

SUPPORTING INFORMATION

Fullerene-capped Copolymers for Bulk Heterojunctions: Device Stability and Efficiency Improvements

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Instrumentation

Fourier Transform Infra-Red measurements (FT-IR) spectra were performed on a Bruker Tensor 27 spectrometer with a beam diameter of 0.6 mm, a resolution of 4 cm⁻¹ and a spectral range between 4000 cm⁻¹ and 400 cm⁻¹. The different samples were analysed qualitatively after evaporation of a drop of solution containing 1 g mL⁻¹ on an ATR cell. The spectra were all corrected by the reference spectrum.

MALDI-TOF mass spectra were performed on a Voyager mass spectrometer (Applied Biosystems). The unit was equipped with a pulsed nitrogen laser (337 nm). The spectra were made in positive ionization mode with reflectron, and an acceleration voltage of 20 kV. The samples were dissolved in THF at 5 mg mL⁻¹. Dithranol matrix was prepared by dissolving 10 mg of product in 1 mL of dichloromethane. A cationizing agent solution (NaI) in methanol (10 mg mL⁻¹) was also prepared. These different solutions were combined in a 10:1:1 ratio (matrix:sample:cationizing agent). A drop of this solution was deposited on the target and dried under vacuum.

TGA measurements were taken using PERKIN ELMER Thermogravimetric Analyzer TGA 7.

Differential scanning calorimetry (DSC) analyses were performed using the DSC Q100 (TA Instruments). The samples were subjected to two heating cycles (50 to 250 °C) and a cooling cycle. All measurements were made at a constant rate of 10 °C min⁻¹.

The UV-visible absorption spectra of films were obtained on the spectral range from 200 to 900 nm on two spectrometers: a Varian Cary 3E and SAFAS UVmc². The spectra were all corrected by the reference spectrum. The films were prepared by deposition of solutions of polymers and copolymers by spin-coating with a SCS P6700 device on quartz plates. In each series of experiments, the thickness was kept constant and verified by profilometry (KLA Tencor, Alpha Step IQ).

Chemicals

Solvents were distilled over their respective drying agents under reduced pressures and stored under inert atmosphere. Tetrahydrofuran (THF, JT Baker, 99%) was distilled over CaH_2 and then cryo-distilled over sodium benzophenone just prior use (i.e., within 30 min). Dichloromethane (DCM, Xilab, 99%) was cryo-distilled after refluxing 1 h over CaH_2 . Diethylether (JT Baker, 99%) and toluene (JT Baker, 99%) were first distilled over CaH_2 and cryo-distilled over polystyryl-lithium just before use. Methanol (Xilab, 99%) was cryo-distilled after refluxing overnight over Mg turnings. Triethylamine (TEA, Aldrich, 99%) was cryo-distilled following overnight stirring over KOH pellets. Hexane (JT Baker, 95%), acetic acid (Aldrich, 99%), ethylacetate (JT Baker, 99%) and diisopropylethylamine (DIEA, Aldrich, 99%) were used as received without purification. Bromohexane (98%), 3-bromothiophene (97%), 1,3-bis(diphenylphosphino)propane nickel(II) chloride $[\text{Ni}(\text{dppp})\text{Cl}_2]$, *N*-bromosuccinimide (99%), sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), 3-bromo-1-propanol (97%), sodium azide (NaN_3 , $\geq 99.5\%$), tetrabutylammonium iodide (Bu_4NI , 98%), dicyclohexano-18-crown-6 (98%), 2-butanone ($\geq 99.9\%$), α -bromoisobutryl bromide (98%), bipyridine ($\geq 99.9\%$), copper(I) iodide (CuI , $\geq 99.9\%$), C_{60} (99.9%), triethylamine (TEA, 99.5%), ammonium chloride (NH_4Cl), and potassium hydroxide (KOH), were used as received from Aldrich without purification. Mg turnings (98%, Aldrich) were dried overnight in an oven at $150\text{ }^\circ\text{C}$ before use. *Tert*-butylmagnesium chloride ($t\text{-BuMgCl}$, 1 M solution in THF), *iso*-propylmagnesium chloride ($i\text{-PrMgCl}$, 2 M solution in THF), ethynylmagnesium bromide (0.5 M solution in THF), were used as received from Aldrich without purification. Copper(I) bromide (CuBr , Aldrich, 98%) was purified by stirring overnight in a mixture of acetic acid and water (1:1), then filtered, rinsed sequentially with ethanol and ether and dried in vacuum oven for about 24 h at $40\text{ }^\circ\text{C}$. It was kept under an inert atmosphere until use. Typically, CuBr (2 g) was washed with a mix of acetic acid (50 mL) and water (50 mL).

Styrene (Aldrich, 99%), was cryo-distilled over CaH_2 just prior to polymerisation. 2,5-Dibromo-3-hexylthiophene and was distilled twice under high vacuum (10^{-5} mbar) just prior to use. In between manipulations it was stored at $4\text{ }^\circ\text{C}$ in a flame-dried glass sealed vessel.

Synthetic techniques

All reactions were performed under highly controlled Schlenk conditions: reaction vessels were thoroughly flame dried; covering gases (nitrogen) was dried by passage through CaH_2 filters.

Synthesis of 3-hexylthiophene

In a 500 mL flask equipped with condenser, magnesium (15.13 g, 0.62 mol) and dry diethyl ether (210 mL) were introduced and cooled to 0 °C. Bromohexane (82.25 g, 70 mL, 0.5 mol) was added very slowly by dropping funnel. The resulting mixture was stirred under nitrogen for 3 h and transferred to a dropping funnel (250 mL) fitted to another 1 L flask equipped with condenser containing 3-bromothiophene (50 g, 28 mL, 0.306 mol) and Ni(dppp)Cl₂ (0.75 g, 1.38 mmol) in dry diethyl ether (100 mL). After cooling with an ice bath, the Grignard reagent was added dropwise and the resulting adduct was allowed to warm to room temperature and stirred for 3 days under nitrogen. To terminate the reaction, slightly acidified (HCl) water was added (100 mL) slowly. To recover the monomer, chloroform (200 mL) was added, and the organic layer washed 3 times with water and dried over Na₂SO₄. The crude product was distilled under reduced pressure to obtain in the pure form as a colourless oil (45 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ_H 0.90 (t, 3H, (CH₂)₅-CH₃), 1.32 (m, 6H, CH₂-CH₂-(CH₂)₃-CH₃), 1.63 (q, 2H, CH₂-CH₂-(CH₂)₃-CH₃), 2.63 (t, 2H, CH₂-CH₂-(CH₂)₃-CH₃), 6.92 (m, 1H, CH Ar), 6.95 (m, 1H, CH Ar), 7.23 (m, 1H, CH Ar).

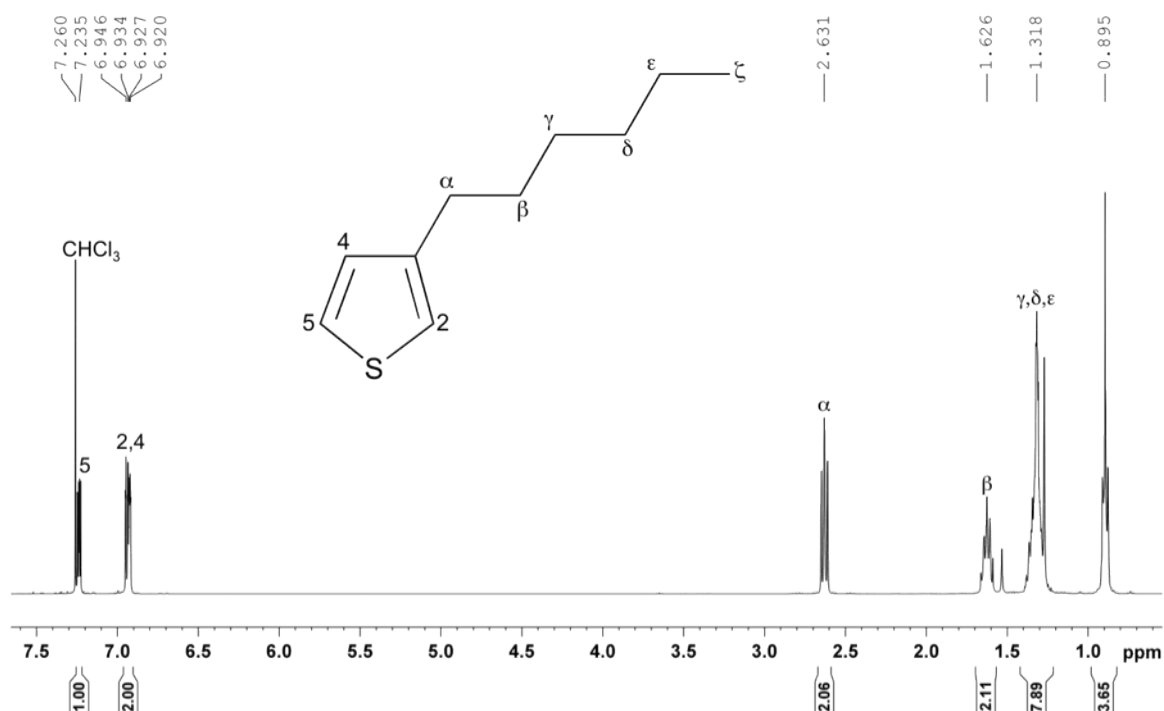


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of 3-hexylthiophene. Impurity at *ca* 1.5 ppm is water in the CDCl₃.

