Supporting Information for

To branch or not to branch: C-H selectivity of thiophene-based donor-acceptor-donor monomers for use in direct arylation polycondensation exemplified by PCDTBT

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Instrumentation

NMR spectroscopy. ^{1}H (500.13 MHz) and ^{13}C (125.77 MHz) NMR spectra were recorded on a Bruker Avance III spectrometer using a 5 mm ^{1}H/^{13}C/^{19}F/^{31}P gradient probe. $CDCl_3$ and $C_2D_2Cl_4$ were used as solvent and reference ($CDCl_3$. δ(^{1}H) = 7.26 ppm, δ(^{13}C) = 77.0 ppm; $C_2D_2Cl_4$. δ(^{1}H) = 5.98 ppm).

High temperature size exclusion chromatography (HT-SEC). HT-SEC was performed on a PL GPC 220 (Agilent Laboratories, US) using 2xMixed-B-LS PLgel, 300 x 7,5 mm columns packed with 10 μm particles (Agilent Laboratories, US). 1,2,4-trichlorobenzene was used as mobile phase at a flow rate of 1 mL/min was used. UV-vis detection was done at 386 nm. All measurements were carried out at 150 °C. The molar masses were calculated with both relative and universal calibration, using polystyrene standards. Usage of the UV-detector enabled the analysis of small amounts of sample (~ 0.15 mg/mL).

UV/vis spectroscopy. UV/vis spectra were recorded on a Lambda 650 S spectrometer from Perkin Elmer in film or in chlorobenzene solutions (c = 0.02 mg/mL). The bandgap of the polymers was determined by the absorption onset.

OPV device fabrication. Photovoltaic devices were fabricated in the standard indium tin oxide (ITO) | poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) | polymer:$PC_{71}BM$ | Ca/Al layer sequence. For the active layer, the chloroform fraction of the polymer was used. ITO on glass anodes were first cleaned with acetone and isopropanol, followed by oxygen plasma treatment. A ~40-nm-thick layer of PEDOT:PSS was spin-coated onto plasma-treated substrates, annealed at 230 °C for 10 min, and transferred into a nitrogen-filled glovebox for the subsequent fabrication steps. Photoactive layers were spin-coated from 1,2-dichlorobenzene (*o*-DCB) solution ($PC_{71}BM$, 48 mg/mL in *o*-DCB and polymer, 12 mg/mL, were mixed in a 1:1 ratio to give the active blend mixture) in air to give ~90 nm thick films. Finally, after keeping the films at 10^{-7} mbar for at least 12h, a Ca (7nm)/Al (100nm) electrode was evaporated at ~10^{-7} mbar and the devices were encapsulated using an epoxy resin.

OPV device testing. Device external quantum efficiency (EQE) was measured using a tungsten lamp with a monochromator at intensities of ~1 mW cm^{-2}. Short circuit currents were recorded using a Keithley 237 source meter. The current–voltage characteristics of the device were measured under simulated 100 mW cm^{-2} AM 1.5 illumination using an Abet Technology solar simulator. The spectral mismatch of the simulator was calibrated to a silicon reference cell.

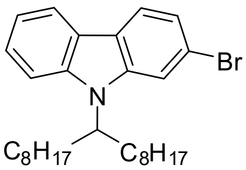
Photoluminescence spectra and photoluminescence quantum efficiency. The measurement was carried out on films deposited on quartz glass (Spectrosil 2000) or chlorobenzene solutions (0.02 mg/ml) in a Hellma quartz cuvette (1 mm beam path) via excitation of the sample with a 532 nm laser. The sample was placed inside an integrating sphere purged with nitrogen. The light collected was coupled through a fibre into a spectrometer (Shamrock SR303i, Andor Technologies). Three individual measurements were performed to calculated the quantum yield according to deMello *et al.* [5]

MALDI-ToF-MS. MALDI-ToF-MS measurements were performed with a Bruker Autoflex III TOF/TOF mass spectrometer (Bruker Daltonik GmbH, Germany) operating in positive reflector mode. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) was used as matrix. Matrix and analyte were dissolved in THF and mixed as follows: 10 µL dithranol (20 mg/mL), 1 µL analyte (1 mg/mL). 1 µL of the mixture was spotted on the sample probe and allowed to dry. Poly(ethylene oxide) was used for external calibration.

Materials. All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. TBT, Br_2TBT, Br_2Cbz, Cbz(Bpin)$_2$ and PCDTBT were synthesized according to the literature. [1–4]

Synthesis Protocols

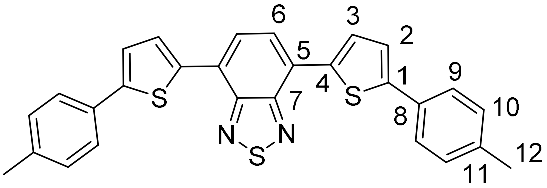
*2-Bromo-9-(heptadecan-9-yl)-carbazol*e, **Br_1Cbz**



2,7-Dibromo-9-(heptadecan-9-yl)-carbazole (**Br_2Cbz**, 3.00 g, 5.32 mmol) was dissolved in dry THF (50 mL) and cooled to -78°C. *n*-BuLi (2.5 M in hexane, 2.2 mL, 5.50 mmol, 1.18 eq.) was added dropwise. The reaction mixture was stirred at -78°C for 1 h. Methanol (2 mL) was added dropwise. After allowing the mixture to warm to rt overnight, the solvent was removed under reduced pressure. The residual suspension was purified *via* column chromatography (*iso*-hexanes:ethyl acetate 10:1) and the product was obtained as a colorless solid in 97% yield (2.5 g, 5.16 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.05 (br s, 1H), 7.94 (br s, 1H), 7.36-7.74 (m, 3H), 7.31 (br d, ^3J = 8.4 Hz, 1H), 7.22 (t, ^3J = 7.7 Hz, 1H), 4.48 (br s, 1H), 2.23 (m, 2H), 1.85-1.97 (m, 2H), 1.09-1.27 (m, 22H), 0.93-1.05 (m, 2H), 0.83 (t, ^3J = 6.7 Hz, 6H).

