

Supporting Information

N-Type Complementary Semiconducting Polymer Blends

William W. McNutt[†], Aristide Gumyusenge[†], Luke A. Galuska[§], Zhiyuan Qian[§], Jiazhi He[†], Xiaodan Gu[§], Jianguo Mei^{†‡}*

[†]Department of Chemistry and [‡]Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, United States

[§]School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, MS 39406, USA

Corresponding Author

*Email: jgmei@purdue.edu (J.M.).

Materials and Synthesis

All reagents and starting materials were purchased from Sigma-Aldrich and SunaTech and used without further purification unless otherwise noted.

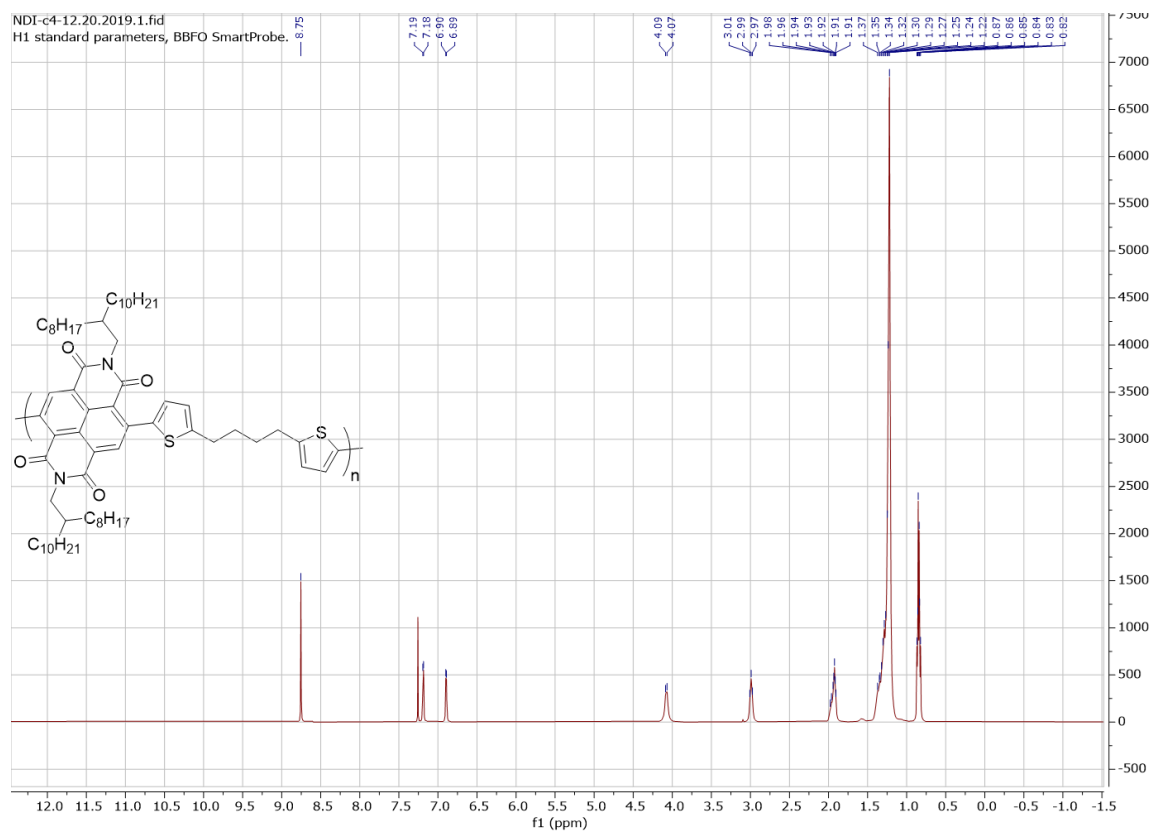
Tin-spacer monomers were synthesized as previously reported.¹

