Supporting Information

Symmetry Breaking in Side Chains Leading to Mixed Orientations and Improved Charge Transport in Isoindigo-*alt*-Bithiophene Based Polymer Thin Films

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Supporting tables

Table S1. Set up conditions of the Berkovich tip

Depth (nm)	Strain rate (1/s)	Drift time (min)	Poisson ratio
1500	0.05	6	0.5

Table S2. Physical Properties of the three polymers

Polymer	M_n [a] (kDa)	PDI	$\lambda_{max, sol}$ [b] (nm)	$\lambda_{max, film}$ [c] (nm)	T_d [d] (°C)	Optical band gap [e] (eV)
P1	35.6	5.1	668, 723	648, 716	393	1.61
Ref-1	8.5	1.9	648, 723	580, 635, 707	396 [1]	1.58
Ref-2	28.8	4.0	665, 713	651, 720	392 [2]	1.55

[a] Trichlorobenzene as eluent at 150 °C. [b] In dilute chloroform solutions. [c] As thin films. [d] Decomposition temperature. [e] Estimated from thin-film absorption onset.

Table S3. Quantified distributions of (010) for P1, Ref-1 and Ref-2.

χ		85.5	80.5	75.5	70.5	65.5	60.5	55.5	50.5	45.5	40.5	35.5	30.5	25.5	20.5	15.5
Percentages of polymers	P1	0.115	0.109	0.097	0.093	0.065	0.037	0.018	0.008	0.010	0.016	0.025	0.061	0.083	0.112	0.151
	Ref-1	0.095	0.110	0.126	0.120	0.098	0.088	0.065	0.050	0.044	0.029	0.024	0.021	0.026	0.037	0.066
	Ref-2	0.131	0.126	0.124	0.115	0.098	0.082	0.067	0.058	0.050	0.040	0.033	0.026	0.022	0.017	0.011

Table S4. Quantified distributions of (100) for P1, Ref-1 and Ref-2.

χ		10.5	15.5	20.5	25.5	30.5	35.5	40.5	45.5	50.5	55.5	60.5	65.5	70.5	75.5	80.5	85.5
Percentages of polymers	P1	0.070	0.055	0.032	0.014	0.011	0.011	0.016	0.020	0.033	0.048	0.064	0.084	0.102	0.126	0.150	0.165
	Ref-1	0.153	0.124	0.088	0.055	0.038	0.026	0.023	0.024	0.025	0.034	0.042	0.051	0.065	0.073	0.099	0.083
	Ref-2	0.178	0.144	0.123	0.109	0.097	0.082	0.064	0.047	0.034	0.025	0.019	0.016	0.012	0.013	0.026	0.010

