Electronic Supplementary Material (ESI) for Polymer Chemistry. This journal is © The Royal Society of Chemistry 2017

Supporting Information

Simultaneous Doping and Crosslinking of Polythiophene Films

P. Reinold,^a K. Bruchlos,^a S. Ludwigs*^a

^aInstitute of Polymer Chemistry, University of Stuttgart

Pfaffenwaldring 55, 70569 Stuttgart, Germany

E-mail: sabine.ludwigs@ipoc.uni-stuttgart.de

I. Synthesis	p. 01
II. Optical properties in neutral state	р. 25
III: Electrochemistry	р. 27
IV. Chemical Doping	р. 36

I. Synthesis

Methods

All reactions were performed under an argon atmosphere. Chemicals were purchased from Sigma-Aldrich or TCI Chemicals and used without further purification. THF was dried using a solvent purification system MB-SPS-800 from MBraun. All other solvents were dried using the respective established methods. ¹H and ¹³C NMR spectra were measured using a Bruker Avance 250 DPX spectrometer at 250 and 63 MHz, respectively. SEC was performed on a SECcurity system from PSS in THF at an elution rate of 1 mL/min and a temperature of 30 °C. High Resolution ESI and EI mass spectra were measured at the Institute of Organic Chemistry (University of Stuttgart) in the positive mode on micrOTOF-Q (Bruker Daltonics) or Finnigan MAT 95 spectrometers, respectively. IR spectra were recorded in the Attenuated Total Reflection (ATR) mode on a Bruker IFS 66/S device. TGA measurements were conducted at the Institute of Inorganic Chemistry (University of Stuttgart) on a Netzsch STA 449 C instrument under an argon atmosphere with a heating rate of 10 K/min. The decomposition temperature T_d was determined at a mass loss of 3%.

a) Backbone synthesis



Scheme S1. Detailed synthethic route to alkyne functionalized precursor polymers P(3HT-co-3TBT).

3-Chloromethylthiophene (2)

Thiophene-3-methanol (1, 15.0 g, 131.4 mmol, 1 eq) was dissolved in 330 mL of CH_2CI_2 and conc. aqueous HCl (37%, 330 mL, 3.90 mol, 30 eq) was added. The mixture was stirred at room temperature for 10 h. The aqueous phase was extracted two times with CH_2CI_2 . The organic phases were washed with water, two times with saturated NaHCO₃ solution and again with water. After drying over Na₂SO₄ and removal of the solvent *in vacuo*, the product was obtained as a colorless oil which slowly degraded at room temperature while developing a brownish color. The product was thus immediately used without further purification in the next step.

Yield: 16.54 g (124.6 mmol, 95%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 7.34-7.29 (m, 2H), 7.13 (d, *J* = 4.8 Hz), 4.63 (s, 2H).



Triisopropyl-(4-thiophen-yl-but-1-inyl)-silane (3)

1-(Triisopropylsilyl)-1-propyne (10.26 g, 52.2 mmol, 1 eq) was dissolved in 250 mL dry THF under an argon atmosphere. The mixture was cooled to -78 °C and *n*BuLi (1.6 M in hexane, 34.2 mL, 54.8 mmol, 1.05 eq) was added dropwise. The mixture was stirred for 2 h after which 3-chloromethylthiophene (**2**, 6.90 g, 52.2 mmol, 1 eq) was added. The reaction mixture was further stirred for 15 h at room temperature and then quenched by addition of water. The phases were separated and the aqueous phase was extracted three times with diethyl ether. The organic phases were washed with water and brine, dried over Na₂SO₄ and the solvent was removed *in vacuo*. The crude product mixture was further purified by column chromatography (silica, CH₂Cl₂:cyclohexane = 5:95) to obtain the title compound as a clear oil.

Yield: 7.97 g (27.3 mmol, 52%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 7.24 (dd, J = 4.9 Hz, 2.9 Hz, 1H), 7.03-6.99 (m, 2H), 2.88 (t, J = 7.3 Hz, 2H), 2.55 (t, J = 7.3 Hz, 2H), 1.09-0.97 (m, 21H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 141.16, 128.18, 125.35, 120.92, 108.30, 81.13, 29.92, 21.44, 18.72, 11.39. HRMS (ESI+): calcd for [M+Na]⁺ m/z = 315.1573, found m/z = 315.1579.





