

Supporting Information

Designing Donor-Acceptor Copolymers for Stable and High-Performance Organic Electrochemical Transistors

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I. General Procedures and OECT Device Fabrication and Testing Procedures

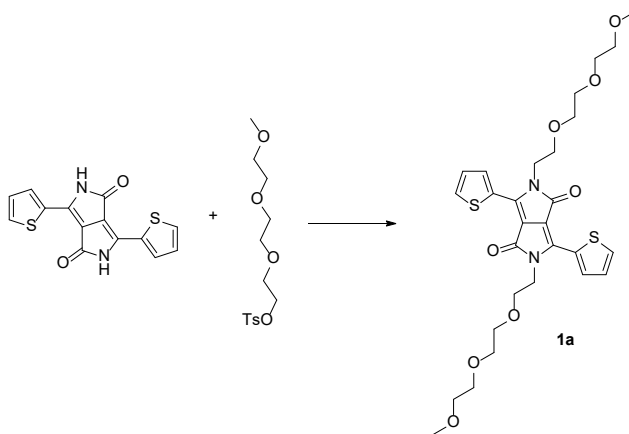
All reagents were purchased from the suppliers noted, and they were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 298 K using a Bruker ARX 400 or Bruker Avance-III-800 spectrometer with the materials dissolved in deuterated chloroform unless otherwise specified. Size exclusion chromatography (SEC) was performed either on a high-temperature size exclusion chromatography system at 150 °C using 1,2,4-trichlorobenzene (TCB) as the mobile phase or using tetrahydrofuran (THF) at 40 °C as the mobile phase with molecular weight values being based on polystyrene standards. Ultraviolet-visible-near infrared (UV-Vis-NIR) light spectra were measured with an Agilent Technologies Cary 6000i UV-Vis-NIR spectrophotometer ($350\text{ nm} \leq \lambda \leq 2000\text{ nm}$). Cyclic voltammetry (CV) was performed using a BioLogic SP-150 electrochemistry setup. 2D-grazing-incidence wide-angle X-ray scattering (GI-WAXS) measurements were carried out at Argonne National Laboratory. The PProDOT-DPP thin film used for the 2D GI-WAXS experiments reported here was prepared by spin-coating the PProDOT-DPP solution (10 mg mL^{-1} in CHCl_3) onto SiO_2 substrates at a rotational rate of 1,500 rpm.

OECTs based on PProDOT-DPP were fabricated using glass substrates (Dow Corning, $2 \times 2\text{ cm}^2$ in size). The glass substrates were cleaned with deionized (DI) water, ethanol, and acetone, in a sequential manner, and then dried in an oven for 30 min at $\sim 110\text{ }^\circ\text{C}$. Patterned Ti (5 nm)/Au (20 nm) source and drain electrodes were then thermally deposited onto the substrates using shadow masks, achieving channel length and width of 200 μm and 2,500 μm , respectively. The polymer, PProDOT-DPP, was dissolved in chloroform at a concentration of 10 mg mL^{-1} and stirred overnight, and it was then spin-coated onto the substrates at 1,500 rpm for 20 s. After the spin-coating process, the devices were placed in vacuum for 1 h to remove the residual solvents.

Afterwards, the OECT channels were covered by patterned polydimethylsiloxane (PDMS) masks to protect the channel areas, while unwanted PProDOT-DPP was etched by oxygen plasma (PE-25, Plasma Etch, Inc.) for 1 h, resulting in well-patterned PProDOT-DPP that was left only in the OECT channels.

During the electrical characterization of the OECTs, the OECT channels were surrounded by PDMS micro-wells to confine the liquid electrolytes. Lithium salts (LiCl or LiPF₆, Sigma-Aldrich) were dissolved in DI water at a concentration of 0.1 M such that they could serve as the electrolytes. The electrolytes were then placed in the PDMS wells using a pipette. The OECT electrical measurements were performed using a Keysight B2902, and an Ag/AgCl reference electrode was immersed in the electrolytes to serve as the gate electrode.

