

## Electrochromic and Liquid Crystalline Polycarbonates Based on Telechelic Oligothiophenes

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### **S1. General**

**General Synthetic Details.** Commercially available reagents were used as received from the chemical suppliers. The synthesis of T6-diol has been published elsewhere.<sup>1</sup> Polymerization reactions were carried out under an inert atmosphere of argon in flame-dried glassware. THF was dried using a Solvent Purification System. All reactions were monitored using F250 silica gel 60 M analytical TLC plates, with UV detection ( $\lambda = 254$  and 365 nm). Silica gel (60Å, 40–63  $\mu\text{m}$ ) was used as stationary phase for column chromatography.

NMR experiments were acquired with working frequencies of 300 MHz for <sup>1</sup>H, and 75 MHz for <sup>13</sup>C experiments. The shifts were reported in parts per million (ppm) and referenced to the residual resonance signals of commercially available deuterated chloroform:  $\delta_{\text{H}}=7.26$  ppm,  $\delta_{\text{C}}=77.23$  ppm. High-resolution mass spectra were recorded on a quadrupole mass analyzer instrument equipped with a direct insertion probe (ionization 70 eV) and an electron spray ionizer. Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida.

**Electrochemistry and Spectroelectrochemistry Experiments.** Acetonitrile (ACN) was refluxed over calcium hydride prior to distillation and was stored under argon in contact with activated molecular sieves. Anhydrous propylene carbonate (PC) of 99.7% purity was used as received from Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl)imide (LiBTI) was dried under vacuum at 120 °C for 24 h prior to use. Dichloromethane (DCM) was obtained from an anhydrous solvent system and kept under inert atmosphere. Room temperature X-band EPR was performed on a commercial Bruker Elexsys E580 spectrometer equipped with the Bruker ER 4122SHQE high-Q resonator. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat. CV and DPV experiments using a platinum disk electrode (0.02 cm<sup>2</sup>) as working electrode were carried out in a one compartment electrochemical cell kept under an argon blanket, with a Ag/Ag<sup>+</sup> reference electrode and platinum foil as a counter electrode; all potentials were reported vs. Fc/Fc<sup>+</sup> redox couple. Spectroelectrochemistry was carried out on thin films spray coated onto ITO coated glass slides. The films were sprayed from a 2 mg/mL toluene solutions of the polymer, and contacts were made using copper tape. The coated ITO slides were transferred to an argon filled glovebox, in which the electrochemical cells were assembled. The cells were sealed with Teflon tape and taken out of the glovebox to perform the initial electrochemical reduction break-in cycles and the subsequent spectroelectrochemical experiments.

**X-ray Scattering Experiments.** Transmission, wide-angle X-ray scattering measurements were performed using copper anode X-ray tube, operated at 35 kV/30 mA, as X-ray source, Osmic confocal Max-Flux optics, and a two pin-hole collimation system. The patterns were recorded on a two-dimensional (2D) area detector (Bruker HI-STAR) for a macroscopically oriented fiber with a diameter of 0.7 mm which was prepared by extrusion. The fiber sample was mounted vertically towards the 2D detector.

**Space-charge-limited current (SCLC) devices.** SCLC devices were fabricated by thermally evaporating a 7 nm thick MoO<sub>3</sub> layer onto clean ITO-patterned glass slides, followed by spin coating a 15 mg/mL solution of T6PC in toluene at 1000 rpm for 45 s. The top gold electrode was thermally evaporated to form a 80 nm thick layer defining an active area of 0.07 cm<sup>2</sup>. The thermally annealed device was set on a hotplate at 90 °C for 10 min then ramped down in 10 °C increments over 1h. The devices remained in an argon-filled glovebox at room temperature for 48 h before electrical testing. Devices were tested in the dark by scanning voltage bias from 0.1V to +10V, and the hole mobility was extracted from the current density-voltage (J-V) curves following the SCLC model:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of T6PC (taken to be equal to 3 based on other conjugated polymers),  $\mu$  is the charge carrier mobility and L is the T6PC active layer thickness (measured to be 80 nm via profilometry).

