Supporting Information

Ethynylene-Linked Donor-Acceptor Alternating Copolymers

Wade A. Braunecker,*[,†] Stefan D. Oosterhout,[†] Zbyslaw R. Owczarczyk,[†] Ross E. Larsen,[†] Bryon W. Larson,[‡] David S. Ginley,[†] Olga V. Boltalina,[‡] Steven H. Strauss,[‡] Nikos Kopidakis,[†] and Dana C. Olson[†]

[†]*National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401*

[‡]*Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523*

Email: Wade.Braunecker@nrel.gov

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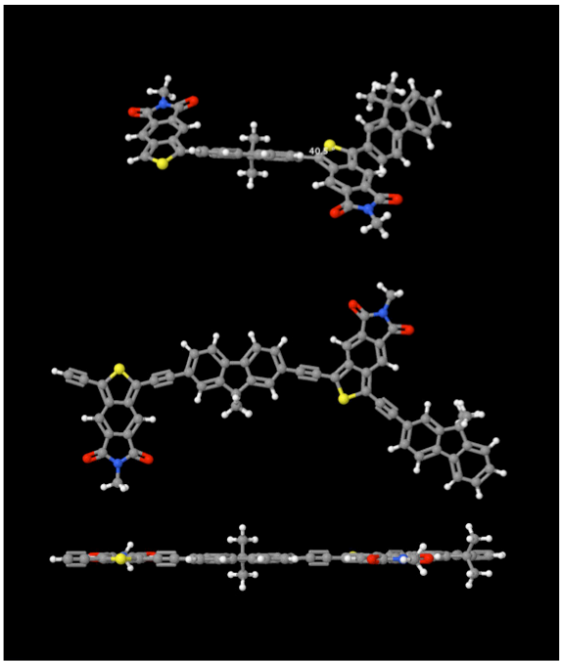


Figure S1. Illustration of the twist in *P*-TID-FLR (top) and planarity of *P*-TID-≡-FLR (middle and bottom).

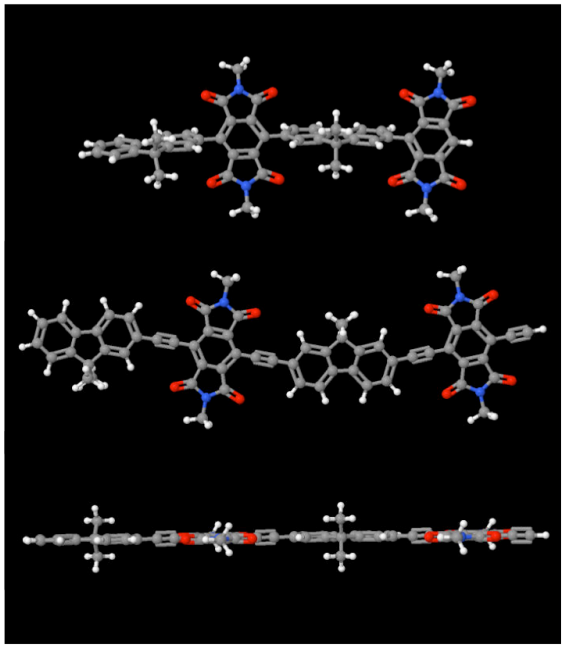


Figure S2. Illustration of the twist in *P*-PMDI-FLR (top) and planarity of *P*-PMDI-≡-FLR (middle and bottom).

II. Absorbance Spectra

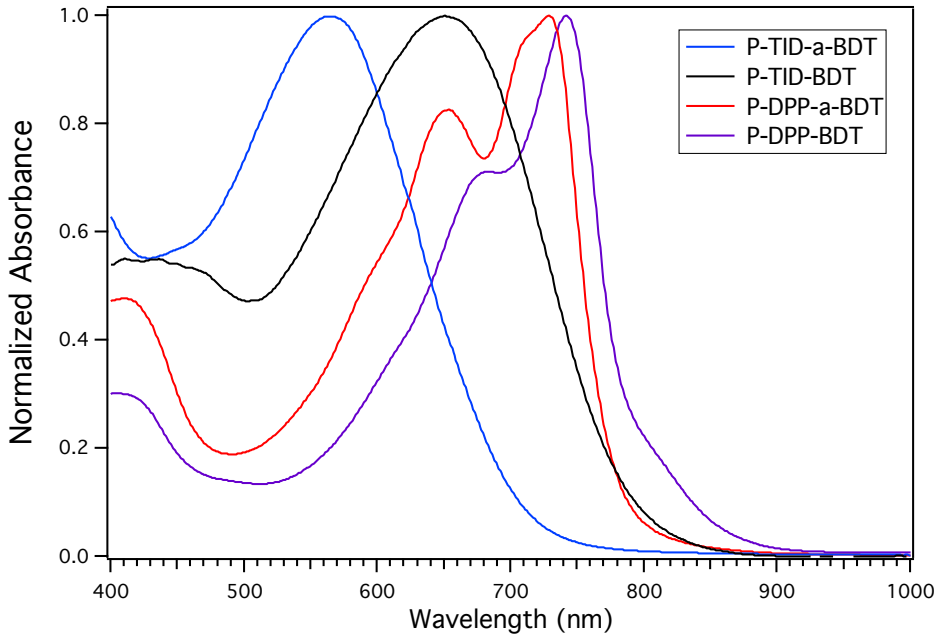


Figure S3. Effect of ethynylene linkages on polymer absorbance (normalized) in $CHCl_3$ solution.

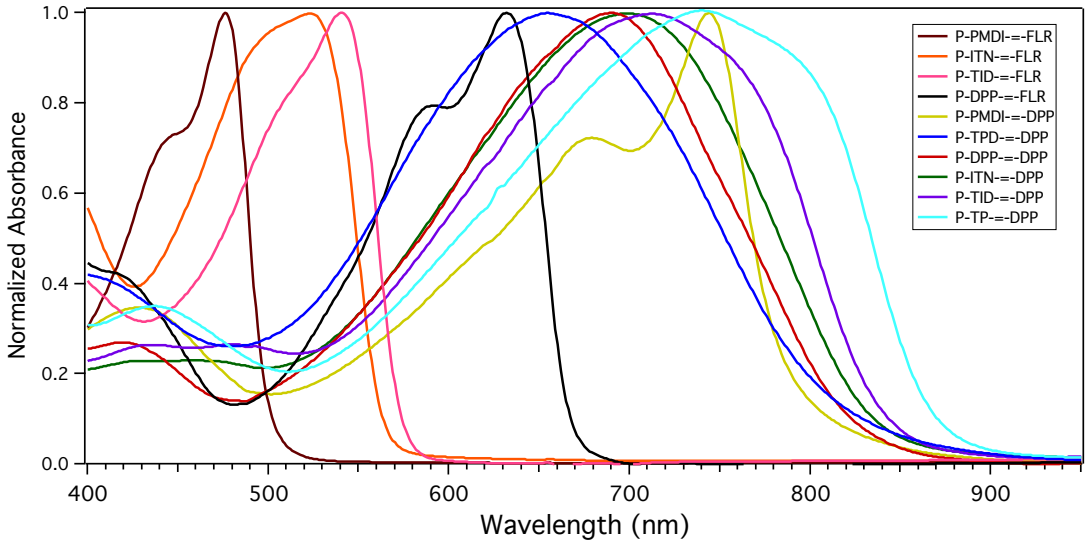
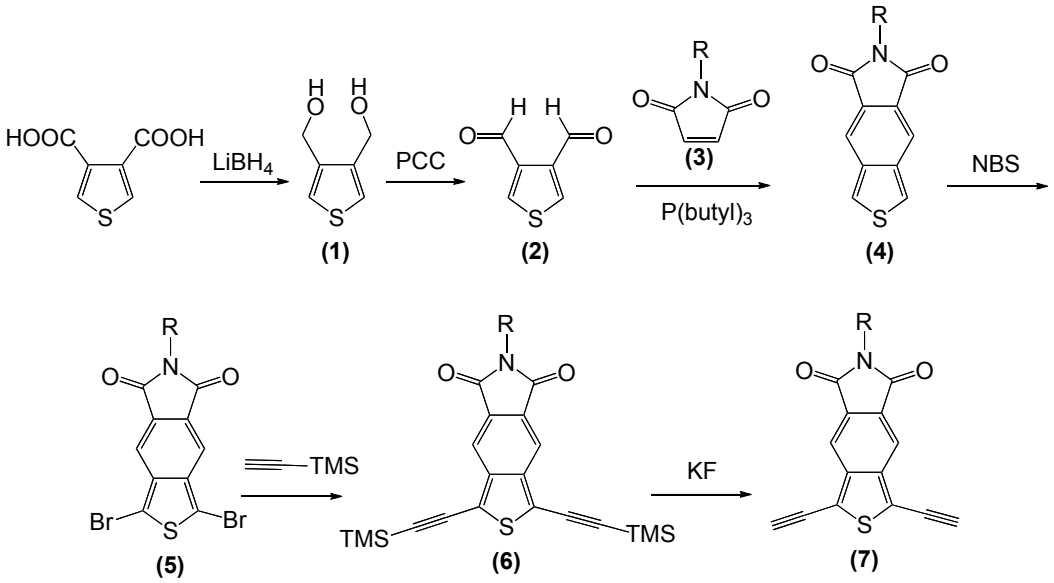


Figure S4. Normalized absorbance spectrum of polymers in solution ($CHCl_3$).

III. Synthetic Procedures



Scheme S1

Compounds **1, 2,** and **3a-5a** (where R = *n*-octyl), were synthesized according to a literature procedure.[1]

1-(2-hexyldecyl)-pyrrole-2,5-dione (**3b**). This compound was synthesized according to a literature procedure[2] developed for *N*-alkyl-pyrrole-2,5-dione derivatives in 78% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (s, 2H), 3.35 (d, 2H, *J* = 7.6 Hz), 1.70 (br m, 1H), 1.22 (br m, 24H), 0.83 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 134.1, 42.3, 37.1, 32.1, 32.0, 31.6, 30.1, 29.8, 29.7, 29.5, 26.4, 22.8, 14.3.

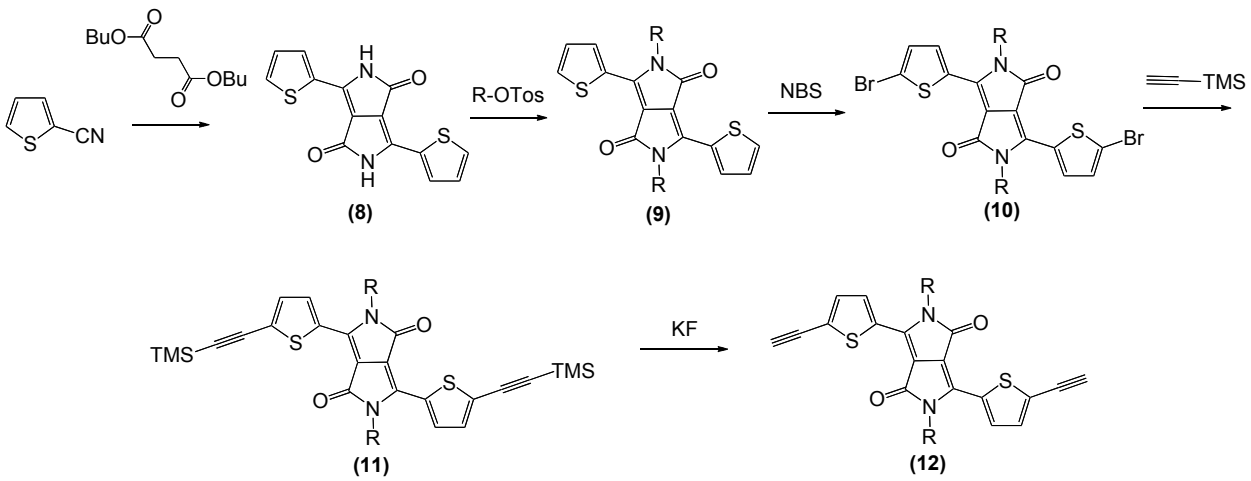
6-(2-hexyldecyl)-thieno[3,4-*f*]isoindole-5-7-dione (**4b**). This compound was synthesized according to a modified literature procedure.[1] Dialdehyde (**2**) (0.70 g, 5.0 mmol) and maleimide (**3b**) (1.6 g, 5.0 mmol) were dissolved in 50 mL anhydrous methylene chloride and stirred in an ice bath. To this cooled solution, a 10 mL solution of methylene chloride containing ~0.1 eq. DBU (75 μL, 0.5 mmol) and 1.5 eq. tri-*n*-

butylphosphine (1.87 mL, 7.5 mmol) was added dropwise. The reaction was stirred for 1 hr at r.t., after which it was concentrated in vacuo and the residue was purified via flash chromatography in hexane:ethyl acetate (4:1). After removing the solvent, the red solid was recrystallized twice from methanol to give 1.7 g (80%) of yellow crystals ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 2H), 8.00 (s, 2H), 3.62 (d, 2H, J = 7.6 Hz), 1.90 (br m, 1H), 1.23 (br m, 24H), 0.83 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 138.6, 126.3, 123.0, 119.7, 42.9, 37.1, 32.1, 32.0, 32.8, 31.8, 30.2, 29.9, 29.7, 29.5, 26.5, 22.9, 14.3.

1,3-Dibromo-6-(2-hexyldecyl)-thieno[3,4-*f*]isoindole-5-7-dione (**5b**). This compound was synthesized according to a modified literature procedure.[1] NBS (0.90 g, 5.0 mmols) was added to a stirred solution of compound (**4b**) (1.04 g, 2.43 mmols) in a mixture of 25 mL of chloroform and 25 mL of acetic acid. The mixture was stirred at r.t. overnight, and then stirred at 60 °C for 2 hrs. The mixture was quenched with water, the organic layer was separated, and the water layer was extracted 3× with 10 mL of chloroform. The combined chloroform extracts were washed with a sodium bicarbonate solution. After drying over $MgSO_4$, the solvent was evaporated, and the residue was purified via flash chromatography using methylene chloride:hexane (1:3) as the eluent to afford 0.93 g (65%) of a bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 2H), 3.62 (d, 2H, J = 7.6 Hz), 1.90 (br m, 1H), 1.23 (br m, 24H), 0.83 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 138.1, 127.5, 118.6, 110.1, 42.9, 37.1, 32.1, 32.0, 31.8, 30.2, 29.9, 29.7, 29.5, 26.5, 22.9, 14.3.

6-(2-hexyldecyl)-1,3-bis((trimethylsilyl)ethynyl)-thieno[3,4-*f*]isoindole-5,7-dione (**6**). To a flask containing **5b** (0.200 g, 0.342 mmol), pre-complexed $PdCl_2(PPh_3)_2$ (12.1 mg, 0.017 mmol), and CuI (3.3 mg, 0.017 mmol) that had been evacuated and refilled with nitrogen 3x was added an oxygen free (nitrogen purged) mixture of THF (2 mL) and diisopropylamine (1 mL). To this solution was added nitrogen purged ethynyltrimethylsilane (122 μL, 0.855 mmol). The solution was heated at 40 °C overnight, afterwhich the solvents were removed by evaporation. The residue was purified via column chromatography using methylene chloride:hexane (1:2) as the eluent to afford 0.195 g (92%) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 2H), 3.61 (d, 2H, J = 7.2 Hz), 1.90 (br m, 1H), 1.23 (br m, 24H), 0.83 (t, 6H), 0.31 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 140.8, 127.5, 120.6, 119.1, 108.1, 94.9, 43.0, 37.1, 32.1, 32.0, 31.8, 30.1, 29.8, 29.7, 29.5, 26.5, 22.9, 14.3, 0.0.

1,3-diethynyl-6-(2-hexyldecyl)-thieno[3,4-*f*]isoindole-5,7-dione (**7**). To a flask containing **6** (0.195 g, 0.315 mmol) and 300 mg of KF was added 5 mL of nitrogen-purged THF and 3 mL of nitrogen-purged H_2O. The biphasic system was stirred rapidly for 20 min, after which the product was extracted with methylene chloride. The residue was purified via column chromatography using methylene chloride:hexane (1:2) as the eluent to afford 0.108 g (72%) of a yellow-green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 2H), 3.86, (s, 2H), 3.61 (d, 2H, J = 7.6 Hz), 1.90 (br m, 1H), 1.23 (br m, 24H), 0.83 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 141.3, 128.0, 119.6, 118.8, 89.1, 74.7, 43.1, 37.1, 32.1, 32.0, 31.8, 30.1, 29.9, 29.7, 29.5, 26.5, 22.9, 14.3.



