Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Flow Synthesis of Conjugated Polymers: Exploring the Effects of Solvent and Catalyst on Molecular Weight

Jin Woo Jeon and Ye-Jin Hwang*

Department of Chemistry and Chemical Engineering, Education and Research Center for Smart Energy and Materials, Inha University, 100 Inha-ro, Michuhol-gu, Incheon, Republic of Korea

Phone: (+82)-32-860-7464; Fax: (+82)-32-860-7725; Email: yjhwang@inha.ac.kr

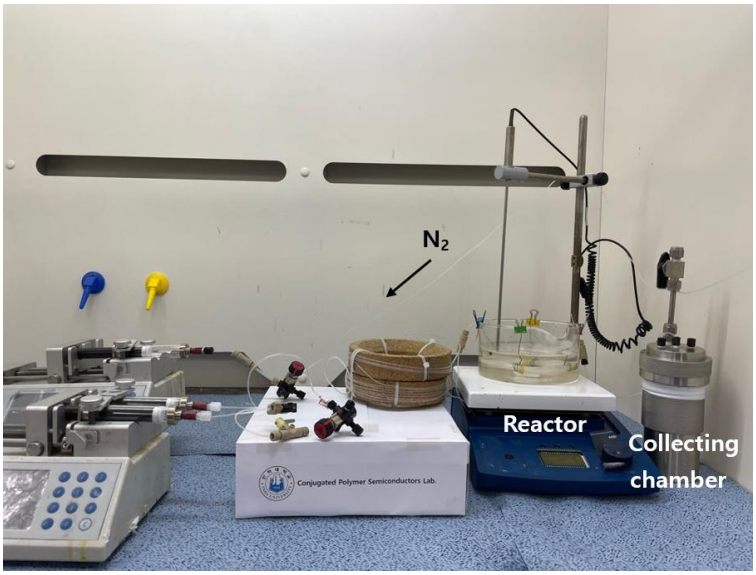

Figure S1. An image of the flow synthesis system used in this study.

Table S1. Molecular weight and *Đ* of PTB7 synthesized by flow system from three times of repeated runs.

entry	catalyst	solvent	M_n[kDa]	M_w[kDa]	*Đ*
1[a]	$Pd(PPh_3)_4$	toluene	3.13	4.25	1.36
2[a]	$Pd(PPh_3)_4$	toluene	3.16	4.26	1.35
3[a]	$Pd(PPh_3)_4$	toluene	2.71	3.47	1.28
4[a]	$Pd(PPh_3)_4$	chlorobenzene	3.13	7.46	2.38
5[a]	$Pd(PPh_3)_4$	chlorobenzene	3.18	7.67	2.41
6[a]	$Pd(PPh_3)_4$	chlorobenzene	3.56	8.23	2.32
7	$Pd(PPh_3)_4$	o-xylene	3.29	7.20	2.19
8	$Pd(PPh_3)_4$	o-xylene	3.49	8.42	2.41
9	$Pd(PPh_3)_4$	o-xylene	3.25	7.47	2.30
10	$Pd(PPh_3)_4$	toluene/DMF	59.54	146.34	2.46
11	$Pd(PPh_3)_4$	toluene/DMF	55.12	125.32	2.27
12	$Pd(PPh_3)_4$	toluene/DMF	58.12	123.12	2.12
13	$Pd(PPh_3)_4$	chlorobenzene/DMF	53.59	106.08	1.98
14	$Pd(PPh_3)_4$	chlorobenzene/DMF	55.24	116.81	2.12
15	$Pd(PPh_3)_4$	chlorobenzene/DMF	52.80	113.76	2.16
16	$Pd(PPh_3)_4$	o-xylene/DMF	58.70	132.10	2.25
17	$Pd(PPh_3)_4$	o-xylene/DMF	55.97	127.97	2.29
18	$Pd(PPh_3)_4$	o-xylene/DMF	61.34	145.90	2.38
19	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene	42.44	92.41	2.18