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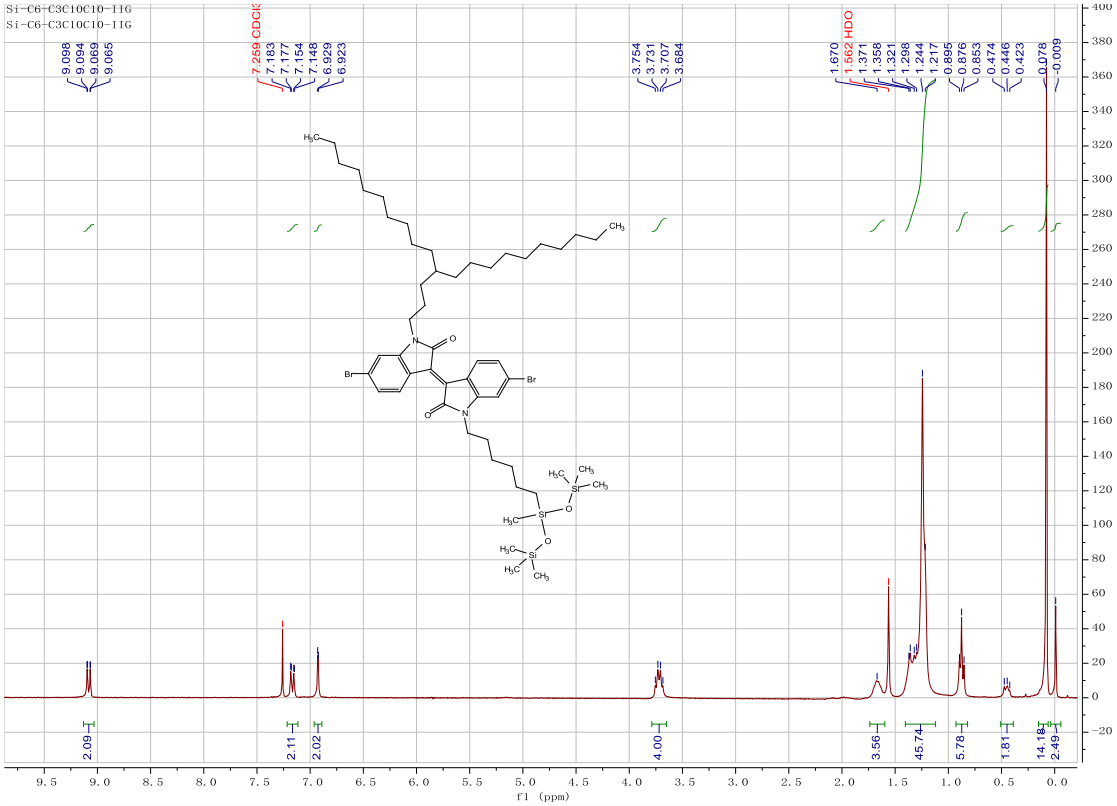
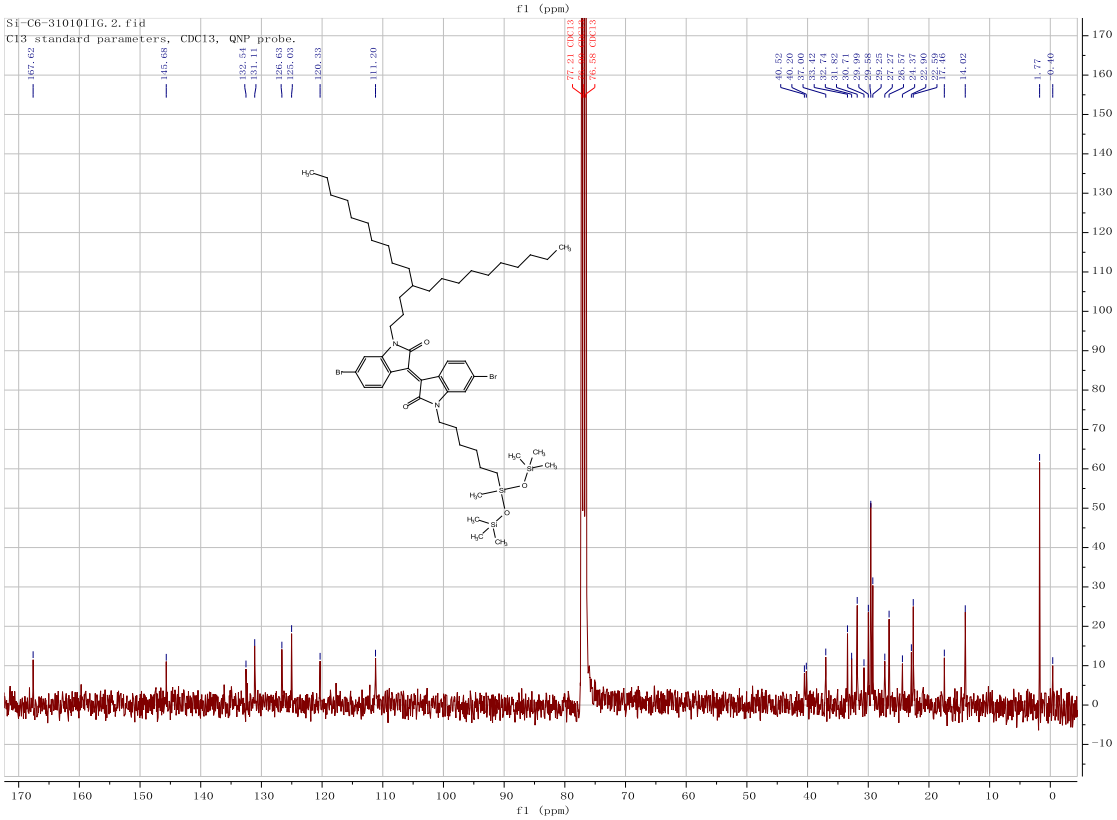
Supporting figures





