Supplementary Information

Continuous flow synthesis of conjugated polymers

Helga Seyler, David J. Jones, Andrew B. Holmes and Wallace W. H. Wong,*

Bio21 Institute, School of Chemistry, University of Melbourne, Victoria 3010, Australia

Contents:

General experimental. Monomers **1**,[1] **2**,[1] **3a**,[2] **3b**,[3] **5**[4] and **7**[5] were synthesized according to procedures described in the literature. Monomers **4** and **6** were purchased from Luminescence Technology Corp. (http://www.lumtec.com.tw/). Polymers synthesised in this study, including **PFO**,[1] **PCDHTBT**,[6] and **MEH-PPV**,[5, 7] have been reported in the literature. For **PTB**, analogous polymers with side chain variations have also been reported.[4] Commercial reagents were used as purchased without further purification.

The continuous flow experiments were conducted using a Vapourtec R2+R4 unit (http://www.vapourtec.co.uk/). All solutions were degassed and reactions were performed under anaerobic conditions. Perfluoroalkoxy PFA (10 mL internal volume) or stainless steel (10 mL internal volume) tubing material was used in the reactor setups. The Vapourtec R4-pumping module equipped with manual loaded sample loops was used. The reactants were channeled into the tube reactor by pumping solvent from a reservoir. Residence times in the reactor coils were defined by the flow rate and the volume of the reactor. As the Stille reaction and the synthesis of **MEH-PPV** via the Gilch route require anhydrous conditions, the flow reactor system was thoroughly dried by first flushing with anhydrous methanol followed by dried acetone before refilling with anhydrous reaction solvent.

^{1}H and ^{13}C NMR measurements were and carried out from $CDCl_3$ solutions on a 500 MHz instrument. Gel permeation chromatography (GPC) data was obtained using a Viscotek GPC Max VE2001 solvent/sample module equiped with a Viscotek VE3580 refractive index detector. Toluene was used as the eluent with a 200 µl sample volume injection. Samples were passed through three 30 cm, PL gel (5 µm) mixed C columns and one 30 cm, PL gel (3 µm) mixed E column at 0.6 mL/min. Molecular mass distributions were calculated relative to narrow polystyrene reference standards.

Synthetic procedures

Synthesis of poly(9,9-dioctylfluorene) **PFO**

2,7-Dibromo-9,9-dioctylfluorene (2.74 g, 5 mmol), 9,9-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (3.21 g, 5 mmol) and tetrakis(triphenylphosphine)palladium(0) (115 mg, 2 mol%) were dissolved in toluene (25 mL). The solution was degassed by bubbling with nitrogen for 15 min and this was used as the stock monomer solution for both batch and flow experiments. The base solution of Et_4NOH (25 mL, 1 M, aq.) was also degassed thoroughly and used for both batch and flow reactions. More stock solutions were prepared as required.

Batch reaction: The monomer stock solution (5 mL) and aqueous base solution (5 mL) were added to a Schlenk tube and heated at 90 °C. Samples were taken from the reaction mixture at specific reaction times of 0.5, 1, 1.5, 2, 3, 4, 5 and 24 h and subjected to GPC analysis. After 24 h, the reaction was allowed to cool and the product was precipitated in MeOH. The residue was redissolved in toluene and filtered through a plug of silica followed by re-precipitation in MeOH. A pale yellow amorphous solid (250 mg, 64% yield) was collected by filtration and dried under vacuum.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.83 (t, *J* 7 Hz, -CH_3), 1.1-1.3 (br m, -CH_2-), 2.14 (br m, -CH_2-), 7.70 (br m, ArH), 7.85 (br m, ArH). GPC data: M_n = 29000; M_w = 81000; M_w/M_n = 2.8.

Flow reactions: For each flow reaction run, monomer stock solution (2 mL) and aqueous base solution (2 mL) were injected into the sample loops. Using the 10 mL PFA coil reactor unit, retention time of approximately 1 h was achieved at flow rates of 0.08 mL/min for each of the pump channels. The temperature of the coil reactor was adjusted on the Vapourtec R4 heating unit as required. Upon collection of the polymeric products, the same work-up procedure was used as the batch reaction above before GPC analysis. The NMR and GPC data for the flow reaction performed at 120 °C for 1 h are given below.

UV-vis λ_{max} = 386 nm (solution) and 387 nm (film). PL λ_{max} = 418 nm (solution) and 435 nm (film). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.86 (t, *J* 7 Hz, -CH_3), 1.1-1.3 (br m, -CH_2-), 2.17 (br m, -CH_2-), 7.72 (br m, ArH), 7.87 (br m, ArH). ^{13}C-NMR ($CDCl_3$, 500 MHz) δ ppm: 14.1, 22.6, 23.9, 29.2, 30.1, 31.8, 40.4, 55.4, 120.0, 121.5, 126.2, 127.2, 128.8, 140.0, 140.5, 151.8. GPC data: M_n = 23000; M_w = 63000; M_w/M_n = 2.8.

Synthesis of polymer **PCDHTBT**

Batch reaction: 9-(Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (132 mg, 0.2 mmol), 4,7-bis(5-bromo-4-hexylthieny-2-yl)-2,1,3-benzothiadiazole (126 mg, 0.2 mmol) and tetrakis(triphenylphosphine)palladium(0) (5 mg, 2 mol%) were dissolved in toluene (2 mL). The solution was degassed by bubbling with nitrogen for 15 min and a degassed solution of

Et_4NOH (2 mL, 1 M, aq.) was added. The reaction was heated at 90 °C and monitored via GPC after 14h and 36h. After 72 h the polymer was end-caped with phenyl boronic acid (9 mg, 0.07 mmol) and bromobenzene (0.6 mL, 5 mmol). The reaction was allowed to cool and the product was precipitated in MeOH. The residue was purified by Soxhlet extraction with acetone and petroleum spirits 40-60 °C. The remaining solid was extracted with $CHCl_3$ and the product was precipitated with methanol. A dark red amorphous solid (130 mg, 74% yield) was collected by filtration and dried under vacuum. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.82 (t, *J* 7.1 Hz, $-CH_3$), 0.89 (br m, $-CH_3$), 1.1-1.25 (br m, $-CH_2-$), 1.26-1.35 (br m, $-CH_2-$), 1.43 (br s, $-CH_2-$), 1.80 (br m, $-CH_2-$), 2.00 (br m, $-CH_2-$), 2.36 (br m, $-CH_2-$), 2.88 (br s, $-CH_2-$), 4.64 (br m, -CH-), 7.43-7.47 (br m, ArH), 7.59 (br s, ArH), 7.76 (br s, ArH), 7.93 (br s, ArH), 7.14-7.20 (br m, ArH). GPC data: M_n = 19000; M_w = 39000; M_w/M_n = 2.1.

Flow reactions: A stock solution containing the Pd-catalyst (2 mol%), the carbazole- and benzothiadiazole monomers (1 mL, 0.2 M) and the aqueous base solution (1 mL) were degassed and filtered prior injection into the sample loops. Using the PFA coil reactor units (2 x 10mL), retention time of approximately 2 h was achieved at flow rates of 0.08 mL/min for each of the pump channels. The temperature of the coil reactor was set at 120 °C on the Vapourtec R4 heating unit. Following the work-up described for the batch reaction, a dark red polymer (70 mg, 79%) was obtained.

UV-vis λ_{max} = 510 nm (solution) and 530 nm (film). PL λ_{max} = 643 nm (solution) and 673 nm (film). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.82 (m, $-CH_3$), 0.90 (br m, $-CH_3$), 1.23-1.18 (br m, $-CH_2-$), 1.33-1.27 (br m, $-CH_2-$),1.44 (br s), 1.80 (br m, $-CH_2-$), 2.00 (br m, $-CH_2-$), 2.38 (br m, $-CH_2-$), 2.89 (br s, $-CH_2-$), 4.65 (br m, -CH-), 7.48-7.44 (br m, ArH), 7.59 (br s, ArH), 7.76 (br s, ArH), 7.94 (br m, ArH), 8.21-8.15 (br m, ArH). ^{13}C-NMR ($CDCl_3$, 500 MHz) δ ppm: 14.0, 14.1, 22.6, 22.7, 27.0, 29.2, 29.4, 29.5, 31.3, 31.8, 33.9, 56.7, 109.6, 112.1, 120.2, 120.6, 121.7, 123.11, 125.3, 125.8, 130.6, 131.5, 132.0, 137.3, 139.2, 139.8, 140.9, 142.6, 152.8. GPC data: M_n = 12000; M_w = 23000; M_w/M_n = 1.9.

