

Supporting Information

Combining Flow Synthesis and Heterogenous Catalysis for the Preparation of Conjugated Polymers

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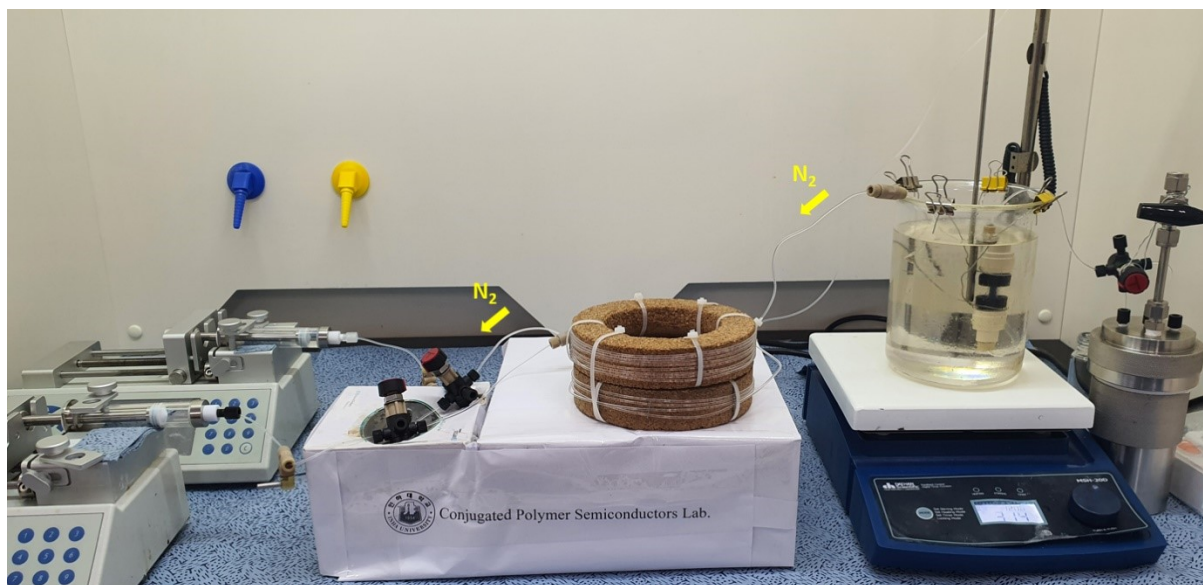


Figure S1. Picture of customized flow system with packed bed column reactor.

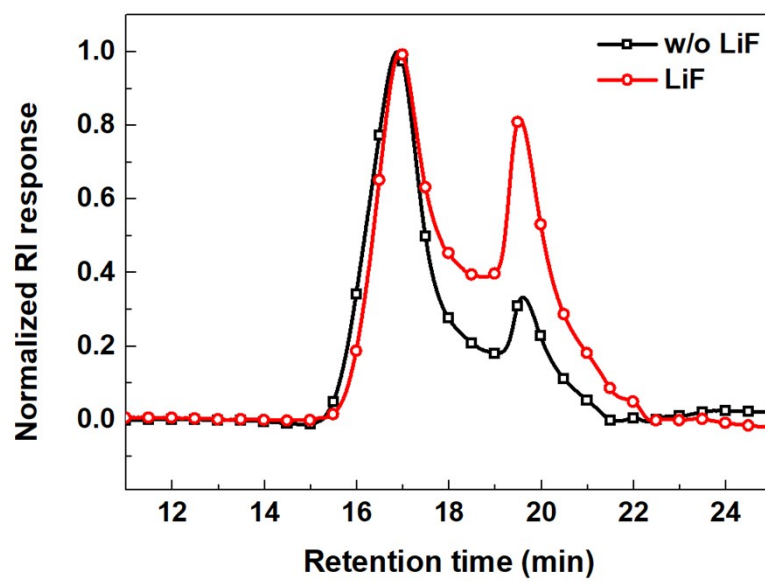


Figure S2. Normalized GPC traces of PTB7 product after batch reaction without and with LiF**Table S1.** GPC data of batch reaction without and with LiF

entry	System	M_n [kDa]	M_w [kDa]	\mathcal{D}
1	w/o LiF	7.3	26.1	3.581
2	LiF	4.4	17.0	3.872

Table S2. Reproducibility data of molecular weights and \mathcal{D} for heterogeneous batch and heterogeneous flow synthesis.