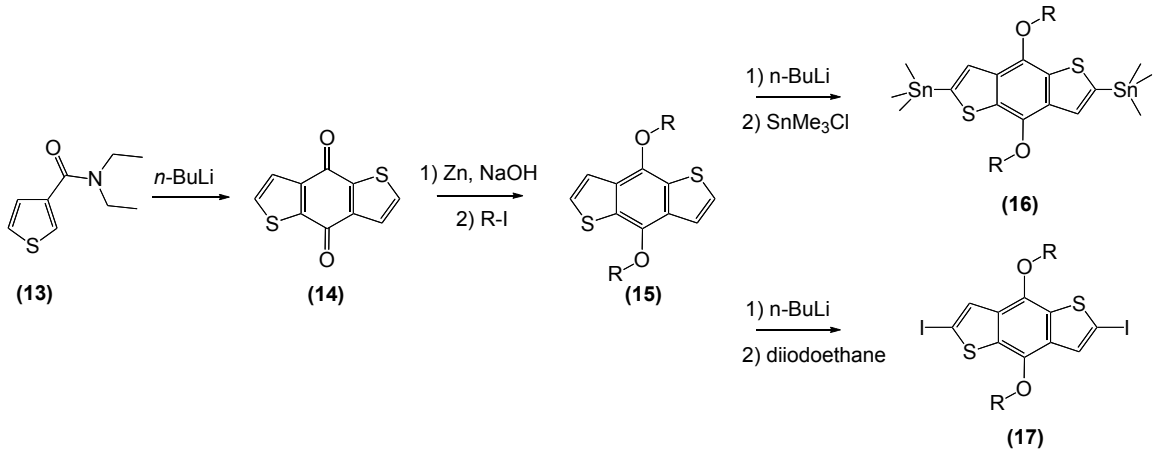
Scheme S2

Compounds **8**-**10**, where R = 2-hexyldecyl, were synthesized according to a literature procedure.[3]

2,5-bis(2-hexyldecyl)-3,6-bis(5-((trimethylsilyl)ethynyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**11**). To a flask containing **10** (0.445 g, 0.490 mmol), pre-complexed $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol), and CuI (4.7 mg, 0.025 mmol) that had been evacuated and refilled with nitrogen 3x was added an oxygen free (nitrogen purged) mixture of THF (3 mL) and diisopropylamine (2 mL). To this solution was added nitrogen purged ethynyltrimethylsilane (172 μL, 1.23 mmol). The solution was heated at 35 °C for 3 hrs, afterwhich the solvents were removed by evaporation. The residue was purified via column chromatography using ethyl acetate:hexane (1:10) as the eluent to afford 0.360 g (82%) of a deep purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, 2H), 7.26 (d, 2H), 3.90, (d, 4H), 1.86 (br, 2H), 1.23 (br m, 48H), 0.82 (t, 12H), 0.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 139.8,

135.5, 133.8, 130.7, 128.6, 109.1, 104.3, 97.0, 46.6, 37.9, 32.1, 32.0, 31.4, 30.2, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3, 0.0.

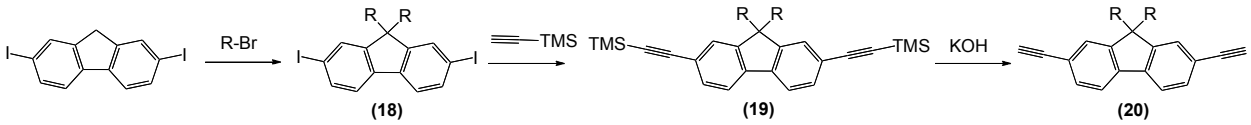
3,6-bis(5-ethynylthiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**12**). To a flask containing **11** (0.360 g, 0.382 mmol) and 300 mg of KF was added 10 mL of nitrogen-purged THF and 3 mL of nitrogen-purged H_2O. The biphasic system was stirred rapidly overnight at r.t., after which the product was extracted with methylene chloride. The residue was purified via column chromatography using ethyl acetate:hexane (1:10) as the eluent to afford 0.228 g (75%) of a deep purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, 2H), 7.26 (d, 2H), 3.90, (d, 4H), 1.86 (br, 2H), 1.23 (br m, 48H), 0.82 (t, 12H), 0.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 139.6, 135.2, 134.0, 130.7, 127.0, 109.0, 85.4, 76.3, 46.6, 37.9, 32.1, 32.0, 31.4, 30.2, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.



Scheme S3

Compounds **13**,[4] **14**,[4] **15**,[1] and **16**[1] were synthesized according to literature procedures.

2,6-Diiodo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b′*] dithiophene (17). This procedure is based on a modified literature procedure for an analgous 2,6-diiodo-4,8-bis(alkoxy)benzodithiophene compound.[5] Anhydrous nitrogen-purged THF (15 mL) was added to compound **15** (0.221 g, 0.5 mmol), and the solution was cooled to -78 °C in a dry ice bath. 2.5 eq. of n-BuLi (2.5 M THF solution, 0.5 mL) was added dropwise. The solution was stirred at -78 °C for 30 min, was removed from the ice bath for 30 min while stirring, and was then recooled to -78 °C. 1,2-diiodoethane (0.366 g, 1.3 mmol) was added in one portion. The reaction was stirred at -78 °C for one more hr before it was allowed to warm to r.t. Water (30 mL) was added to quench the reaction, and the product was extracted with methylene chloride (30 mL). The methylene chloride solution was dried over $NaSO_4$, after which the solvent was distilled off. The residue was purified via column chromatography using methylene chloride:hexane (3:10) as the eluent to afford 0.320 g (93%) of a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 4.08 (d, 4H), 1.90-1.35 (m, 18H), 0.99 (t, 6H), 0.94 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.1, 132.4, 130.4, 78.4, 76.5, 40.8, 30.6, 29.4, 24.0, 23.3, 14.4, 11.5.



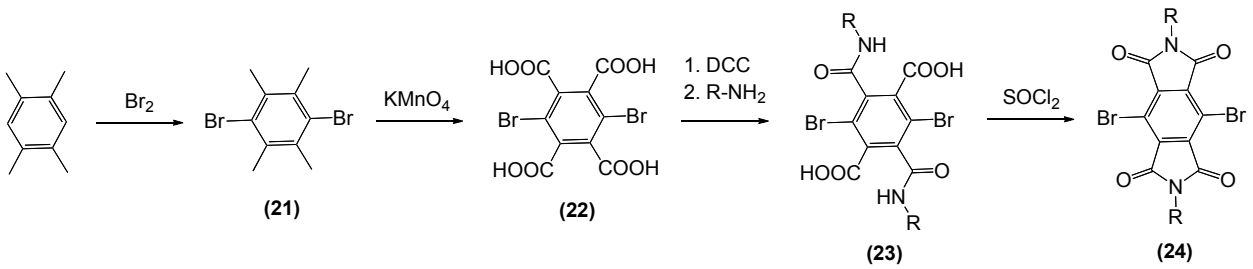
Scheme S4

Compounds **18**-**20**, where R = 2-ethylhexyl, were all synthesized using a literature procedure[6] for derivatives where R = *n*-octyl.

9,9-bis(2-ethylhexyl)-2,7-diiodo-9*H*-fluorene (**18**). Compound **18** was isolated in 77% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (t, 2H), 7.63 (d, 2H), 7.39 (d, 2H), 1.90 (d, 4H), 0.95-0.65 (m, 22H), 0.53 (t, 6H), 0.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 140.1, 136.1, 133.6, 121.6, 92.6, 55.4, 44.4, 34.9, 33.9, 28.3, 27.4, 23.0, 14.4, 10.6.

(9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(trimethylsilane) (**19**). Compound **19** was isolated in 91% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H), 7.42 (m, 4H), 1.93 (d, 4H), 0.95-0.65 (m, 22H), 0.50 (m, 8H), 0.25 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ150.8, 140.8, 131.0, 127.4, 121.4, 119.7, 106.0, 94.0, 54.8, 44.5, 34.7, 33.3, 27.9, 27.0, 22.7, 14.1, 10.3, 0.0.

9,9-bis(2-ethylhexyl)-2,7-diethynyl-9*H*-fluorene (**20**). Compound **20** was isolated in 95% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, 2H), 7.47 (m, 4H), 3.10 (s, 2H), 1.95 (d, 4H), 0.95-0.65 (m, 22H), 0.50 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ151.1, 141.3, 131.4, 128.0, 120.6, 120.1, 84.7, 77.3, 55.1, 44.6, 34.9, 33.7, 28.2, 27.2, 22.9, 14.2, 10.5.



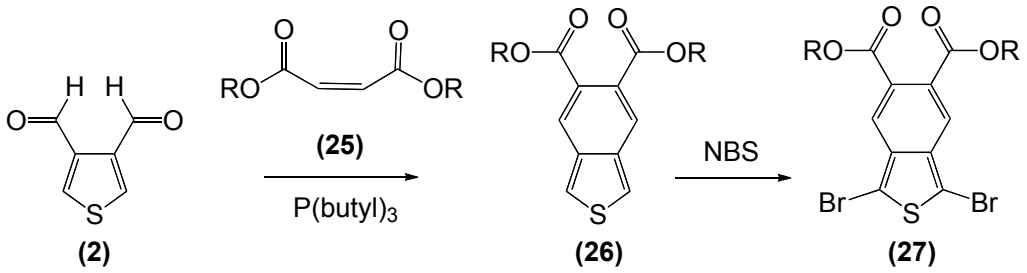
Scheme S5

Compounds **21** and **22** were synthesized according to a literature procedure.[7]

2,5-Dibromo-3,6-bis(2-hexyldecylcarbamoyl)terephthalic acid (**23**). A solution of 3,6-Dibromobenzene-1,2,4,5-tetracarboxylic acid (**22**) (3.00 g, 7.28 mmol) was prepared in anhydrous THF (50 mL) under nitrogen. A separate solution of dicyclohexylcarbodiimide (DCC) (3.60 g, 17.5 mmol) was prepared in anhydrous THF (30 mL) under nitrogen. The DCC solution was added slowly to the former solution, resulting in the formation of a precipitate. The solution was refluxed for 2 hrs under nitrogen, after which it was cooled to r.t. and the precipitate quickly filtered off on the benchtop. The solution was put back under nitrogen, and 2-ethylhexylamine (2.44 mL, 14.9 mmol) was added dropwise (the reaction was very exothermic). This solution was stirred overnight at r.t., afterwhich a small amount of precipitate was again filtered off. The solvent was removed with a rotary evaporator and the residue was dried at 60 °C overnight under vacuum. The yield was nearly quantitative. This product was used in the next step without further purification or characterization.

4,8-Dibromo-2,6-bis(2-hexyldecyl)pyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetraone (**24**). The residue of **23** (1.00 g, 1.58 mmol) was dissolved in 10 mL of

anhydrous DMF under nitrogen. Thionyl chloride (0.575 mL, 7.9 mL) was added slowly. The reaction needed to stir 18 hrs at r.t. before it was complete. After this time, 20 mL of ethyl acetate was added in one portion and 20 mL of water and was added dropwise to quench the reaction. The reaction was stirred vigorously for 30 min. The organic layer was washed twice more with water before the ethyl acetate was removed on a rotarty evaporator. The brown color of the material was removed by washing several times with hexane to leave a yellow powder. This powder was twice recrystallized from 4:1 hexane:ethyl acetate to give a highly pure (>99%) material by 1H NMR. The following NMR signals agree very well with literature values for this compound.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (d, 4H), 1.94 (m, 2H), 1.4 (m, 16H), 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ164.0, 136.3, 114.3, 43.1, 38.4, 30.7, 28.7, 24.1, 23.1, 14.2, 10.6.



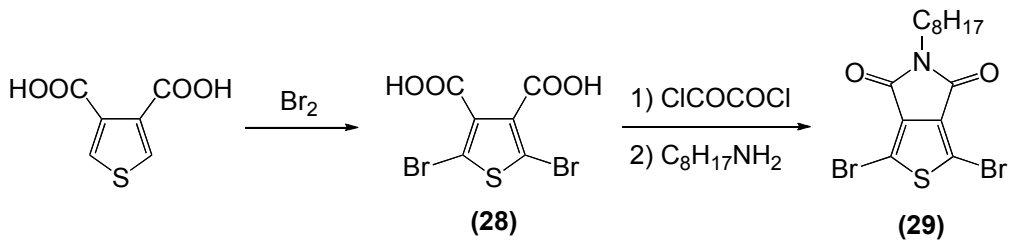
Scheme S6

Bis(2-hexyldecyl) maleate (**25**). Maleic anhydride (0.60 g, 6.1 mmol) was added with 2-hexyl-1-decanol (3.02 g, 12.5 mmol) to 20 mL of anhydrous toluene. The reaction was heated at 70 °C overnight, at which point the mono adduct had been formed. Toluene was removed with a rotary evaporator. Dowex 50x8-100 ion exchange resins (0.1 g) were then added, and the reaction was heated at 100 °C under vacuum for 2 days.

Column chromatography was performed in 10:1 hexane:ethyl acetate. The product had an R_F value of approximately 0.75 in this system, the free alcohol an R_F ~ 0.5, and the mono-adduct an R_F ~0.05. The pure product was obtained in ~50% yield (1.8 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 (s, 2H), 4.06 (d, 4H), 1.65 (br m, 2H), 1.25 (m, 48H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ165.4, 129.7, 68.2, 37.2, 31.9, 31.8, 31.1, 30.0, 29.6, 29.3, 26.6, 22.7, 14.1.

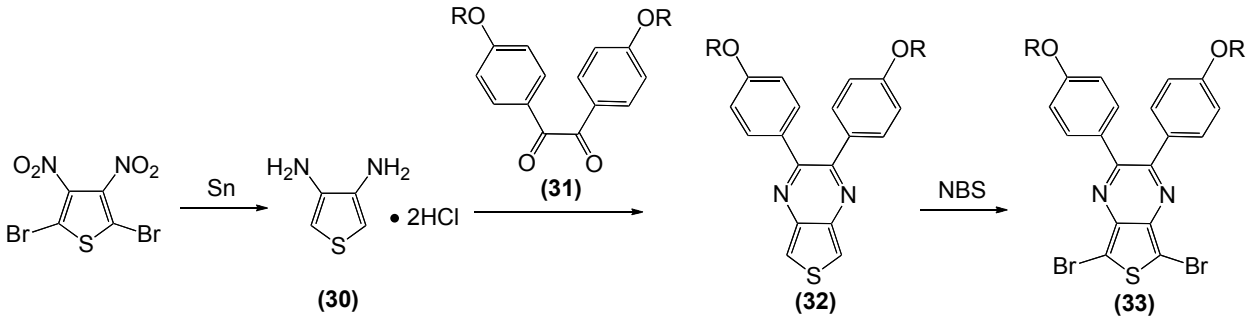
Bis(2-hexyldecyl) benzo[*c*]thiophene-5,6-dicarboxylate (**26**). This compound was synthesized in an analogous manner to compound **4** in approximately 90% yield as a yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 2H), 7.86 (s, 2H), 4.19 (d, 4H), 1.75 (br m, 2H), 1.25 (m, 48H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ168.2, 137.0, 127.4, 124.9, 120.7, 68.6, 37.6, 32.1, 31.5, 30.2, 29.9, 29.8, 29.6, 27.0, 26.9, 22.9, 14.3.

Bis(2-hexyldecyl) 1,3-dibromobenzo[*c*]thiophene-5,6-dicarboxylate (**27**). This compound was synthesized in an analogous manner to compound **5** in approximately 45% yield as a red oil. It was used immediately for polymerization, as the product did not appear to be oxidatively stable and became discolored at r.t., as has been observed for analogous compounds.[9] . ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 2H), 4.19 (d, 4H), 1.75 (br m, 2H), 1.25 (m, 48H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ167.5, 136.2, 129.0, 123.8, 107.5, 69.0, 37.6, 32.1, 31.5, 30.2, 29.9, 29.8, 29.6, 27.0, 26.9, 22.9, 14.3.



Scheme S7

Compounds **28**[10] and **29**[1] were synthesized according to literature procedures.



Scheme S8

Compounds **30**[11] and **31**-**33**[12] were synthesized according to literature procedures.