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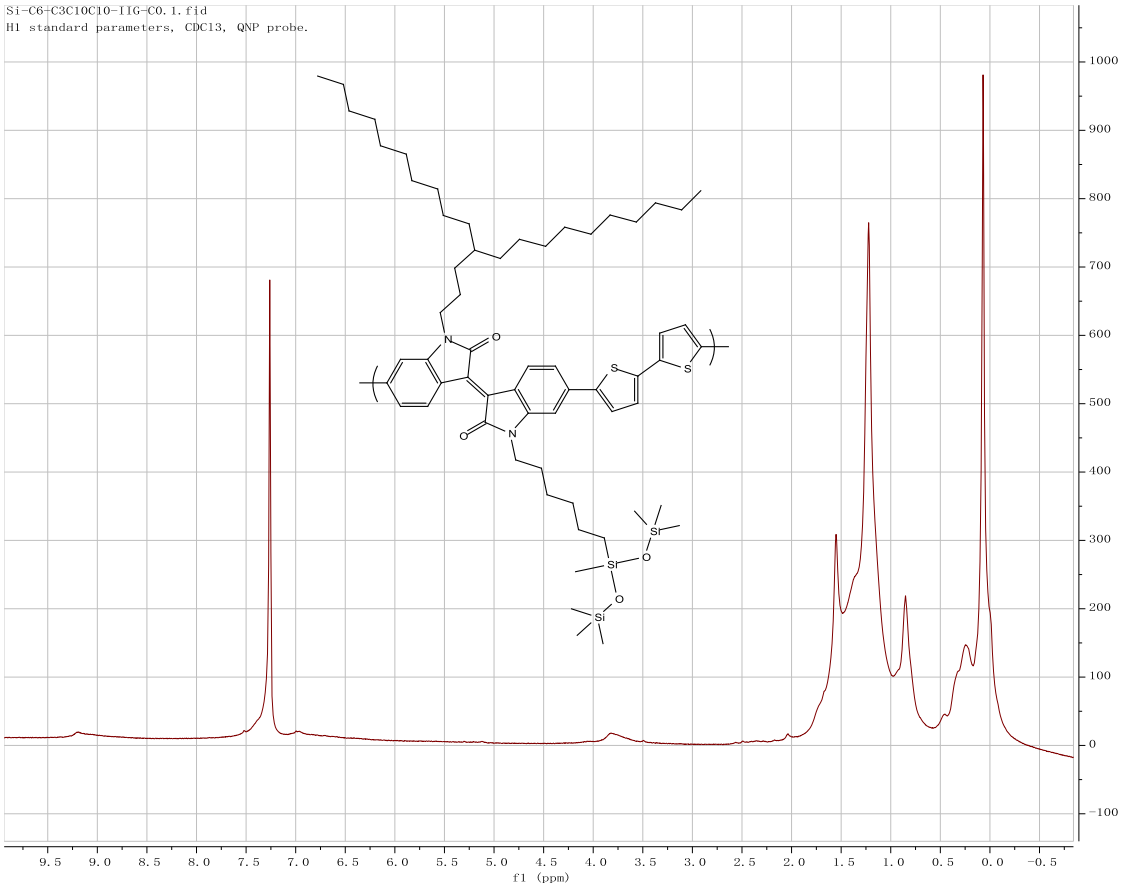

Figure S1. NMR spectra of the monomer and P1.

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Workbook: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\TCB(PLgel Olexis 200ul)(20160712)New.plw

Sample Details

Sample Name: Si-C3-IIG

Acquired: 5/11/2017 7:13:48 PM — By Analyst: Administrator

Batch Name: Sample101(XGB)

Filename: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\sample101(xgb)-0001.cgrm

Concentration: 0.10 mg/ml — K of Sample: 12.1000

Injection Volume: 200.0 ul — Alpha of Sample: 0.7070

LIMS ID: — Bottle ID:

Analysis Using Method: PS(20170307)XP

Comments: PS(20170307)XP

Results File: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\sample101(xgb)-0001.rst

Calibration Used: 3/9/2017 9:23:30 AM

Calibration Type: Narrow Standard — Curve Fit Used: 5

Calibration Curve: y = 21.836347 - 2.999090x^1 + 0.313850x^2 - 0.019755x^3 + 0.000633x^4 - 0.000008x^5

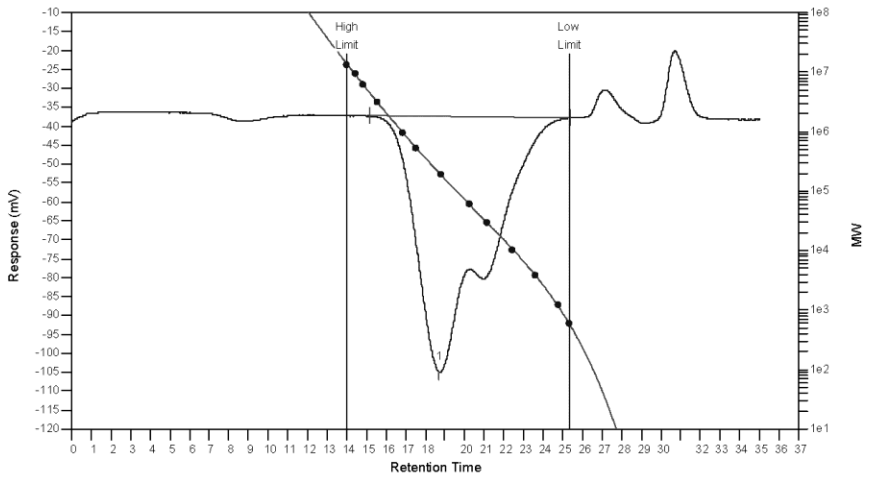
High Limit MW RT: 14.02 mins — Low Limit MW RT: 25.32 mins

High Limit MW: 13572985 — Low Limit MW: 595

K: 12.1000 — FRM Name:

Alpha: 0.7070 — Flow Marker RT: 0.00 mins

FRCF: 1.0000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	198941	35608	183374	493989	948123	152843	5.1498

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Figure S2. GPC curve and result of P1. The data was collected with trichlorobenzene as solvent at 150 °C.

