Effects of Side Chain Length and Functionality on Polar Poly(Dioxythiophene)s for Saline-Based Organic Electrochemical Transistors

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Increased solubility, $E_{ox (onset)}$, stability, μC^* , and faster (de)doping kinetics in OECTs

Abstract

Understanding the impact of side chains on the aqueous redox properties of conjugated polymers is crucial to unlocking their potential in bioelectrochemical devices, such as organic electrochemical transistors (OECTs). Here, we report a series of polar propylenedioxythiophenebased copolymers functionalized with glyme side chains of varying length as well as an analogue with short hydroxyl side chains. We show that long polar side chains are not required for achieving high volumetric capacitance (C*), as short hydroxy substituents can afford facile doping and high C* in saline-based electrolytes. Furthermore, we demonstrate that varying the length of the polar glyme chains lead to subtle changes in material properties. Increasing the length of glyme side chain is generally associated with an enhancement in OECT performance, doping kinetics, and stability, with the polymer bearing longest side chains exhibiting the highest performance $([\mu C^*]_{OECT} = 200 \pm 8 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1})$. The origin of this performance enhancement is investigated in different device configurations using in-situ techniques (e.g., time-resolved spectroelectrochemistry and chronoamperometry). These studies suggest the performance improvement is not due to significant changes in C* but rather due to variations in the inferred mobility. Through a thorough comparison of two different architectures, we demonstrate that device geometry can obfuscate the benchmarking of OECT active channel materials, likely due to contact resistance effects. By complementing all electrochemical and spectroscopic experiments with *in-situ* measurements performed within a planar OECT device configuration, this work seeks unambiguously assign material design principles to fine tune properties of to poly(dioxythiophene)s relevant for application in OECTs.

Introduction

The electrochemical functionality of π -conjugated polymers has been leveraged to develop devices with a broad range of applications, including optical displays,^{1,2} energy storage devices,^{3,4} neuromorphic computing elements,^{5,6} and bio-electronic interfaces.^{7,8} In recent years, the field of organic bioelectronics has undergone significant advancements, as it has become increasingly apparent that π -conjugated polymers offer highly desirable properties for interfacing with living systems mechanical conformability, low-voltage operation, facile chemical modification, and compatibility with biological media. This has led to a renewed interest in developing active

materials for bioelectrochemical devices, such as organic electronic ion pumps,⁹ neural probes,^{10,11} artificial muscles,^{12,13} and organic electrochemical transistors (OECTs).¹⁴ In particular, OECTs have garnered significant attention due to their ability to transduce cellular ion fluxes (*e.g.*, protons, metal cations, and neurotransmitters) into exogeneous electrical signals with extremely high signal fidelity.^{14,15}

In general, the operation of these devices relies on the simultaneous transport of ions and electrons during electrochemical doping of the active polymer. Upon device biasing, Faradaic electron transfer between the conjugated polymer active layer and the underlying electrode introduces electronic charge carriers into the backbone π -system. These charge carriers are stabilized by concomitant counterion transport through the polymer-electrolyte interface and into the bulk of the active layer. For many electrochemical devices, specific electrolyte formulations are chosen based on application targets and constraints, such as the electrolyte conductivity, environmental stability, and the width of the electrochemical window of the electrolyte. These constraints are especially relevant in biological applications, such as OECTs, where the conjugated polymer active layer typically will interface electrochemically with aqueous media. This requires the rapid and reversible transport of hydrated ions from a saline electrolyte, at physiological temperature and pH, into the bulk of the polymer film.

Considering the fundamental aqueous electrolyte limitation in these bioelectrochemical applications, the design of the active material requires unique considerations. For p-type systems, the polymer backbone must be sufficiently electron rich to allow for oxidative doping within the relatively narrow electrochemical window of water. For solution-processed materials, solubilizing side chains generally must be sufficiently hydrophilic to promote the uptake and transport of aqueous ions within the film.¹⁶ Here, a careful hydrophobic-hydrophilic balance is required to promote aqueous electrolyte compatibility, as the incorporation of polar and hydrophilic functionalities (*e.g.*, ionic groups or exceedingly long ethylene oxide chains) may increase the propensity of film delamination and introduce instabilities during electrochemical doping.^{17,18} Long side chains also decrease the relative electroactive fraction of the total film volume. This may reduce the volumetric capacitance (C^*) and impede electronic carrier mobility (μ), which are thought to be critical for OECT performance.¹⁹ Therefore, the optimal balance between side chain length, polymer polarity, and electroactive mass fraction needs to be achieved.

Most commonly, polar glyme (G) side chains (also referred to as glycol, ethylene oxide, or oligoether chains) have been introduced to improve aqueous compatibility of conjugated polymers. Since the first demonstration of this approach in the early 1990s,²⁰ similar strategies have been adapted to develop a wide range of conjugated polymers for aqueous-based OECTs.²¹⁻²³ These glyme side chains are thought to facilitate electrolyte uptake, improve charge carrier stabilization, and enhance charge storage and transport in aqueous media. While other polar moieties, such as amides,²⁴ esters,²⁵ sulfonates,^{26,27} alcohols,²⁸ and carboxylic acids²⁹ have been incorporated into side chains to improve the aqueous redox activity of solution-processed conjugated polymer, materials with glyme side chains remain among the most prevalent, versatile, and highest performing aqueous OECT active materials tested to date.^{16,30-33}

In this context, glyme side chains have been appended to many different \Box -conjugated polymer backbones, most commonly polythiophene motifs. Several studies have evaluated the effect of the length and substitution pattern of glyme side chains on the electrochemical properties, solid-state microstructure, and associated OECT performance of polar polythiophenes.^{30,34-37} Among thiophene-derived materials, poly(3,4-propylenedioxythiophene)s or poly(ProDOT)s, are an alternative class of p-type materials for OECTs. Recently, we reported a poly(ProDOT) functionalized with glyme side chains that exhibited exceptional electrochemical properties (*e.g.*, fast doping kinetics, high capacitance, and redox stability) in aqueous media as well as high OECT device performance.³⁸ However, when compared to other polythiophene derivatives, the impact of polar side chain structure in these aqueous-compatible poly(ProDOT)s remains relatively unexplored.

This work presents a family of aqueous compatible ProDOT-based copolymers with polar side chains of varied length to establish design principles for p-type OECT active materials. This family is based on a previously studied polymer, G3-DMP (reported as ProDOT(OE)-DMP) in prior work),³⁸ which consists of a glyme-functionalized ProDOT comonomer and a second comonomer, herein referred to as DMP, with small dimethyl substituents. By varying the length of the glyme chains on the polar comonomer, we yield a series of materials (G*x*-DMP, *x* = 2, 3, 4, **Figure 1**b) in which the side chain is progressively lengthened from two to four ethylene oxide units. Additionally, this work investigates a hydroxy functionalized OH-DMP polymer, in which the polar comonomer is functionalized with two short alcohol groups rather than glyme side chains. This hydroxy functionality was accessed through a previously reported hydrolysis process of a

ProDOT polymer prepared with 2-butyloctyl ester side chains (BOE-DMP).^{39,40} These materials allow for an investigation into the effect side chain length and functionality on the fundamental redox properties, including the oxidation onset and volumetric capacitance, in a biologically relevant sodium chloride electrolyte. We also present the *in situ* optical response of the materials, both when directly adsorbed to an electrode and when incorporated as an OECT device channel, in order to gain insight into the potential- and time-dependent evolution of charge carriers in the active films. Lastly, integration of the glyme-based materials into both planar and interdigitated OECTs allows for the characterization of device performance, kinetics, stability, and the assessment of geometry-dependent effects.