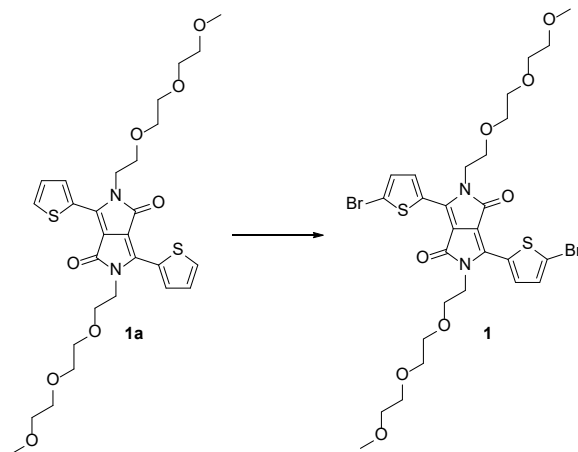
II. Synthetic Procedures



Compound 1a. 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1.00 g, 3.33 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (2.21 g, 7.32 mmol), and potassium carbonate (1.38 g, 9.99 mmol) were added to dimethylformamide (DMF, 50 mL). The mixture was heated to 100 °C and allowed to stir for 24 h under nitrogen. The reaction mixture was cooled, poured into water, extracted with dichloromethane (DCM), and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by silica

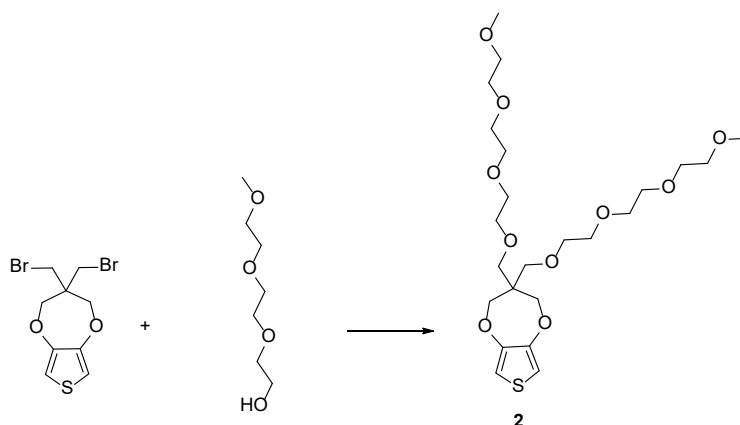
chromatography (CH₂Cl₂:Ethyl Acetate = 10:1) to give the product (**1a**) as a purple solid. (753mg, 38%) ¹H NMR (400 MHz, CDCl₃, ppm) δ: 8.74 (dd, *J* = 3.9, 1.2 Hz, 2H), 7.63 (dd, *J* = 5.0, 1.2 Hz, 2H), 7.24 (dd, *J* = 5.0, 3.9 Hz, 2H), 4.27 (t, *J* = 6.3 Hz, 4H), 3.79 (t, *J* = 6.3 Hz, 4H), 3.70 – 3.44 (m, 16H), 3.34 (s, 6H).

*Spectroscopic data are in agreement with previous literature.*¹



Compound 1. Compound **1a** (700 mg, 1.18 mmol) and *N*-bromosuccinimide (431 mg, 2.42 mmol) were added to 20 mL of chloroform. The mixture was stirred under N₂ at 60 °C for 1.5 h. After removal of the solvent under reduced pressure, the residue was purified by silica chromatography (CH₂Cl₂:Ethyl Acetate = 20:1) to give the product (**1**) as a dark purple solid. (712 mg, 80%) ¹H NMR (400 MHz, CDCl₃, ppm) δ: 8.49 (d, *J* = 4.2 Hz, 2H), 7.21 (d, *J* = 4.1 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 4H), 3.89 – 3.41 (m, 20H), 3.35 (s, 6H).

