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ESI

Determining the sequence and backbone structure of “semi-statistical” copolymers as donor-acceptor polymers in organic solar cells

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Experimental

Materials

2,6-Dibromo-4,8-didodecylbenzo[1,2-b:4,5-b']dithiophene, 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazol, 2,5-bis(trimethylstannyl)thiophene and phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) were provided by Merck Ltd. Anhydrous chlorobenzene (99.9 %) was purchased from ACROS Organics and used without further purification. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) was purchased from sigma Aldrich and recrystallised from chloroform to obtain $Pd_2(dba)_3.CHCl_3$. Tri(*o*-tolyl)phosphine was purchased from Sigma Aldrich and recrystallised from hexane. Tetrabutylammonium hexafluorophosphate (99.9 %), silver nitrate, ferrocene (99.9 %), butylated hydroxytoluene and 2-tributylstannyl thiophene were purchased from Sigma-Aldrich and used without further purification.

Methods

NMR. ^{1}H NMR was run on a Bruker Avance 300 MHz spectrometer in deuterated chloroform at 25 °C. High temperature and in-situ kinetic data was obtained using Bruker Avance III 400 MHz spectrometer at 100 °C.

Optoelectronic properties. UV-Vis spectra where obtained using an Agilent Technologies Cary 60 UV-Vis spectrometer. Samples were made up to a concentration of 0.01 mg/ml by serial dilution in chlorobenzene. Cyclic voltammetry was conducted on a CH-Instruments 600 E potentiostat using a 3 mm glassy carbon disc electrode which was polished with 0.05 µm alumina powder, rinsed sequentially with acetone, IPA and MilliQ water prior to each use. The counter electrode was a platinum wire coil which was annealed in a blue flame prior to use. The reference electrode was Ag/Ag+, the silver wire was polished and rinsed sequentially with acetone, IPA and MilliQ water the wire was then placed into a glass capillary tube fitted with a vycor frit and filled with 0.01 mM $AgNO_3$ solution. The system was calibrated using the ferrocene(Fc)/ferrocenium(Fc+) redox couple. 0.100 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as the supporting electrolyte. Analytes were dissolved at a concentration of 2 mg/ml in a solution of 2 mg/ml of $TBAPF_6$ in chlorobenzene, drop cast onto the clean glassy carbon disk electrode and allowed to dry under ambient conditions.

Gel permeation chromatography. GPC was run on an Agilent PL220 instrument equipped with differential refractive index (DRI) and viscometry (VS) detectors. The system was equipped with 2 x PLgel Olexis columns (300 x 7.5 mm) and a PLgel Olexis 10 µm guard column. The mobile phase was 1,2,4-trichlorobenzene (TCB) with 250 ppm BHT (butylated hydroxytoluene) as the stabilising additive. Samples were run at 1 ml/min at 160 °C. The system was calibrated between M_p = 164 and 6,035,000 g/mol using 12 polystyrene narrow standards (Agilent EasyVials) to create a third order calibration. Analyte samples were filtered through a stainless steel frit with 10 µm pore size at 140 °C prior to injection. Experimental molar mass (M_n, GPC) and dispersity ($Đ$) values of synthesised polymers were determined by conventional calibration using Agilent GPC/SEC software.

TGA Measurements. TGA spectra were recorded on a Mettler Toledo TGA/DSC1. Samples were analysed from 25 to 600 °C at a 10 °C min^{-1} heating rate under a nitrogen atmosphere.

Experimental Procedures

In-situ kinetics. All solids were dried overnight under vacuum at < 1 mbar at 25 °C, 99.9 % anhydrous chlorobenzene was purged with nitrogen prior to use. 1 ml, 0.100 M stock solutions of 2,6-dibromo-4,8-didodecylbenzo[1,2-b:4,5-b']dithiophene (BnDT) 68.5 mg (0.100 mmol), 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazol (BT) 55.0 mg (0.100 mmol) and 2-(tributylstannyl)thiophene 37.3 mg (32 µL, 0.100 mmol) were made up and stored under an atmosphere of nitrogen. 1 ml of catalyst solution was made up from of $Pd_2(dba)_3.CHCl_3$ 2.0 mg (2 µmol) and of $P(o\text{-tolyl})_3$ 3.6 mg 6 µmol. To a dry NMR tube fitted with a Young's tap, under a blanket of Argon 50 µL BnDT, 50 µL BT, 100 µL 2-(tributylstannyl)thiophene and 100 µL catalysts solutions were added with an additional 100 µL of dry chlorobenzene. A capillary tube filled with degassed 1,1,2,2-tetrachloroehtane-D2 was added as a locking agent. The NMR tube was placed in liquid nitrogen to effectively halt any reaction prior to loading. An NMR was taken at 25 °C before the probe cavity was heated to 100 °C and a second spectrum (T 373 K, t = 0) was taken, after which the ^{1}H NMR spectrum was recorded every 120 seconds for two hours.

Polycondensation kinetics. To a dry 100 ml, 3-neck-round bottom flask 275.3 mg (0.500 mmol) 4,7-dibromo-5,6-bis(octyoxy)-benzo-2,1,3-thiadiazole, 342.3 mg (0.500 mmol) 2,6-dibromo-4,8-di(dodecyl)benzo-[1,2-b:4,5-b']dithiophene and 409.8 mg (1.000 mmol) of 2,5-bis(trimethylstannyl)thiophene were added. The central neck was fitted with a condenser, the top of which was sealed with a rubber septum and the remaining two necks were fitted with rubber septa. The system was evacuated and refilled with nitrogen gas for three cycles. 48.0 mL of dry, degassed chlorobenzene was cannulated into the flask, which thereafter was kept under a positive nitrogen pressure.

To a separate glass sinter vial 31.1 mg (0.030 mmol) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct and 54.8 mg of P(*o*-tolyl)$_3$ (0.18 mmol) were added. The glass sinter vial was sealed with a rubber septum, evacuated and back filled with nitrogen for three cycles. 3 ml of dry chlorobenzene was added via a degassed syringe.

The main reaction vessel was refluxed to 133 °C. A t = 0 sample (100 µL) was taken before 2 ml of the fully solvated catalyst solution was added via a degassed syringe. Further 100 µL samples were taken at t = 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60, 120, 180, 240, 300 and 1440 min, and quenched by bubbling with air. Monomer conversion was followed by ^{1}H NMR in d-chloroform at 25 °C.

Statistical Polymer Synthesis. To a dry 100 ml, 2-neck 100 ml round bottom flask 55.1 mg (0.100 mmol) 4,7-dibromo-5,6-bis(octyoxy)-benzo-2,1,3-thiadiazole, 68.5 mg (0.100 mmol) 2,6-dibromo-4,8-di(dodecyl)benzo-[1,2-b:4,5-b']dithiophene and 77.8 mg (0.190 mmol) of 2,5-bis(trimethylstannyl)thiophene were added. The central neck was fitted with a condenser, the top of which was sealed with a rubber septum, and the remaining neck was fitted with rubber septum. The system was evacuated and refilled with nitrogen gas for three cycles. 8.0 mL of dry, degassed chlorobenzene was cannulated into the flask, which thereafter was kept under a positive nitrogen pressure.

To a separate glass sinter vial 4.1 mg (0.004 mmol) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct and 7.3 mg (0.024 mmol) of P(*o*-tolyl)$_3$ were added. The glass sinter vial was sealed with a rubber septum, evacuated and back filled with nitrogen for three cycles. 3 ml of dry chlorobenzene was added *via* a degassed syringe. 2.0 ml of the premixed catalyst solution was then added to the reaction mixture.