Figure 1. Structure of ProDOT-DMP copolymers studied in this work. a) Repeat unit structure of the ProDOT-DMP backbone. b) Polar side chains appended to the backbone, including oligo(ethylene) glyme-derived side chains: G2- (diglyme, green), G3- (triglyme, purple), G4- (tetraglyme, orange), as well as BOE- (2-butyoctylester, black), and OH-DMP (hydroxy, blue).

Experimental Section

Materials and Methods

The detailed synthesis and characterization of polymers and molecular precursors (including NMR, GPC, and elemental analyses) as well as processing methods are outlined in section **1** of the SI (**Figures S1-S8**). The side chain cleavage process of BOE-DMP toward OH-DMP consisted of a thin film hydrolysis process outlined in section **2.4** of the SI. Briefly, films of BOE-DMP were cast from chloroform solution onto glassy carbon and ITO electrode substrates, *vide infra*. The film was then heated in 2 M KOH in methanol (55 °C) for 4 hours (**Figure S10**)

then gently rinsed with methanol and deionized water and allowed to dry at room temperature in the dark.

Polymer Characterization

Aqueous cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (**Figures 2a**, **S9, and S11** were performed using a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software. For CV and DPV, polymer samples were prepared by drop casting on a polished glassy carbon disk electrode (mass = $16 \mu g$, area = 0.07 cm^2), as described in section **2.3** of the SI. Both CV and DPV were performed under an argon blanket in degassed 0.1 M NaCl (biotechnology grade, Amresco) in ultrapure water (18.2 M Ω cm). A glassy carbon rod was used as the counter electrode, and a Ag/AgCl electrode (3 M NaCl/H₂O inner solution, BASi) was used as the reference electrode. CV was performed by scanning across the indicated voltage range at scan rates ranging from 2–2000 mV s⁻¹ (**Figure S12**). Note that drop casting was performed carefully to ensure that no part of the polymer film overlapped with the edge of the insulating electrode body, as this was found to drastically influence the recorded peak shape, current density, and overall apparent charge passed in the voltammogram (**Figure S9**).

For potential-dependent UV-Vis-NIR spectroelectrochemical measurements, polymer films were coated onto ITO/glass electrodes (7 mm x 50 mm x 0.7 mm, sheet resistance 8-12 Ω sq⁻¹, Delta Technologies Ltd) from chloroform. G2-DMP polymer was spray-coated from chloroform due to solubility limitations,⁴¹ while all other materials were all blade-coated onto the ITO electrodes (see section **2** of the SI for details). The voltage-dependent UV-Vis-NIR absorbance spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer in conjunction with a Princeton Applied Research 273A potentiostat/galvanostat (CorrWare software). The polymer-coated ITO electrodes were immersed in a quartz cuvette and incorporated into a three-electrode cell. The polymer-coated ITO served as the working electrode, a Pt flag served as the counter electrode, and a Ag/AgCl (3 M NaCl/H₂O inner solution, BASi) was used as the reference. The electrolyte was a degassed 0.1 M NaCl aqueous solution (ultrapure water, 18.2 MΩ cm). Before recording the voltage-dependent spectra, the polymer films were subjected to 10 cyclic voltammograms (-0.5 V to +0.8 V vs. Ag/AgCl at 50 mV s⁻¹) to electrochemically condition the films. Steady-state spectra were recorded at applied DC voltages from -0.3 V to +0.8 V vs.

Ag/AgCl per steps of 0.1 V, after holding the film at each voltage for ~30 seconds dwell time until the transient current reached a steady state.

Electrochemical impedance spectroscopy (EIS) was performed on a Reference 3000 Gamry potentiostat/galvanostat/ZRA utilizing the Gamry Framework 6.5 software. Films of G3-, G4-, and BOE-DMP polymers were obtained by blade coating on clean ITO/glass slides as described above, while G2-DMP was spray cast from a dilute chloroform solution (4 mg/mL). OH-DMP films were accessed from the blade-coated BOE-DMP samples, processed by the hydrolysis procedure described above. Irregular portions of the film were removed by wiping with a cotton swap, yielding rectangular films for analysis. The polymer-coated ITO was configured as a working electrode into a three-electrode cell. In this case, a stainless-steel plate was used as the counter electrode and a Ag/AgCl electrode (described above) as reference. The cell was filled with a 0.1 M NaCl aqueous electrolyte (ultrapure water) degassed with argon. The cell was kept under an argon blanket throughout the entire measurement. The working and counter electrodes were positioned 1 cm apart, with the polymer-coated side of the ITO electrode directly facing the stainless-steel plate, as shown in Figure S13a. Prior to performing EIS studies, the films were electrochemically conditioned via 10 CV scans from -0.8 V to +0.8 V vs. Ag/AgCl at 50 mV s⁻¹. For EIS measurements, a 5 mV AC bias was superimposed on a range of DC biases to set the oxidation state/doping level of the polymer. Films were held at a given voltage for 60 seconds before the EIS measurement to ensure steady-state behavior. The measurement was performed starting with the film in its most dedoped state (-0.3 or -0.4 V), and then performed iteratively by increasing the DC offset by 0.1 V steps. EIS was performed at low frequencies (10 Hz–0.1 Hz) to capture the capacitance associated with the faradaic doping/dedoping reactions. Representation of raw Nyquist and Bode plots are shown for each material in SI Figures S15-S16). The experimental impedance spectra were fitted using the Zview software (Scribner Associates Inc., USA). The lowfrequency region of the EIS spectrum was fit with an $R-Q_0$ series circuit, where R represents the charge transfer resistance and Q_o represents a constant phase element that captures the pseudocapacitive behavior of the polymer film (more details in section 3.2 of the SI). Once the EIS measurement was completed, the films were dedoped by holding at -0.8 V vs. Ag/AgCl for 30 s. Next, the films were rinsed with copious amounts of DI water and dried at room temperature. No salt deposits were observed on the dry films. To calculate the volume of the film, the thicknesses of the dry, dedoped films were measured using a Bruker Dektak XT profilometer,

while the film length and width were calculated using manual calipers after the EIS measurement. Film length, width, and thickness ranged from 1.50-1.88 cm, 0.32-0.69 cm, 85-259 nm, respectively. The calculated capacitance *C* was normalized to film volume to give the volumetric capacitance *C**. At least three separate films were studied for each polymer to ensure reproducibility of the impedance characteristics and *C** value.

