Supporting Information

A high mobility DPP-based polymer obtained via direct (hetero)arylation polymerization

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Polymerization

P1

2,5-Bis(2-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (63.6, 0.1 mmol) (**M2**), 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (101.9 mg, 0.1 mmol) (**M1**), Herrmann-Beller's catalyst (1.9 mg, 2% mol), tris-*o*-methoxyphenylphosphine (2.8 mg, 8% mol), cesium carbonate (74.9mg, 0.23 mmol) and pivalic acid (3.1 mg, 30 % mol) were loaded in an oven dried 5 mL microwave tube. The tube was sealed and purged under vacuum for 15 min. After equilibration with argon, neat and argon-saturated toluene (0.5 mL) was added to the tube. The latter was heated at 120 °C using a slow temperature ramp. After heating for 16 hours, 0.2 mL of toluene was added in order to keep the polymer in solution. 4 hours later the oil bath was removed and the mixture was left to cool. Precipitation in methanol followed by a filtration afforded a crude black material. Successive sohxlets using acetone, hexanes and chloroform were used to remove low molecular weights materials. The residual fraction was solubilize in o-DCB (boiling) and precipitate in methanol. After filtration, the polymer was solubilized in o-DCB and washed using a palladium scavenger overnight. Extraction using hot water and precipitation in methanol afforded **P1** as black material (140mg, 93%).

P2

2,5-Bis(dodecyl)-3,6-bis(4-methylthiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (66.5, 0.1 mmol) (**M4**), 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromo-4-methylthiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (104.7 mg, 0.1 mmol) (**M3**), Herrmann-Beller's catalyst (1.9 mg, 2% mol), tris-*o*-methoxyphenylphosphine (2.8 mg, 8% mol), cesium carbonate (74.9mg, 0.23 mmol) and pivalic acid (3.1 mg, 30 % mol) were loaded in an oven dried 5 mL microwave tube. The tube was sealed and purged under vacuum for 15 min. After equilibration with argon, neat and argon-saturated toluene (0.5 mL) was added to the tube. The latter was heated at 120 °C using a slow temperature ramp. After heating for 16 hours, 0.2 mL of toluene was added in order to keep the polymer in solution. 4 hours later the oil bath was removed and the mixture was left to cool. Precipitation in methanol followed by a filtration afforded a crude black material. Successive sohxlets using acetone and hexanes were used to remove low molecular weights materials. The chloroform fraction was reduced and precipitate in methanol. After filtration, the polymer was solubilized in o-DCB and washed using a palladium scavenger overnight. Extraction using hot water and precipitation in methanol afforded **P2** as black material (95mg, 61%).

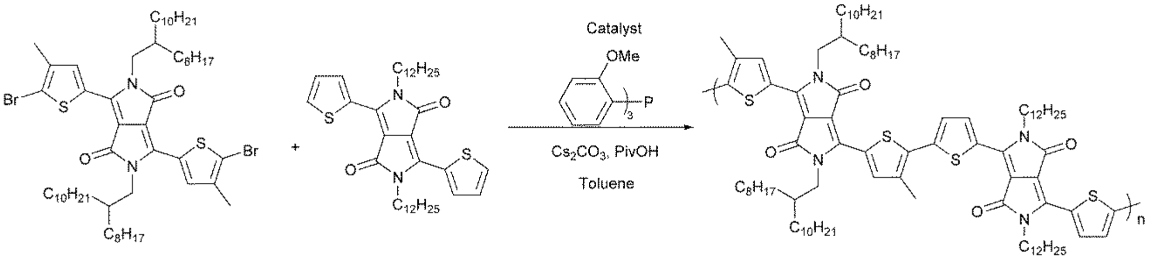
P3

2,5-Bis(dodecyl)-3,6-bis(5-bromo-4-methylthiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (79.4, 0.1 mmol) (**M6**), 2,5-bis(2-octyldodecyl)-3,6-bis(4-methylthiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (88.9 mg, 0.1 mmol) (**M5**), Herrmann-Beller's catalyst (1.9 mg, 2% mol), tris-*o*-methoxyphenylphosphine (2.8 mg, 8% mol), cesium carbonate (74.9mg, 0.23 mmol) and pivalic acid (3.1 mg, 30 % mol) were loaded in an oven dried 5 mL microwave tube. The tube was sealed and purged under vacuum for 15 min. After equilibration with argon, neat and argon-saturated toluene (0.5 mL) was added to the tube. The latter was heated at 120 °C using a slow temperature ramp. After heating for 16 hours, 0.2 mL of toluene was added in order to keep the polymer in solution. 4 hours later the oil bath was removed and the mixture was left to cool. Precipitation in methanol followed by a filtration afforded a crude black material. Successive sohxlets using acetone and hexanes were used to remove low molecular weights materials. The chloroform fraction was reduced and precipitate in methanol. After filtration, the polymer was solubilized in o-DCB and washed using a palladium scavenger overnight. Extraction using hot water and precipitation in methanol afforded **P3** as black material (120mg, 83%).

P4

2,5-Bis(2-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (63.6, 0.1 mmol) (**M2**), 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromo-4-methylthiophene-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2H,5H)-dione (104.7 mg, 0.1 mmol) (**M3**), Herrmann-Beller's catalyst (1.9 mg, 2% mol), tris-*o*-methoxyphenylphosphine (2.8 mg, 8% mol), cesium carbonate (74.9mg, 0.23 mmol) and pivalic acid (3.1 mg, 30 % mol) were loaded in an oven dried 5 mL microwave tube. The tube was sealed and purged under vacuum for 15 min. After equilibration with argon, neat and argon-saturated toluene (0.5 mL) was added to the tube. The latter was heated at 120 °C using a slow temperature ramp. After heating for 16 hours, 0.2 mL of toluene was added in order to keep the polymer in solution. 4 hours later the oil bath was removed and the mixture was left to cool. Precipitation in methanol followed by a filtration afforded a crude black material. Successive sohxlets using acetone and hexanes were used to remove low molecular weights materials. The chloroform fraction was reduced and precipitate in methanol. After filtration, the polymer was solubilized in o-DCB and washed using a palladium scavenger overnight. Extraction using hot water and precipitation in methanol afforded **P4** as black material (128mg, 84%).

