Supplementary Material (ESI) for Polymer Chemistry

Supporting Information:

Synthesis

Poly-3-bromo-4-hexylthiophene, 1a (1% brominated). To a solution of P3HT (300 mg, 1.8 mmol) in 150 mL of $CHCl_3$ was added 3.4 mg (0.01 equivalent) of NBS. The mixture was stirred at room temperature overnight in the absence of light. The reaction mixture was then heated to 50 ºC for 2 h after which it was cooled down to room temperature and washed with saturated $NaHCO_3$ solution and brine. After the separation of organic layer, the aqueous layer was further extracted with $CHCl_3$ and the combined organic layers were dried over $MgSO_4$. The concentrated mixture was poured into methanol and filtered, giving the target compound as a deep violet solid. Yield: 275 mg, 91%).^{1}H-NMR in $CDCl_3$: 6.96, s, 1H (thiophene H4 position); 2.78, t, 2H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.89, t, 3H (methyl).

Poly-3-bromo-4-hexylthiophene, 1b (5% brominated). To a solution of P3HT (300 mg, 1.8 mmol) in 150 mL of $CHCl_3$ was added 16 mg (0.05 equivalent) of NBS. The following steps are the same as those for **1a.** Yield: 266 mg, 87%.^{1}H-NMR in $CDCl_3$: 6.96, s, 0.95H (thiophene H4 position); 2.78, t, 1.9H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.35, m, 4H (other methylene); 0.89, t, 3H (methyl). For the brominated thiophene rings, α-methylene protons appear at 2.60 ppm. Its respective peak integration (0.1H) is consistent with a 5% post-functionalized P3HT.

Poly-3-bromo-4-hexylthiophene, 1c (10% brominated). To a solution of P3HT (200 mg, 1.2 mmol) in 100 mL of $CHCl_3$ was added 23.7 mg (0.11 equivalent) of NBS. The following steps are the same as those for **1a**. (Yield: 180 mg, 62%). The ^{1}H-NMR result

showed 10% bromination of thiophene 3-position. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.9H (thiophene H4 position); 2.79, t, 1.8H (α-methylene); 1.70, m, 2H (β-methylene); 1.43, m, 2H and 1.35, m, 4H (other methylene); 0.90, t, 3H (methyl). For the brominated thiophene rings, α-methylene protons appear at 2.60 ppm. Its respective peak integration (0.2H) is consistent with a 10% post-functionalized P3HT.

Poly-3-bromo-4-hexylthiophene, 1d (20% brominated). Using a similar procedure as explained above for **1a**, the 20% brominated P3HT was synthesized from P3HT (400 mg, 2.4 mmol) in 175 mL of $CHCl_3$ and 86 mg (0.2 equivalent) of NBS. Yield 380 mg, 65%.^{1}H-NMR in $CDCl_3$: 6.96, s, 0.82H (thiophene H4 position); 2.78, t, 1.64H (α-methylene); 1.68, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.86-0.89, dt, 3H (methyl). For the brominated thiophene rings, α-methylene protons appear at 7.01 and 2.60 ppm, respectively. Its respective peak integration (0.36H) is consistent with a ~18% post-functionalized P3HT.

Poly-3-bromo-4-hexylthiophene, 1e (30% brominated). To a solution of P3HT (320 mg, 1.8 mmol) in 150 mL of $CHCl_3$ was added 103 mg (0.3 equivalent) of NBS. The following steps are the same as those for **1a** (Yield: 300 mg, 82%).^{1}H-NMR in $CDCl_3$: 6.96, s, 0.7H (thiophene H4 position); 2.78, t, 1.5H (α-methylene); 1.68, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.86-0.89, dt, 3H (methyl). For the brominated thiophene rings, α-methylene and methyl protons appear at 2.60 and 0.86 ppm, respectively. Their respective peak integrations (0.5H and 0.9H) is consistent with a >25% post-functionalized P3HT.

1-(4'-Bromophenyl)-1-(2",2",6",6"-tetramethyl-1-piperidinyloxy)ethyl, 2. To a solution of 4-bromostyrene (25.33 g, 0.138 mol) and 2,2,6,6-tetramethyl-1-piperidinyloxy

(TEMPO) (21.63 g, 0.138 mol) in 1:1 toluene/ethanol (850 mL) was added (*R*,*R*)[N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato] manganese(III) chloride (Jacobsen's catalyst; 13.22 g, 0.021 mol) followed by di-tert-butyl peroxide (20.2 g, 0.138 mol) and sodium borohydride (10.51 g, 0.279 mol). The reaction mixture was then stirred at room for 5 days under constant flow of air through the solution. The reaction mixture was then evaporated to dryness, partitioned between CH_2Cl_2 (250 mL) and water (400 mL), and the aqueous layer further extracted with CH_2Cl_2 (3 × 200 mL). The combined organic portions were dried over $MgSO_4$ and loaded onto 160 g of silica gel and evaporated to dryness. The crude loaded silica gel (divided in three portions) then dispersed in hexane, packed in a column on top of fresh silica gel and eluted with hexane. The solvent polarity was gradually increased by addition of ethylacetate to 5%. The desired bromo-substituted alkoxamine, **5**, was obtained as white solid upon addition of ethanol to the concentrate. The product was further purified by recrystallization from ethanol. Yield 23.1 g (49%). ^{1}H-NMR in $CDCl_3$: 7.41, d, 2H and 7.17, d, 2H (aromatic protons); 4.71, q, 1H (CH-O); 1.46, b, 2H, 1.43, b, 2H and 1.35, b, 2H (piperidinyl CH_2); 1.42, d, 3H, (CH_3); 1.25, s, 3H, 1.13, s, 3H, 0.99, s, 3H and 0.62, s, 3H (piperidinyl CH_3).

1-[4-(4'-trimethylene-1,3,2-dioxaborolan-2-yl)phenyl]-1-(2,2,6,6-tetramethyl-1-piperidinyloxyl)ethane, 3. To a solution of **2** (3.10 g, 9.0 mmol) in 160 mL of THF under nitrogen at -78 °C, *n*-BuLi (2.5 M in hexane, 7.2 mL, 18 mmol) was injected using a syringe. The mixture was then allowed to warm up to 0 °C over 2 h and again cooled down to -78 °C. Triethylborate (4.6 mL, 27 mmol) was injected into the reaction and the mixture was allowed to warm up gradually to room temperature. It was stirred overnight followed by addition of aqueous NH_4Cl (10%). The organic phase was separated and the

aqueous layer was subjected to extraction with ether. The organic layers were combined, washed with brine (5%) and dried over $MgSO_4$. The mixture was evaporated to dryness, dissolved in 150 mL of $CHCl_3$ and stirred with $MgSO_4$ (9 g) and 1,3-propandiol (1.0 mL, 14 mmol) overnight. Following filtration, the organic layer was washed with water (2 ×100 mL) and dried over $MgSO_4$. The solvent was removed under vacuum and a white precipitate was formed upon addition of methanol. The product was further purified by recrystallization from methanol. Yield 2.20 g (70%). ^{1}H-NMR in CD_2Cl_2: 7.66, d, 2H and 7.28, d, 2H (aromatic protons); 4.76, q, 1H (CH-O); 4.13, t, 4H (ester α-methylene); 2.04, m, 2H (ester β-methylene); 1.47, b, 2H, 1.45, b, 2H and 1.35, b, 2H (piperidinyl CH_2); 1.42, d, 3H, (CH_3); 1.28, s, 3H, 1.15, s, 3H, 1.02, s, 3H and 0.62, s, 3H (piperidinyl CH_3).

Tempo(1%)-P3HT macroinitiator, 4a. Partially (1%) brominated poly-3-bromo-4-hexylthiophene, **1a** (208 mg), Tempo-styrene boronic ester **3** (15 mg) and $Pd(PPh_3)_4$ (5 mg, 0.0043 mmol) were dissolved in 30 mL THF and degassed by three cycles of freeze-pump-thaw. Under a flow of nitrogen, a degassed solution of K_2CO_3 (55 mg in 0.2 mL, 0.2 mmol) in water was added to this mixture through a cannula. The reaction mixture was heated at 60 ºC for 2 days under nitrogen. The concentrate was poured into MeOH and the precipitate was centrifuged and washed several times with MeOH. The crude was filtered through a short column of alumina using $CHCl_3$. The dark purple product, re-precipitated upon addition of the concentrate to MeOH, centrifuged and washed several time with MeOH and dried at 50 ºC under vacuum. Yield 210 mg.

Tempo(5%)-P3HT macroinitiator, 4b. Partially (5%) brominated poly-3-bromo-4-hexylthiophene, **1b** (228 mg), Tempo-styrene boronic ester **3** (34 mg, 0.1mmol) and $Pd(PPh_3)_4$ (5 mg, 0.0043 mmol) were dissolved in 30 mL THF and degassed by three

cycles of freeze-pump-thaw. Under a flow of nitrogen, a degassed solution of K_2CO_3 (55 mg in 0.2 mL, 0.2 mmol) in water was added to this mixture through a cannula. The following steps are the same as those for **4a**. Yield 215 mg.

Tempo(10%)-P3HT macroinitiator, 4c. Partially (10%) brominated poly-3-bromo-4-hexylthiophene, **1c** (162 mg), Tempo-styrene boronic ester **3** (35 mg, 0.10 mmol) and $Pd(PPh_3)_4$ (5 mg, 0.0043 mmol) were dissolved in 20 mL THF. The mixture was purged with N_2 for 20 min before a degassed solution of K_2CO_3 (55 mg in 0.2 mL, 0.2 mmol) in water was added to this mixture through a cannula. The following steps are the same as those for **4a**. Yield 150 mg (84%). ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.9H (thiophene H4 position); 4.72, q, 0.1H (CH-O); 2.60-2.78, t, 2H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.89, t, 3H (methyl). For the tempo grafted thiophene rings, H4 and α-methylene protons appear at 7.02 and 2.60 and ppm, respectively.

