Supporting information

High-efficiency synthesis of naphthalene-diimide-based conjugated polymer using continuous flow technology for organic field-effect transistors

Weiwei Wang,[ac] Ruikun Chen,[ac] Yaohui Hu,[a] Hongbo Lu,[ac] Longzhen Qiu,[ac] Yunsheng Ding,[c] Dengrong Sun,*[b] and Guobing Zhang*[ac]

[a]National Engineering Lab of Special Display Technology, State Key Lab of Advanced Display Technology, Academy of Photo-Electronic Technology, Hefei University of Technology, Hefei, 230009, China.

[b]Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea.

[c]School of Chemistry and Chemical Engineering, Hefei University of Technology, Key Laboratory of Advance Functional Materials and Devices of Anhui Province, Hefei, 230009, China.

Experimental section

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene were synthesized according to the methods reported in literatures.[S1] 4,9-Dibromo-2,7-bis(2-decyltetradecyl)naphthalene-diimide (2Br-NDI) was purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd., Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, tri(*o*-tolyl)phosphine ($P(o\text{-}tol)_3$), and other chemicals were purchased from Sigma-Aldrich Chemical Company and Sinopharm Chemical Reagent Co. Ltd., China. Chemical regents were purchased and used as received. The polymer tubing (Polytetrafluoro ethylene, PTFE, *D*: 1 mm) was purchased from Health & Science (USA).

Measurements and characterization

Nuclear magnetic resonance (NMR) spectra were record using an Agilent VNMRS600 machine. Gel permeation chromatography (GPC) analyses were performed on a Waters 1515 instrument equipped with a guard column MIXED 7.5×50 mm PL column and two MIXED-C 7.5×300 columns and a differential refractive index detector using chloroform (HPLC grade) as the eluent at 35 ^{o}C with a flow rate of 1 mL/min. Absorption spectra were measured using polymer solution in chloroform and films cast onto quartz glass using Agilent Cary 5000 model spectrophotometer. Electrochemical cyclic voltammetry (CV) was conducted under nitrogen using a CHI 660D electrochemical analyzer in anhydrous acetonitrile solution containing 0.1 M tetra-*n*-butylammounium hexafluorophosphate with a scan rate of 0.1 V/s. A platinum (Pt) electrode was used as both the working and auxiliary electrode. The Ag/Ag^+ electrode was used as the reference electrode. Grazing-incidence-X-ray diffraction (GIXD) measurements were performed using 3C beamlines at the Pohang Accelerator Laboratory (PAL) in Korea. The fabrication of GIXD samples was same as the devices (In the Section of Device Fabrication), and the film thickness was about 90 nm. The atomic force microscopy (AFM) images were obtained using a SPA300HV instrument.

Fabrication and performance of the organic field effect transistors (OFETs)

Bottom-gate/top-contact (BG/TC) OFETs devices were fabricated on a gate of *n*-

doped Si with a 300 nm thick SiO_2 dielectric layer. A chloroform solution (~ 6 mg/mL) was dropped onto the ocadecyltri-chlorosilane (OTS)-treated Si/SiO_2 and spin-coated at 3500 rpm for 40 s. The film thickness was about 90 nm. The polymer films were annealed in glove box. The Au source-drain electrodes were prepared by thermal evaporation. The OTFTs devices had a channel length (L) of 130 μm and a channel wide (W) of 760 μm. The devices were characterized under vacuum conditions using a Keithley 4200 semiconductor parametric analyzer. Mobility (μ) was obtained using the following equation in the saturation regime: $I_d = (W/2L)Ci\mu(V_g\text{-}V_{th})^2$, where I_d is the drain current, C_i is the capacitance of the gate dielectric, V_g is the gate-source voltage and V_{th} is the threshold voltage.

General procedures for continuous flow synthesis and purification (P7 – P105)

2Br-NDI (0.1 mmol, 0.11 g), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.1 mmol, 0.049 g), and anhydrous chlorobenzene (10 mL) were added to a 100 mL Schlenck tube. After the tube was charge with nitrogen through a freeze-pump-thaw cycle for three times, $Pd_2(dba)_3$ (4 mg) and P(*o*-tol)$_3$ (5 mg) were added quickly in one portion. The degassed chlorobenzene solvent is pumped through the PTFE tubing until it is completely filled with no air bubbles visible. Then the syringe (maximum volume of 20 mL) was charged with the solutions and placed onto the syringe pump and rapidly connected to the PTFE tubing. The whole reactors were exposed under air directly. The heating section of PTFE tube was arranged in a loose spiral of length 1 m. The reaction mixture is then injected in the flow reactor at the certain rate. The reaction mixture is heated with the temperature of 110 ^oC for **P7–P70** and 120 ^oC for **P105**. Once the reaction is completed, the polymer solution is slowly poured in methanol (80 mL) and was stirred for another 2 h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol and hexane for removal of low molecular weight. Finally, the remaining solid was extracted with hot chloroform. After removal of the solvent under reduced pressure, the black-blue solid was collected (**P7**: 22 mg, 20%; **P21**: 61 mg, 55%; **P35**: 75 mg, 68%; **P70**: 76 mg, 69%; **P105**: 80 mg, 72%.). Molecular weights are obtained using Gel permeation chromatography (Table 1 and Figures S12-16). The structures of the polymers were characterized using NMR (Figure S1-5).