For OH-DMP and BOE-DMP, comparative characterizations of these two materials showing the effect of the hydrolysis process may be found in **Figures S11**, **S14**, **S16**, **S17**, **S21**, and **S24**.

OECT Device Testing

For planar OECTs (pOECTs), all polymers were processed by spin coating from chloroform solutions onto patterned Cr/Au contacts. The channel dimensions (Wd/L) of the pOECT devices ranged from 40 to 940 nm. The OECT device characteristics were measured using a Ag/AgCl pellet gate electrode in 0.1 M aqueous NaCl electrolyte using a data acquisition system (USB-6211 from National Instrument Corp.) and a Keithley 2400 SMU (Tektronix). Extensive details about sample preparation and pOECT device characterization are described in section 6 of the SI. For the interdigitated OECTs (iOECTs), films were cast from polymer solutions onto interdigitated Pt electrodes obtained from MicruX Technologies (electrode model ED-IDE1-Pt with 90 pairs of interdigitated electrode arms, ~90 unique channels, channel length = $10 \mu m$, average channel width = 0.27 cm, overall total nWL⁻¹ \approx 24,700). All polymers were blade-coated from chloroform solutions, except for G2-DMP, which was spray cast. iOECT devices were characterized in 1x PBS (pH=7.4, Sigma Aldrich) using a Ag/AgCl wire as the gate electrode. A buffered electrolyte was used to prevent long-term pH changes when testing redox stability over 1,000 ON/OFF cycles. Devices were measured using Agilent 16422a test fixture, which was controlled by an Agilent E5263A 2 Channel IV Analyzer equipped with two source measure units (Agilent E5291A and E590A), along with Keysight software. Additional details about iOECT sample preparation, processing, and analysis are described in section 7 of the SI.

Results and Discussion

Polymer Design and Preparation

A family of five electron-rich alternating copolymers with a common 3,4propylenedioxythiophene (ProDOT) backbone motif (**Figure 1**a) was designed and synthesized. For all materials, one ProDOT comonomer is symmetrically di-substituted at the 2-position of the propylene bridge with side chains of various lengths and polarities, including the glymes and hydroxy groups (**Figure 1**b). Meanwhile, the alternating comonomer, 3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (herein referred to as DMP), is symmetrically disubstituted with two relatively small methyl groups. This minimally substituted DMP unit has previously been incorporated into the backbones of materials for various electrochemical applications because it is associated with high charge storage capacity, low oxidation onsets (E_{ox}), and redox stability.^{38,40,42} Here, the DMP unit also controls the solubility of the final polar material. Homopolymers and materials rich in glyme-functionalized ProDOTs tend to delaminate, disperse, or even dissolve in common electrolytes and solvents upon p-doping.^{17,18,43,44} Therefore, the incorporation of the DMP unit lowers the solubility of the final polymer, allowing for a balance of polarity and solubility to be achieved.

An in-depth account of the synthetic techniques used to prepare these materials can be found in section **1** of the SI. In short, typical transetherification, Williamson etherification, and bromination methods were used to prepare ProDOT comonomers, followed by direct (hetero)arylation polymerization (DHAP) to synthesize the final polymers. The chemical structure, molecular weight, and purity of all synthesized products and intermediates are confirmed by NMR, GPC, and elemental analyses (**Figures S1-S8**). The number average molecular weights (M_n) and dispersity (D) of the polymers ranged from 13-66 kg mol⁻¹ and 1.6-2.5, respectively. As indicated in **Table 1**, the M_n scaled with side chain length, where the monomer with the longest side glyme chains, G4-DMP, produced the polymer with the largest M_n (66 kg mol⁻¹) and vice-versa. While an estimation, these M_n values determined by GPC indicate an approximate average degree of polymerization (X_n) of 22, 33, and 85 for G2-, G3-, and G4-DMP, respectively. The trend between side chain length and polymer molecular weight is rationalized by (i) the increase in hydrodynamic radius (i.e. more conformational freedom of side chains), (ii) the greater molecular weight of the repeat unit, and (iii) the increased solubility of the polymers with larger side chains in the polymerization medium, which allows for longer reaction times and thereby higher M_n . Correspondingly, the materials with glyme side chains demonstrate varying degrees of solubility in chloroform (approximately 5 mg/mL for the 13 kg/mol batch of G2-DMP, 30 mg/mL for G3-DMP, and \geq 40 mg/mL for G4-DMP).

As explained earlier, the polar side chains appended to the poly(ProDOT) backbone were chosen to explore a range of length and functionality used to support mixed ionic/electronic conduction in aqueous media. The G2-, G3-, and G4-DMP polymers are functionalized with polar glyme-based side chains consisting of two, three, and four ethylene oxide units, respectively, whereas OH-DMP is functionalized with two hydroxy groups. OH-DMP was prepared from an ester-functionalized soluble precursor polymer, BOE-DMP. The branched aliphatic ester groups appended to BOE confer solution processability while also allowing for further postpolymerization modification. BOE-DMP was processed from solution into thin films, followed by treatment with KOH/methanol to hydrolyze the esters and leave short hydroxy groups appended to the polymer backbone, as described in section **2.4** of the SI. This side chain hydrolysis process, which was adapted according to previous literature^{39,40} allows us to prepare a polymer with short polar side chains (OH-DMP) that would otherwise not be solution processable if it were polymerized outright from the corresponding repeat unit comonomers. As shown by the FTIR spectra (Figure S24), the hydrolysis converted most of the ester groups into alcohol functionalities, which is evidenced by the substantial loss in the intensity of the carbonyl stretch at ~ 1720 cm⁻¹. Accordingly, we expand the library of polar-functionalized ProDOT polymers from only glyme materials (Gx-DMP) and may evaluate subtle effects of side chain functionality and size.

Typically, long polar side chains are utilized to enhance ion transport and promote doping of solution-processed polymers in aqueous media.^{45,46} By studying OH-DMP, we can evaluate whether short polar side chains induce the same properties as long glyme side chains and whether they confer any unique advantage to OECT material design. In OH-DMP, the hydroxy groups are conjoined to the ProDOT repeat unit through a small methylene linkage. Consequently, OH-DMP has a lower side chain density relative to G2-DMP, G3-DMP, and G4-DMP, which may enhance interchain interactions that are necessary for efficient electronic transport. By minimizing the side chain density in OH-DMP, we also expect to increase the electroactive mass of the film (*i.e.*, the mass percentage of the conjugated backbone relative to the whole polymer). Therefore, we predict a higher C^* for OH-DMP relative to all glyme-functionalized polymers (Gx-DMP), which have

with longer side chains and thus lower electroactive masses. Finally, because hydroxy groups in OH-DMP act as hydrogen bond donors, they may induce unique polymer-electrolyte interactions in aqueous media that are not observed for the other side chains.