4,7-Bis(5-p-tolylthiophen-2-yl)benzo[2,1,3]thiadiazole, **tol_2TBT**



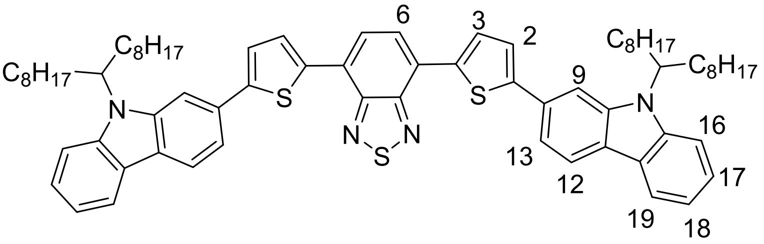
4,7-Di(2-thienyl)-2,1,3-benzothiadiazole (392 mg, 1.30 mmol), 4-bromotoluene (669 mg, 3.91 mmol, 3 eq), pivalic acid (136 mg, 1.33 mmol, 1 eq) und cesium carbonate (1.27 g, 3.89 mmol, 3 eq) were dissolved in degassed toluene (4.71 mL) and purged with nitrogen. The catalyst $Pd_2(dba)_3$ (23.9 mg, 0.03 mmol, 2 mol%) and P(o-anisyl)$_3$ (36.8 mg, 0.10 mmol, 8 mol%) were added and the mixture was stirred at 100°C overnight. The reaction mixture was purified *via* column chromatography (gradient *iso*-hexanes:dichloromethane 2:1 to 1:1) and the product was obtained as a red solid in 71% yield (444 mg, 0.92 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.11 (d, ^3J = 3.8 Hz, 2H, H-3), 7.89 (s, 2H, H-6), 7.61 (d, ^3J = 7.8 Hz, 4H, H-9), 7.38 (d, ^3J = 3.8, 2H, H-2), 7.23 (d, ^3J = 7.8 Hz, 4H, H-10), 2.40 (s, 6H, H-12).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 152.6 (7), 145.8 (1), 138.2 (4), 137.8 (11), 131.4 (8), 129.6 (10), 128.6 (3), 125.7 (5 and 9), 125.3 (6), 123.6 (2), 21.2 (12).

MS (APCI): *m/z* 481.08 (100) $[M+H]^+$

4,7-Bis(5-(9-(heptadecan-9-yl)-9H-carbazol-2-yl)thiophen-2-yl)benzo[2,1,3]thiadiazole, **Cbz_2TBT**

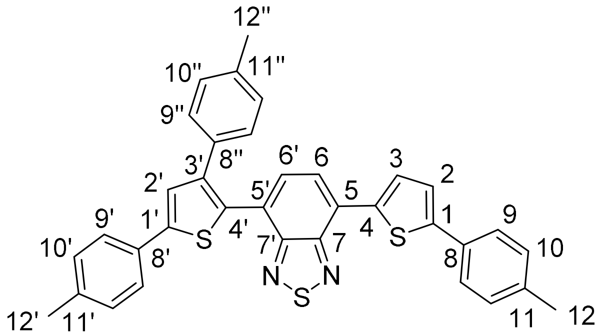


4,7-Di(2-thienyl)-2,1,3-benzothiadiazole (100 mg, 0.33 mmol), 2-bromo-9-(heptadecan-9-yl)-carbazole (484 mg, 0.99 mmol), pivalic acid (34 mg, 0.33 mmol) und cesium carbonate (325 mg, 1.0 mmol) were dissolved in degassed toluene (4.8 mL) and purged with nitrogen. The catalyst $Pd_2(dba)_3$ (23.9 mg, 0.03 mmol, 2 mol%) and $P(o\text{-anisyl})_3$ (36.8 mg, 0.10 mmol, 8 mol%) were added and the mixture was stirred at 100°C for 72 h. The reaction mixture was purified *via* column chromatography (*iso*-hexanes:dichloromethane 6:1) and the product was obtained as a deep purple solid in 77% yield (283 mg, 0.26 mmol).

^{1}H NMR (500 MHz, $C_2H_2Cl_4$, 393K): δ (ppm) = 8.23 (d, ^3J = 3.8 Hz, 2H, H-3), 8.14 (d, ^3J = 8.0 Hz, 2H, H-12), 8.12 (d, ^3J = 7.8 Hz, 2H, H-19), 7.98 (s, 2H, H-6), 7.84 (br s, 2H, H-9), 7.62 (d, ^3J = 8.0 Hz, 2H, H-13), 7.54 (br d, 2H, H-16), 7.53 (d, ^3J = 3.8 Hz, H-2), 7.46 (t, ^3J = 7.8 Hz, 2H, H-17), 7.26 (t, ^3J = 7.8 Hz, 2H, H-18), 4.67 (m, 2H, N-CH), 2.38 (m, 4H, N-CH-CH_2), 2.09 (m, 4H, N-CH-CH_2), 1.45-1.05 (44H, CH_2), 0.86 (t, 12H, CH_3).

MS: (ESI); *m/z* = 1108.64 $[M+H]^+$.