General procedures for flask synthesis and purification (P0)

2Br-NDI (0.1 mmol, 0.11 g), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.1 mmol, 0.049 g), and anhydrous chlorobenzene (10 mL) were added to a 100 mL Schlenck tube. After the tube was charged with nitrogen through a freeze-pump-thaw cycle for three times, $Pd_2(dba)_3$ (4 mg) and P(*o*-tol)$_3$ (5 mg) were added quickly in one portion. The mixture was stirred at 110 ^oC for 35 min. After being cool to room temperature, the reaction mixture was poured into 80 mL methanol and was stirred for another 2 h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol, the solid was extracted with hot hexane. After removal of the solvent under reduced pressure, a black-blue solid was collected (76 mg, 69%). GPC: M_n = 4.86 kg/mol, M_w = 13.21 kg/mol, *PDI* = 2.72 (Figure S11).

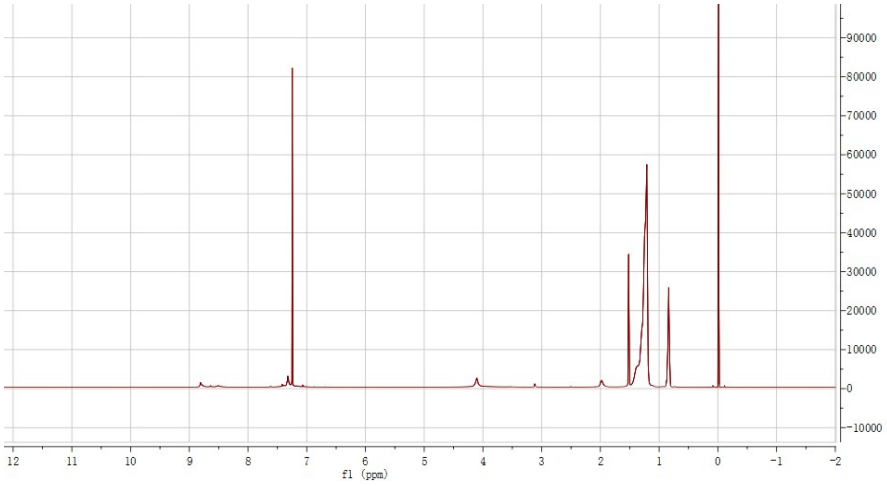


Figure S1. ^{1}H NMR spectra of **P7** prepared by flow synthesis ($CDCl_3$).

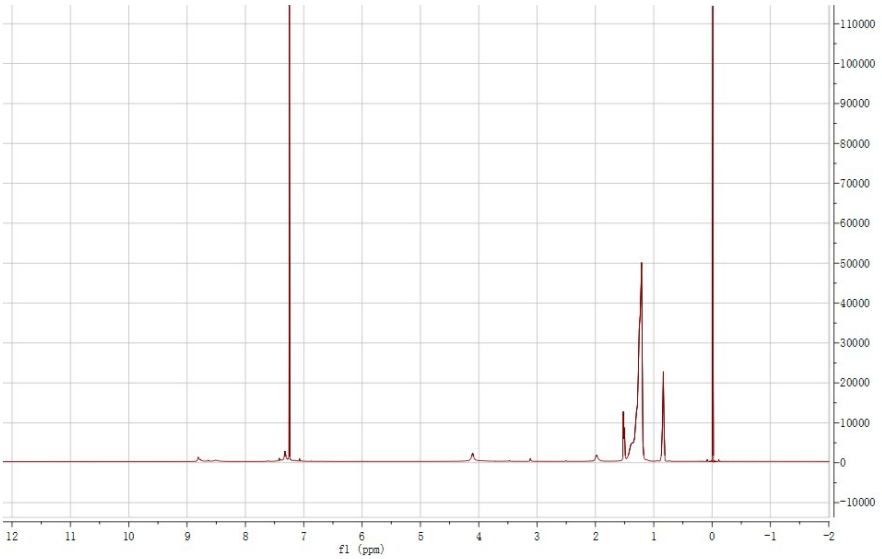


Figure S2. ^{1}H NMR spectra of **P21** prepared by flow synthesis ($CDCl_3$).

