Supplementary Information

Electrochromic Polymers Processed from Environmentally Benign Solvents

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Materials and Methods

All chemicals were purchased from Sigma Aldrich, Fisher Scientific, or VWR International and used as received unless otherwise noted. Chromium (IV) oxide (CrO₃) was purchased from Alpha Aesar and was used as received. Palladium (II) acetate (Pd(OAc)₂, 99+%) was purchased from Strem Chemicals and used as received. Propylene carbonate (PC) was purified using Vacuum Atmospheres Solvent Purifier prior to use. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized from hot ethanol prior to use. All materials were synthesized using standard Schlenck line techniques under an argon atmosphere. Monomers were purified via column chromatography using 60 Å silica gel (230-400 mesh). ¹H and ¹³C NMR spectra were obtained using a Bruker Avance IIIHD 500 MHz NMR spectrometer at room temperature using 15-20 mg/mL solutions in CDCl₃. Chemical shifts are reported in ppm and referenced to the residual solvent peak. Polymer molecular weights are reported relative to polystyrene standards and were determined via size-exclusion chromatography (SEC) using a Shimadzu Prominence SEC system operated at 35 °C using HPLC grade tetrahydrofuran (THF) as the eluent. Polymer-THF solutions with a nominal concentration of 10 mg/mL were filtered prior to injection into the SEC system. Optical microscopy images were collected from an Olympus BX51, with 500X magnification in transmission mode. Contact angle measurements were performed on a Rame-Hart Inc. Model 300 Goniometer, with a 2 µL drop of water used for each measurement. Atomic Force Microscopy height and phase images were collected with a Bruker Dimension Icon, in tapping mode, with a Bruker RTESP-150 probe.

Film Preparation

Tin-doped indium oxide (ITO) coated glass slides (7x50x0.7 mm) with a resistance of R_s = 8-12 Ω /sq were purchased from Delta Technologies and cleaned prior to use by sonication in acetone, acetonitrile, and isopropyl alcohol for 5-10 min. After each sonication cycle, the electrodes were rinsed thoroughly with the respective solvent. Polymer solutions of 5 mg/mL were used to deposit films to an optical density of 1.0-1.3 onto clean electrodes using a handheld airbrush (Iwata-Eclipse HP-BC, 15 psi).

Film Characterization

Electrochemical measurements were performed with a three-electrode cell using a platinum flag as the counter electrode, a Ag/Ag⁺ reference electrode (10 mM AgNO₃ in 0.5 M TBAPF₆-ACN, $E_{1/2}$ for Fc/Fc⁺: 46 mV), and the polymer coated ITO slides as the working electrode in a 1 cm path length quartz cuvette. A 0.5 M solution of TBAPF₆ in propylene carbonate was used as the supporting electrolyte solution for electrochemical and spectroelectrochemical experiments. The voltage and current were controlled and monitored using an EG&G Princeton Applied Research potentiostat/galvanostat controlled by CorrWare software. Films were characterized with cyclic voltammetry (CV) between -0.5 V and 0.8 V vs. Ag/Ag⁺ using a scan rate of 50 mV/s. Optical absorbance spectra of the polymers both as a function of potential as well as in their as cast states were acquired using a Cary 5000 UV-Vis-NIR spectrophotometer scanning from 300-1600 nm. Polymer film haze was measured using the same Cary 5000 spectrophotometer with an integrating sphere attachment (DRA 2500). Switching speeds were determined by square-wave potential absorptiometry by monitoring the transmittance at λ_{max} for each polymer while switching between -0.5 V and 0.8 V at varying pulse lengths. Colorimetric coordinates were quantified by converting the absorbance spectra to CIELAB $L^*a^*b^*$ color coordinates. Photography was performed using a Nikon D90 SLR camera with a Nikon 18-105 mm VR lens and the pictures are presented without manipulation except for cropping.