*Spectroscopic data are in agreement with previous literature.*¹



Compound 2. 3,3-bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (5.00 g, 14.6 mmol), triethylene glycol monomethyl ether (7.20 g, 43.8 mmol), and sodium hydride (3.51 g, 60% dispersion in mineral oil) were added to 100 mL of dimethylformamide (DMF). The mixture was stirred under N₂ at room temperature for 30 min and then the temperature was raised to 100 °C. Then, the reaction was allowed to stir at this temperature for 12 h. The reaction mixture was cooled, extracted with DCM, and dried over Na₂SO₄. After removal of solvent under reduced pressure, the residue was purified by silica chromatography (CH₂Cl₂:Ethyl Acetate = 10:1) to give the product (**2**) as a near-colorless oil. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 6.44 (s, 2H), 4.01 (s, 4H), 3.66 – 3.51 (s, 28H), 3.37 (s, 6H).

*Spectroscopic data are in agreement with previous literature.*²

0.00071 mmol), pivalic acid (1.45 mg, 0.00142 mmol), potassium carbonate (8.50 mg, 0.0615 mmol), and 5 mL of dimethylacetamide (DMAc) were added. The resulting solution was bubbled with N₂ for 20 min, and the mixture was stirred at 130 °C under N₂ for 24 h. After the polymerization was complete, *N,N*-diethyl-2-phenyldiazenecarbothioamide was added, and the mixture was stirred for 30 min at 60 °C before being precipitated into hexanes. The solid was collected in a Soxhlet thimble, and it was then purified by Soxhlet extraction under N₂ using successive washes with hexanes, methanol, acetone, and chloroform. The collected polymer solution from the chloroform fraction was reprecipitated into hexanes and dried at 60 °C under vacuum, providing 69.8 mg (92% yield) of a black solid product.

