Supporting information for:

Using Bis(pinacolato)diboron to Improve the Quality of Regio-Regular Conjugated Co-Polymers

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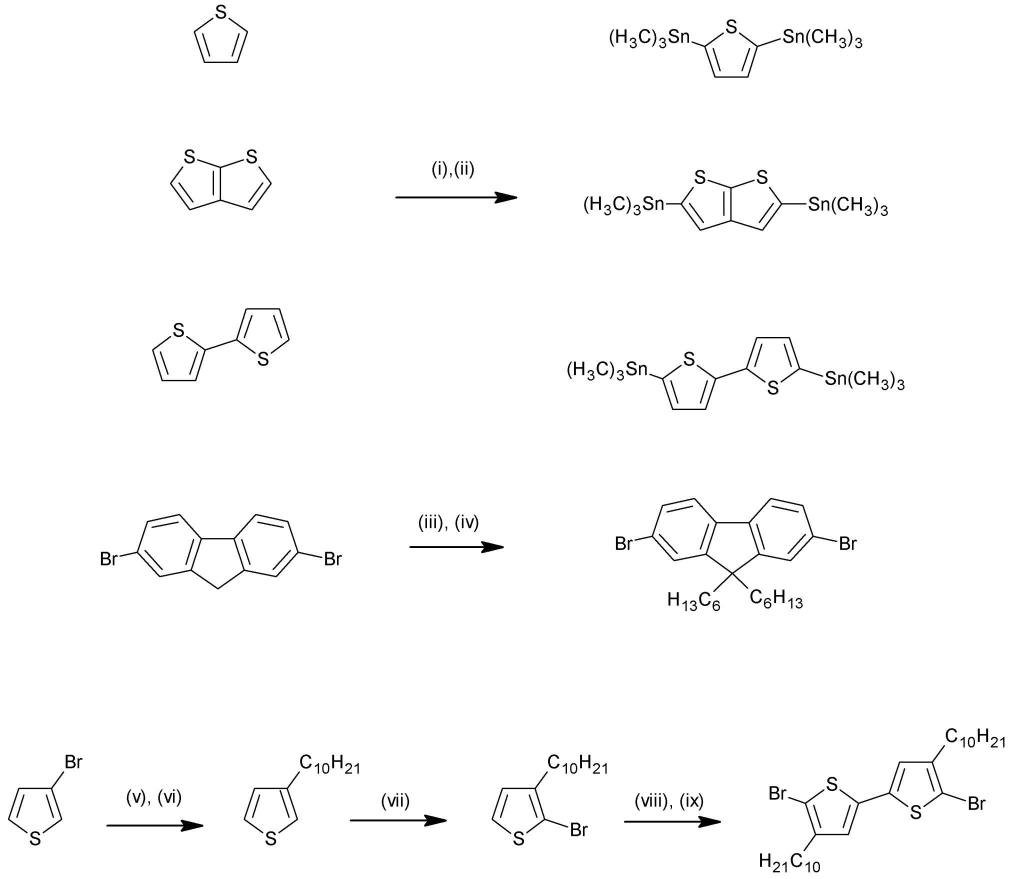
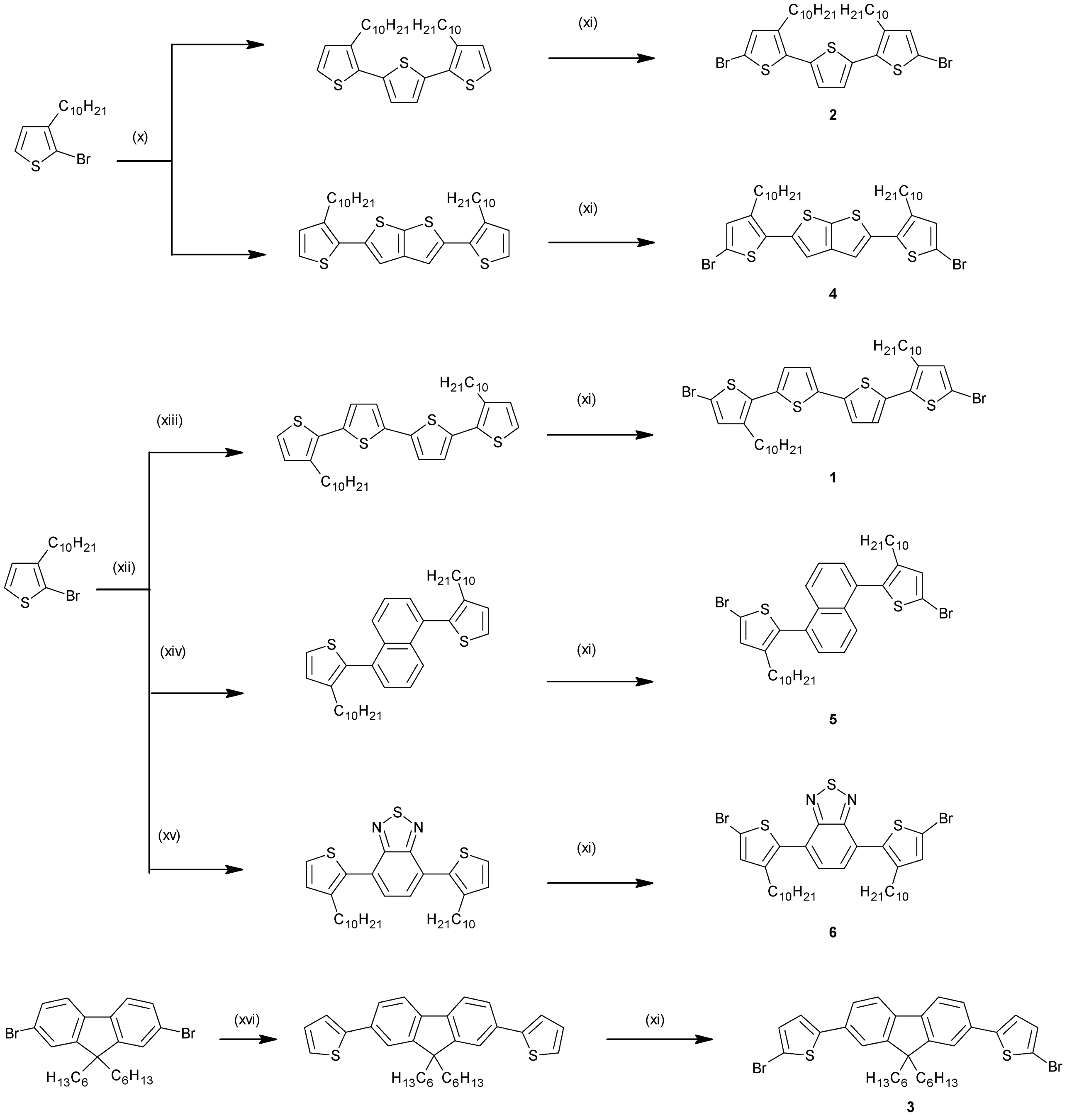
Scheme S1. Synthesis route of the monomers for the Stille polymerization.