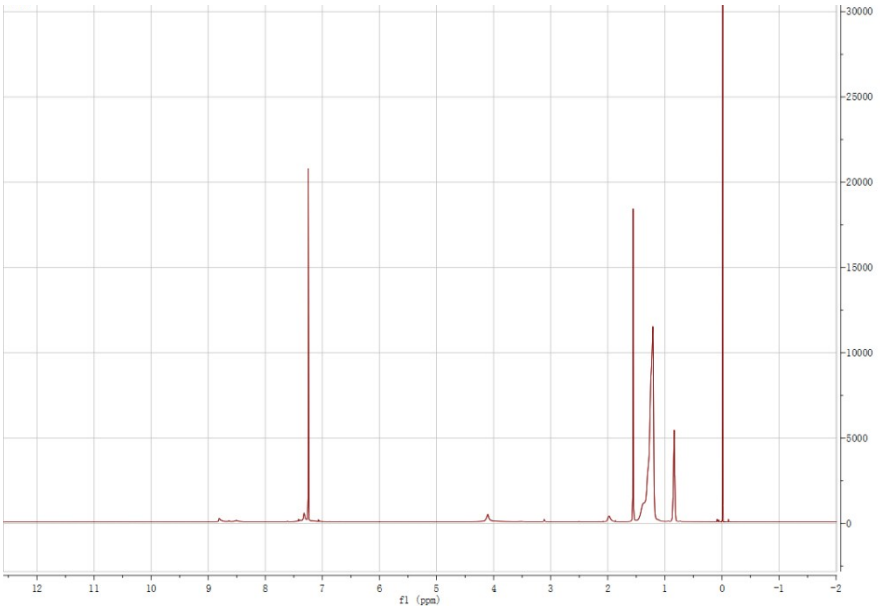


Figure S3. ^{1}H NMR spectra of **P35** prepared by flow synthesis ($CDCl_3$).

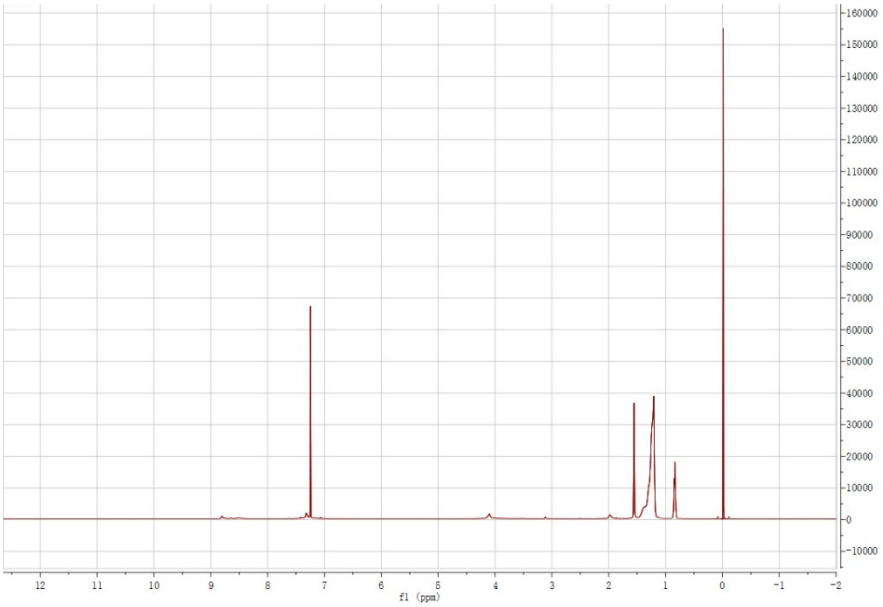


Figure S4. ^{1}H NMR spectra of **P70** prepared by flow synthesis ($CDCl_3$).

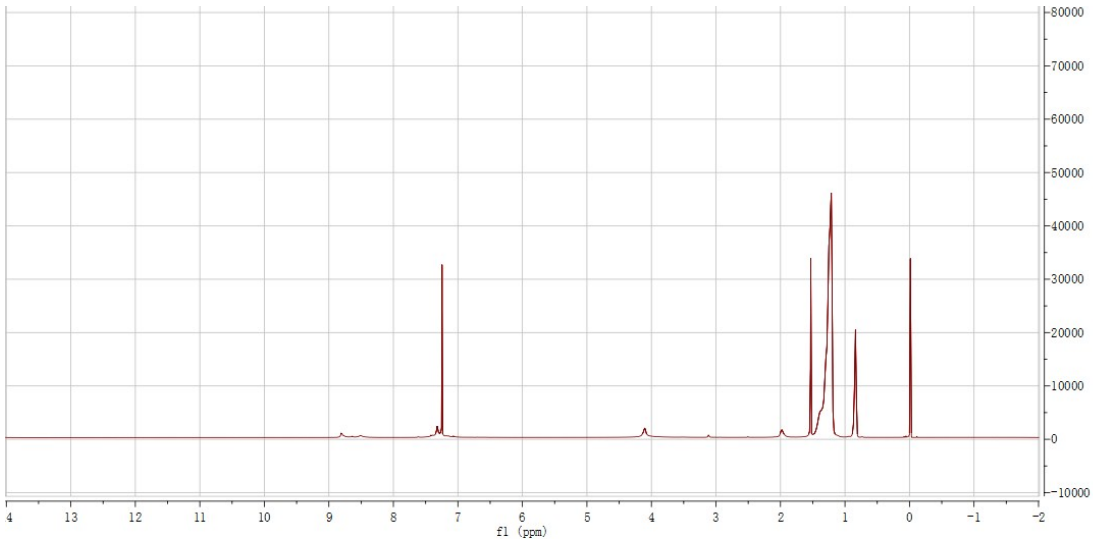


Figure S5. ^{1}H NMR spectra of **P105** prepared by flask synthesis ($CDCl_3$).