Aqueous Electrochemical Characterization

For many bioelectrochemical devices, such as OECTs, the ability of the polymeric active layer to undergo electrochemical doping in biological media is paramount. Therefore, the electrochemical properties of each polymer were studied by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) in a degassed 0.1 M NaCl/H₂O electrolyte. The onsets of oxidation ($E_{ox(onset)}$) were extracted from the DPV traces, whereas the peak volumetric capacitance (C^*) was determined by EIS (**Table 1**). Details regarding sample preparation and electrochemical analysis are clarified in the *Experimental Section* and the SI.

First, we note that OH-DMP shows a drastically lower $E_{ox(onset)}$ and an enhanced *C** when compared to its precursor polymer, BOE-DMP (106 ± 7 F cm⁻³ for OH-DMP vs. ~40 F cm⁻¹ for BOE-DMP) (**Figure S14**). The long aliphatic side chains in BOE-DMP encumber reversible transport of aqueous ions and prevent reproducible doping (see section **3** of the SI for more details). By converting these side chains to short polar hydroxy groups, the post-polymerization hydrolysis effectively transforms an otherwise redox inactive material into a material that is highly dopable, yet still insoluble, in aqueous media.

Polymer	M _n (kg/mol) ^a	Đ	$E_{ox(onset)} (V)^b$	C*EIS (F cm ⁻³) ^c
OH-DMP	-	-	-0.39	106 ± 7
G2-DMP	13	1.6	-0.30	86 ± 5
G3-DMP	23	2.0	-0.23	81 ± 6
G4-DMP	66	2.5	-0.18	91 ± 8

Table 1. Number average molecular weight (M_n), dispersity (D), and redox properties of polar ProDOT copolymers in 0.1 M NaCl/H₂O.

^{*a*} M_n was determined by GPC (CHCl₃, 40 °C) vs. PS standards. No molecular weight information is provided for OH-DMP, as it could not be analyzed by GPC due to its insolubility, though we assume the approximate X_n is equal to that of the BOE-DMP precursor ($M_n = 63$ kg/mol, D = 2.3, and inferred $X_n = 83$). ^{*b*} Onsets of oxidation (E_{ox(onset)}) were extracted from DPV measurements, with voltages reported vs. the Ag/AgCl reference electrode (3 M NaCl/H₂O). ^{*c*} Average voltagedependent volumetric capacitance (*C**) for films measured by EIS in a degassed 0.1 M NaCl/H₂O electrolyte. The capacitances were normalized to the volume of the dedoped film, dried overnight in ambient conditions after biasing. Standard deviations are reported from *C** measurements performed on 3+ different films, which were cast and measured separately.

By evaluating the redox properties of the polar ProDOT copolymers (OH-DMP and Gx-DMP), we gain insight into how side chain length and functionality impact the resulting electrochemical properties. First, all polymers are sufficiently electron rich and hydrophilic for electrochemical doping in aqueous media, as evidenced by their low $E_{ox(onset)}$ (**Figure 2**a) and broad current response over the voltage range tested. The cyclic voltammograms also show multiple anodic waves (**Figure 2**a), which suggests that several distinct oxidation steps occur during doping reaction. Typically, the origin of these sequential processes is thought to be associated with the progressive oxidation of chromophore sub-populations with varying extents of order.^{42,47,48} Ion diffusion limitations were evaluated by quantifying the peak current density (i_p) as a function of scan rate (v) (**Figure S12**). All materials maintain a roughly linear dependence of i_p on scan rates up to 50 mV s⁻¹, hence demonstrating that ion diffusion is not limiting at the scan rate used in **Figure 2**a.

For the polymers with glyme side chains (G*x*-DMP), increasing the length of the side chain is associated with an increase in $E_{ox(onset)}$, with each additional ethylene oxide unit resulting in an anodic shift of approximately +0.10 V (**Table 1**). Polymer OH-DMP, which lacks any solubilizing side chains, has the lowest $E_{ox(onset)}$ (-0.39 V vs. Ag/AgCl) among all materials tested at. Comparatively, the $E_{ox(onset)}$ of OH-DMP is 0.09-0.21 V lower than that of the G*x*-DMP materials, depending on the analogue. This inverse trend between side chain length and $E_{ox(onset)}$ could be due to several factors. First, the reduced side chain bulk may result in less steric hindrance to both inter- and intra-chain interactions that assist the stabilization of charge carriers. A recent study showed that chemically doped films of OH-DMP show significantly more carrier delocalization when compared to G3-DMP, even at similar doping levels, which could support this hypothesis.⁴⁰ Additionally, reduction of side chain bulk may also change the nature of the polymer-electrode interface to facilitate charge transfer. For OH-DMP, another possible contribution to its low $E_{ox(onset)}$ lies in the unique hydrogen bonding character of the hydroxy substituents. These hydroxy groups act as both hydrogen bond donors and acceptors, whereas the ether groups in the G*x*-DMP analogues are only weak hydrogen bond acceptors. The hydrogen bonds formed in aqueous media promote polymer-electrolyte interactions and facilitate the uptake of hydrated ions.^{49,50} However, a similar trend in the $E_{ox(onset)}$ was observed for OH-DMP relative to G3-DMP when tested in a polar aprotic electrolyte,⁴⁰ where the hydrogen bonding character of the OH-DMP is expected to play a lesser role in the redox response of the material. Therefore, for the results shown here in aqueous media, we assume that the lower $E_{ox(onset)}$ of OH-DMP is not only due to the unique hydrogen bonding character of the hydroxy side chains but also is due to its smaller size relative to the glyme chains. The incorporation of long, electronically insulating side chains increases the principal $E_{ox(onset)}$ of the polymers, likely by obstructing inter- and intra-chain interactions and raising the ionization energy.



Figure 2. a) Cyclic voltammograms of polar ProDOT copolymer films drop cast on glassy carbon disk electrodes (4 μ L of 4 mg/mL CHCl₃ solution), performed at 50 mV s⁻¹ in degassed 0.1 M aqueous NaCl/H₂O under an argon blanket. b) Volumetric capacitance (*C**) of ProDOT copolymer derivatives, determined by EIS in degassed 0.1 M aqueous NaCl/H₂O. Error bars represent standard deviations of measurements performed on 3+ different films.