1,7-Bis-trifluoromethyl[60]fullerene. The compound $C_{60}(CF_3)_2$ was synthesized according to literature procedures,[13] but isolated in high purity by a more efficient single-stage HPLC method not previously described. The crude trifluoromethylfullerene product mixture, along with unreacted C_{60}, was dissolved in a 50/50 v/v mixture of toluene/heptane and then filtered through a 0.45 μm PTFE membrane filter before HPLC separation (10 x 250 mm Cosmosil Buckyprep-M column, 5 mL/min flow rate, diode array detection) using the same eluent mixture for the mobile phase. The fraction collected at 11.1 – 12.0 minutes corresponded to +99% purity $C_{60}(CF_3)_2$. ^{19}F NMR (376.07 MHz, C_6F_6) δ –72.3 (s). APCI-MS (–) obs. 858.95, calc. 858.62.

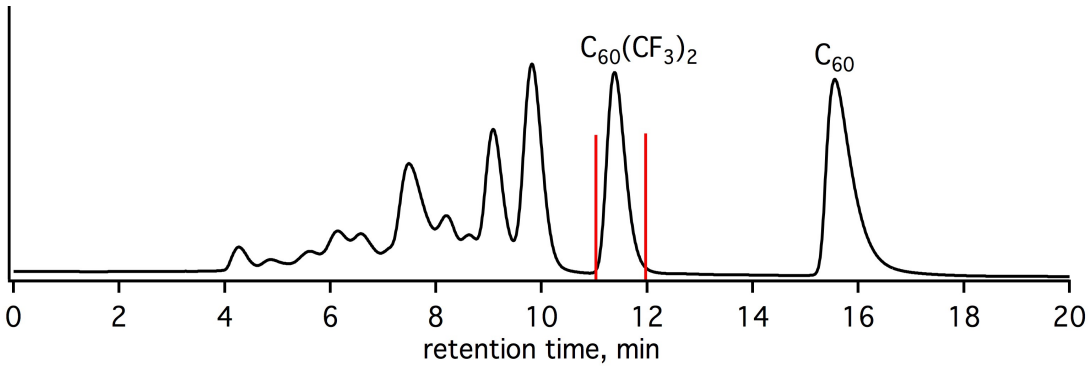


Figure S5. HPLC chromatogram of the crude products after trifluoromethylation of C_{60} showing the collected fraction corresponding to $C_{60}(CF_3)_2$ denoted by red vertical bars (11.1-12.0 minutes). The flow rate was 5 mL/min with 50/50 v/v toluene/heptane mixture as eluent.

Typical Proceedure for Stille Coupling Polymer Synthesis. Compound **5a** (100 mg, 0.21 mmol), compound **16** (163 mg, 0.21 mmol), $Pd_2(dba)_3$ (2 mol %) and tri(o-tolyl)phosphine (12 mol %) were placed in a flask, purged with three nitrogen/vacuum cycles, and subsequently dissolved in 5 mL of dry oxygen free chlorobenzene. The mixture was stirred for 36 h at 110 °C, after which 20 μL of 2-bromothiophene was injected as a capping agent. The reaction was stirred for 2 h at 110 °C before 20 μL of 2-(tributyltin)thiophene was injected to complete the end capping. After an additional 2 h of stirring, a complexing ligand (N,N-diethylphenylazothioformamide) was stirred with the polymer to remove any residual catalyst before being cooled to r.t. and precipitated into methanol (100 mL). The precipitate was purified via Soxhlet extraction with methanol and acetone. Typical yields were around 80%.

Typical Proceedure for Sonogashira Coupling Polymer Synthesis. Compound **20** (88 mg, 0.20 mmol), compound **24** (119 mg, 0.20 mmol), $Pd(PPh_3)_4$ (6 mg, 5.2 μmol), and CuI (2 mg, 10.5 μmol) were mixed placed in a flask, purged with three nitrogen/ vacuum cycles, and subsequently dissolved in anhydrous oxygen free diisopropylamine (2 mL) and toluene (4 mL). The solution was stirred for 30 min at r.t. and at 60 °C for 6 h, after which 20 μL of ethynyltrimethylsilane was injected as a capping agent. After an additional 2 h of stirring, a complexing ligand (N,N-diethylphenylazothioformamide) was stirred with the polymer to remove any residual catalyst before being cooled to r.t. and precipitated into methanol (100 mL). The precipitate was purified via Soxhlet extraction with methanol and acetone. Typical yields were around 80%.

IV. ^{1}H NMR Spectra of New Monomers and Polymers.

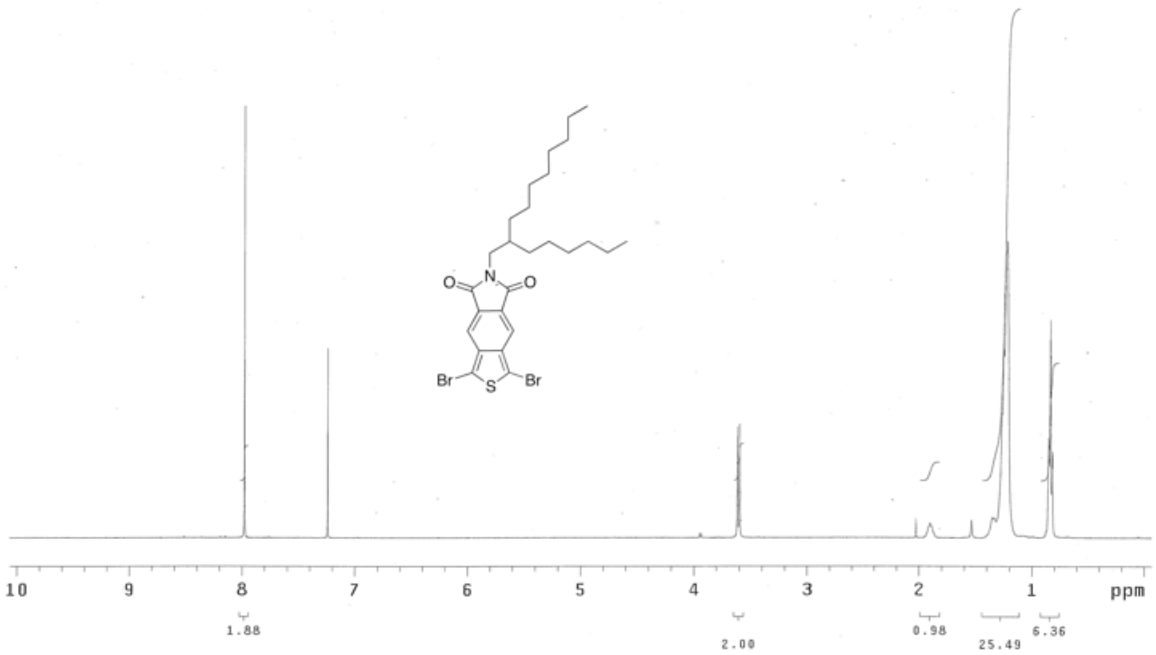


Figure S6. ^{1}H NMR spectrum of 1,3-dibromo-6-(2-hexyldecyl)-thieno[3,4-*f*]isoindole-5-7-dione (**5b**).

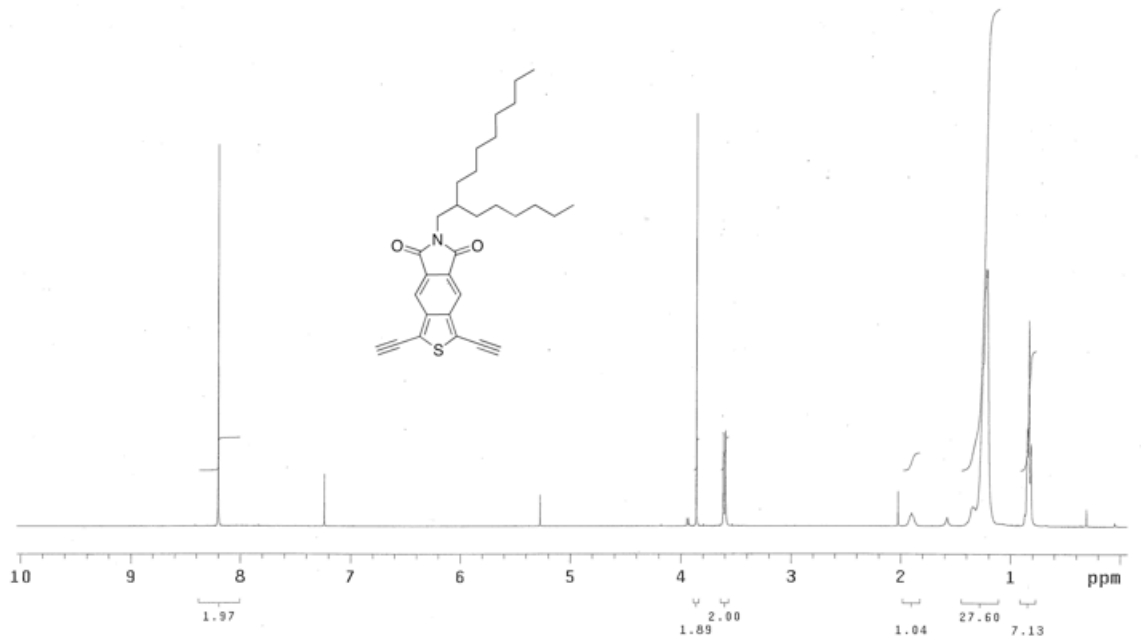


Figure S7. ^{1}H NMR spectrum of 1,3-diethynyl-6-(2-hexyldecyl)-thieno[3,4-*f*]isoindole-5,7-dione (**7**).

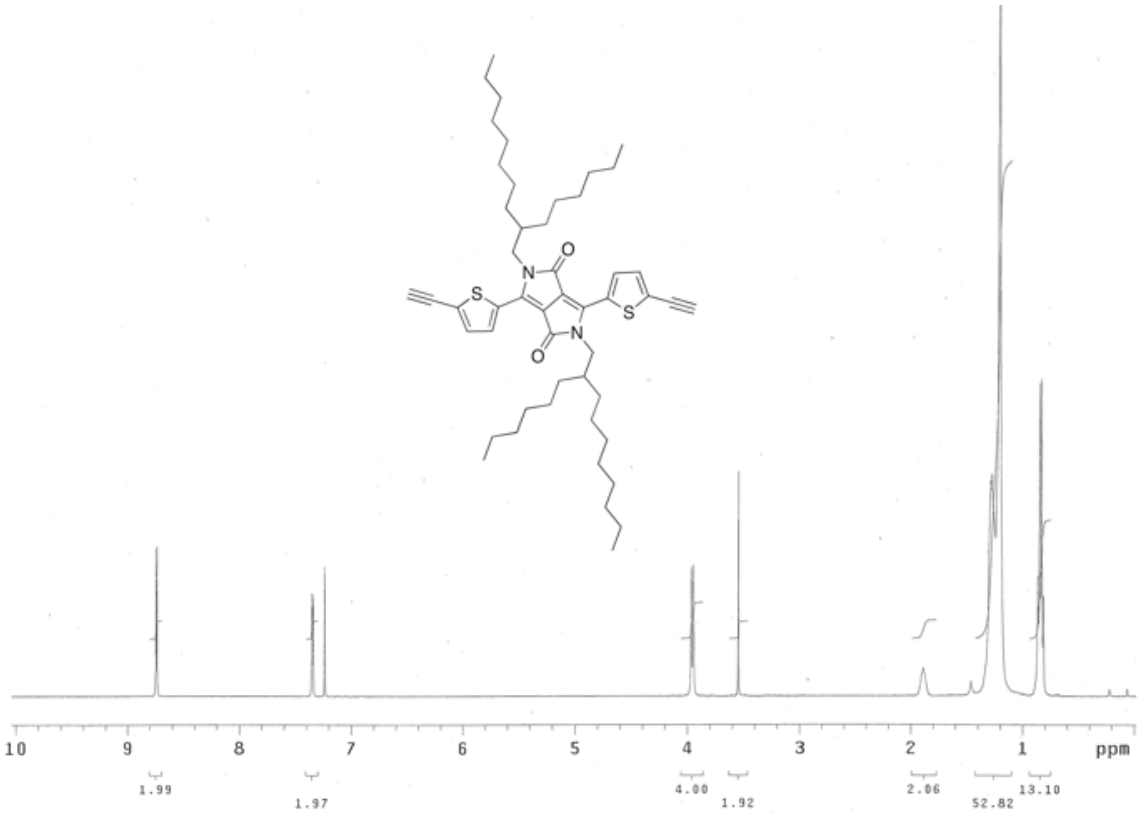


Figure S8. ^{1}H NMR spectrum of 3,6-bis(5-ethynylthiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**12**).

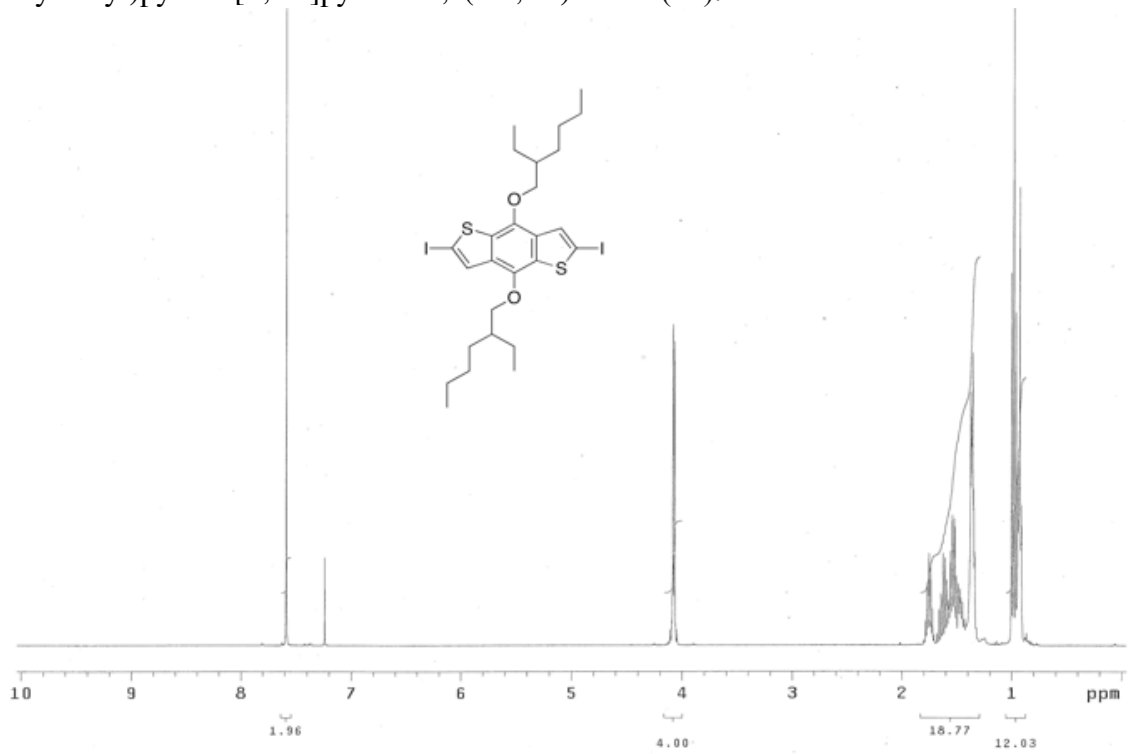


Figure S9. ^{1}H NMR spectrum of 2,6-diiodo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′] dithiophene **(17).**

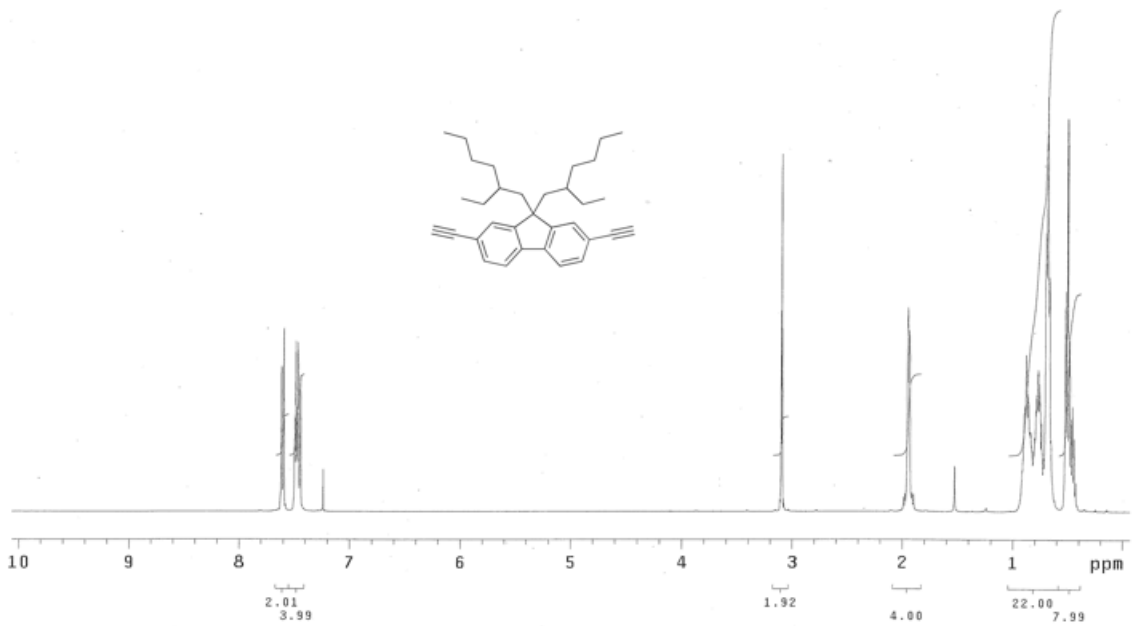


Figure S10. [1]H NMR spectrum of 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9*H*-fluorene (**20**).