The reaction mixture was refluxed at 133 °C for 24 hours, the resulting polymeric solution was then reduced under vacuum to approximately 2 ml. The polymer was precipitated into 150 ml of methanol and filtered through a cellulose thimble. The polymer was then purified by Soxhlet extraction with acetone, hexanes and chloroform. The chloroform fraction was precipitated into 150 ml of methanol and collected by vacuum filtration. The polymer was dried under vacuum at 40 °C for 24 hours.

The resulting polymer was characterised by ^{1}H NMR (Figure S1) δ(ppm) =: 8.70-8.43 (2H, d) corresponding to the two hydrogens an the benzodithiophene unit, 7.74-7.16 (4H, m) result from the four protons of the bridging thiophene, 4.34 (4H, s) is assigned the α-CH$_2$ protons of the alkoxy side chains on the BT unit, 3.29 (4H, s) are assigned to the α-CH$_2$ of the alkyl side chains of the BnDT unit, 2.50-0.68 area is assigned to the remaining protons of the alkyl side chains on both the BT and BnDT unit. Characterisation by TGA (Figure S2) shows the T_D = 329 °C. Molecular weight averages as determined by GPC (Figure S3) are M_n = 17,600 g/mol, M_w = 44,800 g/mol and the dispersity = 2.55. The optical properties were characterised by UV/Vis and CV (Figure S4 and Figure S5, respectively).

ESD deposition. Electrospray deposition solutions were prepared as follows: PTBnDT at a concentration of 70 mg/L in a 3:1 mixture by volume of toluene/methanol; PTBT at a concentration of 60 mg/L in a 5:1 mixture by volume of toluene/methanol; PTBnDT-stat-PTBT (with a nominal 1:1 ratio of TBnDT to TBT) at a concentration of 40 mg/L in a 5:1 mixture by volume of toluene/methanol.

Au(111) on mica substrates (Georg Albert PVD) were cleaned in ultrahigh vacuum through repeated cycles of Ar^+ sputtering (1 keV, 3 mA/cm^2) and subsequent annealing at 500°C for 10 min. The surface was checked for atomic flatness and cleanliness with in situ STM measurements before each polymer deposition.

Each polymer was deposited for 10-40 min by ESD in vacuum (Molecularspray Ltd.) onto the Au(111) substrate, and with sample currents varying between 10-30 pA. After deposition, the pressure in the preparation chamber reverted to its base value of 4×10^{-10} mbar, and the sample was annealed to 100°C. The sample was then transferred without breaking the vacuum to the analysis chamber (base pressure, $<2 \times 10^{-10}$ mbar) and imaged by STM at −153°C.

STM acquisition and analysis. STM images were acquired in the constant-current mode, using an electrochemically etched tungsten tip. The bias voltage (V_{bias}) was applied to the sample with respect to the tip. The WSxM software was used to process the STM images [I. Horcas, et al., Rev. Sci. Instrum. 78, 013705 (2007)].

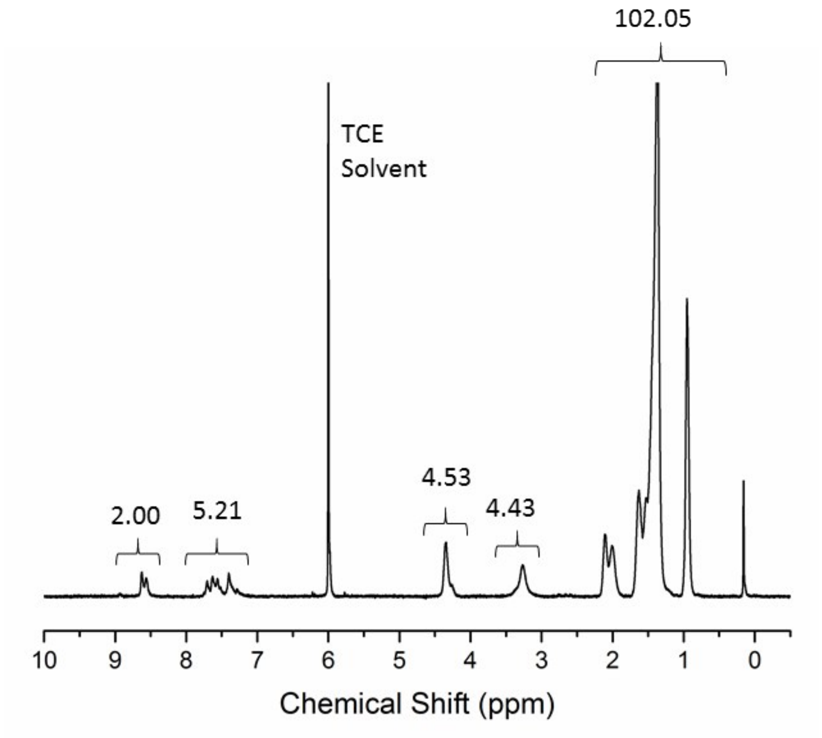

Figure S1. *^{1}H NMR of statistical PTBnDT-stat-PTBT in 1,1,2,2-tetrachloroethane-D_2.*

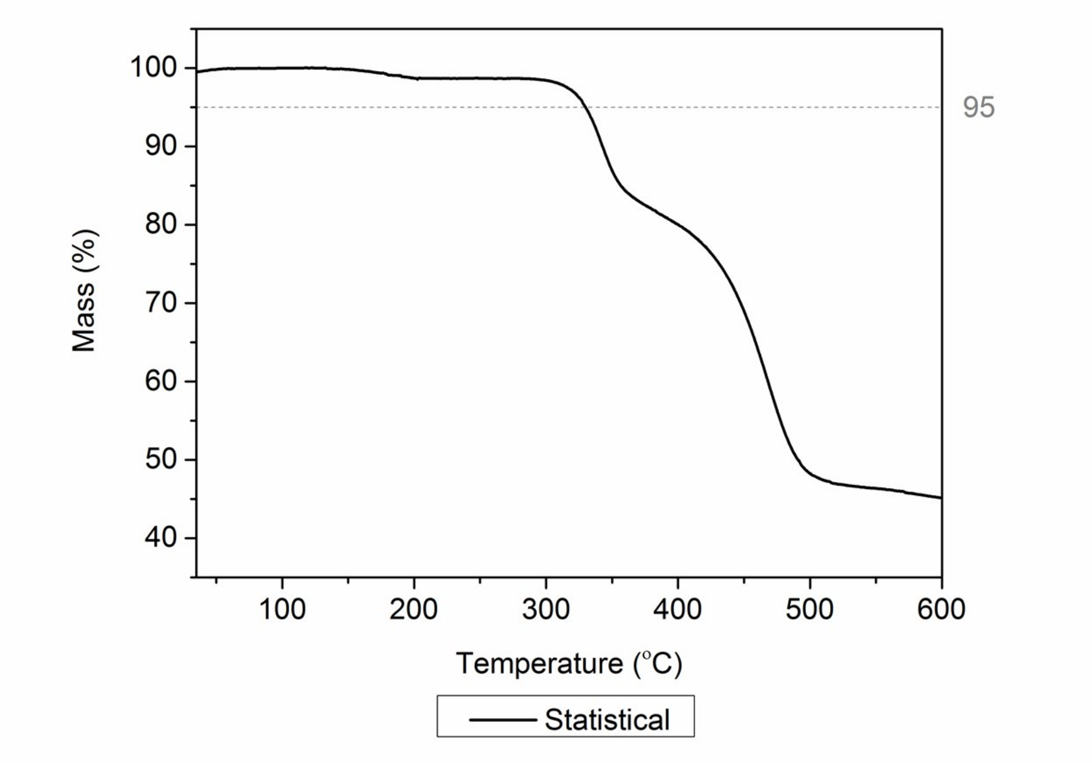

Figure S2. TGA of statistical PTBnDT-stat-BTBT.

