Electronic Supplementary Information

Molecular weight tuning of low bandgap polymers by continuous flow chemistry: increasing the applicability of PffBT4T for organic photovoltaics†

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1. Continuous flow set-up and operation

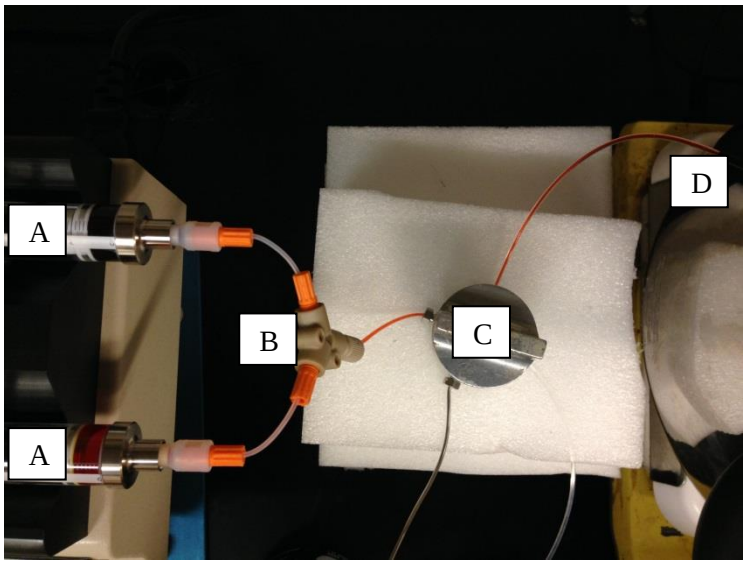

Figure S1: Reagents are injected into the continuous flow reactor (D) by two SGE gastight syringes (A), a T-piece mixer (B) and a 4-way valve (C).

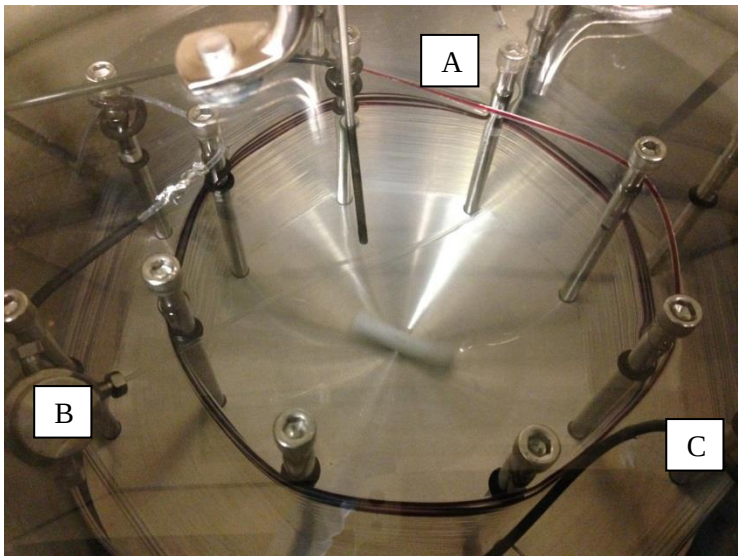

Figure S2: The tubular flow reactor is immersed in an oil bath. The incoming reaction mixture (A) rapidly turns deep purple. Before exiting the reactor (C), the reaction mixture is diluted (B) by a stream of fresh solvent, in which also the palladium scavenging agent is dissolved.

2. Modified processing chuck

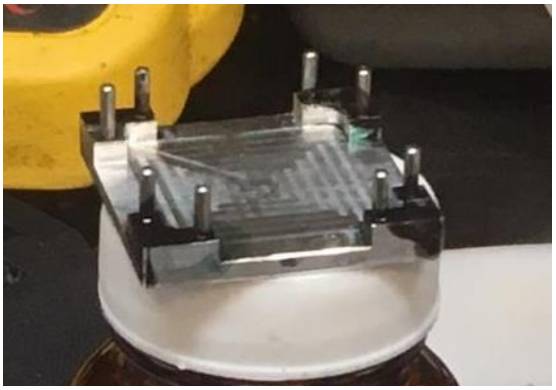

Figure S3: The modified processing chuck, which allows elevation of the glass substrate from the cold metal surface. The substrate rests on the four corners and is kept in place with 8 pins.