¹³C-NMR spectrum of compound **3** (63 MHz, CDCl₃).

(4-(2,5-Dibromothiophen-3-yl)-but-1-inyl)-triisopropylsilane (4)

Triisopropyl-(4-thiophen-yl-but-1-inyl)-silane (**3**, 7.97 g, 27.3 mmol, 1 eq) was dissolved in 100 mL of a 1:1 mixture of glacial acetic acid and chloroform. NBS (9.70 g, 54.5 mmol, 2 eq) was added and the mixture was stirred in the dark for 3 h. More NBS (6.79 g, 38.2 mmol, 1.4 eq) was added and the bromination reaction was allowed to proceed for 60 h at room temperature until TLC analysis showed full conversion of the starting material to the dibrominated product. The reaction was quenched by addition of water, the phases separated and the aqueous phase was extracted two times with chloroform. The organic phases were washed with water and saturated NaHCO₃ solution, dried over Na₂SO₄ and the solvent evaporated. The crude product mixture was further purified by column chromatography (silica, petroleum ether) and the clean product obtained as a slightly yellowish liquid.

Yield: 7.71 g (17.3 mmol, 63%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 6.94 (s, 1H), 2.75 (t, J = 7.0 Hz, 2H), 2.51 (t, J = 7.0 Hz, 2H) 1.10-0.94 (m, 21H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 140.96, 131.39, 110.53, 108.96, 107.07, 82.07, 28.80, 20.15, 18.71, 11.37. HRMS (EI+): calcd for [M]⁺ m/z = 447.9891, found m/z = 447.9880.



¹H-NMR spectrum of compound **4** (250 MHz, CDCl₃).



¹³C-NMR spectrum of compound **4** (63 MHz, CDCl₃).

2,5-Dibromo-3-hexylthiophene (6)

3-Hexylthiophene (**5**, 15.0 g, 89.1 mmol, 1 eq) was dissolved in 150 mL of dry THF and cooled to 0 °C. NBS (39.6 g, 222.5 mmol, 2.5 eq) was added and the mixture stirred under the exclusion of light at 0 °C for 2 h. At this point the conversion was found to be incomplete by TLC. The reaction was further stirred in the dark at rt overnight until TLC indicated nearly quantitative conversion of the monobrominated compound to the desired product. The reaction mixture was then diluted with diethyl ether and saturated NaHCO₃ solution was added. The layers were separated and the organic layer was washed two times with water and one time with brine, dried over Na₂SO₄ and the solvent removed *in vacuo*. The crude product was further purified by column chromatography using cyclohexane as the eluent to obtain the desired compound as a slightly orange oil.

Yield: 24.2 g (74.2 mmol, 83%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 6.78 (s, 1H), 2.51 (t, J = 7.6 Hz, 2H), 1.60-1.48 (m, 2H), 1.37-1.27 (m, 6H), 0.92-0.86 (t, J = 6.6 Hz, 3H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 143.15, 131.11, 110.44, 108.06, 31.71, 29.70, 29.63, 28.93, 22.71, 14.22. HRMS (EI+): calcd for [M]⁺ m/z = 323.9183, found m/z = 323.9176.



¹³C-NMR spectrum of compound **6** (63 MHz, CDCl₃).

P(3HT-co-3TBT) (73/27)

[4-(2,5-Dibromothiophen-3-yl)-but-1-inyl]-triisopropylsilane (**4**, 540 mg, 1.2 mmol, 0.3 eq) and 2,5-dibromo-3-hexylthiophene (**6**, 913 mg, 2.8 mmol, 0.7 eq) were dissolved in 4 mL of dry THF under an argon atmosphere. A solution of *t*BuMgCl (2.0 M in Et₂O, 2.0 mL, 4.0 mmol, 1 eq) was added *via* syringe. After stirring at room temperature for 2 h the mixture was diluted to a total volume of 20 mL with dry THF. After addition of the catalyst Ni(dppp)Cl₂ (21.6 mg, 0.04 mmol, 0.01 eq) the mixture was allowed to react for 2 h at room temperature. The polymer **P(3HT-***co***-3TBT)** was precipitated into methanol, collected by centrifugation and dried in a vacuum oven at 50 °C overnight.