Entry	Reactor type	Reaction time	Temp. [°C]	M_n [kDa]	M_w [kDa]	\mathcal{D}
1	flow	30 min	120	7.9	21.5	2.70
2	flow	30 min	120	9.1	32.8	3.58
3	flow	30 min	120	7.6	28.9	3.78
4	batch	72 hr	120	9.3	27.8	2.99
5	batch	72 hr	120	7.4	27.4	3.71
7	batch	72 hr	120	5.7	22.0	3.88
8	flow*	30 min	120	4.9	28.7	5.86
9	flow*	30 min	120	6.1	27.1	4.44

* flow synthesis without N₂ interlayer.

Table S3. Molecular weights and \mathcal{D} of PTB7 products with temperature of 110 °C, 120 °C and 130 °C.

entry	Reaction time (min)	Temp. [°C]	M_n [kDa]*	M_w [kDa]*	\mathcal{D} *
1	30	110	16.87 ± 0.5	36.25 ± 1.08	2.15 ± 0.02
2	30	120	19.12 ± 0.96	36.16 ± 1.65	1.89 ± 0.05

3 30 130 10.63 ± 2.10 35.9 ± 1.01 2.59 ± 0.25

* Molecular weights and molecular weight dispersity were averaged over three or more repeated runs. Only first 0.5 mL samples were collected and characterized.

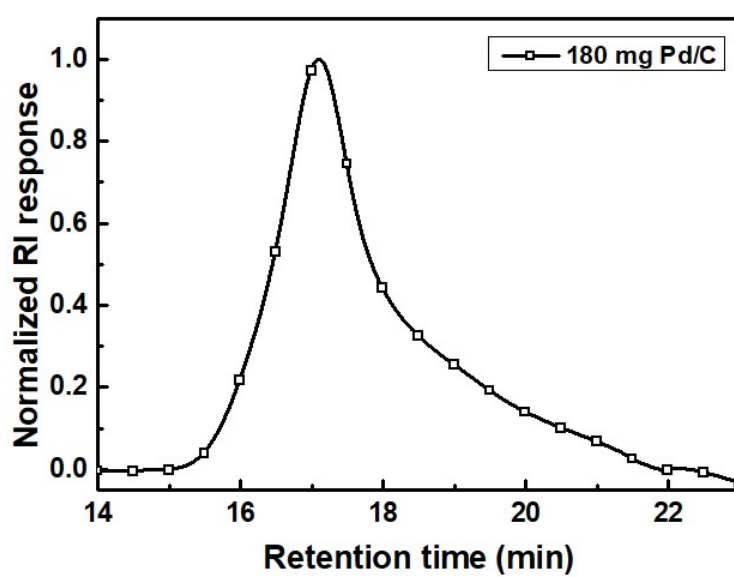


Figure S3. PTB7 samples collected all regions of the reaction mixture at same reaction conditions with 180 mg of Pd/C in the column reactor.

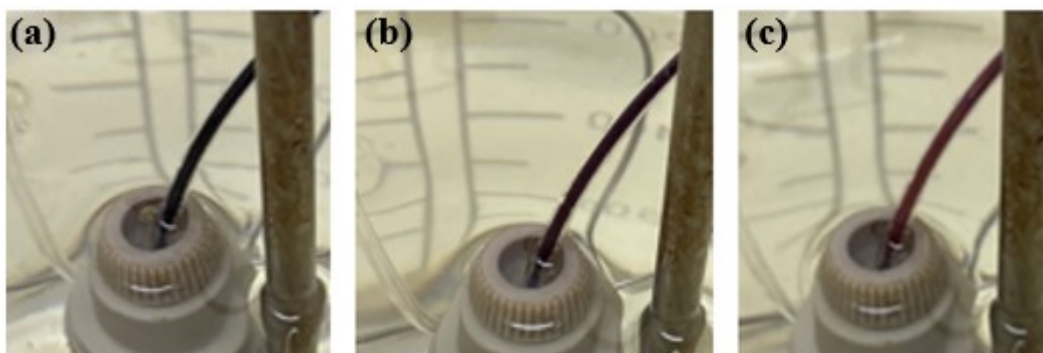


Figure S4. Picture of product color existing column by region. (a) region 1-2, (b) region 3, (c) region 4

