the intensity of semiquinone radical increased upon photoirradiation owing to the proton-coupled electron transfer from the hydroquinone to quinone unit [46]. The results indicate that poly23DHN acts as an n-type D+A semiconductor, in which the hydroquinone and quinone units behave as the donor and acceptor, respectively, promoting both WOR and ORR under visible light.

The other polymers produce almost no  $\text{H}_2\text{O}_2$  (Figure 2A). PolyCC and polyDPM also contain hydroquinone and quinone units (Figure S13); however, they form multibranch polymers (Figure 1A), as confirmed by the broad chemical shifts in the  $^{13}\text{C}$  NMR spectra (Figure 3C). The extended  $\pi$ -conjugation resulted in broad light absorption extending into the NIR region (Figure 2B). The VB levels of polyCC and polyDPM lie at 1.17 and 1.04 V (vs. RHE), respectively (Figure 4A), which are more negative than the potentials required for both  $4\text{e}^-$  and  $2\text{e}^-$  WOR. This suggests that the multibranch structures create shallow VB levels that are inactive for WOR. In contrast, poly45DFCC is a linear polymer (Figure 3C) with a relatively deep VB level (1.82 V, Figure 4A) but exhibits a large  $R_{\text{CT}}$  even under photoirradiation (Figure 4B), indicating low conductivity. It showed weak H-bonding features (Figure S15), weak  $\pi$ -stacking diffraction (Figure 3E), and no ESR signal (Figure 3D). The results indicate that bulky F groups sterically hinder H-bonding and  $\pi$ -stacking (Figure 1C), creating a less conductive polymer with discretized bands (Figure 4A). As shown in Figure 2A, other linear (poly45DMeCC) [32] and multibranch polymers (poly4FCC, poly4MeCC, poly4CyCC, and poly4CO<sub>2</sub>MeCC) [32] produced almost no  $\text{H}_2\text{O}_2$ , indicating that polymers synthesized with monocyclic CCs are inactive. In addition, polymers synthesized from DHN bearing —OH groups at different positions (1,8, 1,5, and 2,6) were also inactive. Oxidation of these derivatives produces multibranch polymers with broad light absorption (Figure 2B) [32, 47], resulting in shallow VB levels insufficient for WOR (Figure 4A). Therefore, the linear poly23DHN powder, with appropriately positioned VB levels created by H-bonding and  $\pi$ -stacking D+A interactions, exhibits superior photocatalytic activity.

### 2.5 | DFT Calculations of D+A Structures

DFT calculations were performed to confirm the semiconducting structure of poly23DHN created via H-bonding and  $\pi$ -stacking D+A interactions (Figure 1Bb). Figure 5 shows the optimized structures of the models consisting of hydroquinone (D) and quinone (A) units calculated using Grimme's dispersion correction parameter [48], and the Cartesian coordinates of the models are shown in Table S1. Both the D/A stack (a) and D/D stack (b)



**FIGURE 4** | Electrochemical, solubilization/insolubilization, and immobilization properties of the polymers. (A) Electronic band structures of the polymers. (B) EIS Nyquist plots of polymer-loaded FTO electrodes measured in 0.1 M  $\text{Na}_2\text{SO}_4$  at a bias of 1.2 V (vs. Ag/AgCl), where the equivalent circuit model contains ohmic resistance ( $R_s$ ), double-layer capacitance ( $C_{DL}$ ), and charge-transfer resistance ( $R_{CT}$ ). (C) Amount of  $\text{H}_2\text{O}_2$  produced during photoirradiation of poly23DHN dispersed in water or dissolved in a MeCN/water (25/5 vol/vol) mixture (solution (30 mL), polymer (50 mg),  $\text{O}_2$  (1 bar),  $\lambda > 420$  nm (Xe lamp), 298 K, 6 h). (D) Preparation procedure of photocatalyst sheets and their activity for  $\text{H}_2\text{O}_2$  generation (water (30 mL), sheet,  $\text{O}_2$  (1 bar),  $\lambda > 420$  nm (Xe lamp), 298 K).

