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Investigating the Active Layer Thickness Dependence of Non-Fullerene Organic Solar Cells Based on PM7 Derivatives

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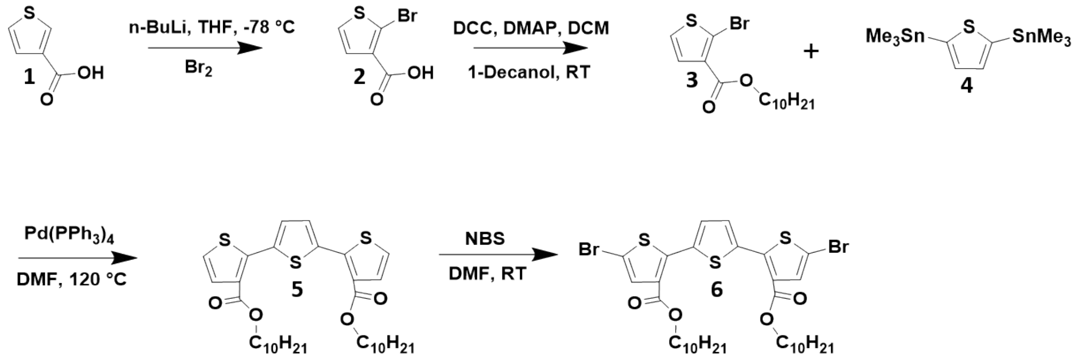
Materials

All starting materials were purchased from a commercial supplier and were used without further purification. 3-thiophenecarboxylic acid (**1**) was purchased from TCI America, thiophene-3,4-dicarboxylic acid (**7**) was purchased from Santa Cruz Biotechnology and 2-(tributylstannyl)thiophene (**10**) was purchased from Sigma Aldrich. ITIC-4F was purchased from Sigma Aldrich. Monomer **13** was purchased from SunaTech and monomer **14** was synthesized according to a literature procedure.[1]

Synthetic Procedures, Characterization and Spectra

Synthetic Scheme 1



2-bromothiophene-3-carboxylic acid (2)[2]: 3-Thiophenecarboxylic acid (5 g, 39.0 mmol) was added to a dry 300 mL round bottom flask equipped with a stir bar and was transferred into a glove box. The flask was filled with 100 mL of dry THF and subsequently removed from the dry box and immediately placed under a constant flow of argon. The reaction vessel was chilled to -78 °C and 2 equivalents of 2.5 M *n*-butyllithium in hexanes (31.2 mL, 78 mmol) was added dropwise over 30 minutes. The reaction mixture was allowed to react for 3 hours at -78 °C followed by the dropwise addition of liquid bromine (2.1 mL, 40.7 mmol) at -78 °C. The mixture was allowed to react and slowly warm up to room temperature over 16 hours. A small amount of HCl (2 mL of 1 M) was added to the reaction mixture turning the mixture into a clear solution. The solvent was removed under reduced pressure followed by the addition of ethyl acetate which was added to a separatory funnel and extracted with 1 M HCl twice. The organic layer was combined, dried over Na_2SO_4 and filtered. The organic solvent was removed under reduced pressure to produce an impure white powder which was recrystallized using a water/ethanol 4:1 mixture to produce white crystals (6.5 g, 80%). ^{1}H NMR (300 MHz, C_2D_6OS): δ (ppm) 13.11 (bs, 1H), 7.61 (d, *J* = 6 Hz, 1H), 7.33 (d, *J* = 6 Hz, 1H); ^{13}C NMR (75 MHz, C_2D_6OS): 162.79, 132.00, 129.42, 127.68, 118.67. FTMS-ESI MS (*m/z*) $[M-H+]^-$ Calcd for $C_5H_2O_2BrS$, 204.896; found 204.896.

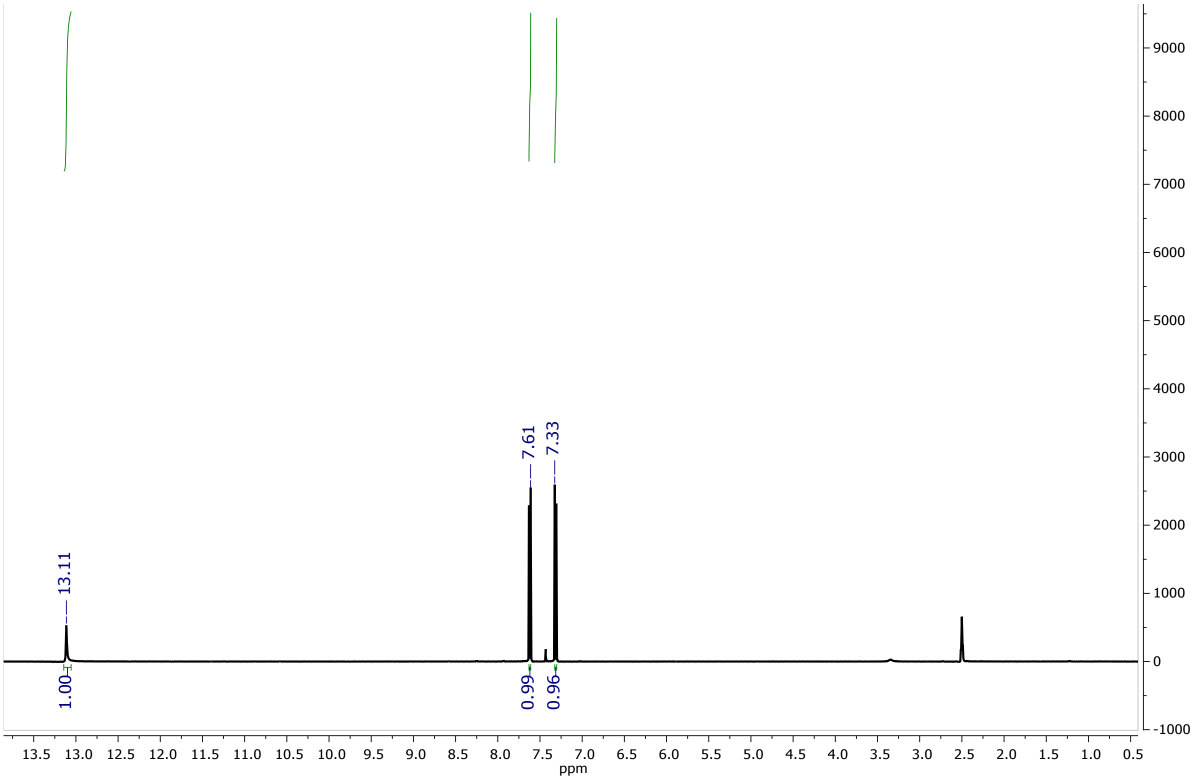


Figure S1. ^{1}H NMR of 2

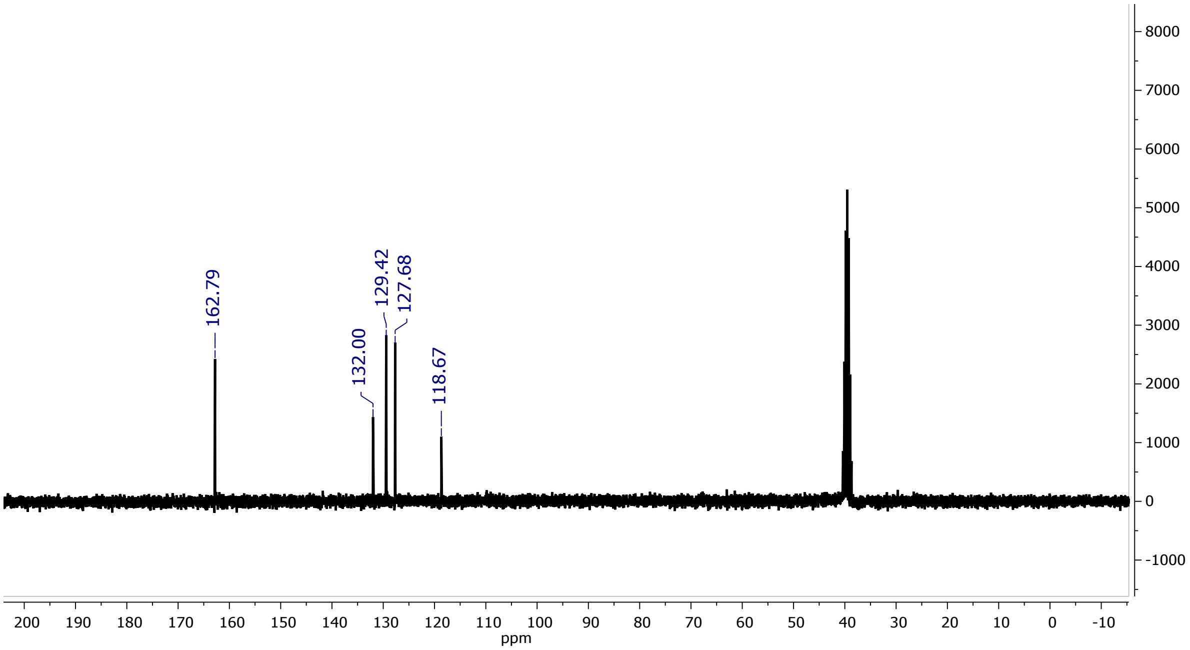


Figure S2. ^{13}C NMR of 2

decyl 2-bromothiophene-3-carboxylate (3)[3]: A 100 mL round bottom flask with a magnetic stir bar was flamed dried before 20 mL of dry dichloromethane (DCM) and 3-thiophenecarboxylic acid (2 g, 9.66 mmol) was added into the flask. The solution was stirred and degassed with argon for 15 minutes before 0.3 equivalents of 4-dimethylaminopyridine (354 mg, 2.90 mmol) was added followed by 1.3 equivalents of *N,N'*-dicyclohexylcarbodiimide (2.6 g, 12.6 mmol). Then 1.3 equivalents of 1-decanol (2.0 g, 12.6 mmol) was added into the mixture and the reaction was left to react for 14 hours at room temperature. The solvent was removed under reduced pressure and the remaining contents were purified using a short silica plug using a 9:1 hexane:DCM ratio to afford a colorless oil (3.1 g, 92%). ^{1}H NMR (300 MHz, CDCl$_3$): 7.36 (d, *J* = 6 Hz, 1H), 7.22 (d, *J* = 6 Hz, 1H), 4.28 (t, *J* = 6 Hz, 2H), 1.80-1.70 (m, 2H), 1.49-1.24 (m, 14H), 0.88 (t, *J* = 6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): 162.19, 131.47, 129.56, 125.89, 119.70, 63.51, 32.02, 29.66, 29.65, 29.36, 28.73, 26.16, 22.81, 14.26. FTMS-ESI MS (*m/z)* [M+Na]$^+$ Calcd for $C_{15}H_{23}O_2BrSNa$, 369.049; found 369.049.