(i) n-BuLi, hexane / TMEDA, 0ºC (ii) $(CH_3)_3SnCl$, hexane, 0ºC (iii) KOH (aq) 50%, TBACl, DMSO, 60 ºC (iv) $C_6H_{13}Br$, 60 ºC (v) $C_{10}H_{21}Br$, Mg, THF, Reflux (vi) $Ni(dppp)Cl_2$, THF, reflux (vii) NBS, DMF, 0 ºC (viii) LDA, THF -78 ºC (ix) $CuCl_2$, THF, -78 ºC - 20ºC

Scheme S2 Synthesis of the macro monomers



(x) 2,5-bis(trimethylstannyl)thiophene or 2,5-bis(trimethylstannyl)thieno[2,3-b]thiophene, DMF / Toluene (3:1), $Pd(PPh_3)_4$, 110 ºC (xi) NBS, THF, 0 ºC (xii) Mg, THF, reflux (xiii) 5,5'-dibromo-2,2'-bithiophene, $Ni(dppp)Cl_2$, THF / Toluene (4:3), reflux (xiv) 1,5-diiodonaphthalene, $Ni(dppp)Cl_2$, THF / Toluene (4:3), reflux (xv) 4,7-dibromo-2,1,3-benzothiadiazole, $Ni(dppp)Cl_2$, THF / Toluene (4:3), reflux (xvi) (2-thienyl)borane, K_3PO_4, $Pd(PPh_3)_4$, DMF, 110 ºC

General. Kumada couplings and Bipi polymerizations were performed under dry conditions and nitrogen atmosphere. NBS brominations were performed under nitrogen atmosphere, with exclusion of light.

5,5'-bis(trimethylstannyl)-2,2'-bithiophene[1]**.** The procedure for the synthesis of 2,5-bis(trimethylstannyl)-thiophene was followed to prepare 5,5'-bis(trimethylstannyl)-2,2'-bithiophene in 47% yield as light green crystals. δ_H(300 MHz, $CDCl_3$) 7.26 (d, J=3.3, 2H), 7.07 (d, J=3.3, 2H), 0.37 (s, 18H). δ_C(50 MHz, $CDCl_3$) 143.24, 137.27, 136.07, 125.07, -8.00.

5,5'-dibromo-4,4'-didecyl-2,2'-bithiophene. The synthetic route original proposed by McCoulough et al. required the use of a tedious reverse phase chromatography step, limiting the use of the synthesis[2]. By using a slightly modified method, based on selective lithiation of 2-bromo-alkylthiophene by LDA, we where able to synthesize **8** in good yield.

