Electronic Supplementary Material (ESI) for Polymer Chemistry.

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

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): δ = 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.

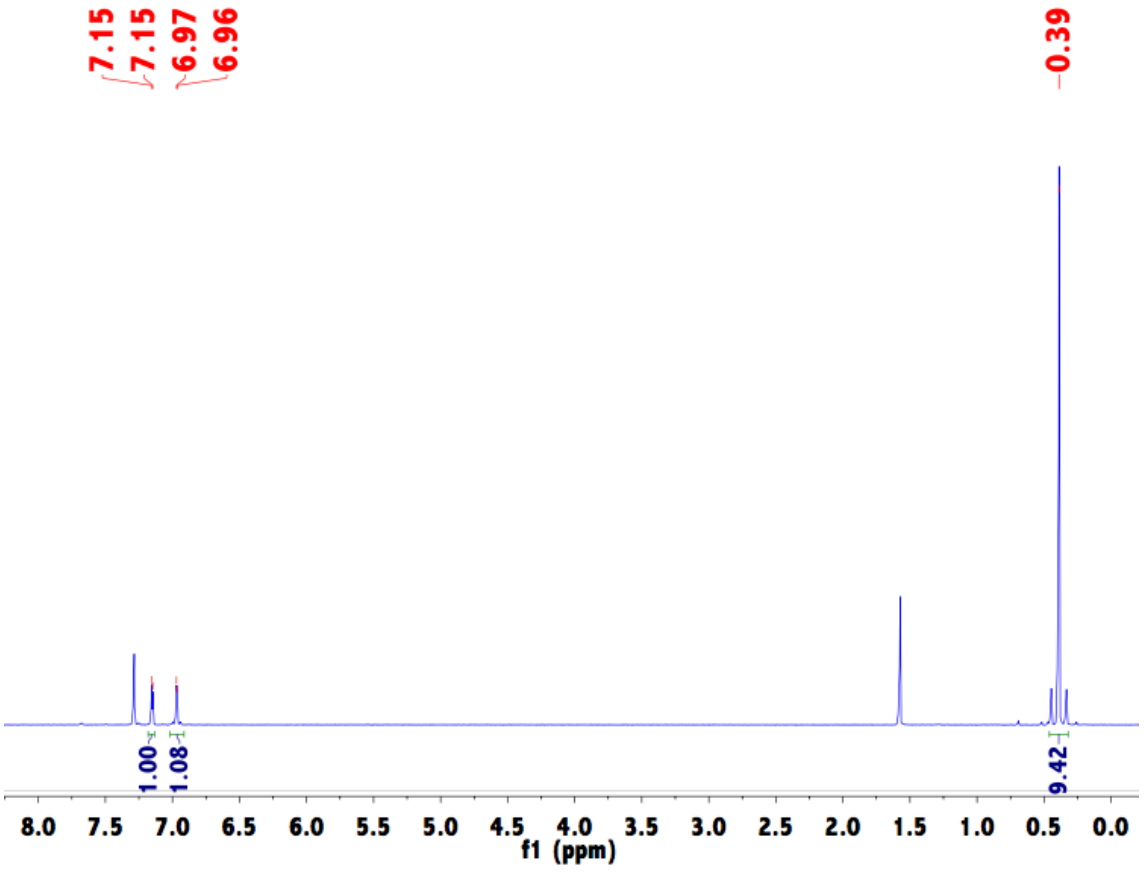

Figure S1 ^{1}H NMR spectrum of (5-bromothien-2-yl)trimethylstannane in $CDCl_3$ (499.9 MHz).

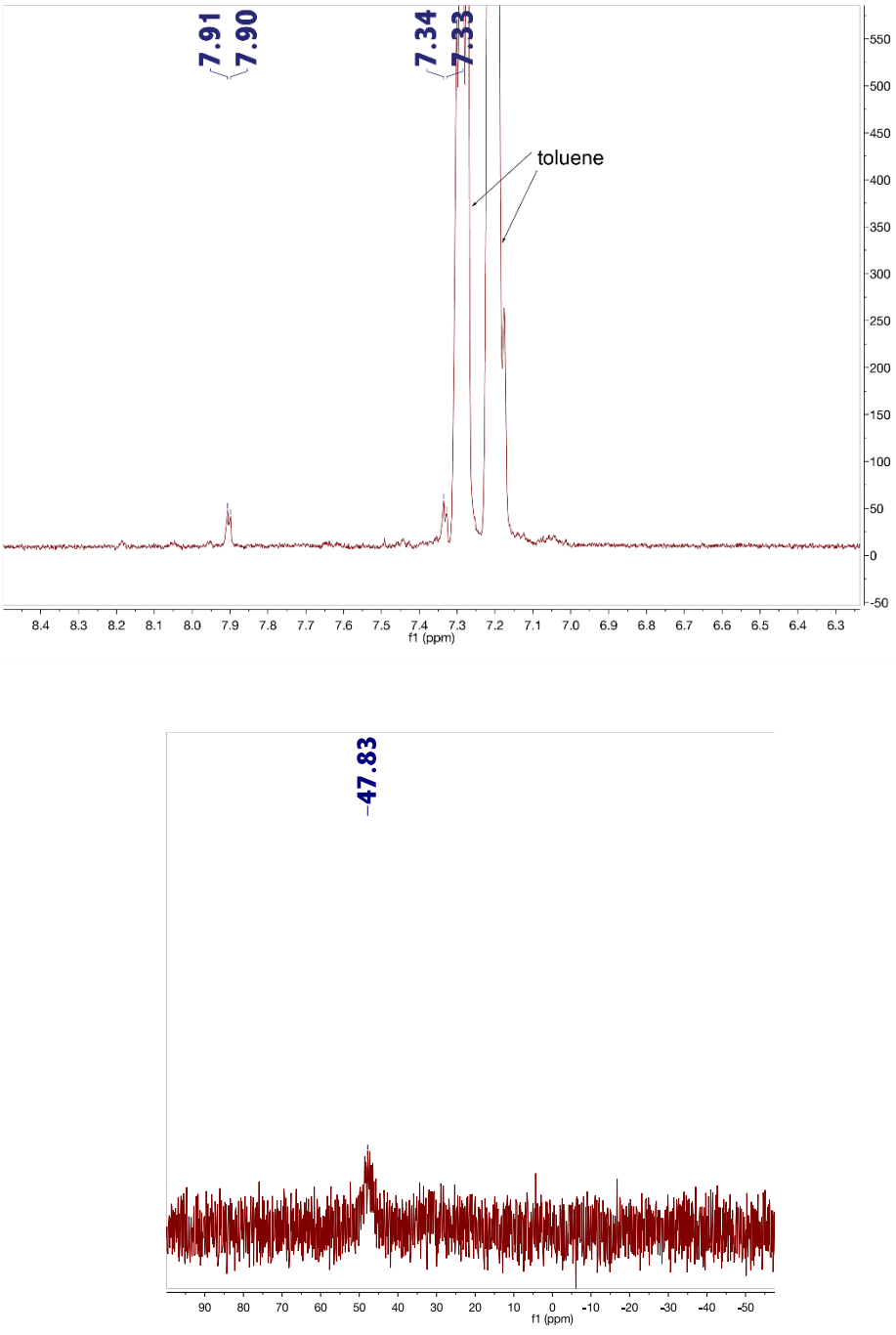

Figure S2 ^{1}H (top, 499.9 MHz) and ^{11}B NMR spectrum (bottom, 160.3 MHz) of toluene solution of crude bromobis[(5-bromo)2-thienyl]borane in $CDCl_3$.

