SUPPORTING INFORMATION

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

Brandon T. DiTullio,^a[‡] Lisa R. Savagian,^{b‡} Olivier Bardagot,^c Michel De Keersmaecker,^a Anna M. Österholm,^a Natalie Banerji,^c John R. Reynolds^{a,b*}

[‡]These authors contributed equally to this work

^a School of Chemistry and Biochemistry, Center for Organic Photonics and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA

^bSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA

^c Department of Chemistry, Biochemistry and Pharmaceutical Sciences (DCBP), University of Bern, 3012 Bern, Switzerland

Author Contributions: 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 input from MD, NB, JRR, and AMÖ.

*Corresponding author email: reynolds@chemistry.gatech.edu

TABLE OF CONTENTS

1. Pol	lymer Synthesis and Characterization	4				
1.1.	Materials and methods					
1.2.	Synthesis of Polymer G2-DMP	5				
1.3.	Synthesis of Polymer G4-DMP					
2. Pol	lymer Processing					
2.1.	Spray Coating					
2.2.	Blade Coating					
2.3.	Drop Casting					
2.4.	Thin film hydrolysis towards OH-DMP	20				
3. Ele	ectrochemical Characterization	21				
3.1.	DPV and CV	21				
3.2.	EIS	23				
4. GI	WAXS					
5. Spe	ectroscopic Characterization					
5.1.	UV-Vis-NIR absorbance spectroelectrochemistry	33				
5.2.	ATR-FTIR	37				
6. pOECT devices						
6.1.	Fabrication	37				
6.2.	Thickness-absorbance calibration curve					
6.3.	Chronoamperometry coupled with Vis-NIR spectroelectrochemistry	40				
6.4.	Transfer characteristics	48				
6.5.	Time-resolved Vis-NIR spectroelectrochemistry	55				
7. iOI	ECT devices					
7.1.	Fabrication	64				
7.2.	Device Parameters and Characteristics	64				
7.3.	Active Layer Delamination	68				
References						

1. Polymer Synthesis and Characterization

1.1. Materials and methods

All reagents were purchased and used as received from commercial suppliers: $Pd(OAc)_2$ (99.9%, Acros Organics), pivalic acid (99%, TCI America), K₂CO₃ (anhydrous, VWR), diethyleneglycol monomethyl ether (98%, Aldrich), triethyleneglycol monomethyl ether (98%, TCI America), tetraethyleneglycol monomethyl ether (98%, Acros Organics), Nbromosuccinimide (99% NBS, Sigma Aldrich), NaH (90%, Sigma Aldrich). and diethyldithiocarbamic acid diethylammonium salt (97%, TCI America). Dimethylacetamide (HPLC grade DMAc, VWR) was degassed by argon bubbling and stored over molecular sieves prior to use. Silica (60 Å porosity) used for column chromatography was purchased from Sorbent Technologies, Inc. ¹H NMR and ¹³C NMR spectra for all monomers and molecular precursors were acquired on a Varian Mercury Vx 300 MHz instrument using CDCl₃ as the solvent at 25 °C. ¹H-NMR spectroscopy of polymers G2-DMP and G4-DMP was performed using a Bruker AVIII-400 MHz instrument with CDCl₃ as the solvent at 50 °C. The residual CHCl₃ peak was used as a reference for all reported chemical shifts (¹H: δ = 7.26 ppm, ¹³C: δ = 77.16 ppm). Gel permeation chromatography (GPC) was performed using a chloroform Tosoh EcoSEC GPC instrument with an RI detector to determine the number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (Đ) relative to polystyrene (PS) standards at 40°C. Elemental analysis was conducted by Atlantic Microlab Inc. G2-DMP was synthesized twice to ensure there was enough material for all the experimentation in this study. All the monomer and polymer characterization was performed for both materials, confirming their purity. Molecular weights and dispersities of the batches were comparable ($M_n = 13.4 \text{ kg mol}^{-1}$, $D = 1.6 \text{ and } M_n = 10.2 \text{ kg mol}^{-1}$, D = 1.4 vs. PS in CHCl₃ at 40°C). The solution UV-Vis and cyclic voltammograms were identical.

Polymer **G3-DMP** ($M_n = 22.5 \text{ kg mol}^{-1}$, D = 1.6 vs. PS in CHCl₃ at 40°C) and **BOE-DMP** ($M_n = 72.6 \text{ kg mol}^{-1}$, D = 2.3 vs. PS in CHCl₃ at 40°C) were synthesized as reported in previous publications.^{1,2} The chemical characterization (NMR, elemental analyses, and chromatography traces) for these polymers can be found in the indicated literature references.^{1,2} Compound **1**

(Bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) was prepared using published procedures³ and characterized by ¹H-NMR and GC-MS analysis. Similarly, compound **3** (6,8-dibromo-3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) was synthesized and purified according to published procedures^{1,4} and characterized by ¹H-NMR and GC-MS.

1.2. Synthesis of Polymer G2-DMP

Scheme S1. Synthesis of compound 2.



Compound 2 (3,3-bis((2-(2-methoxyethoxy)ethoxy)methyl)-3,4-dihydro-2H-thieno[3,4b][1,4]dioxepine)

Under an inert atmosphere of argon, neat sodium hydride (NaH, 0.631 g, 26.31 mmol, 3 equiv.) and a stir bar were added to a flame-dried 250 mL round bottom flask. Next, compound 1^3 (3.00 g, 8.77 mmol, 1 equiv.) and 100 mL of anhydrous *N*,*N*-dimethylacetamide (DMAc) were mixed separately and added to the flame-dried 250 mL round bottom flask via cannulation. The resulting mixture of NaH, compound **1**, and DMAc was purged with argon while stirring at room temperature for 30 min. Diethylene glycol monomethyl ether (3.16 g, 26.31 mmol, 3 equiv.) was then added dropwise to the reaction mixture while stirring. After addition, the reaction mixture was heated to 120 °C and allowed to stir vigorously for 16 h under positive argon pressure. Once the reaction was complete, the mixture was cooled to ambient temperature, extracted with dichloromethane (DCM), and washed with deionized water. The organic layer was then washed repeatedly with brine. The organic phase was collected and subsequently concentrated under

reduced pressure by rotary evaporation and purified by column chromatography using a 4:1 mixture of ethyl acetate (EtOAc) and hexanes as a mobile phase. The product, compound **2**, was obtained as a clear oil with a faint yellow hue in a 68% yield (2.52 g). ¹H-NMR (300 MHz, CDCl₃, 25°C), δ (ppm) 6.44 (s, 2H), 4.02 (s, 4H), 3.70-3.50 (br, 20H), 3.37 (s, 6H). ¹³C-NMR (300 MHz, CDCl₃, 25°C) δ 149.61, 105.13, 73.48, 71.93, 71.07, 70.48, 70.33, 70.02, 58.99, 47.71. HR-MS (ESI) m/z calculated for C₁₉H₃₃O₈S[m+1] 421.19, found 421.1891.



Figure S1. ¹H-NMR spectrum of compound 2 in CDCl₃.



Figure S2. ¹³C-NMR spectrum of compound 2 in CDCl₃.

Scheme S2. Synthesis of polymer G2-DMP.



Polymer G2-DMP

Polymer G2-DMP

Compound 2 (0.1454 g, 1.0 equiv.), compound 3¹ (0.1182 g, 1.0 equiv.), pivalic acid (PivOH, 0.011 g, 0.30 equiv.), potassium carbonate (K₂CO₃, 0.1433 g, 3.0 equiv.), and a stir bar were added to a flame-dried and evacuated 15 mL Schlenk flask at room temperature. The reagents were then dissolved by addition of anhydrous DMAc (3.5 mL). Following addition, the flask was sealed and allowed to stir while concurrently purging with argon for 10 min. Finally, palladium (II) acetate (0.0016 g, 2 mol %), was added to the reaction mixture, which was then heated to 140 °C and allowed to stir for 12 h under positive argon pressure. After the flask was removed from heat and allowed to cool to 50 °C, the reaction vessel was charged with \sim 30 mg of diethylammonium diethyldithiocarbamate (palladium scavenger) and stirred for an additional 2 h. The polymer was then precipitated into methanol and filtered into a soxhlet extraction thimble. Washes were performed using methanol, acetone, hexanes, and DCM before finally dissolving the polymer into chloroform (CHCl₃). After dissolution, the CHCl₃ was removed under reduced pressure via rotary evaporation until ~2 mL of polymer solution remained. The polymer was then precipitated in methanol and dried under high vacuum overnight. The product was obtained as a purple, flaky solid in 78 % yield (0.52 g). ¹H-NMR (400 MHz, CDCl₃, 50°C) δ (ppm) 4.18 (s, 4H), 3.85 (s, 4H), 3.77-3.45 (m, 20H), 3.36 (s, 6H), 1.15 (s, 6H). Anal. calcd. for C₂₈H₄₀O₁₀S₂: C, 55.98; H, 6.71; S, 10.67, Found: C, 55.22; H, 6.44; S, 10.48. $M_n = 13.4 \text{ kg mol}^{-1}$, $D = 1.6 \text{ vs. PS in CHCl}_3$ at 40°C.



Figure S3. ¹H-NMR spectrum of polymer G2-DMP in CDCl₃.



Figure S4. Gel permeation chromatogram of polymer G2-DMP in CHCl₃ at 40° C. $M_n = 13.4$ kg mol⁻¹, D = 1.6 vs. PS.

1.3. Synthesis of Polymer G4-DMP

Scheme S3. Synthesis of compound 4.