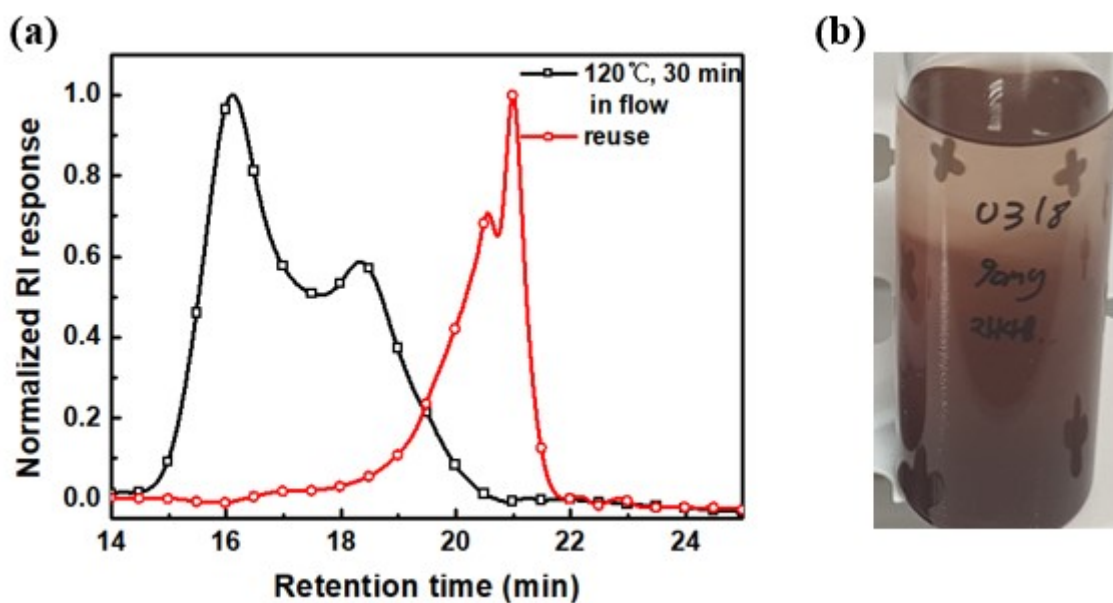


Figure S5. (a) Normalized GPC traces of PTB7 synthesized in flow at 120 °C for 30 minutes with a fresh Pd/C and reused Pd/C, and (b) picture of the sample collected from the reaction with reused Pd/C in methanol.

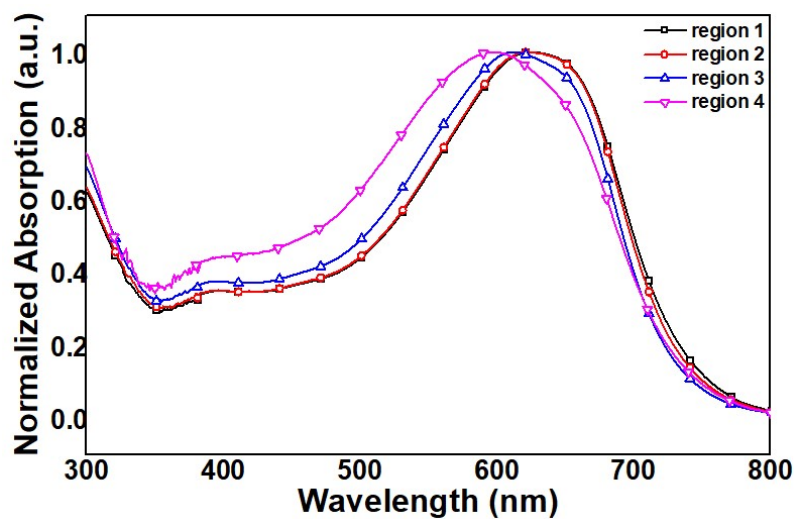


Figure S6. Absorption spectrum of PTB7 solution by different regions.

