

# Supporting Information

## Azido-Functionalized Thiophene as a Versatile Building Block to Cross-Link Low-Bandgap Polymers

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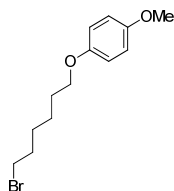
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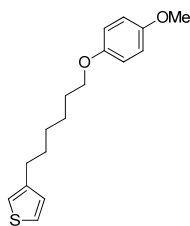
## 1 Materials and methods

2,5-bis(trimethylstannyl)thiophene **7** was obtained from Sigma-Aldrich and recrystallized before it was used in polymerizations. 4,7-bis(5-bromo-2-yl)-2,1,3-benzothiadiazole **10** and 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9"-hepta-decanylcabazole **11** were obtained from SunaTech and used as received. The reference polymers PDPP[T]<sub>2</sub>-T **P6** and PDPP[Py]<sub>2</sub>-T **P8** without azide functionalization were prepared as previously reported.<sup>1</sup> The PCDTBT reference **P9** was synthesized following a published procedure.<sup>2</sup>

## 2 Monomer synthesis

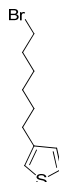


**3-(p-Methoxyphenoxy)hexylbromide 1.** In a dry 1 L flask sodium methoxide (21.76 g, 0.40 mol) was dissolved in ethanol (460 mL) and 4-methoxyphenol (40 g, 0.33 mol) was added. Finally an excess of 1,6-dibromohexane (195 mL, 1.3 mol) was added and the mixture was refluxed for 2 h. After cooling to room temperature, diethylether (250 mL) was added and the solution was washed with water. The aqueous phase was extracted with diethylether (3 x 50 mL), the combined organic layers were dried over MgSO<sub>4</sub>, filtrated and the residual solvent was removed under reduced pressure using rotary evaporation. Unreacted 1,6-dibromohexane can be removed via distillation (60-100 °C,  $5 \times 10^{-3}$  mbar). The product was purified by distillation (140-180 °C,  $5 \times 10^{-3}$  mbar) with a heated distilling connecting tube (100 °C) to avoid solidification of the product. The product **1** was obtained as 39 g of a white crystalline solid (136 mmol, 42%).

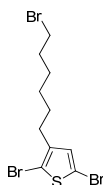


**3-(6-(4-Methoxyphenoxy)hexyl)thiophene 2.** In a dry 250 mL three-necked flask magnesium (1.69 g, 69.6 mmol) was provided under argon atmosphere. Anhydrous diethylether (140 mL) was poured into a dropping funnel from which 5 mL were added dropwise to the magnesium and stirred at rt. 3-(p-methoxyphenoxy)hexylbromide (20.0 g, 69.6 mmol) was transferred into a second dropping funnel, which was mounted on top of the first, and melted via a heat gun (250 °C). The molten starting material was slowly added to the residual anhydrous diethylether (135 mL) in the first dropping funnel. Afterwards approximately 20% of the diethylether solution were dropped to the suspended magnesium and the suspension stirred until the reaction started. Then the residual solution was slowly added dropwise to the reaction mixture and stirred for 16 h at rt and thereafter 3 h under reflux. In a second dry 250 mL flask Ni(dppp)Cl<sub>2</sub> (69.0 mg, 0.13 mmol) and 3-bromothiophene (6.0 mL, 63.3 mmol) were mixed under argon atmosphere. The Grignard-suspension in the other flask was slowly transferred via a cannula to the second flask. For this the second flask was cooled in an ice bath during the transfer. Subsequently the reaction mixture was stirred for three days under reflux in the dark. The reaction was stopped through addition of HCl (1 M, 12.5 mL, 12.5 mmol) and H<sub>2</sub>O (70 mL). The organic phase was separated from the aqueous phase, which was then extracted with diethylether (3 x 100 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtrated and the residual solvent was removed under reduced pressure.

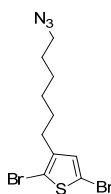
The crude product was purified via vacuum distillation at  $2\text{--}5\cdot 10^{-3}$  mbar without water cooling of the distillation apparatus and yielded 10.95 g of 3-(6-(4-methoxyphenoxy)hexyl)thiophene **2** (37.7 mmol, 60%) as white crystals.



**3-(6-Bromohexyl)thiophene 3.** In a dry 250 mL flask 3-(6-(4-methoxyphenoxy)hexyl)thiophene (10.9 g, 37.5 mmol) was dissolved in anhydrous DCM (120 mL) under argon atmosphere at rt. Afterwards boron tribromide (3.0 mL, 31.77 mmol) and then a boron tribromide solution in DCM (1 M, 10.0 mL, 10.0 mmol) were added and the mixture stirred under reflux. The reaction was monitored via gas chromatography. After 1.5 h the reaction was stopped through addition of saturated  $\text{NH}_4\text{Cl}$  solution (70 mL). The organic phase was separated from the aqueous phase, which was then extracted with DCM (3 x 100 mL). The combined organic phases were washed with  $\text{H}_2\text{O}$  (1 x 100 mL), saturated  $\text{NaHCO}_3$  solution (1 x 100 mL) and again with  $\text{H}_2\text{O}$  (1 x 100 mL). The organic phase was dried over  $\text{MgSO}_4$ , filtrated and solvents were removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane) to yield 7.98 g of 3-(6-bromohexyl)thiophene **3** (32.3 mmol, 86%) as a yellowish oil.

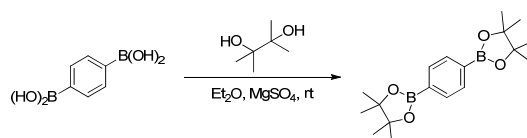


**2,5-dibromo-3-(6-bromohexyl)thiophene 4.** In a 250 mL flask 3-(6-bromohexyl)thiophene (7.98 g, 32.3 mmol) was dissolved in THF (40 mL) and afterwards acetic acid (40 mL) added. N-Bromosuccinimide (12.64 g, 71.0 mmol) was added in the dark and the reaction mixture stirred for 24 h at rt. The reaction was monitored via gas chromatography. The reaction was stopped through addition of H<sub>2</sub>O (200 mL) and diluted with diethylether (100 mL). The organic phase was separated from the aqueous phase, which was then extracted with diethylether (3 x 100 mL). The combined organic phases were washed with saturated NaHCO<sub>3</sub> solution (70 mL), sodium hydroxide (5 w%, 50 mL) and brine (100 mL). The organic phase was dried over MgSO<sub>4</sub>, filtrated and solvents were removed under reduced pressure. The crude product was purified via column chromatography (silica gel, hexane). Drying in a vacuum oven yielded 12.32 g of 2,5-dibromo-3-(6-bromohexyl)thiophene **4** (30.41 mmol, 94%) as a yellowish oil.



**3-(6-azidohexyl)-2,5-dibromothiophene 5.** In a 100 mL flask 2,5-dibromo-3-(6-bromohexyl)thiophene (4.0 g, 9.88 mmol) was dissolved in DMSO (30 mL) and sodium azide (1.28 g, 19.8 mmol) added afterwards. The reaction mixture was stirred for 10 min at rt and sonicated for 3 min to facilitate the dissolving of sodium azide. Thereafter the reaction mixture was stirred for additional 2 h at rt. The reaction was stopped through addition of H<sub>2</sub>O (50 mL),

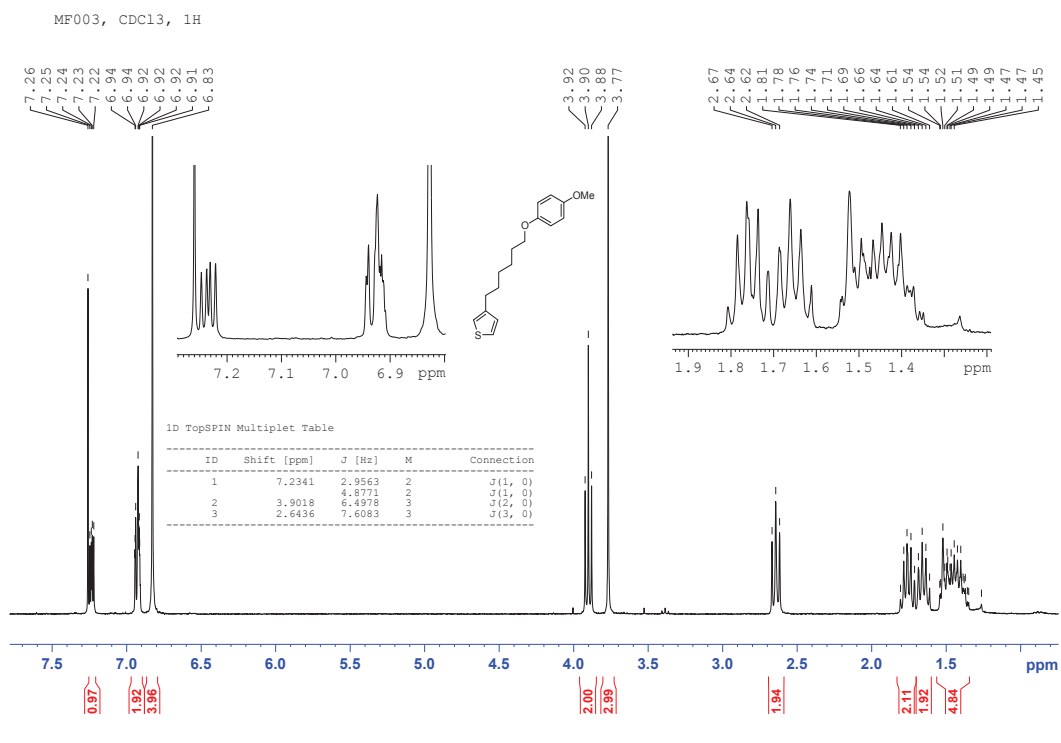
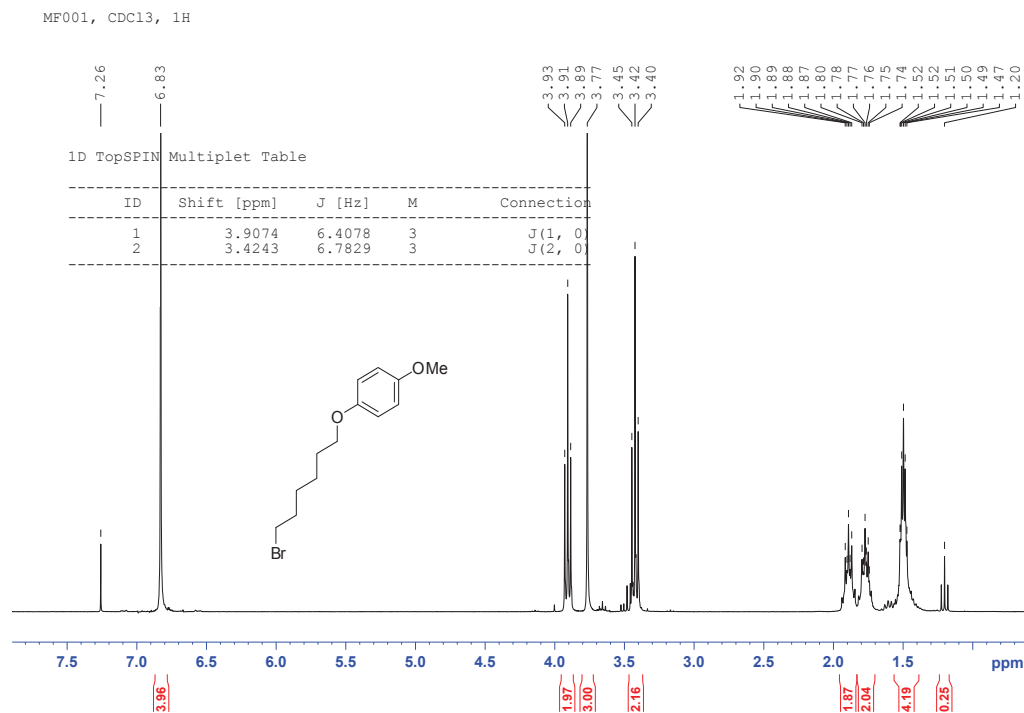
the organic phase was separated from the aqueous phase, which was then extracted with diethylether (3 x 50 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over  $\text{MgSO}_4$ , filtrated and solvents were removed under high vacuum overnight. The crude product was purified via column chromatography (silica gel, cyclohexane / ethyl acetate 1:0, 10:1, 5:1, 2:1). After drying under high vacuum 3.17 g of 3-(6-azidohexyl)-2,5-dibromothiophene **5** (8.64 mmol, 87%) could be obtained as a yellowish oil.



**1,4-Benzenediboronic acid dipinacol ester 9.** To a 250 mL three necked flask was added 1,4-phenylenediboronic acid (4.50 g, 27.1 mmol), anhydrous pinacol (7.06 g, 59.7 mmol) and dry THF (90 ml). After stirring for 5 minutes all starting materials were dissolved and anhydrous  $\text{MgSO}_4$  (7.52 g, 62.4 mmol) was added. The flask was sealed with a rubber septum and flushed with argon. The reaction was stirred vigorously overnight at 80 °C. After cooling, the Solids were removed by filtration and washed with THF. The crude filtrate was concentrated in vacuo, redissolved in hexane/ethyl acetate 1:1 and filtered through a silica gel plug using hexane/ethyl acetate 1:1 as the eluent. Solvents were removed under reduced pressure and the residue was dried under high vacuum to yield 8.94 g of 1,4-benzenediboronic acid dipinacol ester **9** (27.1 mmol, 100%) as a white, highly crystalline solid.