20	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene	46.17	106.71	2.31
21	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene	44.16	88.81	2.01
22	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene	55.16	130.47	2.37
23	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene	50.59	109.32	2.16
24	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene	48.65	94.81	1.95
25	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene	40.98	77.92	1.90
26	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene	43.79	90.19	2.06
27	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene	40.23	87.13	2.17
28	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene/DMF	15.45	66.14	4.28
29	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene/DMF	14.79	62.00	4.19
30	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	toluene/DMF	14.82	61.10	4.12
31	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene/DMF	11.65	51.96	4.46
32	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene/DMF	11.00	42.25	3.84
33	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	chlorobenzene/DMF	10.03	39.78	3.97
34	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene/DMF	12.58	45.05	3.58
35	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene/DMF	12.50	46.51	3.72
36	$Pd_2(dba)_3$+$P(o\text{-}tol)_3$	o-xylene/DMF	12.26	47.33	3.86

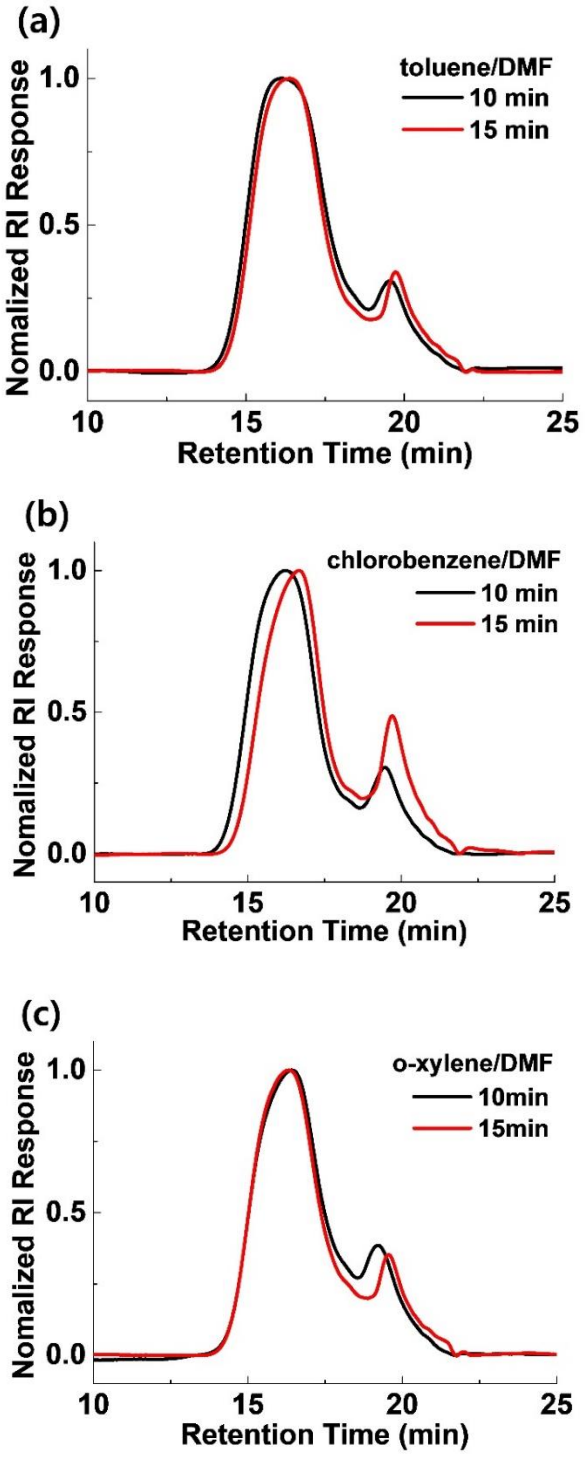

Figure S2. GPC traces of PTB7 synthesized for 10 and 15 min by using $Pd_2(dba)_3$/$P(o\text{-}tol)_3$ (a) in a toluene/DMF, (b) in a chlorobenzene/DMF, and (c) in a o-xylene/DMF.

