Supporting Information

Hybrid Conjugated Polymers with Alternating Dithienosilole or -Germole and Tricoordinate Boron Units

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Synthesis procedure for (5-bromothien-2-yl)trimethylstannane .......................... 2
NMR and MALDI-TOF mass spectra of the monomer FBDT2Br .................. 3—7
NMR spectra of the polymers

1H NMR.................................................................................. 8—9
11B NMR................................................................................. 10
13C NMR................................................................................. 10—12
19F NMR.................................................................................. 12
29Si NMR................................................................................ 13
MALDI-TOF mass spectra.......................................................... 14—15
DSC traces of pDTSFBDT and pDTGFBDT........................................ 15—16
Absorption and fluorescence spectra of pDTSBDT.............................. 16
Absorption and fluorescence spectra of pDTSFBDT.............................. 17
Fluorescence spectra of 0.5wt% PMMA films....................................... 17
Cyclic voltammograms ................................................................ 18
AFM images .............................................................................. 19
Synthesis procedure for (5-bromothien-2-yl)trimethylstannane

To 2,5-dibromothiophene (11.1 g, 45.9 mmol) in 300 mL of dry ether, n-BuLi (18.3 mL, 2.5 M in hexane) were added dropwise at -78 °C. After stirring the reaction mixture at -78 °C for 0.5 h, a solution of trimethyltin chloride (10.0 g, 50.2 mmol) in THF (20 mL) was added dropwise. The reaction was allowed to slowly warm up to room temperature, stirred over night at room temperature, and then quenched by addition of water. The organic layer was extracted with DCM (3×10 mL) and all solvents were removed from the combined extracts via rotary evaporation. The product was purified by distillation under high vacuum (140-160 °C) to give a colorless oil (7.5 g, 50% yield).\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C): \(\delta = 7.15\) (d, J = 3.3 Hz, 1H), 6.97 (d, J = 3.3 Hz, 1H), 0.39 (s/d, J\(^{117/119}\)Sn, H = 60 Hz, 9H, SnMe\(_3\)). The spectrum is shown in Figure S1.

Figure S1  \(^1\)H NMR spectrum of (5-bromothien-2-yl)trimethylstannane in CDCl\(_3\) (499.9 MHz).
Figure S2 $^1$H (top, 499.9 MHz) and $^{11}$B NMR spectrum (bottom, 160.3 MHz) of toluene solution of crude bromobis[5-bromo[2-thienyl]borane in CDCl$_3$. 
Figure S3  $^1$H NMR spectrum of FBDTBr2 in CDCl$_3$ (599.7 MHz).
Figure S4  $^{11}$B NMR spectrum of $\text{FBDTBr}_2$ in CDCl$_3$ (192.4 MHz).

Figure S5  $^{19}$F NMR spectrum of $\text{FBDTBr}_2$ in CDCl$_3$ (470.4 MHz).
Figure S6  $^{13}$C NMR spectrum of FBDTBr$_2$ in CDCl$_3$ (150.8 MHz).
Figure S7  MALDI-TOF mass spectrum of FBDTBr2 (Matrix: 1,1,4,4-Tetraphenyl-1,3-butadiene, negative mode).
Figure S8  $^1$H NMR spectrum of pDTSBDT (400 MHz).

Figure S9  $^1$H NMR spectrum of pDTGBDT (400 MHz).
Figure S10  $^1$H NMR spectrum of pDTSFBDT (400 MHz).

Figure S11  $^1$H NMR spectrum of pDTGFBDT (400 MHz).
Figure S12  $^{11}$B NMR spectra of the borane-dithienosilole/dithienogermole copolymers (160.4 MHz).

Figure S13  $^{13}$C NMR spectrum of pDTSBBDT (125.7 MHz).
Figure S14  $^{13}$C NMR spectrum of pDTGBDT (125.7 MHz).

Figure S15  $^{13}$C NMR spectrum of pDTSFBDT (125.7 MHz).
Figure S16  $^{13}$C NMR spectrum of pDTGFBDT (125.7 MHz).

Figure S17  $^{19}$F NMR spectra of pDTSFBDT and pDTGFBDT (470 MHz).
Figure S18  $^{29}$Si NMR spectra of pDTSBDT and pDTSFBDT (99.3 MHz).

Figure S19  A high resolution mass pattern of pDTSBDT. (Matrix: trans-2[3-(4-t-butyphenyl)-2-methyl-2-propenylidene]malononitrile)
**Figure S20** A high resolution mass pattern of pDTGBDT. (Matrix: \(\text{trans-2[3-(4-t-butyphenyl)-2-methyl-2-propenylidene]malononitrile}\))

**Figure S21** A high resolution mass pattern of pDTSFBDT. (Matrix: \(\text{trans-2[3-(4-t-butyphenyl)-2-methyl-2-propenylidene]malononitrile}\))
Figure S22  A high resolution mass pattern of pDTGFBDT. (Matrix: trans-2[3-(4-r-butylphenyl)-2-methyl-2-propenylidene]malononitrile)

Figure S23  Second cycle of DSC for pDTSFBDT.
Figure S24  Second cycle of DSC for pDTGFBDT.

Figure S25  Absorption (solid lines) and fluorescence (dashed lines) spectra of pDTSBDT in solution and as film.
Figure S26  Absorption (solid lines) and fluorescence (dashed lines) spectra of pDTSFBDT in solution and as film.

Figure S27  Fluorescence spectra of 0.5wt% PMMA films of pDTSBDT and pDTSFBDT.
Figure S28  Full cyclic voltammetry data of (a) reductive and (b) oxidative waves of the borane-dithienosilole/dithienogermole copolymers.
Figure S29  AFM topographical (top) and cross-section (bottom) images of spin-coated films of pDTGBDT (left) and pDTGFBDT (right). The position of the cross-section image is shown as a green line in the topographical image. The pDTGBDT film displayed triangular-shaped aggregates (Fig. 6, left) that are aligned in the same direction. It is speculated that the aggregates formed under the moment of spin-coating.