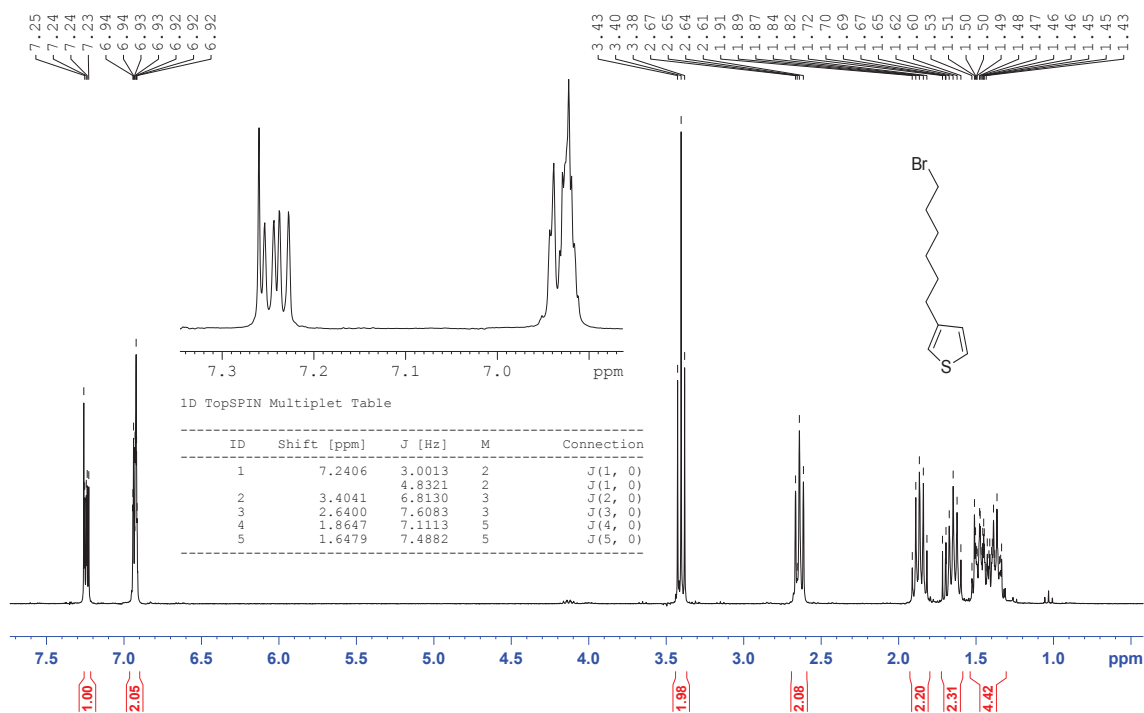
### 3 Monomer Characterization

#### 3.1 <sup>1</sup>H-NMR spectra of monomer compounds.

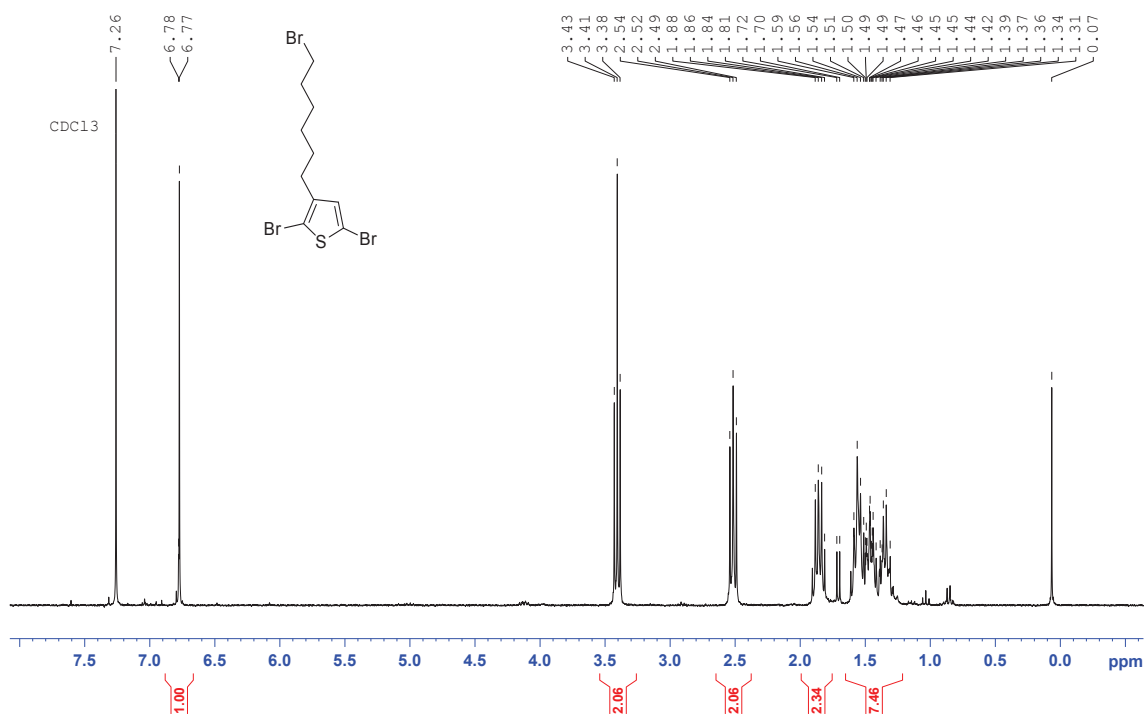


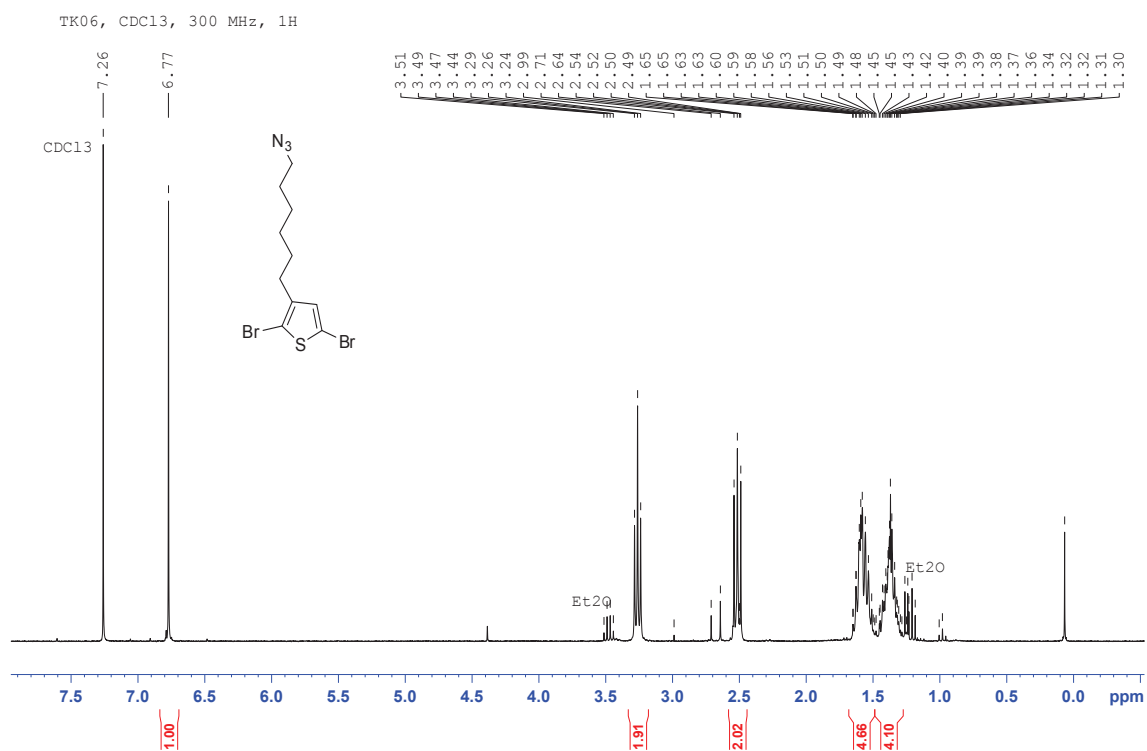


MF005, CDC13, 1H

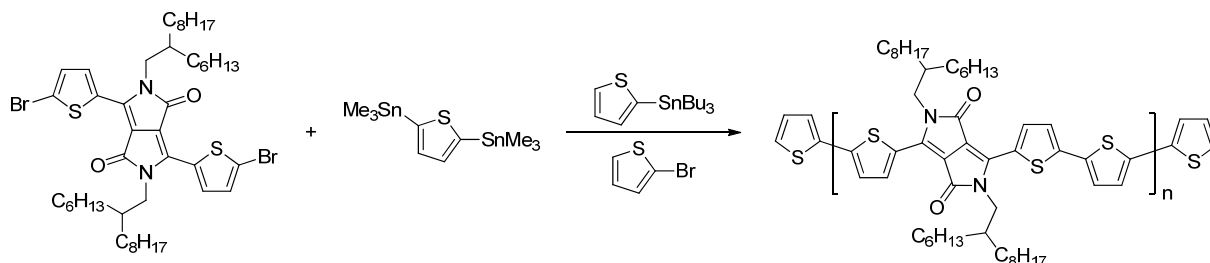


TK05, CDC13, 300 MHz, 1H

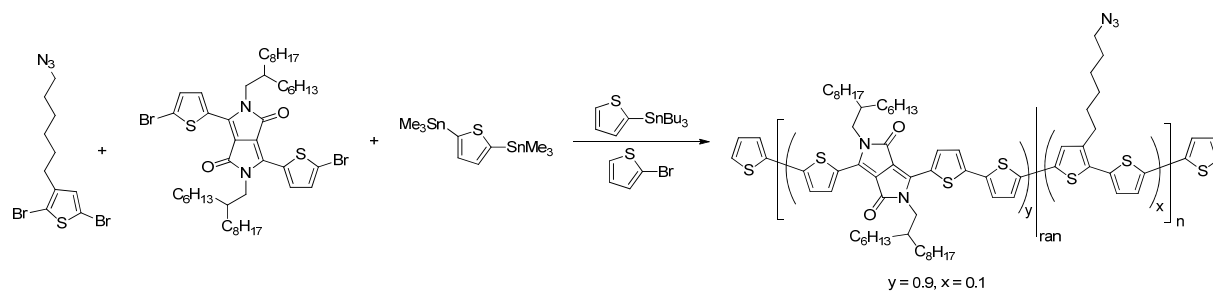




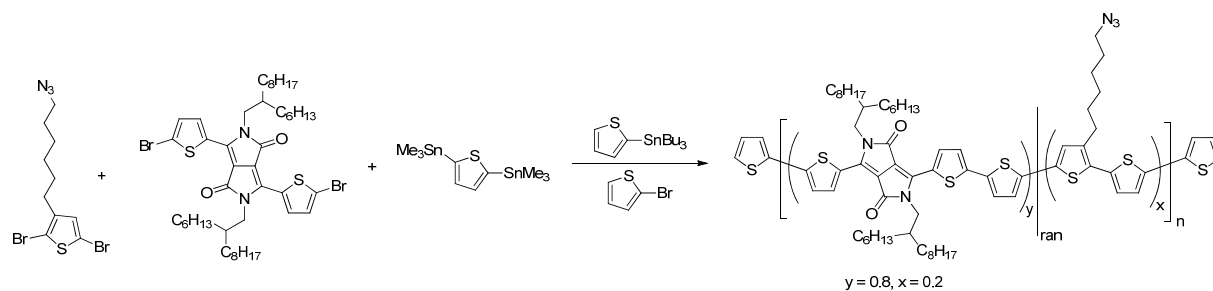
## 4 Polymer syntheses



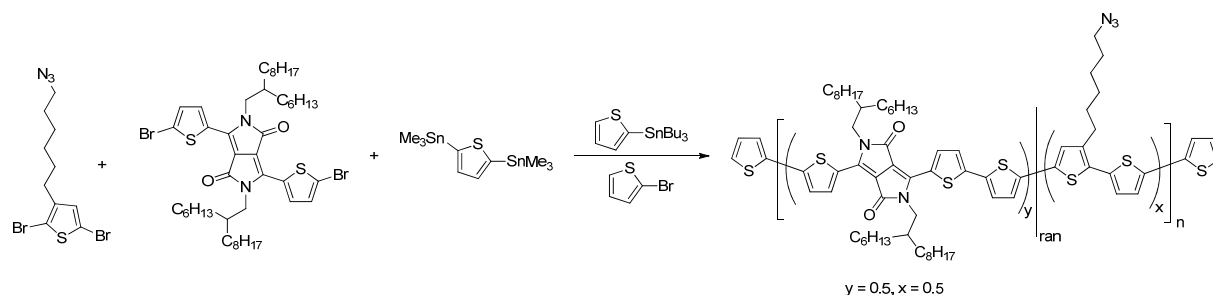
**P1: PDPP[T]<sub>2</sub>-T** Similarly to an previously reported procedure,<sup>1</sup> an oven dried microwave vial was loaded with DPP[T]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (99.38 mg, 110 μmol), 2,5-bis(trimethylstannyl)thiophene (44.89 mg, 110 μmol) and tri-*o*-tolylphosphine (4.00 mg, 13 μmol). Dry and degassed chlorobenzene (2.5 mL) was added and the polymerization mixture was purged with argon for 10 min. Finally tris(dibenzylideneacetone)dipalladium(0) (3.04 mg, 3.7 μmol) was added, the vial was sealed with a septum cap and the vial atmosphere exchanged three times with argon. The mixture was stirred for 30 min at 180 °C in the microwave. After cooling to 50 °C 2-tributyltinthiophene (25 μL, 79 μmol) was added to the viscous green solution using a microliter syringe. The mixture was again heated at 180 °C for 5 min in the microwave, cooled to 50 °C and finally 2-bromothiophene (40 μL, 413 μmol) was added. The mixture was heated to 180 °C for 10 min in the microwave. After cooling to room temperature the polymer was precipitated in 250 mL methanol, filtrated over a 0.45 μm PTFE filter and dried in high vacuum. The crude polymer was subjected to soxhlet extraction using acetone, hexane and dichloromethane. The dichloromethane fraction was concentrated under reduced pressure and precipitated in 150 mL methanol. The precipitate was filtrated over a 0.45 μm PTFE filter and dried in high vacuum to obtain 85.0 mg PDPP[T]<sub>2</sub>-T (94%) as a dark purple solid.



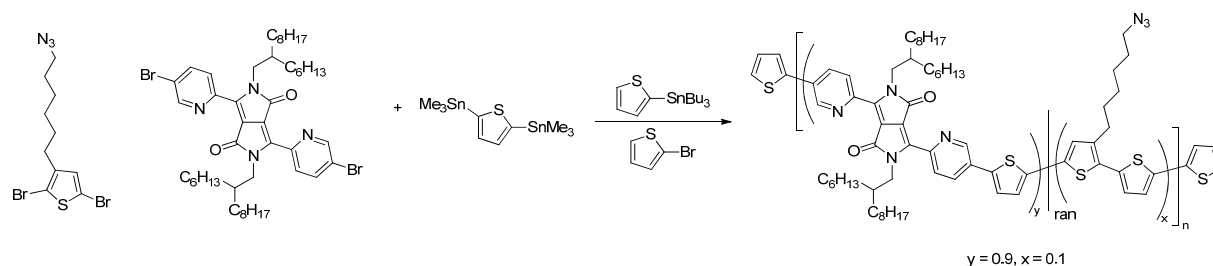
**P2: PDPP[T]<sub>2</sub>-T(5mol%Az).** An oven dried microwave vial was loaded with 3-(6-azidoheptyl)-2,5-dibromothiophene (5.96 mg, 16  $\mu$ mol), DPP[T]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (149.60 mg, 182  $\mu$ mol), 2,5-bis(trimethylstannyl)thiophene (74.48 mg, 165  $\mu$ mol) and tri-*o*-tolylphosphine (6.68 mg, 22  $\mu$ mol). Dry chlorobenzene (4 mL) was added and the polymerization mixture was purged with argon for 10 min. Finally tris(dibenzylideneacetone)dipalladium(0) (5.17 mg, 5.7  $\mu$ mol) was added, the vial was sealed with a septum cap and the vial atmosphere exchanged three times with argon. The mixture was stirred for 30 min at 180 °C in the microwave. After cooling to 50 °C 2-tributyltinthiophene (25  $\mu$ L, 79  $\mu$ mol) was added to the viscous green solution using a microliter syringe. The mixture was again heated at 180 °C for 5 min in the microwave, cooled to 50 °C and finally 2-bromothiophene (40  $\mu$ L, 413  $\mu$ mol) was added. The mixture was heated to 180 °C for 10 min in the microwave. After cooling to room temperature the polymer was precipitated in 250 mL methanol, filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum. The crude polymer was subjected to soxhlet extraction using acetone, hexane and dichloromethane. The dichloromethane was concentrated under reduced pressure and precipitated in 150 mL methanol. The precipitate was filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum to obtain 132 mg PDPP[T]<sub>2</sub>-T(10%Az) (93%) as a dark purple solid.



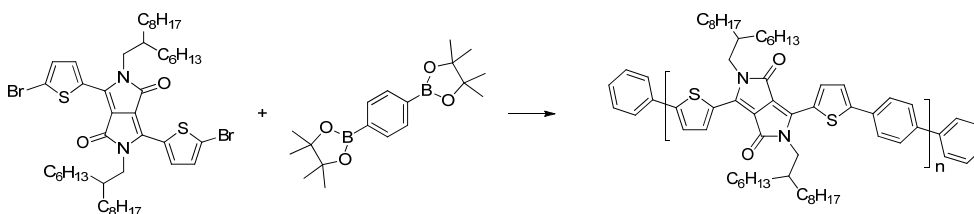
**P3: PDPP[T]<sub>2</sub>-T(10mol%Az).** An oven dried microwave vial was loaded with 3-(6-azidoheptyl)-2,5-dibromothiophene (15.04 mg, 41  $\mu$ mol), DPP[T]<sub>2</sub>{2HD}2Br<sub>2</sub> (149.90 mg, 165  $\mu$ mol), 2,5-bis(trimethylstannyl)thiophene (84.65 mg, 207  $\mu$ mol) and tri-*o*-tolylphosphine (7.55 mg, 25  $\mu$ mol). Dry chlorobenzene (4 mL) was added and the polymerization mixture was purged with argon for 10 min. Finally tris(dibenzylideneacetone)dipalladium(0) (5.85 mg, 6.4  $\mu$ mol) was added, the vial was sealed with a septum cap and the vial atmosphere exchanged three times with argon. The mixture was stirred for 30 min at 180 °C in the microwave. After cooling to 50 °C 2-tributyltinthiophene (25  $\mu$ L, 79  $\mu$ mol) was added to the viscous green solution using a microliter syringe. The mixture was again heated at 180 °C for 5 min in the microwave, cooled to 50 °C and finally 2-bromothiophene (40  $\mu$ L, 413  $\mu$ mol) was added. The mixture was heated to 180 °C for 10 min in the microwave. After cooling to room temperature the polymer was precipitated in 250 mL methanol, filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum. The crude polymer was subjected to soxhlet extraction using acetone, hexane, dichloromethane and chloroform. The dichloromethane and chloroform fractions were combined, concentrated under reduced pressure and precipitated in 150 mL methanol. The precipitate was filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum to obtain 142 mg PDPP[T]<sub>2</sub>-T(20%Az) (96%) as a dark purple solid.