Tempo(20%)-P3HT macroinitiator, 4d. Same procedure as above, with the exception that **1d** (270 mg, 1.48 mmol), is used to obtain **4d**. Yield 288 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.8H (thiophene H4 position); 4.72, q, 0.2H (CH-O); 2.60-2.78, t, 2H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.86-0.89, t, 3H (methyl). For the tempo grafted thiophene rings, H4 and α-methylene protons appear at 7.02 and 2.60 and ppm, respectively.

Tempo(30%)-P3HT macroinitiator, 4e. Same procedure as above, with the exception that **1e** (162 mg, 0.85 mmol), is used to obtain **4e**. Yield 150 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.8H (thiophene H4 position); 4.72, q, 0.2H (CH-O); 2.60-2.78, t, 2H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene);

0.86-0.89, t, 3H (methyl). For the tempo grafted thiophene rings, H4 and α-methylene protons appear at 7.02 and 2.60 and ppm, respectively. Traces for tempo-modified ends are observable at 7.14, 4.72, 1.13, 0.95, 0.79 and 0.49 ppm.

Poly(hexylthiophene)-*1%graft*-poly(ST-*stat*-CMS) (ST/CMS, 2:1), 5a. A mixture of **4a** (100 mg), styrene (2 mL) and chloromethylstyrene (1.25 mL) was purged with nitrogen for 20 min before heating to 100 ºC for 24 h. The product was poured into MeOH and centrifuged. The crude was dissolved in $CHCl_3$ and loaded on Silica gel. Flash chromatography was performed to remove the styrene homopolymer with an increasing solvent gradient of acetone in MeOH (from 20 to 50 and 100% to remove any monomers) followed by $CHCl_3$ in acetone (from 10 to 20, 40 and 80% to remove oligomers and/or copolymers of ST/CMS). Finally the product was eluted with $CHCl_3$ and the concentrate poured into MeOH. The product was centrifuged, washed with MeOH and vacuum dried. Yield 103 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 1H (thiophene H4 position); 2.79 and 2.60, t, 2H (α-methylene); 1.69, m, 2H (β-methylene); 1.42, m, 2H and 1.34, m, 4H (other methylene); 0.90, t, 3H (methyl). Broad peaks at 7.0-7.2, 6.3-6.7, 4.4-4.6 ppm were attributed to the side chain (CMS and ST) phenyl protons and chloromethylene ones, respectively.

Poly(hexylthiophene)-*5%graft*-poly(ST-*stat*-CMS) (ST/CMS, 3:1), 5b. A mixture of **4b** (41 mg), styrene (2 mL) and chloromethylstyrene (0.84 mL) was purged with nitrogen for 20 min before heating to 110 ºC for 24 h. The following steps are the same as those for **5a**. Yield 120 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.9H (thiophene H4 position); 2.78 and 2.60, t, 2H (α-methylene); 1.70, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.89, t, 3H (methyl); Also observable is a shoulder at 0.82 ppm.

Broad peaks at 7.0-7.2, 6.3-6.7, 4.4-4.6 ppm were attributed to the side chain (CMS and ST) phenyl protons and chloromethylene, respectively.

Poly(hexylthiophene)-*10%graft*-poly(ST-*stat*-CMS) (ST/CMS, 5:1), 5c. A mixture of **4c** (43 mg), styrene (2 mL) and chloromethylstyrene (0.5 mL) was purged with nitrogen for 20 min before heating to 100 ºC for 6 h. The following steps are the same as those for **5a**. Yield 95 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.9H (thiophene H4 position); 2.78 and 2.60, t, 2H (α-methylene); 1.70, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.89, t, 3H (methyl); Also observable is a shoulder at 0.82 ppm. Broad peaks at 7.0-7.2, 6.3-6.7, 4.4-4.6 ppm were attributed to the side chain (CMS and ST) phenyl protons and chloromethylene, respectively.

Poly(hexylthiophene)-2*0%graft*-poly(ST-*stat*-CMS) (ST/CMS, 5:1), 5d. A mixture of **4d** (41 mg), styrene (2 mL) and chloromethylstyrene (0.5 mL) was purged with nitrogen for 20 min before heating to 100 ºC for 6 h. The following steps are the same as those for **5a**. Yield 203 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.8H (thiophene H4 position); 2.78 and 2.60, t, 2H (α-methylene); 1.70, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m, 4H (other methylene); 0.89, t, 3H (methyl); Also observable is a shoulder at 0.82 ppm. Broad peaks at 7.0-7.2, 6.3-6.7, 4.4-4.6 ppm were attributed to the side chain (CMS and ST) phenyl protons and chloromethylene, respectively.

Poly(hexylthiophene)-*30%graft*-poly(ST-*stat*-CMS) (ST/CMS, 5:1), 5e. A mixture of **4e** (43 mg), styrene (2 mL) and chloromethylstyrene (0.5 mL) was purged with nitrogen for 20 min before heating to 100 ºC for 6 h. The following steps are the same as those for **5a**. Yield 161 mg. ^{1}H-NMR in $CDCl_3$: 6.96, s, 0.7H (thiophene H4 position); 2.78 and 2.60, t, 2H (α-methylene); 1.70, m, 2H (β-methylene); 1.42, m, 2H and 1.33, m,

4H (other methylene); 0.89, t, 3H (methyl); Also observable is a shoulder at 0.82 ppm. Broad peaks at 7.0-7.2, 6.3-6.7, 4.4-4.6 ppm were attributed to the side chain (CMS and ST) phenyl protons and chloromethylene ones, respectively.

P3HT-*n%graft*-(ST-*stat*-N_3MS), 6 (N_3MS denotes azidomethylstyrene). To a solution of ~100 mg of P3HT-*n%graft*-(ST-stat-CMS), **5** in chlorobenzene (CB, 70 mL) was added excess (4 or more equivalents) of sodium azide in DMF (30 mL). The CB to DMF mixing ratio (70:30) was chosen to keep both the polymer and sodium azide dissolved upon mixing. The mixture was heated at 100 ºC for 3-6 h under nitrogen. After cooling the mixture to room temperature, it was poured into MeOH (200 mL) and stirred. The precipitate was centrifuged, washed with MeOH/H2O (4:1 v/v) and MeOH sequentially and vacuum dried. The product, if needed, can be further purified by Soxhlet extraction using MeOH and hexane sequentially. Conversion to the azide form is quantitative.

P3HT-*5%graft*-(ST-*stat*-NMS)-*graft*-C_{60}, 7b. A mixture of **6b** (20 mg) and C_{60} (34 mg) in 50 mL 1,2-dichlorobenzene (1,2-DCB) purged with Ar for 30 min and stirred at 70 ºC for 5 days. The reaction mixture was poured into 150 mL of hexane and the precipitate was centrifuged. The crude was re-dissolved in CB and re-precipitated in hexane 4 times after which the absorption spectrum remained essentially the same. The hexane was decanted and the product was dissolved in CB, sealed under Ar and kept at -10 ºC until further use. Elemental analysis (based on GPC, NMR and TGA results) calculated: C = 82.12; H = 4.92; N = 4.49; found: C = 81.94; H = 4.83; N = 4.32.

P3HT-*10%graft*-(ST-*stat*-NMS)-*graft*-C_{60}, 7c. A mixture of **6c** (20 mg) and C_{60} (16 mg) in 25 mL DCB, purged with Ar for 30 min, was stirred at 70 ºC for 5 days. The

following steps were the same as described for **7b**. Calculated: C = 82.54; H = 5.88; N = 2.30; found: C = 82.36; H = 6.81; N = 1.94.

P3HT-*20%graft*-(ST-*stat*-NMS)-*graft*-C_{60}, 7d. A mixture of **6d** (40 mg) and C_{60} (40 mg) in 50 mL DCB, purged with Ar for 30 min, was stirred at 70 ºC for 5 days. The following steps were the same as described for **7b**. Calculated: C = 86.70; H = 5.55; N = 2.10; found: C = 86.24; H = 6.36; N = 2.06.

P3HT-*30%graft*-(ST-*stat*-NMS)-*graft*-C_{60}, 7e. A mixture of **6e** (21 mg) and C_{60} (26 mg) in 25 mL, DCB purged with Ar for 30 min, was stirred at 70 ºC for 5 days. The following steps were the same as described for **7b**. Calculated: C = 85.89; H = 4.63; N = 1.82; found: C = 85.69; H = 6.38; N = 1.69.

P3HT-1*%graft*-(ST-*stat*-NMS)-*graft*-PCBM, 8a. A mixture of **6a** (15 mg) and PCBM (15 mg) in 25 mL, DCB purged with Ar for 30 min, was stirred at 85 ºC for 1 day. The reaction mixture was poured into 150 mL of hexane and the precipitate was centrifuged. The crude was re-dissolved in CB and re-precipitated in hexane 2 times (NMR spectroscopy confirmed the absence of the esteric methyl protons at 3.66 ppm due to free PCBM). The hexane was decanted and the product was dissolved in CB and vial sealed under Ar until further use.

P3HT-*5%graft*-(ST-*stat*-NMS)-*graft*-PCBM, 8b. A mixture of **6b** (20 mg) and PCBM (48 mg) in 25 mL, CB purged with Ar for 30 min, was stirred at 85 ºC for 5 days. The following steps were the same as described for **8a**. Calculated: C = 79.15; H = 5.60; N = 4.61; found: C = 79.40; H = 5.34; N = 4.58.

P3HT-*10%graft*-(ST-*stat*-NMS)-*graft*-PCBM, 8c. A mixture of **6c** (20 mg) and PCBM (16 mg) in 10 mL CB purged with Ar for 30 min and stirred at 85 ºC for 2 days.