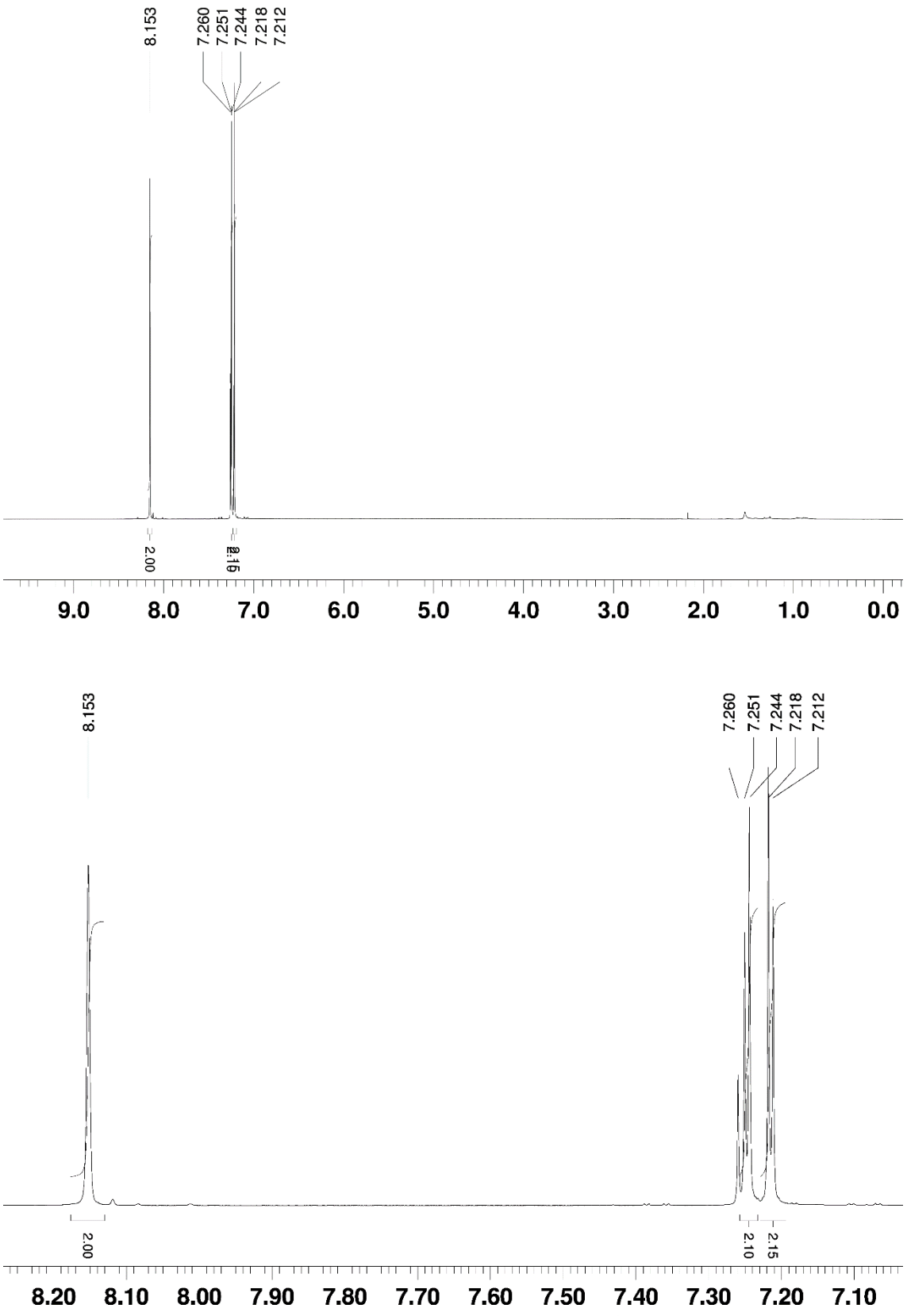

Figure S3 ^{1}H NMR spectrum of **FBDTBr2** in $CDCl_3$ (599.7 MHz).

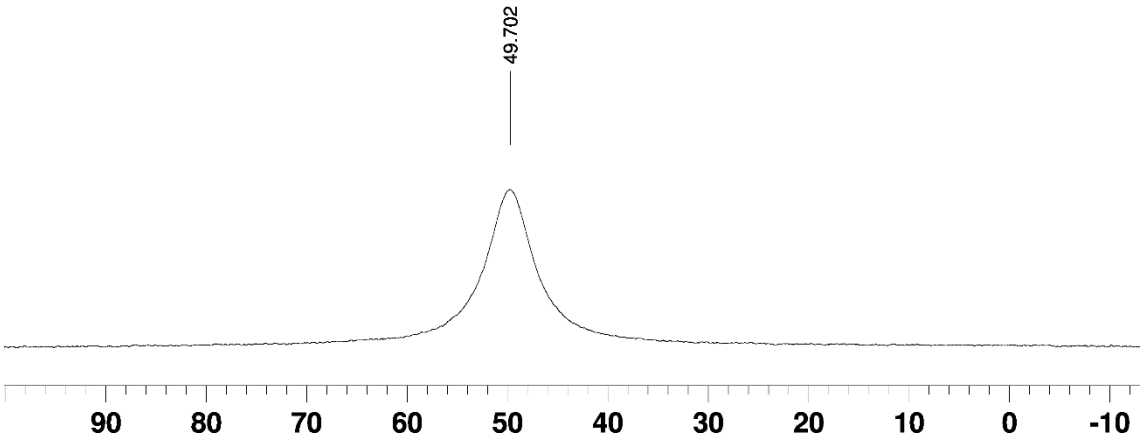

Figure S4 ^{11}B NMR spectrum of **FBDTBr2** in $CDCl_3$ (192.4 MHz).

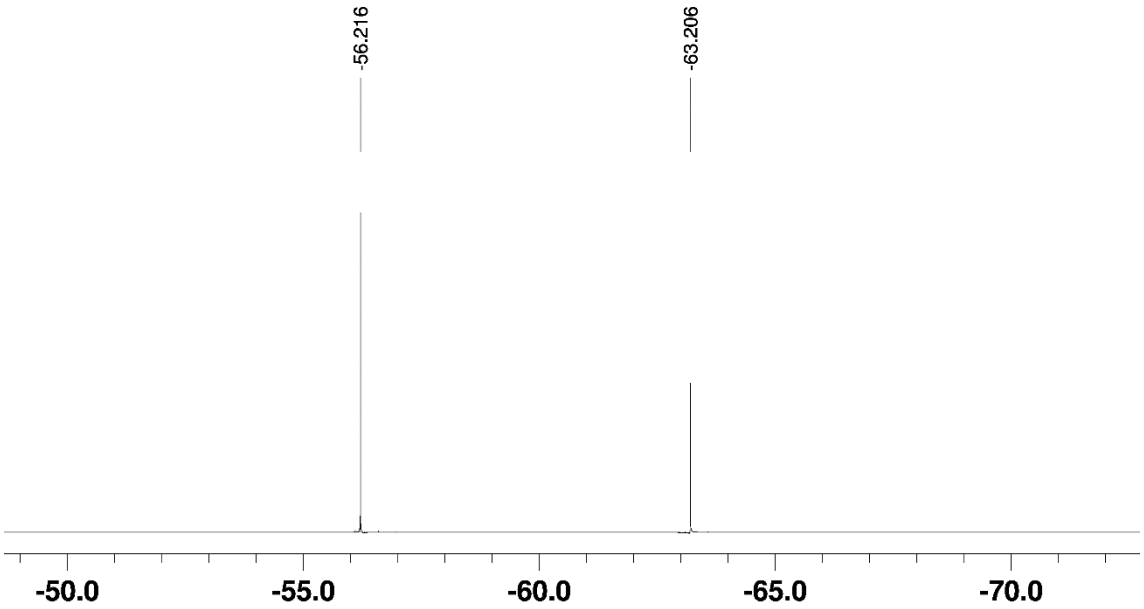

Figure S5 ^{19}F NMR spectrum of **FBDTBr2** in $CDCl_3$ (470.4 MHz).

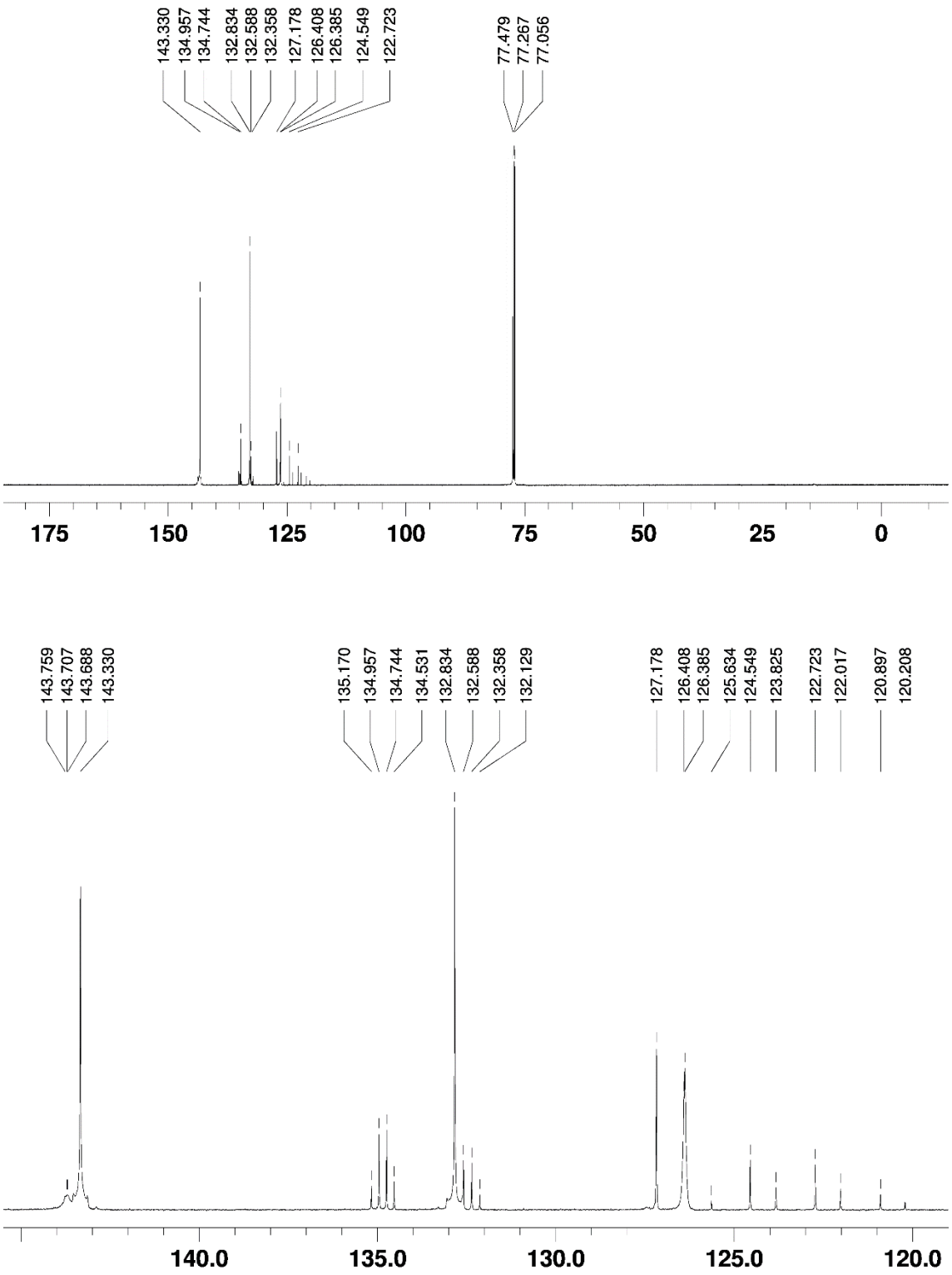

Figure S6 ^{13}C NMR spectrum of **FBDTBr2** in $CDCl_3$ (150.8 MHz).