4-(3,5-Di-p-tolylthiophen-2-yl)-7-(5-p-tolylthiophen-2-yl)benzo[2,1,3]thiadiazole, **tol$_3$TBT**



Tol$_2$TBT (100 mg, 0.21 mmol), 4-bromotoluene (110 mg, 0.68 mmol), pivalic acid (22 mg, 0.22 mmol) und cesium carbonate (203 mg, 0.62 mmol) were dissolved in degassed toluene (4 mL) and purged with nitrogen. The catalyst Pd$_2$(dba)$_3$ (3.8 mg, 2 mol%) and P(o-anisyl)$_3$ (5.9 mg, 8 mol%)) were added and the mixture was stirred at 100°C for 72 h. The solvent was removed, the reaction mixture was suspended in chloroform and the solid was filtered off. The solution was poured into *iso*-hexanes. This procedure was repeated 4 times prior to further purification *via* column chromatography (*iso*-hexanes:dichloromethane 2:1). The product was obtained as a red solid in 14% yield (7.5 mg, 0.013 mmol).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 8.09 (d, ^3J = 3.9 Hz, 1H, H-3), 7.71 (d, ^3J = 7.6 Hz, 1H, H-6), 7.61 (d, ^3J = 7.7 Hz, 1H, H-9’), 7.59 (d, ^3J = 7.7 Hz, 1H, H-9), 7.44 (d, ^3J = 7.6 Hz, 1H, H-6‘), 7.41 (s, 1H, H-2‘), 7.36 (d, ^3J = 3.9 Hz, 1H, H-2), 7.25-7.20 (5H, H-10, H-10‘, H-9’’), 7.08 (d, ^3J = 8.0 Hz, 2H, H-10’’), 2.39 (s, 6H, H-12, H-12‘), 2.34 (s, 3H, H-12’’).

^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 154.2 (7), 152.3 (7’), 145.9 (1), 145.2 (1’), 142.0 (3’), 138.1 (4), 137.9 and 137.8 (11,11’), 136.8 (11’’), 134.0 (8’’), 131.5 (4’), 131.4 and 131.3 (8,8’), 130.3 (6’), 129.6 (10,10’), 129.3 (10’’), 128.8 (3), 128.7 (9’’), 126.3 (5), 126.0 (5’), 125.8 (2’,9,9’), 124.9 (6), 123.6 (2), 21.23 (12,12’), 21.18 (12’’).

MS (APCI): *m/z* 571.13 (100) [M+H]$^+$.

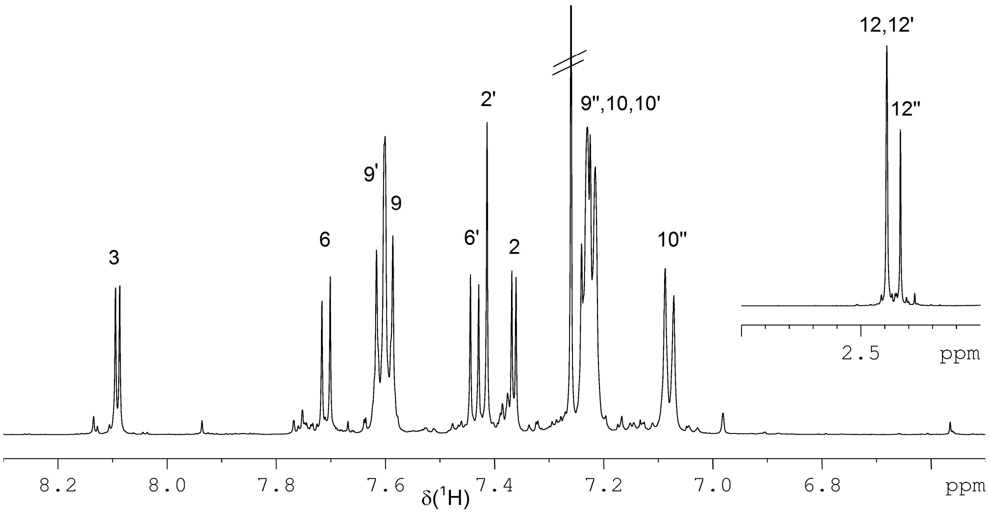


Figure SI-1. ^{1}H NMR spectrum of **tol$_3$TBT** ($CDCl_3$, 30°C)

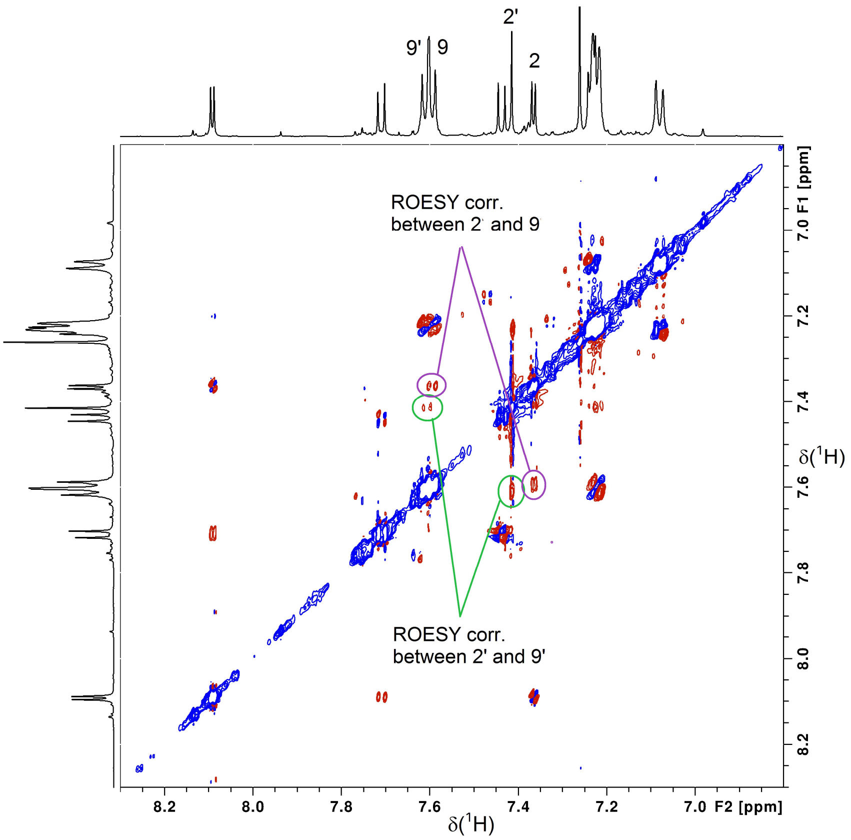


Figure SI-2. ROESY spectrum (region) of **tol$_3$TBT** showing a through-space correlation between protons 2' (singlet) and 9' proving γ-substitution and the complementary correlation between protons 2 (doublet) and 9 ($CDCl_3$, 30°C).