Catalyst optimization (for P4)



Catalyst	Mn	IP	Yield	Temperature
	kDa		%	°C
Pd(Herrmann-Beller)	46	2.5	84	120
$PdCl_2(MeCN)_2$	37	2.6	84	120
Pd(Herrmann-Beller)	27	4.0	83	130
$Pd(OAc)_2$	0	0	0	120

P1 - The polymer was isolated as a black powder (140 mg, 93%).

Figure S1. DSC thermogram of **P1** at a rate of 20 °C/min (cooling-heating (blue-green))

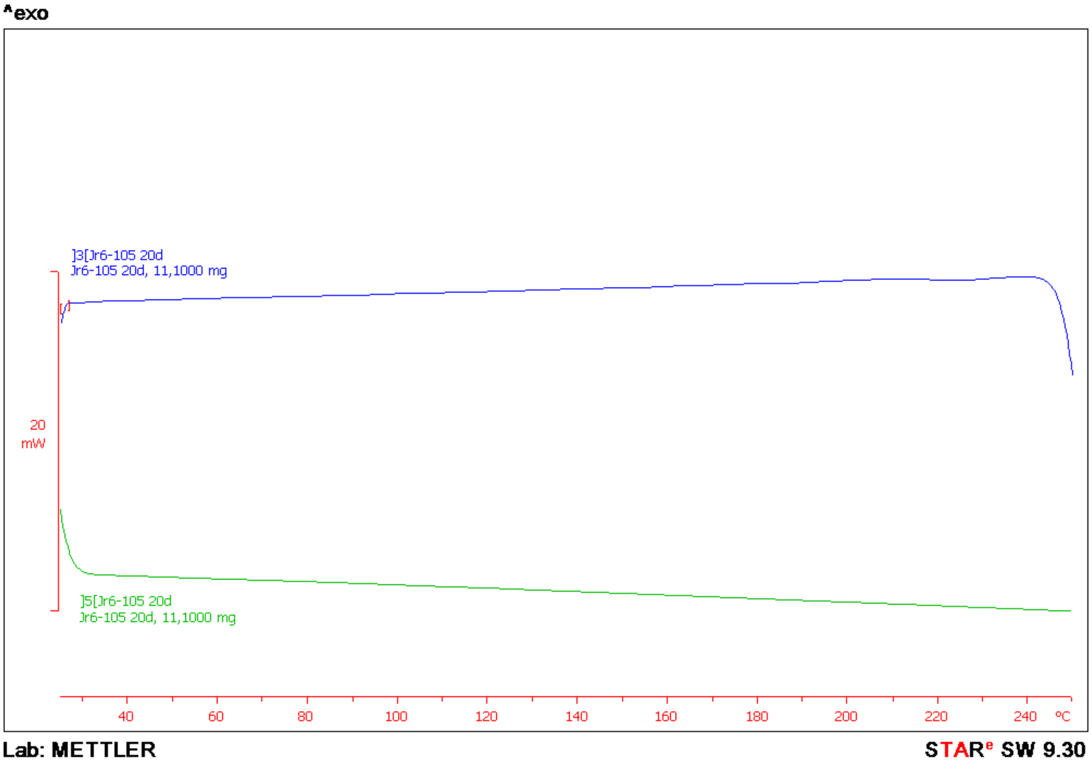


Figure S2. WAXS experiment of **P1** (powder)

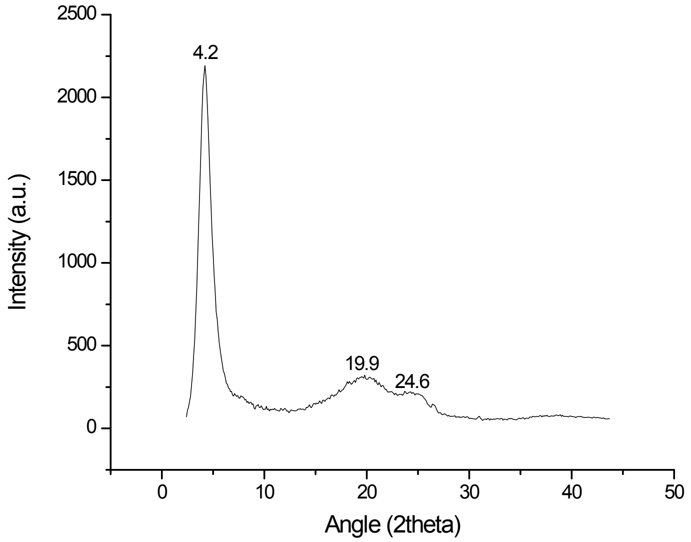


Figure S3. Cyclic voltammogram of **P1** cast on a platinum wire

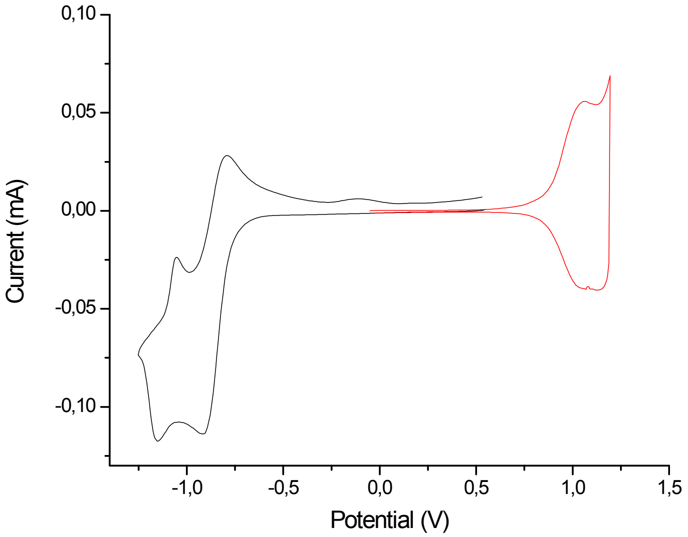
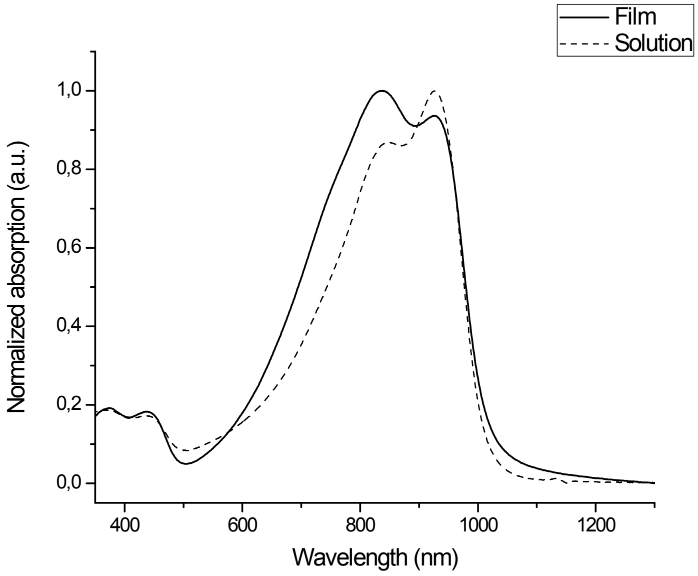


Figure S4. Normalized UV-visible absorption spectra of **P1** in solution in chloroform and in solid state cast on a glass substrate



P2 - The polymer was isolated as a fine black powder (95 mg, 61%).