Compound 4 (3,3-di(2,5,8,11,14-pentaoxapentadecyl)-3,4-dihydro-2H-thieno[3,4b][1,4]dioxepine)

Sodium hydride (NaH, 0.631 g, 26.31 mmol, 3 equiv.) and a stir bar were added to a flame-dried 250 mL round bottom flask under inert atmosphere. Compound 1^{3,4} (3.00 g, 8.77 mmol, 1 equiv.) and 100 mL of anhydrous DMAc were mixed separately and added to the flame-dried 250 mL round bottom flask via cannulation. The resulting mixture of NaH, compound 1, and DMAc was purged with argon while stirring at room temperature for 30 min. Tetraethylene glycol monomethyl ether (5.48 g, 26.31 mmol, 3 equiv.) was then added dropwise to the reaction mixture while stirring. After addition, the reaction mixture was heated to 120 °C and allowed to stir vigorously for 16 h under positive argon pressure. Once the reaction was complete, the mixture was cooled to ambient temperature, extracted with DCM, and washed with deionized water. The organic layer was then washed repeatedly with brine. The organic phase was collected and subsequently concentrated under reduced pressure via rotary evaporation and purified by column chromatography using an EtOAc/hexanes (4:1) mobile phase. The product was obtained as a highly viscous, clear oil with a faint yellow hue in a 49% yield (2.58 g). ¹H-NMR (300 MHz, CDCl₃, 25°C) δ (ppm) 6.44 (s, 2H), 4.01 (s, 4H), 3.70-3.50 (br, 36H), 3.37 (s, 6H). ¹³C-NMR δ 149.68, 105.19, 73.56, 71.94, 71.12, 70.65, 70.62, 70.59, 70.53, 70.36, 70.11, 59.05, 47.77. HR-MS (ESI) m/z calculated for $C_{27}H_{49}O_{12}S$ [m+1] 597.29, found 597.2939.



Figure S5. ¹H-NMR spectrum of compound 4 in CDCl₃.



Figure S6. ¹³C-NMR spectrum of compound 4 in CDCl₃.

Scheme S4. Synthesis of polymer G4-DMP.



Polymer G4-DMP

Polymer G4-DMP

Compound 4 (0.2156 g, 1.0 equiv.), compound 3¹ (0.1450 g, 1.0 equiv.), pivalic acid (PivOH, 0.013 g, 0.30 equiv.), potassium carbonate (0.1758 g, 3.0 eq.), and a stir bar were added to a flamedried and evacuated 15 mL Schlenk flask at room temperature. The reagents were then dissolved by addition of anhydrous DMAc (4.2 mL). Following addition, the flask was sealed and allowed to stir while concurrently purging with argon for 10 min. Then, palladium (II) acetate (0.0019 g, 2 mol%), was added to the reaction mixture, which was then heated to 140 °C and allowed to stir for 12 h under positive argon pressure. After the flask was removed from heat and allowed to cool to 50 °C, the reaction vessel was charged with ~30 mg of diethylammonium diethyldithiocarbamate (palladium scavenger) and stirred for an additional 2 h. The polymer was then precipitated into methanol and filtered into a soxhlet extraction thimble. Washes were performed using methanol, acetone, hexanes, and tetrahydrofuran before finally dissolving the polymer into chloroform. After dissolution, the chloroform was removed under reduced pressure via rotary evaporation until ~ 2 mL of polymer solution remained. The polymer was then precipitated in methanol and dried under high vacuum overnight. The product was obtained as a shiny purple, fibrous solid in 86 % yield (0.29 g). ¹H NMR (400 MHz, CDCl3, 50 °C) δ (ppm) 4.19 (s, 4H), 3.85 (s, 4H), 3.77-3.45 (m, 36H), 3.35 (s, 6H), 1.15 (s, 6H). Anal. calcd. for $C_{36}H_{56}O_{14}S_2$: C, 55.65; H, 7.27; S, 8.24, Found: C, 55.38; H, 7.04; S, 8.53. $M_n = 65.9 \text{ kg mol}^{-1}$, D = 2.5 vs. PS in CHCl₃ at 40°C.



Figure S7. ¹H-NMR spectrum of polymer G4-DMP in CDCl₃.



Figure S8. Gel permeation chromatogram of polymer G4-DMP in CHCl₃ at 40 °C. $M_n = 65.9$ kg mol⁻¹, D = 2.5 vs. PS.

2. Polymer Processing

For pOECT characterizations, all polymers were spin coated (see **Section 6**). For the rest of samples (those used for electrochemical, optical, microstructural characterization, as well as iOECT devices), all polymers were blade coated from solution onto the electrodes to ensure uniform thickness, except for G2-DMP, which was spray-cast due to poor solubility.

2.1. Spray Coating

Spray coating was performed using an Iwata-Eclipse HP-BC airbrush with nitrogen (20 psi) as the carrier gas. Polymers were dissolved at 4 mg/mL in chloroform and spray-cast onto room-temperature substrates.

2.2. Blade Coating

Polymers were dissolved at 15 mg/mL in room temperature chloroform by stirring in a closed vial overnight. The solutions were blade-coated using a custom-built blade coater consisting of a clean and unmodified glass blade. The gap height was ~200 μ m and the blade was pulled at a speed of 4 mm s⁻¹. The blade-coating stage was heated to 30 °C while coating. Films of thicknesses ranging from 150-250 nm were obtained.

2.3. Drop Casting

Polymers were dissolved in room-temperature chloroform overnight at a concentration of 4 mg/mL. Identical masses of each polymer were drop-casted (four 1- μ L aliquots, 4 μ L total volume, 16 μ g total polymer mass) onto a polished glassy carbon (GC) disk electrode (active area = 0.07 cm²).

As stated in the main text, drop casting was performed carefully to ensure that no part of the conjugated polymer film overlapped with the edge of the insulating electrode body, as this was found to drastically influence the peak shape, current density, and overall charge passed in the voltammogram (**Figure S9**). While these coating differences may seem trivial, drop-casting onto disk electrodes can be extremely difficult to execute properly, especially considering the relatively small active area of most common disk electrodes (0.01–0.07 cm²) and the low surface tension of organic solvents used for processing. Based on these variables, the analysis of the relative peak

position and current density of the redox response can be inaccurate. In addition, calculation of the mass-normalized redox capacity and charge density are also subject to error, seeing as the overall charge passed during the CV experiment also can depend on casting technique. The best way to ensure the polymer is only deposited on the active electrode area and does not extend up to or beyond the interface between the active area and the electrode body electrode is to drop-cast in extremely small aliquots and avoid coating the full active area of the disk electrode (as shown in scheme *A* of **Figure S9**). Consequently, this technique calls into question the conventional practice of normalizing current to the surface area of the electrode for an adsorbed layer when, in fact, the polymer film (which contributes to much of the current density) does not have a well-defined surface area. For polymers adsorbed onto electrodes, normalization to mass may ultimately be a more meaningful practice.

The voltammetric characteristics of the film cast by scheme *A* are more capacitive and closely resemble the redox properties of the analogous films drop-casted directly onto GC and ITO plate electrodes. In contrast to GC disk electrodes, GC and ITO plate electrodes do not have an insulating plastic body (schemes *D* and *E*, **Figure S9**) on which the polymer may contact. This demonstrates that the previously described differences are, in fact, due to "overcoating" the polymer film beyond the active area of the disk electrodes. Interestingly, the redox properties do not differ greatly between films cast onto ITO/glass and GC plate electrodes. Small differences in the oxidation onset ($E_{ox(onset)}$) may be due to either (1) changes in film morphology induced by different surface energy, surface roughness, or charge transfer resistances between the two systems. The enhanced current density observed for the GC plate electrode may be the result of a greater relative contribution from background capacitive charging of the larger GC electrode surface. Notably, the sharpness and breadth of the redox peaks does not depend strongly on the conductivity of the underlying electrode. Nonetheless, the precision of the drop casting method is critical to extract valid material properties. Given the similarities to the plate-based CVs, drop-casting scheme *A* is preferred and therefore was employed in this study.



Figure S9. *Top:* Schematic showing different methods for drop casting polymer solutions onto glassy carbon disk electrodes (schemes A, B, C), a glassy carbon plate electrode (scheme D), and an ITO/glass plate electrode (scheme E). *Bottom Left:* Repeat unit structure of G4-DMP. *Bottom Right:* Cyclic voltammogram of drop cast films of G4-DMP (16 µg) in 0.1 M NaCl/H₂O recorded at 50 mV s⁻¹, using various electrodes and drop casting methods.

2.4. Thin film hydrolysis towards OH-DMP

The polymer BOE-DMP was cast from solution onto the electrode substrate via bladecoating or drop casting. The substrate was then suspended with tweezers into a solution of 2 M KOH in methanol heated to 55 °C for 4 hours while the solution gently stirred. During the side chain saponification process, white solid particulates accumulated in the KOH solution and on the surface of the film. After the hydrolysis was complete, the film was gently rinsed with clean methanol and deionized water, then allowed to dry at room temperature.



Figure S10. Schematic showing coating of polymer BOE-DMP and thin film saponification process to access polymer OH-DMP.

3. Electrochemical Characterization

Details surrounding sample preparation and analysis are reported in the Experimental section of the main text and in Section 2 of the SI. Cyclic voltammograms (CV) are reported in **Figure S9**.





Figure S11. Differential pulse voltammetry (DPV) performed on electrochemically conditioned films of a) G2-, b) G3-, c) G4-, d) OH-, e) BOE-DMP in Ar-degassed 0.1 M NaCl/H₂O.