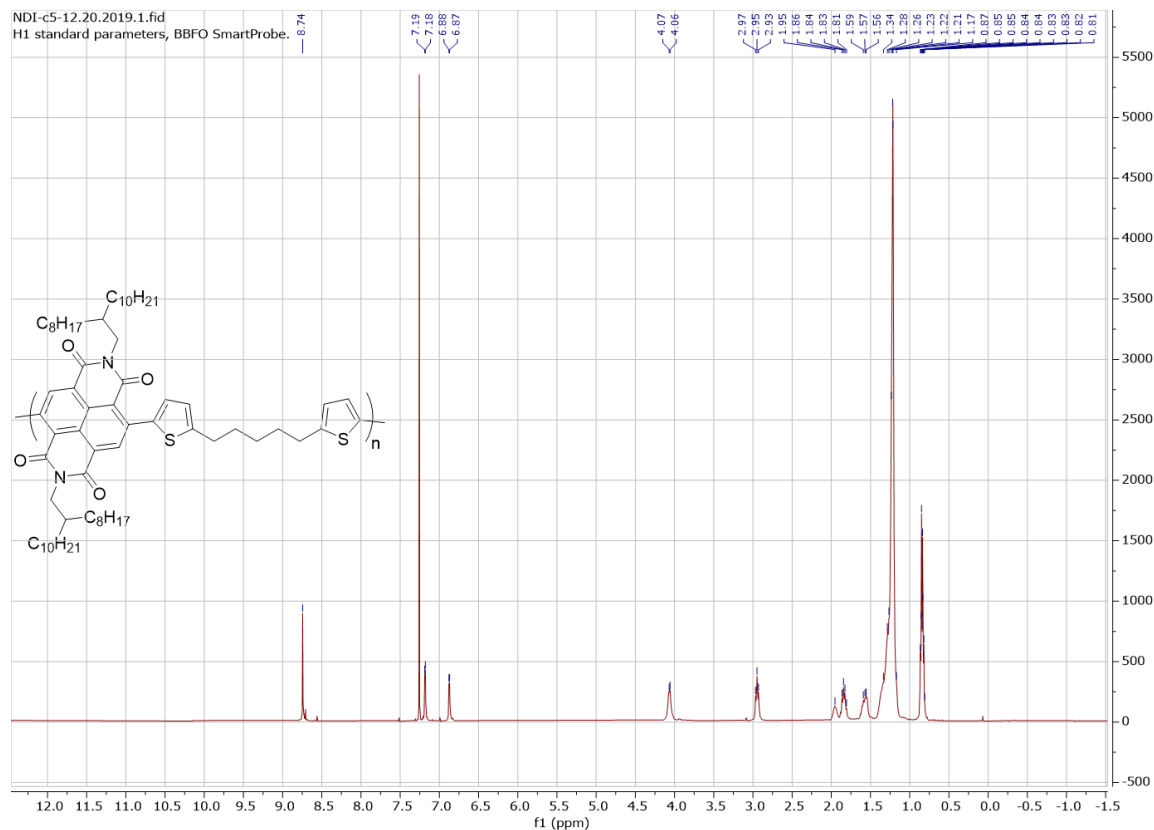
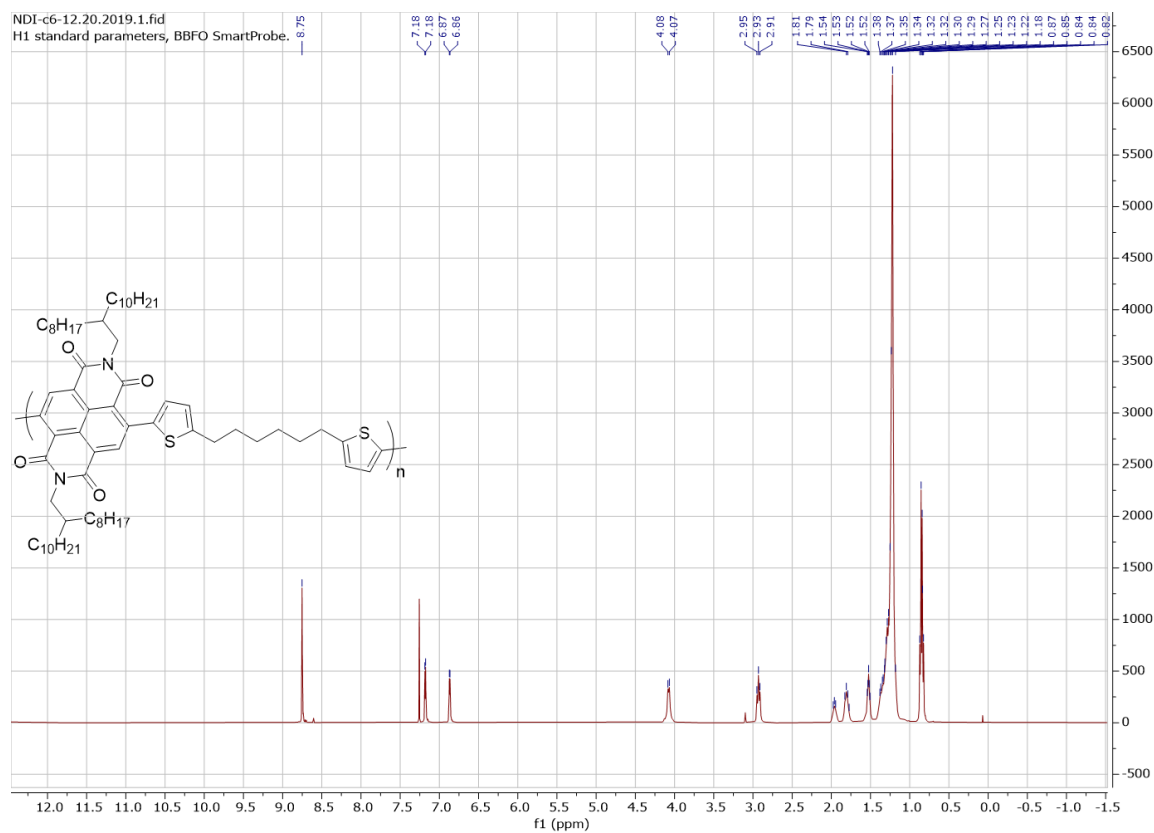
General Method for NDI-C_m Polymerization

4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (0.17 mmol) and ditin monomer (1 eq) were added into a 50 mL Schlenk tube. Upon stirring, the monomers were dissolved in 10 mL of anhydrous toluene and degassed with nitrogen for 15 min. Pd₂(dba)₃ (4.0 mol %) and tris(*o*-tolyl) phosphine (8.0 mol %) were added under nitrogen. The reaction was heated to 100°C and run for 24 hours. After the polymerization was complete, the mixture was taken up and precipitated into methanol. The solids were collected by a high-quality glass thimble, which was purified by Soxhlet extraction with acetone, hexane, and chloroform. The chloroform or hexane fraction was precipitated into methanol. The collected polymer was dried at 60 °C under vacuum with the yields in the range of 61%–78%.

P(NDI2OD-T2) Polymerization

4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (0.17 mmol) and bistin-bithiophene (1 eq) were added into a 50 mL Schlenk tube. Upon stirring, the monomers were dissolved in 10 mL of anhydrous toluene and degassed with nitrogen for 15 min. Pd₂(dba)₃ (2.0 mol %) and tris(*o*-tolyl) phosphine (16 mol %) were added under nitrogen. The reaction was heated to 100°C and run for 1 hours. After the polymerization was complete, the mixture was taken up and precipitated into methanol. The solids were collected by a high-quality glass thimble, which was purified by Soxhlet extraction with acetone, hexane, and chloroform. The chloroform fraction was precipitated into methanol. The collected polymer was dried at 60 °C under vacuum with a yield of 90%.





S-5

Experimental Details

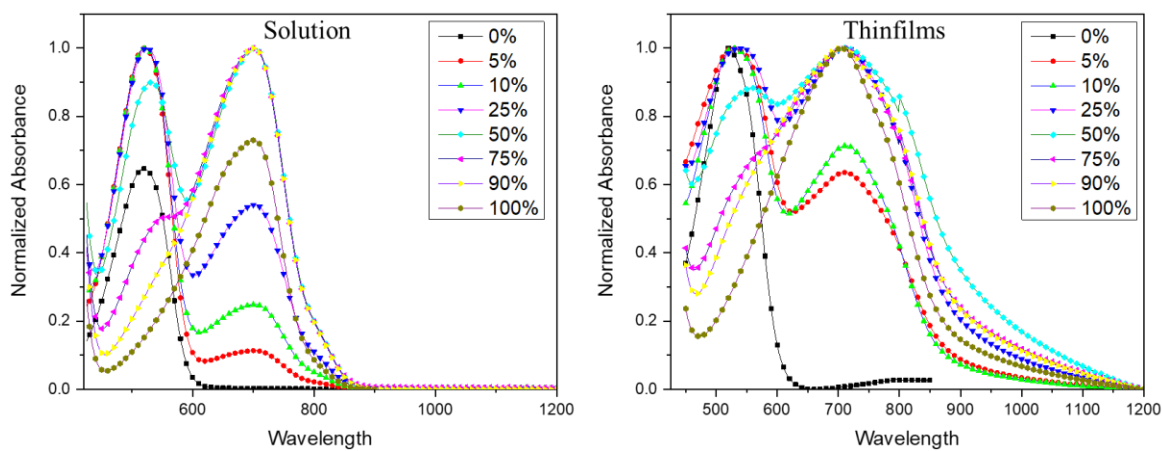


Figure S2 – UV-vis Spectra of NDI-C3 *c*-SPBs (0-100% P(NDI2OD-T2)) in chloroform solution and spin-cast thinfilms.