Synthesis of 2,5-dibromo-3-hexylthiophene

N-bromosuccinimide (80.65 g, 0.453 mol) was added to a stirred solution of 3-hexylthiophene (42.15 g, 0.25 mol) in acetic acid (320 mL) and CH₂Cl₂ (320 mL). The mixture was stirred at room temperature for 24 h under nitrogen. The organic layer was washed five times with water, five times with a saturated aqueous NaHCO₃ solution, dried over Na₂SO₄, filtered and concentrated. The crude product was recovered as pale yellow oil by two successive secondary vacuum distillations (5×10^{-4} mbar) (58 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ_{H} 0.89 (t, 3H, (CH₂)₅-CH₃), 1.30 (m, 6H, CH₂-CH₂-(CH₂)₃-CH₃), 1.55 (q, 2H, CH₂-CH₂-(CH₂)₃-CH₃), 2.51 (t, 2H, CH₂-CH₂-(CH₂)₃-CH₃), 6.78 (s, 1H, CH aromatic). δ_{C} 14.1 ((CH₂)₅-CH₃), 22.6 ((CH₂)₄-CH₂-CH₃), 28.8 ((CH₂)₂-CH₂-(CH₂)₂-CH₃), 29.5 ((CH₂)₃-CH₂-CH₂-CH₃), 29.6 ((CH₂)₃-CH₂-CH₂-CH₃), 31.6 (CH₂-CH₂-(CH₂)₃-CH₃), 107.92 (C2 Ar), 110.31 (C5 Ar), 130.89 (C4 Ar), 142.91 (C3 Ar).

Note: the relative integration of this peak with the peak corresponding to the proton in position 2 located at 7.1 ppm (a witness to the monobromothiophene impurity) indicated a purity of 99.5%.

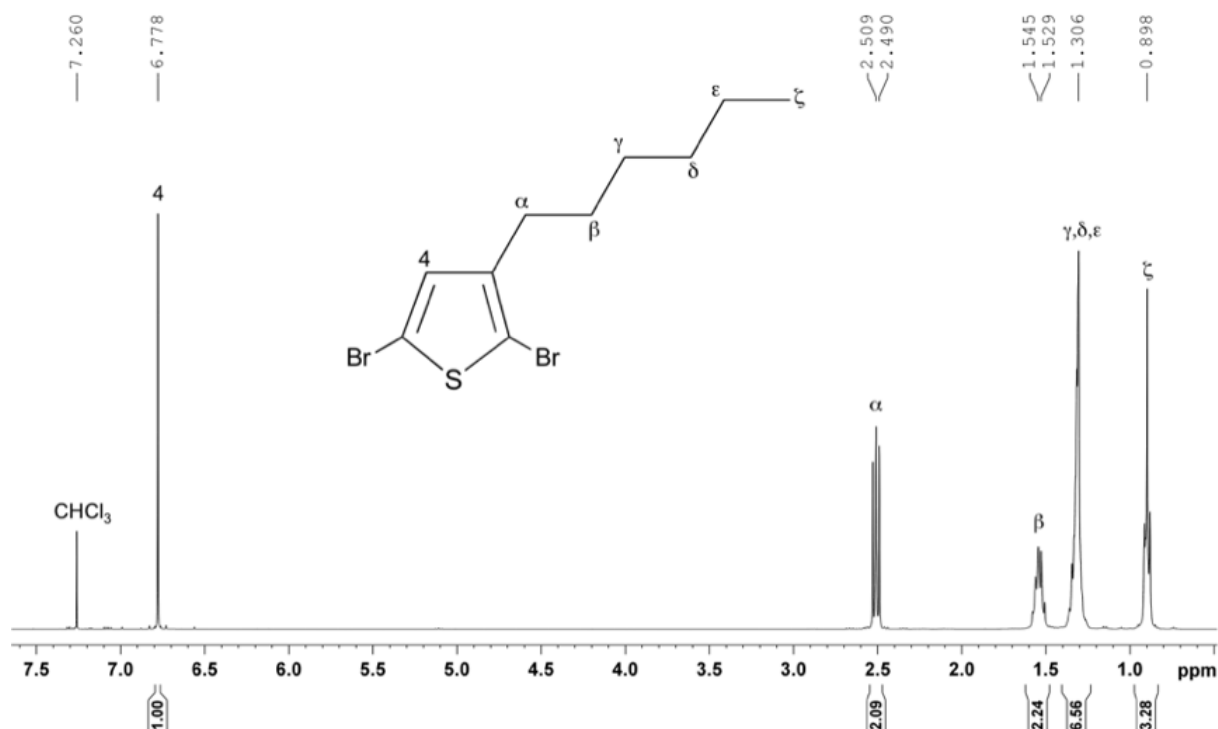


Figure S2. ¹H NMR (400 MHz, CDCl₃) spectrum of 2,5-dibromo-3-hexylthiophene.

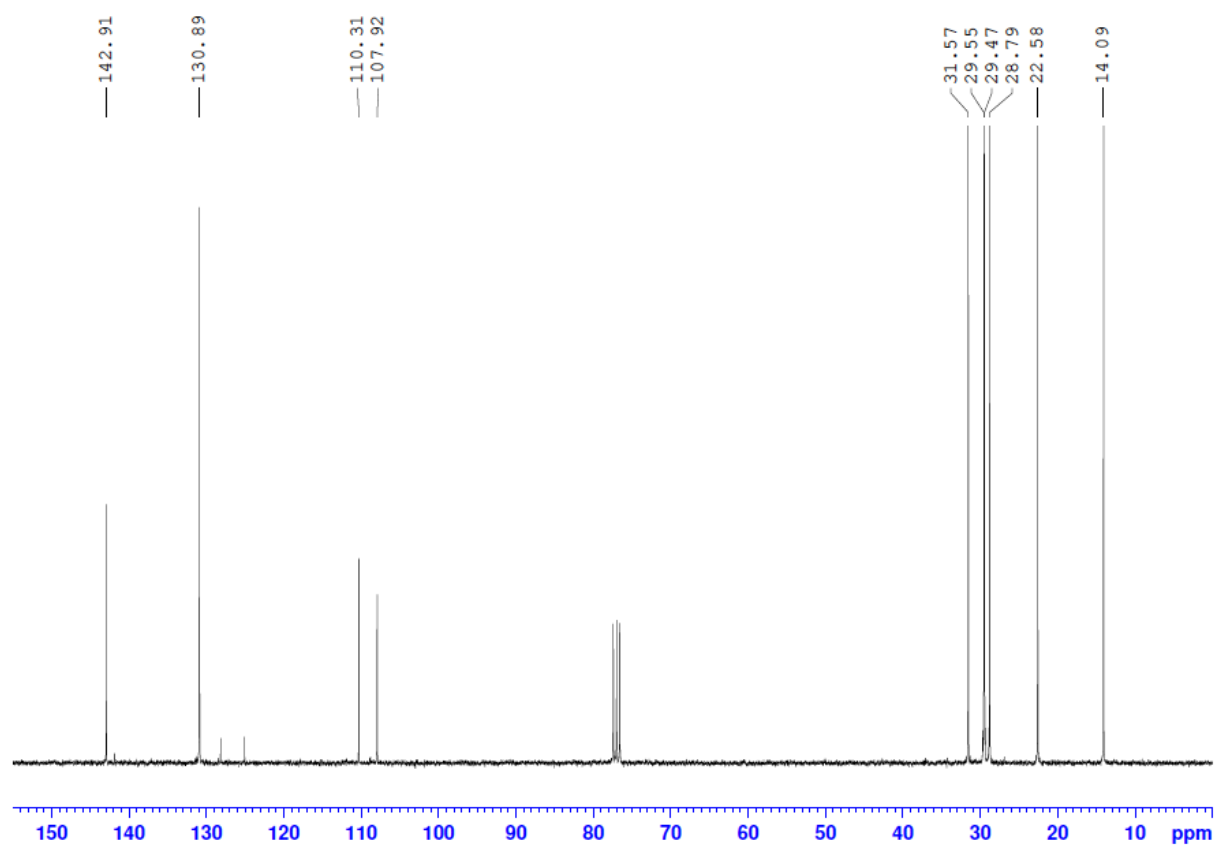


Figure S3. ^{13}C NMR (100 MHz, CDCl_3) spectrum of 2,5-dibromo-3-hexylthiophene.

Synthesis of ω -ethynyl-P3HT

In a typical experiment, *tert*-butylmagnesium chloride (13.8 mL as a 1 M solution in THF, 13.8 mmol) was added by syringe to 2,5-dibromo-3-hexylthiophene (4.5 g, 13.8 mmol) dissolved in THF (30 mL) at room temperature and the mixture stirred for 2.5 h. On dilution by adding THF (120 mL), Ni(dppp)Cl₂ (0.074 g, 0.136 mmol, 0.98 mol% with respect to the monomer) was added in one shot, and the mixture stirred for 30 min at room temperature. The termination of the polymers with the Grignard functionalization agent was carried out in a one-shot addition using 50-60 mol % with respect to the monomer, thus in this case, ethynylmagnesium bromide (8 mmol, 16 mL of a 0.5 M solution in THF) was added. Finally the reaction was quenched by adding HCl (5 M) and poured into methanol (800 mL) to precipitate the polymer. It was recovered directly in an extraction thimble to be washed by Soxhlet extraction with methanol, hexane and chloroform. ω -ethynyl-P3HT was isolated from the chloroform extraction and concentrated under reduced pressure, precipitated into methanol, filtered with a G₄ crucible, dried overnight under vacuum and finally stored under inert atmosphere with protection from light. ¹H NMR (400 MHz, CDCl₃): δ_{H} 0.93 (t, 3nH, (CH₂)₅-CH₃), 1.3-1.4 (m, 6nH, CH₂-CH₂-(CH₂)₃-CH₃), 1.7 (m, 2nH, CH₂-CH₂-(CH₂)₃-CH₃), 2.57 (m, chain-end CH₂-CH₂-(CH₂)₃-CH₃), 2.80 (t, 2nH, CH₂-CH₂-(CH₂)₃-CH₃), 3.52 (s, 1H, -C \equiv C-H), 6.98 (s, 1nH, CH aromatic); δ_{C} 67.98 ppm (-C \equiv CH), Regioregularity estimated at 97% by ¹H NMR. SEC (THF, 254 nm, UV): M_{n} = 14000 g mol⁻¹, D = 1.1.

