Simplified Methods for the Functionalisation of 3-Hexoxythiophenes at 5-Position and Further Reactions to Alkynyl and Vinyl Derivatives.

Supporting Information

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General: All chemicals were used as supplied. Dry solvents stored over molecular sieve were used for all reactions except the Suzuki coupling. Reactions were performed in flame dried flasks under nitrogen atmosphere. 3-Hexoxythiophene 1, 4-hexoxythiophene-2-boronicacid 4 and diethyl-(2,5-dibromothiophen-3-yl)methylphosphonate 13 were synthesised by literature procedures.[1,2,3]

Chromatography: TLC plates and silica gel were purchased from Machery Nagel GmbH & Co KG.

Analytical methods: NMR experiments were recorded on a Varian MercuryPlus 200 (1H NMR / 199.98 MHz; 13C NMR / 50.29 MHz) and Bruker DRX-400 (1H NMR / 400.14 MHz; 13C NMR / 100.62 MHz). 1H NMR resonances are referenced relative to tetramethylsilane (TMS) and 13C NMR spectra to CDCl3 at 77.3 ppm. Data are reported as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dddd = doublet of doublets of doublet of doublets. If a signal can not be assigned to a special carbon or hydrogen clearly, the possible atom numbers are separated by a slash, e.g. 2/5/7. If one signal belongs to two or more carbon or hydrogen atoms, the atom numbers are separated by a comma, e.g. 2,5,7. High and low resolution EI (electron ionisation at 70 eV) mass spectra measurements were performed by the Institut für Organische Chemie, Technische Universität Braunschweig using a ThermoFinnigan MAT 95. Peak matching method was used at a resolution of 10000 with PFK as mass calibrant. Data are reported relative to the base ion, which is set to 100%. For recording GC-MS spectra, an Agilent 6890 gas chromatograph, equipped with a 30 m analytical column (Phenomenex ZB5-MS, 30 m x 0.25 mm ID, t=0.25 µm), was used. A split injection port at 250°C was used for sample introduction and the split ratio was set to 10:1. Start temperature was set to 70°C for 3 minutes. The rate of heating was 10 °C per minute to a final temperature of 310°C. The helium carrier gas flow rate was set to 1.0 ml/minute (constant flow mode). The transfer line was kept at 250°C. A JMS-T100GC (GCAccuTOF, JEOL, Japan) time of flight mass spectrometer was used in electron ionization (EI) mode at 70eV. The source and transfer line temperature were set at 200°C and 270°C respectively. The detector voltage was set at 2000V. The acquisition range was from m/z 41 to 700 with spectrum recoding interval of 0.4 s. The system was tuned with PFK to achieve a resolution of 5000 (FWHM) at m/z 292.9824. UV-Vis and IR spectra were measured on Carry 100 Bio (Varian) and an ATR Diamond Tensor 27 (Bruker) instruments, respectively. IR bands are characterised by intensity: w - weak, m - medium, s - strong Elemental analyses was
performed by Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. Melting points were determined using a Stuart Melting Point SMP3 instrument.

**Cyclic Voltammetry**: Cyclic Voltammetry was performed using a Metrohm μAutolab equipped with a 1 mm platin disc working electrode, a platin wire counter electrode and a saturated Ag/AgCl reference electrode. The ferrocene/ferrocenium redox couple was determined at 0.65 V. The electrolyte Bu₄NPF₆ was dissolved in acetonitrile to generate a 0.1 M stock solution. Monomer concentrations were set to 0.1 mM.
4-Hexoxy-3-iodothiophene (5):

Diisopropylamine (3.40 g, 33.60 mmol, 1.1 eq) and THF (30 ml) were cooled to –80 °C. n-Butyllithium (20.5 ml, 32.80 mmol, 1.1 eq, 1.6 M in hexane) was added slowly. The resulting solution was warmed to 0 °C for five minutes and recooled to –80 °C.