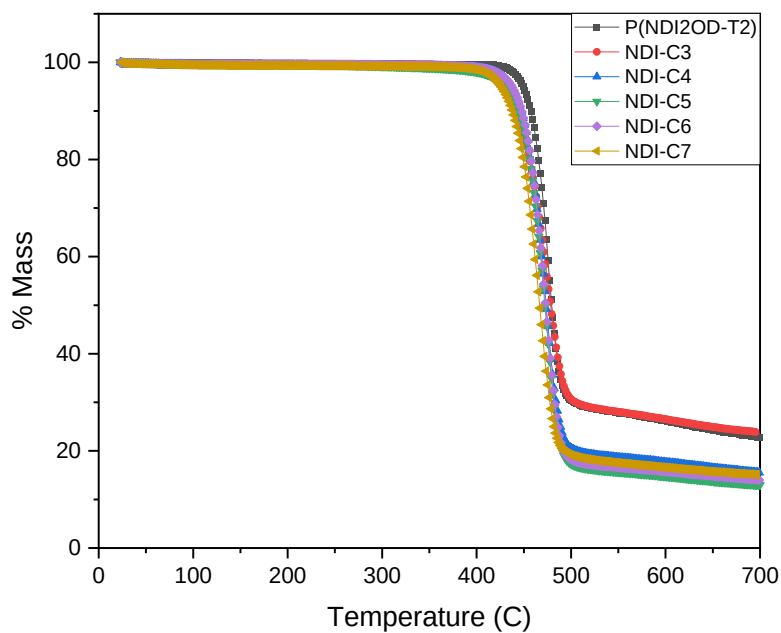
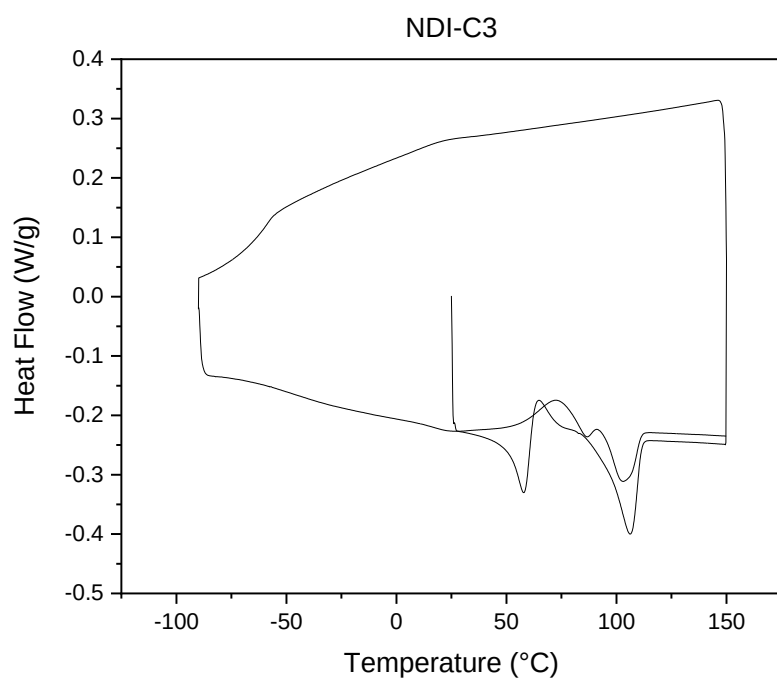
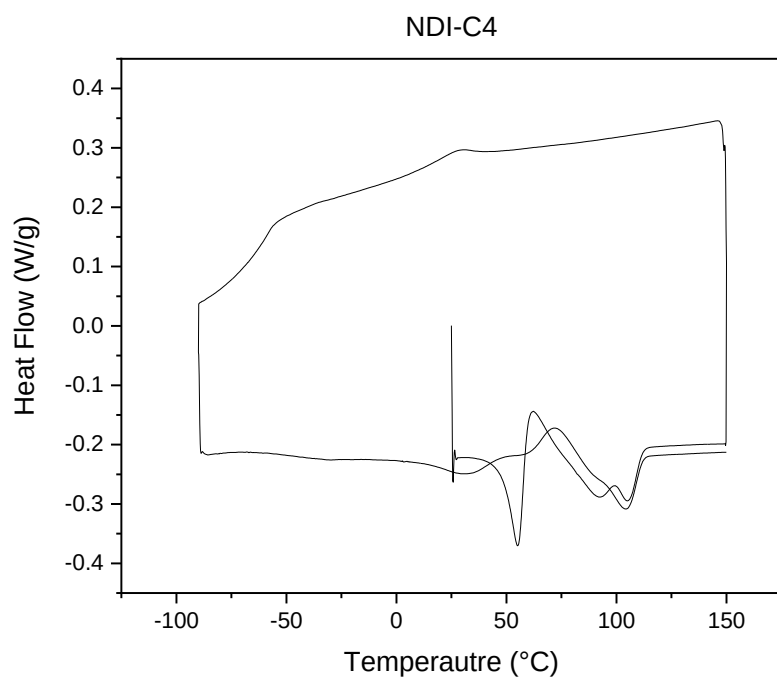
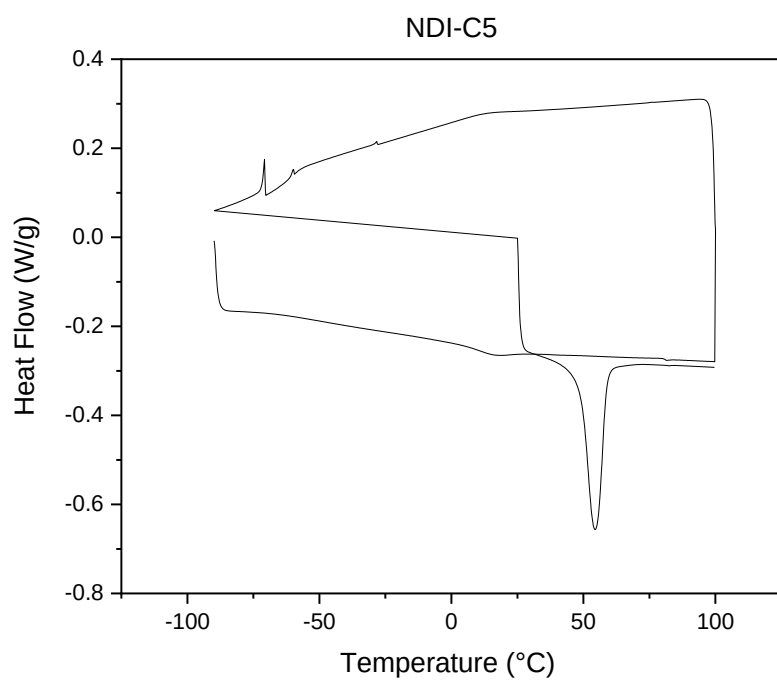
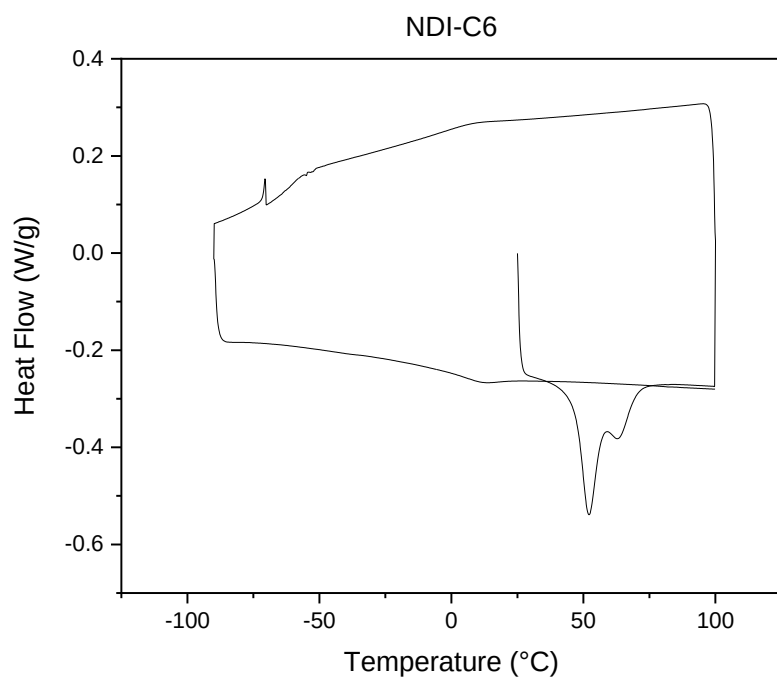