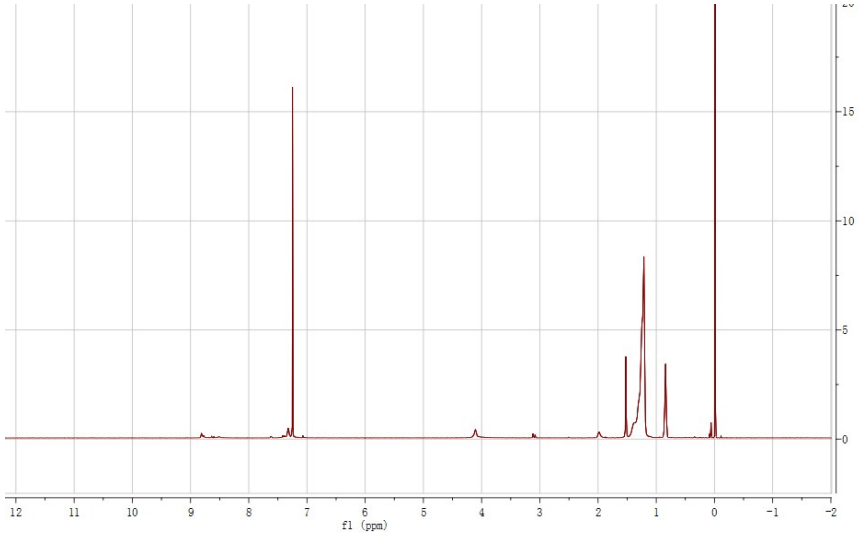


Figure S6. ^{1}H NMR spectra of **P0** prepared by flask synthesis ($CDCl_3$).

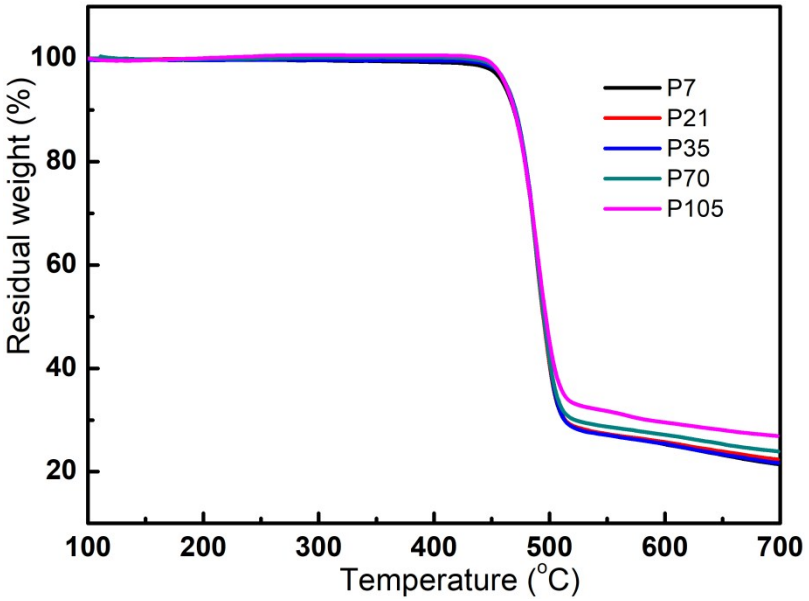


Figure S7. TGA plots of polymer prepared by flow synthesis.

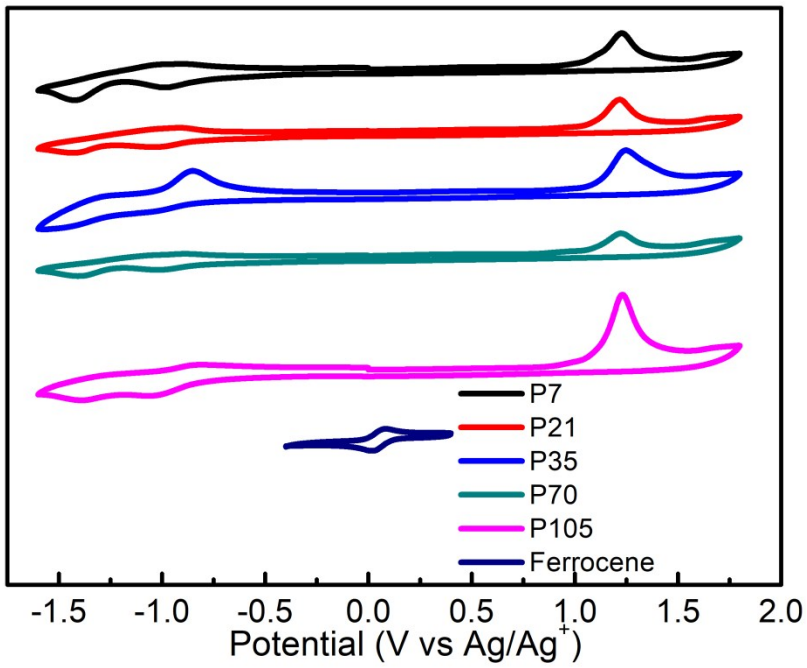


Figure S8. The CV curves of polymers synthesized by flask synthesis and continuous flow synthesis.