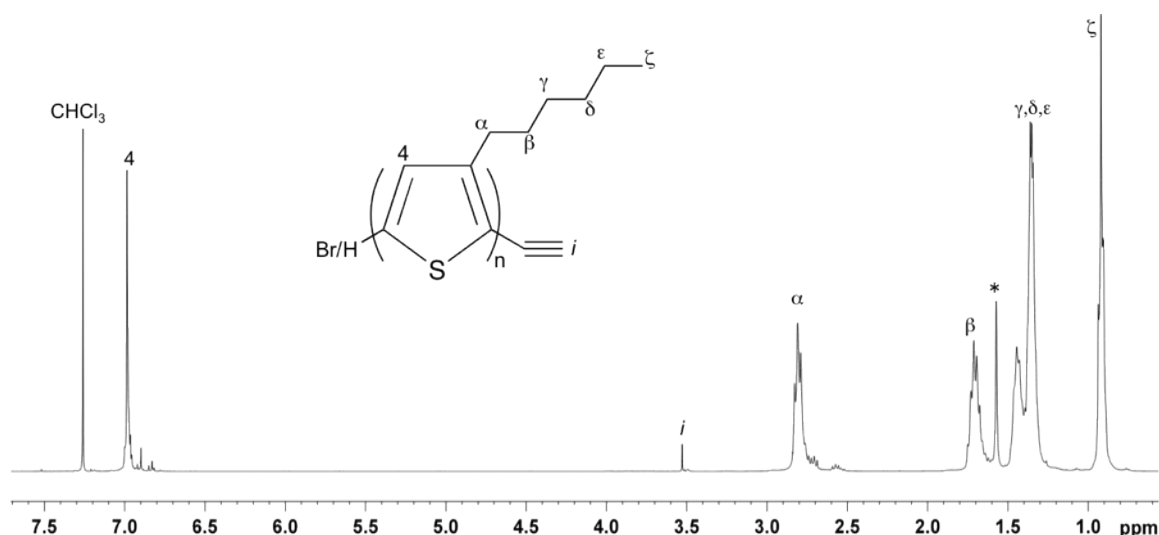


Figure S4. ¹H NMR (400 MHz, CDCl₃) spectrum of ω -ethynyl-P3HT.

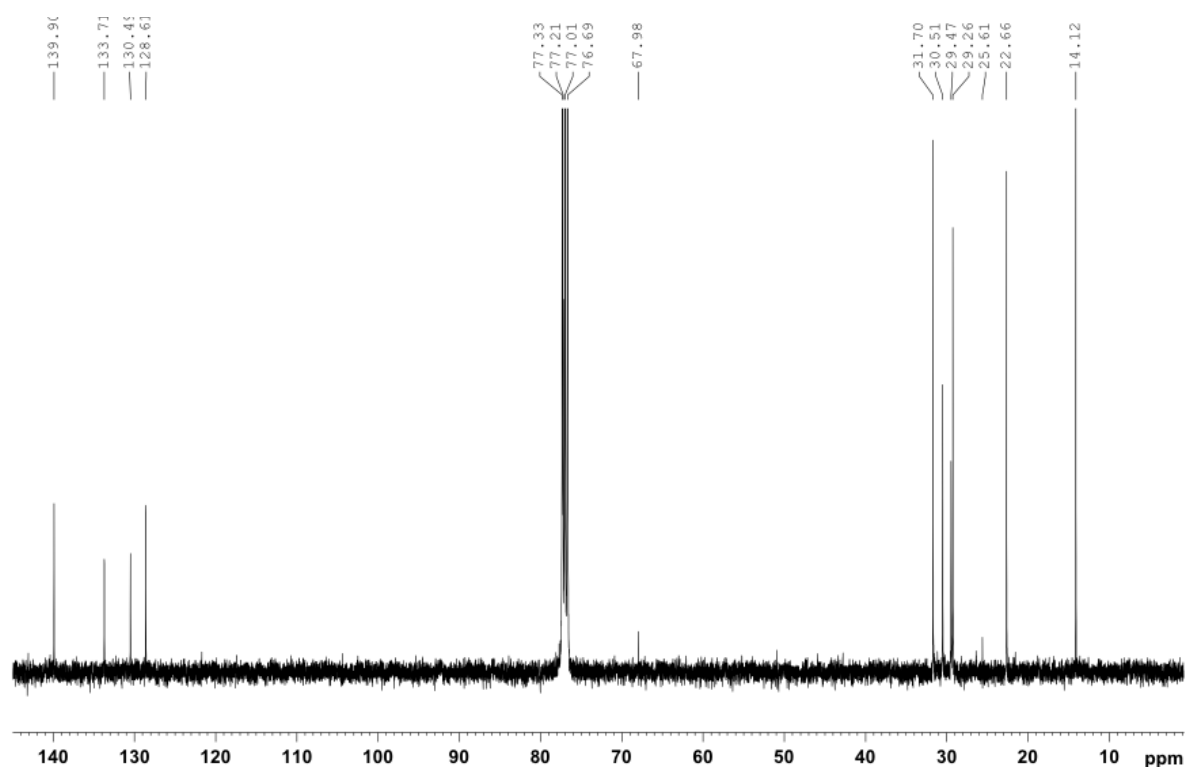


Figure S5. ^{13}C NMR (100 MHz, CDCl_3) spectrum of ω -ethynyl-P3HT.

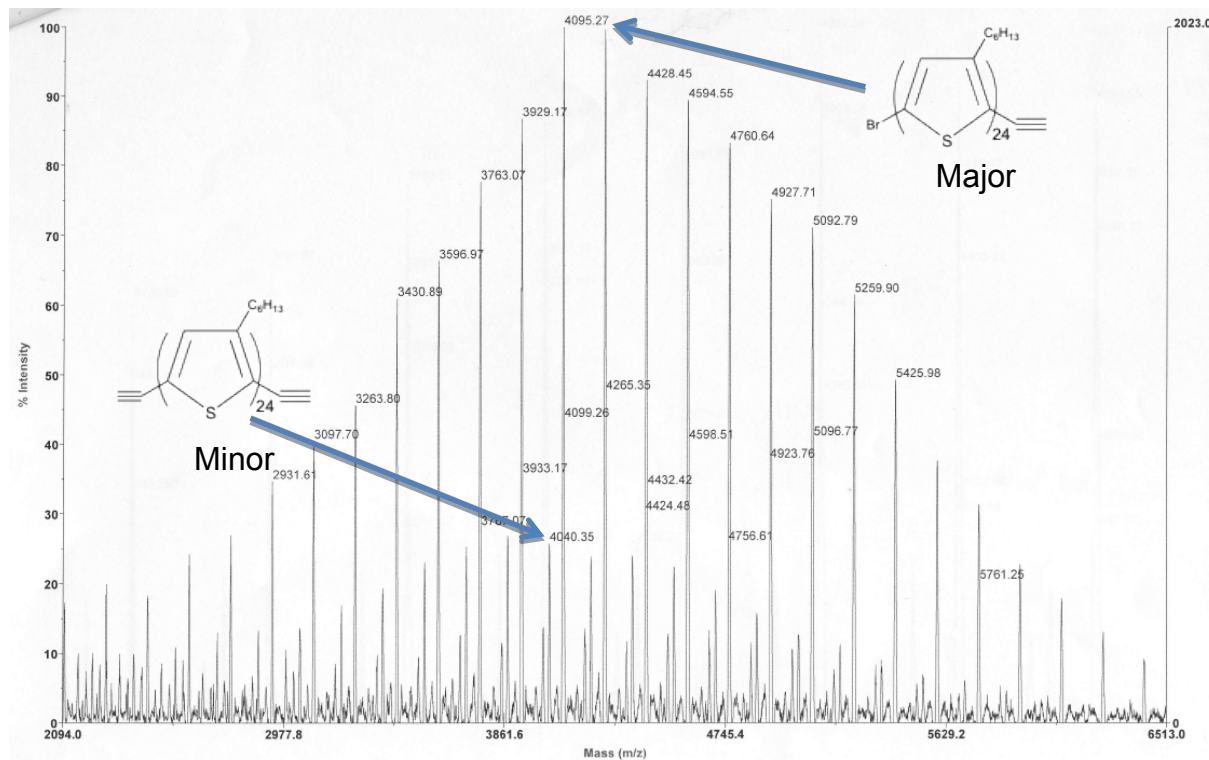


Figure S6. Representative MALDI-TOF mass spectra of ω -ethynyl-P3HT, showing that *ca* 21% of chains carried both ends terminated with ethynyl groups. Note the considerably lower

recorded molar mass than that of the GPC due to the difficulty in making high molar mass P3HT “fly”.