Figure S3 – TGA thermograms of NDI-C_m and P(NDI2OD-T2) polymers





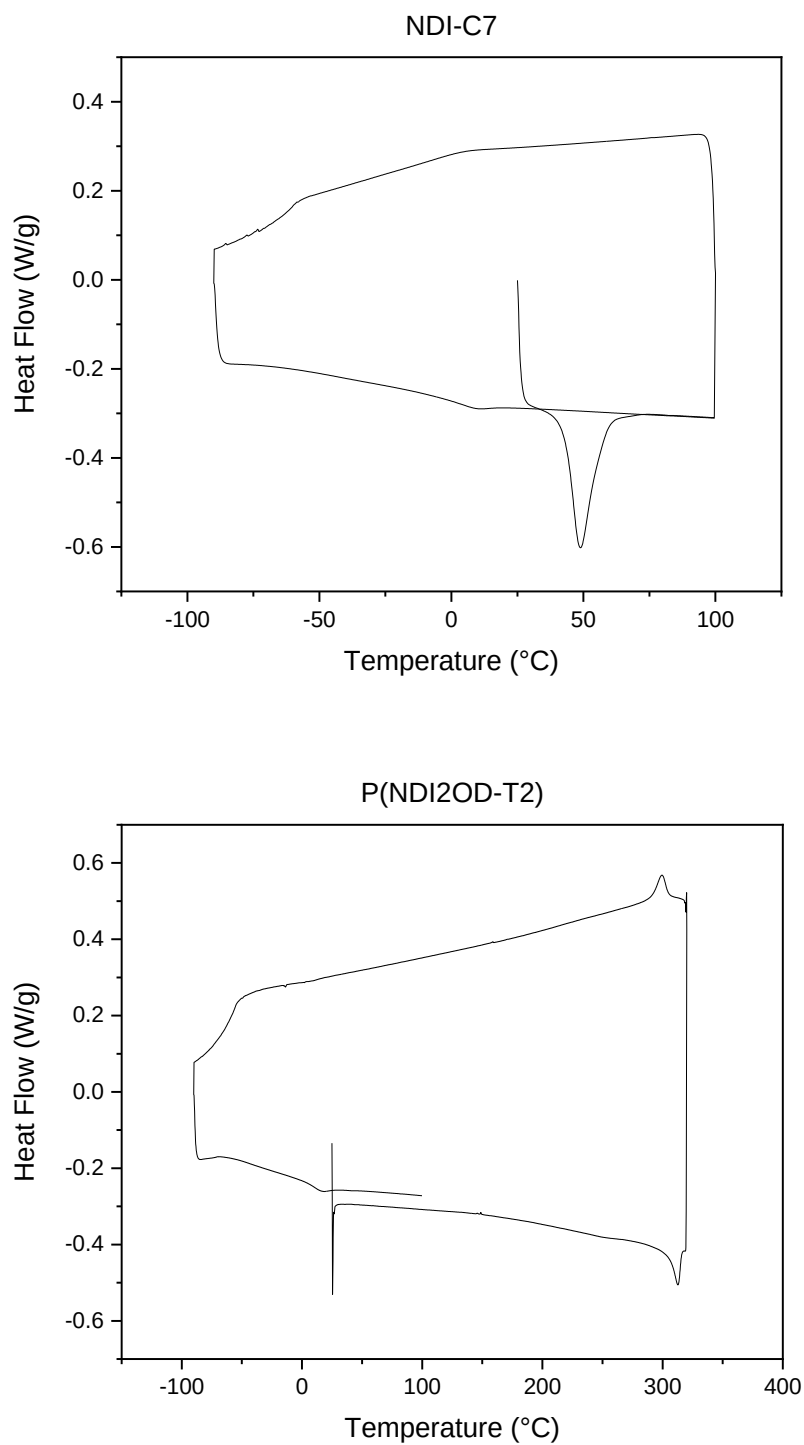


Figure S4 – DSC thermograms for NDI- C_m and P(NDI2OD-T2). Polymers recorded at 10°K/min.