**P4: PDPP[T]<sub>2</sub>-T(25mol%Az).** An oven dried microwave vial was loaded with 3-(6-azidohexyl)-2,5-dibromothiophene (48.30 mg, 132  $\mu$ mol), DPP[T]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (120.17 mg, 132  $\mu$ mol), 2,5-bis(trimethylstannyl)thiophene (108.17 mg, 264  $\mu$ mol) and tri-*o*-tolylphosphine (9.89 mg, 33  $\mu$ mol). Dry chlorobenzene (4.8 mL) was added and the polymerization mixture was purged with argon for 10 min. Finally tris(dibenzylideneacetone)dipalladium(0) (7.71 mg, 8.4  $\mu$ mol) was added, the vial was sealed with a septum cap and the vial atmosphere exchanged three times with argon. The mixture was stirred for 30 min at 180 °C in the microwave. After cooling to 50 °C 2-tributyltinthiophene (25  $\mu$ L, 79  $\mu$ mol) was added to the viscous green solution using a microliter syringe. The mixture was again heated at 180 °C for 5 min in the microwave, cooled to 50 °C and finally 2-bromothiophene (40  $\mu$ L, 413  $\mu$ mol) was added. The mixture was heated to 180 °C for 10 min in the microwave. After cooling to room temperature the polymer was precipitated in 250 mL methanol, filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum. The crude polymer was subjected to soxhlet extraction using acetone, hexane and dichloromethane. The remaining precipitate was refluxed for 16 h in chloroform. The obtained solution was filtrated, concentrated under reduced pressure and precipitated in 150 mL methanol. Filtration over a 0.45  $\mu$ m PTFE filter and drying in high vacuum yielded 84 mg (57%) PDPP[T]<sub>2</sub>-T(50%Az) as a dark purple solid.



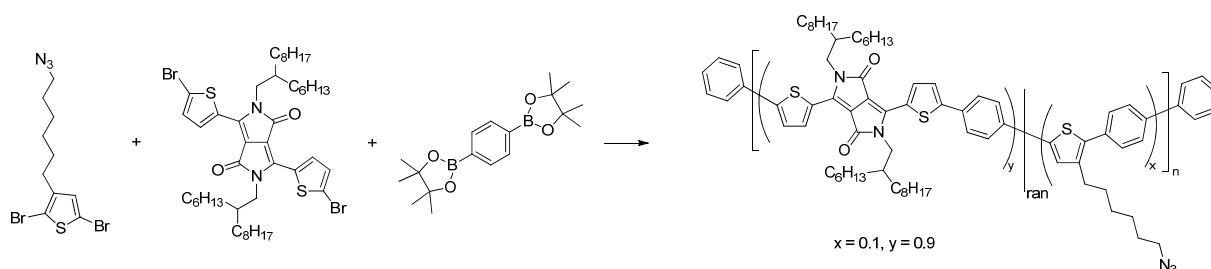
**P6: PDPP[Py]<sub>2</sub>-T(5mol%Az).** An oven dried microwave vial was loaded with 3-(6-azidohexyl)-2,5-dibromothiophene (6.15 mg, 17  $\mu$ mol), DPP[Py]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (135.03 mg, 151  $\mu$ mol), 2,5-bis(trimethylstannyl)-thiophene (68.5 mg, 167  $\mu$ mol) and tri-*o*-tolylphosphine (6.38 mg, 21  $\mu$ mol). Dry and degassed chlorobenzene (4 mL) was added and the polymerization mixture was purged with argon for 10 min. Finally tris(dibenzylideneacetone)dipalladium(0) (4.90 mg, 5.35  $\mu$ mol) was added, the vial was sealed with a septum cap and the vial atmosphere exchanged three times with argon. The mixture was stirred for 60 min at 180  $^{\circ}$ C in the microwave. After cooling to 50  $^{\circ}$ C 2-tributyltinthiophene (25  $\mu$ L, 79  $\mu$ mol) was added to the blue solution using a microliter syringe. The mixture was again heated at 180  $^{\circ}$ C for 10 min in the microwave, cooled to 50  $^{\circ}$ C and finally 2-bromothiophene (25  $\mu$ L, 258  $\mu$ mol) was added. The mixture was heated to 180  $^{\circ}$ C for 10 min in the microwave. After cooling to room temperature the polymer was directly precipitated into methanol (200 mL). The precipitate was filtrated through a soxhlet thimble and was further purified by soxhlet extraction using methanol, acetone, hexane and chloroform. The chloroform fraction only contained 15 mg of product and was discarded. The hexane fraction was concentrated to dryness under reduced pressure and redissolved in a minimal amount of chloroform before it was precipitated in methanol (200 mL). The precipitate was filtrated over a 0.45  $\mu$ m PTFE filter and dried in high vacuum to obtain 109 mg PDPP[Py]<sub>2</sub>-T(10%Az) (85%) as a dark purple solid.



**P7: PDPP[T]<sub>2</sub>-Ph.** A schlenk tube with a PTFE sealed screw cap was loaded with DPP[T]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (551.49 mg, 608  $\mu$ mol), freshly recrystallized 1,4-benzenediboronic acid dipinacol ester (200.72 mg, 608  $\mu$ mol) and triphenylphosphine (27.13 mg, 103  $\mu$ mol). The solids were dissolved in degassed toluene (22 mL) and 4.4 mL (ratio 5:1) of an aqueous, degassed 2 M tribasic potassium phosphate solution were added. Furthermore, 3 drops of Aliquat 336 were added as a phase transfer catalyst and the mixture was purged with argon for 30 min. Pd<sub>2</sub>(dba)<sub>3</sub> (23.68 mg, 26  $\mu$ mol) as added, the tube was sealed tightly and an inert atmosphere was ensured by 10 vacuum/argon cycles. The reaction mixture was protected from light and stirred at 115 °C for 18 h. The green suspension was then cooled to room temperature using an ice bath, benzeneboronic acid pinacol ester (60 mg, 294  $\mu$ mol) was added and the mixture was again degassed by 5 vacuum/argon cycles. Endcapping was performed for 30 min at 115 °C and the mixture was again cooled to room temperature before bromobenzene (100  $\mu$ L, 1 mmol) was added and the mixture was finally heated to 115 °C for 2 h. After cooling to room temperature, the reaction mixture was transferred into a separating funnel using chloroform and water. The organic phase was poured into 200 mL of 25% aqueous ammonia solution and refluxed at 80 °C for 15 min in the dark. The phases were separated and the organic layer was stirred with a mixture of ethylenediaminetetraacetic acid (EDTA, 600 mg, 2 mmol) and tetrapotassium EDTA salt (900 mg, 2 mmol) for 15 min before 200 mL water were added and the mixture was stirred vigorously for 2 h in the dark. The organic phase was isolated, washed with water twice, dried over MgSO<sub>4</sub> and filtrated through mineral wool. The solution was then concentrated to 20 mL

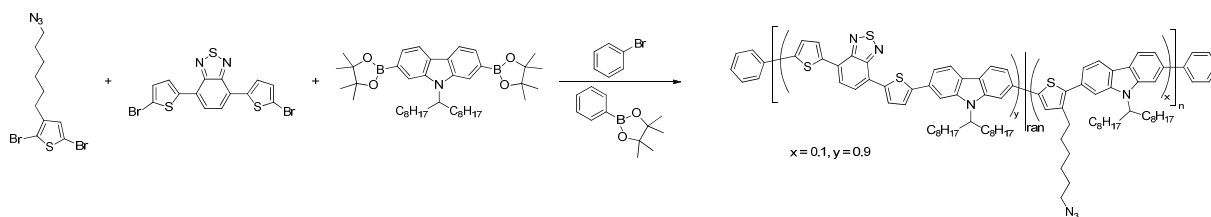


and precipitated into 1.2 L of methanol. The precipitate was filtered through a glas frit, washed with methanol and dried *in vacuo* overnight. The crude polymer was further purified by soxhlet extraction using acetone, hexane and dichloromethane as solvents. The remaining solid was put into a flask and refluxed in chloroform for 1 h. The solution was filtered, concentrated under reduced pressure and precipitated into methanol (1.2 L). The precipitate was filtered through a glas frit and dried *in vacuo* for 2 h at 55 °C and at room temperature overnight to obtain 444 mg (86%) PDPP[T]<sub>2</sub>-Ph as a purple film.



**P8: PDPP[T]<sub>2</sub>-Ph(5mol%Az).** 3-(6-Azidoheptyl)-2,5-dibromothiophene (6.31 mg, 17  $\mu$ mol) was weighed into a snap cap vial. A schlenk tube with a PTFE sealed screw cap was loaded with DPP[T]<sub>2</sub>{2HD}<sub>2</sub>Br<sub>2</sub> (142.90 mg, 158  $\mu$ mol), freshly recrystallized 1,4-benzenediboronic acid dipinacol ester (57.70 mg, 175  $\mu$ mol) and triphenylphosphine (6.18 mg, 24  $\mu$ mol). Degassed toluene (6 mL) was used to transfer the 3-(6-azidoheptyl)-2,5-dibromothiophene into the schlenk tube and 0.6 mL (ratio 10:1) of an aqueous, degassed 2 M tribasic potassium phosphate solution were added. Furthermore, 3 drops of Aliquat 336 were added as a phase transfer catalyst and the mixture was purged with argon for 30 min. Pd<sub>2</sub>(dba)<sub>3</sub> (5.27 mg, 5.8  $\mu$ mol) as added, the tube was sealed tightly and an inert atmosphere was ensured by 10 vacuum/argon cycles. The reaction mixture was protected from light and stirred at 120 °C for 2 h. The green suspension and was then cooled to room temperature using an ice bath, benzeneboronic acid pinacol ester (60 mg, 294  $\mu$ mol) was added and the mixture was again degassed by 5 vacuum/argon cycles.

Endcapping was performed for 30 min at 120 °C and the mixture was again cooled to room temperature before bromobenzene (100  $\mu$ L, 1 mmol) was added and the mixture was finally heated to 120 °C for 1 h. After cooling to room temperature, the reaction mixture was transferred into a separating funnel using chloroform and water. The organic phase was poured into 70 mL of 25% aqueous ammonia solution and refluxed at 80 °C for 10 min in the dark. The phases were separated and the organic layer was stirred with a mixture of ethylenediaminetetraacetic acid (EDTA, 250 mg) and tetrapotassium EDTA salt (250 mg) for 15 min before 70 mL water were added and the mixture was stirred vigorously for 1 h in the dark. The organic phase was isolated, washed with water twice, dried over  $\text{MgSO}_4$  and filtrated through mineral wool. The solution was then concentrated to 15 mL and precipitated into 150 mL of methanol. The precipitate was filtered through a soxhlet thimble and was then further purified by soxhlet extraction using acetone, hexane and dichloromethane as solvents. The remaining solid was put into a flask and refluxed in chloroform overnight. The solution was filtered, concentrated under reduced pressure and precipitated into methanol (200 mL). The precipitate was filtered through a 0.45  $\mu\text{m}$  PTFE filter and dried *in vacuo* at room temperature overnight to obtain 89 mg (67%) PDPP[T]<sub>2</sub>-Ph as a purple film.



**P10: PCDTBT(5mol%Az).** 3-(6-Azidoheptyl)-2,5-dibromothiophene (6.83 mg, 19  $\mu\text{mol}$ ) was weighed into a snap cap vial. A schlenk tube with a PTFE sealed screw cap was loaded with 4,7-bis(5-bromo-2-yl)-2,1,3-benzothiadiazole (77.67 mg, 170  $\mu\text{mol}$ ), 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-hepta-decanylcarbazole (123.7 mg, 188  $\mu\text{mol}$ ) and tri-*o*-

tolylphosphine (6.72 mg, 22  $\mu$ mol). Degassed toluene (7 mL) was used to transfer the 3-(6-azidohexyl)-2,5-dibromothiophene into the schlenk tube and 0.7 mL (ratio 10:1) of an aqueous, degassed 2 M tribasic potassium phosphate solution were added. Furthermore, 3 drops of Aliquat 336 were added as a phase transfer catalyst and the mixture was purged with argon for 30 min.  $\text{Pd}_2(\text{dba})_3$  (5.13 mg, 5.6  $\mu$ mol) as added, the tube was sealed tightly and an inert atmosphere was ensured by 10 vacuum/argon cycles. The reaction mixture was protected from light and stirred at 120 °C for 2 h. The red suspension and was then cooled to room temperature using an ice bath, benzenboronic acid pinacol ester (40 mg, 196  $\mu$ mol) was added and the mixture was again degassed by 5 vacuum/argon cycles. Endcapping was performed for 30 min at 120 °C and the mixture was again cooled to room temperature before bromobenzene (100  $\mu$ L, 1 mmol) was added and the mixture was finally heated to 120 °C for 1 h. After cooling to room temperature, the reaction mixture was transferred into a separating funnel using chloroform and water. The phases were separated and the organic layer was stirred with a mixture of ethylenediaminetetraacetic acid (EDTA, 250 mg) and tetrapotassium EDTA salt (250 mg) for 15 min before 70 mL water were added and the mixture was stirred vigorously for 1 h in the dark. The organic phase was isolated, washed with water twice, dried over  $\text{MgSO}_4$  and filtrated through mineral wool. The solution was then concentrated to 15 mL and precipitated into 150 mL of methanol. The precipitate was filtered through a soxhlet thimble and was then further purified by soxhlet extraction using acetone, hexane, dichloromethane and chloroform as solvents. The chloroform and the dichloromethane fractions were combined, filtrated, concentrated under reduced pressure and precipitated into a methanol/water mixture (200 mL / 20 mL). The precipitate was filtered through a 0.45  $\mu$ m PTFE filter and dried *in vacuo* at room temperature overnight to obtain 56 mg (43%) PCDTBT(10%Az) as a red solid.