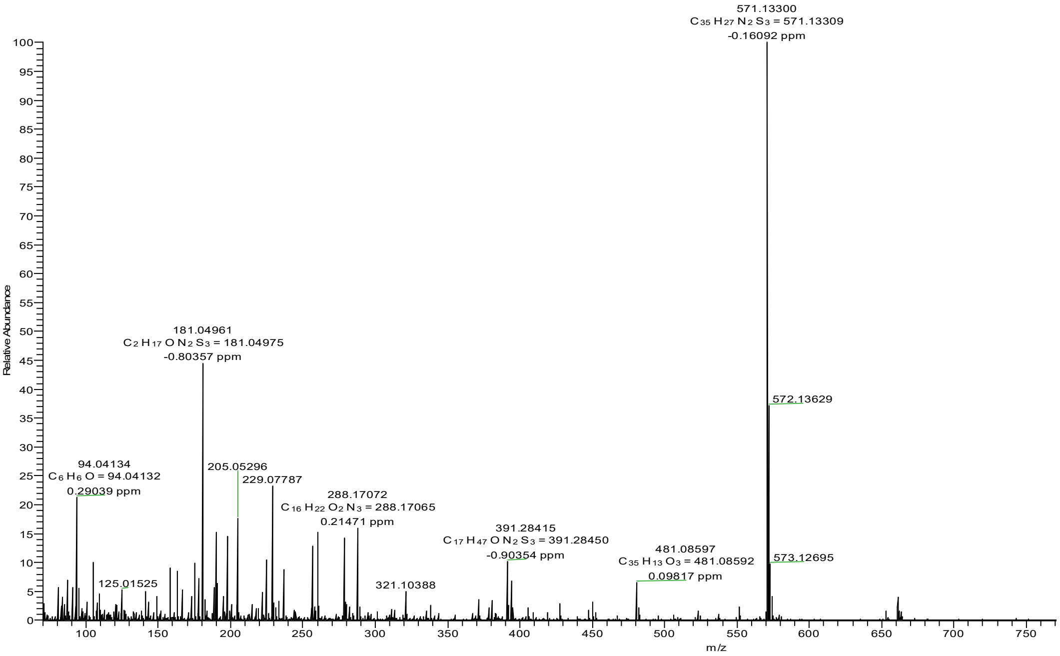


Figure SI-3 Mass spectrum of **tol$_3$TBT**; substance ionized *via* APCI.

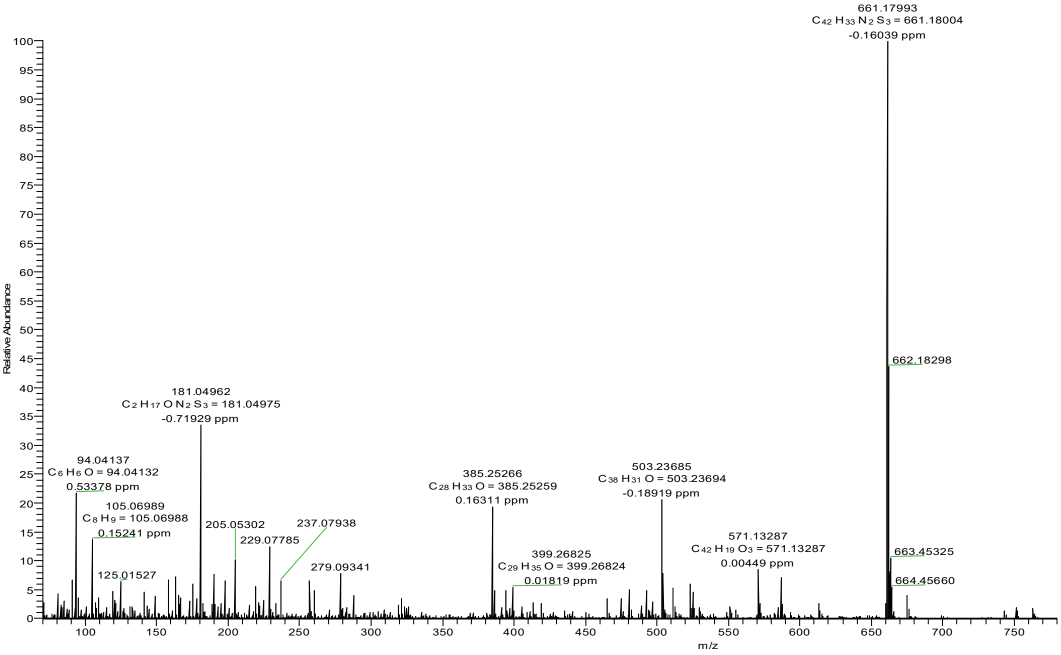
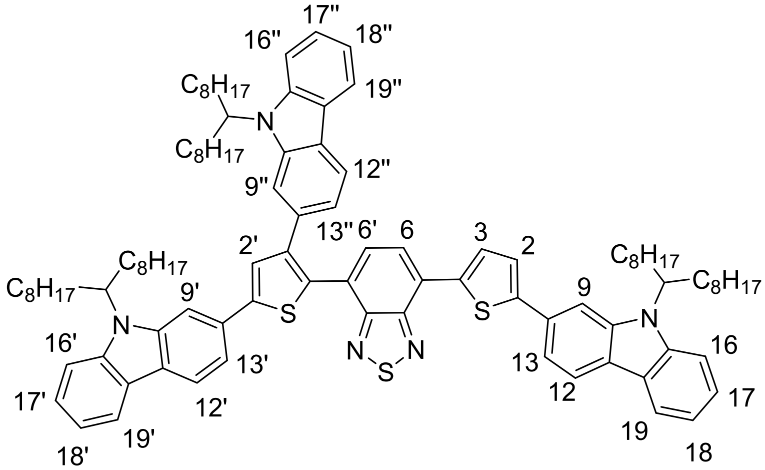


Figure SI-4 Mass spectrum of **tol$_4$TBT**; substance ionized *via* APCI.

