Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Propylenedioxythiophene (ProDOT) – Phenylene Copolymers Allow a Yellow-To-Transmissive Electrochrome

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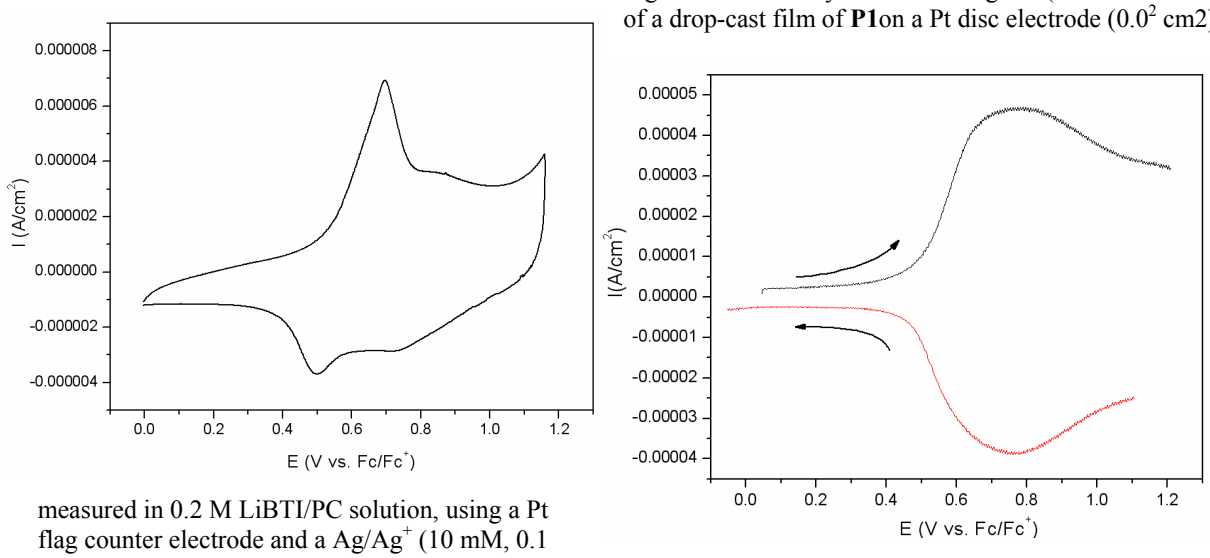
Synthetic Details

Solvents were degassed via the freeze-pump-thaw method 5 times prior to reaction. 1,4-Benzenediboronicacid bis(pinecol) ester was recrystallized from methanol. All other reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. ^{1}H-NMR and ^{13}CNMR spectra were collected on a Varian Inova 2 500 MHz instrument using $CDCl_3$ as a solvent and the residual $HCCl_3$ peak as references (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.23 ppm). Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 40^{o} 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. 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). Absorption spectra and chronoabsorptometry measurements were performed using a Varian Cary 500 UV-vis / NIR spectrophotometer. Electrochemical measurements were carried out using an EG&G Princeton Applied Research model 273A potentiostat / galvanostat used under the control of Corrware II in a 3-electrode cell configuration, using ITO working electrodes, Ag/Ag^{+} (used for non-aqueous solutions) reference electrodes, and Pt wire counter electrodes. The ITO electrodes were purchased from Delta Technologies, Ltd. (7 x 50 x 0.7 mm, sheet resistance, R_s 8-12 Ω/sq). Films were spray cast onto the ITO coated glass slides using 25 psi from 2 mg/mL solutions (pre-filtered with 0.45 μm PTFE syringe filters) in toluene. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen.