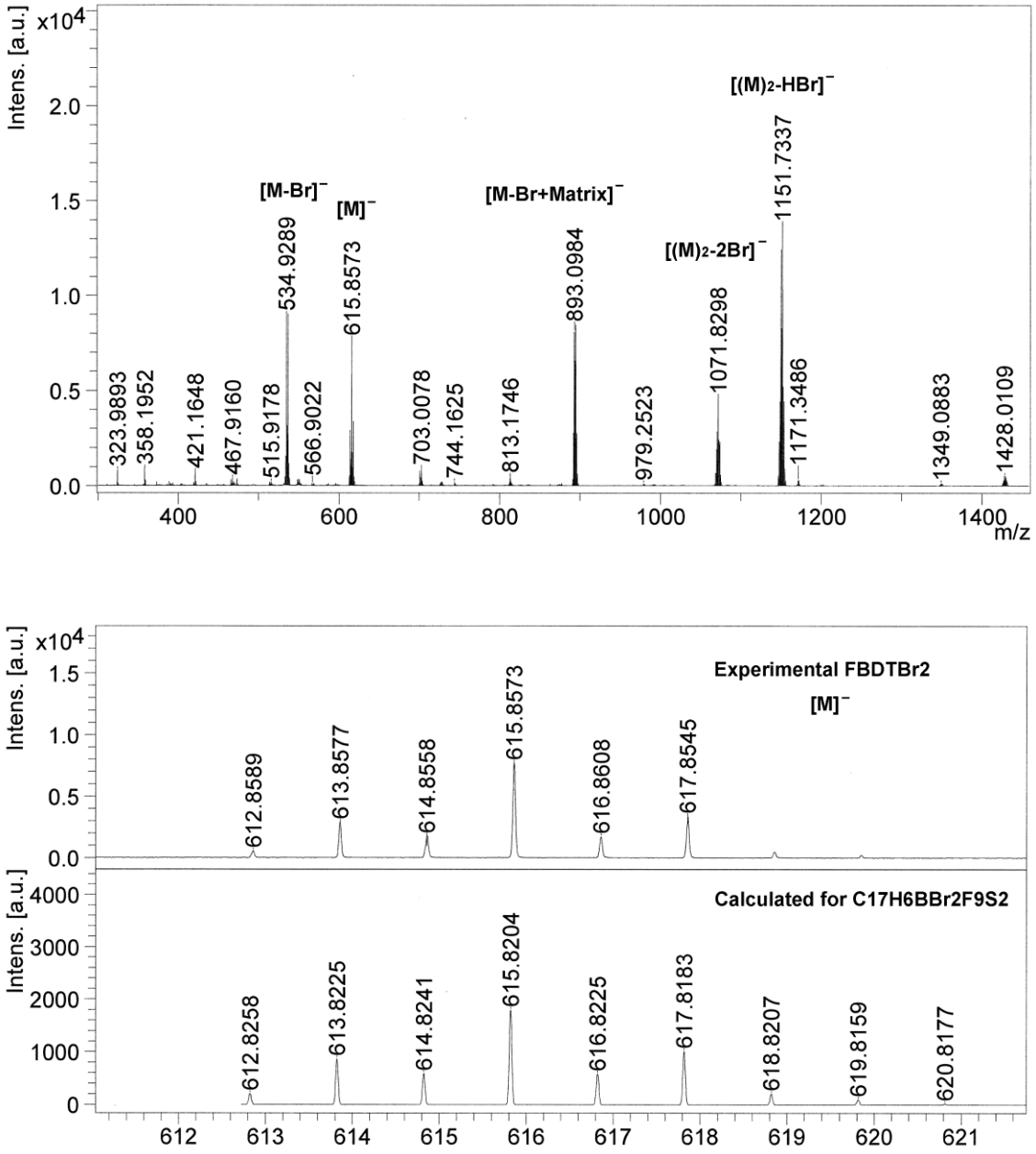

Figure S7 MALDI-TOF mass spectrum of **FBDTBr2** (Matrix: 1,1,4,4-Tetraphenyl-1,3-butadiene, negative mode).

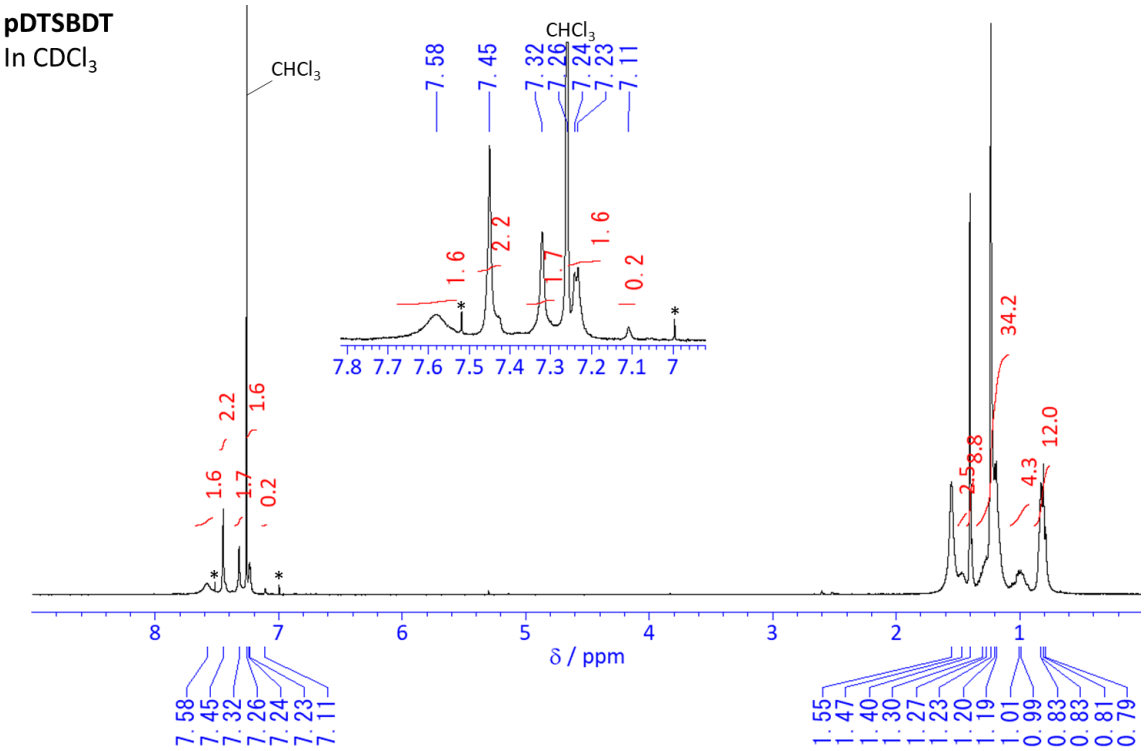

Figure S8 ^{1}H NMR spectrum of **pDTSBDT** (400 MHz).

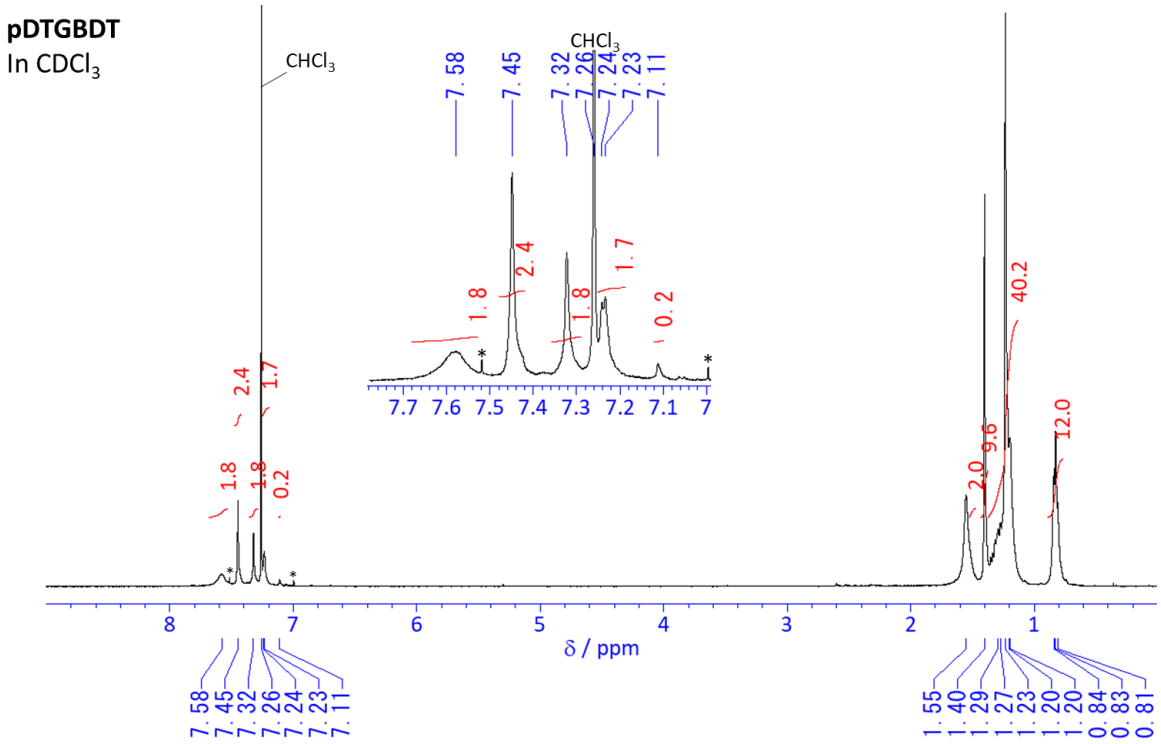

Figure S9 ^{1}H NMR spectrum of **pDTGBDT** (400 MHz).