4-(3,5-Bis(9-(heptadecan-9-yl)-9H-carbazol-2-yl)thiophen-2-yl)-7-(5-(9-(heptadecan-9-yl)-9H-carbazol-2-yl)thiophen-2-yl)benzo[2,1,3]thiadiazole, **Cbz$_3$TBT**



Cbz$_2$TBT (250 mg, 0.23 mmol), 2-brom-9-(heptadecan-9-yl)-carbazole (263 mg, 0.54 mmol), pivalic acid (24 mg, 0.23 mmol) und cesium carbonate (221 mg, 0.68 mmol) were dissolved in degassed toluene (9 mL) and purged with nitrogen. The catalyst Pd$_2$(dba)$_3$ (4.1 mg, 2 mol%) and P(o-anisyl)$_3$ (6.4 mg, 8 mol%) were added and the mixture was stirred at 100°C for 72 h. The solvent was removed and the reaction mixture was purified *via* column chromatography (gradient *iso*-hexanes:ethyl acetate 1:0 to 15:1) and the product was obtained as a deep purple solid in 18% yield (62 mg, 0.04 mmol). The starting material could be recovered in 62% yield.

^{1}H-NMR (500 MHz, $C_2H_2Cl_4$, 393K): δ (ppm) = 8.20 (d, ^3J = 3.9 Hz, 1H, H-3), 8.16 (d, ^3J = 7.9 Hz, 1H, H-12‘), 8.15-8.07 (5H, H-12, H-12‘‘, H-19, H-19‘, H-19‘‘), 7.90 (s, 1H, H-9‘), 7.80 (s, 1H, H-9), 7.77 (d, ^3J = 7.5 Hz, 1H, H-6), 7.72 (s, 1H, H-2‘), 7.68 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-13‘), 7.60 (d, ^3J = 7.5, 1H, H-6‘), 7.58 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-13), 7.55 (d, 1H, H-16‘), 7.53 (d, 1H, H-16), 7.50 (s, 1H, H-9‘‘), 7.49 (d, ^3J = 3.8 Hz, 1H, H-2), 7.48-7.35 (5H, H-13‘‘, H-16‘‘, H-17, H-17‘,H-17‘‘),H-13‘‘), 7.30-7.20 (3H, H-18, H-18‘, H-18‘‘), 4.66 (m, 2H, N-CH), 4.38 (m, 1H, N-CH), 2.37 (m, 4H, N-CH-CH_2), 2.07 (m, 4H, N-CH-CH_2), 1.99 (m, 2H, N-CH-CH_2), 1.77 (m, 2H, N-CH-CH_2), 1.45-0.90 (72H, CH$_2$), 0.90-0.80 (18H, CH$_3$).

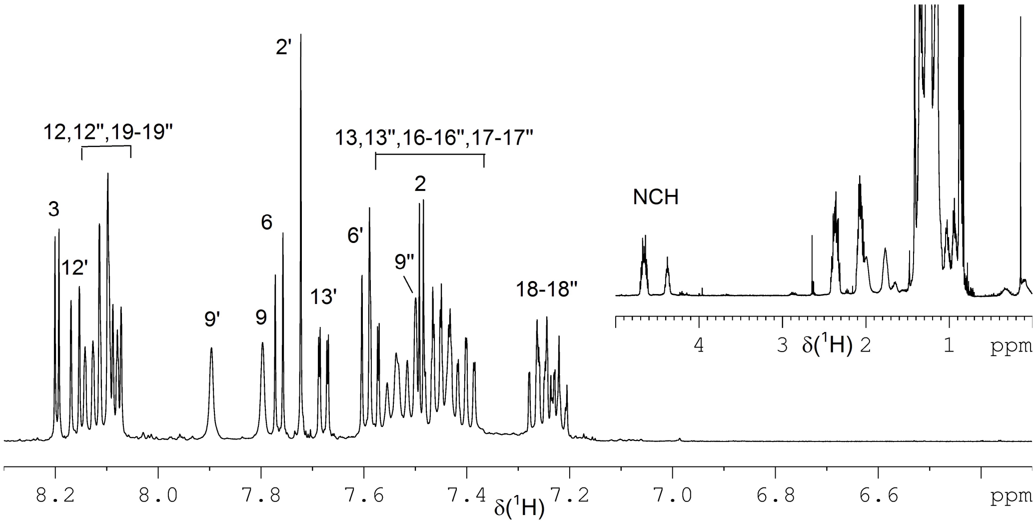


Figure SI-5. ^{1}H NMR spectrum of **Cbz$_3$TBT** ($C_2D_2Cl_4$, 120°C)

