

RESEARCH ARTICLE

Unencapsulated Self-Hydroadaptive Organic Heterojunctions for Underwater Physiological Monitoring

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ABSTRACT

Water exposure is generally considered detrimental to organic semiconductor films, causing irreversible defects, dielectric perturbation, and device failure. Here, n-type giant-molecule-type organic semiconductors GSY-C4 and GSY-C10 with tailored alkyl chains were developed for waterproof organic photodetectors (OPDs). D18:GSY-C4 and D18:GSY-C10 bulk heterojunctions enabled stable underwater photoplethysmography sensing, with peak responsivities of ~ 1.31 and $\sim 0.7 \text{ A W}^{-1}$, respectively. Short-term water exposure did not cause obvious irreversible degradation, but induced water-triggered adaptive structural reorganization, supported by reduced lamellar d-spacing, increased lamellar coherence length, and preserved π - π stacking. After 4 h water immersion, unencapsulated D18:GSY-C4 arrays ($n = 49$) showed a $\sim 9\%$ reduction in dark-current density and nearly unchanged responsivity (R_λ) and specific detectivity (D^*). Moreover, key current parameters could be recovered through ethanol rinsing and mild annealing at 100°C for 20 min. D18:GSY-C10 OPDs maintained underwater functionality for 9 days with $<10\%$ variation in dark- and photocurrent densities, highlighting alkyl-chain engineering as an effective strategy for aqueous-stable organic optoelectronics.

1 | Introduction

Waterproof organic optoelectronic devices are critical for reliable biosensing in aqueous biological environments, such as on skin surfaces or within bodily fluids. These devices enable real-time optical signal capture for novel disease diagnosis and treatment monitoring [1–5]. Photoplethysmography (PPG) sensors based on organic photodetectors (OPDs), leveraging organic heterojunctions, are particularly promising for noninvasive physiological monitoring. They capitalize on the inherent advantages of organic semiconductors, including solution processability, flexibility,

thinness, and light weight [6–8], which are essential for seamless integration into wearable and implantable biosensing platforms [9–11]. Recent studies have further demonstrated the potential of organic and hybrid photodetectors in in-chip visual processing, pulse monitoring, responsivity-noise trade-off regulation, and multimodal spectral adaptation [12, 13].

However, water has a profound influence on the structure and carrier dynamics of conjugated organic semiconductors. Previous studies have suggested that water molecules generate deep-level trap states via the formation of irreversible “bound water”

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[14–16], trapping bulk carriers and degrading mobility. Consequently, early efforts mainly focused on eliminating “deep-layer water” to achieve trap-free charge transport [17–19]. However, recent studies have revealed that water penetration can preserve the mesoscale morphology and molecular orientation in polymers, inducing only localized disorder. The intrinsic structural elasticity efficiently buffers water-induced volume deformation to preserve charge-transport channels, enabling these polymers to outperform their rigid inorganic counterparts [20, 21].

This directs our attention to how the adsorption–desorption cycles of thermally removable, reversible water (<150°C) at interfaces in organic semiconductors regulate device performance [14]. Vertically stacked layers are the standard organic photodiode architecture for efficient charge transport and collection [22]. However, their multilayer structure presents inherent vulnerabilities at two critical sites: the interlayer interfaces and the donor–acceptor (D:A) heterointerfaces within the bulk heterojunctions (BHJs). Both interfaces exhibit high moisture sensitivity and structural instability [23]. Therefore, research strategies have mainly prioritized encapsulation-based protection for BHJ layers. Recent advances include in situ growth of hole-transport layers to stabilize top-interface contacts and confinement within viscoelastic polymer matrices for robust sealing, collectively promoting waterproof technology in organic photodiodes [24, 25].

However, the aqueous stability of the D:A interfaces has received little attention, yet these interfaces are critical sites for dark-current generation and carrier recombination [26–28]. Aqueous erosion creates irreversible D:A interfacial traps, while dielectric effects from water permeation through nano-voids lead to irreversible device failure [23]. Nevertheless, existing researches have neglected the intrinsic water resistance of organic photosensitive layers, and the fundamental mechanisms of water–BHJ interactions remain underexplored, particularly for encapsulation-free BHJs with intrinsic water tolerance. For OPDs, the device performance is governed not only by photocurrent, but also by dark-current density and specific detectivity (D^*) [21, 29]. Incorporating alkyl or nonconjugated segments into acceptor backbones can partially interrupt backbone conjugation and may limit photocurrent, but this strategy can also suppress dark-current density and improve OPD detectivity [30, 31].

Notably, giant-molecule-type organic semiconductors (GOSs), which are low-molecular-weight macromolecular acceptors constructed from non-fullerene acceptor segments and alkyl-chain linkers, possess precisely defined chemical structures and stable BHJ morphology, offering a promising platform for developing stable optoelectronic devices [32–35]. Leveraging this advantage, we developed alkyl-tailored n-type GOSs (GSY-C4/C10) and D18:GSY-C4/C10 BHJs that demonstrate water-stable, recoverable optoelectronic performance. Remarkably, transient water exposure (4 h) did not induce permanent degradation at the D:A interfaces. Instead, water triggers adaptive structural reorganization, characterized by reduced lamellar d-spacing, increased lamellar coherence length, and preserved π – π stacking, resulting in denser lamellar packing while maintaining the conjugated backbone framework. The unencapsulated OPDs maintained stable photodetection performance during 9 days of water submersion, demonstrating their capability for continuous biosignal monitoring under humid or aqueous conditions.

2 | Results and Discussion

To develop underwater-stable BHJs for waterproof OPDs (Figure 1a), a molecular design strategy based on alkyl chain engineering is proposed. N-type GOSs GSY-C4 and GSY-C10 featuring butyl (C4) and decyl (C10) alkyl chains (Figures S1–S6) were synthesized, respectively, and blended with the polymer donor D18 to form the BHJ active layer (Figure 1b). Alkyl-chain length is expected to regulate BHJ molecular packing and hydrophobic shielding, thereby promoting compact lamellar stacking (Figure 1c). This compact architecture is proposed to provide a structural basis for water resistance.