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Sample Details

Sample Name: Si-IIG

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Batch Name: Sample101(XGB)

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Concentration: 0.10 mg/ml — K of Sample: 12.1000

Injection Volume: 200.0 ul — Alpha of Sample: 0.7070

LIMS ID: — Bottle ID:

Analysis Using Method: PS(20170307)XP

Comments: PS(20170307)XP

Results File: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\sample101(xgb)-0002.rst

Calibration Used: 3/9/2017 9:23:30 AM

Calibration Type: Narrow Standard — Curve Fit Used: 5

Calibration Curve: y = 21.836347 - 2.999090x^1 + 0.313850x^2 - 0.019755x^3 + 0.000633x^4 - 0.000008x^5

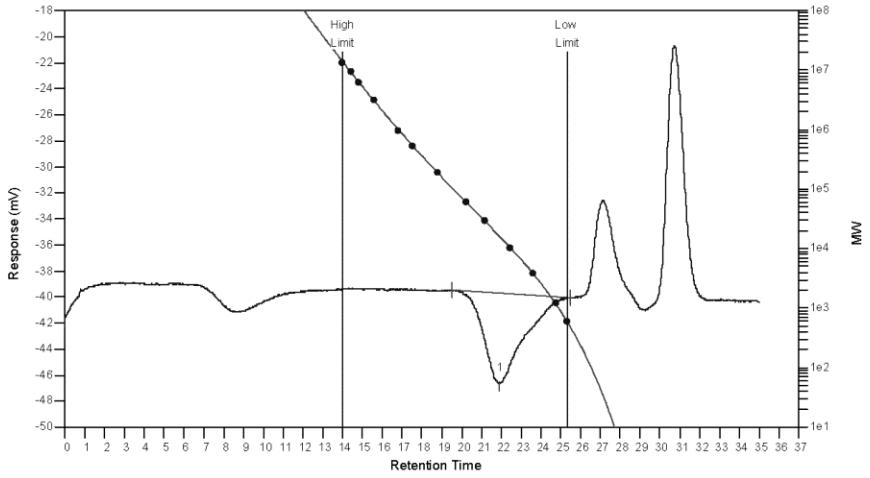
High Limit MW RT: 14.02 mins — Low Limit MW RT: 25.32 mins

High Limit MW: 13572985 — Low Limit MW: 595

K: 12.1000 — FRM Name:

Alpha: 0.7070 — Flow Marker RT: 0.00 mins

FRCF: 1.0000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16479	8462	15690	23107	30674	14672	1.85417

Figure S3. GPC curve and result of Ref-1. The data was collected with trichlorobenzene as solvent at 150 °C.

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Workbook: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\TCB(PLgel Olexis 200ul)(20160712)New.plw

Sample Details

Sample Name: C3-IIG

Acquired: 5/11/2017 8:37:22 PM — By Analyst: Administrator

Batch Name: Sample101(XGB)

Filename: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\sample101(xgb)-0003.cgrm

Concentration: 0.10 mg/ml — K of Sample: 12.1000

Injection Volume: 200.0 ul — Alpha of Sample: 0.7070

LIMS ID: — Bottle ID:

Analysis Using Method: PS(20170307)XP

Comments: PS(20170307)XP

Results File: C:\Cirrus Workbooks\TCB(PLgel Olexis 200ul)(20160712)New\sample101(xgb)-0003.rst

Calibration Used: 3/9/2017 9:23:30 AM

Calibration Type: Narrow Standard — Curve Fit Used: 5

Calibration Curve: y = 21.836347 - 2.999090x^1 + 0.313850x^2 - 0.019755x^3 + 0.000633x^4 - 0.000008x^5