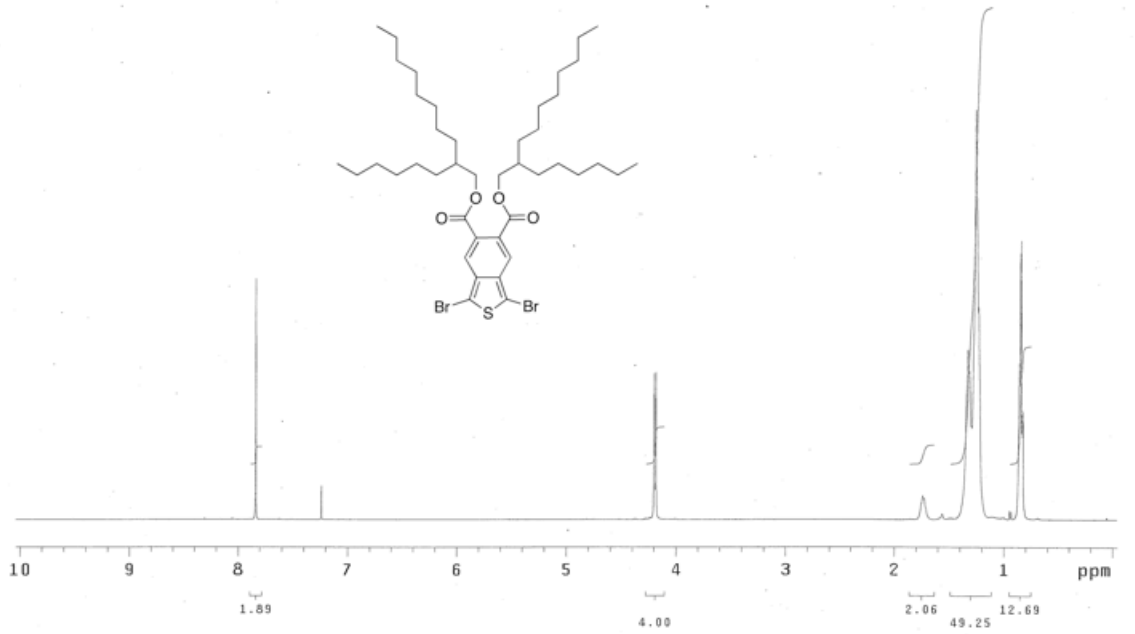


Figure S11. [1]H NMR spectrum of bis(2-hexyldecyl) 1,3-dibromobenzo[*c*]thiophene-5,6-dicarboxylate (**27**).

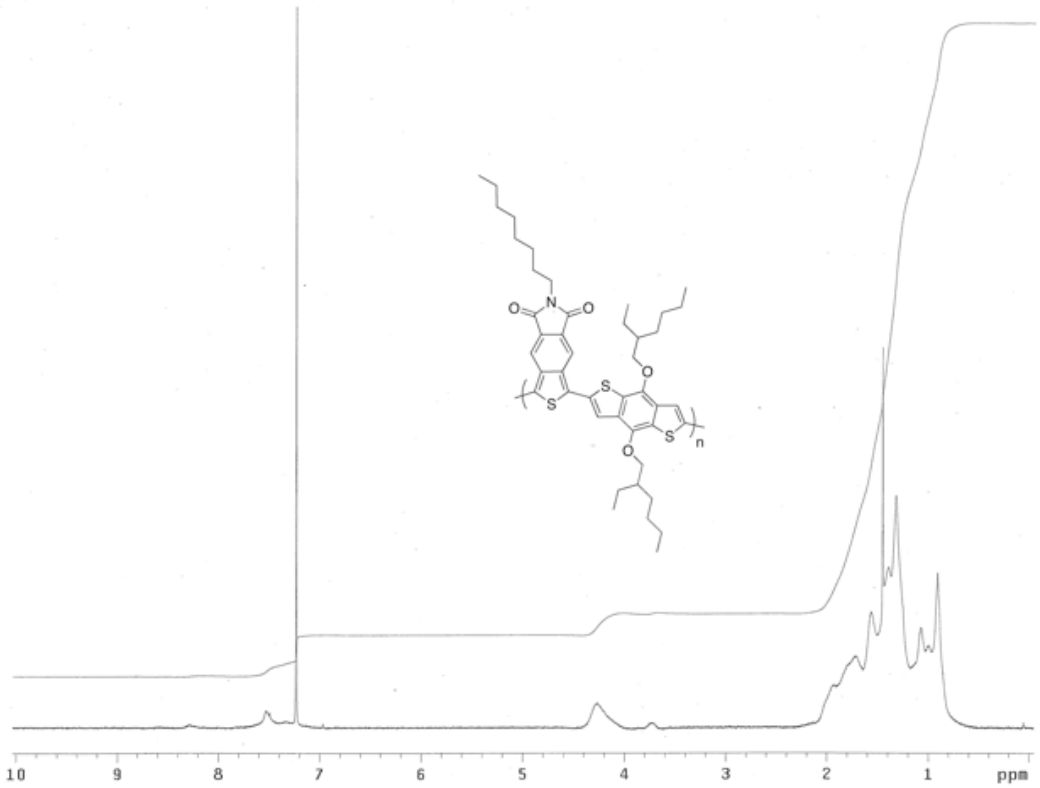


Figure S12. ^{1}H NMR spectrum of *P*-TID-BDT at 50°C in $CDCl_3$.

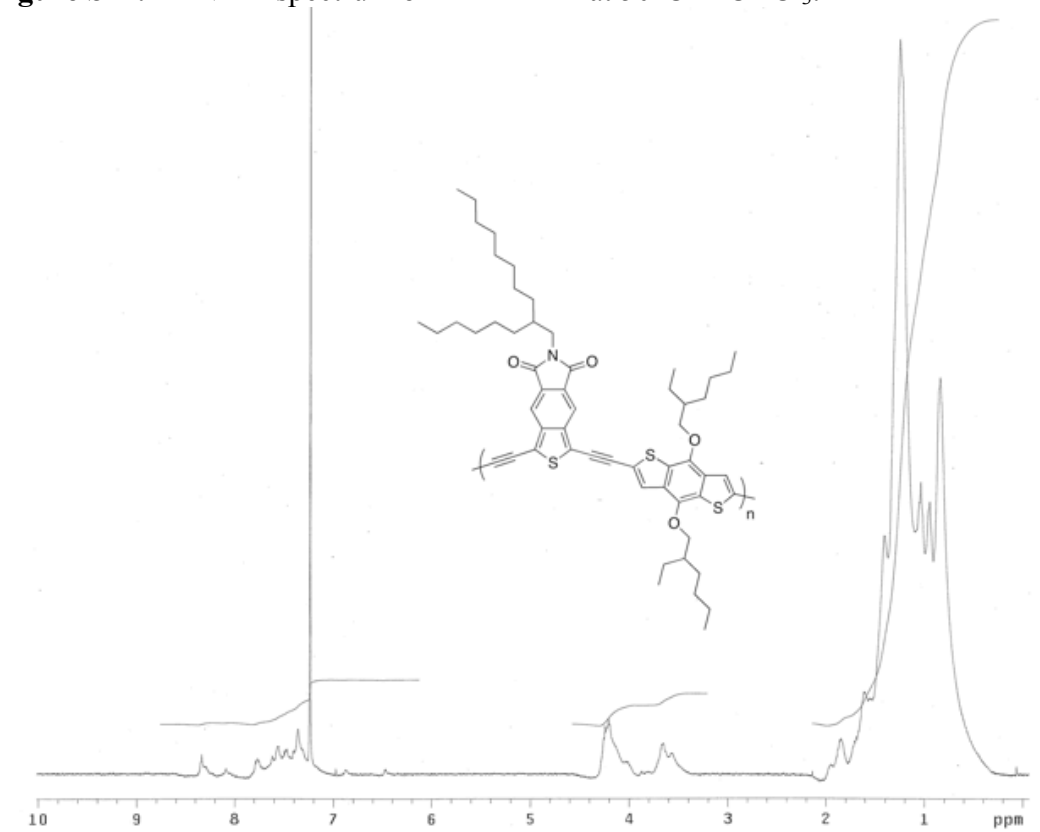


Figure S13. ^{1}H NMR spectrum of *P*-TID-≡-BDT at 50°C in $CDCl_3$.

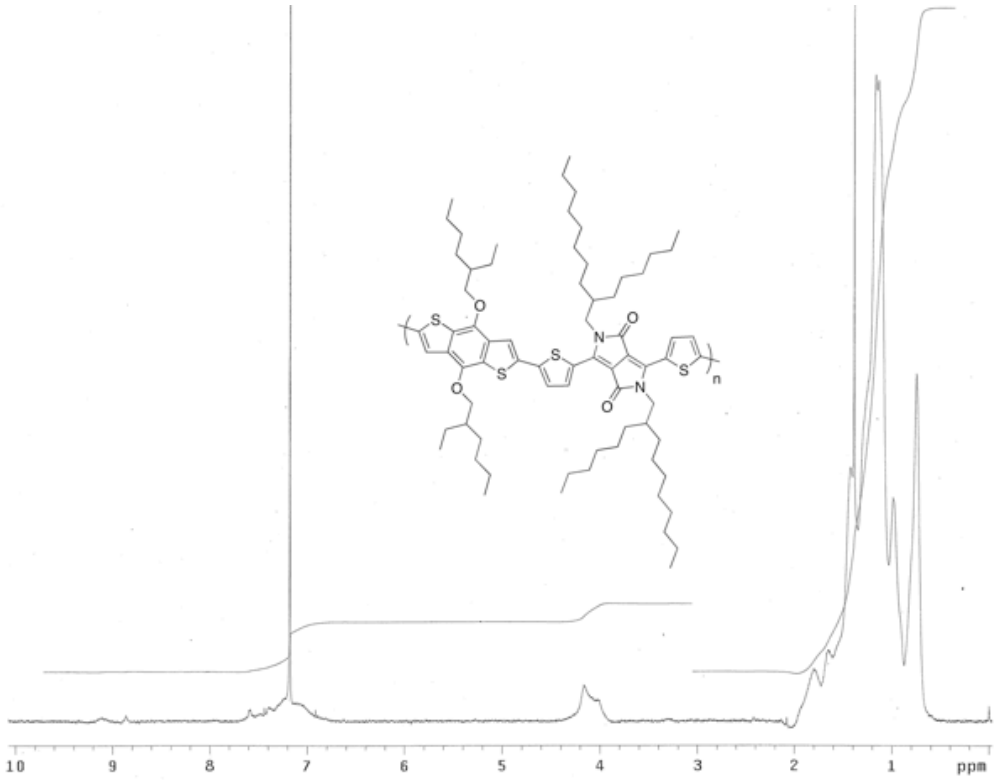


Figure S14. ^{1}H NMR spectrum of *P*-DPP-BDT at 50°C in CDCl.

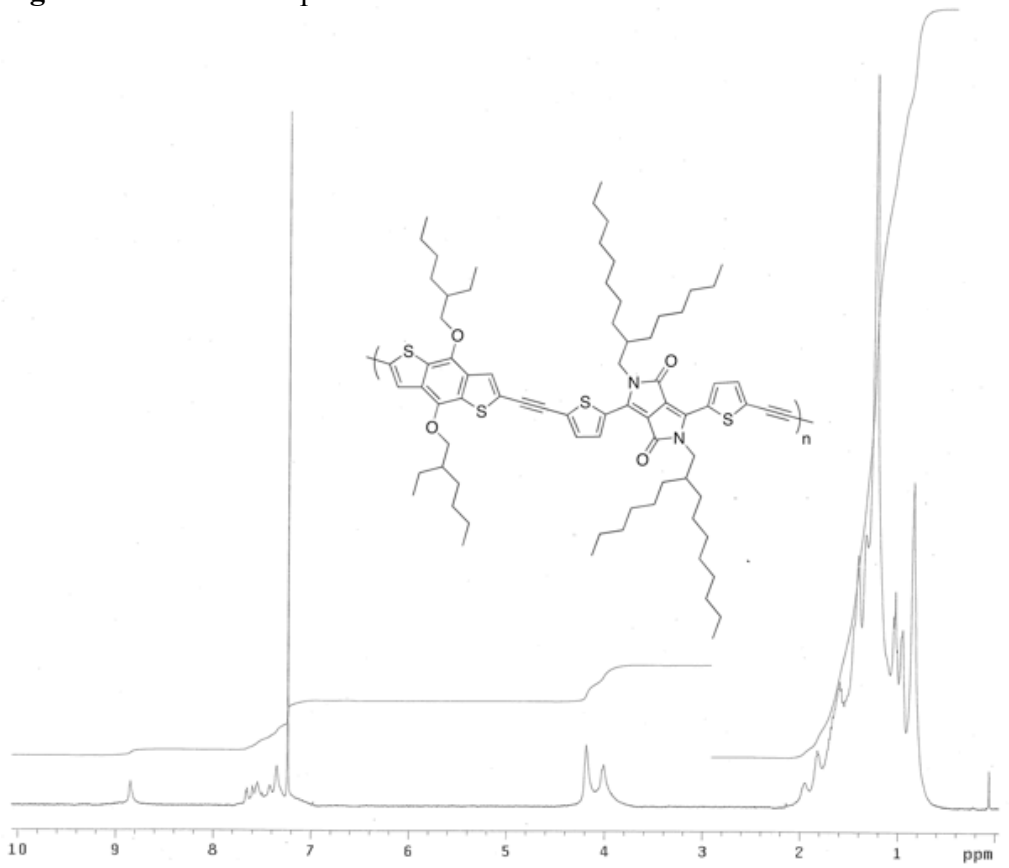


Figure S15. ^{1}H NMR spectrum of *P*-DPP-≡-BDT at 50°C in $CDCl_3$.

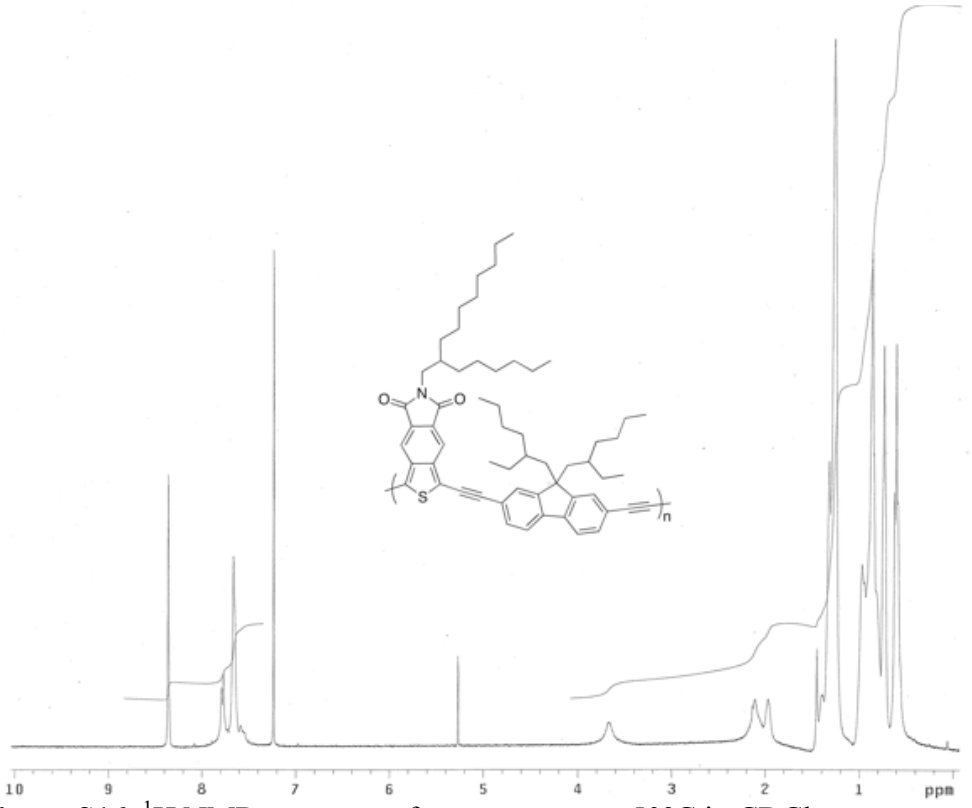


Figure S16. ^{1}H NMR spectrum of *P*-TID-≡-FLR at 50°C in $CDCl_3$.