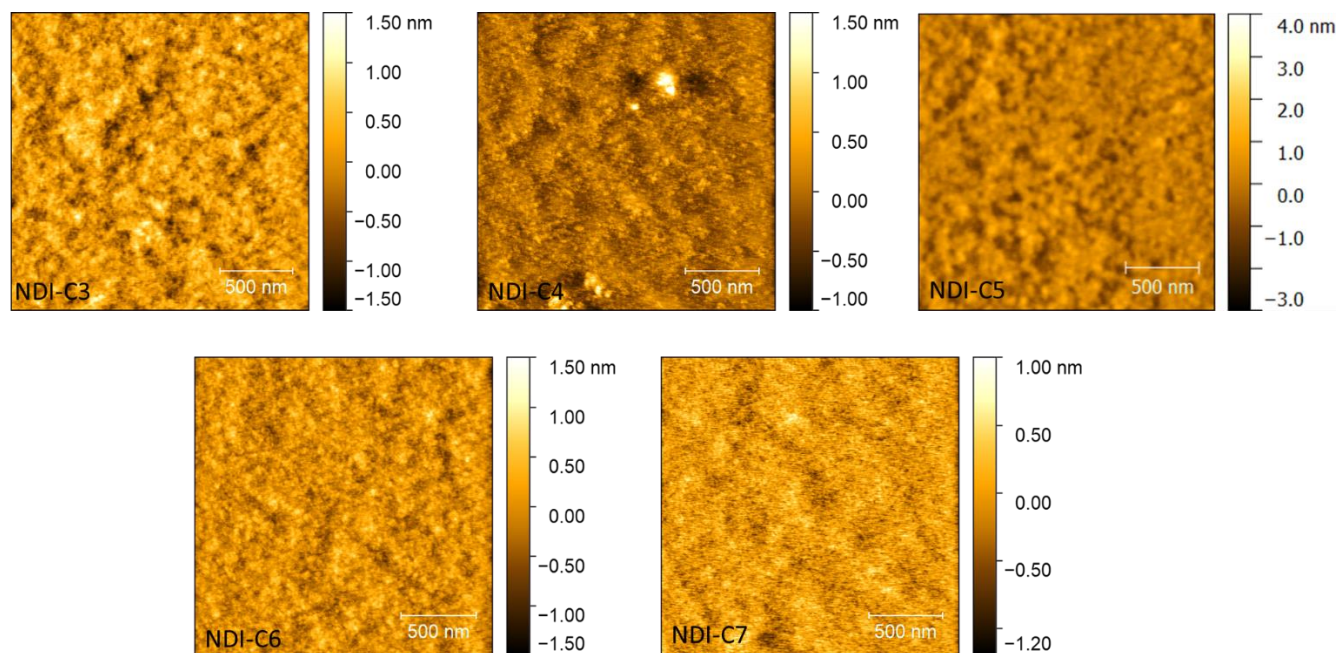


Figure S5 – AFM images of pure NDI-C_m Polymers

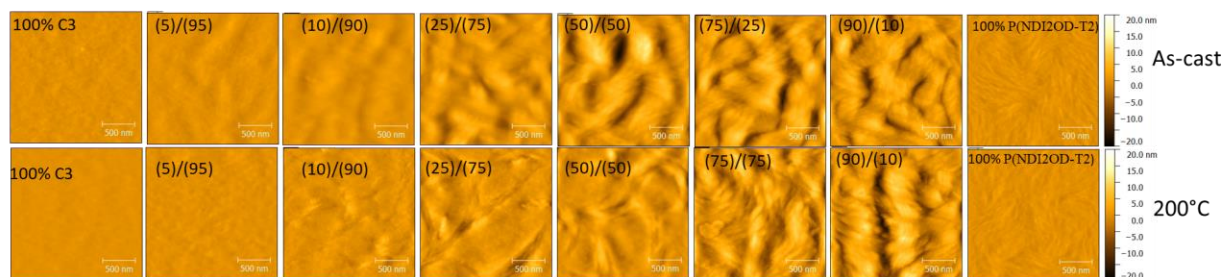


Figure S6 – Height images demonstrating surface morphology evolution with blending ratios for NDI-C3 blends, top row as cast films, bottom row after annealing at 200°C.