During water immersion, BHJ films undergo hydration: partial water molecules occupy grain boundaries while the remainder penetrates disordered intergranular zones. This process is proposed to induce moderate structural reorganization while preserving the polymer network integrity [14, 20]. In this design, alkyl-chain-regulated packing is expected to promote denser lamellar organization and help maintain charge-transport pathways during water exposure (Figure 1c). Meanwhile, water adsorption may cause a transient increase in dark-current density (J_{dark}) through reversible interfacial/dielectric perturbation. Crucially, the key current-density parameters (J_{dark} , J_{light}) are designed to be recoverable after targeted ethanol rinsing and mild thermal annealing at 100°C for 20 min, corresponding to reversible solvation/desolvation through removal of surface/interface-adsorbed water [14] (Figure 1d).

Organic photodetectors adopt vertical ITO/Ca₂Nb₃O₁₀ (CNO)/D18:GSY-C4(GSY-C10)/AgO_x/Ag architectures (Figure 2a), where the AgO_x hole-transport layer forms in situ via Ag electrode oxidation [24] (Figures S7–S9). The wide-bandgap CNO remains transparent under visible-light illumination and functions as an electron-transport layer [36, 37] (Figures S10 and S11), enable superior charge extraction through optimal band alignment (Figure S12). Alkyl-chain elongation in GSY elevates HOMO while lowering LUMO energy levels (Figure S13), inducing redshifted absorption and photoluminescence (Figures S14 and S15).

Devices exhibit efficient J_{dark} suppression under reverse bias in Figure 2b,c, with J_{dark} values of $\sim 8 \mu\text{A cm}^{-2}$ for D18:GSY-C4 and $\sim 2 \mu\text{A cm}^{-2}$ for D18:GSY-C10 at -1 V , together with stable photoresponse over 1200 s on–off cycles (Figure S16). Under 530 nm illumination with incident power densities ranging from 0.5 to 5.1 mW cm^{−2}, the photocurrent density increases with increasing light intensity, reaching $\sim 7.1 \text{ mA cm}^{-2}$ for D18:GSY-C4 and $\sim 1.1 \text{ mA cm}^{-2}$ for D18:GSY-C10 at -1 V . Time-resolved photoluminescence (TRPL) characterization further reveals that D18:GSY-C4 exhibits a longer slow lifetime component ($\tau_2 = 259.7 \text{ ns}$) than D18:GSY-C10 ($\tau_2 = 176.0 \text{ ns}$), suggesting more favorable long-lived excited-state/charge-transfer dynamics in D18:GSY-C4 (Figure S17). In addition, the external quantum efficiency (EQE) spectra indicate bias-enhanced photocarrier collection and internal gain behavior, with EQE values exceeding 100% (Figure S18). Photocurrent effectively modulates with light intensity and bias (Figure 2b,c), while efficient rectification in dark state enables stable reverse-bias