We note that for the DPV trace of BOE-DMP (**Figure S11**), there is a small but reproducible oxidation wave at approximately +0.3 V. This is a rather minor contribution to the overall electrochemical response of BOE-DMP, especially when compared to the other materials. In addition, this wave is not detectable by CV (**Figure S14a**). In fact, this polymer shows no change in the neutral state absorbance spectra until +0.8 V (**Figure S21**), and no capacitive response is detected by EIS until +0.6 V (**Figure S14b**). Accordingly, we conclude that this small electrochemical process is not indicative of the bulk doping of BOE-DMP. Instead, we ascribe the more anodic process ($E_{ox onset} = +0.85$ V) to be associated with the doping reaction, as it most closely corresponds to other potential-dependent changes in C* and optical absorption.



Figure S12. Peak current densities for cyclic voltammetry (CV) performed at various scan rates for a) G2-, b) G3-, c) G4-, and d) OH-DMP. Points joined by solid lines represent experimental data. Dashed lines represent the linear extrapolation of the data recorded at low scan rates ($v \le 50$ mV s⁻¹) and fit to a linear regression. Scan-rate dependence of BOE-DMP was not performed due to its poor redox activity and stability in the aqueous NaCl electrolyte.

3.2. EIS

The experimental configuration used for electrochemical impedance spectroscopy (EIS) is depicted schematically in **Figure S13**a. Further experimental details for EIS are provided in the main text. The equivalent circuit representing the data is shown in **Figure S13**b. One series combination of the circuit consists of an equivalent series resistance (R_s) that encompasses the resistance of the electrolyte, leads, interconnects, and polymer film, as well as a double-layer capacitor (C_{DL}) that accounts for double capacitive charging at the polymer-electrolyte interface. These two elements represent physical processes that dominate the impedance response across the high frequency range (Hz-kHz for these samples). At low frequencies (~mHz–Hz), the impedance behavior is dominated by the charge transfer resistance at the polymer-electrode interface (R_{CT}) in series with a constant phase element (Q_o) representing the imperfect pseudo-capacitive behavior of the film (**Figure S13**b).^{5,6} For reported capacitance values, the value of the Q_o exponent (α) is found to be > 0.8, suggestive of capacitive behavior and validating the use of a constant phase element to extract capacitance values. As described in previous literature,^{7,8} the capacitance of the film was calculated using the following equation for an *R-Q_o* series circuit:

$$C = [Q_o * R_{CT}^{-(\alpha-1)}]^{1/\alpha}$$



Figure S13. a) Schematic depiction of a three-electrode cell used for EIS measurement, showing a reference electrode (RE), polymer-coated working electrode (WE), and counter electrode (CE), as well as argon (Ar) gas source used as a blanket to minimize oxygen contamination. b) Equivalent circuit for the doping and ion interaction process in the polymer, as adapted from the literature.^{5,6}



Figure S14. a) Cyclic voltammograms of BOE-DMP and OH-DMP films in 0.1 M NaCl/H₂O on a glassy carbon disk electrode and recorded at 50 mV s⁻¹. b) Voltage-dependent volumetric capacitance C* for BOE-DMP and OH-DMP extracted from EIS, as described above. Error bars for OH-DMP represent the standard deviation of values for three different films, cast and measured separately. BOE-DMP showed no appreciable capacitive response until +0.6 V vs. Ag/AgCl.

We note that the capacitive behavior of BOE-DMP presented in **Figure S14**b is not repeatable upon multiple doping/de-doping cycles. We hypothesize that the hydrophobic BOE side chains prevent the facile transport of ions in and out of the film, and therefore charged states remain trapped in the film, even upon de-doping to large negative voltages. This is supported by the spectroelectrochemical data, which clearly show residual absorbance of charge carriers around 900 nm when applying -0.8 V after the first doping process (**Figure S21**). Accordingly, EIS was not repeated many times for BOE-DMP, as the material showed little capacitive response and irreversible doping within the aqueous electrolyte.

Regarding the C* of each material, we may also consider the C* normalized to the electroactive mass fraction of the material, *i.e.*, the relative ratio of the mass of the conjugated backbone to the entire polymer (backbone and side chains). Assuming a uniform, homogeneous density of 1 g cm⁻³, the C* may be scaled accordingly to understand the underlying influence of side chain length on charge storage. For instance, in polythiophenes functionalized with glyme side chains of varying length, it was found that normalization of the C* for the electroactive mass fractions yielded similar values, suggesting that the primary mechanism by which longer side chains reduce C* was indeed through a reduction in relative electroactive mass of the film.⁹ In the case of the DMP copolymers in this work, the electroactive mass normalized volumetric capacitance values were found to be 111.6, 154.4, 167.0, and 211.1 F gelect. mass⁻¹ for OH-, G2-, G3-, and G4-DMP, respectively (assuming a uniform density of 1 g cm⁻³ for both backbone and side chain). Under this limited assumption, these findings suggest that the mechanism for the enhancement of C* for OH-DMP is not merely through a reduction in electroactive mass. In fact, the materials with the longer side chains have the higher capacitance when normalized to the estimated mass of the conjugated backbone. Accordingly, the longer polar side chains on G4-DMP may actually confer a greater fundamental charge storage capacity to the conjugated backbone itself. Without further experiments, we cannot unequivocally prove that this is the case, nor can we identify the origin of such a potential effect. Nonetheless, the fundamental mechanism underlying such C* variations are worthy of further exploration.



Figure S15. a) Nyquist and b) Bode plots of G*x*-DMP polymers for EIS data collected using the electrochemical cell shown in **Figure S13**a. Data are shown for three representative DC offset potentials. In the Bode plots, the frequency (logarithmic scale) is plotted as a function of the phase shift, Φ . The Nyquist plots have the negative imaginary impedance, -*Z*", plotted versus the real part of the impedance, *Z*'.



Figure S16. a) Nyquist and b) Bode plots of the BOE-DMP (top, black) and OH-DMP (bottom, blue) polymers for EIS data collected using the electrochemical cell shown in **Figure S13**a. Data are shown for three representative DC offset potentials. In the Bode plots, the frequency (logarithmic scale) is plotted as a function of the phase shift, Φ . The Nyquist plots have the negative imaginary impedance, -Z", plotted versus the real part of the impedance, Z'.

4. GIWAXS

Polished Si wafers were cleaned with piranha etch, followed by rinsing with deionized water and isopropyl alcohol. The substrates were then dried under a nitrogen stream and cleaned for 10 minutes in a UV/O_3 chamber. Films were cast from solution using either blade or spray coating onto cleaned Si wafers. Film treatment toward polymer OH-DMP was performed as described in **Section 2.4** above.

Grazing-incidence wide angle X-ray scattering (GIWAXS) of G2-, G3-, G4-, and BOE-DMP was performed at the Stanford Synchrotron Radiation Lightsource (SLAC National Accelerator Laboratory, BL 11-3). The measurements used a beam energy of 12.7 keV and an angle of incidence of approximately 0.13° . The distance between the sample and detector was approximately 250 mm, and scattering patterns were calibrated using a LaB₆ standard. GIWAXS of OH-DMP was performed at beamline 11-BM of NSLS II at Brookhaven National Laboratory. The beam energy was 13.5 keV, and the incident angle of the measurement was 0.12° . The sample distance was approximately 259 mm.

For processing raw scattering data, software packages Nika¹⁰ and WAXStools¹¹ were used as loaded into IgorPro Version 6.37. Images were reduced to *intensity vs. q* plots (line cuts) *via* integration of cake segments and analyzed using peak fitting in Origin Pro 2016. D-spacings were calculated using the equation $d = 2\pi/q$. Out-of-plane $(15^\circ > \chi > 0^\circ)$ and in-plane $(85^\circ > \chi > 70^\circ)$ line cuts for G2-, G3-, G4-, and BOE-DMP were corrected for detector geometry and film thickness (measured using Bruker Dektak XT profilometer). Out-of-plane $(0^\circ > \chi > -15^\circ)$ and inplane $(85^\circ > \chi > 70^\circ)$ line cuts of the OH-DMP sample were arbitrarily normalized, as this film was collected under a slightly different geometry at a different beamline. Irrespective of the normalization, the peaks identified integrated intensity profile provides information about the lattice spacing. For all GIWAXS patterns, intensity is represented on a linear scale.



Figure S17. Representative GIWAXS patterns for ProDOT copolymer films cast on polished Si wafers. Casting method (*blade* or *spray* coating) is indicated in white text. a) G3-DMP, blade coated, b) G3-DMP, spray coated, c) G2-DMP, spray coated, d) G4-DMP, blade coated, e) BOE-DMP, blade coated, f) OH-DMP, blade coated. Scattering intensities are represented on a linear

color scale, with red representing the greatest scattering intensity. Red line in panel f is a detector artifact.

GIWAXS was performed on neat ProDOT copolymer films cast on Si wafers to better understand the extent of ordering in the materials. All polymers were blade coated from chloroform solutions, except for G2-DMP. Due to the poor solubility of G2-DMP, this material could not be dissolved at concentrations required to fabricate comparable films by blade coating. Accordingly, GIWAXS samples of G2-DMP were spray cast from dilute chloroform solutions. In films, the microstructure does not seem to depend on the processing method. The scattering patterns of sprayand blade-coated films of polymer G3-DMP are strikingly similar (**Figure S17**). For G2-DMP, spin-coating and spray-coating from chloroform also yields identical scattering patterns (**Figure S17**). Therefore, we assume that processing effects are minimal, especially because the processing solvent, film thicknesses, and solution ages were identical.