Table S4. Reproducibility data of molecular weights and \mathcal{D} for 1st region

entry	Temp. [°C]	M_n [kDa]	M_w [kDa]	\mathcal{D}
1	120	18.9	36.1	1.91
2	120	20.8	38.9	1.87
3	120	19.1	34.7	1.82
4	120	18.4	35.3	1.92
5	120	18.7	36.3	1.94
6	110	16.8	36.1	2.15
7	110	16.2	34.8	2.15
8	110	17.2	37.3	2.17
9	110	17.3	36.8	2.13
10	130	16.8	36.1	2.15
11	130	16.2	34.8	2.15
12	130	17.3	36.8	2.13

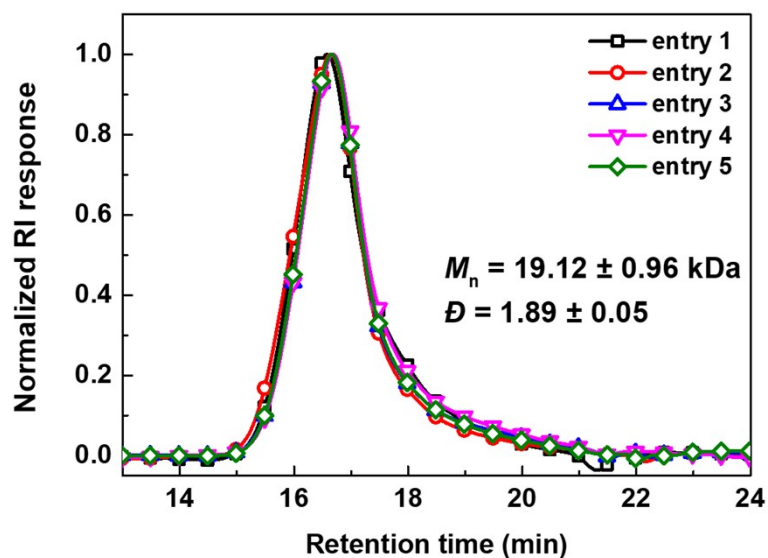


Figure S7. Normalized GPC traces of five repeated runs of PTB7 synthesis in flow at the same reaction conditions. (90 mg of Pd/C in the column reactor, reaction temperature of 120 °C, and residence time of ca. 30 min)

Table S5. The amount of the palladium before and after the reaction.

Mean Data: Pd/C							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Pd 340.458	2453180.7	24.58 mg/L	0.514	79820 ppm	1669.9	2.09%	
Si 251.611	26093.6	0.232 mg/L	0.0018	752.4 ppm	5.89	0.78%	
Mean Data: Pd/C used							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Pd 340.458	1928155.8	19.43 mg/L	0.440	62680 ppm	1419.8	2.26%	
Si 251.611	132062.5	1.205 mg/L	0.0224	3885 ppm	72.4	1.86%	

Table S6. The amount of the palladium residue in polymer samples after the reaction.

Mean Data: Pd/C(hetero flow)							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Pd 340.458	1428.9	0.042 mg/L	0.0004	423.1 ppm	3.79	0.90%	
Mean Data: Pd(PPh) ₄ (homo flow)							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Pd 340.458	131862.7	1.583 mg/L	0.0230	1439 ppm	20.9	1.45%	

Mean Data: Pd/C + TPP (flow)		Calib.		Sample		Std.Dev.	RSD
Analyte	Mean Corrected Intensity	Conc. Units	Std.Dev.	Conc. Units	Std.Dev.		
Pd 340.458	17214.6	0.221 mg/L	0.0009	585.8 ppm	2.39		0.41%

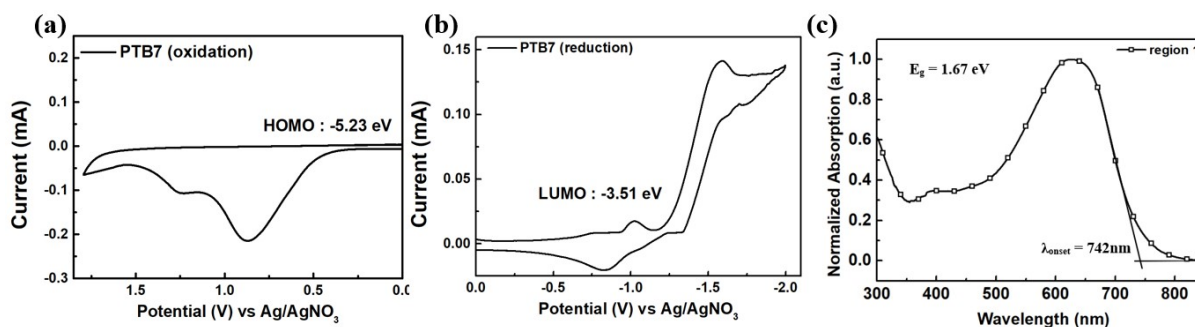


Figure S8. Cyclic voltammograms of PTB7 thin film in 0.1 M Bu₄NPF₆ solution in acetonitrile, oxidation scans (a) and reduction scans (b), and UV-vis absorption spectrum of PTB7 as a thin film on glass substrate (c).