Yield: 394 mg

¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 7.07 (s), 6.98 (s), 3.08 (br), 2.80 (br), 2.66 (br), 1.71 (br), 1-36 (br), 1.04 (br), 0.91 (br). ¹³C-NMR (63 MHz, CDCl₃): δ [ppm] = 140.04, 137.58, 133.84, 130.64, 128.75, 107.87, 81.68, 31.86, 30.68, 29.63, 29.43, 29.05, 22.82, 21.08, 18.79, 14.29, 11.44. Repeating unit ratio 3HT/3TBT = 73/27. SEC (THF): $\overline{M_n}$ = 18000 g/mol, $\overline{M_w}$ = 23000 g/mol, PDI = 1.3



Figure S1a. ¹H-NMR spectrum of **P(3HT-***co***-3TBT) (73/27)** (250 MHz, CDCl₃).



Figure S1b. ¹³C-NMR spectrum of P(3HT-co-3TBT) (73/27) (63 MHz, CDCl₃).

Additionally, a polymer batch with a repeating unit ratio of 3HT/3TBT = 91/9 was synthesized employing the same reaction protocol.

¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 7.07 (s), 6.98 (s), 3.07 (br) 2.81 (br), 2.61 (br), 1.71 (br), 1.36 (br), 1.04 (br), 0.91 (br). SEC (THF): $\overline{M_n}$ = 21000 g/mol, $\overline{M_w}$ = 40000 g/mol, PDI = 1.9



Figure S1c. ¹H-NMR spectrum of P(3HT-co-3TBT) (91/09) (250 MHz, CDCl₃).



Figure S2. SEC traces of precursor polymers P(3HT-co-3TBT).

b) Synthesis of triphenylamine azides



Scheme S2. Synthetic route towards triphenylamine azide compounds TPA-N₃ (11) and spTPA-N₃ (13).

4-Nitrotriphenylamine (9)

Diphenylamine (**8**, 5.00 g, 29.6 mmol, 1 eq) and NaH (1.11 g, 46.0 mmol, 1.6 eq) were suspended in 30 mL of DMAc. The suspension was stirred at room temperature for 30 min and then cooled to 0 °C in an ice bath. 4-Fluoronitrobenzene (**7**, 5.00 g, 35.5 mmol, 1.2 eq) in 30 mL of DMAc was added slowly at this temperature and the mixture was heated to 100 °C and stirred for 1 h. The reaction was quenched by pouring into dilute aqueous HCl. Recrystallization of the crude product from a 1:1 mixture of water and isopropanol and subsequent purification *via* column chromatography (silica, petroleum ether: $CH_2CI_2 = 2:1$) yielded the title compound as an orange crystalline solid.

Yield: 6.91 g (23.8 mmol, 81%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 8.04 (d, J = 9.4 Hz, 2H), 7.40-7.34 (m, 4H), 7.24-7.17 (m, 6H), 6.92 (d, J = 9.4 Hz, 2H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 153.59, 145.75, 140.24, 130.04, 126.63, 125.85, 125.57, 118.22. HRMS (ESI+): calcd for [M+Na]⁺ m/z = 313.0947, found m/z = 313.0953.



¹³C-NMR spectrum of compound **9** (63 MHz, CDCl₃).

4-Aminotriphenylamine (10)

A mixture of 4-nitrotriphenylamine (**9**, 2.00 g, 6.9 mmol, 1 eq) and palladium on carbon (10 w%, 0.10 g, 0.01 eq) in 14 mL of ethanol was heated to reflux. After careful addition of hydrazine monohydrate (2.1 mL, 42.6 mmol, 6.2 eq) *via* syringe the mixture was stirred under reflux overnight. The mixture was cooled down to room temperature, the catalyst removed by filtration and the resulting clear solution poured into water to precipitate the product. The white crystalline solid was collected by suction filtration and dried in a vacuum oven at 50 °C overnight.