Synthesis of polymer **PTB**

Batch reaction with conventional heating: 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (362 mg, 0.5 mmol) and dodecyl 4,6-dibromo-thieno[3,4-*b*]thiophene-2-carboxylate (240 mg, 0.5 mmol) were dissolved in *p*-xylene (2.35 mL). The solution was degassed by bubbling with nitrogen for 15 min and tetrakis(triphenylphosphine)-palladium(0) (12 mg, 2 mol%) was added. The reaction was heated at 130 °C and monitored via GPC after 1, 2, 3 and 4h. After 14 h the mixture was allowed to cool, the product was precipitated in MeOH and washed twice with methanol and petroleum spirits. A black amorphous solid (334 mg, 89%) was collected by filtration and dried under vacuum.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.77-2.27 (br m, -CH_2-, CH_3), 3.6-4.7 (br m, O-CH_2-), 6.5-8.2 (br m, ArH). GPC data: M_n = 15000; M_w = 28000; M_w/M_n = 1.9.

Batch reaction with microwave heating: 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b'*]dithiophene (309 mg, 0.4 mmol) and dodecyl 4,6-dibromo-thieno[3,4-*b*]thiophene-2-carboxylate (204 mg, 0.4 mmol) and tetrakis(triphenylphosphine)-palladium(0) (12 mg, 2.5 mol%) were placed in a microwave vial and sealed with a septum cap under inert atmosphere. Degassed and dried *p*-xylene (2 mL) was added and the reaction was heated in the microwave reactor (Biotage Initiator Sixty) at 120 °C for 5 min, 140 °C for 5 min and 170 °C for 40 min. The resulting polymeric product (200 mg, 62% yield) was isolated in the same fashion as the batch reaction with conventional heating above.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.73-2.3 (br m, CH_3, -CH_2-), 3.5-4.7 (br m, O-CH_2-), 6.7-8.1 (br m, ArH). GPC data: M_n = 16000; M_w = 34000; M_w/M_n = 2.1.

Flow reactions: A stock solution (1.65 mL, 0.2 M) containing 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (255 mg, 0.33 mmol), dodecyl 4,6-dibromo-thieno[3,4-*b*]thiophene-2-carboxylate (171 mg, 0.33 mmol) and tetrakis(triphenylphosphine)-palladium(0) (8 mg, 2 mol%) were pumped into the stainless steel coil reactor units (2 × 10 mL). The temperature was set at 170 °C and retention time of approximately 1 h was achieved at a flow rate of 0.33 mL/min. The crude polymer solution was collected and the same work-up procedure was used as the batch reaction. A black polymer (197 mg, 75%) was isolated.

UV-vis λ_{max} = 660 nm (solution) and 665 nm (film). No significant PL response was observed in solution or thin film. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.8-2.14 (br m, -CH_2-, CH_3), 3.6-4.7 (br m, O-CH_2-), 6.5-8.1 (br m, ArH). ^{13}C-NMR ($CDCl_3$, 500 MHz) δ ppm: 11.3, 14.1, 22.7, 23.2, 23.89, 26.0, 29.5, 29.8, 32.1, 40.6, 65.9, (aromatic signals are very broad with low S/N ratios). GPC data: M_n = 17000; M_w = 29000; M_w/M_n = 1.7

Synthesis of poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) **MEH-PPV**

Batch reaction: Potassium *tert*-butoxide (5 mL, 1 M) was added to anhydrous THF (20 mL). α,α'-Dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (0.5 g, 1.2 mmol) in anhydrous THF (5 mL) was added dropwise using a syringe pump at a rate of 20 mL/h. The reaction was allowed to stir for 5 h at 25 °C and the product was precipitated in MeOH. A red amorphous solid (0.25 g, 77% yield) was collected by filtration and dried under vacuum.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.92 (br m, -CH_3), 1.01 (br m, -CH_3), 1.37 (br m, -CH_2-), 1.54 (br m, -CH_2-), 1.83 (br m, -CH-), 3.9-4.1 (br m, -OCH_2- and -OCH_3), 7.20 (br m, vinyl-H), 7.4-7.5 (br m, ArH). GPC data: M_n = 70000; M_w = 200000; M_w/M_n = 2.8.

Batch reaction with initiator: Potassium *tert*-butoxide (4 mL, 1 M) and 4-methoxyphenol (0.5 mg, 0.5 mol%) were added to anhydrous THF (6 mL). α,α'-Dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (0.34 g, 0.8 mmol) in anhydrous THF (10 mL) was added dropwise using a syringe pump at a rate of 20 mL/h. The reaction was allowed to stir for 5 h at 25 °C and the product was precipitated in MeOH. A red amorphous soild (0.17 g, 82% yield) was collected by filtration and dried under vacuum.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.92 (br m, -CH_3), 1.02 (br m, -CH_3), 1.37 (br m, -CH_2-), 1.5-1.7 (br m, -CH_2-), 1.83 (br m, -CH-), 3.9-4.1 (br m, -OCH_2- and -OCH_3), 7.20 (br m, vinyl-H), 7.4-7.5 (br m, ArH). GPC data: M_n = 69000; M_w = 121000; M_w/M_n = 1.7.

Flow reaction with initiator: The base solution was prepared by adding potassium *tert*-butoxide (4 mL, 1 M) and 4-methoxyphenol (0.5 mg, 0.5 mol%) to anhydrous THF (6 mL). The monomer solution was prepared by dissolving α,α'-dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (0.34 g, 0.8 mmol) in anhydrous THF (10 mL). The base and monomer solutions were injected into the sample loops and the reactants were pushed through the coil reactor at 25 °C. The flow rate was adjusted to give a retention time of 30 min in the 10 mL coil reactor. The polymeric product was collected and precipitated in MeOH. A red amorphous solid (0.15 g, 72% yield) was collected by filtration and dried under vacuum.

UV-vis λ_{max} = 500 nm (solution) and 500 nm (film). PL λ_{max} = 558 nm (solution) and 590 nm (film). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm: 0.92 (br m, -CH_3), 1.02 (br m, -CH_3), 1.37 (br m, -CH_2-), 1.5-1.7 (br m, -CH_2-), 1.83 (br m, -CH-), 3.9-4.1 (br m, -OCH_2- and -OCH_3), 7.20 (br m, vinyl-H), 7.4-7.5 (br m, ArH). ^{13}C-NMR ($CDCl_3$, 500 MHz) δ ppm: 11.4, 14.1, 23.1, 24.3, 29.2, 30.9, 39.9, 56.1, 56.5, 71.3, 109.1, 110.1, 126.4, 127.3, 128.6, 129.7, 151.5. GPC data: M_n = 55000; M_w = 90000; M_w/M_n = 1.6.