3. Dependence of the photoactive layer film formation on molecular weight and the processing set-up

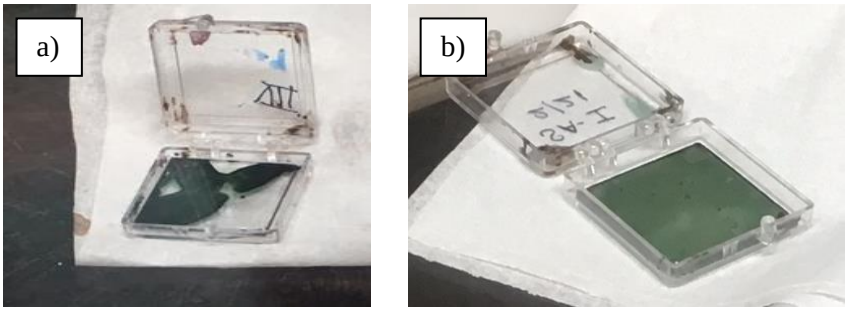

Figure S4: a) Example of incomplete coverage of the substrate and gelation in case of higher molecular weight PffBT4T-2OD with the initial processing set-up (commercial sample of Solarmer, M_n = 57.2 kDa); b) Example of a properly spin-coated active layer, with lower molecular weight PffBT4T-2OD (Table 5, entry 5) and using the initial processing set-up.

4. *J*-*V* curves

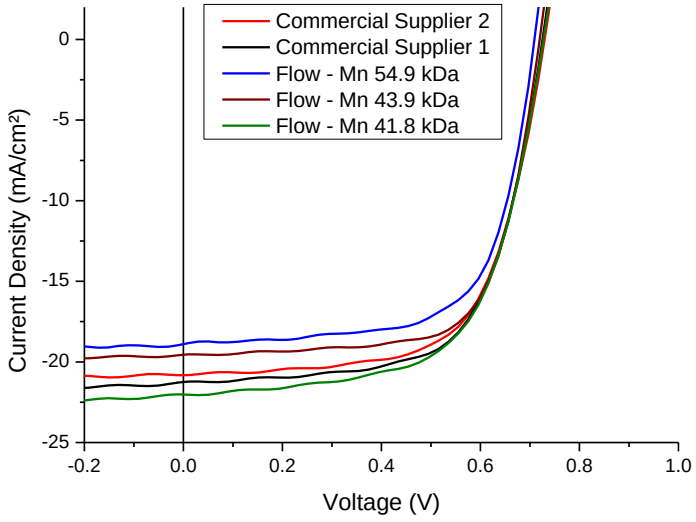

Figure S5: *J*-*V* curves of (maximum efficiency) BHJ OPV devices based on PffBT4T-2OD from commercial sources and synthesized by flow.

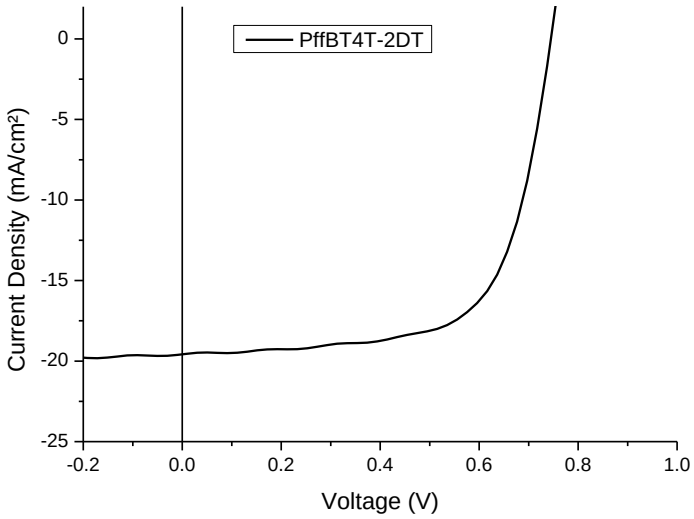

Figure S6: *J*-*V* curve of an average efficiency BHJ OPV device based on PffBT4T-2DT synthesized by flow.

5. Flow parameters and GPC data

Table S1: Overview of the flow parameters and GPC data of all polymers synthesized within this project.