To further evaluate the redox properties of these polar ProDOT copolymers, EIS was used to determine the C^* of each material in aqueous media. The volumetric capacitance C^* is thought to be an important parameter for benchmarking OECT channel materials.¹⁹ A range of DC offsets was used to study the voltage-dependent C^* in a degassed 0.1 M NaCl/H₂O electrolyte. The

extraction of C^* was performed by fitting the low frequency impedance spectrum (0.1-100 Hz) to a modified Randles circuit (Figure S13b). Quantifiable capacitive behavior was observed for each material, starting around the $E_{ox(onset)}$ (Figure 2b). The evolution of the voltage-dependent C^* for the polar ProDOT copolymers roughly follows to the *i*-V trace in the CV, as anticipated. The glyme-based Gx-DMP materials show peak C^* values ranging from 80-90 F cm⁻³, with no apparent trend with respect to side chain length within this range. This result is markedly different than a trend identified in a similar study of glyme-functionalized polythiophenes, which showed a substantial dependence of C^* on side chain length.³⁴ One potential reason for this disparity lies in the distinct molecular design of the two systems. In the family of polythiophenes reported previously, the glyme side chains are directly linked to the β -position of the thiophene ring, *i.e.*, an sp^2 carbon involved in the π -system. Thus, length-dependent variations of side-chain conformation and ordering may have a greater influence on the ability of the π -conjugated backbone to stabilize charge carriers. Meanwhile, in poly(ProDOT)s, the side chains are symmetrically and tetrahedrally substituted onto an sp³ carbon that does not participate in the backbone π -conjugation. Accordingly, it is reasonable to assume that the mere side chain length (at least within the narrow range studied here) has a relatively weaker influence on material properties relating to charge storage.

When comparing OH-DMP to the Gx-DMP polymers, we see that the small hydroxy-based side chains of OH-DMP confer the highest C^* across the entire voltage range tested (106 ± 7 F cm⁻³, **Figure 2**b). We note that this increase in volumetric capacitance likely arises from the volumetric contraction of the film that occurs during the hydrolysis process, which increases the carrier density, as has been shown for chemically doped films of OH-DMP.⁴⁰ So, while adding long glyme side chains is a common approach for conferring aqueous redox activity in conjugated polymers, the higher C^* obtained for OH-DMP demonstrates that such side chains are not necessary for achieving mixed conduction and high C^* in conjugated polymers. Conceptually, this result is consistent with a finding presented in a recent study in which high C^* was achieved in so-called "side chain-free" materials based on poly(benzimidazobenzophenanthroline) (although the structures of these materials were not verifiable).^{51,52}

Microstructural and Optical Characterization

Investigating how polar side chain length and functionality impacts the structural organization of polymers in thin films may help elucidate the structure-property relationships relevant to device performance in bioelectrochemical applications. This thin-film ordering was investigated using grazing incidence wide-angle X-ray scattering (GIWAXS) and UV-Vis-NIR spectroelectrochemistry in different crystallographic directions and on varying length scales. For all films, the GIWAXS diffraction patterns of the ProDOT copolymer films do not suggest the presence of any significant degree of crystalline microstructure or long-range order (Figure S17). Nonetheless, some face-on texturing relative to the substrate is evidenced by the notable out-ofplane (q_z) scattering around q \approx 1.6 Å⁻¹, which we tentatively assign to relatively disordered, lowcoherence π -stacks (020). All polymers have similar π -stacking distances considering the standard error of the measurement (d₍₀₂₀₎ \approx 4.0 Å, **Table S1**). The π -stacking diffraction peak overlaps with a broad, amorphous scattering halo which is commonly attributed to side chain disorder in alkylfunctionalized polythiophenes.⁵³ Scattering at low q_z (0.3–0.4 Å⁻¹) is attributed to the lamellar stacking (100) direction and corresponds to the distance between adjacent polymer chains ($d_{(100)}$). Across the Gx-DMP series, the lamellar stacking moderately increases with the length of the side chain by approximately 1-2 Å per additional ethylene oxide unit. Seeing as the length of one ethylene oxide repeat in polyethylene oxide unit is approximately 3.5 Å (depending on the conformation/solvation), 54,55 this 1-2 Å change in $d_{(100)}$ is smaller than anticipated, likely due to the side chain tilt angle and/or conformational differences in the solid state. Films of OH-DMP show the tightest lamellar spacing, which likely arises from the reduced side chain length. A more in-depth analysis of the GIWAXS data can be found in section 4 of the SI.

UV-Vis-NIR spectroelectrochemical absorbance spectra demonstrate that the ProDOT copolymers can all be doped in saline aqueous media (**Figure 3**a). Note that the dedoped spectra were normalized and the doped spectra were scaled accordingly to preserve the peak ratios. At -0.4 V vs. Ag/AgCl (solid line) a band centered at ~550 nm is observed and corresponds to the neutral state with a peak and shoulder at ~580 and ~620 nm assigned to 0-1 and 0-0 vibronic transitions, respectively.⁵⁶ Note that the relative intensities of these features are thought to be related the nature and extent of HJ aggregation in the film.⁵⁷ The neutral signatures vanish upon doping at +0.8 V with a concomitant rise of a broad (bi)polaronic band extending beyond 1300 nm, due to singly and doubly charged species typically referred to as polarons and bipolarons.⁵⁸⁻⁶⁰ The full

spectroelectrochemical characterization from -0.4 V to +0.8 V in steps of 0.1 V is shown in **Figure S18**.



Figure 3. a) Superimposed UV-Vis-NIR absorbance spectra of spray-casted polar ProDOT copolymer films biased at -0.4 V (dedoped, solid lines) and +0.8 V (doped, dotted lines) vs. Ag/AgCl in degassed 0.1 M NaCl/H₂O. The dedoped spectra were normalized and the doped spectra scaled accordingly to preserve the peak ratios. The OH-, G2-, G3-, and G4-DMP polymers correspond to blue, green, purple, and orange lines, respectively. The vertical grey lines show the

wavelengths sampled to obtain plots b and c. (b-c) Evolution of the steady-state absorbance upon electrochemical doping from -0.6 V to +0.8 V ($\Delta V = +0.1$ V) at b) 550 nm and c) 900 nm.

Generally, all polymers behave similarly as highlighted by wavelength samplings at 550 nm and 900 nm given in Figure 3b-c. The overlay of these wavelength samplings as well as at 1300 nm for each polymer is shown in **Figure S19**, while the voltage-dependent decay of the 0-0 vibronic band at 620 nm is depicted in Figure S20. By oxidizing the material at higher applied potentials (> -0.2 V), incremental doping of the polymer film is indicated by the decay of the neutral band (\sim 550 nm) and the rise of the polaron band (\sim 900 nm). Above +0.3 V, the \sim 900 nm polaron band decreases again, with a concomitant rise of the signature above 1300 nm arising from bipolarons (as depicted in Figures S18-S19).⁵⁸⁻⁶⁰ An exception is observed for OH-DMP, which maintains a maximum absorbance at 900 nm above +0.3 V. This likely indicates a spectral overlap of different charge carriers at these voltages, which we attribute to residual polaronic absorption and a change in the overlapping bipolaronic band (e.g. a shifting or broadening) compared to the Gx-DMP polymers (Figure 3a). The voltage at which the neutral absorbance begins to decay increases for polymers with longer polar side chains, which is consistent with the DPV data. Note that at +0.7 V, the neutral band has completely disappeared with only minimal changes observed at higher voltages, indicating the films are doped and depleted of detectable neutral chromophores (Figure 3b). Upon reduction, the absorbance spectra of the neutral state are recovered indicating that the doping reaction is reversible — a key characteristic for active channel materials in bioelectrochemical devices such as OECTs.