Yield: 1.31 g (5.0 mmol, 72%)

¹H-NMR (250 MHz, CDCl₃): δ[ppm] = 7.23-7.16 (m, 4H), 7.04-6.89 (m, 8H), 6.65 (d, J = 8.7 Hz, 2H), 3.60 (s, 2H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 148.36, 142.29, 139.51, 129.13, 127.80, 122.76, 121.70, 116.66. HRMS (ESI+): calcd for [M+H]⁺ m/z = 261.1386, found m/z = 261.1388.



¹H-NMR spectrum of compound **10** (250 MHz, CDCl₃).



¹³C-NMR spectrum of compound **10** (63 MHz, CDCl₃).

TPA-N₃ (11)

4-Aminotriphenylamine (**10**, 660 mg, 2.5 mmol, 1 eq) was dissolved in a mixture of conc. HCI (37%, 0.5 mL) and water (6.6 mL) and the mixture was cooled down to 0 °C in an ice bath. The diazonium salt of the compound was formed by slow addition of a solution of sodium nitrite (185 mg, 2.7 mmol, 1.1 eq) in 2.6 mL of water which caused a significant color change of the reaction mixture to orange-red. After stirring the reaction for an additional hour at 0 °C, sodium azide (198 mg, 3.9 mmol, 1.2 eq) in 2.6 mL of water was added slowly. The mixture was allowed to react for an additional hour. The product was extracted from the solution with CH_2Cl_2 and the organic phase was washed with water, saturated NaHCO₃ solution, water and brine and dried over Na₂SO₄. After removal of the solvent *in vacuo* the crude product mixture was purified by column chromatography (silica, cyclohexane: $CH_2Cl_2 = 2:1$) to obtain the title compound as a white solid. Since **11** degrades to a variety of colored products under UV light, it should be purified, stored and handled in the dark.

Yield: 661 mg (2.3 mmol, 77%)

¹H-NMR (250 MHz, CD₂Cl₂): δ [ppm] = 7.28-7.22 (m, 4H), 7.09-6.99 (m, 8H), 6.93 (d, J = 9.0 Hz, 2H). ¹³C-NMR (63 MHz, CDCl₃): δ [ppm] = 147.74, 145.12, 134.24, 129.43, 125.68, 124.08, 122.98, 120.01. HRMS (ESI+): calcd for [M+H]⁺ m/z = 287.1291, found m/z = 287.1293. IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2079 (-N₃).



Figure S3a. ¹H-NMR spectrum of compound 11 (250 MHz, CD₂Cl₂).



Figure S3b. ¹³C-NMR spectrum of compound **11** (63 MHz, CDCl₃).



Figure S3c. ATR-IR spectrum of compound 11.

6-Bromo-N-(4-(diphenylamino)phenyl)hexanamide (12)

6-Bromohexanoyl chloride (0.29 mL, 1.9 mmol, 1 eq) was dissolved in 8 mL of dichloromethane and cooled to 0 °C in an ice bath. 4-Aminotriphenylamine (**10**, 500 mg, 1.9 mmol, 1 eq) and triethylamine (0.27 mL, 1.9 mmol, 1 eq) in 38 mL of dichloromethane were added dropwise by syringe. The ice bath was removed and the solution stirred for 12 h at room temperature. It was diluted with Et_2O and washed two times with saturated ammonium chloride solution, water and brine, dried over Na₂SO₄ and the solvent was removed *in vacuo*. The crude product was further purified *via* column chromatography (silica, CH_2CI_2) to obtain the product as a colorless oil which crystallized slowly to a white solid upon standing at room temperature.