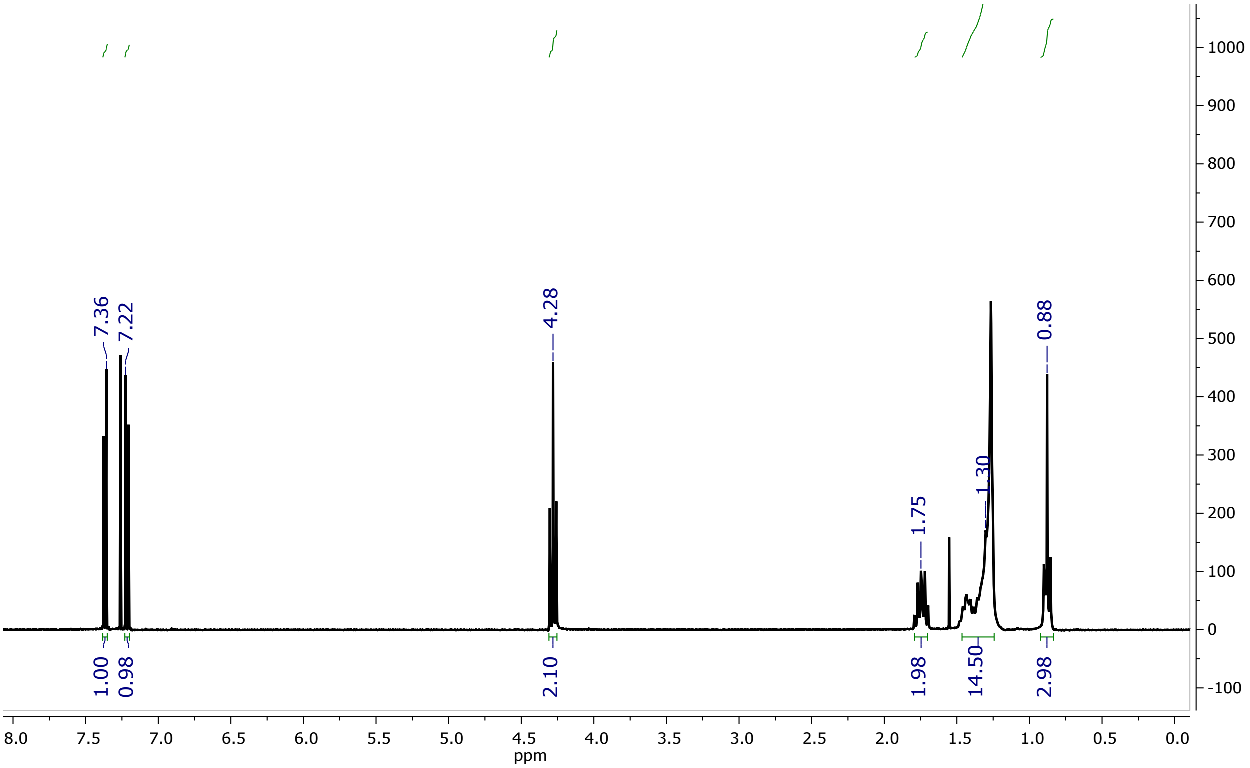


Figure S3. ^{1}H NMR of 3

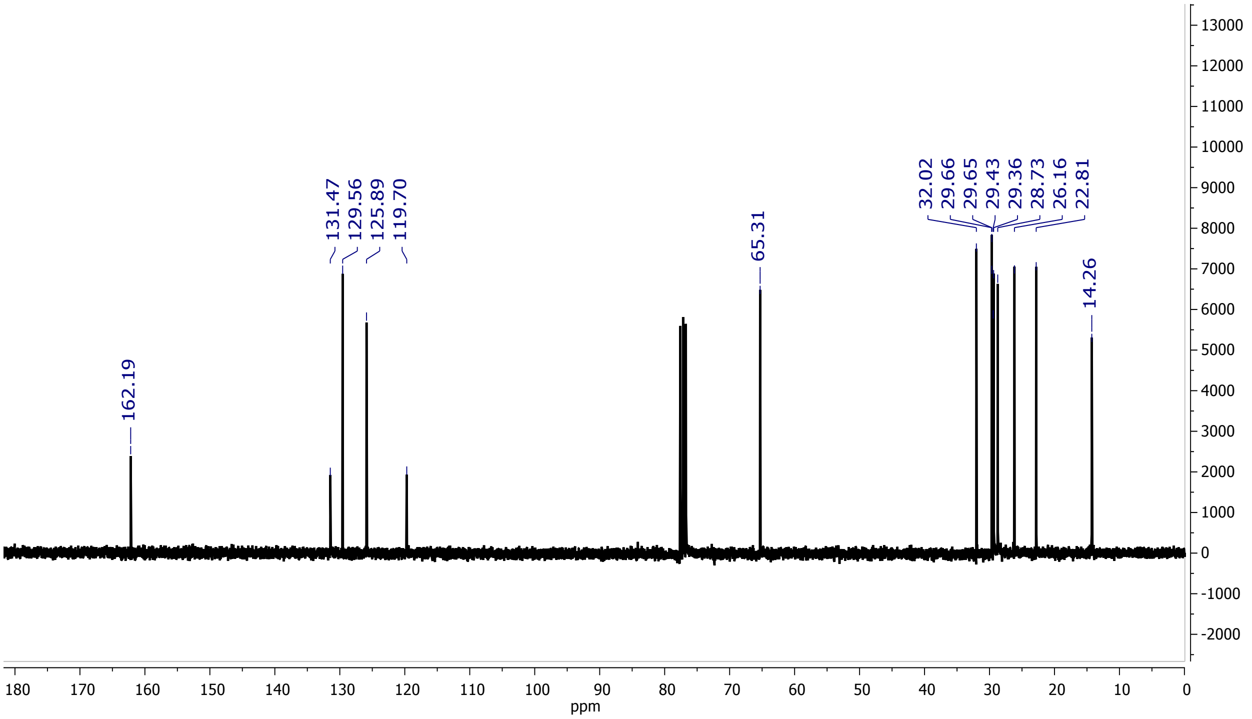


Figure S4. ^{13}C NMR of 3

didecyl [2,2':5',2''-terthiophene]-3,3''-dicarboxylate (5)[3]: A dry 100 mL round bottom flask equipped with a stir bar and compound 3 (1.5 g, 4.32 mmol) was transferred into a glove box. Compound 4 (700 mg, 1.71 mmol) and Tetrakis(triphenylphosphine)palladium(0) (140 mg, 0.12 mmol) was added to the flask. The reaction flask was removed from the glove box and immediately placed under a constant pressure of argon, followed by the addition of 20 mL of recently argon purged dimethylformamide. The reaction flask was heated to 125 °C and stirred for 24 hours. The solvent was removed under reduced pressure and the remaining mixture was purified using silica gel chromatography using hexane:DCM (5:2) as the eluent to produce a yellow oil (955 mg, 91%).^{1}H NMR (300 MHz, $CDCl_3$): 7.45 (d, *J* = 3 Hz, 2H), 7.39 (s, 2 H), 7.14 (d, *J* = 3 Hz, 2H), 4.22 (t, *J* = 6 Hz, 4H), 1.72-1.61 (m, 4H), 1.38-1.17 (m, 28H), 0.85 (t, *J* = 6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.79, 142.34, 135.88, 130.47, 128.96, 127.96, 123.81, 64.79, 31.81, 29.47, 29.23, 29.21, 28.54, 25.96, 22.59, 14.03. FTMS-ESI MS (*m/z*) $[M+Na]^+$ Calcd for $C_{34}H_{48}O_4S_3Na$, 639.261; found 639.258.

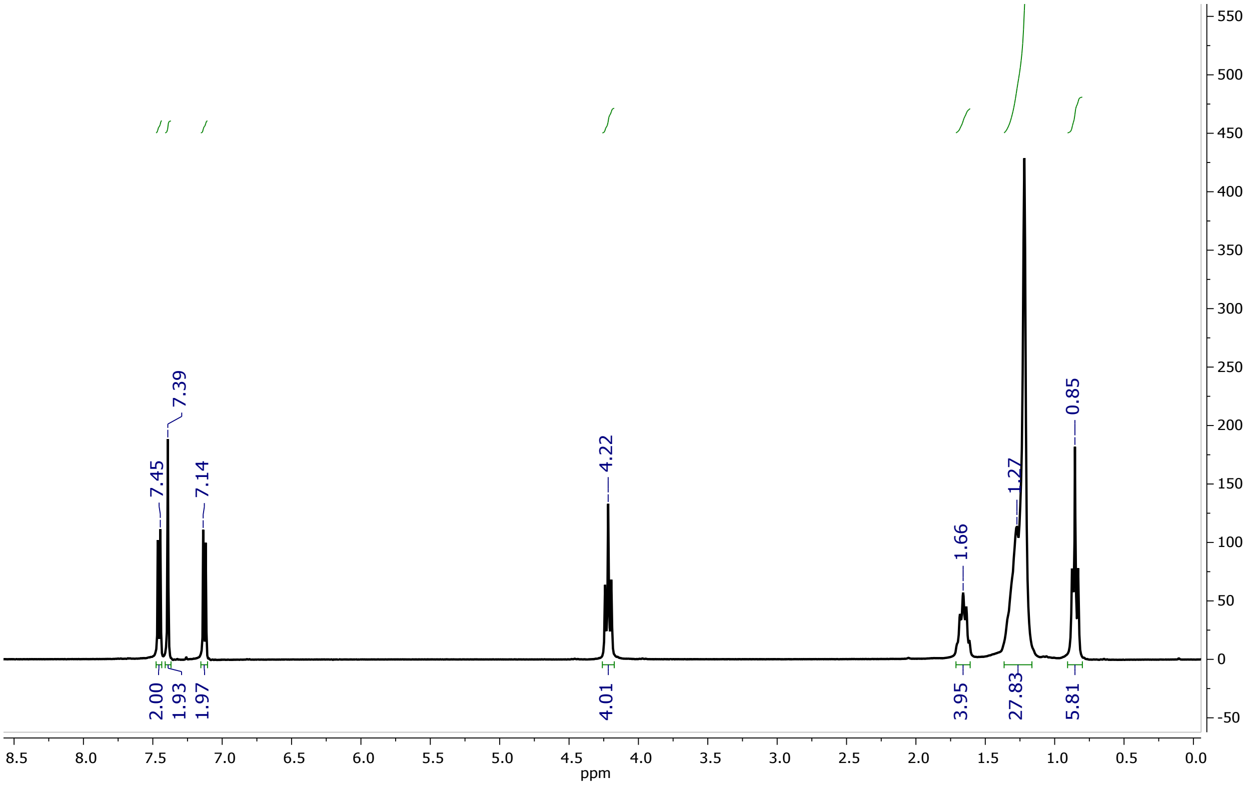


Figure S5. ^{1}H NMR of 5

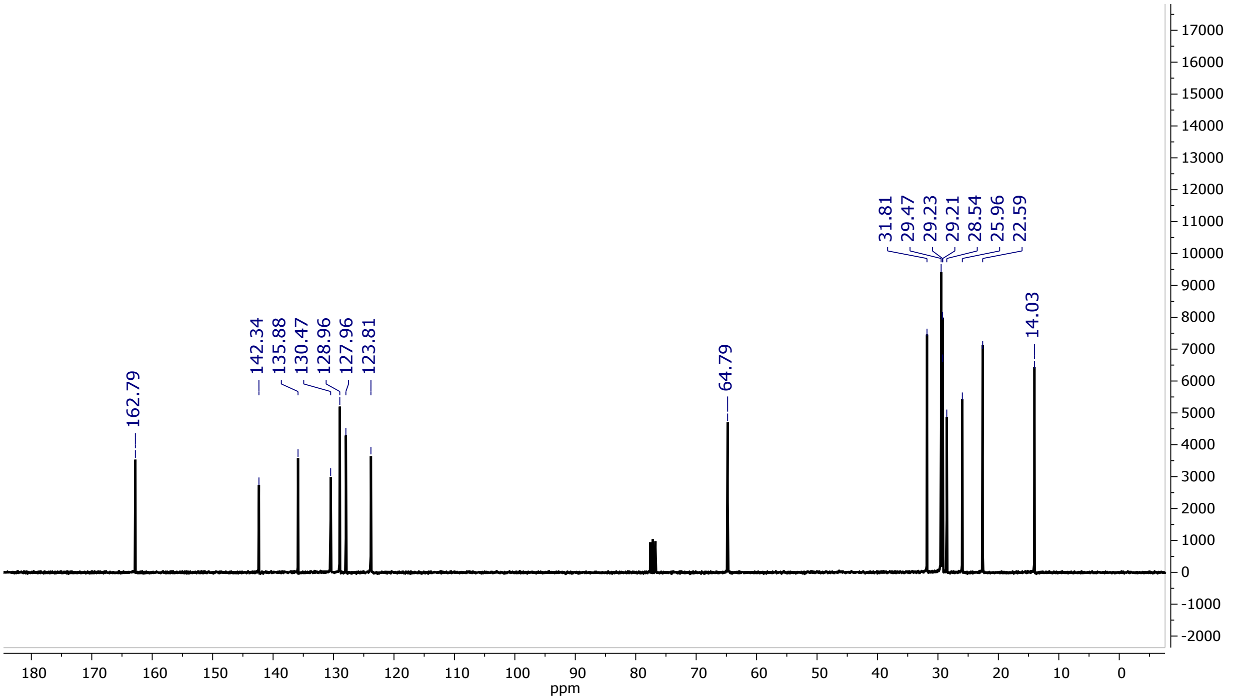


Figure S6. ^{13}C NMR of 5

didecyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3,3''-dicarboxylate (6)[3]: To a 100 mL round bottom flask was added a stir bar, compound 5 (700 mg, 1.13 mmol) and 30 mL of DMF. Then 2.7 equivalents of NBS (545 mg, 3.06 mmol) was added to the solution in small portions. The reaction was sealed, protected from light and stirred for 16 hours at room temperature. Subsequently, the solvent was removed under reduced pressure followed by an extraction using DCM and water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified using silica gel chromatography using hexane:DCM (4:1) as the eluent to produce a orange solid (750 mg, 85%).^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44 (s, 2H), 7.33 (s, 2H), 4.22 (t, J = 6 Hz, 4H), 1.72-1.62 (m, 4H), 1.36-1.21 (m, 28H), 0.88 (t, J = 6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.00, 143.63, 135.43, 132.97, 129.54, 128.64, 111.19, 65.49, 32.04, 29.70, 29.67, 29.45, 29.41, 28.69, 26.14, 22.83, 14.27. FTMS-ESI MS (*m/z)* $[M+Na]^+$ Calcd for $C_{34}H_{46}O_4Br_2S_3Na$, 795.082; found 795.079.