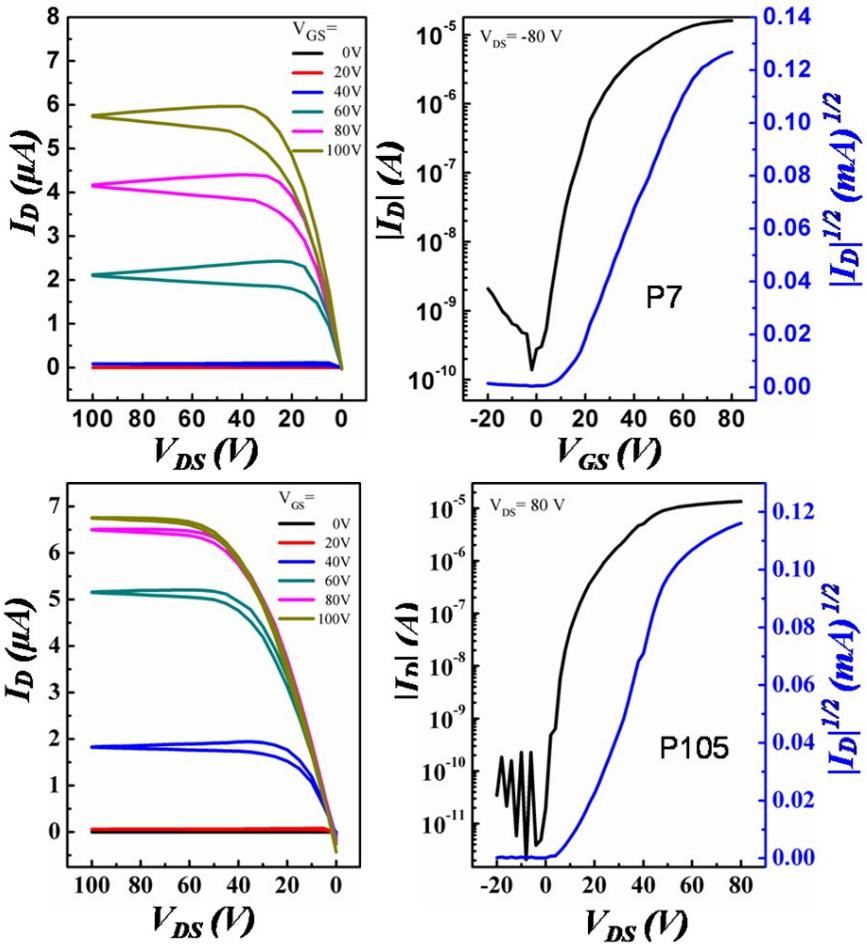


Figure S9. Output and transfer curves of OFETs based on P7 and P105 prepared by continuous flow synthesis.

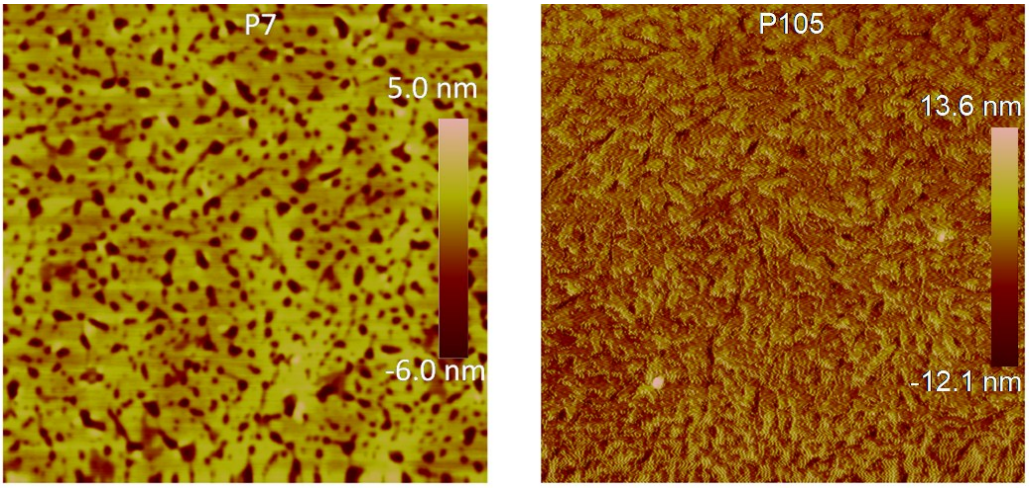


Figure S10. AFM height images of polymer films spin-coated on OTS-treated SiO_2/Si substrates.

Table S1. Device performances of polymer-based OFETs.