Synthesis of 3-azido-1-propanol

3-Bromo-1-propanol (4) (10 g, 72 mmol), NaN_3 (7 g, 108 mmol), $(\text{C}_4\text{H}_9)_4\text{NI}$ (4 g, 11 mmol) and dicyclohexano-18-crown-6 (20 mg, 0.05 mmol) were dissolved in 2-butanone (50 mL) and the mixture was stirred under reflux for 24 h. The mixture was filtered, the solid rinsed with acetone and the combined solutions concentrated. After distillation, the pure product was obtained as a colourless oil (6 g, 83 %). ^1H NMR (400 MHz, CDCl_3): δ_{H} 1.52 (s, 1H, $\text{CH}_2\text{-OH}$), 1.83 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 3.45 (t, 2H, $\text{CH}_2\text{-N}_3$), 3.75 (t, 2H, $\text{CH}_2\text{-OH}$) ppm; δ_{C} : 31.45 ($\text{CH}_2\text{-CH}_2$), 48.51 ($\text{CH}_2\text{-N}_3$), 59.98 ($\text{CH}_2\text{-OH}$) ppm.

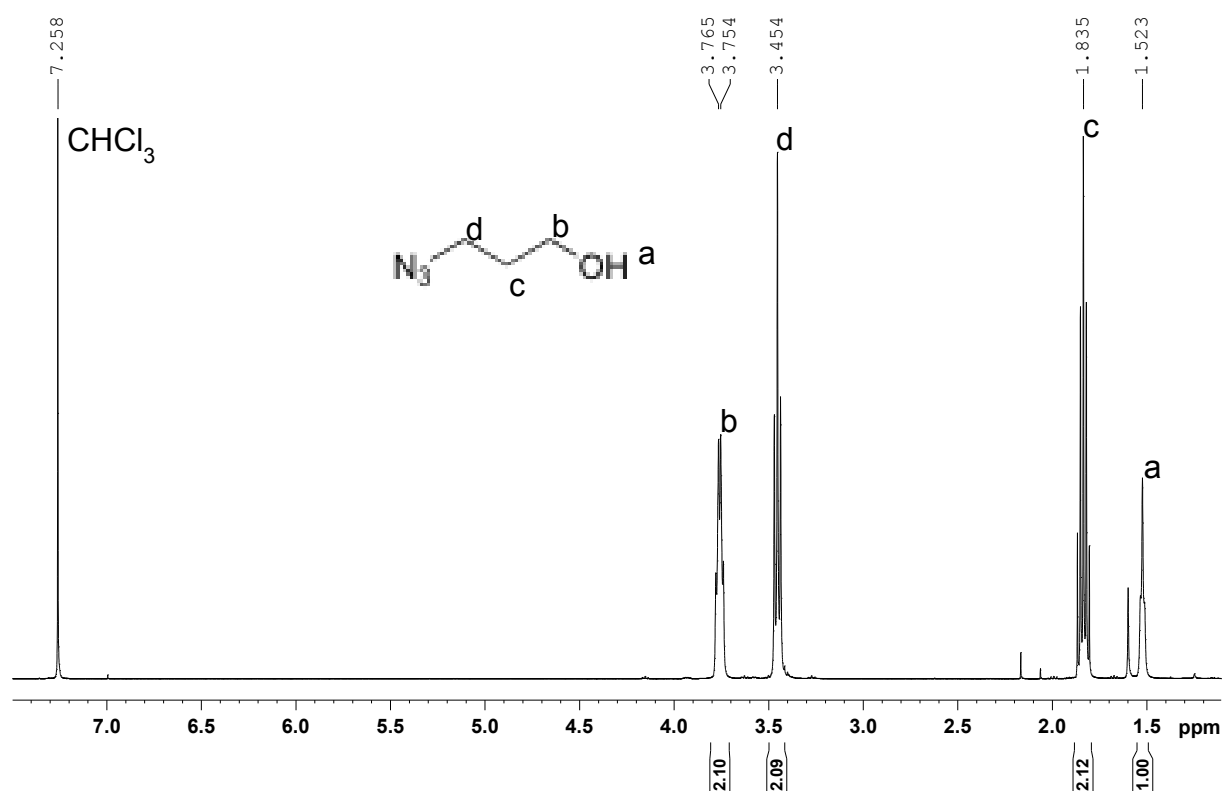


Figure S7. ^1H NMR (400MHz, CDCl_3) spectrum of 3-azido-1-propanol.

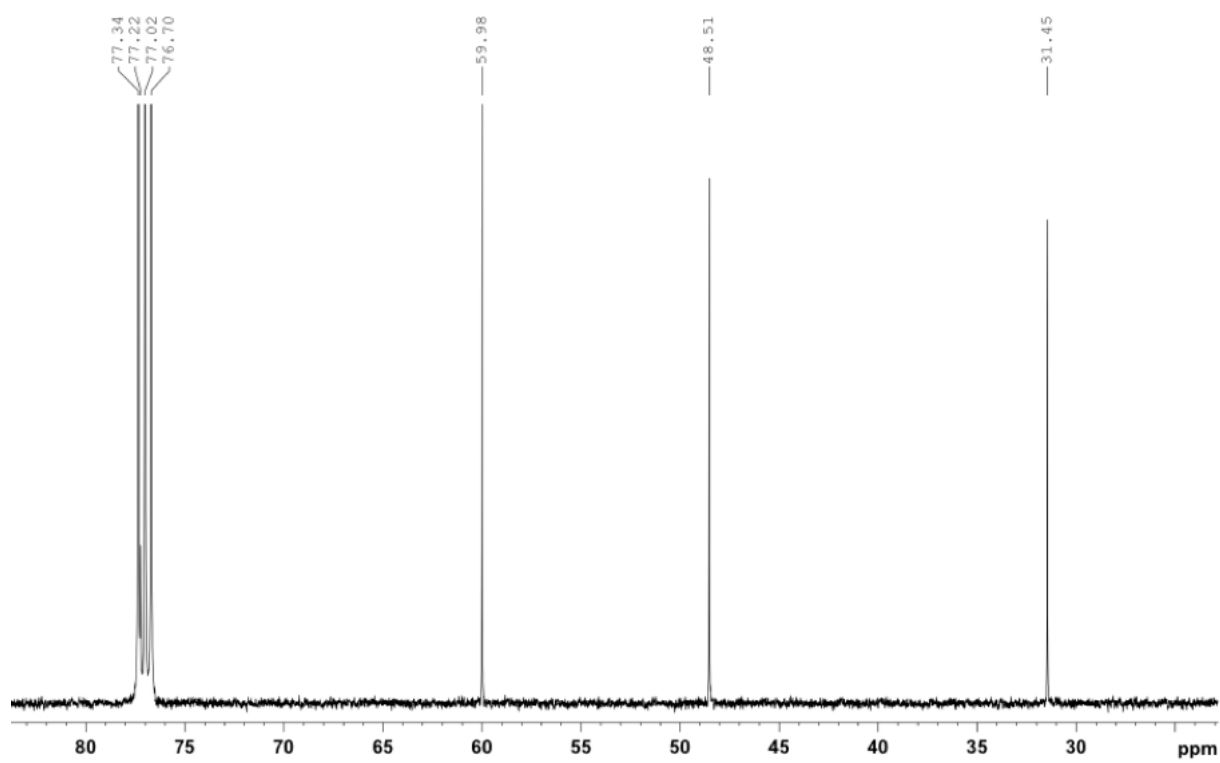


Figure S8. ¹³C NMR (100MHz, CDCl₃) spectrum of 3-azido-1-propanol.

Synthesis of 3-azidopropyl-2-bromoisobutyrate

A solution of α -bromoisobutyryl bromide (11.95 g, 6.43 mL, 52 mmol, 1.05 eq.) in THF (50 mL) was added dropwise to a solution of 3-azido-1-propanol (5 g, 49.5 mmol) and triethylamine (6.5 g, 9 mL, 64.4 mmol) in THF (50 mL) at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at 25 °C. Excess acid bromide was quenched by addition of degassed methanol (50 mL). The formed triethylammonium bromide salt was filtered off and the solution was concentrated. The crude product was dissolved in CH_2Cl_2 , washed 3 times with a saturated ammonium chloride solution and 3 times with distilled water. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered and concentrated, yielding pale yellow oil, which was dried under vacuum (9 g, 81%). ^1H NMR (400 MHz, CDCl_3): δ_{H} 1.92 (s, 6H, $(\text{CH}_3)_2\text{C}$), 1.96 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 3.44 (t, 2H, $\text{CH}_2\text{-N}_3$), 4.27 (t, 2H, $\text{CH}_2\text{-O-C(=O)}$); δ_{C} 27.97 ($\text{CH}_2\text{-N}_3$), 30.70 ($(\text{CH}_3)_2\text{-C}$), 48.03 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$), 55.66 (C-Br), 62.74 ($\text{CH}_2\text{-O}$), 171.53 (C=O).