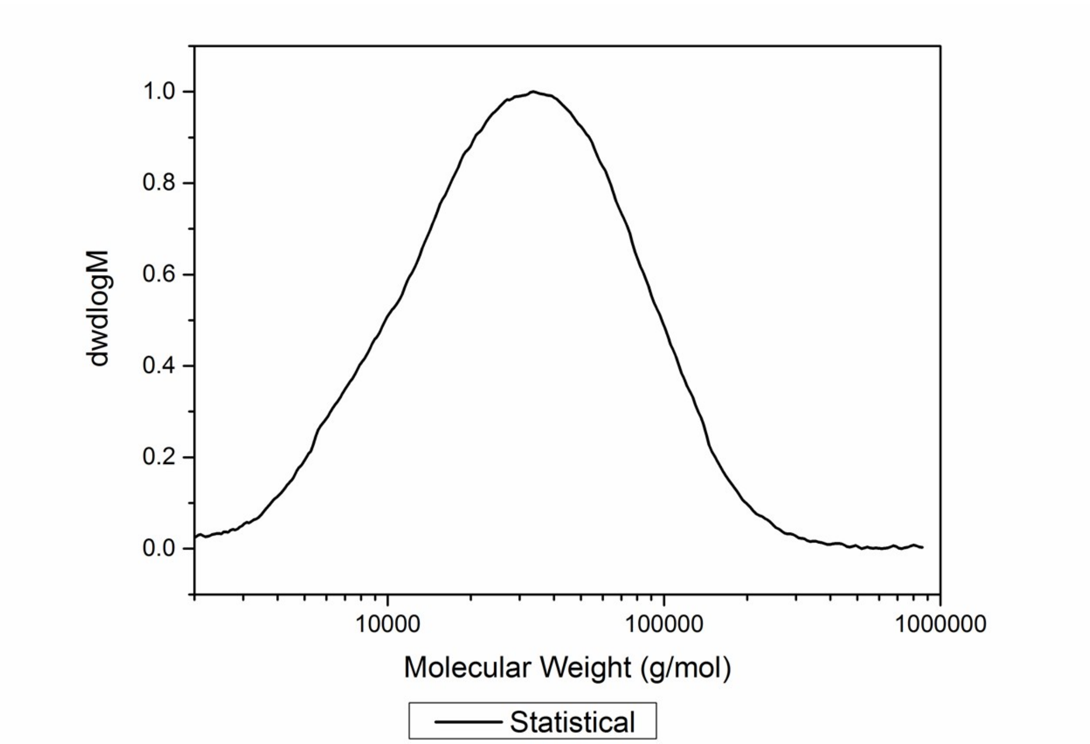

Figure S3. Molecular weight distribution of PTBnDT-stat-PTBT.

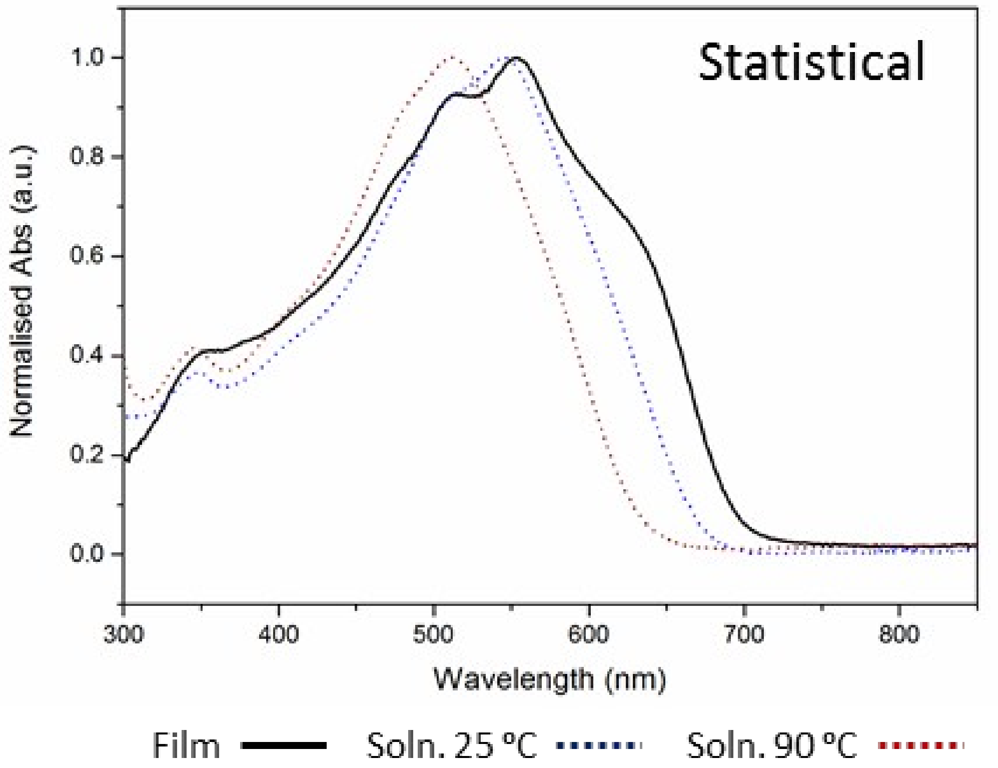

Figure S4. UV/Vis trace of PTBnDT-start-PTBT, thin film on ITO and, hot and cold solution of chlorobenzene.