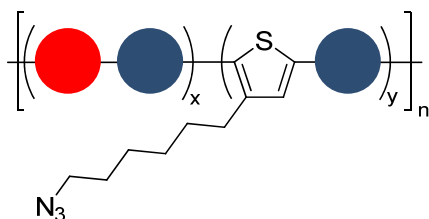
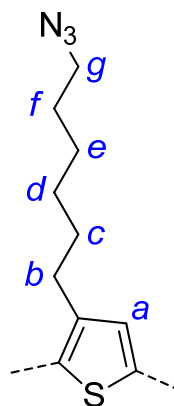
## 5 Polymer Characterization

### 5.1 Polymer NMR

The built-in mole fraction  $\chi_{\text{NMR}}(y)$  of the 6-azido-hexyl functionalized thiophene moiety in the polymers was determined by correlating the  $-\text{CH}_2-\text{N}_3$  signal ( $H_g$ , 2 H) at  $\sim 3.35$  ppm as well as the  $\alpha\text{-CH}_2$  group at  $\sim 2.89$  ppm ( $H_b$ , 2 H) to an alkyl signal of the regular sidechains (either at the DPP moiety for **P2-P8** or the carbazole moiety for **P10**). In the case of any DPP polymers the tertiary  $-\text{CH}-$  signal at the sidechain branching point (at  $\sim 2.07$  ppm, corresponds to 2 H due to two sidechains per DPP moiety) was used. For the PCDTBT system either the  $-\text{CH}-$  signal at the sidechain branching point at  $\sim 4.77$  ppm (1 H) or the  $-\text{CH}_2-$  group at  $\sim 2.46$  ppm was used. The built-in mole fractions of the two repeating units x and y were calculated as follows:

$$\chi_{\text{NMR}}(x) = \frac{H_{\text{reference}}}{H_{\text{reference}} + \frac{H_b + H_g}{2}}$$

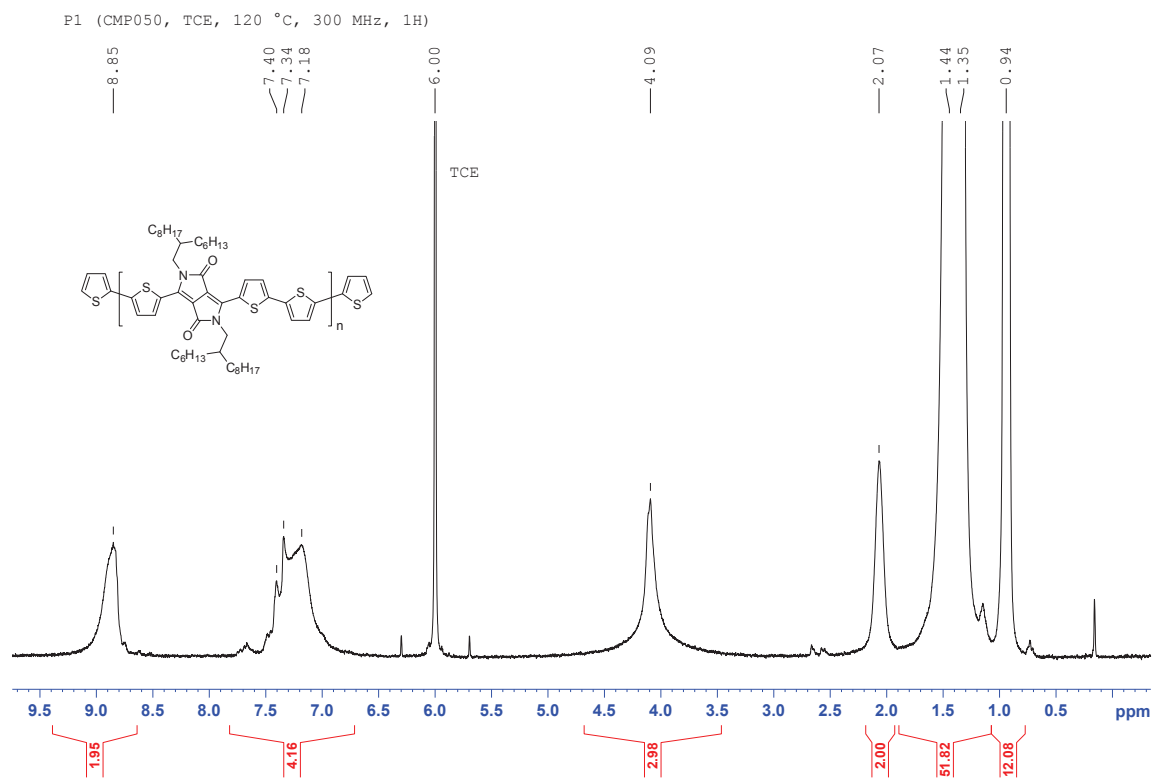
$$\chi_{\text{NMR}}(y) = \frac{\frac{H_b + H_g}{2}}{H_{\text{reference}} + \frac{H_b + H_g}{2}}$$

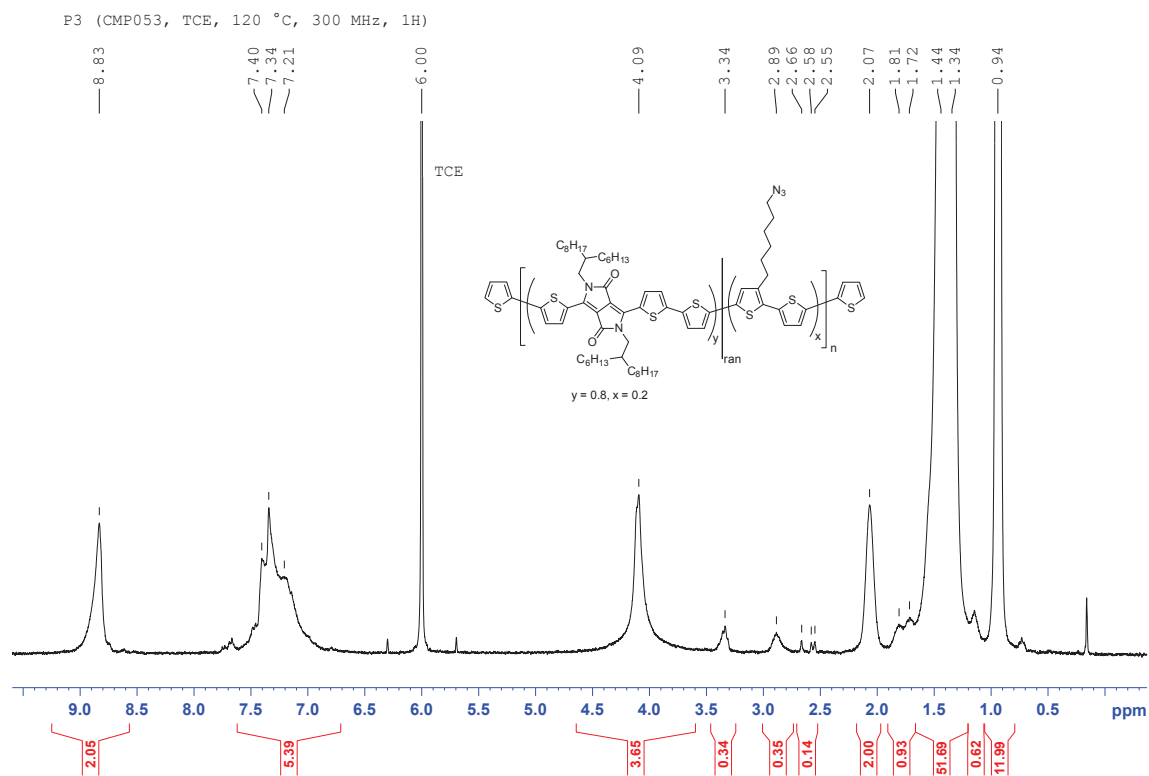
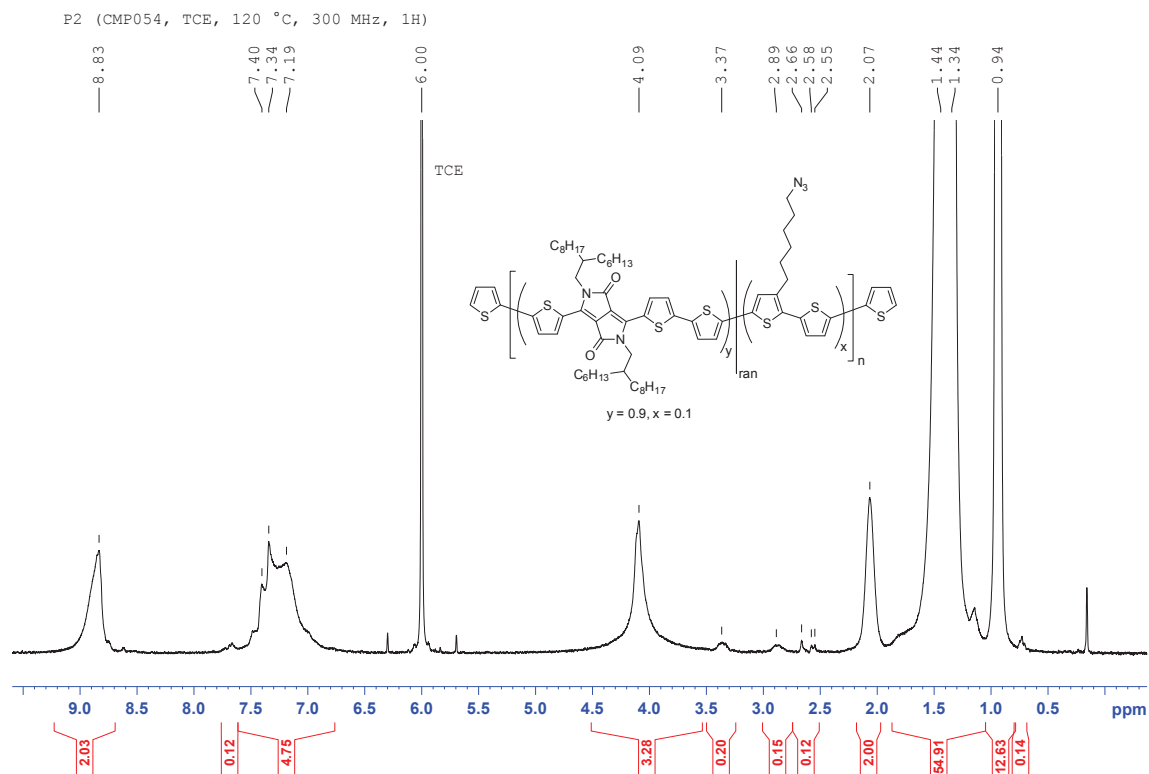


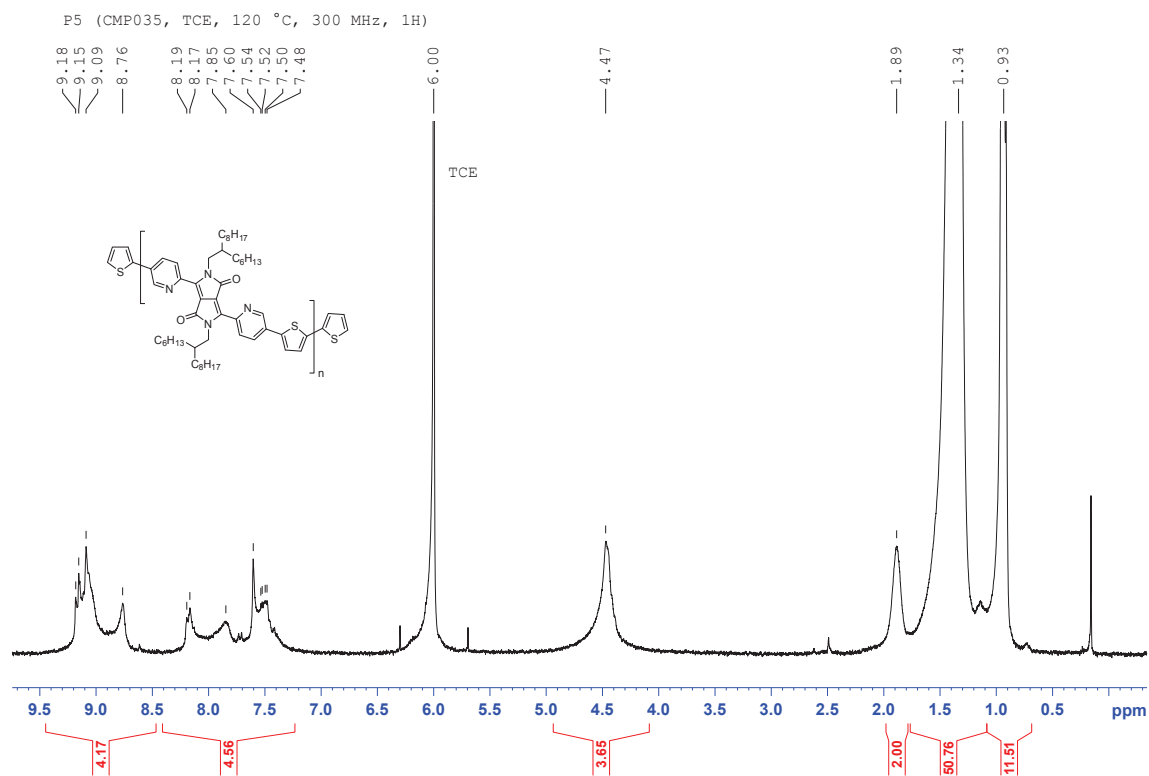
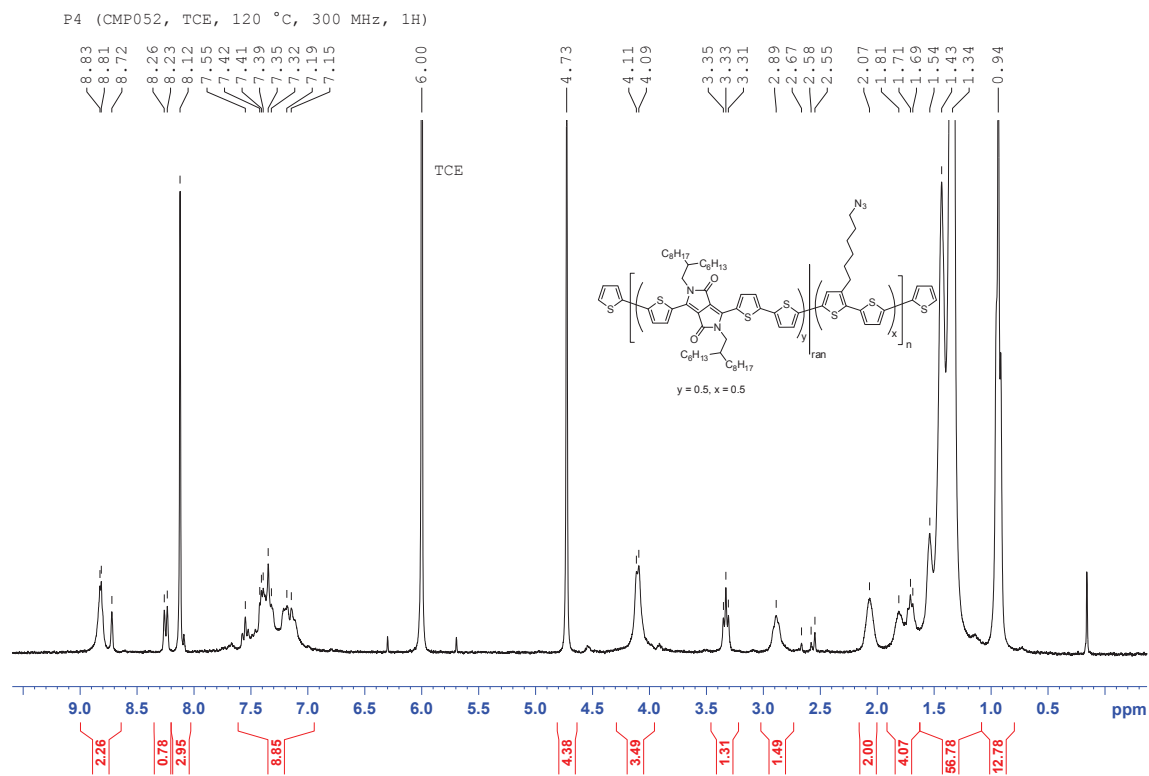
Where  $H_{\text{reference}}$  is the signal of either the DPP or carbazole sidechain as described above and  $H_b$  and  $H_g$  are the signals from the azido-functionalized thiophene moiety