The following steps were the same as described for **8a**. Calculated: C = 81.55; H = 5.73; N = 1.90; found: C = 81.49; H = 7.09; N = 1.82.

P3HT-*20%graft*-(ST-*co*-NMS)-*graft*-PCBM, 8d. A mixture of **6d** (20 mg) and PCBM (20 mg) in 10 mL CB, purged with Ar for 30 min, was stirred at 85 ºC for 2 days. The reaction mixture was poured into 90 mL of hexane and the precipitate was centrifuged. The crude was purified with the same procedure described for **8a**. Calculated: C = 85.03; H = 6.16; N = 2.04; found: C = 85.50; H = 6.77; N = 2.37.

P3HT-*30%graft*-(ST-*stat*-NMS)-*graft*-PCBM, 8e. A mixture of **6e** (21 mg) and PCBM (26 mg) in 15 mL CB, purged with Ar for 30 min, was stirred at 85 ºC for 2 days. The crude was purified with the same procedure described for **8a**. Calculated: C = 84.86; H = 5.97; N = 2.23; found: C = 84.67; H = 6.44; N = 1.88.

NMR Spectra

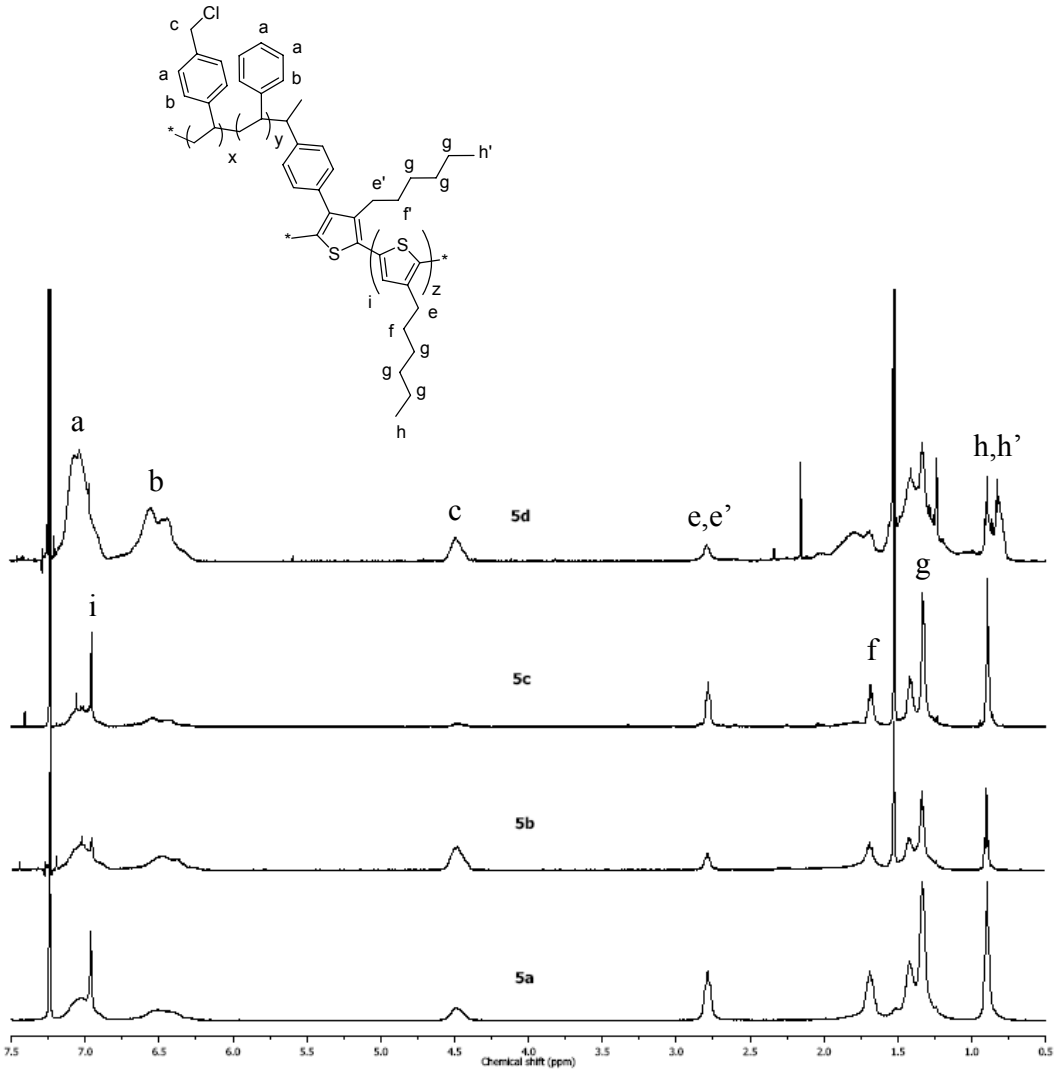

Figure S1. ^{1}H-NMR spectrum of **5a-d** in $CDCl_3$. Peaks at 7.24 and 1.54 ppm are due to solvent and trace water, respectively. The peak at 2.15 in **5d** corresponds to residual acetone in this sample. The peaks at 4.5 and 6.5 ppm assigned to -CH_2Cl and the aromatic protons of ST/CMS, respectively.

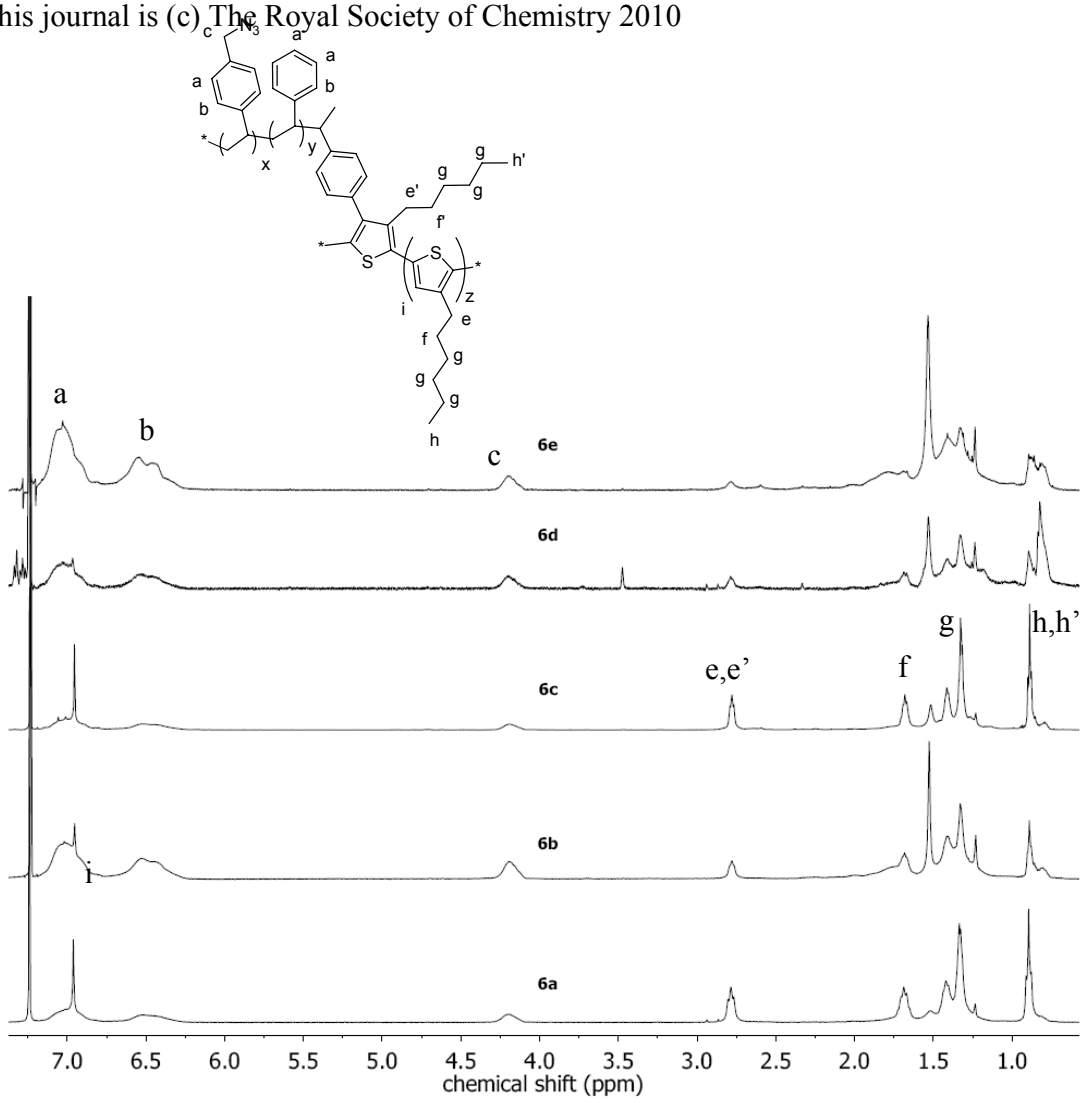

Figure S2. ^{1}H-NMR spectrum of **6a-e** in $CDCl_3$. The peaks assigned to -CH_2N_3 and the aromatic protons of ST/CMS are observed at 4.2 and 6.5 ppm, respectively. Peaks at 7.24 and 1.54 ppm are due to solvent and trace water, respectively.