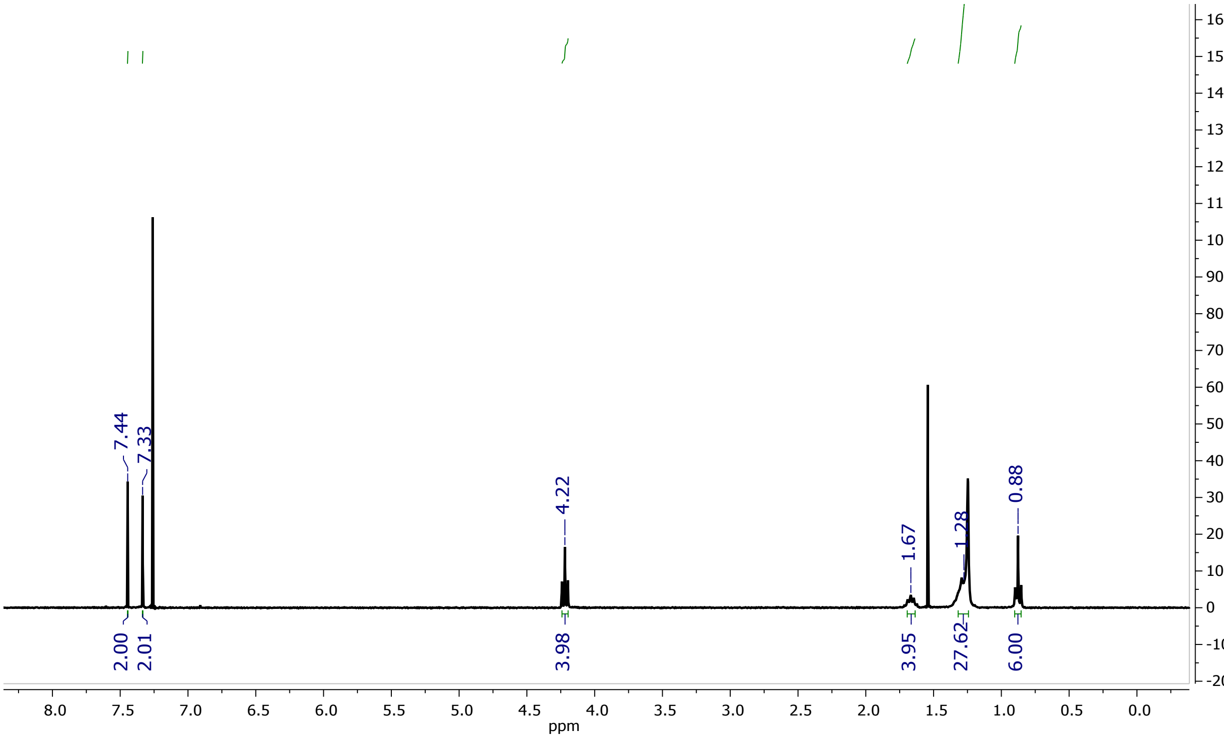


Figure S7. ^{1}H NMR of 6

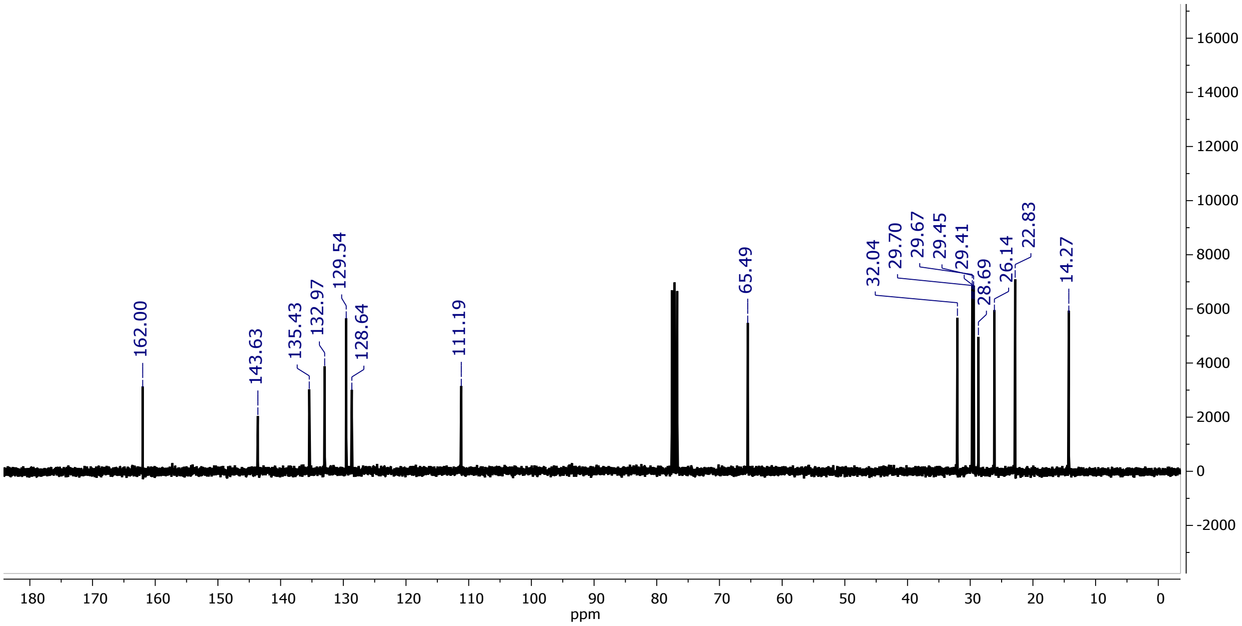
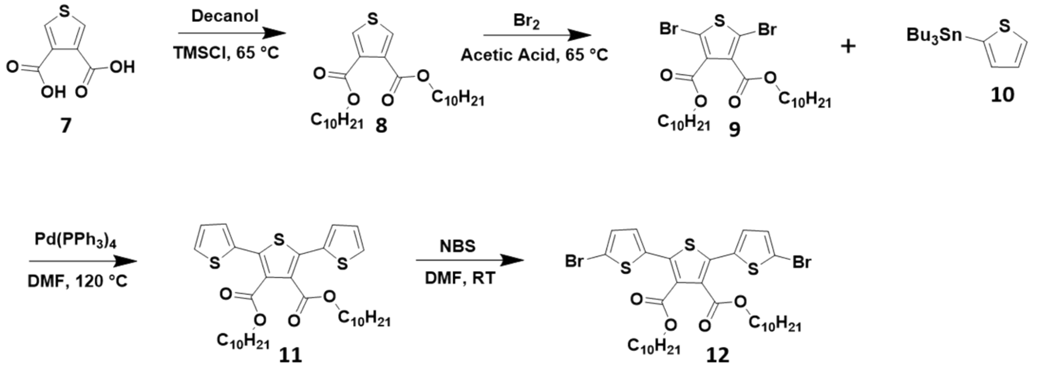


Figure S8. ^{13}C NMR of 6

Synthetic Scheme 2



didecyl thiophene-3,4-dicarboxylate (8): Trimethylsilyl chloride (8.8 mL, 69.6 mmol) was added to a stirred mixture of 7 (3 g, 17.4 mmol) and 36 mL of 1-decanol dropwise at room temperature. The reaction mixture was then sealed and warmed to 65 °C for 20 hours. The crude reaction was then purified using silica gel column chromatography using DCM:hexane (2:5) as the eluent to produce a colorless oil (7.1 g, 89%).^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.83 (s, 2H), 4.26 (t, *J* = 6 Hz, 4H), 1.76-1.66 (m, 4H), 1.43-1.21 (m, 28H), 0.88 (t, *J* = 6 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): 163.28, 133.80, 131.51, 65.64, 32.00, 29.65, 29.42, 29.40, 28.70, 26.07, 22.79, 14.22. FTMS-ESI MS (*m/z*) [M+Na]$^+$ Calcd for $C_{26}H_{44}O_4SNa$, 475.285; found 475.283.

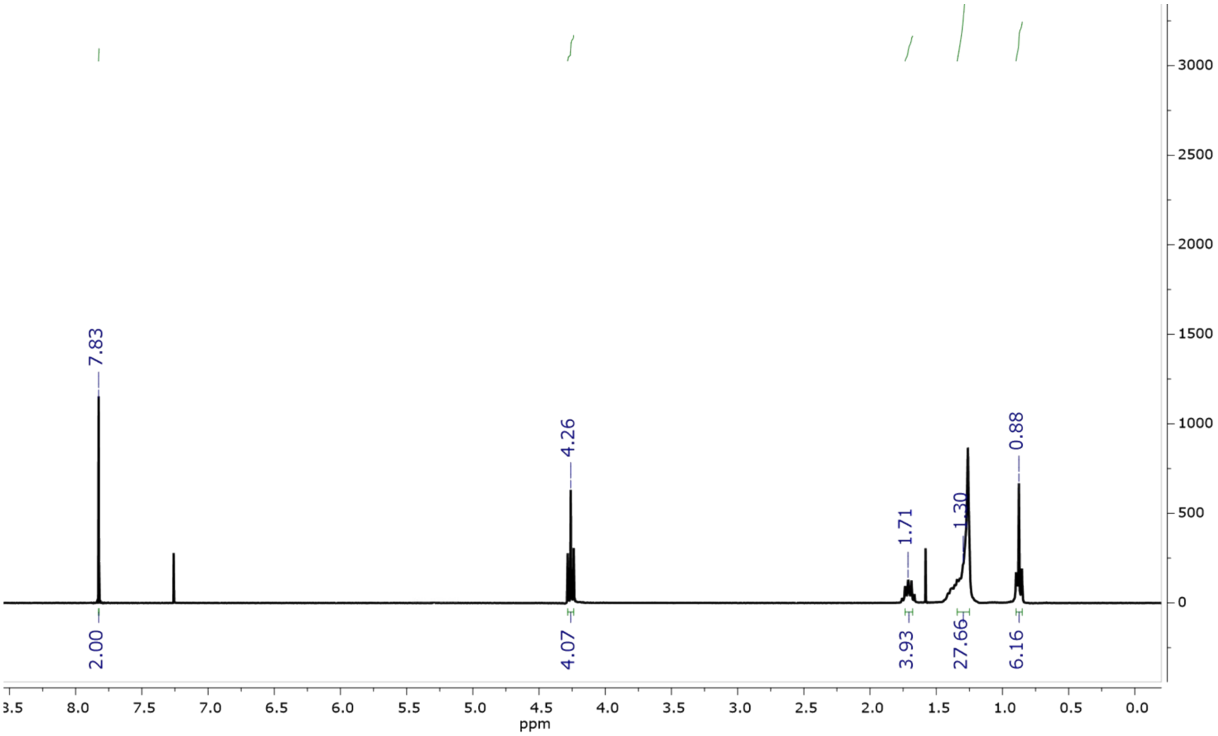


Figure S9. ^{1}H NMR of 8

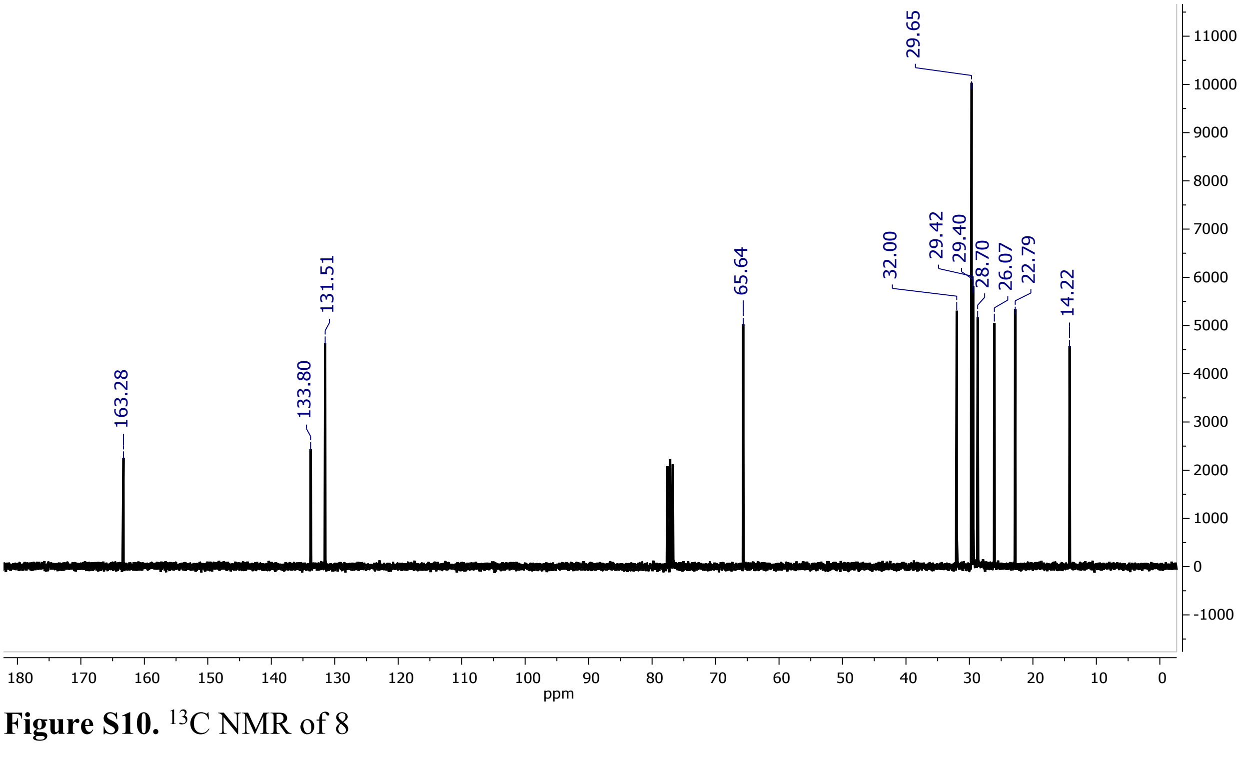


Figure S10. ^{13}C NMR of 8

didecyl 2,5-dibromothiophene-3,4-dicarboxylate (9): A 200 mL round bottom flask was equipped with a stir bar, compound 8 (4 g, 8.84 mmol) and 75 mL of acetic acid. Next, liquid bromine (2.5 mL, 48.8 mmol) was added to the stirred solution dropwise at room temperature. After complete addition of Br_2, the reaction mixture was heated to 65 °C and stirred for 20 h. The reaction was then cooled down to room temperature and an aqueous solution of Na_2SO_3 was added to quench the remaining Br_2. The mixture was then extracted with methylene chloride, dried over Na_2SO_4, filtered and dried under reduce pressure to produce a crude oil. The oil was purified *via* silica gel column chromatography using DCM:hexane (2:5) as the eluent to produce a colorless oil (2.6 g, 48%).^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.27 (t, J = 6 Hz, 4H), 1.76-1.66 (m, 4H), 1.44-1.20 (m, 28H), 0.87 (t, J = 6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 161.74, 134.04, 115.69, 66.37, 32.03, 29.68, 29.66, 29.45, 29.38, 28.61, 26.06, 22.82, 14.26. FTMS-ESI MS (*m/z)* $[M+Na]^+$ Calcd for $C_{26}H_{42}O_4Br_2SNa$, 631.106; found 631.104.