Scheme S1. Monomer synthesis

Synthesis of 2-butyloctanoic acid

A solution of 1-butyloctanol (26.08 g, 0.14 mole) in acetone (280 mL) was prepared in a one liter three-neck round-bottom flask equipped with a Teflon stir bar and addition funnel. The resulting solution was cooled to 0 °C using an ice water bath. In a separate flask, chromium (VI) oxide (CrO₃) (56.0 g, 0.56 mole) was dissolved in 230 mL of 6 M sulfuric acid (H₂SO₄) to generate the Jones Reagent. The Jones Reagent solution was transferred to the addition funnel and subsequently added dropwise to the alcohol solution over several hours. After completing the addition of the Jones Reagent, the resulting reaction mixture was allowed to warm to room temperature and stir overnight. After stirring overnight, 100 mL of isopropyl alcohol (IPA) was added to the reaction mixture and the mixture was filtered through celite. The reaction mixture was extracted with ether and brine, dried with magnesium sulfate (MgSO₄), and filtered. The collected filtrate was then concentrated via rotary evaporation and dried under vacuum overnight yielding a pale green oil (75% yield). ¹H NMR: (500 MHz, CDCl₃), δ (ppm): 0.85-0.93 (br, m, 6H), 1.22-1.35 (br, m, 12H), 1.43-1.52 (br, m, 2H), 1.57-1.65 (br, m, 2H) 2.40-2.40 (m, 1H). ¹³C NMR: (500 MHz, CDCl₃),), δ (ppm): 13.74, 13.88, 22.42, 22.45, 27.15, 29.05, 29.36, 31.48, 31.71, 32.01, 45.37, 182.82. HR ESI MS calc'd for C₁₂H₂₃O₂: 199.1704 Found: 199.1709

Synthesis of ProDOT-BOE-H₂

A solution of Br₂ProDOT (2.1 g, 6.15 mmol), 2-butyloctanoic acid (3.07 g, 12.28 mmol), and potassium carbonate (K₂CO₃) (3.40 g, 24.6 mmol) were added to a 250 mL three-neck roundbottom flask, equipped with a Teflon stirbar and reflux condenser, and was sealed with rubber septa. The atmosphere was rendered inert by flushing the flask for 30 min with argon (Ar). N,N-Dimethylformamide (DMF) was then added via cannula and the reaction mixture was heated using an oil bath set to 100 °C. After stirring for 21 h, the reaction mixture was cooled to ambient temperature and extracted using diethyl ether and DI water followed by brine. The combined organic fractions were dried with MgSO₄, concentrated via rotary evaporation, and purified via column chromatography using 10:1 hexanes:ethyl acetate as the mobile phase. The recovered product was concentrated via rotary evaporation and then dried under vacuum overnight to yield a pale yellow oil (86% yield). ¹H NMR: (500 MHz, CDCl₃), δ (ppm): 0.85-0.93 (br, m, 12H), 1.22-1.35 (br, m, 24H), 1.43-1.52 (br, m, 4H), 1.57-1.65 (br, m, 4H), 2.30-2.40 (m, 2H), 4.04 (s, 2H), 4.19 (s, 2H), 6.47 (s, 2H). ¹³C NMR: (500 MHz, CDCl₃),), δ (ppm): 14.05, 14.21, 22.73, 22.75, 27.55, 29.36, 29.72, 31.79, 32.14, 32.47, 45.82, 46.13, 62.68, 72.69, 105.59, 149.18, 176.11. HR ESI MS calc'd for C₃₃H₅₇O₆S: 581.3870 Found: 581. 3861

Synthesis of ProDOT-BOE-Br₂

ProDOT-BOE-H₂ (1.5 g, 2.51 mmol) was dissolved in 25 mL of anhydrous tetrahydrofuran (THF) under an Ar atmosphere and the resulting solution was cooled to 0 °C using an ice water bath. *N*-Bromosuccinimide (NBS) (0.920 g, 5.17 mmol) was subsequently added slowly under Ar and the resulting reaction mixture was covered with foil and stirred overnight. After stirring overnight, the THF was removed under reduced pressure and the crude reaction mixture was filtered through a silica plug using hexanes and then 10:1 hexanes:ethyl acetate as the mobile

phase. The collected fractions were concentrated via rotary evaporation and then dried under vacuum overnight to yield a pale yellow oil (71% yield). ¹H NMR: (500 MHz, CDCl₃), δ (ppm): 0.85-0.93 (br, m, 12H), 1.22-1.35 (br, m, 24H), 1.43-1.52 (br, m, 4H), 1.57-1.65 (br, m, 4H), 2.30-2.40 (m, 2H), 4.12 (s, 2H), 4.20 (s, 2H). ¹³C NMR: (500 MHz, CDCl₃), δ (ppm): 13.90, 14.06, 22.58, 22.61, 27.42, 29.20, 29.59, 31.65, 31.96, 32.28, 45.64, 46.16, 62.38, 73.04, 91.48, 146.38, 175.82. HR ESI MS calc'd for C₃₃H₅₅O₆Br₂S: 737.2081 Found: 737.2077

