

Supporting Information

Broadly absorbing black to transmissive switching electrochromic polymers

By Pengjie Shi, Chad M. Amb, Eric P. Knott, Emily J. Thompson, David Y. Liu, Jianguo Mei, Aubrey L. Dyer and John R. Reynolds*

The George and Josephine Butler Polymer Research Laboratory
Department of Chemistry
Center for Macromolecular Science and Engineering
University of Florida
Gainesville, Florida 32611 (USA)
E-mail: reynolds@chem.ufl.edu

Experimental Section

Instrumentation ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Mercury 300 spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. High-resolution mass spectrometry was performed by the Spectroscopic Services at the Department of Chemistry of the University of Florida with a Finnigan MAT 96Q mass spectrometer. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Atlantic Microlab, Inc. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 40 °C, using two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL min⁻¹. Injections were made at 0.05 - 0.07 % w/v sample concentration using a 220.5 μL injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA). Electrochemistry was performed using a three-electrode cell with a platinum wire or a platinum flag as the counter electrode, a silver wire quasi-reference electrode calibrated using a 5 mM solution of Fc/Fc^+ in 0.1 M electrolyte solution, and a platinum button or ITO-coated glass slide (7 $\times$ 50 $\times$ 0.7 mm, 20 Ω /cm²) as the working electrode. The ITO electrodes were purchased from Delta Technologies, Ltd. All potentials were reported vs Fc/Fc^+ . An EG&G Princeton Applied Research model 273 potentiostat was used under the control of CorrWare

II software from Scribner and Associates. All absorption spectra including spectroelectrochemistry studies were performed using a Varian Cary 500 Scan UV-Vis/NIR spectrophotometer. *In situ* colorimetric measurements were performed using a Minolta CS100 Colorimeter in transmission mode with a GraphicLite LiteGuard II standard D50 light source. The light source and the sample to be measured were placed in a color viewing booth. The interior of the light booth is coated with a standard gray neutral 8 (GTI Graphic Technology, Inc.) matte latex enamel (equivalent to Munsell N8) to allow for accurate assessment of color of the sample during measurement. Photography was performed in the same light booth using either a Nikon D90 at a exposure time of 1/40~1/25 sec, f-stop of f/5.3, ISO sensitivity of 200 or 400, and focal length of 75~80 mm, or a Canon EOS REBEL XSi at a exposure time of 1/125~1/60 sec, f-stop of f/4~f/5.6, ISO sensitivity of 200, and focal length of 18~55 mm. The photograph file-type was JPEG and the files were cropped to only the polymer film to exclude extraneous background using Adobe Photoshop. No additional alterations to the photography files were performed.