## **S2. Synthetic Procedures and Characterization of Products**

**Poly(6,6'-(4',3''''-bis(hexyl)-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''-hexathiophene-5,5''''''-diyl)-dihexyl) carbonate (T6PC).** To a solution of T6-diol<sup>1</sup> (259 mg, 0.30 mmol) and triphosgene (32.8 mg, 0.11 mmol) in dry THF (5 mL) is added anhydrous pyridine (0.1 mL) diluted in dry THF (1 mL) dropwise at room temperature. Gelation occurs after 90 minutes, after which 5 mL of dry THF are added to the reaction mixture, which is then left stirring at room temperature overnight. The reaction mixture is subsequently diluted with chloroform and poured in water, extracted twice with chloroform. After drying over magnesium sulfate, the combined organic extracts are concentrated to a red solid, which is dissolved in a minimum amount of chloroform and precipitated in methanol. The filtered precipitate is then fractionated using methanol, hexanes and chloroform in a Soxhlet apparatus. Precipitation of the concentrated chloroform fraction in methanol affords T6PC (210 mg, 0.236 mmol, 79 %) as an orange solid after filtration. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.10 (d, J = 3.7 Hz, 1H), 7.01 (d, J = 3.8 Hz, 1H), 6.96 (d, J = 3.5 Hz, 1H), 6.93 (s, 1H), 6.67 (d, J = 3.5 Hz, 1H), 4.14 (t, J = 6.6 Hz, 2H), 2.85-2.65 (m, 4H), 1.68 (m, 6H), 1.43 (m, 6H), 1.34 (m, 4H), 0.90 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  155.59, 145.30, 140.57, 136.74, 135.89, 135.33, 134.79, 128.92, 126.48, 126.22, 125.10, 124.13, 123.94, 123.66, 68.09, 31.87, 31.57, 30.64, 30.25, 29.73, 29.45, 28.80, 25.68, 22.82, 14.54, 14.07. Anal. calcd for C<sub>49</sub>H<sub>60</sub>O<sub>3</sub>S<sub>6</sub>: C 66.17, H 6.80 found C 66.08, H 6.73.