5.32 g (52.6 mmol) diisopropylamine was added to 80 mL of THF and the solution was cooled to 0°C. 19.12 mL (47.8 mmol) of 2.5M n-Buli in 20mL of dry THF was added drop wise. The resulting mixture was stirred at 0°C for 30 min before cooling to -78°C and subsequent dropwise addition of 14.5 g (47.8 mmol) 2-bromo-3-decylthiophene in 40 mL THF. The reaction mixture was stirred 60 min at -78°C, before 8.0 g (58.8 mmol) copper(II)chloride was added in one portion. The reaction mixture was kept at -78°C for 30 min in which the color of the reaction mixture changed from clear green/turquoise to clear blue to clear purple to clear brown to turbid brown. The cooling was removed and the reaction mixture was allowed to warm up to RT overnight. The reaction mixture was worked up by acidification of the reaction mixture with dilute hydrochloric acid to neutral pH followed by extraction with ether (3 x 150 mL), washing the combined ether layers with water (2 x 150 mL) followed by drying of the ether layer over Na_2SO_4. The solvent was removed under reduced pressure and the resulting brown oil was purified using column chromatography (silica gel, hexane) to give 14.72 g crude product. The crude product was dissolved in a small amount of chloroform and precipitated in methanol cooled to 0°C, dried under vacuum at RT and finally recrystallized from ethyl acetate to give 12.085 g (20 mmol, 84%) of product as fluffy bright yellow crystals.

δ_H($CDCl_3$, 300 MHz) 6.75 (s, 2H), 2.50 (t, J = 7.5, 4H), 1.56 (m, 4H), 1.30 (m, 28H) 0.87 (t, J = 4.8, 6H). δ_C($CDCl_3$, 300 MHz) 142.93, 136.15, 124.41, 107.84, 31.90, 29.62, 29.53, 29.39, 29.34, 29.20, 22.69, 18.42, 14.13

1,5-bis(3-decylthiophen-2-yl)naphthalene. Magnesium (193 mg, 7.98 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (2.251 g, 7.33 mmol) in 5.5 mL ether was added drop wise and the mixture was refluxed for several hours. The Grignard reagent was then added drop wise to a mixture of 1,5-diiodonaphthalene (1.359 g, 3.58 mmol) and Ni(dppp)Cl_2 (21 mg, 0.039 mmol) in 26 mL ether/toluene (1:2) and refluxed overnight. The mixture was quenched with 80 mL NH_4Cl and extracted with DCM (3 x 100 mL). The organic layers were washed with aq. sat. Na_2CO_3 (150 mL), brine (150 mL), and water (100 + 200 mL) and dried on Na_2SO_4. The solvent was removed and the obtained oil was purified by column chromatography (silica gel, pet. ether) and recrystallized from isopropanol/methanol (3:1), which yielded 0.957 g (1.67 mmol, 47%) of the title compound as white powder.

δ_H(500 MHz, $CDCl_3$) 7.78 (d, *J* = 8.7, 2H), 7.48 – 7.43 (m, 4H), 7.37 (d, *J* = 5.2, 2H), 7.07 (d, *J* = 5.2, 2H), 2.38 (t, 4H), 1.52 – 1.43 (m, 4H), 1.27 – 1.12 (m, , 28H), 0.86 (t, *J* = 7.1, 6H). δ_C(125 MHz, $CDCl_3$) 140.92, 135.20, 133.22, 132.21, 129.26, 128.38, 126.71, 125.26, 124.37, 31.87, 30.52, 29.53, 29.48, 29.30 (2 signals), 29.19, 28.72, 22.66, 14.11. IR (cm^{-1}): 3061, 2953, 2922, 2852, 1713, 1590, 1500, 1465, 1393, 1377, 1310, 1227, 1208, 1092, 1069, 1016, 946, 901, 876, 835, 792, 720, 687, 655. HRMS (APCI) calculated for $[M+H]^+$ 573.3583, found 573.3583. Calcd for $C_{38}H_{52}S_2$: C, 79.66; H, 9.15; S, 11.19. Found: C, 79.34; H, 9.04; S, 11.11.

1,5-bis(5-bromo-3-decylthiophen-2-yl)naphthalene 5. 1,5-bis(3-decylthiophen-2-yl)naphthalene (0.841 g, 1.47 mmol) was dissolved in 50 mL THF and NBS (0.708 g, 3.95 mmol) in 15 mL THF was added drop wise over 40 minutes. The yellow mixture was stirred overnight and then quenched with 200 mL 2M HCl and extracted with DCM (3 x 200 mL). The organic layers were washed with brine (200 mL) and dried on Na_2SO_4. The solvent was removed under reduced pressure and the product was recrystallized from isopropanol/methanol (3:1), yielding 0.868 g (1.19 mmol, 81%) of **5** as a white powder.

δ_H(500 MHz, $CDCl_3$) 7.90 – 7.76 (m, 2H), 7.51 – 7.40 (m, 4H), 7.03 (s, 2H), 2.31 (bs, 4H), 1.50 – 1.40 (m, 4H), 1.32 – 1.01 (m, 28H), 0.87 (t, *J* = 7.0, 6H). δ_C(125 MHz, $CDCl_3$) 141.70, 136.62, 133.03, 131.17, 131.05, 129.55, 126.90, 125.52, 110.97, 31.87, 30.31, 29.52, 29.43, 29.29, 29.23, 29.05, 28.69, 22.66, 14.10. IR (cm^{-1}): 2945, 2921, 2849, 1591, 1504, 1467, 1448, 1393, 1373, 1261, 1209, 1183, 1102, 1069, 1018, 984, 968, 953, 913, 888, 875, 856, 827, 811, 794, 742, 732, 722, 664, 640, 593, 571. HRMS (APCI) calculated for $[M+H]^+$ 731.1773, found 731.1772. Calcd for $C_{38}H_{50}Br_2S_2$: C, 62.46; H, 6.90; S, 8.78. Found: C, 62.44; H, 6.85; S, 8.76.