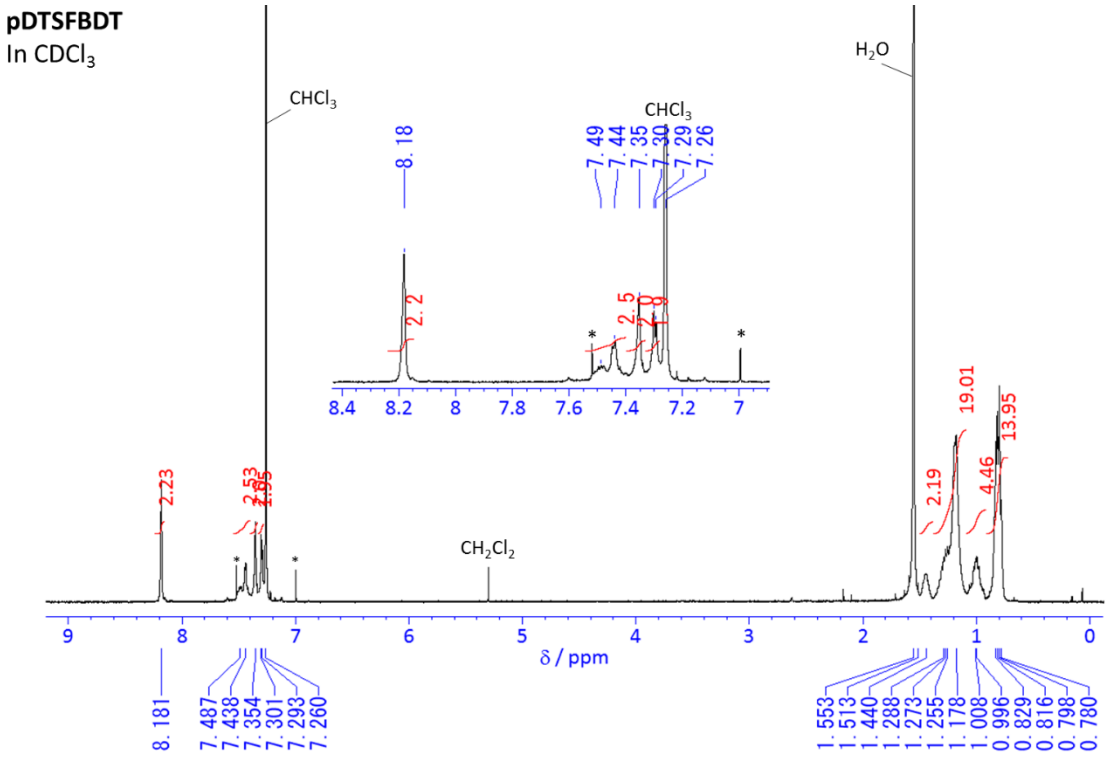

Figure S10 ^{1}H NMR spectrum of **pDTSFBDT** (400 MHz).

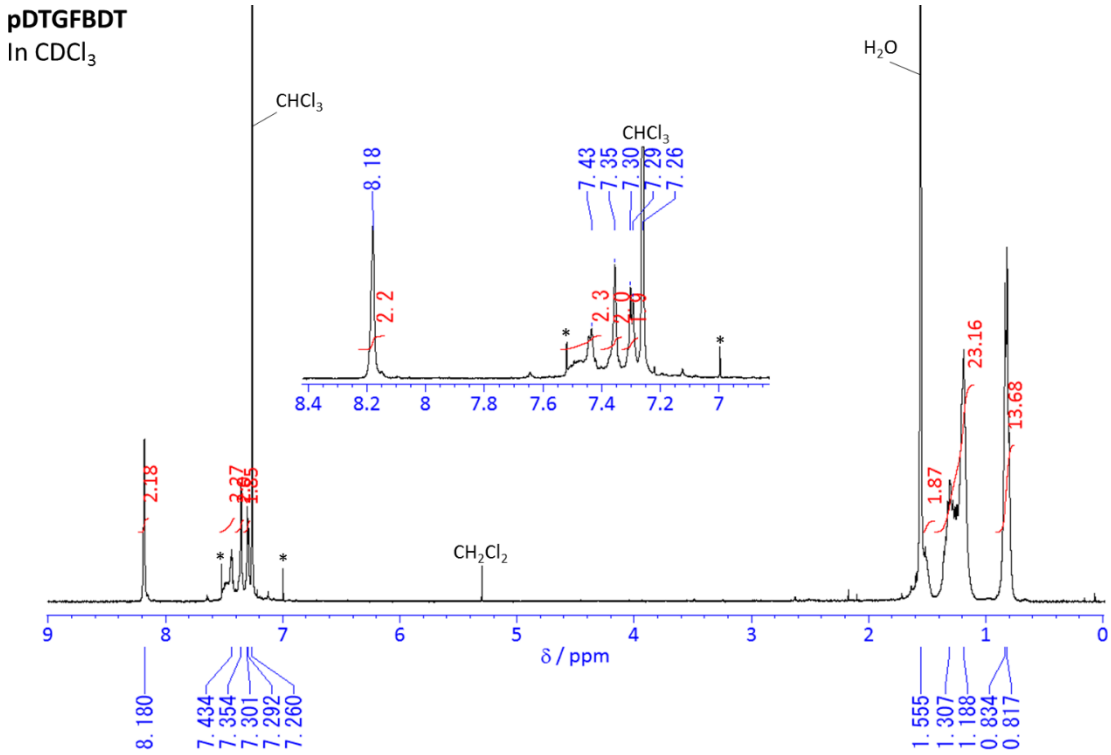

Figure S11 ^{1}H NMR spectrum of **pDTGFBDT** (400 MHz).

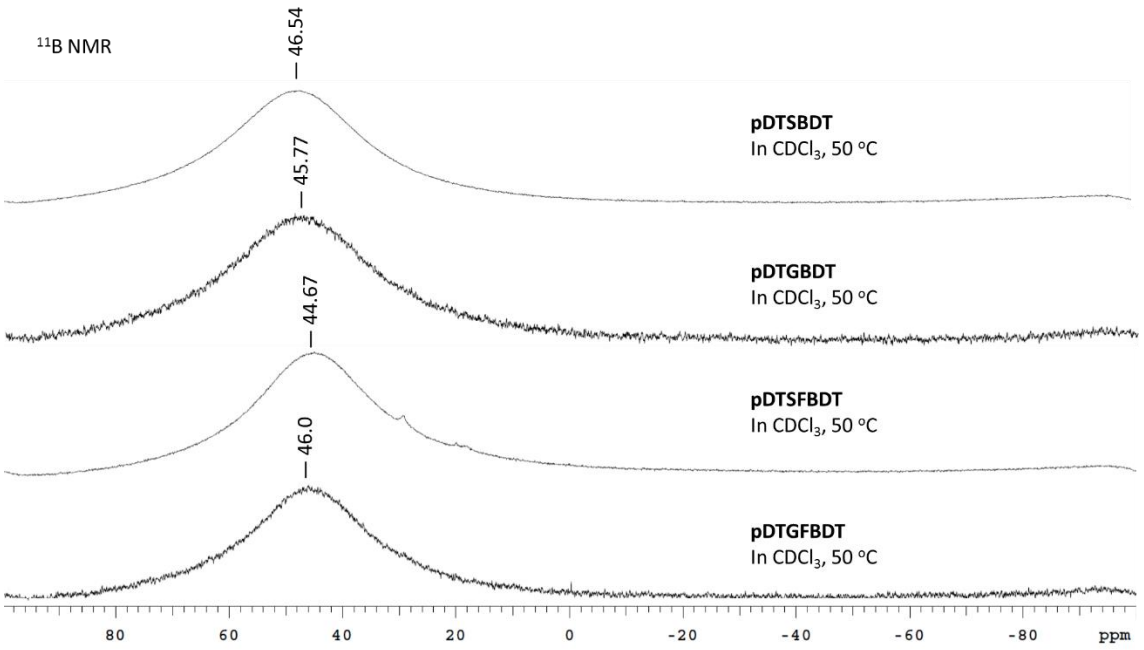

Figure S12 ^{11}B NMR spectra of the borane-dithienosilole/dithienogermole copolymers (160.4 MHz).