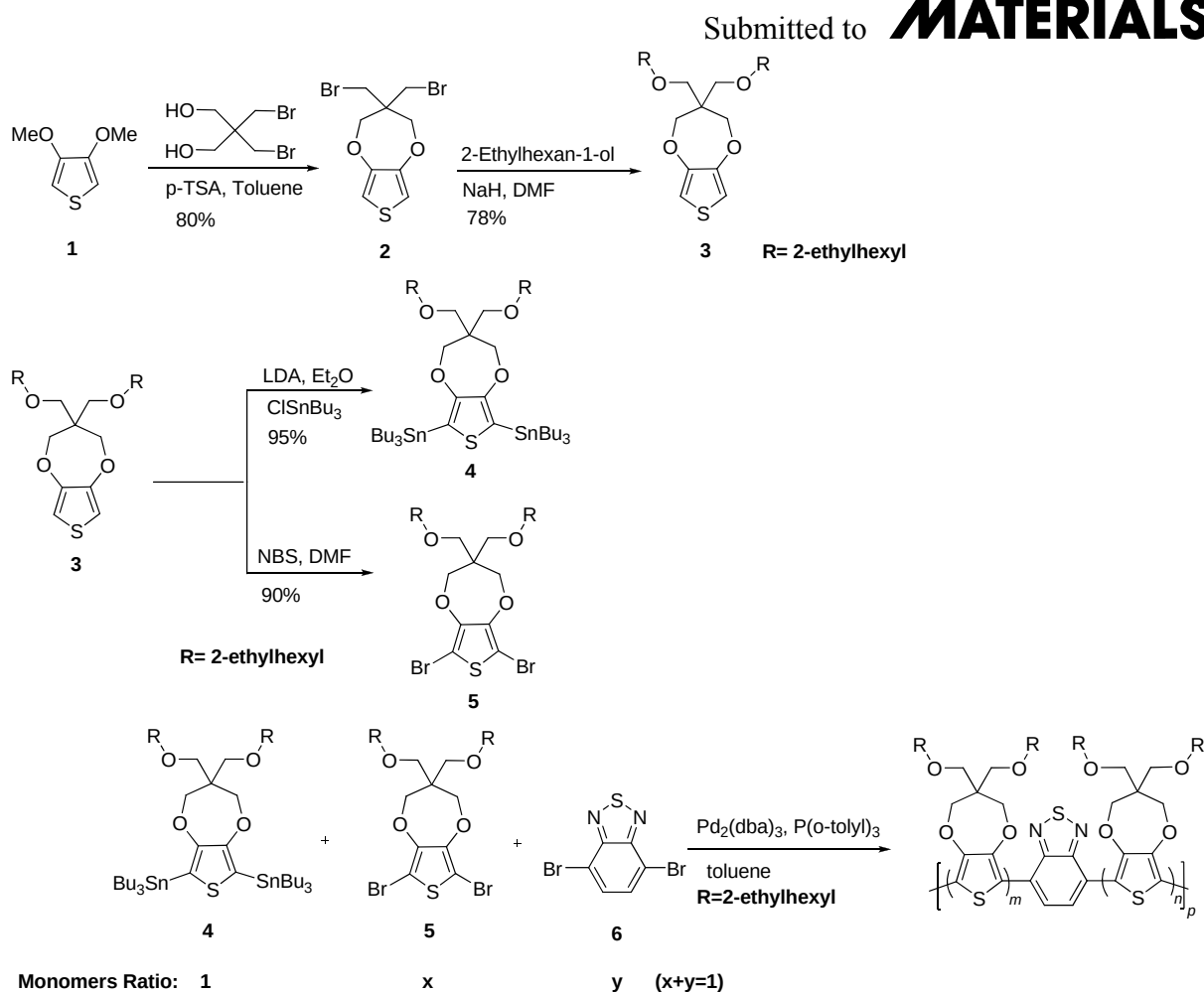
Absorptive/Transmissive ECD The window-type device was constructed using ITO/glass (25 x 37.5 x 1.1 mm, 8-12 Ω , Delta Technologies, Ltd.) coated with the electrochromic polymer **ECP-3** at one electrode and the minimally color-changing polymer, PProDOP-N-C18, at the other. The polymer was spray-cast from methylene chloride as previously described. The gel electrolyte was comprised of LiBTI dissolved in propylene carbonate to a concentration of 0.5 M followed by the addition of 1.1 g of poly(methyl methacrylate) ($M_n \sim 1,000$ kDa) per 10 mL of electrolyte. A layer of the gel was spread onto one of the polymer-coated ITO electrodes and the device assembled using 3M tape as a spacer and epoxy as a sealant on the outer edges of the glass. The device schematic is shown in Figure S3.

Reflective ECD The reflective device was constructed using ITO/glass (25 x 37.5 x 1.1 mm, 8-12 Ω , Delta Technologies, Ltd.) coated with the electrochromic polymer **ECP-3**. The polymer was spray-cast from toluene as previously described to an optical density such that

the absorption at λ_{max} was ~ 0.8 a.u.. The gel electrolyte was comprised of LiBTI dissolved in propylene carbonate to a concentration of 0.5 M followed by the addition of 1.1 g of poly(methyl methacrylate) ($M_n \sim 1,000$ kDa) per 10 mL of electrolyte. Titanium dioxide (Acros) was added to the gel and stirred until the gel was an opaque white. A layer of the gel was spread onto one of the polymer-coated ITO electrodes and the device assembled using double-sided tape as a spacer and epoxy as a sealant on the outer edges of the glass. The device schematic is shown in Figure S3 and device spectra in Figure S4.

Materials All chemical reagents and dehydrated solvents were commercially available and used without further purification unless otherwise noted. All reactions were carried out with oven-dried glassware and dry solvents in a nitrogen atmosphere unless otherwise stated. For column chromatography, Whatman Purasil silica gel (230-400 Mesh, pore diameter 6 nm) was used. **3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (3)** and **4,7 dibromobenzo[c][1,2,5]thiadiazole (6)** were prepared as previously described.^[1,2]

- [1] B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarley, J. R. Reynolds, *Macromolecules* **2004**, 37, 7559.
- [2] B. A. DaSilveira Neto, A. S. A. Lopes, G. R. Ebeling, S. Goncalves, V. E. U. Costa, F. H. Quina, J. Dupont, *Tetrahedron* **2005**, 61, 10975.