Synthesis of P1: 6,8-dibromo-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine[1] (799.87mg, 1.169mmol) was weighed in a small vial, then washed with hexanes (10mL) into schlenk tube, then the hexanes were removed in vacuo. 1,4-Benzenediboronicacid bis(pinecol) ester (387.7mg, 1.1748mmol), K_3PO_4 (3.184g, 0.015mol), $P(o\text{-}tol)_3$ (20mg,0.06571mmol), Pd_2dba_3 (10.7mg, 0.01169mmol,1mol% Pd/Br), and one drop of aliquat 336 were then added to the tube. The mixture was placed under vacuum for 2 hours. The tube was backfilled with argon gas, and the vacuum-purge cycle was repeated 3 times. Toluene (15 mL) and water (5 mL)were then added, and the mixture was stirred at 85°C for 3 days. 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane[2] (550mg, 2.7mmol) was then added, and the mixture was stirred for 8 hours at 85°C, then Bromobenzene (0.37mL, 3.5mmol) was added and the mixture was stirred overnight. Toluene (20 mL) was then added, and then the mixture was precipitated into a mixture of methanol (200mL) and of 1M HCl (25mL). The mixture was filtered into a 25X80mm cellulose thimble, washed 3times with methanol (30 mL) and again three times with DI water (30 mL). The precipitate was then purified by soxhlet extractions: methanol (one day), acetone (one day), hexanes (one day), and chloroform (one day). The chloroform soluble fraction was treated with a spatula tip amount of diethylammonium dithiocarbonate and stirred for 10 minutes, then the solution was concentrated to ~50mL. This concentrated solution was then pippetted dropwise into 200mL of

HPLC grade methanol, and the resulting precipitate was filtered on a nylon filter membrane. The polymer was then collected and dried in vacuo to yield a brown solid. Yield 83%(530mg). GPC M_w = 42,230, M_n = 24,968, PDI = 1.69. ^{1}H NMR ($CDCl_3$): δ 7.78 (br s, 4H), 4.2 (br s, 4H), 3.58 (br s, 4H), 3.36 (br s, 4H), 1.6-1.2 (br, 20H), 0.96 (br s, 14H) Anal. calcd. for $C_{38}H_{54}O_4S$ C 72.33, H 9.01, Found C 72.47, H 9.81.

Figure S1. Left: Cyclic voltammagram (25 mV/s scan rate) of a drop-cast film of **P1**on a Pt disc electrode (0.0^2 cm2)



measured in 0.2 M LiBTI/PC solution, using a Pt flag counter electrode and a Ag/Ag^+ (10 mM, 0.1 M Bu_4NPF_6 in MeCN) reference electrode. Right: Differential pulse voltammagram (2 mV step, 0.038 s step time, 100 mV pulse amplitude) of the same drop cast film.

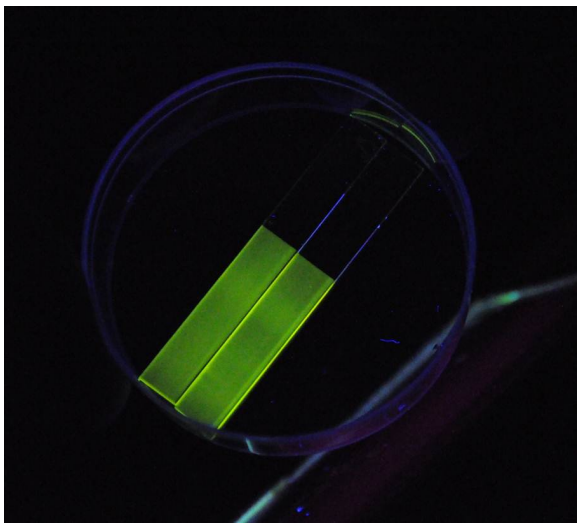


Figure S2. Photograph showing the yellow-green emmission of a spray-cast films of P1 excited at 354 nm.