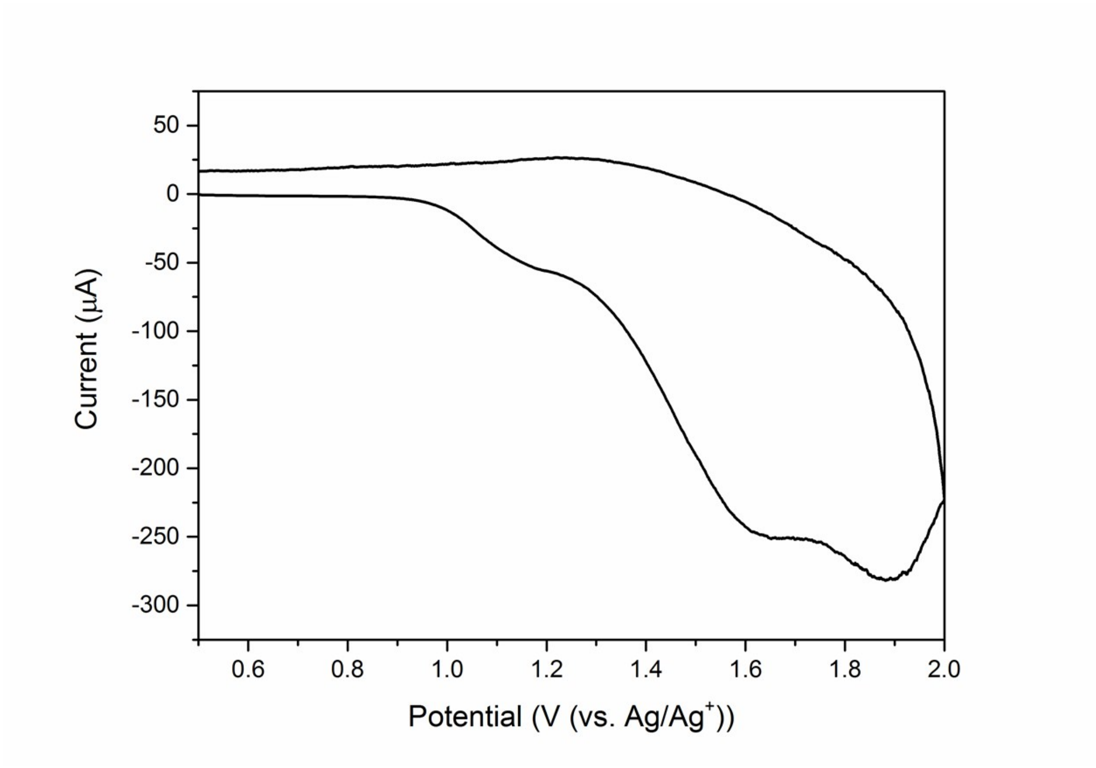

Figure S5. Cyclic voltamogramme of PTBnDT-stat-PTBT showing the oxidation peak.

Alternating Polymer Synthesis. To a dry 100 ml, 2-neck 100 ml round bottom flask 142.9 mg (0.200 mmol) of 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole and 162.0 mg (0.190 mmol) of (4,8-didodecylbenzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) were added. The central neck was fitted with a condenser, the top of which was sealed with a rubber septum, and the remaining neck was fitted with rubber septum. The system was evacuated and refilled with nitrogen gas for three cycles. 8.0 mL of dry, degassed chlorobenzene was cannulated into the flask, which thereafter was kept under a positive nitrogen pressure.

To a separate glass sinter vial 4.1 mg (0.004 mmol) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct and 7.3 mg (0.024 mmol) of P(*o*-tolyl)$_3$ were added. The glass sinter vial was sealed with a rubber septum, evacuated and back filled with nitrogen for three cycles. 3 ml of dry chlorobezene was added *via* a degassed syringe. 2.0 ml of the premixed catalyst solution was then added to the reaction mixture.

The reaction mixture was refluxed at 133 °C for 24 hours, the resulting polymeric solution was then reduced under vacuum to approximately 2 ml. The polymer was precipitated into 150 ml of methanol and filtered through a cellulose thimble. The polymer was then purified by Soxhlet extraction with acetone, hexanes, chloroform and chlorobenzene (owing to the limited solubility of the alternating polymer). The chlorobenzene fraction was precipitated into 150 ml of methanol and collected by vacuum filtration. The polymer was dried under vacuum at 40 °C for 24 hours.

The resulting polymer was characterised by ^{1}H NMR (Figure S6) δ(ppm) =: 8.57 (2H, s) corresponding to the two hydrogens an the benzodithiophene unit, 7.83-7.62 (2H d) result from the protons of the bridging thiophene unit which are spatially close to the BnDT unit, 7.62-7.43 (2H, d) arise from the remaining two protons on thiophene bridging unit which are spatially close to the BT unit, 4.34 (4H, s) is assigned the α-CH$_2$ protons of the alkoxy side chains on the BT unit, 3.29 (4H, s) are assigned to the α-CH$_2$ of the alkyl side chains of the BnDT unit, 2.50-0.68 area is assigned to the remaining protons of the alkyl side chains on both the BT and BnDT unit. Characterisation by TGA (Figure S7) show the T_D = 326 °C. Molecular weight averages as determined by GPC (Figure S8) are M_n = 27,500 g/mol, M_w = 52,800 g/mol and the dispersity = 1.92. The optical properties were characterised by UV/Vis and CV (Figure S9 and Figure S10, respectively).

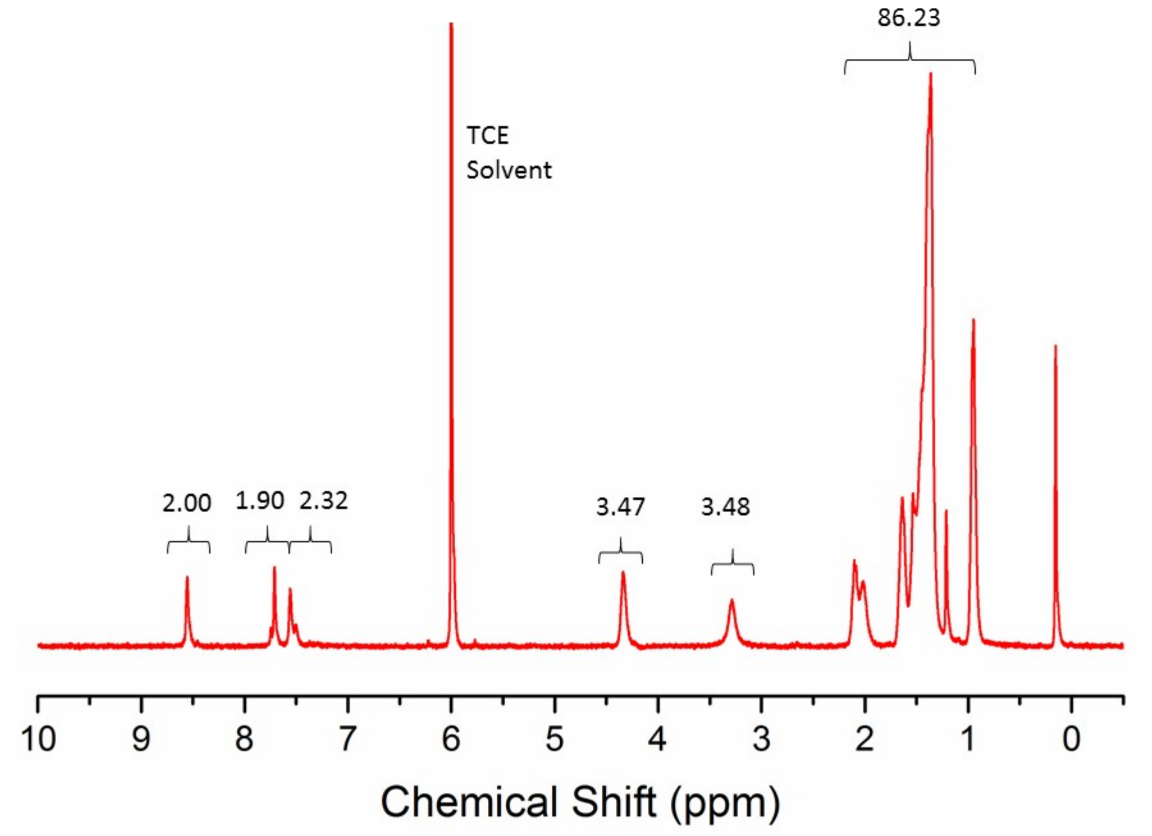

Figure S6. ^{1}H NMR of alternating PBnDTDTBT in 1,1,2,2-tetrachloroethane-D2.

