Supporting Information for

A General Protocol for the Polycondensation of Thienyl MIDA-Boronate Esters to Form High Molecular Weight Copolymers

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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), toluene, d_8-THF, CH_2Cl_2, *n*-hexane, *o*-$C_6H_4Cl_2$, MeCN, CD_3CN, ethyl acetate, Et_2O, C_6D_5Br, mesitylene, Et_3N, and 2,6-di-*tert*-butylpyridine (*t*Bu_2Py) were distilled from K, NaK alloy, or CaH_2 under N_2 gas atmosphere and stored over molecular sieves or K mirror as appropriate. 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, D_2O, and alkaline aqueous solutions were thoroughly degassed by a continuous bubbling flow of N_2 gas for at least one hour. *N*-Methyliminodiacetic disilyl ester (TMS_2-MIDA),[1] 5-bromo-4-hexylthien-2-yl-MIDA-boronate, **1**,[2] 4,4'-bis(dodecyl)-2,2'-bithiophene, **13**,[3] 4,7-bis(5-bromo-3-hexylthiophene-2-yl)-2,1,3-benzothiadiazole, **9**,[4] were prepared according to literature procedures. 4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene, **2**, 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole, **8**, and 2,5-dibromothieno[3,2-b]thiophene, **12**, were purchased from TCI (98%), and used without further purification. 5,5'-dibromo-2,2'-bithiophene, **11**, was purchased from Alfa Aesar (99%) and used as received. 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole, **7**, was purchased from Alfa Aesar (98%) and recrystallised from EtOH before use. All other materials were purchased from commercial vendors and used as received. Room temperature (RT) refers to 23 ^{o}C (± 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; ^{19}F, 376.6 MHz) or Bruker AV-500 (^{1}H, 500 MHz, ^{13}C, 125.8 MHz; ^{11}B, 160.5 MHz; ^{27}Al, 130.3 MHz; ^{19}F, 470.7 MHz; ^{17}O, 67.8 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 $CDCl_3$ δ_H = 7.26) or TMS (δ_H = 0.00), and the central peak of $CDCl_3$ triplet (δ_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 $[Al(D_2O)_6]^{3+}$; ^{19}F, C_6F_6; ^{17}O, D_2O. 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. Alternatively, GPC analyses were performed in chlorobenzene solution (~1 mg mL^{-1}) at 70 °C using a Polymer Laboratories solvent/sample module with 2 × PL gel 10 μm mixed-B and a PL gel 500 A column, and equipped with an ERC 7515A RI detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Experiments were carried out with injection volume of 100 μL, flow rate of 0.5 mL min^{-1}. Results were analysed using toluene as internal marker, and in-house customised LabView 8.5 software, and processed using OriginLab Pro 8.5 software. GPC analyses in 1,2,4-trichlorobenzene solution at 160 °C were performed by PSS Polymer Standards Service GmbH, Mainz, Germany.

UV-vis spectroscopy analyses were performed in spectroscopy grade chloroform or chlorobenzene solution (1×10^{-5} M) at room temperature using an Agilent Technologies Cary 5000 UV-vis-NIR spectrophotometer.

MALDI-TOF analyses were performed using a Shimadzu Axima Confidence spectrometer using a 4k PPG as a calibration reference. 1 μL of a solution of dopant NaI in THF (10 mg mL^{-1}) was spotted onto a well of the MALDI plate and the solvent left to evaporate. Polymer samples solutions were made up to 10 mg mL^{-1} in THF. A solution of matrix dithranol was made up to 10 mg mL^{-1} in THF. 2 μL of sample solution and 20 μL of matrix solution were thoroughly mixed and 1 μL of this solution was spotted onto a well with no dopant, and 1 μL spotted by a layered method with the NaI. The solvent was allowed to evaporate before being

placed in the spectrometer. Samples were run in positive polarity mode in either linear or reflectron mode. Results were and processed using OriginLab Pro 8.5 software.

X-Ray crystallographic analyses were carried out by Dr. Inigo Vitorica-Yrezabal and Dr. James Raftery (for **3**), and Dr. Jay J. Dunsford (for **10**). Data for compounds **3** and **10** were recorded on an Agilent Supernova diffractometer, with Mo Kα radiation (mirror monochromator, λ =0.7107). The CrysAlisPro[5a] software package was used for data collection, cell refinement and data reduction. The CrysAlisPro software package was also used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Structures were solved using direct methods and refined against F^2 using the OLEX2[5b] software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically.

Crystallographic data for **3** and **10** have been deposited with the Cambridge Crystallographic Data Center under the references: CCDC 1493979 and 1493980, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) *via* www.ccdc.cam.ac.uk/data_request/cif

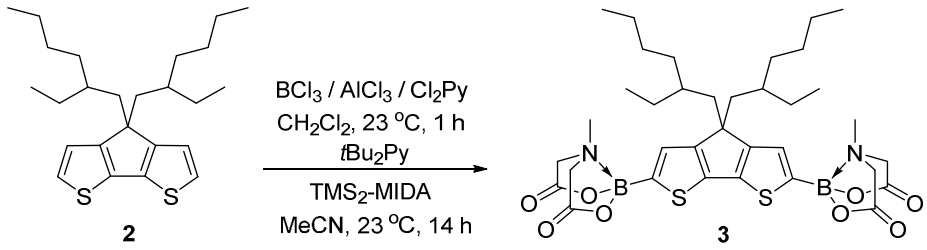
Elemental analyses were performed by the Micro Analytical Laboratory, School of Chemistry, University of Manchester.

Monomer synthesis procedures

General Procedure (GP1) Optimised for multigram-scale bis-borylation of bithiophenes. 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 bithiophene (1.0 equiv) was added, keeping the temperature at 18-25 °C. After stirring at ambient temperature for 1 h, 2,6-di-*tert*-butylpyridine (*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 relevant work up procedures.
It should be noted that in experiments where *t*Bu_2Py is not added the *in-situ* conversion to **3** is significantly lower, with protodeboronation products observed even before work up. This is attributed to the strongly Brønsted acidic by-product $[HCl_2Py]^+$ from S_EAr reacting with a four coordinate thienylBCl_2(L) species (L = $MIDA^{2-}$ or MeCN). *t*Bu_2Py deprotonates $[HCl_2Py]^+$ and generates a less acidic solution resulting in no protodeboronation in-situ.

Workup Procedure 1 (WP1), optimised for the synthesis of **3**: The crude reaction mixture was concentrated under reduced pressure at ambient temperature to remove TMSCl and solvents. The crude product was washed thoroughly with anhydrous toluene. The residue was redissolved in anhydrous ethyl acetate, filtered through a plug of dry Celite, and concentrated under reduced pressure at ambient temperature. Then it was recrystallised from a concentrated solution in anhydrous MeCN layered with anhydrous Et_2O. Decantation of the solvents and drying under reduced pressure (1×10^{-2} mbar), afforded the desired pure product.
Workup Procedure 2 (WP2), optimised for the synthesis of **10**: The crude reaction mixture was concentrated under reduced pressure at ambient temperature to remove TMSCl and solvents. The crude product was redissolved in anhydrous hot THF, filtered through a short plug of Et_3N-treated silica gel (40-63 μm), and concentrated under reduced pressure at ambient temperature. The residue was sequentially washed thoroughly with anhydrous hexane (3 × 15 mL), Et_2O (3 × 15 mL), and cold ethyl acetate (3 × 15 mL). Further drying at 40 °C under reduced pressure (1×10^{-2} mbar) afforded the desired pure product.

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



According to **GP1**: 4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene (1.0 g, 2.48 mmol) reacted with BCl_3 (5.2 mL of 1.0 M in CH_2Cl_2, 5.22 mmol), Cl_2Py (0.77 g, 5.22 mmol), and $AlCl_3$ (0.66 g, 4.97 mmol), in CH_2Cl_2 (15 mL). Subsequent addition of tBu$_2$Py (1.0 g, 5.22 mmol), followed by esterification with TMS_2-MIDA (1.52 g, 5.22 mmol) in MeCN (20 mL) afforded after workup (following **WP1**), 1.44 g (81%) of a pure product as a colourless solid. When workup followed standard purification using non-purified "wet" solvents and silica gel chromatography,[2] the yield of **3** decreased to 23%, along with **4** being isolated in 32%. X-Ray quality crystals of **3** were grown from a concentrated solution in MeCN, layered with Et_2O.

^{1}H NMR (400 MHz, d_8-THF): δ 7.20 (s, 2 H), 4.16 (dm, $^2J_{(H,H)}$ = 16.6 Hz, 4 H, 2 × CH_2), 3.90 (dm, $^2J_{(H,H)}$ = 16.6 Hz, 4 H, 2 × CH_2), 2.67 (6 H, 2 × NCH_3), 1.94 (d, J = 4.9 Hz, 4 H, 2 × CH_2), 1.03 – 0.94 (m, 16 H, 8 × CH_2), 0.79 (t, $^3J_{(H,H)}$ = 7.0 Hz, 6 H, 2 × CH_3), 0.69 (m, 2 H, 2 × CH), 0.59 (m, 6 H, 2 × CH_3)

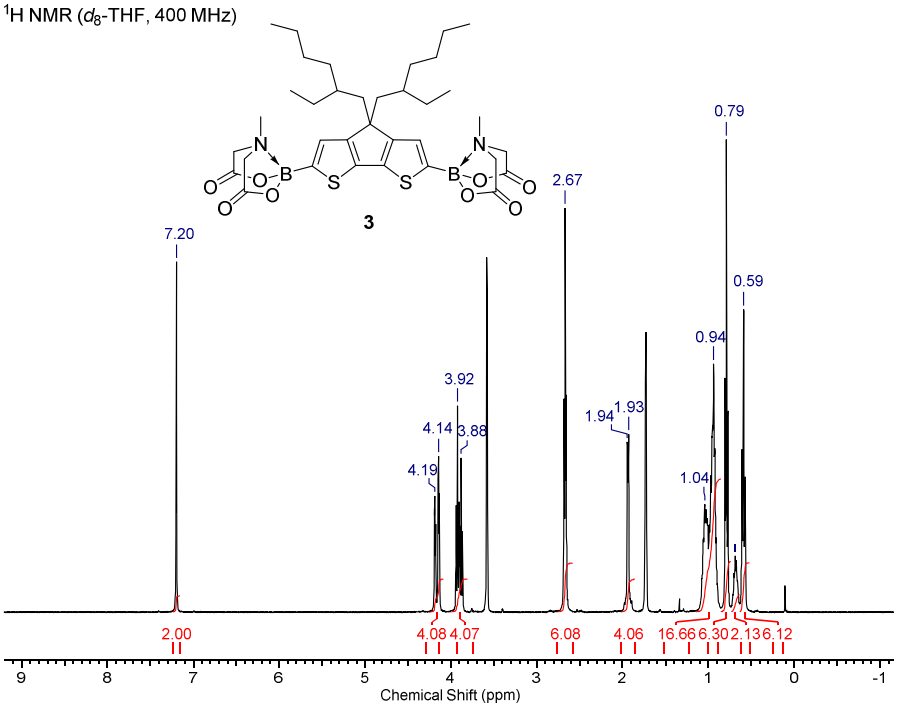
^{13}C{^{1}H} NMR (125.8 MHz, CD_3CN): δ 169.1 (4 C_{quat}), 161.8 (2 C_{quat}), 141.9 (2 C_{quat}), 129.6 (2 CH), 62.5 (4 CH_2), 53.9 (C_{quat}), 48.5 (2 CH_3), 43.9 (2 CH_2), 36.1 (2 CH), 34.9 (2 CH_2), 29.5 (2 CH_2), 27.9 (2 CH_2), 23.6 (2 CH_2), 14.5 (2 CH_3), 11.1 (2 CH_3)

^{11}B NMR (128.4 MHz, d_8-THF): δ 11.0 (s)

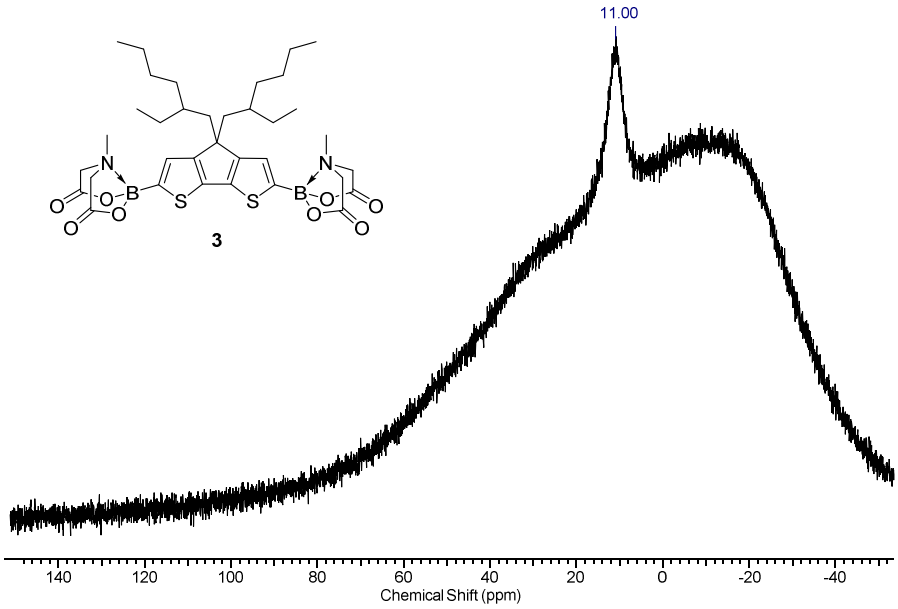
HRMS (APCI): calcd. for $C_{35}H_{50}N_2O_8S_2B_2H^+$ $[M + H^+]^+$ 713.3286, found 713.3289

Elemental Microanalysis: Expected C = 59.00, H = 7.07, N = 3.93. Found C = 58.87, H = 7.58, N = 3.86

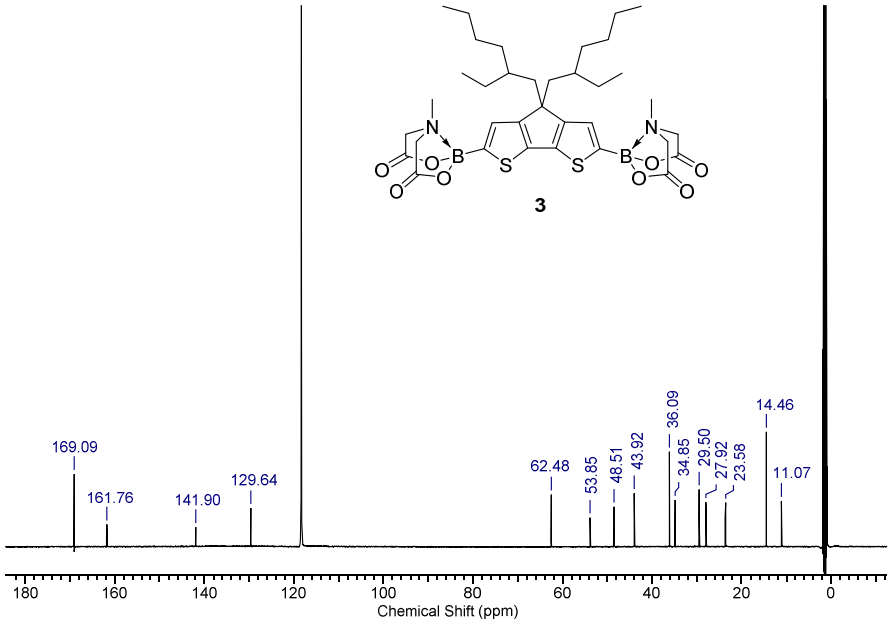
^{1}H NMR (d_8-THF, 400 MHz)



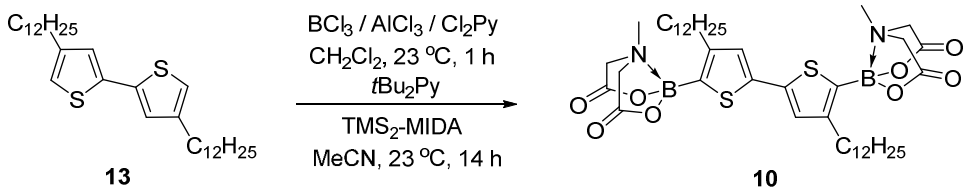
^{11}B NMR (d_8-THF, 128 MHz)



$^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz)



4,4'-bis(dodecyl)-2,2'-bithiophene-2,7-diyl-MIDA-boronate, 10



According to **GP1**: 4,4'-bis(dodecyl)-2,2'-bithiophene, **13**, (1.00 g, 1.99 mmol) reacted with BCl_3 (4.2 mL of 1.0 M in CH_2Cl_2, 4.18 mmol), Cl_2Py (0.622 g, 4.18 mmol), and $AlCl_3$ (0.560 g, 3.98 mmol), in CH_2Cl_2 (15 mL). Subsequent addition of tBu$_2$Py (0.804 g, 4.18 mmol), followed by esterification with TMS_2-MIDA (1.224 g, 4.18 mmol) in MeCN (40 mL) afforded after workup (following **WP2**), 0.93 g (57.4%) of a pure product as a pale yellow solid. When workup followed standard purification using non-purified "wet" solvents,[2] the isolated yield of **10** decreased to 8.4%. X-Ray quality crystals were grown from slow cooling a warm concentrated solution of **10** in MeCN.

^{1}H NMR (500 MHz, d_8-THF, 55°C): δ 7.14 (s, 2 H), 4.16 (d, $^2J_{(H,H)}$ = 17.0 Hz, 4 H), 3.94 (d, $^2J_{(H,H)}$ = 17.0 Hz, 4 H), 2.68 (s, 6 H, 2 × NCH_3), 2.60 (t, $^3J_{(H,H)}$ = 7.7 Hz, 2 × $CH_2C_5H_{11}$), 1.64 (tt, $^3J_{(H,H)} \approx$ 7.4 Hz, 2 × $CH_2CH_2C_4H_9$), 1.30 (m, 36 H, 18 × CH_2), 0.89 (t, $^3J_{(H,H)}$ = 6.9 Hz, 6 H, 2 × CH_3)

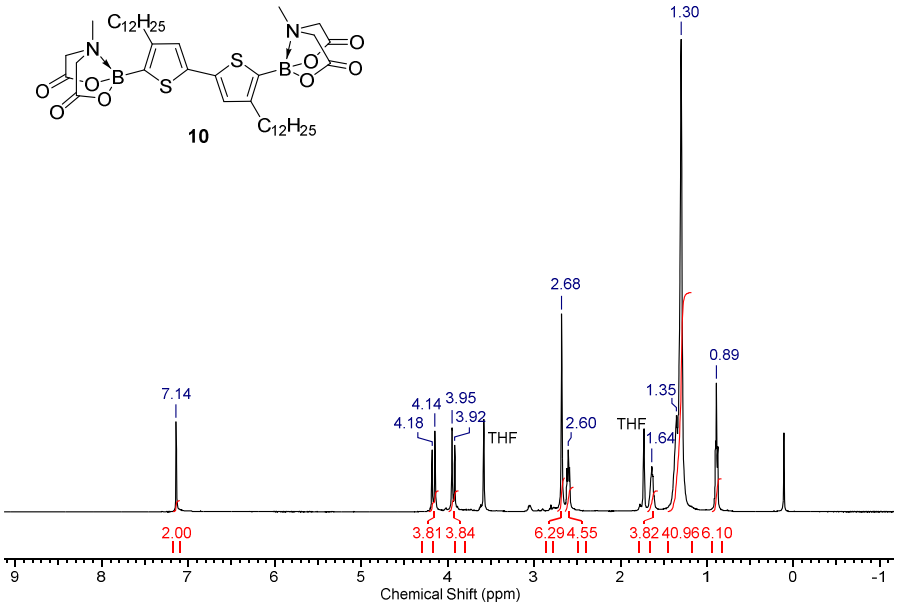
^{13}C{^{1}H} NMR (125.8 MHz, d_8-THF, 55°C): δ 168.0 (2 C_{quat}), 150.6 (C_{quat}), 141.2 (C_{quat}), 128.2 (CH), 62.8 (2 CH_2), 47.8 (CH_3), 32.99 (CH_2), 32.70 (CH_2), 31.56 (CH_2), 30.78 (CH_2), 30.76 (CH_2), 30.75 (CH_2), 30.72 (CH_2), 30.63 (CH_2), 30.40 (CH_2), 23.65 (CH_2), 14.5 (CH_3)

^{11}B NMR (128.4 MHz, d_8-THF, 55°C): δ 11.1 (s)

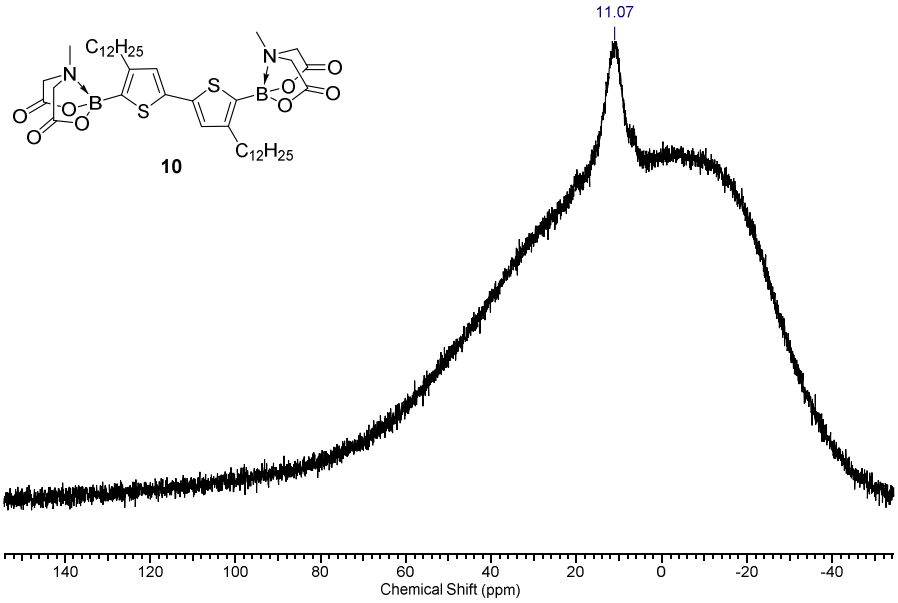
HRMS (APCI): calcd. for $C_{42}H_{66}B_2N_2O_8S_2^-$ $[M + H^+]^-$ 813.4519, found 813.4520

Elemental Microanalysis: Expected C = 62.07, H = 8.19, N = 3.45. Found C = 61.77, H = 8.76, N = 3.63.

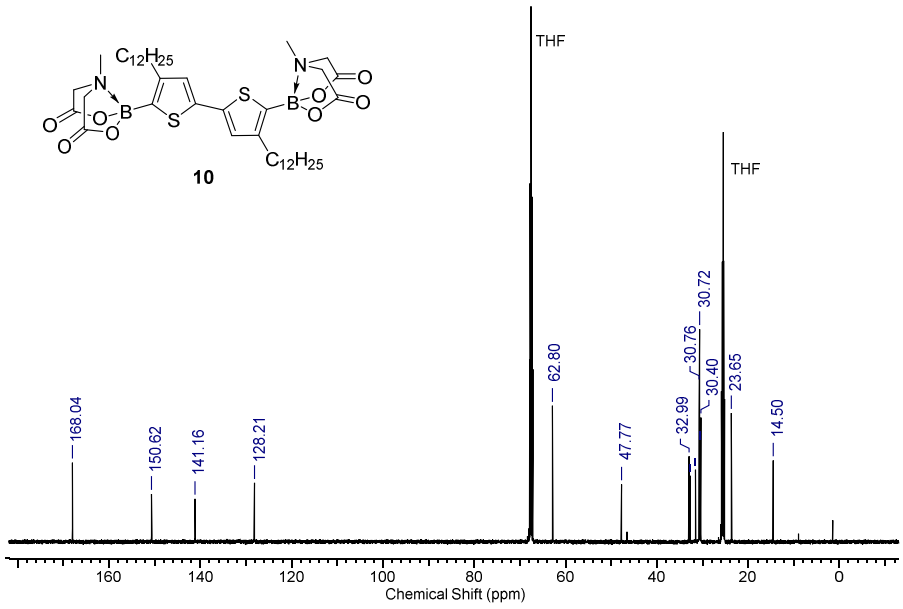
^{1}H NMR (d_8-THF, 55 °C, 500 MHz)



^{11}B NMR (d_8-THF, 55 °C, 128 MHz)



$^{13}C\{^{1}H\}$ NMR (d_8-THF, 55 °C, 125.8 MHz)



Monomer hydrolysis reactions procedures

Stability and Hydrolysis Kinetics of MIDA Boronate Ester Monomers, using D_2O (base-free)

Under anhydrous conditions, all thienyl MIDA boronate ester monomers remained unchanged in solution for weeks. They are structurally and thermally stable, as confirmed *via* variable temperature NMR spectroscopy experiments (at least to 100 °C). For example, the diastereotopic CH_2 protons of thienyl-BMIDA maintained their $^2J_{HH}$ coupling over this temperature range, indicating no N→B bond dissociation (Figure S1).

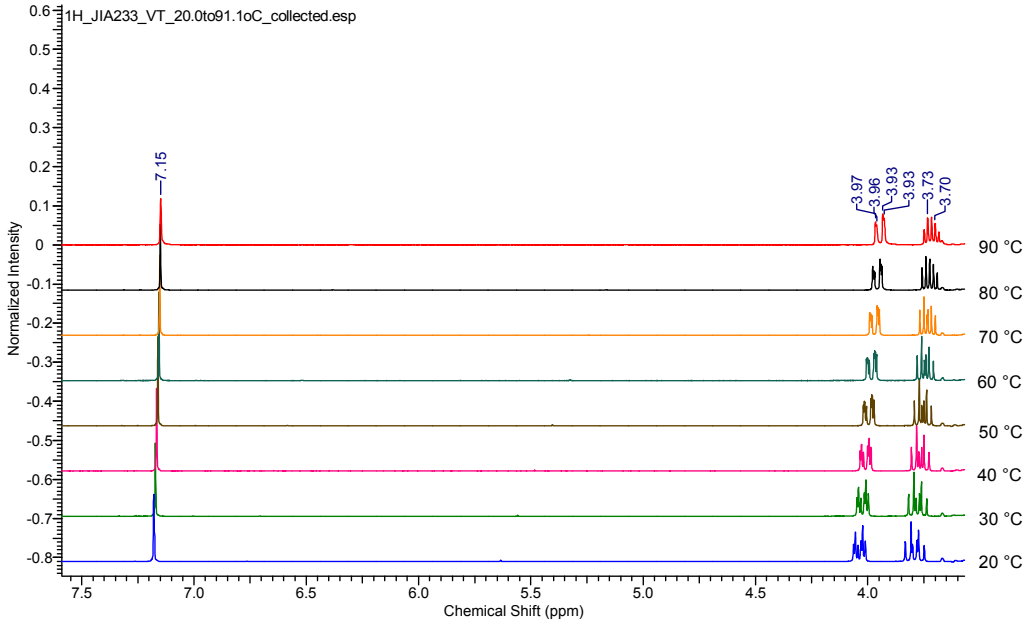
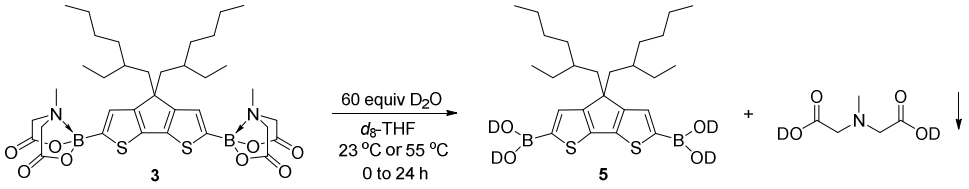


Figure S1. Variable-temperature ^1H NMR spectra (partial range) of **3** in anhydrous d_8-dioxane.