### S3. Supporting Figures

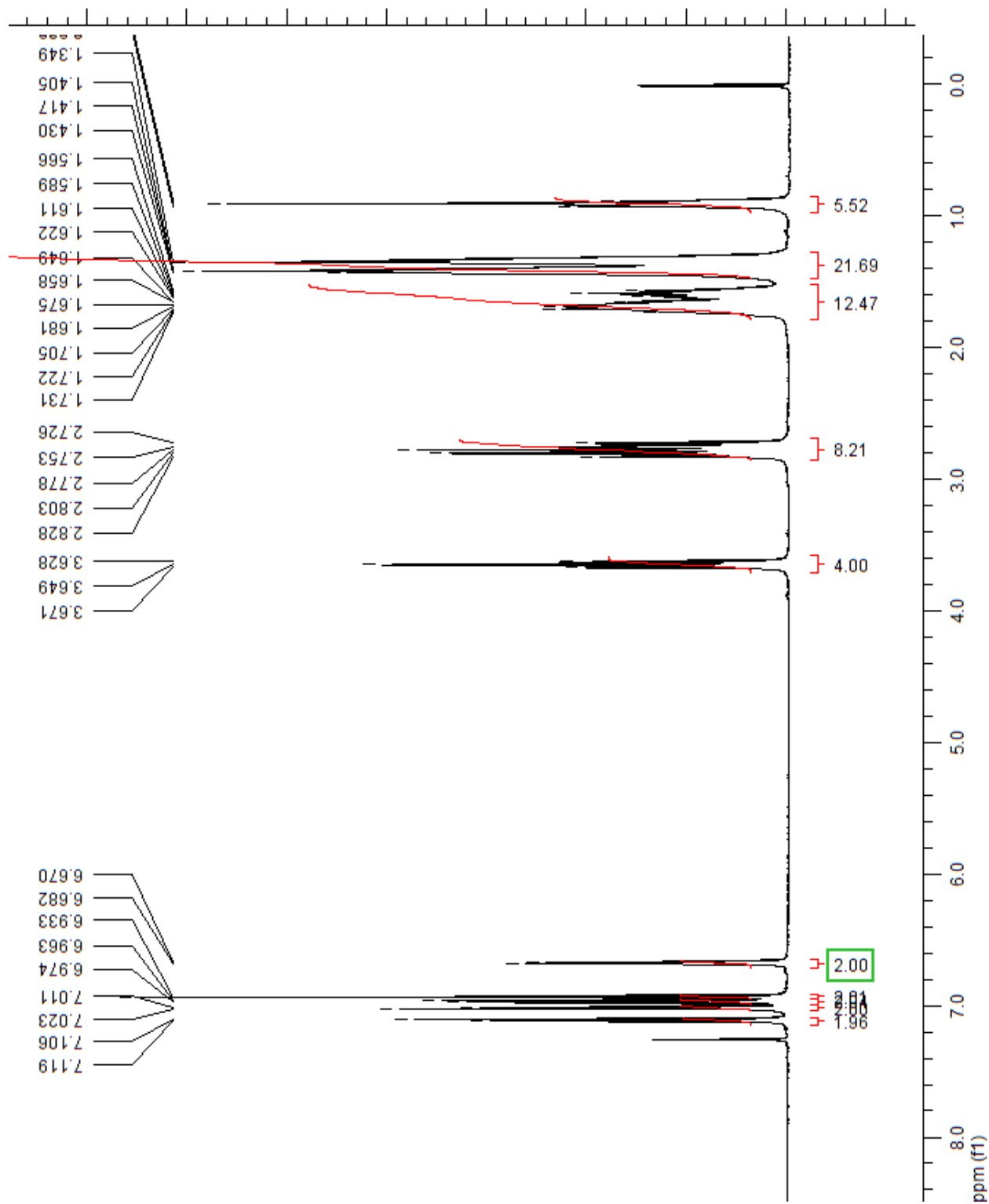


Figure S1. <sup>1</sup>H-NMR spectrum of T6-diol in CDCl<sub>3</sub>.

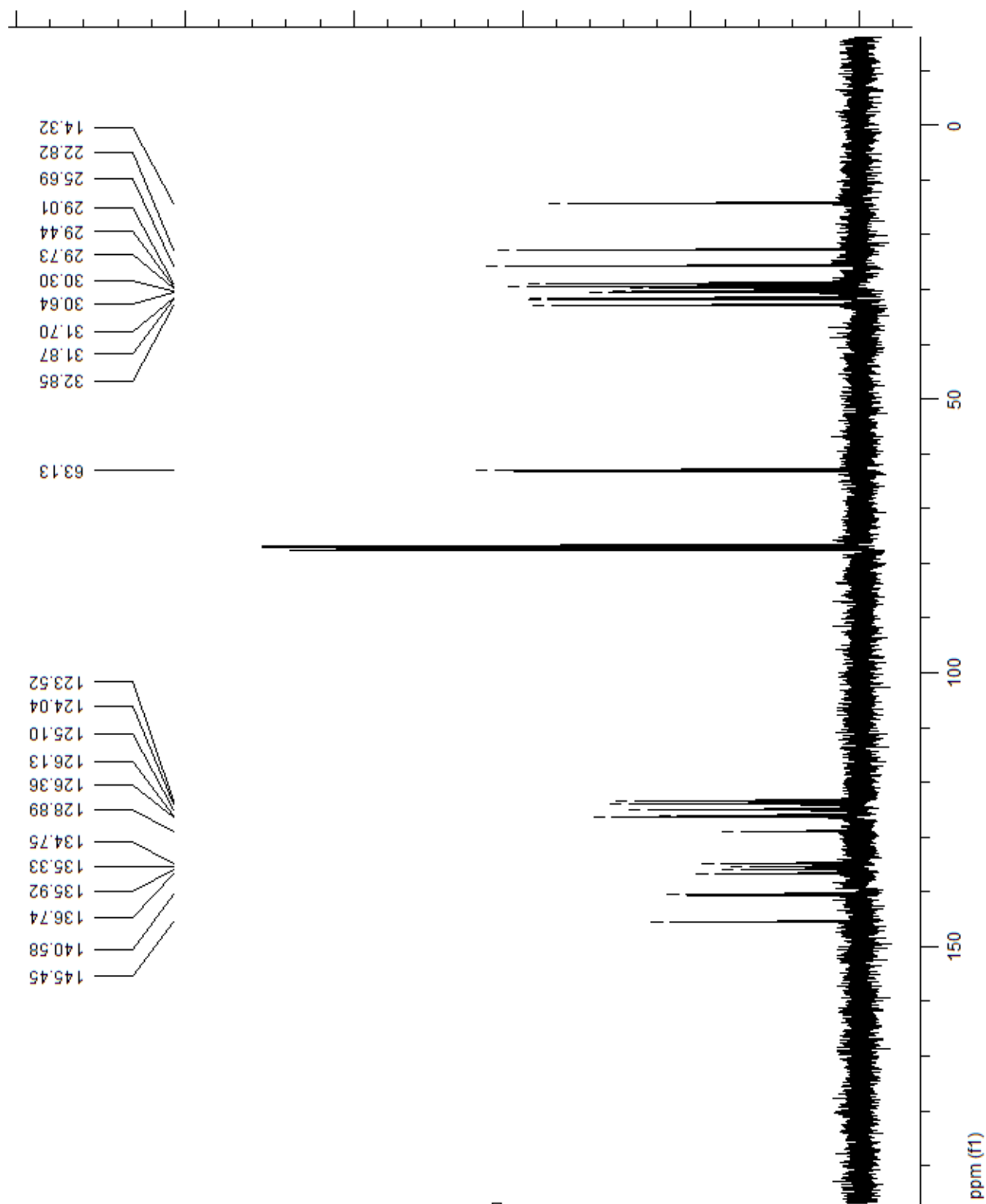


Figure S2.  $^{13}\text{C}$ -NMR spectrum of T6-diol in  $\text{CDCl}_3$ .