Polymer	Casting	d (020)	Std. Error	d (100)	Std. Error
	method	(Å)	(Å)	(Å)	(Å)
G2-DMP	Spray	3.99	0.01	20.98	0.01
G3-DMP	Spray	3.94	0.03	21.13	0.38
G3-DMP	Blade	4.03	0.02	22.53	0.05
G4-DMP	Blade	4.01	0.02	23.10	0.08
BOE-DMP	Blade	4.26	0.03	21.41	0.05
OH-DMP	Blade	4.02	0.02		

Table S1. Estimated lattice spacing for polar-functionalized ProDOT copolymers extracted from out-of-plane GIWAXS line-cuts. Uncertainties represent standard error of at least two separate films measurements.

Scattering in the q_z direction at low q (0.3–0.4 Å⁻¹) is attributed to the lamellar stacking (100) direction and corresponds to the distance between adjacent polymer chains. Across the G*x*-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 PEO unit is approximately 3.5 Å (depending on the conformation/solvation),^{12,13} this change in d(100) is a bit smaller than anticipated, likely due to the side chain tilt angle and/or conformational differences in the solid state. OH-DMP shows the smallest lamellar spacing, which likely arises from the reduced side chain length.

Conversion of BOE-DMP to OH-DMP is associated with the emergence of a prominent peak at higher q in the out-of-plane direction ($q_z \approx 1.6 \text{ Å}^{-1}$), which we speculatively attribute to possible π -stacking (020) that results from the removal of side chain. However, further studies would need to be performed to prove this. Upon side chain removal, the lamellar spacing (100) decreases from 21.4 Å in BOE-DMP to 15.0 Å in OH-DMP (Table S1). The magnitude of the lamellar spacing in OH-DMP is a bit larger than anticipated considering the expected size of the propylene bridge and side chains combined. Without further studies, we cannot definitively understand why the OH-DMP has a lamellar spacing 15.0 Å. However, we speculate that this could be attributed to the presence of uncleaved side chains expanding the lamellar structure and/or increased void volume in the film. These materials are predominantly amorphous in the as-cast state. If substantial ordering is induced by doping, as has been shown to occur for other materials, ¹⁴⁻¹⁶ more substantial differences might be observed in the scattering patterns of electrochemically conditioned or doped films. However, considering that X-ray methods only probe regions with enough coherence for appreciable diffraction, it is important to note that these methods would still fail to characterize amorphous domains of the film, which play a substantial role in the redox process, especially for regulating ion transport.

5. Spectroscopic Characterization



5.1. UV-Vis-NIR absorbance spectroelectrochemistry

Figure S18. UV-Vis-NIR steady-state absorbance spectra for voltages from -0.3/-0.4 V to +0.8 V vs. Ag/AgCl in 0.1 V increments of as-spray-cast a) OH-, b) G2-, c) G3-, d) G4-DMP on ITO/glass (degassed 0.1 M NaCl/H₂O).



Figure S19. Evolution of the steady-state absorbance upon electrochemical doping from -0.6 V to +0.8 V ($\Delta V = +0.1$ V) vs. Ag/AgCl at 550 nm, 900 nm, and 1300 nm respectively for a) OH-, b) G2-, c) G3-, d) G4-DMP (degassed 0.1 M NaCl/H₂O electrolyte).



Figure S20. Evolution of the steady-state absorbance upon electrochemical doping from -0.6 V to +0.8 V ($\Delta V = +0.1$ V) vs. Ag/AgCl at 620 nm, which is attributed to the 0-0 vibronic transition of the neutral state (degassed 0.1 M NaCl/H₂O electrolyte).



Figure S21. UV-Vis-NIR absorbance spectra of thin polymer films cast on ITO/glass, showing as-cast BOE-DMP (black, dry and pristine film before any base treatment), post-hydrolysis OH-DMP (red, dry film immediately after hydrolysis), and conditioned OH-DMP (blue, in degassed 0.1 M NaCl/H₂O electrolyte and held at a dedoping voltage of -0.4 V vs. Ag/AgCl).



Figure S22. Normalized UV-Vis-NIR absorbance spectra of G3-DMP films cast on ITO/glass by blade and spray coating. Spectra were recorded when steady state is reached (~30 s) upon biasing at -0.8 V vs. Ag/AgCl in degassed 0.1 M NaCl/H₂O electrolyte.



Figure S23. UV-Vis-NIR steady-state absorbance spectra for BOE-DMP films coated on ITO/glass upon electrochemical doping in a 0.1 M NaCl/H₂O electrolyte, showing irreversibility of the dedoping reaction (red line) after oxidation to +1.0 V vs. Ag/AgCl (line gray line). Pink text highlights the discontinuity at 800 nm due to a change in diffraction grating within the spectrophotometer.
5.2. ATR-FTIR

ATR-FTIR was recorded on a Shimadzu Prestige Infrared Spectrometer using solid polymer samples. BOE-DMP was blade coated onto an ITO/glass substrate and hydrolyzed to OH-DMP (described above in **Section 2.4**). The product OH-DMP polymer was scraped from the electrode and dried under vacuum prior overnight prior to FTIR analysis.



Figure S24. ATR-FTIR spectra of BOE-DMP and OH-DMP thin films (*i.e.*, before and after saponification by base treatment, cf. **Section 2.4**).

6. pOECT devices

6.1. Fabrication

First, ultra-flat quartz-coated glass substrates (S151, Ossila) were cleaned by sequential sonication in 2% Hellmanex III, bi-distilled H₂O, acetone, and isopropyl alcohol (10 min each), followed by UV/O₃ cleaning (30 min). Pre-patterned Cr/Au (10 nm/ 60 nm) electrodes were deposited by thermal evaporation (0.2 Å s⁻¹/ 1.0 Å s⁻¹) onto the cleaned substrates to form the source (S) and drain (D) electrodes. All polymers were dissolved at 20 mg/mL in room temperature chloroform by stirring in a closed vial overnight. Planar organic electrochemical transistors

(pOECT) were fabricated by spin-coating the resulting polymer solution in two subsequent steps (where the first consisted of a ramp to 2000 rpm for 2 s followed immediately by a 1000 rpm hold for 60 s) in ambient conditions onto the S and D electrodes. No post-deposition treatment was performed. The stock solutions were diluted stepwise from 20 to 3 mg/mL to achieve pOECTs with varying thicknesses. A square channel was then defined by removing excess polymer from the S and D electrodes by gently wiping with a high-precision micro-cleaning cleanroom swab (C201, Ossila). The channel width (W), length (L) and the overlap of the polymer with the SD contacts (SD overlap) were estimated from a photograph using ImageJ software. Prior sample encapsulation, the dry absorbance and thickness of some samples were measured to establish a calibration curve (details in subsection **6.2**). All parameters (W, L, SD overlap, and film thickness (d)) are summarized in **Table S2** and **Table S3** for each device. The pOECT devices were completed by encapsulating the sample in a hermetic cell together with a Ag/AgCl quasi-reference pellet electrode (Warner Instruments) and filled with Ar-degassed 0.1 M NaCl electrolyte in bi-distilled H₂O.

6.2. Thickness-absorbance calibration curve

An accurate determination of the film thickness is paramount as the μ C* product directly scales with the thickness d. Therefore, we made a thickness-absorbance calibration curve to decrease errors associated with thickness determination. The Vis-NIR absorbance spectra of dry films were acquired using a halogen lamp (HL-2000), a Vis-NIR spectrophotometer (Flame Vis-NIR), and an NIR spectrophotometer (Flame NIR) from Ocean Insight. The beam spot was roughly of 1 mm in diameter. The blank quartz-coated glass substrate was used as background and subtracted from the sample spectra. The relative Vis-NIR absorbance spectra are shown in **Figure S25**a, and highlight the different thicknesses obtained by solution dilution. While the dry G2-DMP spectrum exhibits a Gaussian-like absorbance profile centered at 550 nm without vibronic features (likely because it is partially doped in ambient conditions in the as-cast state, as indicated by the broad absorbance band around 900 nm), G3- and G4-DMP show a shoulder centered around 600 nm. We tentatively assign this shoulder to the 0-0 vibronic transition. A more pronounced 0-0 transition relative to the 0-1 transition (around 550 nm) is typically associated with greater J-type

aggregation. Assuming similar extents of H-aggregation, the enhanced 0-0 transition is commonly associated with greater ordering in conjugated polymer films. ¹⁷ For these materials, the 0-0 vibronic transition is more pronounced for thinner films (**Figure S25**b). One potential explanation for this trend is that superior ordering is afforded by less entangled polymer chains in more dilute solutions, which were used to spin cast the thinner films. Alternatively, another possible explanation is that there is greater ordering caused by interactions with the substrate surface, which would have a stronger influence for thinner films, as the interfacial region constitutes a greater proportion of the film. To account for this difference in the calibration curve (**Figure S26**), the "max absorbance" for G2-DMP is the absorbance at 550 nm, while for G3- and G4-DMP it is the average of the absorbances at 550 nm and 600 nm.



Figure S25. a) Relative and b) normalized Vis-NIR absorbance spectra of dry as-spin cast films of G2-, G3- and G4-DMP polymers from left to right.

Then, the thicknesses of the corresponding dry films were measured using a Bruker Contour GT-K optical profiler using light interferometry (green light, PSI mode) controlled by Vision 64 software. Each value considered for the calibration curve is the average of 4+ thickness measurements (4+ points on each film). The results are given in **Figure S26**. The linear fits of the data show high R^2 values, superior to 0.99, which validates the determination of the thickness.