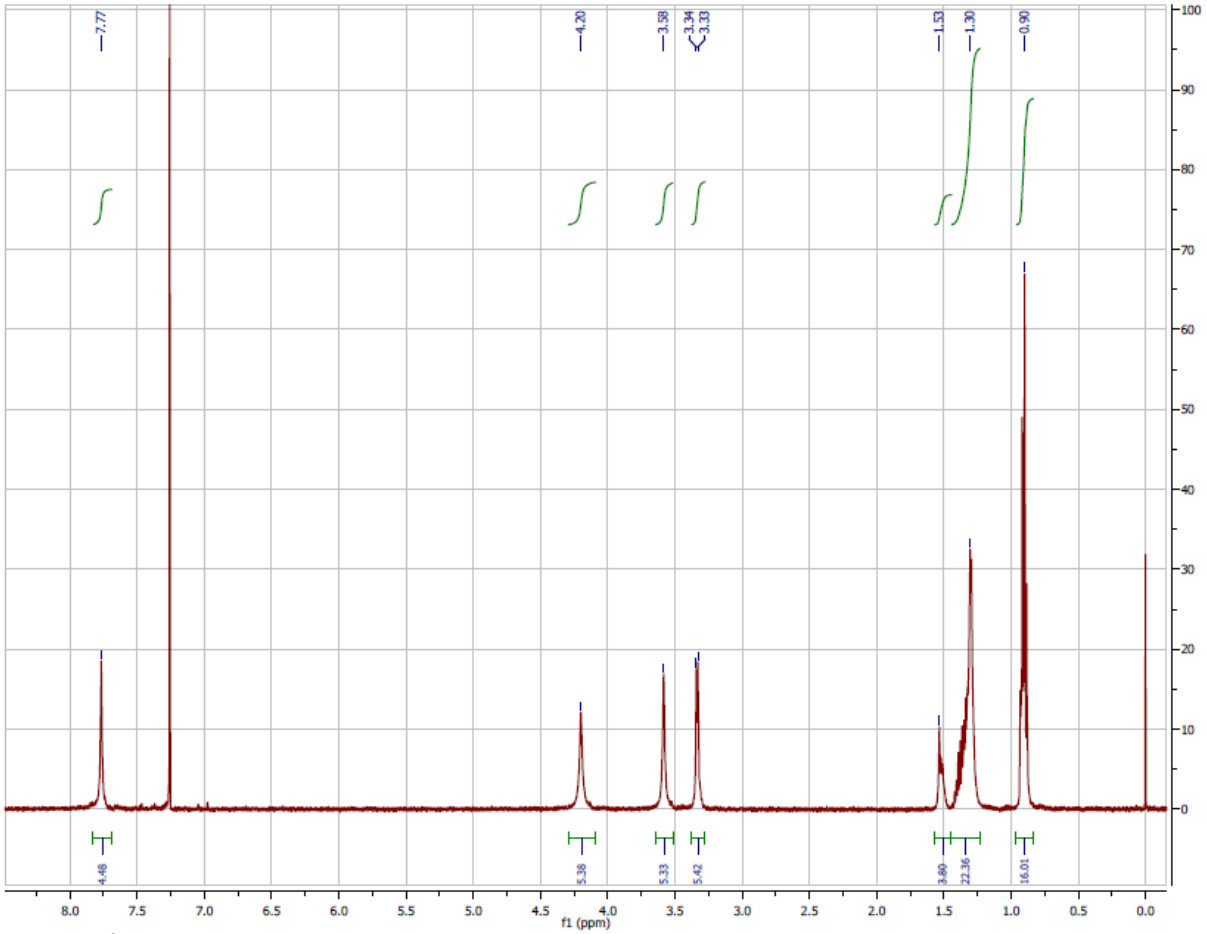
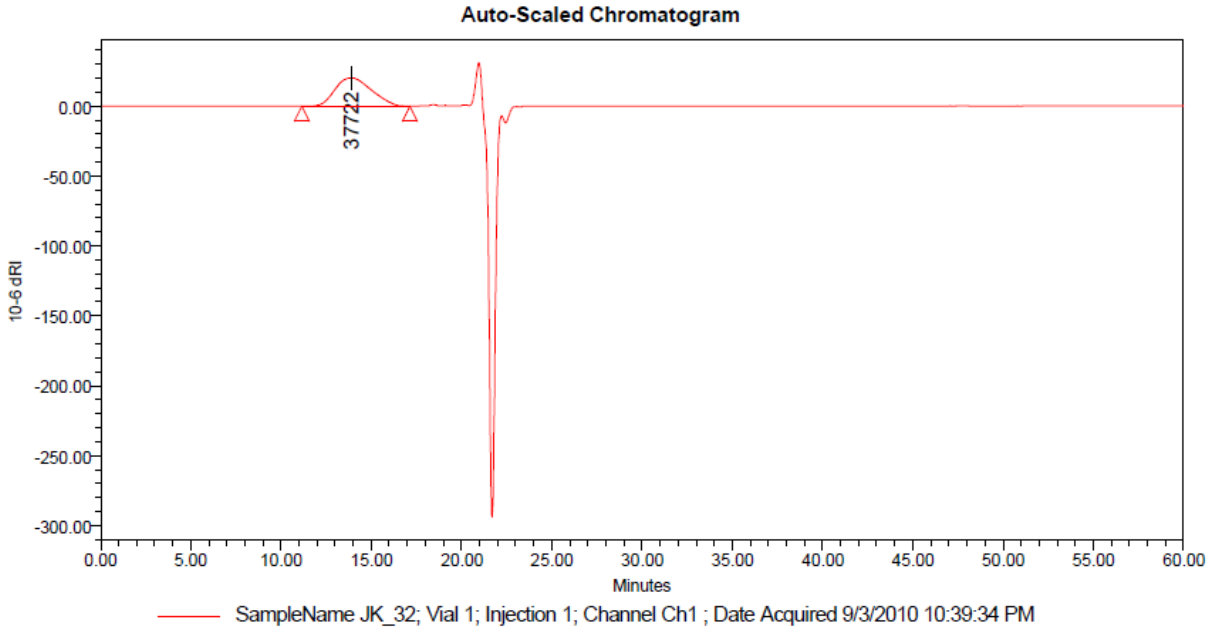