Kinetics experiments for thienyl MIDA boronate esters hydrolysis with THF/D_2O (base-free conditions)

Procedure for kinetics experiments and *in situ* measurements, example procedure for **1**. An oven-dried J. Young's NMR tube was charged under inert atmosphere with **1**, (1.0 equiv.), mesitylene as internal reference (1.0 μL), and dissolved in d_8-THF (0.7 mL). Subsequently, D_2O (30.0 equiv. per BMIDA moiety), was added [**1**]= 6.2×10^{-2} M, and the reaction mixture was vigorously shaken to homogenise before recording its NMR spectrum (t_0). Then the tube was rotated at ambient temperature or heated in an oil bath at 55 °C, and followed by NMR spectroscopy at different reaction times.



[Eq. S1]

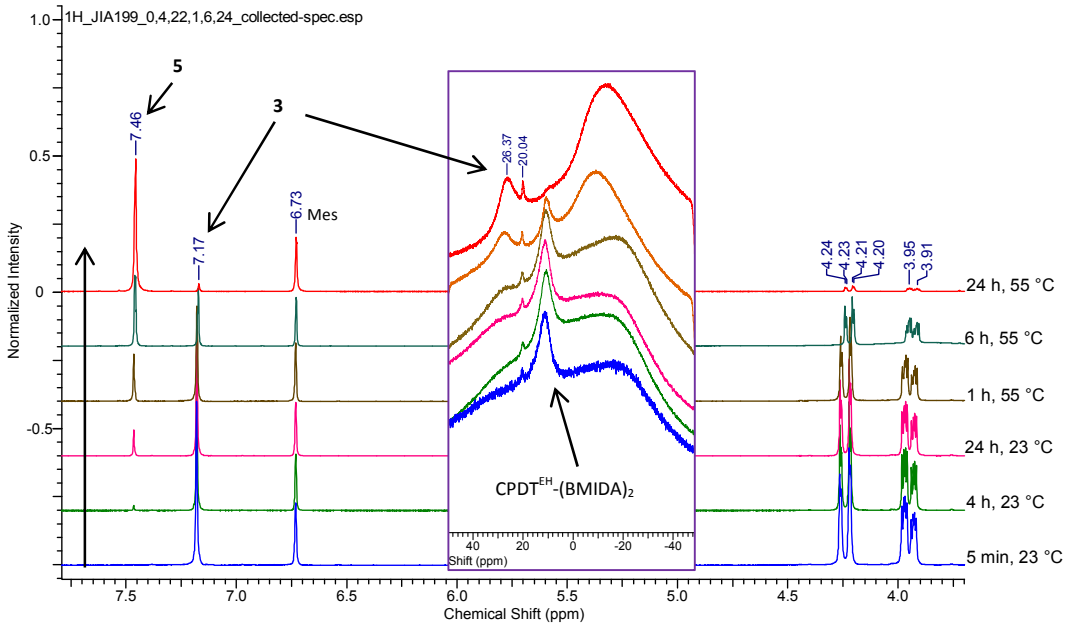
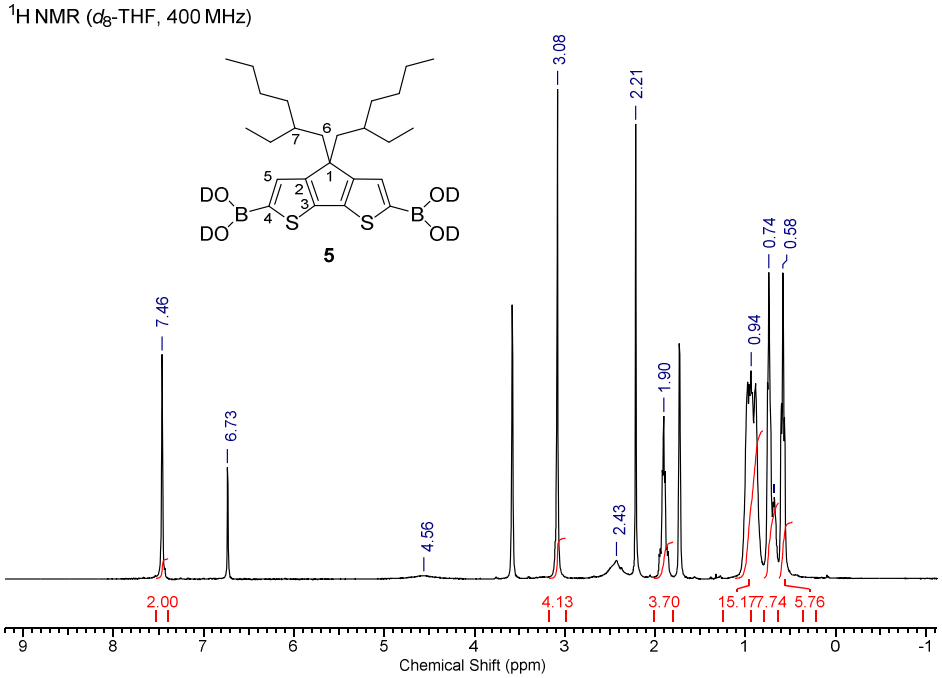


Figure S2. Collected partial ^{1}H NMR spectra in d_8-THF of the hydrolysis of **3** to **5**. Reaction conditions as in Equation S1. Mesitylene added as internal standard. Inset: Collected ^{11}B NMR spectra at the same time intervals.

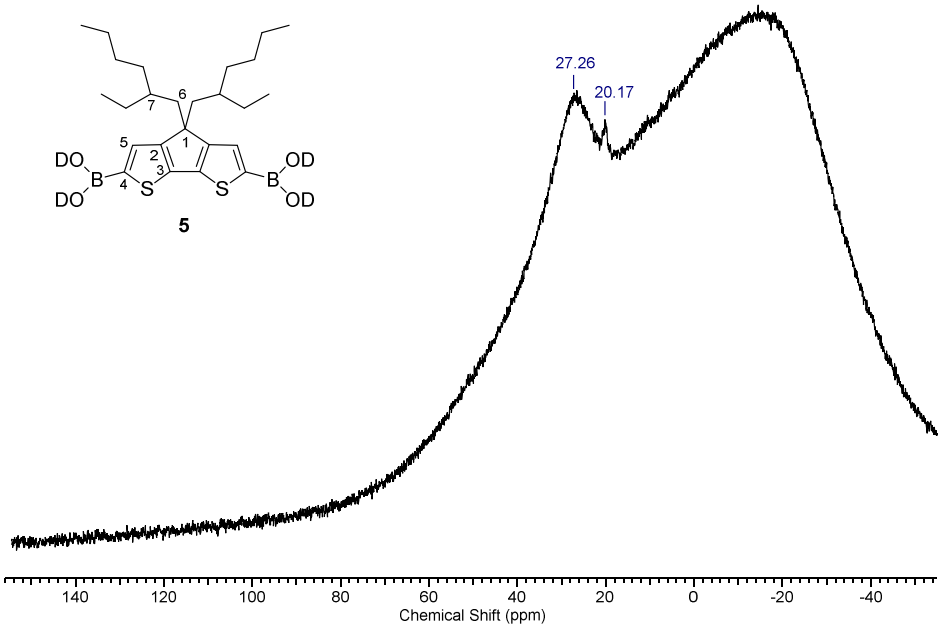
In situ characterisation of **4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diyl-bis-boronic acid, 5**:

^{1}H NMR (400 MHz, d_8-THF): δ 7.46 (s, 2 H), 1.90 (m, 4 H, 2 × CH_2), 0.94 (m, 16 H, 8 × CH_2), 0.74 (t, J = 5.3 Hz, 6 H, 2 × CH_3), 0.68 (m, 2 H, 2 × CH), 0.58 (t, J = 7.1 Hz, 6 H, 2 × CH_3).
^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF): δ 159.8 (2 $C3_{quat}$), 143.2 (2 $C2_{quat}$), 130.1 (2 C5-H), 52.2 ($C1_{quat}$), 43.4 (2 C6-H_2), 34.9 (2 C7-H), 34.0 (2 CH_2), 28.4 (2 CH_2), 27.1 (2 CH_2), 22.7 (2 CH_2), 13.5 (2 CH_3), 9.97 (2 CH_3).
^{11}B NMR (128.4 MHz, d_8-THF): δ 27.3 (bs).



Resonances at 6.73, 2.21, correspond to mesitylene (internal standard). Resonance at 3.08 corresponds to free MIDA (4 H, 2 × CH_2), and 2.43 is H_2O and HDO in THF.

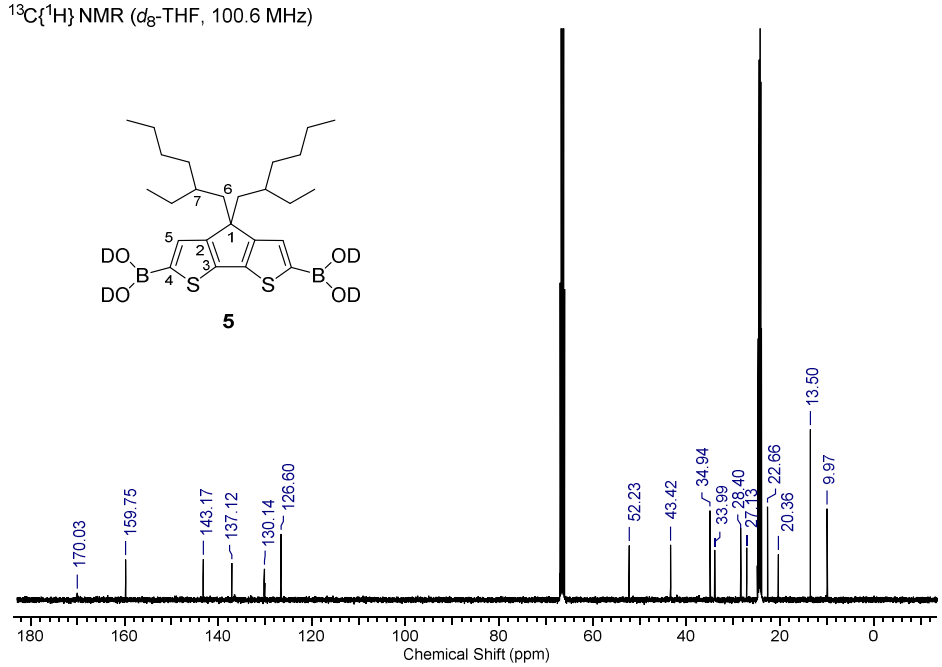
^{11}B NMR (d_8-THF, 128 MHz)



5

Resonance at 20.2 (s), corresponds to $B(OD)_3$

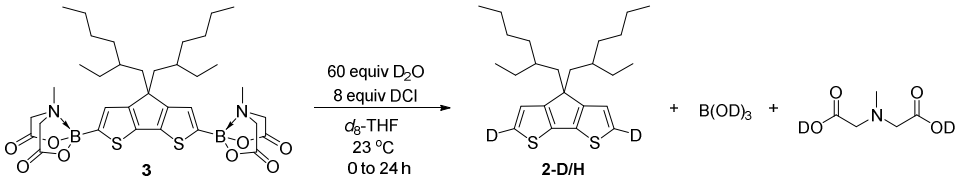
^{13}C{^{1}H} NMR (d_8-THF, 100.6 MHz)



5

Resonances at 137.1, 126.6, 20.4, correspond to mesitylene (internal standard). Resonance at 170.0 (C_{quat}), corresponds to free MIDA.

Hydrolysis and subsequent protodeboronation of **3** to **2-(D)$_2$** was confirmed by reacting **3** in d_8-THF with 8 equivalents of DCl (1 M solution in Et_2O) and then subsequent addition of 60 equivalents of D_2O at 23 °C. Complete deuteration of the alpha position of the CPDT core was observed by *in situ* NMR spectroscopy after addition of D_2O, with no deoboronation occurring under anhydrous conditions.



[Eq. S2]

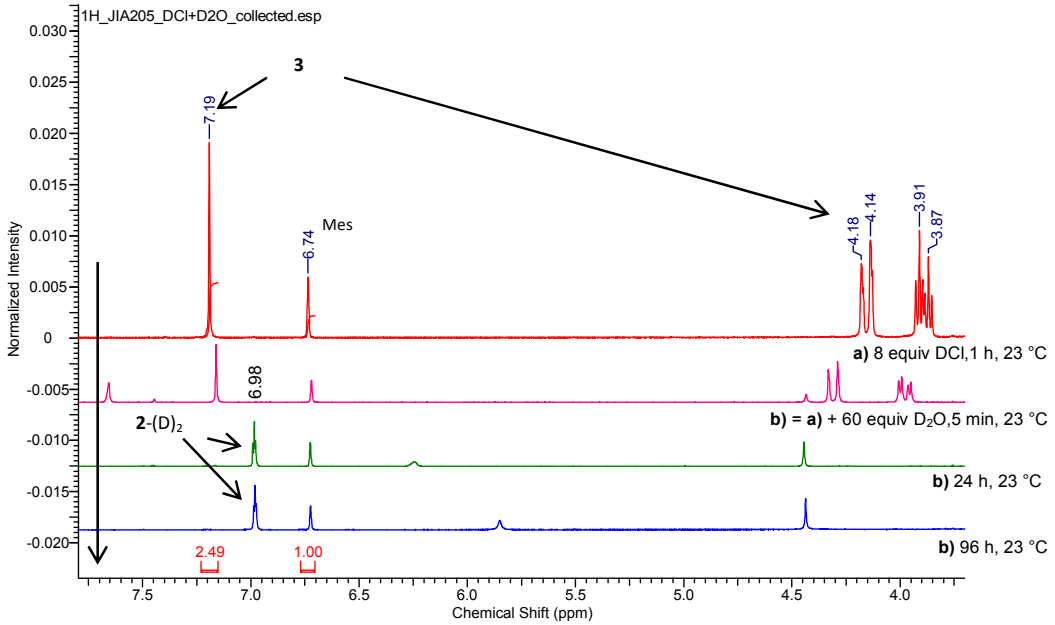
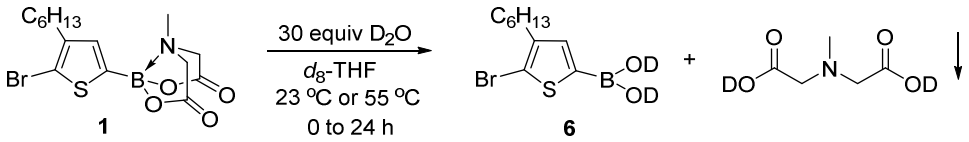


Figure S3. Collected ^{1}H NMR spectra in d_8-THF of the hydrolysis of **3** to **2-(D)$_2$**. Reaction conditions as in Equation S2.

The hydrolysis of BMIDA by water under these conditions is not specific to **3**, **1**, *p*-Me-PhBMIDA and *p*-F-PhBMIDA all undergo slow hydrolysis in THF/water mixtures to form the respective boronic acid with the MIDA diacid precipitating in each case under these conditions.



[Eq. S3]

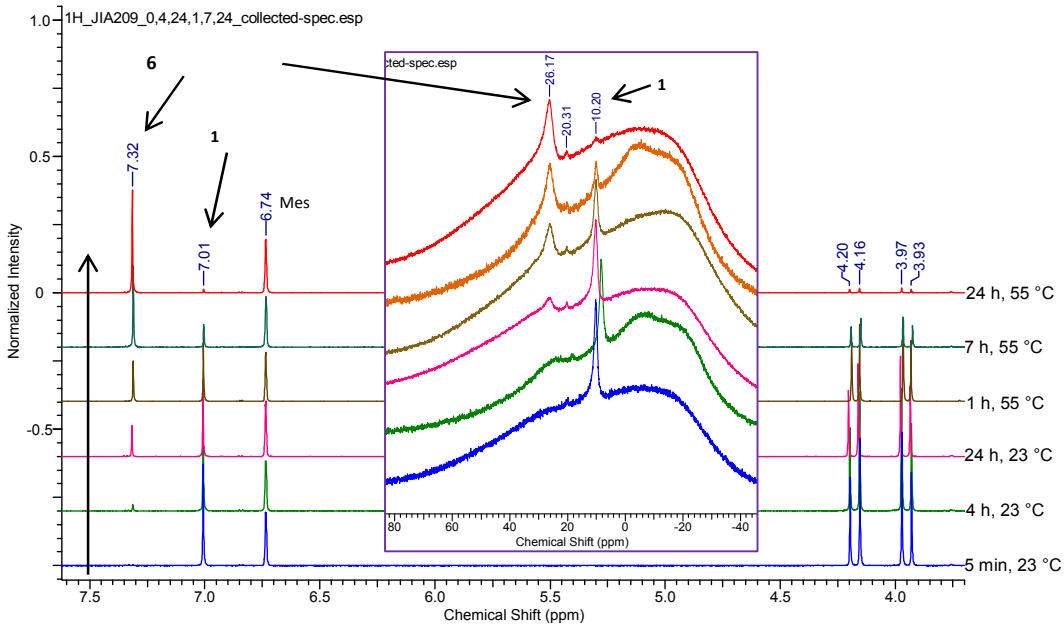
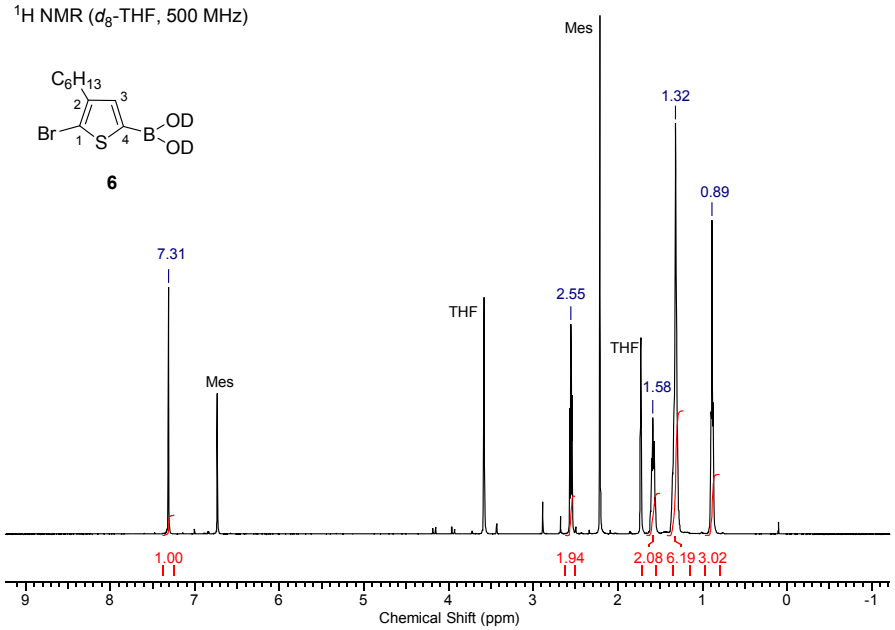


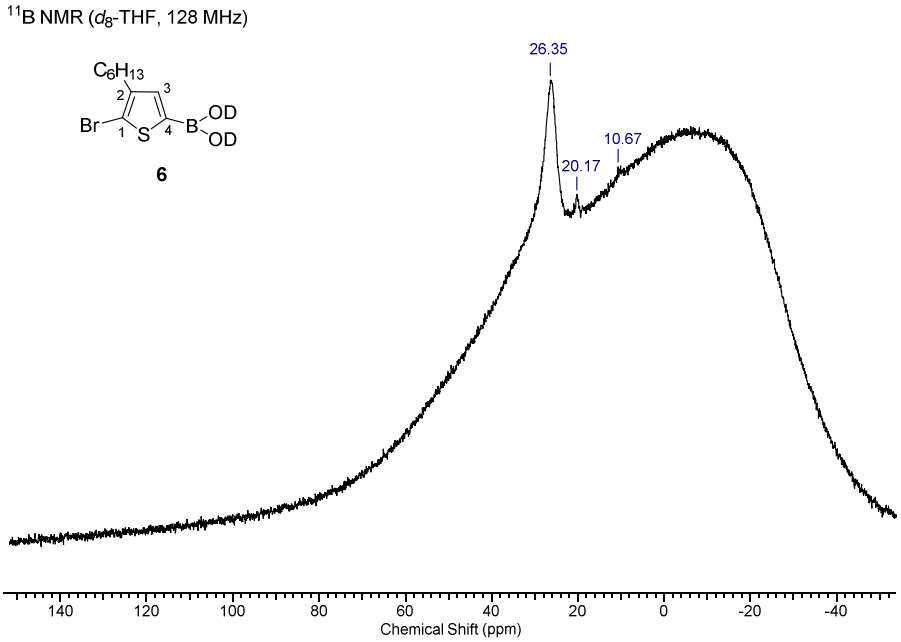
Figure S4. Collected partial ^{1}H NMR spectra in d_8-THF of the base free hydrolysis of **1** to **6**. Reaction conditions as in Equation S3. Mesitylene added as internal standard. Inset: Collected ^{11}B NMR spectra at the same time intervals.

In situ characterisation of **5-bromo-4-hexylthien-2-yl-boronic acid, 6**:

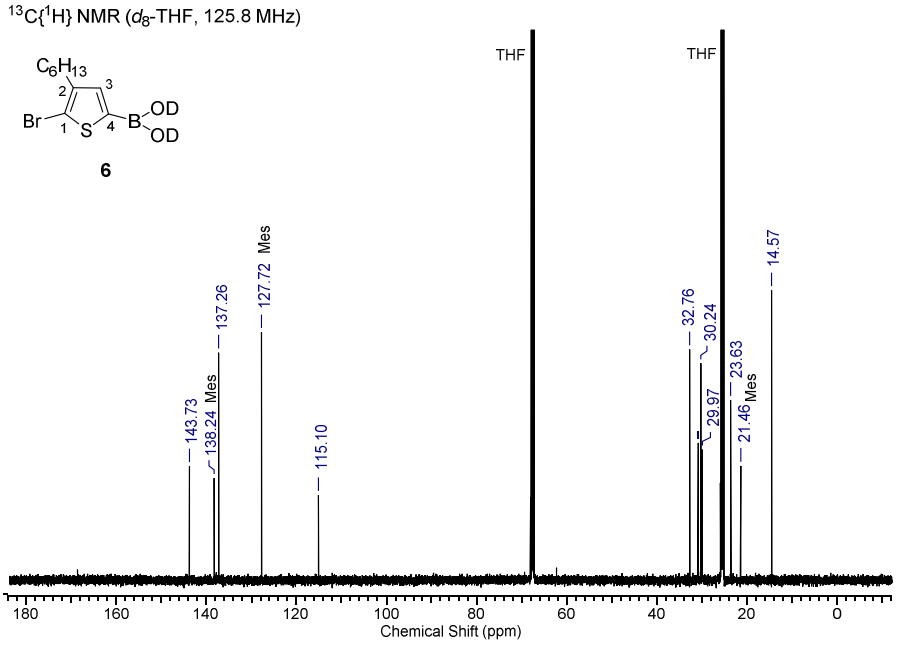
^{1}H NMR (500 MHz, d_8-THF): δ 7.31 (s, H), 2.55 (t, J = 7.63 Hz, 2 H, CH_2), 1.58 (m, 2 H, CH_2), 1.32 (m, 6 H, 3 × CH_2), 0. 89 (t, J = 7.02 Hz, 3 H, CH_3).
^{13}C{^{1}H} NMR (125.8 MHz, d_8-THF): δ 143.7 ($C2_{quat}$), 137.3 (C3-H), 115.1 ($C1_{quat}$), 32.8 (CH_2), 30.9 (CH_2), 30.2 (CH_2), 30.0 (CH_2), 23.6 (CH_2), 14.6 (CH_3).
^{11}B NMR (128.4 MHz, d_8-THF): δ 26.4 (bs).



Resonances at 6.74, 2.22, correspond to mesitylene (internal standard). Small resonances at 7.01, 4.17 (d), 3.95 (d), 2.68, correspond to residual **1**; and 3.43 and 2.89 correspond to free MIDA.

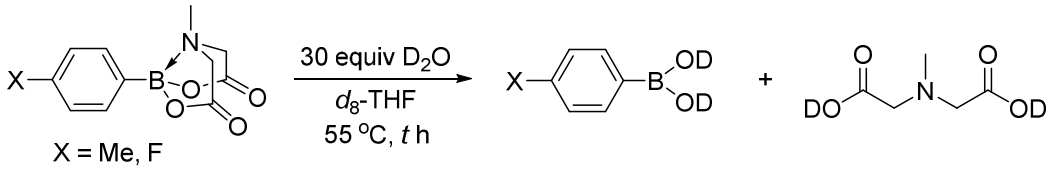


Resonance at 20.2 (s), corresponds to $B(OD)_3$, and small resonance at 10.7 (bs) corresponds to residual **1**.



Resonances at 138.2, 127.7, 21.5, correspond to mesitylene (internal standard).

Comparison of relative rates of hydrolysis of para-substituted arylBMIDAs.



[Eq. S4]

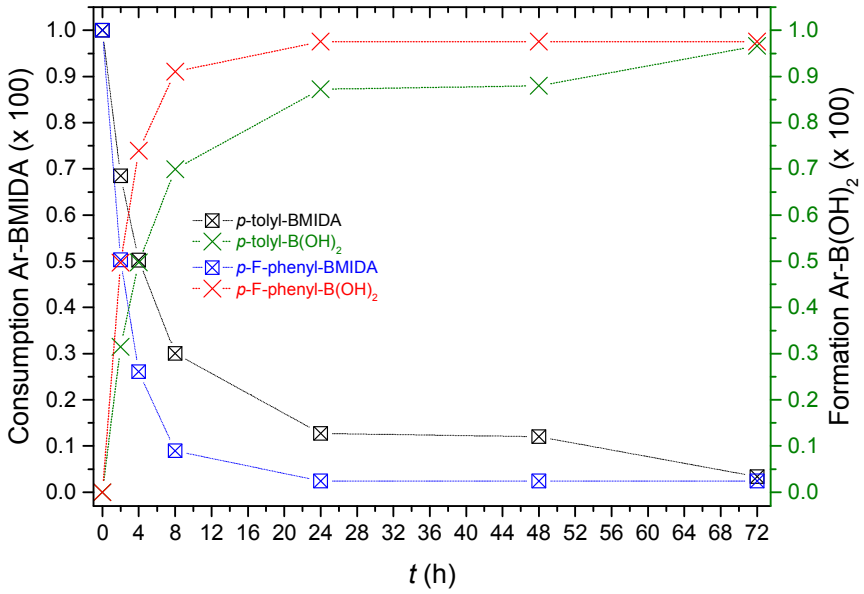
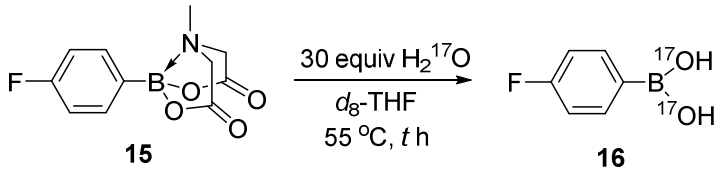


Figure S5. Kinetic profiles of hydrolysis of para-substituted arylBMIDAs under D_2O, and formation of their corresponding boronic acids, as depicted in Equation S4.