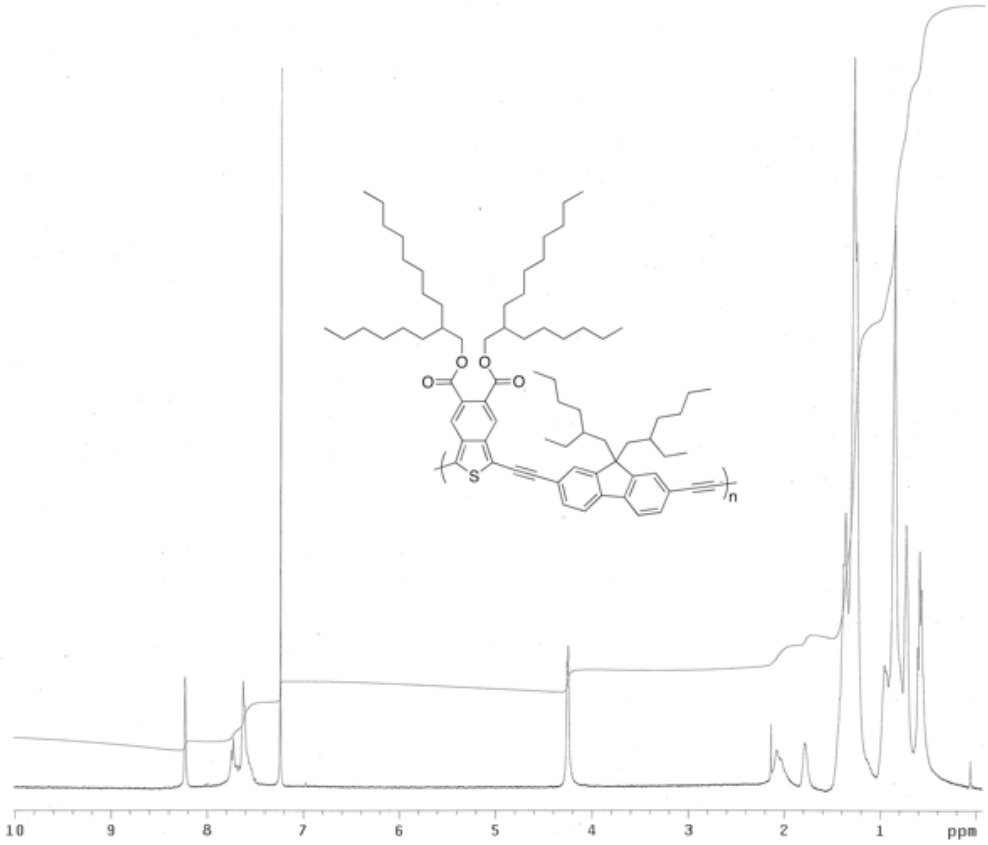


Figure S17. ^{1}H NMR spectrum of *P*-ITN-≡-FLR at 50°C in $CDCl_3$.

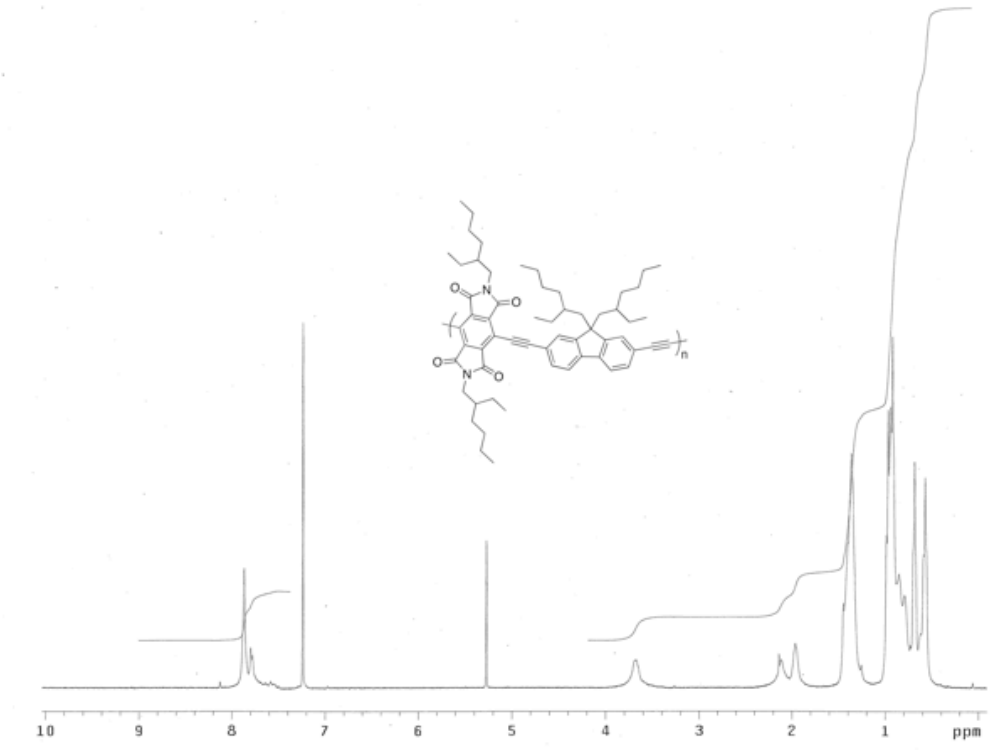


Figure S18. ^{1}H NMR spectrum of *P*-PMDI-≡-FLR at 50°C in $CDCl_3$.

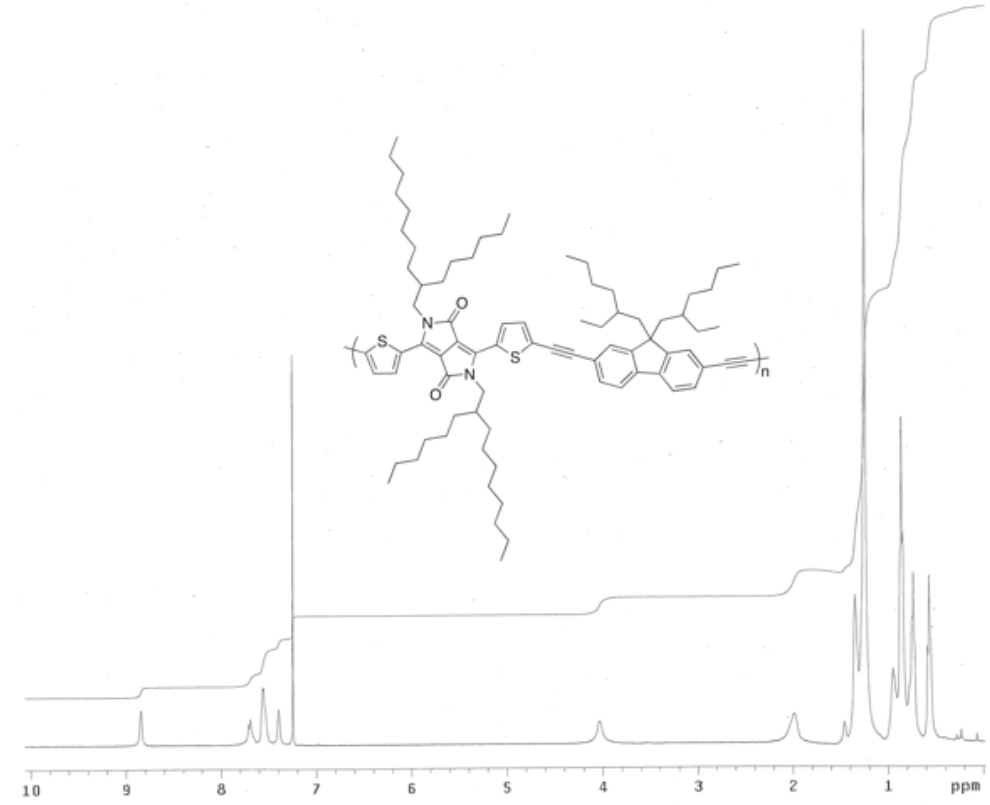


Figure S19. ^{1}H NMR spectrum of *P*-DPP-≡-FLR at 50°C in $CDCl_3$.

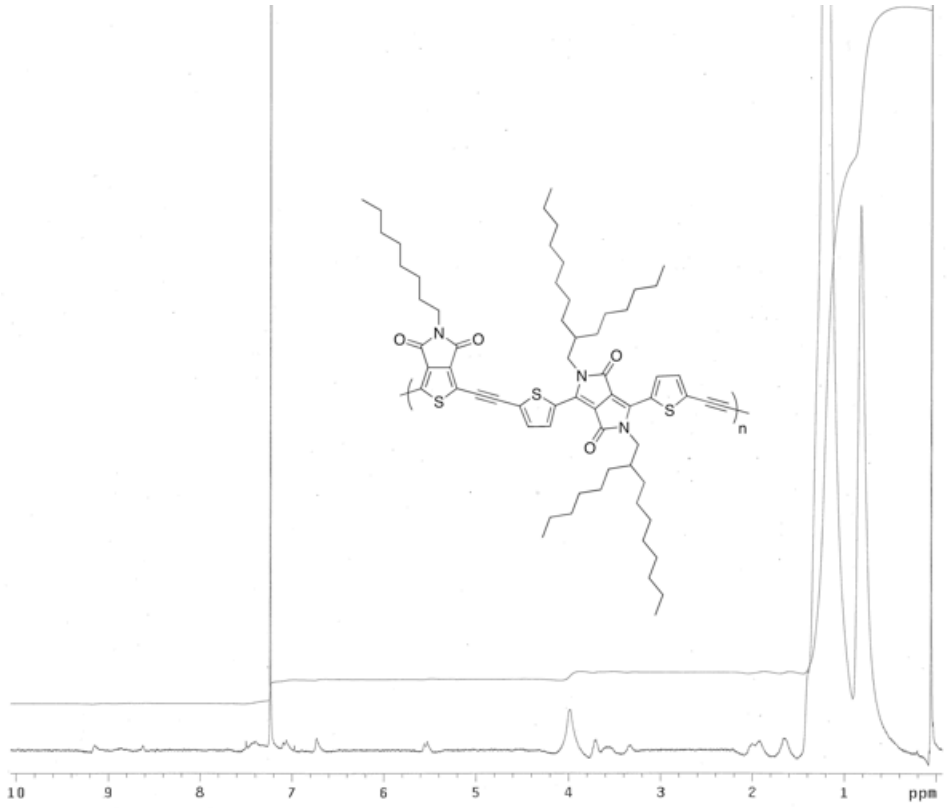


Figure S20. ^{1}H NMR spectrum of *P*-TPD-≡-DPP at 50°C in $CDCl_3$.

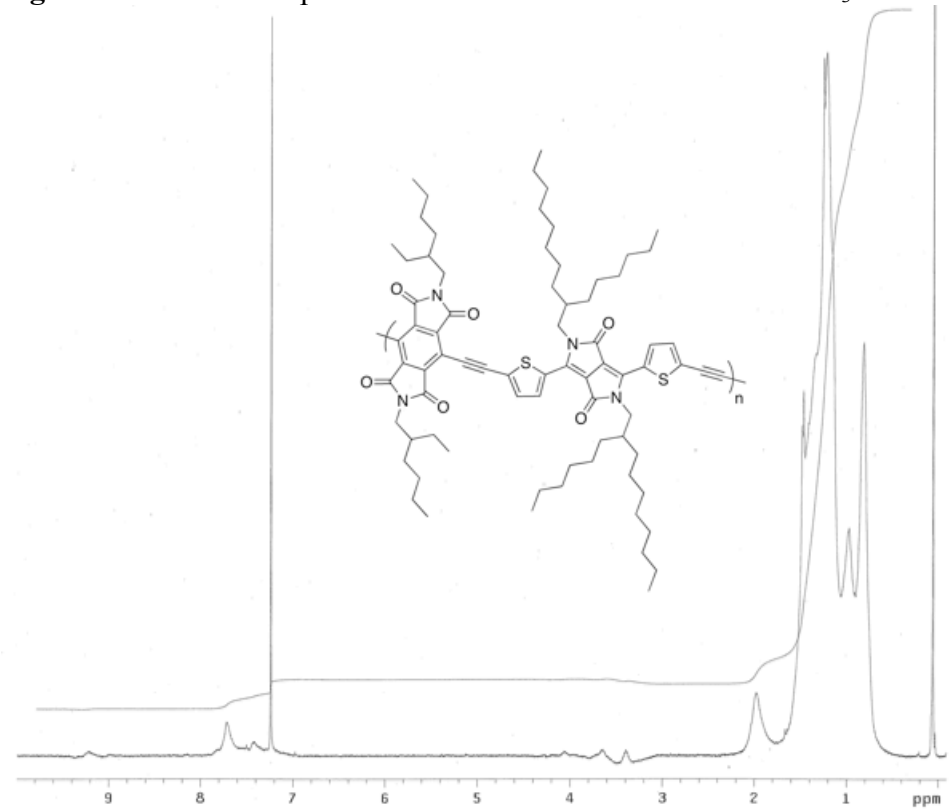


Figure S21. ^{1}H NMR spectrum of *P*-PMDI-≡-DPP at 50°C in $CDCl_3$.

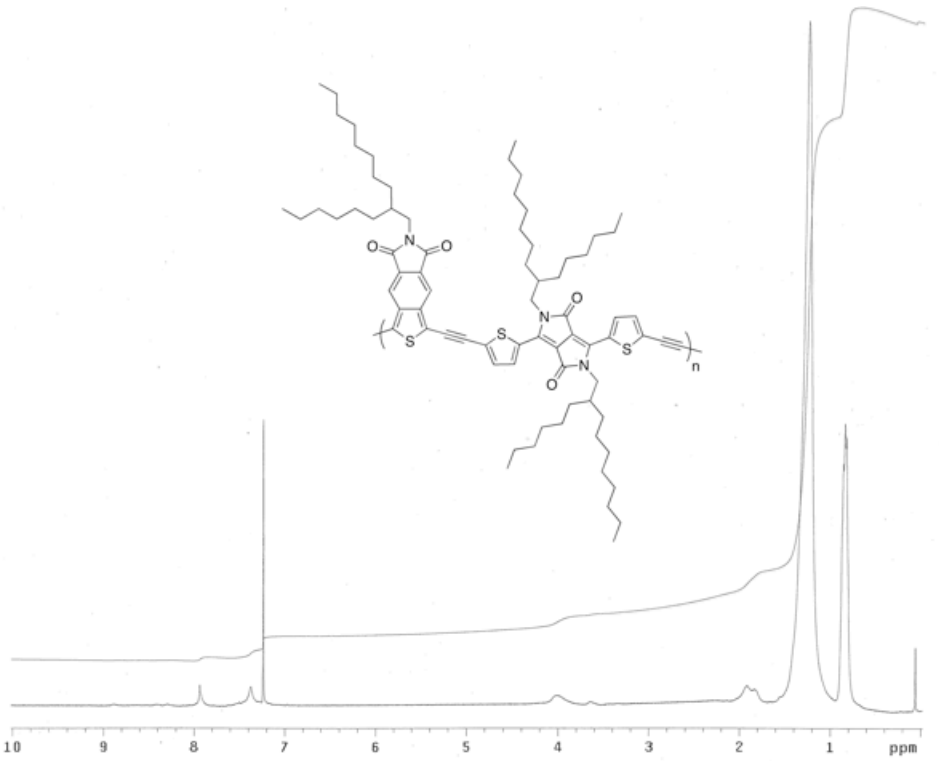


Figure S22. ^{1}H NMR spectrum of *P*-TID-≡-DPP at 50°C in $CDCl_3$.