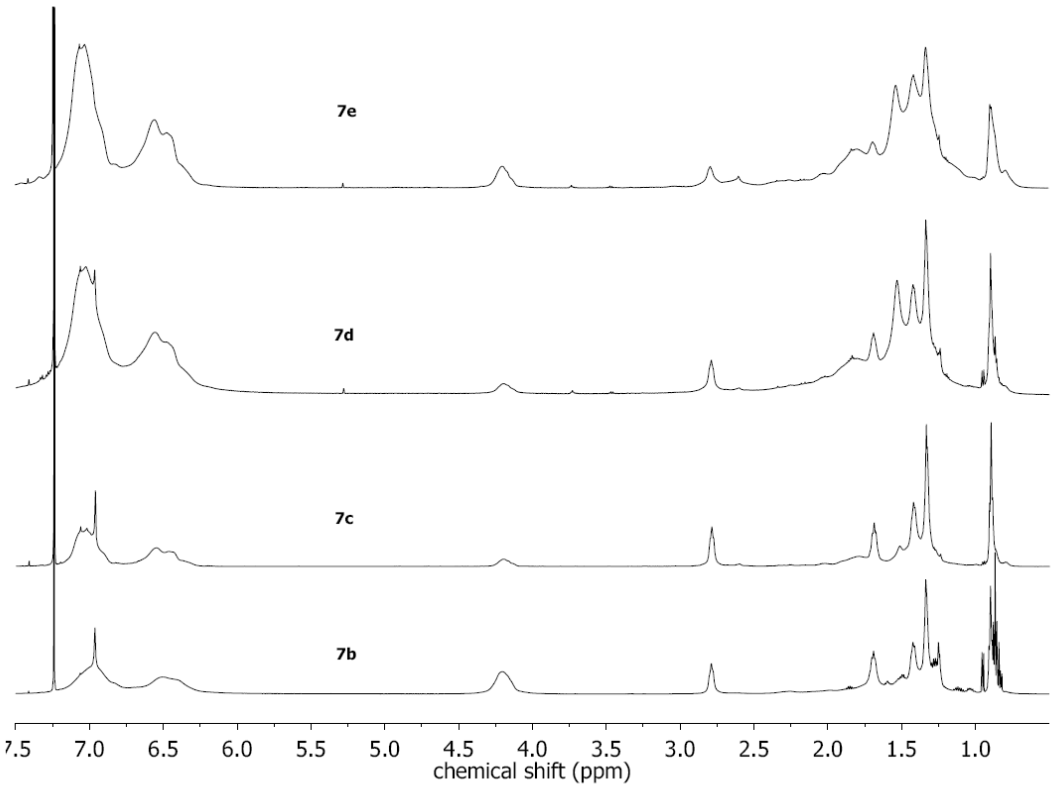

Figure S3. ^{1}H-NMR spectrum of C_{60}-graft copolymers **7b-e** in $CDCl_3$. For proton assignments see **Figure S2**.

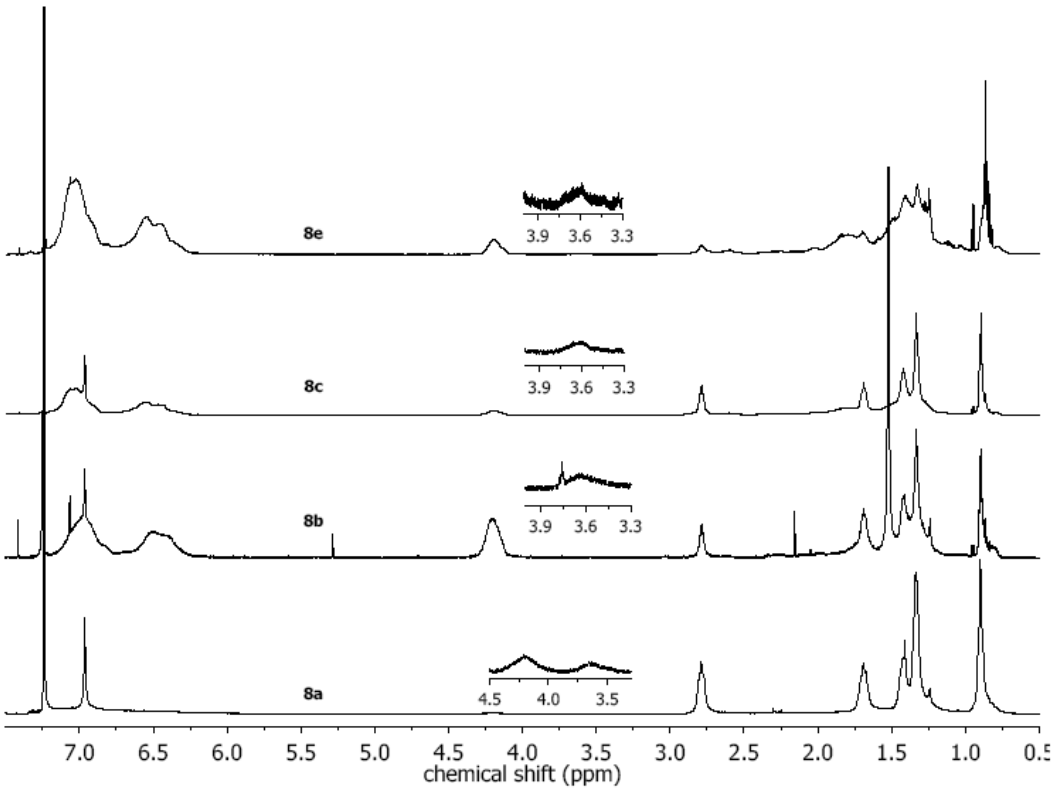

Figure S4. Proton NMR spectrum of the PCBM-graft copolymers **8a-c** and **8e** in $CDCl_3$. For proton assignments see **Figure S2**. The insets show the peak of the methyl ester of PCBM centered at 3.6 ppm and, for the case of **8a**, the residual of $–CH_2N_3$ at 4.2 ppm. The peak at 1.54 is due to residual water.

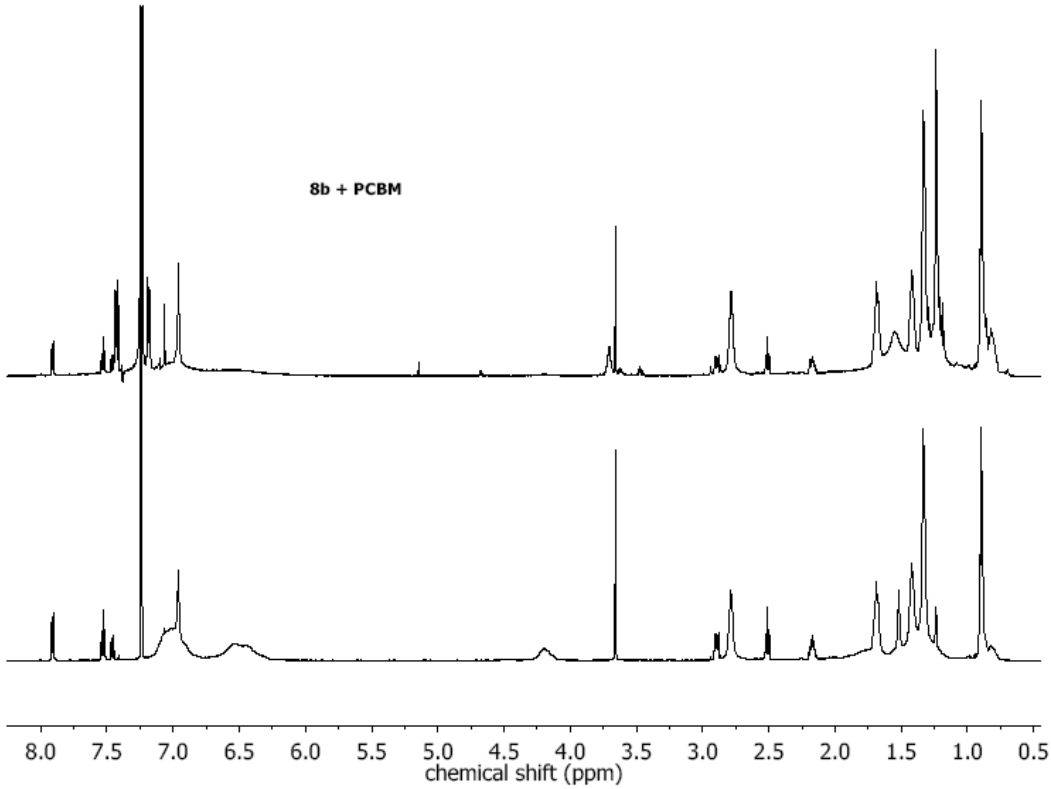

Figure S5. Proton NMR spectrum of the PCBM-graft copolymer **8b** containing free PCBM (top) following the reaction between **6b** and PCBM (bottom) in $CDCl_3$. The PCBM protons are observed at 2.17, 2.51, 2.89, 3.66, 7.46, 7.53 and 7.90 ppm. The residual of $–CH_2N_3$ is centered at 4.2 ppm. The peak at 1.54 is due to residual water.