Hydrolysis of p-Fluorophenyl-MIDA boronate ester with 10% enriched ^{17}O-labelled water confirmed incorporation of ^{17}O on the boronic acid formed, and the NMR chemical shifts match previous reports.[6,7]



[Eq. S5]

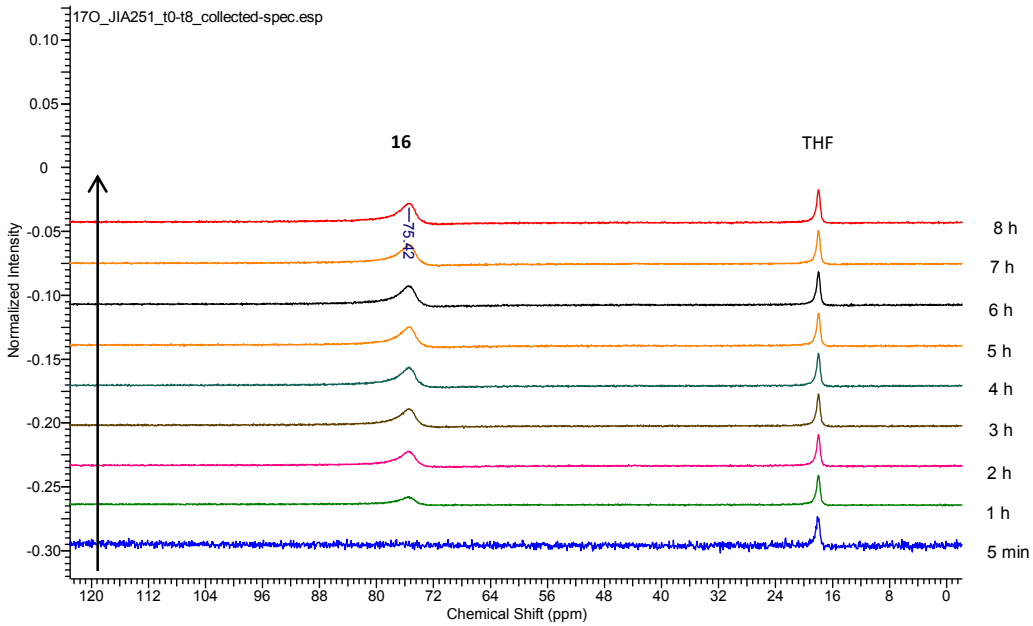
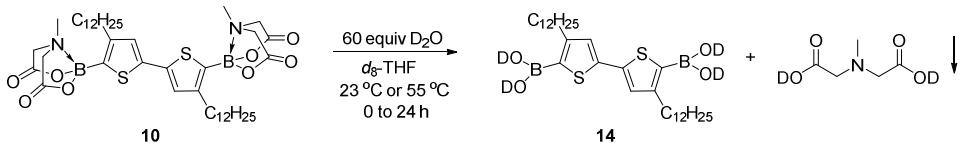


Figure S6. Collected ^{17}O NMR spectra in d_8-THF of the hydrolysis of **15** to **16**. Reaction conditions as in Equation S5.

H_2MIDA precipitates from this reaction mixture as a crystalline solid, isolation and analysis of the ^{17}O NMR spectrum of these crystals revealed no observable ^{17}O incorporation into H_2MIDA.



[Eq. S6]

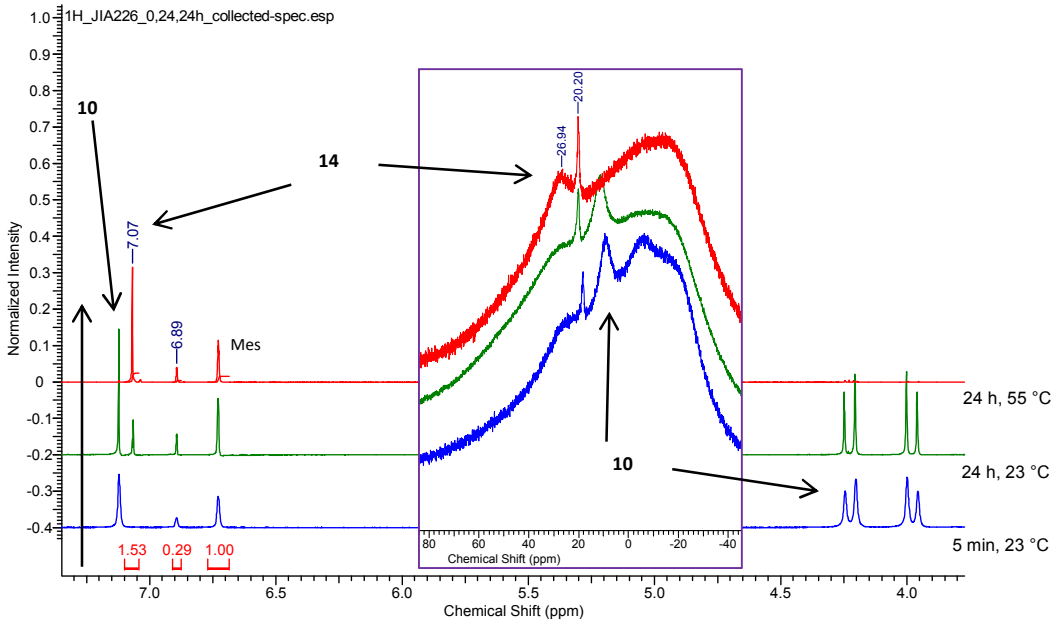
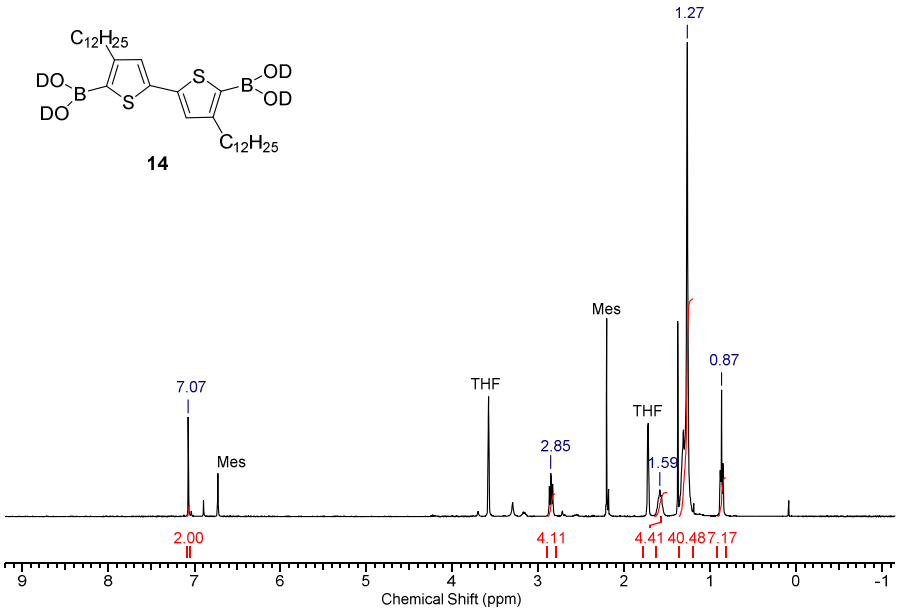


Figure S7. Collected ^{1}H NMR spectra in d_8-THF of the hydrolysis of **10** to **14**. Reaction conditions as in Equation S6. Integration of signal at 6.89 ppm (tentatively assigned as the d_2-isotopomer of the protodeboronation product) remains unchanged over time. Mesitylene added as internal standard. Inset: Collected ^{11}B NMR spectra at the same time intervals.

In situ characterisation of **4,4'-bis(dodecyl)-2,2'-bithiophene-2,7-diyl-bis-boronic acid, 14**:

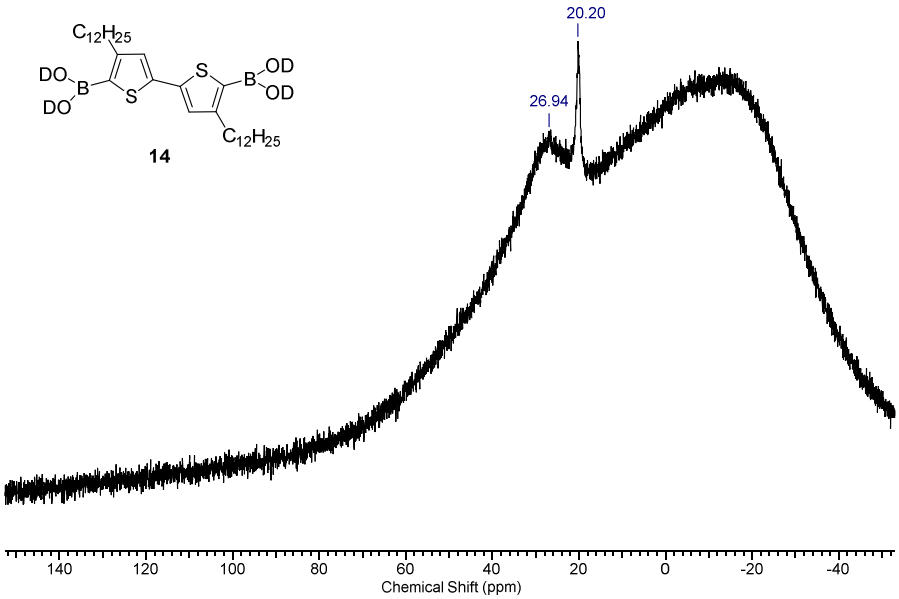
^{1}H NMR (400 MHz, d_8-THF): δ 7.07 (s, 2 H), 2.85 (t, J = 7.6 Hz, 4 H, 2 × CH_2), 1.59 (m, 4 H, 2 × CH_2), 1.27 (m, 40 H, 20 × CH_2), 0.87 (t, J = 6.7 Hz, 6 H, 2 × CH_3).
^{11}B NMR (128.4 MHz, d_8-THF): δ 27.0 (bs).

^{1}H NMR (d_8-THF, 400 MHz)



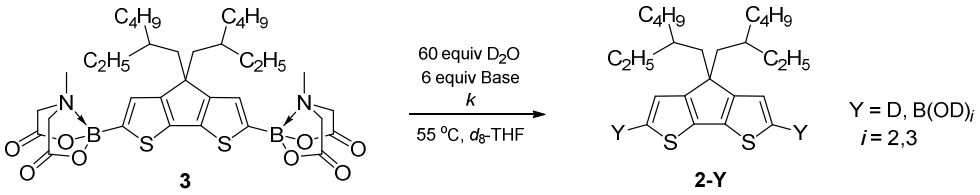
Resonances at 6.73, 2.20, correspond to mesitylene (internal standard). Resonance at 6.89 is tentatively assigned as the d_2-isotopomer of the protodeboronation product .

^{11}B NMR (d_8-THF, 128 MHz)



Resonance at 20.2 (s), corresponds to $B(OD)_3$

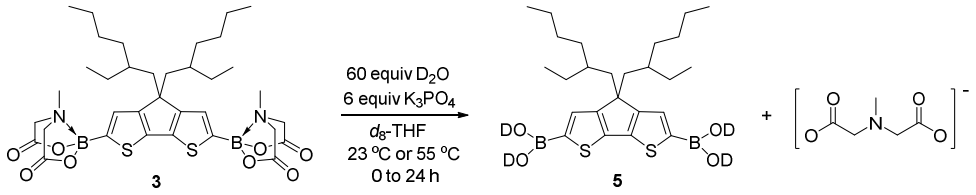
Monomer hydrolysis reactions general procedures



General Procedure (**GP2**) for kinetics experiments and in situ measurements. An oven-dried J. Young's NMR tube was charged under inert atmosphere with **3**, (1.0 equiv.), internal reference (mesitylene), and K_3PO_4 (6 equiv.), followed by addition of d_8-THF and D_2O (60.0 equiv), $[\mathbf{3}]_0 = 3.5 \times 10^{-2}$ M, and the reaction mixture was vigorously shaken to homogenise before recording its NMR spectra. Then it was rotated at ambient temperature or heated in an oil bath at 55 °C, and followed by NMR spectroscopy at different reaction times.

General Procedure (**GP3**) for kinetics experiments and measurements on extracted aliquots. A Schlenk ampoule fitted with a J. Young's tap containing a stirrer bar was charged with **3**, base (K_3PO_4), and d_8-THF, $[\mathbf{3}]_0 = 3.5 \times 10^{-2}$ M. After the mixture was set at 55 °C the desired amount of D_2O was added and the first aliquot was taken out of the reaction mixture for t_0 whilst the remaining mixture was stirred at 900 rpm. Each aliquot was quenched with 0.6 mL of CD_3CN (containing internal reference 0.05% mesitylene v/v) and NMR spectra were recorded. The same procedure was followed for each aliquot at the defined times.

Kinetics studies of the hydrolysis of the BMIDA moiety in 3: K_3PO_4/H_2O system



[Eq. S7]

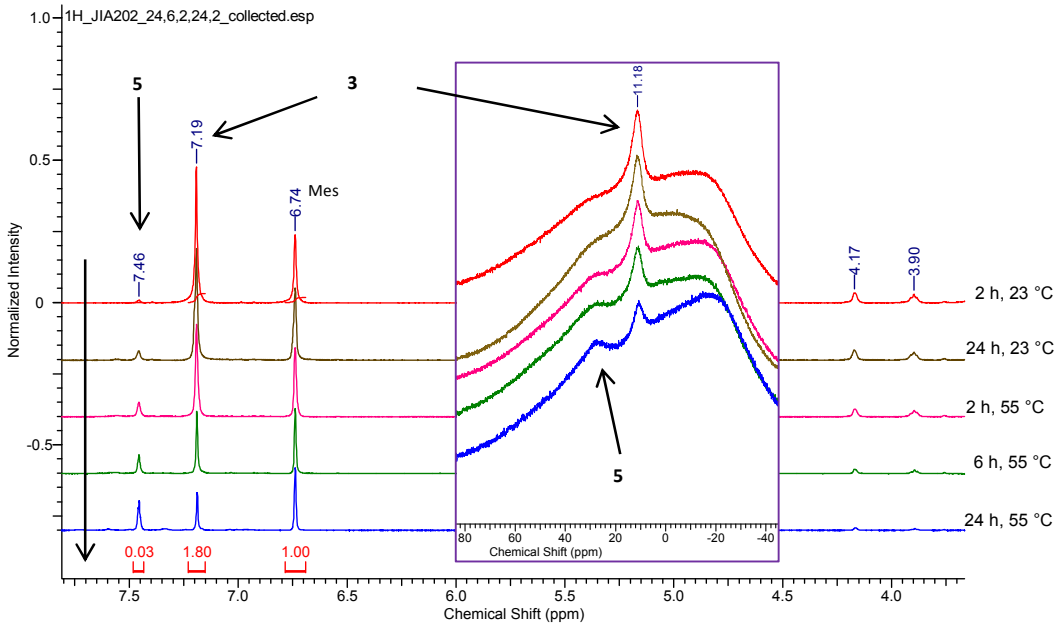


Figure S8. Collected ^{1}H NMR spectra in d_8-THF of the hydrolysis of **3** to **5**. Reaction conditions as in Equation S7 (performed in a J. Young's NMR tube). Inset: Collected ^{11}B NMR spectra at the same time intervals.

Direct comparison between the hydrolysis of **3** under not agitated vs stirred (900 rpm) conditions at 55°C:

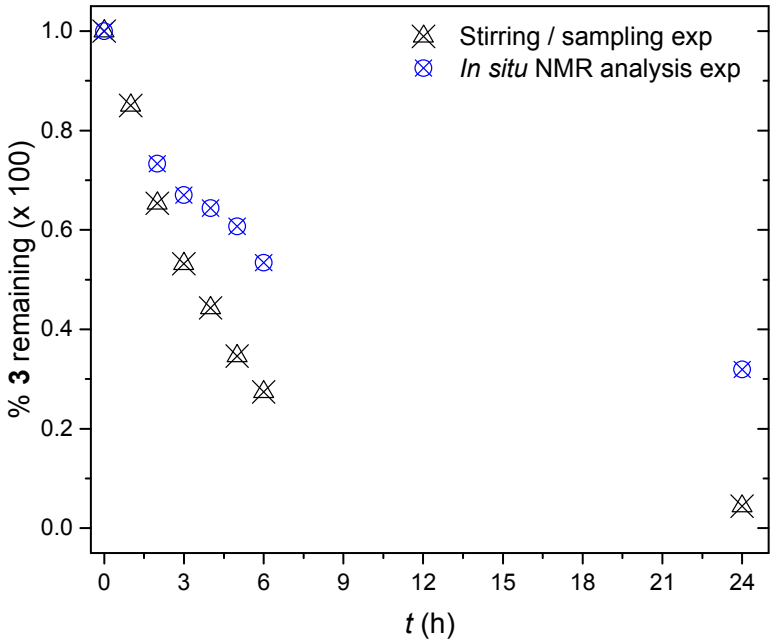
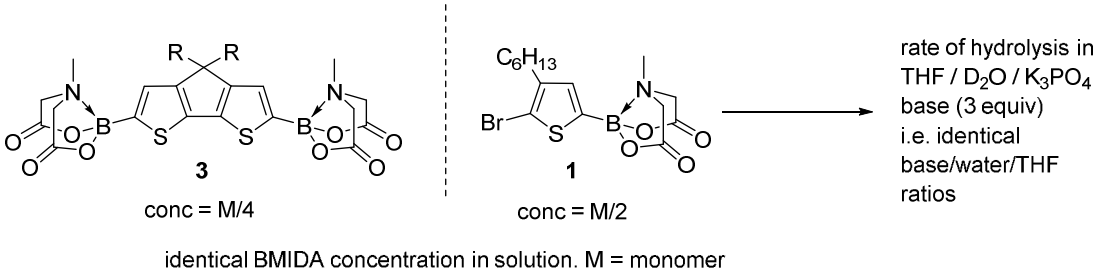


Figure S9. Kinetic profiles of the hydrolysis of **3** under two different experimental conditions: a) In a Schlenk tube fitted with a J. Young valve with stirring (900 rpm), and sampling/quenching for further NMR analyses (Triangle). b) In a J. Young's NMR tube without mixing, and *in situ* NMR analyses (Circle). Reaction conditions: 1:6:60 equivalents of **3**:K_3PO_4:D_2O in d_8-THF at 55 °C, $[\mathbf{3}]_0 = 3.5 \times 10^{-2}$ M.

Direct comparison between hydrolysis rate of **1** and **3**, under D_2O/K_3PO_4

A competitive BMIDA hydrolysis experiment was carried out as follows: hydrolysis of a 2:1 mixture of **1**/**3** in d_8-THF / D_2O (30 equiv. per BMIDA) / K_3PO_4 (3 equiv. per BMIDA) at 55 °C, $[\mathbf{1} + \mathbf{3}]_0 = 6.2 \times 10^{-2}$ M. The reaction mixture was monitored by NMR spectroscopy periodically.



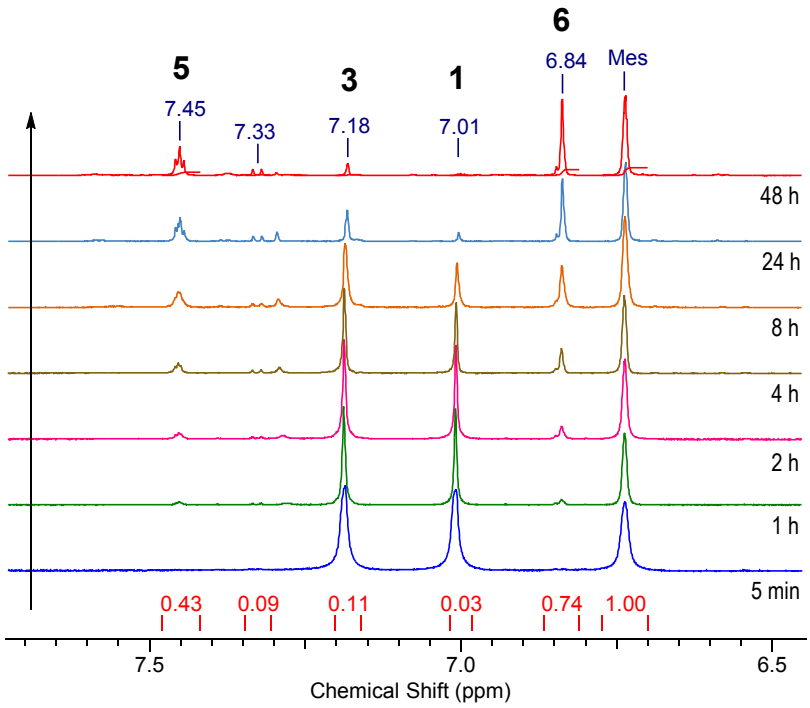


Figure S10. Collected partial ^{1}H NMR spectra of competitive hydrolysis of **1** and **3** (aromatic region, Mes = mesitylene as internal reference).

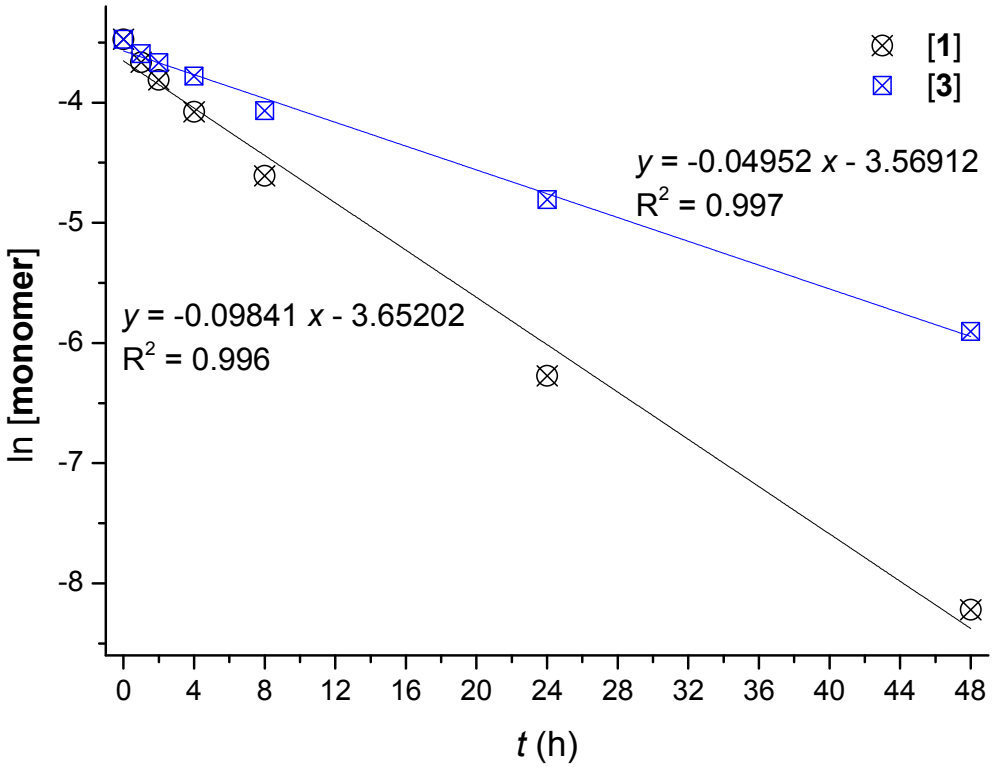


Figure S11. Pseudo-first order BMIDA hydrolysis kinetics of **1** and **3**.

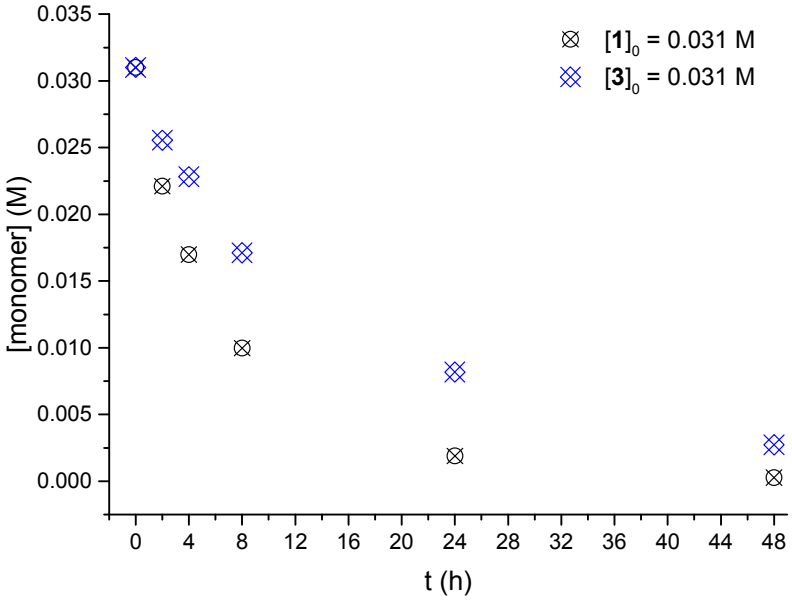


Figure S12. Kinetic profile of the hydrolysis of **1** and **3** in d_8-THF at 55 °C (with D_2O/K_3PO_4 base)

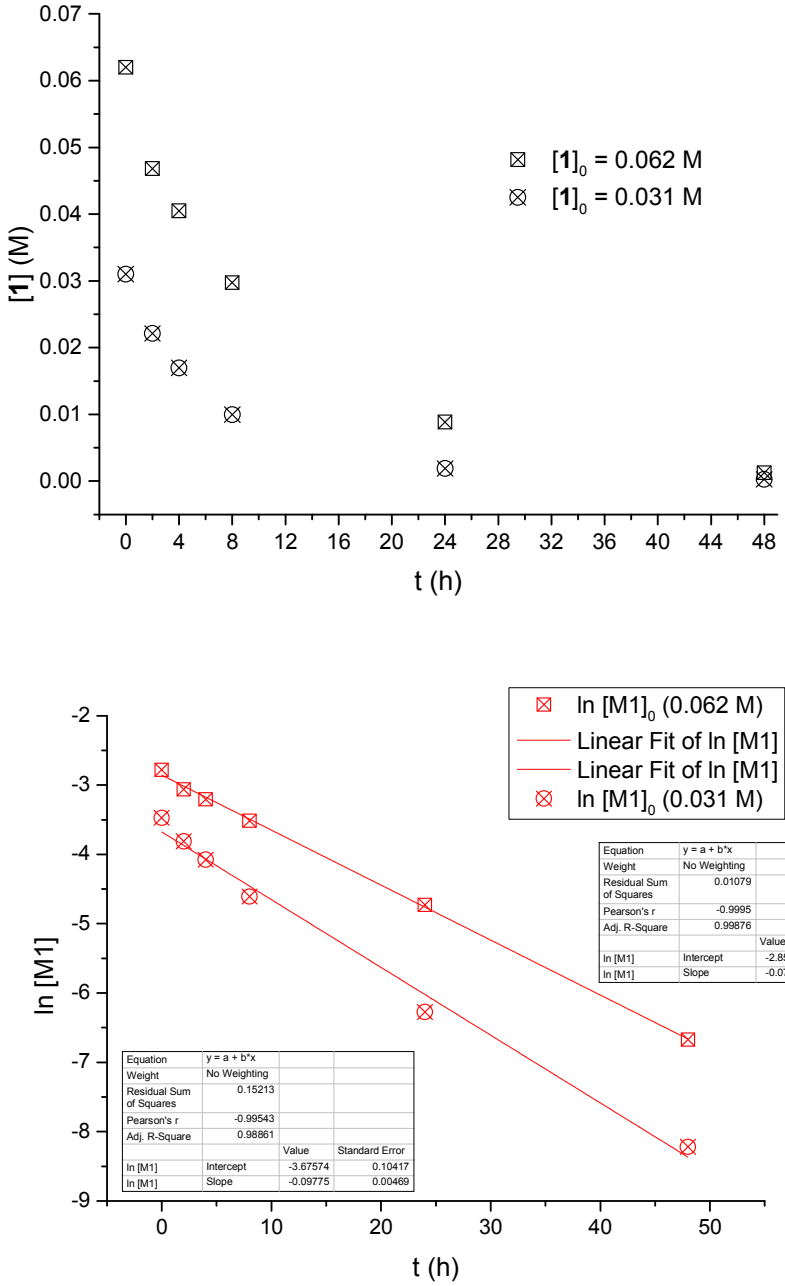


Figure S13. Top, kinetic profile of the hydrolysis of **1** in d_8-THF at 55 ^{o}C in the presence and absence of **3.** Bottom, pseudo first order kinetics showing minimal change in gradients (for the hydrolysis of **1**) in the presence/absence of CPDT-(BMIDA)$_2$ monomer **3**.