NMR Spectra

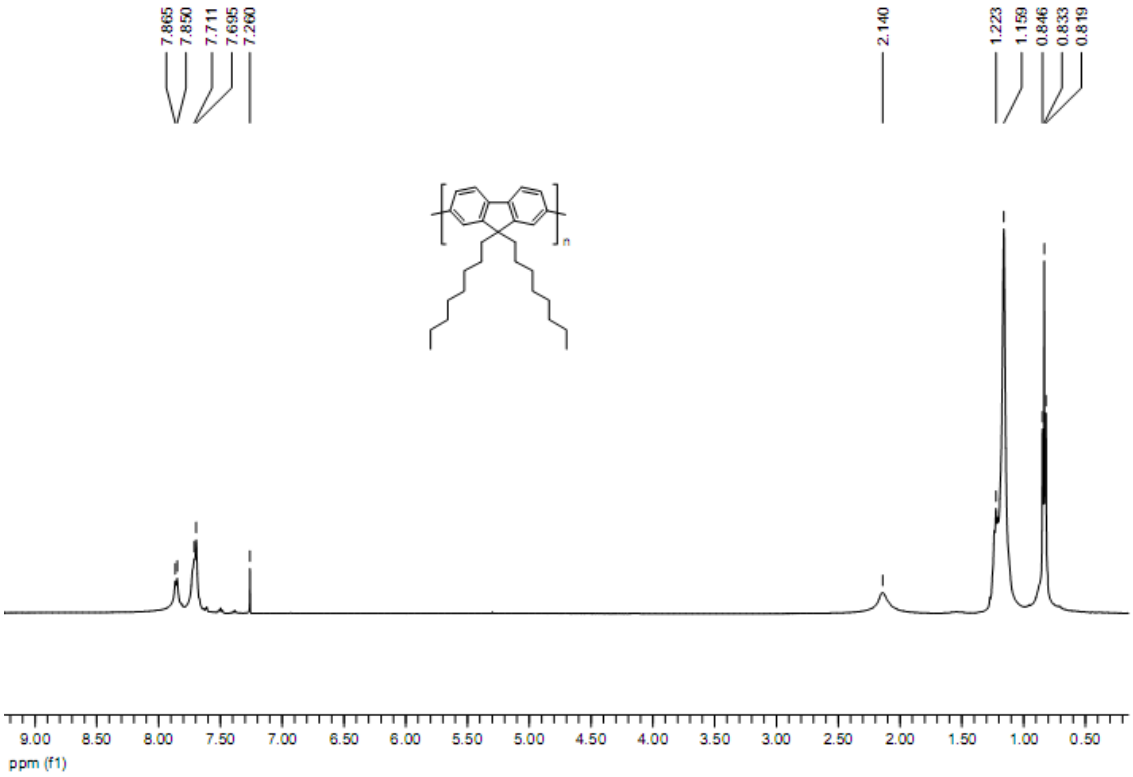

Figure S1. ^{1}H NMR spectrum of **PFO** synthesised in batch reaction measured in $CDCl_3$.

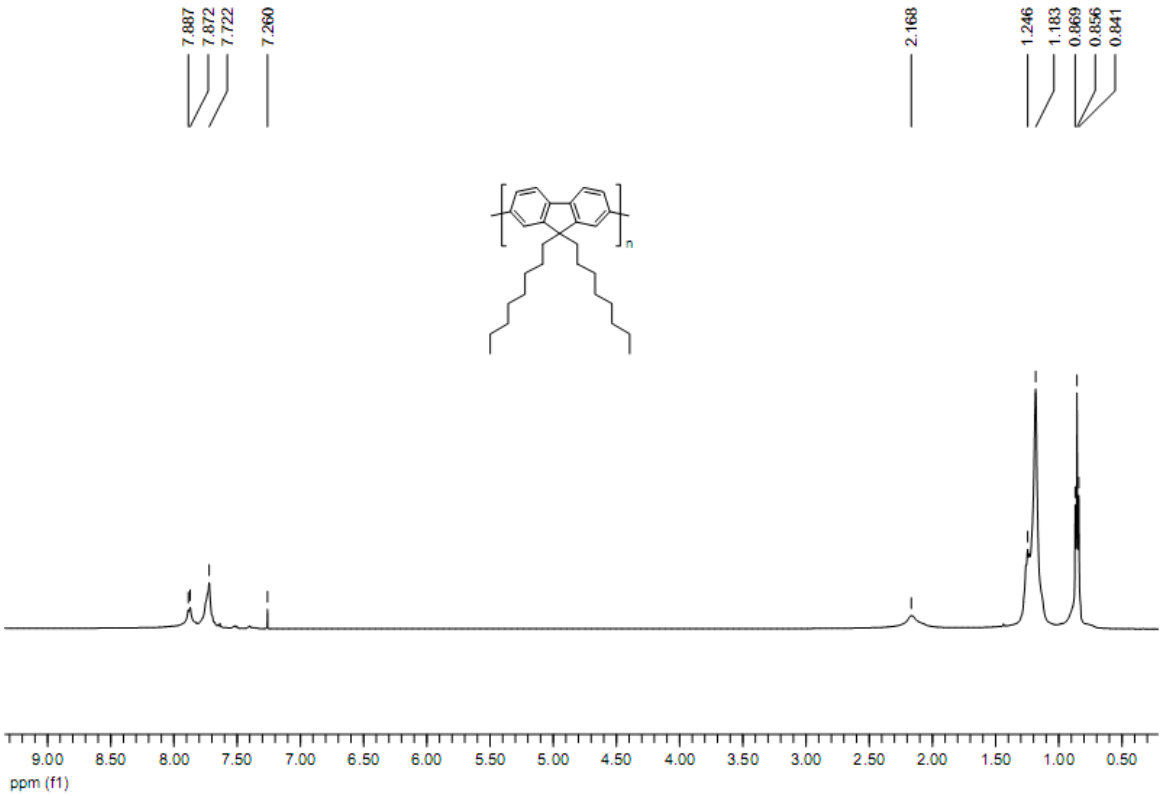

Figure S2. ^{1}H NMR spectrum of **PFO** synthesised in flow reaction measured in $CDCl_3$.

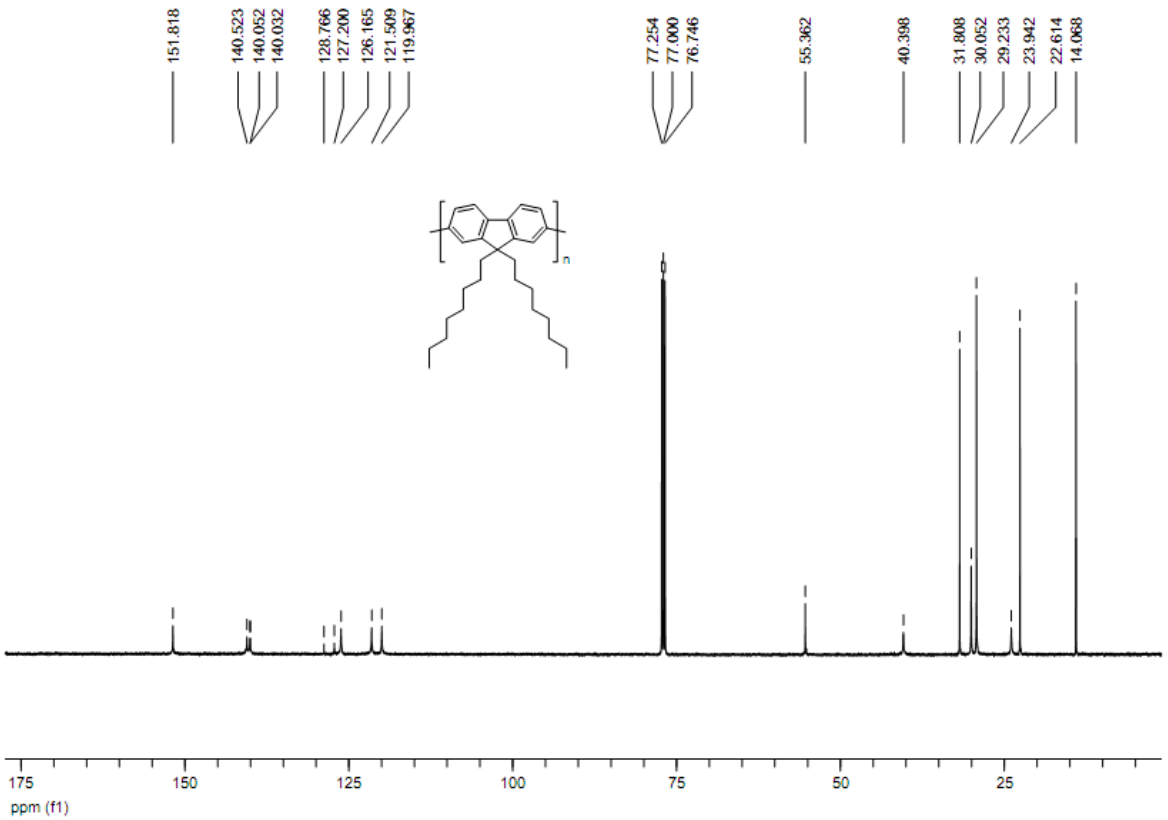

Figure S3. ^{13}C NMR spectrum of **PFO** synthesised in flow reaction measured in $CDCl_3$.