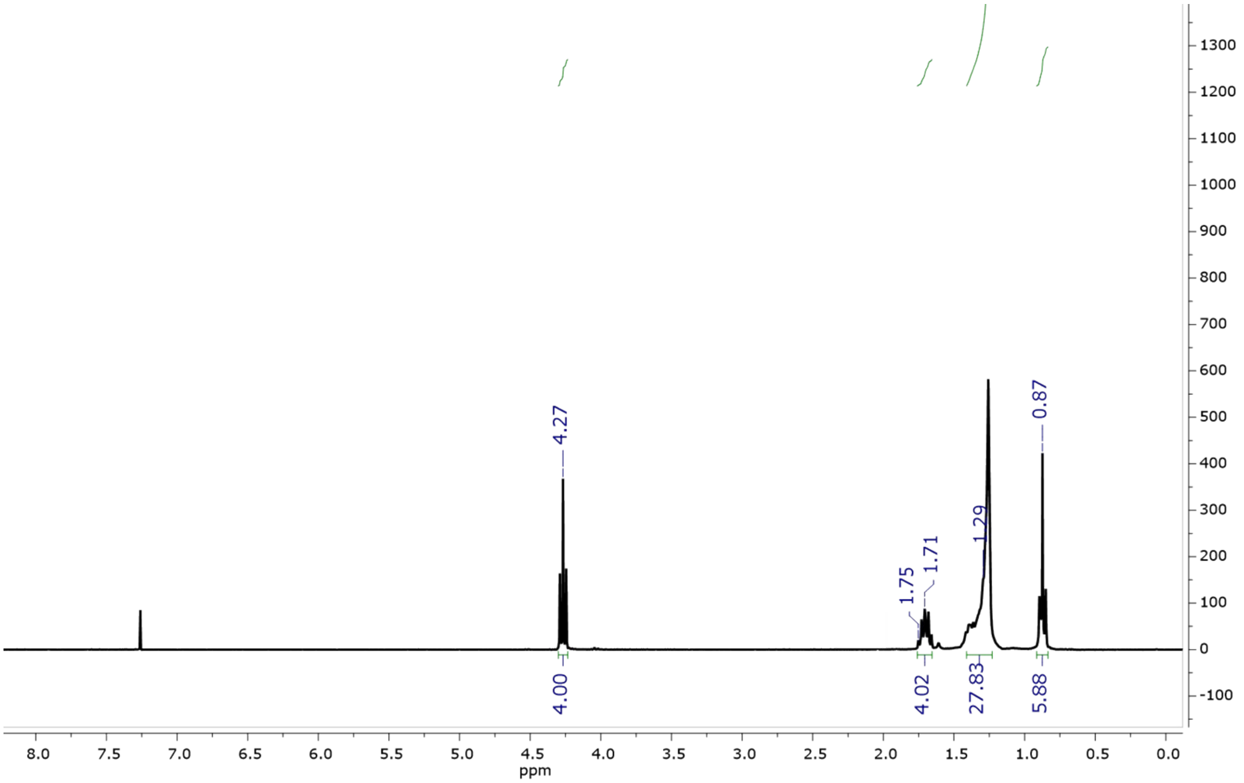


Figure S11. ^{1}H NMR of 9

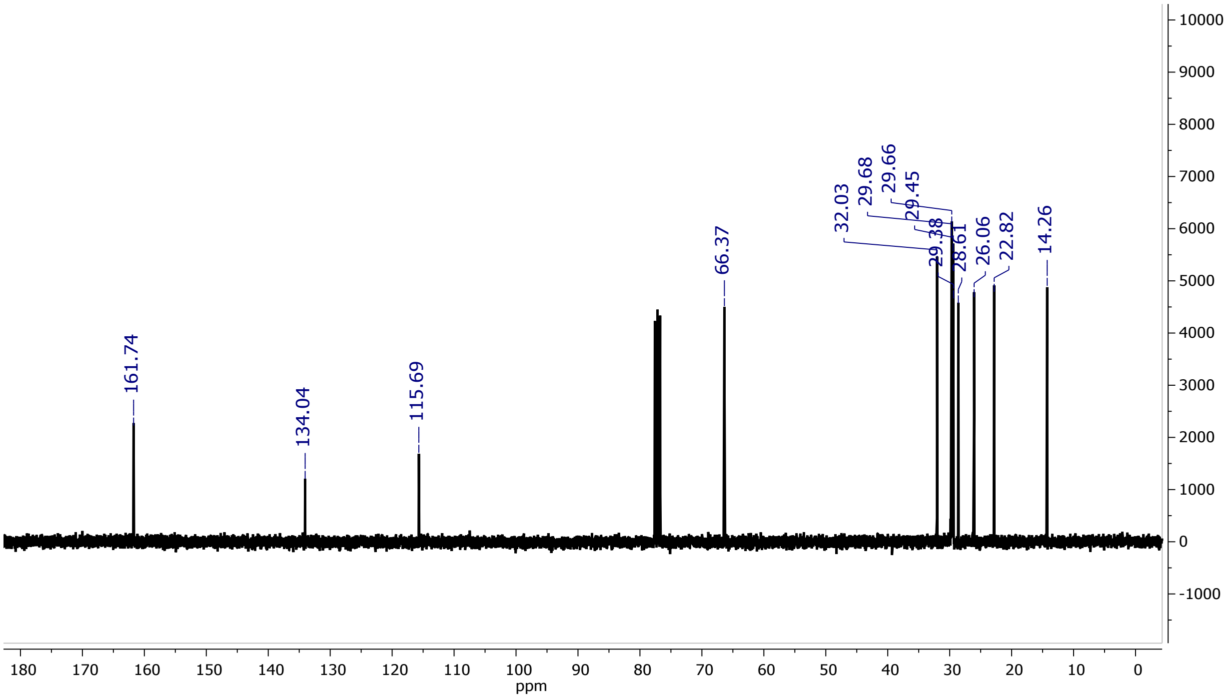


Figure S12. ^{13}C NMR of 9

didecyl [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (11): A dry 100 mL round bottom flask equipped with a stir bar and compound 9 (1.2 g, 1.96 mmol) was transferred into a glove box where tetrakis(triphenylphosphine)palladium(0) (140 mg, 0.12 mmol) was added to the flask. The reaction flask was removed from the glove box and immediately placed under a constant pressure of argon, followed by the addition of 20 mL of recently argon purged dimethylformamide and 2.2 equivalents of compound 10 (1.37 mL, 4.31 mmol). The reaction flask was heated to 125 °C and stirred for 24 hours. The solvent was removed under reduced pressure and the remaining mixture was purified using silica gel chromatography using hexane:DCM (5:2) as the eluent to produce a yellow oil (820 mg, 68%).^{1}H NMR (300 MHz, $CDCl_3$): 7.40-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.07-7.03 (m, 2H), 4.22 (t, *J* = 6 Hz, 4H), 1.68-1.59 (m, 4H), 1.34-1.20 (m, 28H), 0.89 (t, *J* = 6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 163.44, 137.50, 132.23, 129.76, 128.26, 127.37, 127.15, 65.53, 31.56, 29.22, 29.19, 28.99, 28.95, 28.08, 25.56, 22.35, 13.79. FTMS-ESI MS (*m/z)* $[M+Na]^+$ Calcd for $C_{34}H_{48}O_4S_3Na$, 639.261; found 639.259.

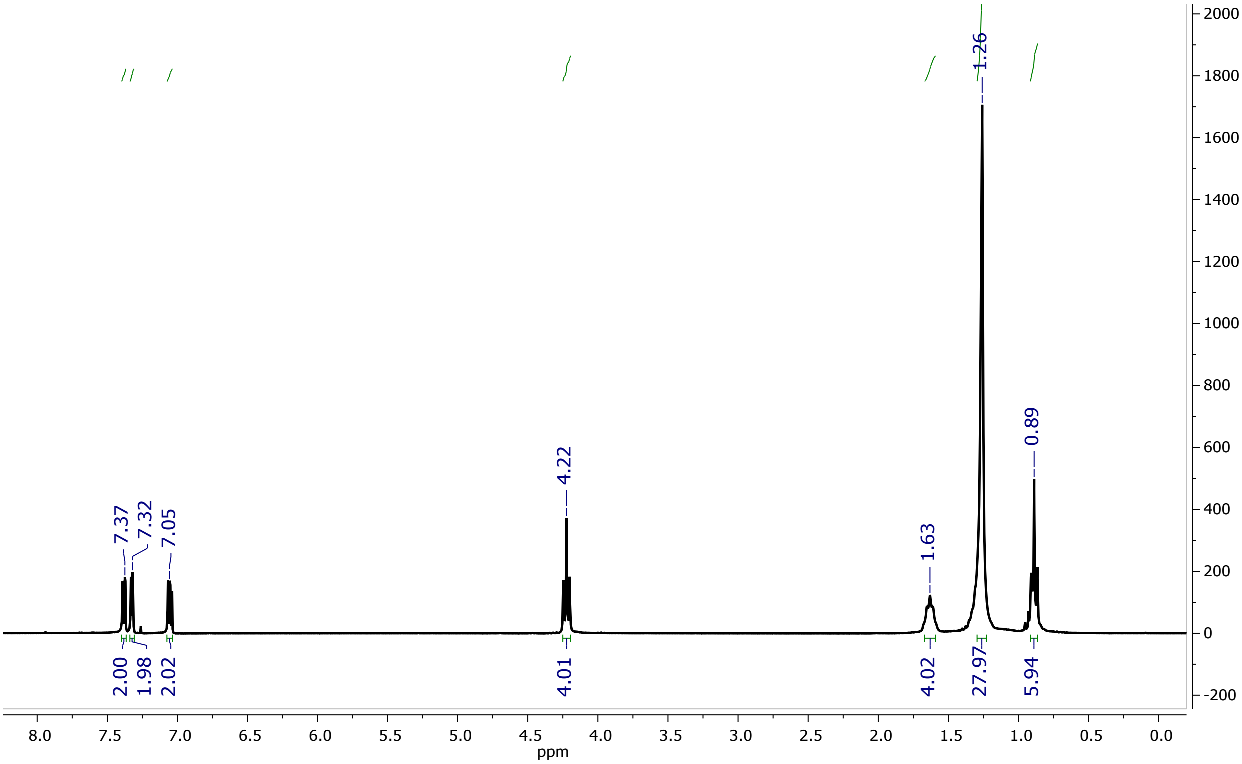


Figure S13. ^{1}H NMR of 11

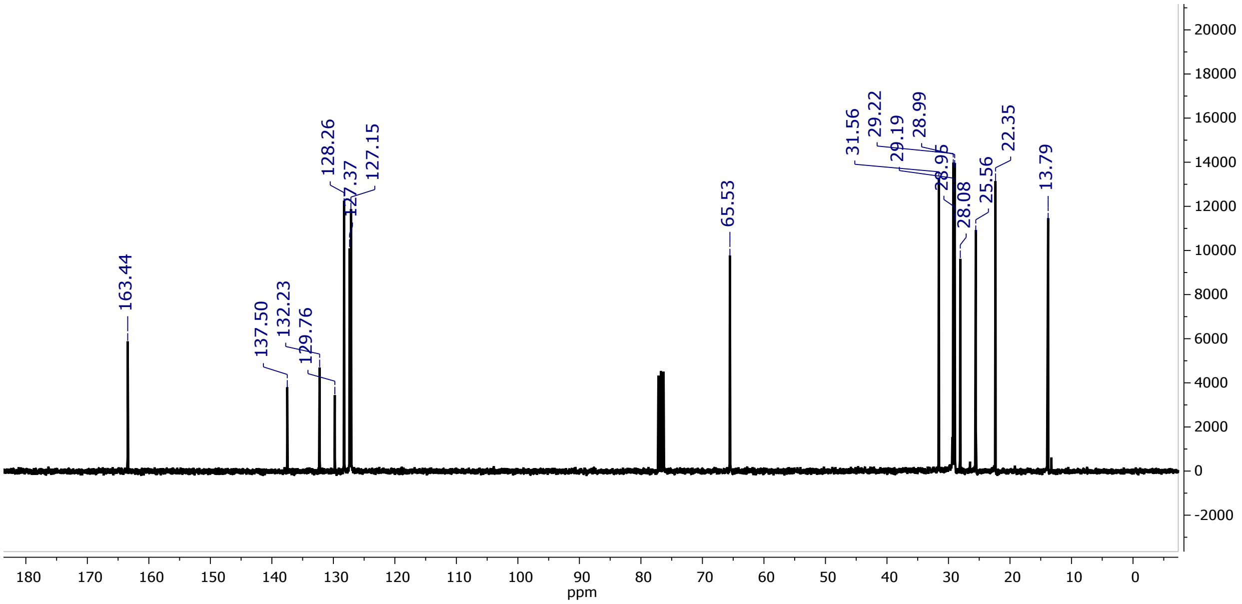


Figure S14. ^{13}C NMR of 11

didecyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (12): To a 100 mL round bottom flask was added a stir bar, compound 5 (540 mg, 0.87 mmol) and 20 mL of DMF. Then 2.3 equivalents of NBS (358 mg, 2.01 mmol) was added to the solution in small portions. The reaction was sealed, protected from light and stirred for 16 hours at room temperature. Subsequently, the solvent was removed under reduced pressure followed by an extraction using DCM and water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified using silica gel chromatography using hexane:DCM (4:1) as the eluent to produce an orange solid (550 mg, 81%).^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.06 (d, J = 3 Hz), 7.02 (d, J = 3 Hz), 4.22 (d, J = 6 Hz), 1.69-1.59 (m, 4H), 1.34-1.22 (m, 28H), 0.88 (t, J = 6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 163.50, 137.12, 133.82, 130.37, 129.11, 115.34, 66.22, 32.00, 29.67, 29.65, 29.43, 29.40, 28.53, 26.03, 22.80, 14.25. FTMS-ESI MS (*m/z)* $[M+Na]^+$ Calcd for $C_{34}H_{48}O_4Br_2S_3Na$, 795.082; found 795.080.