Kinetics studies of the hydrolysis of the BMIDA moiety in 3: KOH/H_2O system

In d_8-THF, the hydrolysis of **3** in the presence of 30 equivalents of D_2O and 3 equivalents of KOH per BMIDA moiety is faster than in the absence of base, and different from the K_3PO_4 case. Under these reaction conditions, at 55 °C (in J. Young's NMR tubes), hydrolysis of **3** follows a different rate, compared to its hydrolysis with D_2O both with and without K_3PO_4 (Figure S14).

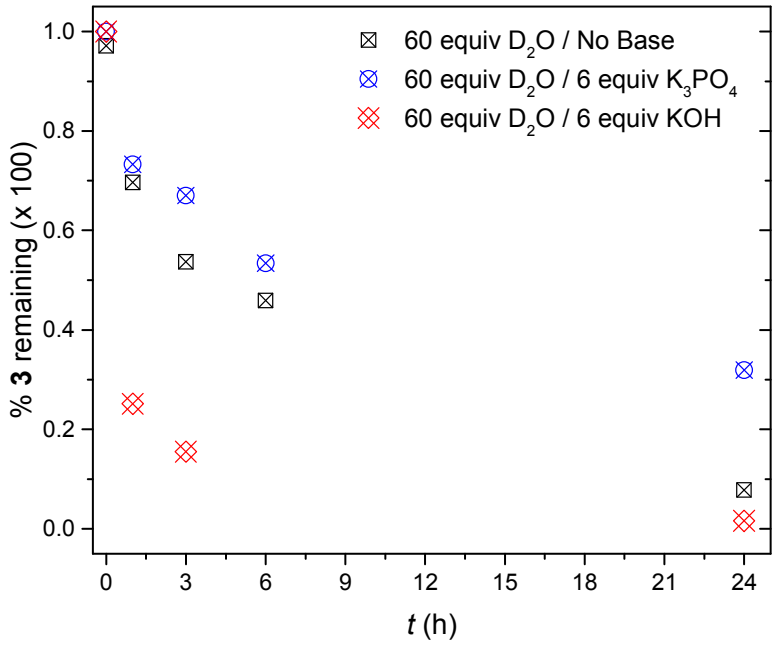
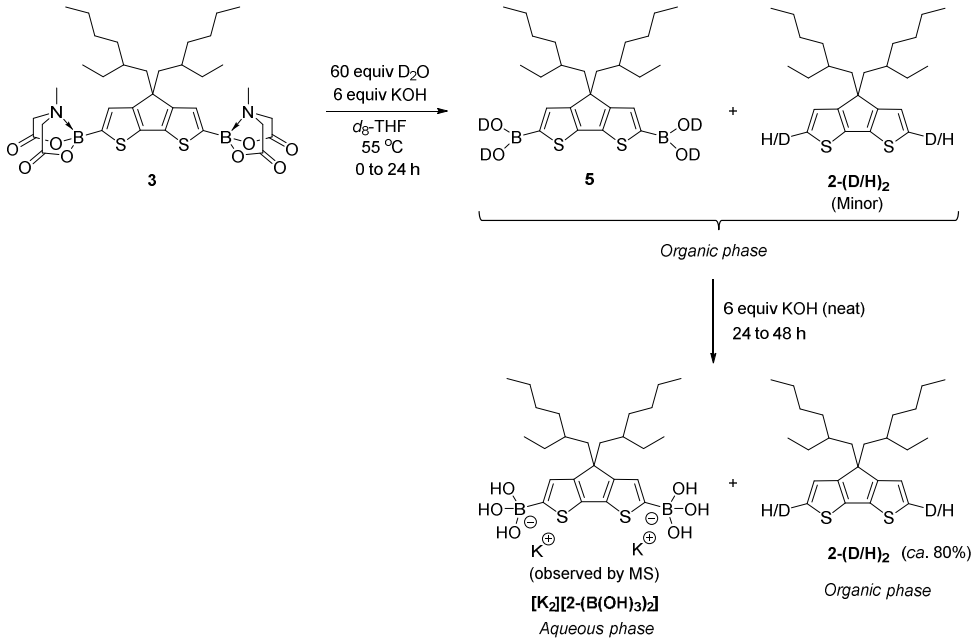


Figure S14. Kinetic profile of the hydrolysis of **3** in d_8-THF at 55 °C comparing the effect of base. Reaction conditions as described in Equation S7. D_2O:Base ratio as indicated.

In an attempt to observe the possible formation of the dianionic borate $[\mathbf{2\text{-}(B(OH)_3)_2}]^{2-}$ an additional quantity of KOH was added to the reaction mixture (additional 6 equiv. of KOH) (Equation S8). This excess of base promoted the complete disappearance of **5** in the organic phase which now consisted mainly of protodeborylated $\mathbf{2\text{-}(D/H)_2}$ with some degree of deuteration (~80% of $\mathbf{2\text{-}(D/H)_2}$, by ^{1}H NMR spectroscopy *versus* an internal standard). As the mass balance indicated that other CPDT-derived species should be present in the aqueous phase, this was isolated and analysed by electrospray ionisation mass spectrometry and NMR spectroscopy. The presence of a peak at *m*/*z* 602.55 confirmed the existence of the anionic borate intermediate, $\mathbf{[K_2][2\text{-}(B(OH)_3)_2]}$.



[Eq. S8]

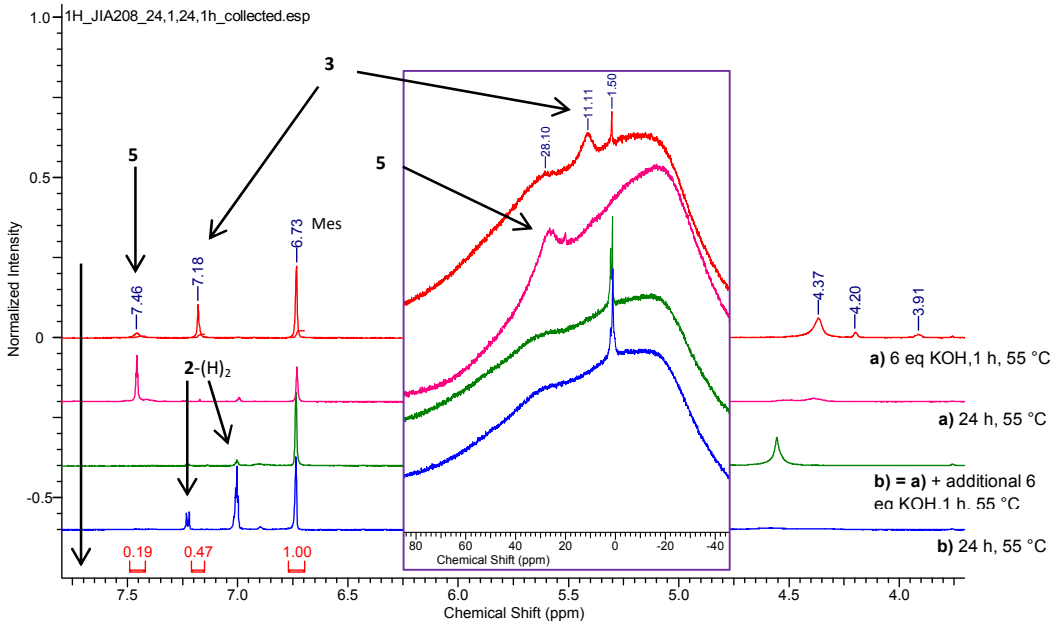
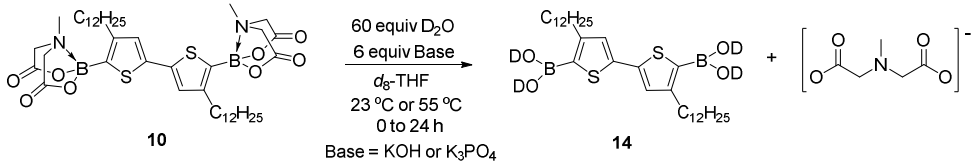


Figure S15. Collected partial ^{1}H NMR spectra of the hydrolysis of **3** to **5**. Reaction conditions as in Equation S8. Inset: Collected ^{11}B NMR spectra at the same time intervals (singlet at 1.50 ppm not assigned).

Kinetics studies of the hydrolysis of the BMIDA moiety in 10: K_3PO_4/H_2O and KOH/D_2O systems



[Eq. S9]

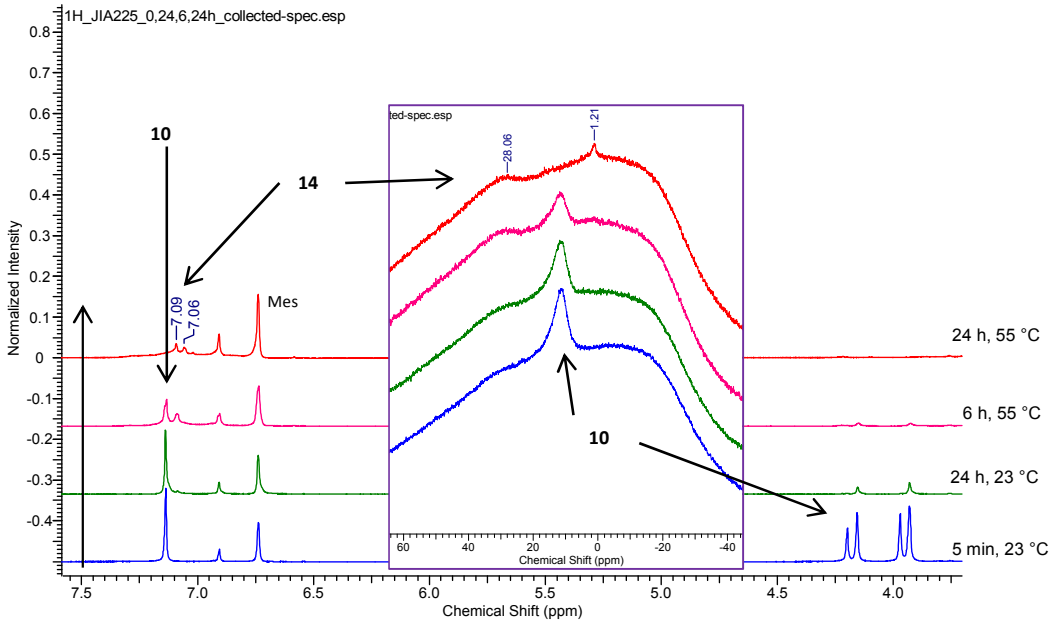


Figure S16. Collected partial ^{1}H NMR spectra in d_8-THF of the hydrolysis of **10** to **14**. Reaction conditions as in Equation S9, **Base = K_3PO_4**. Mesitylene added as internal standard. Integration of signal at 6.89 ppm (tentatively assigned as the d_2-isotopomer of the protodeboronation product) remains unchanged over time. Inset: Collected ^{11}B NMR spectra at the same time intervals.

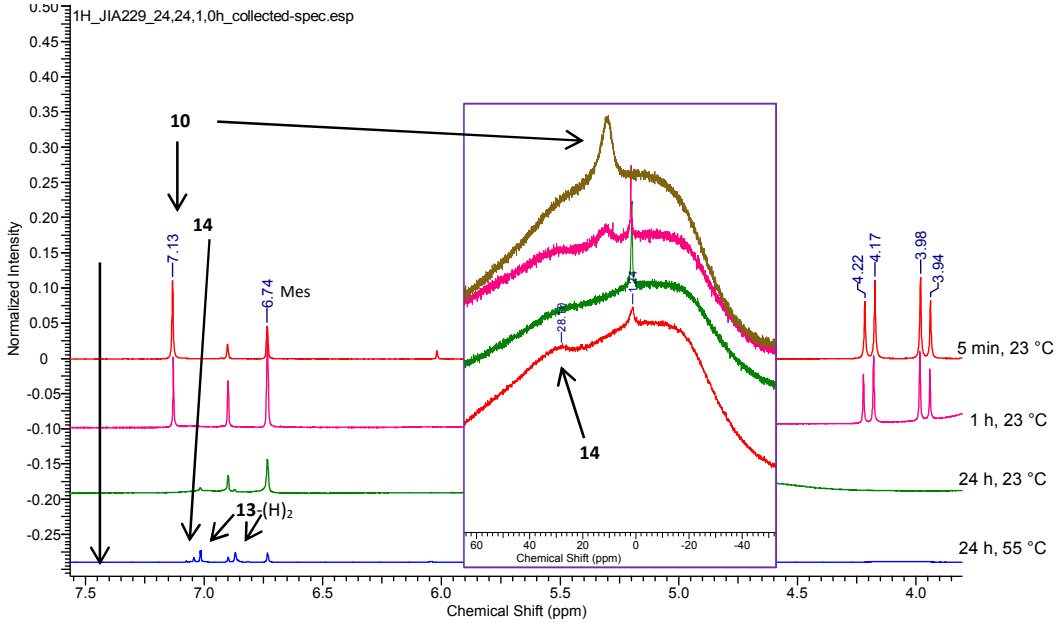
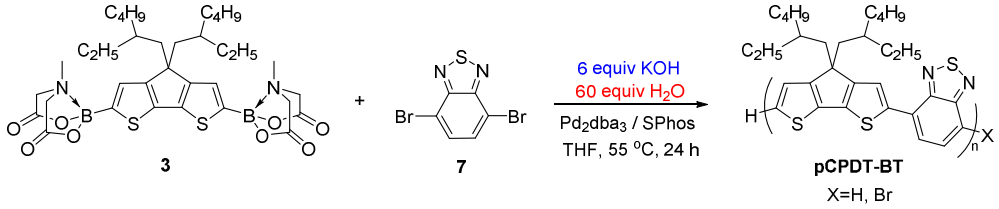


Figure S17. Collected ^{1}H NMR spectra in d_8-THF of the hydrolysis of **10** to **14**. Reaction conditions as in Equation S9, **Base = KOH**. Mesitylene added as internal standard. Integration of signal at 6.89 ppm (tentatively assigned as the d_2-isotopomer of the protodeboronation product) remains unchanged over time. Inset: Collected ^{11}B NMR spectra at the same time intervals.

Polymer synthesis studies

Polymer syntheses general procedures

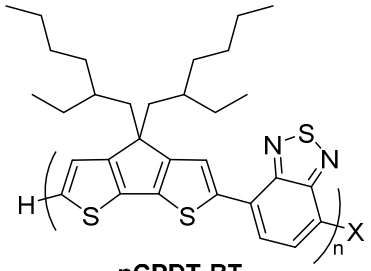


General Procedure (**GP4**) for optimised **pCPDT-BT** synthesis. An oven-dried Radley's carousel tube containing a stirrer bar was charged with **3** (1.0 equiv.), and **7** (1.0 equiv.). Dry and degassed THF was added and the reaction mixture was stirred until all components had completely dissolved, [**3**] = 3.5×10^{-2} M. Then the appropriate quantity of degassed KOH aqueous solution was added (**GP6**), and the system was heated to 55 °C for *ca*. 5 min. Subsequently, a freshly prepared palladium precatalyst in THF solution (**GP5**) was injected and the polymerisation was carried out with vigorous stirring (900 rpm) under a constant flow of N_2 gas. Aliquots of the reaction mixture were taken out of the solution (when required) at different times and precipitated in vigorously stirred HCl-acidified MeOH ([HCl] = 5×10^{-4} M) and NMR spectra recorded. At the end of the reaction, the crude mixture was quenched by precipitating it into an excess (fifty-fold by volume) of HCl-acidified MeOH. The collected polymeric solid material was dried overnight at ambient temperature under reduced pressure (1×10^{-2} mbar). Sequential MeOH, *n*-hexane and chlorobenzene fractions were collected by Soxhlet extraction, for 14 h at each stage or until the solvent in the Soxhlet chamber was colourless.

General Procedure (**GP5**) for preparation of the palladium precatalyst. An oven-dried J. Young's tube was charged under inert atmosphere with 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl "SPhos", and tris(dibenzylideneacetone)dipalladium, Pd_2dba_3 (2:1 mol of L/Pd, *e.g.*, 5 mol % of **3**). 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.

General Procedure (**GP6**) for preparation of KOH aqueous solution. A Schlenk flask was charged with KOH and dissolved with H_2O (1:10 mol of base/H_2O, *e.g.*, 0.63 mmol/6.30 mmol). The solution was degassed by continuous bubbling of N_2 gas for at least 1 h.

Poly[4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl], pCPDT-BT

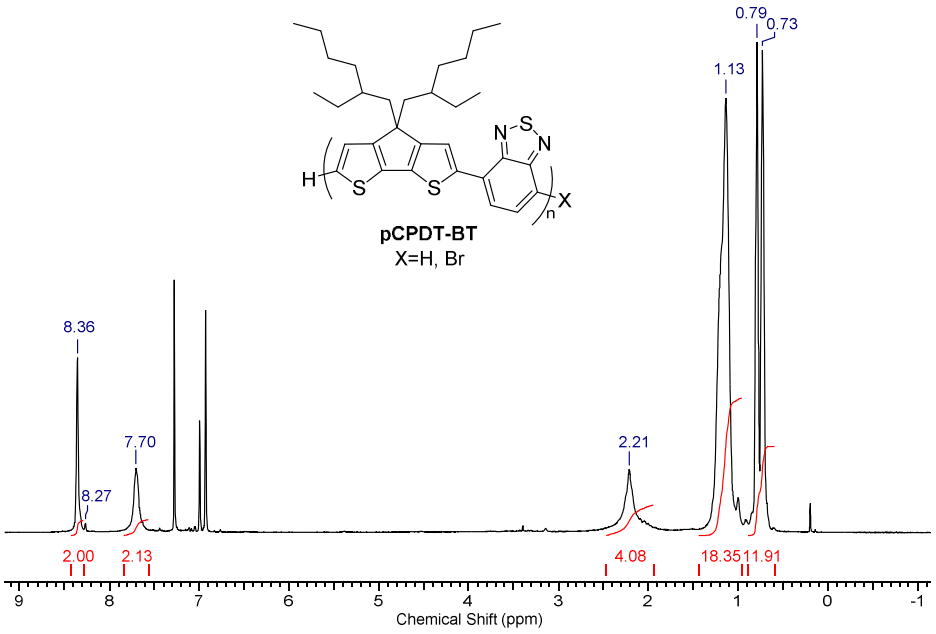


pCPDT-BT
X=H, Br

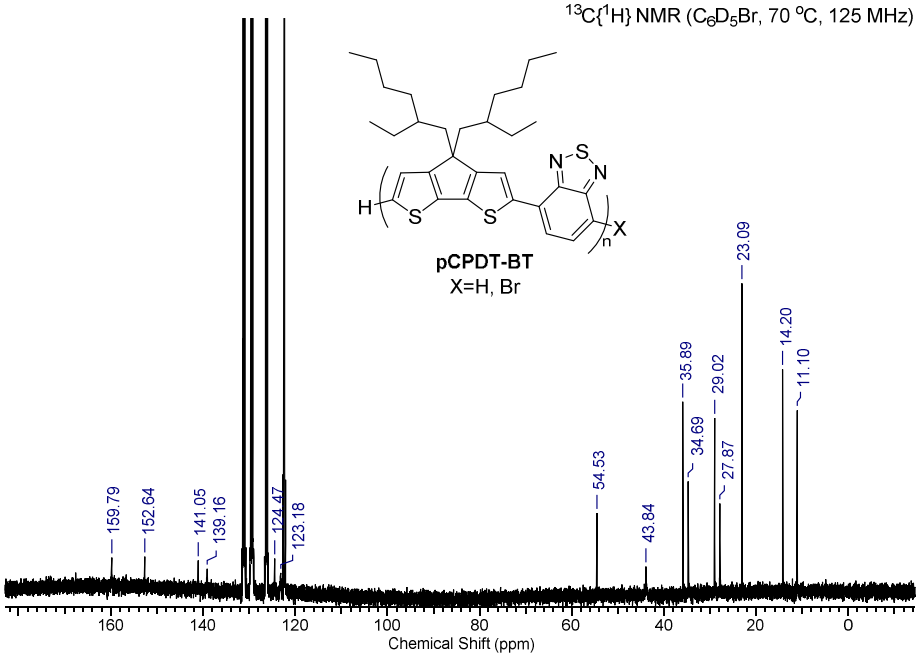
According to **GP4**: **3** (75.0 mg, 0.105 mmol) reacted with: **7** (31.0 mg, 0.105 mmol), KOH (35.3 mg, 0.630 mmol), H_2O (113 µL, 6.300 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (2.4 mg, 0.003 mmol) and SPhos (4.8 mg, 0.006 mmol) in THF (2.90 mL) over 24 h to afford after precipitation with HCl-acidified MeOH 56 mg (>99%) of crude polymer as a dark green solid. After Soxhlet extraction, 55 mg (98%) of dark blue **pCPDT-BT** was recovered from the chlorobenzene fraction.

^{1}H NMR (500 MHz, C_6D_5Br, 70 °C): δ 8.36 (s, 2 H, 2 × CH), 7.70 (bs, 2 H, 2 × CH), 2.21 (bs, 4 H, 2 × CH_2), 1.13 (m, 18H), 0.76 (d, J = 33.0 Hz, 12 H, 4 × CH_3)
^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Br, 70 °C): δ 159.8 (C_{quat}), 152.6, 141.1 (C_{quat}), 139.2, 124.5, 123.2, 54.5 (C_{quat}), 43.8 (CH_2), 35.9 (CH), 34.7 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 23.1 (CH_2), 14.2 (CH_3), 11.1 (CH_3)
Elemental Analysis: Trace of Pd found, <0.1%, by ICP.
UV-vis (C_6H_5Cl solution at 23 °C): λ_{max} = 730 nm; ε = 44294 M^{-1} cm^{-1}
GPC (1,2,4-trichlorobenzene, 160 °C, PS calibration): M_n = 42.5 kDa; M_w = 130.0 kDa

^{1}H NMR (C_6D_5Br, 70 °C, 500 MHz)



^{13}C{^{1}H} NMR (C_6D_5Br, 70 °C, 125 MHz)



GPC analysis from PSS Polymer Standards Service GmbH:

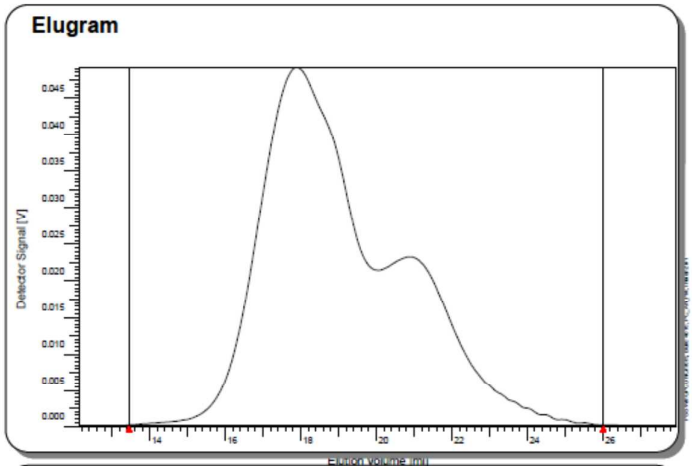
Sample preparation

The samples were weighted exactly and 1,5 ml 1,2,4-Trichlorobenzene were added.

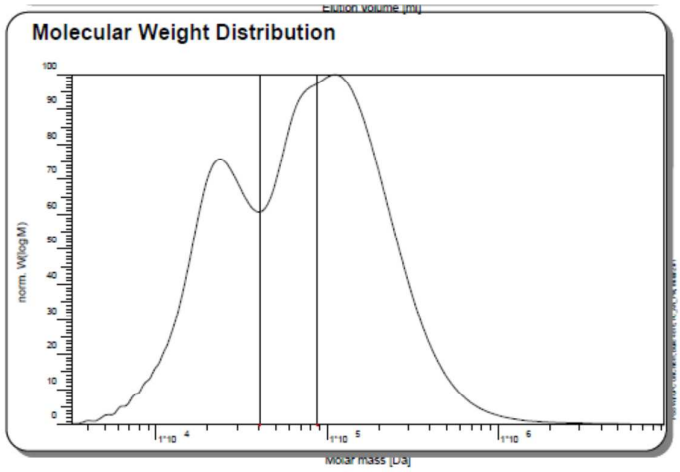
After 2 hours dissolving at 160°C the samples were injected twice with 200 µl into the SEC.

Method Information

Project:	W:\GPC_DATEN\AN\LC\serv_16\serv_16_PG14.LDX	Injection time:	29.04.2016 14:15:28
GPC instrument:	PG 14, Agilent PL-210-HT	Operator:	pm
Calibration type:	Conventional	Calibration fit:	PSS Poly 5
Calibration file:	ps-160°C-SDV AK-TCB-Merck-22-04-16.CAL	Int. standard:	keiner
Vp int. standard calib.:	50,00 mL	Vp int. standard sample:	0,00 mL
Injection volume:	200 µL		
Sample concentration:	3,000 g/L	temperature:	160,0 °C
Eluent:	1,2,4-trichlorobenzene	Flow rate:	1,00 mL/min
Columns:			



Baseline from: 12,14 mL to: 27,95 mL
Integration from: 13,45 mL to: 26,01 mL



Detector	Fraction % M < 40280 Da	Fraction % M < 87680 Da
RID	31,06	54,97

Detector	Fraction % M > 87680 Da
RID	45,03

	Detector	Mn /Da	Mw /Da	Mz /Da	PDI (=Mw/Mn)	Vp /mL	Mp /Da	Area /(mL*V)
—	RID	42500	130000	736000	3,07	17,90	127000	0,1922

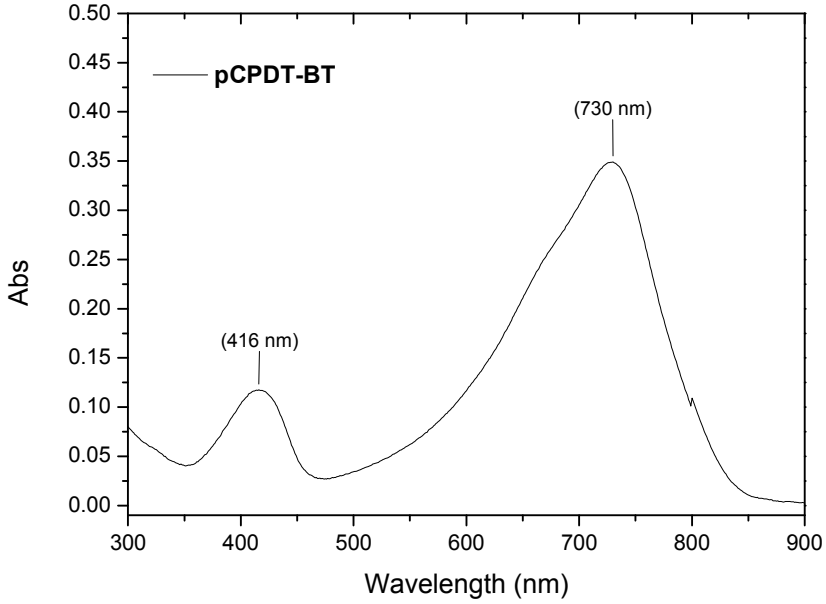


Figure S18. UV-vis spectrum of **pCPDT-BT** in C_6H_5Cl at room temperature.

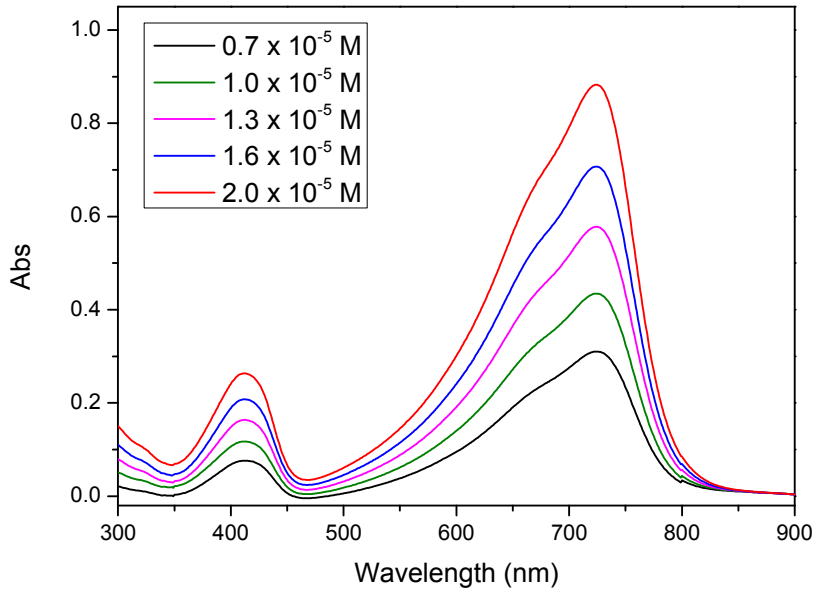


Figure S19: Uv-vis spectra of **pCPDT-BT** in chlorobenzene at varying concentrations at ambient temperature.