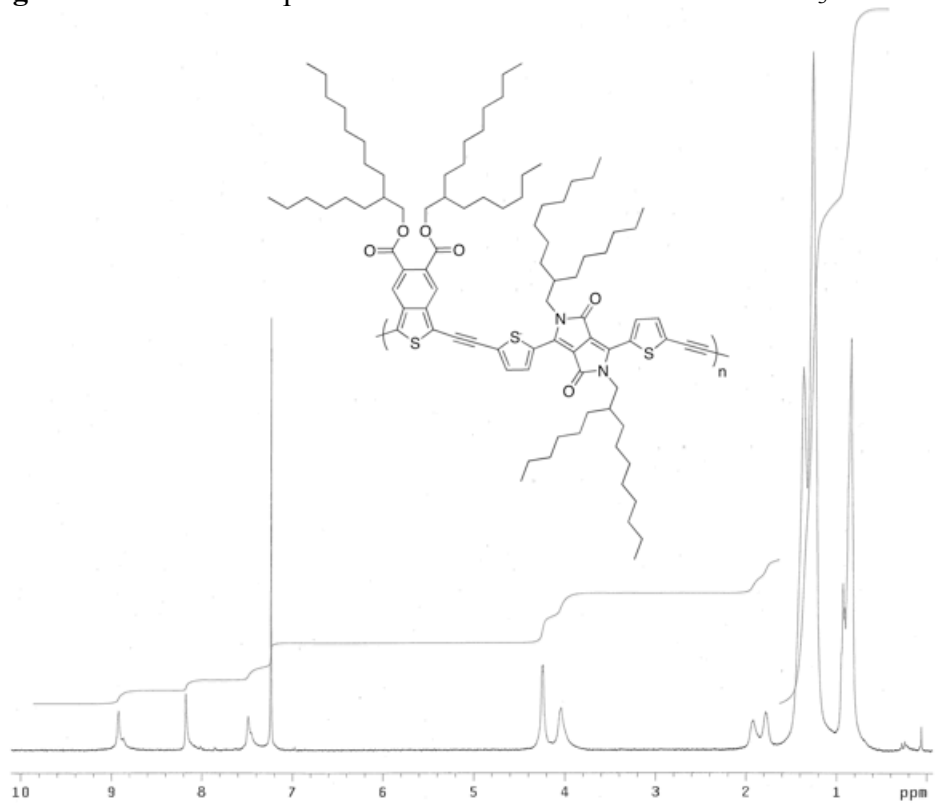


Figure S23. ^{1}H NMR spectrum of *P*-ITN-≡-DPP at 50°C in $CDCl_3$.

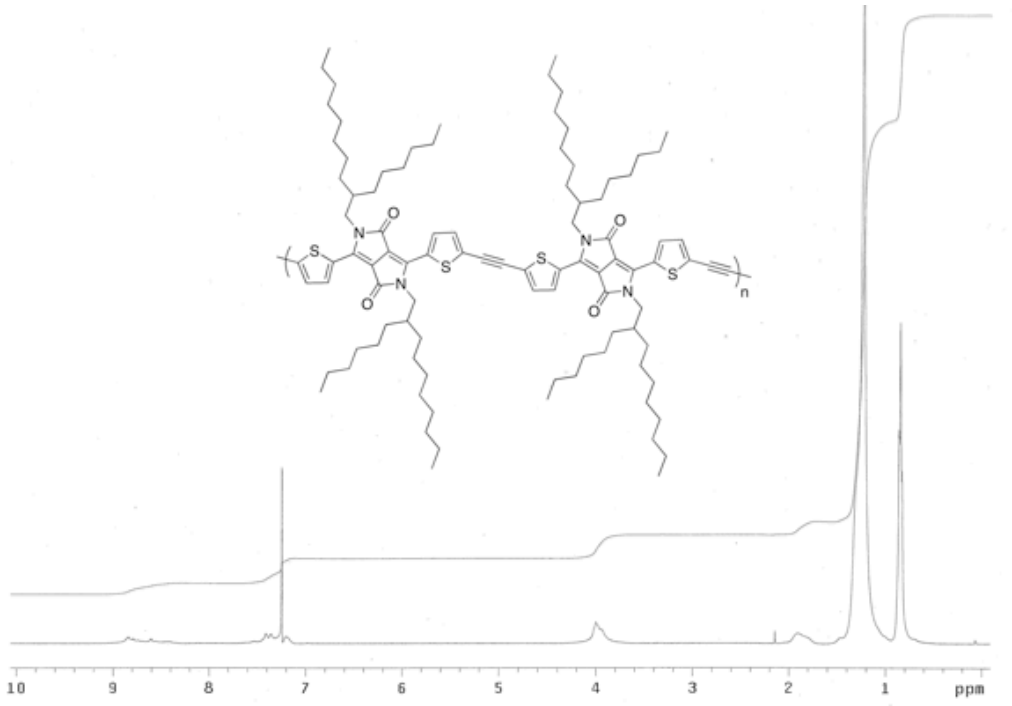


Figure S24. ^{1}H NMR spectrum of *P*-DPP-≡-DPP at 50°C in $CDCl_3$.

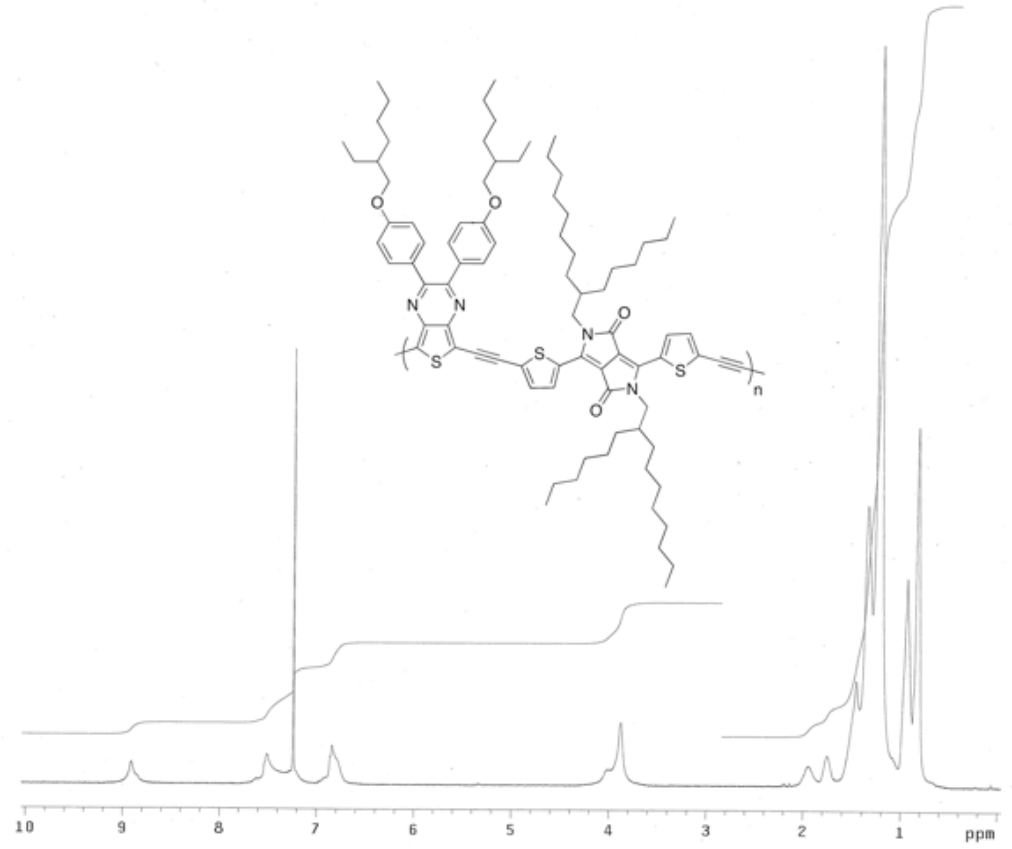


Figure S25. ^{1}H NMR spectrum of *P*-TP-≡-DPP at 50°C in $CDCl_3$.

V. Cyclic Voltammograms.

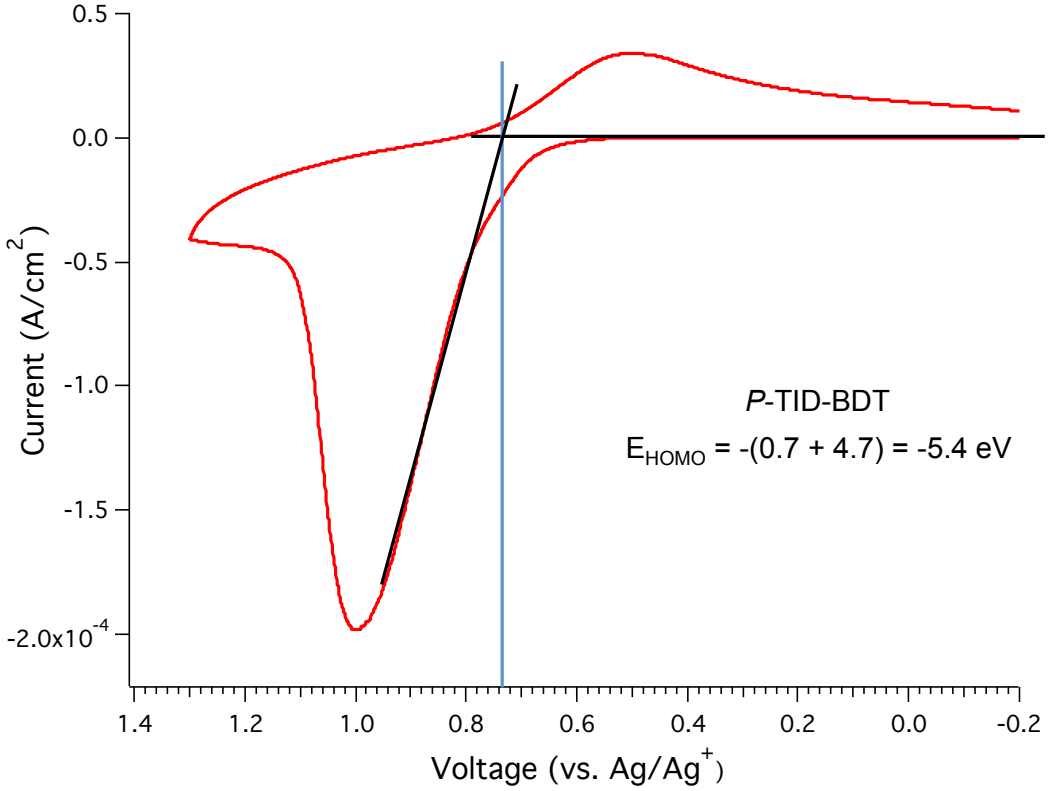


Figure S26.

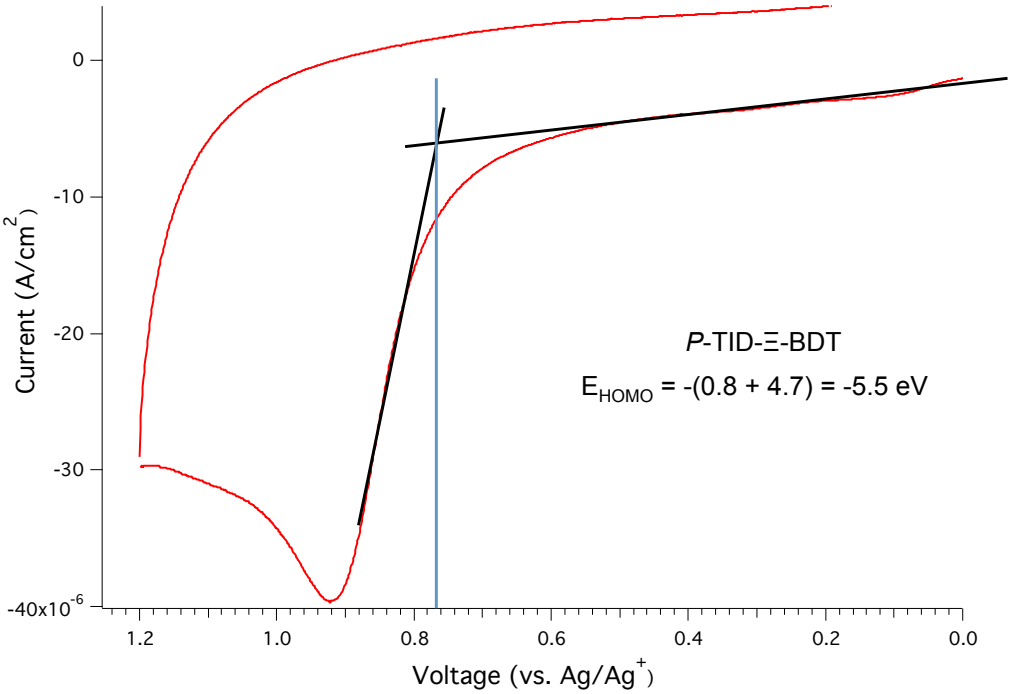


Figure S27.

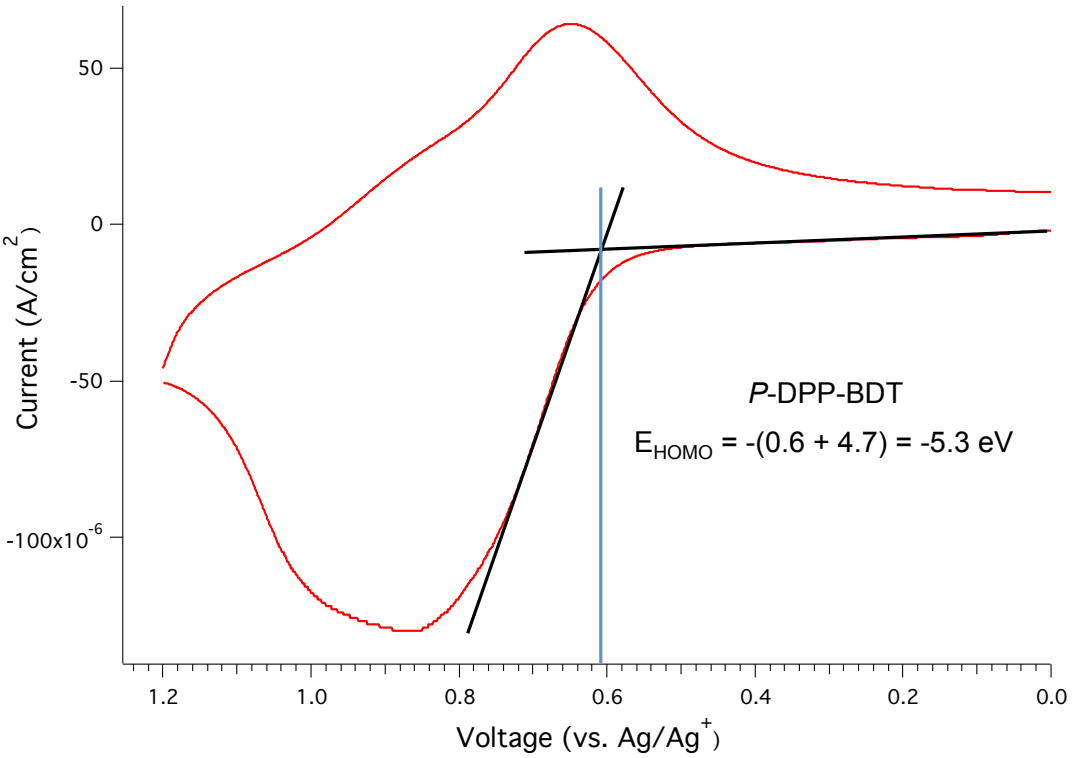


Figure S28.