Injection	Residence time (min)	Temperature (°C)	Flow rate (µL/min)	[M] (mM)	Injected volume (mL)	M_n (kg/mol)	M_w (kg/mol)	$Đ$
1 - PffBT4T-2OD[a,b]								
1	30	117	666	29.6	1.75	43.5	84.6	1.95
2	45	117	444		1.75	41.8	78.4	1.87
3	60	120	333		3.50	37.7	69.3	1.84
2 - PffBT4T-2OD[b]								
1	30	120	666	29.4	1.00	38.1	71.2	1.87
2		130			1.00	32.0	58.1	1.82
3		140			1.00	28.7	49.5	1.72
3 - PffBT4T-2OD[b]								
1	45	120	444	29.4	1.00	43.0	86.1	2.00
2		130			1.00	36.8	69.5	1.89
3		140			1.00	26.8	47.7	1.78
4 - PffBT4T-2OD								
1	30	120	666	29.6	1.75	48.6	101.2	2.08
2		130			1.75	39.9	76.4	1.91
3		140			1.44	30.9	55.1	1.78
5 - PffBT4T-2OD								
1	60	120	333	29.5	1.25	47.8	99.4	2.08
2		130			1.25	41.8	82.6	1.97
3		140			2.45	33.8	60.3	1.78
6 - PffBT4T-2OD								
1	26	120	754	29.6	17.74	54.9	108.1	1.97
7 - PffBT4T-2OD								
1	30	140	333	29.5	1.75	32.0	64.0	2.00
2		130			1.75	39.4	78.4	1.99
3		120			1.75	45.0	94.2	2.09
8 - PffBT4T-2OD								
1	30	130	333	29.2	1.75	40.4	76.5	1.89
9 - PffBT4T-2OD								
1	15	120	1332	29.6	8.99	50.9	103.1	2.03
10 - PffBT4T-2OD								
1	20	120	1000	29.6	9.00	51.8	105.9	2.05
11 - PffBT4T-2OD								
1	10	120	2000	29.6	4.50	47.8	98.5	2.06
2	5	120	4000	29.6	4.50	43.8	88.6	2.02
3	20	120	1000	29.6	4.50	47.8	101.4	2.12
4	20	140	1000	29.6	4.50	32.7	62.6	1.92

Injection	Residence time (min)	Temperature (°C)	Flow rate (µL/min)	[M] (mM)	Injected volume (mL)	M_n (kg/mol)	M_w (kg/mol)	$Đ$
12 - PffBT4T-2OD								
1	26	120	754	19.74	17.74	43.9	89.9	2.05
13 - PffBT4T-2OD								
1	26	120	754	9.87	17.74	26.6	46.7	1.76
PffBT4T-2DT								
1	26	120	754	29.6	18.00	56.1	113.9	2.03
Commercial sample Solarmer								
	N/A	N/A	N/A	N/A	N/A	57.2	130.0	2.27
Commercial sample 1-Material								
	N/A	N/A	N/A	N/A	N/A	41.8	69.7	1.67

[a] Performed without back pressure regulator (leading to gas bubbles and an irregular flow).
[b] The monomers and catalyst were injected as one single solution into the system.

6. ^{1}H NMR spectra and GPC traces

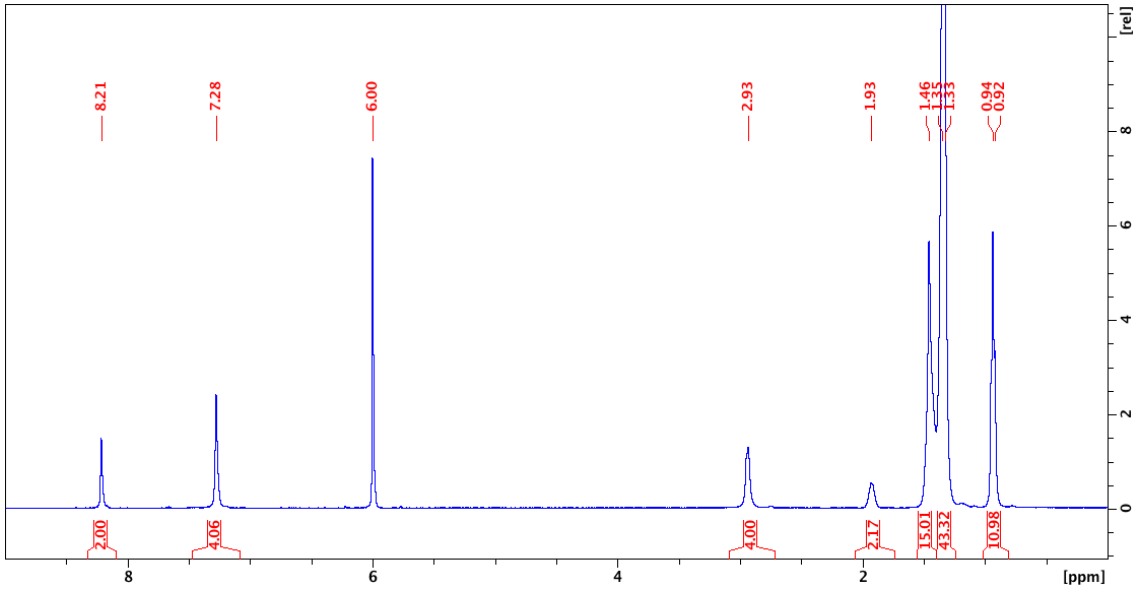

Figure S7: ^{1}H NMR spectrum of PffBT4T-2OD (Table 5, entry 4) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C.