For comparison pCPDT-BT made via Stille coupling has an absorption maxima in ortho-dichlorobenzene at room temperature of 736 nm.[8]

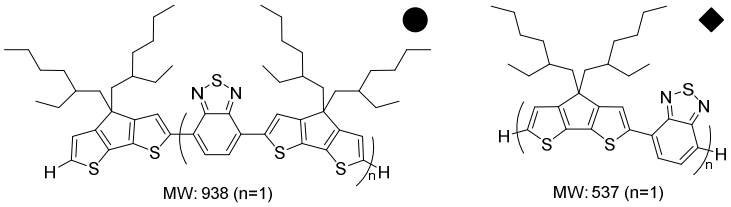


Chart S1. **pCPDT-BT** chain fragments from the reaction of **3** and **7** with 6 equiv. KOH with different end groups observed by MALDI-TOF spectrometry.

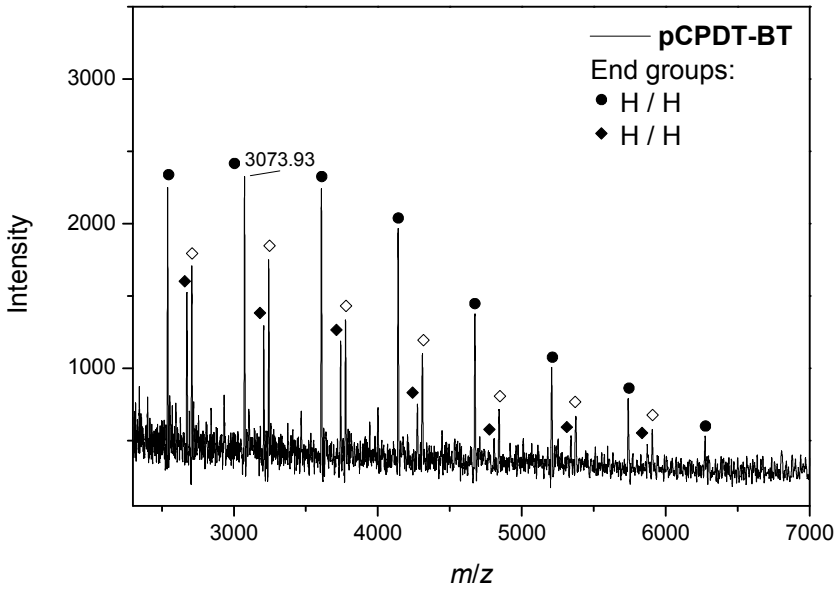
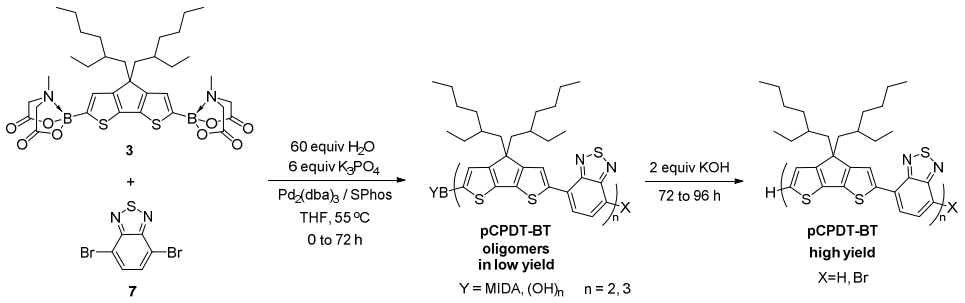


Figure S20. MALDI-TOF spectrum of **pCPDT-BT** (made using 6 equiv. KOH). End groups as shown in Chart S1. Blank diamonds corresponds to ♦ + 35 uma adducts. Sample after Soxhlet fractionation, C_6H_5Cl fraction.

Polymerisation studies of 3 using 7 as a model comonomer

As explained in the main text, polymerisation of **3** with **7** started employing K_3PO_4 as base, Eq. S10:



[Eq. S10]

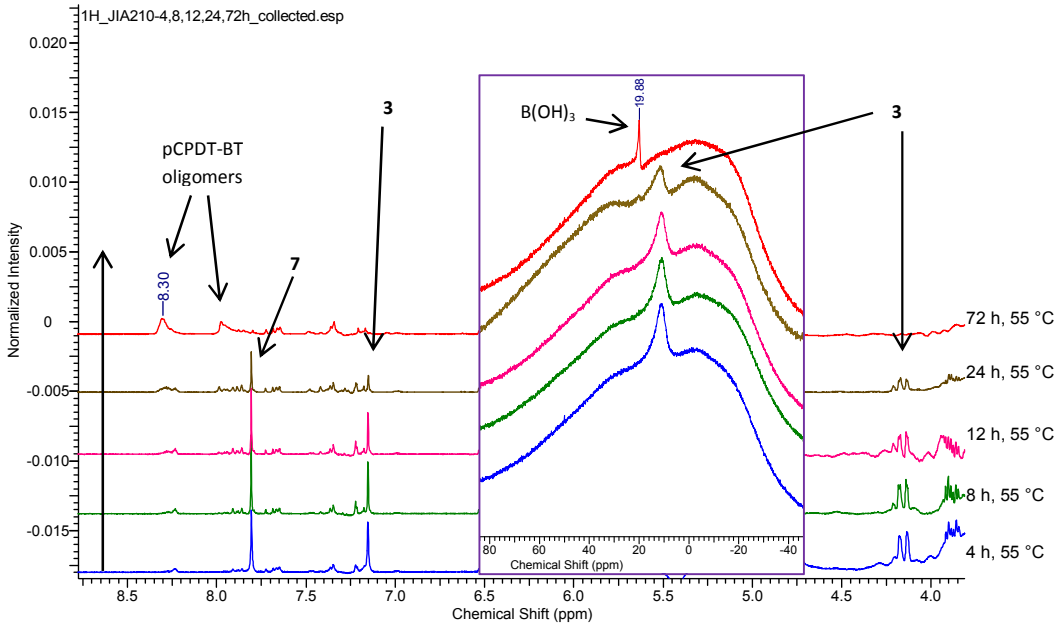


Figure S21. Collected ^{1}H NMR spectra of aliquots extracted from the polymerisation of **3** and **7**. Reaction conditions as in Equation S10. Inset: Collected ^{11}B NMR spectra at the same time intervals. Significant **3** (or other CPDT-BMIDA species) is still present after 24 h at 55^{o}C.

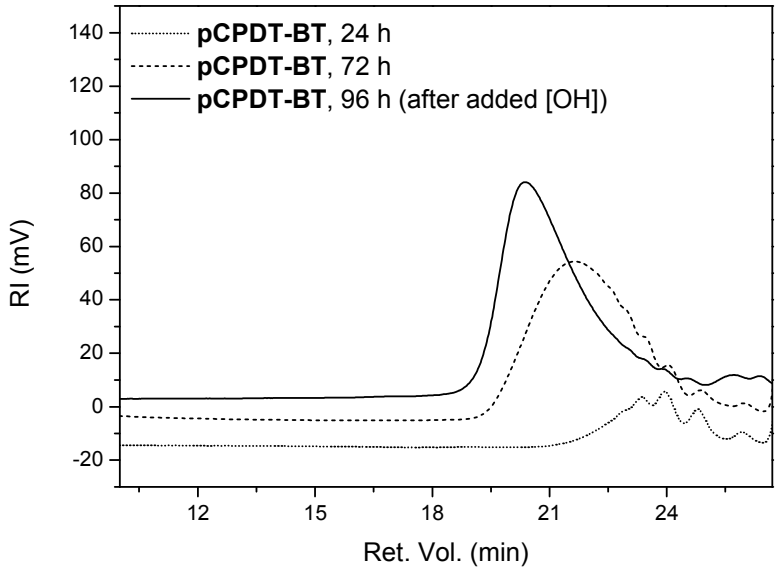
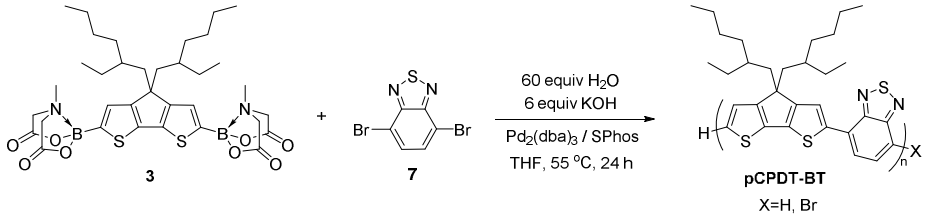


Figure S22. GPC traces of the crude **pCPDT-BT** samples collected at different times of reaction (THF at 35 °C, PS calibration). Reaction conditions as in Equation S10.

When the polymerisation of **3** with **7** employed KOH as base, Eq. S11:



[Eq. S11]

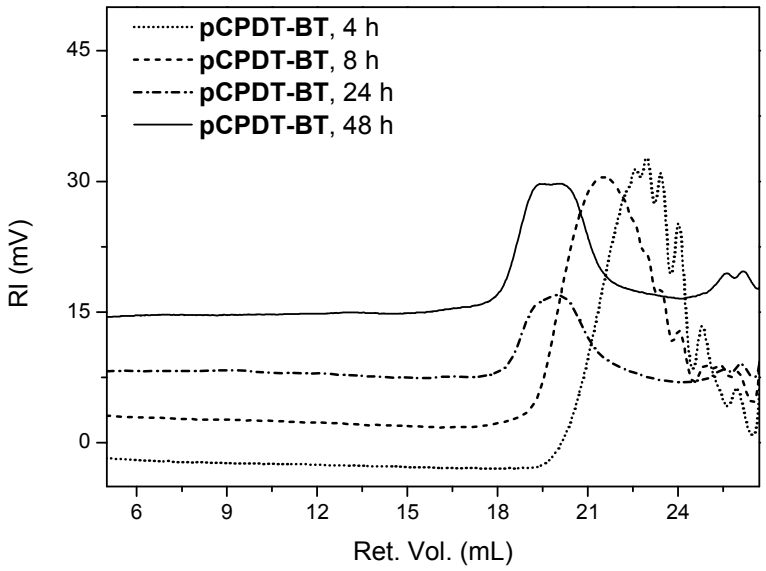


Figure S23. GPC traces of the reaction of **3** and **7** at different times: crude **pCPDT-BT** samples collected (THF at 35 °C, PS calibration). Reaction conditions as in Equation S11. Polymerization is complete after 24 h by GPC analysis.

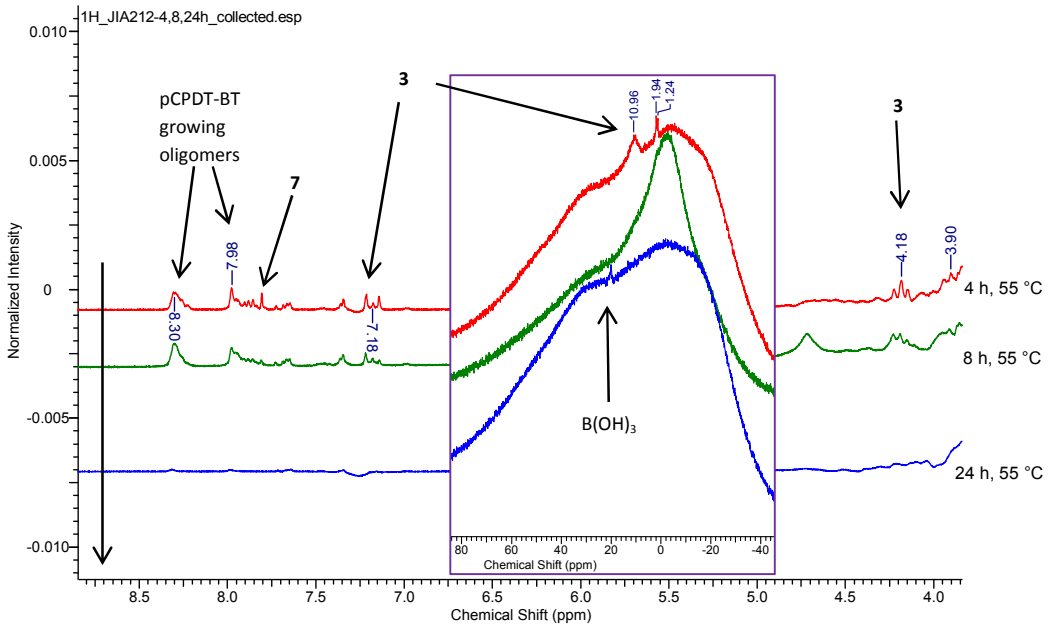
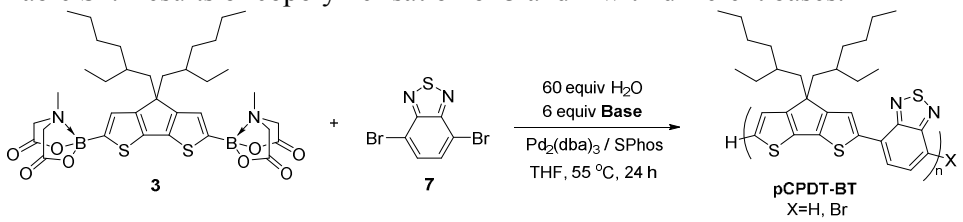


Figure S24. Collected ^{1}H NMR spectra of the polymerisation of **3** and **7**. Reaction conditions as in Equation S11. Inset: Collected ^{11}B NMR spectra at the same time intervals. No **3** (or other CPDT-BMIDA containing moieties) are observed after 24 h at 55^{o}C.

Effect of base on polymerisation of **3** and **7**:

Table S1. Results of copolymerisation of **3** and **7** with different bases.[a]



Entry[b]	Base	Yield[c] (%)	M_n[d] (kDa)	M_w[d] (kDa)	$Đ_M$[d]
1	K_3PO_4	<12	1.5	2.7	1.8
2	KOH	>99	21.5	40.4	1.9
3	[*n*Bu$_4$N][OH]	~75	3.0	5.7	1.9

[a]Reaction conditions: *T*: 55 °C, [**3**] = 3.5 × 10^{-2} M, Base: 6 equiv., H_2O: 60 equiv, $Pd_2(dba)_3$: 2.5 mol%, SPhos: 5 mol%, solvent: THF, *t*: 24 h, reaction quenched with 2.5% HCl-acidified MeOH. [b]Crude polymer samples. [c]Isolated. [d]Determined by GPC (THF at 35 °C, PS calibration).

When co-polymerisation of **3** with **7** was carried out using nBu$_4$NOH as base instead of KOH, (in situ) analysis of the polymerisation progress showed no significant chain growth over time (Reaction conditions as in Table S1):

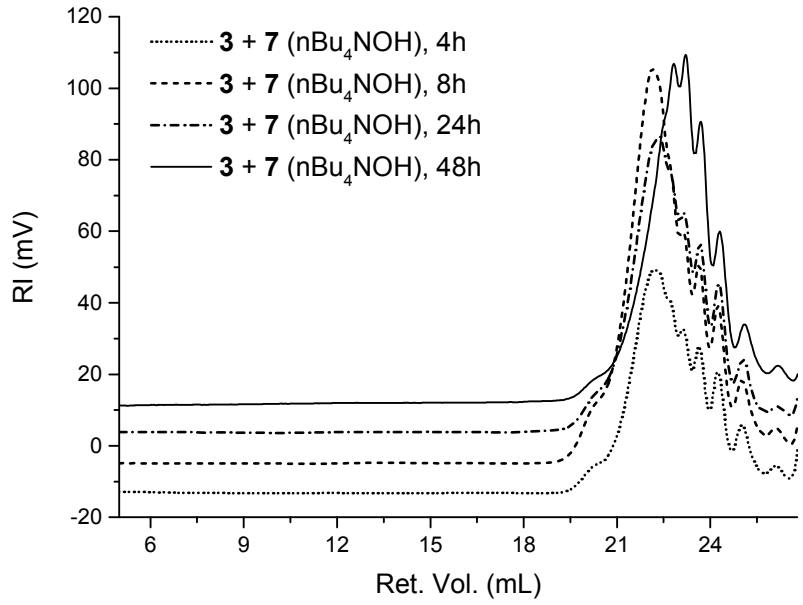


Figure S25. Collected GPC traces of the polymerisation of **3** and **7** using nBu$_4$NOH. Reaction conditions as in Table S1.

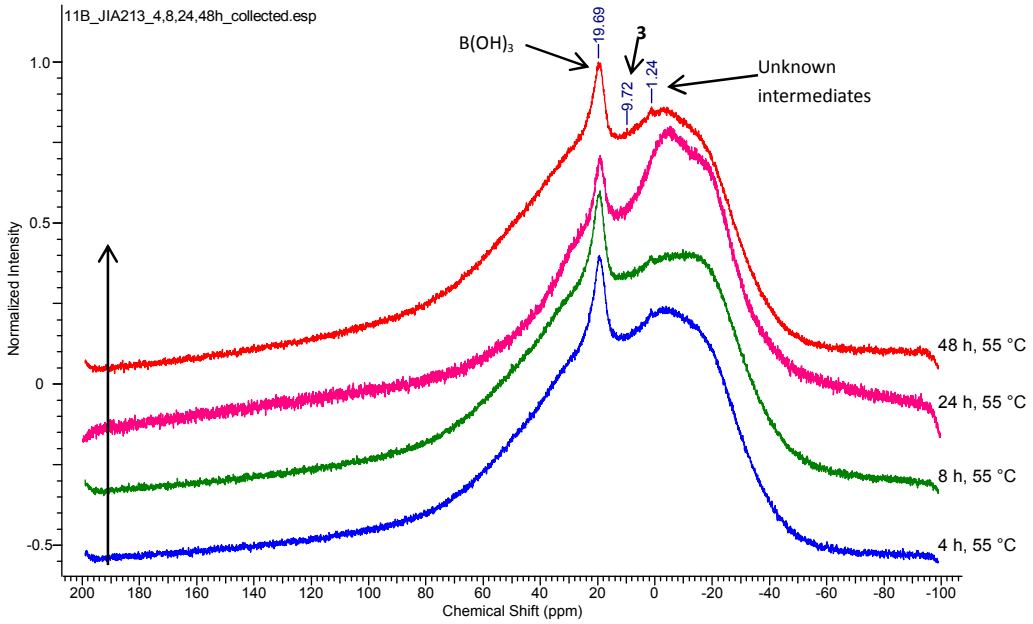


Figure S26. Collected ^{11}B NMR spectra of the polymerisation of **3** and **7** using nBu_4NOH. Reaction conditions as in Table S1. No **3** (or other CPDT-BMIDa species) are observed after 4 h at 55°C.

It is worth to mention that when preparing the samples from KOH as base for GPC analyses in THF, not all the polymeric sample (typically 1 mg/mL) could be fully dissolved even in boiling THF, therefore, the molecular weights quoted in THF are actually lower than the true polymer M_w/M_n values. Thus, for the subsequent GPC analyses, the studies were carried out in chlorobenzene at 70 °C (Figure S27) or in 1,2,4-trichlorobenzene at 160 °C by external company PSS (see above) .

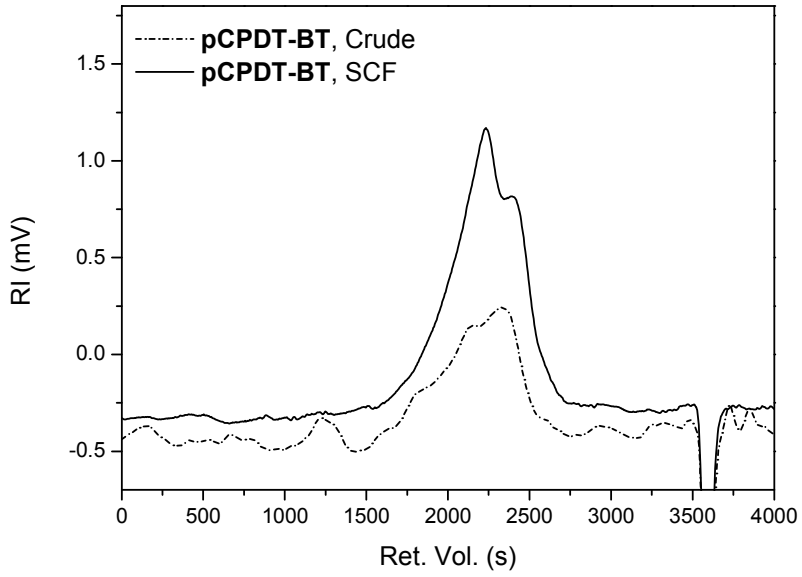
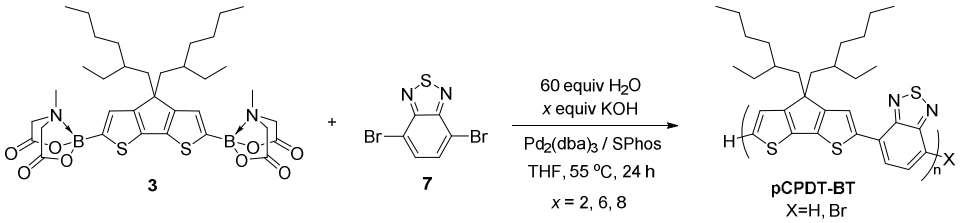


Figure S27. GPC traces of crude, and Soxhlet chlorobenzene fraction (SCF) of **pCPDT-BT** samples (C_6H_5Cl at 70 °C, PS calibration). Peak at 3600 s corresponding to toluene, added as internal marker.

Effect of KOH equivalents on polymerisation of **3** and **7**:

Table S2. Results of copolymerisation of **3** and **7**, utilising different quantities of KOH.[a]



Entry	KOH (equiv)	M_p[b] (kDa)	Soxhlet fraction[c]	Yield[d] (%)
1	2	---[e]	crude	---[e]
2	6	42.5	crude	>99
3	6	30.0[f]	C_6H_5Cl	99
4	8	20.3	crude	95[g]
5	8	18.3	C_6H_5Cl	80[g]

[a]Reaction conditions: *T*: 55 °C, [**3**] = 3.5×10^{-2} M, KOH: *x* equiv, H_2O: 60 equiv, $Pd_2(dba)_3$: 2.5 mol %, SPhos: 5 mol %, solvent: THF, *t*: 24 h, reactions run twice, quenched with 2.5% HCl-acidified MeOH. [b]Determined by GPC (C_6H_5Cl at 70 °C, PS calibration). M_w/M_n not quoted due to traces out of the calibration curve range in the high molecular weight region. [c]Soxhlet-fractionated C_6H_5Cl fraction after sequential extractions with MeOH, and *n*-hexane, for 14 h each or until colourless solvent in the Soxhlet chamber. [d]Isolated. [e]No polymer. [f]Corresponding to the second peak at higher retention time. [g]Average of multiple runs.

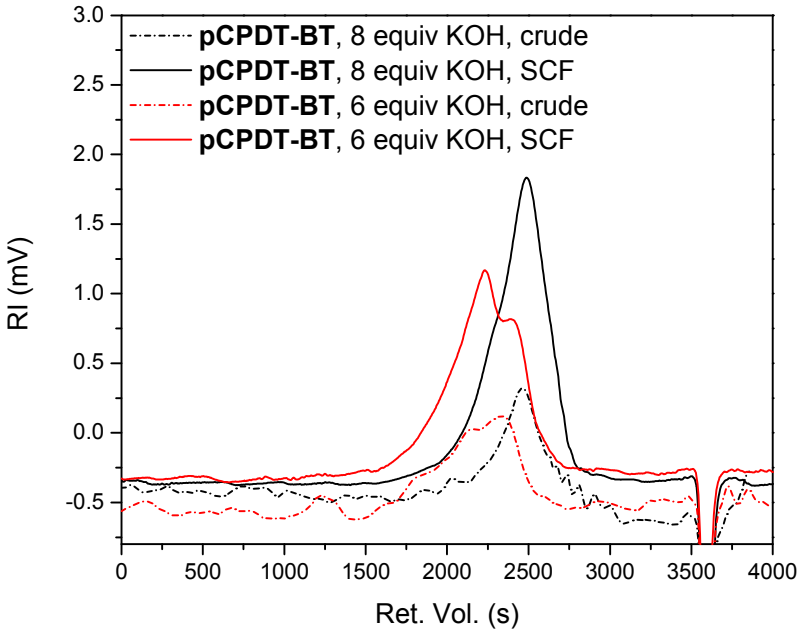


Figure S28. GPC traces of crude and Soxhlet C_6H_5Cl fraction (SCF) samples of **pCPDT-BT** (C_6H_5Cl at 70 °C, PS calibration). Reaction conditions as in Table S2. Negative peak at 3600 s corresponding to toluene, added as internal marker.

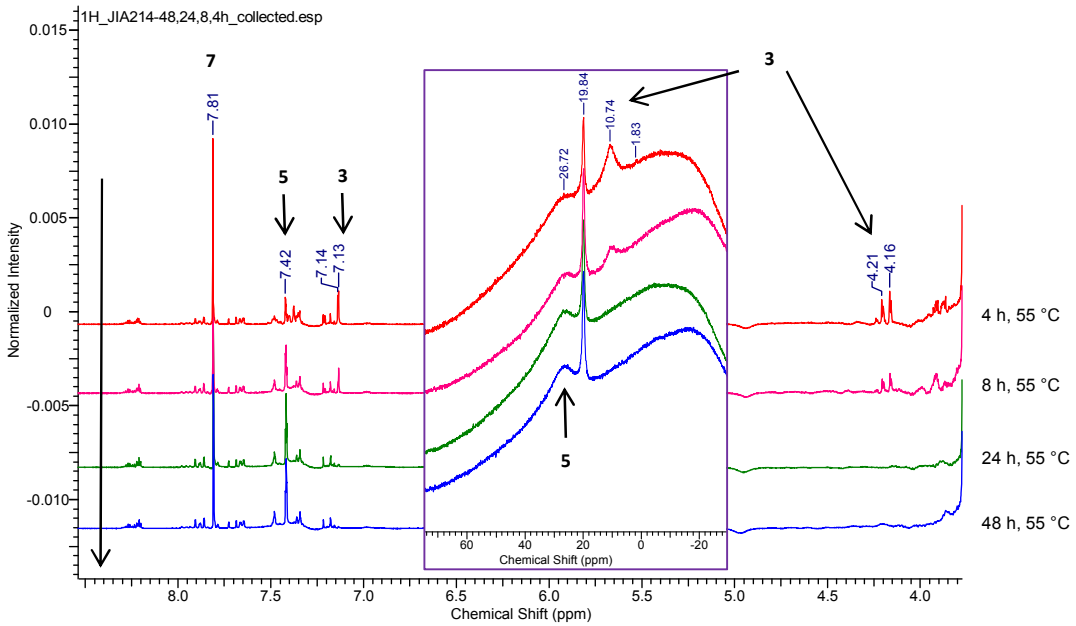


Figure S29. Collected ^{1}H NMR spectra of the polymerisation of **3** and **7**. Reaction conditions as in Table S2 (**2 equiv. KOH**). Inset: Collected ^{11}B NMR spectra at the same time intervals.

Polymerisation using "aged" monomer

Polymerisation of di-MIDA monomers that have been stored for 1 week under ambient conditions produces comparable results to using freshly prepared monomer or monomer stored under inert atmosphere (consistent with NMR spectroscopy studies where there is no observable protodeboronation in these cases).