3-Hexoxythiophene (5.66 g, 30.76 mmol) was added dropwise and the mixture was stirred for 30 minutes. In a separate flask iodine (7.76 g, 30.58 mmol, 1.0 eq) was dissolved in THF (20 ml), transferred into a syringe and added as quickly as possible in one shot to the vigorously stirred thienyllithium solution. The mixture decoloured within some seconds, indicating the end of the reaction. Aqueous Na2S2O3 (40 ml) was immediately added to eliminate residual iodine and lithiated compounds. After warming to room temperature, the reaction mixture was extracted three times with CH2Cl2 (3x 120 ml). The combined organic layers were dried over MgSO4, filtered and evaporated to dryness. Column chromatography (SiO2, Hex:CH2Cl2 5:1, Rf = 0.46) gave a mixture of monoiodothiophene 5 and diiodothiophene 7 as a pale yellow oil (8.4 g, 88%). The ratio of 5 and 7 was determined by 1H NMR and ranged from 6:1 to 9:1. The mixture can be used without further separation for subsequent syntheses of the acetylene derivatives 8, 9 and 10, because the resulting products can be purified by chromatography more easily. When a vacuum distillation was performed after column chromatography (140 – 145 °C/1 mbar) 5 can be isolated in ratios of >50:1.

1H NMR (CDCl3, 200 MHz): δ = 6.89 (d, 4J3,1 = 1.8 Hz, 1 H, 3-H), 6.23 (d, 4J1,3 = 1.8 Hz, 1H, 1-H), 3.88 (t, 3J5,6 = 6.5 Hz, 2H, 5-H), 1.82 – 1.65 (m, 2 H, 6-H), 1.51 – 1.23 (m, 6 H, 7 – 9 H), 0.90 (t, 3J10,9 = 6.6 Hz, 3 H, 10-H); 13C NMR (CDCl3, 50 MHz): δ = 158.1 (s, C-2), 129.3 (d, C-3), 103.4 (d, C-1), 72.5 (s, C-4), 70.5 (t, C-5), 31.8 (t, C-8), 29.3 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); GC: tR [min] = 12.83 (5), 15.99 min (7); GC-MS: tR [min] (M+) = 16.90 (310), 20.11 (436); UV/Vis (CH2Cl2): λ [nm] (ε) = 266 (4800), 234 (8500); FT-IR (ATR): ʋ [cm⁻¹] = 3115 (w), 2952 (w), 2927 (w), 2857 (w), 1538 (s), 1467 (w), 1419 (w), 1354 (s), 1166 (s), 1046 (w), 1025 (m), 971 (w), 939 (w), 904 (w), 862 (w),
817 (m), 726 (w); **Elemental analysis** (C_{10}H_{15}OIS, 310.2): calc. C 38.72 H 4.87 S 10.34 found C 38.70 H 4.73 S 9.87.

The signal of the β-proton at δ = 6.80 ppm (s, 1 H) is characteristic for diiodothiophene 7 in \textsuperscript{1}H NMR (figure 1).

**Figure 1:** \textsuperscript{1}H NMR data of the aromatic region of 5 after column chromatography (left) and distillation (right).
Peak # | RT  | Start | End  | Abs Area | Area(%) | Height
---|-----|-------|------|----------|---------|-------
1   | 16.84 | 16.77 | 17.36 | 144638061 | 94.118 | 16449247
2   | 20.11 | 20.07 | 20.55 | 9039594 | 5.882 | 879549

Figure 4: GC-MS data of 5 after column chromatography and distillation.
4-Hexoxy-2-(trimethylsilylethynyl)thiophene (8):

Trimethylsilylacetylene (2.26 g, 23.00 mmol), diisopropylamine (3.04 g, 30.00 mmol), PdCl$_2$(PPh$_3$)$_2$ (670 mg) and CuI (95 mg) were consecutively added to a stirred solution of pure iodothiophene 5 (5.00 g, 16.12 mmol) in THF (30 ml). After stirring at room temperature for two hours DC indicated consumption of 5 and water (100 ml) was added. The mixture was extracted three times with CH$_2$Cl$_2$ (3 x 80 ml). The combined organic layers were dried (MgSO$_4$), filtered and concentrated in vacuum. Column chromatography (SiO$_2$, Hex:CH$_2$Cl$_2$ 10:1, $R_f$ = 0.39) provided 4.45 g (15.86 mmol, 98%) of 8 as pale yellow oil.

