Experimental Results

Supplementary Material for:

Cyclopentadithiophene polymers synthesised via Suzuki-Miyaura polymerisation of MIDA boronate esters

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Contents:

General Considerations

Experimental procedures. Unless otherwise explicitly stated, all manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 and H_2O levels below 0.5 ppm). Polymerisations were performed in a Radley carousel connected to a Schlenk line. Glassware was dried overnight in a hot oven and heated under vacuum before use. Tetrahydrofuran (THF), CH_2Cl_2, MeCN, CD_3CN, and 2,6-di-*tert*-butylpyridine (tBu_2Py) were distilled from K, or CaH_2 under N_2 gas atmosphere and stored over molecular sieves. All solvents were freeze-pump-thaw degassed prior to use. 2,6-dichloropyridine (Cl_2Py), and K_3PO_4, were dried overnight under reduced pressure (1×10^{-2} mbar at 23 °C), finely ground, and stored under inert atmosphere. Deionised water was thoroughly degassed by a continuous bubbling flow of N_2 gas for at least half an hour. *N*-Methyliminodiacetic disilyl ester (TMS_2-MIDA),[1] $[(Cl_2Py)\cdot BCl_2][AlCl_4]$ borocation,[2] were prepared according to literature procedures. 2-bromo-4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene, **3**, and 4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene, **4**, were synthesised by J. Esquivel-Guzman (OMIC, UoM) according to literature procedures[3] and used as received. Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) were purchased from Acros Organics (98%), and Sigma-Aldrich (98%), respectively. Importantly, it has been reported that commercial samples of $Pd_2(dba)_3$ may contain up to 40% of Pd nanoparticles,[4] therefore all reactions throughout this and previously reported works[5,6] used the same batch of $Pd_2(dba)_3$ in order to minimise variations in the contents of any possible impurities or unknown species between experiments. Thus both palladium precursor and ligand were immediately stored in a glovebox under inert atmosphere after purchasing, and used without further purification. All other materials were purchased from commercial vendors and used as received. Room temperature (RT) refers to 23 ºC (± 2 °C).

Analytical procedures: NMR spectroscopy experiments were performed using Bruker AV-400 (^{1}H, 400 MHz, ^{13}C, 100.6 MHz; ^{11}B, 128.4 MHz; ^{27}Al, 104.3 MHz; or Bruker AV-500 (^{1}H, 500 MHz, ^{13}C, 125.8 MHz; ^{11}B, 160.5 MHz; ^{27}Al, 130.3 MHz; spectrometers. Chemical shift values for ^{1}H and ^{13}C are reported in ppm relative to residual protio solvents (*e.g.*, $CHCl_3$ in $CDCl_3$ $\delta_H = 7.26$) or TMS ($\delta_H = 0.00$), and the central peak of $CDCl_3$ triplet ($\delta_C = 77.0$)) as internal standards, respectively. All other nuclei NMR spectra were referenced to external standards: ^{11}B, BF_3:Et_2O; ^{27}Al, $Al(NO_3)_3$ in D_2O $[Al(D_2O)_6]^{3+}$. In reactions where *in situ* analyses (*e.g.*, borylations or polymerisations) were performed the NMR spectra were recorded in protio solvents, employing a capillary filled with wet d_6-DMSO insert as a locking solvent. All coupling constants (*J*) are reported in Hz. Multiplicity of signals are indicated as "s", "d", "t", "m" for singlet, doublet, triplet, and multiplet, respectively. Unless otherwise stated all NMR spectra are recorded at 293 K. Broad

features in the ^{11}B and ^{27}Al NMR spectra are due to boron materials used in the glassware, and the spectrometer probe, respectively, whilst carbon atoms directly bonded to boron are not observed in the $^{13}C\{^{1}H\}$ NMR spectra due to quadrupolar relaxation effects.

Gel permeation chromatography (GPC) analyses were performed in THF solution (~1 mg mL^{-1}) at 35 °C using a Viscotex GPCmax VE2001 solvent/sample module with 2 × PL gel 10 μm mixed-B and a PL gel 500 A column, and equipped with a Viscotex VE3580 RI detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Samples were filtered through an Acrodisc CR 13 mm syringe filter with 0.45 μm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 100 μL, flow rate of 1 mL min^{-1}. Results were analysed using *n*-dodecane as internal marker, and Malvern OmniSEC 4.7 software, and processed using OriginLab Pro 8.5 software.

HR-MS analyses were performed by the Mass Spectrometry Service, School of Chemistry, University of Manchester. Elemental analyses were performed by the Micro Analytical Laboratory, School of Chemistry, University of Manchester.

Synthetic procedures

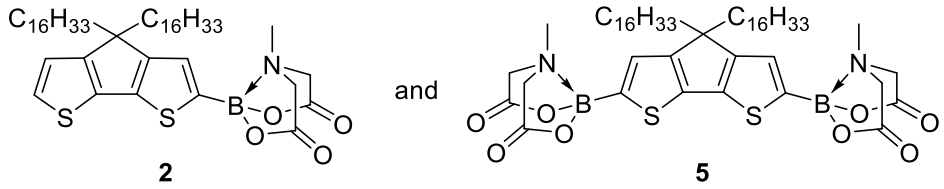
Monomer synthesis An oven-dried Schlenk ampoule fitted with a J. Young's tap containing a stirrer bar was heated under reduced pressure and back filled with N_2. The ampoule was charged with Cl_2Py (2.1 equiv) and $AlCl_3$ (2.0 equiv). Then, anhydrous CH_2Cl_2 was added and the mixture was stirred until the solids completely dissolved. This was followed by addition of BCl_3 (2.1 equiv, 1.0 M solution in CH_2Cl_2), and then the respective cyclopentadithiophene (1.0 equiv) was added, keeping the temperature at 18-25 °C. After stirring at ambient temperature for 1 h, *t*Bu_2Py (2.1 equiv) was injected into the solution. The reaction mixture was then immediately added *via* cannula to TMS_2-MIDA (2.1 equiv) in anhydrous MeCN (pre-charged in a Schlenk ampoule fitted with a J. Young's tap), keeping the temperature at 18-25 °C, and stirring was continued at ambient temperature for 14 h. After the MIDA esterification was accomplished the reaction mixture was subjected to the following work up procedure. The crude reaction mixture was opened to the atmosphere (all operations carried out under air, using bench grade solvents from this point) and concentrated under reduced pressure at ambient temperature to remove TMSCl and solvents. The crude product was redissolved in CH_2Cl_2 (100 mL), washed with water (3 × 100 mL) then brine (100 mL). The organic phase was stirred with anhydrous $MgSO_4$ (~5 g) at ambient temperature for 2 h, it was then filtered, concentrated, and Celite added (~0.1 g), and then the solvent removed under reduced pressure at ambient temperature until dryness. Further purification was accomplished by applying the solids onto a sintered glass frit (Ø 74 mm) pre-packed with ~30 cm^3 of silica gel 60 (Merck 15-40μ fraction) and subjected to DCVC ("Dry Column Vacuum Chromatography")[7] eluting with DCM (dichloromethane)/PE (petroleum ether, 40/60 fraction) 0 : 1 gradient, then EA (ethyl acetate)/DCM (dichloromethane), 1 : 1 gradient. Evaporation of the solvents from EA/DCM fractions and drying under reduced pressure (1×10^{-2} mbar), afforded the desired pure products.