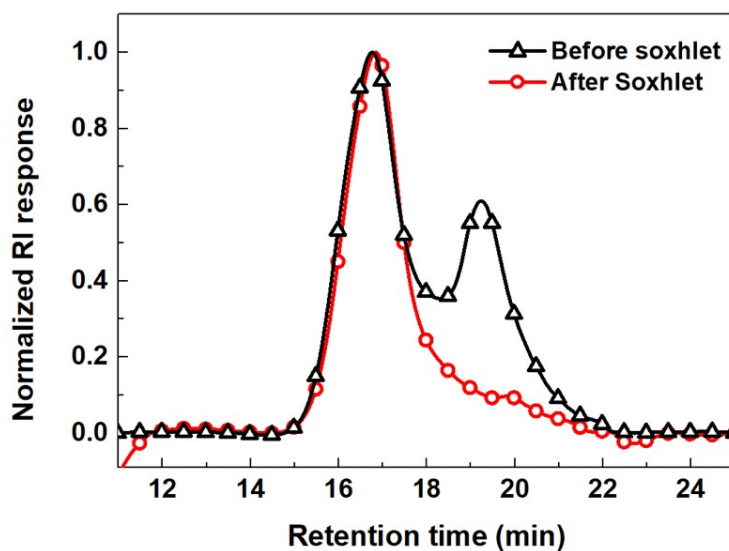


Figure S9. Normalized GPC traces of before and after Soxhlet of PTB7 product using Pd/C in batch reactor.

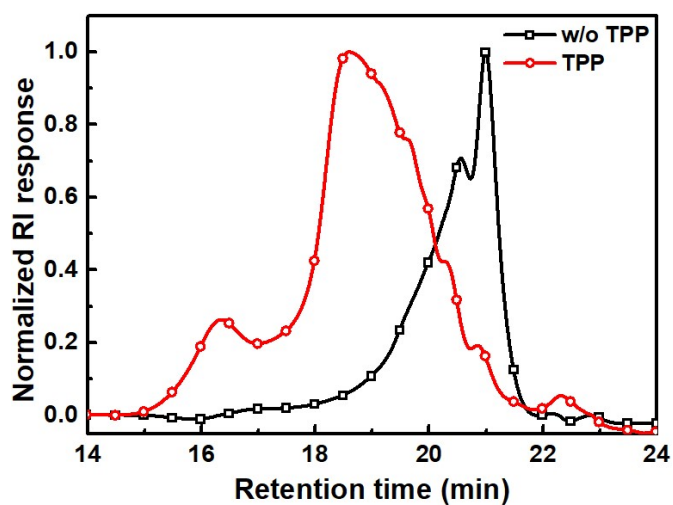


Figure S10. Normalized GPC traces of PTB7 products synthesized with reused Pd/C with triphenylphosphine (TPP) (red line) and without TPP (black line).

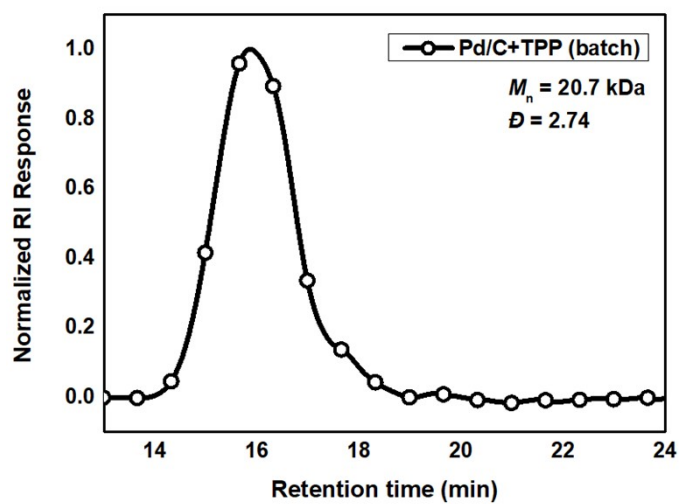


Figure S11. Normalized GPC trace of PTB7 product using Pd/C with TPP in batch reactor.