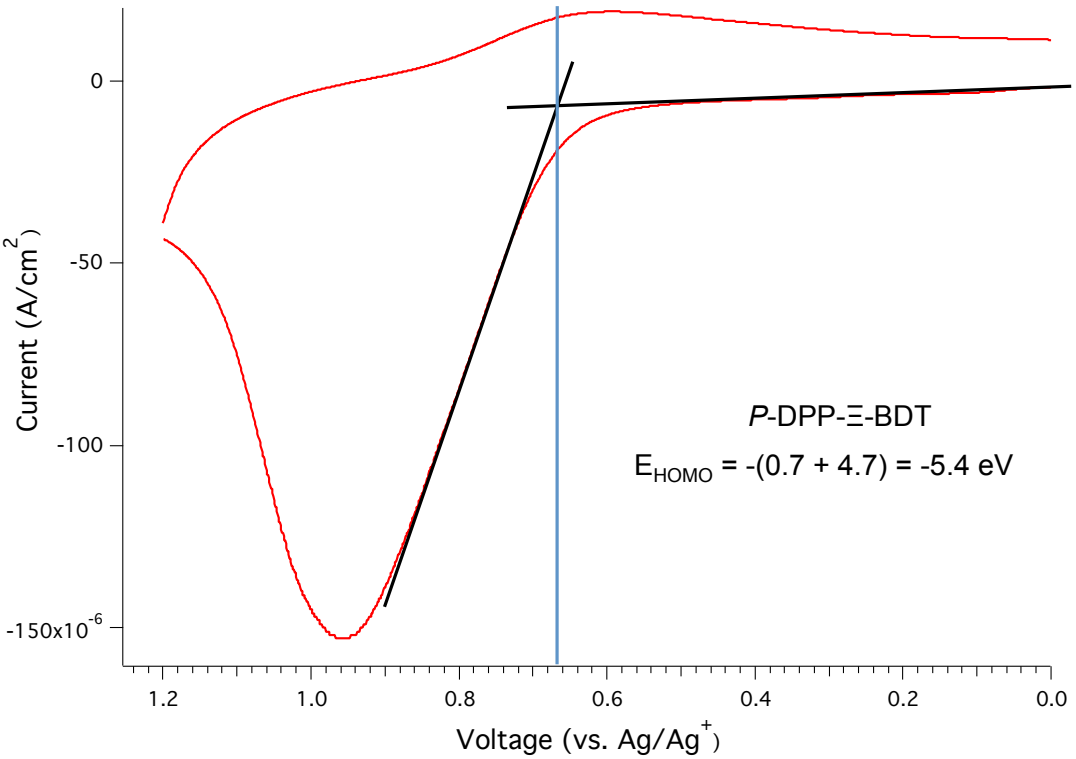


Figure S29.

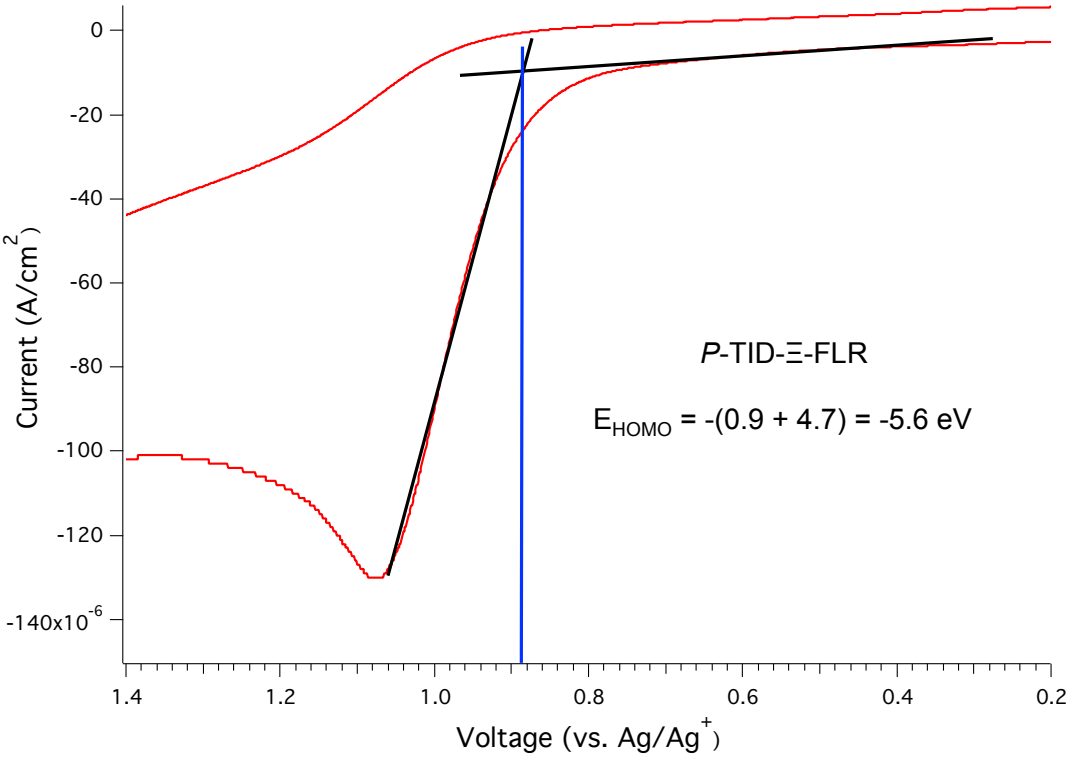


Figure S30.

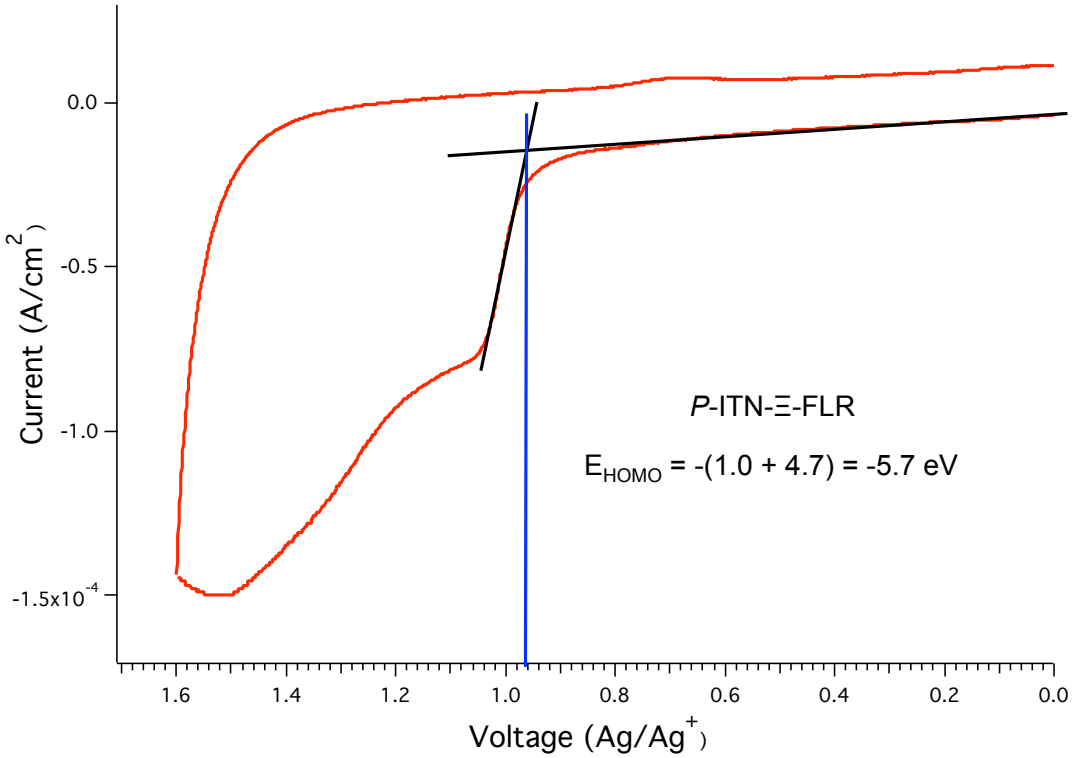


Figure S31.

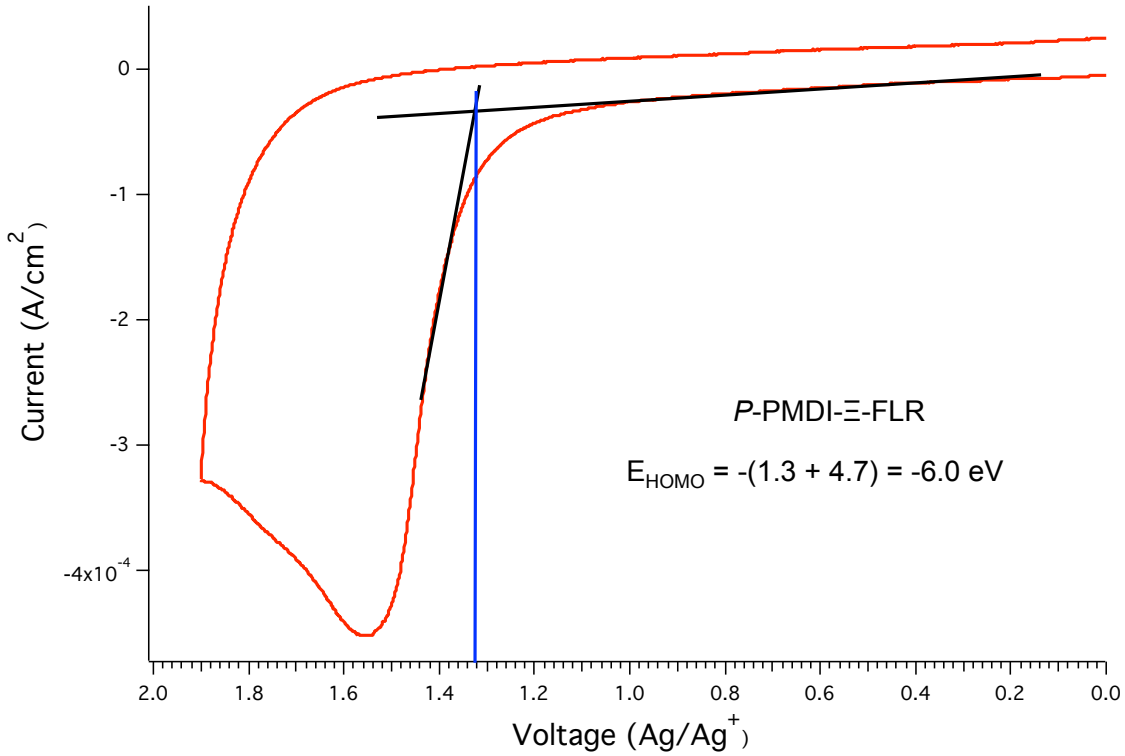


Figure S32.

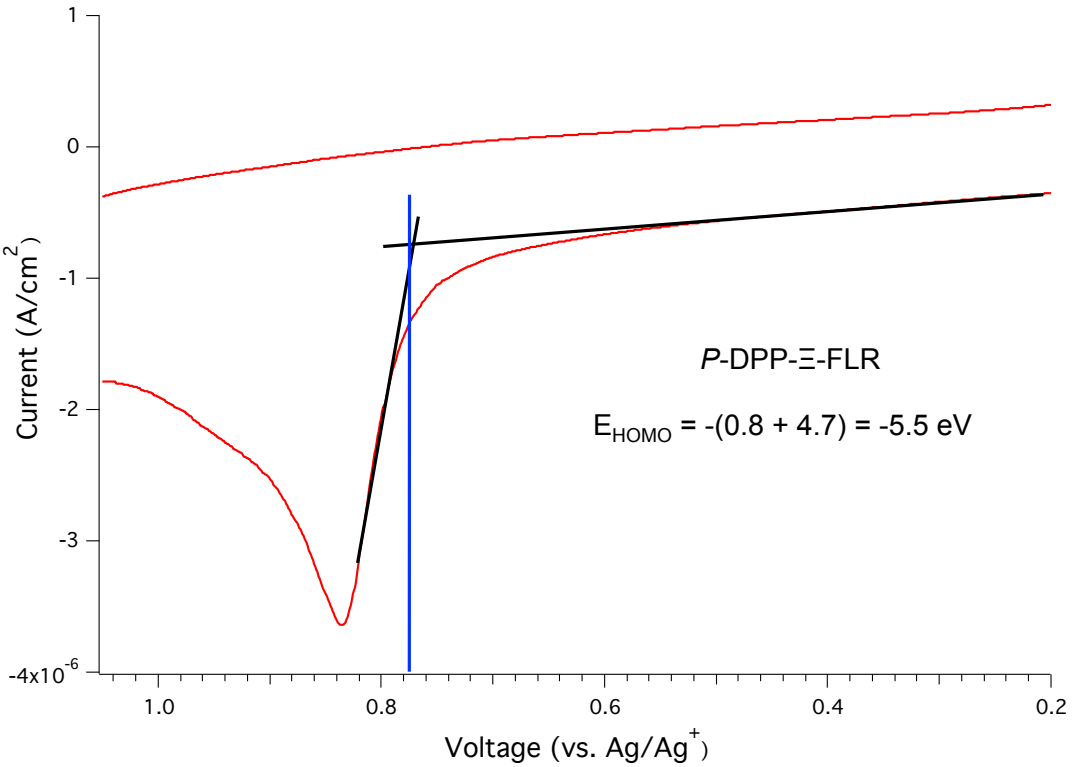


Figure S33.

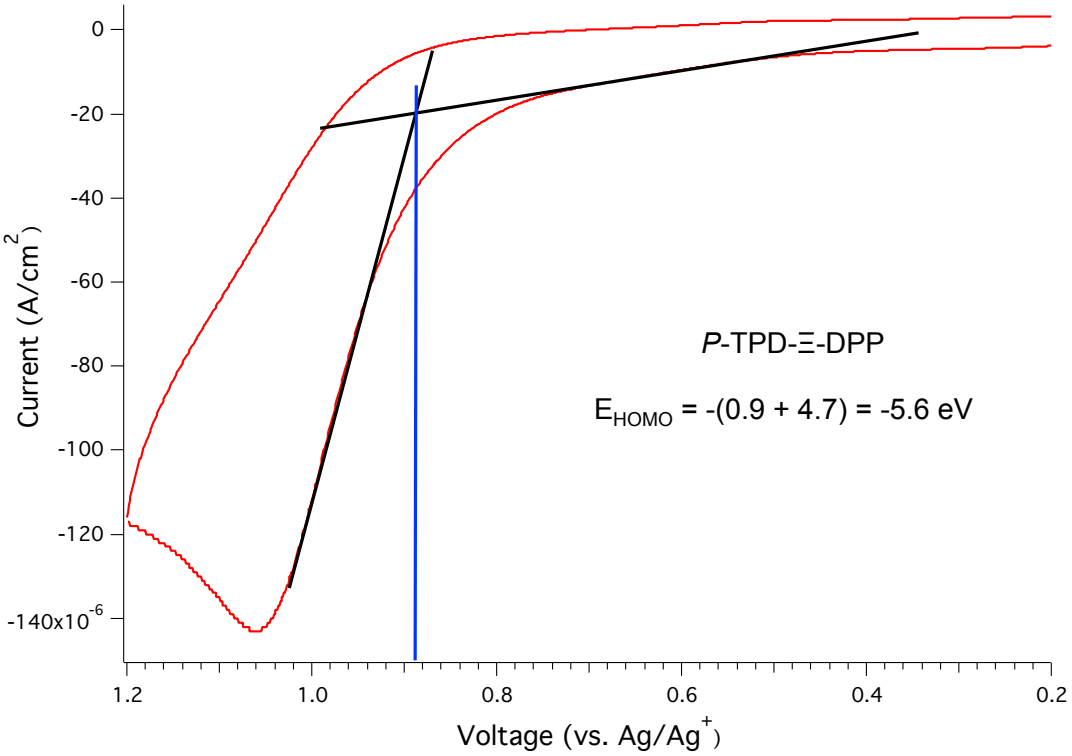


Figure S34.