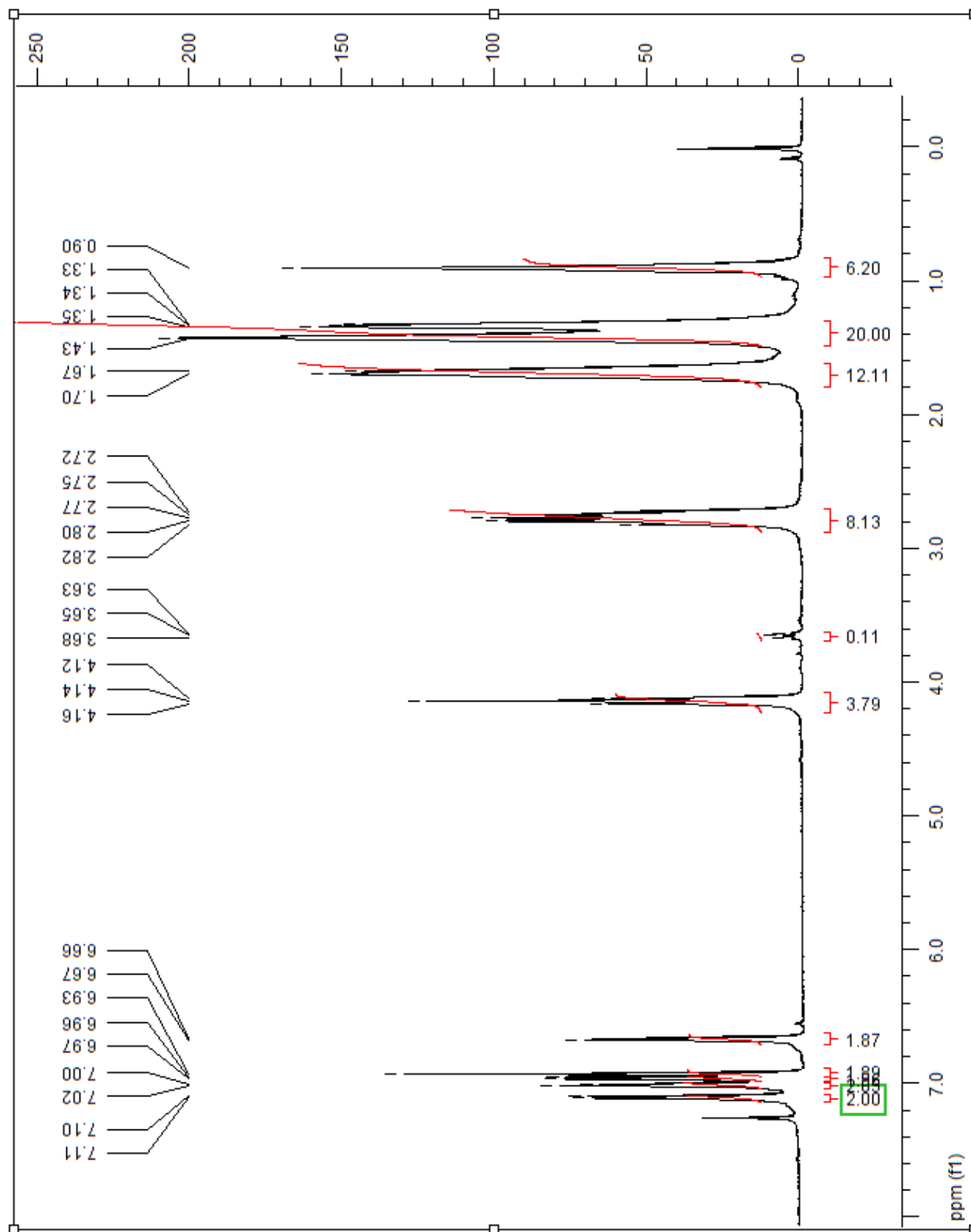


Figure S3. <sup>1</sup>H-NMR spectrum of T6PC in CDCl<sub>3</sub>.