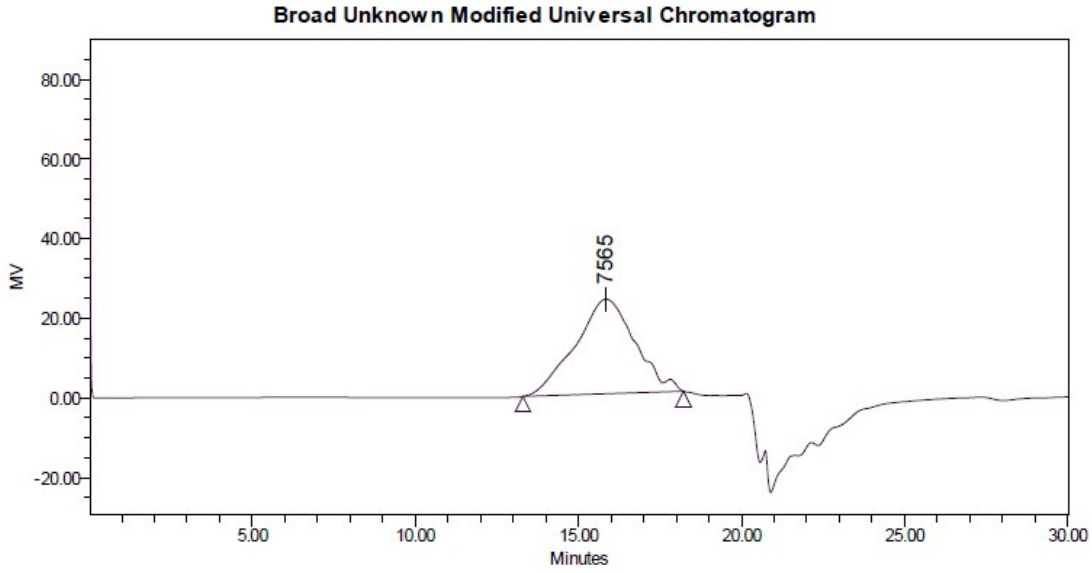
Annealing temperature(^{o}C)	*n*-channel			
	$\mu_{e,max}$ ($cm^2V^{-1}s^{-1}$)	$\mu_{e,avg}$ ($cm^2V^{-1}s^{-1}$)[a]	I_{on}/I_{off}	V_{th} (V)
P7				
rt	0.005	0.004±0.001	3.5×10^5	7.4
180	0.063	0.051±0.008	4.4×10^5	7.7
210	0.24	0.21±0.029	1.2×10^5	13.0
260	0.11	0.099±0.009	1.3×10^5	12.2
P21				
rt	0.16	0.12±0.032	4.7×10^5	36.7
180	0.30	0.15±0.096	1.6×10^6	41.7
210	0.46	0.27±0.12	2.1×10^6	28.4
260	0.50	0.43±0.062	3.5×10^6	20.1
P35				
rt	0.071	0.049±0.011	1.8×10^5	20.0
180	0.16	0.14±0.034	1.9×10^6	32.9
210	0.74	0.70±0.032	1.9×10^6	21.8
260	0.55	0.40±0.035	1.8×10^6	23.5
P70				
rt	0.024	0.02±0.0028	1.2×10^5	19.6
180	0.22	0.17±0.046	1.7×10^5	33.4
210	0.77	0.55±0.15	1.5×10^6	15.4
260	0.64	0.45±0.13	1.0×10^6	25.2
P105				
rt	0.059	0.035±0.021	1.7×10^5	30.8
180	0.33	0.31±0.01	8.7×10^5	26.7
210	0.39	0.25±0.10	6.7×10^6	15.4
260	0.54	0.34±0.16	1.0×10^6	16.6
P0				
rt	0.009	0.007±0.001	1.4×10^5	21.2
180	0.065	0.06±0.005	4.4×10^5	10.0
210	0.098	0.091±0.006	1.8×10^6	8.2
260	0.11	0.090±0.012	3.5×10^5	8.0

[a] Average mobility were obtained from more than 8–10 devices.

Table S2. Crystallographic information of polymer films.

Polymer	Face on				Edge on	
	q^{100} ($Å^{-1}$)	d^{100} ($Å$)	q^{010} ($Å^{-1}$)	d^{010} ($Å$)	q^{100} ($Å^{-1}$)	d^{100} ($Å$)
P35	0.224	28.04	1.61	3.90	0.220	28.55
P70	0.222	28.29	1.60	3.92	0.217	28.94
P0	0.224	28.04	-	-	0.204	30.78