Figure S26. Thickness-absorbance calibration curve of dry as-spin cast films of G2-, G3- and G4-DMP polymers from left to right.

6.3. Chronoamperometry coupled with Vis-NIR spectroelectrochemistry

Before performing chronoamperometry measurements, fresh devices were switched ON and OFF three times to condition the films using voltage pulses of square wave voltage of +0.8 V (dwell time = 5 s) and -0.5 V (dwell time = 30 s) with SD short-circuited. Note that for chronoamperometry, SD contacts were short-circuited to avoid doping inhomogeneity along the channel. Therefore, the voltage sign is based on the analytical electrochemistry configuration where the quasi-reference Ag/AgCl is grounded (*i.e.*, positive voltage induces p-doping). The voltage was applied using a data acquisition system (USB-6211 from National Instrument Corp.). To increase time-resolution, the resulting current was not measured with a Keithley but first converted into a voltage using a low-noise current preamplifier (SR570 from Stanford Research Systems, sensitivity 100 μ A V⁻¹) and measured with the USB-6211 acquisition system, thereby affording a time-resolution of 8 μ s. The voltage was increased from -0.1 V to +0.8 V by steps of 0.1 V. Each step was held for 10 s (dwell time) to ensure the steady-state was reached (Figure S28). After each voltage step, a shutter opens for about one second to record a steady-state absorbance spectrum (instrument detailed in subsection 6.2) before the shutter closes again (Figure S29). The current was recorded in dark conditions to prevent the photo-generation of charges. A blank pre-patterned pOECT substrate was recorded in the same conditions. The

resulting current is shown in **Figure S27**a. By integrating the current over time, we evaluated the charge involved in the electrochemical double-layer at the interface of the SD (working) electrodes (**Figure S27**b). This number was then subtracted to the device data to obtain the total injected charge without contribution from background charging current (**Figure S30**). The total injected charges are converted into volumetric capacitances by dividing by the total film volume and the voltage applied (here 0.1 V) *i.e.*, $C^* = \frac{q}{volume \cdot \Delta V}$. The volumetric capacitance was measured for varying film dimensions (varying the thickness, the channel dimension, and the SD overlap). No significant dimension-dependence was found (**Figure S32**). The length of side chain also has little impact on C* extracted from chronoamperometry, in accordance with EIS data (**Figure 2**b).



Figure S27. a) Time-resolved evolution of the current of a blank pOECT (*i.e.* no polymer coating) in degassed 0.1 M NaCl/H₂O electrolyte. b) Integrated current over time. The dotted black lines correspond to linear fits of the data points between 8 and 10 s, used to remove the steady component after reaching steady-state (leakage current). The intercept of the fit with the y-axis gives the number of charges involved in the double-layer formation at the interface of the SD electrodes upon voltage application (~ 2 μ C at -0.1 V up to 17 μ C at +0.8 V vs. Ag/AgCl). These values are subtracted to the integrated I_{GS} current of the data.



Figure S28. a) Time-resolved evolution of the current of G2-DMP (top, green), G3-DMP (middle, purple) and G4-DMP (bottom, orange,) in pOECTs of similar film volume in degassed 0.1 M NaCl/H₂O electrolyte. The inset number represents the total film volume. b) Integrated current over time. The dotted black lines correspond to linear fits of the data points between 8 s and 10 s, which were used to remove the steady component after reaching steady state (leakage current). The intercept of the fit with the y-axis gives the number of injected charges upon voltage application. Note that these charges are not solely contributing to Faradaic current but also to capacitive current leading to an overestimation of C*. The total injected charge corrected for the blank sample (**Figure S27**) are reported in **Figure S30** and **Table 2**.



Figure S29. Vis-NIR steady-state absorbance spectra from -0.1 V to +0.8 V vs. Ag/AgCl in 0.1 V increments for a) G2-DMP, b) G3-DMP, and c) G4-DMP pOECTs (degassed 0.1 M NaCl/H₂O). The inset number represents the total film volume in 10^{-4} mm³. Analysis is given in caption of **Figure S18**. All samples behave similarly confirming that steady-state was reached during chronoamperometry measurements (*i.e.*, the dwell time was long enough). As a result, the comparison of the volumetric capacitance extracted for each film is relevant as they all reach similar doping extent despite different film volume.



Figure S30. Results of chronoamperometry measurements, corrected for pOECT substrate background noise, for a) G2-DMP, b) G3-DMP, and c) G4-DMP. Inset: total film volume in 10⁴ mm³. The total injected charge (q) result from the integration over time of the total induced current over voltage steps ΔV of 0.1 V. Volumetric capacitance is calculated from $C^* = \frac{q}{volume \cdot \Delta V}$. Note that maximum C* is reached at +0.4 V vs. Ag/AgCl in accordance with EIS data (**Figure 2**b). The corresponding values are reported in **Table S2** and **Table 1**. Similar voltage-dependence between chronoamperometry and EIS data is also globally observed.



Figure S31. Cumulative injected charge for a) G2-DMP, b) G3-DMP, and c) G4-DMP. Following the procedure reported in literature, ¹⁸ an average C* over the doping voltage range is extracted from a linear fit (from +0.2 V to +0.7 V). The corresponding values are reported in **Table S2**. The numbers inset at the top left corner of each plot represents the average C* over doping range,

Polymer	d (nm)	W (mm)	L (mm)	SD overlap (%)	Total volume (10 ⁻⁴ mm ³)	C* _{pOECT} at +0.4 V (F cm ⁻³)	C* _{pOECT} from fit (F cm ⁻³)
G2-DMP	107 ± 20	5.3	2.0	25	14.18	213	182±9
	95 ± 9	5.4	1.0	146	12.62	175	148 ± 5
	55 ± 4	5.0	2.0	86	10.23	248	198 ± 9
	59 ± 8	5.2	2.0	33	8.16	242	185 ± 14
	41 ± 1	2.8	2.0	76	4.04	259	179 ± 10
G3-DMP	58 ± 3	5.3	1.0	183	8.70	217	172 ± 6
	72*	2.3	2.0	94	6.43	220	181 ± 10
	45 ± 2	5.1	1.0	131	5.30	210	140 ± 8
	29 ± 1	4.7	1.0	171	3.69	211	139 ± 8
G4-DMP	$102\pm\!11$	2.4	2.0	66	8.13	208	167 ± 6
	56 ± 1	4.9	1.0	175	7.55	233	179 ± 5
	32 ± 1	5.2	2.0	89	6.29	210	177 ± 10
	55 ± 1	2.9	2.0	73	5.52	202	137 ± 9

corresponding capacitance, $R^2 > 0.98$ showing reasonable fit quality. Numbers inset at the bottom right of each pot represent total film volume in 10^{-4} mm³.

Table S2. Geometric factors and performance of the pOECTs used to determine C^*_{pOECT} . d is the thickness, averaged over 4+ measurements. The error given represents one standard deviation. *Thickness deduced from the calibration curve. Total volume = d*L*W*(1+overlap/100). ' C^*_{pOECT} at +0.4 V' extracted from **Figure S30** and ' C^*_{pOECT} from fit' extracted from **Figure S31**.



Figure S32. Volumetric capacitance as a function of film volume, showing no significant dimension dependence. The final C^*_{pOECT} extracted from chronoamperometry for each polymer a) at +0.4 V and b) from a linear fit in the doping region result from the averaging of 4+ samples.

These chronoamperometry results show a three-fold increase in C^* when compared to the EIS data. We note four possible contributions to this observed discrepancy. (i) It is known that the C^* value extracted from chronoamperometry includes contributions from both non-Faradaic double-layer charging and Faradaic currents. However, the double-layer charging current is expected to be much smaller than the Faradaic contribution. Thus, we do not believe this to be a significant factor. (ii) In contrast to the films measured by EIS, the *in-situ* chronoamperometry experiments were performed on spin-coated films, which has been previously shown to increase the capacitance of ProDOT copolymer relative to blade-coating.¹⁹ (iii) The electrochemical cell architecture, including the working electrode and polymer-electrode interface, are significantly different between the EIS (blade/spray coated on ITO working electrode, please see the Experimental Section for details) and *in-situ* chronoamperometry (spin coated on gold working

electrodes where S/D short-circuited in pOECT setup, as described in section **6.1** of the SI). Further investigation into how pOECT channel geometries might affect the volumetric capacitance would be valuable. (iv) Differences in methods for thickness measurements between EIS (profilometry on dry, dedoped films after biasing in electrolyte) and *in-situ* chronoamperometry (interferometry on dry, dedoped films prior to biasing, see section **6.2** of the SI) could also contribute to these measured differences. Note, we do not believe this to be a major contributor considering the gravimetric capacitance measured in CV was comparable to that of the EIS data. Each of these four factors would increase the C^* measured in chronoamperometry; however, we believe the differences in casting methods and electrochemical cell architecture to be the main reasons for the discrepancy.

6.4. Transfer characteristics

Before measuring the transfer characteristics, fresh devices were switched ON and OFF three times to condition the films using V_{GS} pulses of square wave voltage of -0.8 V (dwell time = 5 s) and +0.5 V (dwell time = 30 s) with SD short-circuited. V_{GS} and V_{DS} voltages were applied using a data acquisition system (USB-6211 from National Instrument Corp.) and the resulting I_{DS} current was recorded with a Keithley 2400 SMU (Tektronix). V_{GS} was swept back and forth from +0.1 V to -0.8 V to +0.1 V at 5 mV s⁻¹. V_{DS} was fixed at -0.6 V prior to applying V_{GS} . Note that here the voltage sign is based on the transistor configuration where the source is grounded (*i.e.*, negative V_{GS} induces doping).