Scheme S1. Synthesis of monomer distannyl ProDOT-(CH₂OEtHx)₂ (**4**), dibromo ProDOT-(CH₂OEtHx)₂ (**5**) and polymers.

6,8-bis(tributylstannyl)-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-

b][1,4]dioxepine (4**)** A solution of n-butyllithium (16.0 mL, 20.4 mmol, 1.28 M in hexane)

was added slowly to diisopropylamine (2.06 g, 20.4 mmol) in ether (50.0 mL) at -78 °C.

After stirring for 1 h at -78 °C, the solution was warmed to room temperature and then cooled

to 0 °C in an ice bath. Compound **3** (3 g, 6.81 mmol) was added, and the mixture was

warmed to room temperature and stirred overnight. After the reaction mixture was cooled to

0 °C again, tributylchlorostannane (6.64 g, 20.4 mmol) was added. The mixture was stirred

for 3 h at 0 °C. After dilution with ether (100 mL), the organic phase was washed with water

and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue

was yellow oil and purified by flash chromatography with hexane as an eluent on treated

silica gel (washed the silica gel with neat triethylamine, then hexane) to give 6.56 g (95%) of

the title compound as colorless oil. ^1H NMR (CDCl_3): δ 3.89 (s, 4H), δ 3.46 (s, 4H), δ 3.30 (d, 4H, J = 5.4 Hz), δ 1.60-0.87 (m, 84H). ^{13}C NMR (CDCl_3): δ 156.59, 122.64, 74.42, 73.56, 70.40, 47.91, 39.84, 30.91, 29.37, 29.28, 27.48, 24.23, 23.33, 14.34, 13.94, 11.33, 10.80. Anal. calcd for $\text{C}_{49}\text{H}_{96}\text{O}_4\text{SSn}_2$: C 57.77, H 9.50, found C 58.04, H 9.62.

6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-

b][1,4]dioxepine (5) Compound **3** (2.0 g, 4.54 mmol) and NBS (2.02 g, 11.35 mmol) were added into a round-bottom flash and then degassed and refilled with argon 3 times. DMF (20 mL) was then added. The reaction mixture was stirred at room temperature for overnight, diluted with ethyl acetate (50 mL), and washed with water (2 times with 200 mL). The organic layer was dried with MgSO_4 . After the solvent was evaporated, the residue was purified by column chromatography with hexane as an eluent to obtain compound **5** as a colorless oil (2.44 g, yield: 90%). ^1H NMR (CDCl_3): δ 4.08 (s, 4H), δ 3.48 (s, 4H), δ 3.29 (d, 4H, J = 5.7 Hz), δ 1.56-0.86 (m, 30H). ^{13}C NMR (CDCl_3): δ 147.23, 91.03, 74.55, 74.50, 69.94, 48.21, 39.82, 30.86, 29.34, 24.20, 23.31, 14.33, 11.37. HRMS (ESI-FTICR): m/z calcd for $\text{C}_{25}\text{H}_{42}\text{Br}_2\text{KO}_4\text{S}$ ($\text{M}+\text{K}^+$) 635.0802 found 635.0798. Anal. calcd for $\text{C}_{25}\text{H}_{42}\text{Br}_2\text{O}_4\text{S}$: C 50.17, H 7.07, found C 50.47, H 7.20.

General Polymerization Procedure. Polymer ECP-1: A solution of compound **4** (0.509 g, 0.5 mmol), compound **5** (0.180 g, 0.3 mmol), compound **6** (0.059 g, 0.2 mmol), tris(dibenzylideneacetone)dipalladium (0) (9 mg, 0.01 mmol) and tri(o-tolyl)phosphine (12 mg, 0.04 mmol) in toluene (20 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 100 °C for 36 h in an oil bath. The solution was then precipitated into methanol (300 mL). The precipitate was filtered through a cellulose thimble and purified via Soxhlet extraction for 24 hours with methanol and then 48 hours with hexane. The polymer was extracted with chloroform, concentrated by evaporation, and then precipitated into methanol again (300 mL). The collected polymer was a black solid (0.29 g, 76 %). ^1H NMR (300 MHz, CDCl_3) δ 8.34-8.20 (m, 2H), 4.17-4.00 (m, 16H), 3.55 (bs, 16H), 3.27 (bs,

16H), 1.45-1.05 (m, 72H), 0.84 (bs, 48H). GPC analysis: See **Table S1**. Anal. for **ECP-1**:

See **Table S1**.