Bromination Procedure. *N*-bromosuccinimide (1.05 mmol) was added to a stirred solution of thienyl MIDA boronate (1.0 mmol) in anhydrous ethyl acetate, covered with foil, and stirred in the dark for 24 h at ambient temperature under inert atmosphere. Subsequently, the system was open to the atmosphere (all further operations carried out under air, using bench grade solvents), the solvent eliminated under reduced pressure, and the crude reaction mixture was redissolved in toluene (50 mL), washed with water (3 × 50 mL) then brine (50 mL). The organic phase was stirred with anhydrous $MgSO_4$ (~5 g) at ambient temperature for 0.5 h. Filtration through a plug of Celite and removal of the solvent under reduced pressure (1×10^{-2} mbar) at ambient temperature afforded the desired pure product.

Polymer synthesis. An oven-dried Radley's carousel tube containing a stirrer bar was charged under inert atmosphere with **1** (1.0 equiv), and K_3PO_4 (3.0 equiv). Dry and degassed THF was added and the reaction mixture was stirred until **1** completely dissolved, [**1**] = 6.1×10^{-2} M. Then, degassed H_2O was added (40.0 equiv), and the system was heated to the reaction temperature (55 °C) for *ca*. 5 min. Subsequently, a freshly prepared palladium precatalyst in THF solution (5 mol%, *vide infra*) was injected and the polymerisation was carried out with vigorous stirring (1000 rpm) and under a constant flow of N_2 gas. Aliquots of the reaction mixture were taken out of the solution at different times and precipitated into vigorously stirred MeCN and NMR spectra recorded. At the end of the reaction, the remaining crude mixture was quenched by precipitating it into an excess (fifty-fold by volume) of MeCN. The filtered solution was analysed by NMR spectroscopy. The collected polymeric solid material was dried overnight at ambient temperature under reduced pressure (1×10^{-2} mbar) for further analyses. Sequential MeOH, *n*-hexane and chloroform fractions were collected by Soxhlet extraction, for 14 h at each stage.

Procedure for preparation of the palladium precatalyst. An oven-dried J. Young's NMR tube was charged under inert atmosphere with the phosphine ligand (2:1 mol of L/Pd) and palladium precursor (*e.g.*, 5 mol% of **1**). Dry and degassed THF (1.0 mL) was added to the mixture, and the tube was rotated at room temperature for 1 h or until complete homogenisation.

4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene-2-yl-MIDA-boronate, **2**



According to **Monomer synthesis**: 4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene **4** (835 mg, 1.33 mmol) reacted with BCl_3 (2.8 mL of 1.0 M in CH_2Cl_2, 2.80 mmol), Cl_2Py (414 mg, 2.80 mmol), and $AlCl_3$ (355 mg, 2.66 mmol), in CH_2Cl_2 (10 mL). Subsequent addition of *t*Bu_2Py (535 mg, 2.80 mmol), followed by esterification with TMS_2-MIDA (815 mg, 2.80 mmol) in MeCN (12 mL) afforded after DCVC, 260 mg (25 %) of **2** as a pure pale yellow solid in the second fractions set. In the subsequent fractions set, 400 mg (32%) of the difunctionalised MIDA boronate ester **5** was also isolated as a pure colourless solid.

2:

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.21 (d, $^3J_{(H,H)}$ = 4.77 Hz, 1 H), 7.13 (s, 1 H), 6.96 (d, $^3J_{(H,H)}$ = 5.02 Hz, 1 H), 3.93 (d, $^2J_{(H,H)}$ = 16.56 Hz, 2 H, CH_2), 3.84 (d, $^2J_{(H,H)}$ = 16.56 Hz, 2 H, CH_2), 2.66 (s, 3 H, *N*CH_3), 1.84 (m, 4 H, 2 × CH_2), 1.11-1.25 (m, 56 H, 28 × CH_2), 0.87 (t, $^3J_{(H,H)}$ = 6.78 Hz, 6 H, 2 × CH_3)

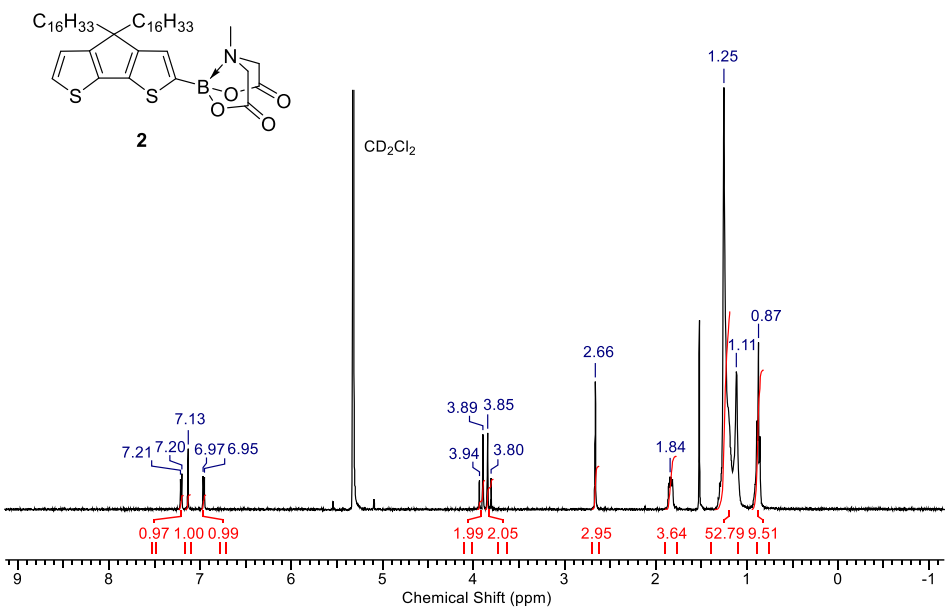
^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 167.2 (C_{quat}), 160.9, 159.7, 136.7, 128.3, 125.9, 122.4, 62.1, 47.9, 38.3, 32.5, 30.6, 30.2, 30.0, 29.9, 25.1, 23.3, 14.4 (2 CH_3)