Table S2. Molecular weight and *Đ* of PTB7 synthesized for 15 min by using $Pd_2(dba)_3$/P(o-tol)$_3$.

entry	solvent	reaction time [min]	M_n[kDa]	M_w[kDa]	*Đ*
1	toluene/DMF	15	11.41	56.55	4.96
2	chlorobenzene/DMF	15	9.45	47.41	5.03
3	o-xylene/DMF	15	11.12	53.15	4.78

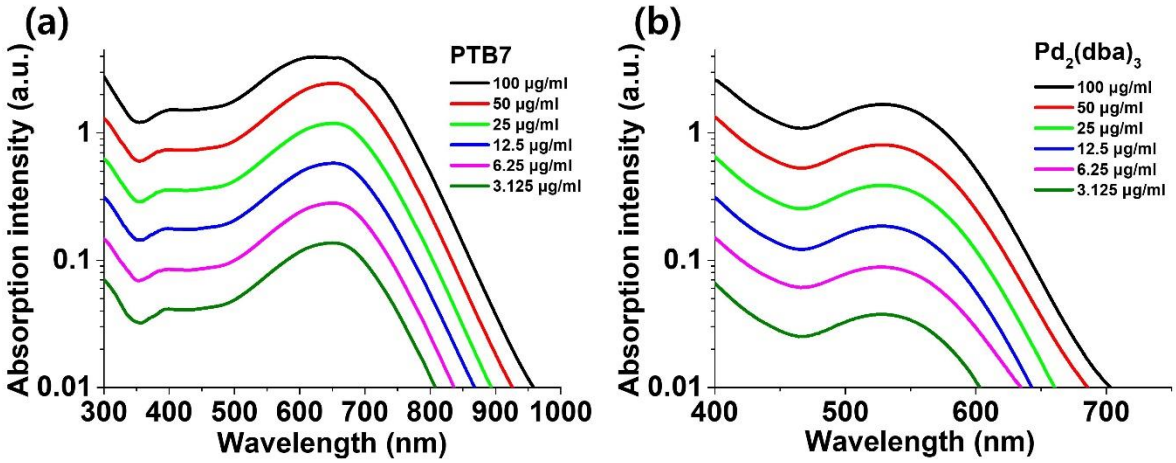

Figure S3. Absorption spectra of standard solutions of (a) PTB7 and (b) $Pd_2(dba)_3$, respectively.

Table S3. Hansen parameters of the solvents and polymer. Parameters of the PTB7 is gained from Manley et al.[1] The others are from Barton.[2]

materials	δ_d	δ_p	δ_h
toluene	18.0	1.4	2.0
chlorobenzene	19.0	4.3	2.0
o-xylene	17.8	1.0	3.1
PTB7	21.05	2.18	5.92