III. Characterization Data

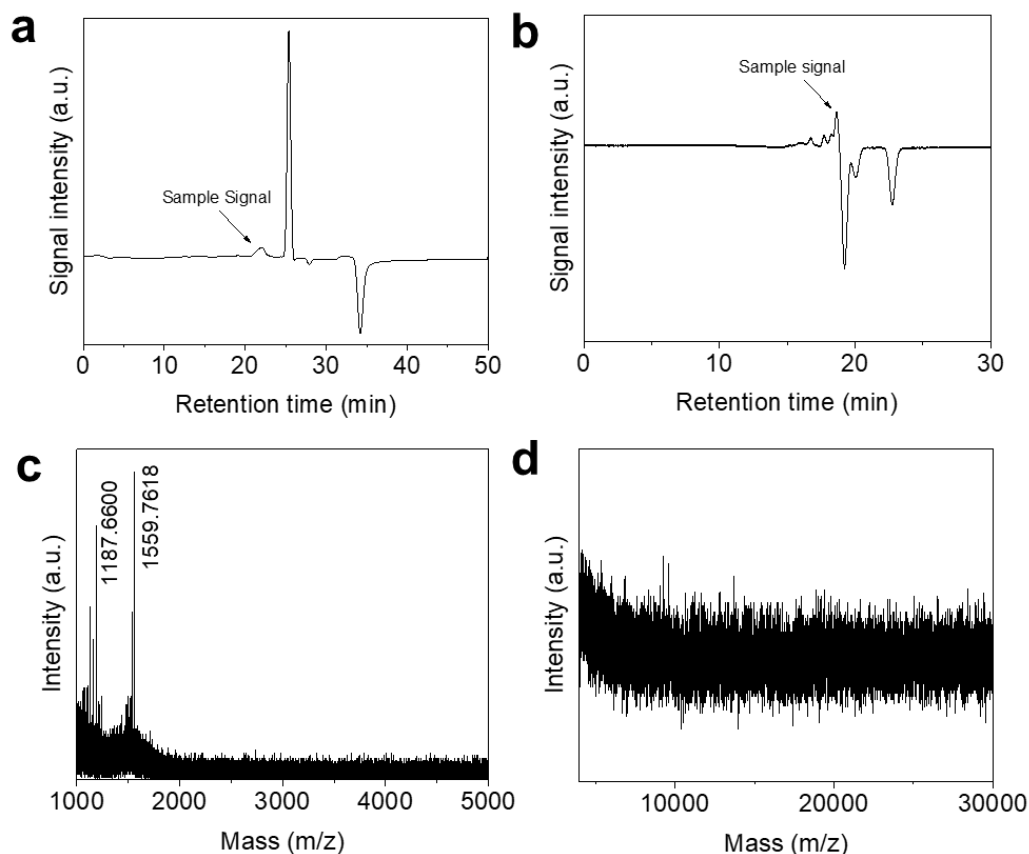


Figure S1. Attempts to estimate the molecular weight of PProDOT-DPP. (a) Size exclusion chromatogram of the PProDOT-DPP polymer collected at 150 °C using 1,2,4-trichlorobenzene (TCB) as the mobile phase. (b) Size exclusion chromatogram of the PProDOT-DPP polymer at 40 °C using tetrahydrofuran (THF) as the mobile phase. Note that the PProDOT-DPP polymer solubility in THF at 40 °C is limited. (c) and (d) MALDI-TOF mass spectra of PProDOT-DPP from a m/z range of 1,000 to 30,000. No peak was detected at values greater than the molecular weight of the monomer.

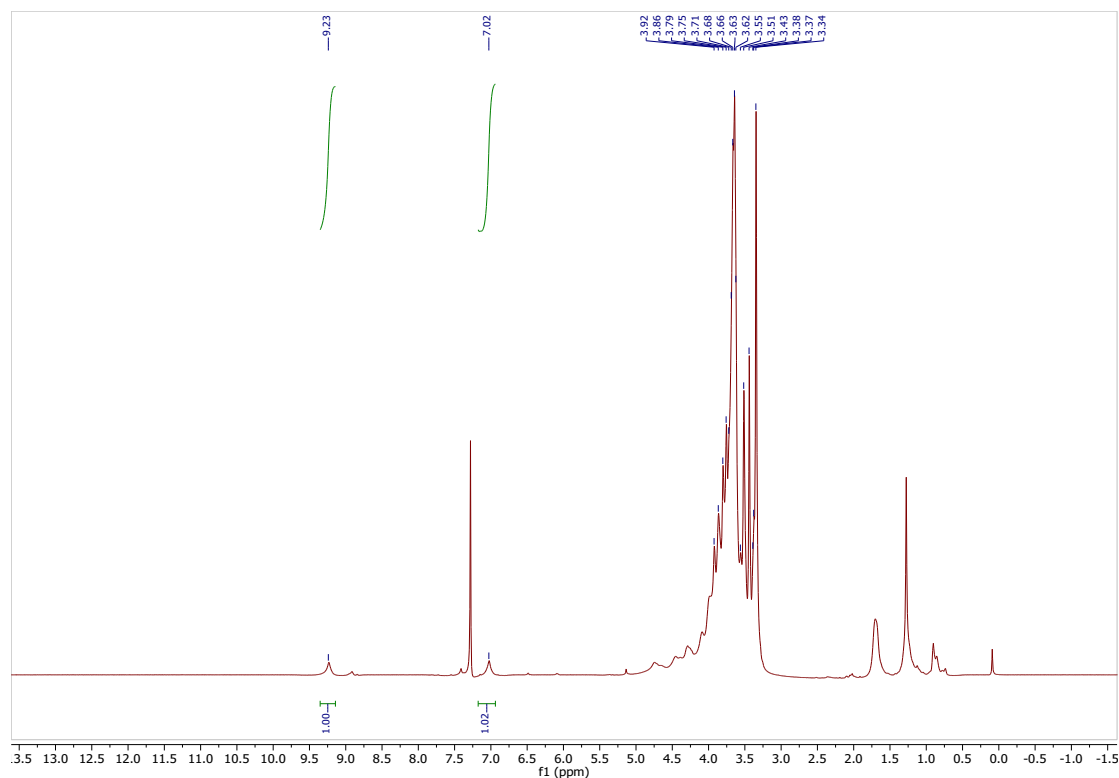


Figure S2. ^1H NMR of PProDOT-DPP in CDCl_3 at 323 K. The two protons remaining on the DPP moiety are integrated.