Yield: 583 mg (1.3 mmol, 70%)

¹H-NMR (250 MHz, CD₂Cl₂): δ[ppm] = 7.40 (d, J = 8.6 Hz, 2H), 7.27-7.20 (m, 5H), 7.05-6.96 (m, 8H), 3.44 (t, J = 6.9 Hz, 2H), 2.34 (t, J = 7.6 Hz, 2H), 1.96-1.84 (m, 2H), 1.79-1.67 (m, 2H), 1.57-1.45 (m, 2H). ¹³C-NMR (63 MHz, CDCl₃): δ[ppm] = 170.94, 147.87, 144.31, 133.05, 129.32, 125.17, 123.90, 122.67, 121.26, 37.44, 33.74, 32.57, 27.87, 24.82. HRMS (ESI+): calcd for [M+Na]⁺ m/z = 459.1042, found m/z = 459.1036.



¹³C-NMR spectrum of compound **12** (63 MHz, CDCl₃).

spTPA-N₃ (13)

6-Bromo-N-(4-(diphenylamino)phenyl)hexanamide (**12**, 400 mg, 0.91 mmol, 1 eq) and sodium azide (310 mg, 4.77 mmol, 5.2 eq) were suspended in 8 mL of dry DMF inside a glove box. The mixture was stirred at room temperature for 16 h and poured into 100 mL of brine. The resulting mixture was extracted two times with EtOAc. The combined organic phases were washed with water 8 times, dried over Na₂SO₄ and concentrated *in vacuo*. The crude product was further purified by column chromatography (silica, CH₂Cl₂) and the product obtained as a colorless oil which crystallized very slowly under storage at -24 °C.

Yield: 353 mg (0.88 mmol, 97%)

¹H-NMR (250 MHz, CD_2CI_2): δ [ppm] = 7.40 (d, J = 8.6 Hz, 2H), 7.27-7.20 (m, 5H), 7.07-6.96 (m, 8H), 3.29 (t, J = 6.9 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 1.79-1.61 (m, 4H), 1.50-1.41 (m, 2H). ¹³C-NMR (63 MHz, CDCI₃): δ [ppm] = 170.94, 147.86, 144.29, 133.08, 129.32, 125.17, 123.89, 122.66, 121.23, 51.36, 37.45, 28.76, 26.48, 25.19. HRMS (ESI+): calcd for [M+Na]⁺ m/z = 422.1951, found m/z = 422.1958. IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2094 (-N₃), 1654 (C=O).



Figure S4a. ¹H-NMR spectrum of compound **13** (250 MHz, CD₂Cl₂).



Figure S4b. ¹³C-NMR spectrum of compound **13** (63 MHz, CDCl₃).



Figure S4c. ATR-IR spectrum of compound 13.

c) Functionalization via copper(I) catalyzed click chemistry



Scheme S3. Polymer analogous functionalization of precursor polymers P(3HT-co-3TBT) with triphenylamine azides 11 and 13 towards CRPs PT-TPA and PT-spTPA.

Polymer analogous reactions to PT-TPA and PT-spTPA

P(3HT-co-3TBT) (73/27 mol%, 100 mg, 0.16 mmol of alkyne groups, 1 eq) was dissolved in 20 mL of dry THF and TBAF solution (1.0 M in THF, 0.8 mL, 0.8 mmol, 5 eq) was added via a syringe. A slight color change from bright orange to orange-red occurred instantly. After stirring for 1 h at 50 °C, the mixture was cooled down to rt. Chloroform and water were added and the layers separated. The aqueous layer was extracted two times with chloroform and the combined organic phases were washed with water four times. After drying the organic phases over Na₂SO₄, the solvent was evaporated. The resulting solid was dissolved in 20 mL of dry THF and transferred into a Schlenk tube. Copper powder (10 mg, 0.16 mmol, 1 eq) and the respective TPA azide compound (**TPA-N**₃ (**11**) or **spTPA-N**₃ (**13**) 0.32 mmol, 2 eq) were added and the mixture was degassed by four cycles of freeze-pump-thaw. [Cu(MeCN)₄]PF₆ (59 mg, 0.16 mmol, 1 eg) was added under a constant stream of argon. The Schlenk tube was sealed and the mixture heated to 45 °C for 68 h. The solution was diluted by addition of chloroform and washed three times with water to dissolve any gel-like particles. The organic phase was dried over Na₂SO₄ and passed over a short aluminium oxide column to remove residual copper salts. The crude polymer product was collected by precipitation in MeOH and purified by Soxhlet extraction with MeOH, EtOAc and CHCl₃. The chloroform fraction was collected. Residual small molecule impurities were separated by preparative SEC.