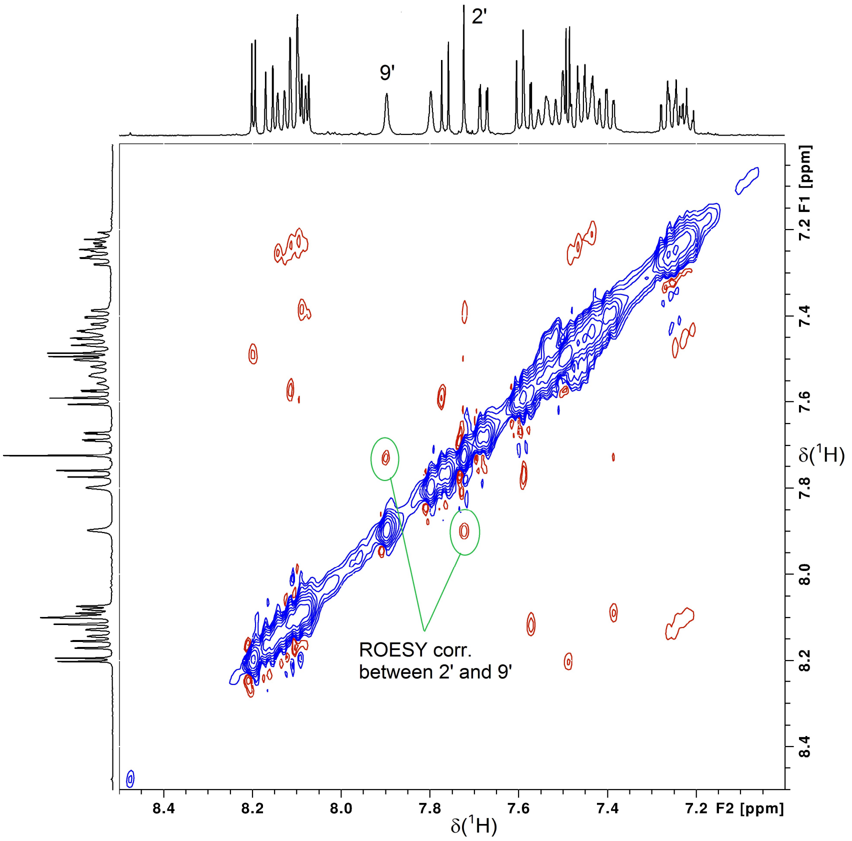
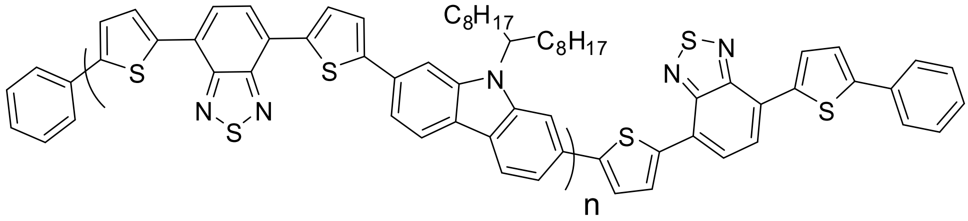


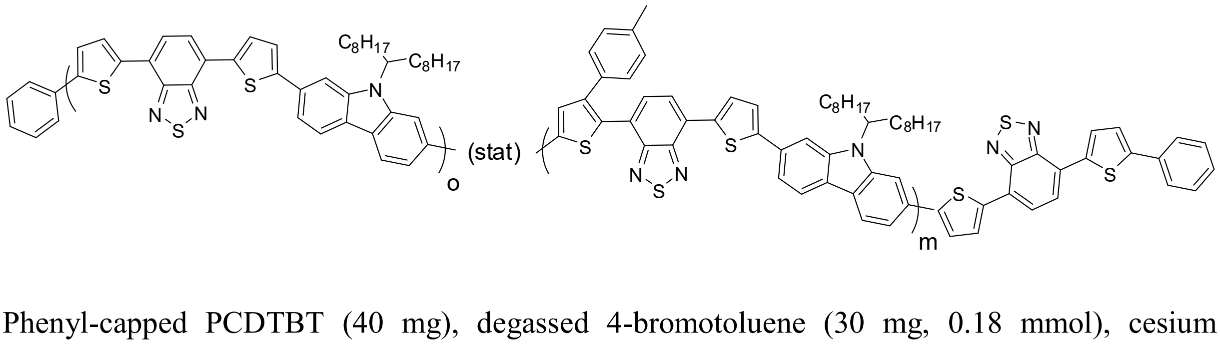
Figure SI-6. ROESY spectrum (region) of **Cbz$_3$TBT** showing a through-space correlation between protons 2' and 9' proving γ-substitution ($C_2D_2Cl_4$, 120°C)

Phenyl-capped PCDTBT



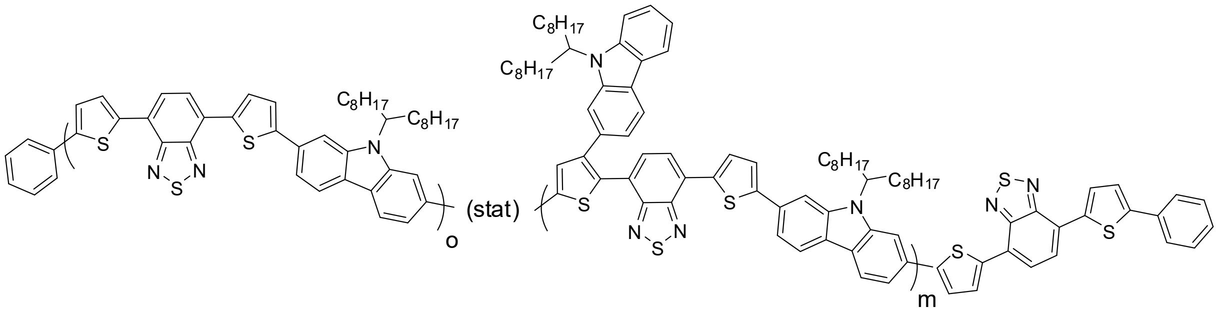
Br$_2$TBT (100 mg, 0.218 mmol), Cbz(Bpin)$_2$ (129.18 mg, 0.196 mmol, 0.9 eq) and phenyl boronic acid (2.66 mg, 0.0218 mmol, 0.1 eq) were placed in a screw-cap vial. The vial was transferred into a nitrogen filled glovebox where the catalyst Pd(PPh$_3$)$_4$ (2.52 mg, 2.18 µmol, 1mol%) was added. 2 drops of Aliquat 336, degassed toluene (4.4 mL) and degassed aqueous potassium carbonate solution (2M, 4.4 mL) were added. The reation mixture was stirred at 80°C for 72 h. After cooling to rt, the aqueous phase was removed and the organic phase was poured into methanol. The polymer was filtered off and washed by successive Soxhlet extraction with methanol, acetone, *iso*-hexanes, chloroform and chlorobenzene. The chlorobenzene fraction was poured into methanol and the polymer was separated *via* centrifugation. The solid was dried under reduced pressure. The polymer was obtained as a deep purple solid in 85% yield (130mg). $M_{\mathrm{n,SEC}}$ = 5.5 kg/mol, $M_{\mathrm{w,SEC}}$ = 21.3 kg/mol (TCB, 150 °C).