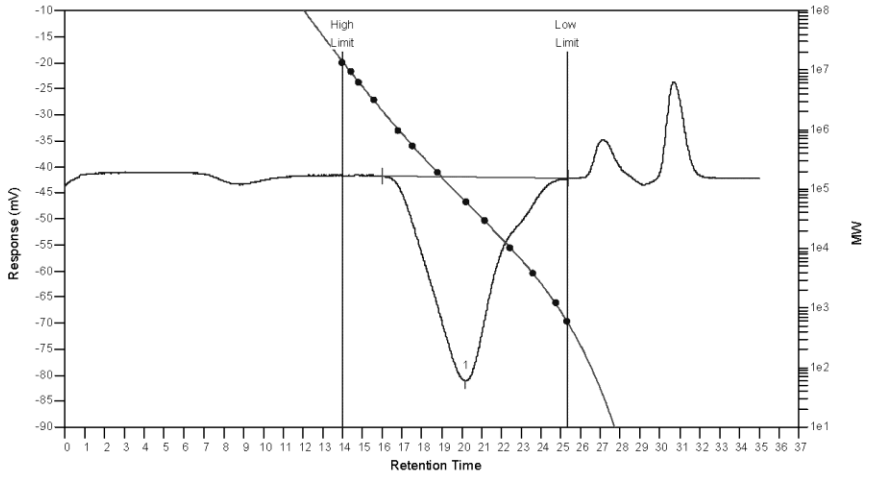
High Limit MW RT: 14.02 mins — Low Limit MW RT: 25.32 mins

High Limit MW: 13572985 — Low Limit MW: 595

K: 12.1000 — FRM Name:

Alpha: 0.7070 — Flow Marker RT: 0.00 mins

FRCF: 1.0000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62113	28815	115400	307560	555006	97361	4.00486

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Figure S4. GPC curve and result of Ref-2. The data was collected with trichlorobenzene as solvent at 150 °C.

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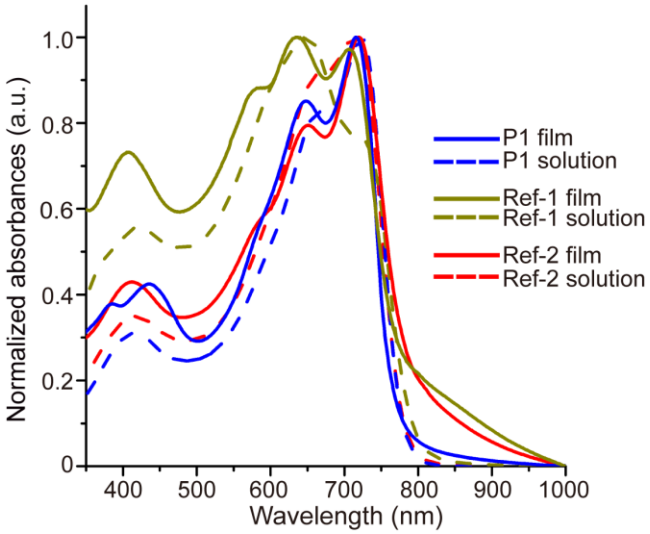

Figure S5. Normalized absorption spectra in dilute solution (chloroform) and thin films (cast from chloroform) of the three polymer thin films.

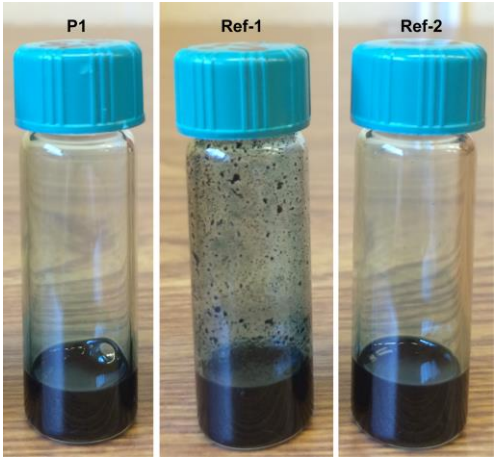

Figure S6. Solutions of the three polymers in chloroform.

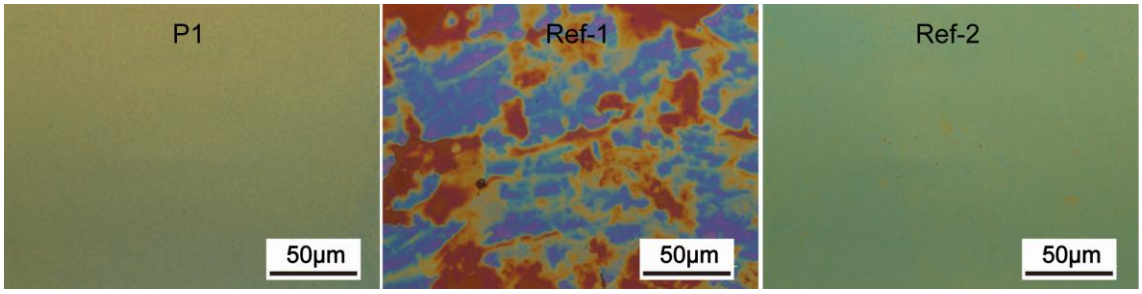

Figure S7. Optical microscopy images of the three polymer thin films.