Figure S3. ^{1}H NMR Spectrum of **P1** in $CDCl_3$ (0.05% tetramethylsilane).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		24980	42263	37722	65758	92134		1.691869		

Peak Results

	Name	RT	Area	Height	Amount	Units
1	PeakRT14	13.900	2836684	20274		

Figure S4. GPC trace for **P1**.

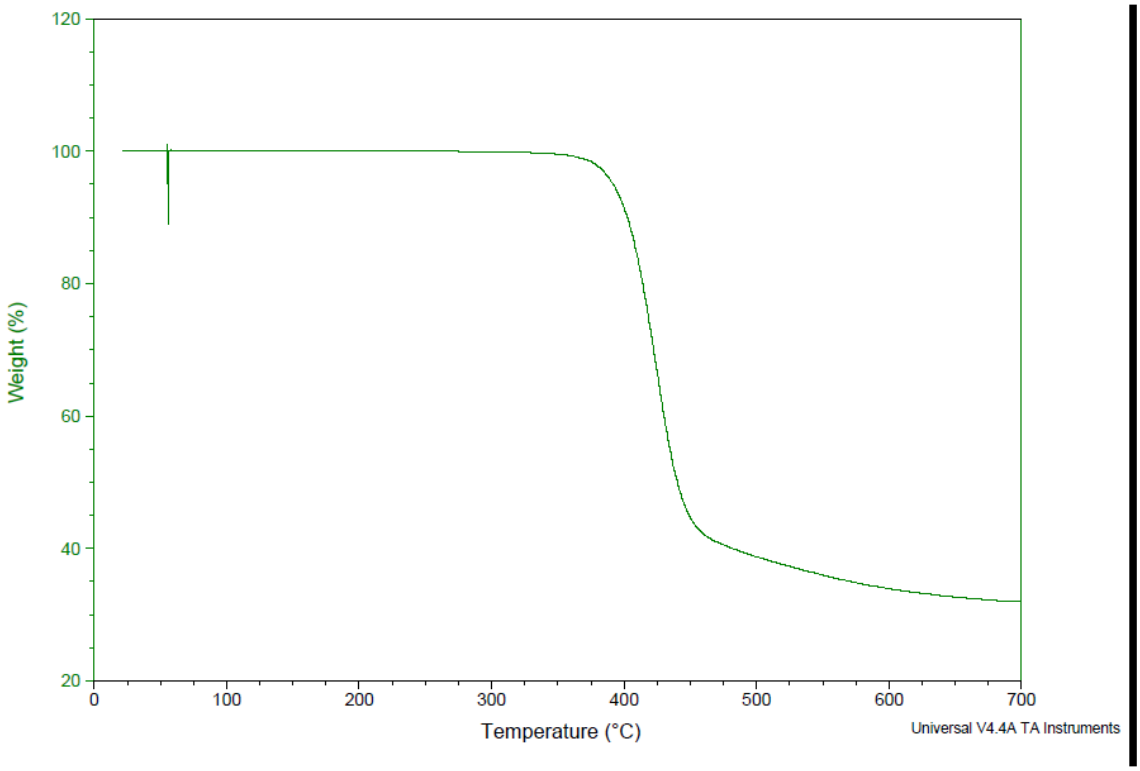


Figure S5. Thermogravimetric analysis scan of **P1** under nitrogen atmospere

[1] B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarleyJ. R. Reynolds, *Macromolecules,* **2004**, *37*, 7559.

[2] Y.-I. Park, J.-H. Son, J.-S. Kang, S.-K.-Kim, J.-H. Leeb and *J.-W.* Park, *Chem. Commun*., **2008**, 2143.