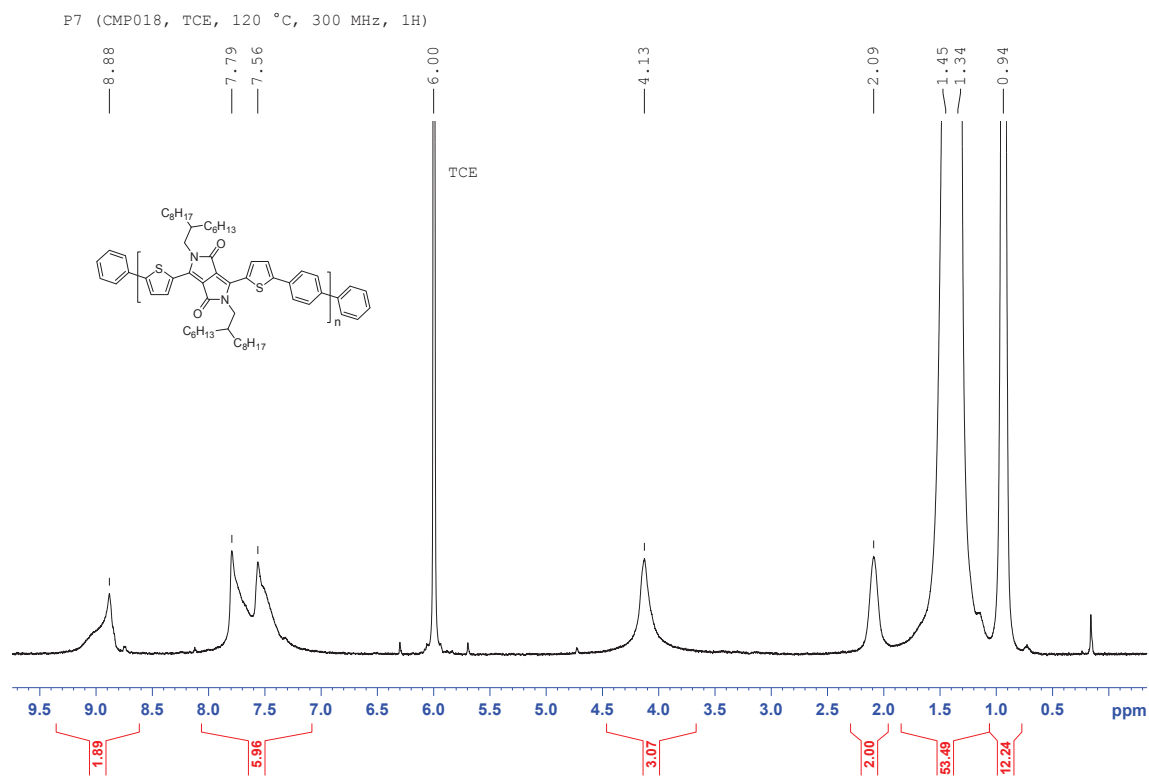
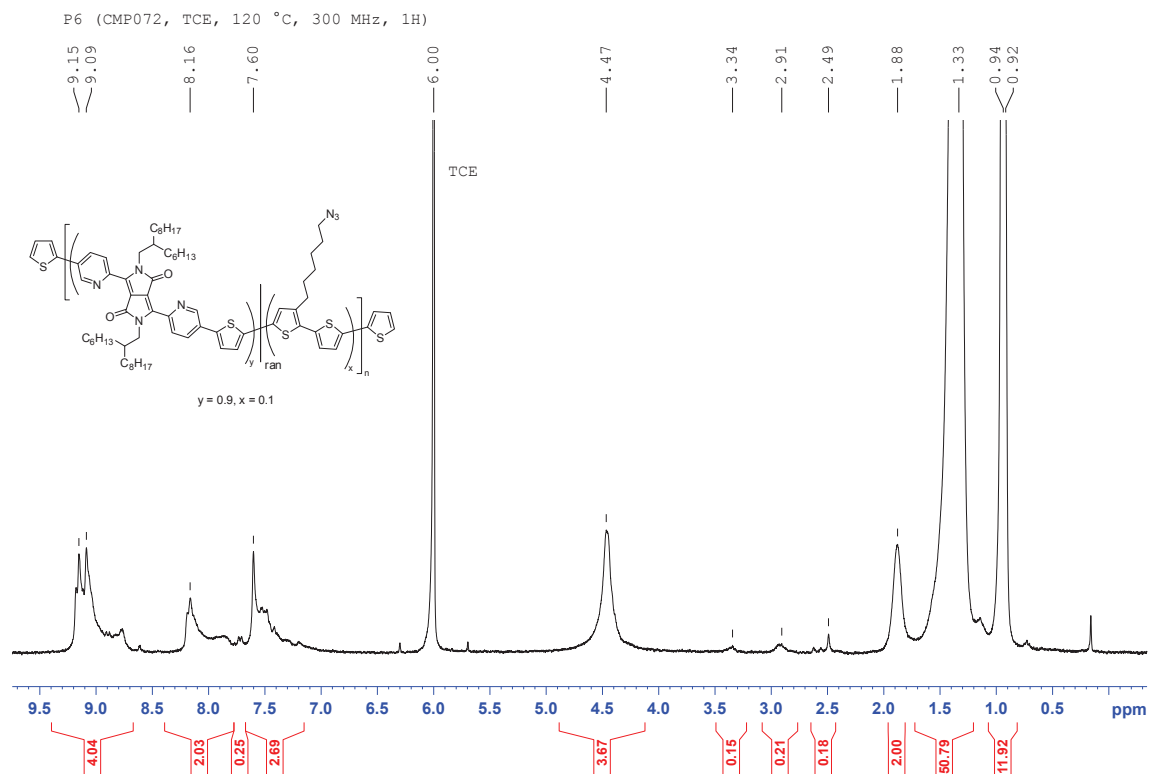
**Table S1.** Calculation of the built-in mole fraction of the azide-functionalized thiophene moiety by  $^1\text{H}$ -NMR.

Polymer	Reference signal	$H_g$	$H_b$	$\chi^{\text{NMR}}(\text{x})$	$\chi^{\text{NMR}}(\text{y})$
P1	2.00	0.00	0.00	1.00	0.00
P2	2.00	0.20	0.15	0.92	0.08
P3	2.00	0.34	0.35	0.85	0.15
P4	2.00	1.31	1.49	0.59	0.41
P5	2.00	0.00	0.00	1.00	0.00
P6	2.00	0.15	0.21	0.92	0.08
P7	2.00	0.00	0.00	1.00	0.00
P8	2.00	0.17	0.17	0.92	0.08
P9	1.00	0.00	0.00	1.00	0.00
P10	1.00	0.14	0.08	0.90	0.10

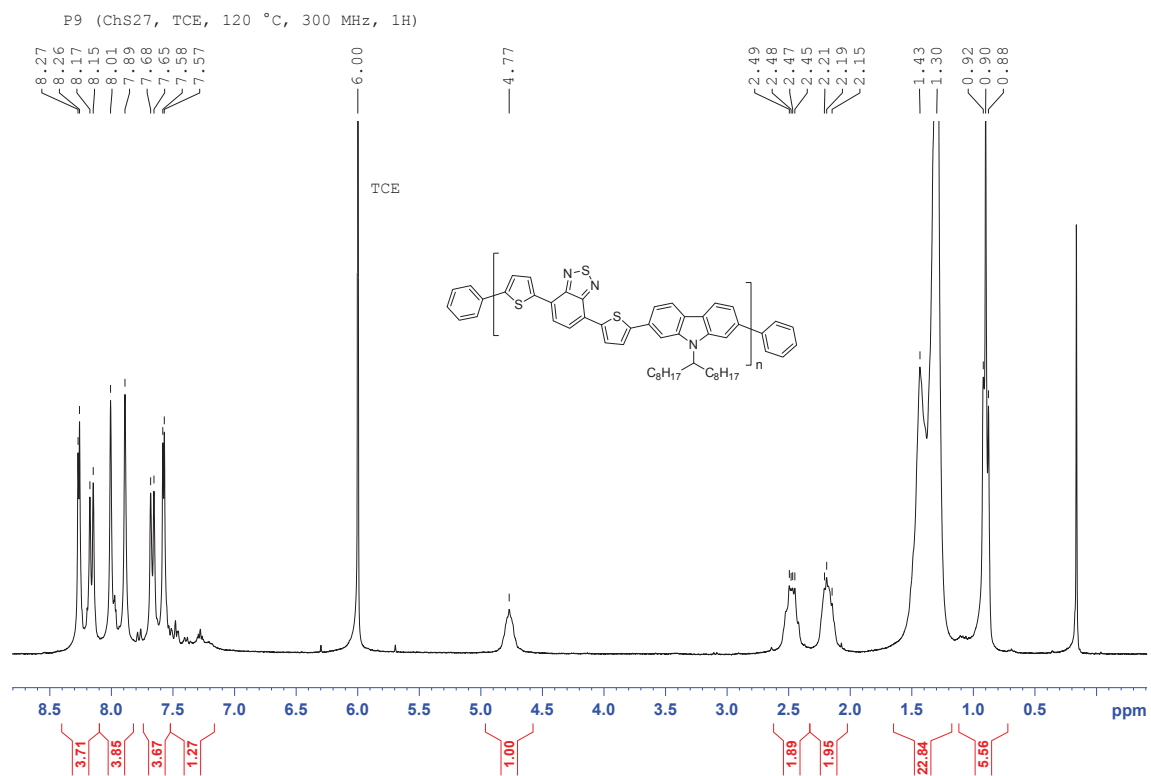
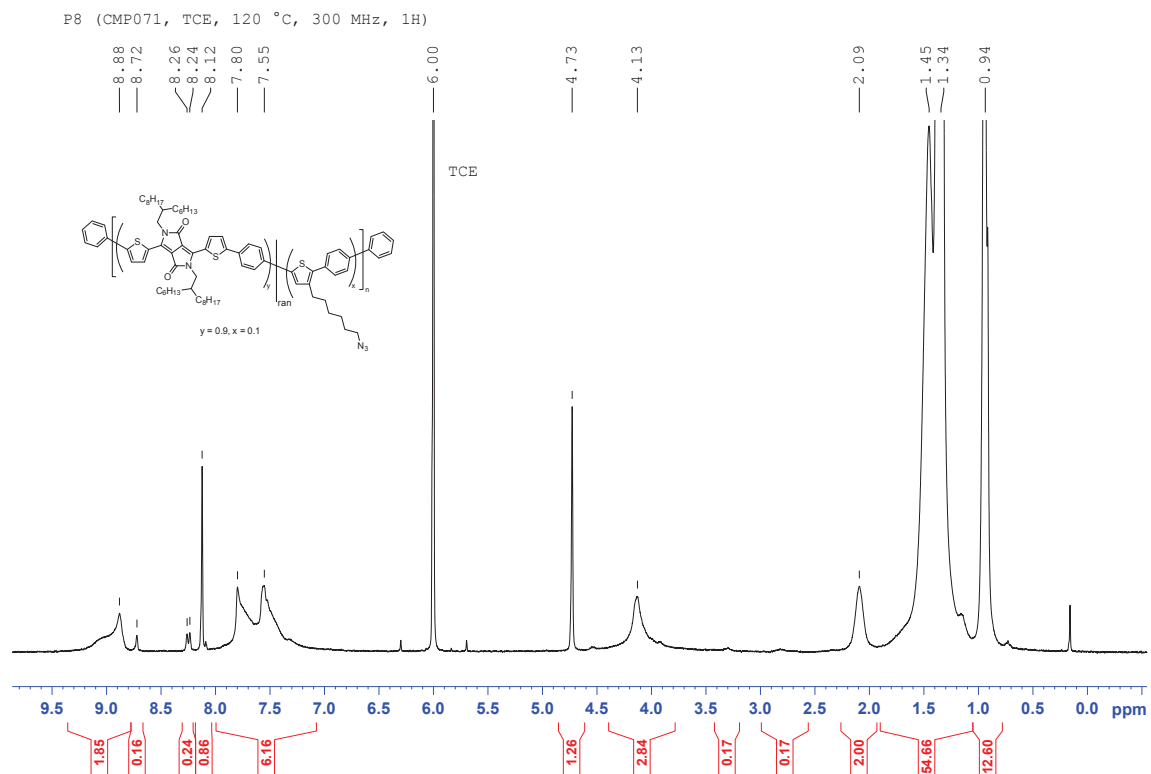


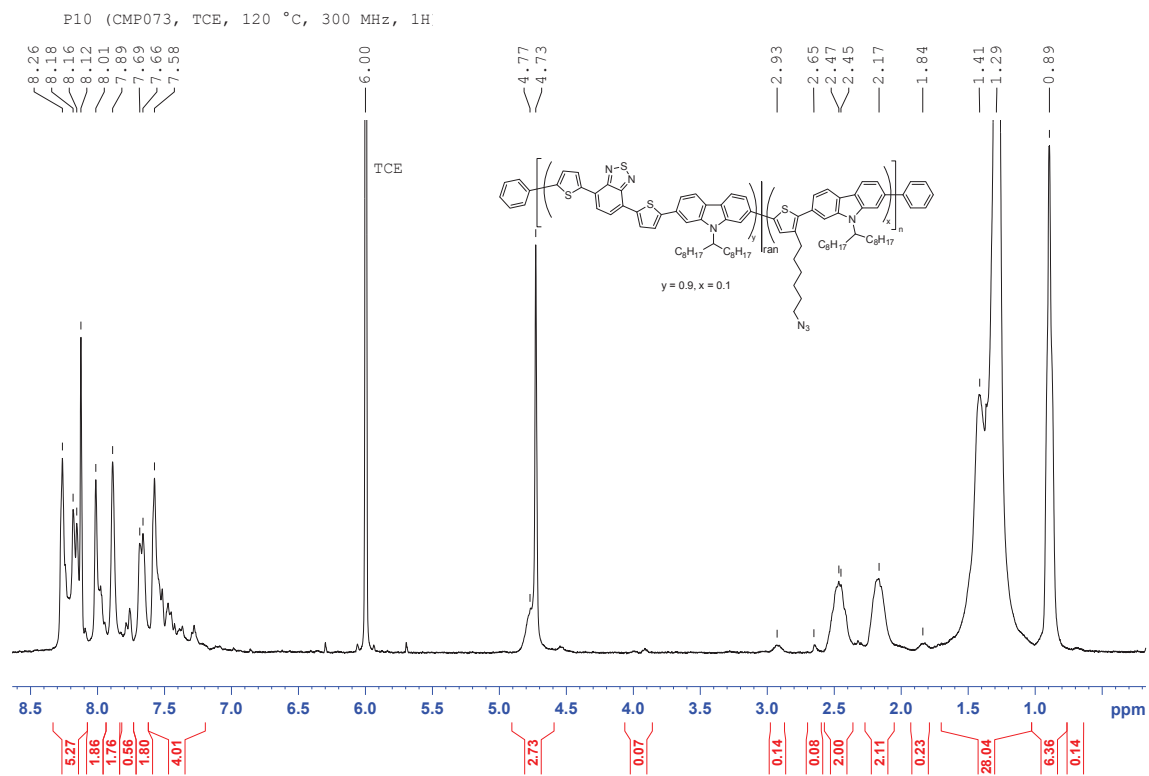




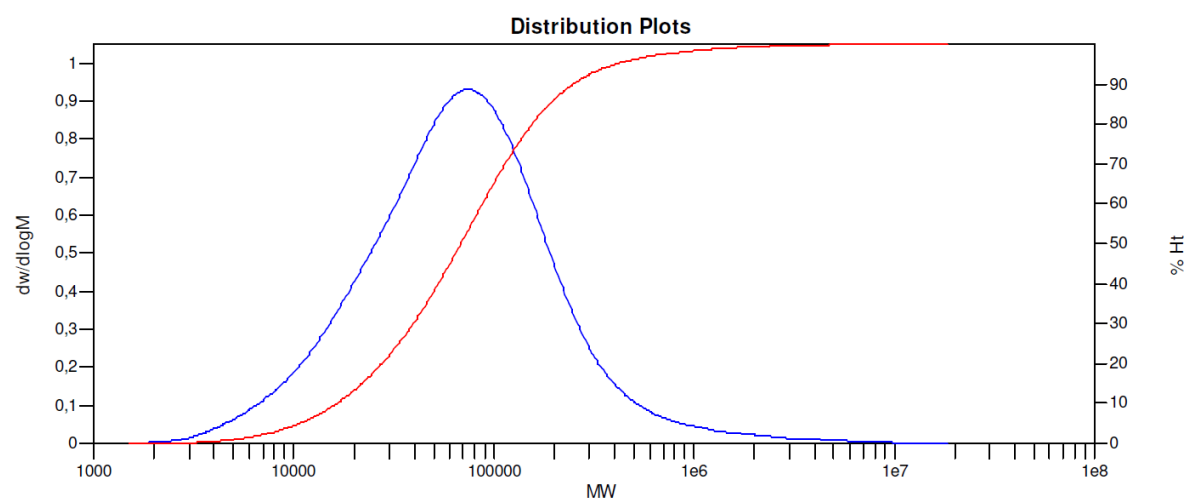








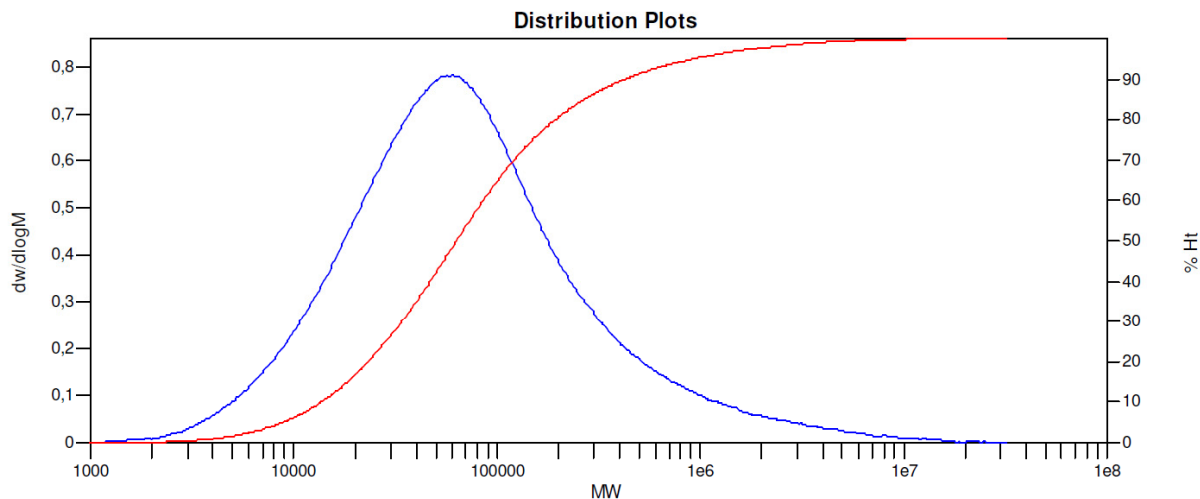
## 5.2 Gel Permeation Chromatography



### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	74390	36932	145504	1488203	6627220	110739	3.93978