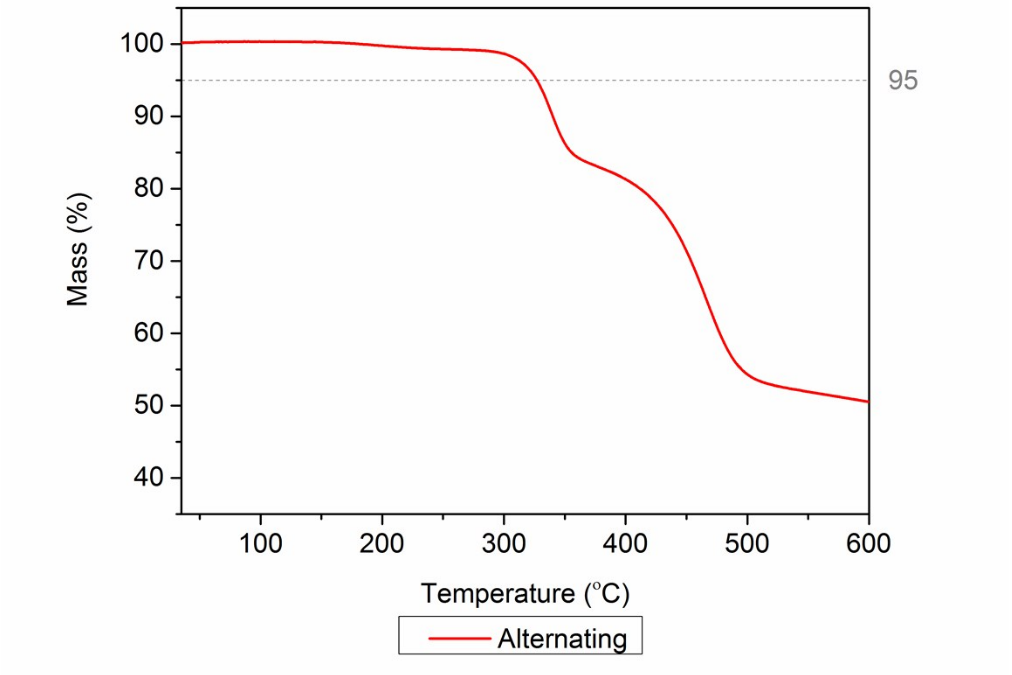

Figure S7. TGA of alternating PBnDTDTBT.

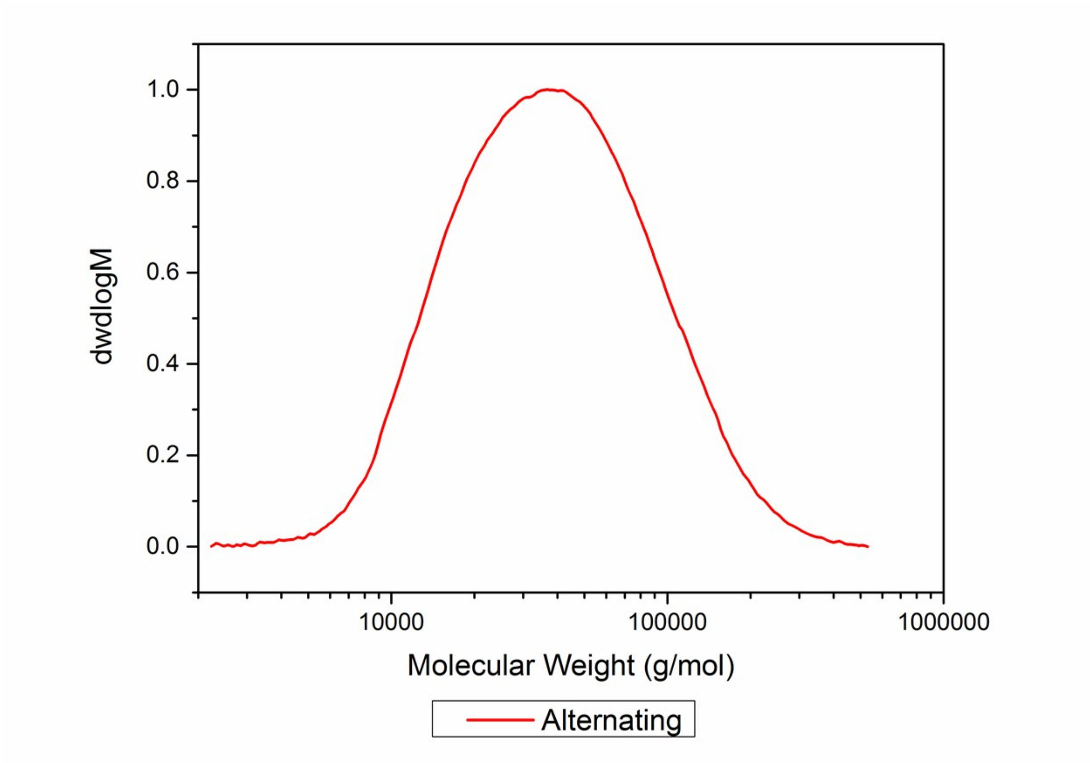

Figure S8. Molecular weight distribution of alternating PBnDTDTBT.

Figure S9. UV/Vis trace of alternating PTBnDTDTBT, thin film on ITO and, hot and cold solution of chlorobenzene.

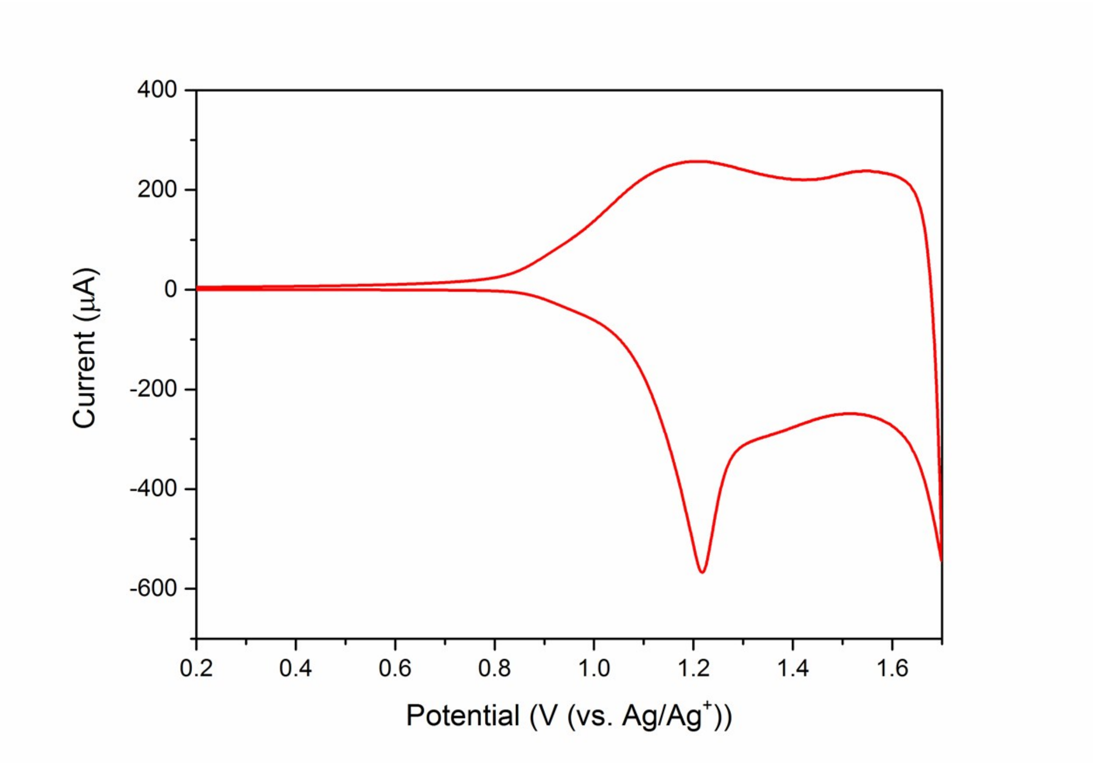

Figure S10. Cyclic voltamogramme of alternating PBnDTDTBT showing the oxidation peak.