Figure S5. DSC thermogram of **P2** at a rate of 20 °C/min (heating-cooling-heating (red-blue-green))

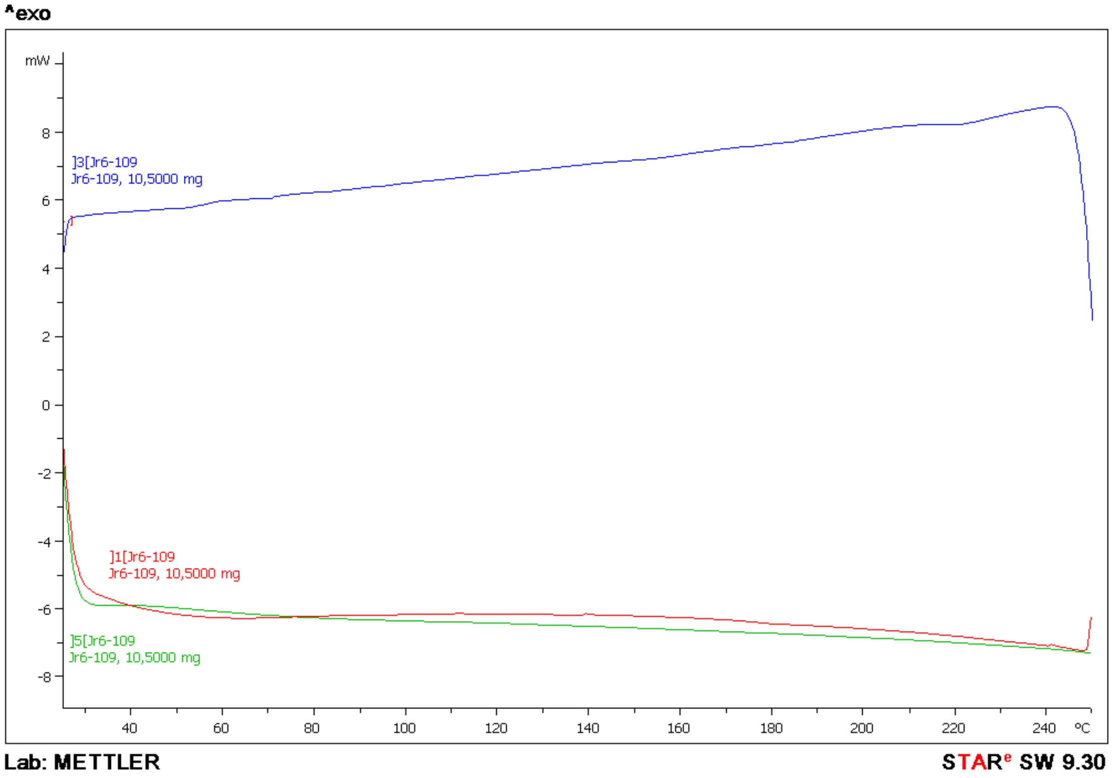


Figure S6. WAXS experiment of **P2** (powder)

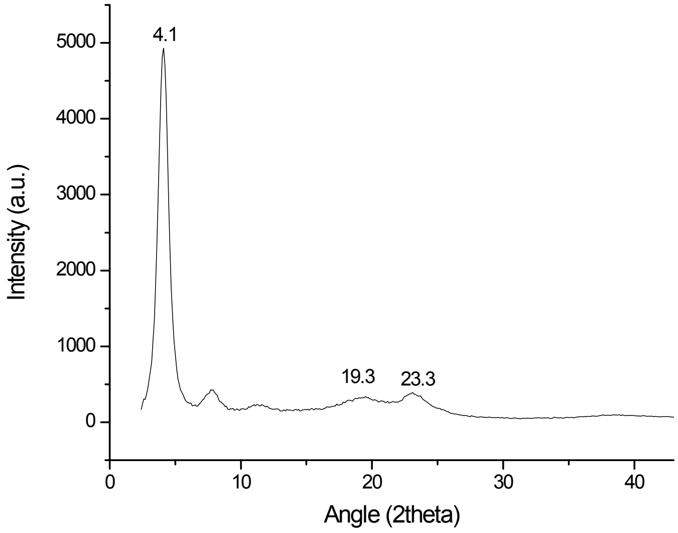


Figure S7. Cyclic voltammogram of **P2** cast on a platinum wire

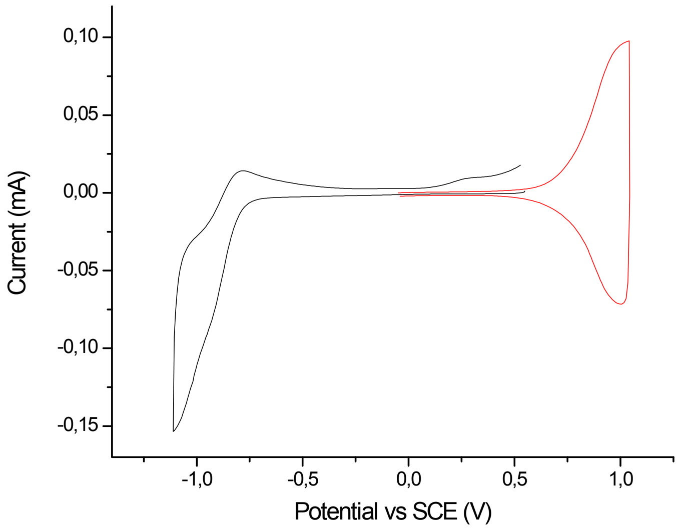
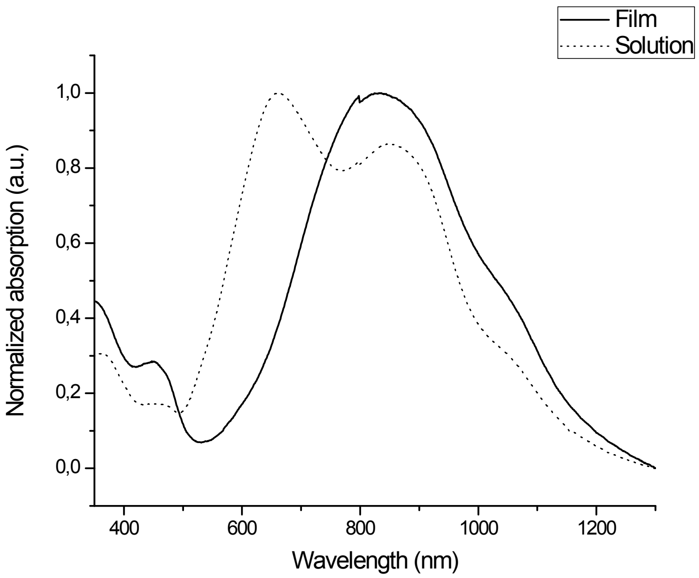