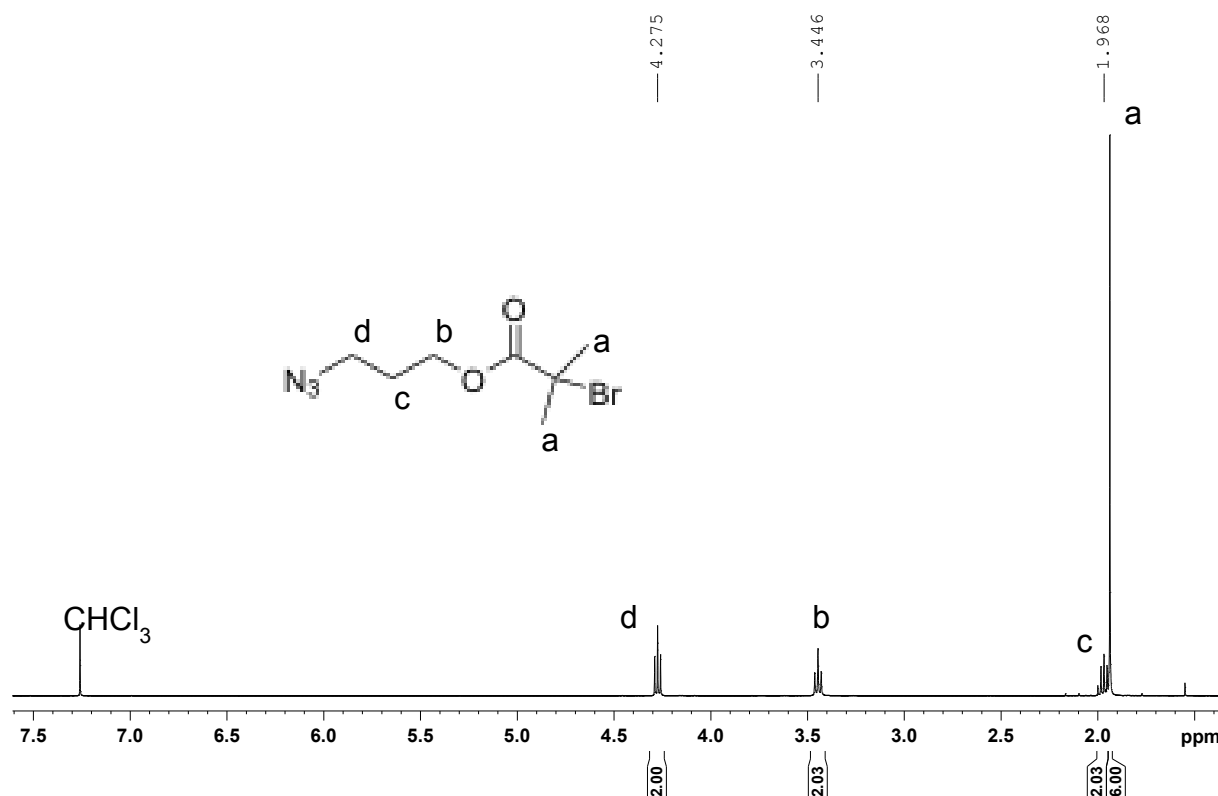


Figure S9. ^1H NMR (400 MHz, CDCl_3) spectrum of 3-azidopropyl-2-bromoisobutyrate.

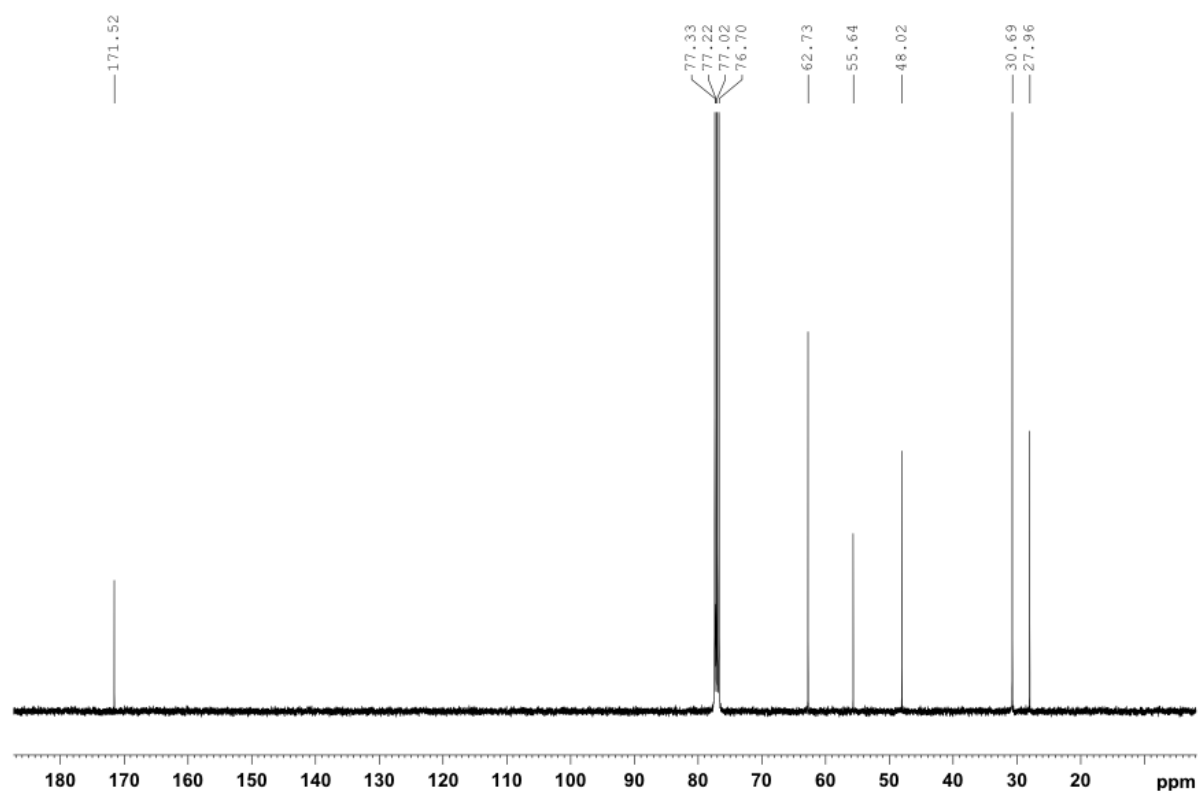


Figure S10. ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3-azidopropyl-2-bromoisobutyrate.

Synthesis of α -azido-polystyrene

Experiments were carried out varying the polymerization time to achieve the required molar mass. Examples are shown in Table S1 below. In the experiment performed to provide the α -azido-polystyrene used in this work (denoted PS2 in Table S1), 3-azidopropyl-2-bromoisobutyrate (**6**) (0.25 g, 1 mmol), freshly purified CuBr (0.143 g, 1 mmol), 2,2'-bipyridyl (0.468 g, 3 mmol) and styrene (5 g, 5.5 mL, 48 mmol) were added to a Schlenk flask. The mixture was stirred for 5 min and degassed three times by freeze-pump-thaw cycles to remove residual oxygen. The polymerization reaction was performed at 130 °C for 25 min. The reaction was stopped by dropping the temperature of the Schlenk flask to 0 °C. The solution was then dissolved in THF and passed through a basic alumina column. After concentration, the polymer was precipitated in methanol and dried overnight under reduced pressure.

PS	Initiator [mg, (mmol)]	CuBr [mg, (mmol)]	Bipyridine [mg, (mmol)]	Styrene [g, (mmol)]	Polymerisation time (min)	M_n (SEC, g mol ⁻¹)	\bar{D}	T_g (°C)
PS1	260 (1.04)	148 (1.03)	487 (3.12)	5 (48)	12	2600	1.08	87
PS2	250 (1.0)	143 (1.0)	468 (3.0)	5 (48)	25	3800	1.17	88
PS3	250 (1.0)	143 (1.0)	468 (3.0)	5 (48)	10	1900	1.21	84
PS4	250 (1.0)	143 (1.0)	468 (3.0)	5 (48)	30	4500	1.30	89
PS5	500 (2.0)	286 (2.0)	936 (6.0)	10 (96)	11	2000	1.11	84
PS6	260 (1.04)	148 (1.03)	487 (3.12)	5 (48)	30	5200	1.29	93

Table S1: Reaction conditions and characteristics of the synthesized α -azido- ω -bromo-polystyrenes (PS1-PS6, SEC in THF, UV-254 nm). DSC characteristics recorded on second heating cycle at 10 °C min⁻¹.

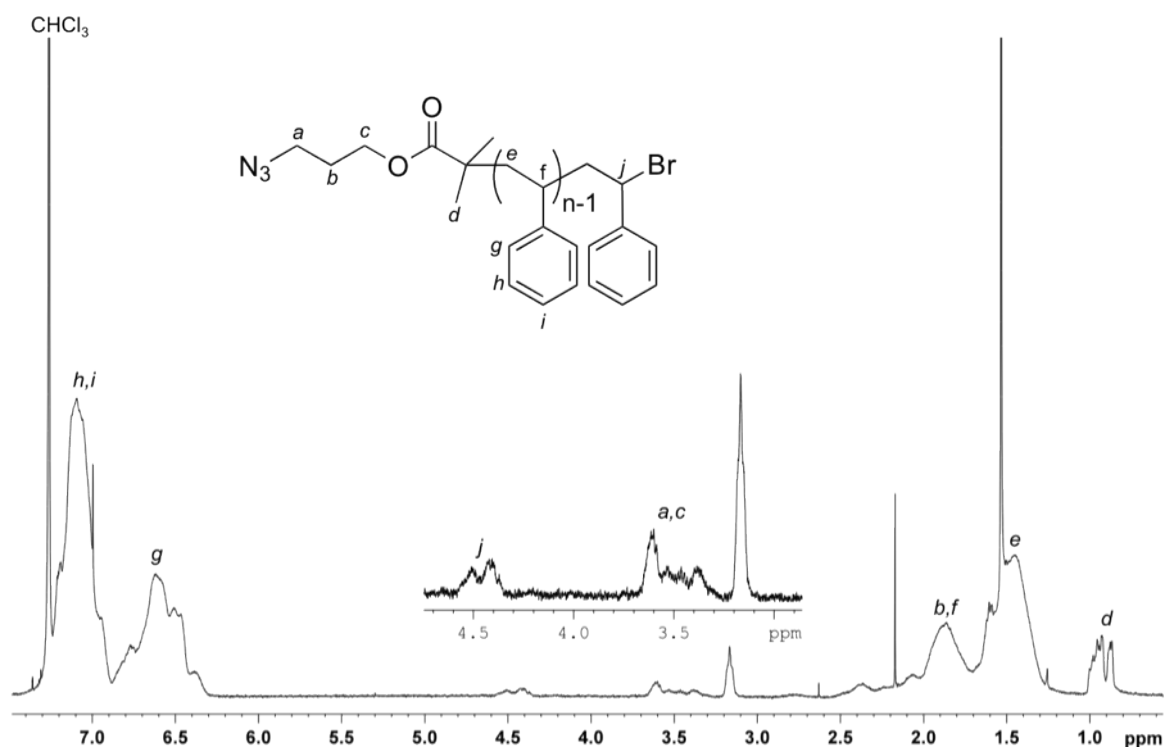


Figure S11. ^1H NMR (400 MHz, CDCl_3) spectrum of the exemplar α -azido- ω -bromo-polystyrene (PS2).