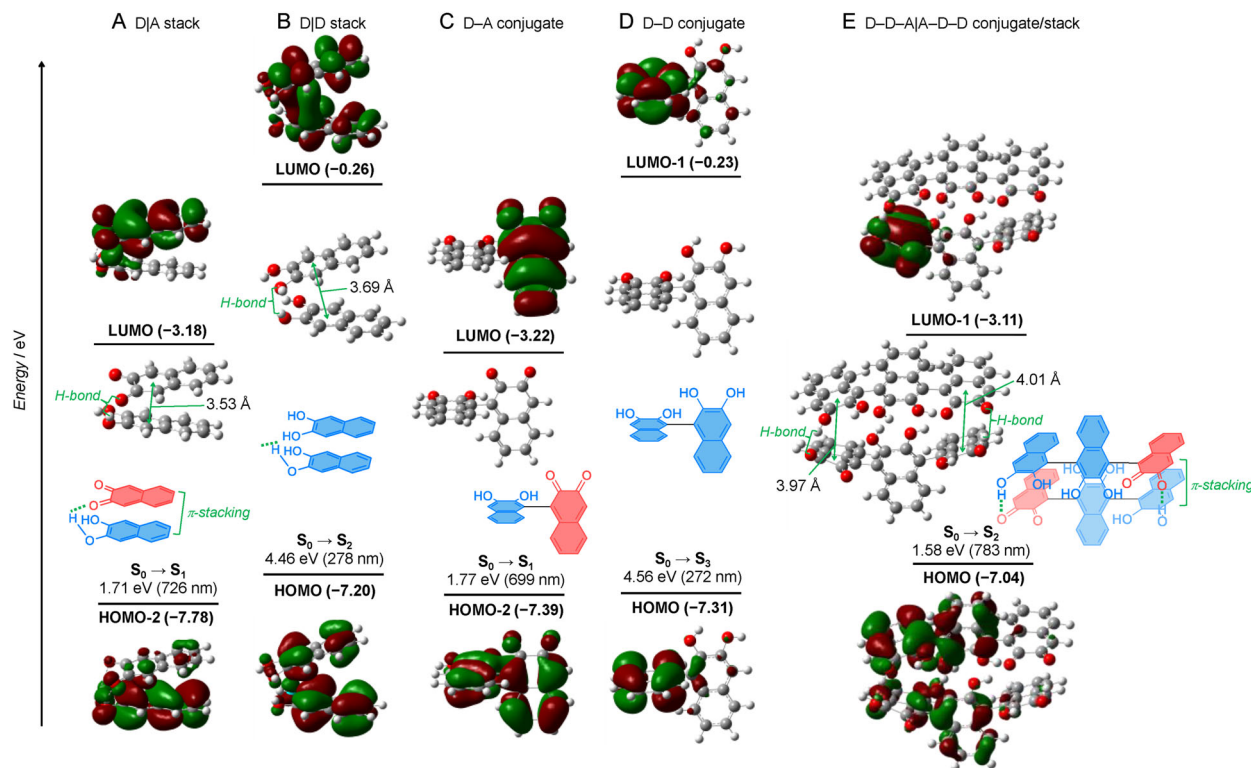
models create H-bonding. The centroid-centroid distance of the two naphthalene rings in the D/A model (3.53 Å) was shorter than that in the D/D model (3.69 Å), confirming stronger D/A  $\pi$ -stacking. In contrast, the D-A conjugate (c) and D-D conjugate (d) models have twisted alignments in which the respective units do not form H-bonds. To reflect the real polymer structure, the D-D-A/A-D-D conjugate/stack model (e) was optimized because poly23DHN comprises  $\sim 70\%$  D and  $\sim 30\%$  A units (Figure S13). The D and A units on both sides of the chains create H-bonding and  $\pi$ -stacking, although the central D units do not interact. The centroid-centroid distances of the terminal D/A pairs are 3.97 and 4.01 Å that are consistent with the  $\pi$ -stacking diffraction confirmed by XRD ( $d = \sim 3.9$  Å, Figure 3E). The results support the hydroquinone-quinone D+A  $\pi$ -stacked architecture, assisted by H-bonding (Figure 1Bb).