General Polymerization Procedure

ProDOT-BOE-H₂, either ProDOT-BOE-Br₂ or ProDOT-OEtHx-Br₂, Pd(OAc)₂, PivOH, and K₂CO₃, were added to a Schlenk flask equipped with a Teflon stir bar and was sealed with a rubber septum. The atmosphere was rendered inert by flushing the vessel with Ar for 20 min. Degassed DMAc was added via syringe under and Ar atmosphere and the reaction flask was placed in an oil bath set to 140 °C. The reaction was then allowed to stir for 18-21 h. After the allotted reaction time, the reaction flask was removed from the oil bath and cooled to room temperature. The reaction mixture was then precipitated into a copious amount of methanol (MeOH) and stirred for 1 h. After 1 h, the precipitate was filtered into a Soxhlet thimble and the polymer was purified with subsequent washes with MeOH, acetone, and hexanes and finally extracted with chloroform. The palladium scavenger diethylammonium diethylcarbamate and 18-crown-6 were added to the polymer/chloroform solution and the mixture was subsequently stirred for 2 h. After 2 h, the solution was concentrated via rotary evaporation and then the concentrated fraction was precipitated in MeOH. The precipitate was then filtered, washed with MeOH, and dried under vacuum.

BOE-co-EtHx: Purple solid. M_n = 149.8 kg/mol, M_w/M_n = 1.7, Yield (%) = 93%. ¹H NMR: (500 MHz, CDCl₃), δ (ppm): 084.-0.94 (br, m), 1.20 (br, s), 1.47-1.70 (br, m), 2.42 (br, s), 3.36 (br, s), 3.64 (br, s), 4.38 (br, s).

BOE: Purple solid. M_n = 81.6 kg/mol, M_w/M_n = 1.8, Yield (%) = 67%. ¹H NMR: (500 MHz, CDCl₃), δ (ppm): 0.82-0.92 (br, m), 1.20-1.35 (br, s), 1.45-1.56 (br, s), 1.58-1.71 (br, m), 2.42 (s), 4.06-4.57 (br, m).



Figure S1. ¹H NMR (500 MHz, 25 °C, CDCl₃) of 2-butyloctanoic acid.



2.88 7 2.48 7 15.27 1 7.47 1 2.25 ≠ 2.17 ≠ 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm Figure S3. ¹H NMR (500 MHz, 25 °C, CDCl₃) of ProDOT-BOE-H₂.

1.32 H

1.00 -=



S9



Figure S6. ¹³C NMR (500 MHz, 25 °C, CDCl₃) of ProDOT-BOE-H₂.





Figure S8. ¹H NMR (500 MHz, 25 °C, CDCl₃) of BOE-co-EtHx.



Figure S9. Size exclusion chromatography elugram obtained for BOE while using THF as the eluent at 35 °C with a flow rate of 1 mL/min.



Figure S10. Size exclusion chromatography elugram obtained for BOE-co-EtHx while using THF as the eluent at 35 °C with a flow rate of 1 mL/min.

Solvent	EtHx	(BOE)-co-(EtHx)	BOE
Chloroform	+	+	+
Toluene	+	+	+
THF	+	+	+
2-Me-THF	+	+	+
Ethyl Acetate	-	-	+
Propyl Acetate	-	-	+

Table S1. Solubility chart of ProDOT polymers used in this study.



Figure S11. Contact angle measurements of redox cycled BOE films spray cast from toluene, 2-Me-THF, ethyl acetate, and propyl acetate.

Casting solvent	Mean contact angle (°)	Std dev (°)	
Toluene	94.9	2.4	
2-Me-THF	109.9	3.0	
Ethyl Acetate	104.5	2.0	
Propyl Acetate	84.7	2.0	

Table S2. Contact angle measurement data for BOE films.



Figure S12. AFM topography images of redox-cycled BOE films cast from toluene, 2-Me-THF, ethyl acetate, and propyl acetate on the scale of 500 nm.



Figure S13. UV-Vis absorbance spectra of 0.2 mg/mL BOE in toluene, 2-Me-THF, ethyl acetate, and propyl acetate



Figure S14. UV-Vis absorbance spectra of EtHx, BOE-co-EtHx, and BOE in 0.2 mg/mL toluene solutions.



Figure S15. Temperature dependent UV-Vis absorbance spectra of EtHx at 0.2 mg/mL in toluene. The arrows indicate optical transitions that occur as the solution temperature is increased.



Figure S16. Temperature dependent UV-Vis absorbance spectra of BOE-co-EtHx at 0.2 mg/mL in toluene. The arrows indicate optical transitions that occur as the solution temperature is increased.