Synthesis of PTBnDT(C_{12})-*stat*-PTBT Polymers. To a dry 100 ml, 2-neck 100 ml round bottom flask 55.1 mg (0.100 mmol) 4,7-Dibromo-5,6-bis(octyoxy)-benzo-2,1,3-thiadiazole, 68.5 mg (0.100 mmol) 2,6-dibromo-4,8-di(dodecyl)benzo-[1,2-b:4,5-b']dithiophene and 77.8 mg (0.190 mmol) of 2,5-bis(trimethylstannyl)thiophene were added. The central neck was fitted with a condenser, the top of which was sealed with a rubber septum and the remaining neck was fitted with rubber septa. The system was evacuated and refilled with nitrogen gas for three cycles. 8.0 mL of dry, degassed chlorobenzene was cannulated into the flask, which thereafter was kept under a positive nitrogen pressure.

To a separate glass sinter vial 4.1 mg (0.004 mmol) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct and 0.024 mmol of the chosen ligand were added. The glass sinter vial was sealed with a rubber septum, evacuated and back filled with nitrogen for three cycles. 3 ml of dry chlorobenzene was added via a degassed syringe. 2.0 ml of the premixed catalyst solution was then added to the reaction mixture.

The reaction mixture was refluxed at 133 °C for 24 hours, the resulting polymeric solution was then reduced under vacuum to approximately 2 ml. The polymer was precipitated into 150 ml of methanol and filtered through a cellulose thimble. The polymer was then purified by Soxhlet extraction with acetone, hexanes and chloroform. The chloroform fraction was precipitated into 150 ml of methanol and collected by vacuum filtration. The polymers were dried under vacuum at 40 °C for 24 hours. The polymers were characterised by ^{1}H NMR (Figure S11 – Figure S14), GPC (Figure S15) and TGA (Figure S16).