Phenyl-capped PCDTBT-*γ*-tol



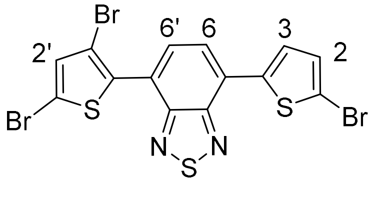
Phenyl-capped PCDTBT (40 mg), degassed 4-bromotoluene (30 mg, 0.18 mmol), cesium carbonate (228 mg) and pivalic acid (23 mg) were placed in a nitrogen-filled screw-cap vial and degassed toluene (2 mL) was added. The reaction mixture was stirred at 100°C for 3 days. The reaction mixture was allowed to cool to room temperature and poured into methanol. The precipitate was filtered of and washed by successive Soxhlet extraction with methanol, acetone, *iso*-propanol and chloroform. The polymer was dissolved in hot chlorobenzene, poured into methanol and separated from the solvent *via* centrifugation. 38 mg of polymeric material was obtained.

Phenyl-capped PCDTBT-γ-Cbz



Phenyl-capped PCDTBT (20 mg), Br₁Cbz (20 mg, 0.08 mmol), cesium carbonate (118 mg) and pivalic acid (13 mg) were placed in a nitrogen-filled screw-cap vial and degassed toluene (2 mL) was added. The reaction mixture was stirred at 100°C for 3 days. The reaction mixture was allowed to cool to room temperature and poured into methanol. The precipitate was filtered of and washed by successive Soxhlet extraction with methanol, acetone, *iso*-propanol and chloroform. The polymer was dissolved in hot chlorobenzene, poured into methanol and separated from the solvent *via* centrifugation. 16 mg of polymeric material was obtained.

4-(5-Bromothiophen-2-yl)-7-(3,5-dibromothiophen-2-yl)benzo[3,1,2]thiadiazole, **Br_3TBT**

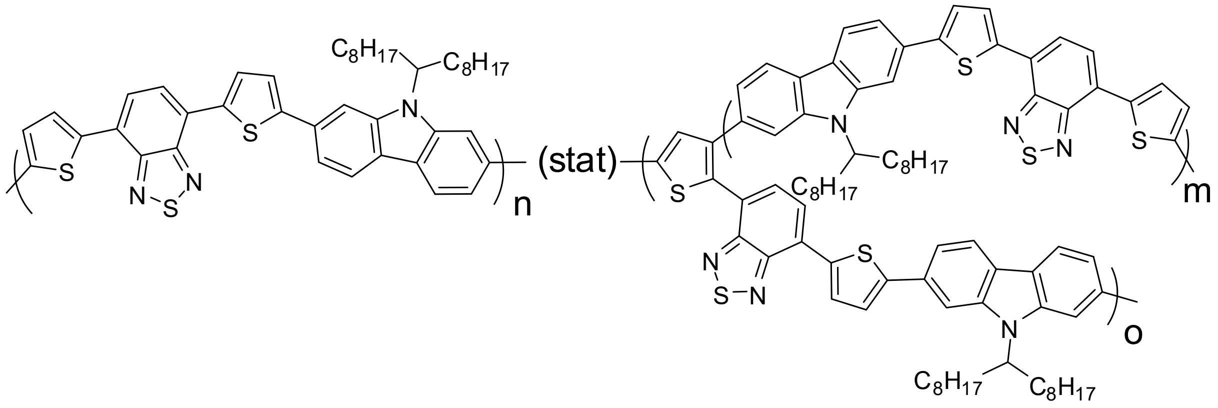


TBT (200 mg, 0.67 mmol) and NBS (360 mg, 1.98 mmol, 3eq.) were dissolved in a chloroform:acetic acid (1:1) mixture. The reaction mixture was stirred for 72h at rt under exclusion of light. Water was added (10 mL) and the organic phase was separated. The aqueous phase was extracted with chloroform three times. Column chromatography (*iso*-hexanes:dichloromethane

9:1) followed by recrystallization from toluene resulted in a concentration of Br_3TBT up to 80%. However, 20% Br_2TBT could not be removed completely.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.06 (d, ^3J = 7.6 Hz, 1H; H-6’), 7.86 (d, ^3J = 7.6 Hz, 1H; H-6), 8.86 (d, ^3J = 4.0 Hz, 1H; H-3), 7.18 (d, ^3J = 4.0 Hz, 1H; H-2), 7.14 (s, 1H; H-2’).

b-PCDTBT-X (X = TBTBr$_3$ feed content in mol %)