Figure S33. Transfer characteristics for pOECTs in degassed 0.1 M NaCl/H₂O electrolyte for a) G2-DMP, b) G3-DMP, and c) G4-DMP. Transfer characteristics were recorded by sweeping V_{GS} at 5 mV s⁻¹ from +0.1 V to -0.8 V with fixed $V_{DS} = -0.6$ V. The distance in inset is the geometric factor Wd/L. g_m is calculated as the derivative of I_{DS} over V_{GS}. The arrows indicate the forward sweep.



Figure S34. Same data as Figure S33 but the square root of I_{DS} is plotted vs V_{GS} to accurately determine the threshold voltage V_{Th} according to $\sqrt{I_{DS}} = \sqrt{\frac{Wd}{2L}\mu C^*} \cdot (V_{Th} - V_{GS})$ in the saturation regime. V_{Th} is defined as the x-intercept of the dotted lines, which are linear fits of the forward $\sqrt{I_{DS}}$ between -0.55 V and -0.69 V, in accordance with the linear extrapolation method.²⁰



Figure S35. Transconductance values as a function of channel geometry (on a linear scale) and biasing parameters of G2-, G3-, and G4-DMP from left to right. Dashed lines are the linear fits y = ax, with intercept forced to be zero in accordance with theory. $[\mu C^*]_{pOECT}$ values are extracted from the slope of the linear fits. The error corresponds to one standard deviation.



Figure S36. Transconductance values as a function of channel geometry (on a linear scale) and biasing parameters of G2-, G3-, and G4-DMP from left to right. Dashed lines are the linear fits y = ax + b, with non-zero intercept ($b \neq 0$). [μC^*]_{pOECT} values are extracted from the slope of the linear fits. The error corresponds to one standard deviation.



Figure S37. Charge carrier mobility (μ) vs. volumetric capacitance (C^*) for published p-type OECT materials. Green, purple, and orange stars indicate the performance of G2-, G3-, and G4-DMP, respectively. All literature values for μ and C^* were adapted from Li *et al.*²¹



Figure S38. Same data as **Figure S33** but plotted on logarithmic y-scale to highlight the I_{ON}/I_{OFF} ratio achieved for each device. The distance in inset is the geometric factor Wd/L.

Polymer	d (nm)	W (mm)	L (mm)	Wd/ L (nm)	V _{Th} (V)	V _{GS} (V)	g _{m_max} (μS)	gmL/Wd (S cm ⁻¹)	I _{ON} /I _{OFF}
G2-DMP	192*	5.0	1.0	940	-0.35	-0.73	2650	27.6	$7 \ge 10^2$
	106 ± 16	2.7	2.0	143	-0.36	-0.78	560	39.1	2×10^3
	88 ± 5	2.7	2.0	119	-0.35	-0.78	370	31.1	3 x 10 ⁵
	40 ± 4	2.6	2.0	52	-0.33	-0.69	120	23.1	1 x 10 ⁵
G3-DMP	72*	3.0	2.0	108	-0.34	-0.78	290	26.9	2 x 10 ⁶
	55 ± 6	2.5	2.0	69	-0.35	-0.78	150	21.8	9×10^4
	40 ± 2	2.6	2.0	52	-0.35	-0.78	120	23.1	3 x 10 ⁵
_	31 ± 2	2.6	2.0	40	-0.35	-0.73	60	15.2	$6 \ge 10^4$
G4-DMP	135*	2.5	2.0	169	-0.37	-0.78	1500	88.9	1 x 10 ⁴
	102 ± 11	2.8	2.0	143	-0.34	-0.73	1060	74.2	6×10^2
	74 ± 7	2.6	2.0	94	-0.36	-0.78	740	78.4	2×10^3
	54 ± 0	2.8	2.0	74	-0.36	-0.78	530	71.4	3 x 10 ⁵
	32 ± 0	2.9	2.0	46	-0.37	-0.78	315	67.9	2 x 10 ⁶

Table S3. Geometric factors and performance of the pOECTs used to determine $[\mu C^*]_{pOECT}$. d is the thickness, averaged over 4+ measurements. The error given is one standard deviation. *Thickness deduced from the calibration curve. The threshold voltage V_{Th} is defined as the x-intercept of the linear extrapolation of the $\sqrt{I_{DS}}$ vs V_{GS} plot (**Figure S34**). V_{GS} is the voltage at the maximum transconductance g_{m_max} . The transconductance per cm g_mL/Wd is given to encourage material-material comparison. I_{ON} and I_{OFF} are defined as I_{max} and I_{min} respectively.

6.5. Time-resolved Vis-NIR spectroelectrochemistry

All time-resolved spectroelectrochemistry experiments were run on conditioned pOECTs after measuring their transfer characteristics. Prior to the experiment, the electrolyte in the cell was replaced with freshly degassed electrolyte and the device held at +0.5 V (dedoping voltage) until a steady dedoped state is reached. Source and drain contacts were short-circuited to avoid doping inhomogeneity along the channel (cf Z factor). Square-wave doping/dedoping voltage pulses were applied using a data acquisition system (USB-6211 from National Instrument Corp.) synchronized with the Vis-NIR spectrophotometers using LabVIEW program. The dedoping voltage was kept at +0.5 V for 30 s, while the doping voltages were decreased stepwise from +0.1 V to -0.8 V in 0.1 V increments, each held for 5 s (transistor configuration, where negative gate voltages result in polymer p-doping). Simultaneously, the Vis-NIR absorbance spectra were recorded continuously with a time-resolution of about 10 ms (instrument detailed in subsection 6.2). The doping/dedoping time constants were quantified by fitting respectively the normalized decay (Figure S40b) and the rise (Figure S40c) of the absorbance intensity at 550 nm (neutral band) with biexponentials. The data are normalized by setting the maximum to one. For all Gx-DMP, the doping process is about 100 times faster than the dedoping process for this device configuration (**Table S4**). Note that, for all devices, a delay ($Delay_{ON}$) was observed between the application of a doping voltage and the biexponential decay of the intensity at 550 nm. This delay was removed before fitting, as previously reported.²² The origins of this delay are mainly (i) the moving front of holes from the electrodes to the center of the channel where the probe beam is focused, which relates to the carrier mobility, (ii) progressive charge transfer between the doped and dedoped parts of the film, and (iii) the ion penetration through the bulk of the film to reach the short-circuited SD contacts to induce charge injection, (iv) the electrolyte polarization. As the beam is systematically centered on the same area for each film and the electrolyte polarization conditions (nature of the salt, concentration, gate-channel distance) are the same for all devices, we believe that comparing the delay for these measurements informs us about the carrier mobilities as well as charge transfer within the channel. We find that the time delay for G4-DMP is consistently shorter (Figure S41a),

in accordance with its faster doping time constant and higher μ , as determined previously by the pOECT results. The shorter delay for the G4-DMP may also suggest better charge transfer, charge transport, and/or a lower *iR* drop across the conducting portions of the film during the doping reaction. Note that no delay is observed for de-doping, where hole injection is not the limiting factor.



Figure S39. Comparison of the b) doping and c) dedoping kinetics of G2- (green), G3- (purple) and G4-DMP (orange) in pOECT devices in degassed 0.1 M NaCl/H₂O. Temporal evolution of the normalized absorbance at 550 nm, upon b) doping at +0.8 V and c) dedoping at -0.5 V. a) Same data than b) but with the delay removed to afford biexponential fitting (solid lines = fit, dotted lines = data points, see Delay_{ON} in **Table S4**).



Figure S40. Thickness dependence of b) doping and c) dedoping kinetics of G2- (top, green), G3- (middle, purple) and G4-DMP (bottom, orange) in pOECT devices in degassed 0.1 M NaCl/H₂O. Temporal evolution of the normalized absorbance at 550 nm, upon b) doping at +0.8 V and c) dedoping at -0.5 V. a) Same data than b) but with the delay removed to afford biexponential fitting (solid lines = biexponential fit, dotted lines = data points, see Delay_{ON} in **Table S4**). The results are compared in **Figure S41** and details of biexponential fits are given in **Table S5** for doping, and **Table S6** for dedoping.



Figure S41. Comparison of a) Delay_{ON}, which corresponds to the time before the exponential decay of the 550 nm absorbance intensity, and the averaged time constants b) τ_{ON} (+0.8 V) and c) τ_{OFF} (-0.5 V) for different channel thickness of G2- (green), G3- (purple) and G4-DMP (orange) in pOECT devices in degassed 0.1 M NaCl/H₂O. All values are reported in **Table S4**. The black arrows highlight the thickness-dependence trends.