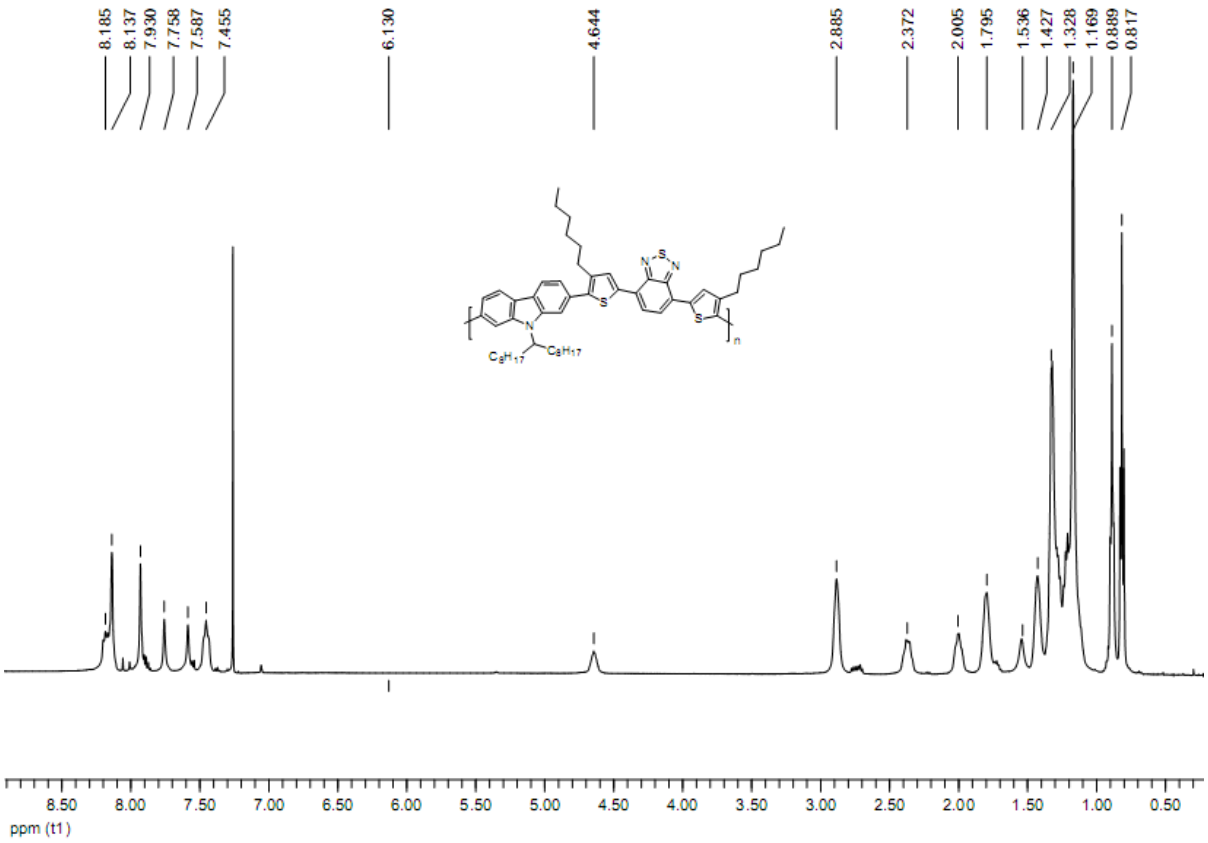

Figure S4. ^{1}H NMR spectrum of **PCDHTBT** synthesised in batch reaction measured in $CDCl_3$.

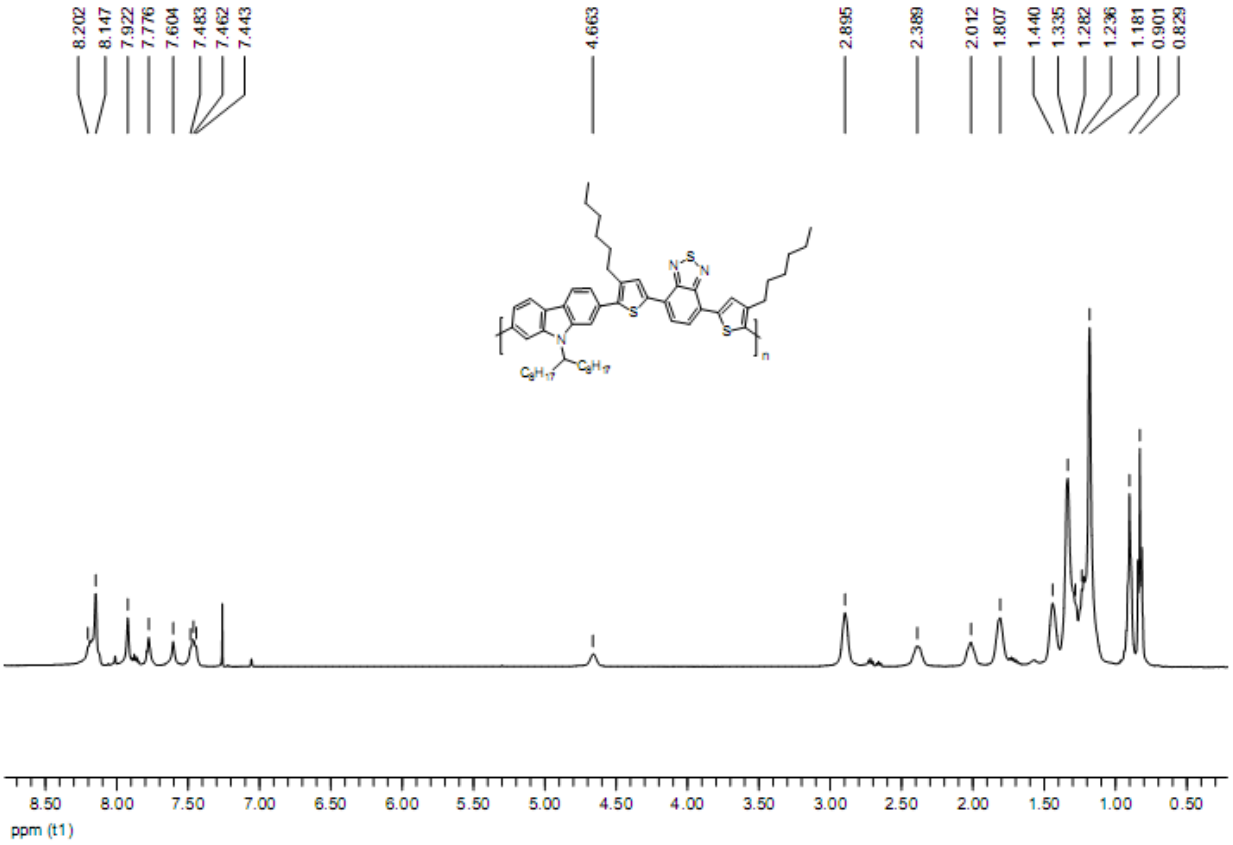

Figure S5. ^{1}H NMR spectrum of **PCDHTBT** synthesised in flow reaction measured in $CDCl_3$.