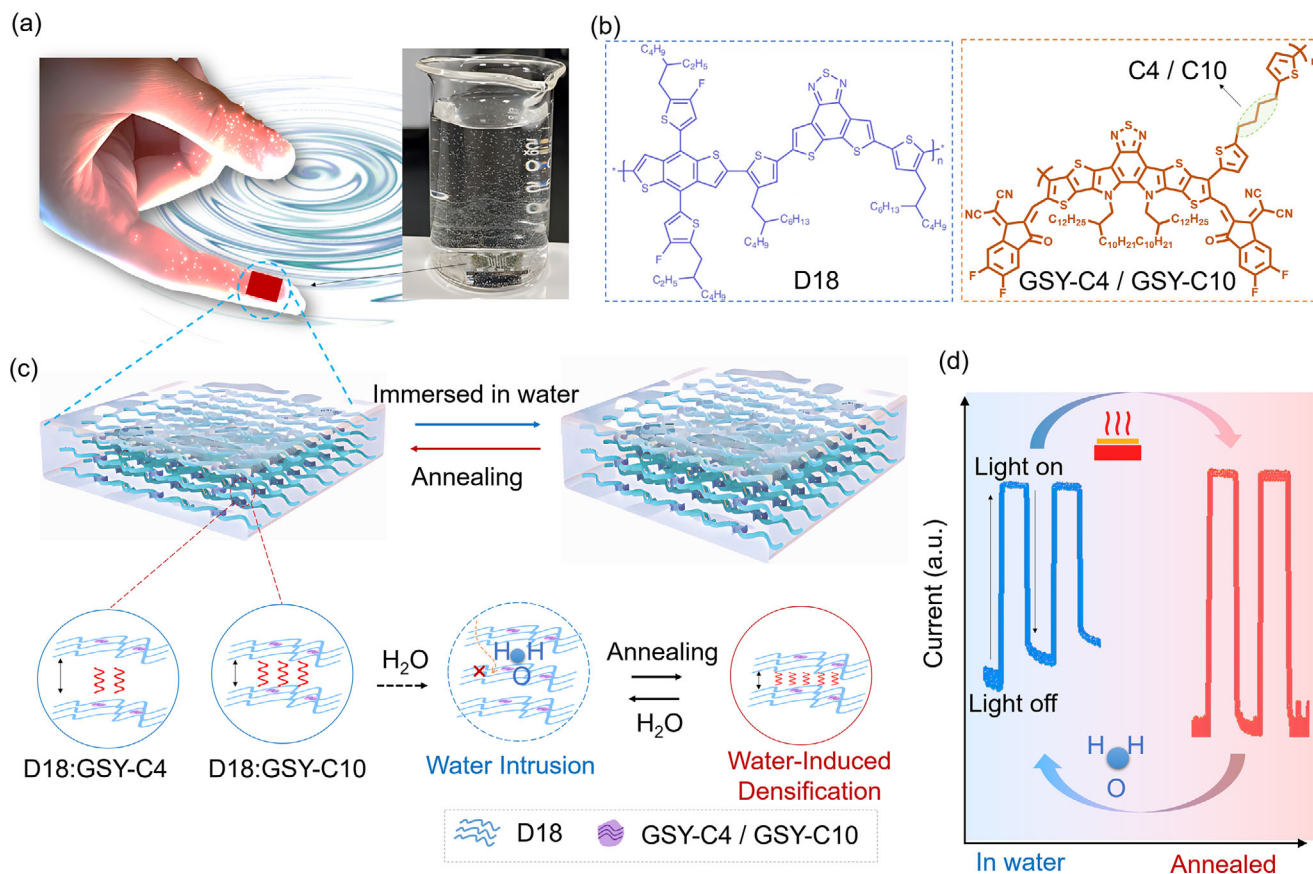


FIGURE 1 | Design strategy for underwater OPD. (a) Schematic of a waterproof OPD based on D18:GSY-C4/D18:GSY-C10 BHJ, with photographic illustration of the device immersed in deionized water. (b) Chemical structures of polymer D18 and giant-molecule-type acceptors GSY-C4 and GSY-C10 (carbon chain length = 4 and = 10 for GSY-C4 and GSY-C10, respectively, indicated by the light-green segment). (c) Schematic illustration of water-induced BHJ structural evolution and lamellar packing reorganization during repetitive water immersion/drying annealing cycles. (d) Current recovery under repeated water immersion-drying annealing cycles.

operation. The spectral responsivity (R_λ) was calculated according to [38]:

$$R_\lambda = \frac{J_{ph}}{P_\lambda} = \frac{J_{light} - J_{dark}}{P_\lambda} \quad (1)$$

where J_{ph} is the photocurrent density and P_λ is the incident light power density. The R_λ exhibits clear bias dependence, reaching a maximum value of 1.31 A W⁻¹ for D18:GSY-C4 (Figure 2d) and 0.70 A W⁻¹ for D18:GSY-C10 at -1 V near 600 nm (Figure 2e).

To further evaluate the weak-signal detection capability, the noise current spectral density (i_n) was measured (Figure 2f). The noise current spectral densities are $\sim 1.9 \times 10^{-13}$ A Hz^{-1/2} for D18:GSY-C4 and $\sim 5.3 \times 10^{-14}$ A Hz^{-1/2} for D18:GSY-C10 at 100 Hz. The D^* was calculated using [38]:

$$D^* = \frac{R_\lambda \sqrt{A}}{i_n} \quad (2)$$

where A is the effective device area of 300 μm × 300 μm. Owing to the reduced dark noise, D18:GSY-C10 exhibits a higher D^* of $\sim 4.2 \times 10^{11}$ Jones, compared with $\sim 2.0 \times 10^{11}$ Jones for D18:GSY-C4 (Figure 2g).

Further, the temporal response characteristics were measured under 532 nm illumination at -1 V. The D18:GSY-C4 device exhibits a rise time of ~ 538 μs and a fall time of ~ 0.9 μs (Figure 2h), while the D18:GSY-C10 device shows a rise time of ~ 661 μs and a fall time of ~ 2.1 μs (Figure 2i). Furthermore, to leverage organic flexibility, D18:GSY-C4 devices were fabricated on PET substrates, exhibiting a R_λ of 120 mA W⁻¹ at -1 V, and distinguishable on-off switching under intensity modulation from 0.1 to 2.2 mW cm⁻² (Figure S19).

To evaluate intrinsic water resistance, we compared unencapsulated D18:GSY-C4/C10 devices with the benchmark all-polymer system D18:PY-IT. Devices were fully immersed in deionized water while monitoring J_{light} and J_{dark} evolution versus time (Figure 3a-c and Figures S20-S22). Post-immersion J - V characterization confirmed enhanced waterproof stability in D18:GSY-C4/C10 relative to D18:PY-IT. D18:GSY-C10 demonstrated exceptional stability during 216 h (9 days) of water immersion, with minimal change in J_{light} and J_{dark} (Figure 3a,d). In contrast, D18:GSY-C4 remained functional for approximately 96 h (4 days) (Figure 3b,e), while the benchmark D18:PY-IT device failed within 4 h (Figure S22), which exhibited a 10-fold increase in J_{dark} . After 24 h, J_{dark} for D18:PY-IT surged by 100-fold (Figure 3c,f), stabilizing transiently before complete failure ($J_{dark} \approx J_{light}$). The underwater stability was quantified by