Analysis of 3 that has been stored under ambient atmosphere as a solid for 18 months.

Monomer **3** stored for 18 months (stored under ambient atmosphere) was analysed by ^{1}H and ^{11}B NMR spectroscopy and found to be in a ~6:1 ratio of **3**/**2** (86% of **3**). Significantly no observable mono-MIDA **4** was observed which would be an effective chain capping species. Therefore the polymerization of this aged monomer was studied.

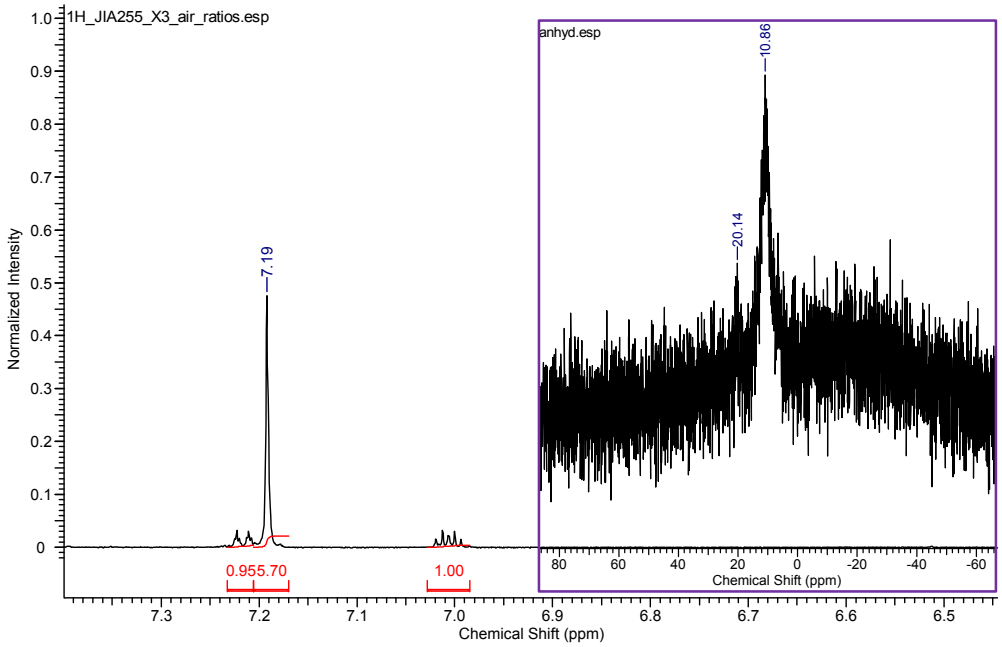


Figure S30. ^{1}H NMR spectrum (of the aromatic region) of monomer **3** (which was initially pristine at t =0) stored for 18-months under ambient atmosphere (spectra in anhydrous d_8-THF). Inset: ^{11}B NMR spectrum of the same sample. Singlet at 7.19 is attributable to **3**, multiplets at 7.0 and 7.21 ppm attributable to **2**.

Subsequently, this sample was utilised for polymerisation under conditions described below. Similar to the described General Procedure (**GP4**) with operations carried out under ambient atmosphere: A Radley's carousel tube containing a stirrer bar was charged with 18-month-old sample **3** (112.0 mg, 0.1572 mmol, from which approximately 0.1352 mmol, equating to 86%, is monomer **3**, by ^{1}H NMR spectroscopy), and **7** (39.7 mg, 0.1352 mmol corresponding to an approximate 1:1 ratio of the bifunctionalised co-monomers). Dry THF was added and the reaction mixture was stirred until all components had completely dissolved, [**3**] = 3.5×10^{-2} M. Then a freshly prepared palladium precatalyst in THF solution (**GP5**) was injected, $Pd_2(dba)_3$ (3.1 mg, 0.003 mmol) and SPhos (6.2 mg, 0.006 mmol), and the system was purged by continuous bubbling of N_2 gas for 60 min. Subsequently, the degassed KOH aqueous solution was added (**GP6**), KOH (45.5 mg, 0.811 mmol), H_2O (0.15 mL, 8.11 mmol), and the

system was heated to 55 °C with vigorous stirring (900 rpm) under a constant flow of N_2 gas for 24 h. At the end of the reaction, the crude mixture was quenched by precipitating it into an excess (fifty-fold by volume) of HCl-acidified MeOH. Crude polymer: 70 mg (97% yield). After Soxhlet extraction (sequential MeOH, *n*-hexane and chlorobenzene), 62 mg (86% yield) of dark blue **pCPDT-BT** was recovered from the chlorobenzene fraction: M_n = 10.0 kDa, M_w = 15.7 kDa (GPC in THF at 35 °C, PS calibration).

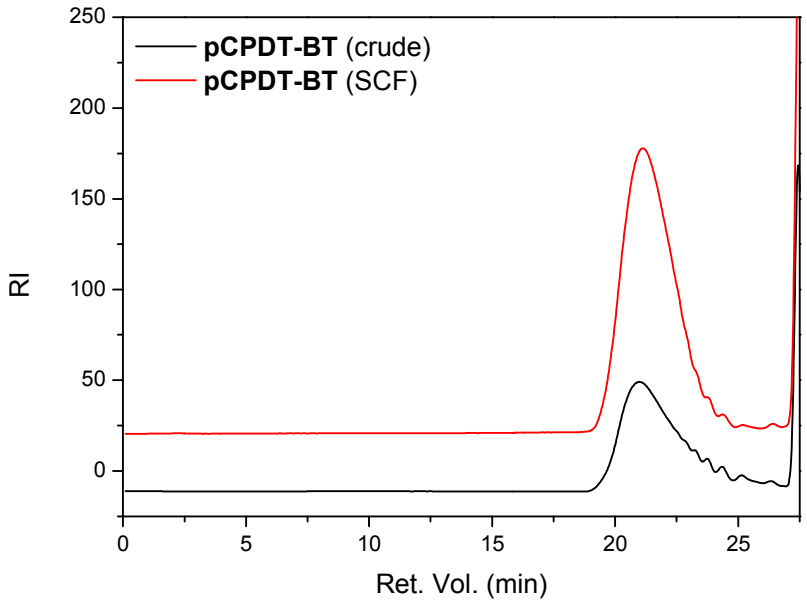
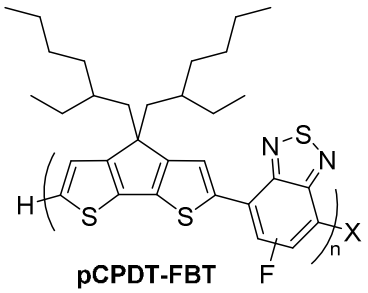


Figure S31. Full GPC elugram traces (crude, and chlorobenzene fraction, SCF, after Soxhlet fractionation) for the copolymerisation of 18-month-old sample of **3** (stored under ambient conditions) with **7** using reaction conditions as described above.

Poly[4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diyl-*alt*-5-fluoro-2,1,3-benzothiadiazole-4,7-diyl], pCPDT-FBT

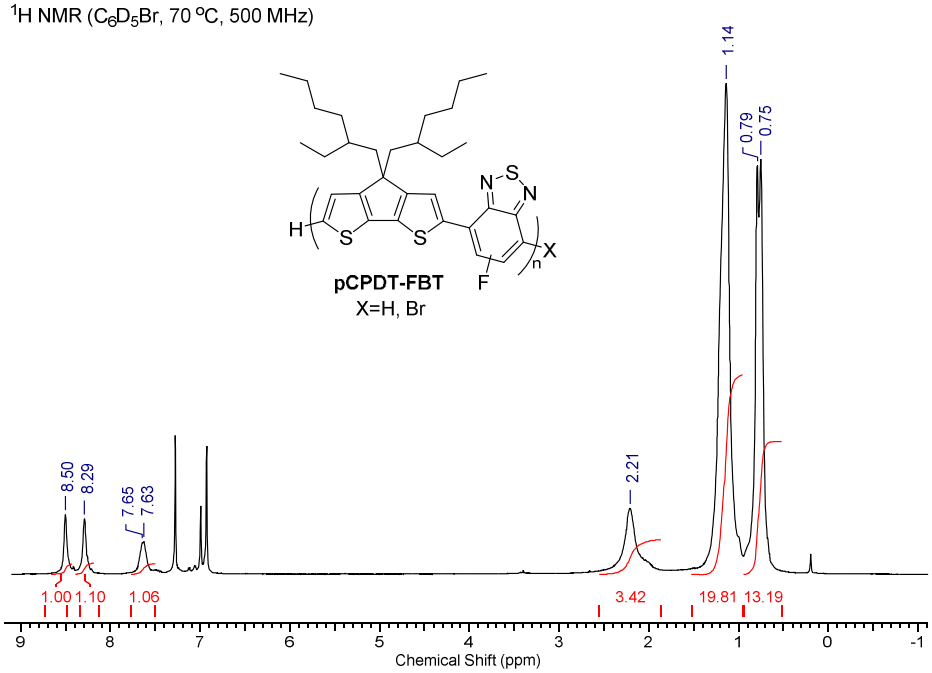


pCPDT-FBT
X=H, Br

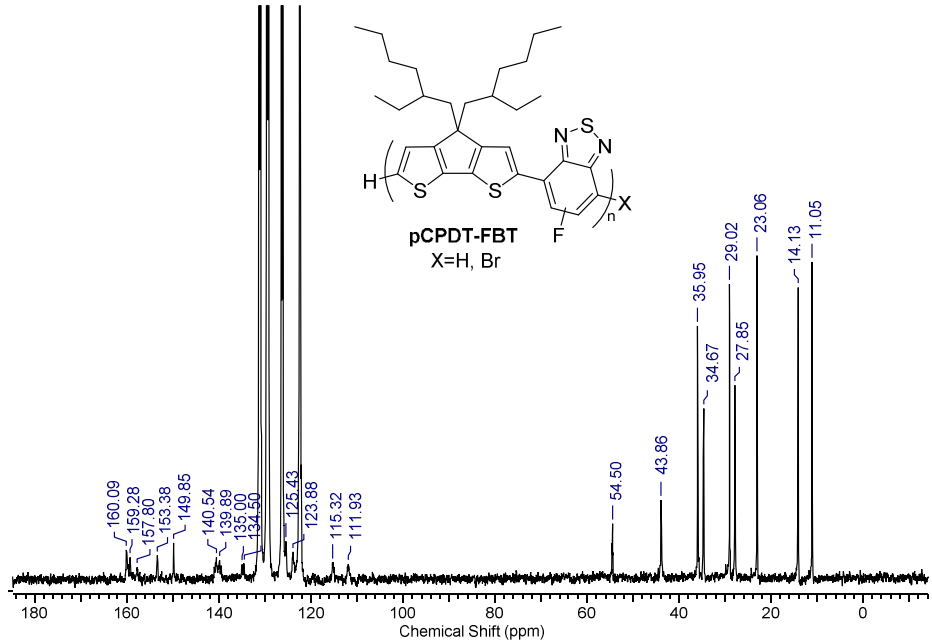
According to **GP4**: **3** (75.0 mg, 0.105 mmol) reacted with: **8** (32.8 mg, 0.105 mmol), KOH (35.3 mg, 0.630 mmol), H_2O (113 µL, 6.300 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (2.4 mg, 0.003 mmol) and SPhos (4.8 mg, 0.006 mmol) in THF (2.90 mL) over 24 h to afford after precipitation with HCl-acidified MeOH 57 mg (>99%) of crude polymer as a dark blue-greenish solid. After Soxhlet extraction, 55 mg (95%) of dark blue **pCPDT-FBT** was recovered from the chlorobenzene fraction.

^{1}H NMR (500 MHz, C_6D_5Br, 70 °C): δ 8.50 (s, 1 H, CH), 8.29 (s, 1 H, CH), 7.64 (bs, 1 H, CH), 2.21 (bs, 4 H, 2 × CH_2), 1.14 (m, 18H), 0.77 (d, J = 19.5 Hz, 12 H, 4 × CH_3)
^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Br, 70 °C): δ 160.1, 159.3 (C_{quat}), 157.8, 153.4, 149.9, 140.5 (C_{quat}), 139.9, 135.0, 134.5, 125.4, 123.9, 115.3, 111.9, 54.5 (C_{quat}), 43.9 (CH_2), 36.0 (CH), 34.7 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 23.1 (CH_2), 14.1 (CH_3), 11.1 (CH_3).
^{19}F NMR (470.7 MHz, C_6D_5Br, 70 °C): δ -107.5
UV-vis (C_6H_5Cl solution at 23 °C): λ_{max} = 717 nm; ε = 45651 M^{-1} cm^{-1}
GPC (1,2,4-trichlorobenzene, 160 °C, PS calibration): M_n = 19.4 kDa; M_w = 38.2 kDa

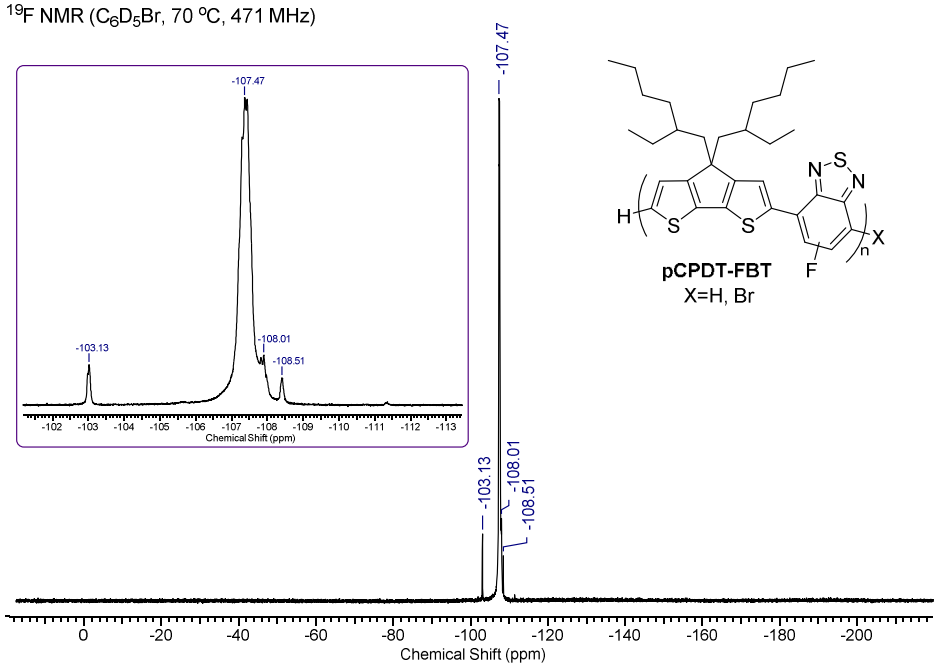
^{1}H NMR (C_6D_5Br, 70 °C, 500 MHz)



^{13}C{^{1}H} NMR (C_6D_5Br, 70 °C, 125 MHz)



^{19}F NMR (C_6D_5Br, 70 ºC, 471 MHz)



pCPDT-FBT
X=H, Br

GPC analysis from PSS Polymer Standards Service GmbH:

Sample preparation

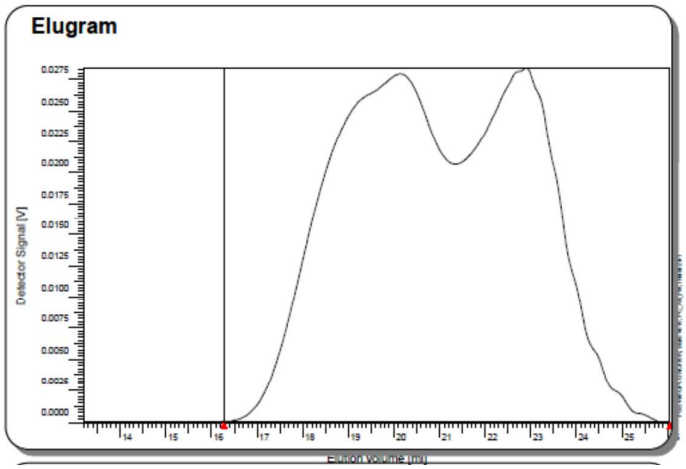
The samples were weighted exactly and 1,5 ml 1,2,4-Trichlorobenzene were added.

After 2 hours dissolving at 160°C the samples were injected twice with 200 µl into the SEC.

Method Information

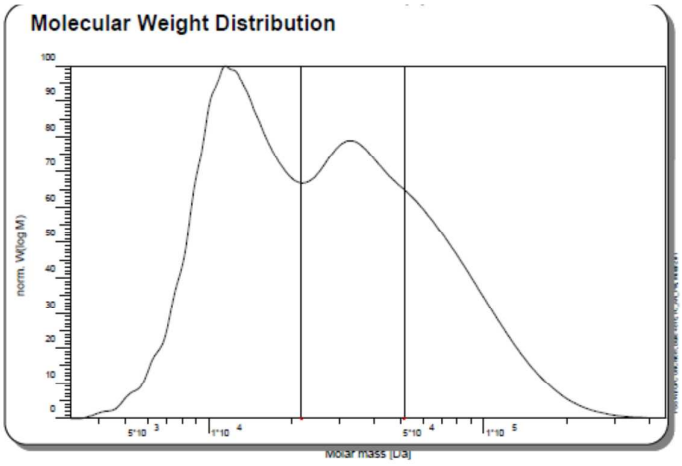
Project:	W:\GPC_DATEN\AN\LC\serv_16\serv_16_PG14.LDX	Injection time:	29.04.2016 17:26:29
GPC instrument:	PG 14, Agilent PL-210-HT	Operator:	pm
Calibration type:	Conventional	Calibration fit:	PSS Poly 5
Calibration file:	ps-160°C-SDV AK-TCB-Merck-22-04-16.CAL	Int. standard:	keiner
Vp int. standard calib.:	50,00 mL	Vp int. standard sample:	0,00 mL
Injection volume:	200 µL		
Sample concentration:	3,000 g/L	temperature:	160,0 °C
Eluent:	1,2,4-trichlorobenzene	Flow rate:	1,00 mL/min
Columns:	SDV, 5 µm, g, lins, 1000, 10e5A		

Elugram



Baseline from: 13,20 mL to: 26,05 mL
Integration from: 16,27 mL to: 26,05 mL

Molecular Weight Distribution



Detector	Fraction % M < 21700 Da	Fraction % M < 51400 Da
RID	44,98	76,21

Detector	Fraction % M > 51400 Da
RID	23,79

	Detector	Mn /Da	Mw /Da	Mz /Da	PDI (=Mw/Mn)	Vp /mL	Mp /Da	Area /(mL*V)
——	RID	19400	38200	74400	1,97	22,91	11500	0,1522

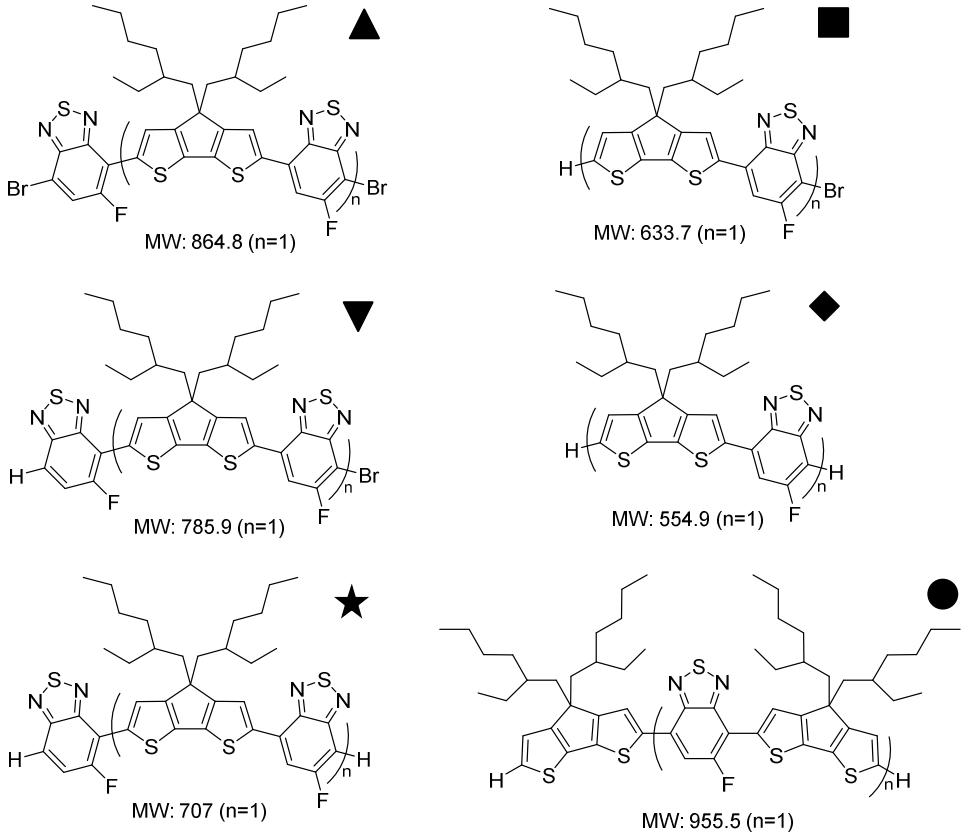


Chart S2. **pCPDT-FBT** chain fragments from the reaction of **3** and **8**, with different possible end groups observed by MALDI-TOF spectrometry.

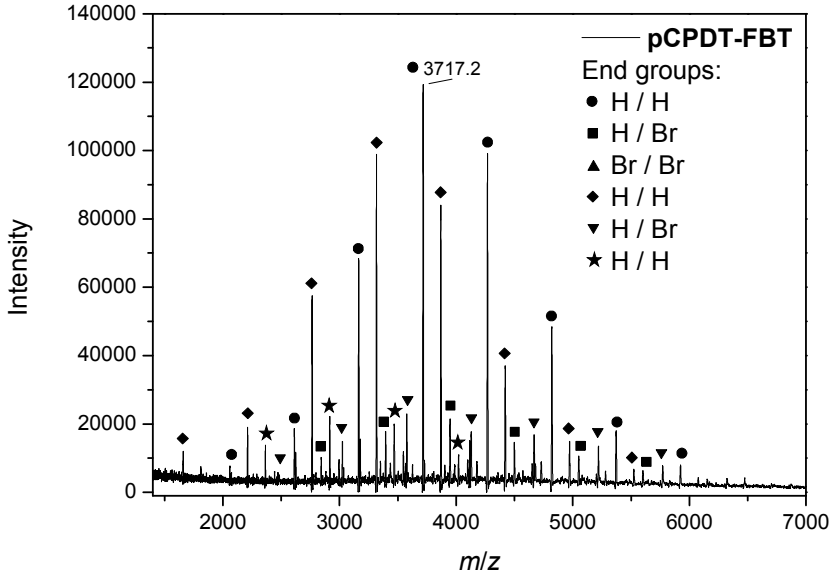


Figure S32. MALDI-TOF spectrum of **pCPDT-FBT**. End groups as shown in Chart S2. Sample after Soxhlet fractionation, C_6H_5Cl fraction.

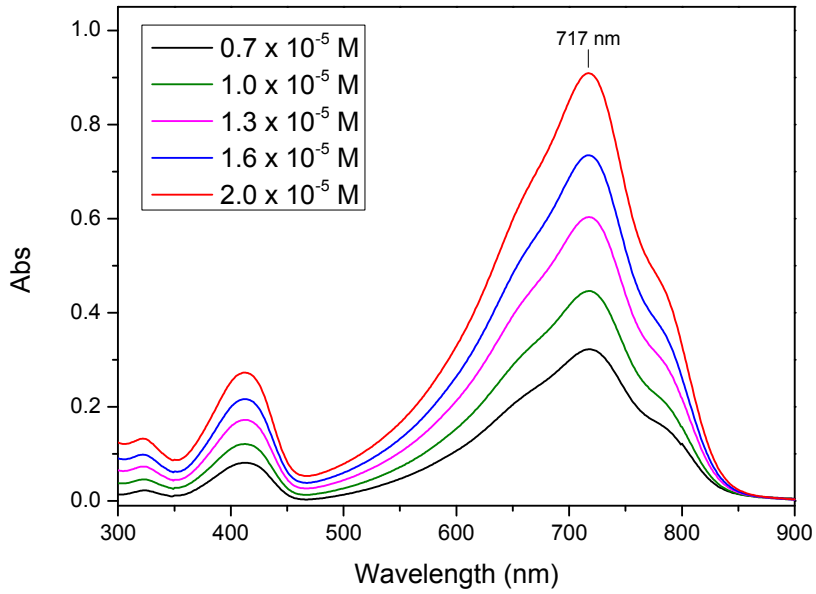
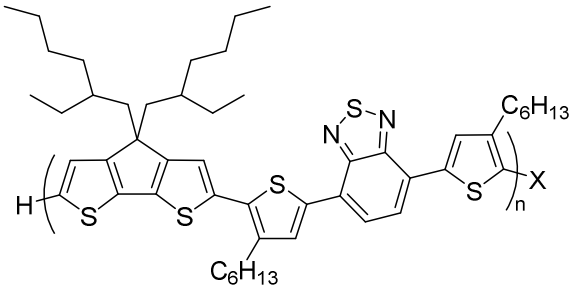


Figure S33: UV-Vis spectra of **pCPDT-FBT** at varying concentrations in chlorobenzene at ambient temperature.

For comparison pCPDT-FBT made via Stille coupling has an absorption maxima in chlorobenzene at room temperature of 720 nm.[9]

Poly[(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene)-2,6-diyl-*alt*-[4,7-bis(3-hexylthiophene-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl], pCPDT-TBTT

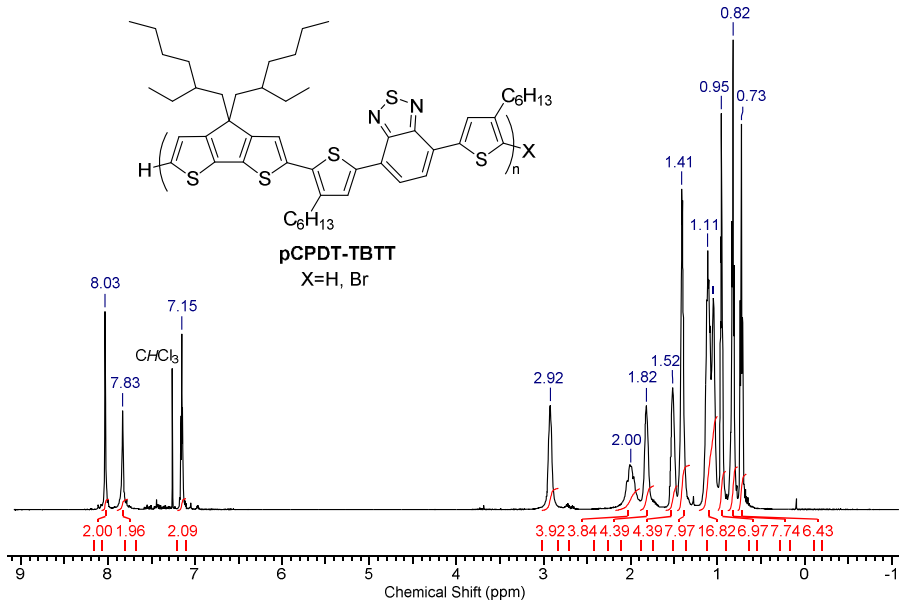


pCPDT-TBTT
X=H, Br

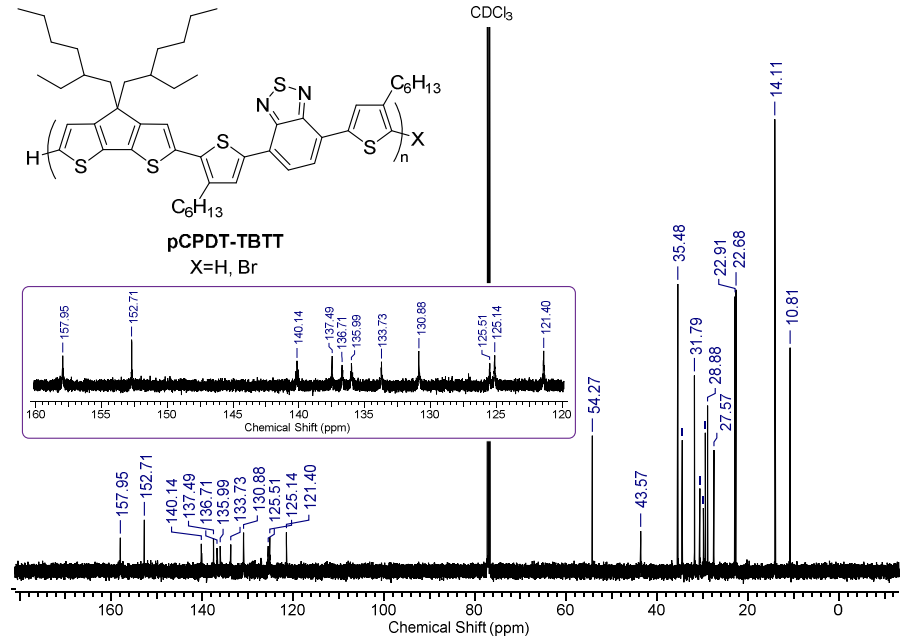
According to **GP4**: **3** (75.0 mg, 0.105 mmol) reacted with: **9** (65.95 mg, 0.105 mmol), KOH (35.3 mg, 0.630 mmol), H_2O (113 µL, 6.300 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (2.4 mg, 0.003 mmol) and SPhos (4.8 mg, 0.006 mmol) in THF (2.90 mL) over 24 h to afford after precipitation with HCl-acidified MeOH 91 mg (>99%) of crude polymer as a dark blue solid. After Soxhlet extraction, 89 mg (98%) of dark blue **pCPDT-TBTT** was recovered from the chlorobenzene fraction.