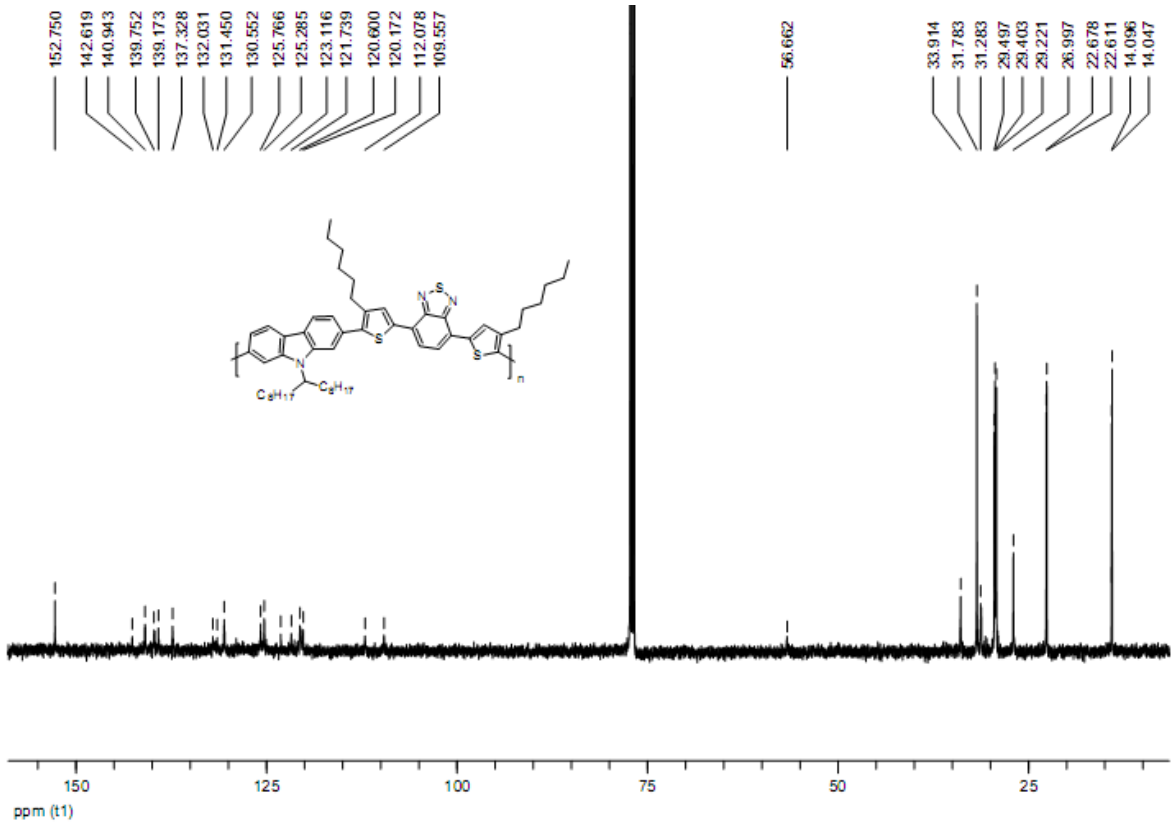

Figure S6. ^{13}C NMR spectrum of **PCDHTBT** synthesised in flow reaction measured in $CDCl_3$.

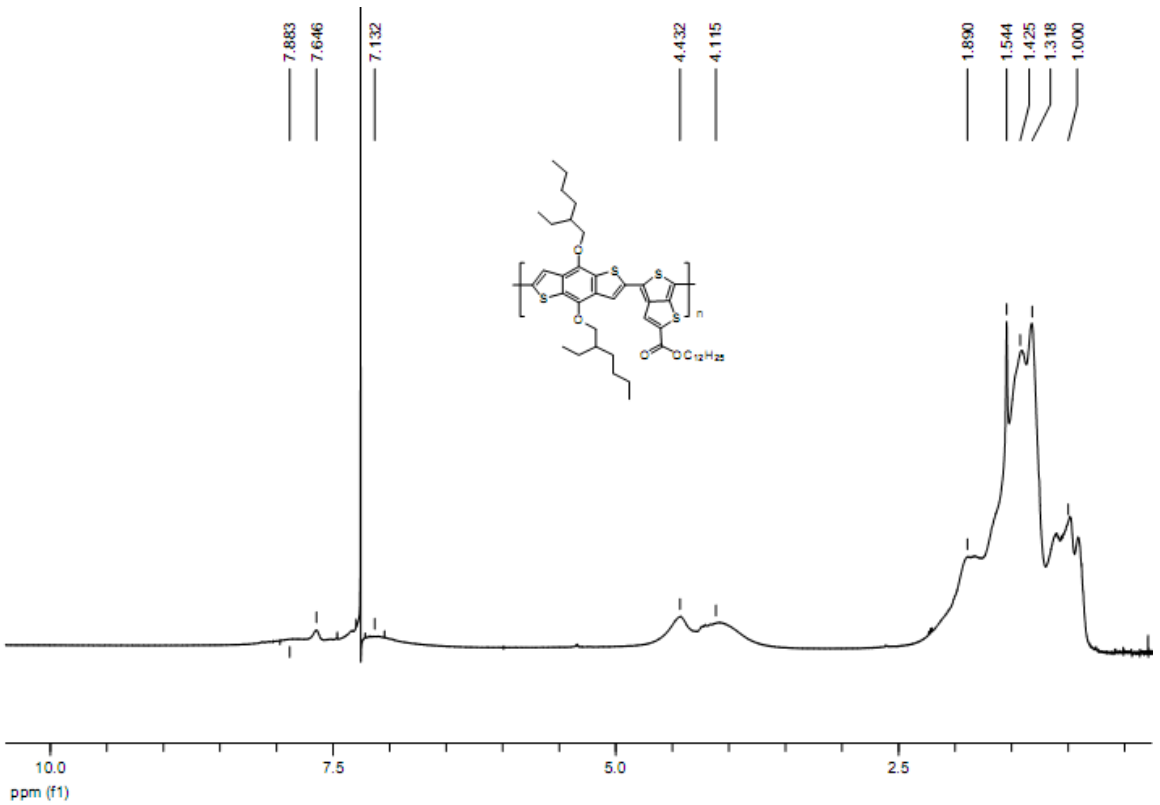

Figure S7. ^{1}H NMR spectrum of **PTB** synthesised in batch (conventional heating) reaction measured in $CDCl_3$.

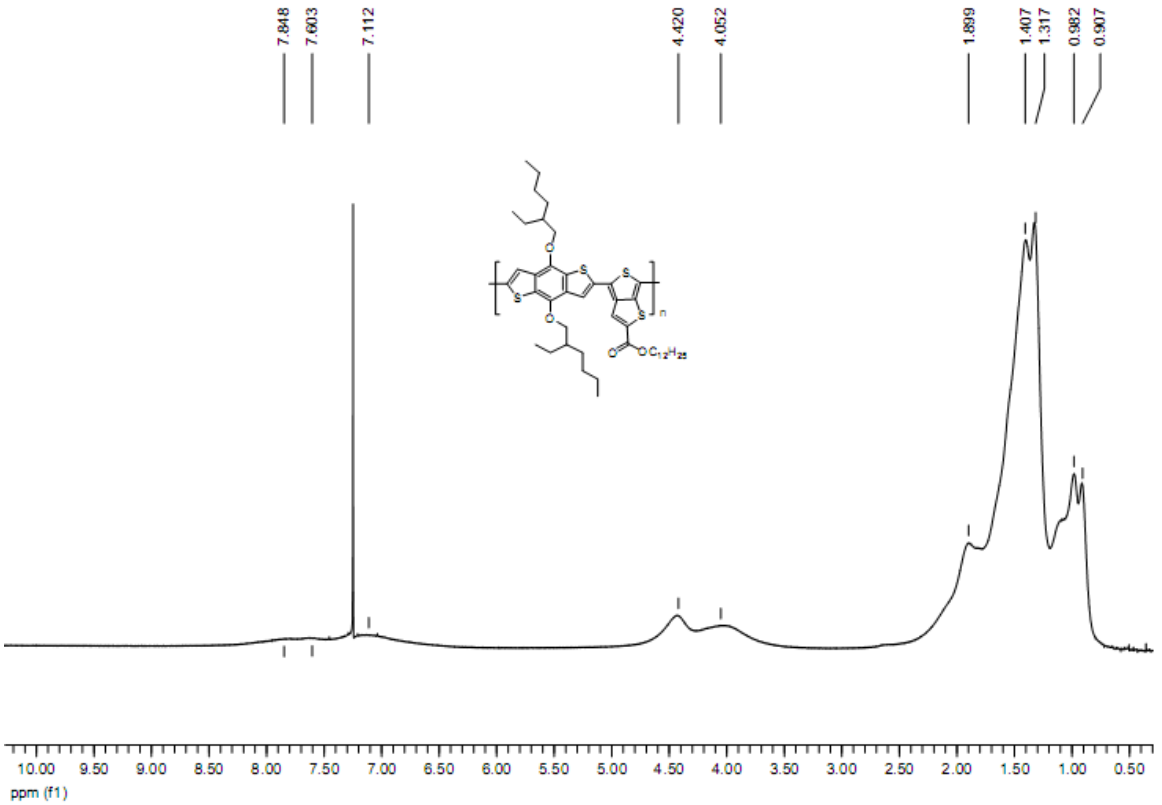

Figure S8. ^{1}H NMR spectrum of **PTB** synthesised in batch (microwave heating) reaction measured in $CDCl_3$.