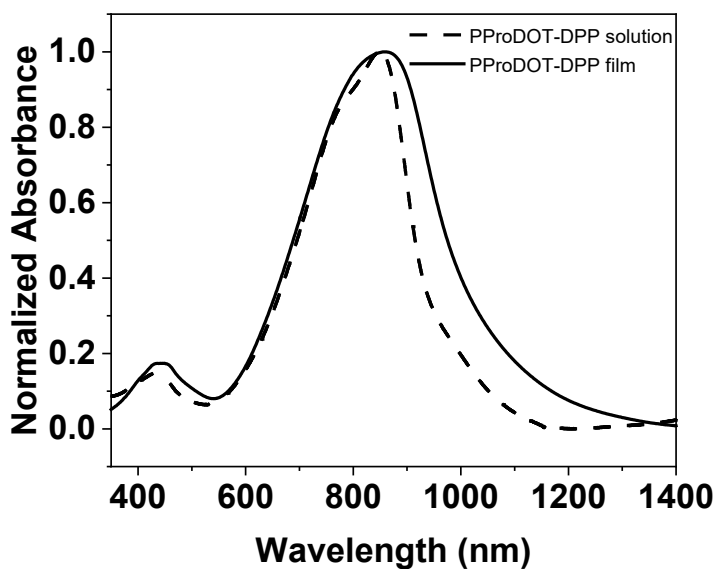


Figure S3. Normalized UV-Vis-NIR light absorption spectra of PProDOT-DPP in a chloroform solution and as a thin film. The PProDOT-DPP exhibited dual-band absorption features both in solution and as a thin film.

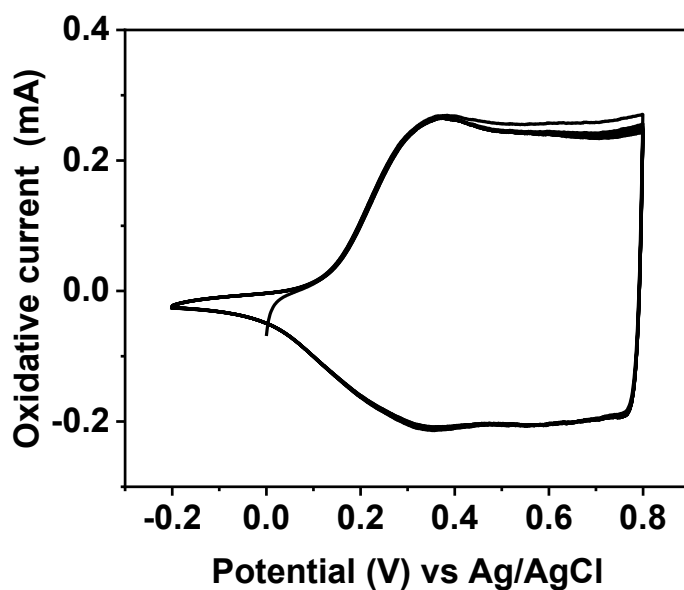


Figure S4. The cyclic voltammograms for the first 10 cycles of a PProDOT-DPP thin film in 0.2 M TBAPF₆ acetonitrile solution electrolyte at a scan rate of 200 mV s⁻¹. The ionization potential (IP) was estimated from the equation: $IP\ (eV) = 4.8 + (E_{\text{onset}} - E_{\text{Fc/Fc}^+})$, where E_{onset} refers to polymer oxidation onset potential vs Ag/AgCl, and $E_{\text{Fc/Fc}^+}$ refers to ferrocene oxidation potential (i.e., +0.37 V, determined experimentally) vs Ag/AgCl.³