Figure S8. Normalized UV-visible absorption spectra of **P2** in solution in chloroform and in solid state cast on a glass substrate



P3 - The polymer was isolated as a black powder (120 mg, 83%).

Figure S9. DSC thermogram of **P3** at a rate of 20 °C/min (heating-cooling-heating (red-blue-green))

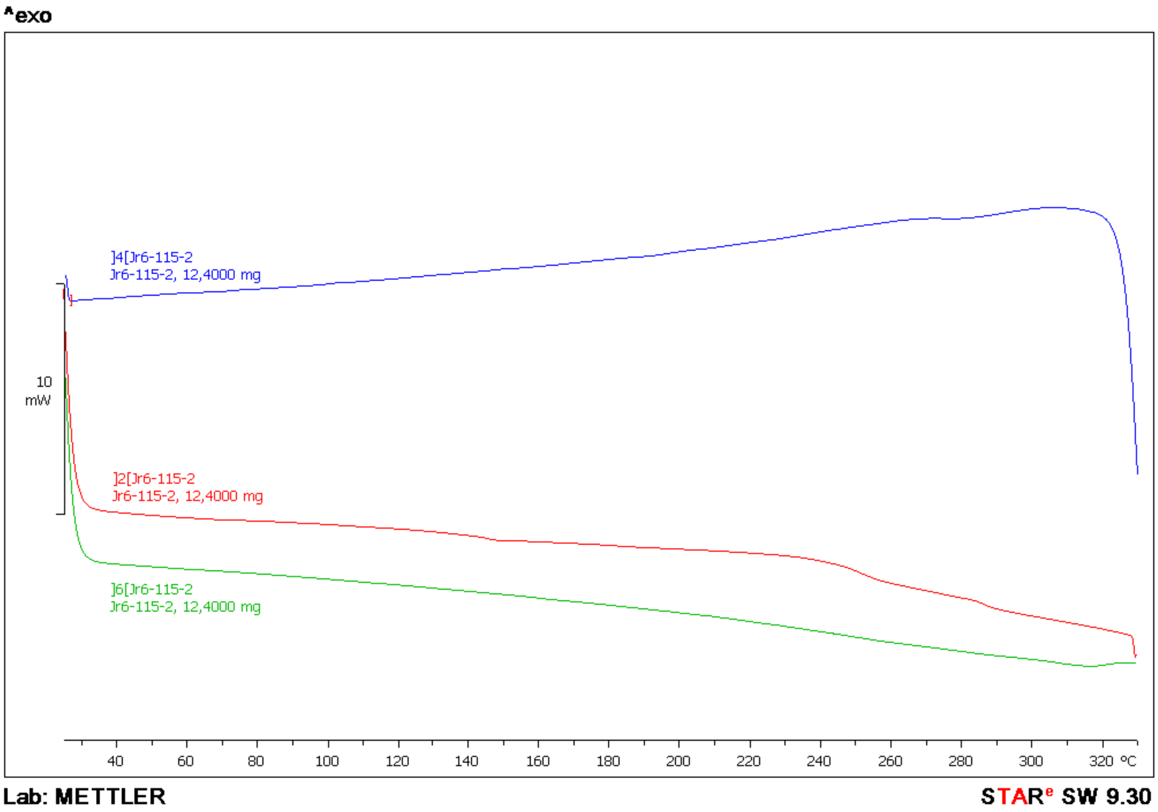


Figure S10. WAXS experiment of **P3** (powder)

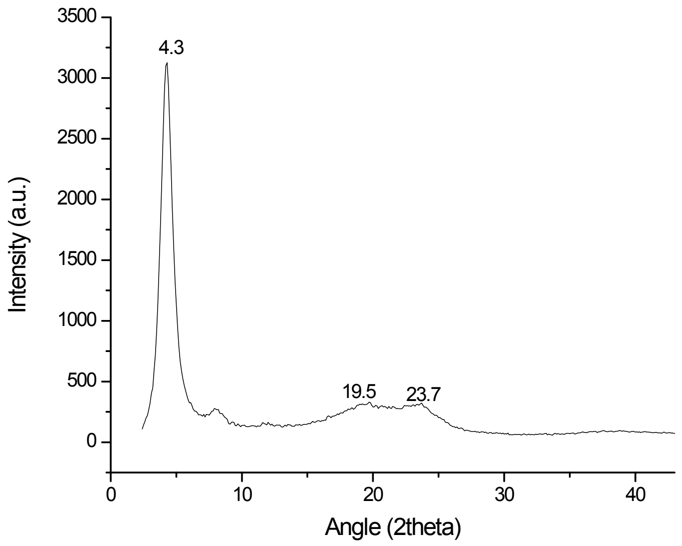


Figure S11. Cyclic voltammogram of **P3** cast on a platinum wire

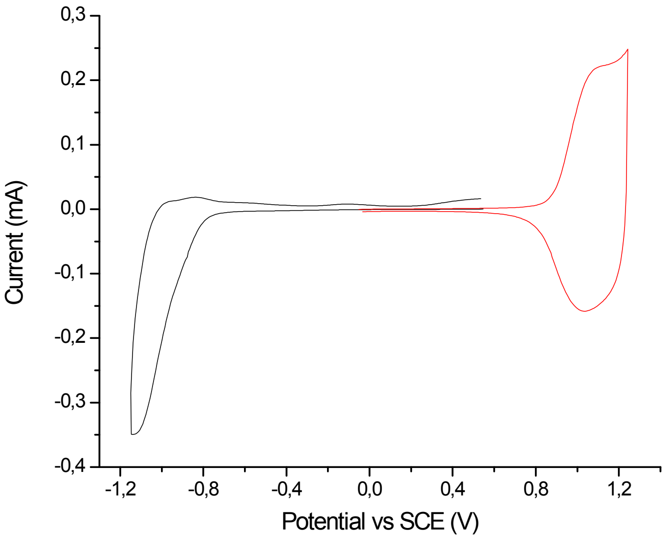


Figure S12. Normalized UV-visible absorption spectra of **P3** in solution in chloroform and in solid state cast on a glass substrate