Poly(1,5-bis(3-decylthiophen-2-yl)naphthalene) PNT-Bipi. Monomer **5** (0.497 g, 0.68 mmol) and bis(pinacolato)diboron (174 mg, 0.68 mmol) were mixed with 22 mL DMF/ toluene (1:3) and degassed. K_3PO_4 (0.750 g, 3.54 mmol) and $Pd(dppf)Cl_2.CH_2Cl_2$ (13 mg, 0.016 mmol) were added and the mixture was heated to 110 ºC and stirred overnight at this temperature. The solvent was removed and the resulting solid was dissolved in chloroform and precipitated in 400 mL cold methanol. The polymer was collected by centrifugation and purified by soxhlet extraction using methanol (400 mL, 23 hours), acetone (400 mL, 23 hours), and chloroform (400 mL, 23 hours). The chloroform was partially evaporated and the product was precipitated in a vortex of cold methanol and collected by centrifugation. The resulting polymer was dried in vacuum, yielding 0.342 g (88%) of PNT-Bipi.

δ_H(400 MHz, $CDCl_3$) 7.95 (bd, J=7.6 Hz, 2H) 7.61-7.46 (b, 4H) 7.20 (b, 2H) 2.39 (b, 4H) 1.61-1.42 (b, 4H) 1.32-1.00 (b, 28H) 0.86 (bt, J= 6.8 Hz, 6H). IR (cm^{-1}): 2920, 2850, 1589,1503, 1455, 1395, 1376, 1207, 1180, 1076, 903, 824, 791, 720, 575, 546. GPC (chloroform): M_n = 10993 g/mol, M_w = 32919 g/mol, PDI = 2.98. MALDI-TOF: see Figure S1

4,7-bis(3-decylthiophen-2-yl)-2,1,3-benzothiadiazole Magnesium (413 mg, 17.01 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (4.295 g, 14.17 mmol) in 11 mL THF was added drop wise and the mixture was refluxed for 3 hours. After cooling to room temperature the Grignard reagent was added drop wise to a mixture 4,7-dibromo-2,1,3-benzothiadiazole (1.705 g, 5.80 mmol) and Ni(dppp)Cl_2 (48 mg, 0.089 mmol) in 49 mL THF/toluene (4:3) and refluxed overnight. The mixture was quenched with 200 mL NH_4Cl and extracted with DCM (3 x 200 mL). The organic layers were washed with aq. sat. Na_2CO_3 (250 mL), brine (200 mL), and water (2 x 200 mL) and dried on Na_2SO_4. The solvent was removed and obtained oil was purified by column chromatography (silica gel, pet. ether) to give a mixture of mono- and bis-coupled products. This mixture was treated with more Grignard reagent.

Magnesium (162 mg, 6.68 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (1.68 g, 5.55 mmol) in 4 mL THF was added drop wise and the mixture was refluxed for 3 hours. After cooling to room temperature the Grignard reagent was added drop wise to Ni(dppp)Cl_2 (28 mg, 0.052 mmol) and the mixture mono- and bis-coupled products in 29 mL THF/toluene (4:3) and refluxed overnight. The mixture was quenched with 100 mL NH_4Cl and extracted with DCM (3 x 90 mL). The organic layers were washed with aq. sat. Na_2CO_3 (120 mL), brine (120 mL), and water (2 x 120 mL) and dried on Na_2SO_4. Solvent were removed and the resulting brown oil was purified by column chromatography (silica gel, pet. ether/DCM 2:1) and recrystallized from acetonitrile at -35°C, which yielded 0.316 g (0.54 mmol, 9%) of the title compound as a dark yellow oil at room temperature.

δ_H(400 MHz, $CDCl_3$) 7.64 (s, 2H), 7.44 (d, *J* = 5.2, 2H), 7.10 (d, *J* = 5.2, 2H), 2.66 (t, *J* = 7.7, 4H), 1.68 – 1.57 (m, 4H), 1.33 – 1.00 (m, 28H), 0.86 (t, *J* = 7.0, 6H). δ_c(125 MHz, $CDCl_3$) 154.25, 141.68, 132.14, 129.87, 129.19, 127.43, 125.83, 31.86, 30.71, 29.55, 29.52, 29.44, 29.37, 29.34, 29.30, 22.66, 14.10. IR (cm^{-1}): 2953, 2922, 2852, 1577, 1537, 1524, 1465, 1436, 1377, 1336, 1269, 1230, 1094, 876, 847, 832, 720, 692, 663. HRMS (APCI) calculated for $[M+H]^+$ 581.3052, found 581.3052.