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 8.03 (s, 2 H, 2 × CH), 7.83 (bs, 2 H, 2 × CH), 7.15 (t, J = 5.04 Hz, 2 H, 2 × CH), 2.92 (bs, 4 H, 2 × CH_2), 2.00 (m, 4 H, 2 × CH_2), 1.82 (bs, 4 H, 2 × CH_2), 1.52 (bs, 4 H, 2 × CH_2), 1.41 (m, 8 H, 2 × CH_2), 1.11-1.05 (m, 18 H), 0.95 (m, 6 H, 2 × CH_3), 0.82 (t, J = 6.79 Hz, 6 H, 2 × CH_3), 0.73 (t, J = 6.79 Hz, 6 H, 2 × CH_3)
^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 50 °C): δ 157.95 (C_{quat}), 152.71 (C_{quat}), 140.14 (C_{quat}), 137.49 (C_{quat}), 136.71 (C_{quat}), 135.99 (C_{quat}), 133.73 (C_{quat}), 130.88 (CH), 125.51 (C_{quat}), 125.14 (CH), 121.40 (CH), 54.27 (C_{quat}), 43.57 (CH_2), 35.48 (CH), 34.48 (CH_2), 31.79 (CH_2), 30.63 (CH_2), 29.79 (CH_2), 29.39 (CH_2), 28.89 (CH_2), 27.57 (CH_2), 22.91 (CH_2), 22.68 (CH_2), 14.11 (CH_3), 14.07 (CH_3), 10.81 (CH_3), 10.79 (CH_3)
UV-vis (C_6H_5Cl solution at 23 °C): λ_{max} = 602 nm; ε = 37789 M^{-1} cm^{-1}
GPC (THF, 35 °C, PS calibration): M_n = 35.6 kDa; M_w = 63.7 kDa

^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 50 °C, 125 MHz)



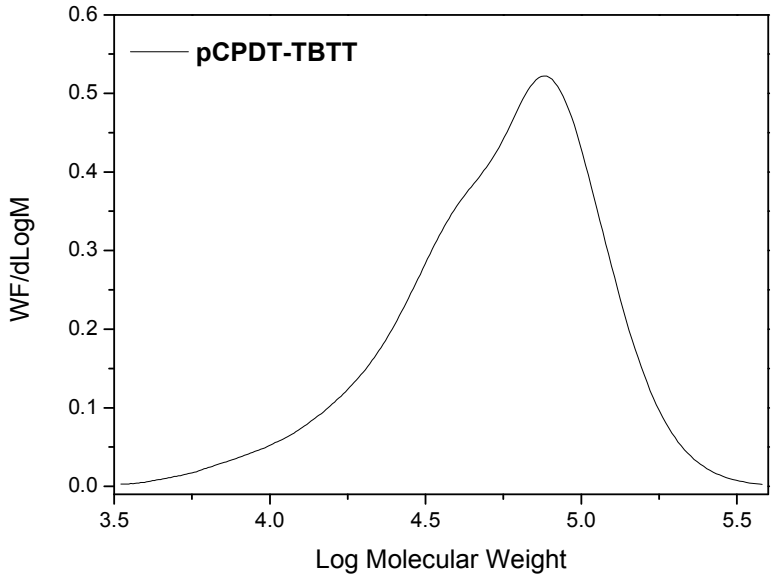


Figure S34. GPC trace of C_6H_5Cl fraction sample of **pCPDT-TBTT** (THF at 35 °C, PS calibration).

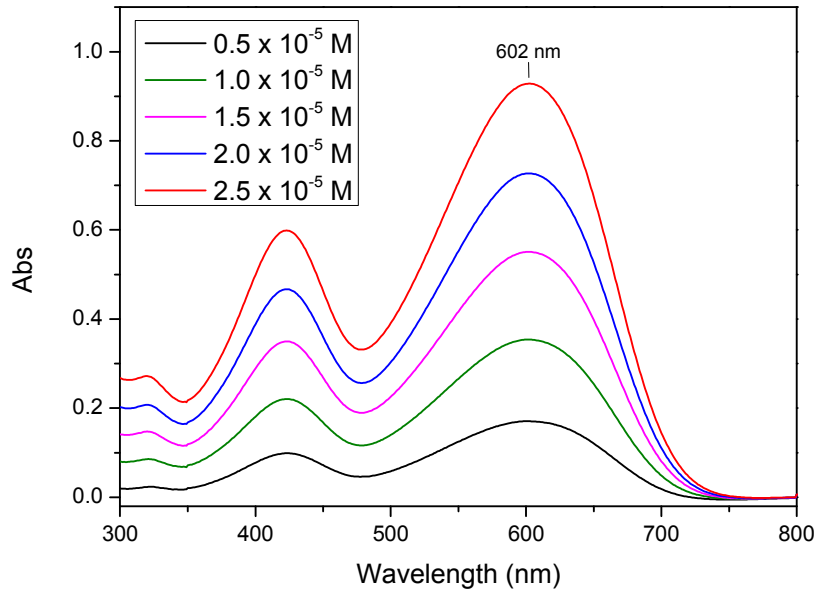


Figure S35: Uv-vis spectra for **pCPDT-TBTT** at varying concentrations in chlorobenzene at ambient temperature.

For comparison pCPDT-TBTT (albeit with octyl substituted CPDT) made via Stille coupling has an absorption maxima at room temperature of 605 nm (although no solvent was stated.[10]

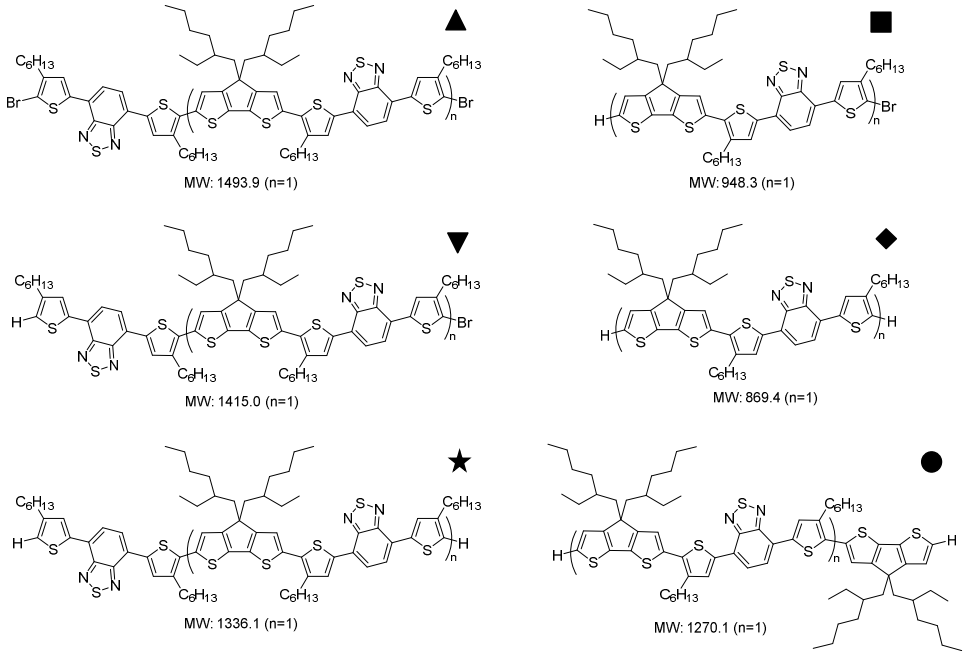


Chart S3. Chain fragments from the reaction of **3** and **9**, with different possible end groups observed by MALDI-TOF spectrometry.

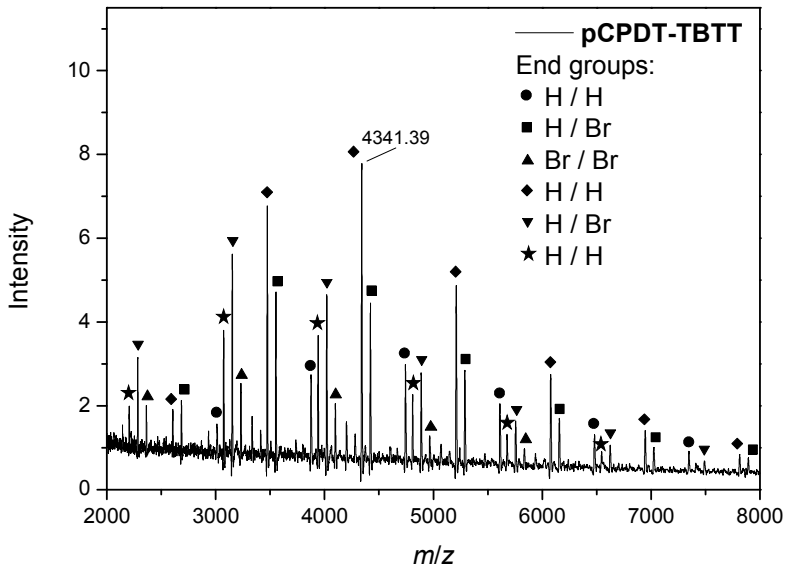


Figure S36. MALDI-TOF spectrum of **pCPDT-TBTT**. End groups as shown in Chart S3 Sample after Soxhlet fractionation, C_6H_5Cl fraction.

When polymerisation of **3** with **9** employed K_3PO_4 instead of KOH as base: 10% yield at 24 h; even at longer reaction time (in an attempt to fully hydrolyse all BMIDA moieties) only 78.6% yield at 48 h.

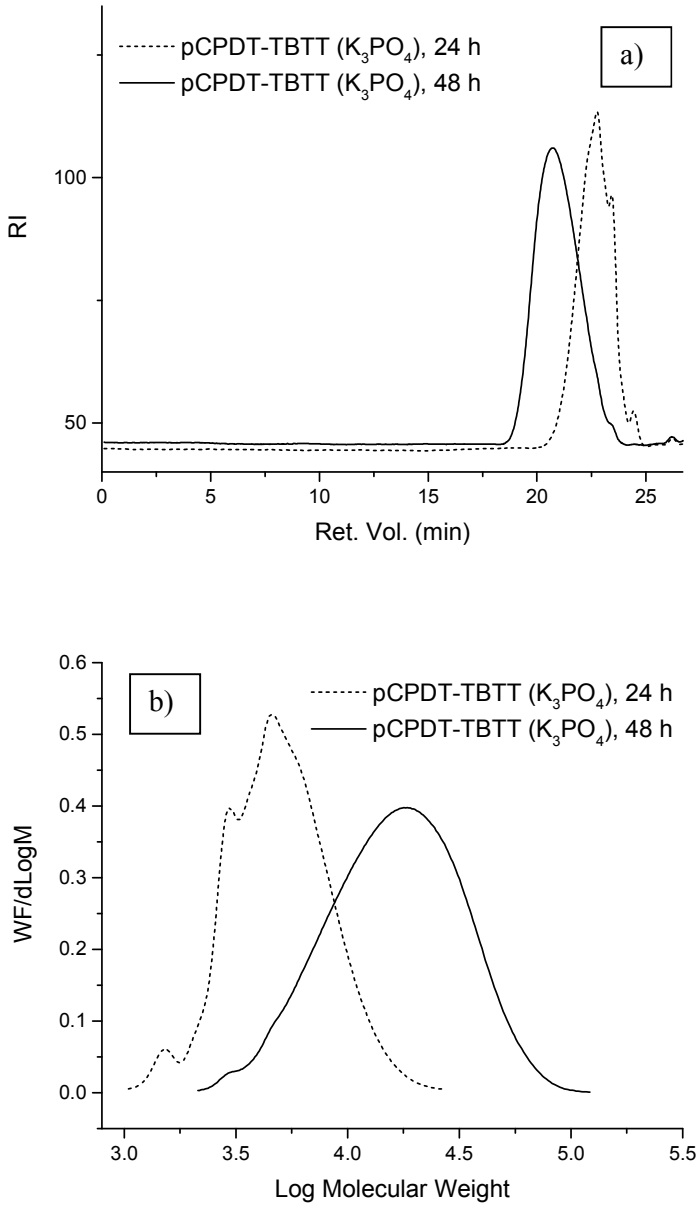


Figure S37. GPC traces (chloroform fraction after Soxhlet fractionation) for the copolymerisation of **3** with **9** using K_3PO_4 as base, at 24 h and 48 h. a) Full GPC elugram traces. b) Molecular weight distribution. (THF at 35 °C, PS calibration)

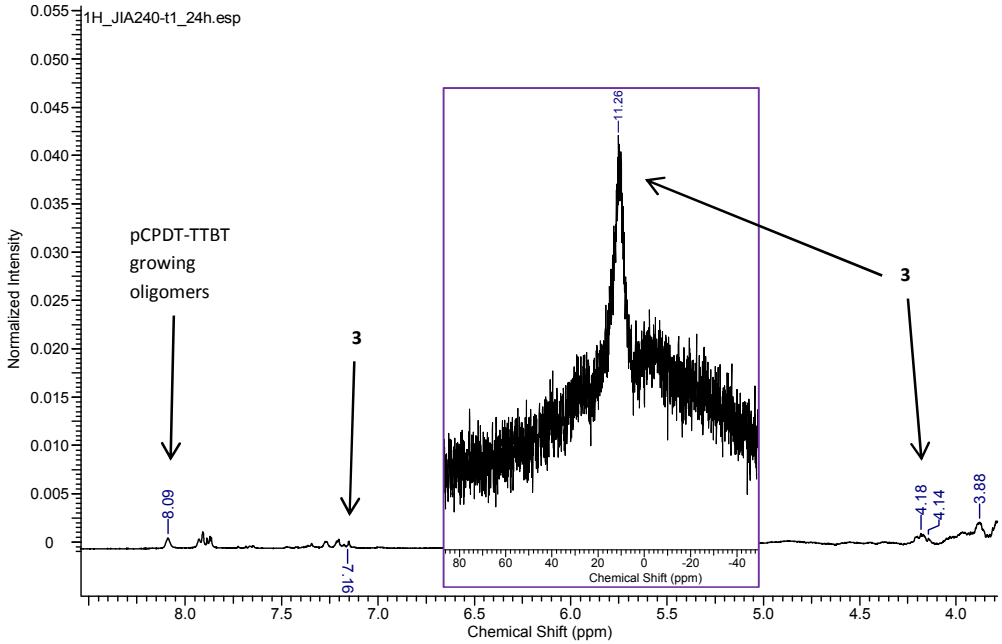


Figure S38. ^{1}H NMR spectrum of the polymerisation of **3** and **9** at 24 h. Reaction conditions as in Equation S11, using K_3PO_4 instead of KOH. Inset: ^{11}B NMR spectrum at the same time.

GPC elugrams of pCPDT-BT and pCPDT-FBT in chlorobenzene at 70°C

Table S3. Results from the copolymerisation of **CPDT^{EH}-(BMIDA)$_2$** and **Acceptor-(Br)$_2$**.[a]

Entry[b]	Acceptor unit	M_n[c] (kDa)	M_w[c] (kDa)	$Đ_M$[c]	M_p[c] (kDa)	Yield[d] (%)	λ_{max}[e] (nm)	ε (M^{-1} cm^{-1})
1	BT	---[f]	---[f]	---[f]	30.0[g]	99	724	44294
2	FBT	---[f]	---[f]	---[f]	12.8[g]	95	717	45651

[a]Reaction conditions: *T*: 55 °C, [**CPDT^{EH}-(BMIDA)$_2$**] = 3.5 × 10^{-2} M, KOH: 6 equiv, H_2O: 60 equiv, $Pd_2(dba)_3$: 2.5 mol %, SPhos: 5 mol %, solvent: THF, *t*: 24 h, reactions run twice, quenched with 2.5% HCl-acidified MeOH. [b]Soxhlet-fractionated C_6H_5Cl fraction after sequential extractions with MeOH, and *n*-hexane, for 14 h each or until colourless solvent in the Soxhlet chamber. [c]Determined by GPC (C_6H_5Cl at 70 °C, PS calibration). [d]Isolated. [e]Determined in C_6H_5Cl solution at room temperature. [f]No M_w/M_n quoted due to traces out of the calibration curve range in the high molecular weight region. [g]Corresponding to the second peak at higher retention time.

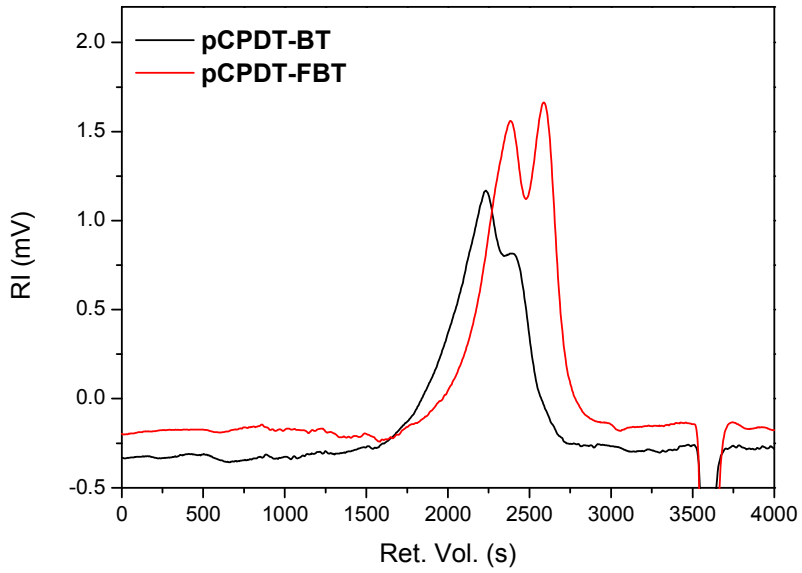


Figure S39. GPC traces of **pCPDT-BT** (black) and **pCPDT-FBT** (red) (C_6H_5Cl at 70 °C, PS calibration). Peak at 3600 s corresponding to toluene, added as internal marker.

Polymerisation of 1 using KOH as base

As explained in the main text, homopolymerisation of **1** was carried out using KOH (3 equiv.) and H_2O (30 equiv.) in THF at 55 °C, (KOH instead of K_3PO_4, as previously reported[2]). 22.3% yield at 8 h; 46.5% yield at 24 h.

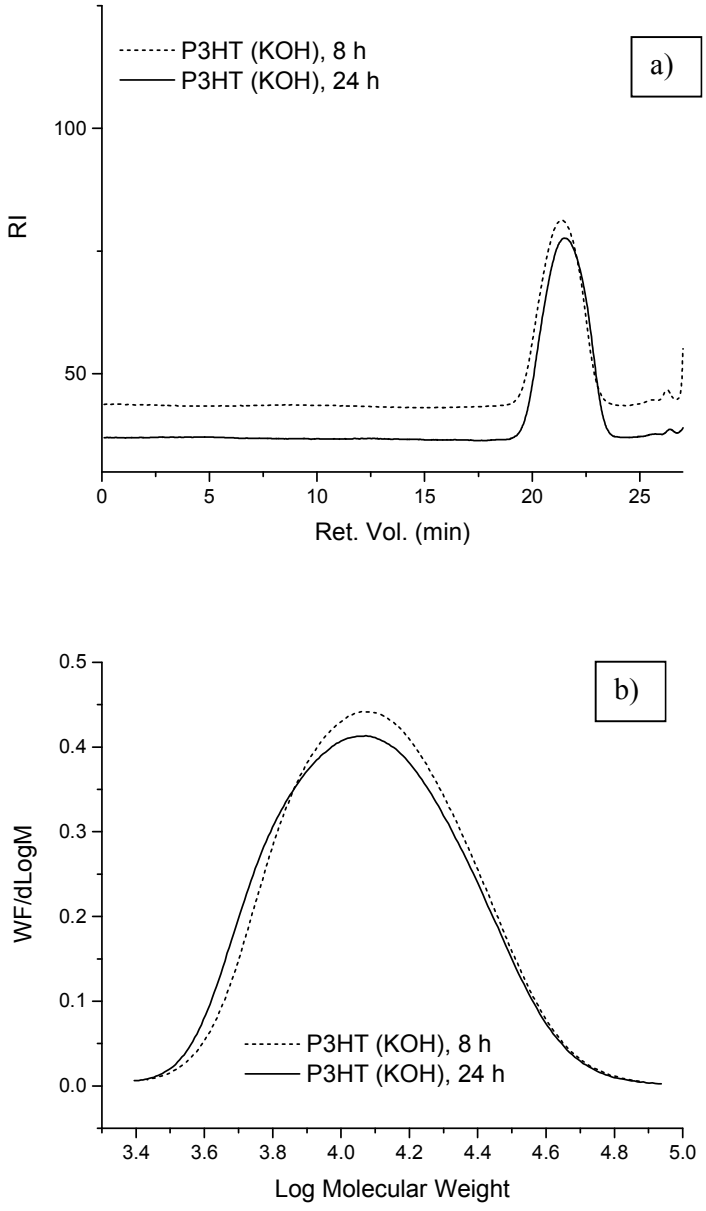
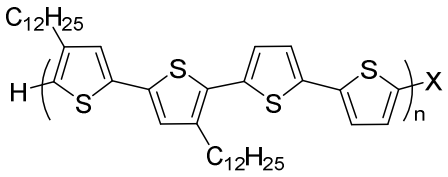


Figure S40. GPC traces (chloroform fraction after Soxhlet fractionation) for the polymerisation of **1** using KOH as base, at 8 h and 24 h. a) Full GPC elugram traces. b) Molecular weight distribution. (THF at 35 °C, PS calibration)

Co-polymerisation of 10 with 11

Poly(3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene), PQT12

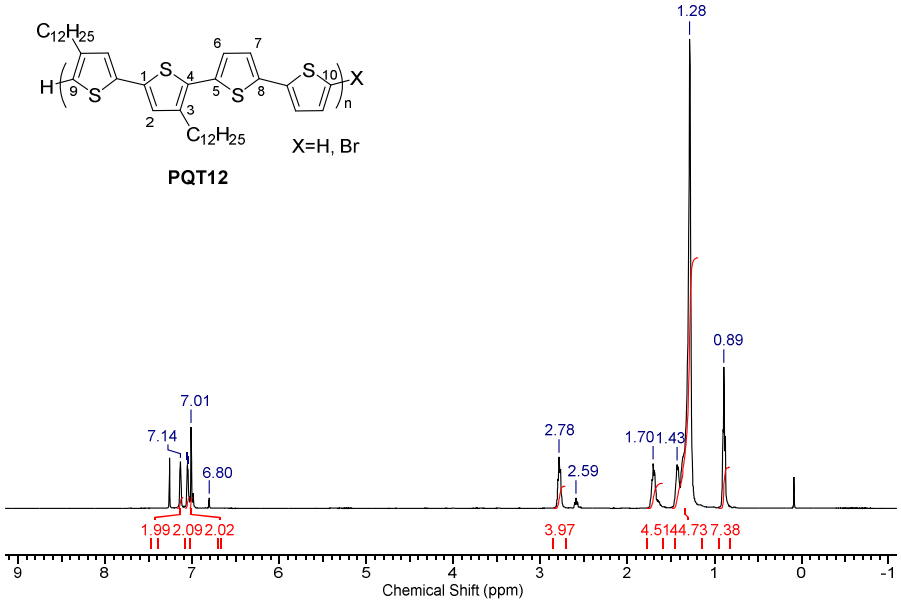


PQT12
X = H, Br

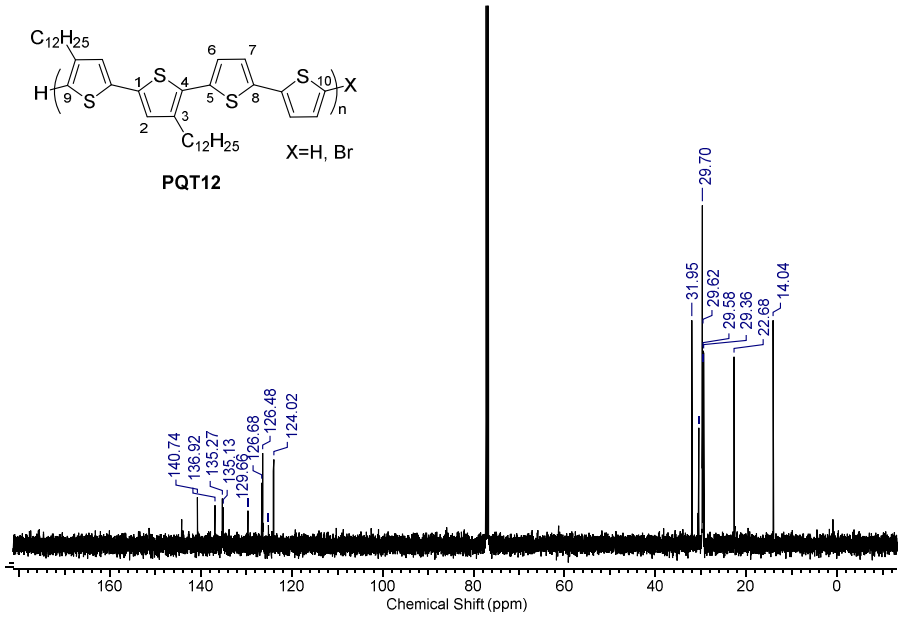
According to **GP4**: **10** (50.0 mg, 0.0615 mmol) reacted with: 5,5'-dibromo-2,2'-bithiophene, **11**, (20.0 mg, 0.0615 mmol), KOH (20.7 mg, 0.3691 mmol), H_2O (66.5 µL, 3.6912 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (1.4 mg, 0.0015 mmol) and SPhos (2.5 mg, 0.003 mmol) in THF (1.70 mL) over 24 h to afford after precipitation with HCl-acidified MeOH 41 mg (>99%) of crude polymer as a dark red solid. After Soxhlet extraction, 33 mg (81%) of dark red **PQT12** were recovered from the chlorobenzene fraction. Additional 7 mg of dark red solid recovered from the hexane fraction completed the mass balance.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, 2 H), 7.05 (d, 2 H), 7.01 (s, 2 × C2-H), 2.78 (t, $^3J_{(H,H)}$ = 7.1 Hz, 2 × $CH_2C_{11}H_{23}$), 1.70 (tt, $^3J_{(H,H)} \approx$ 6.9 Hz, 2 × $CH_2CH_2C_{10}H_{22}$), 1.28 (m, 36 H, 18 × CH_2), 0.89 (t, $^3J_{(H,H)} \approx$ 6.4 Hz, 6 H, 2 × CH_3). Resonances at 6.80 attributed to C9-H terminal groups, 2.59 attributed to CH_2 of a **10**-derived terminal group.
^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 140.74 (C_{quat}), 136.92 (C_{quat}), 135.27 (C_{quat}), 135.13 (C_{quat}), 129.66 (C_{quat}), 126.68 (C-H), 126.48 (C-H), 124.02 (C2-H), 31.95 (CH_2), 30.47 (CH_2), 29.70 (CH_2), 29.62 (CH_2), 29.58 (CH_2), 29.48 (CH_2), 29.36 (CH_2), 22.68 (CH_2), 14.04 (CH_3). Resonances at 125.17 attributed to C9-H terminal groups, 119.17 attributed to C10-H terminal group.
UV-vis ($CHCl_3$ solution at 23 °C): λ_{max} = 470 nm
GPC (C_6H_5Cl, 70 °C, PS calibration): M_n = 9.4 kDa; M_w = 11.9 kDa

^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 50 °C, 125.8 MHz)



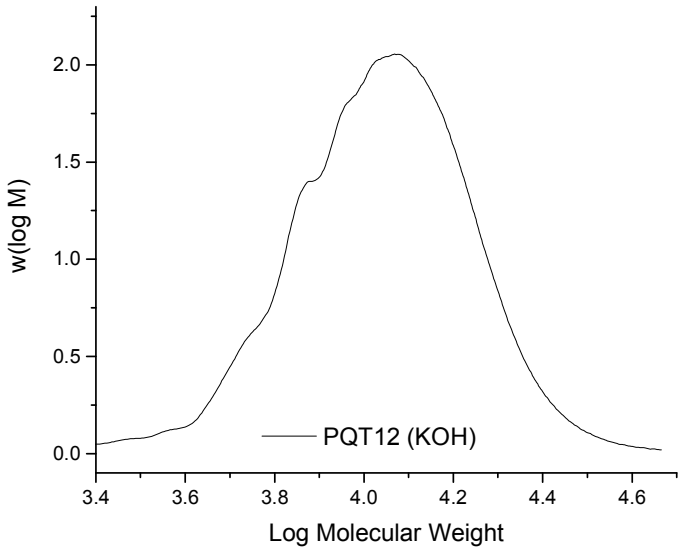


Figure S41. GPC traces of the chloroform fraction sample of **PQT12** synthesised using KOH (C_6H_5Cl at 70 °C, PS calibration).