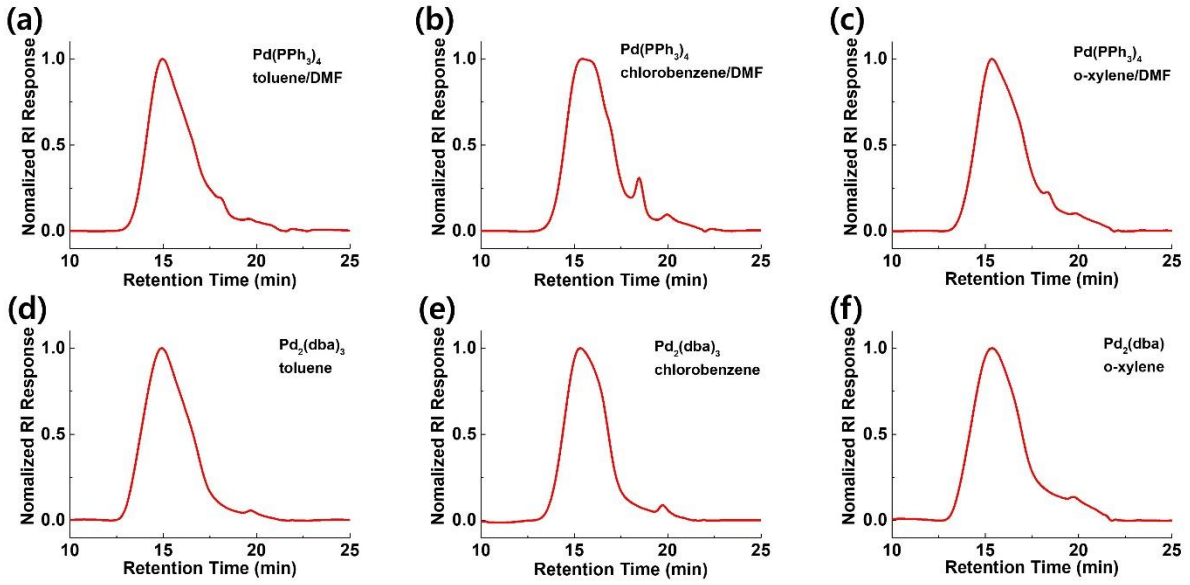

Figure S4. GPC traces of PTB7 synthesized by batch reactor using (a) $Pd(PPh_3)_4$ with toluene/DMF, (b) $Pd(PPh_3)_4$ with chlorobenzene/DMF, (c) $Pd(PPh_3)_4$ with o-xylene/DMF, (d) $Pd_2(dba)_3$/P(o-tol)$_3$ with toluene, (e) $Pd_2(dba)_3$/P(o-tol)$_3$ with chlorobenzene, and (f) $Pd_2(dba)_3$/P(o-tol)$_3$ with o-xylene/DMF.