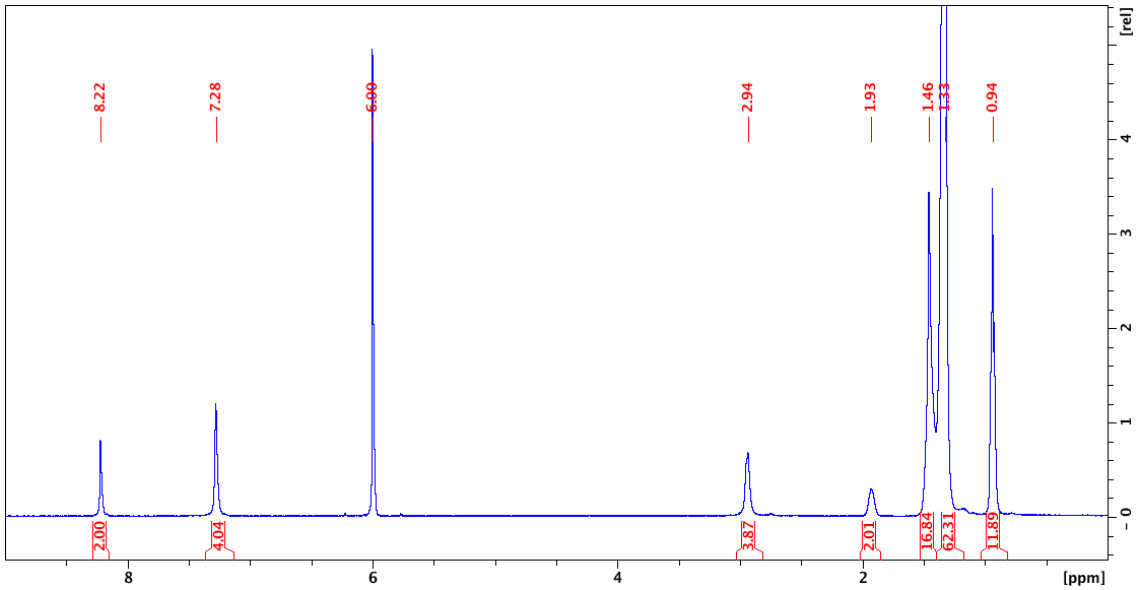

Figure S8: ^{1}H NMR spectrum of PffBT4T-2DT (Table 5, entry 6) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C.

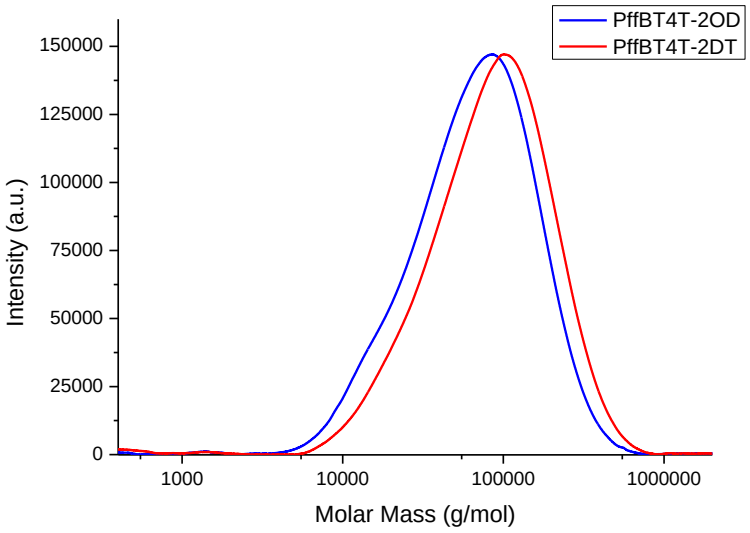

Figure S9: Molar mass distributions obtained from the analytical size exclusion chromatograms of PffBT4T-2OD (Table 5, entry 4) and PffBT4T-2DT (Table 5, entry 6).