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ 11.4 (s)

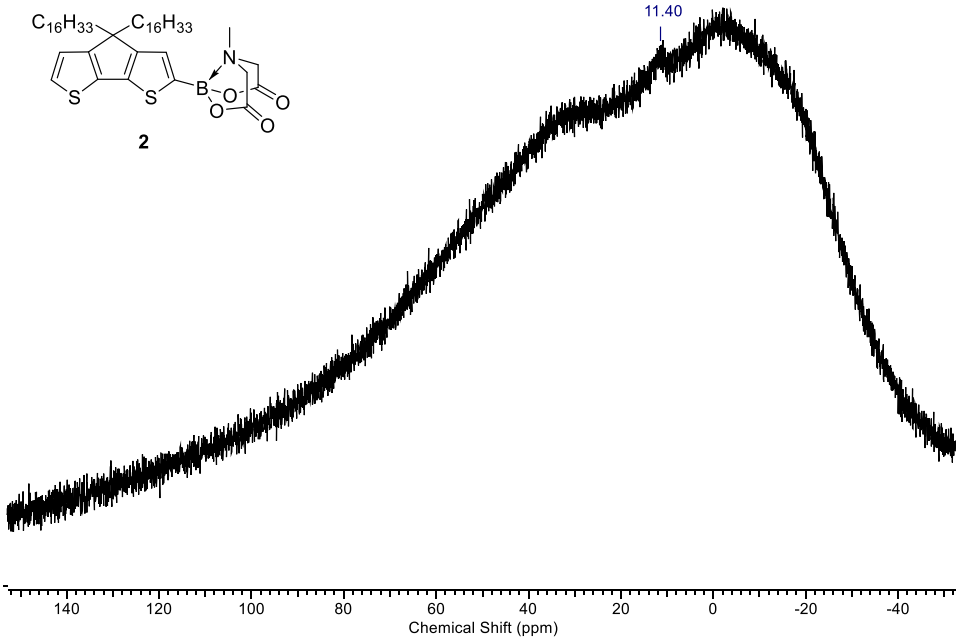
HRMS (APCI): calcd. for $C_{46}H_{76}NO_4S_2BH^+$ $[M + H^+]^+$ 782.5387, found 782.5361

Elemental Microanalysis: Expected C = 70.65, H = 9.80, N = 1.79. Found C = 70.39, H = 10.06, N = 1.75

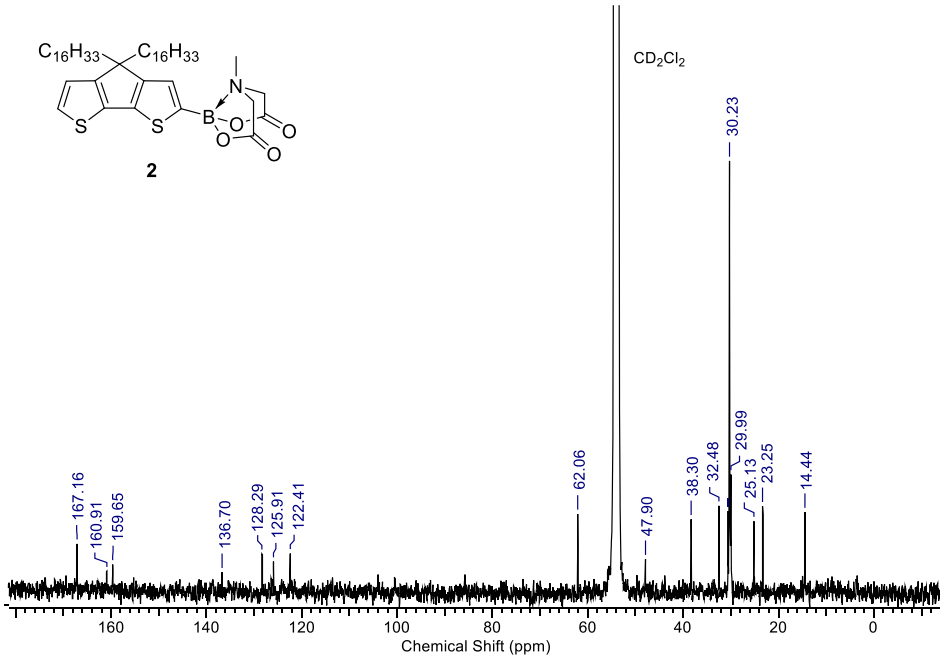
^{1}H NMR (CD_2Cl_2, 400 MHz)



^{11}B NMR (CD_2Cl_2, 128 MHz)



$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz)



5:

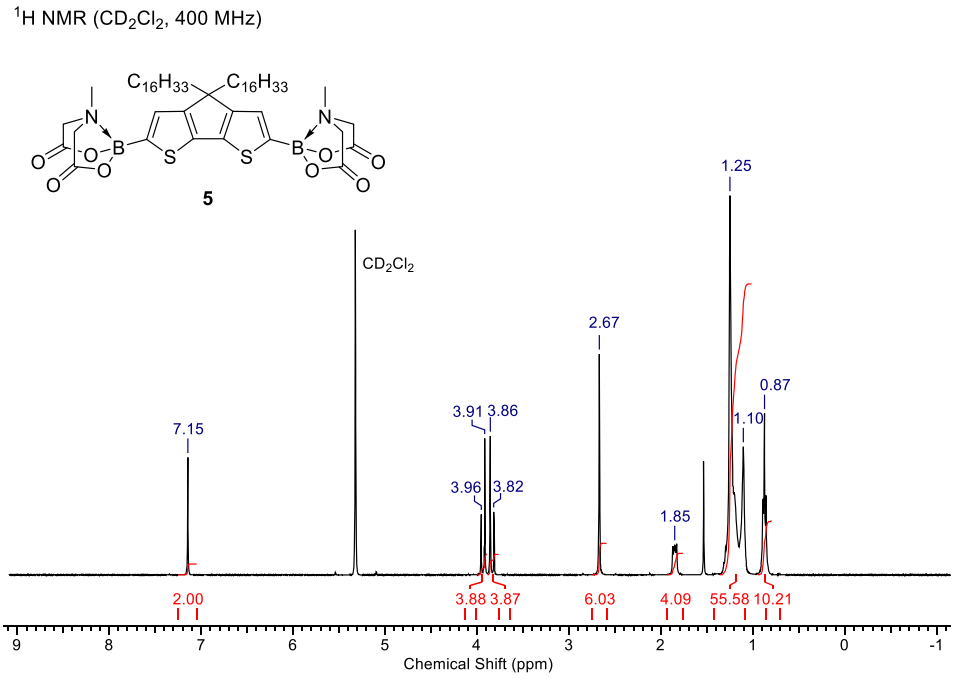
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.15 (s, 2 H), 3.93 (d, $^{2}J_{(H,H)}$ = 16.6 Hz, 4 H, 2 × CH_2), 3.84 (d, $^{2}J_{(H,H)}$ = 16.6 Hz, 4 H, 2 × CH_2), 2.67 (s, 6 H, 2 × *N*CH_3), 1.85 (m, 4 H, 2 × CH_2), 1.10-1.25 (m, 56 H, 28 × CH_2), 0.87 (t, $^{3}J_{(H,H)}$ = 6.78 Hz, 6 H, 2 × CH_3)

^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 167.2 (4 C_{quat}), 161.7 (2 C_{quat}), 142.0 (2 C_{quat}), 128.4 (2 CH), 62.1 (4 CH_2), 48.0, 38.4, 32.5, 30.6, 30.3, 30.2, 30.2, 30.1, 29.9, 25.2, 23.3, 14.4 (2 CH_3)

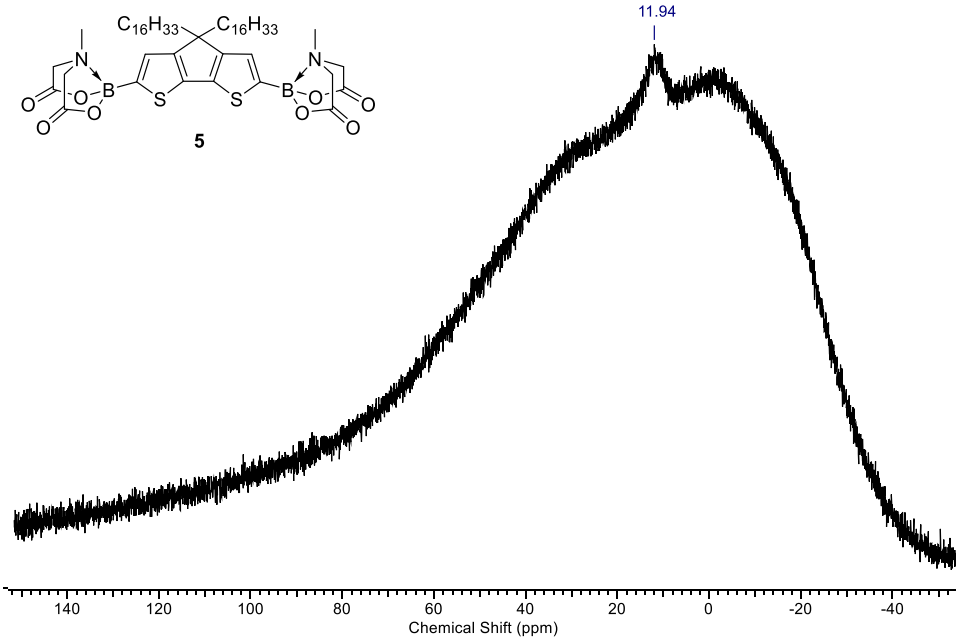
^{11}B NMR (128.4 MHz, CD_2Cl_2): δ 11.9 (s)

HRMS (APCI): calcd. for $C_{51}H_{82}N_2O_8S_2B_2H^+$ $[M + H^+]^+$ 937.5777, found 937.5751

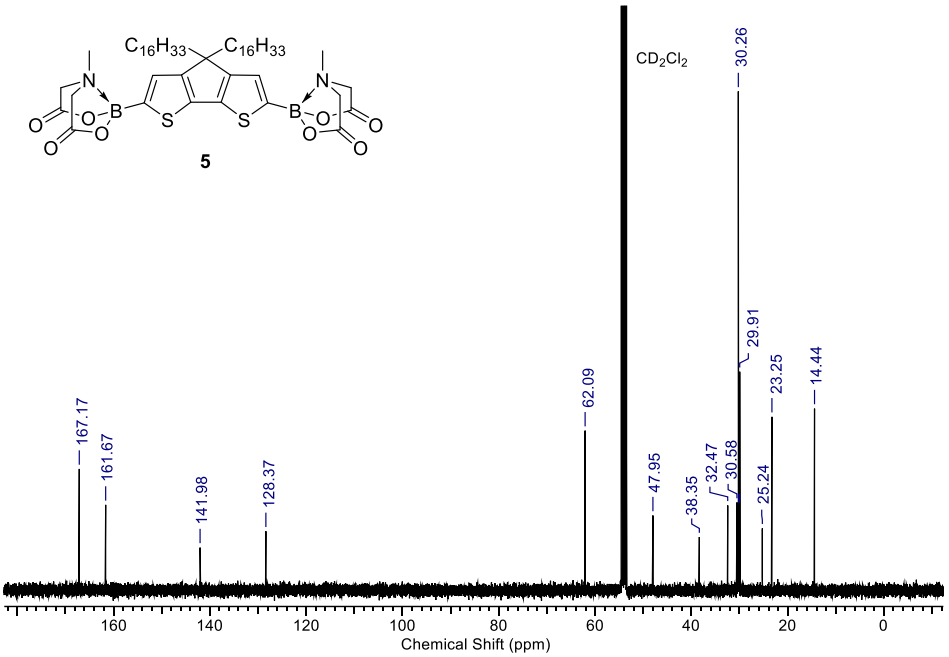
Elemental Microanalysis: Expected C = 65.38, H = 8.82, N = 2.99. Found C = 65.13, H = 9.04, N = 2.89