OECT Characteristics

Next, we incorporated these materials into OECTs to compare their ability to transduce ionic fluxes into electronic outputs in aqueous media. Thus, the electronic performance and cycleto-cycle stability of these materials were studied in OECT devices of varying dimensions and geometric configurations (planar pOECTs and interdigitated iOECTs, see sections **6** and **7** of the SI, respectively). We use μC^* , the product of the carrier mobility (μ) and the volumetric capacitance (C^*) measured in OECTs to benchmark the family of ProDOT copolymers. This μC^* parameter is extracted from the transconductance, device dimensions, threshold voltage, and gatesource voltage using equation 1:¹⁹

$$g_m = \mu C^* \frac{Wd}{L} (V_{Th} - V_{GS}) \tag{1}$$

With g_m , W, d, L, V_{Th} , and V_{GS} representing the transconductance, channel width, channel depth (*i.e.*, film thickness), channel length, threshold voltage, and gate-source voltage at maximum g_m , respectively.

The μC^* of ProDOT copolymers extracted from measurements in iOECTs and pOECTs are compared to understand how material performance is impacted by changing device geometry (Figure 4). Relative to iOECT device measurements (Figures S41-43, Table S7), we observe an approximate thousand-fold increase of μC^* in pOECTs (Error! Reference source not found.). Importantly, pOECTs have simple, rectangular channel geometries (Figure 4a) with W and L of comparable orders of magnitude. In contrast, iOECTs consist of comb-like channel geometries (Figure 4b), with the interdigitated electrode "fingers" giving rise to long effective channel widths, as the total width is the sum of all widths afforded by each individual S and D finger in the device footprint. Accordingly, iOECTs give higher ON currents (IoN) resulting in better signal amplification compared to pOECTs, allowing very small signals such as cellular action potentials to be recorded.⁶¹ However, in contrast to pOECTs, iOECT comb-like channel geometries are also associated with extremely small channel lengths and large effective channel widths (i.e., a high W/L ratio). Liang et al. conducted a thorough and comprehensive study of scaling effects in iOECTs and showed that the enhanced contribution of contact resistance at the polymer-electrode interface in iOECTs with large W/L ratios, resulting in deviations from the expected geometric scaling translated by equation 1, especially for devices with shorter channels.⁶¹ Effects of OECT geometry and bias conditions on contact resistance in devices have also been reported in other extensive studies, especially by Lüssem and coworkers.^{62,63} Thus, for the iOECT measurements in this work, it is likely that contact resistance is the cause for the observed deviation from the relationship between g_m (therefore also μC^*) and channel dimensions implied by equation 1. A similar deviation in device characteristics between iOECTs and pOECTs was recently highlighted by Lill et al.⁶⁴

These effects of device geometry were important to consider when designing the OECT experiments presented below for a couple reasons. First, because of the increased contact

resistance in iOECTs, the μC^* of ProDOT copolymers were only benchmarked in the pOECT device configuration. Second, owing to their enhanced sensitivity and importance in biosensing applications, we conducted long-term iOECT stability measurements to understand how side chain length might impact the output current over time with repeated electrochemical cycling (ON/OFF device switching) in a more application-oriented device configuration. Note, for all OECT device measurements, OH-DMP exhibited extremely poor adhesion to OECT electrode substrates. In fact, the specific processing conditions used for the polymers series (see sections **6.1** and **7.1** of the SI) resulted in consistent film delamination and prevented reliable OECT operation and performance comparison for OH-DMP. Attempts to mitigate delamination were unsuccessful, as discussed in section **7.3** of the SI. Lastly, we further note that we commonly encountered delamination of the G2-DMP when fabricating pOECT devices.



Figure 4. Schematics showing a) planar OECT device using a degassed 0.1 M NaCl/H₂O electrolyte and b) interdigitated OECT device using a 1X PBS electrolyte.

Benchmarking materials

The transistor performance of the Gx-DMP series was evaluated using pOECTs (**Figure** 4a). Details regarding pOECT fabrication and characterization are outlined in section 6 of the SI. All Gx-DMP-based transistors operate in p-type accumulation mode and show reversible transfer characteristics with minimal hysteresis at a 5 mV s⁻¹ scan rate (**Figure S33**). For all polymers tested, the maximum transconductance was observed at V_{GS} \approx -0.8 V with a threshold voltage of V_{Th} \approx -0.35 V (defined as the x-intercept of the linear extrapolation of the $\sqrt{I_{DS}}$ vs V_{GS} plot (**Figure S34**, **Table S3**)). The devices show ON/OFF current ratios (I_{ON/OFF}) exceeding 10⁵, demonstrating potential for large signal amplification (**Figure S33**, **S38**, and **Table S3**).



Figure 5. a) Transconductance values as a function of channel dimensions and biasing parameters of G2-DMP (green triangles), G3-DMP (purple circles), and G4-DMP (orange stars). $[\mu C^*]_{\text{pOECT}}$ values are extracted from the slope of the linear fits (y = ax, dashed lines, $R^2 = 0.99$, 0.97, 0.98, for G2-, G3-, G4-DMP respectively, cf **Figure S35**). All transfer curves are displayed in **Figure S33** and were recorded by sweeping V_{GS} from +0.1 V to -0.8 V at 5 mV s⁻¹ with fixed V_{DS} = -0.6 V. All values of W, d, L, V_{GS} and V_{Th} are reported in **Table S3**. b) Comparison of the doping kinetics of G2- (green), G3- (purple), and G4-DMP (orange) in pOECT devices in a degassed 0.1

M NaCl/H₂O electrolyte. Temporal evolution of the normalized absorbance at 550 nm upon doping at $V_{GS} = -0.8$ V with delay removed (detailed in section **6.5** of the SI, **Figure S39-40**, **Table S4**) to afford biexponential fitting (solid lines = fits, dotted lines = data), as previously done in literature. ⁶⁶ c) Transconductance retention of iOECT devices incorporating G2-, G3-, and G4-DMP performed in a three-electrode interdigitated architecture. All iOECT device data were obtained with a hold time of 3 s, a V_{GS} step size of 1 mV and a step time of 20 ms (comparable to a V_{GS} sweep at a 50 mV s⁻¹ scan rate).

Polymer	μC_{pOECT}^{*} (F cm ⁻¹ V ⁻¹ s ⁻¹) ^{<i>a</i>}	C_{pOECT}^{*} (F cm ⁻³) ^b	μ_{pOECT} (cm ² V ⁻¹ s ⁻¹) ^c	$ au_{ON pOECT}$ $(ms)^d$	$ au_{ m OFF \ pOECT}$ $(ms)^d$
G2-DMP	73 ± 2	$227 \pm 30.$	0.32 ± 0.05	63	6130
G3-DMP	57 ± 3	214 ± 4	0.26 ± 0.02	41	6870
G4-DMP	200 ± 8	213 ± 11	0.94 ± 0.09	22	5610

Table 2. OECT performance of Gx-DMP copolymer series in pOECTs.