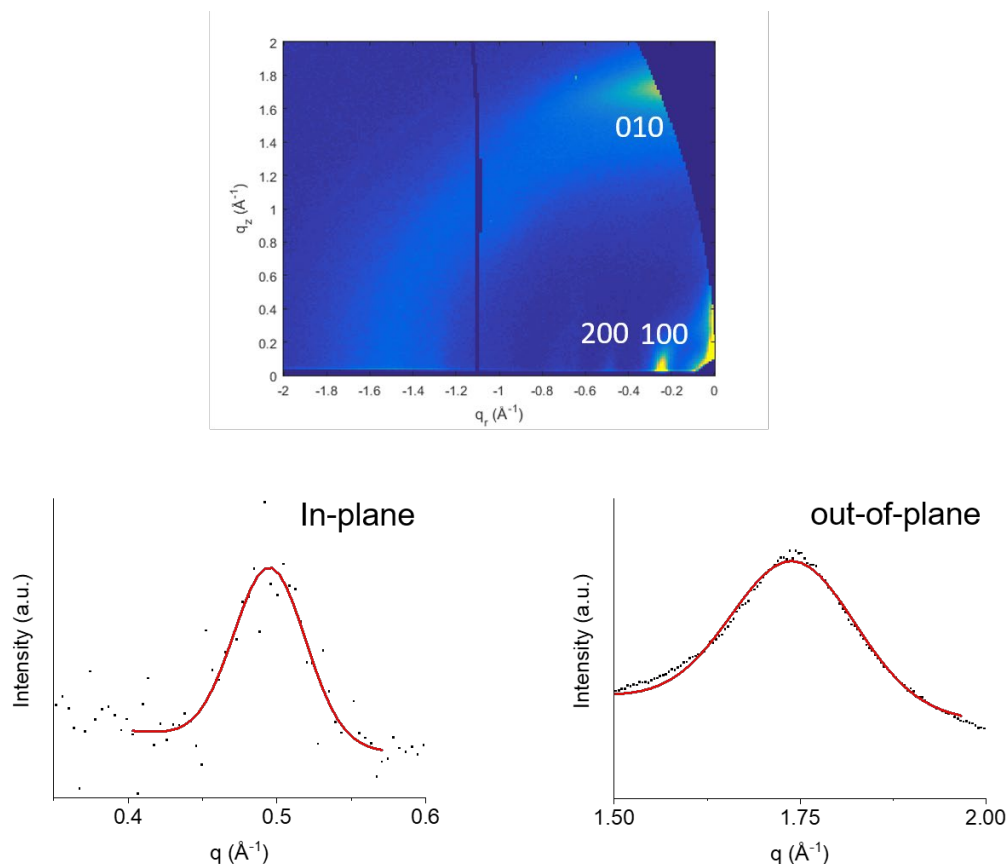


Figure S5. The 2D GIWAXS image, in-plane line cut at (200), and out-of-plane line cut at (010) of PProDOT-DPP. The PProDOT-DPP thin film was prepared by spin-coating the PProDOT-DPP solution (10 mg mL^{-1} in CHCl_3) onto SiO_2 substrates at a rotational rate of 1,500 rpm.