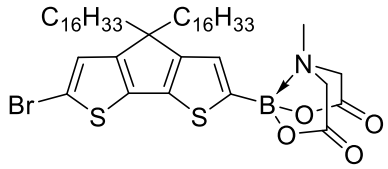
^{11}B NMR (CD_2Cl_2, 128 MHz)



^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz)



6-bromo-4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene-2-yl-MIDA-boronate, 1

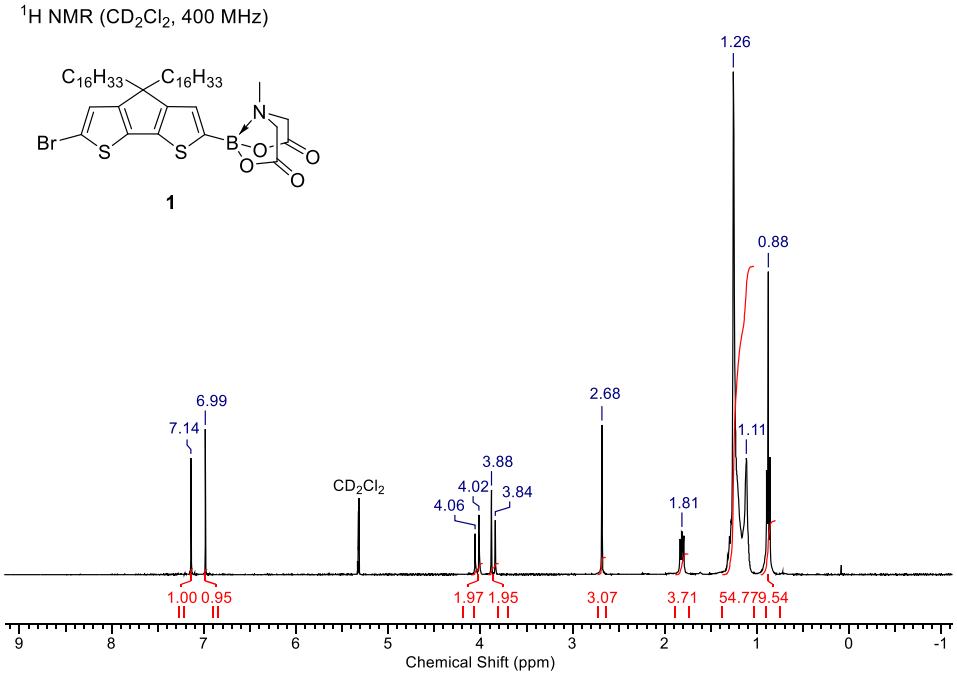


1

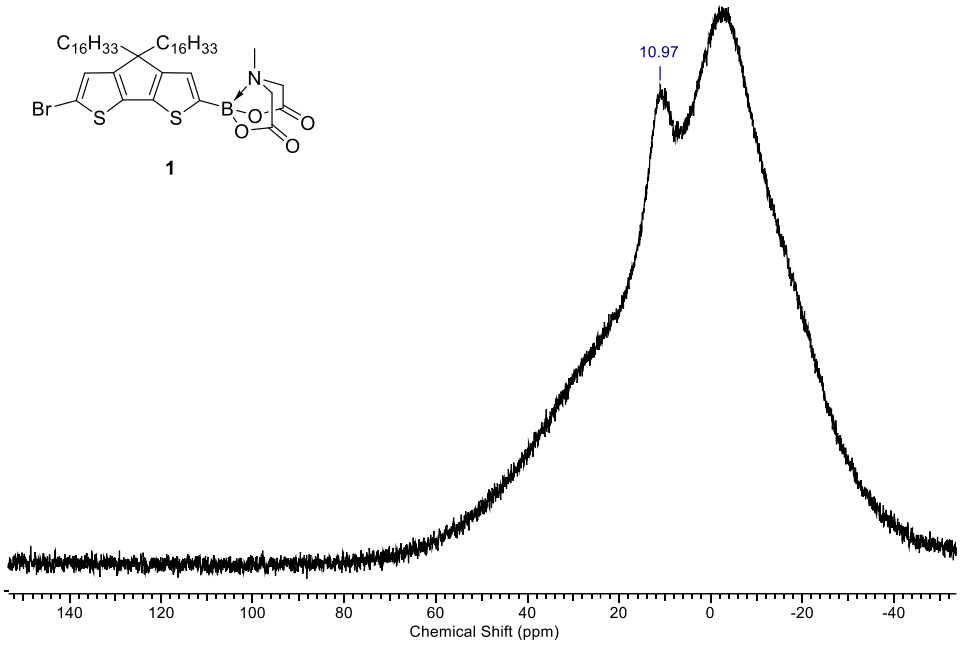
According to the **Bromination Procedure**, 4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene-2-yl-MIDA-boronate, **2** (260 mg, 0.333 mmol) reacted with *N*-bromosuccinimide (62 mg, 0.349 mmol) in anhydrous ethyl acetate (8 mL) over 24 h to afford after work up 147 mg (51%) of a pure product as an pale yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.14 (s, 1 H), 6.99 (s, 1 H), 4.04 (d, $^{2}J_{(H,H)}$ = 16.7 Hz, 2 H), 3.86 (d, $^{2}J_{(H,H)}$ = 16.4 Hz, 2 H), 2.68 (s, 3 H, *N*CH_3), 1.81 (t, $^{3}J_{(H,H)}$ = 8.2 Hz, 4 H, 2 × C*H*$_2$C$_5$H$_{11}$), 1.11-1.26 (m, 56 H, 28 × CH_2), 0.88 (t, $^{3}J_{(H,H)}$ = 6.9 Hz, 6 H, 2 × CH_3)

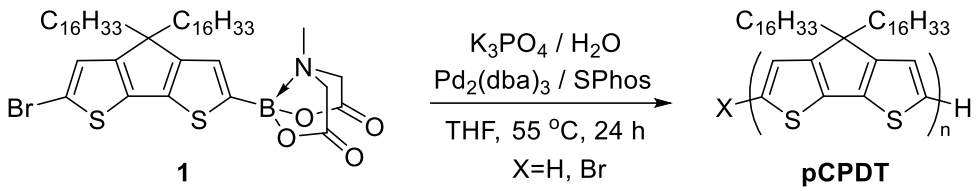
^{11}B NMR (128 MHz, CD_2Cl_2): δ 11.0 (s)