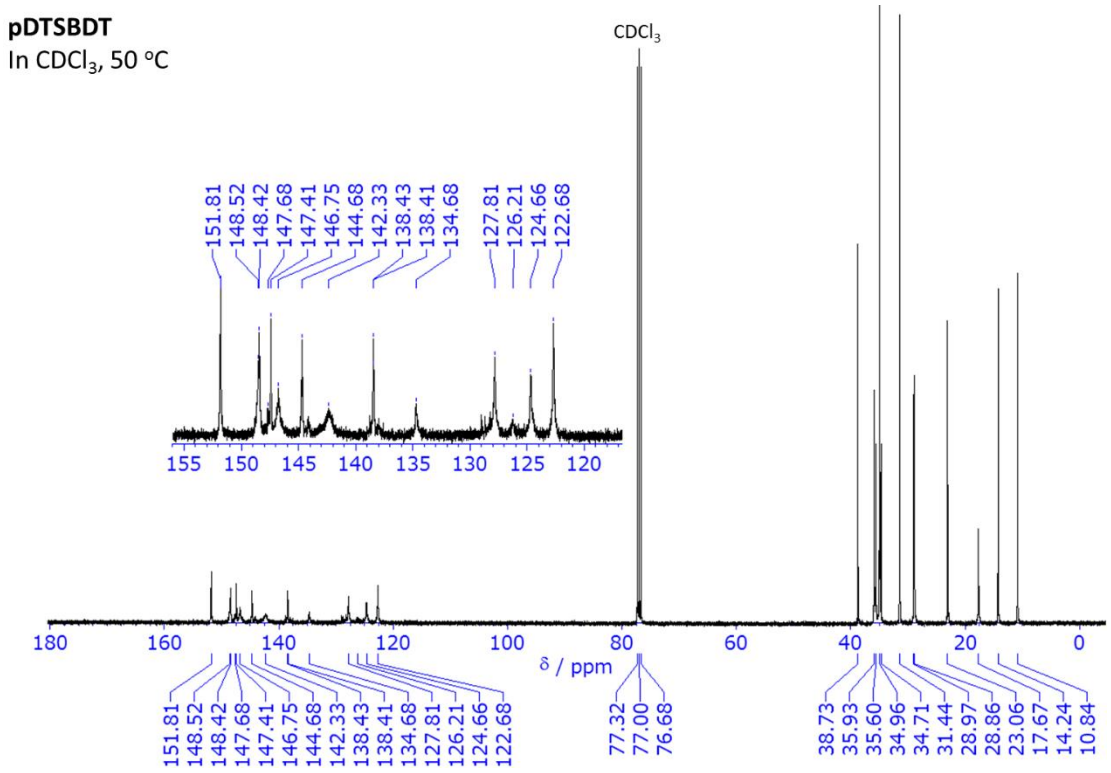

Figure S13 ^{13}C NMR spectrum of **pDTSBDT** (125.7 MHz).

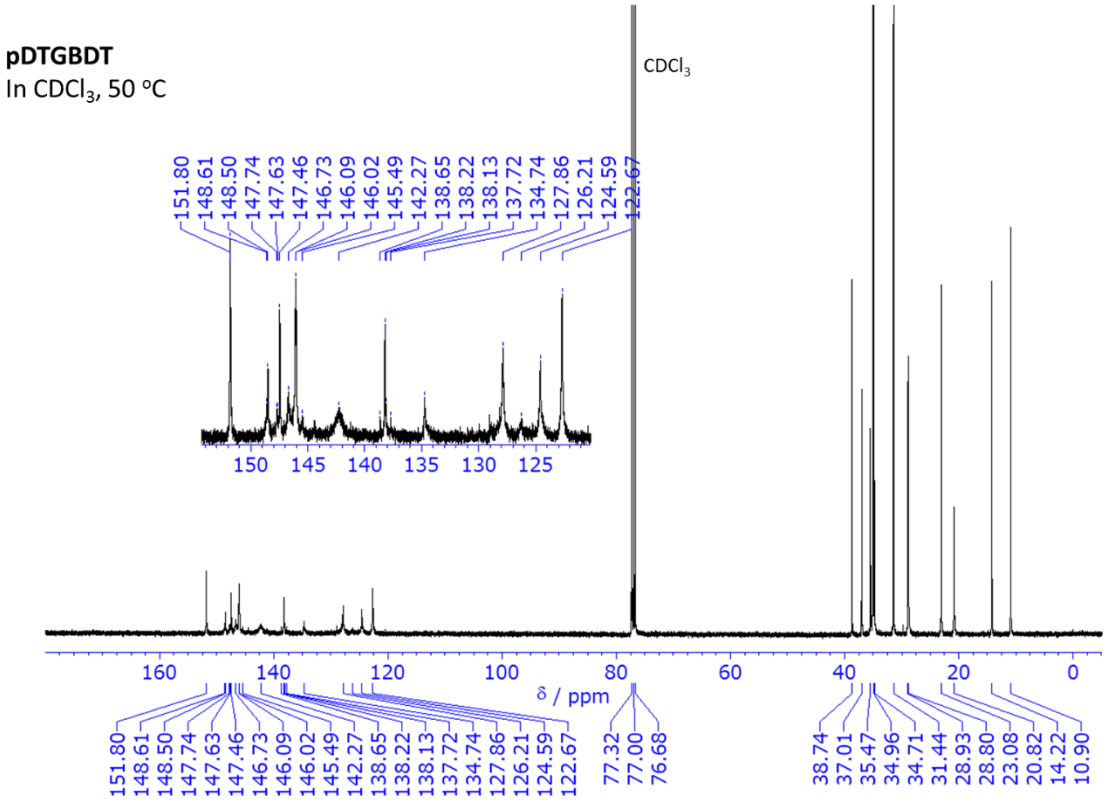

Figure S14 ^{13}C NMR spectrum of **pDTGBDT** (125.7 MHz).

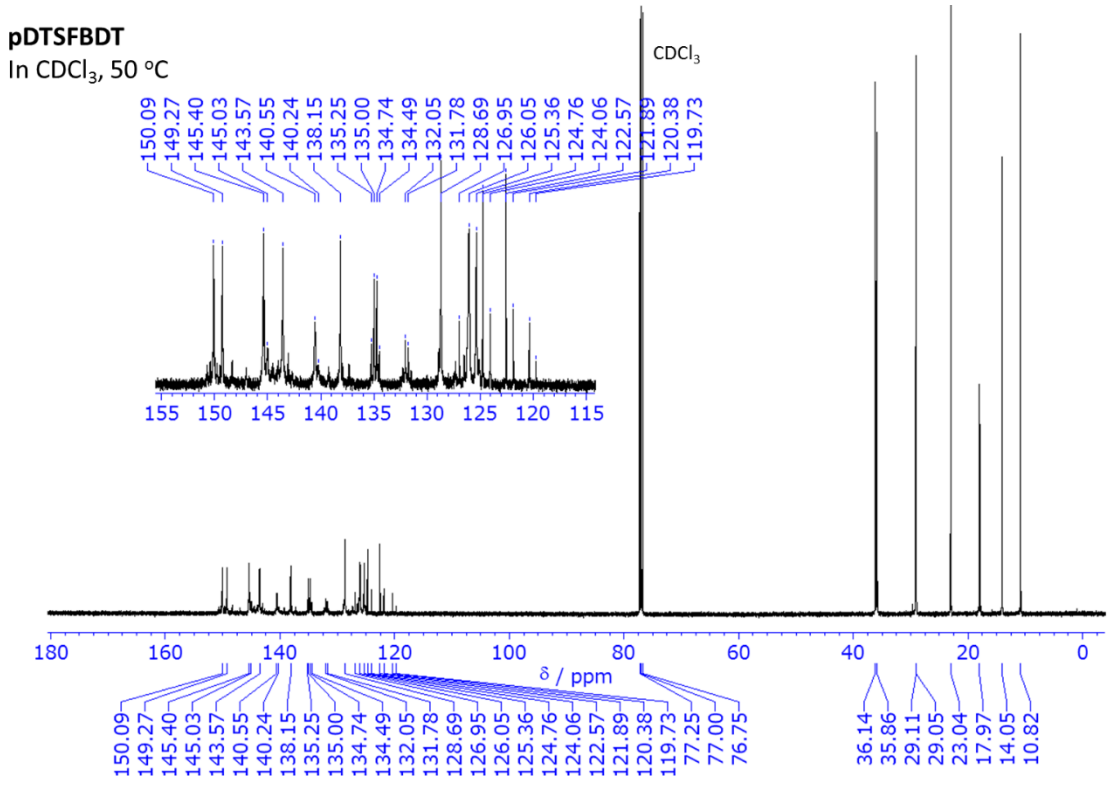

Figure S15 ^{13}C NMR spectrum of **pDTSFBDT** (125.7 MHz).