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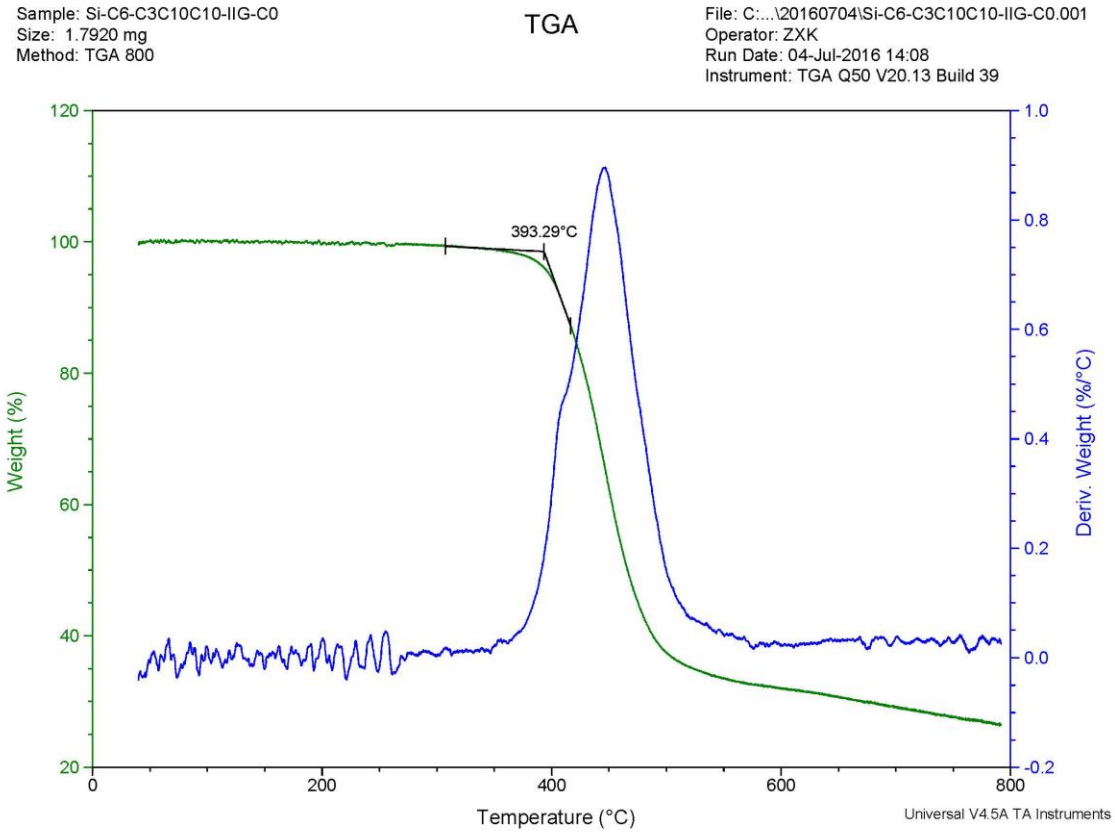

Figure S8. TGA thermogram for P1.

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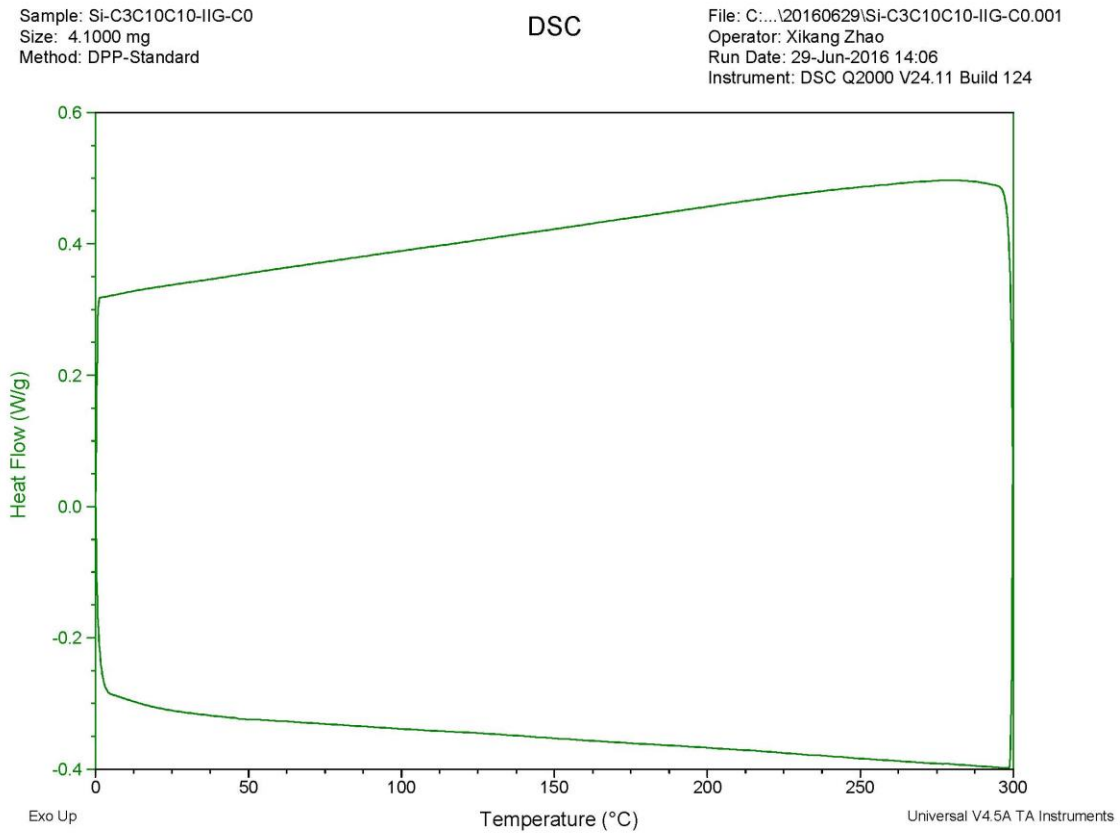