^{11}B NMR (CD_2Cl_2, 128 MHz)



Poly(4,4'-bis(hexadecyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diyl), pCPDT homopolymer



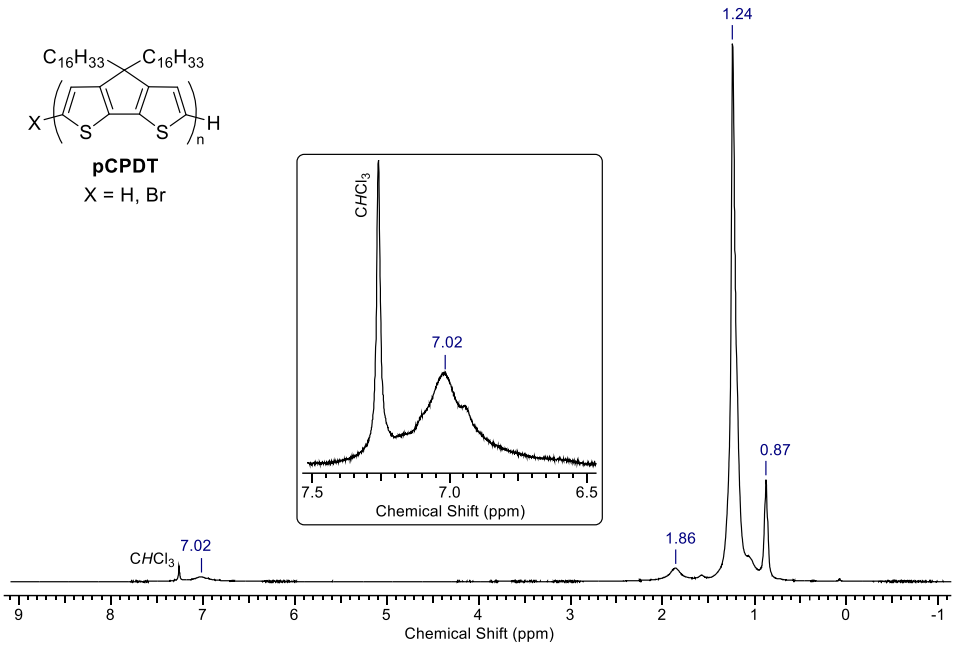
According to **Polymer synthesis**: **1** (146.0 mg, 0.170 mmol) reacted with: K_3PO_4 (108.0 mg, 0.509 mmol), H_2O (122 μL, 3.392 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (3.9 mg, 0.0043 mmol) and SPhos (3.5 mg, 0.0086 mmol) in THF (2.88 mL) over 24 h to afford after precipitation with MeCN 105 mg (99%) of **pCPDT** as a dark blue solid. After sequential Soxhlet extraction with MeOH, *n*-hexane, and chloroform, the last fraction yielded 95 mg (90%) of a dark blue solid. Characterisation of **pCPDT** matches previous reports.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 2 H), 1.86 (m, 4 H, 2 × CH_2), 1.24 (m, 56 H, 28 × CH_2), 0.87 (m, 6 H, 2 × CH_3)

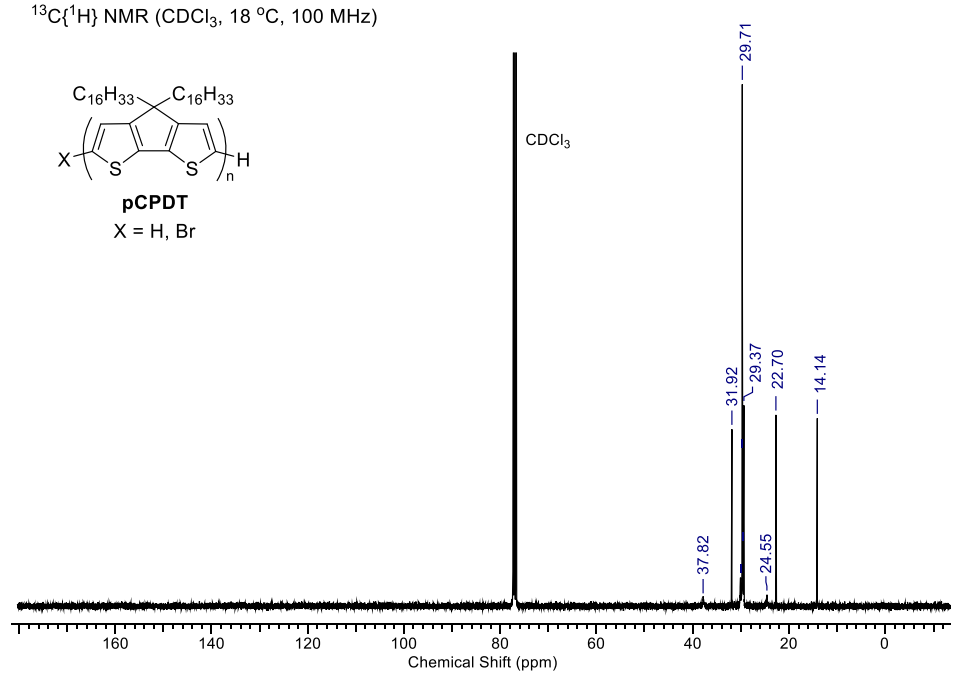
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ (Very weak aromatic and -CR_2 carbon signals, not clearly observed), 37.82, 31.92, 30.09, 29.71, 29.67, 29.64, 29.44, 29.37, 24.55, 22.70, 14.14