$^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ = 6.63 (d, $^4J_{3,1} = 1.7$ Hz, 1 H, 3-H), 5.91 (d, $^4J_{1,3} = 1.7$ Hz, 1H, 1-H), 3.67 (t, $^3J_{5,6} = 6.5$ Hz, 2H, 5-H), 1.59 – 1.42 (m, 2 H, 6-H), 1.27 – 1.00 (m, 6 H, 7 – 9 H), 0.67 (t, $^3J_{10,9} = 6.6$ Hz, 3 H, 10-H), 0.00 (s, 9 H, 13-H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ = 156.7 (s, C-2), 124.4 (d, C-3), 121.9 (s, C-4), 100.0 (d, C-1), 98.8 (s, C-12), 98.0 (s, C-11), 70.5 (t, C-5), 29.3 (t, C-6), 25.8 (t, C-7), 22.8 (t, C-9), 14.2 (q, C-10), 0 (q, C13); MS (EI): e/z % 280 (23) [M$^+$], 196 (52), 181 (100); HRMS (EI): C$_{15}$H$_{24}$OSSi calc. 280.1317 found 280.1321; UV/Vis (CH$_2$Cl$_2$): $\lambda$ [nm] (e) = 335 (900, sh), 297 (9100), 265 (10400), 256 (11400); FT-IR (ATR): $\overline{\nu}$ [cm$^{-1}$] = 3116 (w), 2957 (w), 2931 (w), 2860 (w), 2147 (w), 1545 (m), 1445 (w), 1366 (w), 1249 (w), 1178 (w), 1143 (m), 1025 (w), 839 (s), 758 (m); Elemental analysis (C$_{15}$H$_{24}$OSSi, 280.5): calc. C 64.23 H 8.62 S 11.43 found C 64.13 H 8.32 S 11.07.
2-Ethynyl-4-hexoxythiophene (9):

Trimethylsilyl compound 8 (4.40 g, 15.69 mmol) was dissolved in methanol (20 ml). K$_2$CO$_3$ (5.2 g, 37.63 mmol) was added and the mixture was stirred at room temperature for two hours. DC indicated total consumption of the starting material. After addition of a saturated NH$_4$Cl solution (20 ml), the mixture was extracted with CH$_2$Cl$_2$ (3x 60 ml). The combined organic layers were dried (MgSO$_4$), filtered and evaporated. Column chromatography (SiO$_2$, Hex:CH$_2$Cl$_2$ 5:1, $R_f = 0.30$) afforded 3.24 g (15.55 mmol, 99%) of 9 as pale yellow oil.

$^1$H NMR (CDCl$_3$, 200 MHz): $\delta = 6.91$ (d, $^4J_{3,1} = 1.7$ Hz, 1 H, 3-H), 6.17 (d, $^4J_{1,3} = 1.7$ Hz, 1H, 1-H), 3.91 (t, $^3J_{5,6} = 6.5$ Hz, 2 H, 5-H), 3.30 (s, 1 H 12-H), 1.83 – 1.57 (m, 2 H, 6-H), 1.52 – 1.24 (m, 6 H, 7 – 9 H), 0.90 (t, $^3J_{10,9} = 6.7$ Hz, 3 H, 10-H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta = 156.8$ (s, C-2), 125.1 (d, C-3), 120.8 (s, C-4), 100.1 (d, C-1), 81.4 (d, C-12), 77.5 (s, C-11), 70.6 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); MS (EI): e/z % 208 (20) [M$^+$], 124 (100); HRMS (EI): C$_{12}$H$_{16}$OS calc. 208.0922 found 208.0929; UV/Vis (CH$_2$Cl$_2$): $\lambda$ [nm] ($\varepsilon$) = 291 (6300), 248 (9900); FT-IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3306 (w), 3118 (w), 2954 (w), 2929 (w), 2859 (w), 2105 (m), 1545 (s), 1443 (m), 1364 (m), 1174 (s), 1120 (m), 1023 (m), 874 (w), 829 (m), 711 (m); Elemental analysis (C$_{12}$H$_{16}$OS, 208.3): calc. C 69.19 H 7.74 S 15.39 found C 69.25 H 7.49 S 15.15.
1,2-Bis[4-(hexoxy)thiophen-2-yl]ethyne (10):