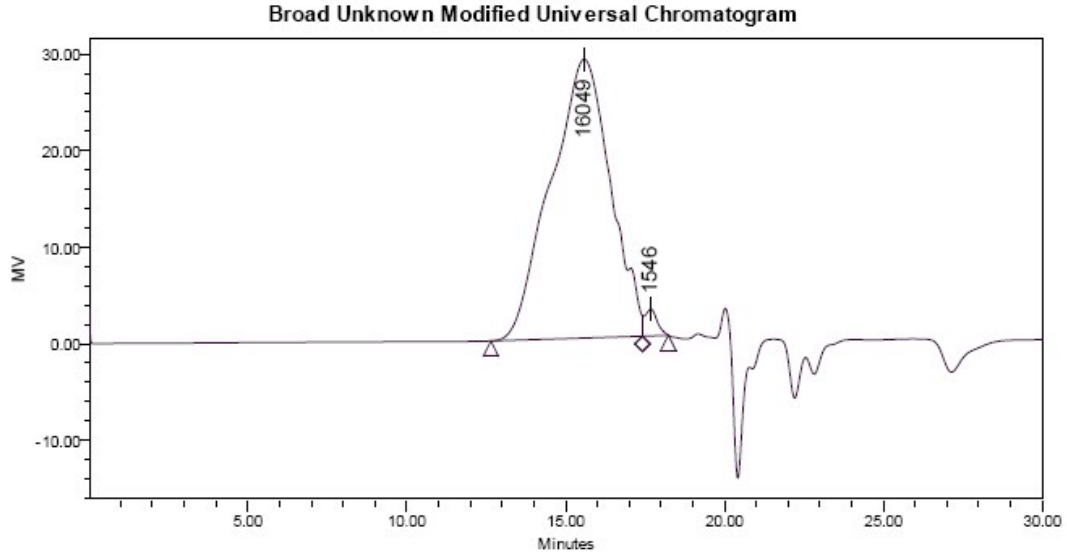
GPC results



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						4862	13211	7565	31050	52123	2.717257	2.350238

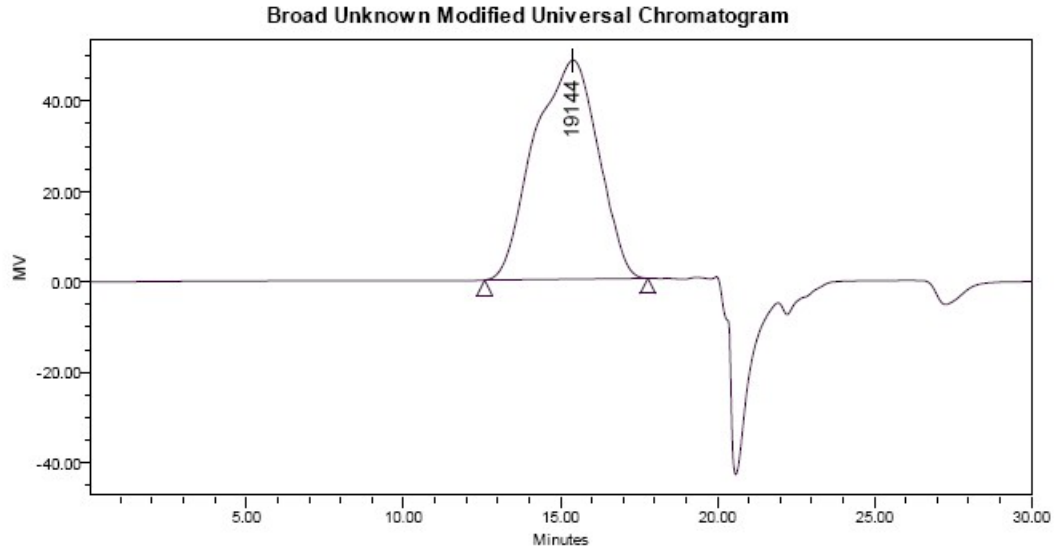
Figure S11. GPC results of **P0** (flask synthesis, 35 min).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						12759	26068	16049	48337	74498	2.043067	1.854256

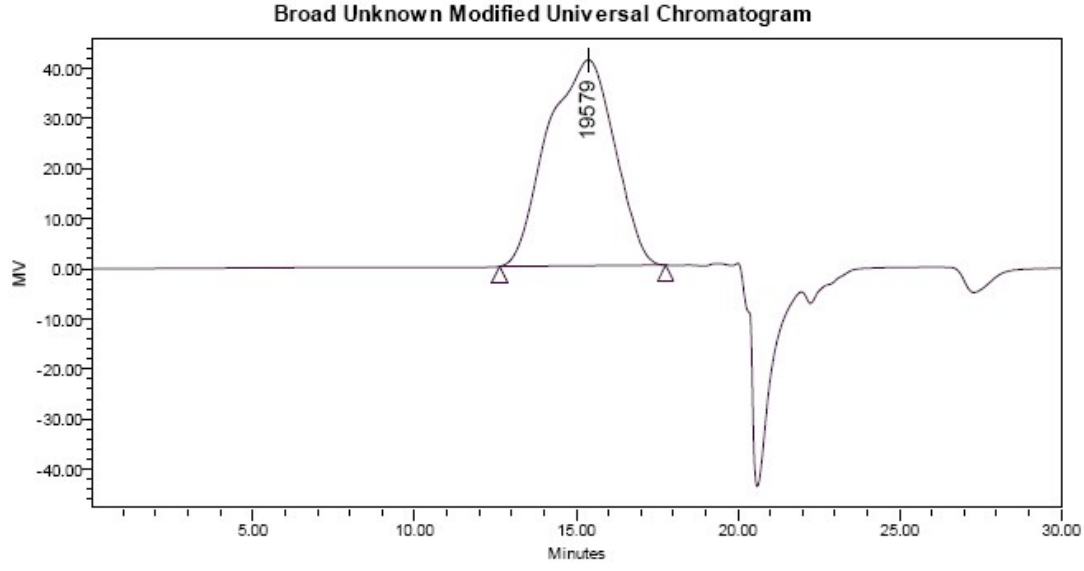
Figure S12. GPC results of **P7** (flow synthesis, 7 min).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						16838	34014	19144	61036	91001	2.020073	1.794408