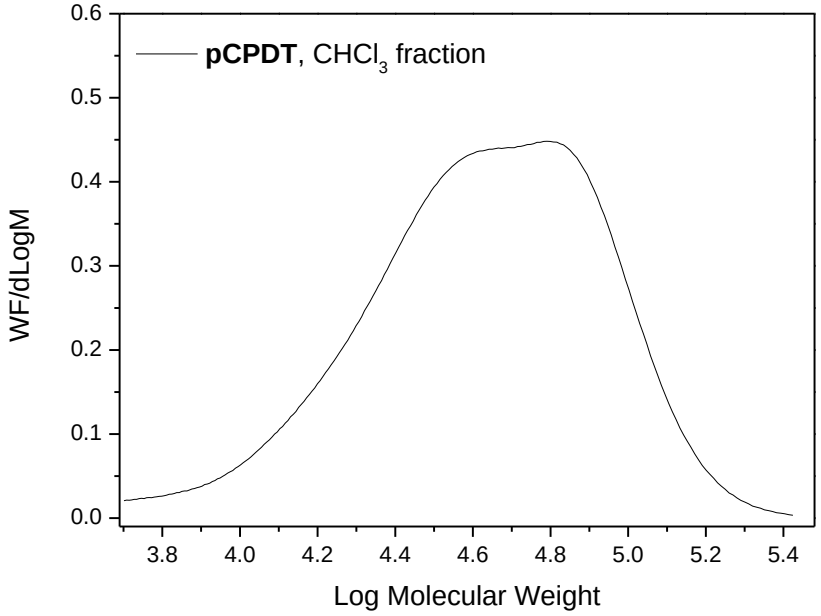
GPC (THF at 35 °C, PS calibration): M_n = 30.6 kDa, M_w = 49.9 kDa

^{1}H NMR ($CDCl_3$, 18 ^{o}C, 400 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 18 ^{o}C, 100 MHz)




pCPDT, CHCl3 fraction
WF/dLogM
0.0
0.1
0.2
0.3
0.4
0.5
0.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
Log Molecular Weight

Analysis of residual unreacted monomer **1** after quenching the polymerisation with MeCN at different reaction times:

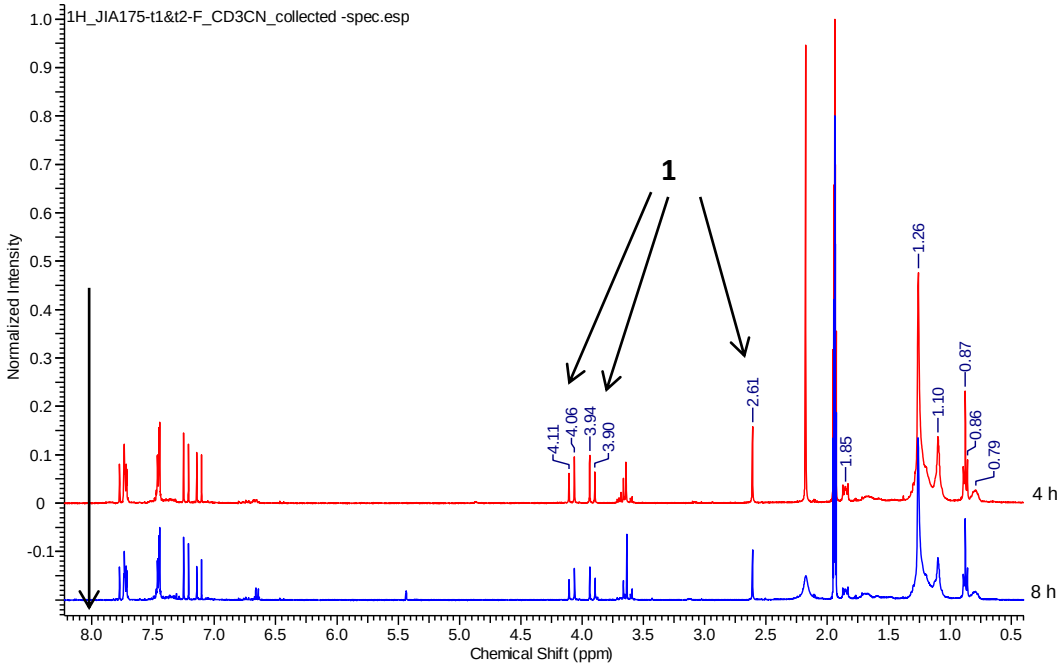
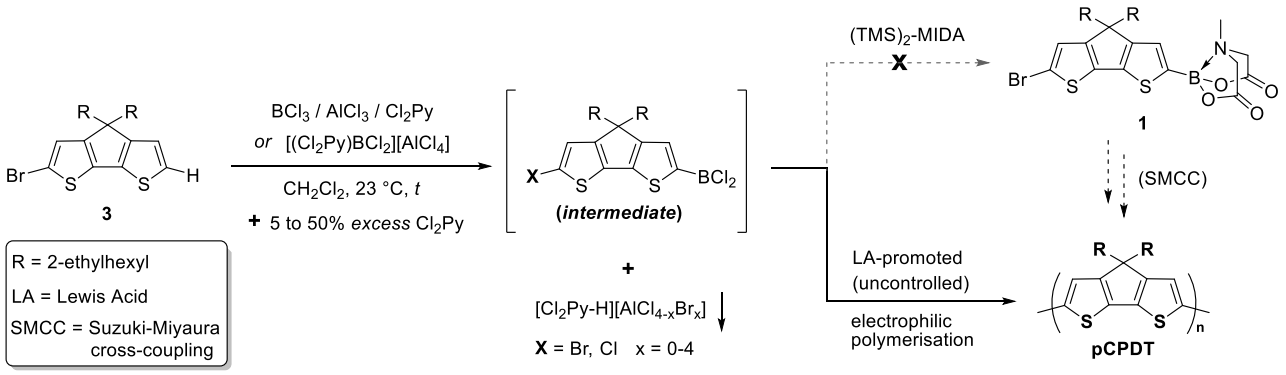


Figure S1. ^{1}H NMR spectra (CD_3CN) of Table 1, entries 1-2, the filtered reaction mixture after precipitation of **1**-derived **pCPDT**. Collected spectra showed remaining unreacted **1** (*N*-Me at 2.61 ppm, CH_2- at 2.56 ppm) after 4 h and 8 h. Other signals corresponding to residual dba and SPhos. No evidence of **3** (deboronated **1**).