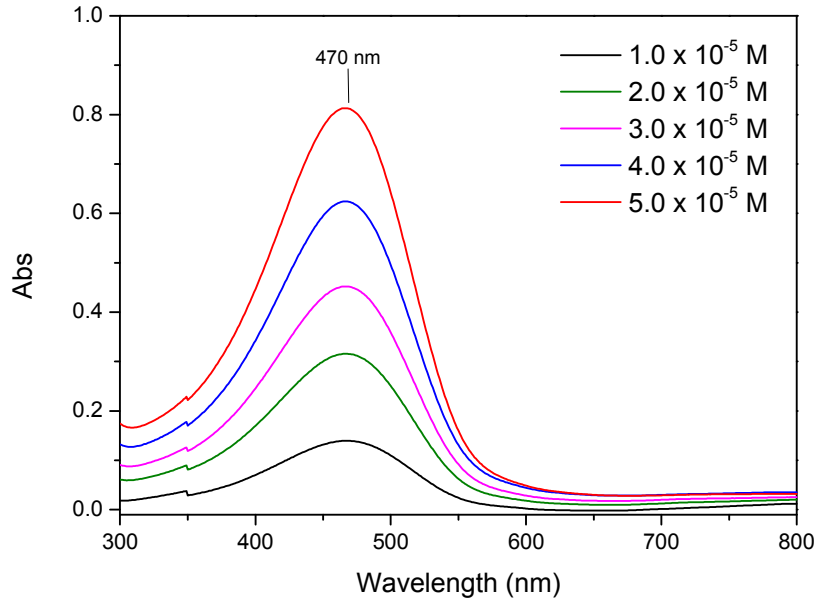


Figure S42: Uv-vis spectra of **PQT12** made using KOH as base, at varying concentrations in chloroform at ambient temperature.

For comparison PQT12 made via Stille coupling has an absorption maxima in chloroform at room temperature of 470 nm.[11]

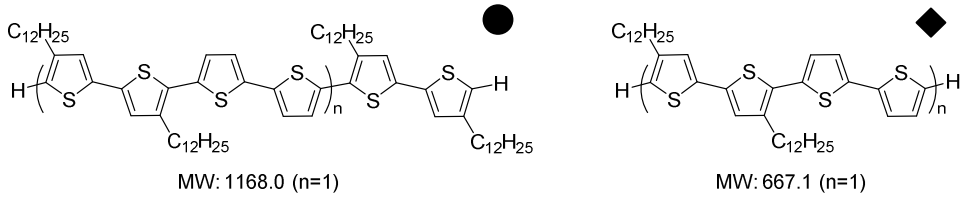


Chart S4. **PQT12** polymeric fragments identified by MALDI-TOF spectrometry.

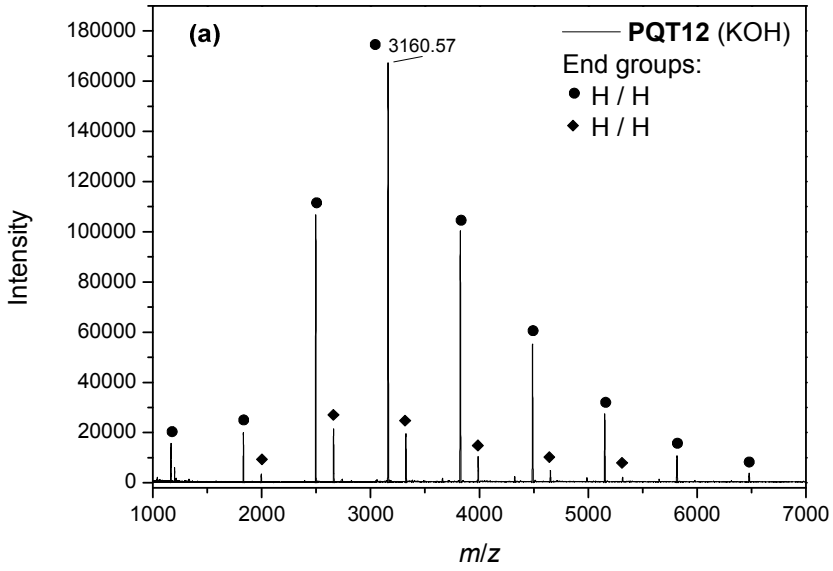
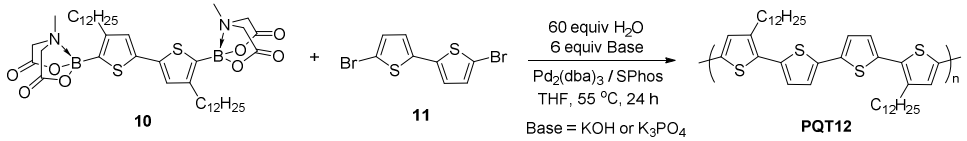


Figure S43. MALDI-TOF spectra of the **PQT12** obtained after using 6 equiv of KOH. End groups as shown in Chart S4. Samples after Soxhlet fractionation, chlorobenzene fraction.

Table S4. Results of copolymerisation of **10** and **11**, with different bases[a]



Entry	Base	Yield[b] (%)	M_n[c] (kDa)	M_w[c] (kDa)	$Đ_M$[c]	M_p[c] (kDa)	λ_{max}[d] (nm)
1	KOH	81	7.2 (9.4)[e]	10.7 (11.9)[e]	1.5 (1.3)[e]	9.5 (10.7)[e]	470
2	K_3PO_4	64	6.7	9.9	1.5	7.4	470

[a]Reaction conditions: *T*: 55 °C, [**10**] = 3.5×10^{-2} M, Base: 6 equiv, H_2O: 60 equiv, $Pd_2(dba)_3$: 2.5 mol%, SPhos: 5 mol%, solvent: THF, *t*: 24 h, reaction quenched with 2.5% HCl-acidified MeOH. [b]Isolated, corresponding to the chloroform fraction after Soxhlet fractionation. [c]Determined by GPC (THF at 35 °C, PS calibration). [d]Determined by UV-vis spectroscopy (solution in $CHCl_3$, 2×10^{-5} M). [e]Determined by GPC (C_6H_5Cl at 70 °C, PS calibration).

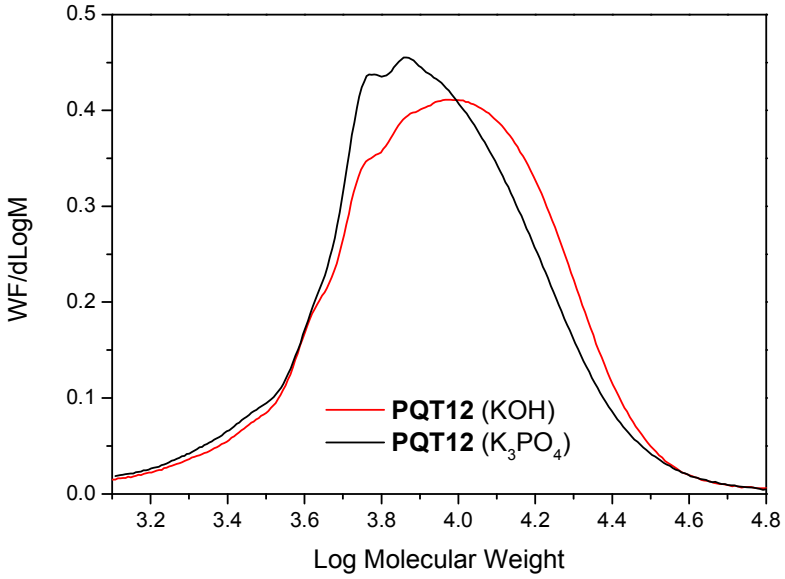


Figure S44. GPC traces of the chloroform fraction samples of **PQT12** synthesised using KOH or K_3PO_4 (THF at 35 °C, PS calibration). Reaction conditions as in Table S3.

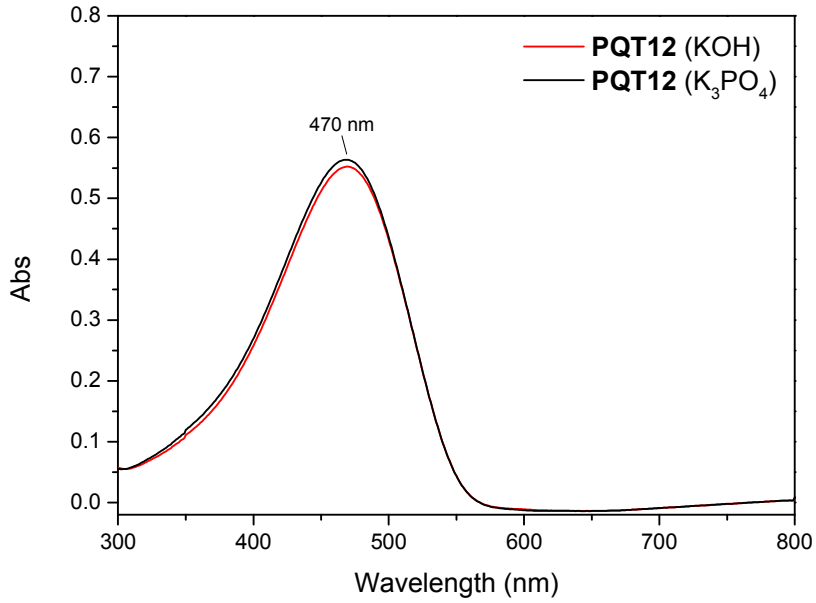
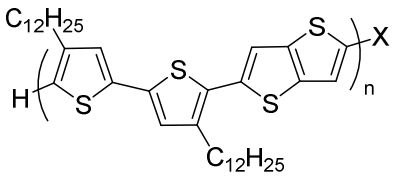


Figure S45: Uv-vis spectra of **PQT12** made using K_3PO_4 or KOH as base, in chloroform at ambient temperature.

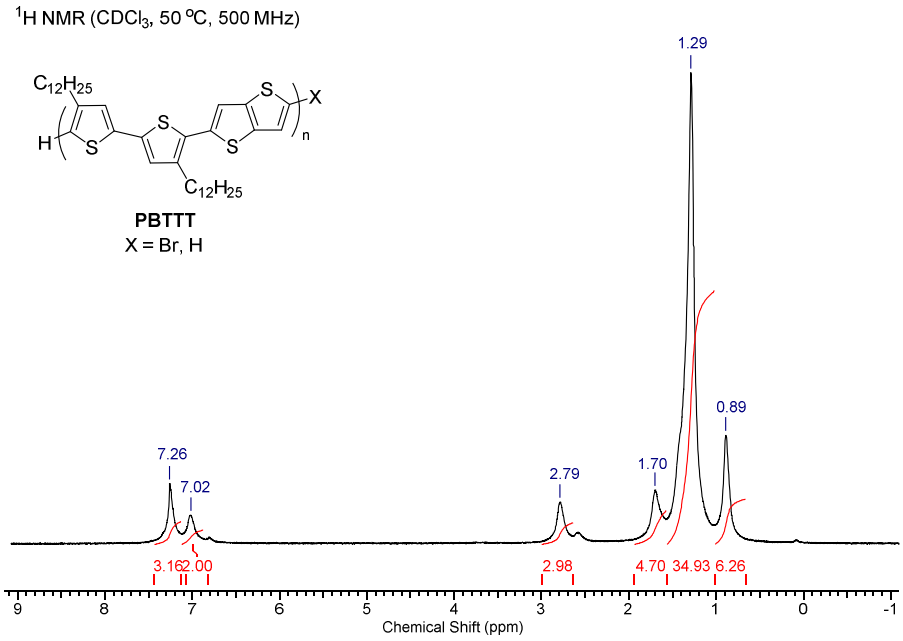
Poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene), PBTTT



PBTTT
X = Br, H

According to **GP4**: **10** (82.0 mg, 0.1009 mmol) reacted with: 2,5-dibromothieno[3,2-b]thiophene, **12**, (30.0 mg, 0.1009 mmol), KOH (34.0 mg, 0.6054 mmol), H_2O (109 µL, 6.054 mmol) in the presence of palladium precatalyst: $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) and SPhos (2.1 mg, 0.005 mmol) in THF (2.90 mL) over 24 h to afford after precipitation with HCl-acidified MeOH 64 mg (>99%) of crude polymer as a dark red solid. After Soxhlet extraction, 38 mg (59%) of dark red **PBTTT** were recovered from the chlorobenzene fraction. Additional 26 mg of dark red solid polymer that was insoluble in hot chlorobenzene completed the mass balance resulting in an effectively quantitative formation of PBTTT.

^{1}H NMR (500 MHz, 50 °C, $CDCl_3$): δ 7.26 (s, 2 H), 7.02 (s, 2 H), 2.79 (t, 2 × CH_2C$_{11}$H$_{23}$), 1.70 (m, 2 × CH$_2$CH_2C$_{10}$H$_{22}$), 1.29 (m, 36 H, 18 × CH$_2$), 0.89 (t, 6 H, 2 × CH$_3$). Small resonances at 6.81 attributed to C-H terminal groups, 2.58 attributed to CH_2 of a **10**-derived terminal group. Signal from residual $CHCl_3$ overlaps with polymer C-H signal.
^{13}C{^{1}H} NMR (125.8 MHz, 50 °C, $CDCl_3$): δ 126.8 (C-H), 117.9 (C-H), 31.9 (CH_2), 30.7 (CH_2), 29.70 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 14.0 (CH_3). Other resonances not observed due to the low solubility and aggregation of the polymer.
UV-vis ($CHCl_3$ solution at 23 °C): λ_{max} = 460 nm; ε = 28600 M^{-1} cm^{-1}
GPC (C_6H_5Cl, 70 °C, PS calibration): M_n = 13.1 kDa; M_w = 31.9 kDa



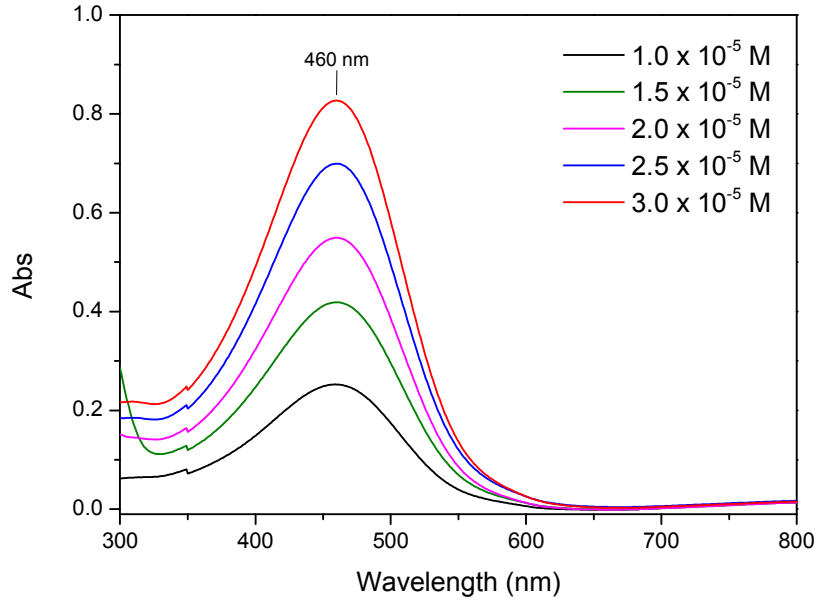


Figure S46: Uv-vis spectra of **PBTTT** made using KOH as base, at varying concentrations in in chloroform at ambient temperature.

For comparison PBTTT made via Stille coupling has an absorption maxima in chloroform at room temperature of 462 nm.[12]

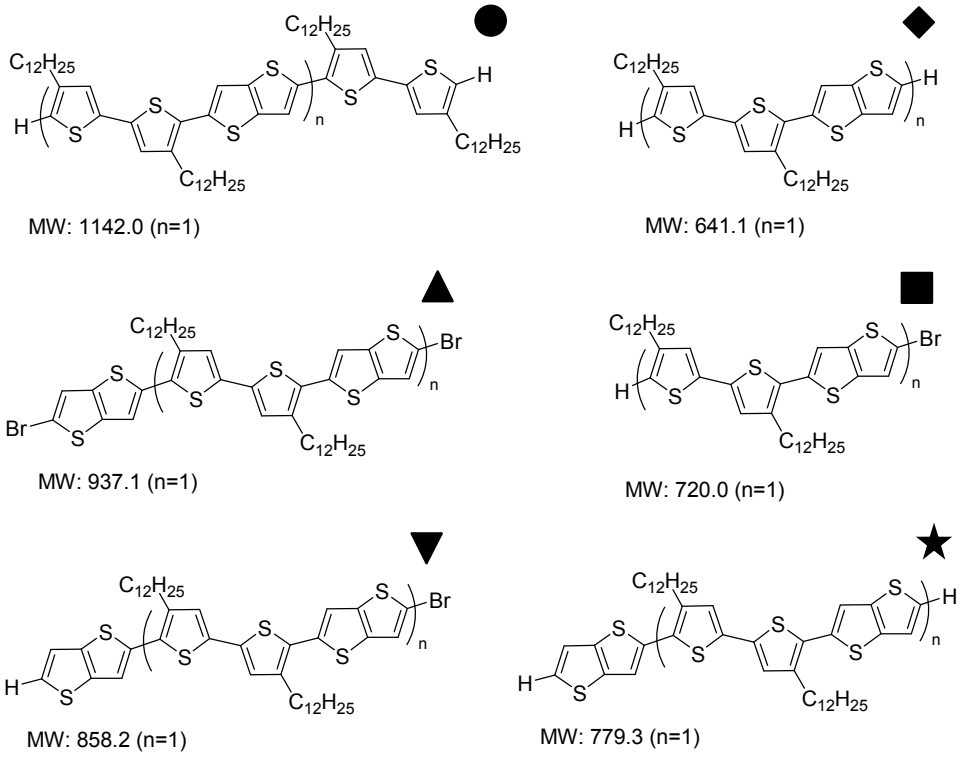


Chart S5**. PBTTT** polymeric fragments identified by MALDI-TOF spectrometry.

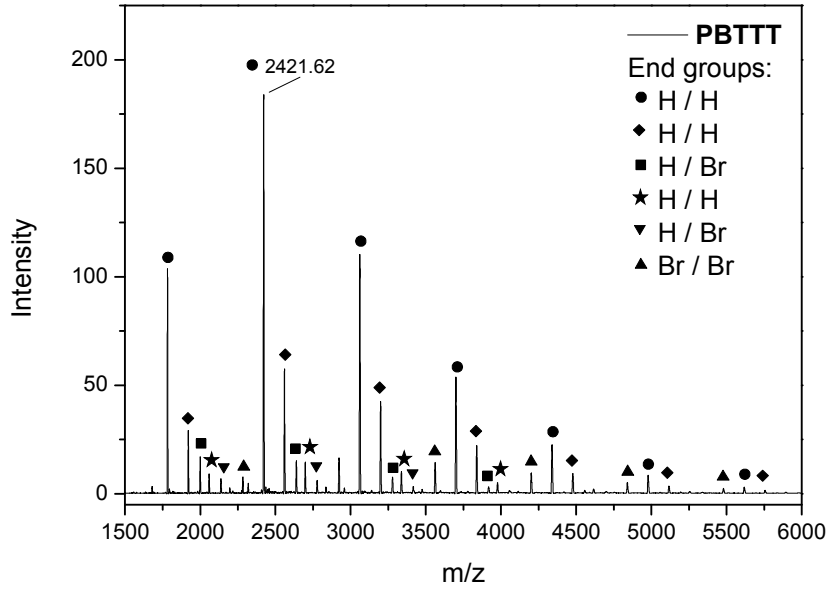
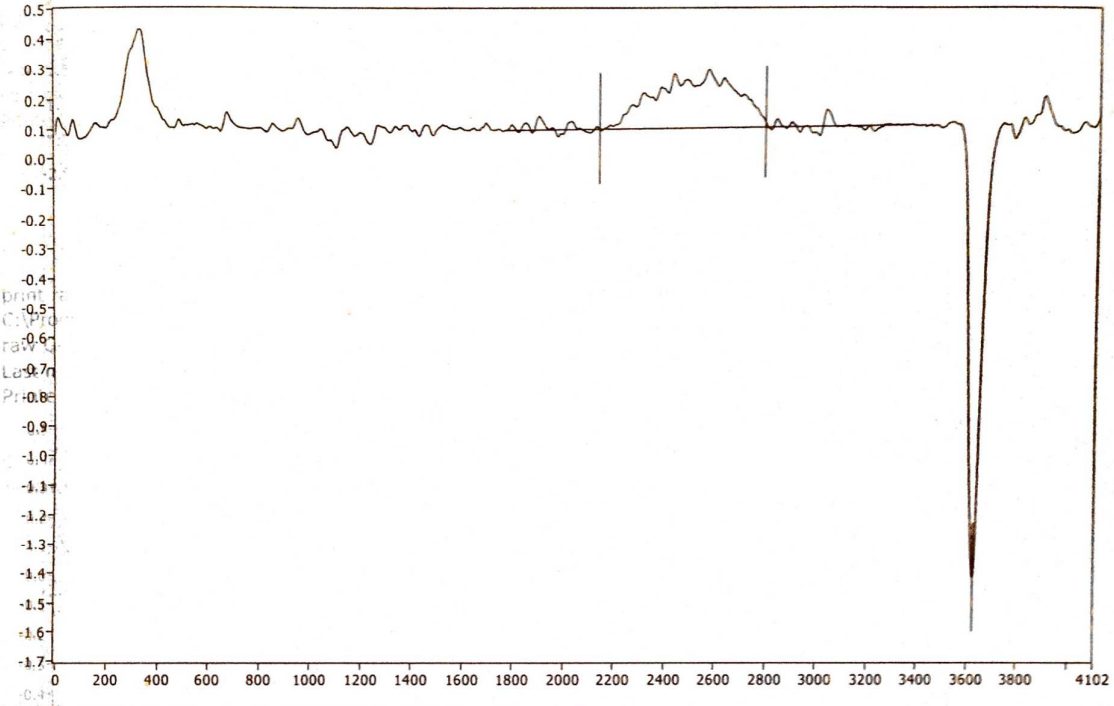


Figure S47: MALDI-TOF spectrum for **PBTTT** obtained after using 6 equiv of KOH. End groups as shown in Chart S5. Sample after Soxhlet fractionation, chlorobenzene fraction.

print GPC

print raw GPC.vi
C:\Program Files\National Instruments\LabVIEW 8.5\GPC\PC GPC aquisition 2011\analysis8.5.llb\print raw GPC.vi
Last modified on 16/01/2012 at 11:54
Printed on 04/07/2016 at 16:51



Instrument	Chlorobenzene
Sample Name	JIA 244
User Name	kn
Date and Time	01/07/2016 17:41
Solvent	Chloro Benzene
Columns	PL 2x MixedB + 500A
Column Temperature / iC	84
Detector 1	ERC 7515A
Detector 1 Temperature / iC	50
Detector 1 Sensitivity	0.3
Detector 2	
Detector 2 Temperature / iC	
Detector 2 Sensitivity	
Injection Volume	0.1ml
Injection Concentration	0.3% w/v
Pump	Gilson 307
Flow rate	0.5 ml/min
Internal Marker	Toluene
Sample rate / s	1
Comment	

Data File:

JIA 244b

Calibration File:

CBPSnew

04 Jul 2016

Unscaled marker time	3707.00
Scaled sample rate	0.9776
Left baseline time	1761.65
Right baseline time	3349.29
Left analysis time	2138.03
Right analysis time	2789.12

Crystallographic details for 3, and 10

Table S5. Crystal structure refinement data for compound **3**, and **10**.

	3	**10**
Identification code	amji306na	amji347
Empirical formula	$C_{28}H_{14}B_2N_2O_8S_2$	$C_{44}H_{69}B_2N_3O_8S_2$
Formula weight	592.15	853.76
Temperature/K	150.01(11)	150.02(13)
Crystal system	Monoclinic	triclinic
Space group	Pn	P-1
a/Å	7.2433(16)	8.2860(2)
b/Å	20.504(4)	10.6177(4)
c/Å	27.708(5)	28.6890(11)
α/°	90	82.158(3)
β/°	90	83.815(3)
γ/°	90	69.036(3)
Volume/Å^3	4115.1(14)	2330.16(15)
Z	4	2
ρ_{calc}g/cm^3	0.956	1.217
μ/mm^{-1}	0.166	0.167
F(000)	1208.0	920.0
Crystal size/mm^3	0.280 × 0.110 × 0.050	0.4 × 0.2 × 0.05
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.648 to 58.29	6.512 to 58.576
Index ranges	-9 ≤ h ≤ 7, -25 ≤ k ≤ 27, -35 ≤ l ≤ 37	-11 ≤ h ≤ 10, -13 ≤ k ≤ 11, -39 ≤ l ≤ 34
Reflections collected	22599	19598
Independent reflections	12113 [R_{int} = 0.1517, R_{sigma} = 0.3520]	10602 [R_{int} = 0.0310, R_{sigma} = 0.0702]
Data/restraints/parameters	12113/26/673	10602/0/537
Goodness-of-fit on F^2	0.962	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.1390, wR_2 = 0.3127	R_1 = 0.0565, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.3032, wR_2 = 0.4249	R_1 = 0.0864, wR_2 = 0.1355
Largest diff. peak/hole / e Å^{-3}	0.62/-0.44	0.28/-0.28
Flack parameter	-0.1(4)	---

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