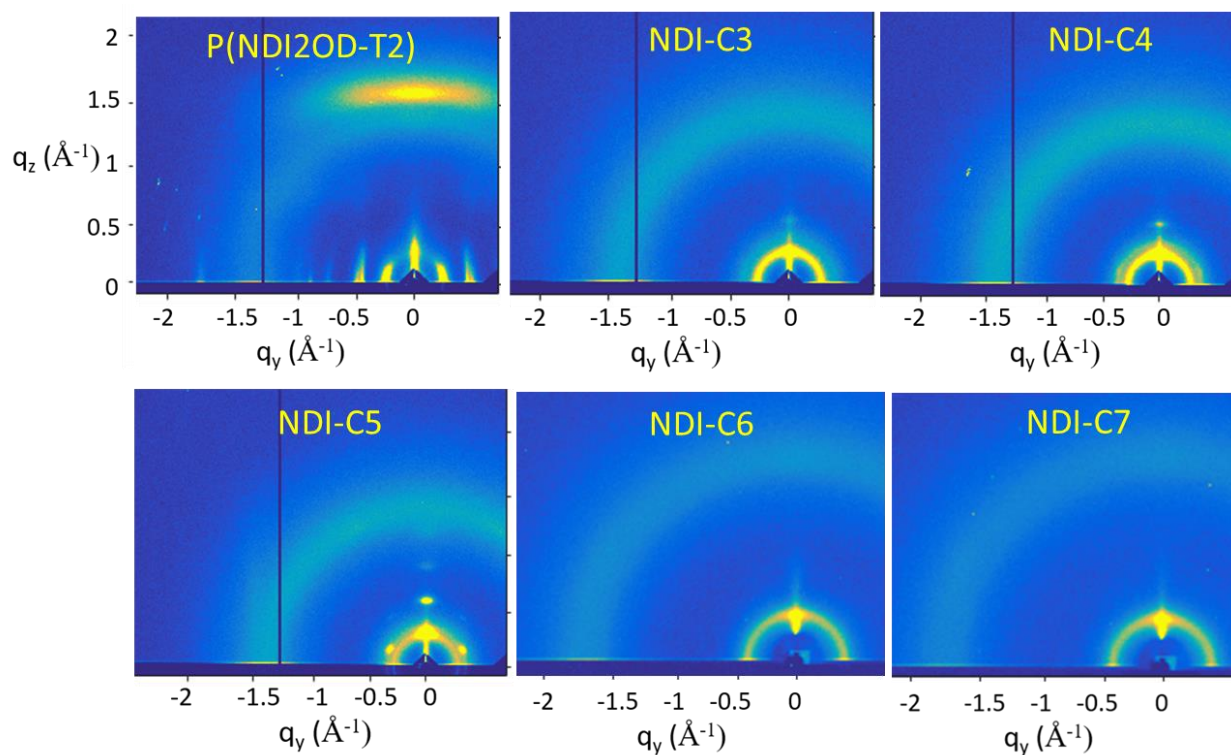


Figure S7 – GIXRD of pure NDI-C_m polymers

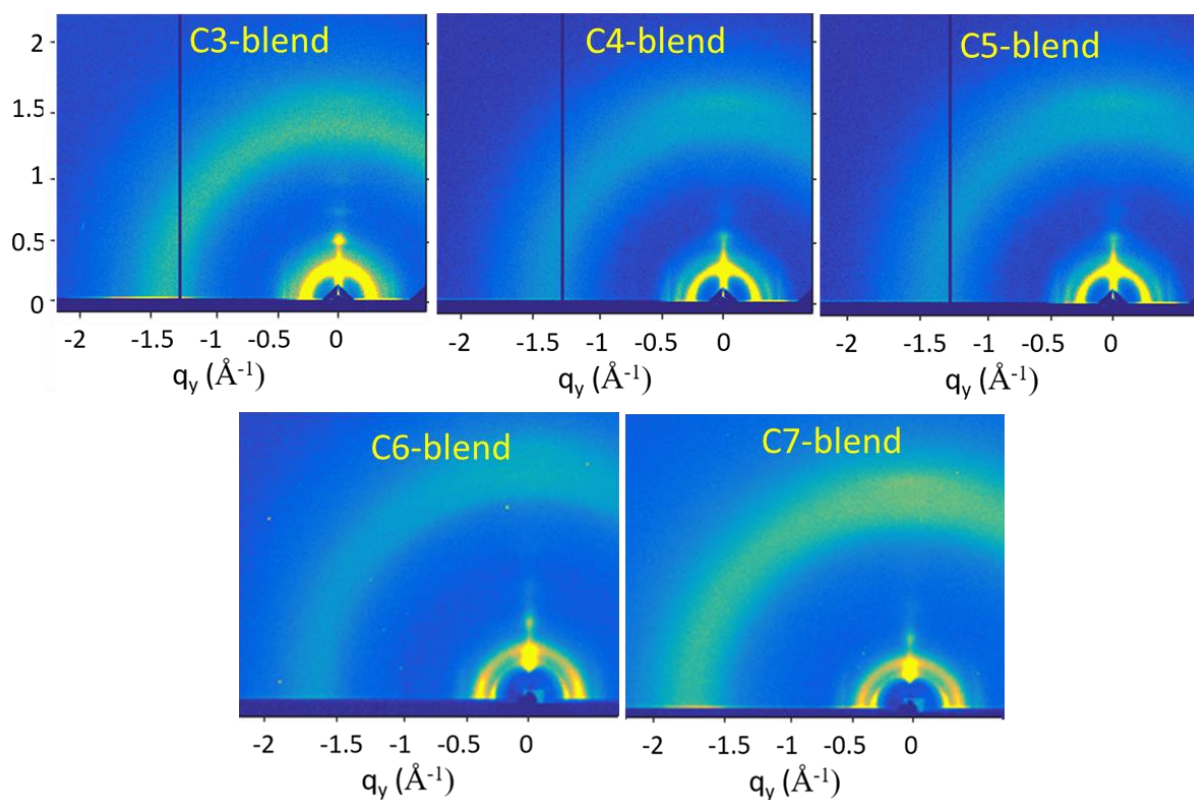


Figure S8 – GIXRD images of NDI-C_m 5% *c*-SPBs

Table S1 – Crystallography Parameters for Melt-Processed Thinfilms of Pure NDI-Cm, 5% *c*-SPBs with P(NDI2OD-T2) and Pure P(NDI2OD-T2)

Material		Out-of-plane π - π stacking		Out-of-plane lamellar	
		Spacing (Å)	FWHM(Å ⁻¹)	Spacing (Å)	FWHM(Å ⁻¹)
NDI-C3	Pure	--	--	21.80	0.043
	5% <i>c</i> -SPB	--	--	22.42	0.059
NDI-C4	Pure	--	--	21.58	0.041
	5% <i>c</i> -SPB	--	0.38	22.20	0.050
NDI-C5	Pure	--	--	20.72	0.039
	5% <i>c</i> -SPB	3.97	0.37	22.23	0.049
NDI-C6	Pure	--	--	21.67	0.124
	5% <i>c</i> -SPB	3.97	0.36	24.07	0.068
NDI-C7	Pure	--	--	21.76	0.128
	5% <i>c</i> -SPB	3.96	0.38	24.04	0.063
P(NDI2OD-T2)	Pure	3.71	0.098	23.52	0.103