2-Iodothiophene 5 (500 mg, 1.61 mmol), 2-ethynylthiophene 9 (416 mg, 2.00 mmol), diisopropylamine (305 mg, 3.01 mmol) and PdCl$_2$(PPh$_3$)$_2$ (70 mg) were dissolved in THF (5 ml) and CuI (20 mg) was added. The solution was stirred at room temperature for three days. DC showed a new spot, which could be assigned to the product later. CH$_2$Cl$_2$ (50 ml) was added and the organic layer was washed first with water (50 ml) and then with brine (50 ml). The organic layer was dried (MgSO$_4$), filtered and evaporated. Column chromatography (SiO$_2$, Hex:CH$_2$Cl$_2$ 2:1, $R_f = 0.78$) gave 10 as a dark red solid (580 mg, 1.48 mmol, 92%). In $^1$H NMR a small amount of a contaminant was observed which can be removed by refluxing the solid in methanol (5 ml). The yellow coloured methanol phase was transferred via a pipette to another flask while still hot. Cooling of the solution in a refrigerator gave yellow crystals (m.p. 71 °C). Alternatively, the red solid can be sublimed (275 °C / 1 mbar) to yield the same yellow solid.

$^1$H NMR (CDCl$_3$, 200 MHz): $\delta = 6.90$ (d, $^4$$J_{3,1} = 1.7$ Hz, 2 H, 3-H), 6.22 (d, $^4$$J_{1,3} = 1.7$ Hz, 2 H, 1-H), 3.93 (t, $^3$$J_{5,6} = 6.5$ Hz, 4 H, 5-H), 1.84 – 1.67 (m, 4 H, 6-H), 1.51 – 1.25 (m, 12 H, 7 – 9 H), 0.90 (t, $^3$$J_{10,9} = 6.5$ Hz, 6 H, 10-H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta = 157.1$ (s, C-2), 124.0 (d, C-3), 121.5 (s, C-4), 100.5 (d, C-1), 86.7 (s, C-11), 70.6 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); MS (EI): e/2 % 390 (53) [M$^+$], 306 (19), 222 (100); HRMS (EI): C$_{22}$H$_{30}$O$_2$S$_2$ calc. 390.1687 found 390.1675; UV/Vis (CH$_2$Cl$_2$): $\lambda$ [nm] ($\varepsilon$) = 342 (14200), 330 (17400), 278 (12000), 261 (12500); FT-IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3125 (w), 2937 (m), 2922 (m), 2865 (m), 2852 (m), 1560 (m), 1484 (w), 1466 (m), 1371 (m), 1345 (w), 1243 (m), 1172 (s), 1125 (m), 1057 (w), 1024 (s), 1003 (w), 958 (w), 869 (m), 712 (w), 691 (w).
827 (m), 732 (m), 700 (s); **Elemental analysis** (C_{22}H_{30}O_{2}S_{2}, 390.6): calc. C 67.65 H 7.74 S 16.42 found C 67.77 H 7.60 S 16.00.

**2-Formyl-4-hexoxythiophene (6):**

Diisopropylamine (20 ml) and THF (50 ml) were cooled to –80 °C. n-Butyllithium (22.5 ml, 36.00 mmol, 1.6 M in hexane) was added slowly. The solution was warmed to 0 °C for five minutes and recooled to –80 °C. 3-Hexoxythiophene (5.48 g, 29.73 mmol) was added dropwise and the mixture was stirred for further 30 minutes. DMF (7.40 g, 84.24 mmol) was added at once to the solution. After one hour at –80 °C the reaction was warmed to 0 °C and stirring was continued for another hour. DC showed almost total conversion of the starting material. The mixture was hydrolyzed with aqueous KOH (5%, 100 ml) and stirred for ten minutes. The aqueous layer was extracted with CH_{2}Cl_{2} (3x 150 ml), the combined organic layers were washed with brine (100 ml), dried (MgSO_{4}) and evaporated. The crude product was purified by column chromatography (SiO₂, Hex:CH_{2}Cl_{2} 3:2, R_f = 0.20) to give 6 as a colourless oil (5.96 g, 28.07 mmol, 94%).