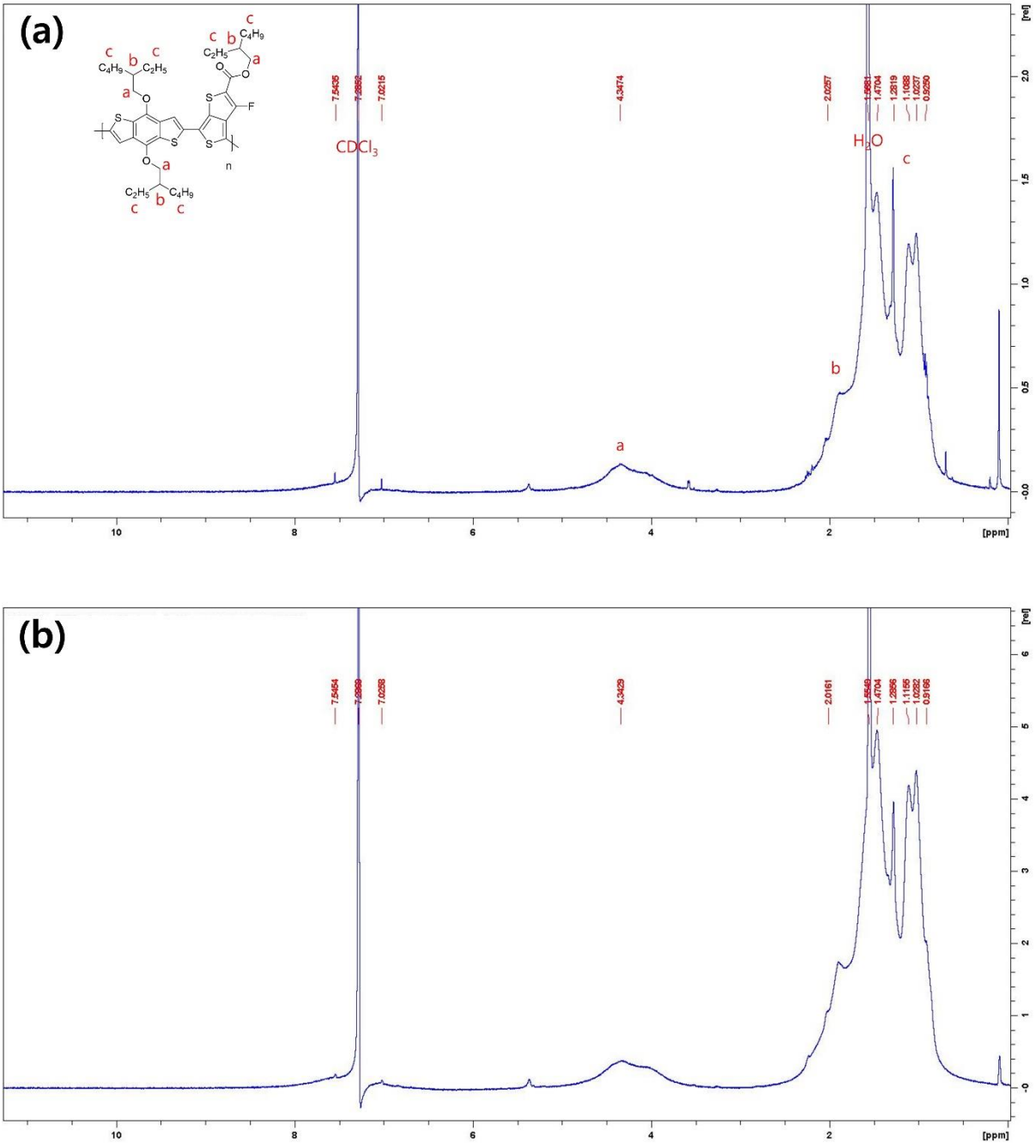

Figure S5. H^1-NMR graph of PTB7 (a) synthesized by flow system, and (b) purchased from Sigma Aldrich.

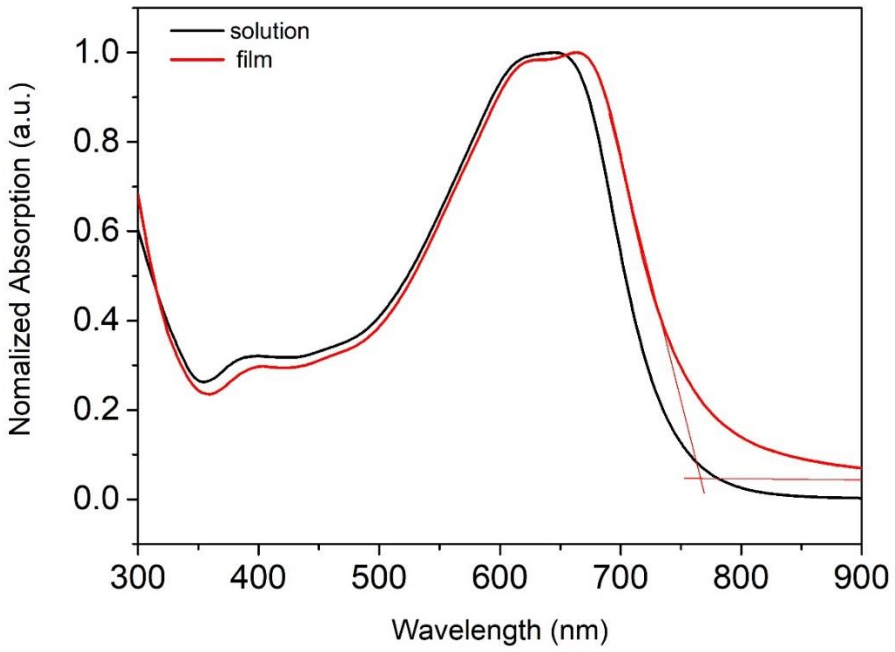

Figure S6. UV-vis absorption spectra of solution and film of PTB7 synthesized by flow system.