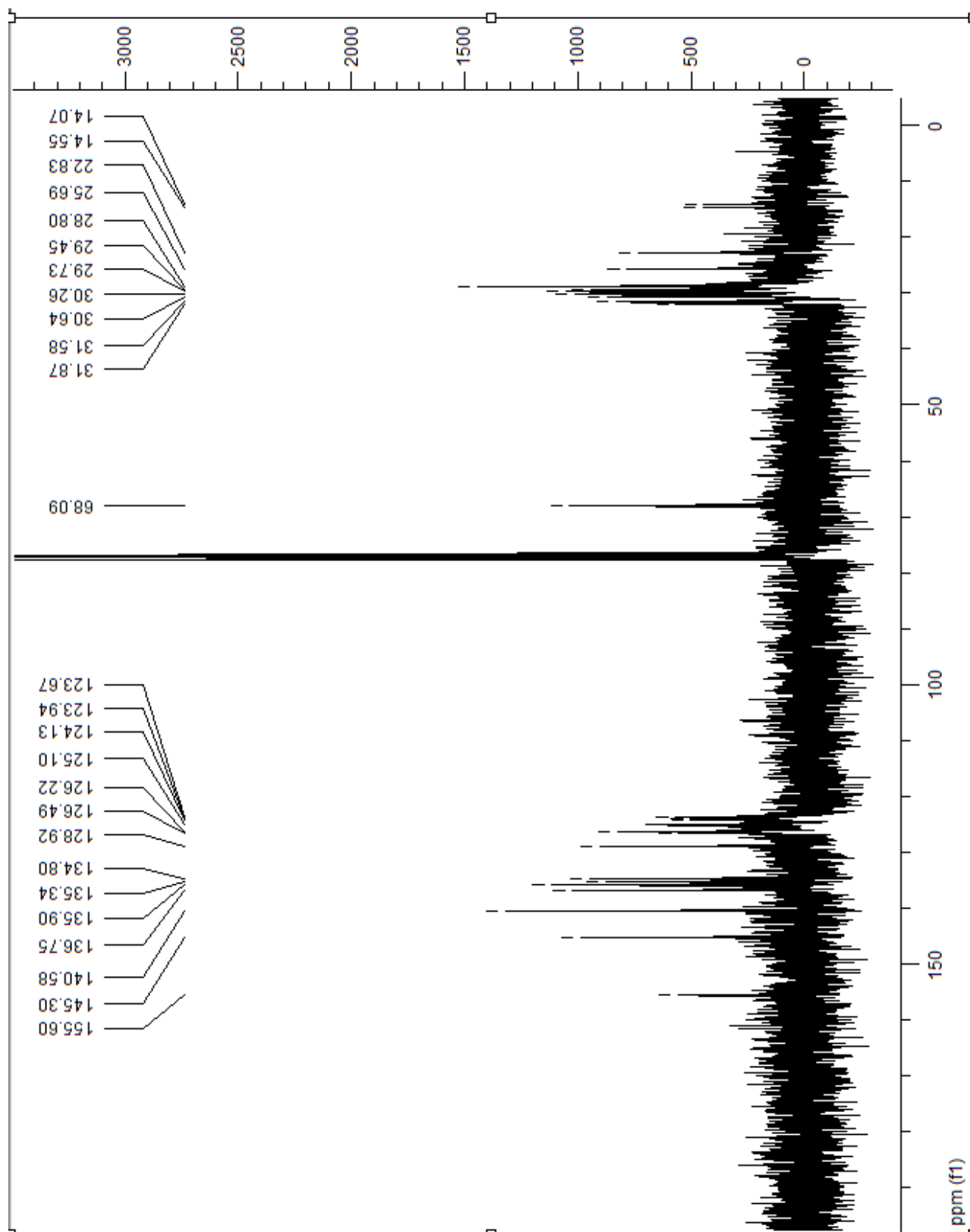
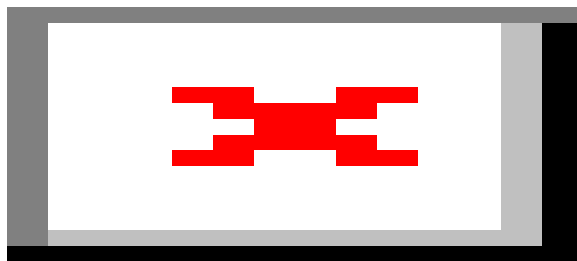
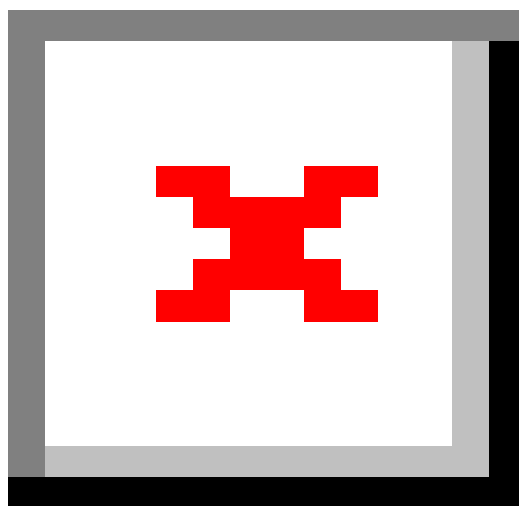


Figure S4.  $^{13}\text{C}$ -NMR spectrum of T6PC in  $\text{CDCl}_3$ .

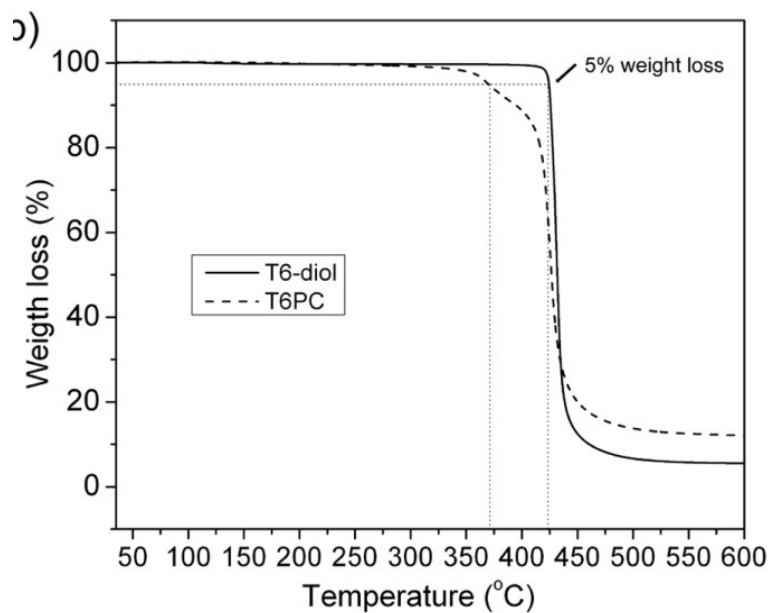


**Figure S5.** Detail of  $^1\text{H}$ -NMR spectrum (a) of the polycarbonate T6PC with the red arrow at 3.65 ppm indicating the protons on the carbon alpha to unreacted terminal alcohols; IR spectra (b) of T6-diol (black line) and T6PC (blue line).

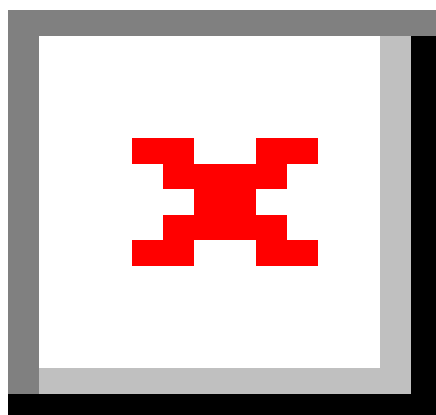


**Figure S6.** Size exclusion chromatography trace for T6PC in THF, calibrated against polystyrene standards.

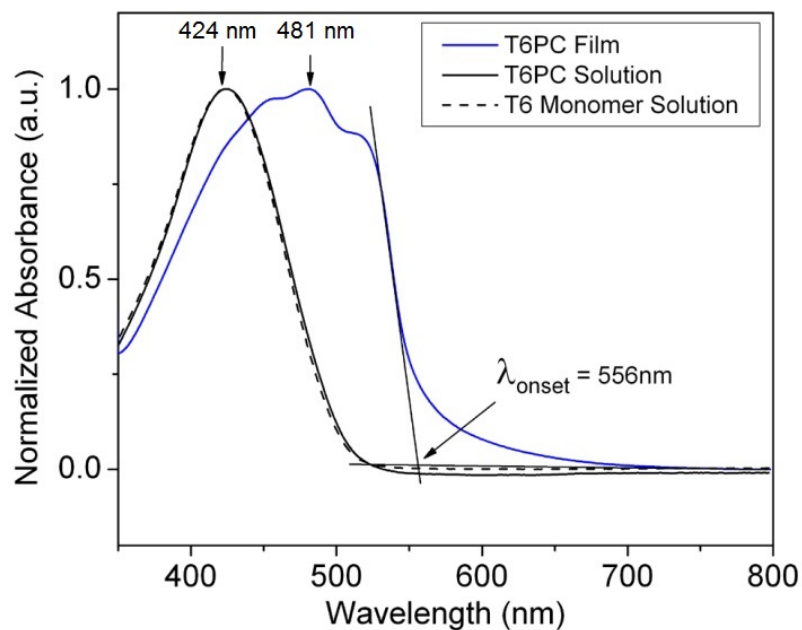




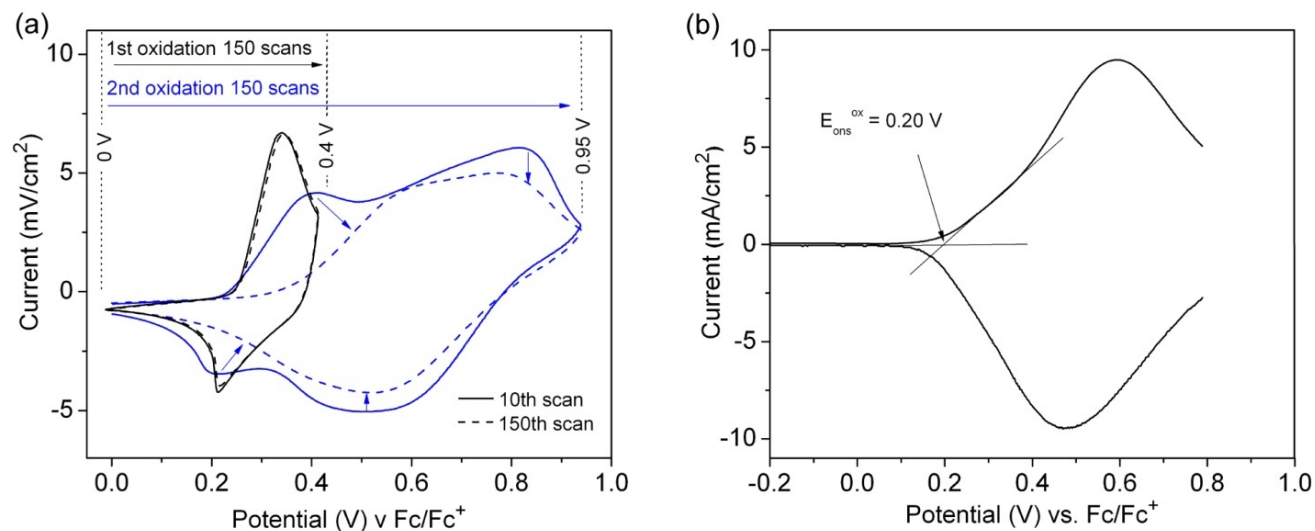
**Figure S7.** TGA thermograms of T6-diol (solid line) and T6PC (dashed line) under nitrogen.



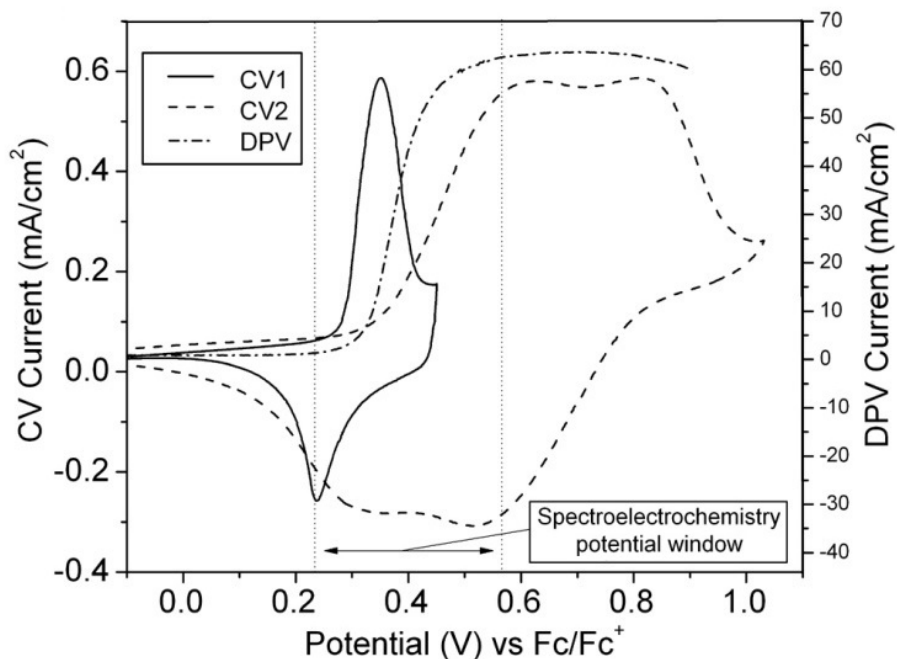
**Figure S8.** Evolution of the DSC heating thermograms of T6PC with increasing room temperature annealing times from 0h to 48h (recorded at 10°C/min).