4,7-bis(5-bromo-3-decylthiophen-2-yl)-2,1,3-benzothiadiazole 6. 4,7-bis(3-

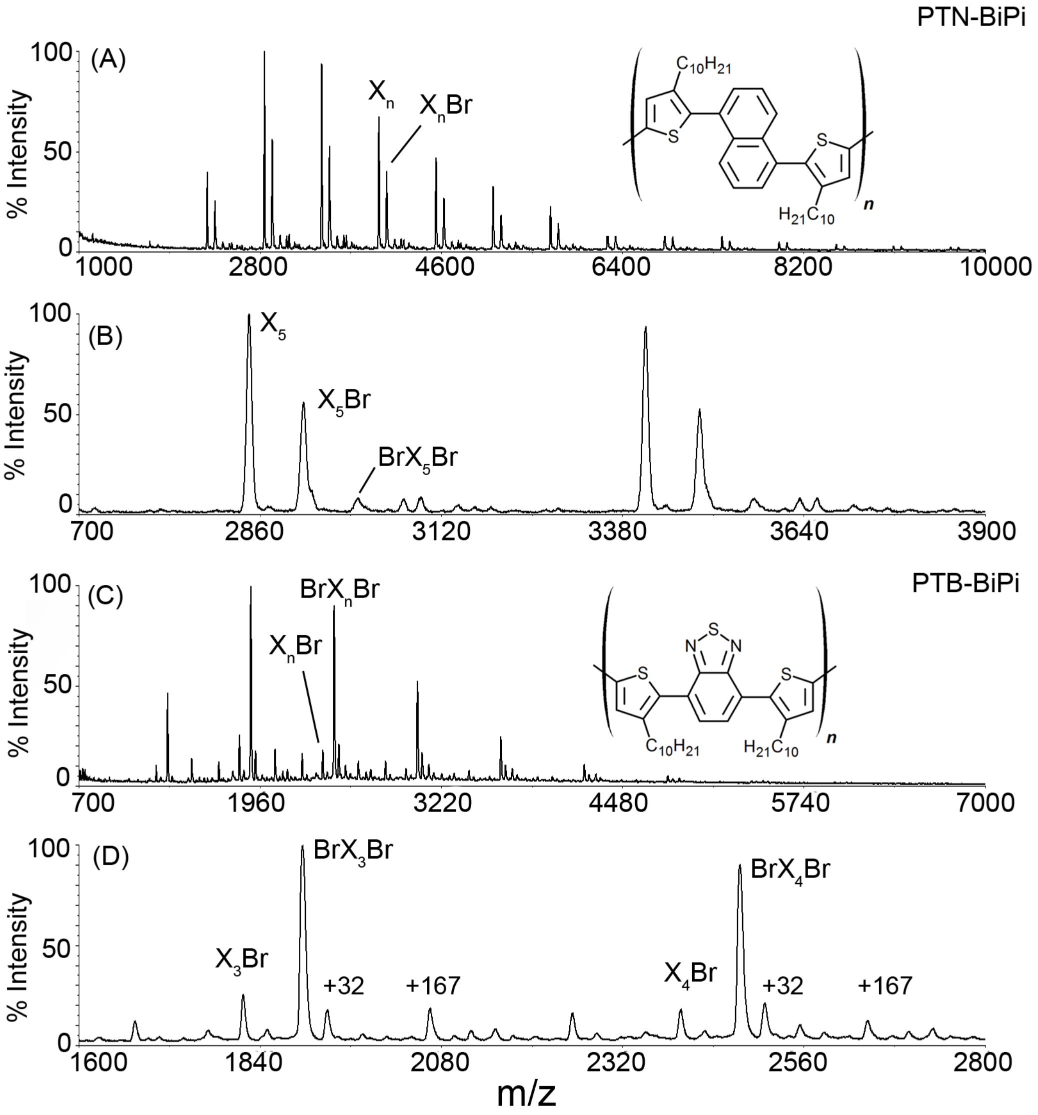
decylthiophen-2-yl)-2,1,3-benzothiadiazole (0.523 g, 0.90 mmol) was dissolved in 25 ml THF and NBS (0.343 g, 1.93 mmol) in 8 mL THF was added drop wise over 40 minutes. The yellow mixture was stirred overnight and then quenched with 100 mL 2M HCl and extracted with DCM (3 x 125 mL). The combined organic layers were washed with brine (150 mL) and dried on Na_2SO_4. The solvent was removed under reduced pressure to give an orange oil, which contained mono- and bis-brominated products (1:1 ratio) and a trace of starting material. Attempts to purify by column chromatography or recrystallization were not successful. Therefore, the mixture was dissolved in 25 mL THF and cooled with an ice-salt bath. NBS (0.175 g, 0.98 mmol) in 10 mL THF was added drop wise over 15 minutes and the reaction mixture was stirred for 2 hours and quenched with 120 mL 2M HCl. The mixture was extracted with DCM (3 x 100 mL), washed with brine (150 mL), and dried on Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, heptane/DCM 1:1), yielding 0.715 g (0.97 mmol, 108%) of **6** as a red oil (that contained traces of solvent).