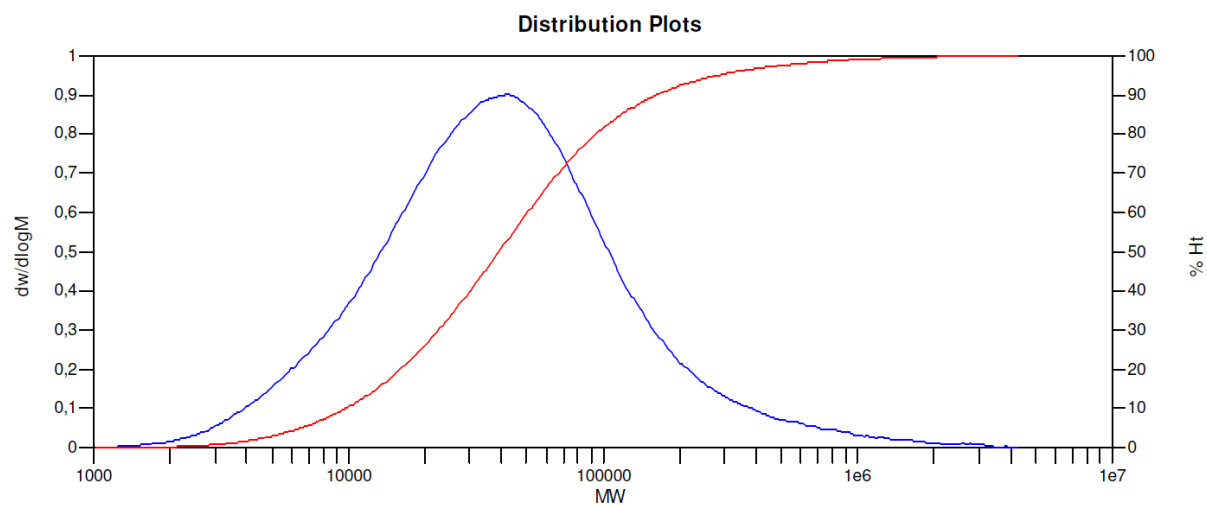
Figure S1. GPC molecular weight distribution of **P1** PDPP[T]<sub>2</sub>-T.



### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	60552	31575	253520	3635108	10483408	163343	8.02914

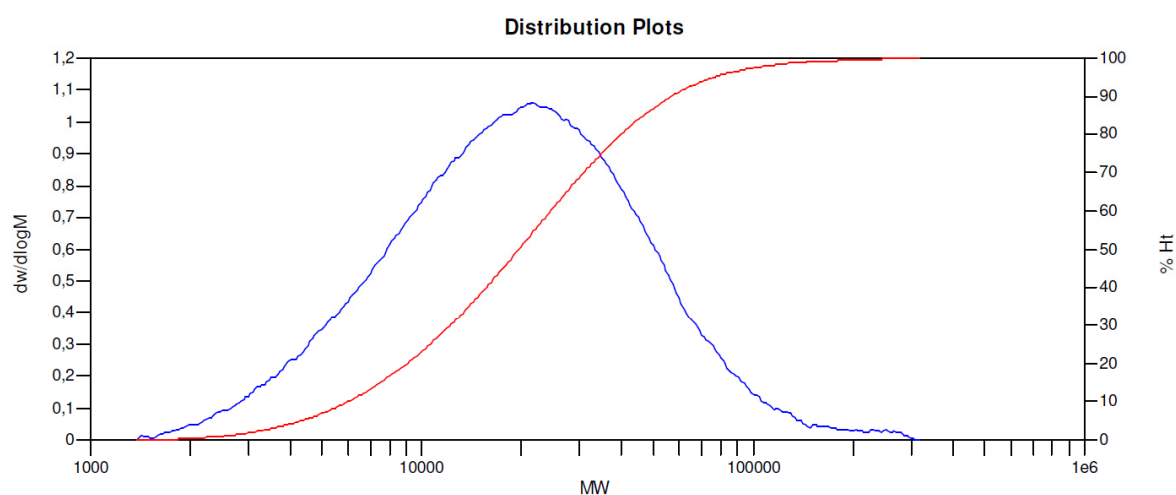
Figure S2. GPC molecular weight distribution of **P2** PDPP[T]<sub>2</sub>-T (10% azide content).



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	42506	22157	84630	508642	1515681	66014	3.81956

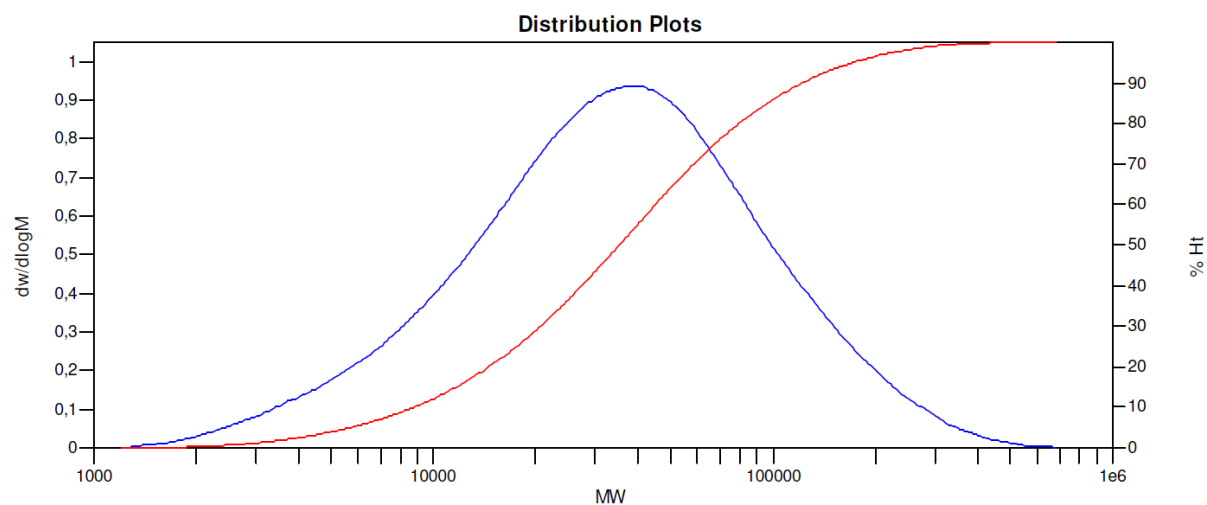
Figure S3. GPC molecular weight distribution of **P3** PDPP[T]<sub>2</sub>-T (20% azide content).



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21456	12949	27537	56517	106264	24719	2.12657

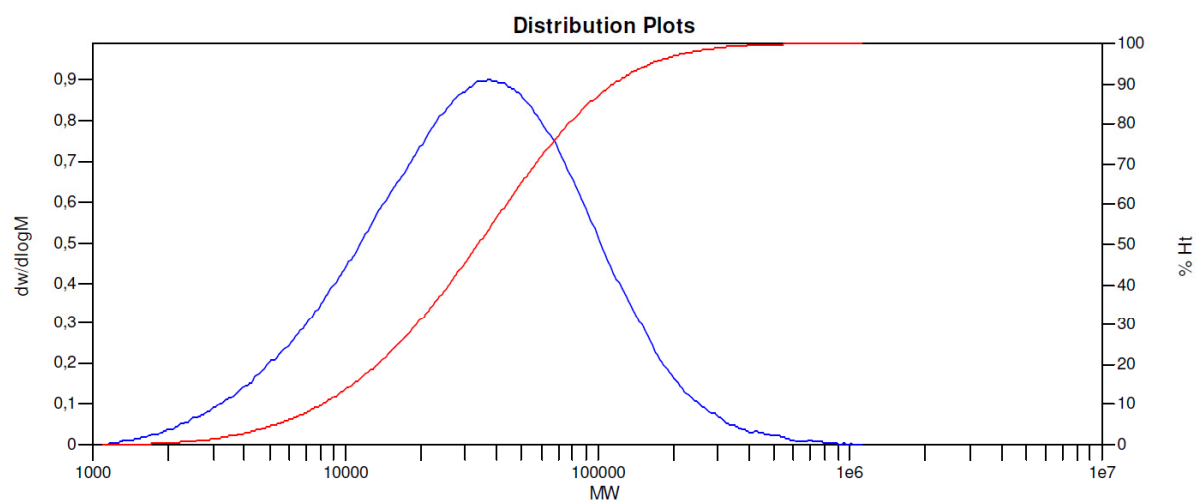
Figure S4. GPC molecular weight distribution of **P4** PDPP[T]<sub>2</sub>-T (50% azide content).



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	37383	19571	54028	119771	208161	47352	2.76062

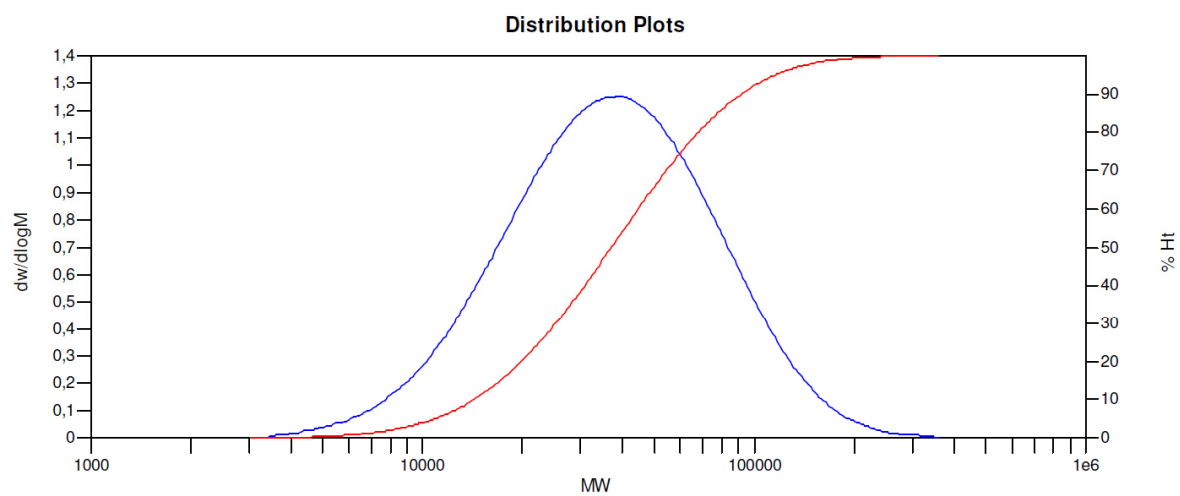
Figure S5. GPC molecular weight distribution of **P5** PDPP[Py]<sub>2</sub>-T.<sup>1</sup>



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	37730	18253	52745	130675	273036	45755	2.88966

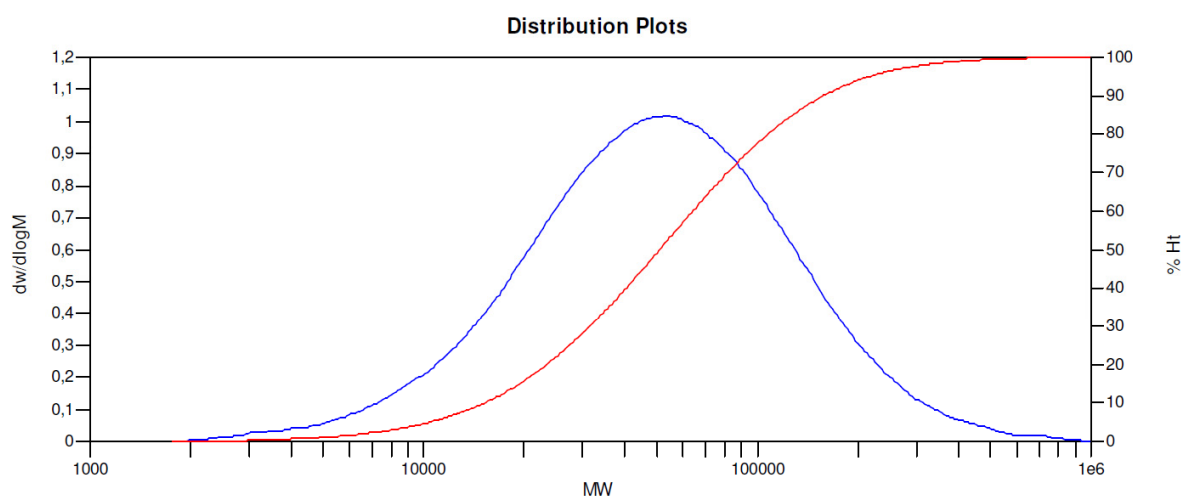
Figure S6. GPC molecular weight distribution of **P6** PDPP[Py]<sub>2</sub>-T (10% azide content).



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	38326	27896	46491	73101	106549	43316	1.66658

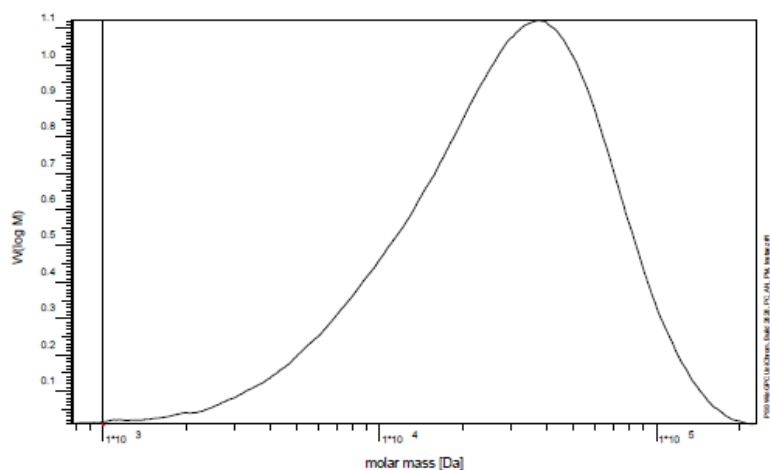
Figure S7. GPC molecular weight distribution of **P7** PDPP[T]<sub>2</sub>-Ph.