Table S1. GPC estimated Molecular Weights in THF, Elemental Analysis of the Polymers

	Monomer 4 ratio	Monomer 5 ratio (x)	Monomer 6 ratio (y)	M _n (g/mol)	M _w (g/mol)	PDI	EA (Calcd/Found)		
							C	H	N
ECP-1	1	0.6	0.4	9,700	15,500	1.6	67.08/66.79	9.51/9.22	1.48/1.39
ECP-2	1	0.7	0.3	10,900	15,200	1.4	67.70/66.99	9.23/9.10	1.07/1.12
ECP-3	1	0.75	0.25	10,500	14,300	1.4	67.83/64.01	9.31/9.10	0.87/0.84
ECP-3-s1	1	0.75	0.25	11,100	14,400	1.3	67.83/65.95	9.31/9.04	0.87/0.96
ECP-3-s2	1	0.75	0.25	10,200	13,700	1.3	67.83/66.18	9.31/9.14	0.87/0.90
ECP-4	1	0.76	0.24	11,000	14,200	1.3	67.86/66.88	9.32/9.24	0.84/0.96
ECP-5	1	0.8	0.2	14,400	19,000	1.3	67.97/63.44	9.38/8.87	0.69/0.75

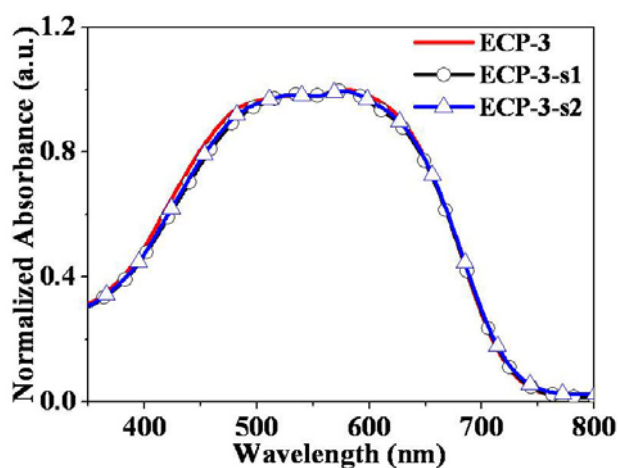


Figure S1. Solution absorption of Polymer **ECP-3**, **ECP-3-s1** and **ECP-3-s2** (monomers ratio: x=0.75, y=0.25) in chloroform (the spectra are normalized at the longer-wavelength absorption maximum of the polymers).

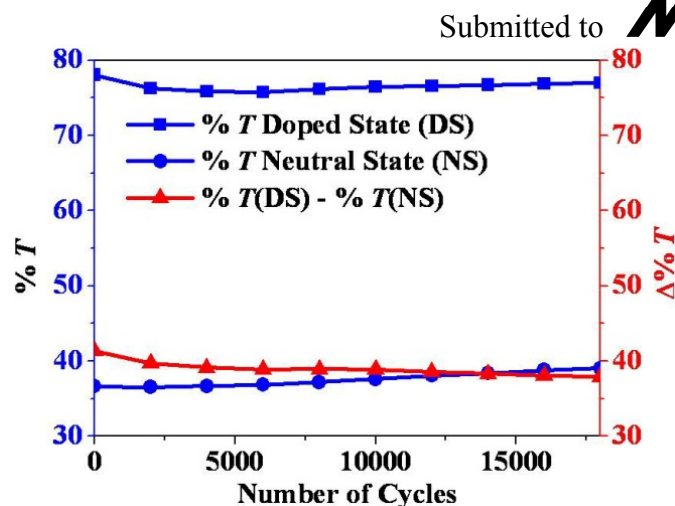


Figure S2. Long-term stability study via square-wave potential stepping while monitoring electrochromic switching of **ECP-3** at 540 nm in 0.1 M LiBTI/propylene carbonate solution switching between -0.72 to +0.48 V (vs. Fc/Fc⁺), and with a switch time of 18,000 cycles (1.5 s step). In blue: %T of oxidized and reduced states, and in red: $\Delta\%T$, as a function of the number of cycles.