δ_H(500 MHz, $CDCl_3$) 7.60 (s, 2H), 7.06 (s, 2H), 2.60 (t, *J* = 7.5, 4H), 1.65 – 1.56 (m, 4H), 1.35 – 1.08 (m, 28H), 0.87 (t, *J* = 7.0, 6H). δ_c(125 MHz, $CDCl_3$) 153.89, 142.42, 133.51, 131.96, 129.67, 126.59, 113.18, 31.87, 30.52, 29.55, 29.49, 29.39, 29.34, 29.32, 29.30, 22.66, 14.10. IR (cm^{-1}): 2951, 2920, 2850, 1726, 1576, 1525, 1485, 1465, 1431, 1376, 1261, 1185, 1070, 1018, 983, 924, 873, 828, 795, 721, 678. HRMS (APCI) calculated for $[M+H]^+$ 739.1242, found 739.1240. Calcd for $C_{34}H_{46}Br_2N_2S_3$: C, 55.28; H, 6.28; N, 3.79; S, 13.02. Found: C, 55.91; H, 6.44; N, 3.74; S, 12.98.

Poly(4,7-bis(3-decylthiophen-2-yl)-2,1,3-benzothiadiazole) PBT-Bipi. Monomer **6** (0.666 g, 0.90 mmol) and bis(pinacolato)diboron (158 mg, 0.62 mmol) were mixed with 25 mL DMF/ toluene (1:3) and degassed. K_3PO_4 (0.804 g, 3.8 mmol) and $Pd(dppf)Cl_2.CH_2Cl_2$ (11 mg, 0.013 mmol) were added and the mixture was heated to 120 ºC and stirred overnight at this temperature. The solvent was removed and the resulting solid was dissolved in chloroform, precipitated in 400 mL cold methanol, and a few drops of conc. HCl were added. The polymer was collected by centrifugation and purified by soxhlet extraction using methanol (400 mL, 23 hours), acetone (2 x 400 mL, 23 hours each), and chloroform (400 mL, 23 hours). The chloroform was partially evaporated and the product was precipitated in a vortex of cold methanol and collected by centrifugation. The resulting polymer was dried in vacuum, yielding 0.233 g (44%) of PBT-Bipi.

δ_H(400 MHz, $CDCl_3$) 7.74-7.61 (m, 2H), 7.07 (s, 2H), 2.76-2.54 (m, 4H), 1.73-1.62 (b, 4H), 1.35-0.92 (b, 28H), 0.85 (bt, J= 6.1 Hz, 6H) IR (cm^{-1}): 2952, 2918, 2849, 1569, 1533, 1483, 1465, 1433, 1376, 1338, 1262, 1184, 1026, 874, 844, 822, 720, 700, 684. GPC (chloroform): M_n = 2941 g/mol, M_w = 4679g/mol, PDI = 1.58. MALDI-TOF: see Figure S1

Figure S1 MALDI-TOF MS spectra of PNT-Bipi and PBT-Bipi



Co-polymerization and MALDI-TOF MS. For a correct analysis and understanding of the recorded MT spectra one has to realize that the schematic representation given for co-polymerizations (Figure S2a) is an over simplification. It does not give any information about the end of the chains, which is exactly what distinguishes different polymer chains in the sample. It are these differences which are visible by MALDI-TOF MS. A more correct representation is given in Figure S2b, which shows that per repeat unit up to 11 possible chains are present, not taking into account side reactions. This also holds for the Stille co-polymerization, discussed in this paper. A detailed representation of the possible end-groups present in PQT-Stille polymerization is given in Figure S3, including a blow up of Figure 1a (n=3). The letter X corresponds with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and Y with monomer 5,5`-dibromo-4,4`-didecyl-2,2`-bithiophene. From the 10 theoretical calculated chains, 9 are visible in the MT spectra. Beside these expected peaks also some other peaks are visible, corresponding to side-reactions concerning the Stille-polymerization. The most abundant peak found was that of the $(XY)_3$ chain, followed by $(XY)_3X$ and $Y(XY)_3$ as one would expect.

Figure S2 (a) common, but incomplete representation of co-polymerizations (b) More correct representation of the chain distribution in co-polymers.