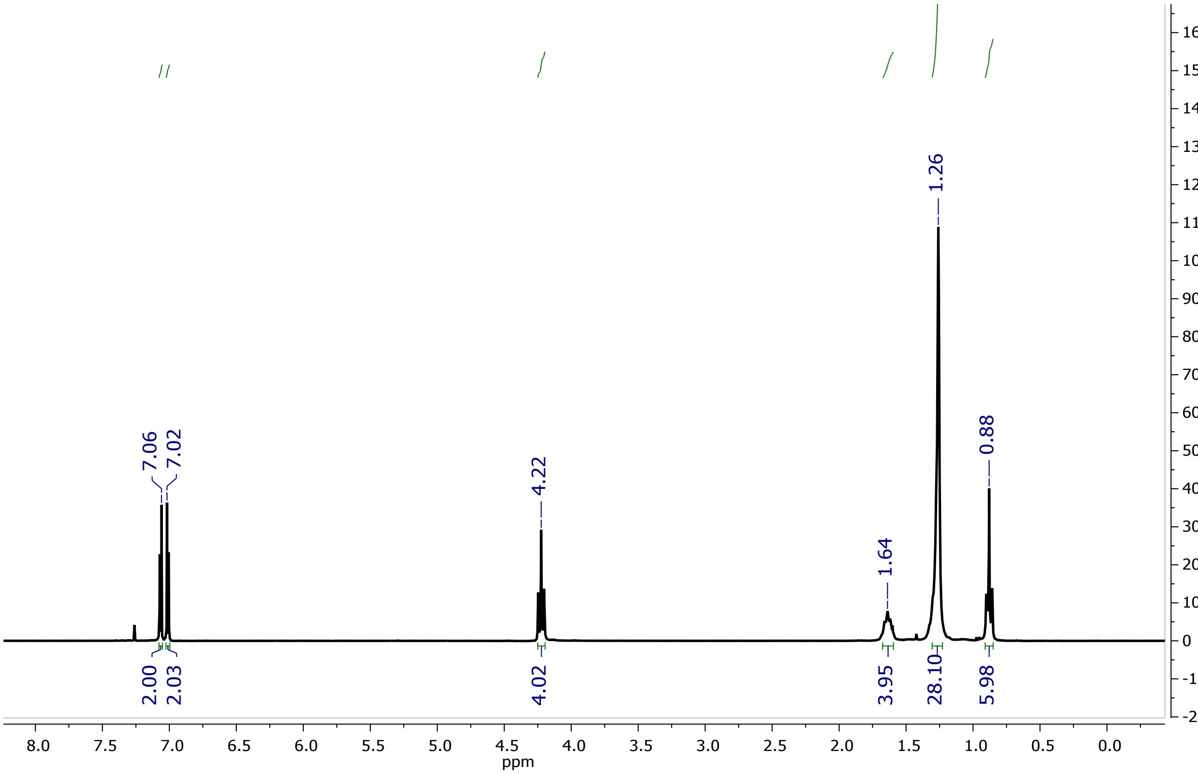


Figure S15. ^{1}H NMR of 12

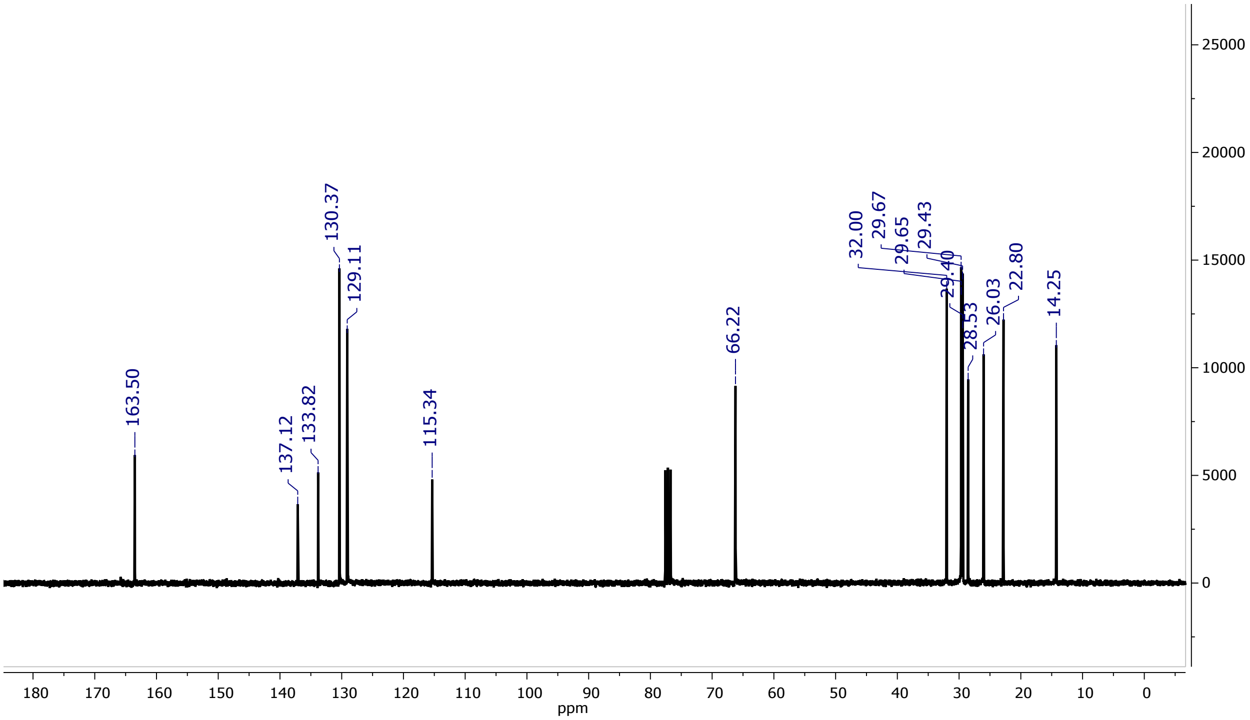
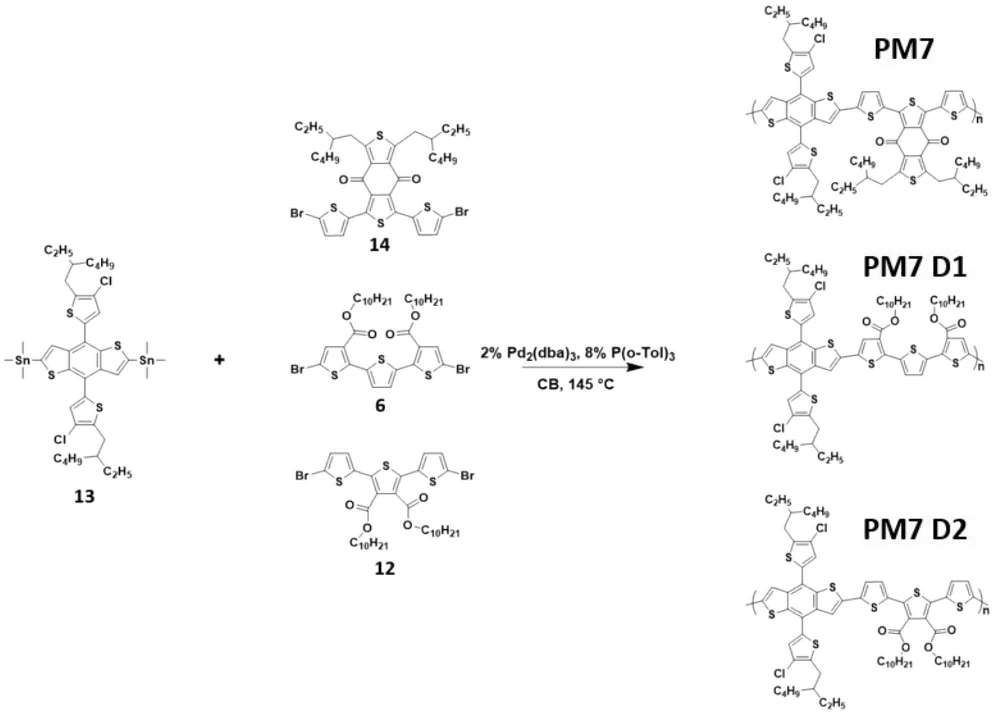


Figure S16. ^{13}C NMR of 12

Synthetic Scheme 3



General polymerization procedure for all polymers. A dry 50 mL round bottom flask was equipped with a magnetic stir bar, designated brominated monomer and compound **13**. The round bottom was transferred into a glove box where $Pd_2(dba)_3$•$CHCl_3$ and P(*o*-tol)$_3$ were added to the flask. The vessel was equipped with a condenser, sealed and removed from the glove box where a constant flow of argon was immediately applied to the flask. Next, 3 mL of dry, recently argon purged chlorobenzene was added to the reaction vessel through the condenser, was heated to 140 °C and allowed to react for 24 hours under argon. The polymerization was then cooled to 90 °C and exposed to air to add an excess amount of Pd scavenger diethylammonium diethyldithiocarbamate and 10 mL of additional chlorobenzene. The mixture was stirred for 1 hour before it was precipitated into 250 mL of methanol. The impure polymer was filtered through a nylon extraction thimble and subjected to successive soxhlet extractions with methanol, acetone, hexanes, dichloromethane and finally chloroform if needed. The soxhlet solution with the desired product was concentrated under reduced pressure and precipitated into methanol. Finally, the pure polymer was collected *via* vacuum filtration and dried under vacuum for 24 hours.

PM7: Monomer 13 (200 mg, 0.205 mmol), Monomer 14 (157 mg, 0.205 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform soxhlet fraction as a dark solid (240 mg, 93%). M_n: 48.8 kg/mol, M_w: 120 kg/mol, *Đ*: 2.45 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_6D_4Cl_2$, 110 °C): δ (ppm) 7.99 (bs, 4H), 7.65 (bs, 4H), 3.62 (m, 4H), 3.17 (bs, 4H), 2.12 (bs, 4H), 1.85-1.50 (m, 32H), 1.35-1.07 (m, 24H). Anal. calcd. for $C_{68}H_{76}Cl_2O_2S_8$: C (65.20%), H (6.12%), S (20.47%); Found: C (65.21%), H (6.24%), S (20.62%).

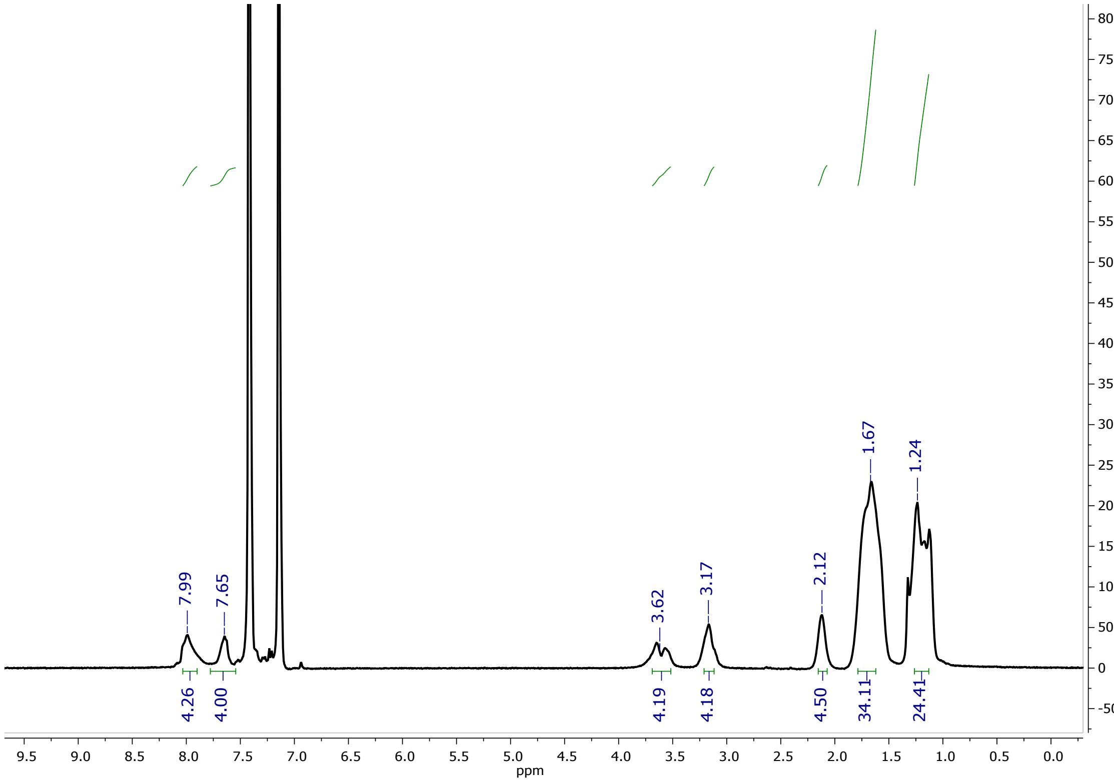


Figure S17. ^{1}H NMR of PM7

PM7 D1: Monomer 13 (200 mg, 0.205 mmol), Monomer 6 (159 mg, 0.205 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform soxhlet fraction as a dark solid (235 mg, 91%). M_n: 49.6 kg/mol, M_w: 111 kg/mol, *Đ*: 2.25 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ (ppm) 7.70 (m, 4H), 7.54 (s, 2H), 7.35 (s, 2H), 4.36 (m, 4H), 2.97 (bs, 4H), 1.91-1.76 (m, 6H), 1.62-1.28 (m, 44H), 1.11-0.89 (m, 18H). Anal. calcd. for $C_{68}H_{84}Cl_2O_4S_7$: C (64.78%), H (6.72%), S (17.80%); Found: C (64.67%), H (6.65%), S (17.60%).