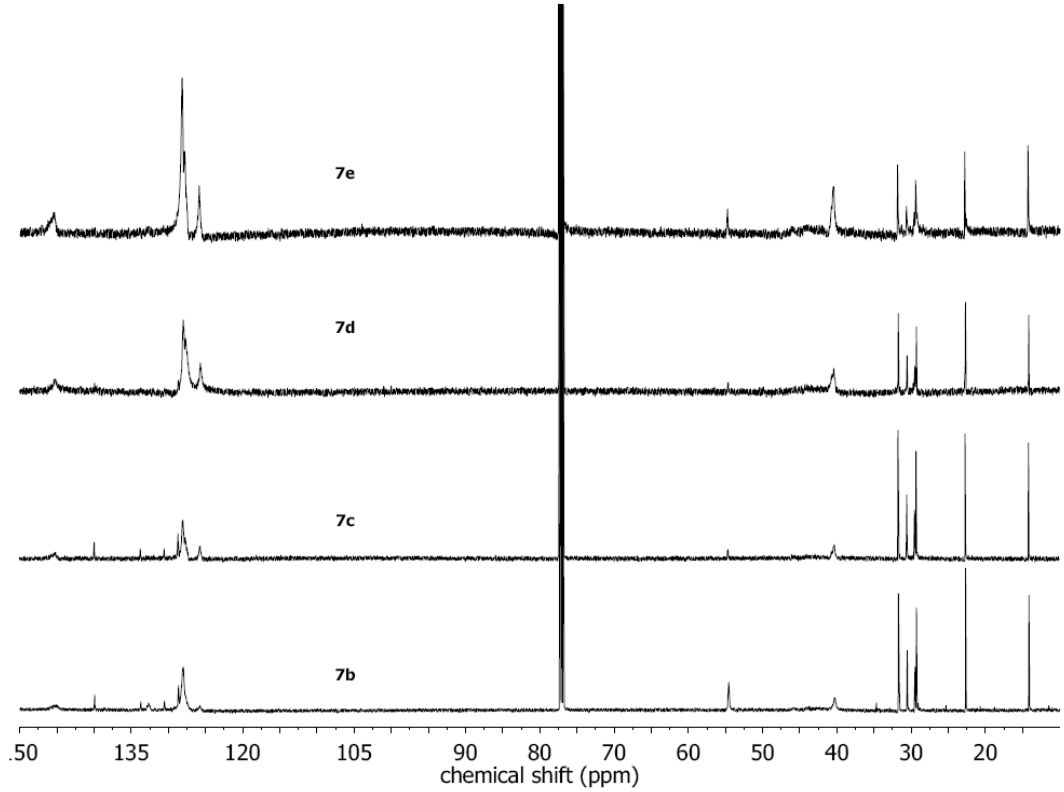

Figure S6. Decoupled ^{13}C NMR of the C_{60}-graft copolymers **7b-e** in $CDCl_3$. Six sharp peaks observed at 14.35, 22.88, 29.49, 29.69, 30.73 and 31.92 ppm are attributed to hexyl chain carbons while broad peaks at 40.47, 43.08 and 46.24 are due to CMS/S side chains. The $–CH_2N$ carbon appears at 57.80. The thiophene carbons are observed between 125-146 ppm in the aromatic region. The broad peak centered at 145 ppm is due to the grafted C_{60}.

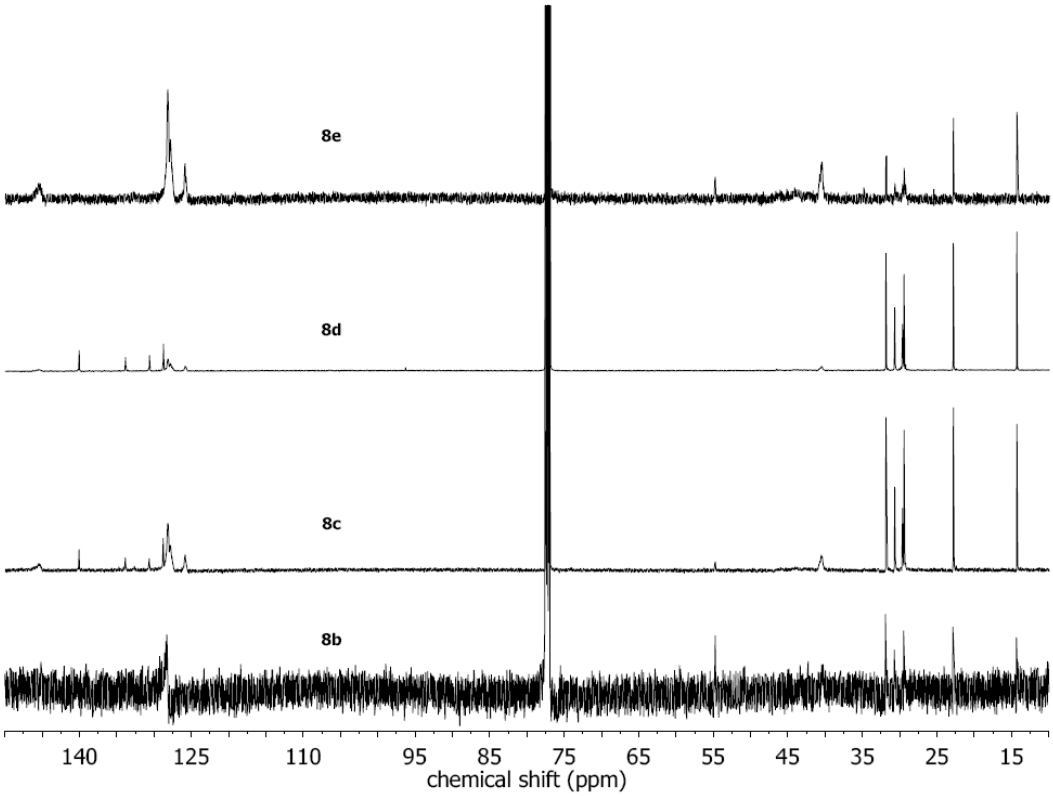

Figure S7. Decoupled ^{13}C NMR of the PCBM-graft copolymers **8b-e** in $CDCl_3$. Six sharp peaks observed at 14.35, 22.88, 29.48, 29.68, 30.73 and 31.92 ppm are attributed to hexyl chain carbons while broad peaks at 40-46 ppm are due to CMS/S side chains. The $-CH_2N$ carbon appears at 54.79. The thiophene carbons are observed between 125-146 ppm in the aromatic region. The broad peak centered at 145 ppm is assigned to the grafted PCBM.

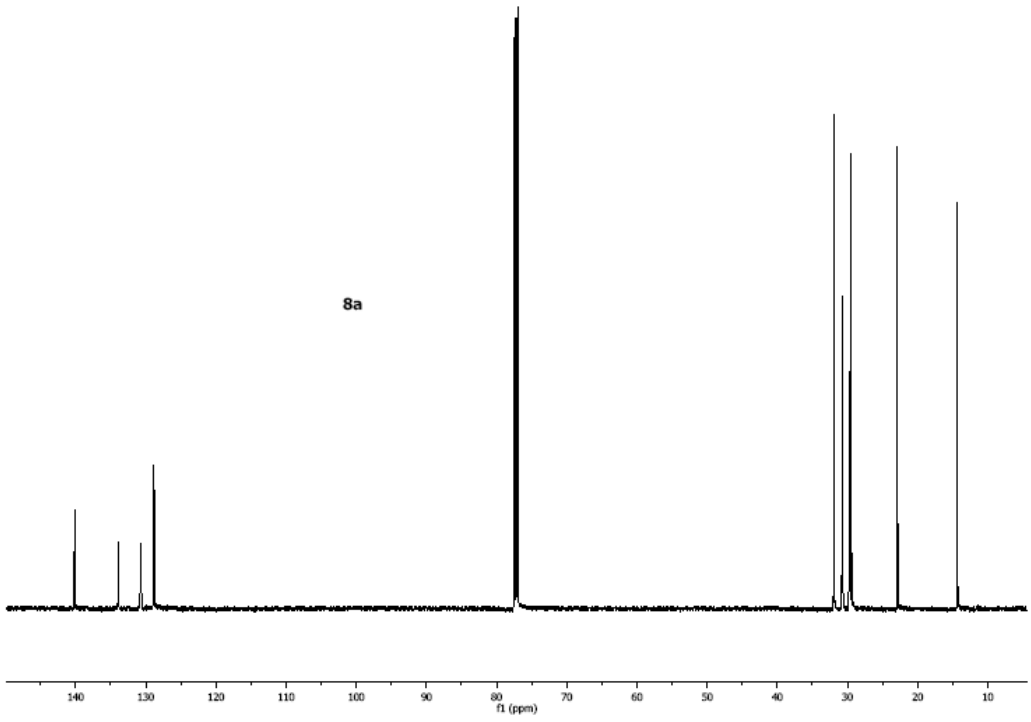

Figure S8. Decoupled ^{13}C NMR of the PCBM-graft copolymer **8a** in $CDCl_3$. Six sharp peaks observed at 14.35, 22.88, 29.49, 29.69, 30.73 and 31.92 ppm are attributed to hexyl chain carbons. The thiophene carbons were observed at 128.82, 130.70, 133.92 and 140.11 ppm in the aromatic region. Due to low content of PCBM, the fullerene carbons are not observable.