Figure S9. DSC thermogram for P1.

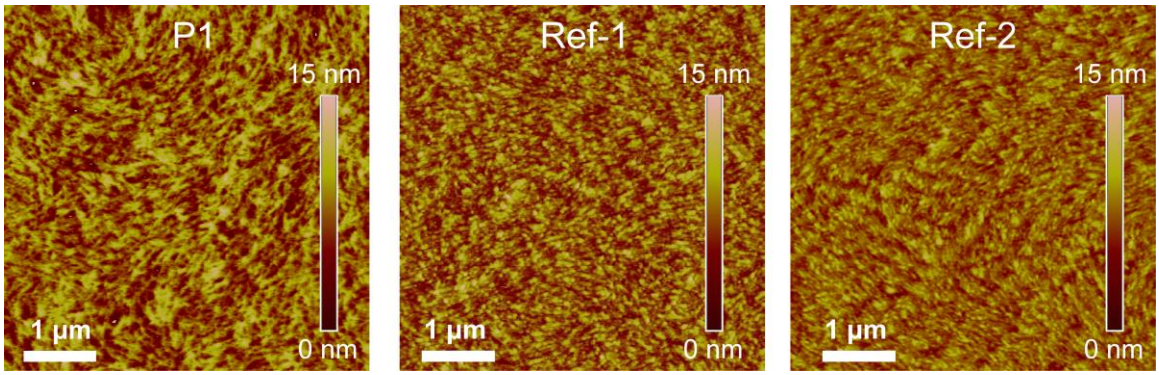

Figure S10. Atomic force microscopy images of the polymer films annealed at 160 °C.

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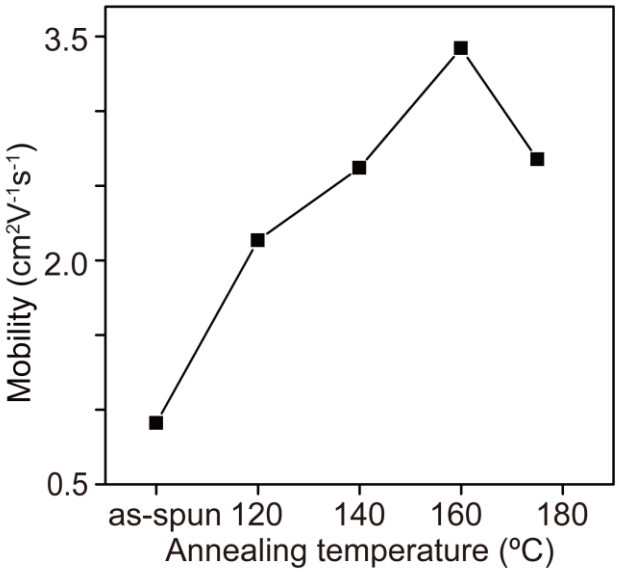

Figure S11. Effect of annealing temperature on field-effect mobility in P1.