^{*a*} Calculated from the slope of the transconductance as a function of pOECT device dimensions (extracted from **Figure 5**a). ^{*b*} Average C_{pOECT}^* extracted from chronoamperometry for each polymer at +0.4 V (**Figure S32**). ^{*c*} Calculated from $\mu C_{pOECT}^*/C_{pOECT}^*$. ^{*d*} Average time constants of the doping/dedoping kinetics extracted from time-resolved spectroelectrochemistry on pOECTs (wavelength sampling at 550 nm). All films are of similar thickness (40-50 nm, **Figure 5**b and **Figure S39**). The thickness dependences of τ_{ON} and τ_{OFF} are given in **Figures S40-41** and **Table S4**.

Next, pOECTs of varying channel dimensions were measured in order to more accurately extract the $[\mu C^*]_{pOECT}$ values from the slope of the linear fits shown in **Figure 5**a (see **Figure S35** for details). The average $[\mu C^*]_{pOECT}$ values for G2-, G3-, and G4-DMP are 73 ± 2 , 57 ± 3 , 200 ± 8 F cm⁻¹ V⁻¹ s⁻¹, respectively with errors being one standard deviation (Error! Reference source not found.).⁶⁷ For reference, if the linear fits are not force fit through the origin (y = ax + b), then the $[\mu C^*]_{pOECT}$ values change to 72 ± 3 , 70 ± 4 , and 236 ± 15 F cm⁻¹ V⁻¹ s⁻¹ for the G2-, G3-, and G4-DMP, respectively (**Figure S36**). Irrespective of the fitting method, both results indicate that the G4-DMP polymer is capable of the largest degree of OECT signal amplification; it is

approximately three-fold larger than its respective shorter side chain analogues. This is the highest reported [μC^*] value for any ProDOT-based active material to date. The transconductances of G2-, G3-, and G4-DMP when corrected for channel dimensions ($g_mL W^{-1} d^{-1}$) are 30 ± 6 , 22 ± 4 , and $76 \pm 7 \text{ S cm}^{-1}$, respectively (errors correspond to one standard deviation averaged over 4+ samples, see **Table S3**). The μ and *C** values for the G*x*-DMP series are compared directly to other reported channel materials in **Figure S37**. We conclude from these results that G4-DMP is highly competitive with the current state-of-the-art OECT channel materials.^{19,30,31,37} We note that scrutinizing the variables that alter OECT performance (*e.g.*, thickness measurement methods, biasing conditions, device geometry, contact resistance, etc.) is crucial to accurately compare any of these reported channel materials.

To elucidate specific structure-property relationships that would explain such results, it is crucial to identify and understand the individual contributions of μ and C^* for the polar ProDOT copolymers in the OECT device. In-situ chronoamperometry was performed on the polymers (Figures S30-S32) in the same pOECT device geometry (S/D short-circuited, thickness measured prior to electrolyte exposure) to account for any possible differences that may arise from their integration into devices. The results do show that the C^* measured by chronoamperometry are roughly three-fold higher (Table S2) than the C* values found with EIS (Table 1). We note four possible contributing factors to this enhancement: (i) differences in casting methods, (ii) other electrochemical cell architectures, (iii) dissimilar metrologies used for thickness measurements (i.e., measured on dry film before chronoamperometry vs. on cycled, de-doped, rinsed, and dried after EIS experiment), and (iv) additional, non-Faradaic double layer current measured in chronoamperometry. Based on extensive analysis, we believe the differences in casting methods and electrochemical cell architecture to be the main reasons for the discrepancy, as is detailed in section 6.3 of the SI. Nonetheless, the chronoamperometry and EIS data both show that C^* is similar for all polymers, thereby demonstrating that the μC^* enhancement must then relate to an improvement of the hole mobility if the materials behave as described in equation 1. In a previous study, a higher OECT hole mobility was also inferred from higher μ C* and similar C* for less semi-crystalline polythiophene films compared to those with higher degrees of crystallinity.⁶⁸ This conclusion is contextualized in the Conclusions and Perspective section.

Interestingly, G4-DMP is not only the highest performing polymer in terms of transconductance (signal amplification), but also exhibits the fastest (de)doping kinetics for rapid

ON/OFF device switching. The kinetics were probed by time-resolved spectroelectrochemistry using square-wave pulses at +0.8 V for doping and -0.5 V for dedoping on pOECTs with shortcircuited source and drain contacts (details in section 6.5 of the SI). The doping/dedoping time constants were quantified by fitting respectively the decay and the rise of the absorbance intensity at 550 nm (neutral band) with biexponentials.⁶⁶ As shown in Figure 5b, G4-DMP dopes two to three times faster than the other polymers (time constants listed in Error! Reference source not found.). These results were confirmed by numerous measurements in which the thicknesses were varied (Figures S40-41, Table S4). Interestingly, the doping time constants are about two orders of magnitude faster than the dedoping time constants. For the doping, a delay is seen before the onset of the biexponential decay of the neutral band (Figures S39b and S40b). This delay corresponds to the time required to propagate doping towards the middle of the channel where the optical response is sampled. The propagation time depends on factors such as the charge transfer between the doped and dedoped parts of the film as well as the hole mobility in the doped segment of the film (see full discussion in section 6.5 of the SI). The shortest delay (*i.e.*, fastest optical response), observed for G4-DMP, is in accordance with the highest hole mobility found and suggests more efficient charge propagation from the electrode to the dedoped region of the channel.

Device stability

Stability testing of the Gx-DMP polymers was performed in iOECTs (**Figure 4**b). Instead of unbuffered 0.1 M NaCl/H₂O, which is the most common electrolyte used in OECT testing (and used in here for pOECT measurements), a 1X phosphate buffered saline (PBS, pH=7.4) solution was employed to mimic physiological conditions and prevent pH variations over extended testing periods. Further details can be found in section **7** of the SI. The transconductance retention was tested in the identical iOECT setups to compare the stability of the materials to rapid device operation. As shown in **Figure 5**c, G4-DMP and G3-DMP perform the best, maintaining > 80% the original transconductance after 1000 device cycles. Notably, the G2-DMP retains only approximately 30% of its initial g_m within 300 cycles. Due to the persistent delamination of the G2-DMP that was observed for pOECTs, it seems likely that this loss in g_m is due to interfacial instabilities. This data provides insight into material stability in a more application-driven electrolyte and OECT device configuration.

Conclusions and Perspective

This work explores the structural effects governing the aqueous redox properties, microstructure, and OECT performance of solution-processable, electron-rich, polar-functionalized copolymers — all based on a DMP (2,2-dimethylProDOT) unit — that are functionalized with side chains of different length, functionality, and polarity. This family includes three materials with hydrophilic glyme (G) side chains of various lengths (G2-, G3-, G4-DMP) as well as an intractable hydroxy-functionalized (OH-DMP) analogue that lacks long solubilizing side chains. The data for these materials suggest there are processing and performance trade-offs for shorter (OH) and longer (G4) polar side chains for conjugated polymers in bioelectrochemical applications.