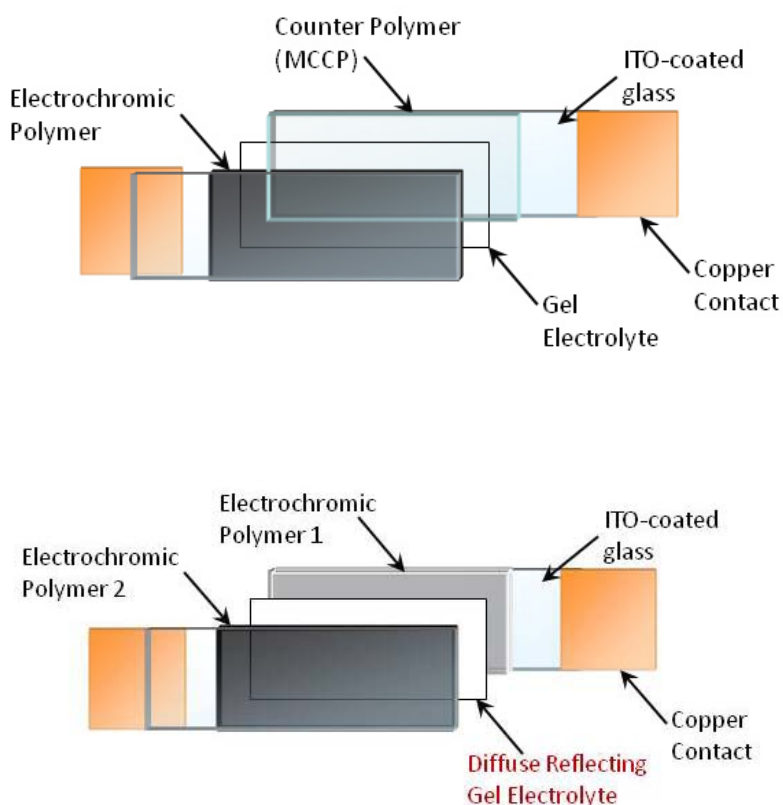


Figure S3. Schematic of a window-type electrochromic device (top) and a reflective electrochromic device (bottom).

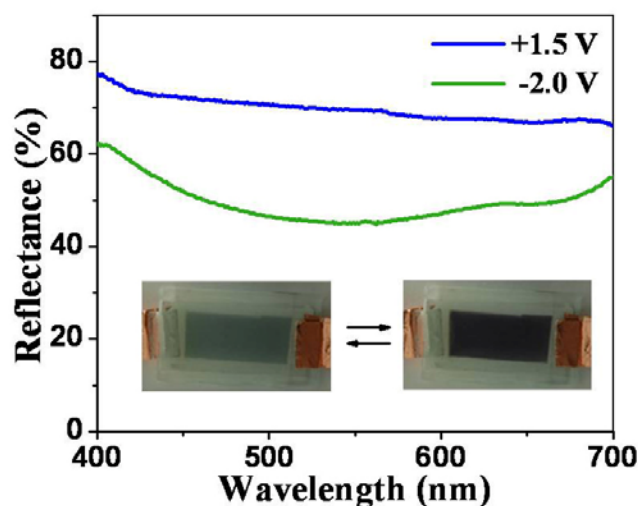


Figure S4. Reflectance spectra of ECD in extreme states of highly absorptive (at an applied cell voltage of -2.0 V) and highly reflective (at an applied cell voltage of 1.5 V). The insets show photographs of the same device in both states.

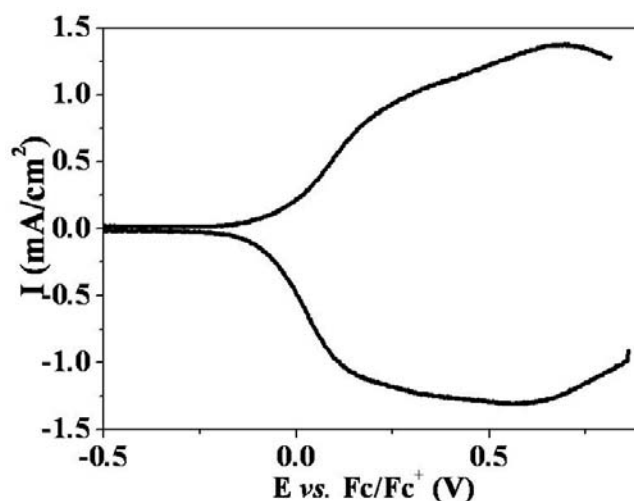


Figure S5. Differential pulse voltammetry of ECP-3 drop-cast from toluene solution onto platinum button electrode ($A = 0.02 \text{ cm}^2$). Measurements were performed in 0.1 M TBAPF₆/propylene carbonate (PC) with a Pt foil counter electrode and a Ag/Ag⁺ reference electrode calibrated vs Fc/Fc⁺ ($E_{\text{Fc/Fc}^+} = 0.087 \text{ V vs Ag/Ag}^+$).