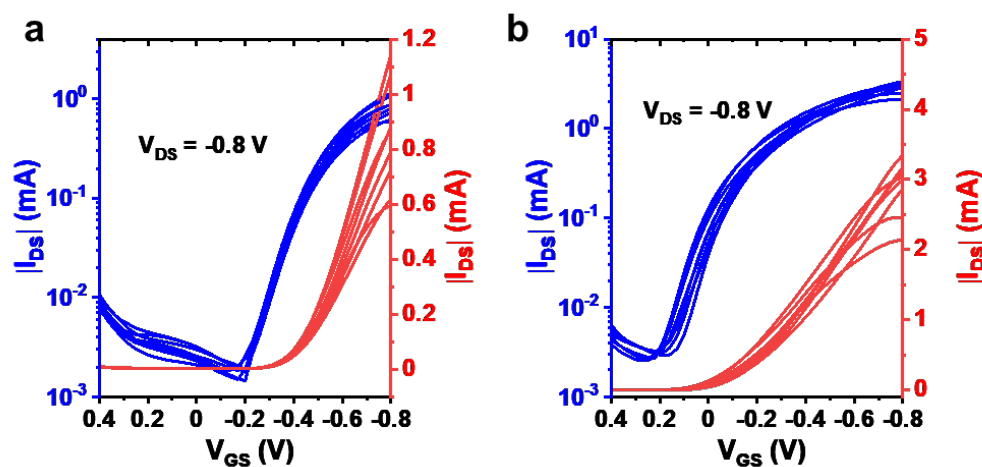


Figure S6. Device-to-device uniformity of PProDOT-DPP OECTs. Transfer curves of 8 individual OECTs using the (a) LiCl and (b) LiPF_6 electrolytes.

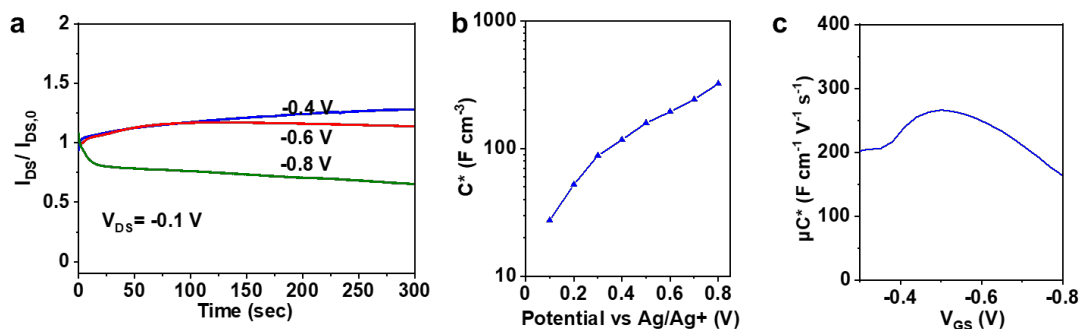


Figure S7. (a) Bias stabilities of PProDOT-DPP OECTs at different V_{GS} values in 0.1 M LiCl. (b) Volumetric capacitance as a function of bias applied to the PProDOT-DPP working electrode via differential capacitance measurements in 0.1 M LiCl. (c) μC^* values of PProDOT-DPP OECTs as a function of V_{GS} in 0.1 M LiCl.

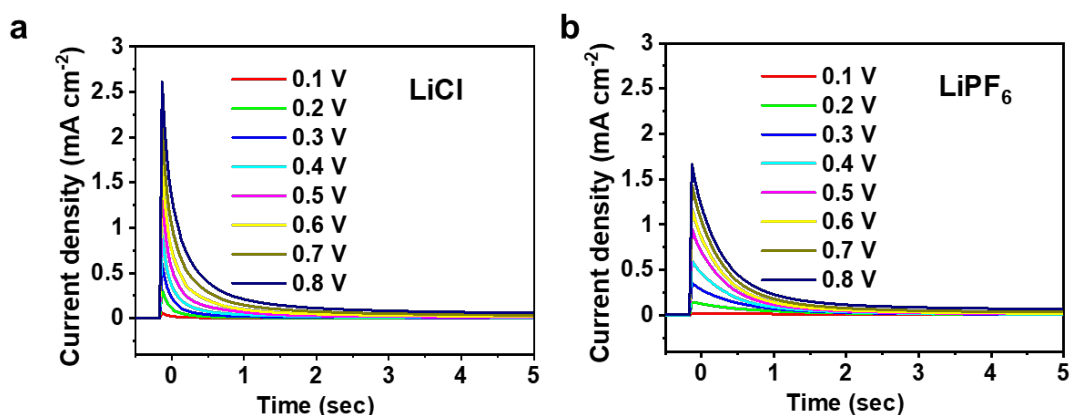


Figure S8. Differential capacitance measurements performed on a PProDOT-DPP on a patterned ITO electrode (0.5 cm²) in 0.1 M (a) LiCl and (b) LiPF₆ aqueous solutions.