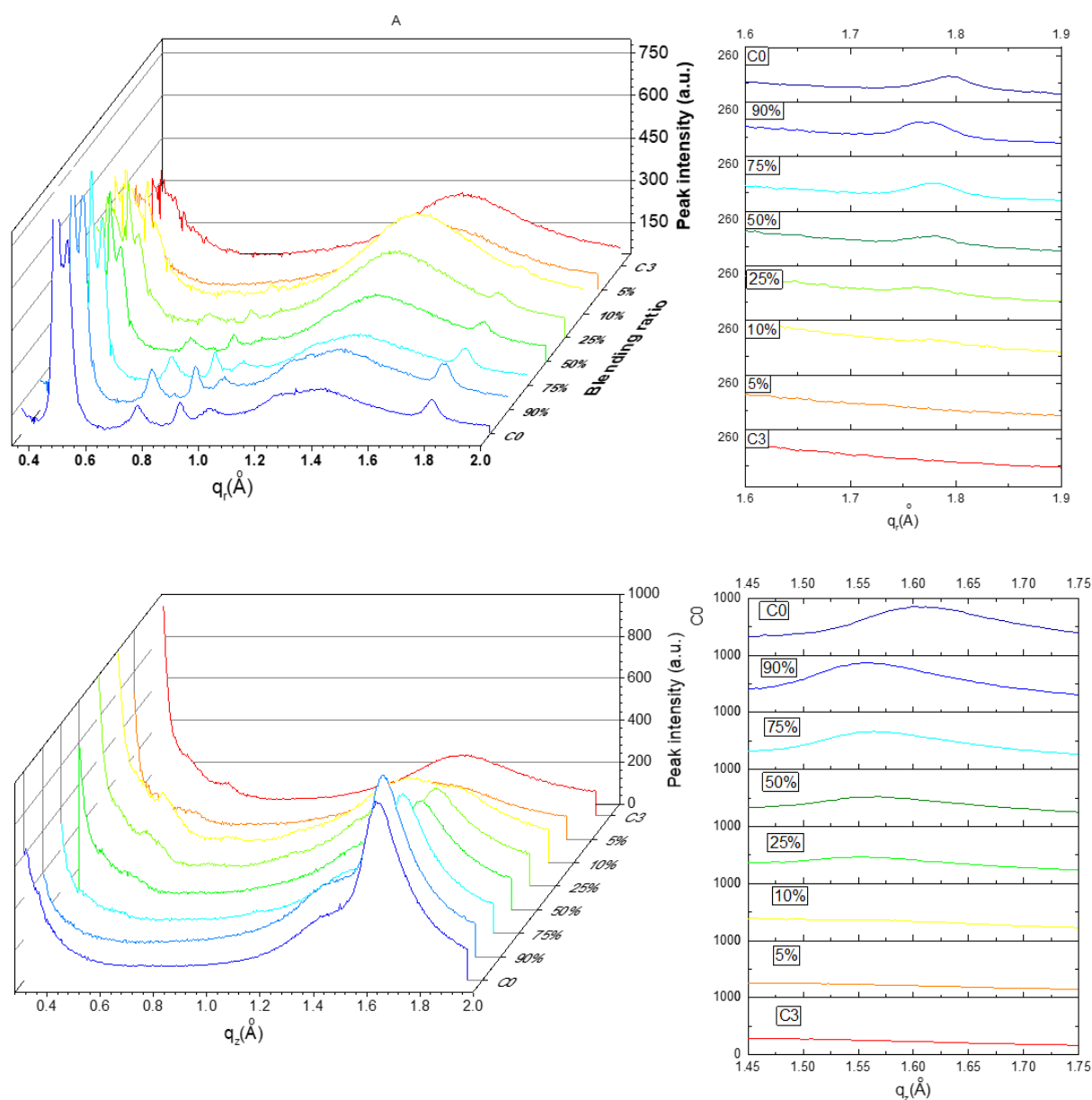


Figure S9 - 1D linecuts of a) the in-plane, b) out-of-plane packing evolution as a function of blending ratios, respectively. Appended are the blown-up overlays of π - π stacking peak positions and intensities for both packing directions.

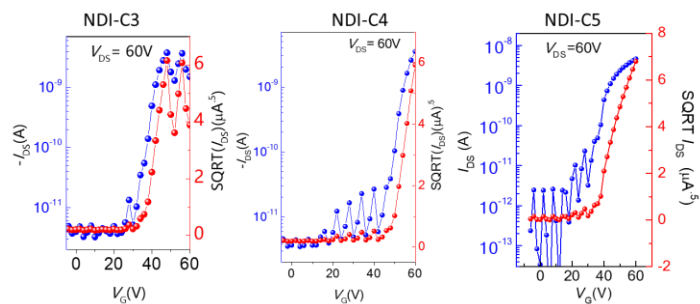


Figure S10 – Transistor Curves of NDI-Cm polymers, NDI-C6/7 were omitted due to no response.