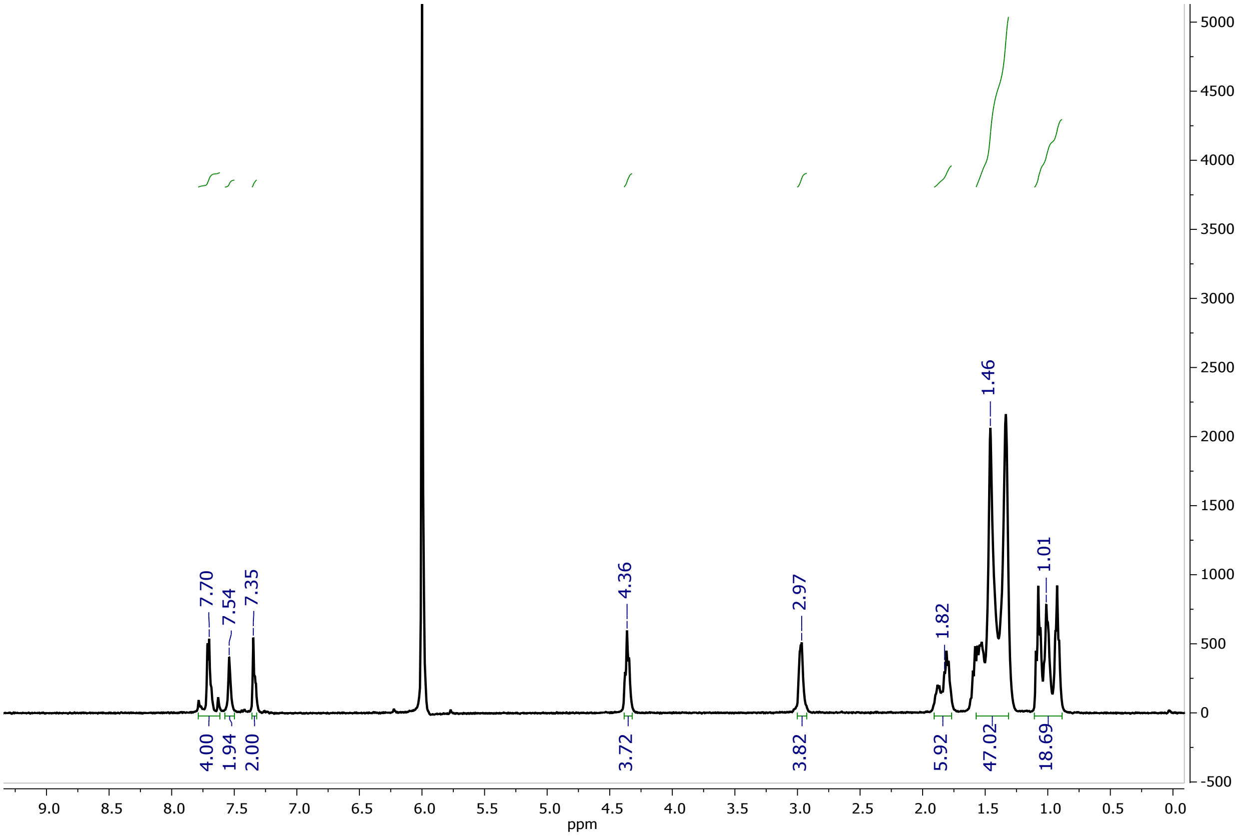


Figure S18. ^{1}H NMR of PM7 D1

PM7 D2: Monomer 13 (232 mg, 0.238 mmol), Monomer 12 (185 mg, 0.238 mmol), $Pd_2(dba)_3{\bullet}CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform soxhlet fraction as a dark green solid (235 mg, 91%). M_n: 45.8 kg/mol, M_w: 94.8 kg/mol, $Đ$: 2.07 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ (ppm) 7.70 (m, 2H), 7.34 (m, 6H), 4.32 (m, 4H), 2.96 (m, 4H), 1.87 (m, 2H), 1.74 (m, 4H), 1.62-1.25 (m, 44H), 1.10-0.88 (m, 18H). Anal. calcd. for $C_{68}H_{84}Cl_2O_4S_7$: C (64.78%), H (6.72%), S (17.80%); Found: C (64.87%), H (6.58%), S (17.74%).

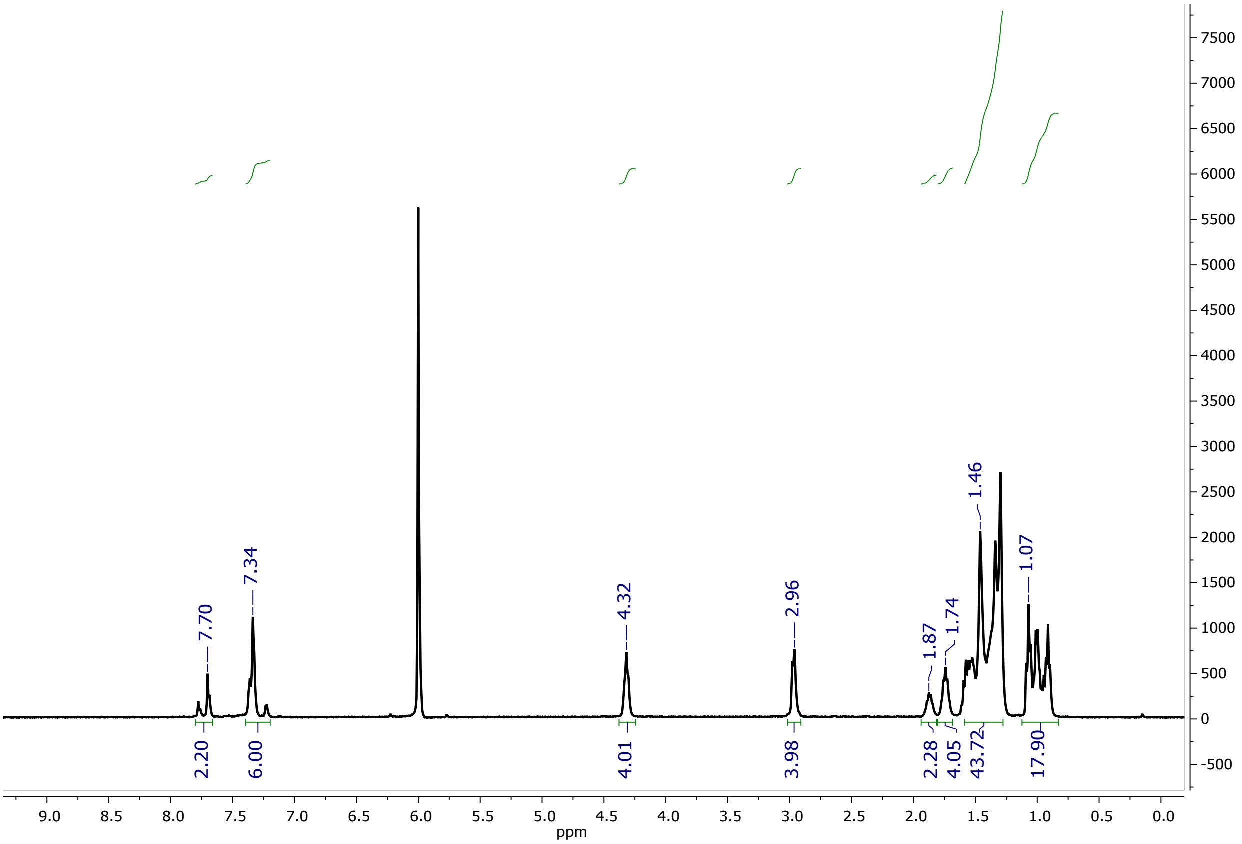


Figure S19. ^{1}H NMR of PM7 D2

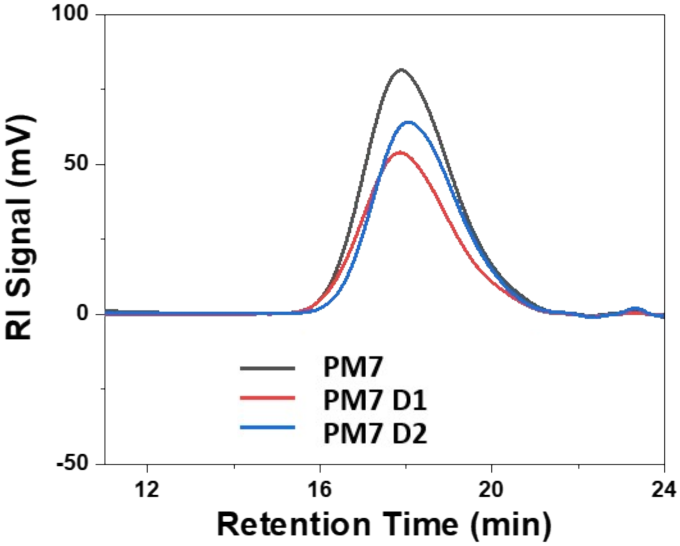


Figure S20. High temperature (140 °C) GPC traces in 1,2,4-trichlorobenzene.

Experimental Section

^1H NMR and ^{13}C NMR spectra for all monomers and molecular precursors were acquired on a Varian Mercury Vx 300 MHz instrument using $CDCl_3$ as solvent; the residual $CHCl_3$ peak was used as a reference for all reported chemical shifts (^1H: δ= 7.26 ppm, ^{13}C: δ= 77.16 ppm). ^1H NMR for all polymers were acquired on a Bruker 400 MHz instrument using 1, 1, 2, 2-tetrachloroethane ($C_2D_2Cl_4$) or 1,2-dichlorobenzene ($C_6D_4Cl_2$) at 100 °C; the residual $C_2H_2Cl_4$ (^1H: δ= 6.0 ppm) or $C_6D_4Cl_2$ (^1H: δ= 7.4 ppm) peak was used as a reference for the reported polymer chemical shifts. Gel permeation chromatography (GPC) was performed using a Tosoh EcoSEC high temperature GPC instrument with RI detector to determine the number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity ($Đ$) for all polymers. Experiments were run using 1, 2, 4-trichlorobenzene (TCB) as eluent at 140 °C at a flow rate of 1 mL/min on two 7.8 mm x 30 cm, 13 µm TSK-Gel GMH_{HR}-H(S) HT2 columns in series. The instrument was calibrated using polystyrene standards (1,390-1,214,000 g/mol) and the data were analyzed using 8321GPC-WS analysis software. The GPC samples were prepared by dissolving the polymers in TCB at a 1 mg/mL concentration and stirred at 110 °C for at least 3 hours before filtering through a 0.45 mm PTFE filter. Elemental analyses were conducted by Atlantic Microlab Inc. UV-vis absorption spectra were obtained on a Cary 5000 spectrometer. Film thicknesses were estimated using a Bruker DektakXT profilometer. Electrochemical analysis was performed using an EG&G Princeton Applied Research model 273A potentiostat-galvanostat. Cyclic voltammetry (CV) was performed at a 20 mV scan rate and differential pulse voltammetry (DPV) were performed using a 2 mV step size, 80 ms step time and 50 mV pulse amplitude. Voltammetry experiments were performed in a glove box using a standard three-electrode cell including a 0.07 cm^2 glassy carbon button working electrode, an Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode and a platinum flag counter electrode. Polymer films were drop casted onto the working electrode from a 1 mg/mL chloroform solution and allowed to air dry. Electrochemical experiments were performed using dry acetonitrile with a $TBAPF_6$ supporting electrolyte at a concentration of 0.5 M in an argon filled glovebox. Ferrocene/ferrocenium (-5.12 V vs vacuum) was used as an internal standard calibrated against the Ag/Ag^+ reference electrode ($E_{1/2}$ = 85 mV).