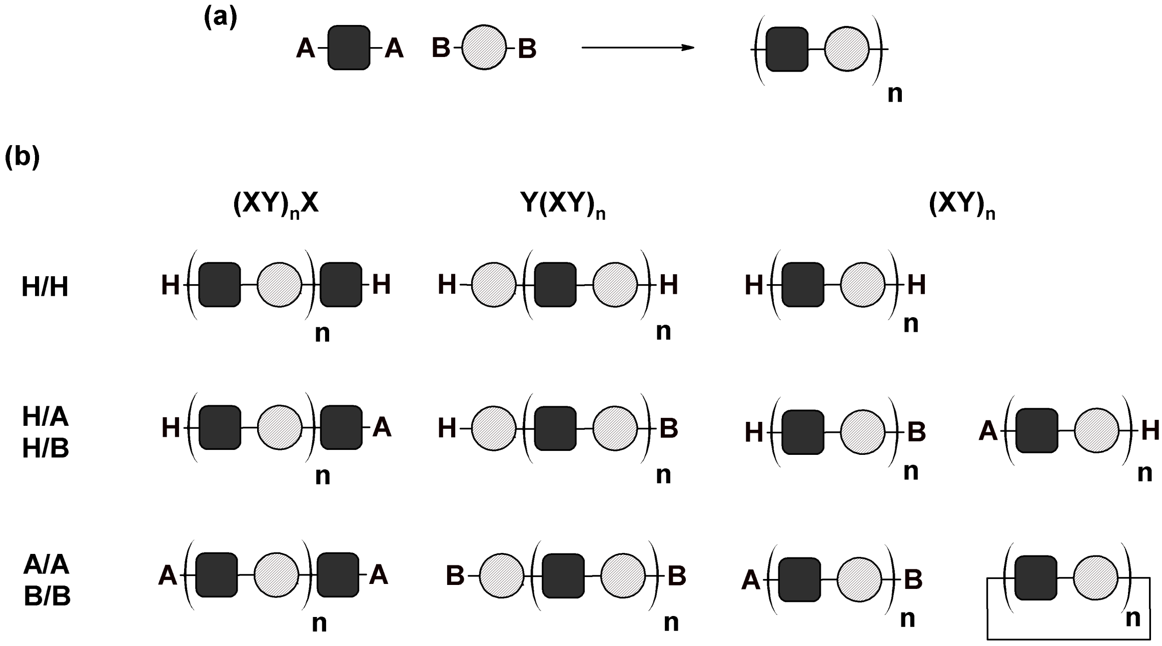
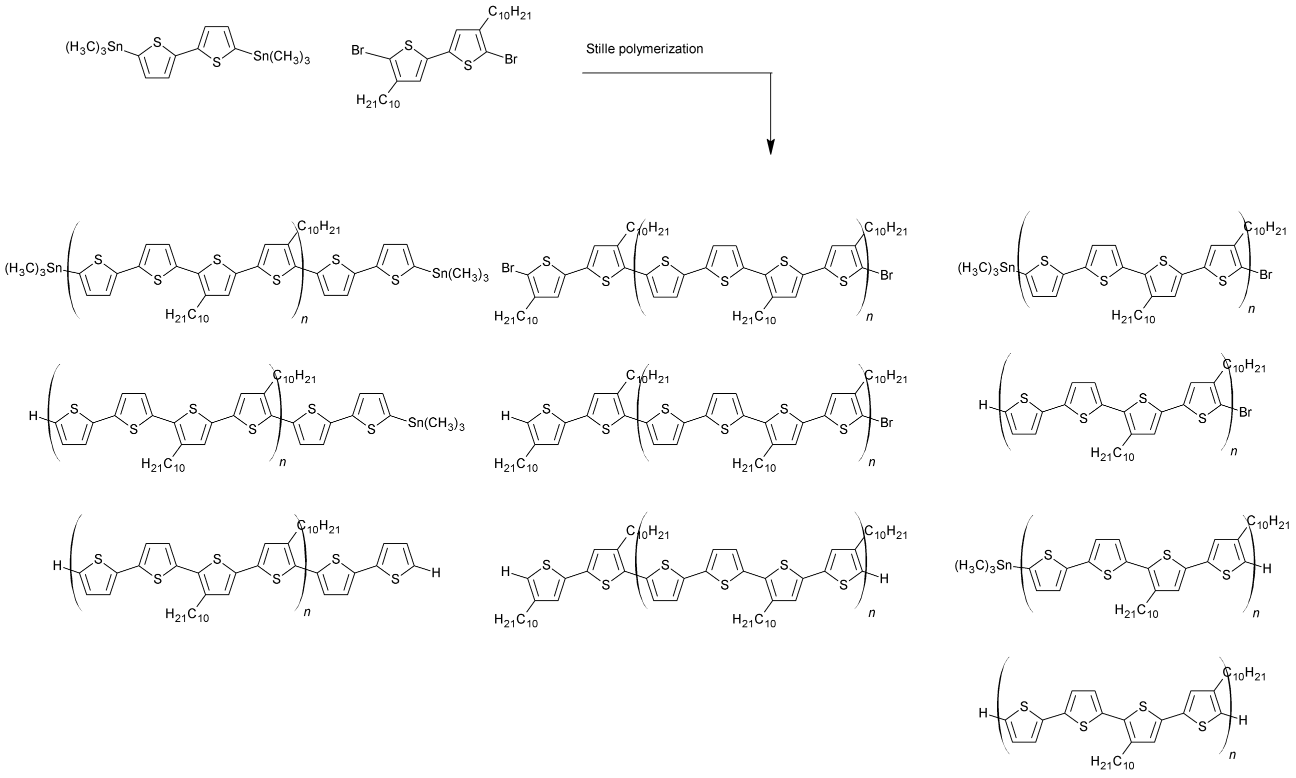
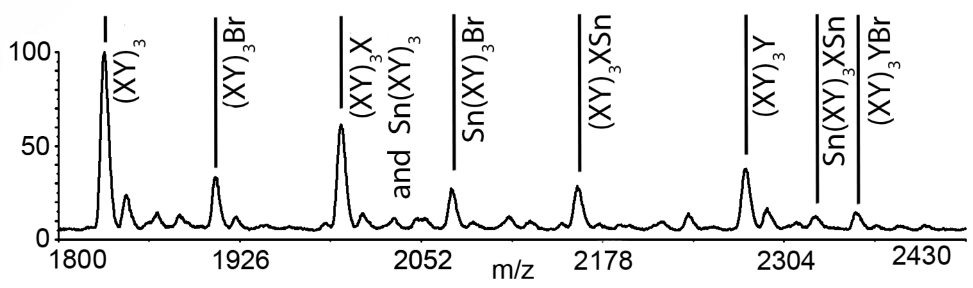


Figure S3 A detailed representation of the possible end-groups present in PQT-Stille. Ring-closure is not taken into account.