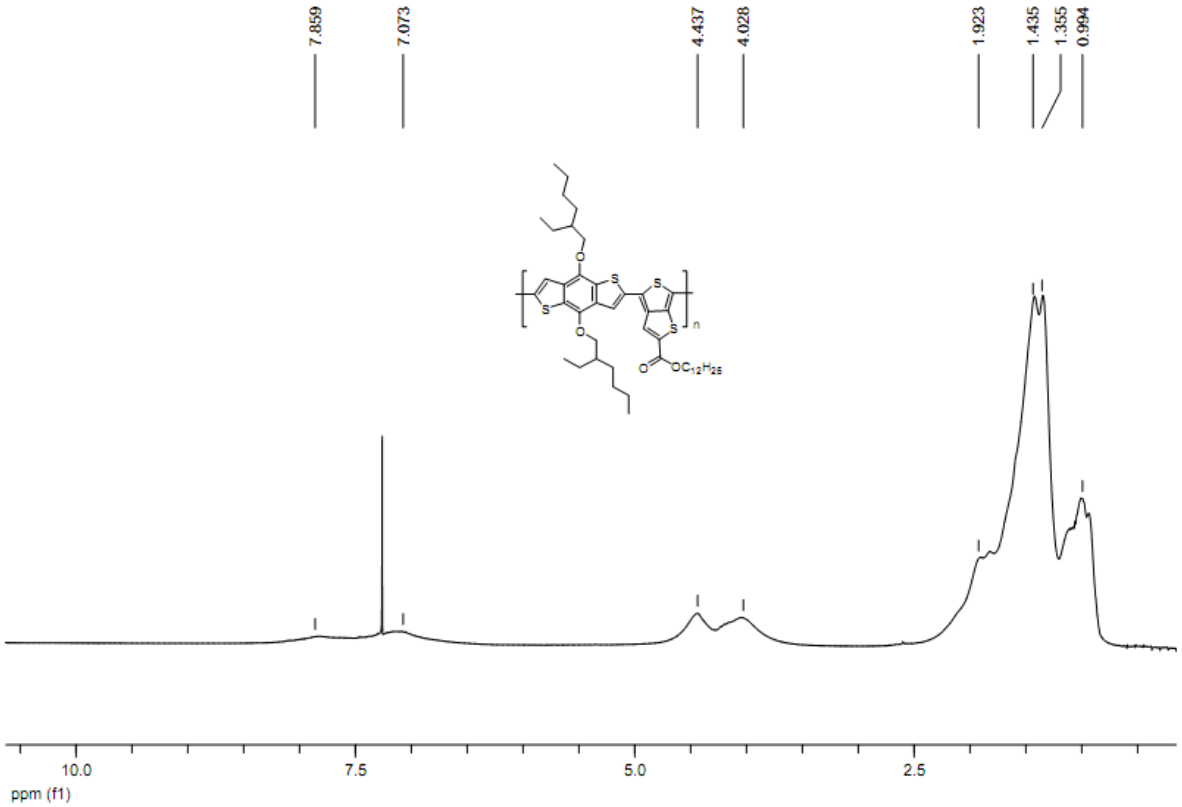

Figure S9. ^{1}H NMR spectrum of **PTB** synthesised in flow reaction measured in $CDCl_3$.

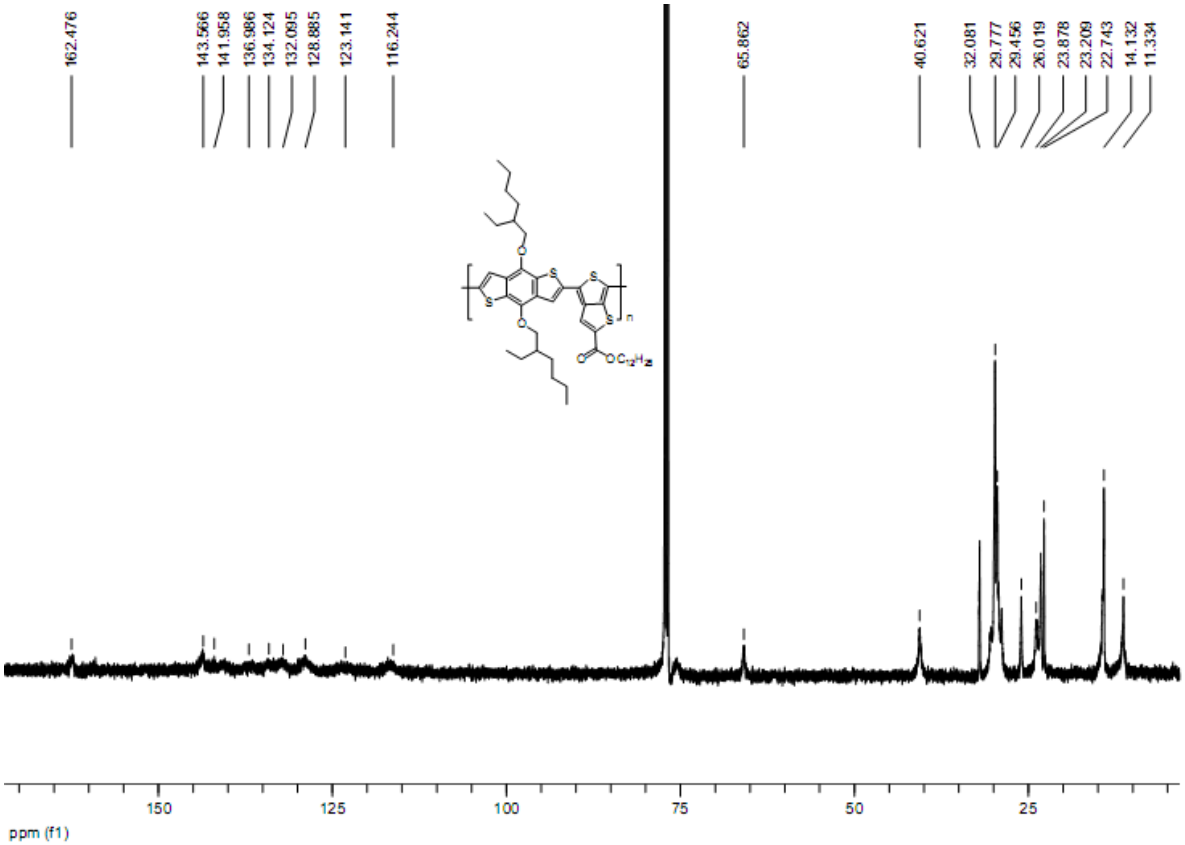

Figure S10. ^{13}C NMR spectrum of **PTB** synthesised in flow reaction measured in $CDCl_3$.

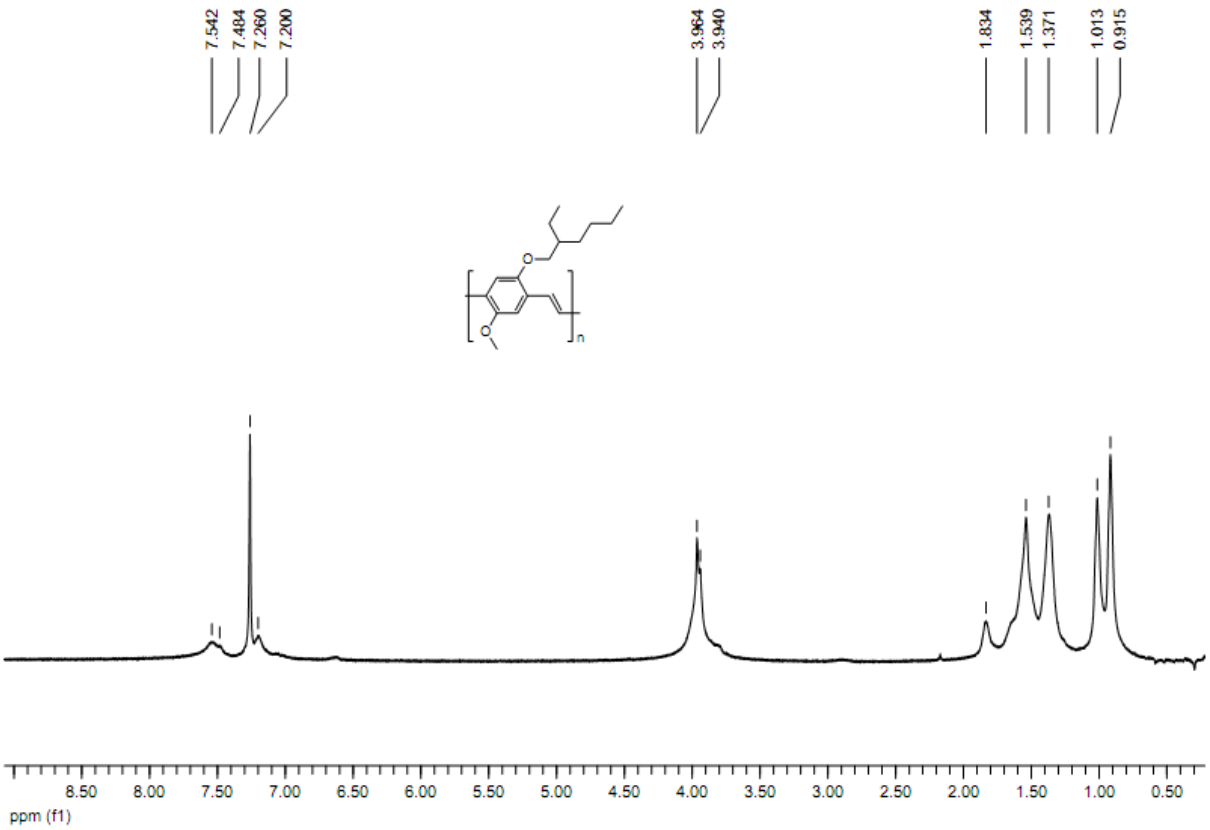

Figure S11. ^{1}H NMR spectrum of **MEH-PPV** synthesised in batch reaction measured in $CDCl_3$.

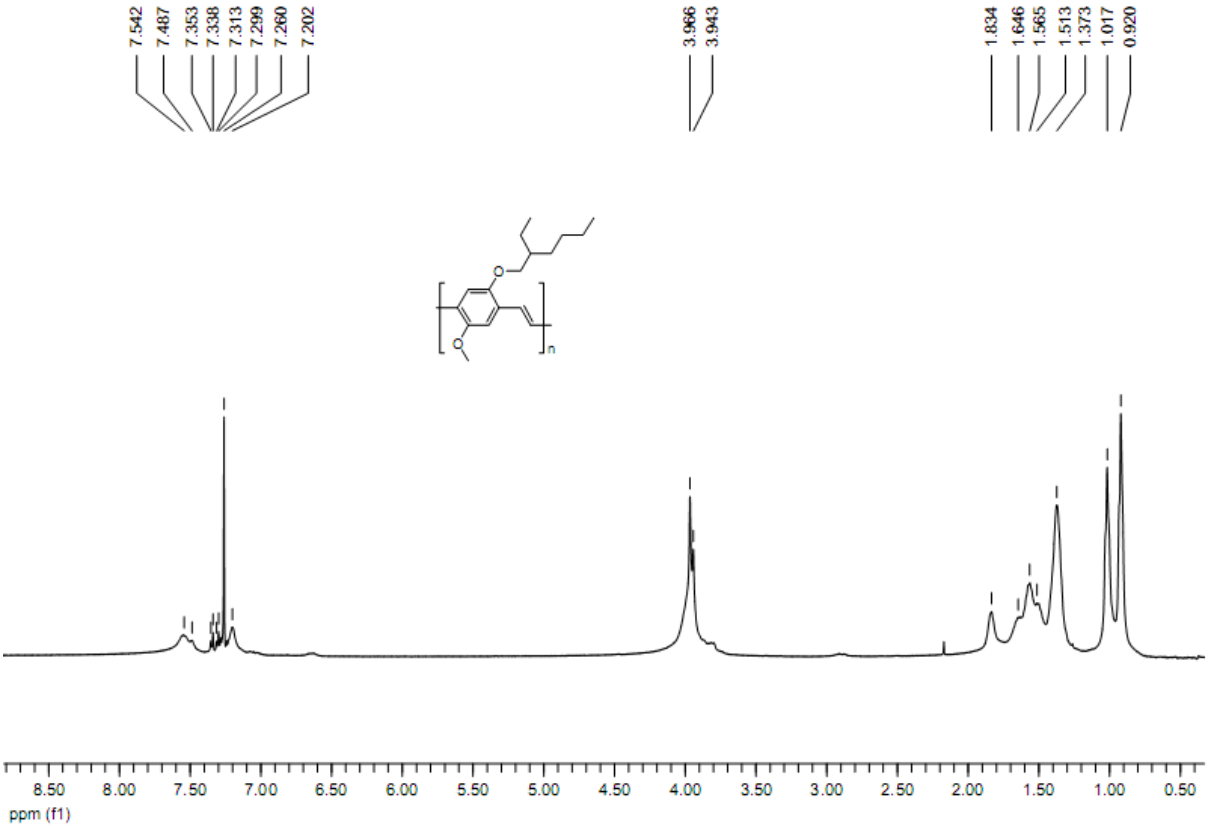

Figure S12. ^{1}H NMR spectrum of **MEH-PPV** synthesised in flow reaction measured in $CDCl_3$.

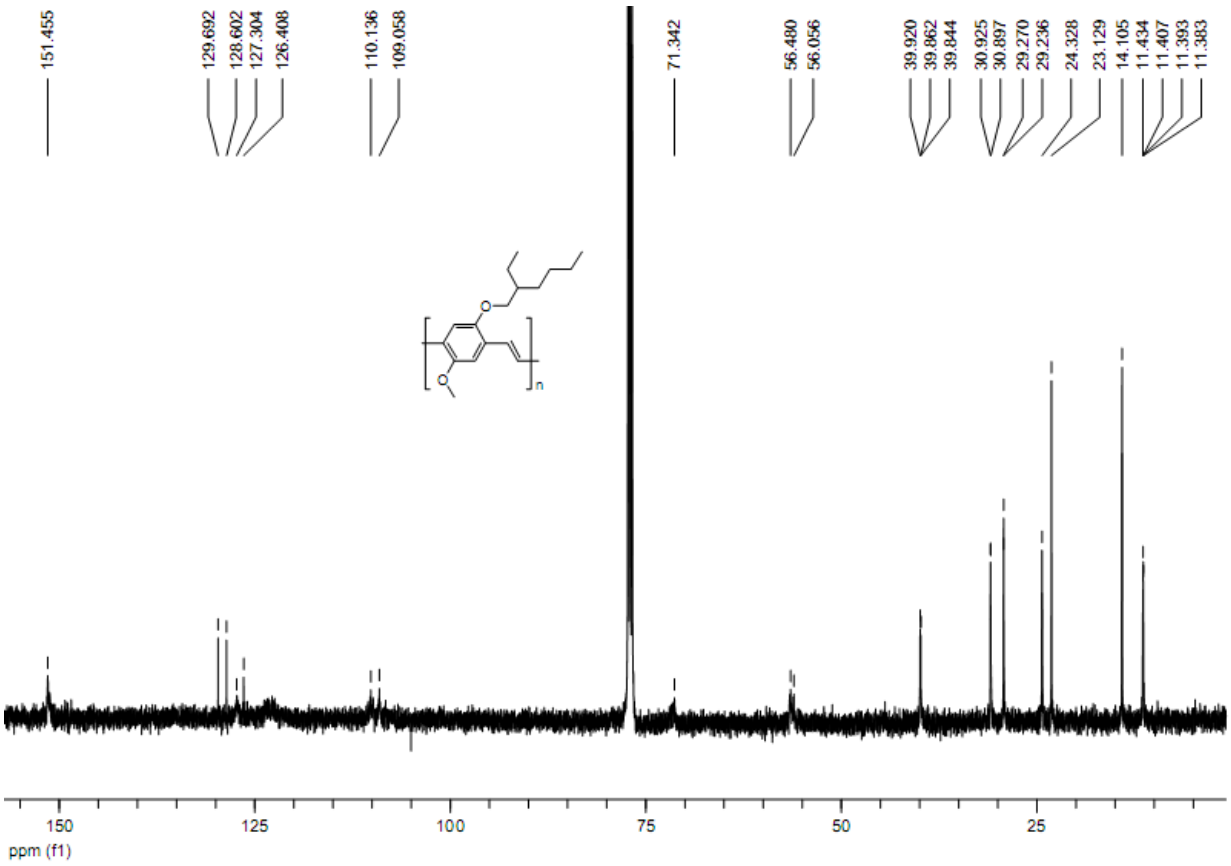

Figure S13. ^{13}C NMR spectrum of **MEH-PPV** synthesised in flow reaction measured in $CDCl_3$.

GPC data

Table S1. Reaction parameters and corresponding GPC data for synthesis of **PFO** vis Suzuki polycondensation.

Entry	Method	Temp. [°C]	Reaction Time [h]	Monomer Conc. [M]	Base Conc. [M]	Pd catalyst [mol%]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
1	Batch	90	1	0.2	1	2	2900	3400	1.2
2	Batch	90	2	0.2	1	2	21000	71000	3.4
3	Batch	90	24	0.2	1	2	29000	81000	2.8
4	Flow	90	1	0.2	1	2	12000	39000	3.4
5	Flow	120	1	0.2	1	2	23000	63000	2.8
6	Flow	120	0.5	0.2	1	2	20000	62000	3.1
7	Flow	150	1	0.2	1	2	17000	54000	3.1
8	Flow	150	1	0.1	1	2	9100	32000	3.5
9	Flow	150	1	0.2	0.2	2	2200	3800	1.7
10	Flow	150	1	0.2	1	0.2	1600	3100	1.9

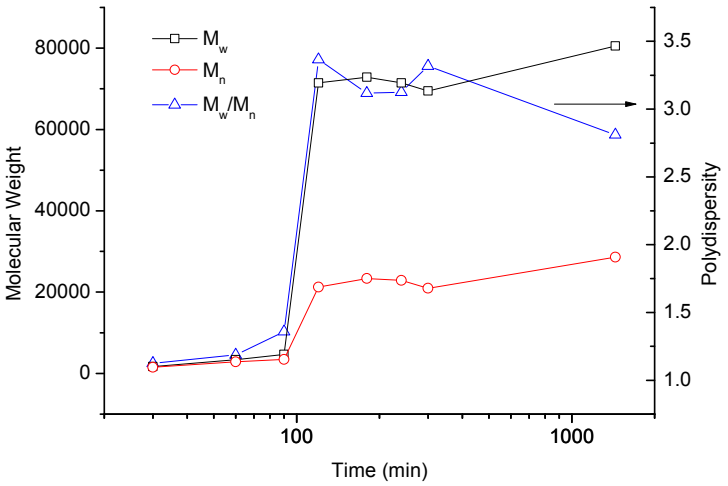

Figure S14. Progress of polymerisation for **PFO** in conventional batch reaction.

Table S2. Reaction parameters and corresponding GPC data for Suzuki polycondensations in batch and flow for **PCDHTBT**.

Entry	Method	Temp. [°C]	Reaction Time [h]	Monomer Conc. [M]	Base Conc. [M]	Pd catalyst [mol%]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
1	Batch	90	14	0.1	1	2	15000	25000	1.6
2	Batch	90	36	0.1	1	2	15000	28000	1.9
3	Batch	90	72	0.1	1	2	19000	39000	2.1
4	Flow	120	2	0.2	1	2	12000	23000	1.9

Table S3. Reaction parameters and corresponding GPC data for Stille polycondensations in batch and flow for **PTB**.

Entry	Method	Temp. [°C]	Reaction Time [h]	Monomer Conc. [M]	Pd catalyst [mol%]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
1	Batch	130	1	0.2	2	800	1000	1.2
2	Batch	130	2	0.2	2	1000	1500	1.4
3	Batch	130	3	0.2	2	2500	4600	2.9
4	Batch	130	4	0.2	2	3900	7400	1.9
5	Batch	130	14	0.2	2	15000	28000	1.9
6	Flow	170	1	0.2	2	17000	29000	1.7

Photophysical data

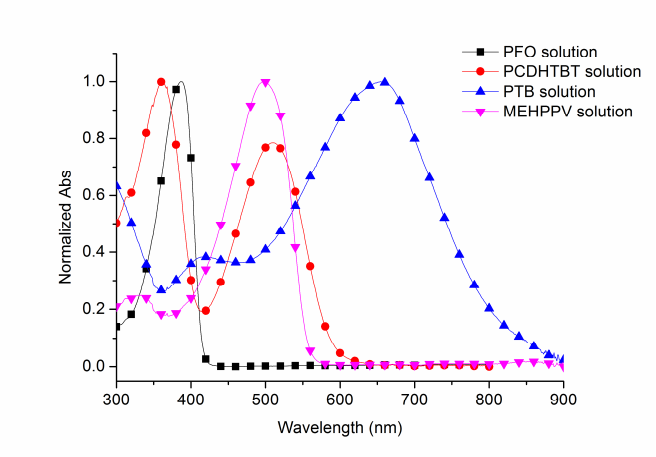

Figure S15. Normalised UV-vis spectrum of polymers synthesised in flow in $CHCl_3$ solution (~ 0.1 mg/L).

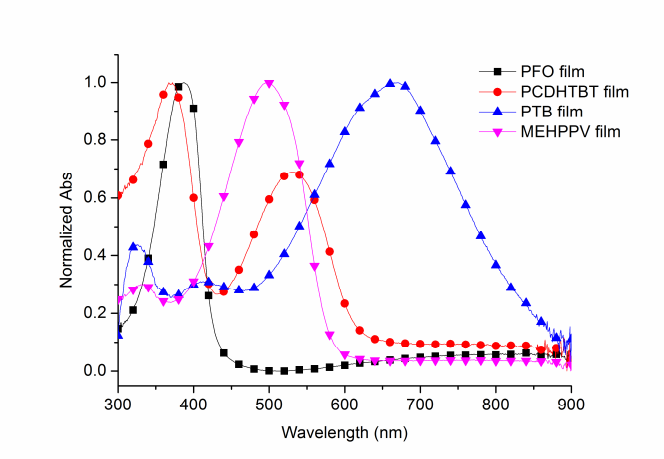

Figure S16. Normalised UV-vis spectrum of polymers synthesised in flow as thin films on glass.

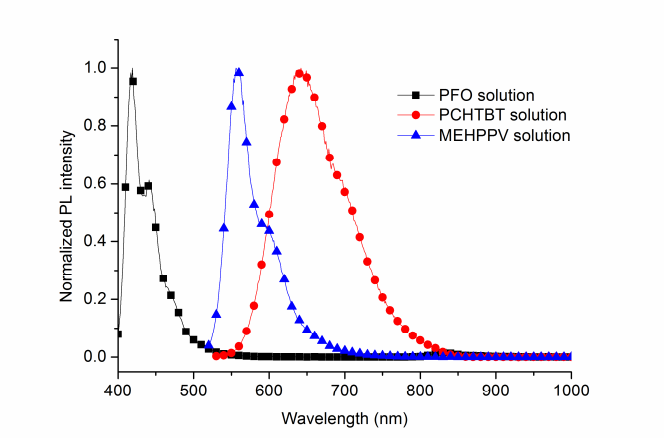

Figure S17. Normalised photoluminescence (PL) spectrum of polymers synthesised in flow in $CHCl_3$ solution (~ 0.1 mg/L). Note: No significant PL was observed for polymer **PTB**.

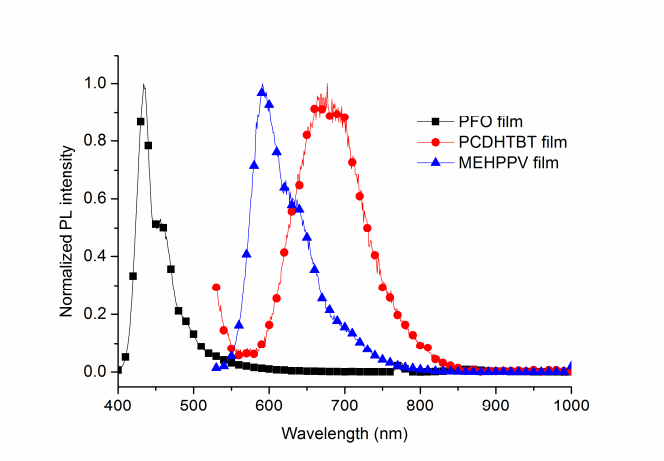

Figure S18. Normalised photoluminescence (PL) spectrum of polymers synthesised as thin films on glass. Note: No significant PL was observed for polymer **PTB**.

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