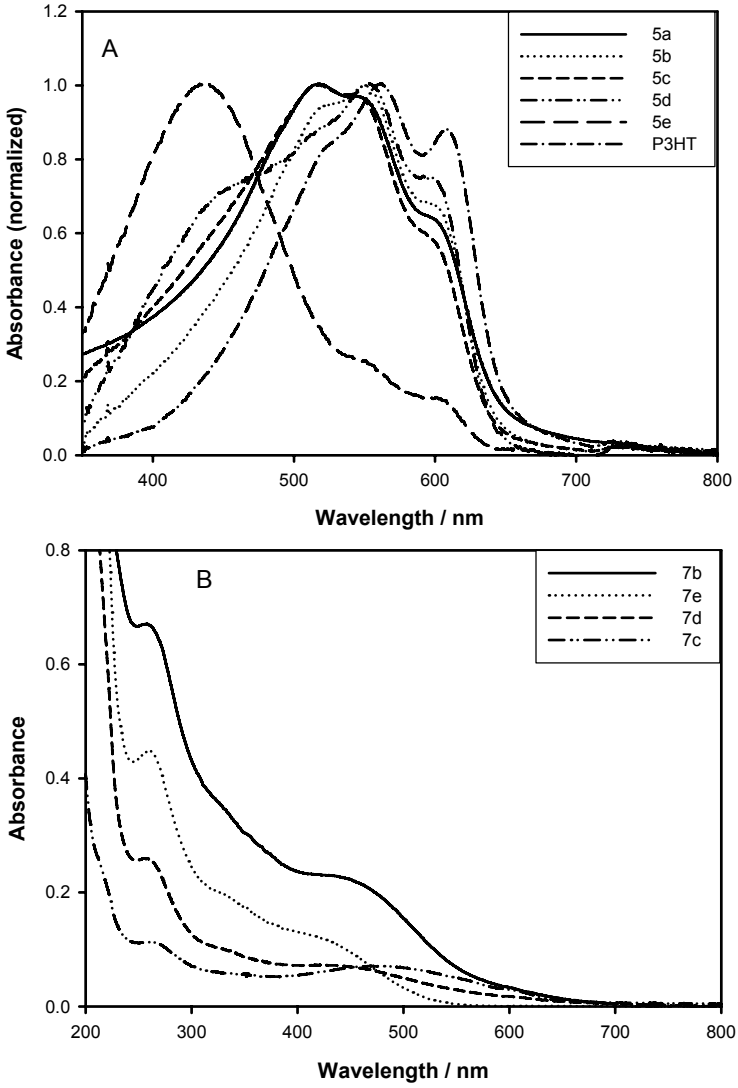

Figure S9. Solid-state absorption spectra of precursors **5a-e** (A) and C_{60}-graft copolymers **7b-e**. In B, film thicknesses are **7b**: 170, **8c**: 100, **8d**: 90 and **8e**: 130 nm.

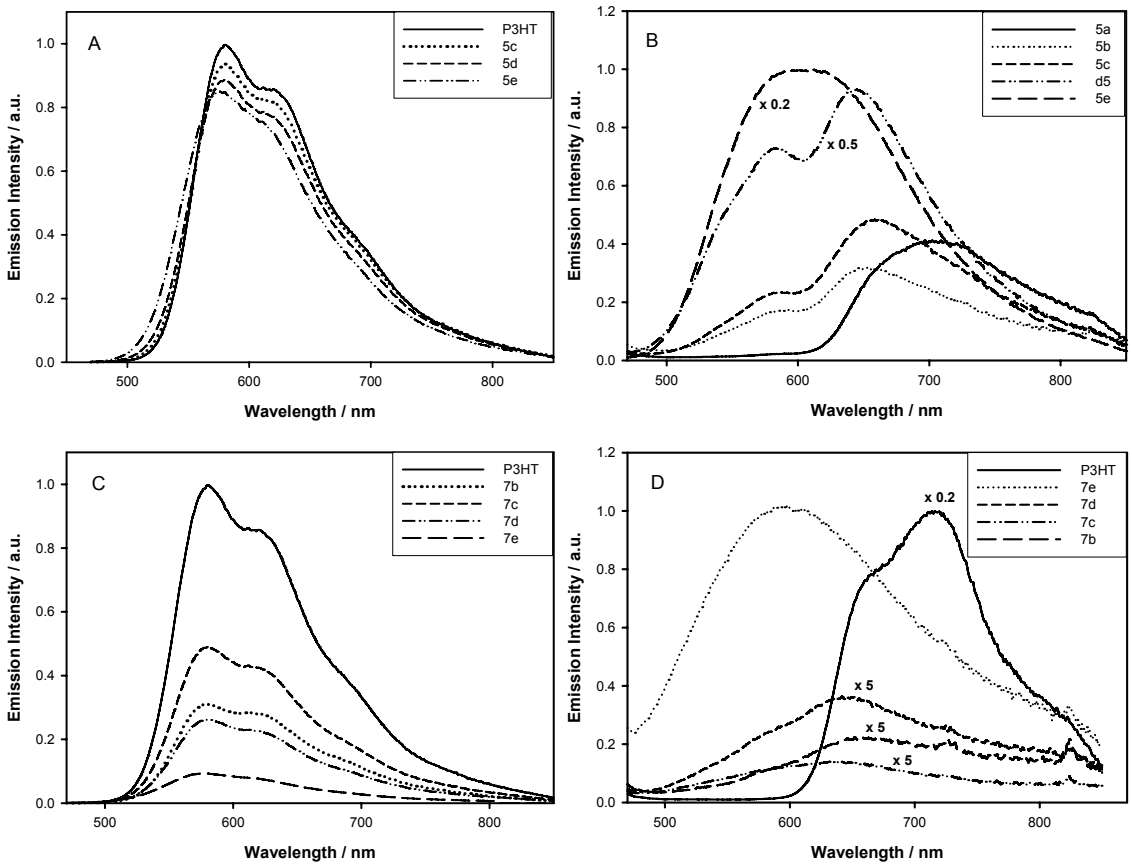

Figure S10. PL spectra of precursors **5c-e** in chloroform (A) and **5a-e** in solid state (B) and the C_{60}-graft copolymers **7b-e** in chloroform (C) and solid state (D). For comparison the normalized PL spectrum of P3HT is shown in A, C and D.

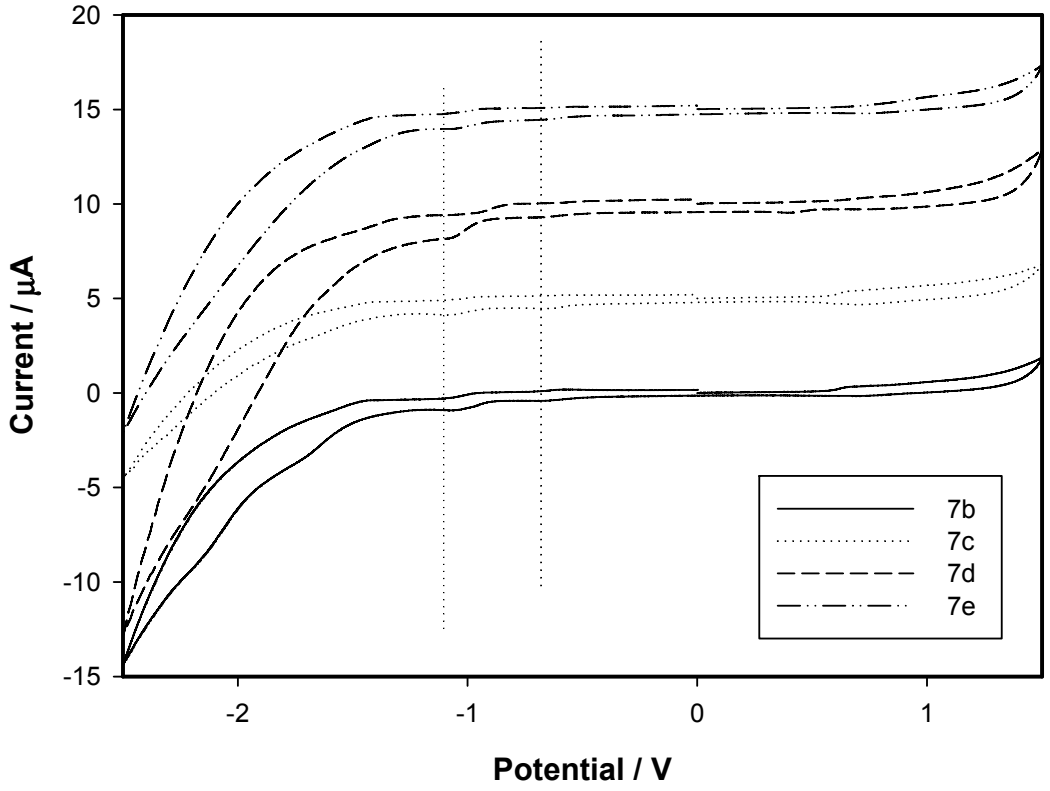

Figure S11. Cyclic voltammogram of graft copolymers **7b-e** in a mixture of chlorobenzene and dichloromethane (2:1 v/v) containing 0.1 M $TBAClO_4$ vs Ag wire at a scan rate of 100 mV/s ($E_{1/2}$ for Fc/Fc^+ couple was observed at 0.487 V in the solvent mixture). The vertical dot-lines show the first and second reduction cathodic peak potentials E_{pc} at -0.68 and -1.10 V, respectively.

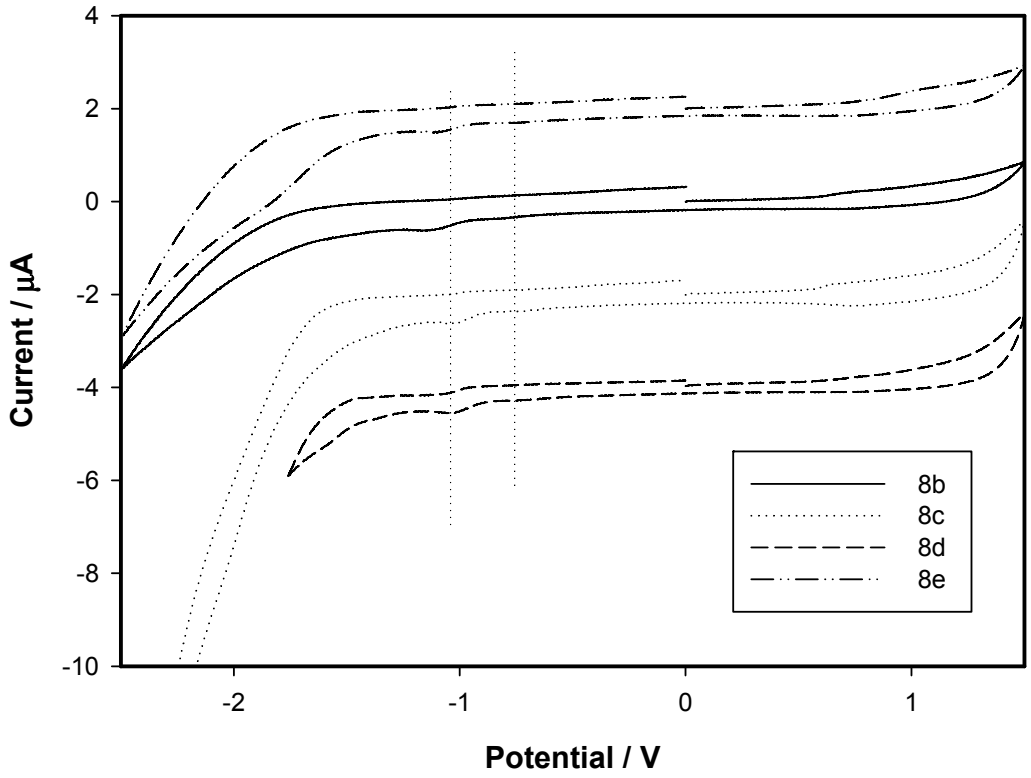

Figure S12. Cyclic voltammogram of graft copolymers **8b-e** in a mixture of chlorobenzene and dichloromethane (2:1 v/v) containing 0.1 M $TBAClO_4$ vs Ag wire at a scan rate of 100 mV/s ($E_{1/2}$ for Fc/Fc^+ couple was observed at 0.487 V in the solvent mixture). The vertical dot-lines show the first and second reduction cathodic peak potentials E_{pc} at -0.75 and -1.05 V, respectively.