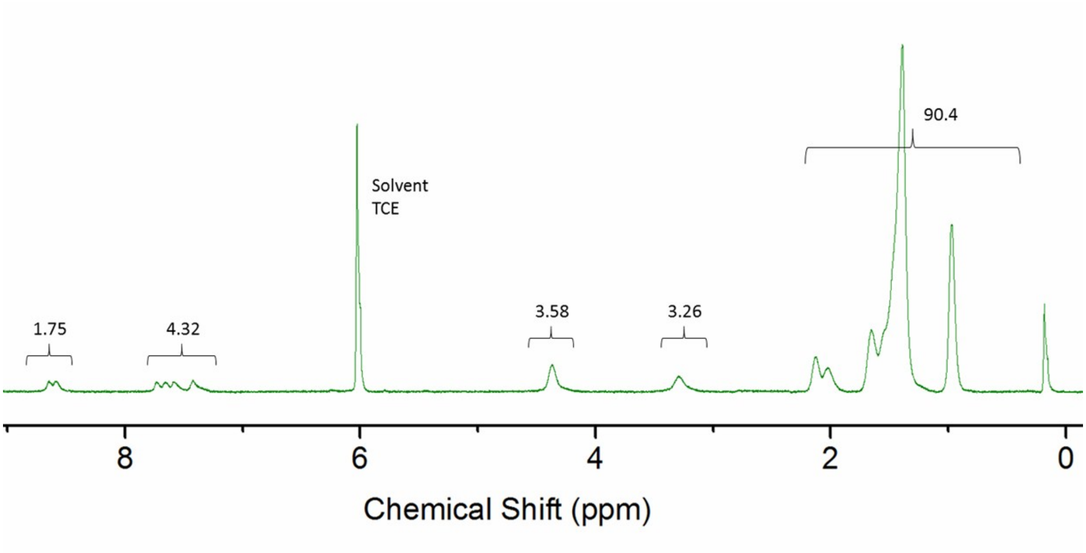

*Figure S11: ^{1}H NMR of PTBnDT(C_{12})-*stat*-PTBT polymer P3.1-XPhos.*

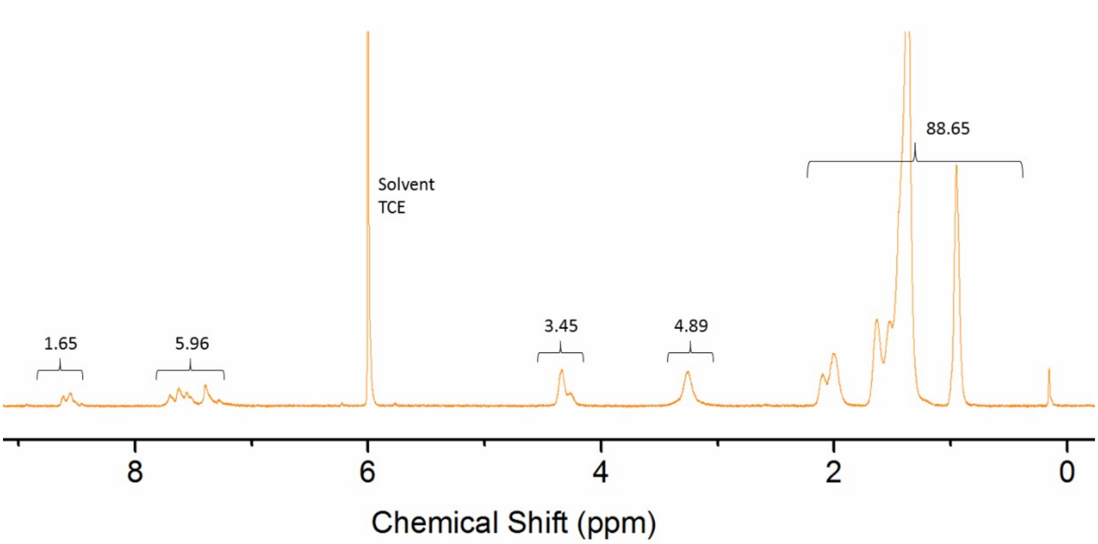

*Figure S12: ^{1}H NMR of PTBnDT(C_{12})-*stat*-PTBT polymer P3.2-DMPP.*

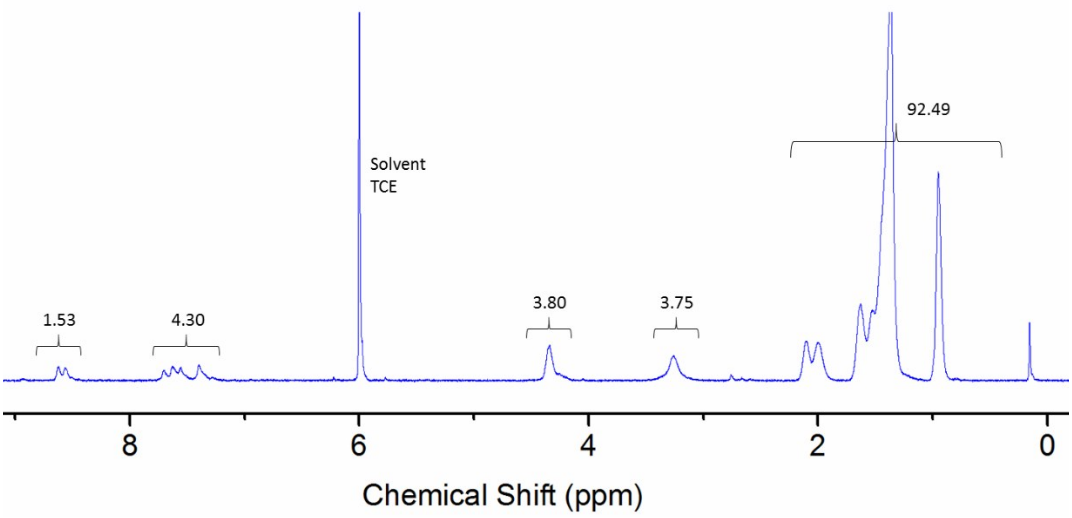

Figure S13: ^{1}H NMR of PTBnDT(C_{12})-stat-*PTBT polymer P3.3-oOMeP.*

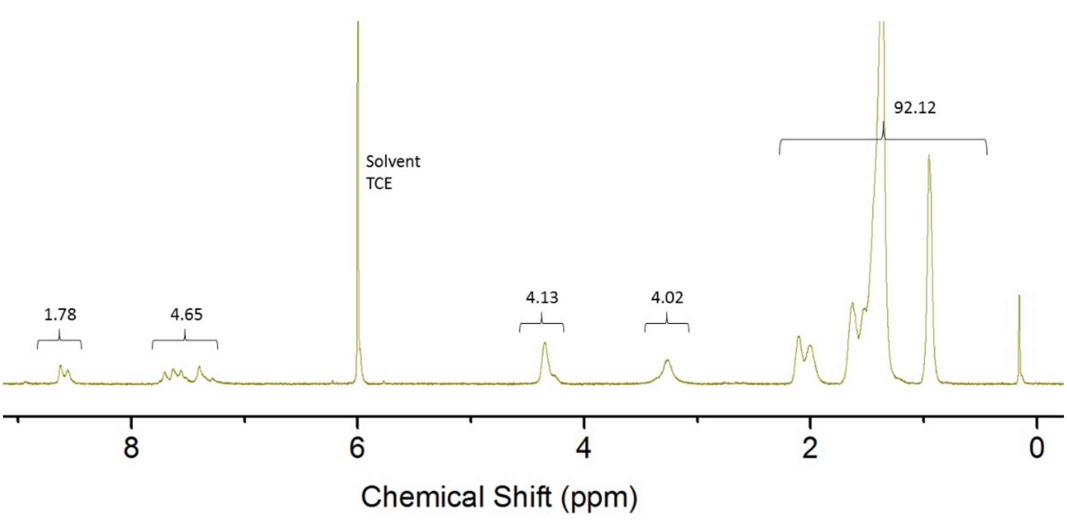

Figure S14. ^{1}H NMR of PTBnDT(C_{12})-stat-*PTBT polymer P3.4-PoTol.*

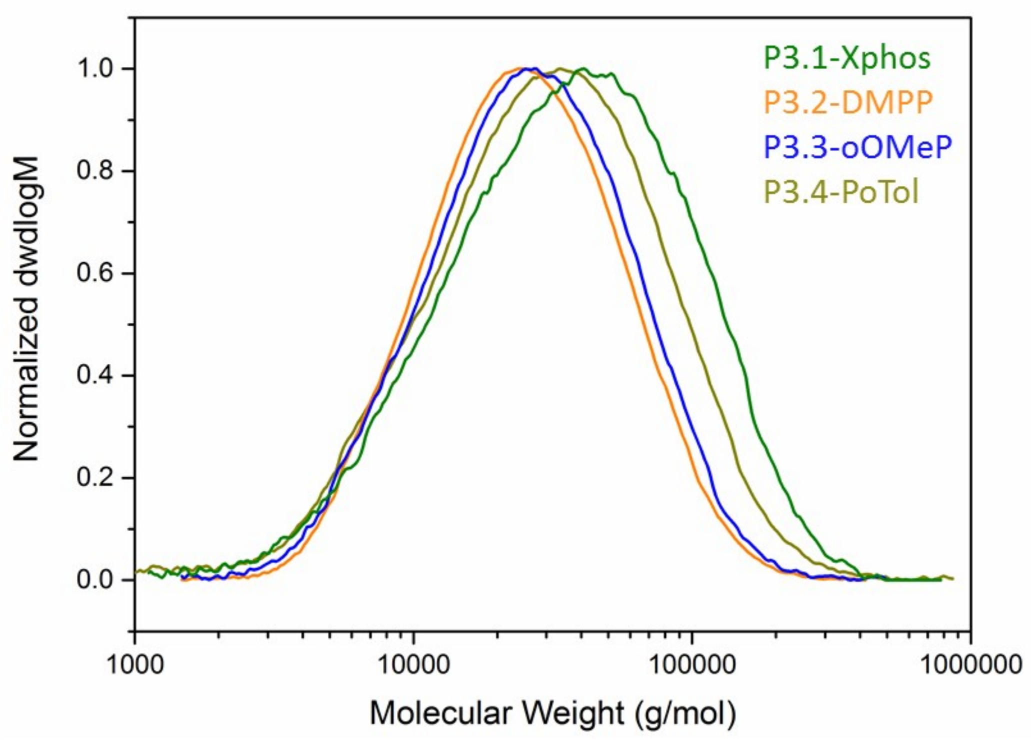

Figure S15 GPC of statistical copolymers

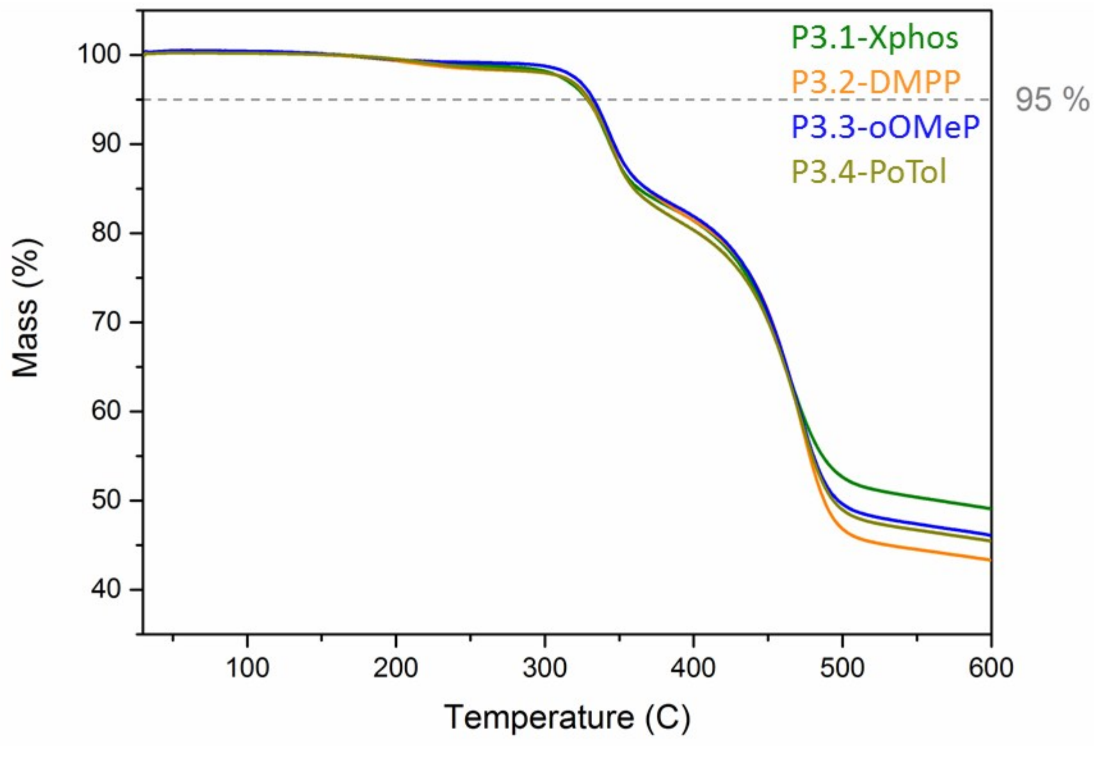

Figure S16 TGA of statistical copolymers

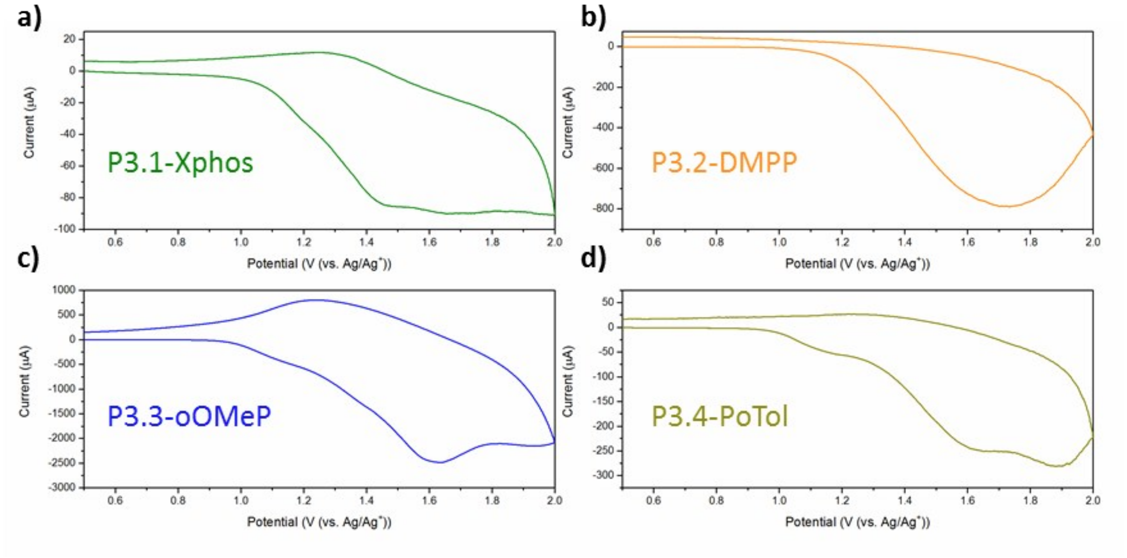

Figure S17 Cyclic voltammograms of polymers synthesised with the use of different ligands in the Stille coupling.

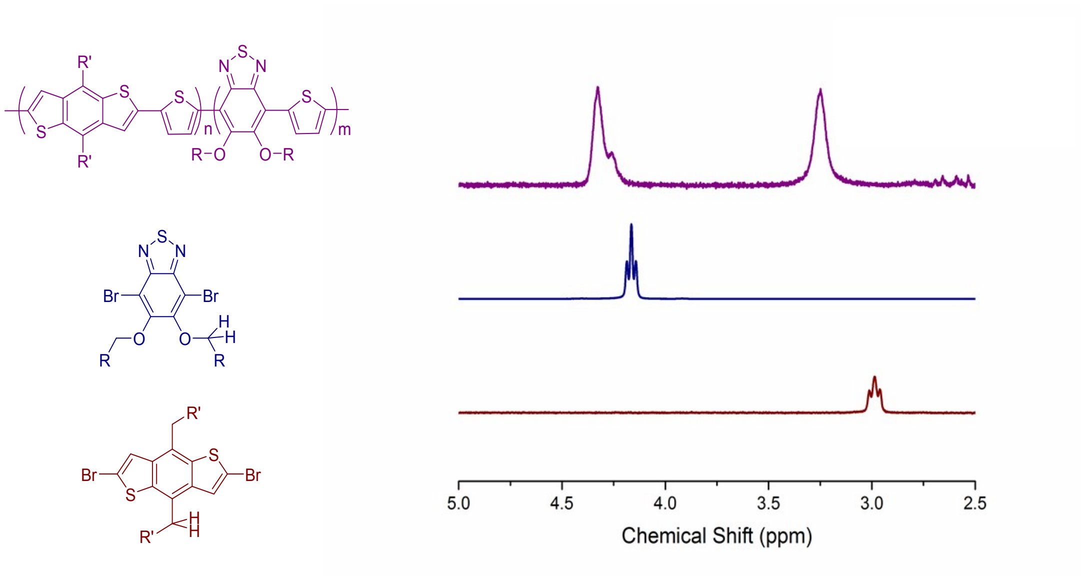

Figure S18: Shift of the α-CH2 protons after the monomers BnDT (red) and BT (Blue) are incorporated into a polymer backbone (purple).