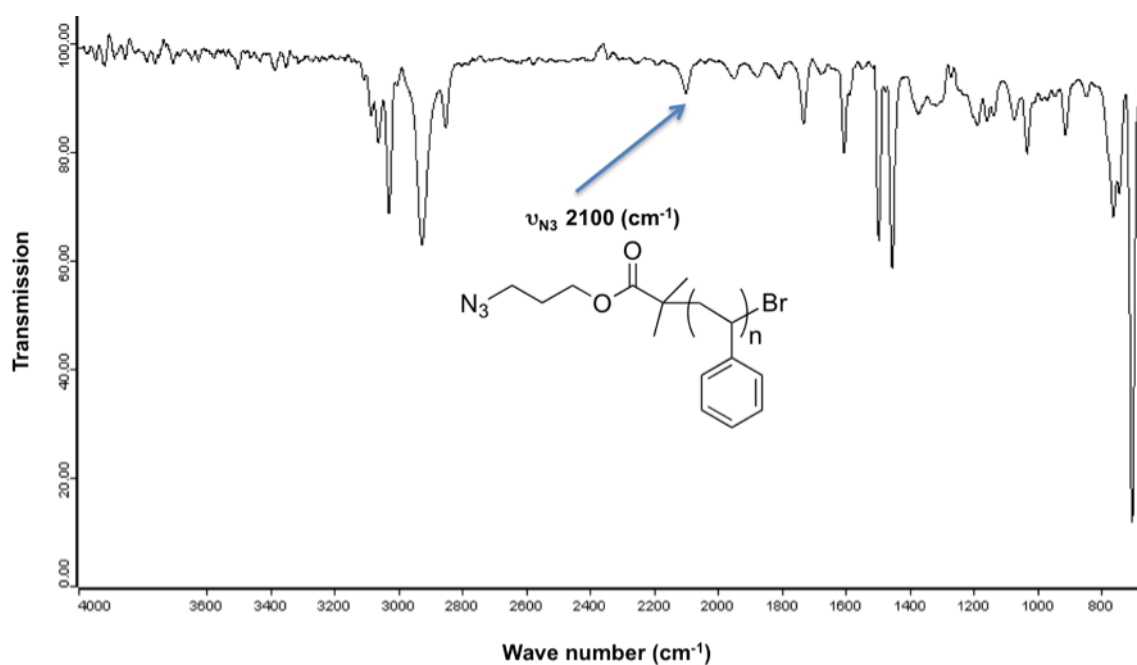


Figure S12. Infra-red spectrum of α -azido- ω -bromo-polystyrene.

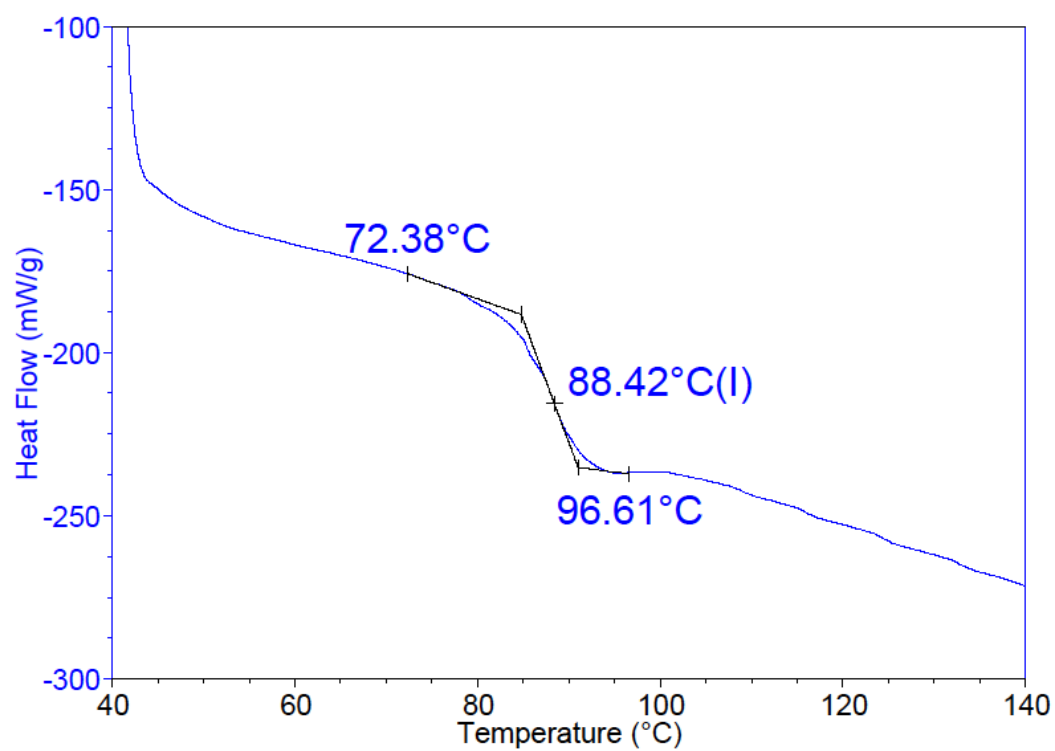


Figure S13. DSC curve of α -azido- ω -bromo-polystyrene, recorded at 10 °C min⁻¹.

Supplementary characterisations of block copolymers

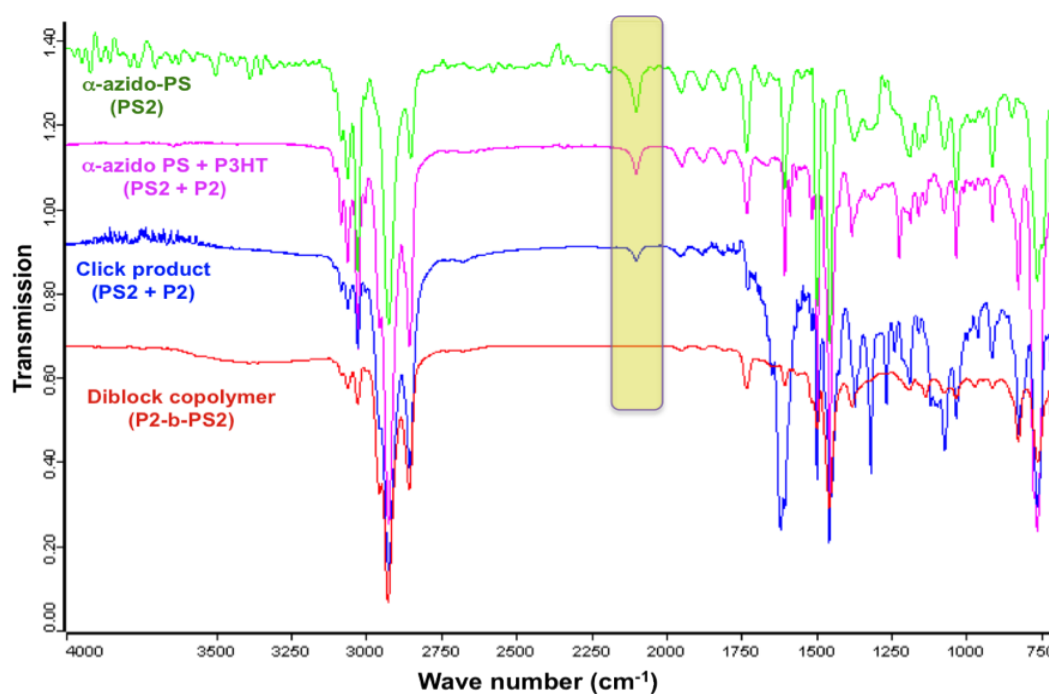


Figure S14. IR spectra, going from top to bottom of: α -azido- ω -bromo-PS (denoted PS2 here); mixture of α -azido- ω -bromo-PS and ω -ethynyl-P3HT (P2); an initial failed reaction using unmodified reaction conditions (see text); and finally the successful “click” product of diblock copolymer P3HT-*b*-PS (labelled P2-*b*-PS2 in the diagram).