Attempted borylation of **3** via C-H electrophilic borylation

Compound 2-bromo-4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene, **3**, a bromo-functionalised thienyl substrate was tested for borylation using either: a) combination of BCl_3 / Cl_2Py / $AlCl_3$ in a 1:1:1 ratio, or b) $[(Cl_2Py)\cdot BCl_2][AlCl_4]$, reaction conditions described in prior work (Scheme S1).[5] The desired dichloroborane-derived product was formed rapidly (<5 min at T = 23 °C) but competitive halogen exchange *via* C-Br activation promoted by $AlCl_3$ species occurred immediately, forming a mixture of borylated thienyl bromides and chlorides, and could not be suppressed even with addition of 50 mol% excess of Cl_2Py and T = 0 °C, as revealed by $[AlCl_{4-x}Br_x]^-$ (x = 0-4) species in the ^{27}Al NMR spectrum (Figure S2). Related aryl halide activations involving $AlCl_3$ have been previously reported.[8] In addition, deborylation occurred over time (*ca*. 2 h at T = 23 °C), and uncontrolled electrophilic polymerisation of the CPDT-derived species was observed (Figure S3). This result is attributed to the more electron rich nature of the CPDT core relative to other bromothienyl substrates previously investigated.[1,5]



Scheme S1. Attempted C-H electrophilic borylation of **3** en route to monomer **1**.

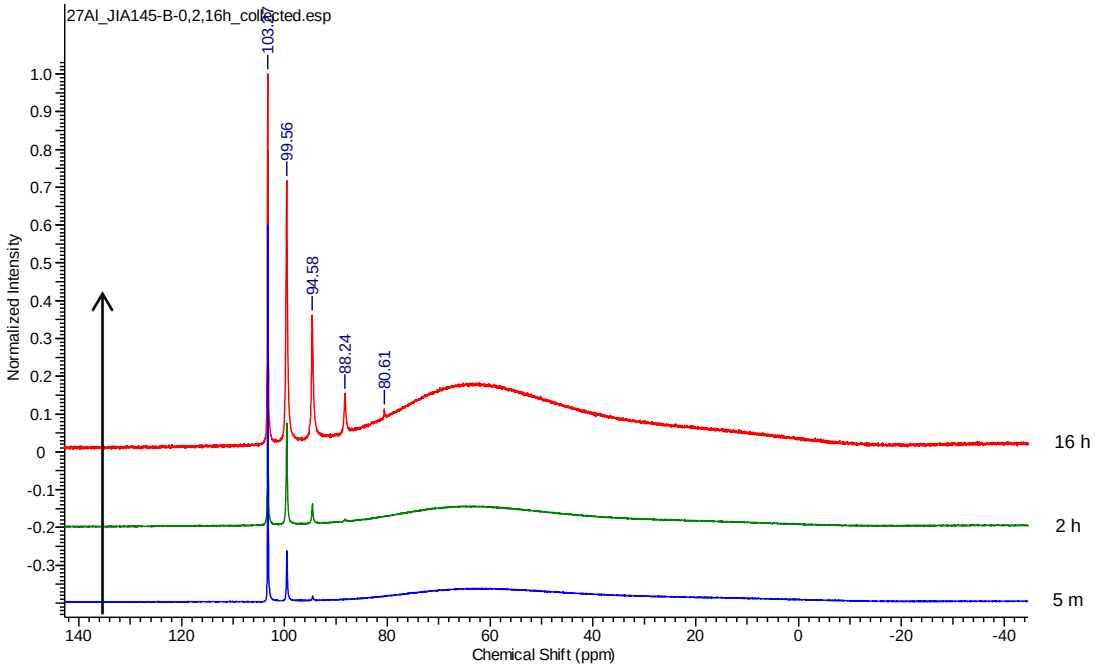


Figure S2. Collected ^{27}Al NMR spectra showing formation of $[AlCl_{4-x}Br_x]^-$ (x = 0-4) due to $AlCl_3$-induced C-Br activation producing borylated thienyl bromides and chlorides. C-H borylation of **3** using a 1:1:1 ratio of BCl_3/$AlCl_3$/Cl_2Py borylating system. *T*: 23 °C, *t*: 0 to 16 h.

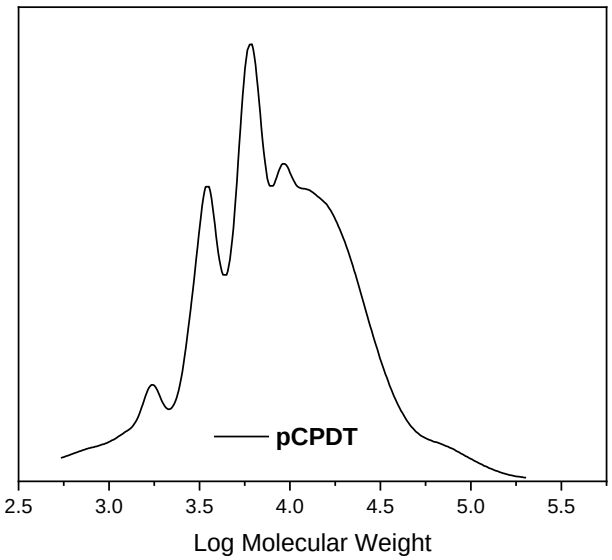


Figure S3. GPC trace of the product obtained from the uncontrolled polymerisation of **3** promoted by $AlCl_3$-derived species. Crude sample showing mixture of oligomers and polymers.

References

1 V. Bagutski, A. Del Grosso, J. Ayuso Carrillo, I. A. Cade, M. D. Helm, J. R. Lawson, P. J. Singleton, S. A. Solomon, T. Marcelli and M. J. Ingleson, *J. Am. Chem. Soc.*, 2013, **135**, 474–487.

2 A. Del Grosso, J. Ayuso Carrillo and M. J. Ingleson, *Chem. Commun.*, 2015, **51**, 2878–2881.

3 P. Coppo, D. C. Cupertino, S. G. Yeates and M. L. Turner, *Macromolecules*, 2003, **36**, 2705–2711.

4 S. S. Zalesskiy and V. P. Ananikov, *Organometallics*, 2012, **31**, 2302–2309.

5 J. Ayuso Carrillo, M. J. Ingleson and M. L. Turner, *Macromolecules*, 2015, **48**, 979–986.

6 J. Ayuso Carrillo, M. L. Turner and M. J. Ingleson, *J. Am. Chem. Soc.*, 2016, **138**, 13361–13368.

7 D. Pedersen and C. Rosenbohm, *Synthesis (Stuttg).*, 2001, **16**, 2431–2434.

8 G. A. Olah, W. S. Tolgyesi and R. E. A. Dear, *J. Org. Chem.*, 1962, **27**, 3441–3449.