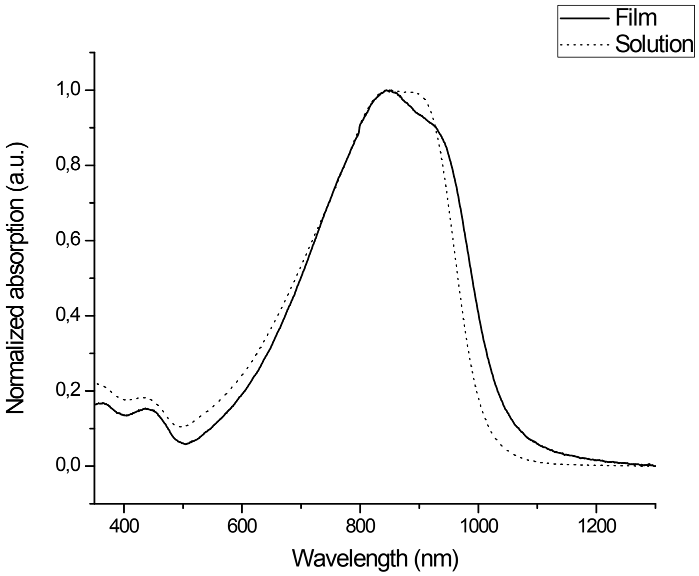
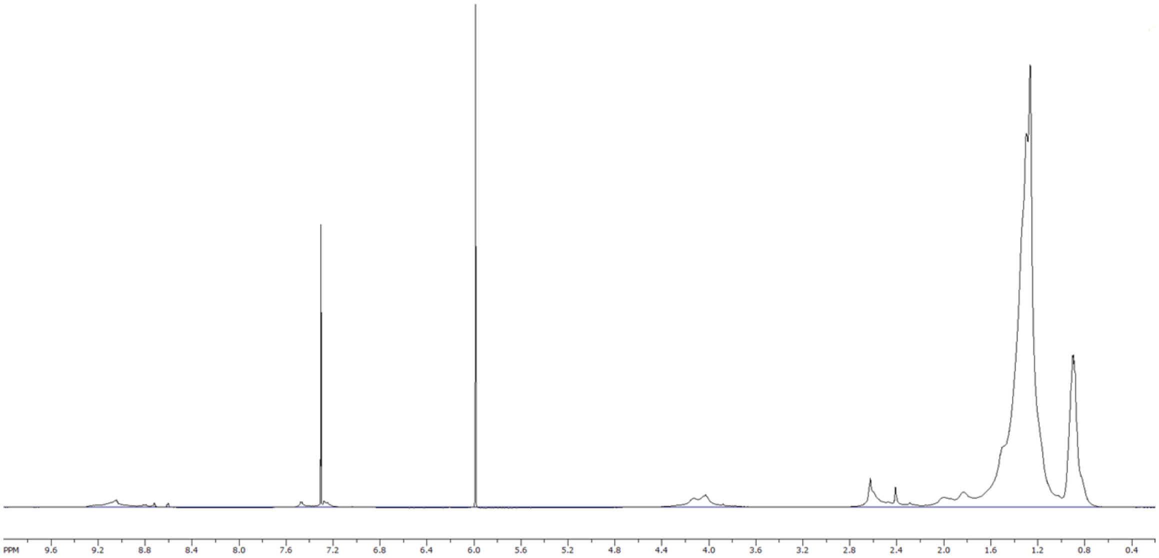


Figure S13. ^{1}H NMR of **P3** (10mg/mL) in *d^2*-tetrachloroethane at 75°C (4000 scans)



P4 - The polymer was isolated as a black powder (128 mg, 84%).

Figure S14. DSC thermogram of **P4** at a rate of 20 °C/min (heating-cooling-heating (red-blue-green))

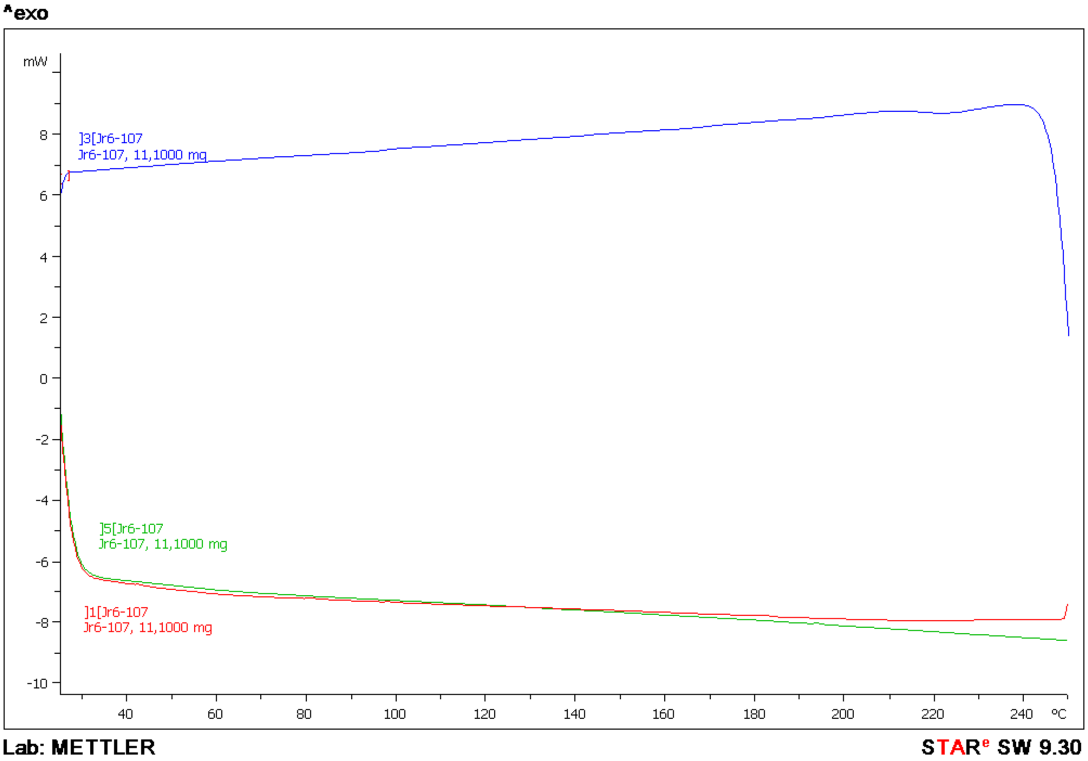


Figure S15. WAXS experiment of **P4** (powder)