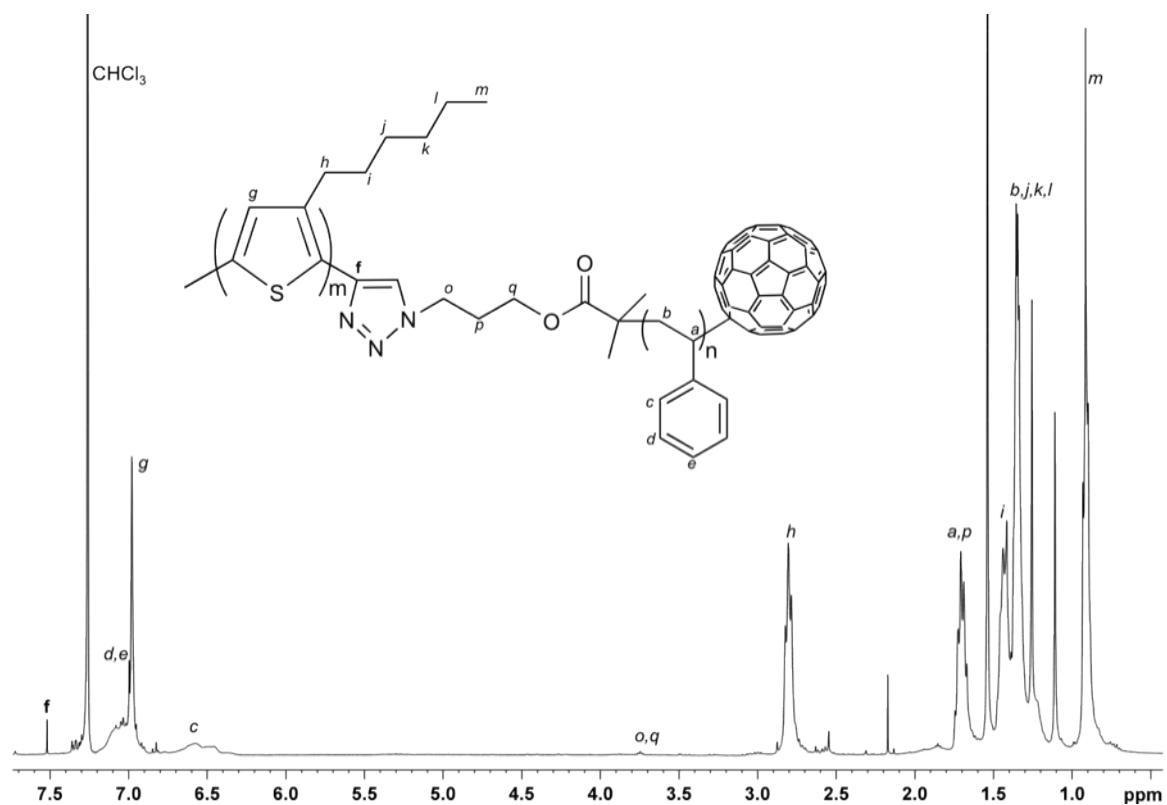


Figure S15. ^1H NMR (400 MHz, CDCl_3) spectrum of P3HT-*block*-PS- C_{60} .

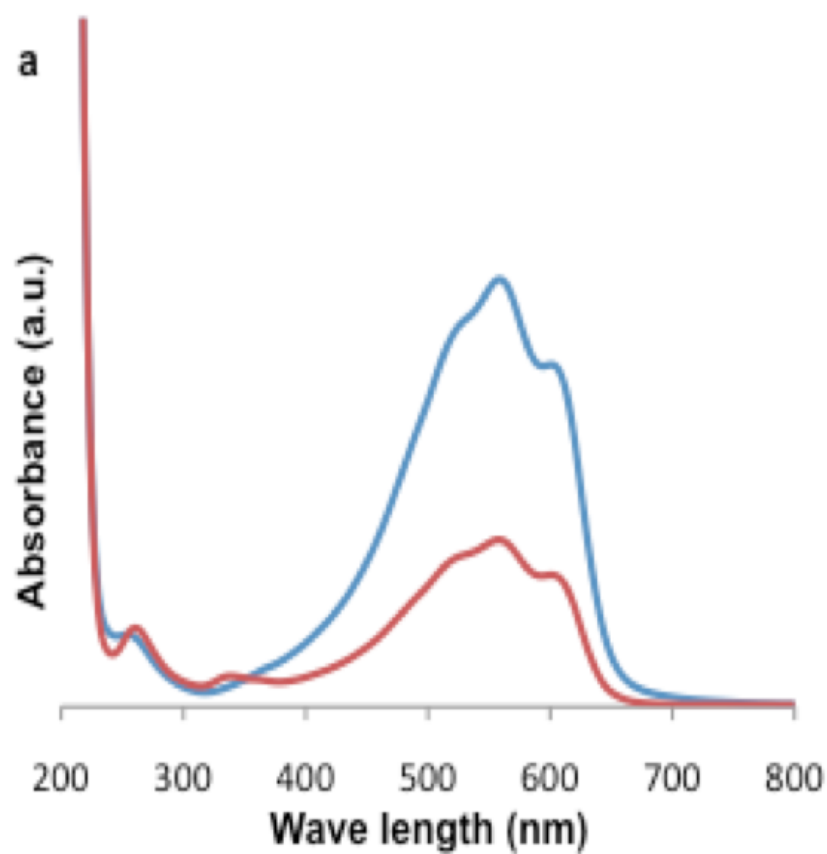


Figure S16. Overlaid UV-visible absorption spectra of P3HT-*b*-PS (blue) and P3HT-*b*-PS-C₆₀ (red). Films made by spin-coating with *o*-dichlorobenzene as solvent.

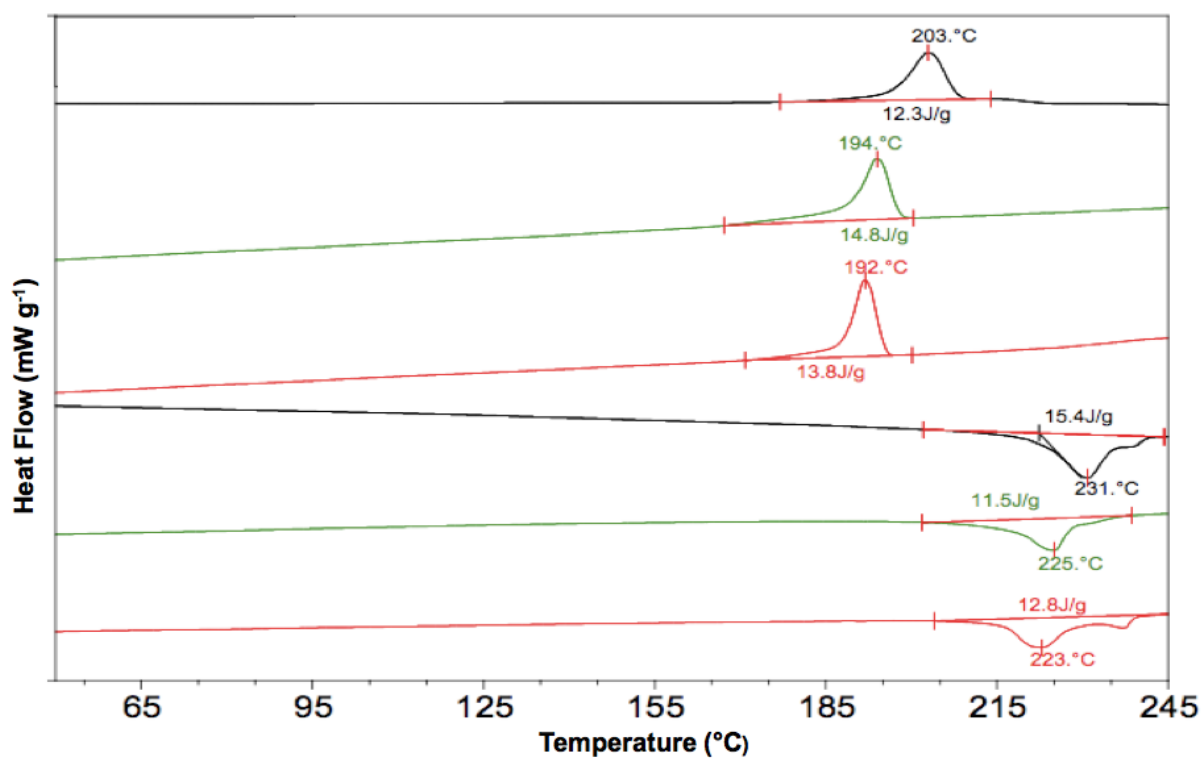


Figure S17. Overlaid DSC curves of P3HT (black), P3HT-*b*-PS (green), and P3HT-*b*-PS-C₆₀ (red). The samples underwent two heating and cooling cycles and a heating rate of 10 °C min⁻¹ was used.