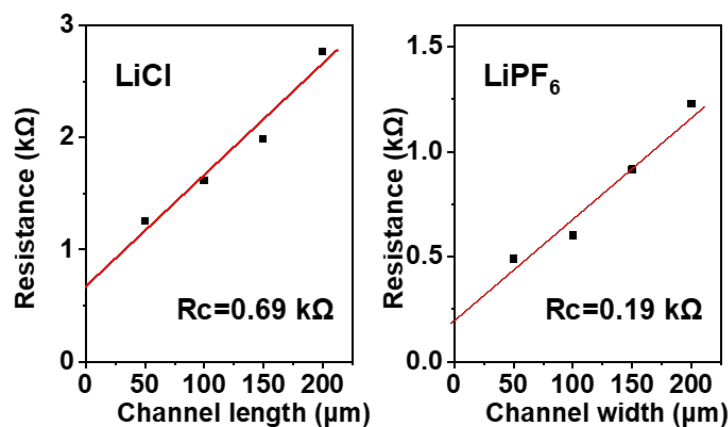


Figure S9. Total resistance of the PProDOT-DPP OECT channel as a function of channel length. The applied V_{GS} was -0.6 V for LiCl and -0.4 V for LiPF₆, and both were evaluated under a constant V_{DS} of -0.1 V.

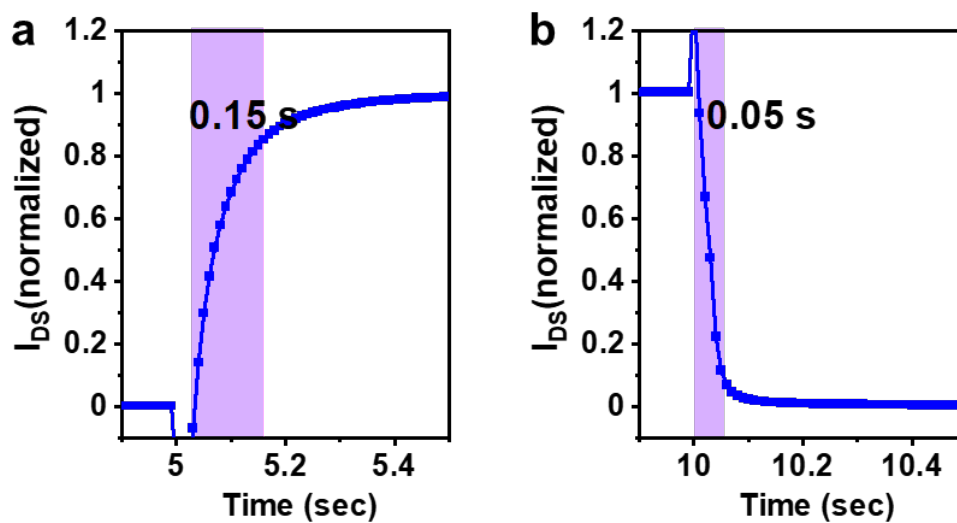
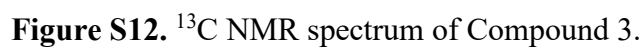


Figure S10. (a) Switching ON and (b) switching OFF responses of PProDOT-DPP OECTs ($V_{GS, on} = -0.4$ V and $V_{GS, off} = 0$ V) in LiCl electrolytes.

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Figure S14. ^{13}C NMR spectrum of Compound 4.

References

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- (3) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, 23 (20), 2367–2371.