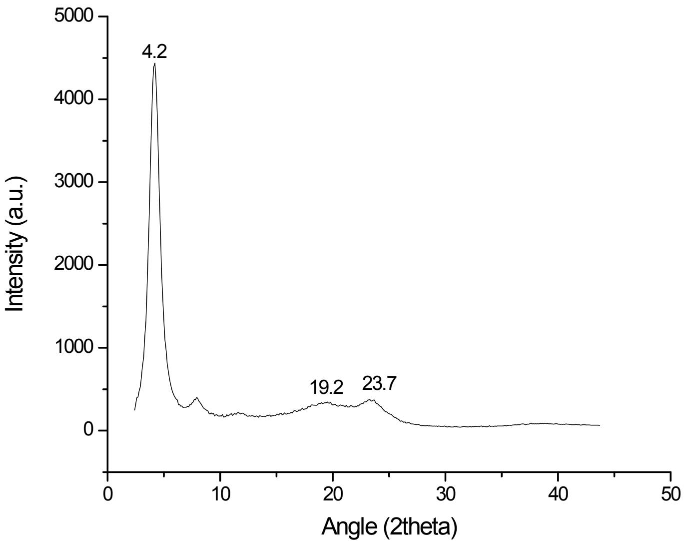


Figure S16. Cyclic voltammogram of **P4** cast on a platinum wire

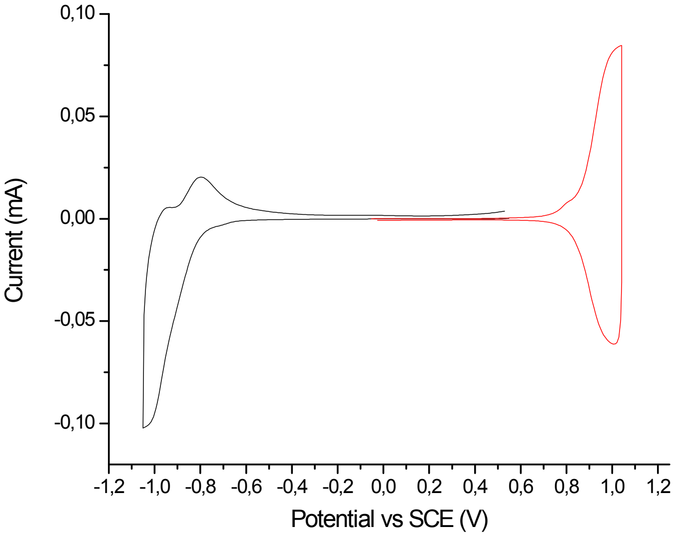


Figure S17. Normalized UV-visible absorption spectra of **P4** in solution in chloroform and in solid state cast on a glass substrate

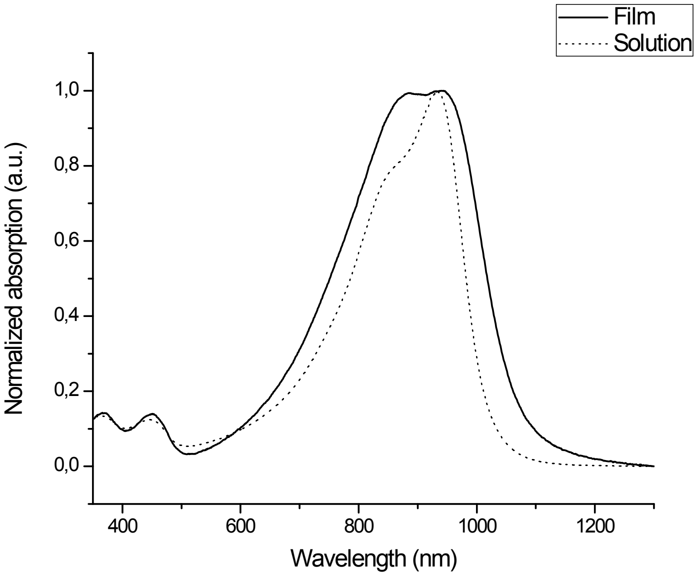
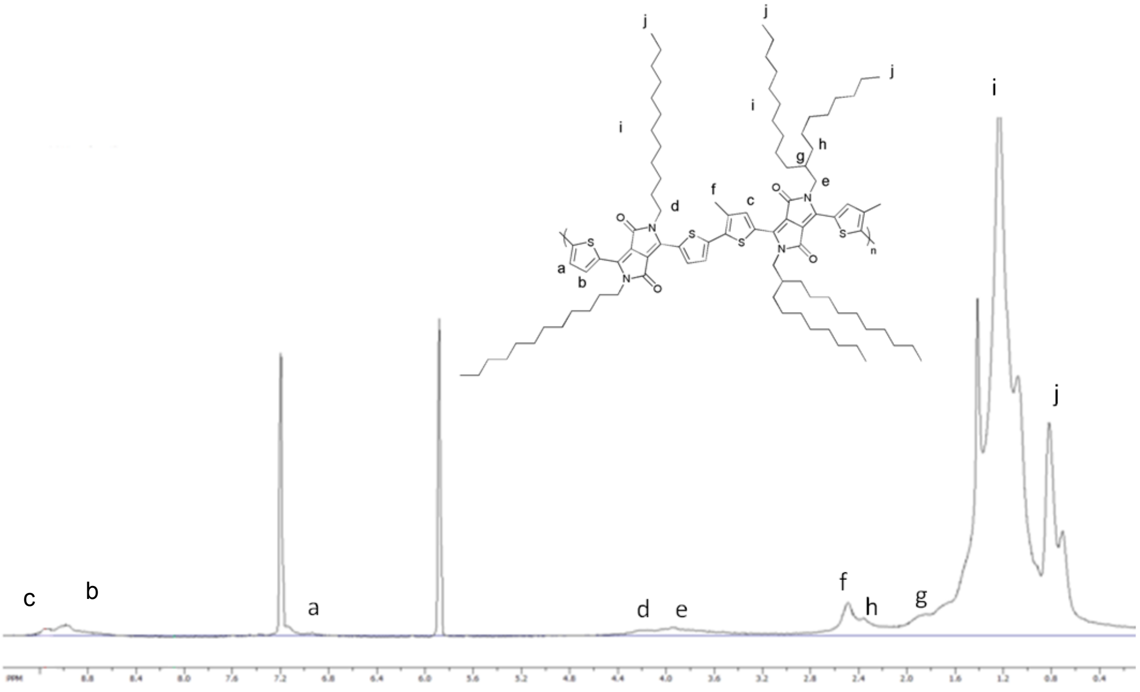