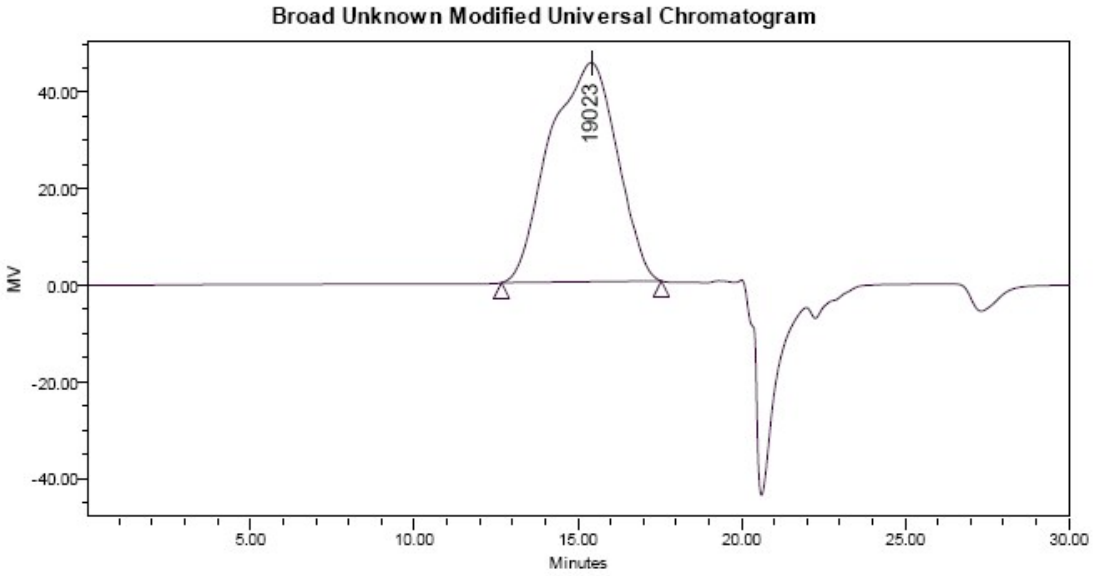
Figure S13. GPC results of **P21** (flow synthesis, 21 min).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						17280	35288	19579	63232	93446	2.040923	1.792895

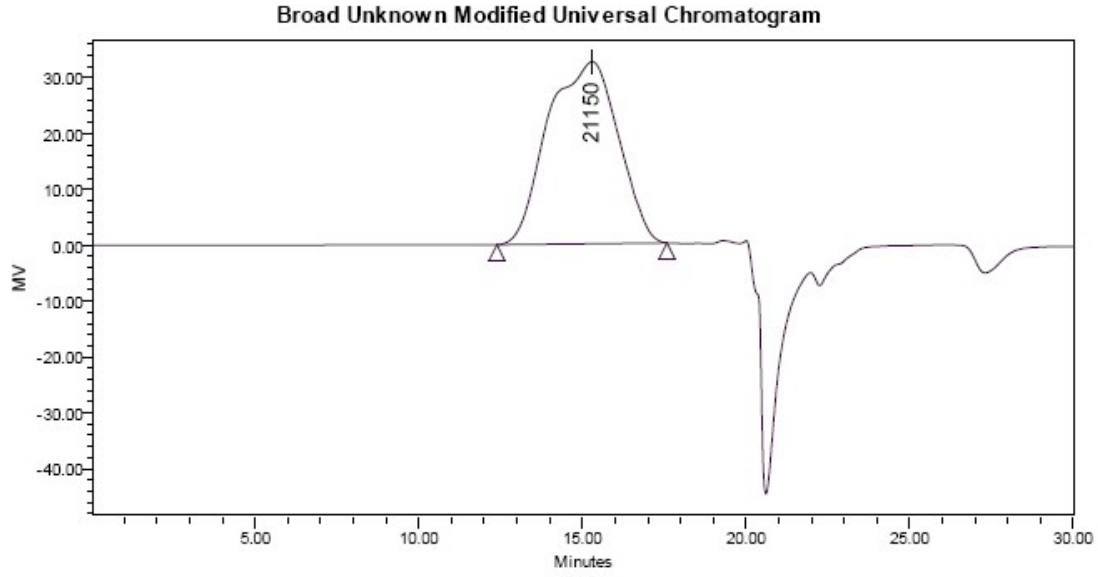
Figure S14. GPC results of **P35** (flow synthesis, 35 min).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						17178	34683	19023	61997	91498	2.018964	1.787554

Figure S15. GPC results of **P70** (flow synthesis, 70 min).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						19266	40002	21150	72312	108082	2.076225	1.807735

Figure S16. GPC results of **P105** (flow synthesis, 105 min).

S1. Ha, J. S.; Kim, K. H.; Choi, D.-H. *J. Am Chem Soc*, **2011**, 133, 10364-10367.