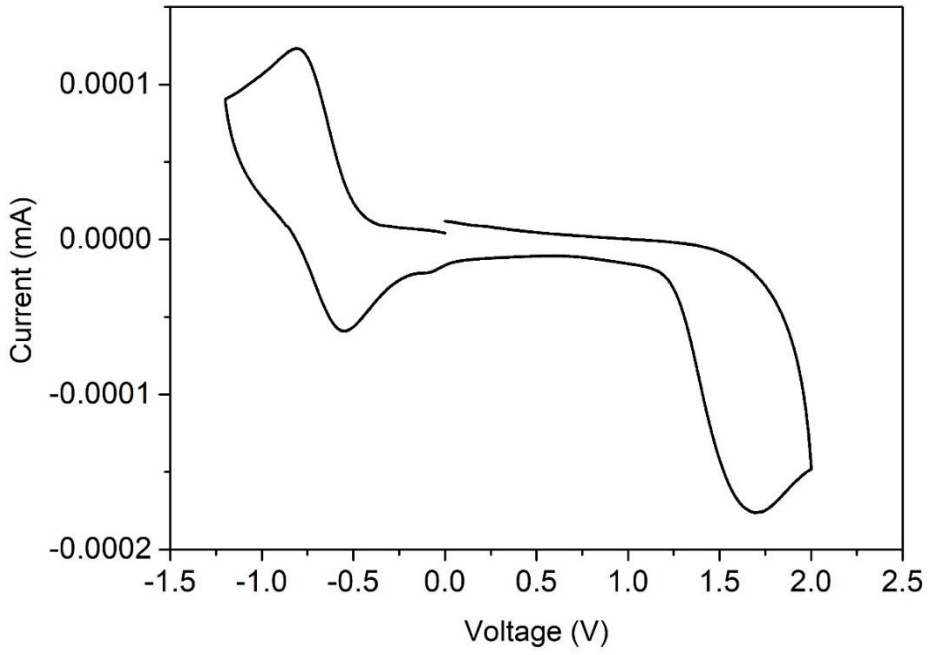

Figure S7. Cyclic voltammogram for PTB7 synthesized by flow system.

Table S4. Optical and electrochemical properties of PTB7 synthesized by flow system.

polymer	λ_{max}^{sol} [nm]	λ_{max}^{film} [nm]	λ_{on}^{film} [nm]	$E_g^{optical}$ [eV][a]	HOMO [eV]	LUMO [eV]	$E_g^{electrical}$ [eV]
PTB7	645	664	767	1.62	-5.41	-3.62	1.79

[a] Optical energy band gap was measured on film.