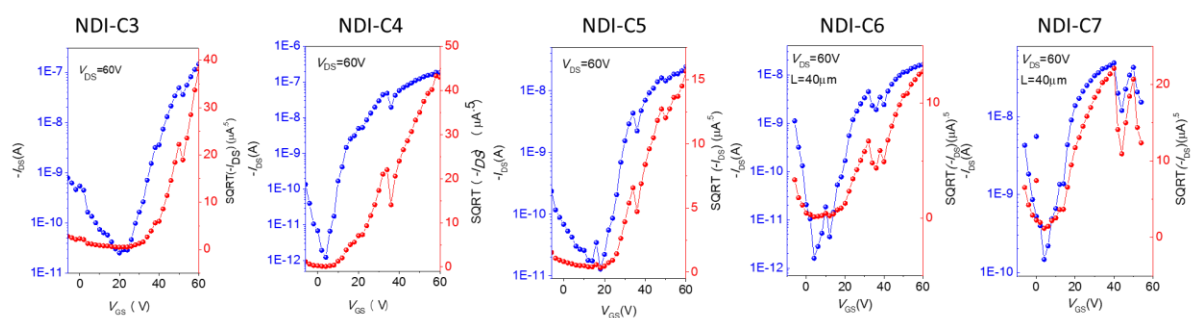


Figure S11 – Transistor curves of NDI-Cm 5% *c*-SPBs

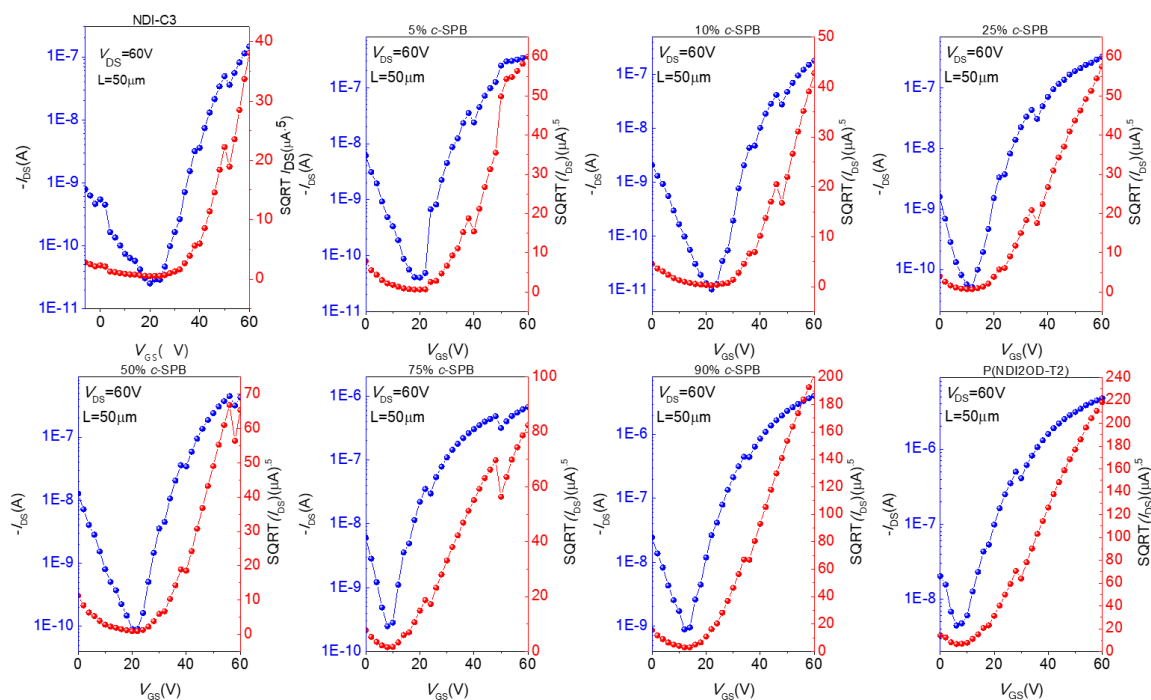


Figure S12 – Transistor curves of NDI-C3 *c*-SPBs from 0-100% P(NDI2OD-T2)

Table S2 – Summarized Transistor Data from NDI-C5 Blending Efficiency

Polymer	Avg. $m_e(\text{cm}^2/\text{Vs})$	Highest $m_e(\text{cm}^2/\text{Vs})$	$I_{\text{ON/OF}}$	$V_{\text{th}}(\text{V})$
NDI-C5	1.10E-5	1.30E-5	2.34E+3	+22.1
5%	1.16E-3	2.14E-3	6.10E+2	+21.7
10%	2.01E-3	3.1E-3	1.74E+3	+22.3
20%	3.02E-3	5.23E-3	1.00E+4	+24.0
30%	3.50E-3	5.4E-3	1.46E+4	+19.4
50%	0.98E-2	3.3E-2	6.10E+3	+21.6
70%	1.50E-2	2.2E-2	4.40E+3	+18.1
90%	3.4E-2	4.5E-2	3.4E+2	+24.2
P(NDI2OD-T2)	0.098	0.178	2.84E+2	+24.0

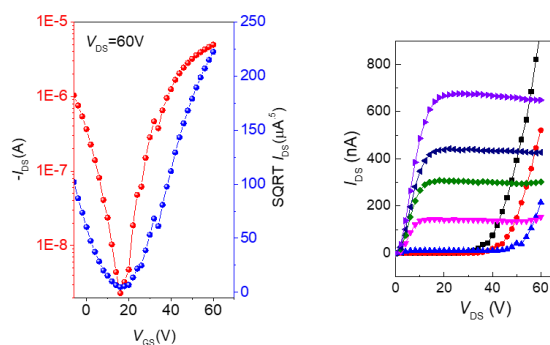


Figure S13 – P(NDI2OD-T2) Transistor and output curves

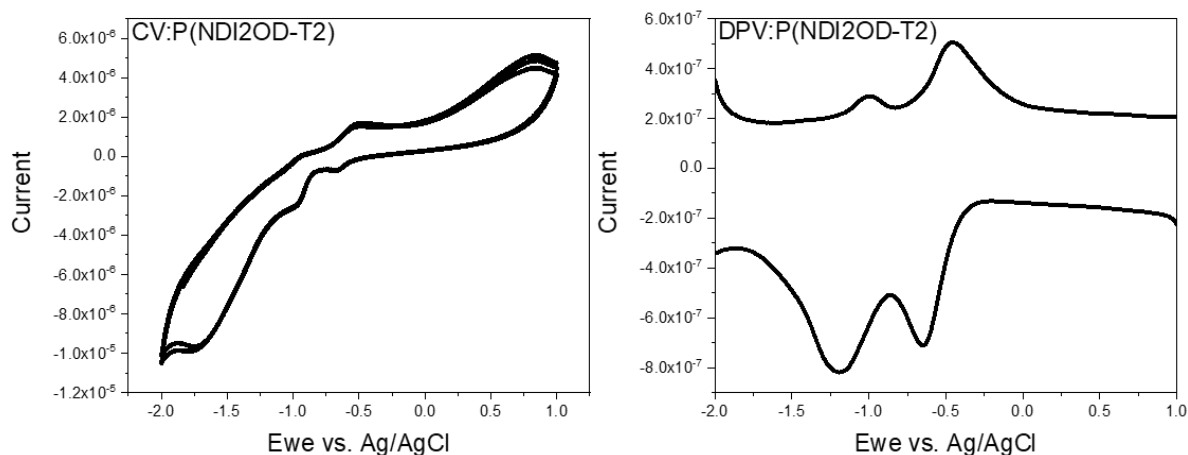


Figure S14 – P(NDI2OD-T2) CV, and DPV curves

References

1. Zhao, X.; Zhao, Y.; Ge, Q.; Butrouna, K.; Diao, Y.; Graham, K. R.; Mei, J., Complementary Semiconducting Polymer Blends: The Influence of Conjugation-Break Spacer Length in Matrix Polymers. *Macromolecules* **2016**, 49 (7), 2601-2608.