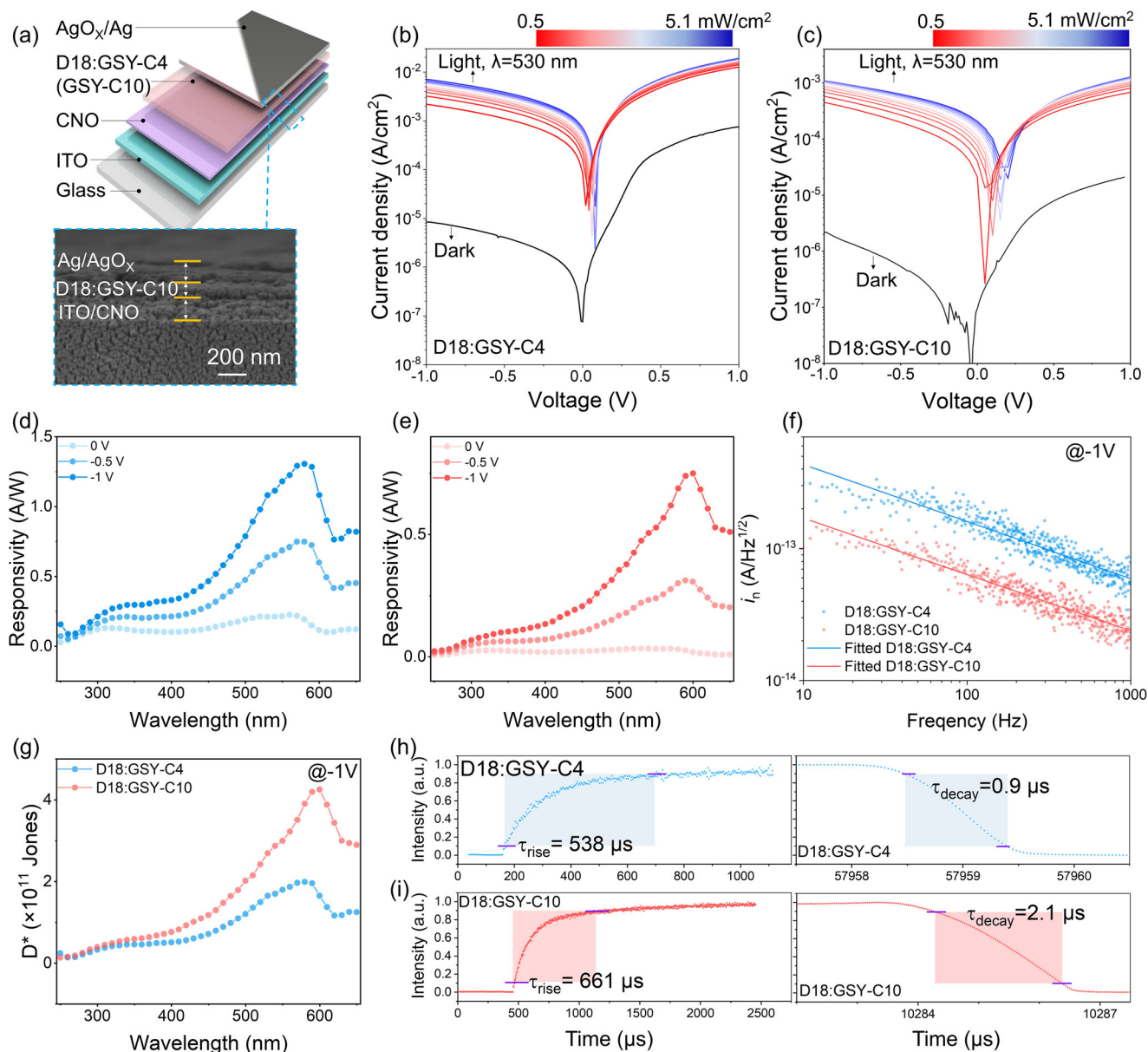


FIGURE 2 | Optoelectronic properties of waterproof OPDs based on D18:GSY-C4/C10 blend films. (a) Schematic device structure and cross-sectional SEM image of the OPDs based on D18:GSY-C4 or D18:GSY-C10. (b) Current density–voltage (J – V) curves of the D18:GSY-C4 OPD under dark and illuminated conditions. (c) J – V curves of the D18:GSY-C10 OPD under dark and illuminated conditions. (d) Spectral responsivity (R_λ) curves of the D18:GSY-C4 OPD under different operating biases. (e) R_λ curves of the D18:GSY-C10 OPD under different operating biases. (f) Noise current spectral density (i_n) of D18:GSY-C4 and D18:GSY-C10 OPDs under dark conditions. (g) D^* spectra of D18:GSY-C4 and D18:GSY-C10 OPDs. Temporal response characteristics of (h) D18:GSY-C4 and (i) D18:GSY-C10 OPDs under 532 nm illumination at -1 V.

light-to-dark current ratios ($J_{\text{light}}/J_{\text{dark}}$; Figure 3g). D18:PY-IT suffered a rapid 60-fold reduction within 24 h, collapsing to a 7000-fold decrease after 168 h (7 days). In contrast, D18:GSY-C4 showed a 267-fold decline at 168 h (7 days), while D18:GSY-C10 maintained essentially unchanged $I_{\text{light}}/I_{\text{dark}}$ ratios over 216 h (9 days).

This performance exceeds state-of-the-art waterproof optoelectronic devices (Figure 3h; Table S1). Conventional perovskite-based [39–41] and organic-based devices [24, 42] typically require protective interlayers or encapsulation yet achieve only 0.0017–100 h of water tolerance. Overcoming these limitations through intrinsic material design, our OPDs exhibit exceptional intrinsic

waterproofing without protective modifications: The D18:GSY-C4 device maintains underwater operation for 96 h (4 days). The D18:GSY-C10 device sets a record with 216 h (9 days) of continuous underwater operation, marking the longest stable performance reported for an underwater OPD.

Atomic force microscopy (AFM) revealed microstructural origins of these differences (Figure 3i,j; Figures S23 and S24; Table S2). After water immersion–drying cycles, D18:GSY-C4 and D18:GSY-C10 films showed reduced surface roughness (0.1–0.2 nm decrease) and increased phase angles (GSY-C4: 1.1° to 1.7°; GSY-C10: 0.93° to 1.5°). These irreversible changes suggest water-triggered molecular rearrangement and heterojunction