PT-TPA: Yield: 55 mg

¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 7.69-7.48 (br), 7.26-6.98 (br), 3.41 (br), 3.22 (br), 2.78 (br), 1.68 (br), 1.35 (br), 0.91 (br). SEC (THF): $\overline{M_n}$ = 21000 g/mol, $\overline{M_w}$ = 26000 g/mol, PDI = 1.2

PT-spTPA: Yield: 75 mg

¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 7.39 (br), 7.17 (br), 6.98 (br), 4.28 (br), 3.14 (br), 2.79 (br), 2.25 (br), 1.86 (br), 1.68 (br), 1.34 (br), 0.90 (br). SEC (THF): $\overline{M_n}$ = 24500 g/mol, $\overline{M_w}$ = 30500 g/mol, PDI = 1.2



Figure S5. ¹H-NMR spectrum of deprotected prepolymer **P(3HT-***co***-3TBT)** compared to the functionalized polymers **PT-TPA** and **PT-spTPA** (250 MHz, CDCl₃).



Figure S6. ATR-IR spectra of protected and deprotected P(3HT-co-3TBT) with a ratio of 73/27 repeating units and the functionalized CRPs PT-TPA and PT-spTPA.



Figure S7. Thermogravimetric analysis of prepolymer P(3HT-co-3TBT), PT-TPA and PT-spTPA. The two separate steps of decomposition likely correspond to pendant group (TIPS and TPA) and polymer backbone decomposition, respectively.

For comparison, P(3HT-co-3TBT) with repeating unit ratio 91/9 was also functionalized with spTPA-N₃ (13) yielding a PT-spTPA batch with lower content of triphenylamine pendant groups.

¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 7.33 (br), 7.16 (br), 6.98 (br), 4.31 (br), 3.16 (br), 2.80 (br), 2.21 (br), 1.88 (br), 1.70 (br), 1.36 (br), 0.91 (br). SEC (THF): $\overline{M_n}$ = 28500 g/mol, $\overline{M_w}$ = 48500 g/mol, PDI = 1.7



Figure S8. ¹H-NMR spectrum of PT-spTPA batch with repeating unit ratio 91/9 (250 MHz, CDCl₃).



Scheme S4. Synthesis of model compound T-TPA (14).

Model compound T-TPA (14)

[4-(2,5-Dibromothiophen-3-yl)-but-1-inyl]-triisopropylsilane (**4**, 280 mg, 0.62 mmol, 1 eq) was dissolved in 10 mL of dry THF and TBAF solution (1.0 M in THF, 3.1 mL, 3.1 mmol, 5 eq) was added. The mixture was heated to 50 °C for 2 h and cooled down to rt. The solution was diluted with CHCl₃ and washed four times with water. The organic phase was dried over Na₂SO₄ and the solvent removed *in vacuo*. The residue was dissolved in 10 mL of dry THF. **TPA-N₃** (**11**, 194 mg, 0.68 mmol, 1.1 eq) and copper powder (20 mg, 0.31 mmol, 0.5 eq) were added and the solution was degassed by four cycles of freeze-pump-thaw. [Cu(MeCN)₄]PF₆ (115 mg, 0.31 mmol, 0.5 eq) was added under argon, the vial was sealed and the mixture heated to 45 °C for 24 h. The copper catalyst was removed by filtration over basic aluminium oxide. The crude product was further purified by column chromatography on silica. First a solvent mixture of cyclohexane:CH₂Cl₂ = 1:1 was used to wash several side products from the column while the strongly fluorescent model compound was found to elute very slowly. The solvent was then changed to 100% CH₂Cl₂ to isolate the desired compound.