**¹H NMR** (CDCl₃, 200 MHz): δ = 9.82 (d, J_{1,1} = 1.2 Hz, 1 H, 11-H), 7.40 (d, J_{3,1} = 1.8 Hz, 1 H, 3-H), 6.22 (dd, J_{1,3} = 1.8 Hz, J_{1,11} = 1.2 Hz, 1 H, 1-H), 3.97 (t, J_{5,6} = 6.5 Hz, 2 H, 5-H), 1.86 – 1.70 (m, 2 H, 6-H), 1.54 – 1.24 (m, 6 H, 7 – 9 H), 0.91 (t, J_{10,9} = 6.5 Hz, 3 H, 10-H); **¹³C NMR** (CDCl₃, 50 MHz): δ = 183.0 (d, C-11), 158.4 (s, C-2), 141.4 (s, C-4), 126.9 (d, C-3), 108.5 (d, C-5), 71.0 (t, C-8), 31.8 (t, C-6), 29.3 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): e/z % 212 (24) [M⁺], 128 (100); **HRMS** (EI): C_{11}H_{16}O_{2}S calc. 212.0871 found 212.0870; **UV/Vis** (CH₂Cl₂): λ [nm] (ε) = 327 (5000), 261 (12800); **FT-IR** (ATR): ν [cm⁻¹] = 3104 (w), 2929 (w), 2858 (w), 1670 (s), 1551 (m), 1441 (s), 1409 (w), 1355 (m), 1231 (m), 1184 (m), 1150 (w), 1020 (m), 917 (w), 877 (w), 836 (w), 725 (m);
Elemental analysis (C$_{11}$H$_{16}$O$_2$S, 212.3): calc. C 62.23 H 7.60 S 15.10 found C 62.02 H 7.47 S 14.70.

4-Hexoxy-2-vinylthiophene (11):

1. method (Stille coupling):
2-Iodothiophene 5 (1.00 g, 3.22 mmol) was dissolved in DMF (50 ml). PdCl$_2$(PPh$_3$)$_2$ (50 mg) and tributylvinylstannane (1.51 g, 4.76 mmol) were added and the mixture was heated to 60 °C for two days. Although DC did not show any changes workup was started. The reaction mixture was cooled to room temperature and water (30 ml) was added. The mixture was extracted with CH$_2$Cl$_2$ (3x 50 ml), dried (MgSO$_4$) and evaporated. Column chromatography (SiO$_2$, Hex:CH$_2$Cl$_2$ 5:1, $R_f = 0.60$) provided 11 as a slightly yellow oil (550 mg, 2.60 mmol, 81%). NMR analysis revealed that 11 is still contaminated with tributyltin units (figure 5, $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ = 28.1, 27.1, 17.8, 13.9).

2. method (Wittig reaction), which is preferred for synthesis 11:
A solution of methyl(triphenyl)phosphonium bromide (3.37 g, 9.42 mmol) and KOtBu (1.37 g, 12.20 mmol) in THF (100 ml) was stirred at 0 °C for 15 minutes. Aldehyde 6 (1.00 g, 4.70 mmol) was added dropwise. After 2.5 h, saturated NH$_4$Cl (50 ml) was added to the mixture. The layers were separated and the aqueous one was extracted three times with CH$_2$Cl$_2$ (3x 50 ml). The combined organic layers were dried (MgSO$_4$), filtered and evaporated. Column chromatography (SiO$_2$, Hex:CH$_2$Cl$_2$ 5:1, $R_f = 0.60$) gave 11 as a colourless oil (970 mg, 4.60 mmol, 98%).