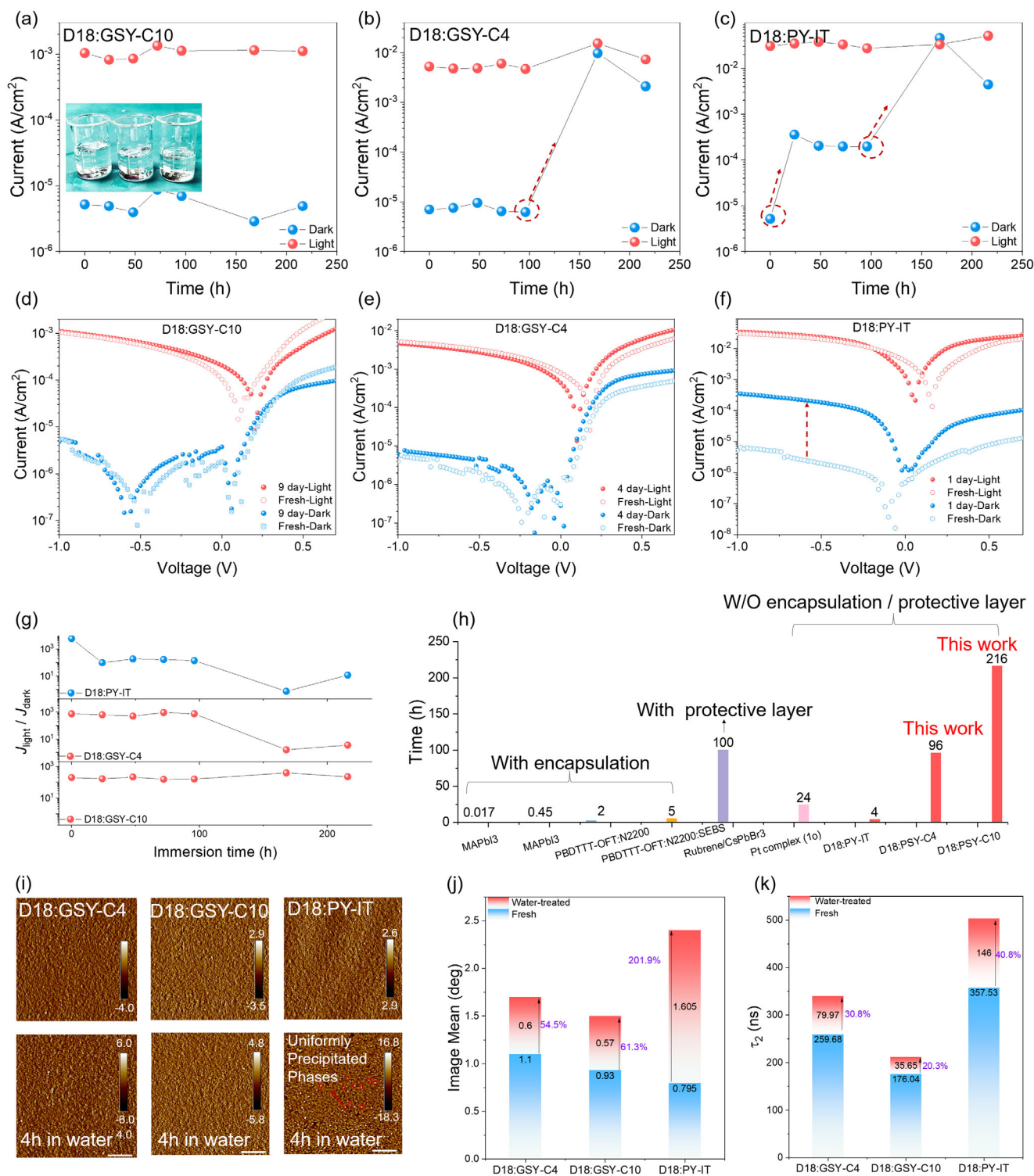


FIGURE 3 | Performance of OPDs immersed in water. (a–c) Evolution of J_{light} and J_{dark} during water immersion for devices based on (a) D18:GSY-C10 photoactive layer (inset: photographs of the corresponding devices immersed in deionized water), (b) D18:GSY-C4 photoactive layer, and (c) D18:PY-IT photoactive layer. (d–f) J - V characteristics under illuminated and dark conditions for (d) fresh D18:GSY-C10 devices and devices after 216 h (9 days) water immersion, (e) fresh D18:GSY-C4 devices and devices after 96 h (4 days) water immersion, and (f) fresh D18:PY-IT devices and devices after 24 h (1 day) water immersion. (g) Evolution of the $J_{\text{light}}/J_{\text{dark}}$ ratio with water-immersion time for the corresponding devices. (h) Comparison of water-immersion stability between this work and reported perovskite- and organic-semiconductor-based devices. (i) Atomic force microscopy (AFM) phase images of the films and (j) Average phase-angle variations of D18:GSY-C4, D18:GSY-C10, and D18:PY-IT photoactive-layer films before and after 4 h water immersion. (k) Fitted slow lifetime component (τ_2) extracted from time-resolved photoluminescence (TRPL) measurements before and after 4 h water immersion.

reconstruction, where surface smoothing likely arises from hydration-swelling and chain mobility during drying [14]. Conversely, D18:PY-IT underwent severe degradation: phase angles surged >200% (0.795° to 2.4°) alongside pervasive nanoparticle-like aggregation, indicating structural collapse. This microstructural failure deactivates devices by impeding exciton dissociation and creating current-leakage pathways at compromised donor-acceptor interfaces.

Time-resolved photoluminescence measurements further support this conclusion from the perspective of excited-state dynamics (Figure 3k; Figures S25 and S26). The fast lifetime component remains nearly unchanged after water treatment for all three blend films. However, the slow lifetime component increases most significantly for D18:PY-IT, from 357.53 to 503.53 ns (~40.8% increase), whereas the increases are smaller for D18:GSY-C4, from 259.68 to 339.65 ns (~30.8% increase), and D18:GSY-C10, from 176.04 to 211.69 ns (~20.3% increase). These results indicate that water exposure modifies long-lived recombination dynamics in all three systems, while the relatively smaller increases in D18:GSY-C4 and D18:GSY-C10 suggest reduced water-induced perturbation of excited-state processes compared with D18:PY-IT.