The same representation can be given for the PQT-BiPi (Figure S4). The use of macro-monomers reduces the amount of possible end-groups from 10 to 6 (not taking ring-closure into account). Even more important, in practice even less end-groups are found as was shown in Figures 2b, 2c, 3c, 4, 5c.

Figure S4 Pd(dppf)Cl_2

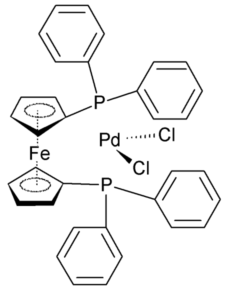
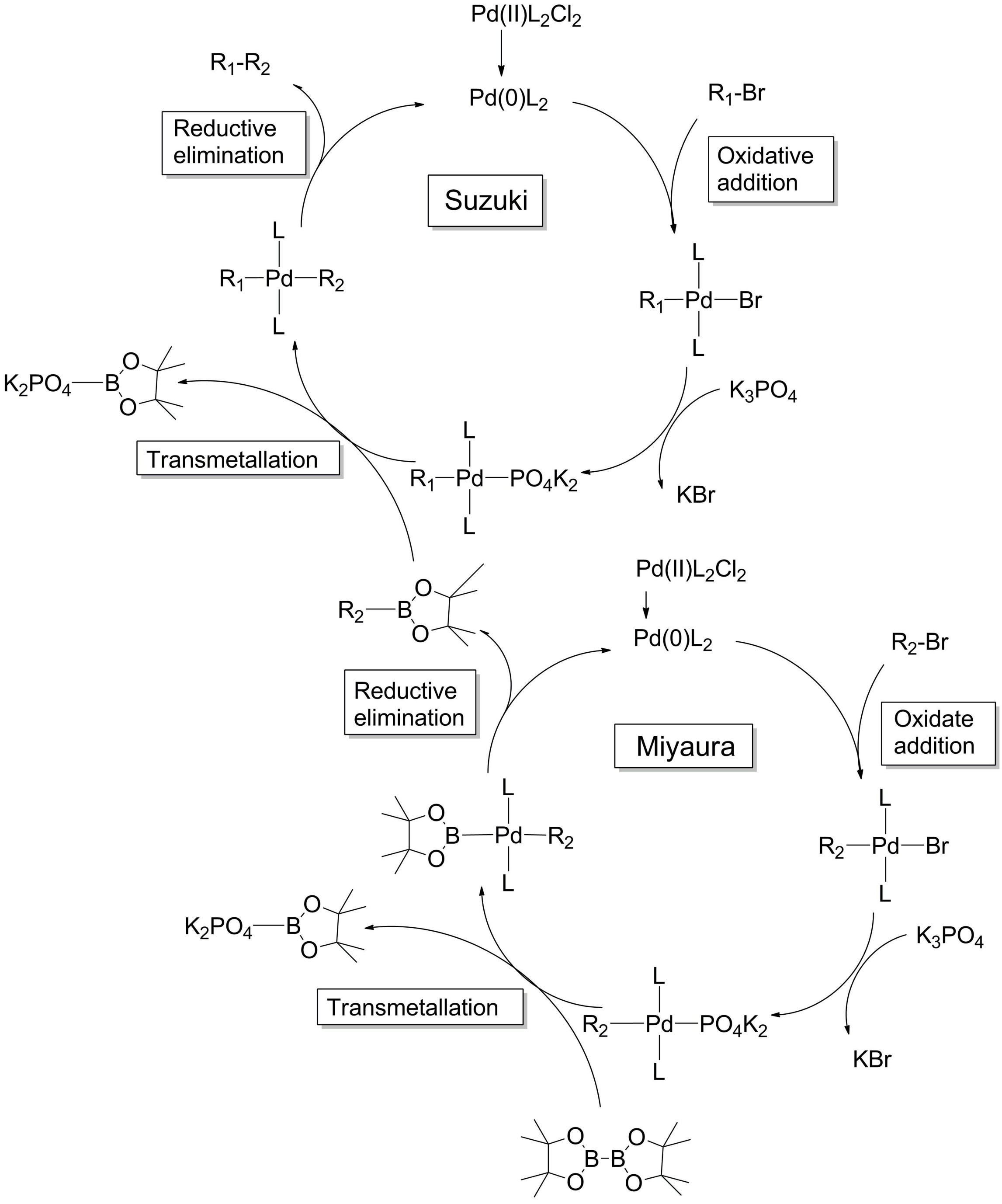


Figure S5 The proposed coupling mechanism of the BiPi polymerization method



(1) Seitz, D. E.; Lee, S.; Hanson, R. N.; Bottaro, J. C. *Synth. Comm.* **1983**, *13*, 121.

(2) Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, M.; Sparrowe, D.; Tierney, S.; McCulloch, I. *J. Am. Chem. Soc.* **2005**, *127*, 1078-1079.