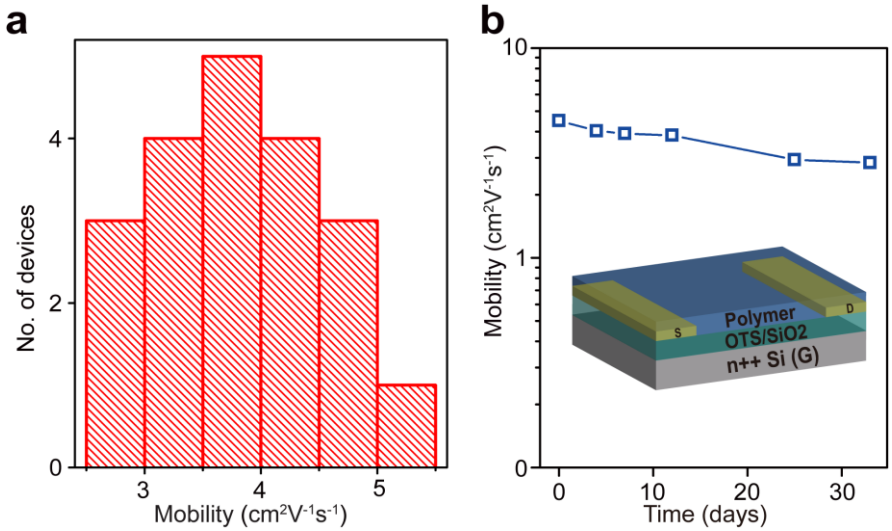

Figure S12. (a) Histogram of the mobility of 20 FETs. (b) Mobility change of field-effect transistors in ambient air as a function of time (day). Inset: A schematic diagram of the FET configuration, where S is the source, D the drain and G the gate.

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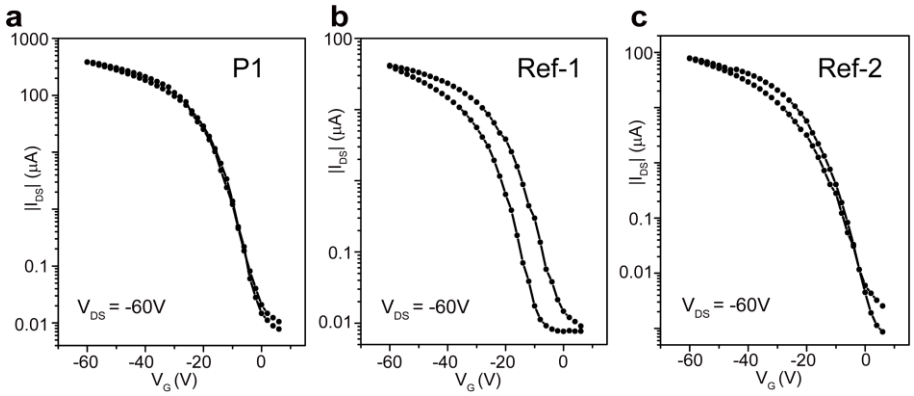

Figure S13. The dual sweep scan of the transfer curves of FETs based on the three polymers.

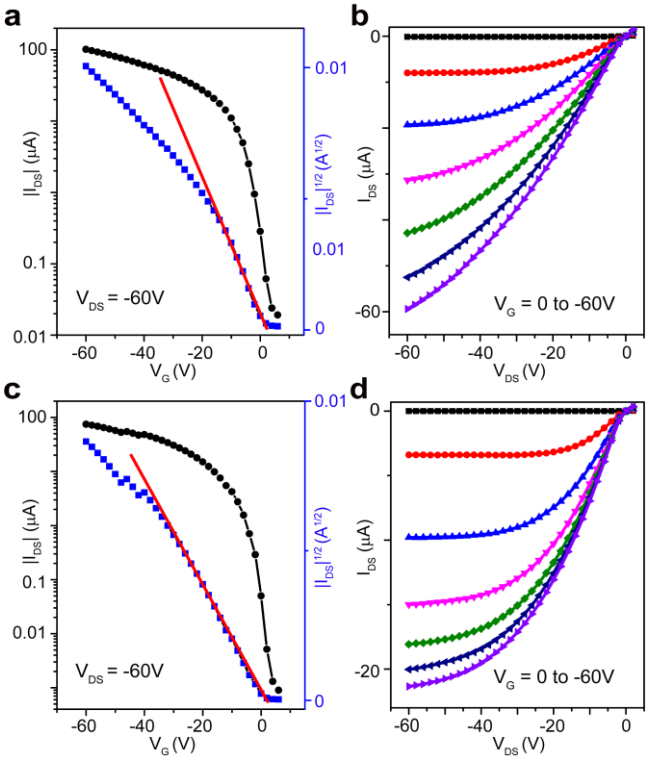

Figure S14. Typical transfers and output characteristics of FETs based on Ref-1 (a, b) and Ref-2 (c, d).

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References

1. Mei, J.; Kim, D. H.; Ayzner, A. L.; Toney, M. F.; Bao, Z., Siloxane-Terminated Solubilizing Side Chains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors. *J. Am. Chem. Soc.* **2011,** *133*, 20130-20133.
2. Lei, T.; Dou, J.-H.; Pei, J., Influence of Alkyl Chain Branching Positions on the Hole Mobilities of Polymer Thin-Film Transistors. *Adv. Mater.* **2012,** *24*, 6457-6461.

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