Figure S18. ^{1}H NMR of **P4** (10mg/mL) in d^2-tetrachloroethane at 75°C (4000 scans)



Characterization

^1H and ^{13}C NMR spectra were recorded using a Varian AS400 in deuterated chloroform or deuterated 1,1,2,2-tetrachloroethane solution at 298 K or 348 K respectively. Chemicals shifts were reported as δ values (ppm) relative to chloroform value of 7.26 ppm. For our size-exclusion chromatography (SEC) measurements, we used a Waters 515 HPLC Pump equipped with a Waters Associates (Model 441) Absorbance Detector, 2 PLgel Mixed C (300 x 7.5 mm) columns and a PLgel Mixec C Guard column at ambient temperature. The experiments were done at ambient temperature and the chloroform flow was set to 1mL/min. The samples (1 mg each) were dissolved in 2 mL of $CHCl_3$ in a 5 mL chromatography vial then stirred for 1 hour to let aggregates completely dissolve. Then, a filtration through a .45 μm cellulose fiber film in a 5 mL chromatography vial lead to a homogenous polymeric solution. The sample was injected though a loop of 100 μL with a glass syringe. Calibration was set with narrow polystyrene standards. A Mettler Toledo TGA SDTA 851e was used to do the thermogravimetric analysis (TGA). The scan range was 50-600°C with a heating rate of 20 °C/min and the experiment was done under nitrogen atmosphere. Degradation temperature was calculated from a 5% weight loss. UV-vis-NIR absorption spectra were recorded using a Varian Cary 500 UV-vis-NIR spectrophotometer using 1 cm path length quartz cells. A polymeric solution was spin-coated on untreated glass substrate in order to perform the solid-state measurement. The optical bandgap was calculated from the onset of the absorption band. The differential scanning calorimetry (DSC) analyses were done with a Mettler Toledo DSC823e under ambient atmosphere using an indium standard for calibration. A successive three step process beginning with a heating to 250°C then a cooling to 25°C and another heating to 250°C was used in order to clearly see thermal processes. The scanning rate was 20°C/min in all cases. Cyclic voltamogramms were recorded from a Solartron 1287 Potentiostat using a three-electrode set-up; a working and counter electrodes in platinum and an Ag/Ag^+ (0.1 M of $AgNO_3$ in anhydrous acetonitrile) reference electrode. The scan rate was 50 mVs^{-1} and the electrolyte was an anhydrous argon saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). Thin films were made by casting a diluted solution of a copolymer on the working electrode, dried under ambient conditions. For each measurement, a new film was cast. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets, assuming an SCE electrode to be at -4.7 eV from vacuum. The WAXS diffraction (powder) measurements were done with a Bruker/Siemens equipped with a Krytalloflex 760 generator (40kV, 40mA), a goniometer and a two-dimensional Hi-Star detector. A sealed tube emitting at 1.5418 Å (copper Kα) nickel-filtered was used as the source. GADDS software was used to control and do the analysis of all experiments. HRMS analyses were performed with an Agilent 6210 LC Time of Flight Mass Spectrometer using a 0.4 mL/min flow of 75% MeOH/25% H_2O (with 5 mM ammonium formate) as eluent. An ESI – Electrospray source was use to ionize the samples, the latter were directly injected without the use of a purification column.

OTFTs fabrication

p-type (BGBC)

Heavily doped n^{++} Si/SiO$_2$ wafer was used as the substrate in bottom-gate bottom-contact OTFT configuration, where the ~300 nm-thick thermally grown SiO$_2$ layer with a capacitance of 11 nF cm^{-2} worked as dielectric and the Si layer worked as the gate electrode. Gold source and drain electrodes were deposited on the substrate by conventional photolithography. The substrate was then cleaned by O$_2$ plasma, acetone, and isopropanol sequentially, and modified with dodecyltrichlorosilane (DTS) in toluene (10 mg mL^{-1}) at 60 °C for 20 min. A polymer semiconductor film (~35 nm) was deposited on the substrate by spin-coating a 10 mg mL^{-1} polymer solution at 3000 rpm for 60 s, followed by annealing at 150 or 200 °C for 15 min in a nitrogen-filled glove box. Then the device was encapsulated with a 500 nm thick poly(methyl methacrylate) (PMMA) layer by spin coating a PMMA solution in butyl acetate (8 wt %) at 3000 rpm for 60 s, and dried at 80 °C for 30 min on a hot plate in the same glove box. The channel length (L) and width (W) are 30 μm and 1 mm, respectively. The devices were characterized in air using an Agilent 4155C Semiconductor Parameter Analyzer. The carrier mobility in the saturated regime, μ, was calculated from the slope of the $(I_{DS})^{1/2}$ versus V_{GS} plot according to the equation of $I_{DS} = \mu C_i \frac{W}{2L}(V_{GS} - V_T)^2$, where I_{DS} is the drain current, C_i is the gate dielectric layer capacitance per unit area, V_{GS} and V_T are the gate voltage and threshold voltage, respectively.