The three-dimensional architecture of poly23DHN creates semi-conducting bands. This was confirmed using time-dependent DFT (TD-DFT) calculations. Figure 5 presents the main transitions and interfacial plots of the respective models, and the main transitions are summarized in Table S2. The D/D stack (b) and D-D conjugate models (d) show high transition energies (4.46 and 4.56 eV, respectively). In contrast, the D/A stack (a) shows a low transition energy (1.71 eV, 726 nm) attributable to the D→A electronic transition along the stacking direction. The D-A conjugate (c) also shows low-energy D→A transition along the chain direction (1.77 eV, 699 nm). Furthermore, the D-D-A/A-D-

D conjugate/stack model (e) shows D→A transitions along both directions. Its transition energy (1.58 eV) agrees with the bandgap energy of poly23DHN (1.56 eV; Figure 4A). Therefore, the D+A interactions along the stacking and chain directions hybridize the molecular orbitals and create D+A semiconducting bands, where the VB consists of hydroquinone units and the CB consists of quinone units.

## 2.6 | Photocatalysis Mechanism

The mechanisms of ORR by  $e^-$  on the quinone unit (A) and WOR by  $h^+$  on the hydroquinone unit (D) were clarified by DFT calculations using the simple D/A stack model, in which the 1,4-carbons of the respective units were terminated with methyl groups (Table S1). The free energies of the intermediates were calculated under applying the CB potential ( $U = 0.40$  V vs. RHE). Figure 6A shows the energy diagrams for the  $2e^-$  ORR at the respective positions of the A unit ( $A_1$ ,  $A_5$ ,  $A_6$ , and  $A_9$ ).  $\text{O}_2$  is reduced by  $e^-$  to form  $\text{OOH}^*$ , which is further reduced by  $e^-$  to produce  $\text{H}_2\text{O}_2$  [49]. The diagram indicates that the path occurring at the  $A_5$ -position (purple) exhibits a stepwise decrease in free energy, suggesting that, as shown in Figure 6C, the  $A_5$ -position is the active site for the  $2e^-$  ORR. Figure 6B shows the energy diagram for WOR on the respective positions of D unit under applying the VB potential ( $U = 1.96$  V vs. RHE). During the WOR, two water molecules are sequentially oxidized by  $h^+$  to form



**FIGURE 5** | Calculated energy levels, molecular orbitals, and optimized structures of the respective models. The results were obtained using TD-DFT/CAM-B3LYP/6-31+G(d,p) with GD3 dispersion correction.