To investigate the alkyl-chain-related water tolerance and structural behavior, the surface wettability of the materials was evaluated. Both GSY-C4 (water contact angle: 95.5°) and GSY-C10 (100.0°) demonstrated significant hydrophobicity, exhibiting incrementally higher contact angles with longer alkyl chains (Figure S27). Critically, this hydrophobic character was preserved in hybrid heterojunction films, where D18:GSY-C4 and D18:GSY-C10 achieved enhanced contact angles of 104.5° and 105.2°, respectively. Grazing-incidence wide-angle x-ray scattering (GIWAXS) analyses (Figure 4a; Figure S28; Tables S3 and S4) revealed alkyl length-dependent crystallization modulation: Longer C10 chains compressed the lamellar d-spacing to 20.9 Å (vs. 21.3 Å for C4), consistent with tighter alkyl-chain packing. Conversely, the π - π stacking distance (~3.8 Å) remained chain-length invariant, demonstrating conjugated core-dominated molecular packing. However, the longer C10 chains slightly reduced long-range ordering, resulting in a shorter π - π stacking coherence length (CCL = 11.5 Å vs. 13.0 Å in the C4 blend).

After 4 h of water immersion, the π - π stacking distance remained almost unchanged (~3.8 Å), indicating that the conjugated backbone packing was largely preserved; however, clear changes in the lamellar d-spacing were observed. Both blends exhibited reduced lamellar d-spacings (21.3 Å to 20.4 Å for D18:GSY-C4; 20.9 Å to 20.4 Å for D18:GSY-C10) accompanied by increased lamellar coherence lengths (from 51.7 Å to 54.3 Å and 49.6 Å to 51.7 Å, respectively). These results suggest water exposure induces a moderate structural reorganization within the active layer, leading to denser lamellar packing while maintaining the π - π stacking framework [43]. Ultraviolet-visible spectroscopy (UV-vis) absorption analysis showed a redshift in the absorption peak (Figure S29), which is consistent with enhanced intermolecular exciton coupling, suggesting reduced lamellar d-spacing and improved structural ordering [44].

To evaluate water-induced trap-related transport, hole-only space-charge-limited current (SCLC) measurements were per-

formed before and after water treatment (Figure 4b and Figure S30). After water treatment, the apparent V_{TFL} of D18:GSY-C4 decreased from 0.122 to 0.084 V, while that of D18:GSY-C10 decreased from ~0.32 to ~0.20 V, indicating reduced effective trap densities. These results suggest that water exposure does not introduce severe trap-limited hole transport in D18:GSY-C4/C10. In contrast, water-treated D18:PY-IT exhibits no well-defined V_{TFL} , suggesting deteriorated trap-related transport behavior.

Cryogenic transmission electron microscopy (cryo-TEM) revealed a solution-phase preassembly behavior (Figure 4c,d): chain entanglement drives the formation of fibrous pre-aggregates and distinct lamellar structures (d-spacing: ~2 nm); such preassembled structures may contribute to the lamellar morphology observed in the solid-state film [45]. The π - π stacking distances were found to be ~0.34 nm in D18:GSY-C4 and D18:GSY-C10, determined from high-resolution TEM micrographs [46] (Figure 4e,f; Figure S31).

Mechanical characterization further supported the structural robustness of the blend films (Table S5). Both films possessed high Young's moduli (≥ 1.4 GPa) and strong interfacial adhesion forces (≥ 32 nN) (Figure 4g and Figure S32). Notably, D18:GSY-C10 showed improved mechanical properties compared with D18:GSY-C4, including a higher Young's modulus (1.6 vs. 1.4 GPa) and stronger adhesion force (42 vs. 32 nN), suggesting enhanced intermolecular cohesion induced by the longer alkyl chains. Pseudo-free-standing tensile testing during cyclic stretching-relaxation (10 cycles, ~8% strain amplitude) further showed that D18:GSY-C10 required significantly higher load (~30 vs. ~20 mN) to sustain equivalent deformation, validating its potential mechanical robustness under dynamic hydraulic stress (Figure S33). Consequently, D18:GSY-C10 displayed higher fracture strength and fracture strain (~73.3 MPa, 16.0%) compared to D18:GSY-C4 (~59.4 MPa, 12.8%) (Figure 4h).

A 7×7 device array of OPDs (D18:GSY-C4) was fabricated to assess device-to-device uniformity and short-term water stability during 4 h water immersion (Figure 5a). Optical microscopy revealed no physical degradation (e.g., corrosion/delamination) post-immersion (Figure 5b). Pre- and post-immersion I - V curves from all 49 devices showed negligible deviation (Figure 5c). Statistical analysis confirmed good array uniformity and reduced J_{dark} : 1.44 $\mu\text{A cm}^{-2}$ (pre-) versus 1.31 $\mu\text{A cm}^{-2}$ (post-), a ~9% reduction (Figure 5d). This decrease suggests water exposure induces denser D:A interfacial packing, suppressing leakage pathways. Minimal J_{light} loss was observed (131.0 vs. 126.0 $\mu\text{A cm}^{-2}$; <4%). Correspondingly, the normalized D^* remains nearly unchanged after 4 h water immersion, with a retention of ~101%, while the R_{λ} retains ~96% of its initial value. These results indicate that short-term water exposure does not significantly degrade the photodetection performance of the D18:GSY-C4 array.