Figure S17. Temperature dependent UV-Vis absorbance spectra of BOE at 0.2 mg/mL in toluene . The arrows indicate optical transitions that occur as the solution temperature is increased.



Figure S18. UV-Vis absorbance of (a) pristine and (b) and films cycled 10 times between -0.5 V and 0.8 V of EtHx, BOE-co-EtHx, and BOE spray-cast from toluene.



Figure S19. UV-Vis absorbance spectra of BOE-co-EtHx of (a) pristine and (b) electrochemically conditioned films to show both were spray cast to similar optical density.



Figure S20. Cyclic voltammograms of EtHx, BOE-co-EtHx, and BOE films spray cast from toluene in 0.5 M TBAPF₆/PC at 50 mV/s.



Figure S21. Cyclic voltammograms for (a) as cast and (b) electrochemically conditioned EtHx films in $0.5 \text{ M TBAPF}_6/PC$ at 50 mV/s.



Figure S22. Cyclic voltammograms for (a) as cast and (b) electrochemically conditioned BOE-co-EtHx films in 0.5 M TBAPF₆/PC at 50 mV/s.



Figure S23. Spectra as a function of potential of EtHx spray cast from (a) toluene and (b) 2-Me-THF by applying potentials from -0.5 V to 0.8 V in 0.1 V intervals in 0.5 M TBAPF₆/PC.



Figure S24. Spectra as a function of potential for BOE-co-EtHx spray cast from (a) toluene and (b) 2-Me-THF from -0.5 V to 0.8 V in 0.1 V intervals in 0.5 M TBAPF₆/PC.



Figure S25. Spectra as a function of potential for BOE spray cast from (a) toluene, (b) 2-Me-THF, (c) ethyl acetate, and (d) propyl acetate from -0.5 V to 0.8 V in 0.1 V intervals in 0.5 M $TBAPF_6/PC$.



Figure S26. Spectra of BOE cast from toluene, 2-Me-THF, ethyl acetate, and propyl acetate in $0.5 \text{ M TBAPF}_6/\text{PC}$ at -0.5 V (solid lines) and 0.8 V (dashed lines) vs. Ag/Ag⁺.



Figure S27. (a) Color coordinates and (b) L* values as a function of potential for EtHx cast from toluene and 2-Me-THF. Arrows in (a) track the color coordinates from pristine films (circled), to -0.5 V, to +0.8 V in 0.5 M TBAPF₆/PC.



Figure S28. (a) Color coordinates and (b) L* values as a function of potential for BOE-co-EtHx cast from toluene and 2-Me-THF. Arrows in (a) track the color coordinates from pristine films (circled), -0.5 V, to +0.8 V in 0.5 M TBAPF₆/PC.

$$\Delta E_{ab}^{*} = \sqrt{(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}}$$
(S1)

Table S3. ΔE^*_{ab} calculations for the ProDOT polymers cast from toluene.

Polymer	ΔE^*_{ab}		
EtHx	n/a		
BOE-co-EtHx	19.0		
BOE	$21.3(27.0)^{a}$		

^acalculated difference between BOE and BOE-co-EtHx.

		ΔE^*_{ab} Compared between Casting Solvents			
Polymer/Solvent		Toluene	2-Me-THF	Ethyl Acetate	Propyl Acetate
EtHx	Toluene	-		_a	_a
	2-Me-THF	6.5	-	_ ^a	_a
BOE-co-EtHx	Toluene	-		_ ^a	_ ^a
	2-Me-THF	16.8	-	_ ^a	_ ^a
	Toluene	-			
BOE	2-Me-THF	5	-		
	Ethyl Acetate	12	7.5	-	
	Propyl Acetate	19.3	14.8	8.7	-

Table S4. ΔE^*_{ab} calculations for the ProDOT polymers cast from toluene, 2-Me-THF, ethyl acetate, and propyl acetate.

^aPolymers not soluble to produce films.



Figure S29. Transmittance at λ_{max} as a function of switching time from 10 to 0.25 seconds for EtHx films spray cast from toluene and 2-Me-THF.



Figure S30. Transmittance at λ_{max} as a function of switching time from 10 to 0.25 seconds for BOE-co-EtHx films spray cast from toluene and 2-Me-THF.



Figure 31. Transmittance at λ_{max} as a function of switching time from 10 to 0.25 seconds for BOE films spray-cast from toluene, 2-Me-THF, ethyl acetate, and propyl acetate.