Figure S19. Transfer characteristics of hole accumulation regimes of **P1**

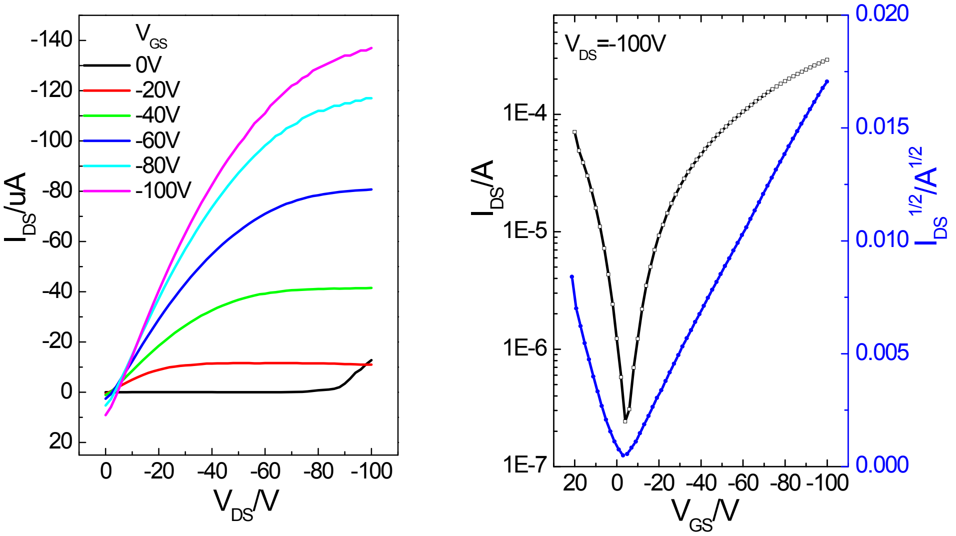


Figure S20. Transfer characteristics of hole accumulation regimes of **P2**

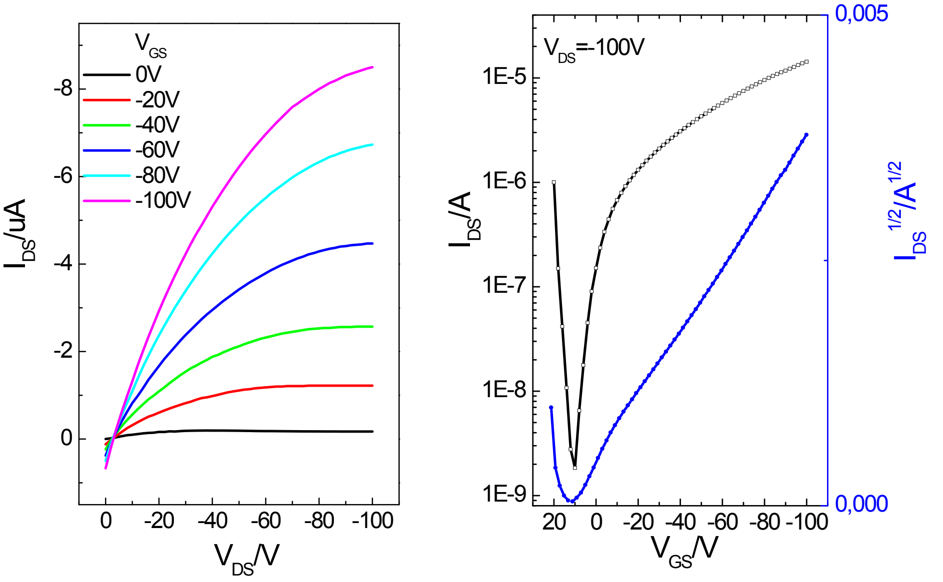
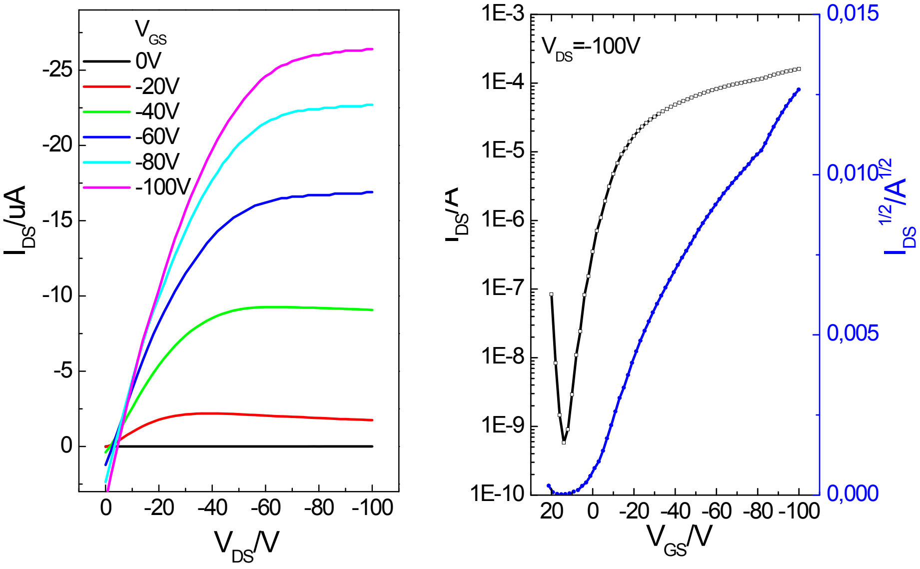


Figure S21. Transfer characteristics of hole accumulation regimes of **P3**



n-type (TGBC)

Top gate bottom contact design was adopted to evaluate the polymer semiconductors. SiO_2/Si wafer patterned with thermally evaporated gold source and drain electrodes was used as the substrate. The patterned substrate was cleaned with air plasma, acetone, and isopropanol, sequentially. On the cleaned substrate, the polymer semiconductor film was formed by spin-coating a polymer solution at 2000 RPM for 60 s, and annealed on a hotplate in nitrogen for 15 min. The Cytop layer (~570 nm with Ci = 3.2 nF cm^{-2}) as the gate dielectric was deposited on the polymer semiconductor layer by spin-coating a Cytop solution at 2000 rpm for 60 s, followed by drying on a hotplate at 100℃ for 30min. Finally, the gate electrode, a 70 nm of Al layer, was deposited by thermal evaporation. The OTFT devices were characterized in air without light on an Agilent 4155C Semiconductor Parameter Analyzer.

Figure S22. *n*- and *p*-type mobilities obtained from TGBC devices

Polymer	$T_{annealing}$	V_{DS}=60V	V_{DS}=-60V
	°C	Mobility	Mobility
		n-type /cm^{2}V^{-1}S^{-1}	p-type /cm^{2}V^{-1}S^{-1}
P1	150	0.19	0.13
P2	200	0.0041	0.0055
P3	150	0.083	0.27
P4	150	0.011	0.92