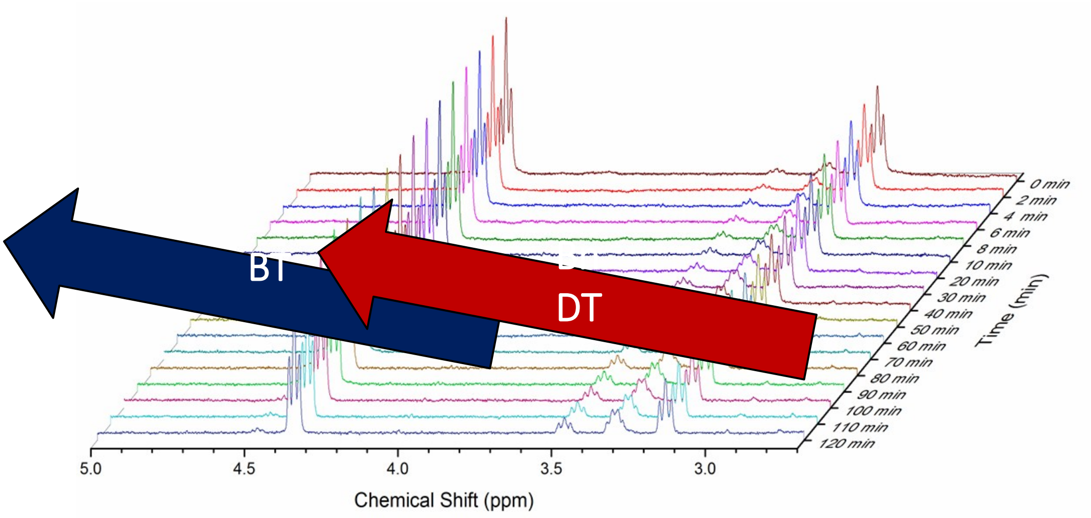

Figure S19: ^{1}H spectra taken in-situ of a competitive Stille coupling between BT and BnDT to a monostannylated thiophene at 100 ˚C over 120 minutes.

The triplet for the BnDT monomer was observed at 3.15 ppm, as the reaction progresses the intensity of this peak diminishes and the emergence of two new triplets is observed. One triplet is centred at 3.30 ppm and the second at 3.45 ppm, which are assigned to the mono (TBnDT) and di-substituted (DTBnDT) BnDT monomer unit respectively (Figure S19). The BT monomer behaves in a similar manner shifting from 4.35 to 4.45 ppm, albeit to a much lesser extent. At t = 120 min a low intensity peak at 4.45 ppm can be observed which is assigned to the mono-substituted BT unit (TBT), while there is no visible peak for the di-substituted species (DTBT) observed within this reaction time frame.