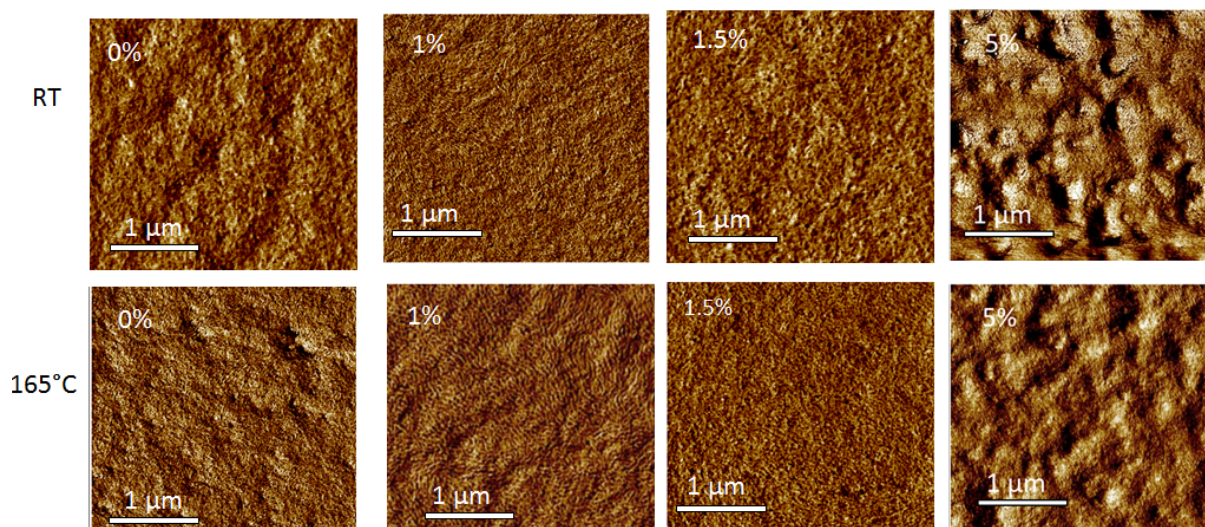


Figure S18. Tapping-mode atomic force microscopy images of a 3 μm x 3 μm region of four films at RT and at 165 $^{\circ}\text{C}$, 10 min used in making devices. -P3HT-PCBM (RT, 165 $^{\circ}\text{C}$); P3HT-PCBM + 1 wt% P3HT-b-PS (RT, 165 $^{\circ}\text{C}$), P3HT-PCBM + 1.5 wt% P3HT-b-PS; P3HT-PCBM + 5wt% P3HT-b-PS.

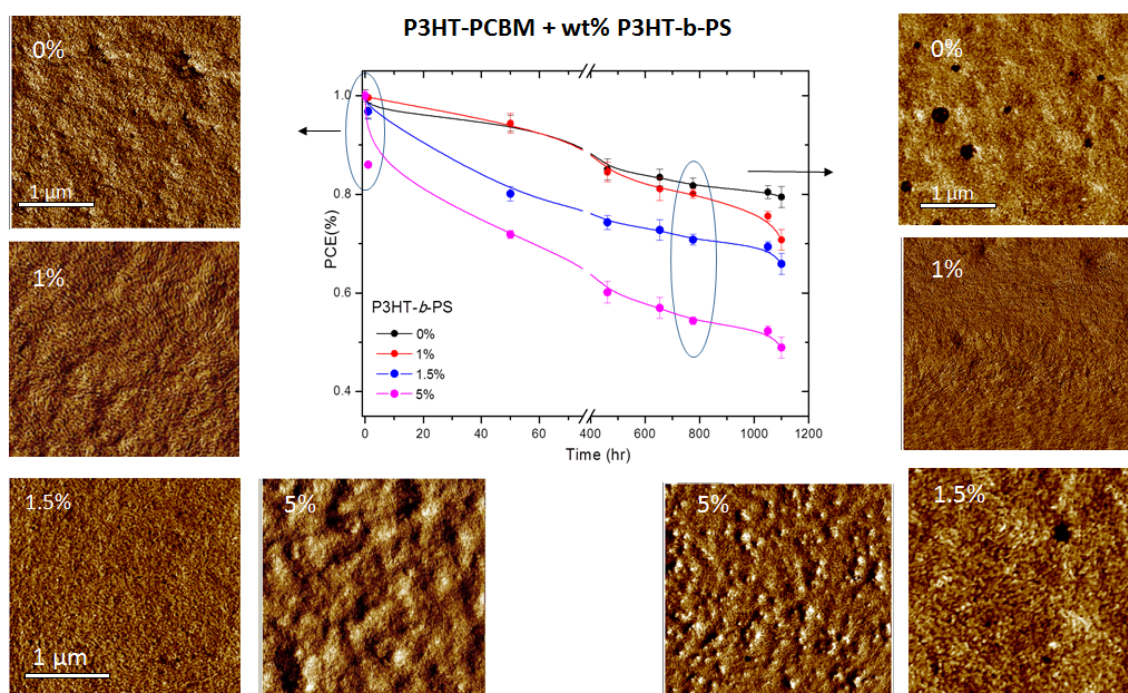


Figure S19: Studies of morphological stability and PCE curves of P3HT-PCBM + (0wt%, 1wt%, 1.5 wt% et 5wt %) P3HT-b-PS under light at 1 h (left) and 800 h (right).

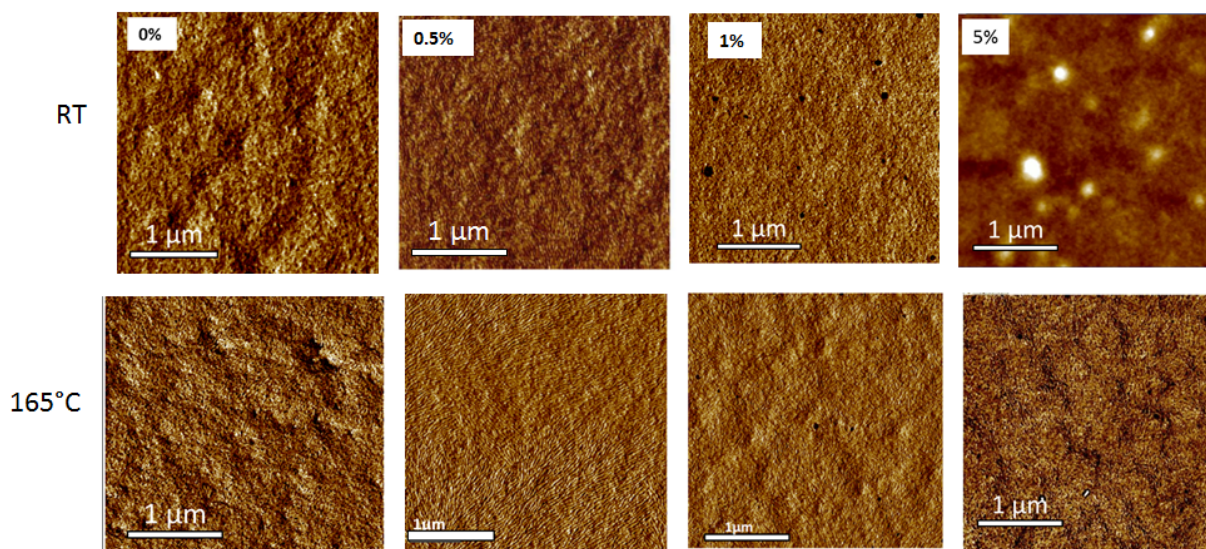


Figure S20. Tapping-mode atomic force microscopy images of a 3 μm x 3 μm region of four films at RT and at 165°C, 10 min used in making devices.

-P3HT-PCBM (RT, 165 °C); P3HT-PCBM + 0.5 wt% P3HT-b-PS-C₆₀ (RT, 165 °C), P3HT-PCBM + 1.5 wt% P3HT-b-PS-C₆₀; P3HT-PCBM + 5wt% P3HT-b-PS-C₆₀.

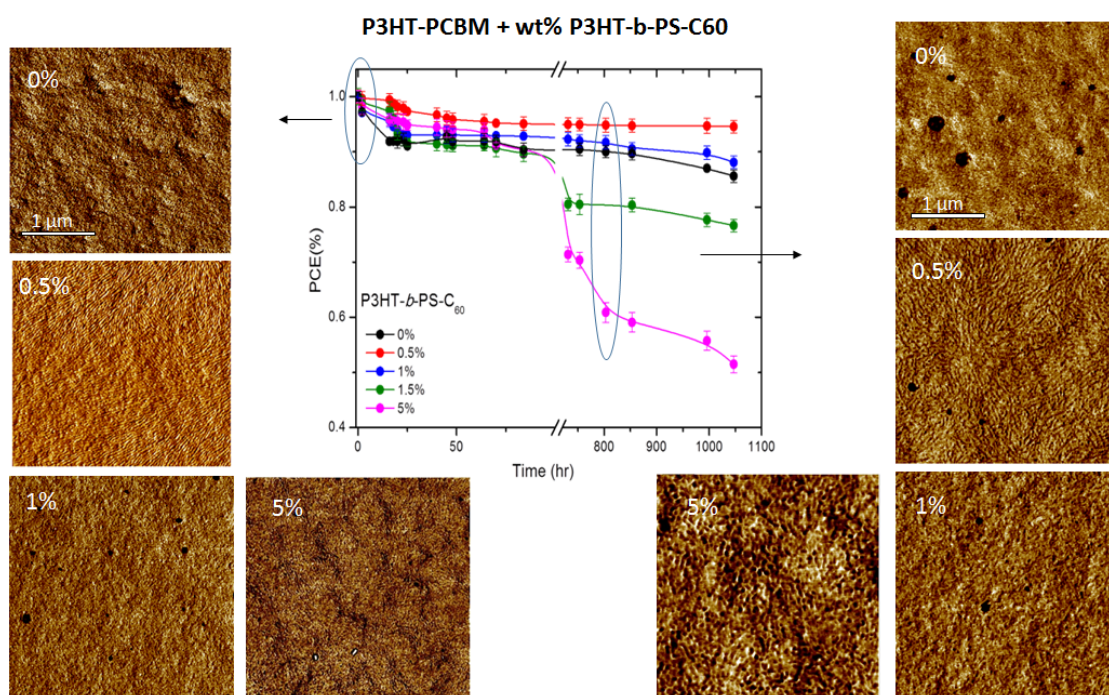


Figure. S21: Studies of morphological stability and PCE curves of P3HT-PCBM + (0wt%, 0.5wt%, 1 wt% et 5wt%) P3HT-b-PS-C₆₀ under light at 1 h and 800 h.