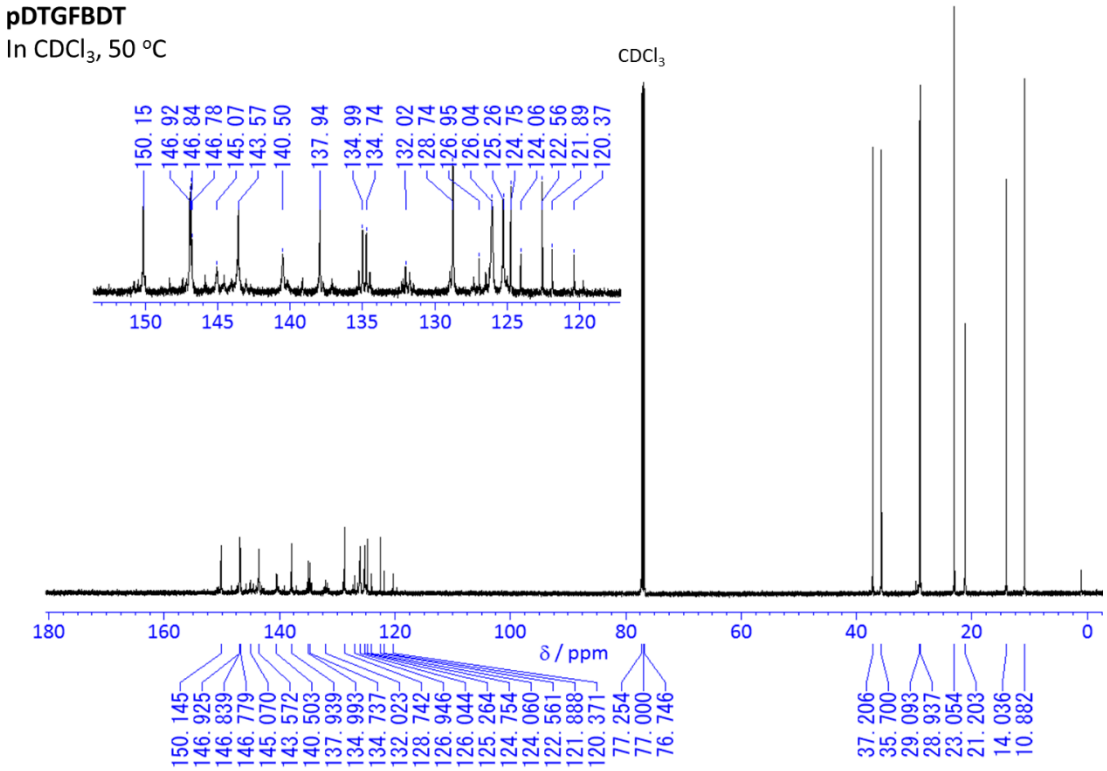

Figure S16 ^{13}C NMR spectrum of **pDTGFBDT** (125.7 MHz).

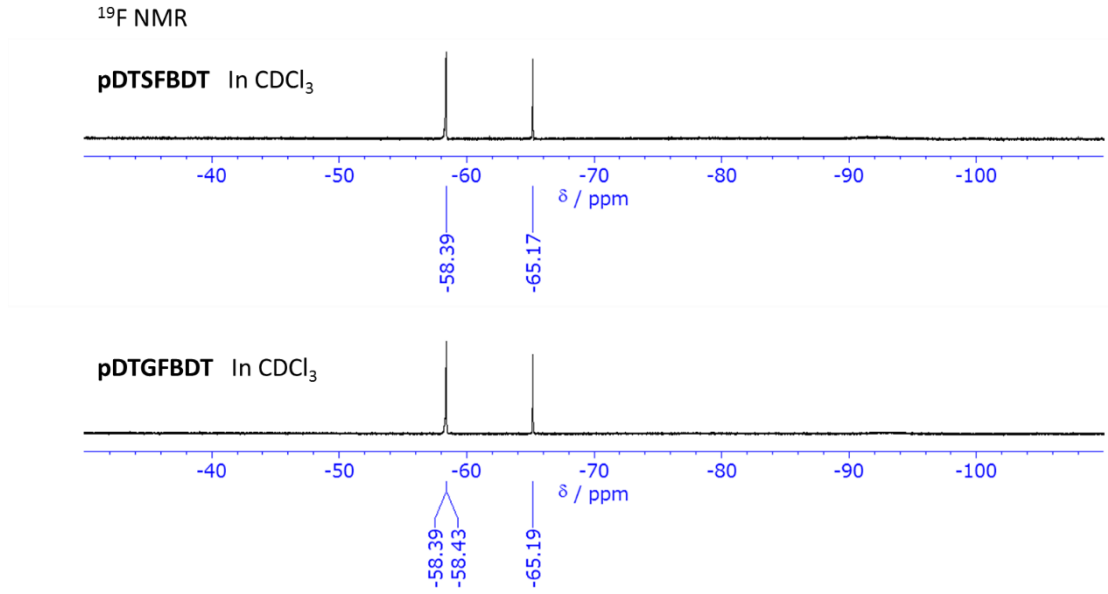

Figure S17 ^{19}F NMR spectra of **pDTSFBDT** and **pDTGFBDT** (470 4 MHz).

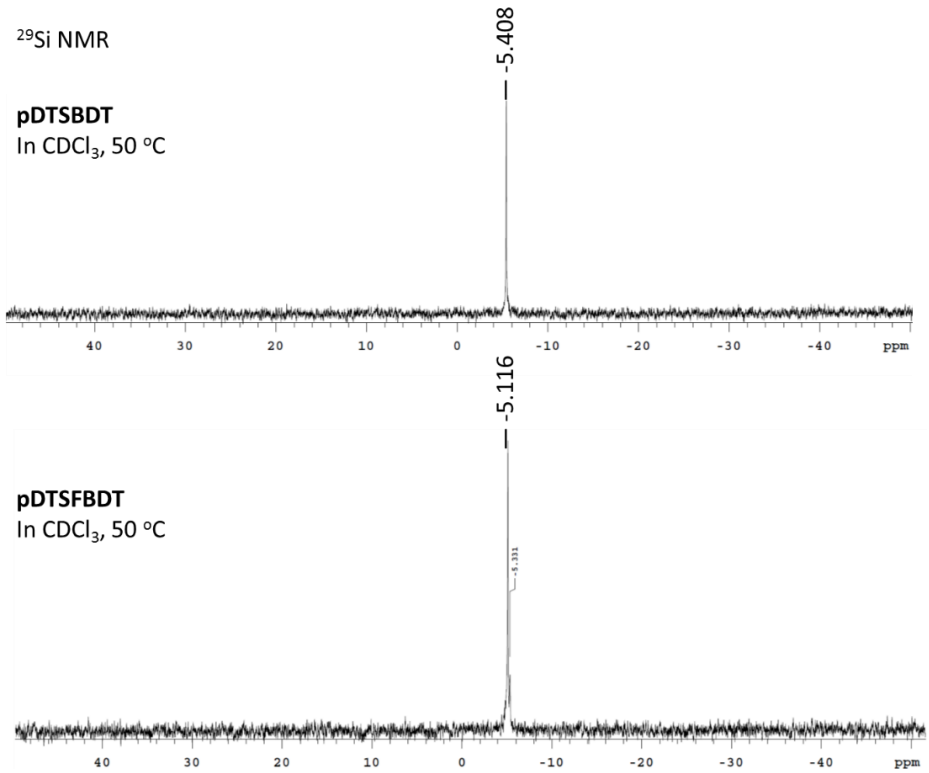

Figure S18 ^{29}Si NMR spectra of **pDTSBDT** and **pDTSFBDT** (99.3 MHz).

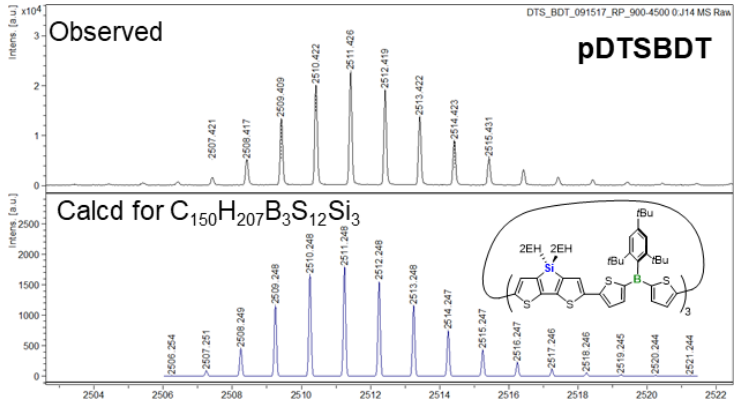

Figure S19 A high resolution mass pattern of **pDTSBDT**. (Matrix: trans-2[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile)

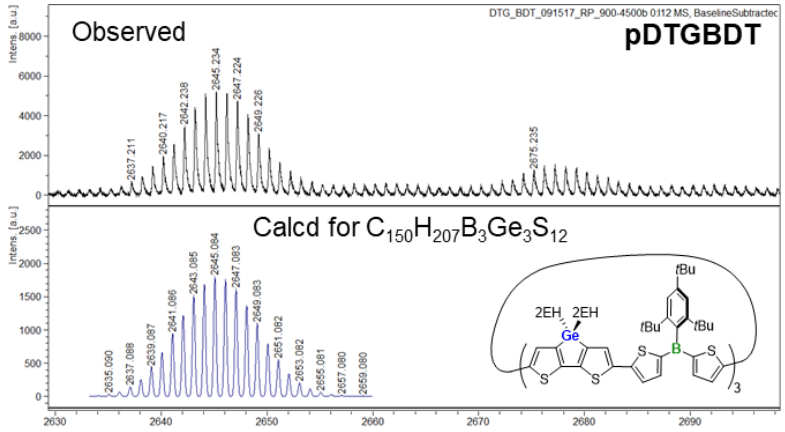

Figure S20 A high resolution mass pattern of **pDTGBDT**. (Matrix: trans-2[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile)