Exemplary for *b*-PCDTBT-4: Br_2TBT (91.22 mg, 0.20 mmol, 0.96 eq.), Br_3TBT (9.37 mg, 0.01 mmol, 0.04 eq.), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxa-borolan-2-yl)-9H-carbazole (146.24 mg, 0.22 mmol, 1.02 eq) and $Pd(PPh_3)_4$ (2.5 mg, 1 mol%) were placed in a screw-cap vial. 2 drops of Aliquat 336, degassed toluene (3 mL) and degassed aqueous potassium carbonate solution (2M, 3 mL) were added. The reation mixture was stirred at 80°C for 72 h. After cooling to rt, the aqueous phase was removed and the organic phase was poured into methanol. The polymer was filtered off and washed by successive Soxhlet extraction with methanol, acetone, *iso*-hexanes, chloroform and chlorobenzene. The chlorobenzene fraction was poured into methanol and the polymer was separated *via* centrifugation. The solid was dried under reduced pressure.

b-PCDTBT-4 was obtained in 16.3% yield (24.5 mg; 10.6 % chloroform fraction and 5.7 % chlorobenzene fraction), *b*-PCDTBT-10 was obtained in 13.3 % yield (6.4 % chloroform fraction and 8.9 % chlorobenzene fraction) and *b*-PCDTBT-20 was obtained in 27.6% yield (16.7 % chloroform fraction and 10.9 % chlorobenzene fraction). For all reactions, significant amount of unsoluble likely cross-linked product was found.

Molecular weights: ***b*-PCDTBT-4** M_n 7.1 kg/mol, M_w 18.4 kg/mol, Đ 2.59; ***b*-PCDTBT-10** M_n 3.6 kg/mol, M_w 8.7 kg/mol, Đ 2.42; ***b*-PCDTBT-20** M_n 4.3 kg/mol, M_w 7.7 kg/mol, Đ 1.79.

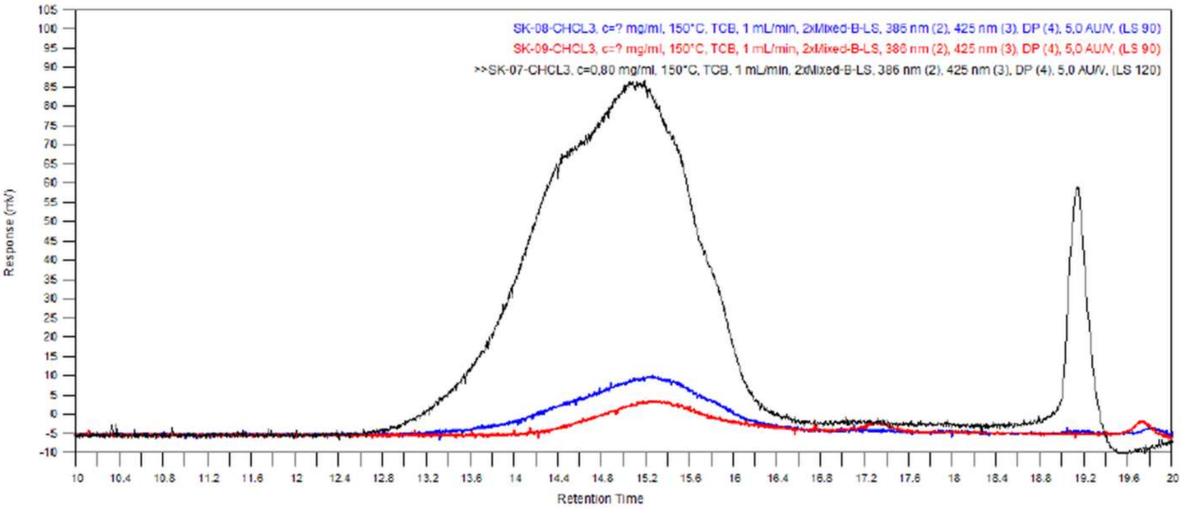


Figure SI-7. Elugrams of ***b*-PCDTBT-4**, ***b*-PCDTBT-10** and ***b*-PCDTBT-20**. Measured in 1,2,4-Trichlorobenzene at 150°C.

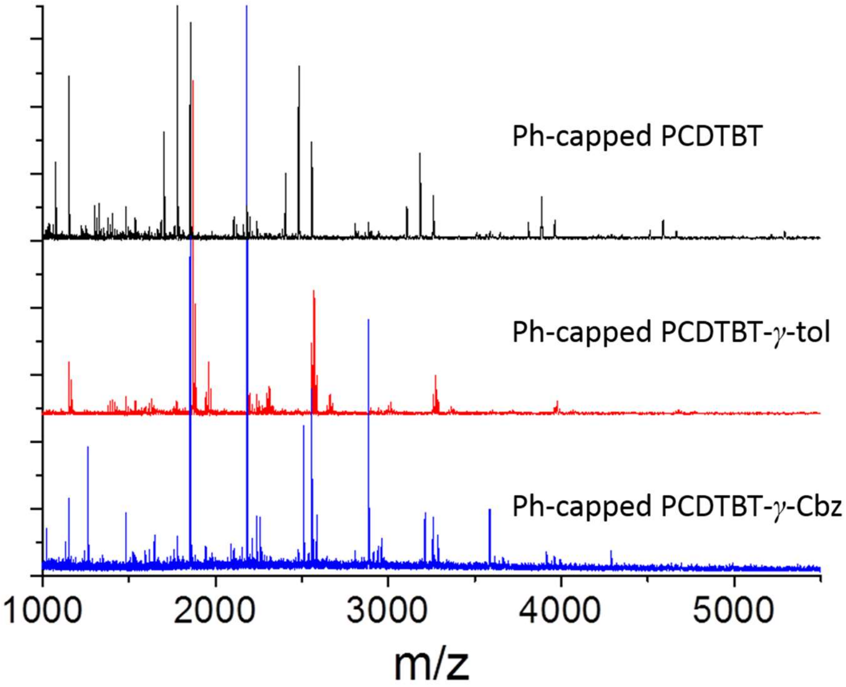


Figure SI-8 MALDI-ToFmass spectra of phenyl-capped PCDTBT (top, black), phenyl-capped PCDTBT-γ-tol (middle, red) and phenyl-capped PCDTBT-γ-Cbz (bottom, blue).

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