Yield: 267 mg (0.46 mmol, 74%)

¹H-NMR (250 MHz, CD_2CI_2): δ [ppm] = 7.61 (s, 1H), 7.51 (d, J = 9.4 Hz, 2H), 7.34-7.27 (m, 4H), 7.16-7.05 (m, 8H), 6.86 (s, 1H), 3.07-2.92 (m, 4H). ¹³C-NMR (63 MHz, CDCI₃): δ [ppm] = 148.49, 147.30, 146.95, 141.46, 131.28, 131.16, 130.98, 129.83, 129.41, 125.22, 124.76, 124.08, 123.64, 123.28, 122.50, 121.83, 121.68, 121.05, 120.25, 119.44, 118.65, 110.89, 109.02, 29.32, 25.79. HRMS (ESI+): calcd for [M+Na]⁺ m/z = 600.9668, found m/z = 600.9677.



Figure S9a. ¹H-NMR spectrum of compound 14 (250 MHz, CD₂Cl₂).



Figure S9b. ¹³C-NMR spectrum of compound **14** (63 MHz, CDCl₃).

II. Optical properties in neutral state

UV/Vis spectra in THF solution (0.1 mg/mL) were recorded on a Lambda 35 spectrometer from Perkin Elmer. Film spectra on glass slides (prepared by spin coating from 5 mg/mL chloroform solutions) were measured using a Zeiss device equipped with a MCS621 Vis II spectrometer cassette and a CLH600F lamp on a THMS 600 hot-stage from LINKAM connected *via* glass fiber optics (Ocean Optics).



Figure S10. Optical absorption properties of protected and deprotected precursor polymer P(3HT-co-3TBT).



Figure S11. a) and b) Absorption spectra of deprotected **P(3HT-***co***-3TBT)** (blue), respective TPA azide compounds **TPA-N**₃ and **spTPA-N**₃ (black) and functionalized polymers **PT-TPA** (green) and **PT-spTPA** (red) in THF solution. Model compound **T-TPA** (14) is shown in brown. c), d) Comparison of solution (solid lines) and film spectra (dashed lines) of **PT-TPA** and **PT-spTPA**. e) Comparison of absorption spectra of **PT-spTPA** with repeating unit ratios of 73/27 and 91/9 in THF solution.

III. Electrochemistry

Thin films of the polymers were prepared by spin coating at room temperature from chloroform solutions (5 mg/mL or 10 mg/mL) onto gold or indium tin oxide (ITO) coated glass slides, as well as interdigitated platinum electrodes from DropSens. The substrates were cleaned by ultrasonication in acetone and isopropyl alcohol. All films were prepared and stored under the exclusion of air under vacuum or nitrogen atmosphere.

Autolab PGSTAT101 or PGSTAT204 potentiostats from Metrohm were used for all electrochemical measurements. Scan rates of 20 mV/s (for cyclic voltammetry and spectroelectrochemistry) and 10 mV/s (for CV coupled with *in-situ* conductance measurements) were applied.

Cyclic voltammetry of thin films was measured at room temperature in a threeelectrode cell with a Pt plate counter electrode and an AgCl-coated silver wire directly immersed into the electrolyte solution as a pseudo-reference electrode. Thin films on gold coated glass were used as the working electrode. Measurements were performed in degassed 0.1 M $NBu_4PF_6/MeCN$ electrolyte under an argon atmosphere and all values are reported against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

For *in-situ* spectroelectrochemistry measurements, ITO coated glass slides (<20 Ω /sq, PGO) covered with the polymer film were used as the working electrode. A similar three-electrode setup with a Pt wire as the counter electrode was used in a custom-built guartz cell which was placed inside the spectrometer beam path and the working electrode arranged perpendicular to the beam. The cell holder was connected to the spectrometer setup (Zeiss device equipped with a MCS621 Vis II spectrometer cassette and a CLH600F lamp) via glass fiber optics (Ocean Optics). Background absorption was measured on a clean ITO slide. All spectra were recorded in transmission mode *in-situ* at each potential step of the electrochemical measurement. Solution spectroelectrochemical measurements of the small molecule model compounds were performed using the same electrolyte containing 1 mg/mL (unless otherwise stated) of the respective analyte in a three-electrode custom-built guartz cell. A polished Pt disk electrode with a diameter of 4 mm was employed as the working electrode and as reflection point for the spectrometer beam, while the counter and reference electrodes consisted of Pt and Ag/AgCl wires, respectively. Absorption spectra were recorded in reflection mode.