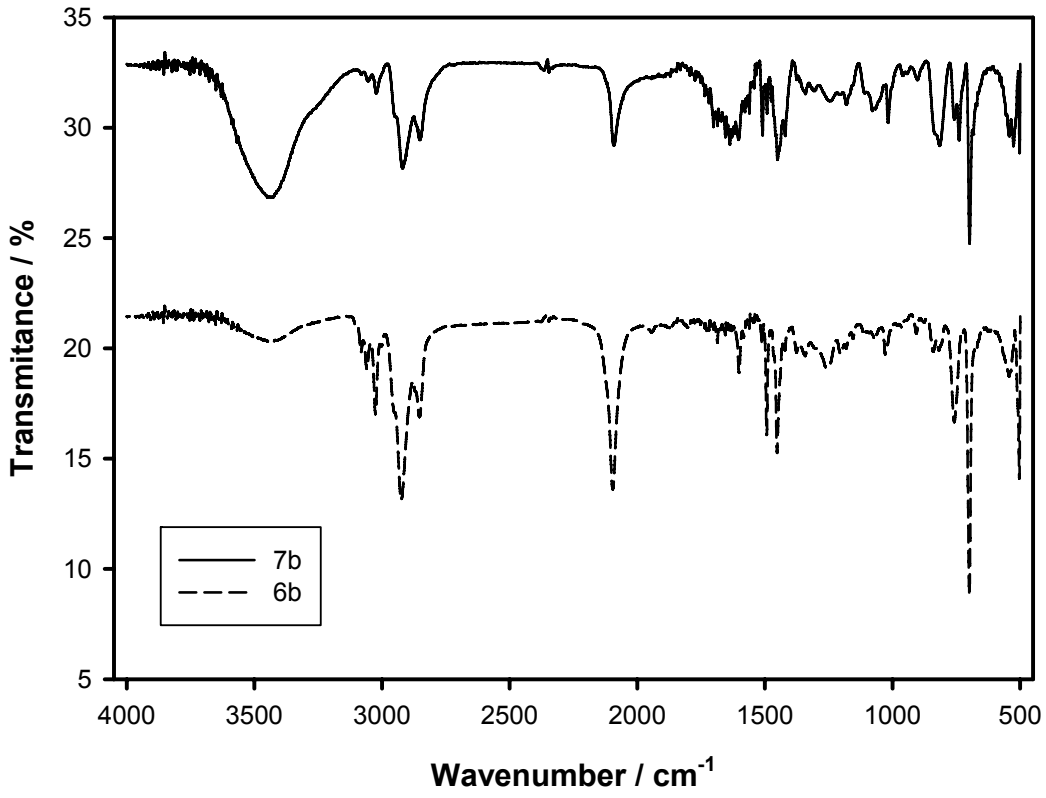

Figure S13. FTIR spectra of C_{60}-graft copolymer **7b** (solid line) and its azide form **6b** (dashed line). The peak at 2095 cm^{-1}, due to the $–N_3$ functional group, is less intense in **7b** for which the peak at 527 cm^{-1} is attributed to the grafted C_{60}.

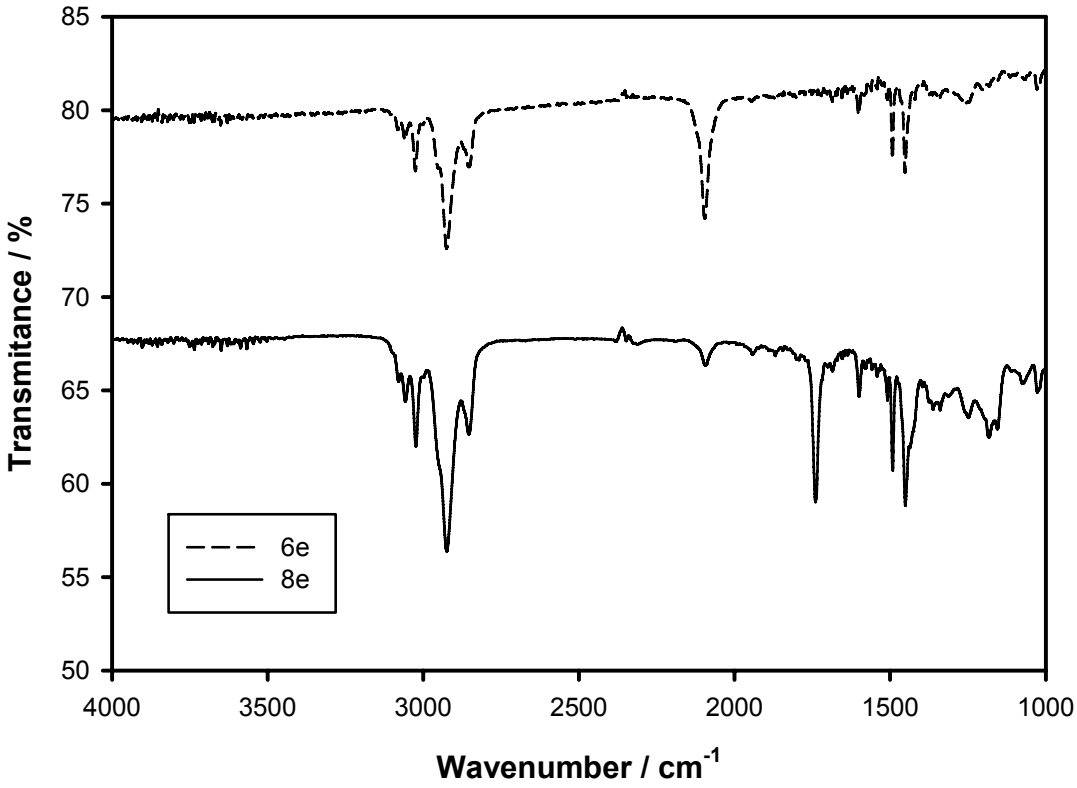

Figure S14. FTIR spectra of PCBM-graft copolymer **8e** (solid line) and its azide form **6e** (dashed line). The peak at 2095 cm^{-1}, due to the $–N_3$ functional group, is less intense in **8e.**

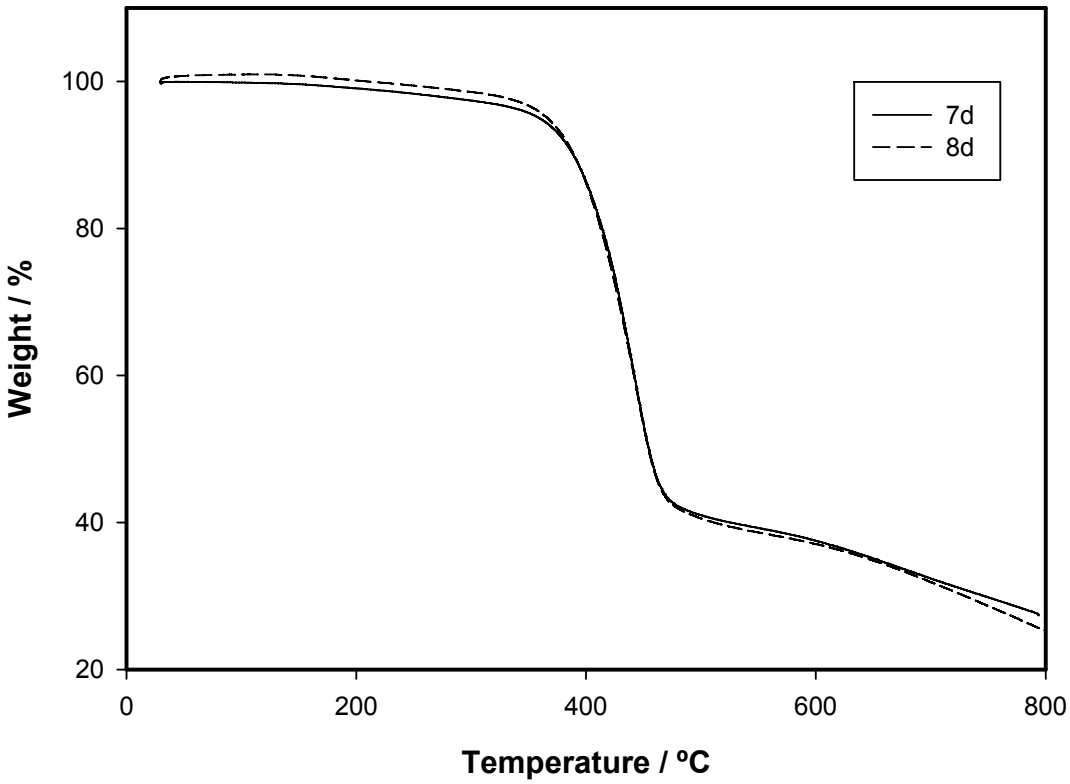

Figure S15. TGA traces of C_{60}-graft **7d** (solid line) and PCBM-graft **8d** (dashed line) copolymers recorded under N_2 at a heating rate of 10 ºC/min.