$^1$H NMR (CDCl$_3$, 200 MHz): $\delta = 6.76$ (dddd, $^{3}J_{11,12\text{trans}} = 17.2$ Hz, $^{3}J_{11,12\text{cis}} = 11.0$ Hz, $^{4}J_{11,3} = 0.5$ Hz, $^{5}J_{11,1} = 0.5$ Hz, 1 H, 11-H), 6.66 (d, $^{4}J_{3,1} = 1.6$ Hz, 1 H, 3-H), 6.07 (d, $^{4}J_{1,3} = 1.6$ Hz, 1 H, 1-H), 5.54 (d, $^{3}J_{12,11} = 17.2$ Hz, 1 H, 12-H$_{\text{trans}}$), 5.12 (d, $^{3}J_{12,11} = 11.0$ Hz, 1 H, 12-H$_{\text{cis}}$),
3.91 (t, $^3J_{5,6} = 6.5$ Hz, 2 H, 5-H), 1.83 – 1.67 (m, 2 H, 6-H), 1.49 – 1.24 (m, 6 H, 7 – 9 H),
0.90 (t, $^3J_{10,9} = 6.6$ Hz, 3 H, 10-H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta = 157.6$ (s, C-2), 141.3 (s, C-4), 130.2 (d, C-11), 118.1 (d, C-3), 113.4 (t C-12), 96.3 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); MS (EI): $m/z$% 210 (18) [M$^+$], 126 (100); HRMS (EI): C$_{12}$H$_{18}$O$_{5}$S calc. 210.1079 found 210.1082; UV/Vis (CH$_2$Cl$_2$): $\lambda$ [nm] ($\varepsilon$) = 298 (5500), 258 (11500); FT-IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3120 (w), 3090 (w), 2954 (w), 2929 (w), 2859 (w), 1623 (w), 1549 (s), 1458 (n), 1361 (m), 1227 (w), 1177 (m), 1149 (m), 1028 (m), 976 (m), 896 (m), 871 (w), 824 (m), 701 (m).

Figure 5: Stannane contamination can be identified by $^{13}$C NMR: left Stille coupling, right Wittig reaction.
(E)-1,2-Bis[4-(hexoxy)thiophen-2-yl]ethene (12):

Vinylthiophene 11 (900 mg, 4.28 mmol) and Grubbs’ 2nd generation catalyst (100 mg, 118 μmol, 3 mol%) were dissolved in toluene (15 ml). The mixture was refluxed for 18 hours. DC indicated almost complete consumption of the starting material. After cooling to room temperature the solvent was evaporated. Column chromatography (SiO2, Hex:CH2Cl2, 5:1, Rf = 0.17) gave a pale yellow solid (810 mg). This solid was recrystallised from ethanol (15 ml) to yield 12 as a pale yellow solid (680 mg, 1.73 mmol, 81%, m.p. 96 – 98 °C).

$^1$H NMR (CDCl3, 200 MHz): δ = 6.88 (s, 2 H, 11-H), 6.71 (d, $^4$J$_{3,1}$ = 1.6 Hz, 2 H, 3-H), 6.17 (d, $^4$J$_{1,3}$ = 1.6 Hz, 2 H, 1-H), 3.92 (t, $^3$J$_{5,6}$ = 6.5 Hz, 4 H, 5-H), 1.84 – 1.67 (m, 4 H, 6-H), 1.53 – 1.22 (m, 12 H, 7 – 9 H), 0.90 (t, $^3$J$_{10,9}$ = 6.7 Hz, 6 H, 10-H); $^{13}$C NMR (CDCl3, 50 MHz): δ = 157.8 (s, C-2), 140.4 (s, C-4), 121.5 (d, C-11), 118.3 (d, C-3), 96.6 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); MS (EI): e/z % 392 (100) [M$^+$], 224 (39), 226 (74); HRMS (EI): C$_{22}$H$_{32}$O$_2$S$_2$ calc. 392.1844 found 392.1840; UV/Vis (CH$_2$Cl$_2$): λ [nm] (ε) = 357 (21300), 285 (11800), 226 (6000); FT-IR (ATR): $\tilde{v}$ [cm$^{-1}$] = 3108 (w), 2957 (w), 2918 (m), 2873 (m), 2853 (m), 1552 (m), 1476 (m), 1458 (m), 1369 (m), 1271 (m), 1202 (m), 1179 (m), 1153 (m), 1074 (w), 1044 (w), 999 (m), 981 (w), 936 (m), 915 (w), 869 (w), 819 (m), 707 (s); Elemental analysis (C$_{22}$H$_{32}$O$_2$S$_2$, 392.6): calc. C 67.30 H 8.22 S 16.33 found C 67.54 H 8.00 S 15.97.
(E)-2,5-Dibromo-3-[2-(4-(hexoxy)thiophen-2-yl)vinyl]thiophene (14):