In-situ conductance profiles were recorded using a setup similar to an electrolyte gated transistor. Interdigitated Pt electrodes from DropSens (comb distance = 5 µm) were used as the working electrodes. A two-potentiostat setup was used, one applying a constant potential bias (10 mV) between the interdigitated combs and the other one controlling the cyclic voltammetry measurement and simultaneously recording the current between working and counter electrode as well as the current between the interdigitated combs. The conductance values G were calculated from the measured current flowing between the combs according to Ohm's law ($G = \frac{1}{R} = \frac{I}{V}$).



Two-potentiostat setup used for measuring potential-dependent conductance profiles of polymer thin films.



Figure S12. a) b) Forward and c) d) backward spectroelectrochemical measurements of precursor polymer **P(3HT-***co***-3TBT)** thin films (first cycle). e) 1st and 2nd cycle CV measurements. f) CV with *in-situ* conductance measurement recorded during electrochemical oxidation on interdigitated Pt electrode (2nd cycle).





Figure S13. a) b) Forward and c) d) backward spectroelectrochemical measurements of **PT-TPA** thin films (first cycle). e) 1st and 2nd cycle CV measurements.





Figure S14. a) b) Forward and c) d) backward spectroelectrochemical measurements of **PT-spTPA** thin films (first cycle). e) 1st and 2nd cycle CV measurements.

CV measurements were performed on the **PT-spTPA** batch with a repeating unit ratio of 91/9 for comparison, showing a significantly higher contribution of the backbone charging and discharging process on the resulting currents due to the lower pendant group content.



Figure S15. 1st and 2nd cycle CV measurements of **PT-spTPA** batch with repeating unit ratio 91/9.

Model compound T-TPA (14)



Figure S16. Solution spectroelectrochemistry measurements of model compound T-TPA (14). a) Charge scan, b) discharge scan.

Model compound spTPA-N₃ (13)



Figure S17. Solution spectroelectrochemistry measurements of model compound spTPA-N₃ (13) in highly dilute solution (0.1 mg/mL). a) b) Forward scan, c) d) backward scan.





Figure S18. Comparison of a) 1st and b) 2nd cycles of **P(3HT-co-3TBT)**, **PT-TPA** and **PT-spTPA** thin films on gold electrodes. Comparison of cyclic voltammetry measurements of c), e), g) 1st and d), f), h) 2nd cycles of **P(3HT-co-3TBT)**, **PT-TPA** and **PT-spTPA** thin films recorded on gold (Au), indium tin oxide (ITO) and interdigitated platinum electrodes (Pt).

IV. Chemical Doping

Thin films were prepared by spin coating the polymers on cleaned glass substrates from toluene solution (5 mg/mL) at room temperature. The substrates were then dipped into solutions of the dopants iron(III) chloride and 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) in acetonitrile for two seconds and one minute, respectively, cleaned in pure acetonitrile and blown dry using a stream of argon. Sheet resistivites of the polymer films were immediately measured using the four-point-probe technique (Signatone SP4 probe head, linear arrangement of tips, spacing = 1 mm, Keithley 2636B SourceMeter). Film thickness t was measured by profilometry with a Veeco Dektak 150 Surface Profiler. Bulk conductivities σ were

then calculated from the measured potentials V and currents I using $\sigma = \left(\frac{\pi}{\ln(2)}t\frac{V}{I}\right)^{-1}$.



Schematic process used for chemical doping of polymer thin films on glass substrates.





Figure S19. Absorption spectra and conductivity measurements of **PT-TPA** doped with a), b) F_4TCNQ and c), d) FeCl₃ solutions of different concentrations in acetonitrile.





Figure S20. Absorption spectra and conductivity measurements of **PT-spTPA** doped with a), b) F₄TCNQ and c), d) FeCl₃ solutions of different concentrations in acetonitrile.