Further validation of imaging fidelity was achieved by optically reconstructing a "human face" pattern. This confirmed the retention of spatial resolution and uniformity post-immersion, thereby demonstrating stable array-level photodetection performance (Figure 5e and Figure S34). To enable biomedical applications that require this stability, we integrated the array into a 3.9×3.9 mm² detection module (Figure 5f). This large-area format enabled microvascular signal capture at the fingertip. Under 660 nm LED

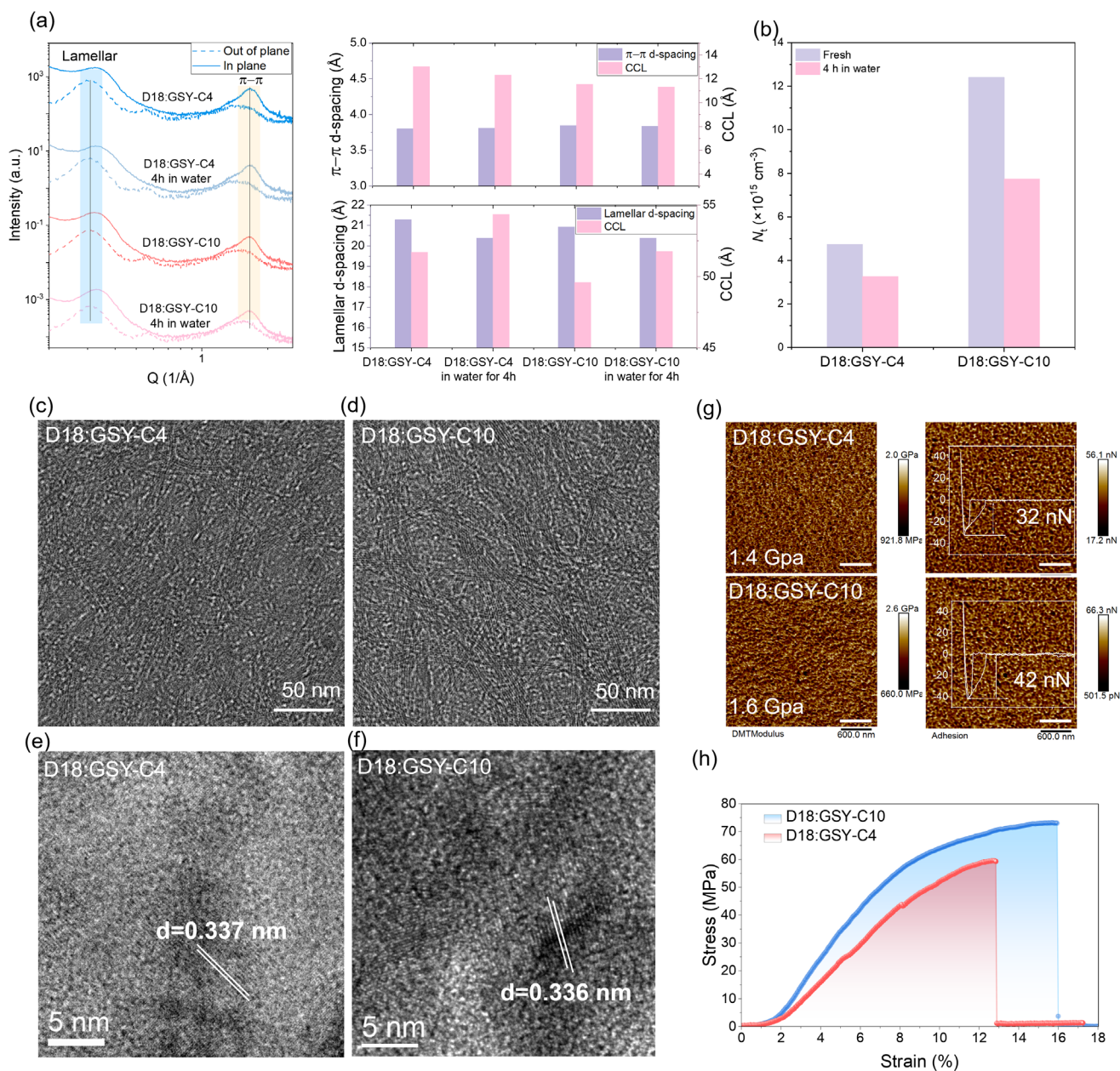


FIGURE 4 | Underwater stability and mechanical properties of D18:GSY-C4/C10 blends. (a Left) Linecut profiles for D18:GSY-C4/D18:GSY-C10 blends in the fresh state and after immersion in water for 4 h (blue rectangle indicates lamellar stacking area; yellow rectangle indicates π - π stacking area). (a Right) Corresponding d-spacing and correlation length (CCL) values. (b) Effective trap densities N_t extracted from hole-only space-charge-limited current (SCLC) measurements of D18:GSY-C4 and D18:GSY-C10 blend films before and after water treatment. (c, d) Cryogenic transmission electron microscopy (cryo-TEM) images of the D18:GSY-C4/D18:GSY-C10 precursor blend solutions. (e, f), High-resolution TEM images of D18:GSY-C4 and D18:GSY-C10 films, after inverse Fourier transform. (g) Young's modulus and adhesion force of D18:GSY-C4/D18:GSY-C10 blends conducted by AFM. (h) Representative stress-strain curves.

illumination of the fingernail, the OPD array detected scattered photons at the fingertip pulp, generating PPG waveform [47] (Figure 5g). Measurements from two volunteers (75 and 66 bpm) confirmed consistent arterial pulsatility and demonstrated the reliability of the module.

To evaluate performance under extreme humidity and full immersion, two scenarios were tested. During high-humidity vapor shock conditions (approximately 95% RH with direct steam exposure), the PPG sensor exhibited a stable signal output,

continuously recording an accurate 66 bpm heart rate (Figure 5h). For direct water immersion, an initial water droplet applied to the Ag/AgO_x electrode generated a transient signal spike within 0.2 s. This phenomenon is attributed to instantaneous electrical conduction through the water phase, prompting rapid signal recovery to baseline. Original waveform morphology was restored within 0.2 s, with subsequent outputs consistently registering 66 bpm. During a second droplet application on the fully immersed device, identical transient spike/recovery behavior induced by water conduction was observed, followed