Solar cells were constructed in the inverted architecture comprising of glass/ITO/ZnO/polymer: ITIC:4F/MoO_3/Ag. Before device processing, the ITO-coated glass substrates (Latech Scientific Supply Pte. Ltd., sheet resistance 10 Ω/sq) were cleaned by sonicating sequentially with sodium dodecyl sulfate in Millipore water, pure Millipore water, acetone and finally isopropanol for 10 minutes each. The cleaned substrates were blown dry with argon and placed in a UV/O_3 chamber for 15 minutes. For the electron transport layer, a ZnO solution was made with 0.11 M Zn acetate dihydrate and 0.11 M ethanolamine combined in 2-methoxyethanol (Sigma Aldrich). This solution was stirred overnight at room temperature, then filtered with a 0.45 µm PTFE syringe filter before use. The ZnO solution was deposited on the cleaned ITO substrates by spin-coating for 30 seconds at 4000 rpm in ambient atmosphere to get a layer thickness of ~30 nm. After spin-coating, the ZnO layer was annealed in air at 150 ˚C for 15 min followed by slow cooling to room temperature and bought into an argon filled glovebox for active layer deposition. The photoactive layer solution for all devices were prepared by dissolving polymer and ITIC-4F (Sigma Aldrich) in of chlorobenzene with 1% DIO as an additive. The ratio of polymer:ITIC-4F used was 1:1 (wt/wt) with a polymer concentration of 20 mg/mL, which produced active layer thickness around 100 nm. For active layer thickness around 180 nm, the active layer solution concentration was doubled. The solution was stirred at 30 ˚C for 12 hours to ensure complete dissolution. The active layer solution was coated on top of the ZnO layer in an Argon-filled glove box at 1500 rpm for 45 seconds. For all devices, the top electrodes MoO_3 and Ag were deposited by vacuum deposition with layer thicknesses of 12 and 160 nm, respectively, to obtain complete solar cell devices with an electrode overlap area of 0.07 cm^2. Fast drying Ag paint (Ted Pella, 16040-30) was applied to the ITO electrodes to improve contact with the device switch-box. An aperture with an area of 4.9 mm^2 was aligned with the electrode overlap area for solar cell characterization. The J-V characteristics of all photovoltaic devices were evaluated under AM 1.5 G solar illumination (100 mW/cm^2) using a Keithley SMU 2410 with a Newport Thermal Oriel 94021 solar simulator calibrated with a reference silicon solar cell.

Device Fabrication at North Carolina State University: The device structure of the OPV cell was ITO/ZnO/Active layer/MoO_X/Ag. ITO patterned glass substrate was cleaned by deionized water, acetone and 2-propanol in ultrasonic bath, followed by UV-ozone treatment. ZnO sol–gel was then spin coated at 4000 RPM onto the ITO substrate and thermal annealed at 150 °C for 30 min. Active layer materials were dissolved in chlorobenzene with a total concentration of 25-35 mg/mL, 1 vol% DIO was added to the solution. The solution was stirred at 40 °C overnight before use, then spin coated on ZnO in a glove box to form BHJ layer. The sample was annealed at 100 °C in a glove box for 5 mins, then transported into a thermal evaporator to coat MoOx (10 nm) and Ag (120 nm) on the BHJ layer under high vacuum. Solar cell was characterized by AM 1.5 G simulator with an intensity of 100 mW cm^{-2}. EQE measurements were conducted using an inhouse setup consisting of a Xenon DC arc lamp, an ORIEL 74125 monochromator, a Keithley 428 current amplifier, an SR 540 chopper system and an SR830 DSP lock-in amplifier from SRS.

Charge transport measurement: The device structure is similar to the OPV device. For the electron-only devices, the MoOx/Ag layers is replaced by PDINO/Al layers. For hole-only devices, the ZnO layer is replaced by a 20 nm thick PEDOT:PSS layer. After device fabrication, the device was put in a cryostat with a pressure of less than 10 mTorr for measurement. Temperature-dependent SCLC characteristics were acquired using a Keithley 4200 semiconductor parameter analyzer.

GIWAXS Characterization: Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA at the beamline 7.3.3. Data was acquired at the critical angle (0.130) of the film with a hard X-ray energy of 10 keV. X-ray irradiation time was 10-30 s, dependent on the saturation level of the detector. Beam center was calibrated using AgBr powder and the sample-to-detector distance was about 330 mm. The π-π coherence lengths (L) are estimated based on the Scherrer Equation ($L=2\pi K/FWHM$), where K is the shape factor (here we use 0.9), and FWHM is the full width at half maximum of the (010) diffraction peaks.

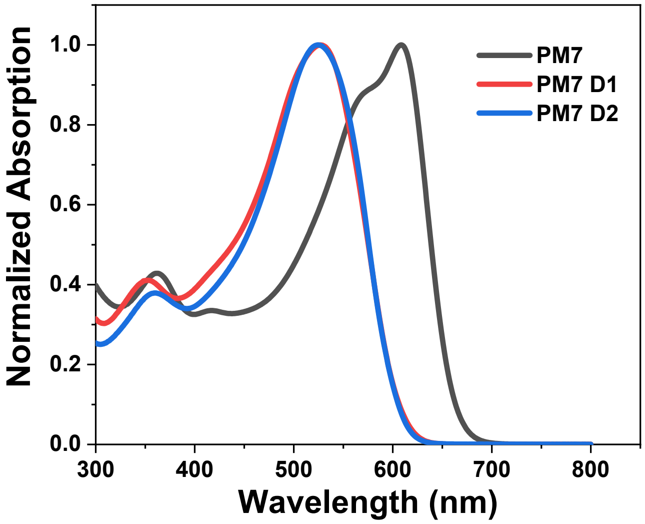


Figure S21. Normalized solution UV/vis absorption of PM7, PM7 D1, and PM7 D2 in dilute chlorobenzene at room temperature.

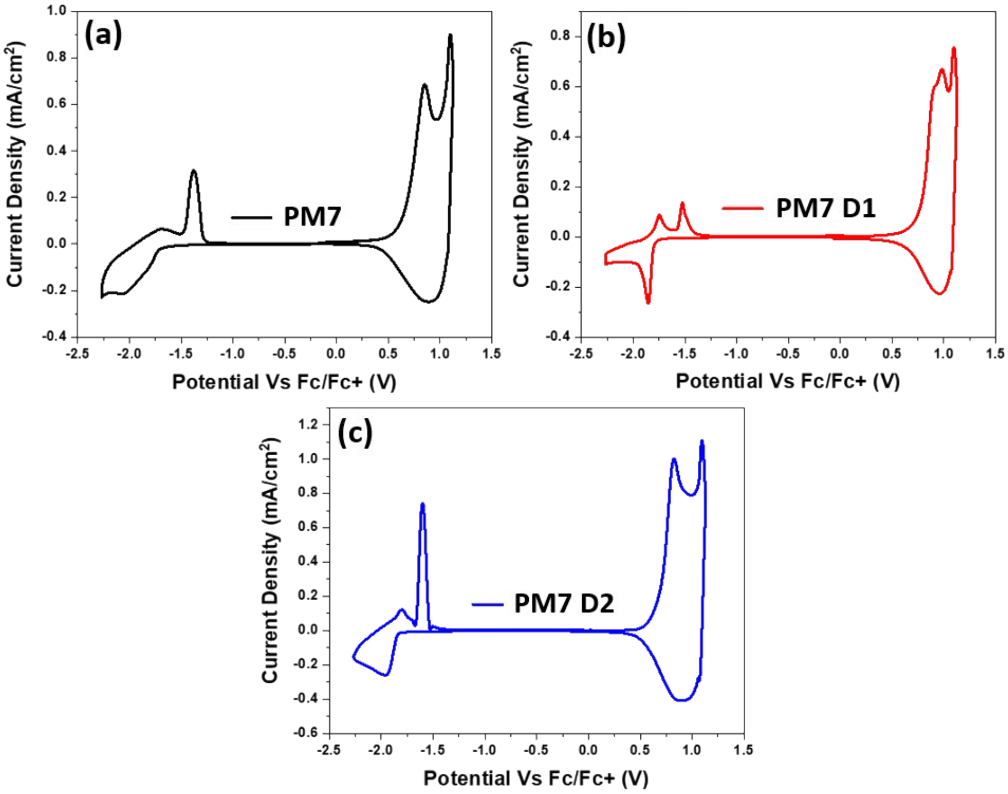


Figure S22. CV traces for PM7 (a), PM7 D1 (b), and PM7 D2 (c) versus Fc/Fc+.

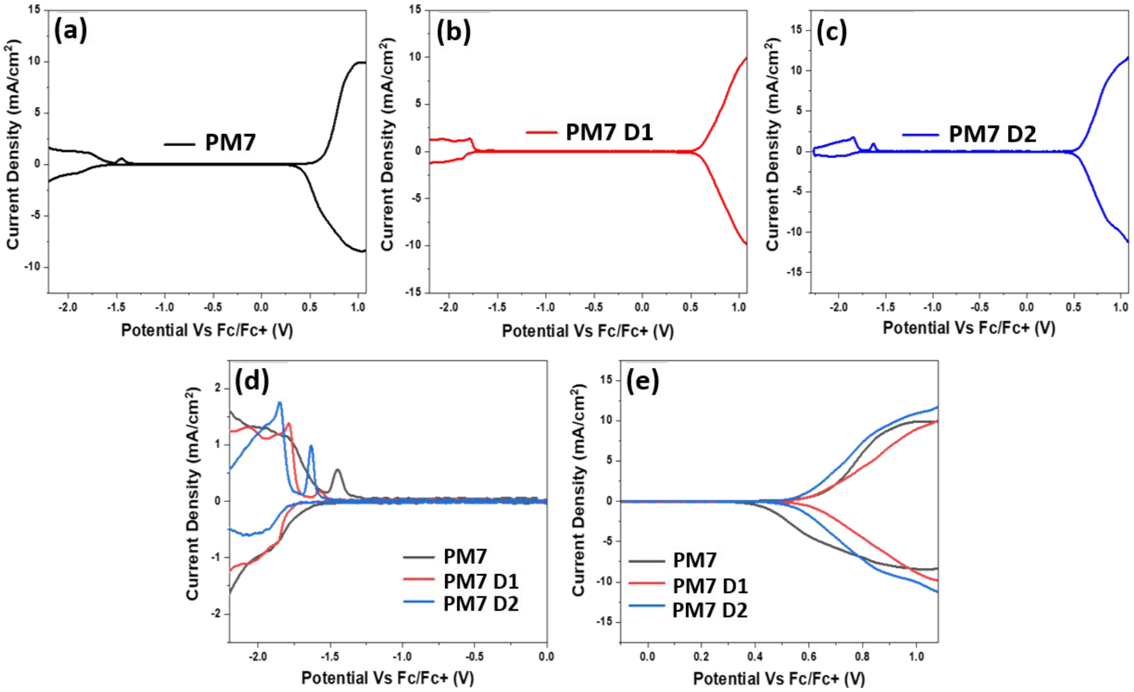


Figure S23. DPV for PM7 (a), PM7 D1 (b), and PM7 D2 (c) versus Fc/Fc+. DPV reduction for all three polymers overlapped (d) and oxidation overlapped (e).

Table S1. Electrochemical Properties and Energy Levels

Polymer	$E_{\text{onset}}^{\text{ox}}$ **(V)**[a]	$E_{\text{onset}}^{\text{red}}$ **(V)**[a]	$E_{\text{gap}}^{\text{echem}}$ **(eV)**	$E_{\text{gap}}^{\text{opt}}$ **(eV)**[c]	**IE (eV)**[b]	**EA (eV)**[b]
PM7	0.62	-1.71	2.33	1.83	-5.74	-3.41
PM7 D1	0.62	-1.78	2.40	1.95	-5.74	-3.34
PM7 D2	0.57	-1.80	2.37	1.98	-5.69	-3.32

[a] Oxidation and reduction potentials were estimated by thin-film electrochemistry using a differential pulse voltammetry (DPV) scan technique. [b] IE and EA state negative values were calculated by assuming saturated calomel electrode (SCE) versus vacuum with respect to Fc/Fc+ to be 5.12 eV using the equation EIE-EA = −e(Eox/red + 5.12). [c] The optical gap was estimated from the onset of the spin-coated films prepared from 10 mg/mL chlorobenzene solutions.

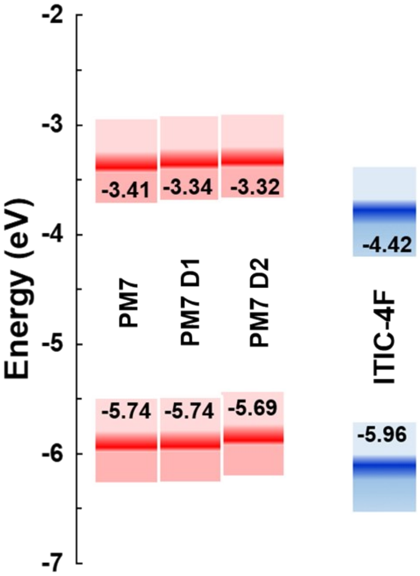


Figure S24. Energy state diagram based on the negative of the IE and EA values; the IEs and EAs were calculated for all materials versus Fc/Fc$^+$ at −5.12 eV, ITIC-4F was referenced from a previous publication where the same electrochemical set-up was used.[4]

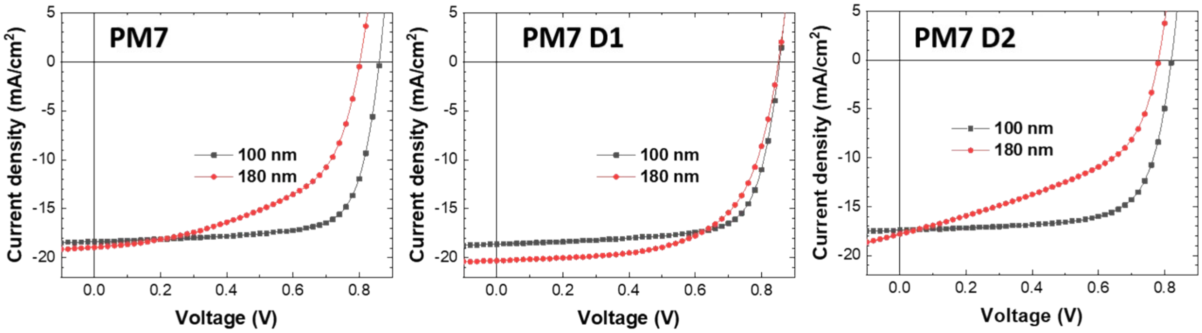


Figure S25. Solar cell *J-V* curves collected at North Carolina State for the polymer:ITIC:4F thick and thin active layer devices.