Polymer	d (nm)	W (mm)	L (mm)	SD overlap (%)	Delay _{ON} (ms)	τ _{ΟΝ} (s)	τ _{OFF} (s)	r ² 0N	r ² off
G2-DMP	106 ± 16	2.7	2.0	70	220	0.070	5.72	0.999	0.998
	88 ± 5	2.7	2.0	95	160	0.052	5.91	0.999	0.998
	68 ± 3	2.6	2.0	90	255	0.034	5.98	0.998	0.998
	40 ± 4	2.6	2.0	72	230	0.063	6.13	0.996	0.999
G3-DMP	72*	3.0	2.0	88	210	0.065	7.91	0.997	0.999
	55 ± 6	2.5	2.0	86	110	0.041	6.87	0.995	0.998
	40 ± 2	2.6	2.0	88	110	0.042	6.97	0.995	0.998
	31 ± 2	2.6	2.0	88	185	0.054	7.93	0.996	0.999
G4-DMP	135*	2.5	2.0	86	170	0.047	6.11	0.997	0.998
	$102\pm\!11$	2.8	2.0	93	220	0.031	6.39	0.997	0.998
	74 ± 7	2.6	2.0	72	140	0.027	5.77	0.997	0.997
	54 ± 0	2.8	2.0	79	70	0.022	5.61	0.996	0.996
	32 ± 0	2.9	2.0	85	95	0.025	6.06	0.990	0.997

Table S4. Geometric factors and performance of the pOECTs used to determine the time constant τ . d is the thickness of dry film, averaged over 4+ measurements prior cell encapsulation. The error given is one standard deviation. *Thickness deduced from the calibration curve. Delay_{ON} corresponds to the time before the exponential decay of the 550 nm intensity which was removed to fit the data. τ_{ON} and τ_{OFF} are the averaged time constants of the biexponential fit of the decay at

+0.8 V (doping, ON) and rise at -0.5 V (dedoping, OFF) of the neutral species (wavelength sampling at 550 nm) respectively. The high $r^2 > 0.995$ obtained demonstrate the fit quality. The samples referred to in main text (**Figure 5**b) are highlighted in bold. Delay_{ON}, τ_{ON} and τ_{OFF} are compared graphically for increasing thickness in **Figure S41**.

Polymer	d (nm)	Delay _{ON} (ms)	$ au_{\mathrm{ON}}(\mathbf{s})$	$ au_{1}\left(s ight)$	A1(%)	$ au_{2}\left(s ight)$	A ₂ (%)	y0 (%)	r ² 0N
G2-DMP	106 ± 16	220	0.070	0.031	71	0.165	29	17	0.999
	88 ± 5	160	0.052	0.025	80	0.155	20	18	0.999
	68 ± 3	255	0.034	0.021	96	0.315	4	13	0.998
	40 ± 4	230	0.063	0.063	100	-	-	9	0.996
G3-DMP	72*	210	0.065	0.054	99	0.817	1	12	0.997
	55 ± 6	110	0.041	0.019	89	0.212	11	20	0.995
	40 ± 2	110	0.042	0.027	93	0.241	7	21	0.995
	31 ± 2	185	0.054	0.039	80	0.114	20	-1	0.996
G4-DMP	135*	170	0.047	0.026	85	0.157	15	19	0.997
	102 ± 11	220	0.031	0.020	97	0.347	3	20	0.997
	74 ± 7	140	0.027	0.022	97	0.202	3	19	0.997
	54 ± 0	70	0.022	0.009	87	0.108	13	25	0.996
	32 ± 0	95	0.025	0.015	87	0.095	13	16	0.990

Table S5. Details of the biexponential fit $(y = A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}} + y_0)$ of the decay at +0.8 V of the neutral species shown in **Figure S40** (normalized absorbance at 550 nm, doping). τ_{ON} is the

averaged time constant ($\tau_{ON} = \tau_1 * A_1(\%) + \tau_2 * A_2(\%)$). The high $r^2_{ON} > 0.990$ obtained demonstrate the satisfying fit quality.

Polymer	d (nm)	$ au_{OFF}\left(s ight)$	$\tau_{1}^{}\left(s\right)$	A ₁ (%)	$\boldsymbol{\tau}_{2}\left(\boldsymbol{s}\right)$	A ₂ (%)	y0 (%)	r² _{OFF}
G2-DMP	106 ± 16	5.72	0.765	50	10.7	50	102	0.998
	88 ± 5	5.91	0.765	50	11.0	50	102	0.998
	68 ± 3	5.98	0.738	49	11.0	51	102	0.998
	40 ± 4	6.13	1.07	46	11.9	54	103	0.999
G3-DMP	72*	7.91	1.14	43	13.0	57	105	0.999
	55 ± 6	6.87	0.932	46	11.9	54	103	0.998
	40 ± 2	6.97	0.945	45	11.9	55	103	0.998
	31 ± 2	7.93	1.15	41	12.7	59	104	0.999
G4-DMP	135*	6.11	0.772	49	11.2	51	102	0.998
	102 ± 11	6.39	0.788	47	11.5	53	102	0.998
	74 ± 7	5.77	0.700	50	10.9	50	102	0.997
	54 ± 0	5.61	0.640	49	11.1	51	102	0.996
	32 ± 0	6.06	0.778	49	11.1	51	102	0.997

Table S6. Details of the biexponential fit $(y = -A_1 e^{-\frac{x}{\tau_1}} - A_2 e^{-\frac{x}{\tau_2}} + y_0)$ associated with the rise of the neutral species at -0.5 V shown in **Figure S40** (normalized absorbance at 550 nm, dedoping). τ_{OFF} is the averaged time constant ($\tau_{OFF} = \tau_1 * A_1(\%) + \tau_2 * A_2(\%)$). The high $r_{\text{OFF}}^2 > 0.996$ obtained demonstrates the adequate fit quality.

7. iOECT devices

7.1. Fabrication

Interdigitated organic electrochemical transistors (iOECTs) were fabricated by blade- or spray-coating polymer films onto interdigitated platinum electrodes obtained from MicruX Technologies (electrode model ED-IDE1-Pt with 90 pairs of interdigitated electrode fingers, 10 μ m arm length, 10 μ m electrode length, Pt thickness \approx 150 nm, active area = 9.6 mm², average width \approx 2.75 mm). Thickness values of dry, de-doped films were measured using a Bruker Dektak XT profilometer. Film thickness values ranged from 80–300 nm. Prior to device testing, excess polymer was removed from the electrode by gently wiping with a cotton swab.

7.2. Device Parameters and Characteristics

Contacts to the source and drain electrodes were made using an MicruX-AIO batch cell testing platform. The batch cell was filled with 1X PBS (pH=7.4, Sigma Aldrich) dissolved in ultrapure water (18.2 M Ω ·cm). A AgCl coated Ag wire was suspended in the electrolyte solution and used as a gate electrode. The cell was connected to an 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). One of the Pt pads (source) was set to the ground unit of the Agilent E5263A, while the other planar Pt pad (drain) was connected to the Agilent E5290A. The Ag/AgCl wire (gate) was connected to the Agilent E591A.

For device testing, transistor characteristics were collected using a Keysight Easy Expert software with a custom I/V sweep configuration. Devices were tested under ambient conditions. Data were collected for at least three separate devices to ensure reproducibility. Error bars represent the standard deviation for the characteristics extracted from these devices. Representative output curves were collected with a V_{DS} step size -1 mV, a delay time of 0.02 s, and a hold time of 3s, scanning V_G every -50 mV and starting in the de-doped "off" state. Representative transfer curves were collected using a V_{DS} = -0.6 or -0.7 V, with a hold time of 3 s, a delay time of 0.02s, and a V_{GS} step size of -1 mV (equivalent to 50 mV s⁻¹), starting in the de-doped "off" state. The peak transconductance (g_m) was calculated by differentiating the transfer curve with respect to the gate voltage. Representative transfer and output curves are shown below.



Figure S42. Example iOECT characteristics for G3-DMP. a) Transfer curves ($V_{DS} = -0.6 V$) showing source-drain current (solid black line) and transconductance (dashed green line). b) Transfer characteristics on logarithmic scale, showing gate current (solid black line) superimposed on drain current (solid green line). c) Output characteristics for various gate voltages. Scan directions are indicated by arrows in all plots.



Figure S43. Example iOECT characteristics for G3-DMP. a) Transfer curves ($V_{DS} = -0.7 V$) showing source-drain current (solid black line) and transconductance (dashed purple line). b) Transfer characteristics on logarithmic scale, showing gate current (solid black line) superimposed

on drain current (solid purple line). c) Output characteristics for various gate voltages. Scan directions are indicated by arrows in all plots.



Figure S44. Example iOECT characteristics for G4-DMP. a) Transfer curves ($V_{DS} = -0.7 V$) showing source-drain current (solid black line) and transconductance (dashed orange line). b) Transfer characteristics on logarithmic scale, showing gate current (solid black line) superimposed on drain current (solid orange line). c) Output characteristics for various gate voltages. Scan directions are indicated by arrows in all plots.

Polymer	d (nm)	Wd/L (mm)	V _{Th} (V)	V _{GS} (V)	gm_max (mS)	g _m L/Wd (S cm ⁻¹)	Apparent μC* ^{<i>a</i>} (F cm ⁻¹ V ⁻¹ s ⁻¹)
G2-DMP	210	5.20	-0.25	-0.63	28	0.054	0.14
	177	4.38	-0.28	-0.59	21	0.048	0.15
	221	5.47	-0.30	-0.65	30	0.055	0.14
G3-DMP	175	4.33	-0.06	-0.56	27	0.062	0.15
	163	4.03	-0.15	-0.56	28	0.069	0.17
	184	4.55	-0.07	-0.55	31	0.068	0.16
	172	4.26	-0.02	-0.53	24	0.056	0.14
	167	4.13	-0.25	-0.65	27	0.065	0.16
G4-DMP	195	4.83	-0.12	-0.59	39	0.081	0.18
	181	4.48	-0.10	-0.55	22	0.049	0.11
	169	4.18	-0.05	-0.49	37	0.088	0.20
	173	4.28	-0.08	-0.58	20	0.047	0.09

^aNote these entries are provided only to demonstrate what μC^* values would be obtained if improperly applying Equation (1) in the main text to iOECT data.