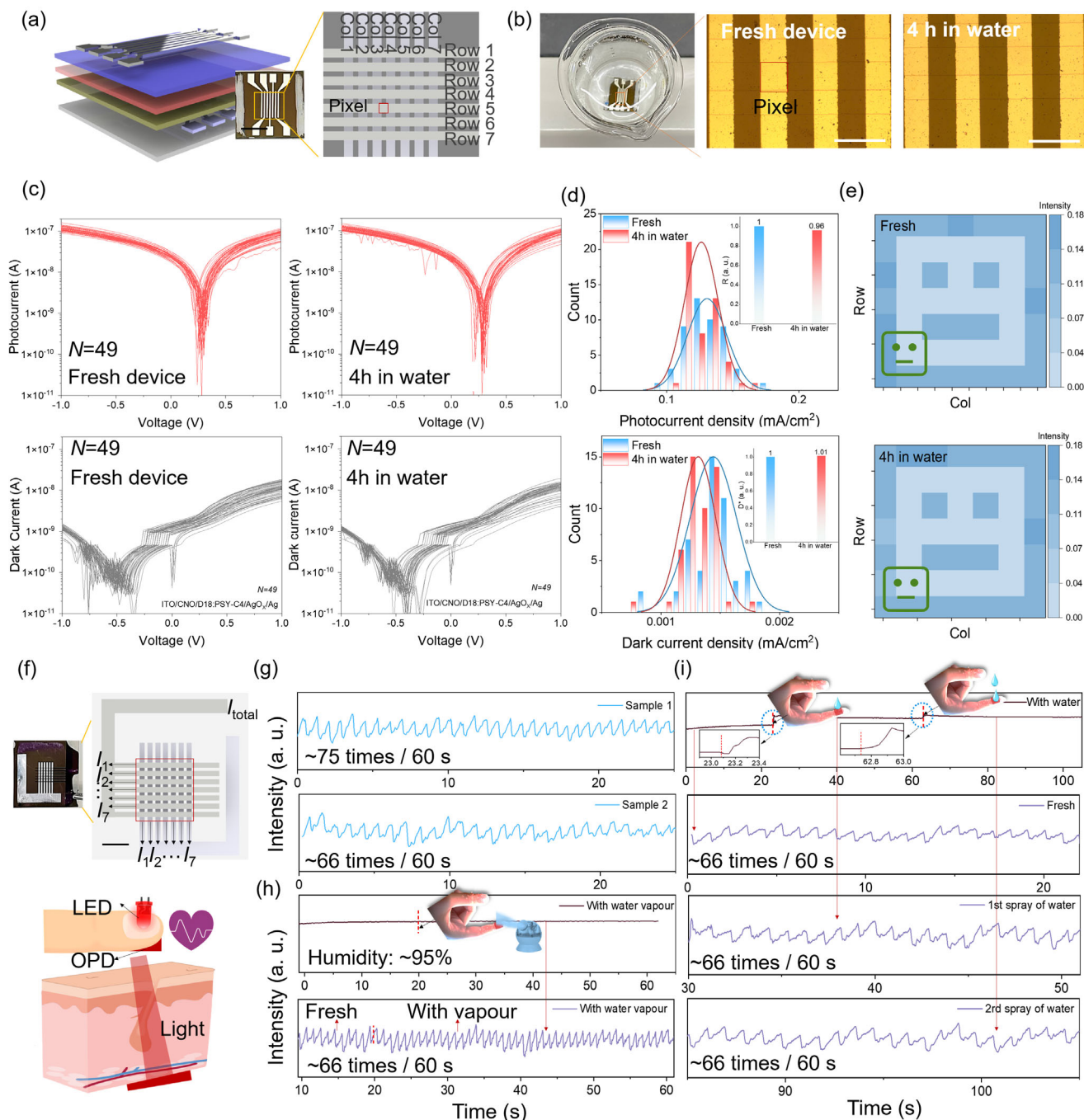


FIGURE 5 | Waterproof PPG OPD based on D18:GSY-C4 for continuous bio-signal monitoring. (a) Schematic diagrams of the waterproof 7×7 OPD array structure (left), photograph of an array (middle), and top-view schematic illustrating pixel arrangement (right), scale bar: 5 mm. (b) Physical device diagram showing the array immersed in water (left), optical microscopy images of the devices in the fresh state (middle) and after immersing in water for 4 h (right). (c) I_{dark} and I_{light} as a function of voltage, measured across all 49 pixels of a fresh OPD array and after being soaked in water for 4 h. (d) Statistical distributions of I_{dark} density and I_{light} density for all 49 pixels in a fresh OPD array and soaked in water for 4 h, Inset: normalized R_{λ} and D^* before and after 4 h water treatment. (e) I_{light} mapping images acquired from a fresh OPD array and soaked in water for 4 h. (f) Serially-connected OPD array; PPG operating principle (schematic, bottom). (g) PPG waveforms obtained from two volunteers using a fresh OPD array. (h) PPG waveforms acquired from a volunteer under high-humidity conditions ($\sim 95\%$ RH). (i) PPG waveform recorded from the OPD array during surface water droplet application inducing complete immersion.

by stable 66 bpm outputs (Figure 5i). These results demonstrate robust operational stability under vapor-phase humidity stress and direct liquid immersion, confirming the OPD's suitability for demanding biomedical environments.

3 | Conclusions

In summary, GOSs GSY-C4 and GSY-C10 with tailored alkyl chains were designed and synthesized, enabling unencapsulated

OPDs with water-stable and recoverable optoelectronic performance for underwater PPG sensing. Short-term water exposure induces moderate structural reorganization within the BHJ active layers, as supported by reduced lamellar d-spacing and increased lamellar coherence length, while the π - π stacking framework is largely preserved. TRPL and SCLC analyses reveal that water exposure induces weaker perturbation of excited-state dynamics and trap-related charge transport in D18:GSY-C4/C10 compared with D18:PY-IT. Consequently, D18:GSY-C10 OPDs maintained stable photoresponse during 9 days of water submersion, and the D18:GSY-C4 array retained nearly unchanged R_L and D^* after short-term immersion. This work provides an alkyl-chain engineering strategy for regulating water-induced structural evolution and enhancing aqueous stability in organic heterojunction photodetectors, offering a promising route toward wearable and biomedical optoelectronic sensors under humid or aqueous conditions.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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