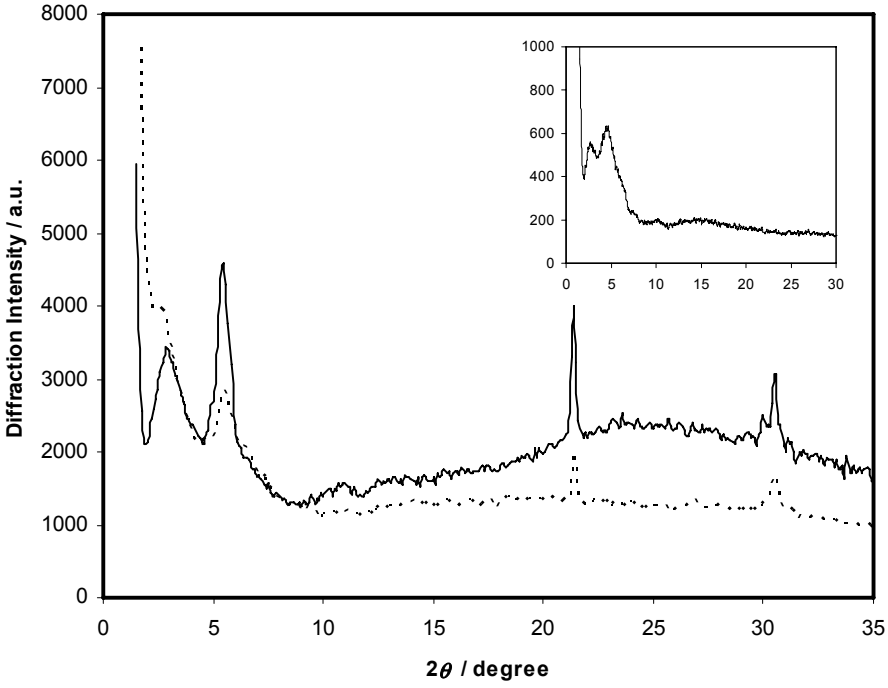

Figure S16. XRD pattern of the precursor copolymers **5a** before (solid line) and after (dashed line) thermal annealing at 150 ºC for 2 h. Films spin-coated on ITO/PEDOT-PSS from a DCB solution. The broad peak centered at 23º for P3HT is due to diffraction from glass while the sharp peaks at 21.4º and 31º are from ITO. The inset shows the XRD pattern of a film of PCBM spin-coated and slow-dried from DCB.

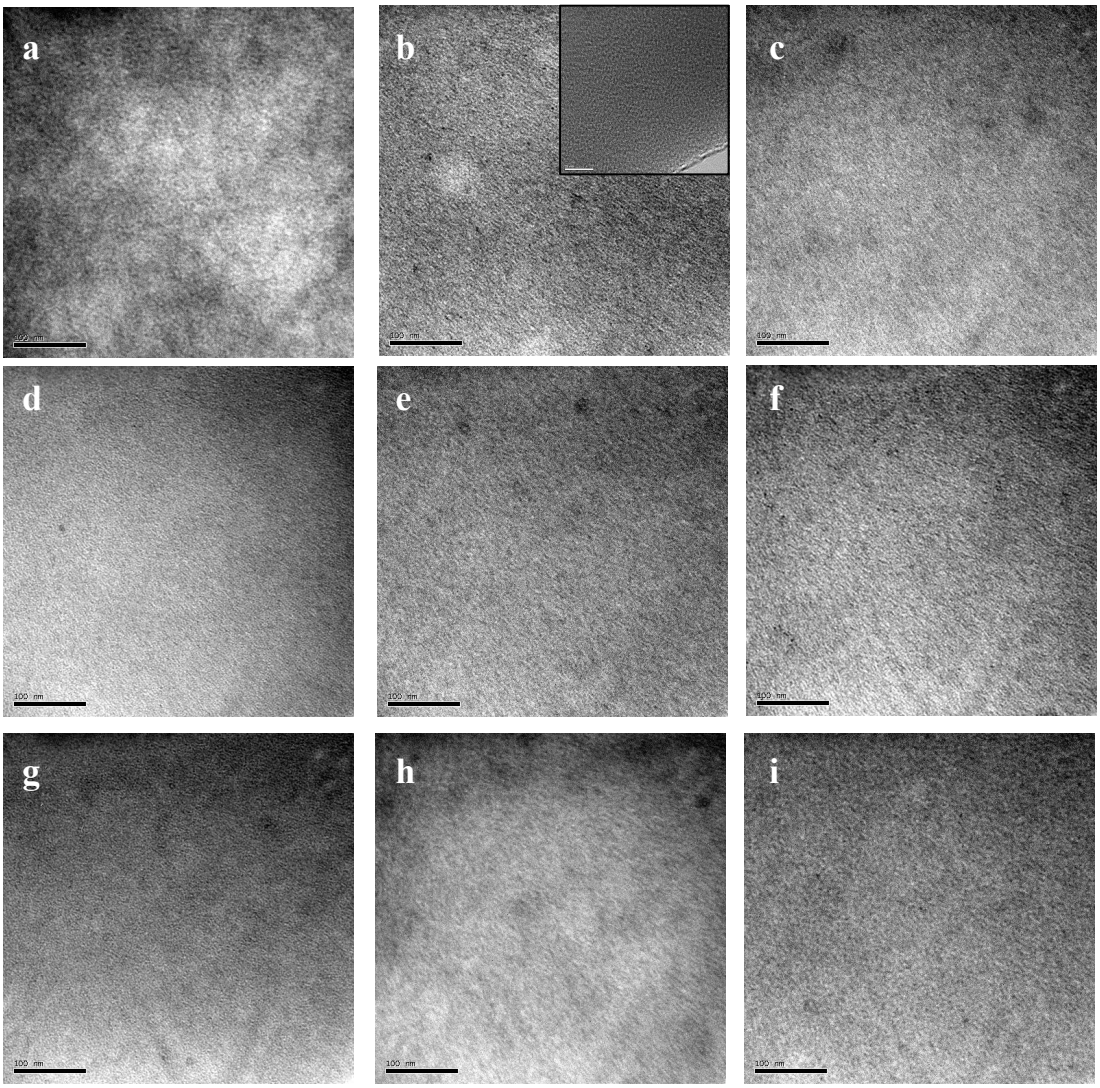

Figure S17. TEM images of the graft copolymer (a) **8a**, (b) **8b**, (c) **8c**, (d) **8d**, (e) **8e**, (f) **7b**, (g) **7c**, (h) **7d** and (i) **7e**. In b the inset shows a higher magnification (scale bar: 20 nm) for a film thermally annealed at 150 ºC for 1 h. Scale bar: 100 nm.

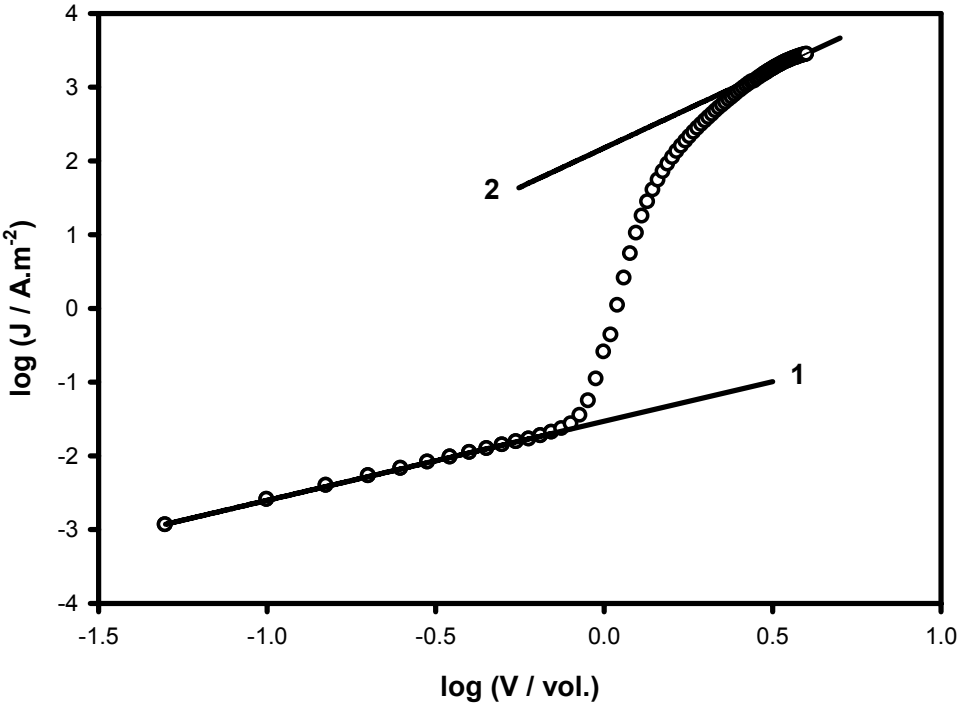

Figure S18. *J-V* characteristic for copolymer **8a** from which the hole mobility is estimated using the SCLC model. Lines show fits to the data points in the ohmic- (slope 1) and SCLC region (slope 2).