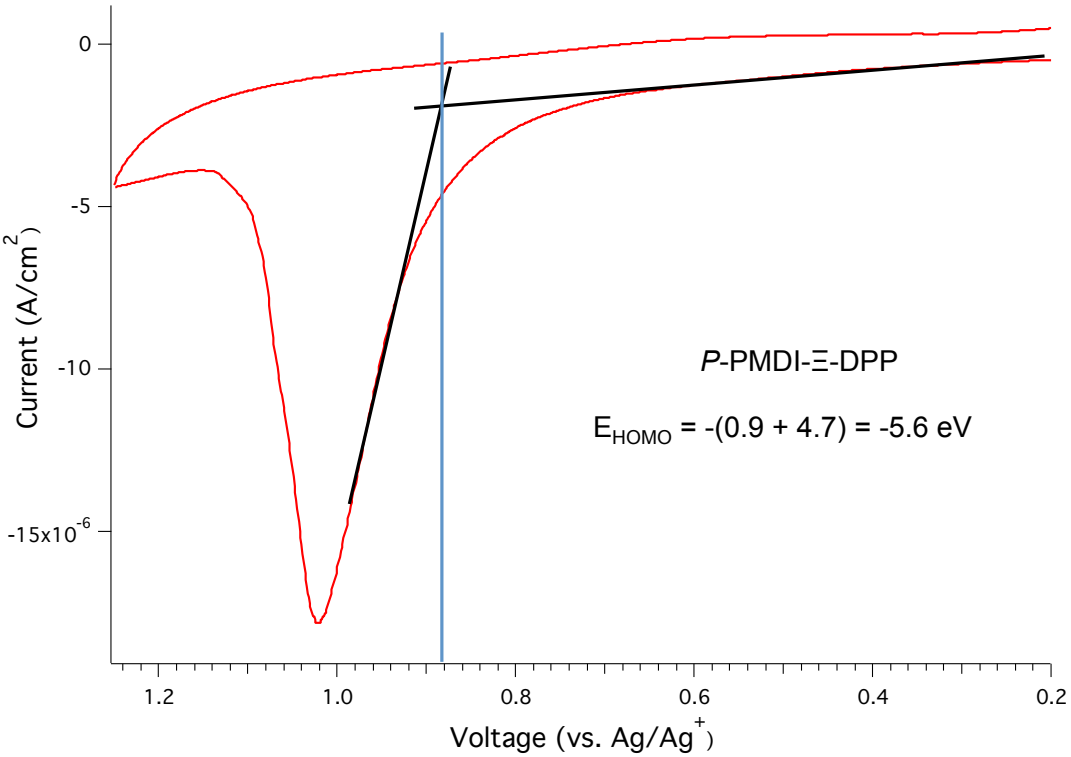


Figure S35.

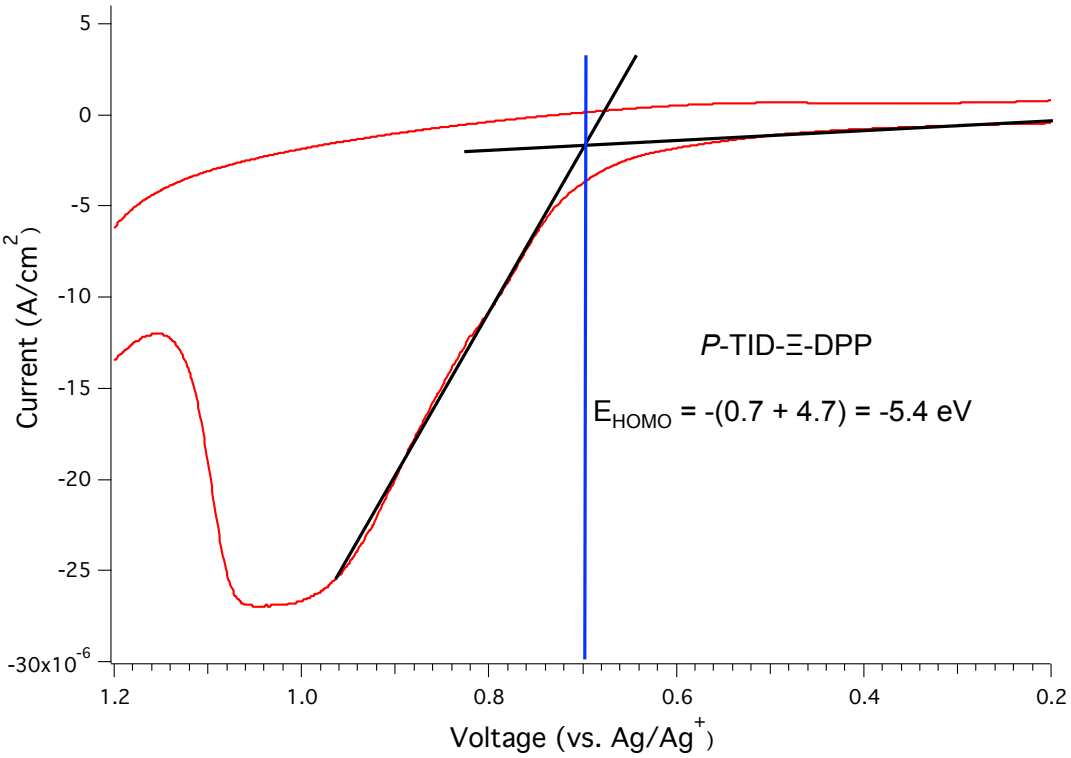


Figure S36.

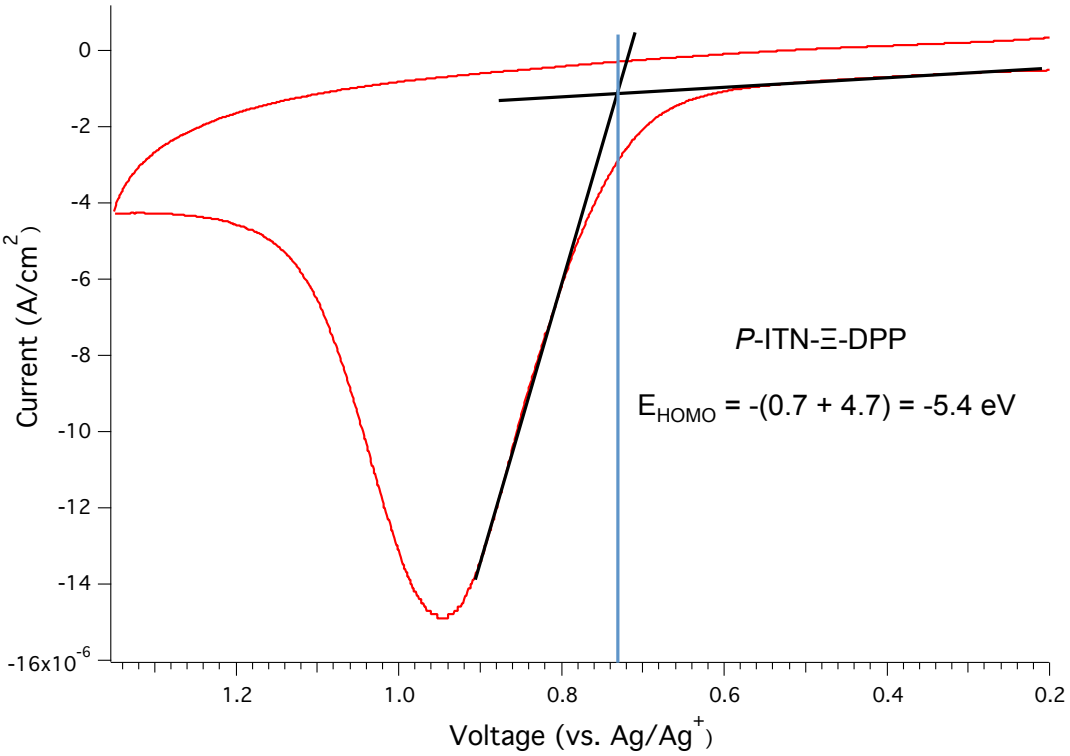


Figure S37.

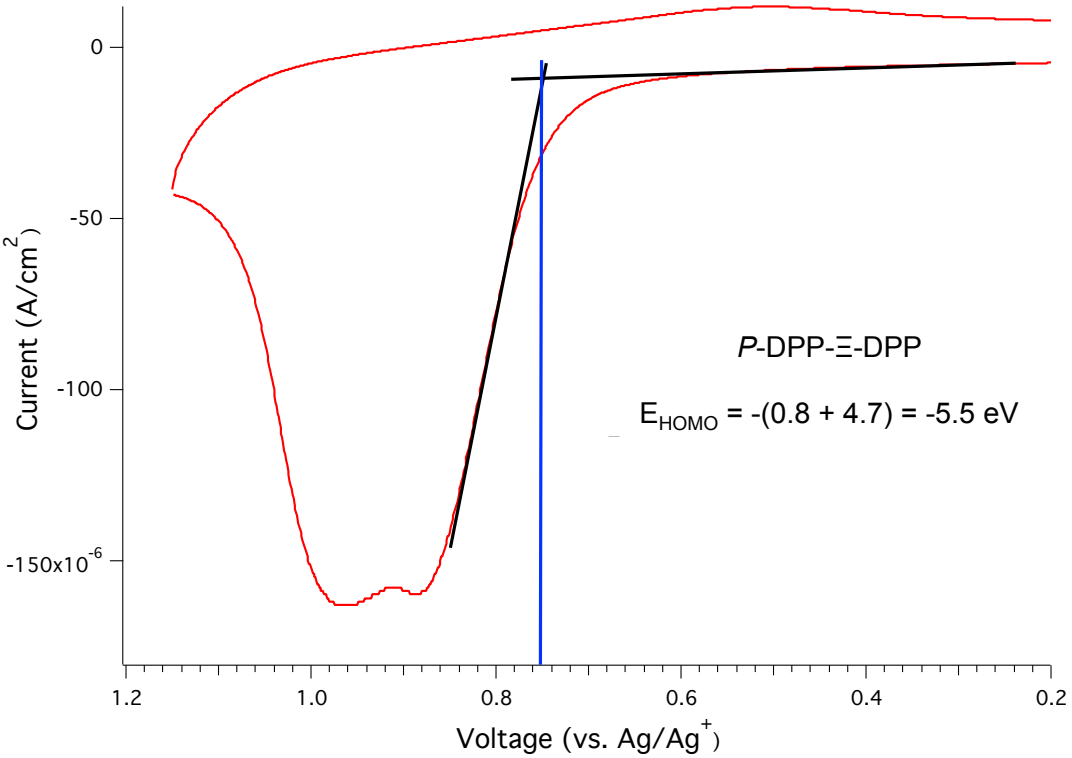


Figure S38.

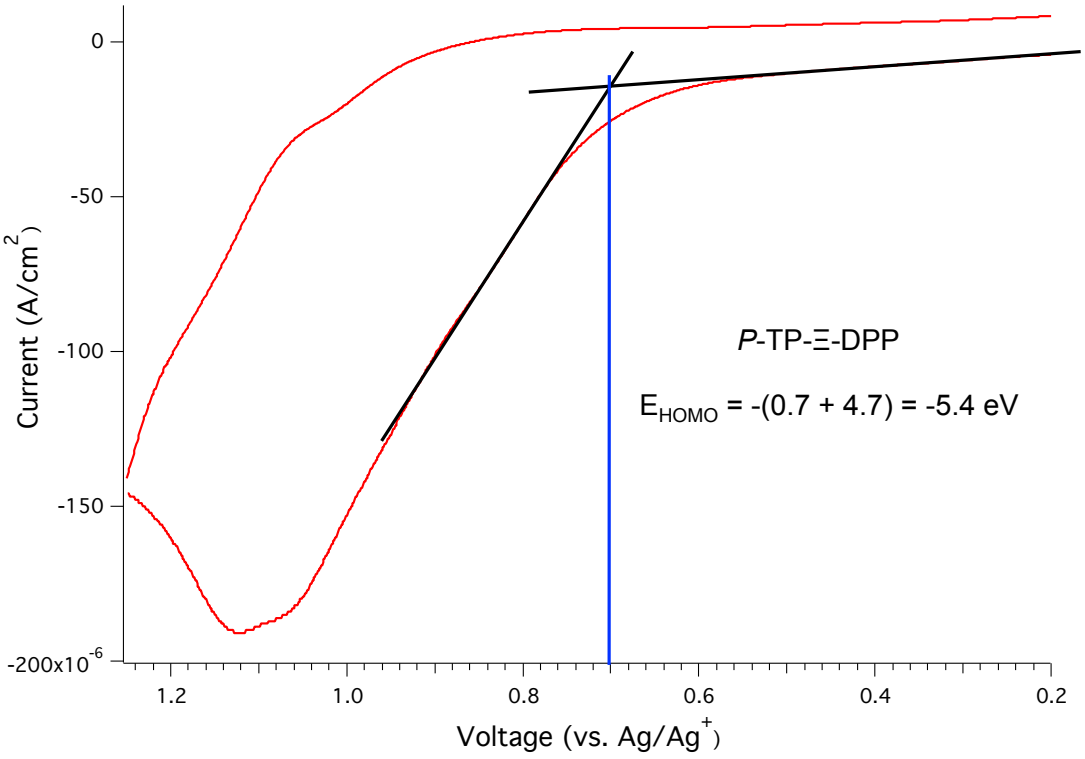


Figure S39.

VI. Time-Resolved Microwave Conductivity (TRMC).

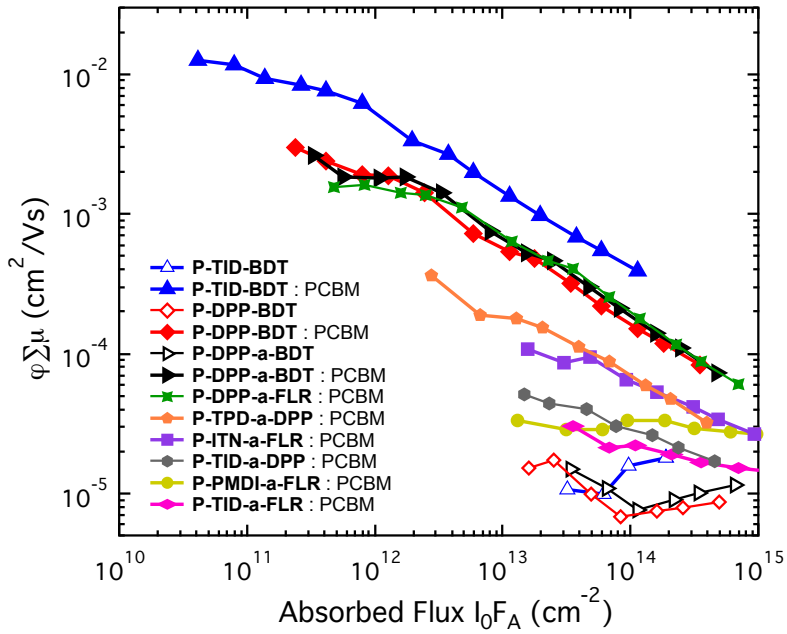


Figure S40. The product of the yield for free carrier generation ϕ and the sum of mobilities $\Sigma\mu$ of electrons and holes obtained from the peak photoconductance, as a function of absorbed photon flux. Thin films of polymers excited at the following wavelengths: *P*-TID-BDT (660 nm), *P*-DPP-BDT (680 nm), *P*-DPP-≡-BDT (680 nm), *P*-PMDI-≡-FLR (480 nm), *P*-ITN-≡-FLR (530 nm), *P*-TID-≡-FLR (540 nm), *P*-DPP-≡-FLR (640 nm), *P*-TPD-≡-DPP (680 nm), *P*-TID-≡-DPP (680 nm). Closed symbols = 1:1 polymer: $PC_{61}BM$ blends; open symbols = pure polymers.

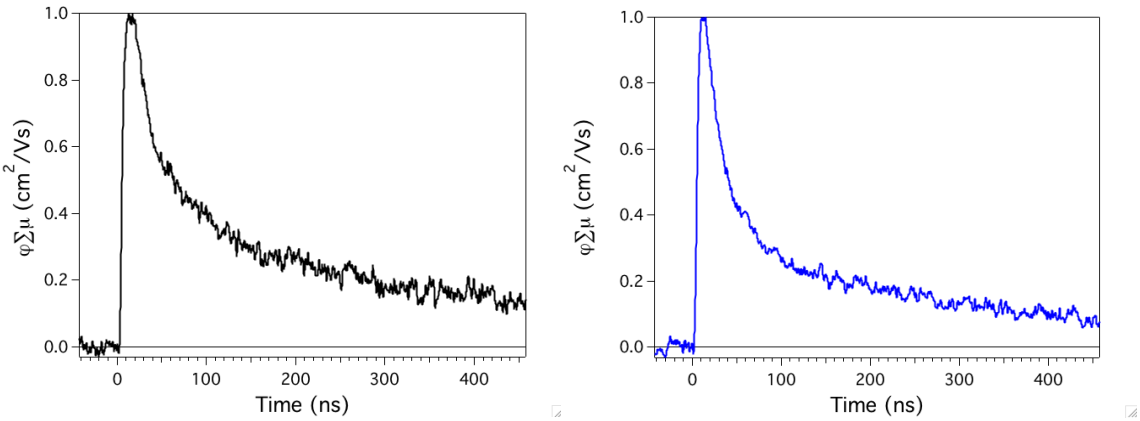


Figure S41. TRMC transients of thin films of *P*-DPP-BDT (left) and *P*-DPP-≡-BDT (right) with 50% blends by weight with PCBM. The absorbed photon flux was 10^{13} photons/cm^2/pulse. Films were photoexcited at 680 nm.

VII. References

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