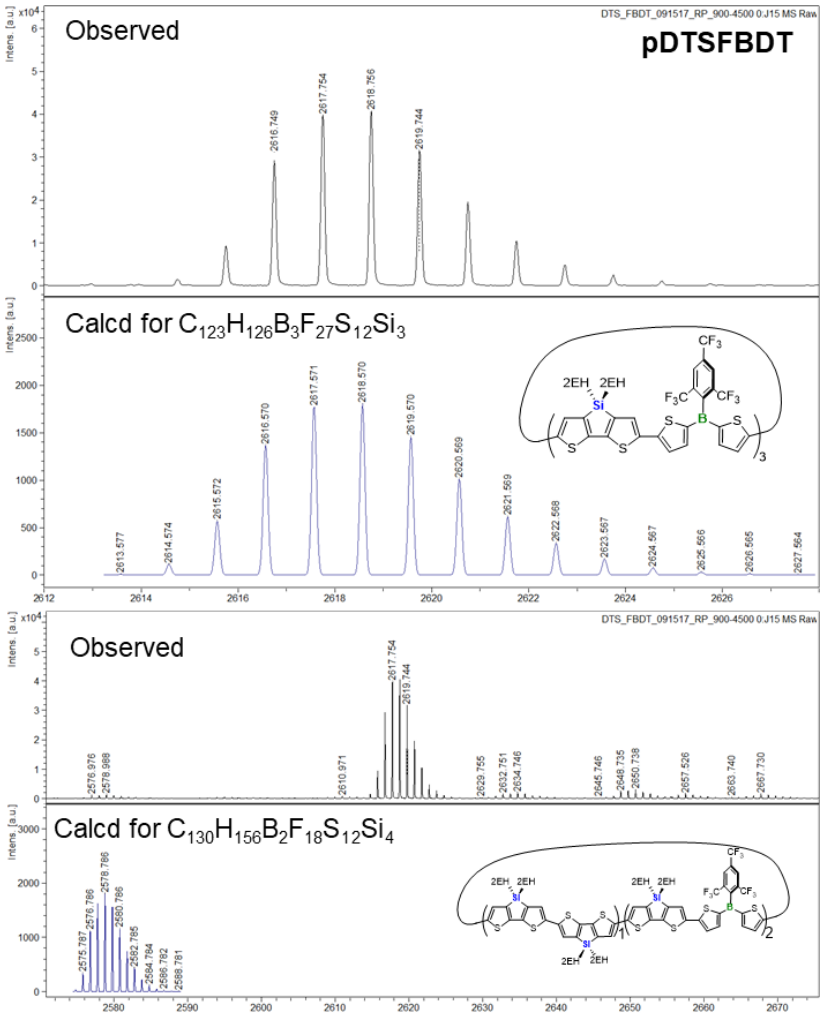

Figure S21 A high resolution mass pattern of **pDTSFBDT**. (Matrix: trans-2[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile)

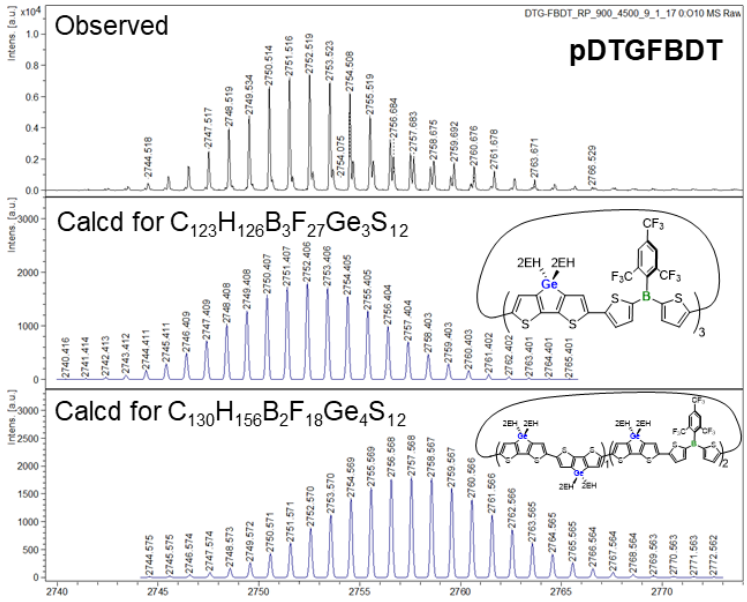

Figure S22 A high resolution mass pattern of **pDTGFBDT**. (Matrix: trans-2[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile)

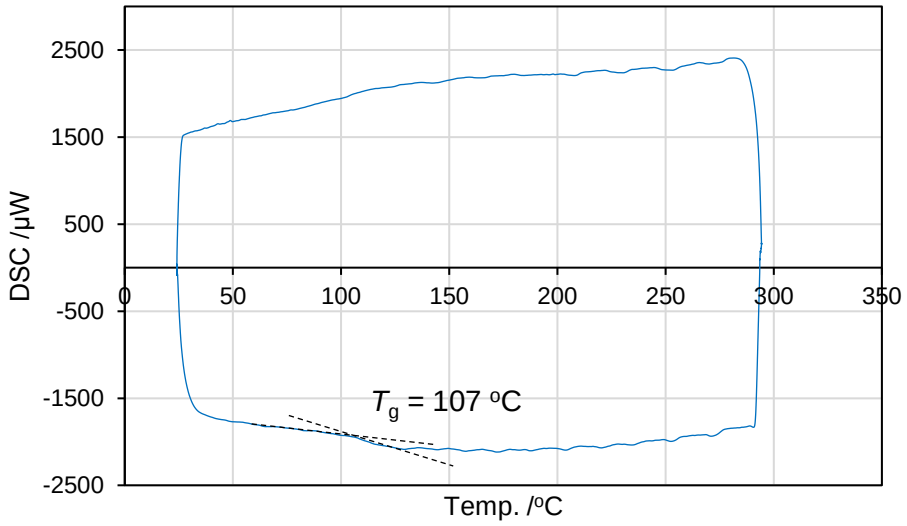

Figure S23 Second cycle of DSC for **pDTSFBDT**.

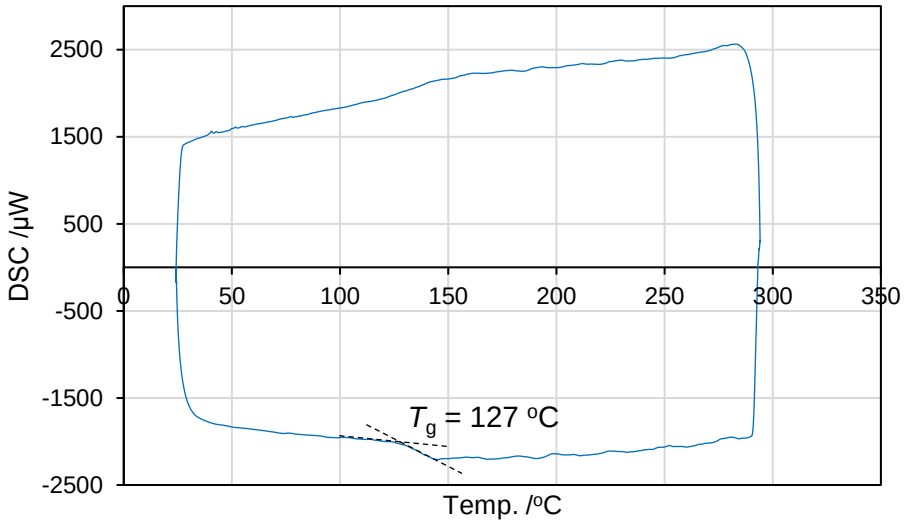

Figure S24 Second cycle of DSC for **pDTGFBDT**.

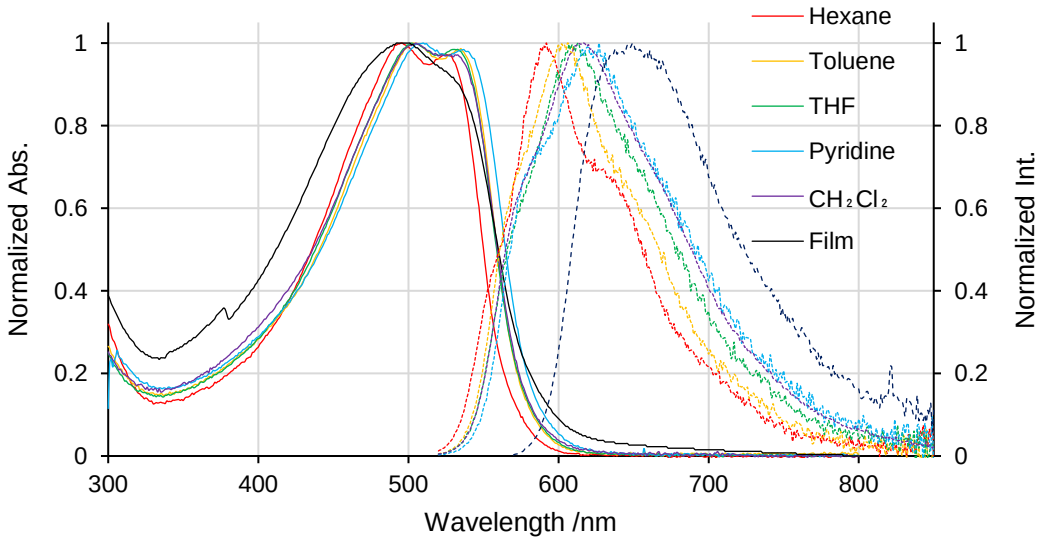

Figure S25 Absorption (solid lines) and fluorescence (dashed lines) spectra of **pDTSBDT** in solution and as film.