2-Formyl-4-hexoxythiophene 6 (1.80 g, 8.48 mmol) and phosphonate 13 were dissolved in DME (20 ml). NaH (420 mg, 10.50 mmol, 1.1 eq, 60% in mineral oil) was added and the reaction mixture was stirred at reflux for 90 minutes. After cooling to room temperature, water (50 ml) was added. The layers were separated and the aqueous was extracted three times with CH₂Cl₂ (3x 50 ml). The combined organic layers were dried (MgSO₄), filtered and evaporated. Column chromatography (SiO₂, Hex:CH₂Cl₂ 2:1, Rf = 0.60) gave 14 as a yellow solid (3.20 g, 7.11 mmol, 83%, m.p. 78 – 80 °C).

1H NMR (TMS, CDCl₃, 200 MHz): δ = 7.13 (s, 1 H, 15-H), 6.89 (d, 3J₁₂,₁₁ = 16.1 Hz, 1 H, 12-H), 6.76 (d, 4J₃,₁ = 1.5 Hz, 1 H, 3-H), 6.74 (d, 3J₁₁,₁₂ = 16.1 Hz, 1 H, 11-H), 6.14 (d, 4J₁,₃ = 1.5 Hz, 1 H, 1-H), 3.92 (t, 3J₅,₆ = 6.5 Hz, 2 H, 5-H), 1.84 – 1.67 (m, 2 H, 6-H), 1.53 – 1.21 (m, 6 H, 7 – 9 H), 0.91 (t, 3J₁₀,₉ = 6.4 Hz, 3 H, 10-H); 13C NMR (CDCl₃, 50 MHz): δ = 157.9 (s, C-2), 140.2 (s, C-4), 138.8 (s, C-14), 127.4 (d, C-15), 124.6 (d, C-12), 119.5 (d, C-11), 118.9 (d, C-3), 112.2 (s, C-13), 110.3 (s, C-16), 97.3 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 26.0 (t, C-7), 22.9 (t, C-9), 14.3 (q, C-10); MS (EI): e/z % 448/450/452 (9/20/11) [M⁺], 206 (100); UV/Vis (CH₂Cl₂): λ [nm] (ε) = 341 (20900), 287 (15100), 274 (15800), 229 (11100); FT-IR (ATR): ν [cm⁻¹] = 3115 (w), 3024 (w), 2951 (w), 2932 (m), 2853 (m), 1620 (w), 1552 (s), 1522 (m), 1452 (s), 1368 (m), 1346 (w), 1270 (m), 1181 (m), 1153 (m), 1127 (m), 1059 (w), 1024 (m), 1005 (m), 945 (s), 929 (m), 895 (w), 870 (m), 827 (w), 812 (m), 729 (w); Elemental analysis (C₁₆H₁₈Br₂O₃S₂, 450.3): calc. C 42.68 H 4.03 S 14.24 found C 42.55 H 4.03 S 14.14.
(E)-2,5-Bis[(4-(hexoxy)thiophen-2-yl)-3-[2-(4-(hexoxy)thiophen-2-yl)vinyl]thiophene (15):

A mixture of dibromide 14 (1.50 g, 3.33 mmol), boronic acid 4 (1.83 g, 8.00 mmol), Pd(PPh₃)₄ (390 mg), 2 M Na₂CO₃ solution (20 ml) and DME (25 ml) was stirred at reflux for two hours. The mixture was cooled to room temperature and water (50 ml) was added. The layers were separated and the aqueous was extracted three times with CH₂Cl₂ (3x 50 ml). The combined organic layers were dried (MgSO₄), filtered and evaporated. Column chromatography (SiO₂, Hex:CH₂Cl₂ 2:1, \( R_f = 0.47 \)) furnished 15 as a yellow oil (1.90 g, 2.89 mmol, 86%). Dissolving the oil in ethanol and cooling it for three days at –18 °C resulted a yellow solid precipitating.

