

Supporting Information

Effect of o-Carborane on the Optoelectronic and Device-Level Properties of Poly(fluorene)s

*Andrew R. Davis, Joseph J. Peterson, Kenneth R. Carter**

Department of Polymer Science and Engineering

University of Massachusetts Amherst

Conte Center for Polymer Research

120 Governors Drive, Amherst, Massachusetts 01003

Experimental

Materials: All reactants, reagents, and solvents were purchased from Aldrich Chemical Co. and used as received unless specified otherwise. All reactions were performed under N₂ atmosphere unless otherwise noted.

Instrumentation: Synthesized polymers were analyzed via ¹H NMR on a Bruker AF 300 (300 MHz). Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and a K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns at 40 °C. Molecular weights are reported relative to poly(styrene) standards. Glass transition temperatures were determined using differential scanning calorimetry (DSC) on a Thermal Analysis (TA) Q-2000 DSC in aluminum pans using a heat-cool-heat cycle at a rate of 10 °C/min. UV-Vis absorbance in CHCl₃ was measured on a Hitachi U-3010 using 1 cm path-length quartz cuvettes. Photoluminescence was measured with a Perkin-Elmer LS-50B fluorescence spectrometer for both spin-coated solid state films on silicon wafers and in dilute CHCl₃ solutions in 1 cm path-length quartz cuvettes. Cyclic voltammetry was performed on a CH Instruments potentiostat in an electrolyte solution of 0.1 M Bu₄NPF₆ in acetonitrile using platinum wires (Bioanalytical System Inc.) as both counter and working electrodes and a silver/silver ion reference electrode (Ag in 0.1 M AgNO₃ solution, Bioanalytical System Inc.).

Synthesis of Carborane-Containing Poly(fluorene) Derivatives: Previously unreported copolymer of fluorene and thiophene with *o*-carborane incorporated directly in the conjugated backbone (PFT-*o*-carb) was synthesized by Stille coupling of the dibromo *o*-carborane monomer [1] (1 equiv.) with 2,5-bis(tributylstannyl)-thiophene (1 equiv.) in the presence of tetrakis(triphenylphosphine) palladium (0.05 equiv) in toluene at 100 °C under N₂ with yields comparable to PF-*o*-carb. ¹H NMR (300 MHz, CDCl₃, δ): 7.63-7.23 (m, 14H, Ar H), 4.15-2.00 (bm, 10H, BH), 2.01-1.68 (m, 8H, CH₂), 1.16-0.8 (m, 52H, alkyl). Number average molecular weight (M_n) = 8.5 kg/mol via GPC (THF vs. polystyrene standards).

The control copolymer of poly(9,9-dihexyl-fluorene -co-thiophene) (PFT) was synthesized by conventional Stille coupling of 2,7-dibromo-9,9-dihexyl-9H-fluorene (1 equiv.) with 2,5-bis(tributylstannyl)-thiophene (1 equiv) in the presence of tetrakis(triphenylphosphine) palladium (0.05 equiv) in toluene at 100 °C under N₂ (40% yield), M_n = 8 kg/mol via GPC (THF vs. polystyrene standards).

Poly(9,9-hiexyl-fluorene) (PF) and its corresponding *o*-carborane-containing copolymer (PF-*o*-carb) were synthesized as described previously [1], M_n = 51 kg/mol and 8.5 kg/mol, respectively, via GPC (THF vs. polystyrene standards). Discrete dimers of fluorene and *o*-carborane-linked fluorene were synthesized as previously reported [1].

Device Fabrication and Characterization: Polymer light emitting diodes (PLEDs) were fabricated using PF, PFT, PF-*o*-carb, and PFT-*o*-carb as active emitting layers. ITO-coated glass was first solvent cleaned and subsequently treated with O₂ plasma for 3 minutes. Poly(ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (1.3wt% in H₂O, Aldrich) was then spin-coated at 4000 RPM and dried under N₂ at 150 °C for 30 minutes. Emissive polymer solutions were then spun from chloroform (10 mg/mL) at 3000 RPM. The coated substrates were dried at 150 °C under N₂ for 1 hour, and devices were completed by the thermal evaporation of 40 nm Ba cathodes capped with 100 nm Al at pressure <10⁻⁵ Torr with active areas of 0.15 cm². Devices were tested in air using a Kiethley 2602 Sourcemeter and a calibrated Ocean Optics USB4000 UV-vis spectrometer.

Bottom-contact thin film transistors (TFTs) were fabricated on highly doped Si with 200 nm of thermally grown SiO₂ serving as the gate and gate dielectric (0.01-0.018 ohm-cm, University Wafer). Gold source and drain contacts (thickness = 50 nm; W/L = 30) were deposited on Si substrates using conventional photolithographic techniques. Thin films of PFT and PFT-*o*-carb were then formed on the substrates using previously reported transfer technique

[2]. TFTs were characterized in air using a Keithley 4200 SCS and a Micromanipulator 6150 probe station.

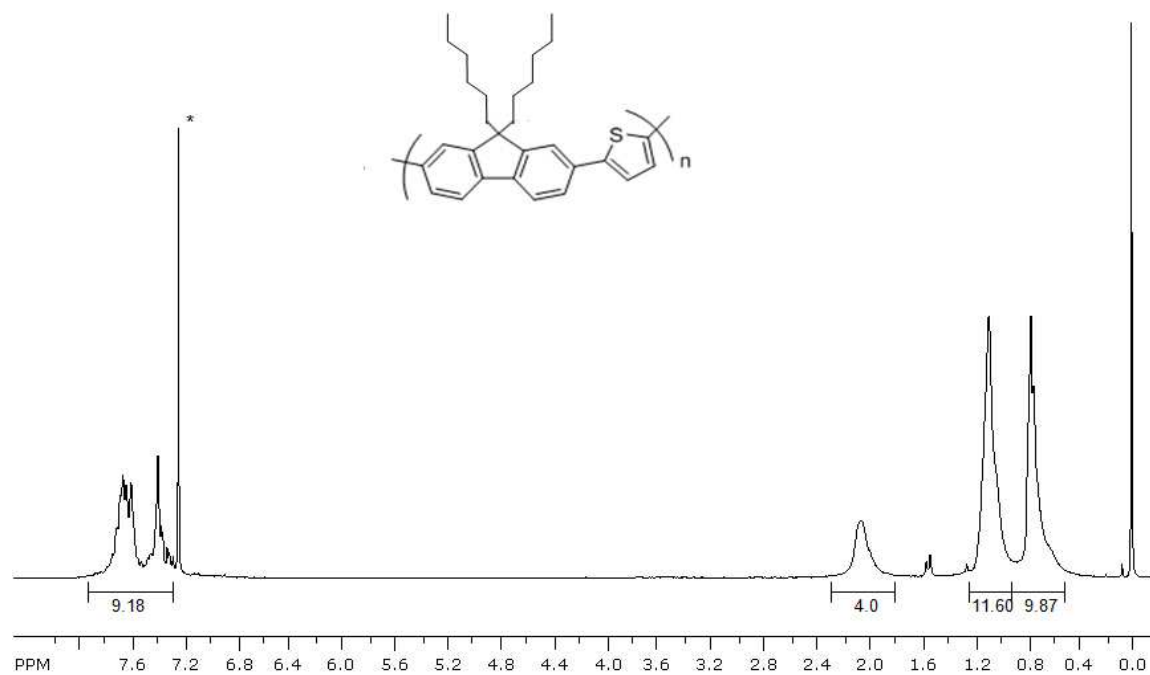


Figure S1- ^1H NMR spectrum of PFT.

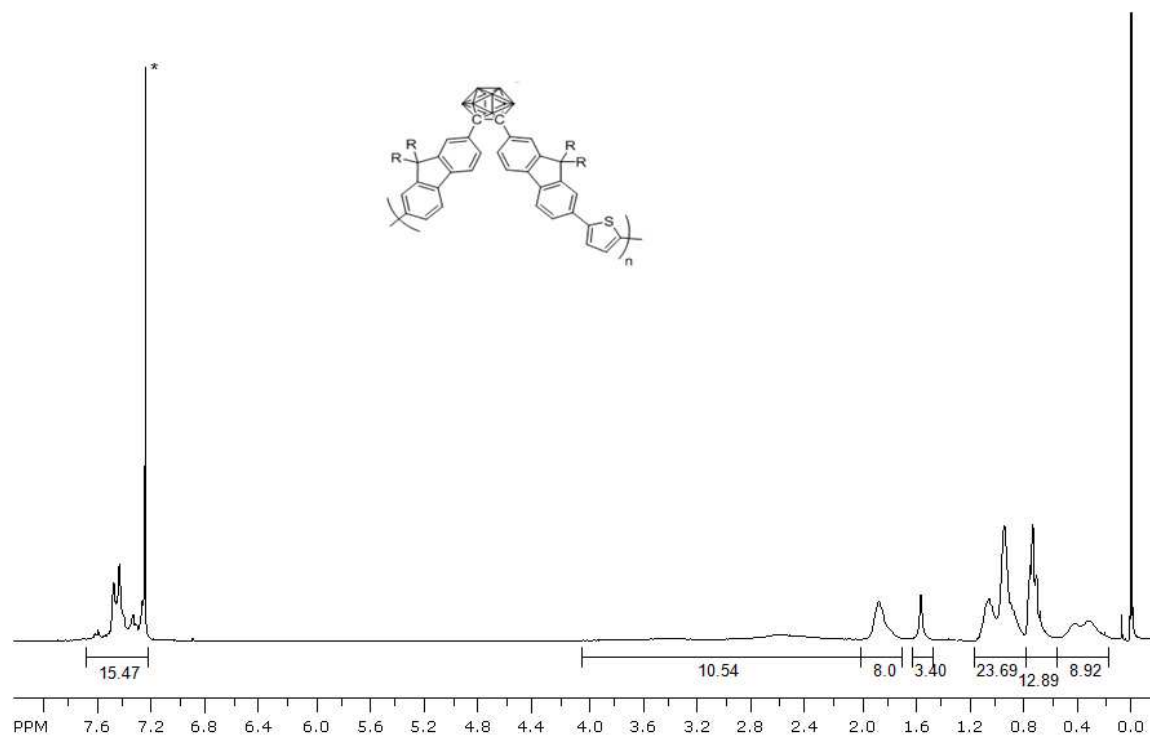


Figure S2 - ^1H NMR spectrum of PFT-*o*-carb. R = hexyl.

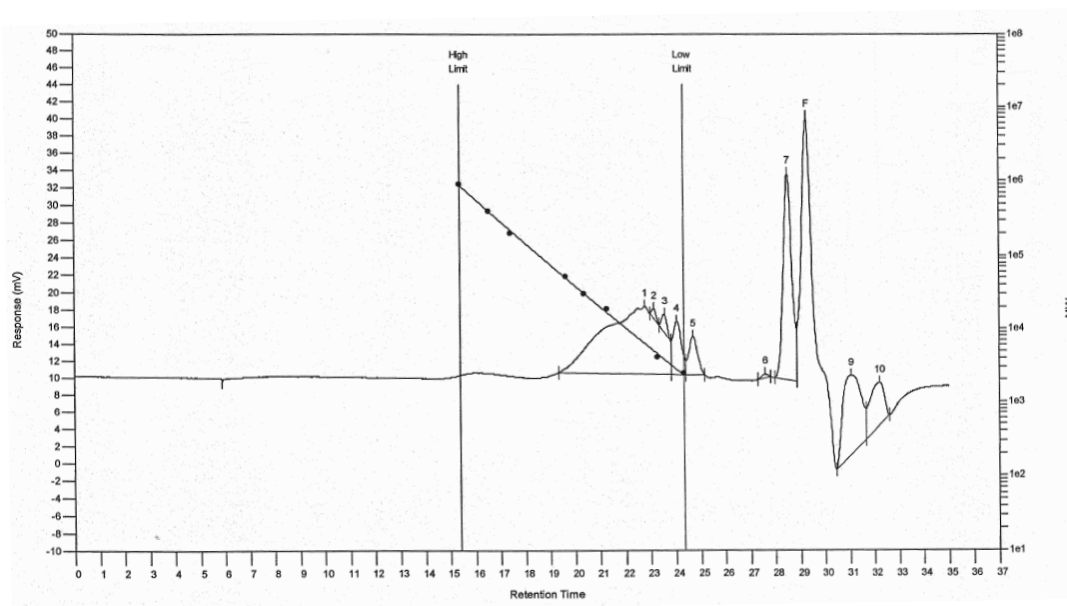


Figure S3 – Analysis of PFT via gel permeation chromatography (THF vs. polystyrene standards).

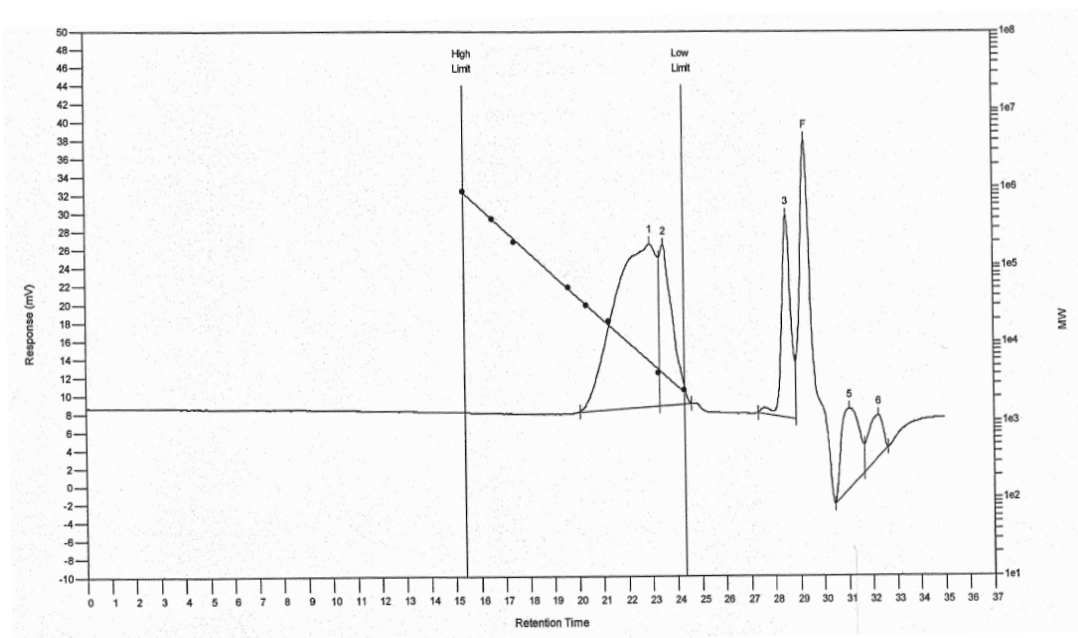


Figure S4 - Analysis of PFT-*o*-carb via gel permeation chromatography (THF vs. polystyrene standards).

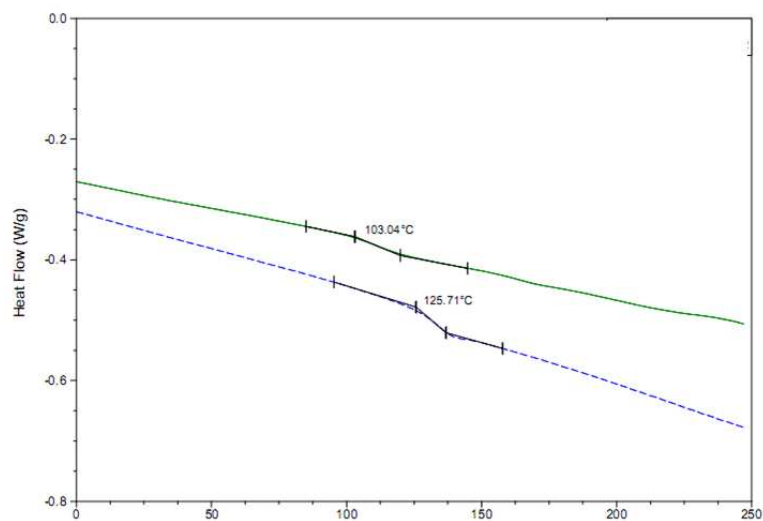


Figure S5 – Glass transition temperatures of PFT (solid green) and PFT-*o*-carb (dashed blue) as determined by differential scanning calorimetry.

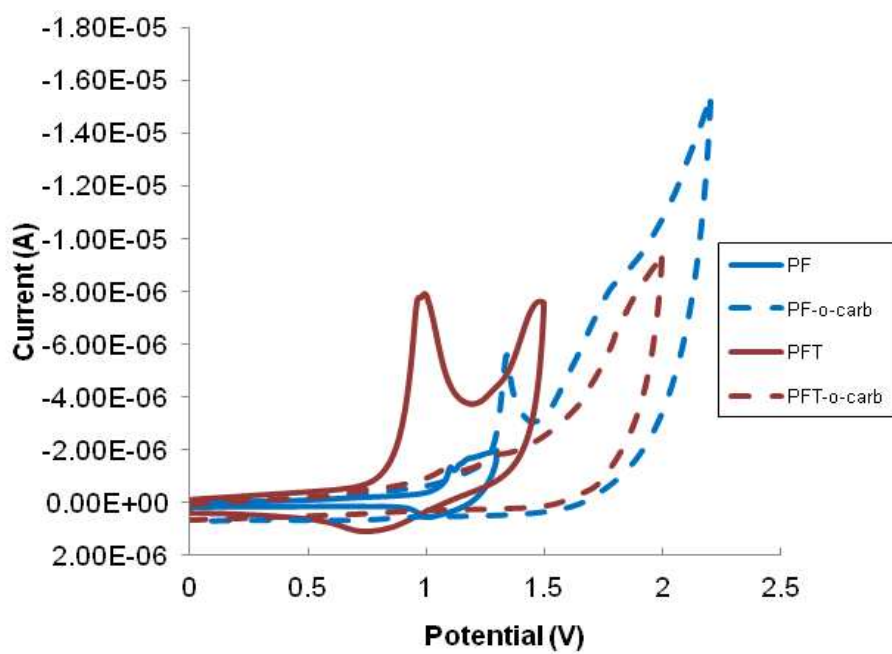


Figure S6 – Cyclic voltammetry (CV) response for poly(fluorene) derivatives measured in dry CH₃CN with 0.1M Bu₄NPF₆ as the electrolyte.

Table S7. Summary of absorption onset wavelength (λ_{onset}), optical bandgap calculated from λ_{onset} , electrochemical oxidation onset (E_{onset}), and HOMO/LUMO levels of poly(fluorene) derivatives. HOMO levels were calculated from the onset of electrochemical oxidation, and LUMO levels were then estimated from the optical band gap.

Sample	λ_{onset} [nm]	Optical Band Gap [eV]	E_{onset} [V]	HOMO/LUMO [-eV]
<i>Polymers</i>				
PF	420	2.96	1.06	5.42 / 2.46
PF- <i>o</i> -carb	384	3.23	1.14	5.50 / 2.27
PFT	481	2.58	0.88	5.24 / 2.66
PFT- <i>o</i> -carb	441	2.81	0.91	5.27 / 2.46
<i>Dimers</i>				
Fluorene	363	3.42	1.14	5.50 / 2.08
Fluorene- <i>o</i> -carb	384	3.23	1.16	5.52 / 2.29

Table S8. Peak emission wavelengths from poly(fluorene) derivatives for photoluminescence in CHCl₃ solution ($\lambda_{PL-soln}$), photoluminescence in thin film ($\lambda_{PL-film}$), and electroluminescence (λ_{EL}).

Sample	$\lambda_{PL-soln}$ [nm]	$\lambda_{PL-film}$ [nm]	λ_{EL} [nm]
PF	416	422	423
PF- <i>o</i> -carb	569	563	570
PFT	469	489	517
PFT- <i>o</i> -carb	602	570	620

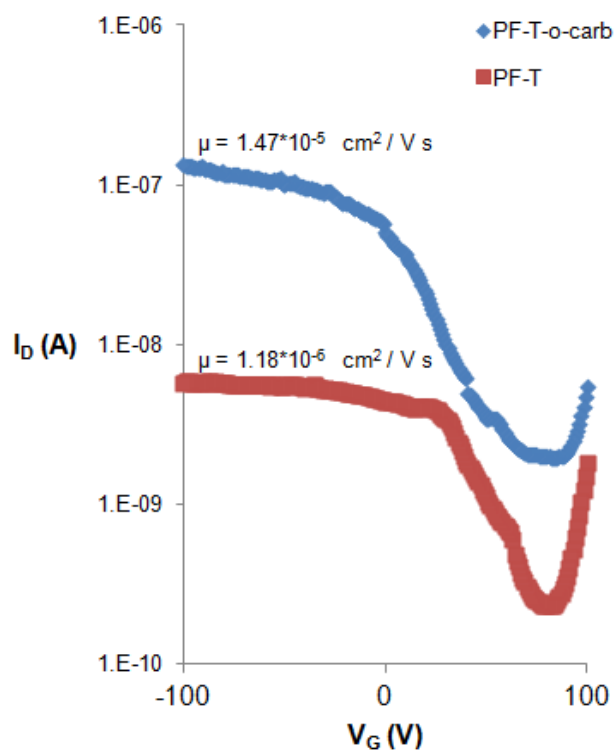


Figure S9. Transfer curves for PFT and PFT-o-carb thin film transistors. Mobilities shown are field-effect hole mobilities calculated for the saturation regime.

References

- [3] J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Macromolecules*. **2009**, 42, 8594.
- [2] Q. Wei, S. Miyanishi, K. Tajima, K. Hashimoto, *Appl. Mater. Inter.* **2009**, 1, 2660.