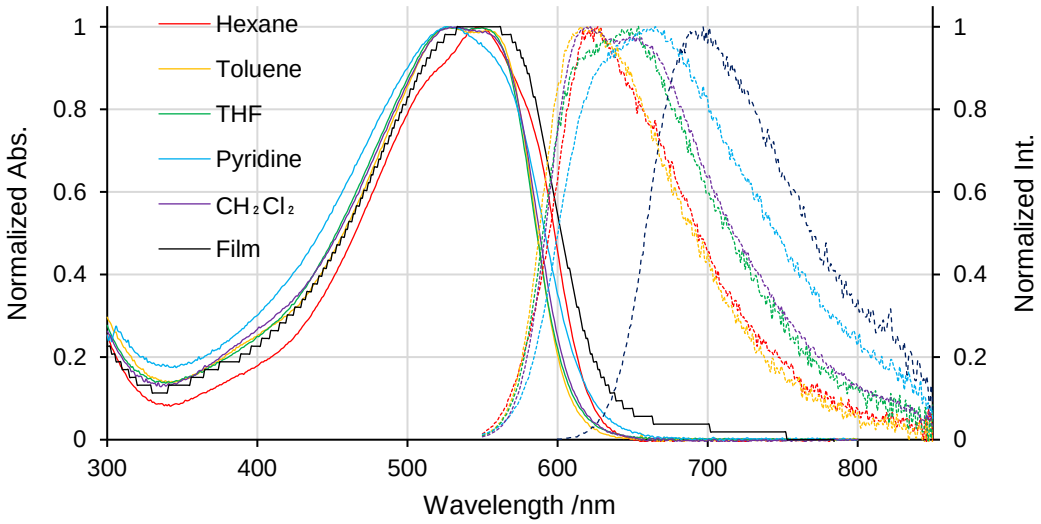

Figure S26 Absorption (solid lines) and fluorescence (dashed lines) spectra of **pDTSFBDT** in solution and as film.

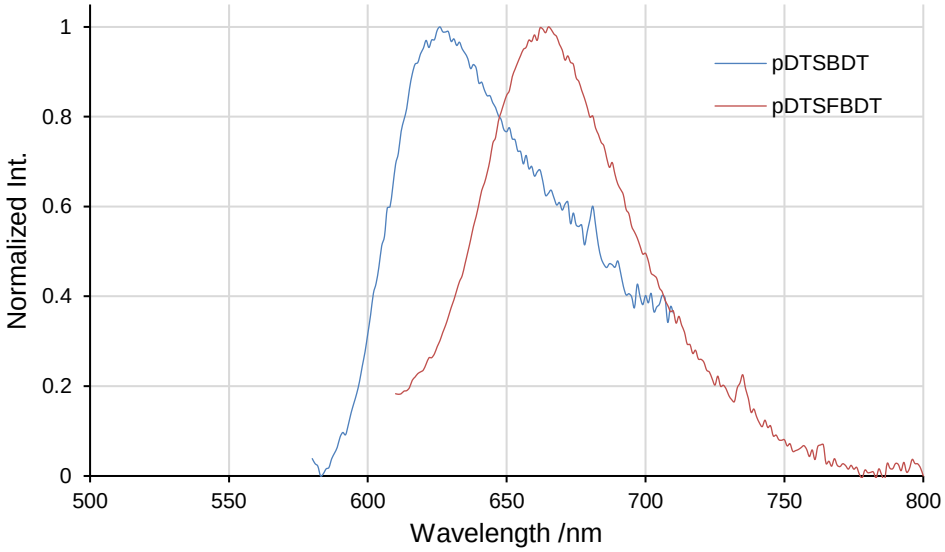

Figure S27 Fluorescence spectra of 0.5wt% PMMA films of **pDTSBDT** and **pDTSFBDT**.

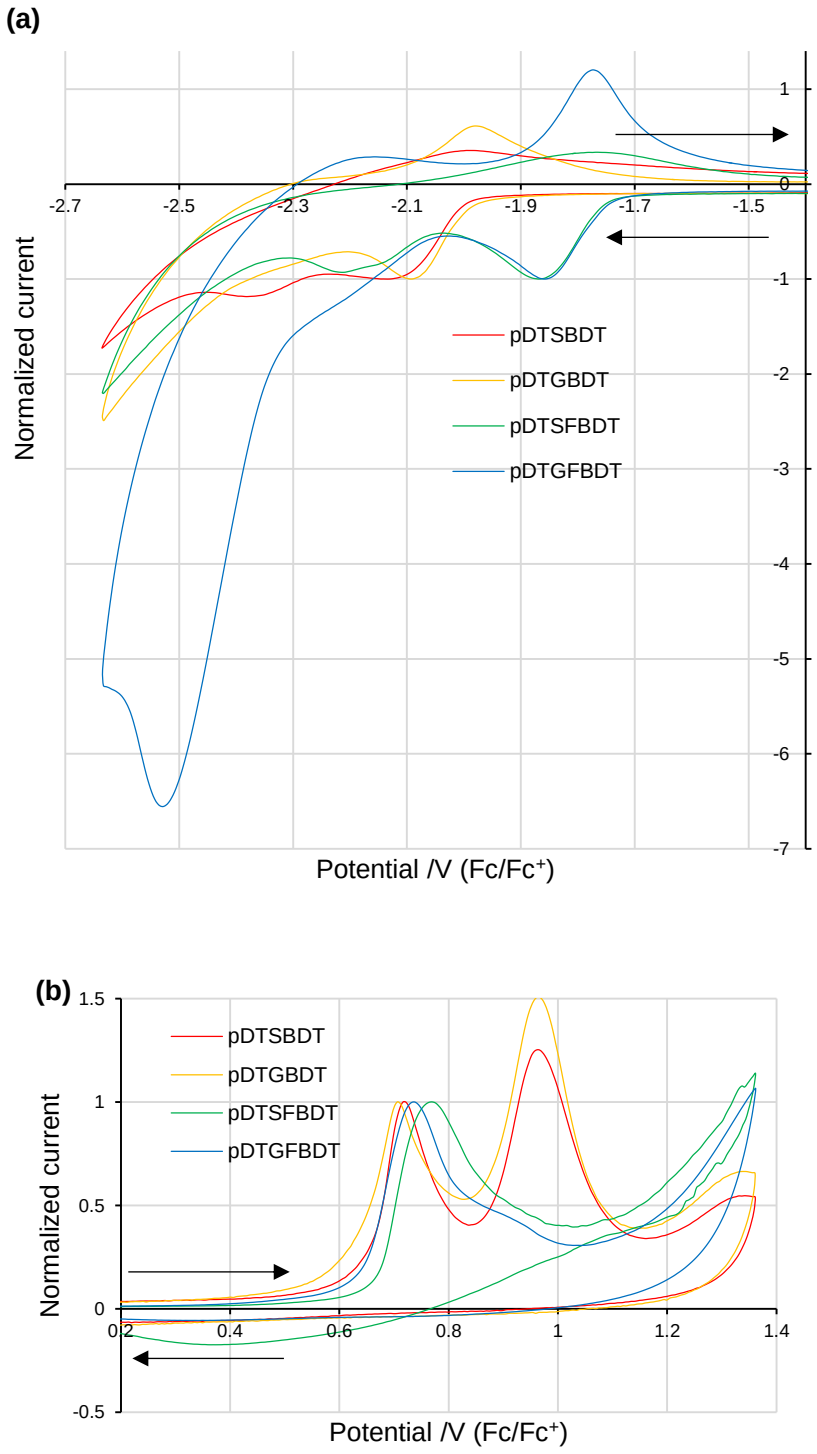

Figure S28 Full cyclic voltammetry data of (a) reductive and (b) oxidative waves of the borane-dithienosilole/dithienogermole copolymers.

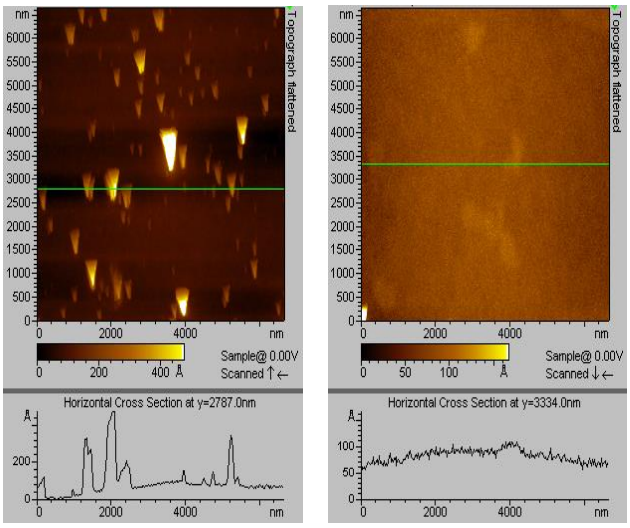

Figure S29 AFM topographical (top) and cross-section (bottom) images of spin-coated films of **pDTGBDT** (left) and **pDTGFBDT** (right). The position of the cross-section image is shown as a green line in the topographical image. The **pDTGBDT** film displayed triangular-shaped aggregates (Fig. 6, left) that are aligned in the same direction. It is speculated that the aggregates formed under the moment of spin-coating.