**MW Averages**

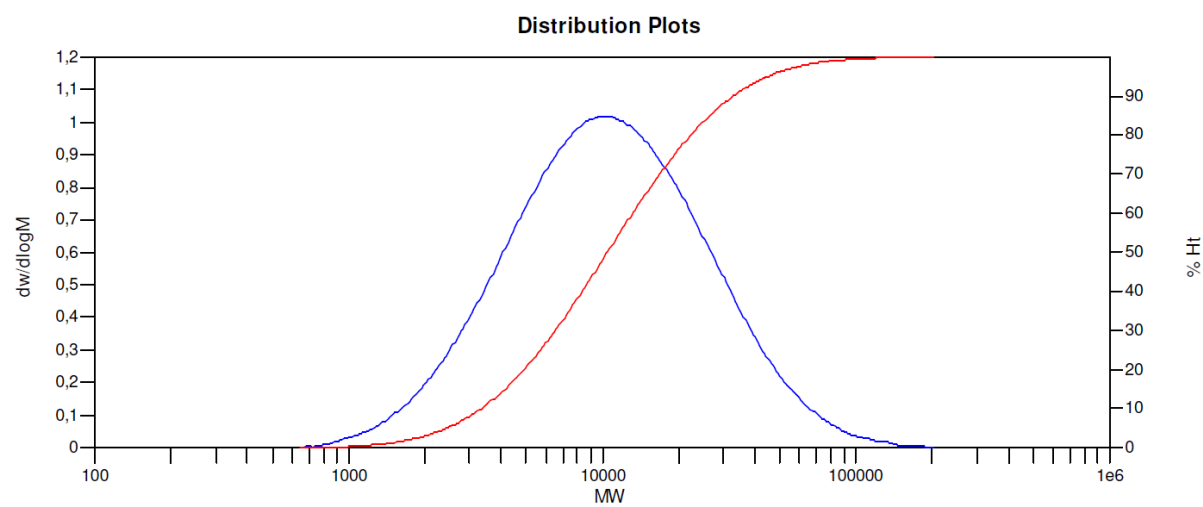
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	53864	31612	74147	156782	289130	66038	2.34553

Figure S8. GPC molecular weight distribution of **P8** PDPP[T]<sub>2</sub>-Ph (10% azide content).



	Detektor	Mn (D)	Mw (D)	Mz (D)	D (Mw/Mn)	Vp (ml)	Mp (D)	Gew.%: < 500 D	Gew.%: 500 - 1000 D
—	GPC-IR4-CH2	16300	36700	59700	2.25	35.08	36700	0.00	0.14

Figure S9. GPC molecular weight distribution of **P9** PCDTBT.



#### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10073	7110	15262	31113	55050	13663	2.14655

Figure S10. GPC molecular weight distribution of **P10** PCDTBT (10% azide content).

**Table S2.** Calculation of the average molecular weight of the polymer's repeating unit and the degree of polymerization.

Polymer	$\chi_{RU}(y)^a$ [%]	$\chi_{RU}(x)^a$ [%]	$M_{RU}(y)^b$ [g/mol]	$M_{RU}(x)^b$ [g/mol]	$\overline{M}_{RU}^c$ [g/mol]	$DP^d$
<b>PDPP[T]<sub>2</sub>-T system</b>						
<b>P1</b>	100	0	831.33	290.43	831.33	44
<b>P2</b>	90	10	831.33	290.43	777.24	41
<b>P3</b>	80	20	831.33	290.43	723.15	31
<b>P4</b>	50	50	831.33	290.43	560.88	23
<b>PDPP[Py]<sub>2</sub>-T system</b>						
<b>P5</b>	100	0	819.23	299.42	819.23	24
<b>P6</b>	90	10	819.23	299.42	767.249	24
<b>PDPP[T]<sub>2</sub>-Ph system</b>						
<b>P7</b>	100	0	823.29	283.39	823.29	34
<b>P8</b>	90	10	823.29	283.39	769.3	41
<b>PCDTBT system</b>						
<b>P9</b>	100	0	702.05	610.94	702.05	23
<b>P10</b>	90	10	702.05	610.94	692.939	10

<sup>a)</sup> molar fraction of repeating unit  $y$  and  $x$  according to feed ratio; <sup>b)</sup> molecular weight of repeating unit  $y$  and  $x$ ; <sup>c)</sup> average molecular weight of the polymer's repeating unit; <sup>d)</sup> degree of polymerization estimated from  $M_n$  and  $\overline{M}_{RU}$ ;



### 5.3 Cyclic Voltammetry

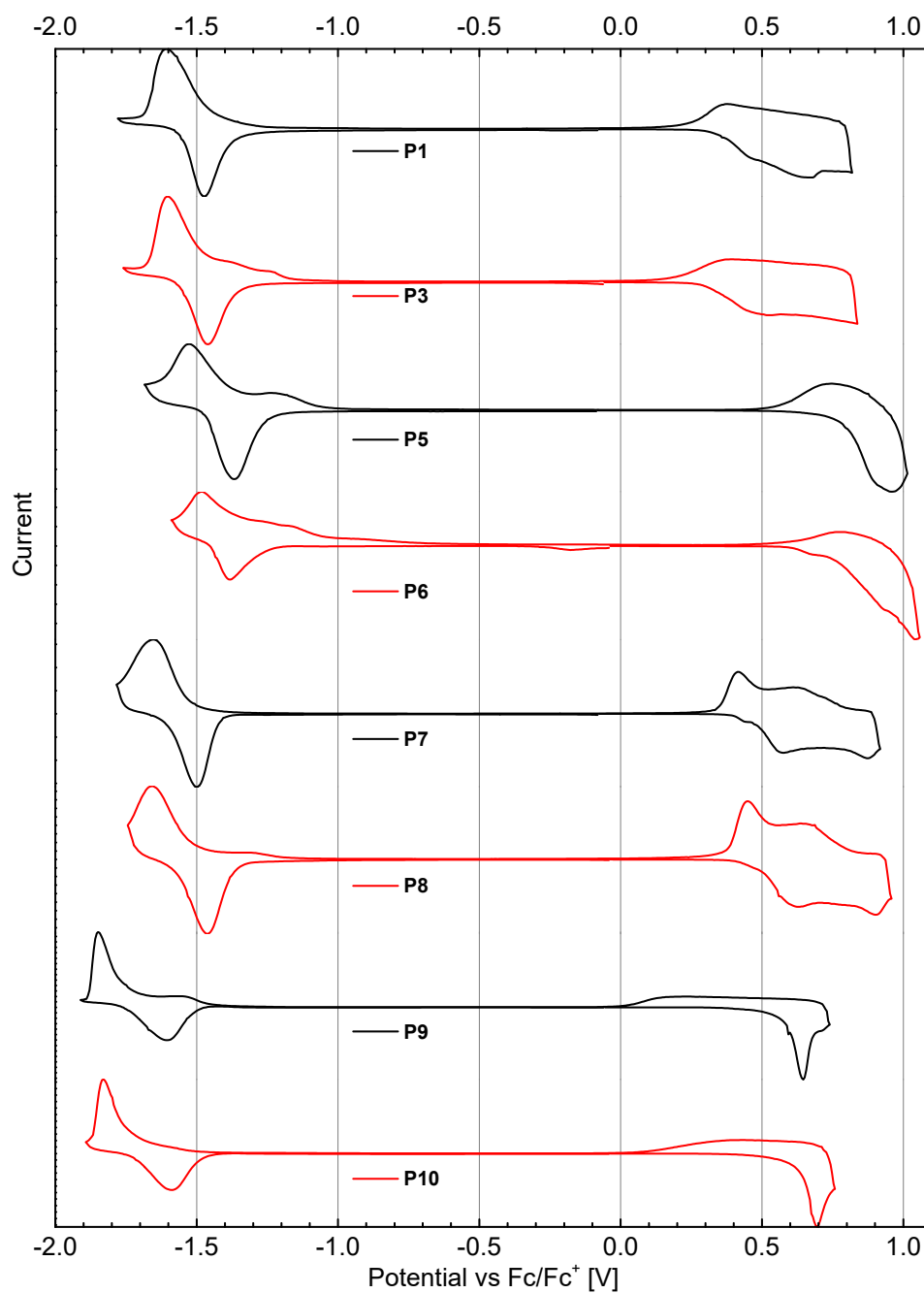


Figure S11. Solid state cyclic voltammetry scans using an acetonitrile / 0.1 M tetra-*n*-butylammonium hexafluorophosphate electrolyte solution at a scan rate of 100 mV s<sup>-1</sup> comparing azide functionalized tercopolymers (red lines) with their respective non-functionalized reference copolymers (black lines).

## 5.4 Infrared spectroscopy

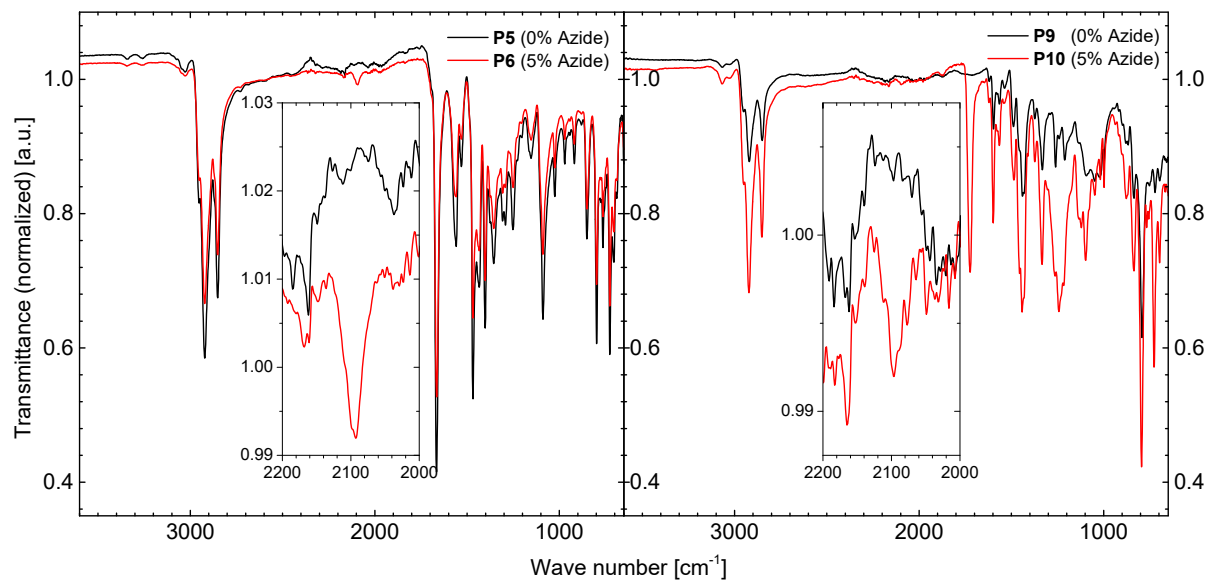


Figure S12. Infrared spectroscopy of the tercopolymers with 5% azide repeating unit content ( $x = 0.1$ , red lines) and their respective non-functionalized reference copolymers (black lines) for the PDPP[Py]<sub>2</sub>-T system (**P5/P6**) and the PCDTBT system (**P9/P10**). Insets show magnification of the characteristic azide vibration at 2100 cm<sup>-1</sup>.

## 5.5 Absorption and photoluminescence spectra

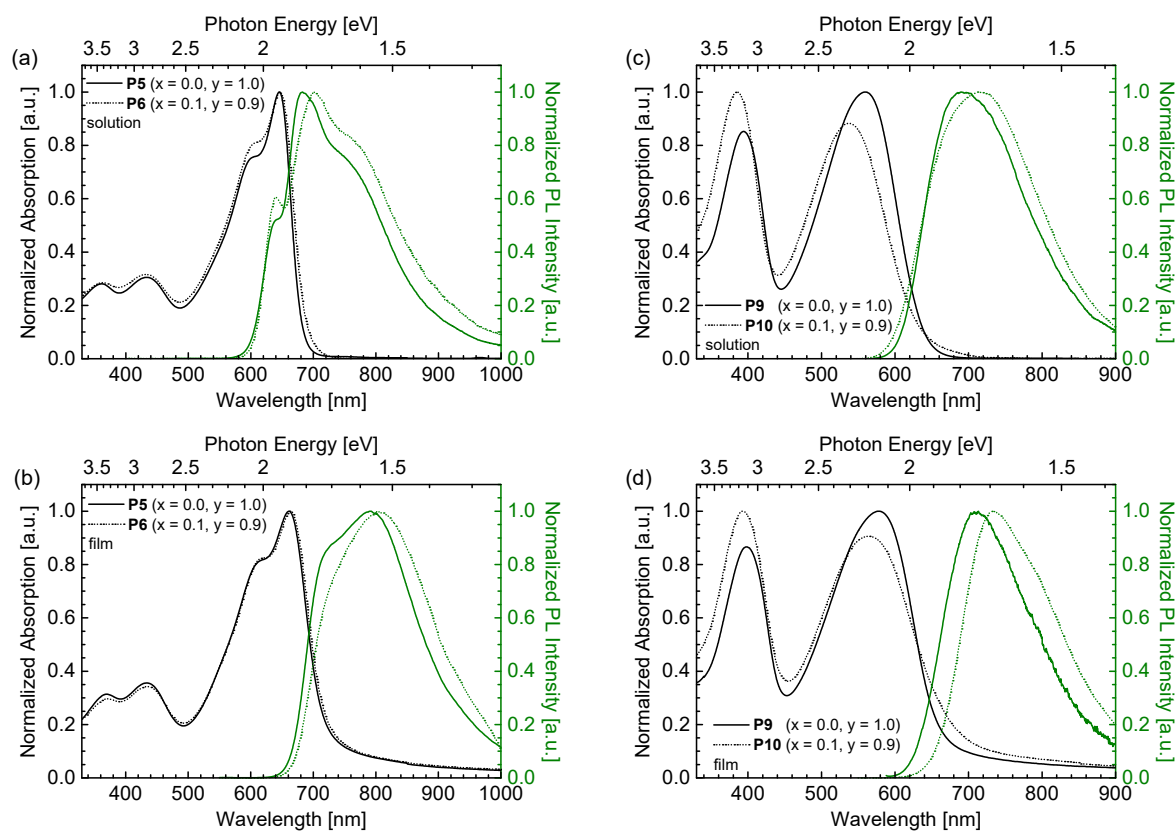


Figure S13. Absorption and photoluminescence spectra of crosslinkable tercopolymers compared to their respective non-functionalized reference polymers: PDPP[Py]<sub>2</sub>-T system **P5/P6** in (a) solution and (b) thin film; PCDTBT system **P9/P10** in (c) solution and (d) thin film.

## 5.6 GIWAXS analysis of neat polymer films

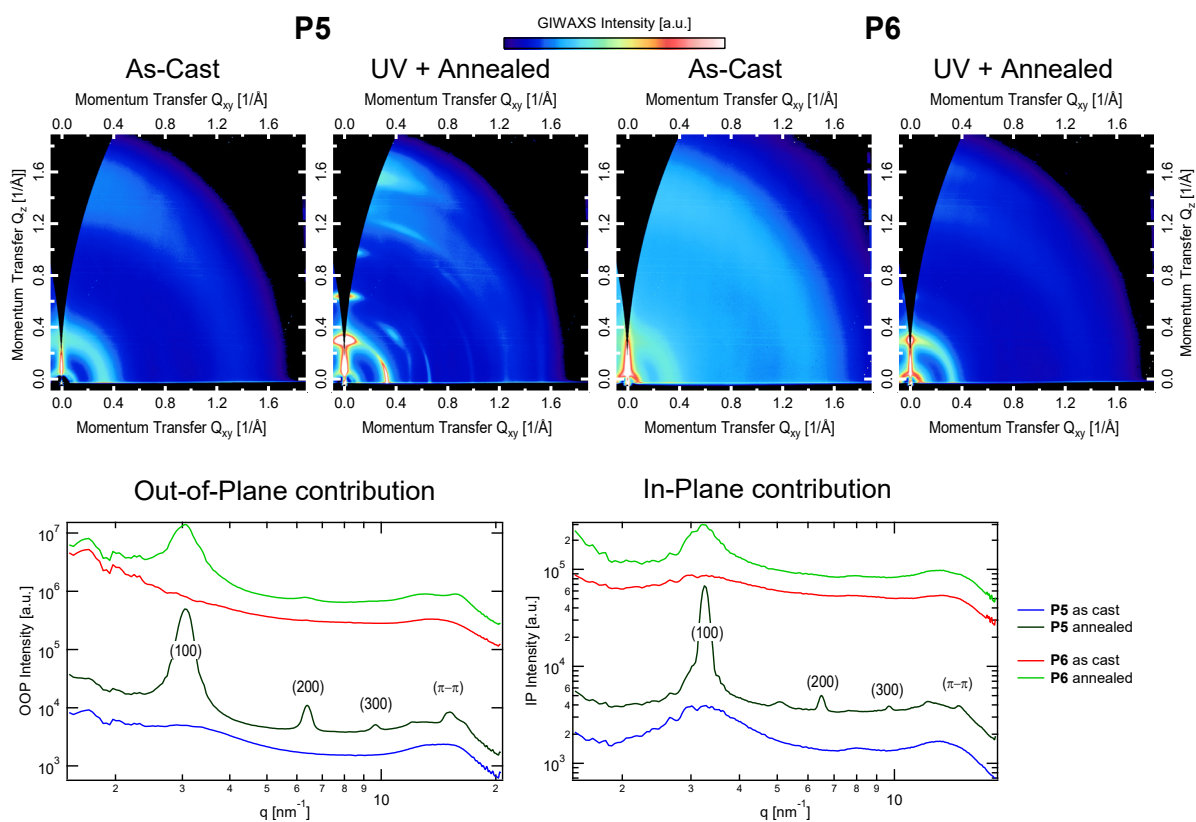


Figure S14. GIWAXS scatter patterns of neat unfunctionalized (**P5**) and azide-functionalized (**P6**) PDPP[Py]<sub>2</sub>-T polymer films.