Table S7. Tabulated device data for ProDOT-based interdigitated iOECTs. Note that all devices have a channel length $L=10 \mu m$ and total width W=(90)*(2.75 mm)=247.5 mm.

7.3. Active Layer Delamination

As stated in the main text, neat films of OH-DMP could not be incorporated into iOECT devices due to persistent delamination from the device substrates. We hypothesize that the delamination could be related to the relatively hydrophobic SU-8 passivation layer around the interdigitated electrodes. Most delamination was observed upon rinsing the film to remove excess KOH and hydrolyzed side chain after the saponification process. Delamination issues were not resolved by processing with various treatments, including pre-treating the surface with UV-Ozone (10 minutes), hydrolyzing the film in an unstirred bath, or pre-treating the electrode with an alkyl phosphonic acid SAM. To circumvent the delamination issues, we incorporated 20 wt.% (relative to BOE-DMP) of an epoxide-based crosslinking agent to the precursor BOE-DMP casting solution prior to film formation. This crosslinking agent, commonly known as GOPS (3-glycidyloxypropyl)trimethoxysilane, Sigma Aldrich), is frequently used to prevent the dispersion of PEDOT:PSS in aqueous OECTs. While the mechanism of crosslinking is not entirely known, it is hypothesized that GOPS crosslinks through sulfonate groups on PEDOT:PSS.¹⁰ While OH-DMP has no sulfonate groups for crosslinking, it is conceivable that the hydroxyl group could add to the unreacted epoxide in GOPS, thereby participating in the crosslinking process.

The resulting film did not delaminate in water, suggesting that the addition of GOPS helped to stabilize the OH-DMP film. However, devices fabricated with OH-DMP+GOPS mixture performed much worse than the Gx-DMP analogues, showing reduced transconductance value for comparable film thickness and device geometry (see **Figure S44** below). In principle, this could be due to the addition of electrochemically inactive GOPS to the film, which would likely lower both C* and μ . Addition of GOPS in similar amounts has been shown to significantly reduce μ of PEDOT:PSS active layers.²³ Accordingly, we were unable to properly characterize the OECT characteristics of OH-DMP, given the drastic influence the GOPS likely had on the material properties. Therefore, we were unable to effectively benchmark OH-DMP as an OECT channel active material. Further efforts ought to be directed at interfacial stabilization for adequate device preparation.



Figure S45. Example iOECT characteristics for OH-DMP (+20 wt% GOPS). a) Transfer curves $(V_{DS} = -0.6 \text{ V})$ showing source-drain current (solid black line) and transconductance (dashed blue line). b) Transfer characteristics on logarithmic scale, showing gate current (solid black line) superimposed on drain current (solid blue line). c) Output characteristics for various gate voltages. Scan directions are indicated by arrows in all plots. The active layer thickness was measured to be 210 nm by profilometry.

References

- Savagian, L. R.; Österholm, A. M.; Ponder, J. F.; Barth, K. J.; Rivnay, J.; Reynolds, J. R. Balancing Charge Storage and Mobility in an Oligo(Ether) Functionalized Dioxythiophene Copolymer for Organic- and Aqueous- Based Electrochemical Devices and Transistors. *Adv. Mater.* 2018, 30, 1804647.
- (2) Österholm, A.; Ponder, J.; De Keersmaecker, M.; Shen, D.; Reynolds, J. Disentangling Redox Properties and Capacitance in Solution-Processed Conjugated Polymers. *Chem. Mater.* 2019, 31 (8), 2971–2982.
- (3) Reeves, B. D.; Grenier, C. R. G. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. Spray Coatable Electrochromic Dioxythiophene Polymers with High Coloration Efficiencies. *Macromolecules* 2004, 37 (20), 7559–7569.
- (4) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. Enhanced Contrast Ratios and Rapid Switching in Electrochromics Based on Poly(3,4-Propylenedioxythiophene) Derivatives. *Adv. Mater.* 1999, *11* (16), 1379–1382.
- (5) Ferloni, P.; Mastragostino, M.; Meneghello, L. Impedance Analysis of Electronically Conducting Polymers. *Electrochim. Acta* **1996**, 41 (1), 27–33.
- (6) Amemiya, T.; Hashimoto, K.; Fujishima, A. Dynamics of Faradaic Processes in Polypyrrole/Polystyrenesulfonate Composite Films in the Presence and Absence of a Redox Species in Aqueous Solutions. J. Phys. Chem. 1993, 97, 4192-4195.
- (7) Brug, G. J.; van den Eeden, A. L. G.; Sluyters-Rehbach, M.; Sluyters, J. H. The Analysis of Electrode Impedances Complicated by the Presence of a Constant Phase Element. *J. Electroanal. Chem.* 1984, 176 (1–2), 275–295.
- (8) Jović, V. D.; Jović, B. M. EIS and Differential Capacitance Measurements onto Single Crystal Faces in Different Solutions: Part I - Ag(111) in 0.01 M NaCl. J. Electroanal. Chem. 2003, 541, 1–11.

- (9) Moser, M.; Savagian, L. R.; Savva, A.; Matta, M.; Ponder, J. F.; Hidalgo, T. C.; Ohayon, D.; Hallani, R.; Reisjalali, M.; Troisi, A.; Wadsworth, A.; Reynolds, J. R.; Inal, S.; McCullough, I. Ethylene Glycol-Based Side Chain Length Engineering in Polythiophenes and its Impact on Organic Electrochemical Transistor Performance. *Chem. Mater.* **2020**, 32, 6618-6628.
- (10) Ilavsky, J. Nika: Software for Two-Dimensional Data Reduction. J. Appl. Crystallogr. 2012, 45 (2), 324–328.
- (11) Oosterhout, S. D.; Savikhin, V.; Zhang, J.; Zhang, Y.; Burgers, M. A.; Marder, S. R.; Bazan, G. C.; Toney, M. F. Mixing Behavior in Small Molecule:Fullerene Organic Photovoltaics. *Chem. Mater.* 2017, 29 (7), 3062–3069.
- (12) Mark, J. E.; Flory, P. J. The Configuration of the Polyoxyethylene Chain. J. Am. Chem. Soc. 1965, 87 (7), 1415–1423.
- (13) Oesterhelt, F.; Rief, M.; Gaub, H. E. Single Molecule Force Spectroscopy by AFM Indicates Helical Structure of Poly(Ethylene-Glycol) in Water. New J. Phys. 1999, 1, 6–6.
- (14) Pittelli, S. L.; De Keersmaecker, M.; Ponder, J. J.; Österholm, A. M.; Ochieng, M. A.; Reynolds, J. R. Structural Effects on the Charge Transport Properties of Chemically and Electrochemically Doped Dioxythiophene Polymers. *J. Mater. Chem. C* 2020, *8* (2), 683–693
- (15) Yee, P. Y.; Scholes, D. T.; Schwartz, B. J.; Tolbert, S. H. Dopant-Induced Ordering of Amorphous Regions in Regiorandom P3HT. J. Phys. Chem. Lett. 2019, 10 (17), 4929–4934.
- (16) Paulsen, B. D.; Wu, R.; Takacs, C. J.; Steinrück, H. G.; Strzalka, J.; Zhang, Q.; Toney, M. F.; Rivnay, J. Time-Resolved Structural Kinetics of an Organic Mixed Ionic–Electronic Conductor. *Adv. Mater.* 2020, 2003404, 1–7.
- (17) Yamagata, H.; Pochas, C. M.; Spano, F. C. Designing J- and H-Aggregates through Wave Function Overlap Engineering: Applications to Poly(3-hexylthiophene). J. Phys. Chem. B 2012, 116, 49, 14494-14503.
- (18) Rivnay, J.; Leleux, P.; Ferro, M.; Sessolo, M.; Williamson, A.; Koutsouras, D. A.; Khodagholy,
 D.; Ramuz, M.; Strakosas, X.; Owens, R. M.; Benar, C.; Badier, J.-M.; Bernard, C.; Malliaras, G.

G. High-performance Transistors for Bioelectronics Through Tuning of Channel Thickness. *Sci. Adv.* **2015**, 1, 4.

- (19) Padilla, J.; Osterholm, A. M.; Dyer, A. L.; Reynolds, J. R. Process controlled performance for soluble electrochromic polymers. *Sol. Energy Mater. Sol. Cells* **2015**, 140, 54-60.
- (20) Ortiz-Conde, A.; García-Sánchez, F. J.; Muci, J.; Barrios, A. T.; Liou, J. J.; Ho, C.-S. Revisiting MOSFET threshold voltage extraction methods. *Microelectron. Reliab.* 2013, 53, 90-104.
- (21) Li, P.; Lei, T. Molecular Design Strategies for High-performance Organic Electrochemical Transistors. *J. Polym. Sci.* **2022**, 60, 3, 377-392.
- (22) Flagg, L. Q.; Giridharagopal, R.; Guo, J.; Ginger, D. S. Anion-Dependent Doping and Charge Transport in Organic Electrochemical Transistors. *Chem. Mater.* **2018**, 30, 15, 5380-5389.
- (23) Håkansson, A.; Han, S.; Wang, S.; Lu, J.; Braun, S.; Fahlman, M.; Berggren, M.; Crispin, X.; Fabiano, S. Effect of (3-Glycidyloxypropyl)Trimethoxysilane (GOPS) on the Electrical Properties of PEDOT:PSS Films. *J. Polym. Sci.* **2017**, *55* (10), 814–820.