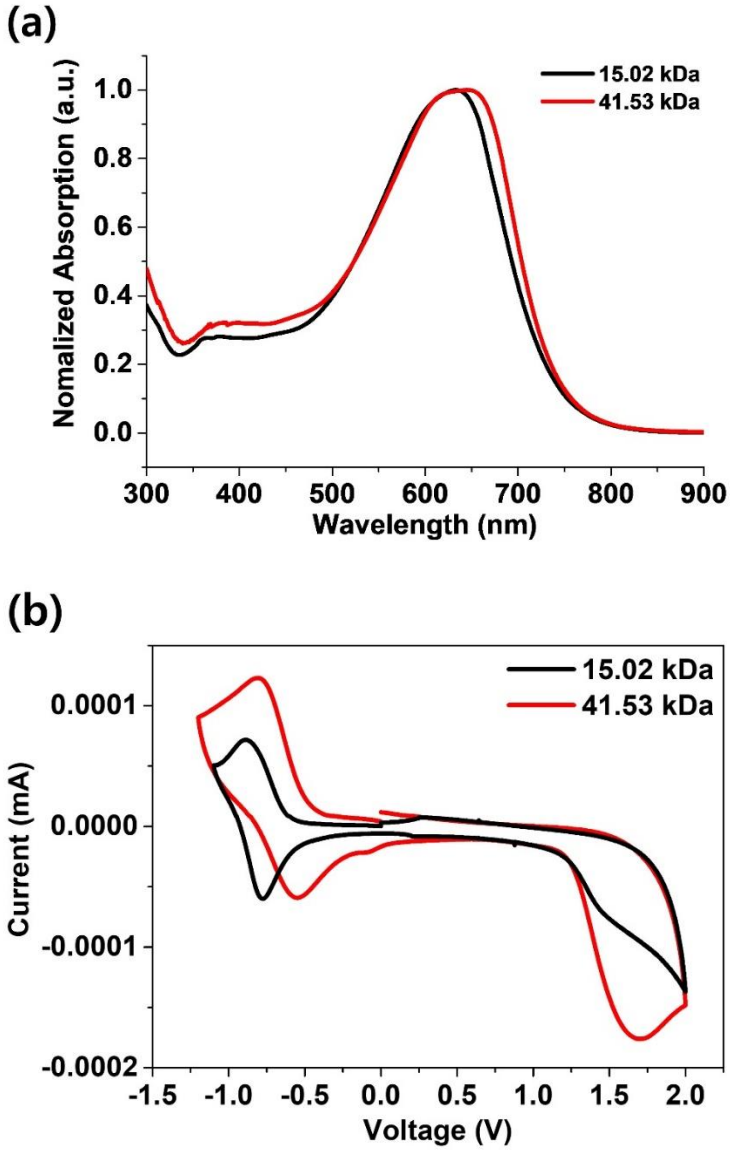

Figure S8. (a) UV-vis absorption spectra of PTB7 thin film and (b) Cyclic voltammogram of PTB7 in two different molecular weights.

Table S5. Optical and electrochemical properties of PTB7 in two different molecular weights.

Entry	M_n [kDa]	λ_{max}^{sol} [nm]	λ_{on}^{sol} [nm]	HOMO [eV]	LUMO [eV]	$E_g^{electrical}$ [eV]
1	15.02	633	737	-5.51	-3.65	1.86
2	41.53	645	748	-5.41	-3.62	1.79

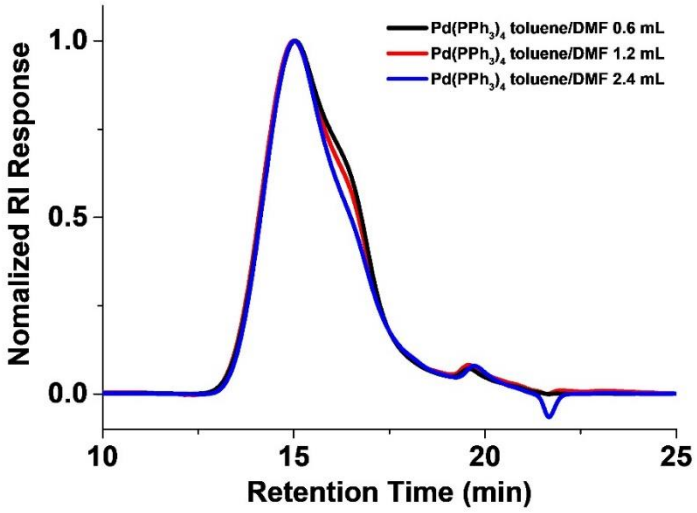

Figure S9. GPC traces of PTB7 synthesized in various reaction volumes.

Table S6. Molecular weight and *Đ* of PTB7 synthesized in various reaction volumes.

reaction volume [mL]	reaction time [min]	M_n[kDa]	M_w[kDa]	*Đ*
1.2	10	57.59	131.59	2.28
0.6	10	58.25	129.69	2.23
2.4	10	54.31	126.08	2.32

Reference

[1] E. F. Manley, J. Strzalka, T. J. Fauvell, N. E. Jackson, M. J. Leonardi, N. D. Eastham, T. J. Marks, L. X. Chen, *Adv. Mater.* **2017**, *29*.

[2] A. F. Barton, *Chem. Rev.* **1975**, *75*, 731-753.