\(^1\)H NMR (CDCl₃, 400 MHz): \( \delta = 7.25 \) (s, 1 H, 15-H), 7.13 (d, \(^3J_{12,11} = 15.9\) Hz, 1 H, 12-H), 6.98 (d, \(^3J_{11,12} = 15.9\) Hz, 1 H, 11-H), 6.84 (d, \(^4J_{18,20} = 1.7\) Hz, 1 H, 18-H), 6.83 (d, \(^4J_{28,30} = 1.7\) Hz, 1 H, 28-H), 6.74 (d, \(^4J_{3,1} = 1.6\) Hz, 1 H, 3-H), 6.24 (d, \(^4J_{30,28} = 1.7\) Hz, 1 H, 30-H), 6.11 (d, \(^4J_{20,18} = 1.7\) Hz, 1 H, 20-H), 6.08 (d, \(^4J_{1,3} = 1.6\) Hz, 1 H, 1-H), 3.97 (t, \(^3J = 6.6\) Hz, 2 H, 5/21/31-H), 3.95 (t, \(^3J = 6.4\) Hz, 2 H, 5/21/31-H), 3.93 (t, \(^3J = 6.4\) Hz, 2 H, 5, 21 or 31-H), 1.82 – 1.73 (m, 6 H, 6,22,32-H), 1.54 – 1.29 (m, 18 H, 7 – 9,23 – 25,33 –35-H), 0.97 – 0.88 (m, 9 H, 10, 26, 36-H); \(^13\)C NMR (CDCl₃, 100 MHz): \( \delta = 157.75 \) (s, C-29), 157.70 (s, C-2), 157.67 (s, C-19), 140.8 (s, C-4), 136.3 (s, C-16), 135.7 (s, C-13), 134.9 (s, C-17), 133.6 (s, C-
27), 132.0 (s, C-14), 123.6 (d, C-11), 121.7 (d, C-15), 121.0 (d, C-12), 119.1 (d, C-28), 117.8 (d, C-3), 116.5 (d, C-18), 98.6 (d, C-30), 96.8 (d, C-20), 96.6 (d, C-1), 70.24 (t, C-5/21/31), 70.20 (t, C-5/21/31), 70.1 (t, C-5/21/31), 31.6 (t, 3 C, C-8,24,34), 29.2 (t, 3 C, C-6,22,32), 25.7 (t, 3 C, C-7,23,33), 22.6 (t, 3 C, C-9,25,35), 14.0 (q, 3 C, C-10,26,36); **MS** (EI): e/z % 656/657/658 (100/42/25) [M\(^+\)]; **HRMS** (EI): C\(_{36}\)H\(_{48}\)O\(_3\)S\(_3\) calc. 656.2487 found 656.2474; **UV/Vis** (CH\(_2\)Cl\(_2\)): \(\lambda\) [nm] (\(\varepsilon\)) = 345 (34900), 288 (20300), 227 (13600), 224 (13700); **FT-IR** (ATR): \(\nu\) [cm\(^{-1}\)] = 3120 (w), 2928 (m), 2856 (m), 1569 (w), 1551 (s), 1526 (m), 1488 (m), 1465 (m), 1350 (s), 1277 (w), 1168 (s), 1151 (s), 1070 (w), 1047 (w), 1031 (m), 1016 (w), 1000 (m), 918 (w), 863 (w), 828 (w), 809 (s), 725 (w).

**CV-data:**
Cyclic voltammetry measurements showed 15s first oxidation peak at 1.12 V (figure 6). This oxidation was irreversible due to the beginning of the polymerisation process. Polymerisation proceeded until the point, where overoxidation takes place. This point is indicated by decreasing currents, whereby the cycles collapse during further measurement. In case of choosing +1.75 V as 1\(^{st}\) reverse potential degeneration begins after ten cycles. For lower reverse potentials, e. g. 1.50 V, degeneration was observed after 30 cycles. It can be concluded, that 15 forms a polymer, which seems not be stable under chosen conditions, especially higher anodic voltages.

**Figure 6:** Cyclic voltammogram of 15. 45 cycles, 1\(^{st}\) reverse potential +1.75 V (left) and +1.50 V (right) respectively. 1\(^{st}\) cycle (black), 10\(^{th}\) cycle (red), 20\(^{th}\) cycle(blue), 30\(^{th}\) cycle(turquoise), 40\(^{th}\) cycle(pink), 45\(^{th}\) cycle(green).
References:

