

Supporting Information

Direct (Hetero)arylation (DHAP) Polymerization of Conjugated Polymers – New A-B-A Monomer Design for P(NDI2OD-T2) & The Challenges of adopting DHAP for Continuous Flow Processes

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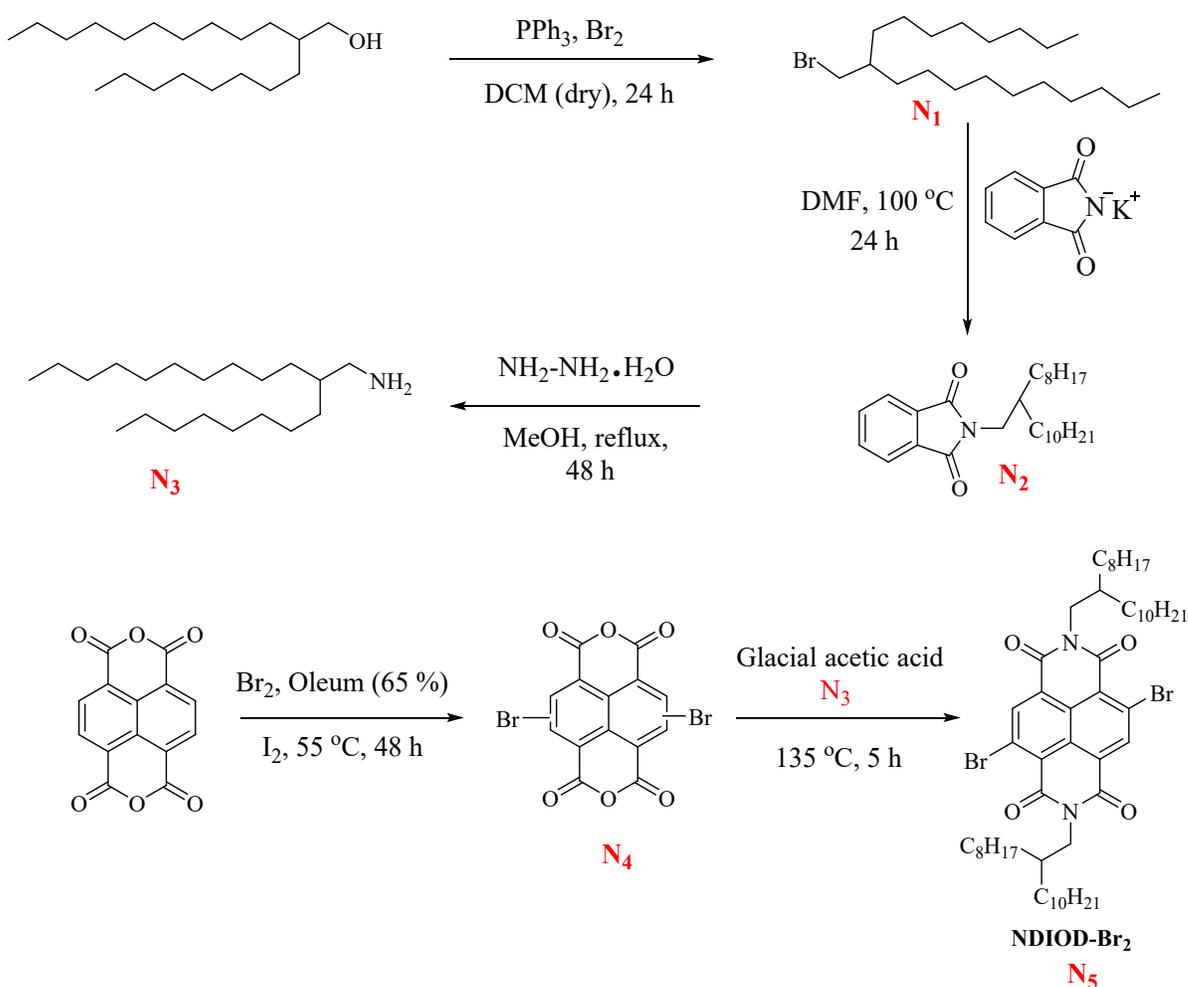
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S1: Synthesis of NDIOD-Br₂ (N5)



Synthesis of 2-octylododecyl bromide (N₁)

In a dry two-necked round bottom flask, PPh₃ (52 g, 201.34 mmol) was dissolved in dry dichloromethane (DCM) (200 mL) and degassed by N₂ for 15 min. Molecular bromine (10.24 mL, 201.34 mmol) was added drop-wise in the reaction mixture. The resulted reaction mixture was stirred at 0 °C for 1 h. Then 2-octyl-1-dodecanol (49 g, 201.34 mmol) was added drop-wise by dropping funnel over a period of 45 min. After the addition, the reaction mixture was stirred at room temperature for 24 h under inert conditions. The dichloromethane was removed by rotatory evaporation. The white solid was suspended in hexane (250 mL), the insoluble part was removed by vacuum filtration using the Buckner funnel. The filtrate was concentrated on the

rotary evaporation to obtain a liquid crude product. The crude product was purified by column chromatography on silica gel using pet ether as the eluent to afford the pure N₁ colourless oil. Yield 62 %. ¹H NMR spectrum (200 MHz instrument, CDCl₃) δ (ppm), 3.53 (2 H, d), 1.80 (1 H, m), 1.26 (32 H, m), 0.88 (6 H, t).

Synthesis of 2-(2-octyldodecyl)isoindoline-1,3-dione (N₂)

In two neck (250 mL) round bottom flask, Potassium phthalimide (23.06 g, 124.50 mmol) was dissolved in dry dimethylformamide (DMF) (55 mL), and reaction mixture was heated at 100 °C for 1 h. After completing 1 h, octyldecyl bromide (N1) (45 g, 124.65 mmol) was added dropwise by dropping funnel. The reaction mixture was refluxed at 100 °C for 24 h. The reaction mixture was cooled and poured in 800 mL deionized water. The solution was extracted with dichloromethane. The organic layer was washed by 0.2 N KOH solution followed by a saturated ammonium chloride (NH₄Cl) solution and dried over sodium sulphate (Na₂SO₄). The solution was concentrated by a rotary evaporator to afford liquid crude product. The liquid crude compound was purified by column chromatography on silica gel using a pet ether and ethyl acetate (95:5 v/v) as eluent to afford colourless oil N₂. Yield 54 %. ¹H NMR spectrum (200 MHz instrument, CDCl₃): δ (ppm), 7.82 (2 H, d), 7.72 (2 H, d), 3.59 (2 H, d), 1.87(1 H, m), 0.87 (6 H, m).

Synthesis of 2-octyldodecan-1-amine (N₃)

2-(2-octyldodecyl)isoindoline-1,3-dione(N₂) (47 g, 110.07 mmol) and hydrazine hydrate (16 g, 330.21 mmol) were taken into a dry two neck round bottom flask. To this reaction mixture methanol (150 mL) was added under an N₂ atmosphere. The reaction mixture was refluxed for 48 h, and reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, methanol was evaporated by rotary evaporation, and the solid residue was diluted by dichloromethane (60 mL). The organic layer was separated by separating funnel. Subsequently, the reaction mixture was washed by KOH solution followed by saturated NaCl solution. The compound was dried over sodium sulfate (Na₂SO₄) and concentrated on rotary evaporation. The crude product was used without further purification. Yield 78 %. ¹H NMR spectrum (200 MHz instrument, CDCl₃): δ (ppm), 5.4 (2 H, d), 1.45 (1 H, m), 1.21 (38 H, m), 0.83 (6 H, m).

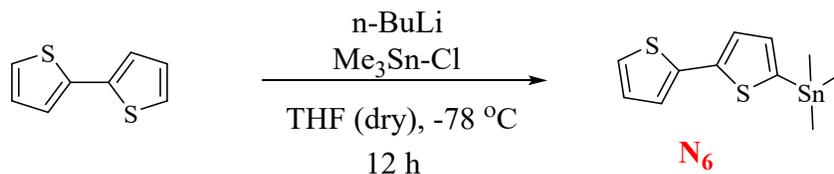
Synthesis of NTCDA-Br₂ (N₄)

A 250 mL two necked round bottom flask was charged with 1, 4, 5, 8-Naphthalenetetracarboxylic dianhydride (4 g, 14.92 mmol) and iodine 164 mg mixed in oleum (65 %). The reaction mixture was stirred at room temperature for 2.5 h under a nitrogen atmosphere. Then, Br₂ (4.53 g, 28.35 mmol) was added dropwise to the reaction mixture using a dropping funnel. The reaction mixture was stirred at 55 °C for 48 h. After completion of the reaction, the reaction mixture was poured drop-wise in ice bath. The yellow precipitate was filtered using Buckner funnel and washed by saturated solution of sodium thiosulfate (Na₂S₂O₃) to remove excess Br₂. The crude product was further washed by 60 mL of water and methanol respectively. The crude product was dried in a vacuum oven at 90 °C for 24 h. The dried product was used as it is for further reaction because the product was not soluble in any organic solvent. The yield of crude product was 75 %.

Synthesis of NDIODBr₂ (N₅)

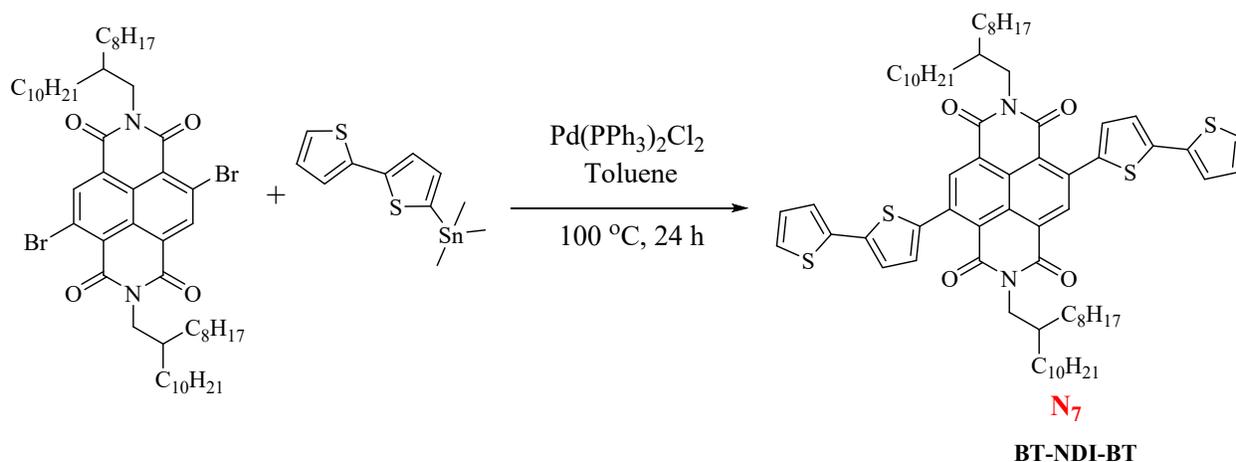
NTCDA-Br₂ (4 g, 9.38 mmol) was dissolved in 90 mL glacial acetic acid. The reaction mixture was stirred and refluxed at 135 °C in a nitrogen atmosphere for 1 h. 2-octyldodecan-1-amine (8.38 g, 28.16 mmol) was added drop-wise in the reaction mixture, then reaction mixture was refluxed at 135 °C for 4 h. The completion of reaction was indicated by change of color from yellow to reddish. The reaction mixture was cooled to room temperature and poured in 1 Lit of deionized water. The organic layer was extracted with dichloromethane (DCM) and successively washed by brine solution. The organic layer was dried over sodium sulfate (Na₂SO₄) and concentrated by rotary evaporation. The resultant reddish viscous compound was purified by column chromatography (silica gel, 200–300 mesh) using petroleum ether and ethyl acetate (98.5:1.5 v/v) as the eluent to give the pure N₅ as solid yellow. Yield 26 %. ¹H NMR spectrum (400 MHz instruments, CDCl₃) δ (ppm), 9.00 (2 H, s), 4.16 (4 H, d), 1.57 (2 H, m), 1.24 (64 H, m), 0.88 (12 H, s). ¹³C NMR Spectrum (100 MHz instrument, CDCl₃) δ (ppm) 161.17, 161.02, 139.15, 128.36, 127.74, 125.27, 124.07, 45.44, 36.45, 31.90, 31.87, 30.01, 29.62, 26.32, 22.65, 14.10. MALDI-TOF MS (Calcd Mol Wt: 985.08); Found Mol Wt: 984.90 [M+H].

S2: Synthesis of [2,2'-bithiophene]-5-yltrimethylstannane (N₆)



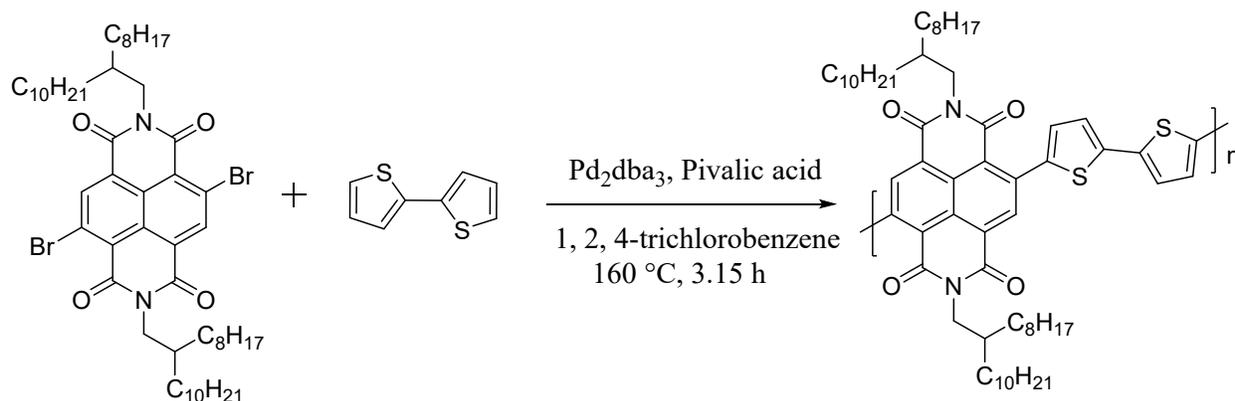
To an oven-dried, two-neck round bottom flask (25 mL) equipped with stir bar was added bithiophene (2 g, 12.03 mmol). The flask was evacuated and filled with nitrogen (N₂) three-times. Dry THF (15 mL) was added, and the mixture was cooled to -78 °C. n-BuLi (0.809 gm, 12.63 mmol) 2.5 molar in hexane was added drop-wise in the reaction mixture and stirred for 1.5 h at -78 °C. Me₃Sn-Cl (2.637 g, 12.03 mmol) was added in portions to the reaction mixture, and it was allowed to warm up slowly overnight from -78 °C to room temperature. NH₄Cl saturated aq (10 ml) was added to the reaction mixture, and it was extracted with diethyl ether three times. The combined organic layers were washed with brine solution and dried with MgSO₄. After drying, the compound was kept in the fridge overnight, and then filtered and filtrate was used without further purification. Yield 60 %. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 7.38 (1 H, dd), 7.28 (1 H, dd), 7.19 (1 H, dd), 7.11-7.10 (2 H, m), 0.49 (9 H, s). ¹³C NMR Spectrum (100 MHz instrument, CDCl₃) δ (ppm) 142.97, 137.94, 135.94, 127.84, 124.84, 123.82, 123.83, 8.12.

S3: Synthesis of BT-NDI-BT (N₇)



An oven dry Schlenk tube (15 mL) containing magnetic stir bar was charged with 4,9-Dibromo-2,7-bis(2-octyl dodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (NDIOD-Br₂) (200 mg, 0.203 mmol), 2,2-bithiophene-5-trimethylstannane (166.99 mg, 0.507 mmol) and Pd(PPh₃)₂Cl₂ (1.42 mg, 1 mol %). After adding monomers and catalyst, the flask was evacuated three times and degassed by nitrogen (N₂). Separately degassed toluene (2 mL) was added in a reaction vessel under inert condition and stirred for 15-20 min at room temperature to fully dissolve the monomer and then kept the reaction vessel in a preheated oil bath at 100 °C with stirring for 24 h. After the completion of reaction, the reaction mixture was precipitated in methanol and filtered using Buckner funnel. The resultant black solid compound was purified by column chromatography (silica gel, 200–300 mesh) using petroleum ether and ethyl acetate (99:1 v/v) as the eluent to obtained the pure N₇ a black solid. Yield 72 %. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ ppm 8.80 (2 H, s), 7.30-7.29 (4 H, m), 7.27-7.26 (4 H, m), 7.08-7.07 (2 H, m), 4.12-4.10 (4 H, d) 1.9 (2 H, m), 1.28-1.22 (75 H, m), 0.88-0.85 (12 H, m). ¹³C NMR Spectrum (100 MHz instrument, CDCl₃) δ (ppm) 161.50, 139.69, 138.34, 135.77, 135.49, 128.84, 126.92, 123.38, 122.97, 121.65, 43.94, 35.50, 30.88, 28.61, 28.29, 21.64, 13.09. MALDI-TOF MS (Calcd Mol Wt: 1155.77); Found Mol Wt: 1155.79 [M+H], 1178.24 [M+Na].

S4: Synthesis of P(NDI2OD-T2) by DHAP method in batch (A)



In a 15 ml oven-dry Schlenk tube equipped with magnetic stirring bar were added NDIOD-Br₂ (100 mg, 0.101 mmol), bithiophene (16.79 mg, 0.101 mmol), pivalic acid (10.31 mg, 0.101 mmol), K₂CO₃ (42 mg, 0.303 mmol) and Pd₂dba₃ (1 mole %). Then the tube was evacuated three-times and purged by nitrogen (N₂). 0.3 mL of degassed T-butyl toluene was added to the reaction mixture under inert conditions. The reaction mixture was stirred for 15-20 min at room temperature to fully dissolve the monomers. The Schlenk tube was kept in a preheated oil bath at 160 °C with stirring for 3.15 h. The polymerization mixture was cooled to room temperature and polymer was dissolved in chloroform and precipitated in methanol. The precipitated polymer was filtered using Buckner funnel. The polymer was purified by Soxhlet extraction using methanol, acetone and hexane (removes catalytic residues and low molecular weight polymer). After the Soxhlet extraction, the polymer was dissolved in chloroform and precipitated in MeOH. The polymer was filtered on Buckner funnel and dried in a vacuum oven to afford deep blue colored polymer. Yield 91 %. ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 90 °C): δ (ppm), 8.91 (2 H), 7.44 (4 H), 4.21 (4 H), 2.11 (2 H), 1.55-1.32 (64 H), 0.93-0.91 (12 H).

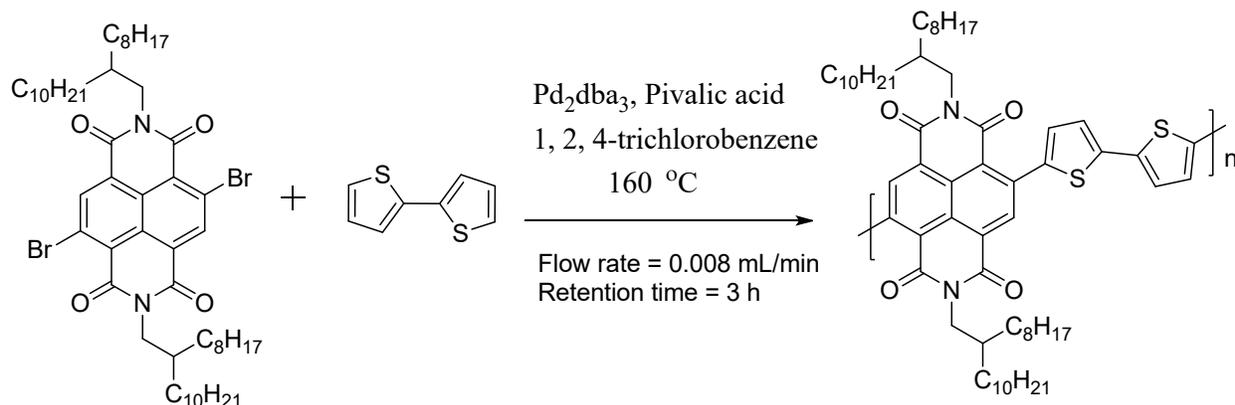
S5: Glass column reactor packing

Activated potassium carbonate (K_2CO_3) (2 g) was mixed with celite (4 g), and then the mixture was crushed using a mortar and pestle until it was homogeneous. The homogenous mixture was prepared under open-air conditions. The mixture was kept at 100 °C for 24 h. The column reactor was filled with the packing material (approximately 1g of mixture for one glass reactor). The glass reactor was connected to the syringe by a PTFE tubing flow system (pre-washed with degassed 1, 2, 4-trichlorobenzene solvent), and the solvent was pumped through it until it filled, with no air bubbles visibly (flow rate 0.1-0.15 mL/min for 1 to 2 h). The reactor was then ready to be used.



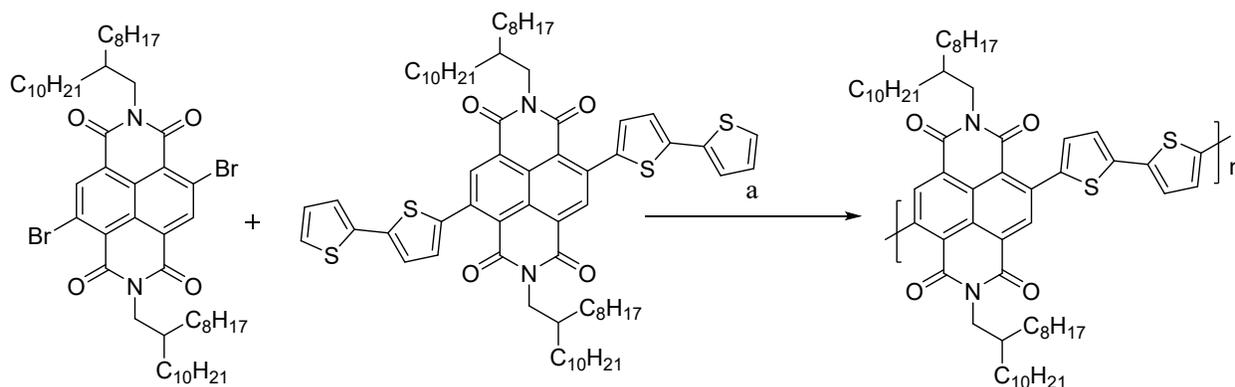
a) Homogeneous mixture of K_2CO_3 and Celite, and b) packed glass column reactor with K_2CO_3 and celite

S6: Synthesis of P(NDI2OD-T2) by DHAP method in continuous flow method (B)



In a 100 mL oven-dry two neck round bottom flask equipped with a stirring bar added NDIOD-Br₂ (500 mg, 0.507 mmol), bithiophene (84.41 mg, 0.507 mmol), pivalic acid (51.83 mg, 0.507 mmol), Pd₂dba₃ (1 mol %). The round bottom flask was evacuated three times and purged with nitrogen. 10 mL of degassed 1, 2, 4-trichlorobenzene was added. The reaction mixture was stirred for 15-20 min at room temperature to fully dissolve the monomers. The reaction mixtures was then taken in a syringe, placed onto the syringe pump, and rapidly connected to the preheated flow reactor by PTFE tubing. The whole reactor was exposed to air directly. The reaction mixture was injected into the flow reactor at a certain flow rate (0.008 ml/min). The flow reactor was heated at 120 °C with a 3 h residence time of polymerization in flow reactor. Once the polymerization was completed, the polymer was precipitated in methanol and stirred for another 2 h. The precipitate was collected by filtration using Buckner funnel. The polymer was purified by Soxhlet extraction using methanol, acetone and hexane (removes catalytic residues and low molecular weight polymer). After the Soxhlet extraction, the polymer was dissolved in chloroform and precipitated in MeOH. The polymer was filtered on Buckner funnel and dried in a vacuum oven to afford deep blue colored polymer. Yield 70 %. ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 90 °C): δ (ppm), 8.91 (2 H), 7.44 (4 H), 4.21 (4 H), 2.11 (2 H), 1.53-1.32 (64 H), 0.93-0.91 (12 H).

S7: Synthesis of P(NDI2OD-T2) by DHAP method in batch with new monomers (C)

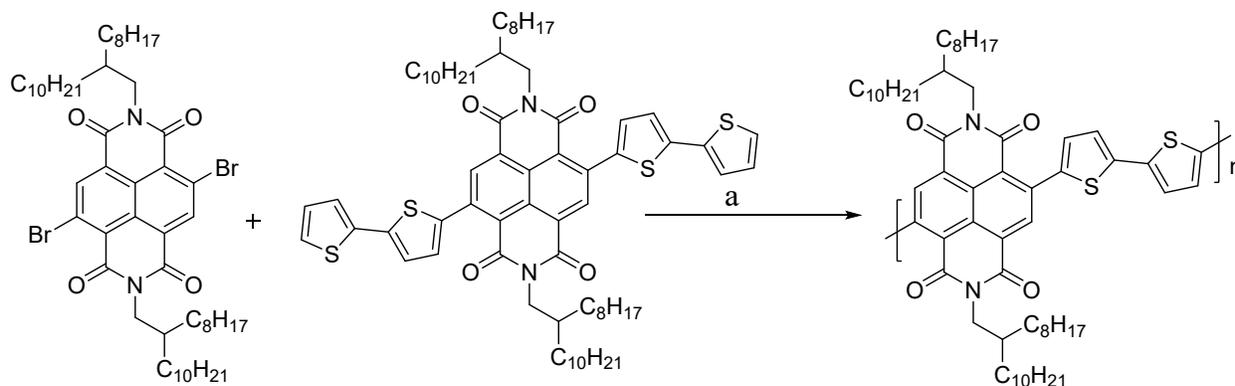


a = polymerization condition

a = Pd₂dba₃, K₂CO₃, Pivalic acid, 1, 2, 4-trichlorobenzene, 120 °C, 4 h.

In a 15 ml oven-dry Schlenk tube equipped with magnetic stirring bar were added NDIOD-Br₂ (N5) (70 mg, 0.071 mmol), (BT-NDI-BT) (N7) (82 mg, 0.071 mmol), pivalic acid (7.61 mg, 0.071 mmol), K₂CO₃ (29.46 mg, 0.213 mmol) and Pd₂dba₃ (1 mol %). The Schlenk tube was evacuated and purged by nitrogen (N₂) three-time. 0.3 mL of degassed 1, 2, 4-trichlorobenzene was added to the reaction mixture under nitrogen condition and stirred for 15 to 20 min at room temperature to fully dissolve the monomers. Then the Schlenk tube was kept in a preheated oil bath at 120 °C with stirring for 4 h. After completion of polymerization, polymer was dissolved in chloroform and precipitated in methanol. The precipitate was collected by filtration using Buckner funnel. The polymer was purified by Soxhlet extraction using methanol, acetone and hexane (removes catalytic residues and low molecular weight polymer). After the Soxhlet extraction, the polymer was dissolved in chloroform and precipitated in MeOH. The polymer was filtered on Buckner funnel and dried in a vacuum oven to afford deep blue colored polymer. Yield 100 %. ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 90 °C): δ (ppm), 8.91 (2 H), 7.44 (4 H), 4.20 (4 H), 2.11 (2 H), 1.54-1.32 (64 H), 0.93-0.92 (12 H).

S8: Synthesis of P(NDI2OD-T2) by DHAP method in continuous flow method with new monomers (D)

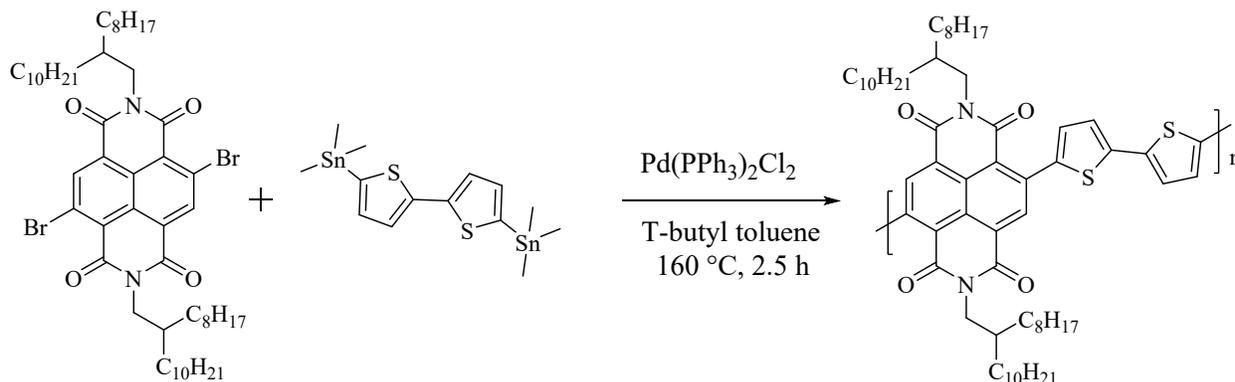


a = polymerization condition

a = Pd₂dba₃, Pivalic acid Flow rate = 0.008mL/min, Residence time 3 h.

In a 100 mL oven-dry two neck round bottom flask equipped with a stirring bar added NDIOD-Br₂ (N₅) (255.68 mg, 0.259 mmol), BT-NDI-BT (N₇) (300 mg, 0.259 mmol), Pd₂dba₃ (1 mol %). The round bottom flask was evacuated three times and purged with nitrogen. 10 mL degassed 1, 2, 4-trichlorobenzene was added. The reaction mixture was stirred for 15-20 min at room temperature to fully dissolve the monomers. The reaction mixture was then taken in a syringe, placed onto the syringe pump, and rapidly connected to the preheated flow reactor by PTFE tubing. The whole reactor was exposed to air directly. The reaction mixture was injected into the flow reactor at a certain flow rate (0.008 ml/min). The flow reactor was heated at 120 °C with a residence time of 3 h polymerization in flow reactor. Once the polymerization was completed, the polymer was precipitated in methanol and stirred for another 2 h. The precipitate was collected by filtration using Buckner funnel. The polymer was purified by Soxhlet extraction using methanol, acetone and hexane (removes catalytic residues and low molecular weight polymer). After the Soxhlet extraction, the polymer was dissolved in chloroform and precipitated in MeOH. The polymer was filtered on Buckner funnel and dried in a vacuum oven to afford deep blue colored polymer. Yield 83 %. ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 90 °C): δ (ppm), 8.91 (2 H), 7.44 (4 H), 4.20 (4 H), 2.11 (2 H), 1.54-1.32 (64 H), 0.93 (12 H).

S9: Synthesis of P(NDI2OD-T2) by Stille Polymerization in Batch (E)



In a 15 ml oven-dry Schlenk tube equipped with magnetic stirring bar were added NDIOD-Br₂ (N₅) (300 mg, 0.304 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (149.28 mg, 0.304 mmol), Pd(PPh₃)₂Cl₂ (1 mol %). The reaction mixture was evacuated by vacuum and filled with nitrogen three times. 1 mL degassed T-butyl toluene was added in the reaction mixture and stirred at room temperature for 15 min to dissolve all monomers. The Schlenk tube was placed in a preheated oil bath under inert condition at 160 °C for 2.5 h. The polymerization mixture was cooled to room temperature and 4 mL chloroform was added. The polymer was precipitated in methanol and filtered using Buckner funnel. The polymer was purified by Soxhlet extraction using methanol, acetone, followed by hexanes (removes catalytic residues and low molecular weight polymer). After the Soxhlet extraction, the polymer was dissolved in chloroform and precipitated in MeOH. The polymer was filtered on Buckner funnel and dried in a vacuum oven to afford deep blue colored polymer. Yield 80 %. ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 90 °C), δ (ppm) 8.91 (2 H), 7.44 (4 H), 4.21 (4 H), 2.12 (2 H), 1.53-1.32 (br, 64 H), 0.94-0.92 (br, 12 H).

Table S1: Optimization table of DHAP-regular monomer polymerization batch and continuous flow (CF) method

Entry No	Types	T (°C)	Time (h)	Conc. ^a (M)	Solvent	Molecular weight ^b			Yield ^d (%)
						Mn (kDa)	Mw (kDa)	\bar{M}_w/\bar{M}_n ^c	
1	DHAP Batch	110	24	0.1	Toluene	-	-	-	-
2	DHAP Batch	110	24	0.3	Toluene	12	20	1.7	95
3	DHAP Batch	160	2.5	0.3	TBT	5	8	1.6	55
4	DHAP Batch	160	3.5	0.3	TBT	15	35	2.3	70
4-r	DHAP Batch	160	3.5	0.3	TBT	25.3	70	2.8	93
5	DHAP Batch	100	4	0.3	CB	15	34.5	2.3	88
5-r	DHAP Batch	110	4	0.3	CB	11.7	31.7	2.7	92
6	DHAP Batch	160	2.5	0.3	TCB	Insoluble Polymer			
7	DHAP Batch	160	1/2	0.3	TCB	-		-	-
8	DHAP Batch	160	1	0.3	TCB	Soluble in hexane			
9	DHAP Batch	160	1.5	0.3	TCB	Insoluble polymer			
10	DHAP Batch	120	3.15	0.3	TCB	48.6	155.6	3.2	91
10-r	DHAP Batch	120	3.15	0.3	TCB	49.8	143.2	2.9	97
11	DHAP Batch	120	3.15	0.1	TCB	-		-	-
12	DHAP Batch	120	3.15	0.05	TCB	-		-	-
13	DHAP Batch	140	3.15	0.3	TCB	16	35.2	2.2	70
14	DHAP CF (6.16 mm)	120	3.00	0.05	TCB	-		-	-
14-r	DHAP	120	3.00	0.05	TCB	-		-	-

	CF (6.16 mm)								
15	DHAP CF (6.16 mm)	110	3.00	0.05	CB	6.5	17.6	2.7	57.3
15-r	DHAP CF (6.16 mm)	110	3.00	0.05	CB	7.5	17.5	2.3	22
16	DHAP CF (3.15 mm)	120	3.00	0.05	TCB	29.5	52.9	1.8	70
16-r	DHAP CF (3.15 mm)	120	3.00	0.05	TCB	18.1	30.6	1.7	77

CF, continuous flow polymerization. a, concentration of NDIOD-Br₂ monomer in taken solvent. b, molecular weight determined by SEC at 140 °C. c, Mw/Mn. d, yield of polymer calculated after Soxhlet extraction. -, no polymerization happened. TBT, T-butyl toluene. CB, chlorobenzene, TCB, 1, 2, 4-trichlorobenzene. r, repetition in entry.

Table S2: Optimization table for DHAP polymerization with new monomer batch and continuous flow method

Entry	Types	T (°C)	Time (h)	Conc. ^a (M)	Solvent	Molecular weight ^b (kDa)			Yield (%)
						Mn	Mw	D _M ^c	
1	DHAP Batch	100	4.00	0.3	CB	23.8	56.2	2.4	80
1-r	DHAP Batch	100	4.00	0.3	CB	33.2	80.2	2.4	100
2	DHAP Batch	120	4.00	0.3	TCB	41.8	85.8	2.1	100
2-r	DHAP Batch	120	4.00	0.3	TCB	99.5	284.2	2.9	100
3	DHAP CF(6.16mm)	120	3.00	0.05	TCB	6.8	13.5	2	75
3-r	DHAP CF(6.16mm)	120	3.00	0.05	TCB	6.2	11.2	1.8	60
4	DHAP CF(3.15 mm)	120	3.00	0.05	TCB	21.5	38.7	1.8	83
4-r	DHAP CF(3.15 mm)	120	3.00	0.05	TCB	20.7	37.5	1.7	83

CF, continuous flow polymerization. a, concentration of NDIOD-Br₂ monomer in taken solvent. b, molecular weight determined by SEC at 140 °C. c, Mw/Mn. d, yield of polymer calculated after Soxhlet extraction. -, no polymerization happened. CB, chlorobenzene. TCB, 1, 2, 4-trichlorobenzene. r, repetition in entry.

Figure S1: ^1H NMR spectrum of NDIOD-Br₂ (CDCl₃)

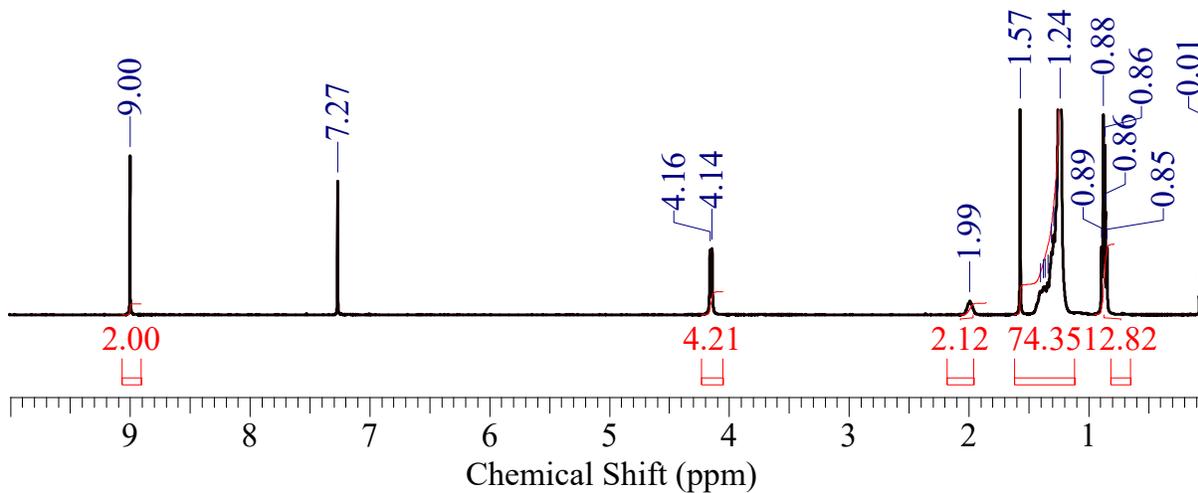


Figure S2: ^{13}C NMR spectrum of NDIOD-Br₂ (CDCl₃)

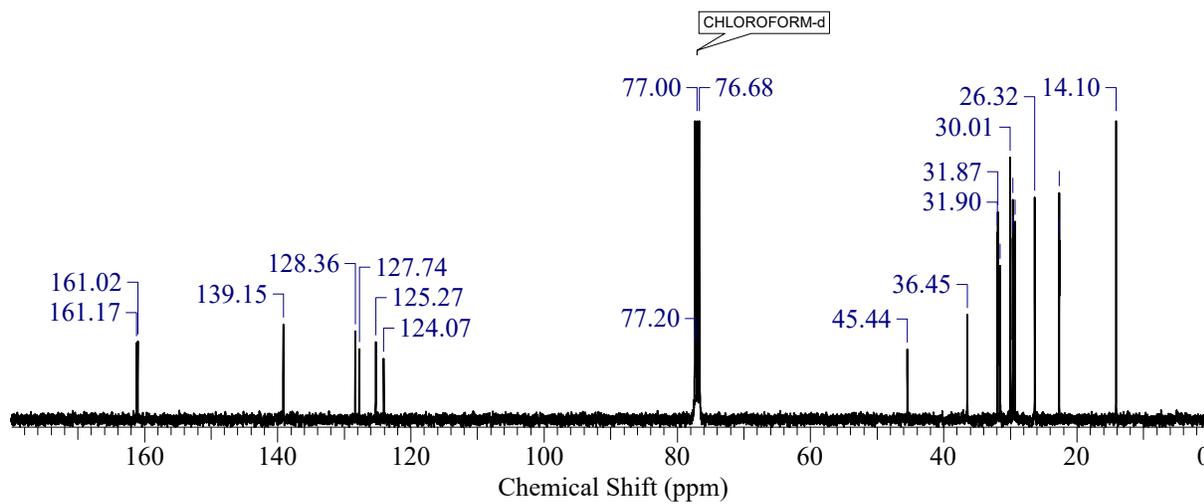


Figure S3: MALDI-TOF spectrum of NDIOD-Br₂

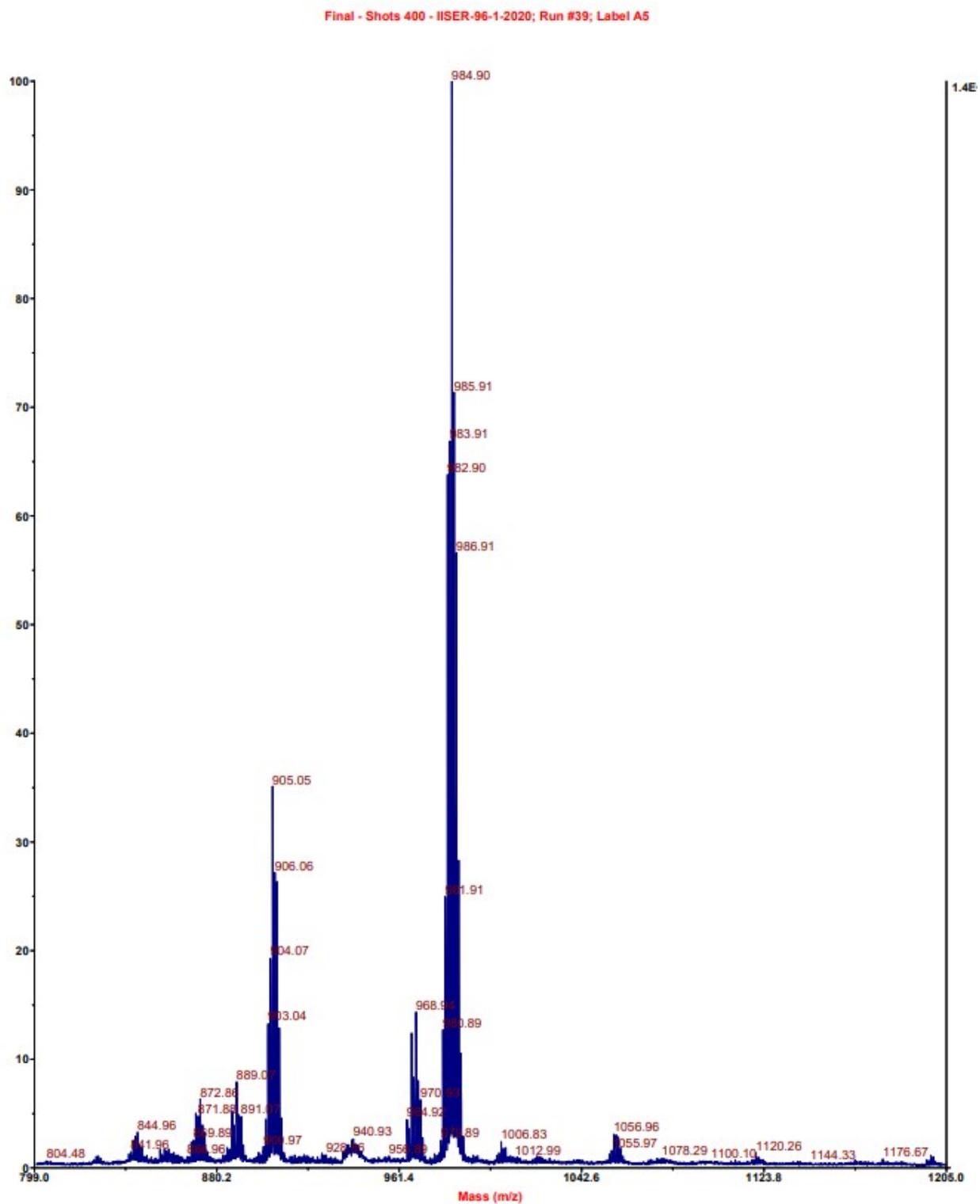


Figure S4: ^1H NMR spectrum for [2,2'-bithiophen]-5-yltrimethylstannane (CDCl_3)

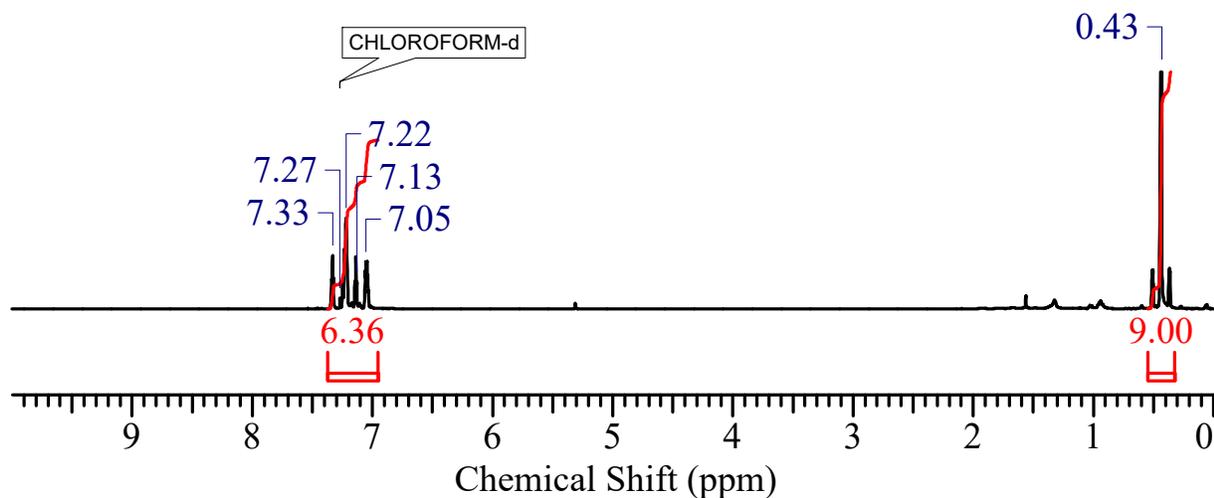


Figure S5: ^{13}C NMR spectrum for [2,2'-bithiophen]-5-yltrimethylstannane (CDCl_3)

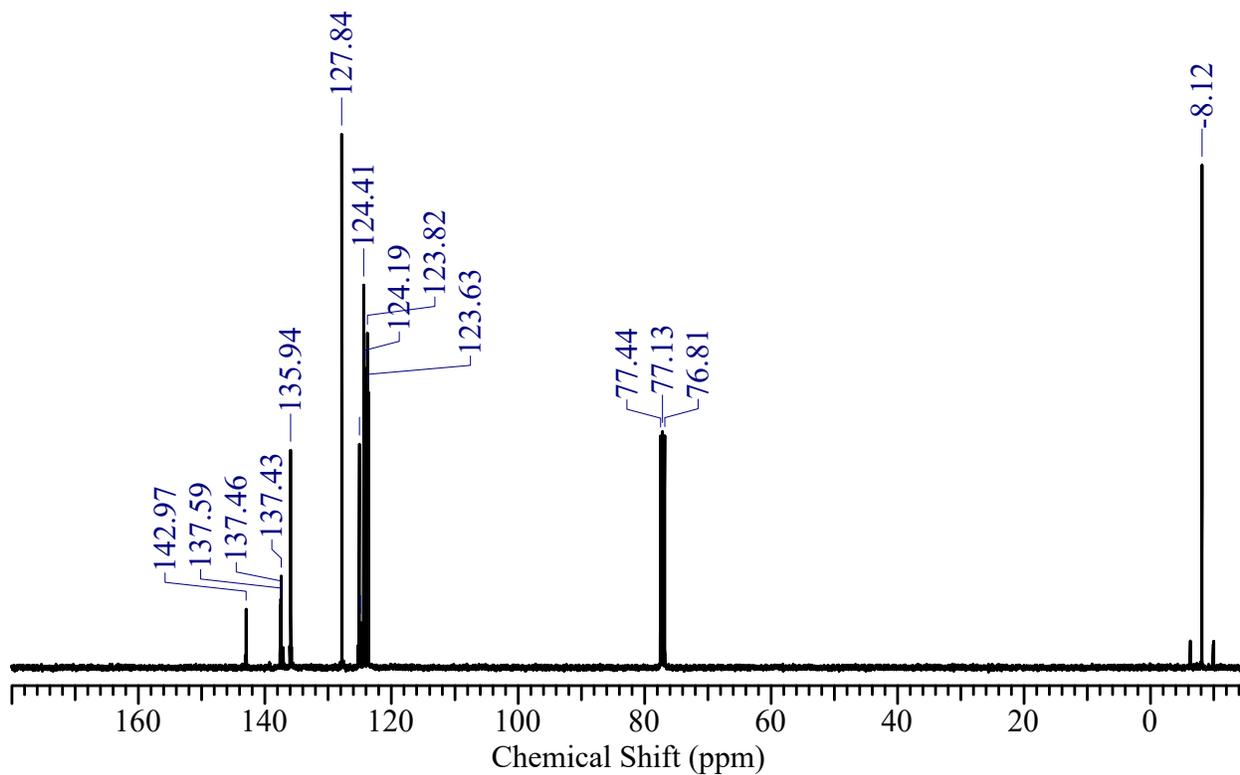


Figure S6: ^1H NMR spectrum for BT-NDI-BT (N7) (CDCl_3)

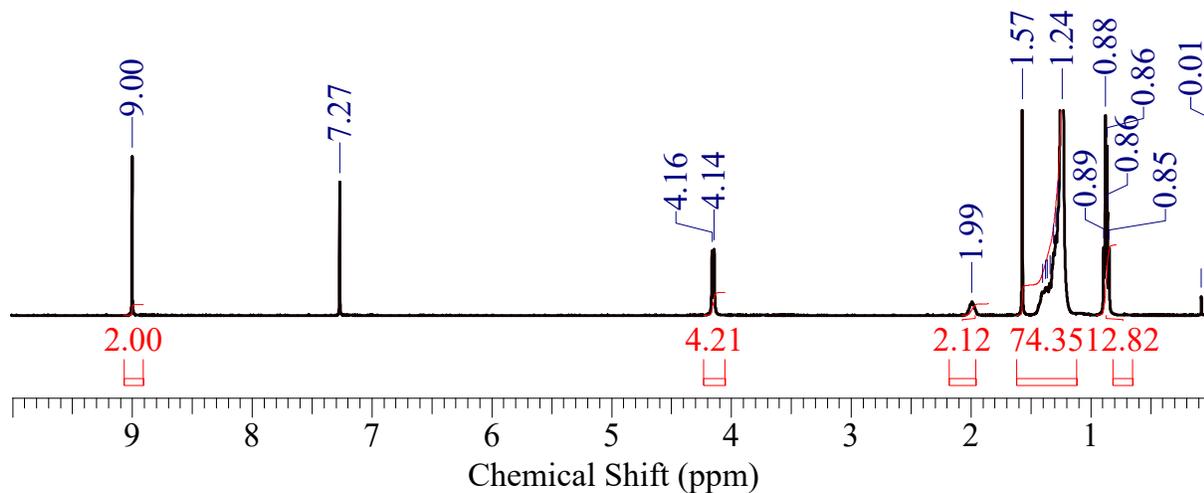


Figure S7: ^{13}C NMR spectrum for BT-NDI-BT N7 (CDCl_3)

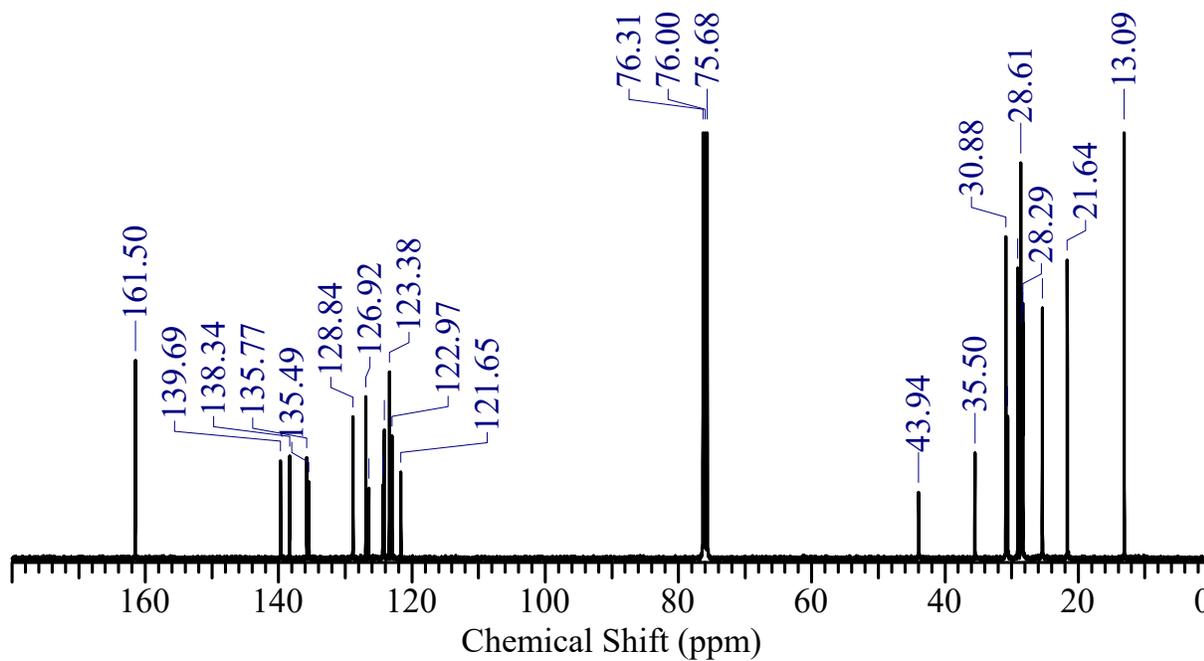


Figure S8: MALDI-TOF spectrum of BT-NDI-BT

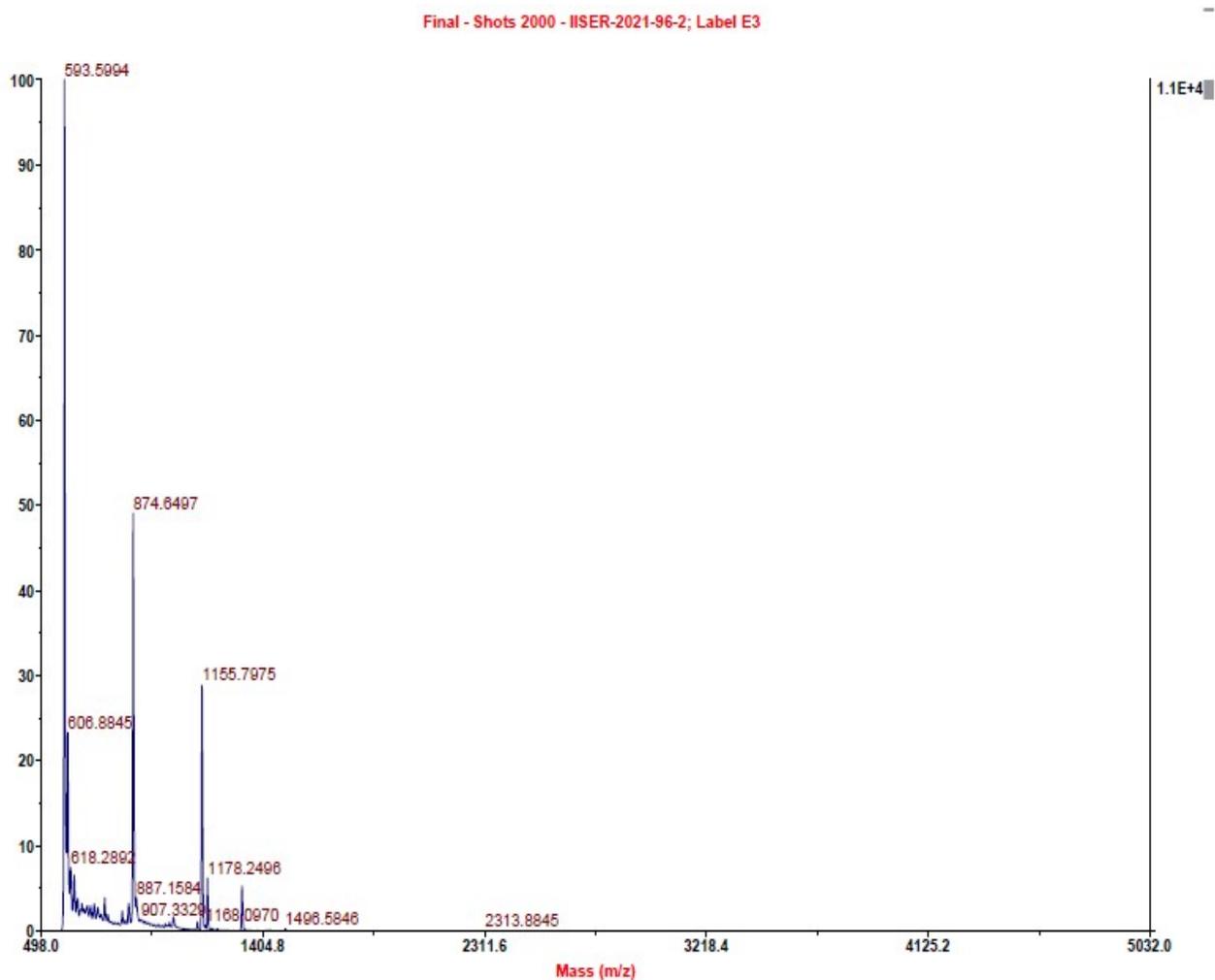


Figure S9: Size exclusion chromatography (SEC) A-E polymers

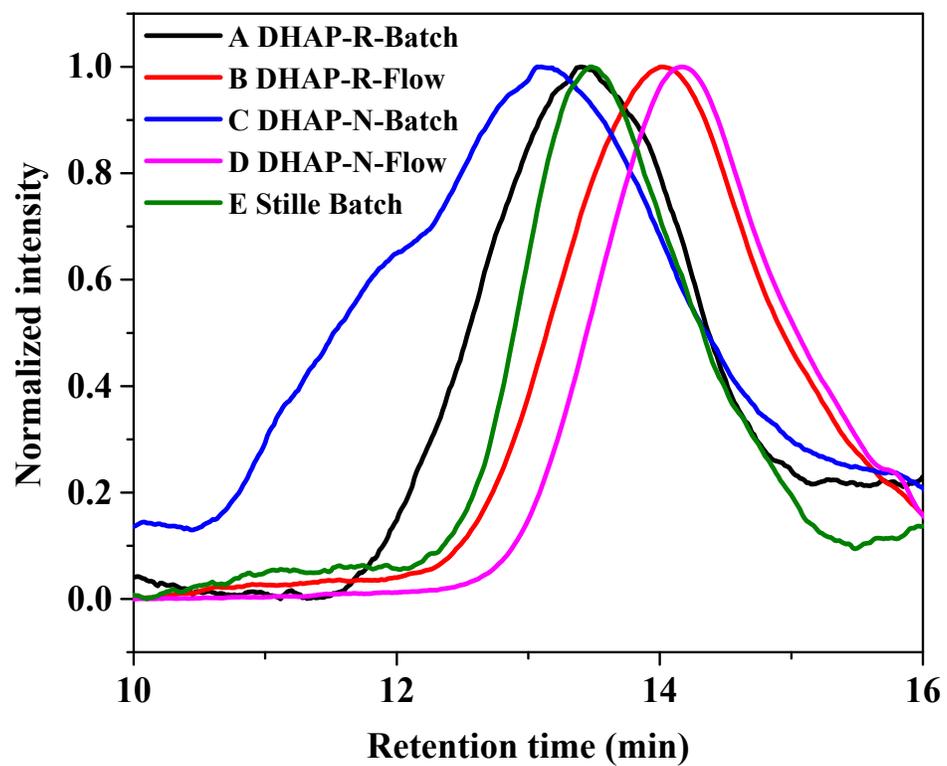


Figure S10: ^1H NMR spectra for E-Stille batch Polymers at 90 °C (TCE- d_2)

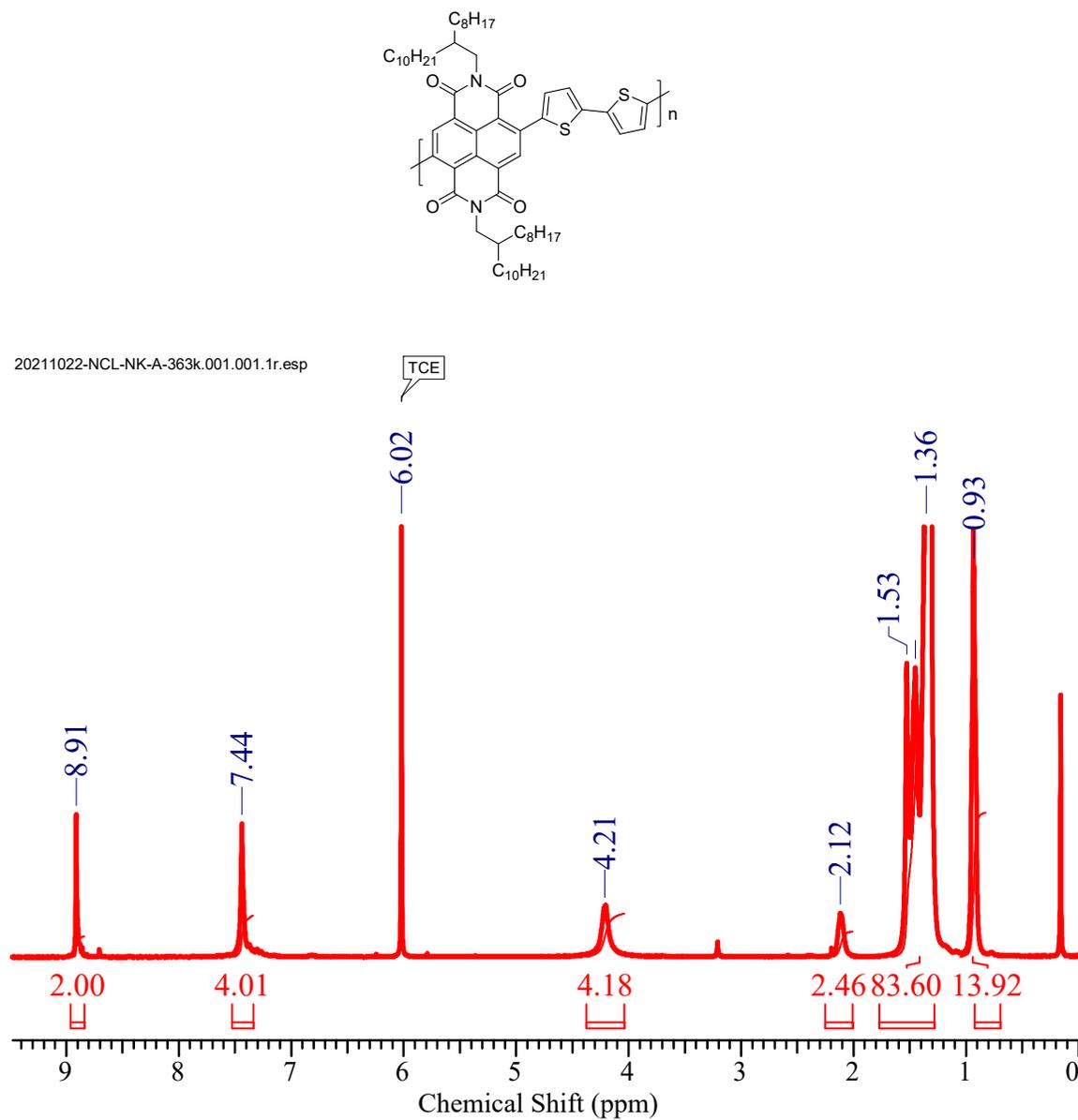


Figure S11: ^1H NMR spectra for A and B Polymers at 90 °C (TCE- d_2)

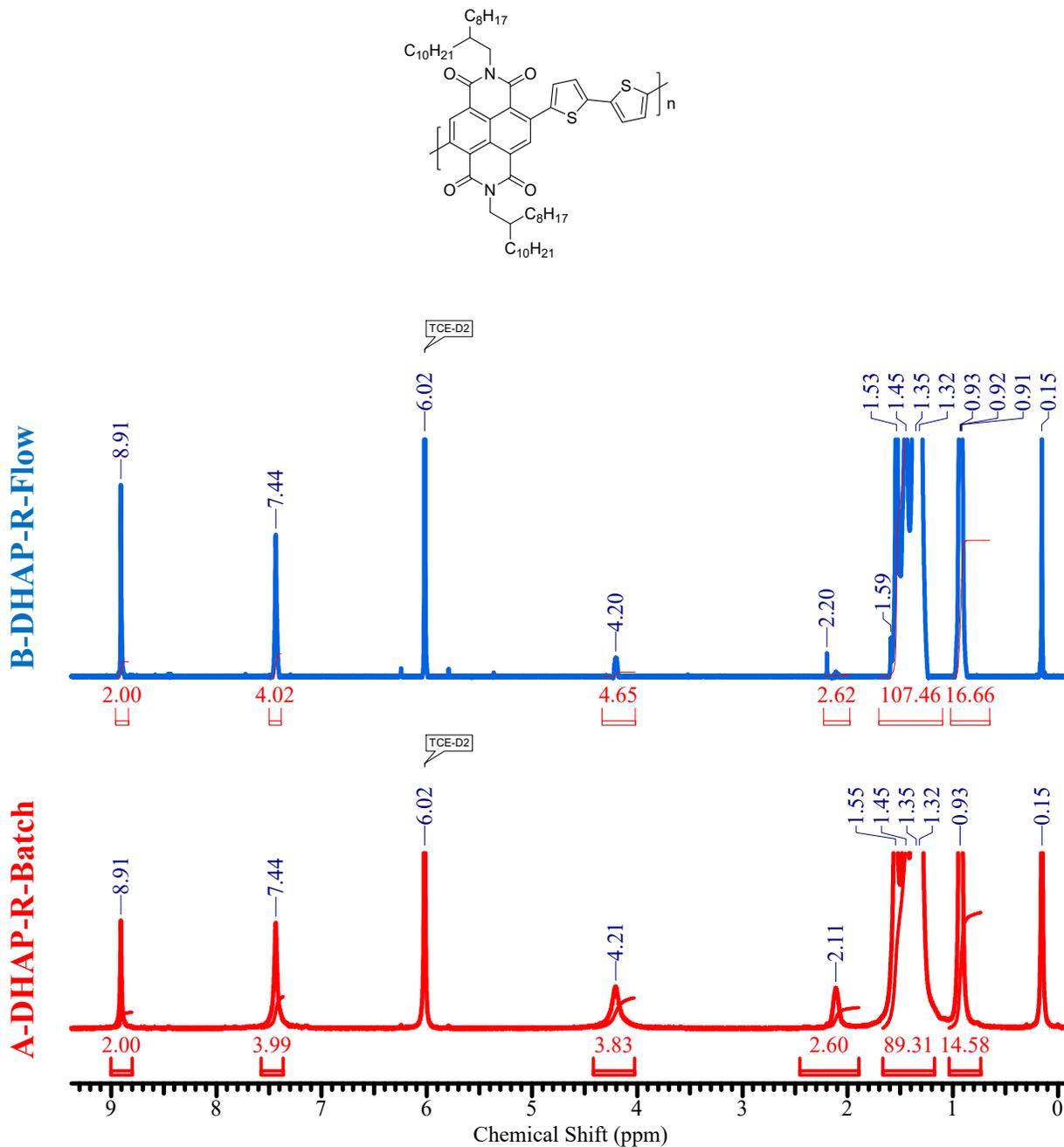


Figure S12 : ^1H NMR spectra for C and D Polymers at 90 °C (TCE- d_2)

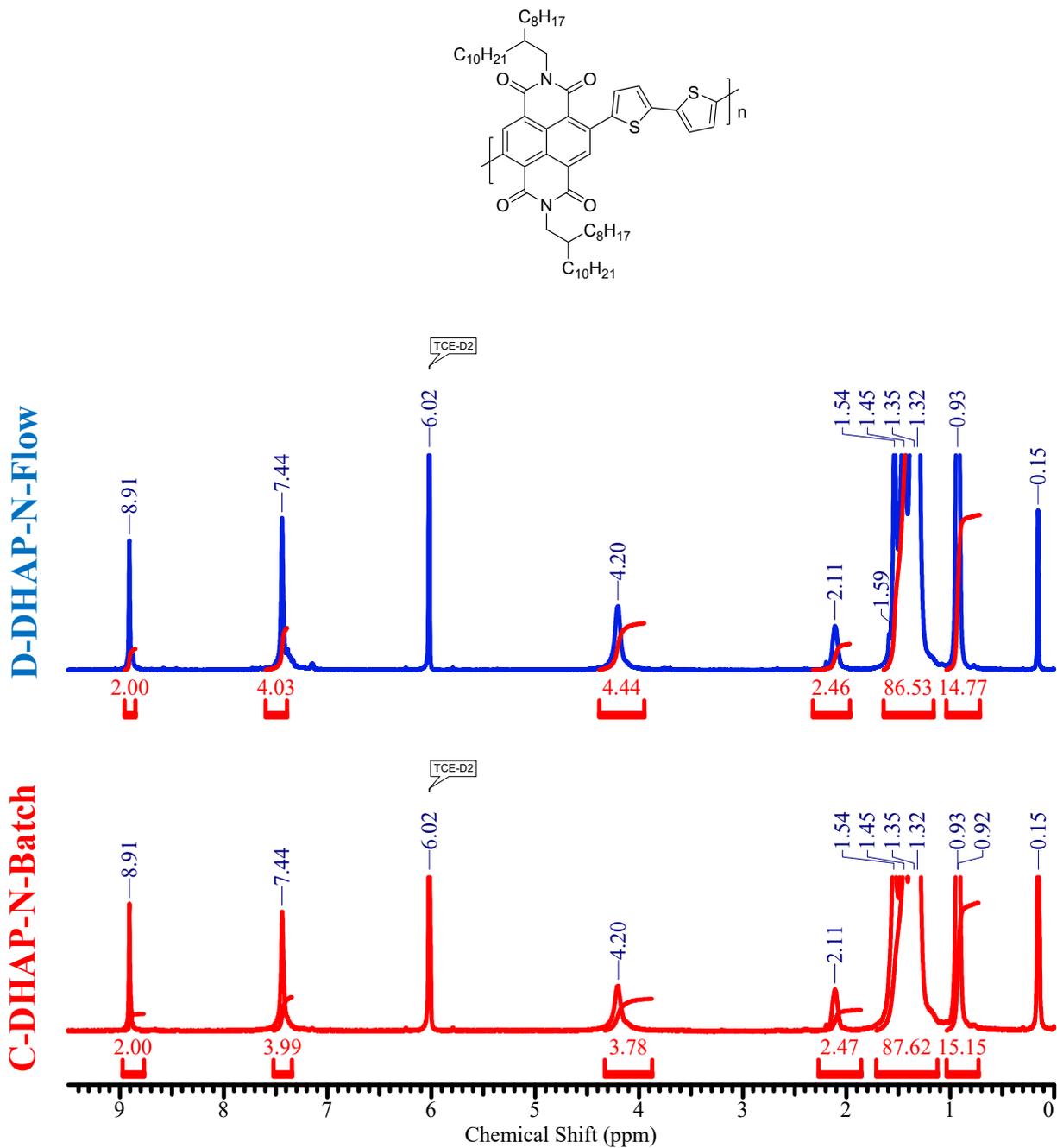


Figure S13: Normalized absorption spectra of polymers recorded in chloroform.

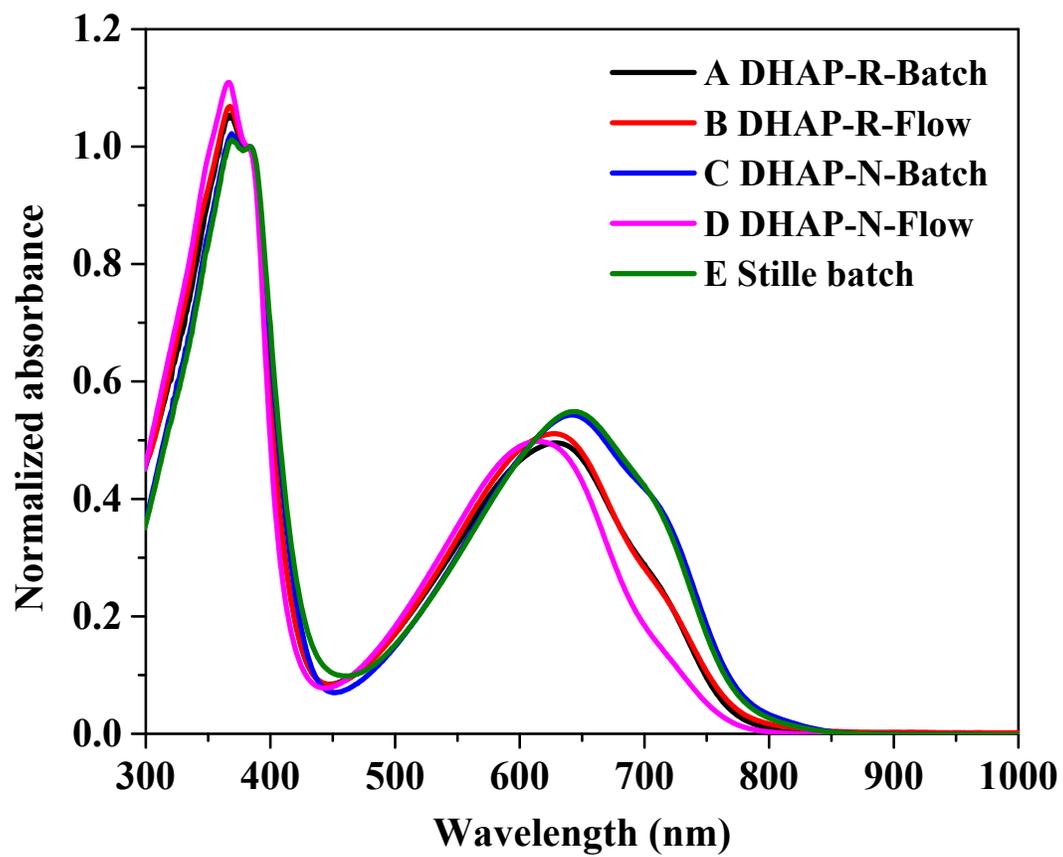


Figure S14: Electrochemical properties of all (A-E) polymers (Cyclic Voltammetry)

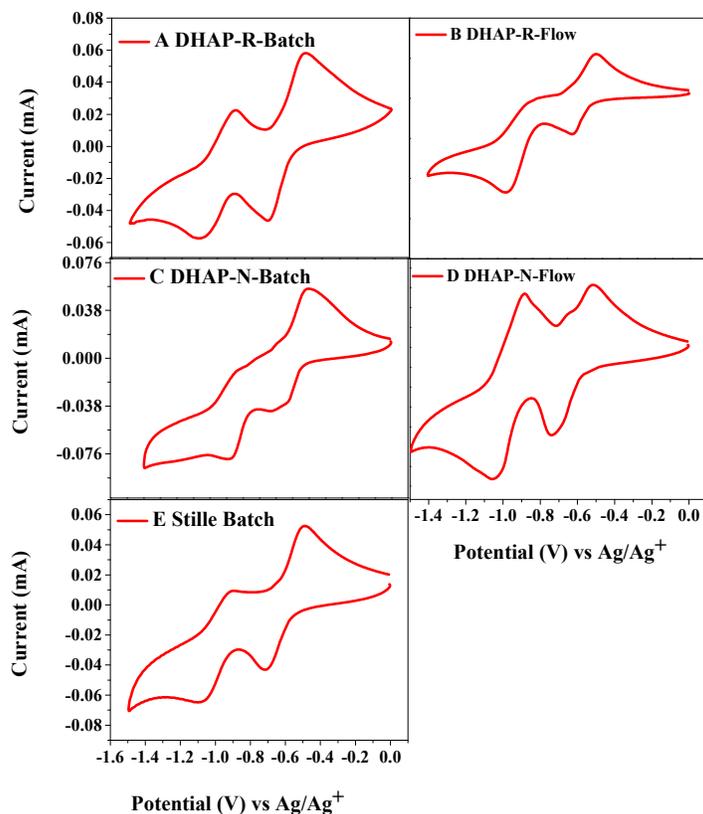


Table S3: HOMO and LUMO energy value calculated from cyclic voltammetry

Polymers	$\lambda_{\text{offset}}(\text{nm})^{\text{a}}$	$E_{\text{g}}^{\text{opt}}(\text{eV})$	LUMO (eV) ^b	HOMO (eV) ^c
A DHAP-R-Batch	843	1.46	-3.83	-5.29
B DHAP-R-Flow	857	1.44	-3.83	-5.28
C DHAP-N-Batch	844	1.46	-3.85	-5.32
D DHAP-N-Flow	846	1.46	-3.82	-5.29
E Stille Batch	857	1.44	-3.83	-5.27

a, thin film absorption spectra. b, cyclic voltammetry. c, cyclic voltammetry.

Figure S15: Thin film UV-visible absorption spectra (substrate used quartz plate)

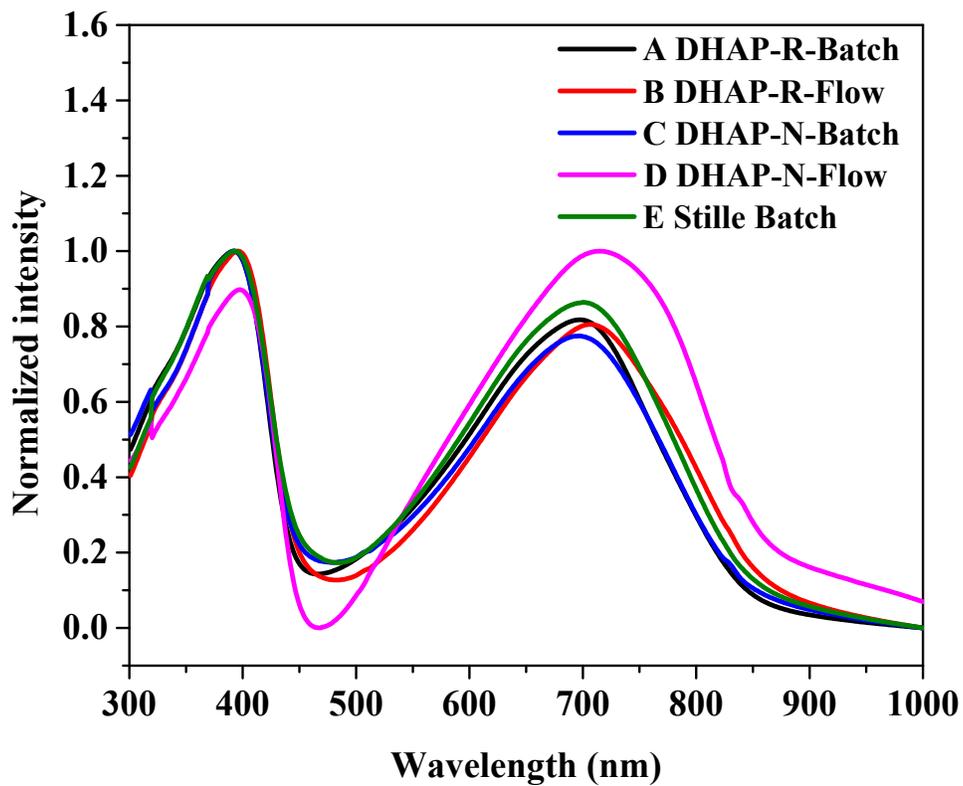


Figure S16: Thermogravimetric analysis (TGA) for A-E polymers

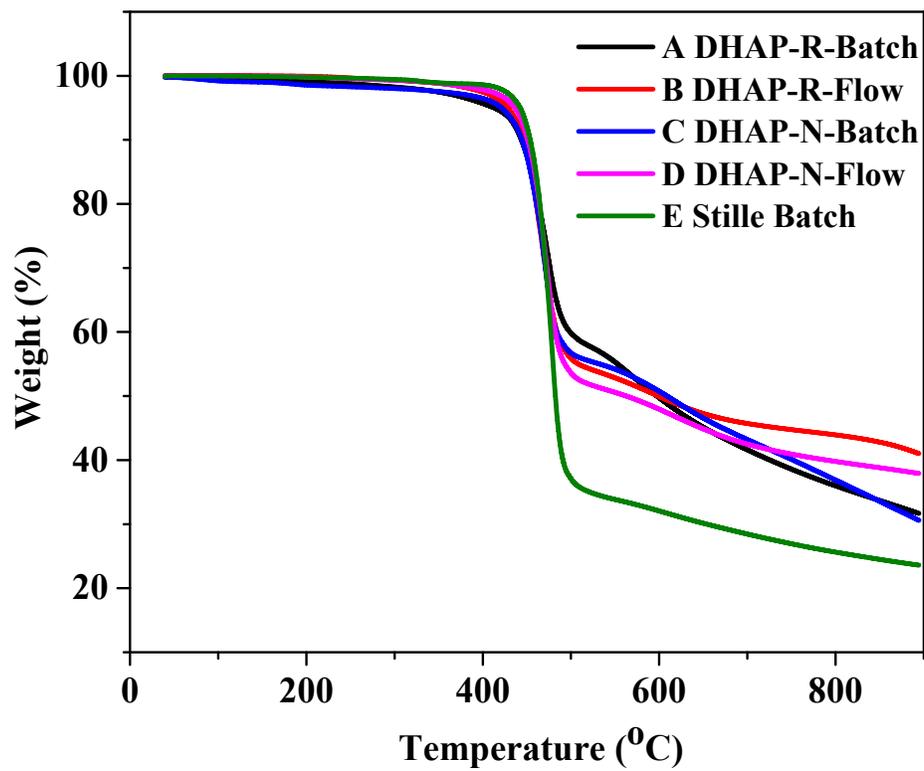


Figure S17: FE-SEM micrographs recorded at various magnifications for polymer samples drop cast from ethanol dispersions.

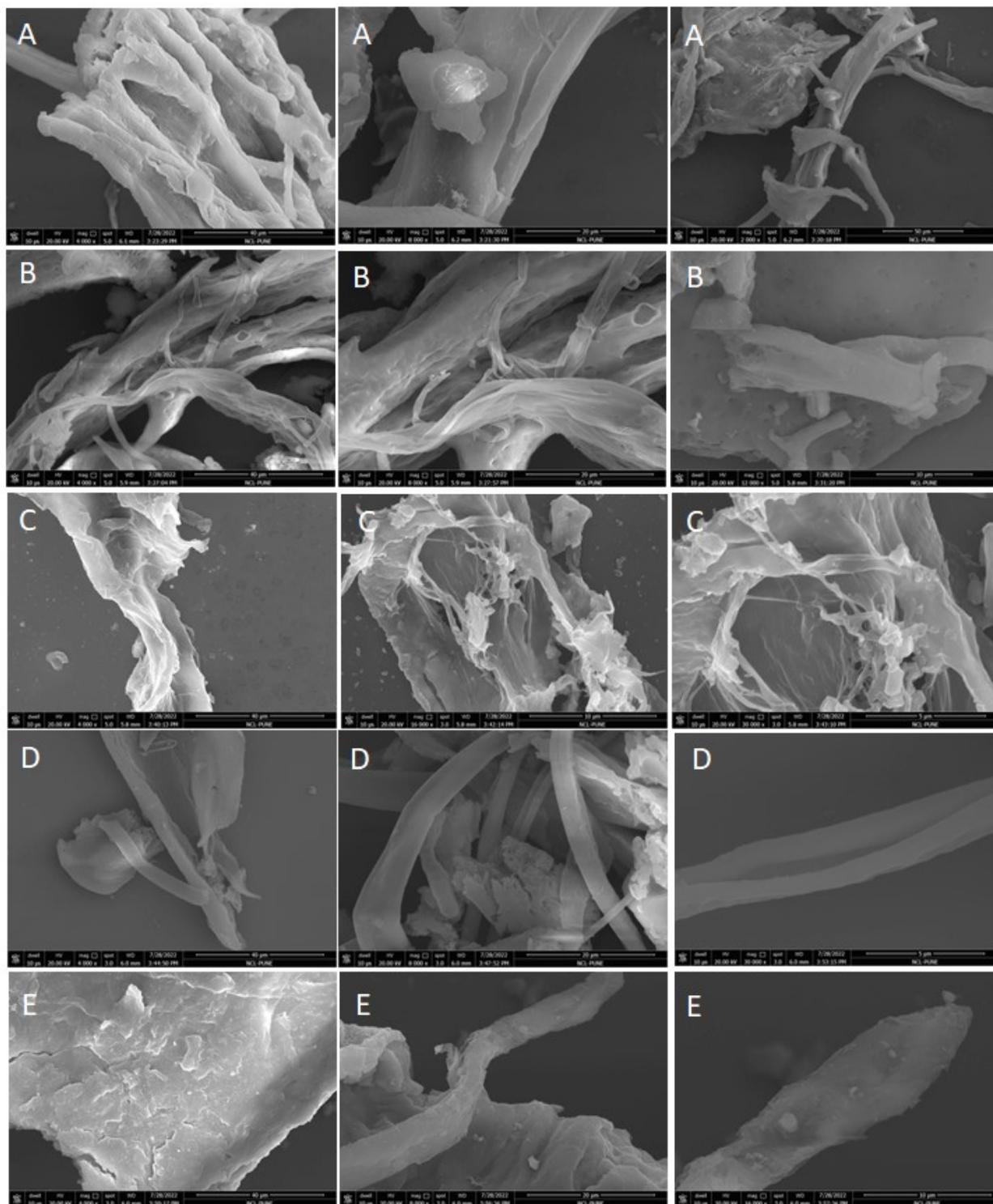


Figure S18: Output and transfer characteristics of polymers A-E after annealing at 100 °C

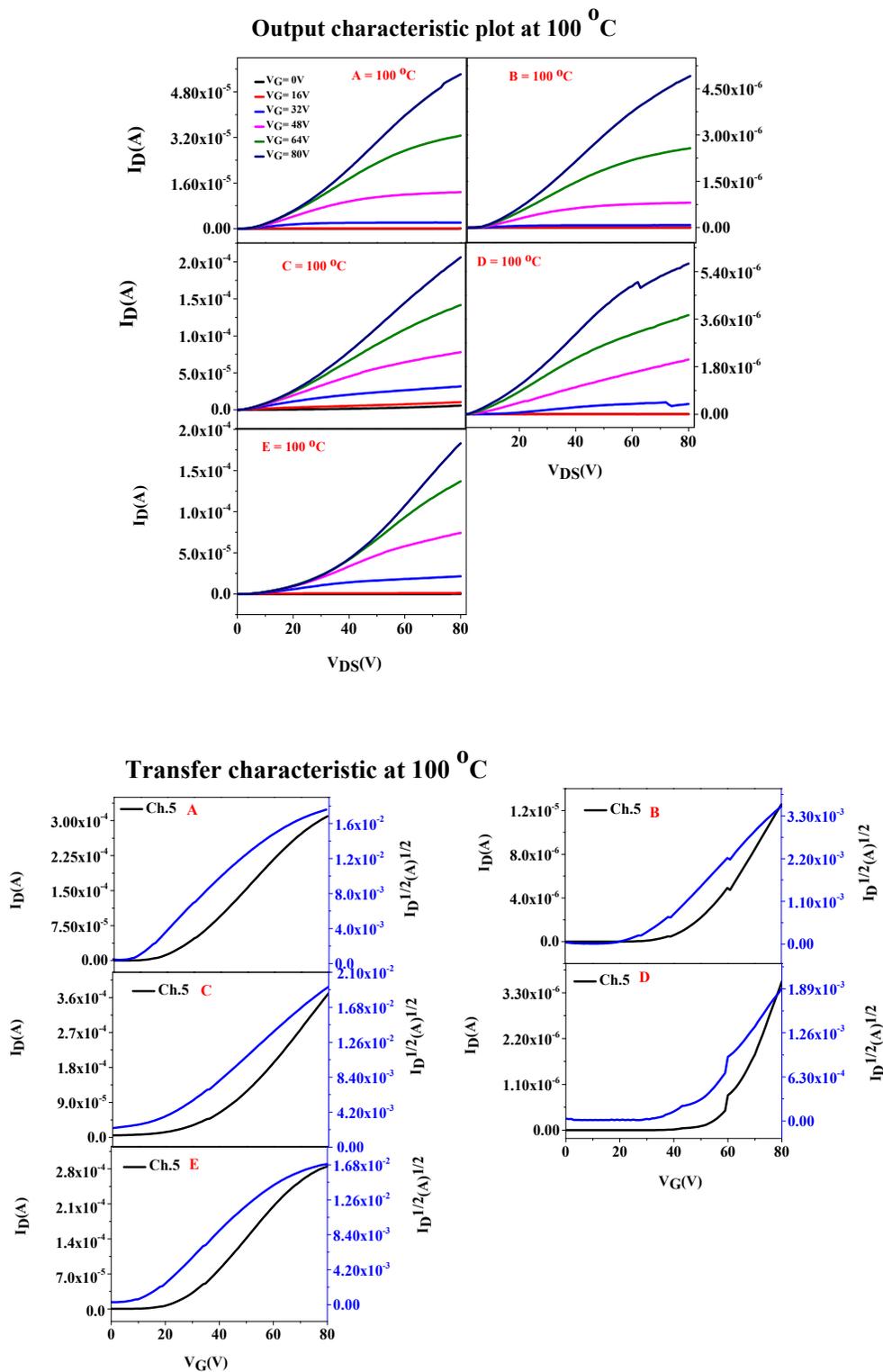


Figure S19: Output and transfer characteristics of polymers A-E after annealing at 150 °C

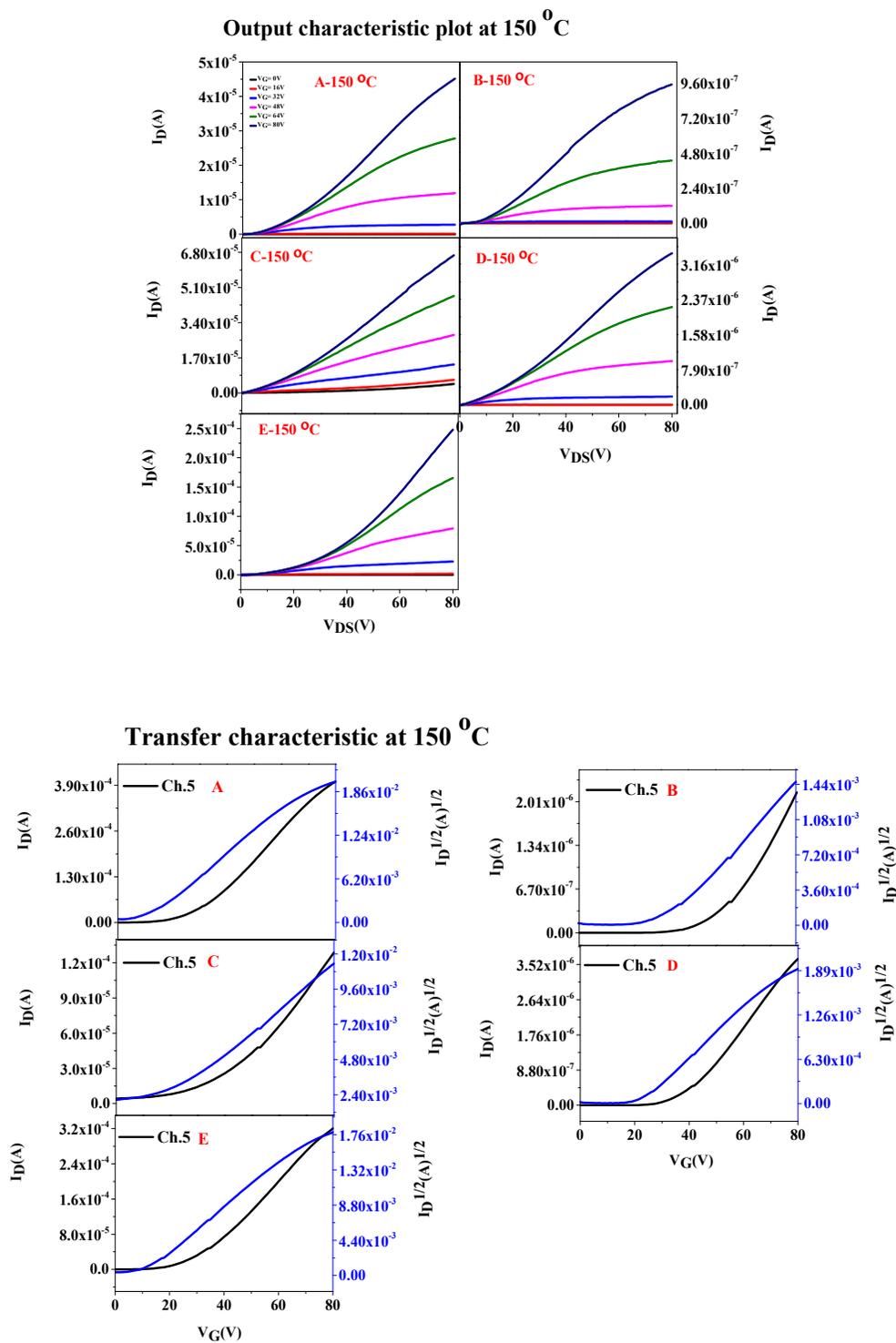


Table S4: Highest Electron mobility values of the polymers at 25 °C and after annealing the devices at 100 °C and 150 °C under argon atmosphere for 15 minutes

Polymer	25 °C			After annealing at 100 °C			After annealing at 150 °C		
	V _T (V)	μ _e (cm ² V ⁻¹ s ⁻¹)	I _{on} /I _{off}	V _T (V)	μ _e (cm ² V ⁻¹ s ⁻¹)	I _{on} /I _{off}	V _T (V)	μ _e (cm ² V ⁻¹ s ⁻¹)	I _{on} /I _{off}
A	20.0	3.30 x 10 ⁻⁴	~10 ²	22.6	1.31 x 10 ⁻³	~10 ³	17.0	8.51 x 10 ⁻⁴	~10 ³
B	21.8	6.96 x 10 ⁻⁵	~10 ²	25.4	1.20 x 10 ⁻⁴	~10 ³	28.2	2.30 x 10 ⁻⁵	~10 ³
C	15.7	1.75 x 10 ⁻³	~10 ³	11.7	3.53 x 10 ⁻³	~10 ³	12.1	1.02 x 10 ⁻³	~10 ³
D	19.2	3.51 x 10 ⁻⁵	~10 ³	40	2.54 x 10 ⁻⁴	~10 ³	20	6.40 x 10 ⁻⁵	~10 ³
E	12.3	8.48 x 10 ⁻⁴	~10 ⁴	12.2	3.54 x 10 ⁻³	~10 ⁴	10.7	4.11 x 10 ⁻³	~10 ³

Figure S20. DSC thermograms comparing the change in enthalpy of melting for P(NDI2OD-T2) polymers after annealing at 150 °C for 10 minutes