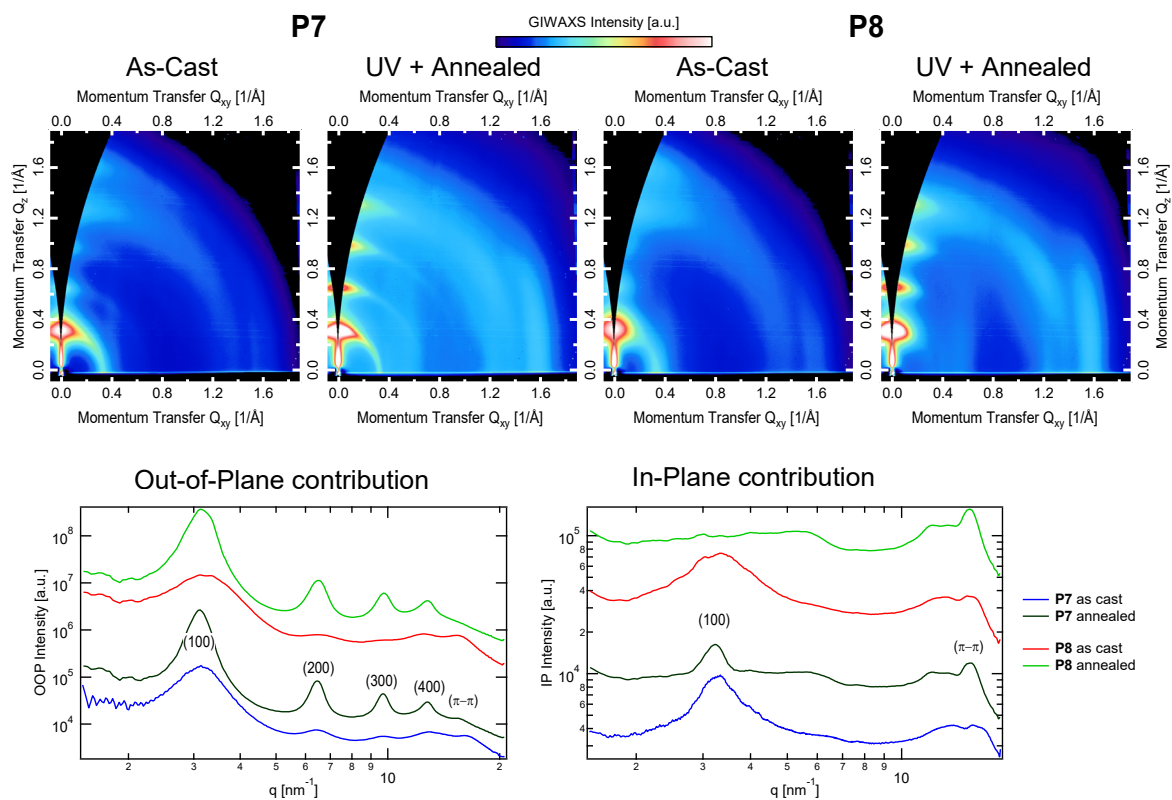


Figure S15. GIWAXS scatter patterns of neat unfunctionalized (**P7**) and azide-functionalized (**P8**) PDPP[T]<sub>2</sub>-Ph polymer thin films.

## 5.7 GIWAXS analysis of PCBM blends

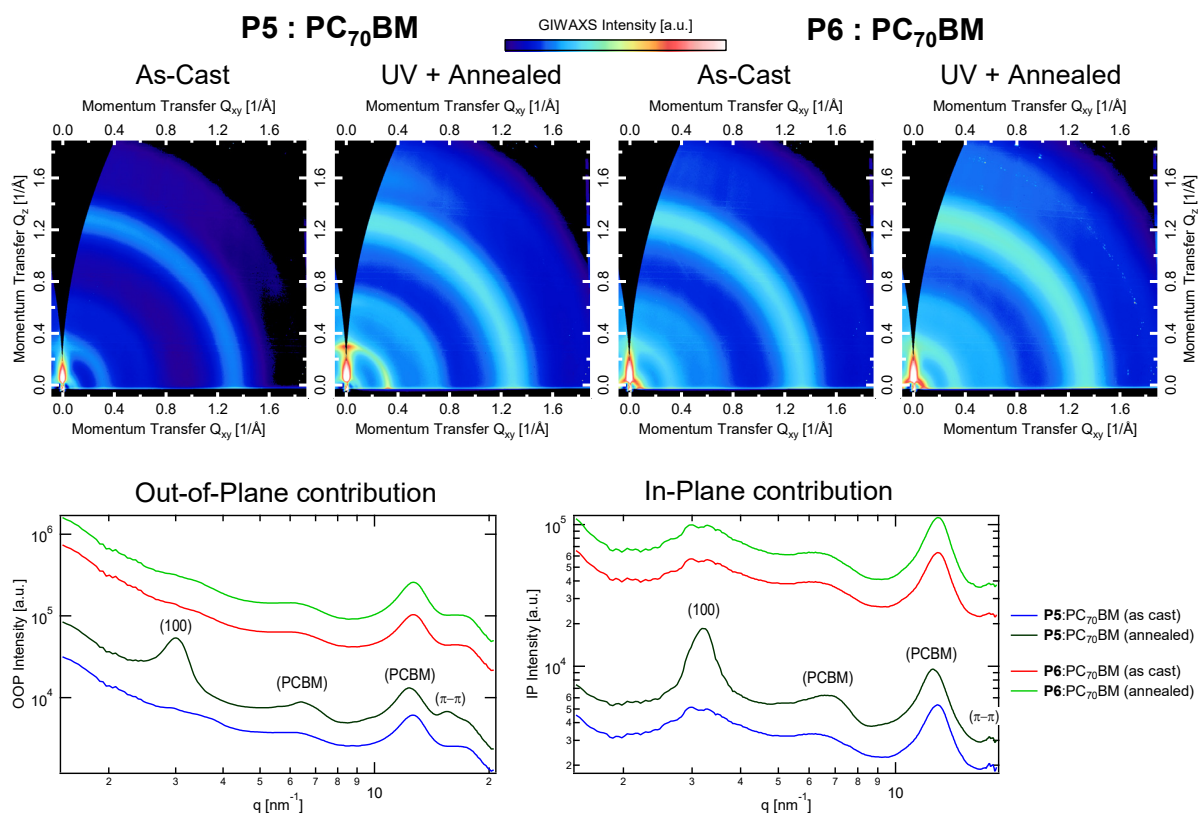


Figure S16. GIWAXS scatter patterns of unfunctionalized (P5) and azide-functionalized (P6) PDPP[Py]<sub>2</sub>-T polymer:PC<sub>70</sub>BM blends.

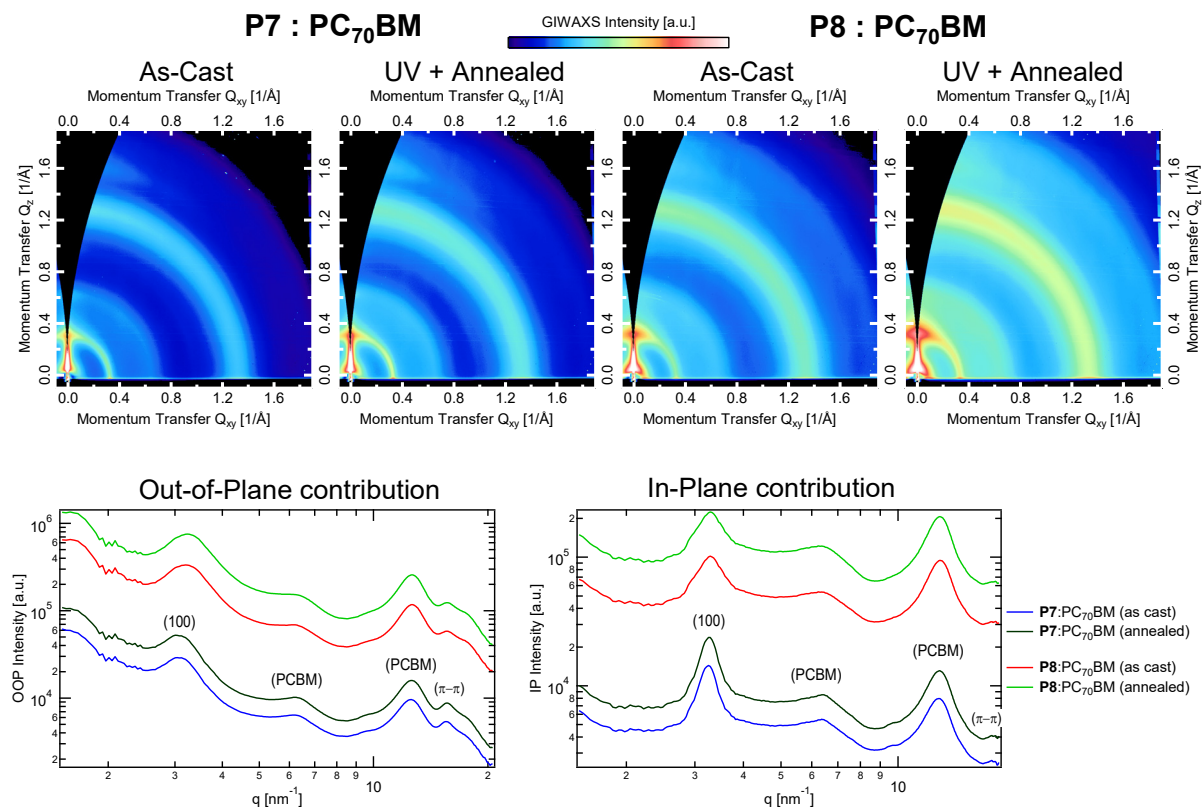


Figure S17. GIWAXS scatter patterns of unfunctionalized (**P7**) and azide-functionalized (**P8**) PDPP[T]<sub>2</sub>-Ph polymer:PC<sub>70</sub>BM blends.

## 5.8 OFET operation in n-channel

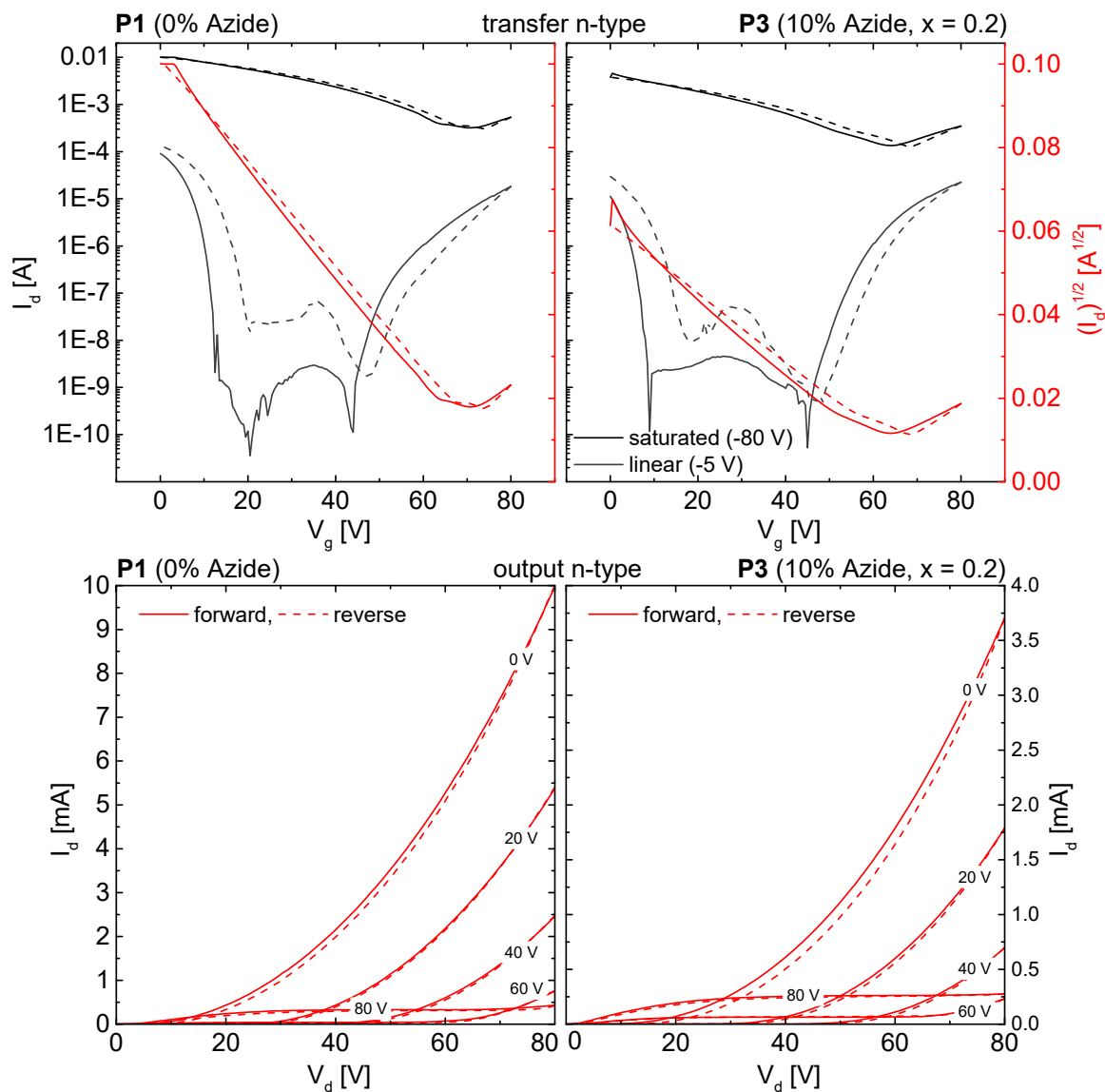


Figure S18. OFET n-type transfer and output  $I$ - $V$  characteristics after annealing at  $250\text{ }^{\circ}\text{C}$  for 15 min of the non-functionalized strictly alternating PDPP[T] $_2$ -T **P1** and the tercopolymer containing 10% azide-functionalized repeating units **P3**. Solid and dashed lines represent the forward and reverse scans in all graphs, respectively. The voltages given in the legend of the output characteristics are the applied gate voltages.



## 6 References

- (1) Mueller, C. J.; Singh, C. R.; Fried, M.; Huettnner, S.; Thelakkat, M. High Bulk Electron Mobility Diketopyrrolopyrrole Copolymers with Perfluorothiophene. *Adv. Funct. Mater.* **2015**, *25*, 2725.
- (2) Blouin, N.; Michaud, A.; Leclerc, M. A Low- Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells. *Adv. Mater.* **2007**, *19*, 2295.