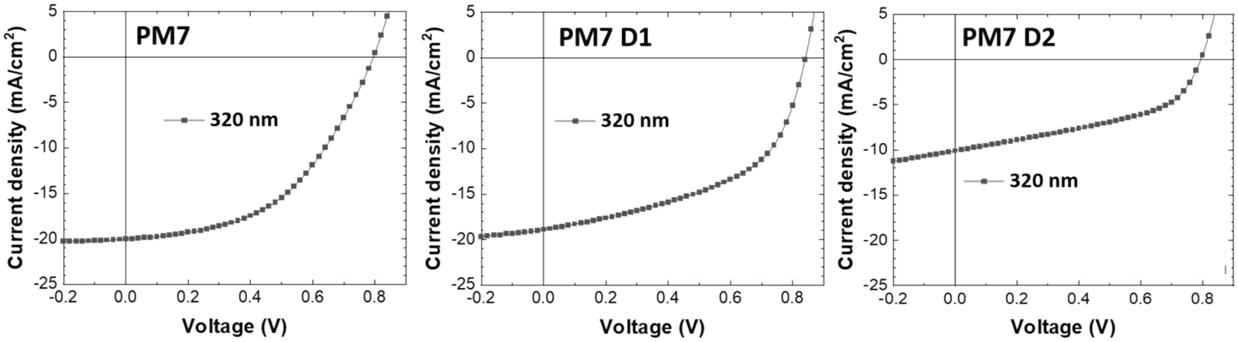


Figure S26. Solar cell *J-V* curves collected at North Carolina State for the polymer:ITIC:4F 320 nm thick active layer devices.

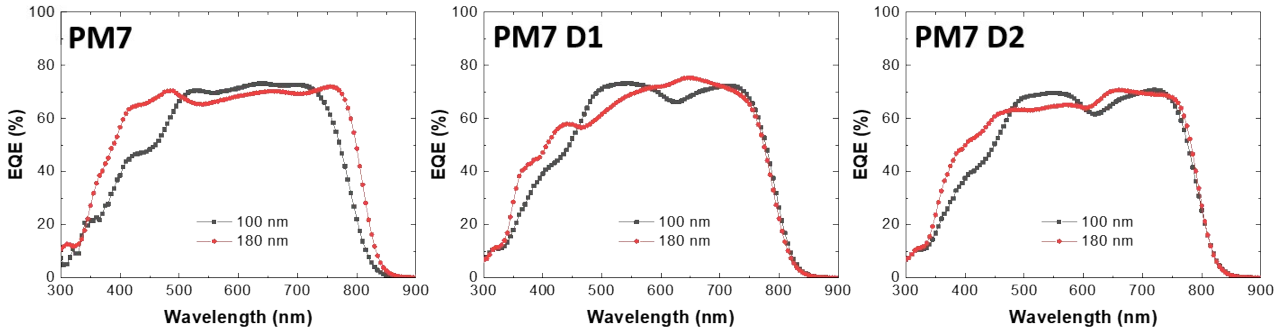


Figure S27. EQE curves for both thick and thin film devices.

Table S2. Integrated EQE Currents

Donor polymer	Integrated J_{SC} (cm^2/Vs)
PM7 – 100 nm	17.02
PM7 – 180 nm	18.70
PM7 D1 – 100 nm	17.37
PM7 D1 – 180 nm	18.43
PM7 D2 – 100 nm	16.65
PM7 D2 – 180 nm	17.34

EQE results were measured at North Carolina State University.

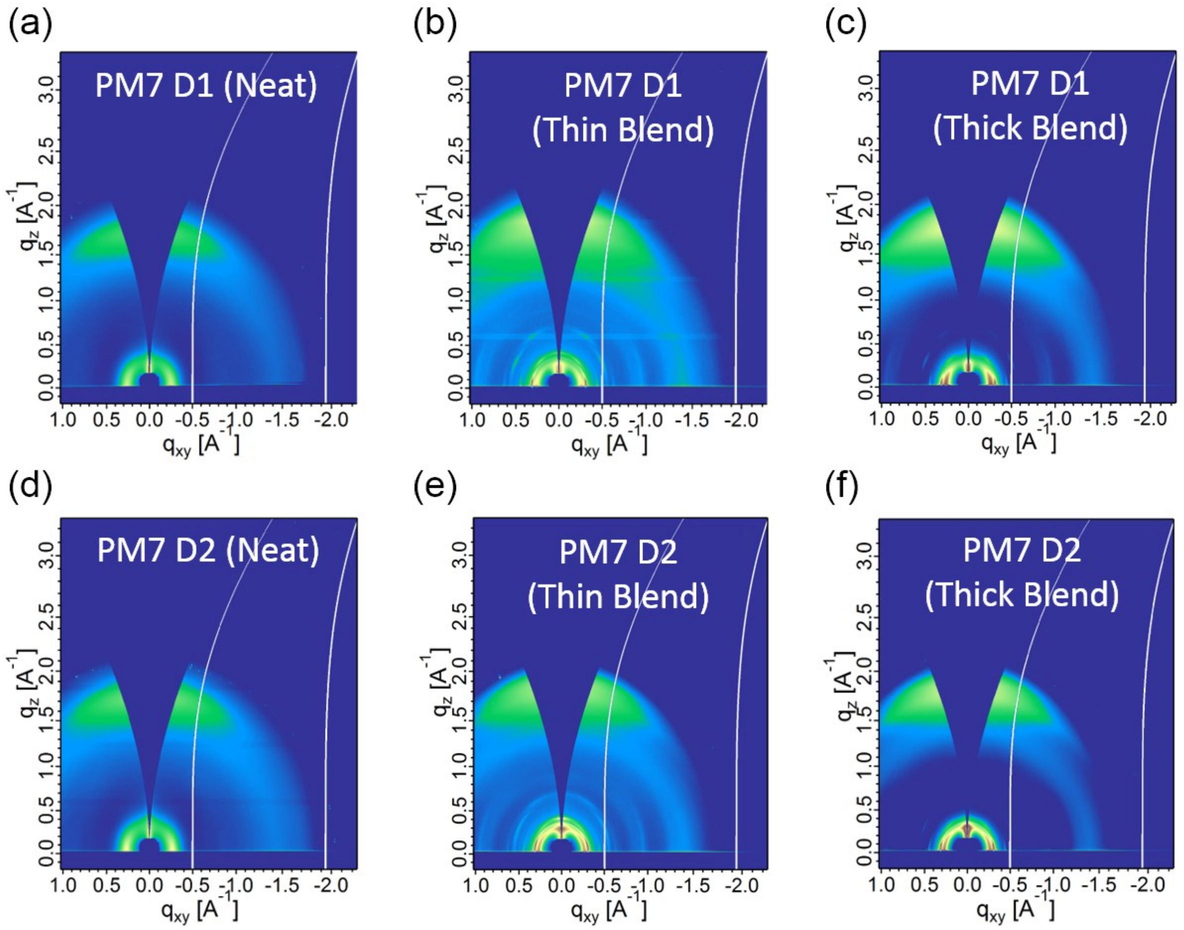


Figure S28. 2D GIWAXS patterns of the neat PM7 D1, D2 (a, d) and the thin (b, e) and thick (c, f) blends PM7 D1 and PM7 D2.

Table S3. The out of plane π-π (010) stacking parameters from GIWAXS.

Sample	π-π stacking: location and distance (OP)		π-π width and coherence length (OP)		Integrated Intensity
	q (Å^{-1})	d (Å)	Δq (Å^{-1})	L_c (Å)	
PM7 D1 (thin)	1.73	3.64	0.23	27	2.15×10^{-6}
PM7 D1 (thick)	1.73	3.64	0.20	32	1.30×10^{-6}
PM7 D2 (thin)	1.79	3.51	0.29	22	2.31×10^{-6}
PM7 D2 (thick)	1.78	3.53	0.26	24	2.07×10^{-6}

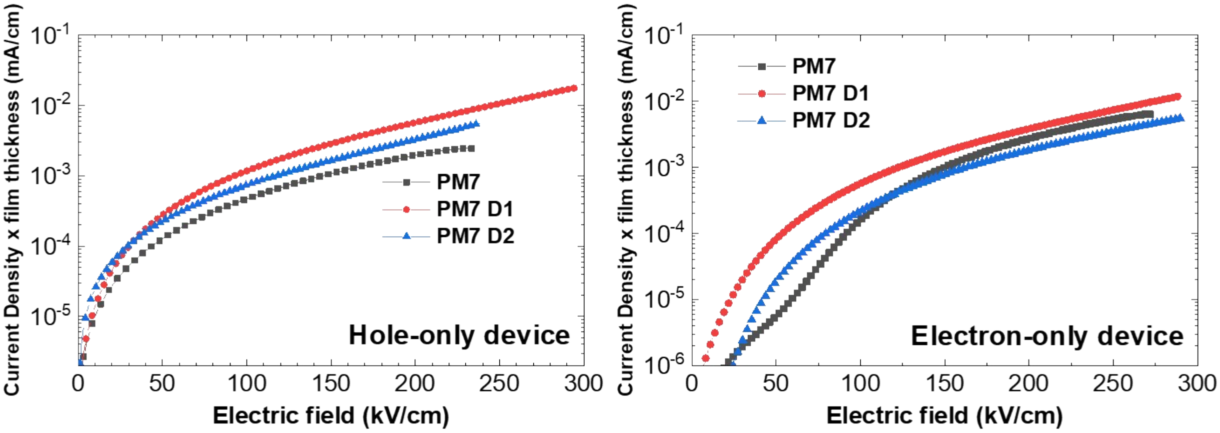


Figure S29. SCLC J-V characteristics of single carrier devices measured at room temperature.

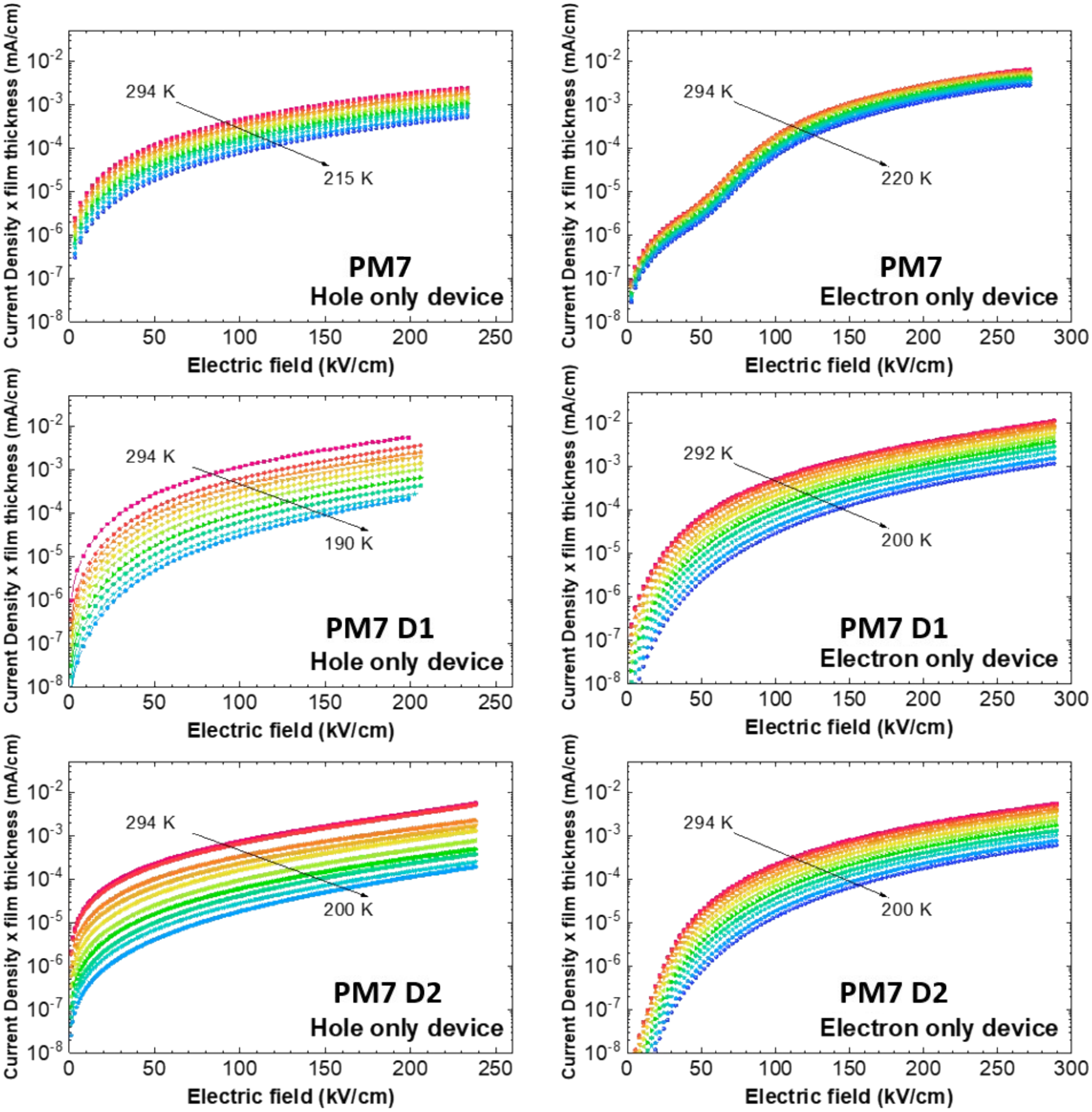


Figure S30. Temperature-dependent J-V characteristics of different hole-only and electron-only devices in a semi-log plot.

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