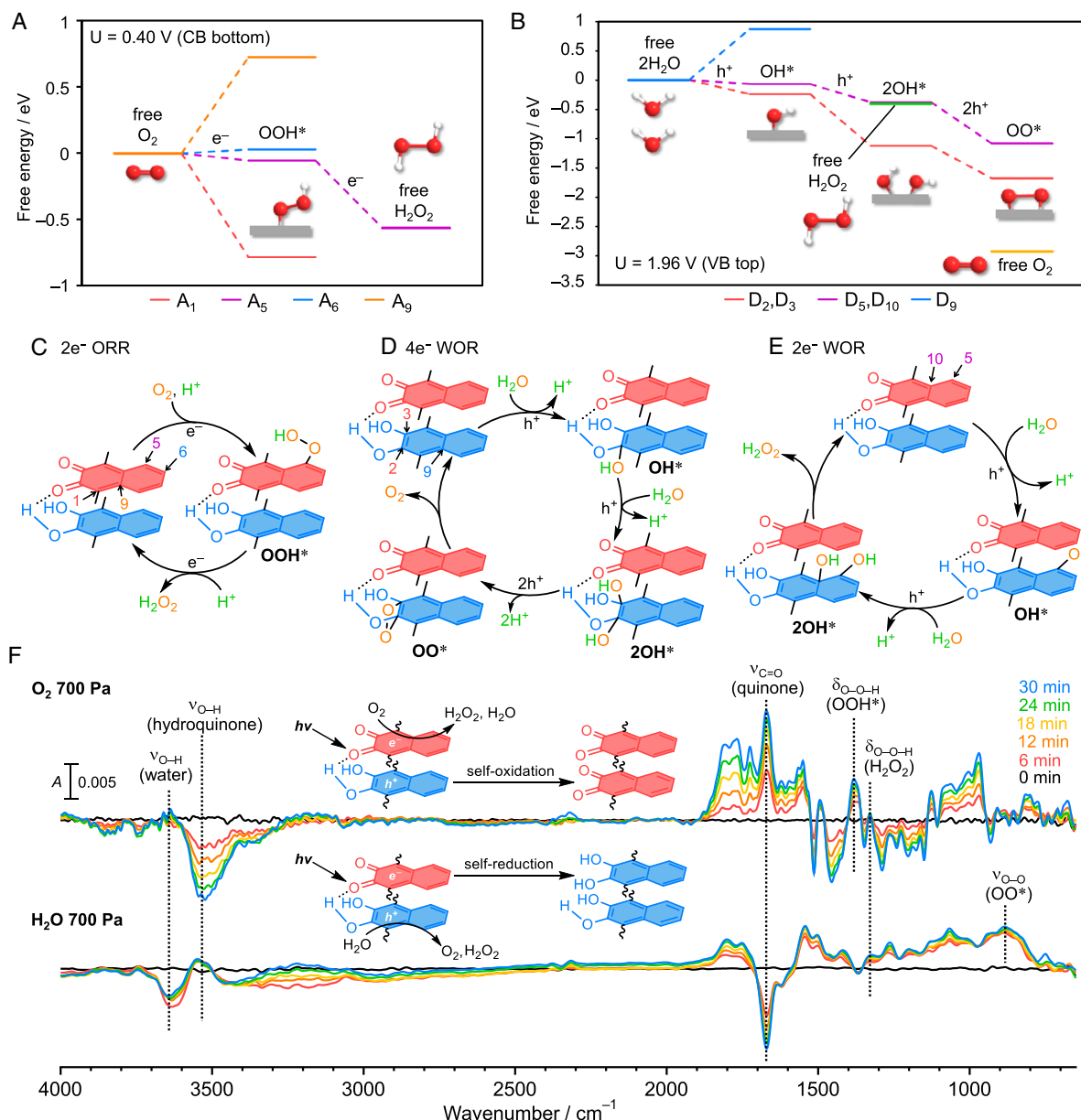
two OH\* intermediates (2OH\*). Coupling of the intermediates produces H<sub>2</sub>O<sub>2</sub> (2e<sup>-</sup> WOR) [49]. In contrast, further oxidation of these two OH\* species by 2h<sup>+</sup> and subsequent coupling produces a bridging OO\* species. Its desorption generates O<sub>2</sub> (4e<sup>-</sup> WOR) [50]. The diagram (Figure 6B) indicates that the D<sub>2</sub>-, D<sub>3</sub>-positions (red) and the D<sub>5</sub>-, D<sub>10</sub>-positions (purple) are active for 4e<sup>-</sup> WOR. In particular, the D<sub>2</sub>-, D<sub>3</sub>-positions (red) allow for a smoother decrease in the free energy for O<sub>2</sub> generation, suggesting that they are the main active sites for 4e<sup>-</sup> WOR (Figure 6D). In contrast, the D<sub>5</sub>-, D<sub>10</sub>-positions (purple) allow H<sub>2</sub>O<sub>2</sub> generation energetically favorably, suggesting that they are active for 2e<sup>-</sup> WOR (Figure 6E). These results support the mechanism of the 2e<sup>-</sup> ORR on the A unit and 2e<sup>-</sup> and 4e<sup>-</sup> WOR on the D unit. To further confirm the mechanism, a poly23DHN solution was photoirradiated under O<sub>2</sub> with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin trapping reagent. ESR analysis of the resulting solution (Figure S19) does not show spin-adduct signal assigned to superoxide radical (O<sub>2</sub><sup>•-</sup>) or hydroxyl radical (OH<sup>•</sup>), indicating that 1e<sup>-</sup> WOR or 1e<sup>-</sup> ORR does not occur. This is consistent with the band positions of poly23DHN (Figure 4A): the VB level (1.96 V vs. RHE) is more negative than the 1e<sup>-</sup> WOR potential (2.73 V vs. RHE) [51] and the CB level (0.40 V vs. RHE) is more positive than the 1e<sup>-</sup> ORR potential (-0.33 V vs. RHE) [51]. The results support the multi-electron transfer mechanism for WOR and ORR (Figure 6C-E).