Importantly, all of the poly(ProDOT)s reported are highly redox active in aqueous NaCl and can be fully doped within the electrochemical window of water. This redox activity allowed us to use both ex- and in-situ aqueous (spectro)electrochemistry to decipher specific structureproperty relationships for the ProDOT copolymer family in traditional electrochemical cells and OECT devices, respectively. First, we see a modest yet reliable positive correlation between the oxidation onset and the length of the polar side chain. Second, EIS data show that short, highly polar side chains can enhance the volumetric capacitance (C^*); the C^* of OH-DMP was between 16-31% higher than polymers in the Gx-DMP series. This demonstrates that similar (if not superior) aqueous redox activity and capacitance can be achieved by replacing the widely used glyme side chains with short hydroxy groups. Provided delamination issues are overcome, this result implies that the cleavable side chain technique may be a promising route to obtain higher performing OECT active materials in the future. Across the Gx-DMP series, we see little influence of the glyme side chain length on the volumetric capacitance measured by both EIS and chronoamperometry. Notably, this result differs from the trend identified for other polar polythiophenes, which showed a substantial dependence of capacitance on the length of the glyme side chain,³⁴ thus introducing more nuance into structure-property relationships. Together, these findings suggest that design strategies for OECT materials cannot be generalized across material classes and instead require careful consideration of the macromolecular architecture (i.e., backbone and side chain combination) at hand. Third, in-situ time-resolved

spectroelectrochemistry (*i.e.*, chronoabsorptometry) measurements show that poly(ProDOT)s with longer glyme side chains result in faster (de)doping kinetics in OECT devices. In sum, the (spectro)electrochemistry data show that these polymers are stable and can be reversibly (de)doped in aqueous media, making them promising candidates for bioelectrochemical applications.

We conclude this work by summarizing and contextualizing our OECT results with a perspective from recent studies. By comparing iOECTs and pOECTs, we find that μC^* , the theorized intrinsic figure-of-merit for OECT channel materials, does not scale with device dimensions as equation 1 would predict for iOECTs. This deviation is likely due to contact resistance effects that distort the relationship between material properties and device performance, as described by others.⁶¹⁻⁶³ Therefore, pOECTs were used to benchmark the Gx-DMP series the results show that the μC^* of G4-DMP (the Gx-DMP derivative with the longest polar side chain) is approximately three times larger than that of the poly(ProDOT)s with shorter glyme side chains. These data imply that side chains with polar functionalities further from the backbone could improve μC^* , a finding that is corroborated by a paper published recently by Chen *et al.*⁶⁶ However, in contrast to their findings, we do not measure a significant change in C^* across the polymer family as the dominant factor in μC^* enhancement. Consequently, based on equation 1, we deduce that a hole mobility enhancement is likely the reason for the observed increase in μC^* for G4-DMP. This improvement in the hole mobility is corroborated by other reports for thiophene copolymers with longer polar side chains.^{37,66} The higher hole mobility deduced for G4-DMP is supported by both the shorter delay in neutral absorbance decay and the faster doping kinetics found using *in-situ* time-resolved spectroelectrochemistry performed on pOECTs. Indeed, a higher hole mobility may afford faster doping fronts from the SD electrodes to the center of the channel where the absorbance is probed. We note that the G3-DMP has a similar implied mobility than the G2-DMP, yet it is noticeably faster to dope. This implies that hole mobility is not the only parameter driving doping kinetics, and other factors such as charge transfer between the doped and de-doped segments, may also play an important role. A recent and thorough study of molecular weight effects in polythiophenes showed a decrease in μC^* with an increase in molecular weight (the opposite trend found here, where the side chain length increases with increasing molecular weight).⁶⁹ Therefore, the results herein provide further evidence that the improved μC^* and (de)doping kinetics is likely a side chain effect caused by having longer polar side chains (or, at least, polar functionalities further from the backbone), rather than by molecular weight.

Assigning unequivocal design rules for this class of materials requires the fundamental understanding of why longer polar side chains might improve OECT performance in the first place. One possible justification supposes that ions are localized further away from delocalized polarons on the doped conjugated backbone, which would conceivably lower the probability of charge trapping and increase the carrier mobility. One other hypothesis is that longer side chains provide a larger volume to accommodate ion and solvent uptake so that conductive pathways are less distorted, hence preserving high carrier mobility upon electrochemical doping. The distortion of conductive pathways by ion intercalation has been previously proposed by Flagg et al. ⁶⁸ While plausible, currently no conclusive evidence confirms these hypotheses. Another possibility is that there are more factors not being accounted for by equation 1 that influence OECT performance.

We believe the comparison of our iOECT and pOECT results (in the context of other findings in the field) provide evidence for the postulation that material-dependent contact resistance may be a more significant factor governing OECT performance than commonly thought. This hypothesis appears especially compelling in light of a recent study where the modification of gold source and drain electrodes with alkane thiol self-assembled monolayers resulted in a three-fold enhancement of the transconductance due to a lessening of the contact resistance at the polymer-electrode interface (in addition to tuning the work function of the gold).⁷⁰ In other types of organic transistors, like OFETs, there have been studies to account for material-dependent contact resistance effects to better compare channel materials.⁷¹⁻⁷⁶ As we have shown in this work, meaningful comparison of materials based solely on device characteristics are complex, especially when these devices are fabricated differently, designed with vastly disparate geometries, and are measured with varied metrologies. Future studies outlining any material- or geometry-dependent contact resistances will be helpful to unambiguously outline structure-property interrelationships that govern OECT active material performance.

This work has elucidated a number of key structure-property relationships for a family of poly(ProDOT)s with different side chain length, functionality, and polarity. Many of these polymers in the family are demonstrated to be high-performing accumulation mode OECT channel materials, as shown by their high transconductances. This high performance is further evidenced by the finding that longer glyme side chains resulted in enhanced aqueous OECT stability with transconductance retention over 80% after 1000 ON/OFF cycles (G2- << G4- < G3-DMP). The G4-DMP — given its higher OECT performance, (de)doping kinetics, stability, improved

processability, and versatility in accessing a wide range of molecular weights — is especially promising for bioelectronic applications.

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Author Contributions

LRS and BTD contributed equally to this work. LRS and BTD designed and conceptualized the study. BTD synthesized, purified, and characterized polymers. LRS performed CV, DPV, EIS,

FT-IR, spectroelectrochemistry, processed GIWAXS data, and configured/tested iOECT devices. BTD and OB fabricated and electrically characterized pOECT devices and performed all *in-situ* pOECT chronoamperometry and time-resolved spectroelectrochemistry. OB processed all pOECT data. MD assisted in EIS configuration and interpretation. LRS, BTD, and OB performed all data analysis and wrote the manuscript, with inputs from JRR, NB, MD, and AMÖ.

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