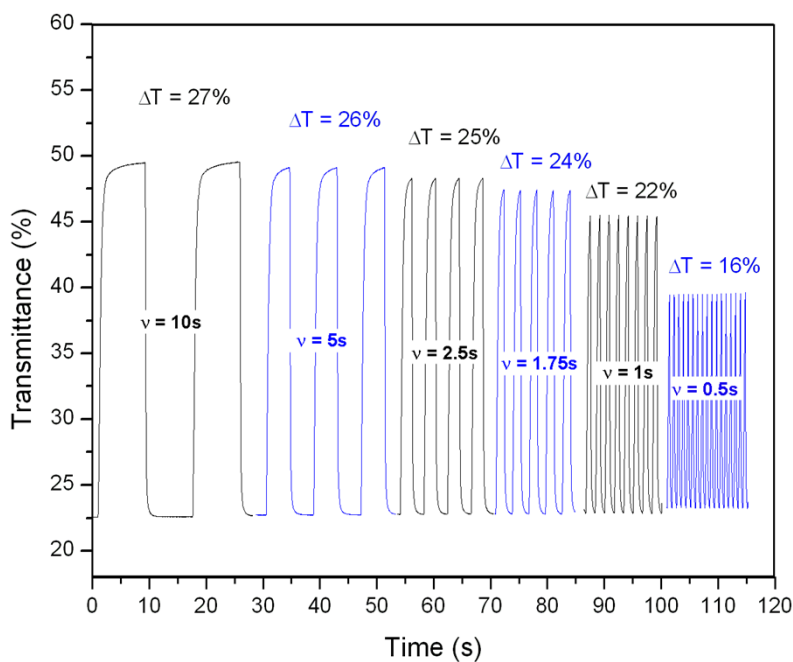
**Figure S9.** UV-vis spectra of T6-diol (dashed, black line) and T6PC in THF solution (solid, black line) and T6PC thin film sprayed onto ITO-coated glass slide (blue line)



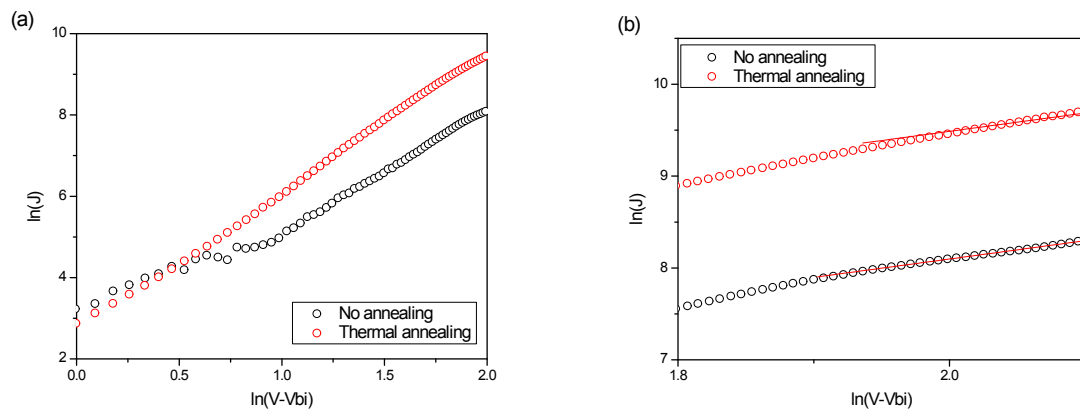
**Figure S10.** Tenth (solid lines) and 150th (dashed lines) cyclic voltammograms (a) from 0 to 0.4 V (black lines) and from 0 to 0.95 V (blue lines) of T6PC drop-cast onto Pt-button electrodes in 0.1 M LiBTI/ACN under inert atmosphere. Differential pulse voltammogram (b) of T6PC drop-cast onto Pt-button electrodes under the same conditions.



**Figure S11.** Cyclic voltammograms from -0.1 to 0.45 V (black line) and from -0.1 to 1.05 V (dashed line) and DPV (dash-dot line) of T6PC sprayed onto ITO-coated glass slides in 0.1 M LiBTI/PC under inert atmosphere



**Figure S12.** Switching speed experiment featuring square-wave potential step absorptometry (% transmittance at 454 nm) of T6PC films on ITO slides in the LiBTI/PC electrolyte, from 10s to 0.5s switching times.



**Figure S13.** (a) Current density-Voltage on a natural logarithmic plot, and (b) SCLC region of the plot showing SCLC fit to extract hole carrier mobility on T6PC-based device.

#### S4. References

1. C. B. Nielsen, A. Angerhofer, K. A. Abboud, and J. R. Reynolds, *J. Am. Chem. Soc.*, 2008, **130**, 9734–9746.