In situ DRIFTS analysis was performed to confirm the proposed pathways (Figure 6C-E). The poly23DHN powder was photoirradiated with O<sub>2</sub> or water vapor (700 Pa) at 323 K. Figure 6F (top) shows the changes in the spectra monitored with O<sub>2</sub> in the absence of water. Photoirradiation increases the bands at

1380 and 1330 cm<sup>-1</sup>, assigned to δ<sub>O-O-H</sub> bending vibrations of OOH\* and H<sub>2</sub>O<sub>2</sub>, respectively, generated by ORR [52, 53], which agree with the 2e<sup>-</sup> ORR mechanism (Figure 6C). In this case, the hydroquinone ν<sub>O-H</sub> (3500 cm<sup>-1</sup>) decreases, associated with an increase in the quinone ν<sub>C=O</sub> (1670 cm<sup>-1</sup>). This suggests that without water (an electron donor), the h<sup>+</sup> photogenerated on the hydroquinone unit leads to self-oxidation, confirming the localization of h<sup>+</sup> on the D unit. Figure 6F (bottom) shows the changes in the DRIFTS spectra monitored with water in the absence of O<sub>2</sub>. Photoirradiation decreases the water ν<sub>O-H</sub> band (3600 cm<sup>-1</sup>), confirming WOR by h<sup>+</sup>. Simultaneously, the bands at 880 cm<sup>-1</sup> assigned to ν<sub>O-O</sub> of the bridging OO\* intermediate [54] and at 1330 cm<sup>-1</sup> assigned to δ<sub>O-O-H</sub> of H<sub>2</sub>O<sub>2</sub> increase, confirming the generation of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> by WOR. In this case, the quinone ν<sub>C=O</sub> (1670 cm<sup>-1</sup>) decreases, suggesting that, without O<sub>2</sub> (electron acceptor), the photogenerated e<sup>-</sup> is localized on the quinone unit and promotes its self-reduction. These DRIFTS results support the ORR and WOR pathways (Figure 6C-E).

## 2.7 | Performance of poly23DHN

The poly23DHN is active only in the solid state; photoirradiation of poly23DHN dissolved in a MeCN/water mixture produced almost no H<sub>2</sub>O<sub>2</sub> (Figure 4C (center)). This is because, as shown in Figure 1Ba, the dissolution of polymer disassembles H-bonding and π-stacking and leads to a loss of semiconducting properties. As shown in Figure S20, when the powder was dissolved in an MeCN/water mixture, the absorption band in the visible region disappeared, confirming disassembly. The dissolved polymer was recovered by evaporation, and the obtained powder was



**FIGURE 6** | ORR and WOR pathways on poly23DHN determined by DFT calculations and DRIFTS analysis. DFT-calculated free-energy diagrams for (A) ORR at  $U = 0.40$  V versus RHE (CB bottom) and for (B) WOR at  $U = 1.96$  V versus RHE (VB top). Proposed reaction pathways for (C)  $2e^-$  ORR, and (D)  $4e^-$  WOR and (E)  $2e^-$  WOR (CAM-B3LYP/6-31+G(d,p) with GD3 dispersion correction). (F) Time-dependent changes in the DRIFTS spectra of poly23DHN measured with (top)  $O_2$  or (bottom) water (700 Pa) under photoirradiation ( $\lambda > 300$  nm) at 323 K.

reused for the photoreaction in water. As shown in Figure 4C (right), the powder generated  $H_2O_2$  in an amount comparable to that obtained using the fresh powder (left), indicating that the insolubilization of poly23DHN spontaneously regenerates its semiconducting properties. The poly23DHN dissolved in acetone was recrystallized by evaporation. The SEM, TEM, and size distributions of the recovered powder were similar to those of the fresh powder (Figures S2, S3, and S21). In addition, the hydroquinone/quinone ratio of the polymer remained unchanged (Figures S13 and S22). Furthermore, the ESR, XRD, UV-vis, and EIS data were unchanged (Figures S23–S26). Therefore, the insolubilization of poly23DHN reconfigures its semiconducting structure via spontaneous H-bonding and  $\pi$ -stacking (Figure 1B, a  $\rightarrow$  b), driving its heterogeneous photocatalysis behavior.

Notably, the poly23DHN powder could be reused for repeated photoreactions without a loss of activity (Figure S8). The recovered polymer showed morphology, composition, structure, and semiconducting properties identical to those of the fresh polymer (Figures S2, S3, S13, S21–S26). In addition,  $^1H$  NMR spectrum of the post-photoreaction solution showed no signal assigned to the decomposition products of polymer (Figure S27), indicating that the polymer is robust and stably promotes photocatalysis. The action spectrum for  $H_2O_2$  generation on poly23DHN (Figure 2C) revealed that the apparent quantum yield ( $\Phi_{AQY}$ ) at 420 nm was 4.8%. Figure S28 summarizes the  $\Phi_{AQY}@420$  nm values in the reported organic semiconductor photocatalysts for  $H_2O_2$  generation. The  $\Phi_{AQY}@420$  nm of poly23DHN is moderate among the reported values (0.1%–18%), although all

reported catalysts require harsh reaction conditions or expensive reagents for their synthesis. The poly23DHN can be synthesized using inexpensive reagents at room temperature and can stably generate  $\text{H}_2\text{O}_2$  without a decrease in activity; therefore, these properties may contribute to the development of cost-effective photocatalysts.

Another notable feature of poly23DHN is the ease of immobilization onto several substrates because many  $-\text{OH}$  groups have a high adhesive capability [24, 26, 27], and the insolubilization of polymer spontaneously reconfigures the semiconducting architecture via H-bonding and  $\pi$ -stacking. Therefore, as shown in Figure 4D, photocatalyst sheets can be easily prepared by placing a poly23DHN-dissolved solution onto substrates such as FTO glass and cotton cloth, followed by drying. These sheets, when immersed in water and photoirradiated under  $\text{O}_2$ , stably generated  $\text{H}_2\text{O}_2$  without peeling off the polymer fragments. The  $\text{H}_2\text{O}_2$  concentrations exceeded 100  $\mu\text{M}$ , which was enough to promote several oxidation reactions catalyzed by horseradish peroxidase [55]. Some photocatalyst sheets of organic semiconductor powders have been reported, in which they were immobilized by a vapor deposition of  $\text{g-C}_3\text{N}_4$  [56] or by a growth of COFs on a surface-treated substrate in the solvent for 3 days [57]. In contrast, poly23DHN can be immobilized using a simple drop-drying procedure. Therefore, the soluble, reconfigurable, and sticky properties of poly23DHN pave the way for the facile synthesis of active powdered photocatalysts for artificial photosynthesis.

### 3 | Conclusion

We have demonstrated that poly23DHN, synthesized via the polymerization of inexpensive DHN at room temperature, acts as a heterogeneous photocatalyst for  $\text{H}_2\text{O}_2$  generation in water with  $\text{O}_2$ . Poly23DHN is a 1,4-conjugated linear polymer composed of hydroquinone (D) and quinone (A) units. The polymer is soluble in polar organic solvents but insoluble in water. The insolubilization spontaneously induces H-bonding and  $\pi$ -stacking interactions between the D and A units, creating a D+A semiconducting architecture that facilitates carrier transport along both the chain and stacking directions. The polymer powder dispersed in water under  $\text{O}_2$  stably promoted WOR and ORR, producing  $\text{H}_2\text{O}_2$  under broad-wavelength light irradiation up to 700 nm. Furthermore, a simple drop-drying process enabled the facile immobilization of poly23DHN onto various substrates while maintaining high photocatalytic activity. These easy-to-synthesize, easy-to-handle, and easy-to-process linear polymers may contribute to the development of scalable, cost-effective semiconductors for artificial photosynthesis.

#### Author Contributions

**Koki Yoshida:** conceptualization, investigation, formal analysis, visualization, writing – original draft. **Yasuhiro Shiraishi:** conceptualization, methodology, validation, supervision, funding acquisition, visualization, project administration, writing – review and editing. **Satoshi Ichikawa:** data curation, formal analysis. **Shunsuke Tanaka:** data curation, formal analysis. **Takayuki Hirai:** supervision, project administration, writing – review and editing.

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#### Conflicts of Interest

The authors declare no conflicts of interest.

#### Data Availability Statement

All experimental data in this article and Supporting Information are available from the corresponding author upon request.

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### Supporting Information

Additional supporting information can be found online in the Supporting Information section.

**Supporting File:** anie72595-sup-0001-SupMat.pdf.