

Supporting Information:

Isoindigo-based Binary Polymer Blends for Solution-Processing of Semiconducting Nanofiber Networks

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Materials Synthesis and Characterization

P1, P2, P3, and C3 were synthesized as previously reported¹⁻⁶ and characterized by NMR, UV-Vis absorption, and GPC. The NMR spectrum and the GPC analysis results of the newly-reported C3 are shown in Figure S1 and S2. Polystyrene (Mw 192,000) was purchased from Sigma-Aldrich and used as received. A 10 mg/mL solution was obtained by stirring overnight in chloroform. Solutions of all the three polymers were obtained in chloroform (10 mg/mL) and stirred overnight. The corresponding blends were obtained by allowing the respectively vol% to mix together for at least 1 hour to ensure mixing. Thin films used for morphology studies, GIXRD studies, as well UV-Vis measurements were obtained by spin coating (2000 rpm, 1 min) the solutions on cleaned substrates and then annealed to 140°C inside the N₂ glovebox.

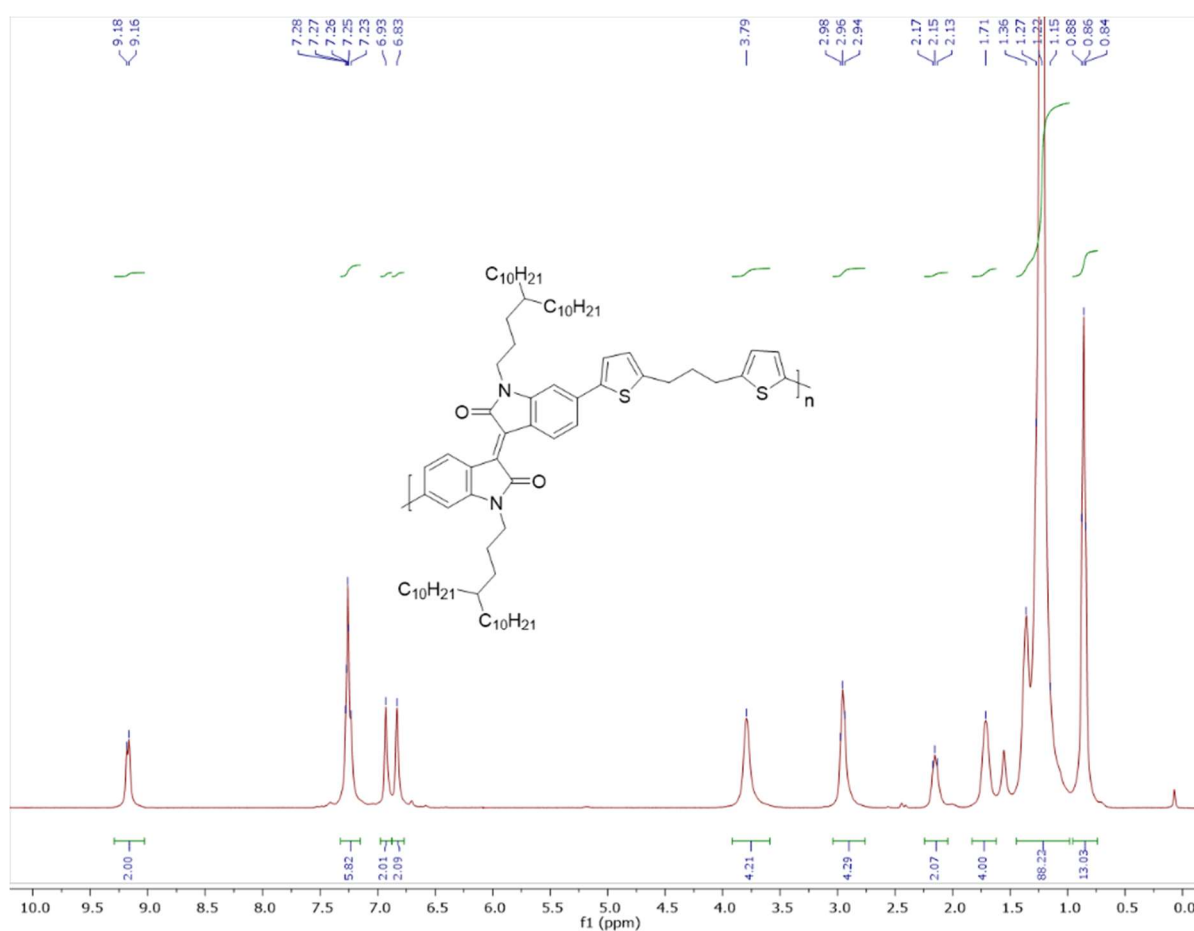
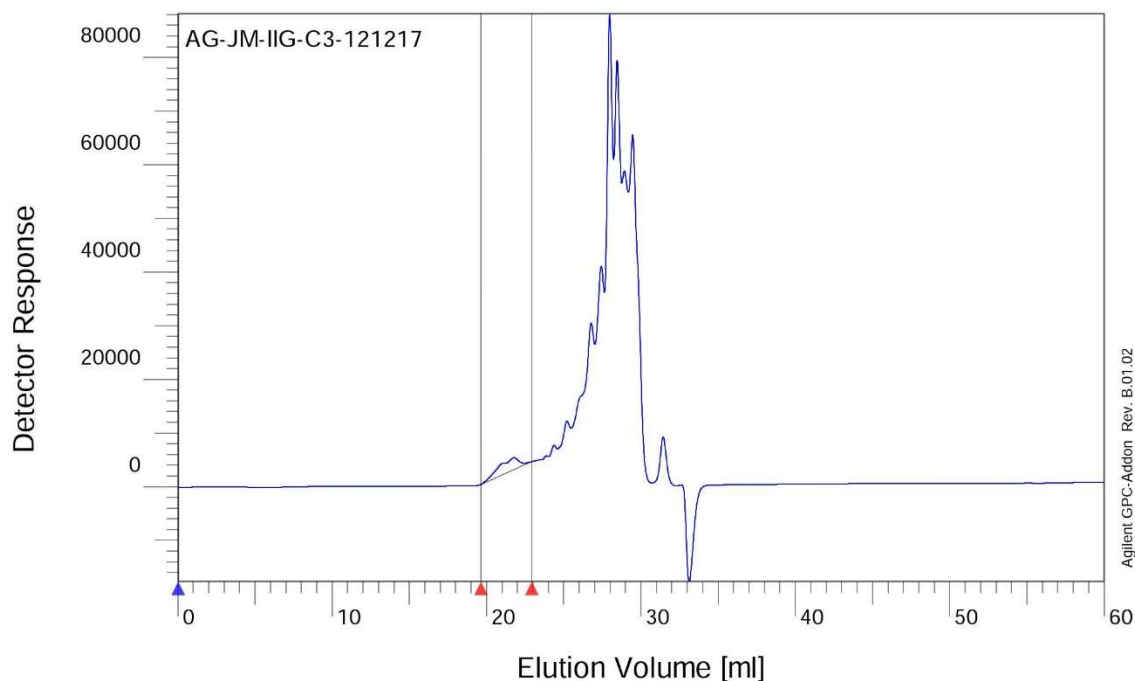


Figure S1. NMR spectra of C3

Sample : AG-JM-IIG-C3-121217
Injection Date : 12-Dec-17, 13:54:20
Calibration File : C:\Chem32\1\DATA\Calibrations\2017April20.CAL
Calibration Date : Monday 01/30/17 16:49:48
Baseline from : 19.648 min
Mass Distr. from : 19.648 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Detector 1 : RID1A, Refractive Index Signal
Operator : VA

Baseline to : 22.915 min
Mass Distr. to : 22.915 min
MHK - K (Cal.): 1.000000E+0 ml/g
Flowrate : 1.000 ml/min
Inject volume : 100.000 ul
Delay volume : 0.000 ml
Acquisition interval : 0.430 sec



RID1A

Mn :	2.7292e4	g/mol
Mw :	3.2629e4	g/mol
Mz :	3.8829e4	g/mol
Mv :	0.000000	g/mol
D :	1.1956e0	
[n]:	0.000000	ml/g
Vp :	2.1708e1	ml
Mp :	2.2220e4	g/mol
A :	3.7367e3	ml*V
10%:	1.7424e4	g/mol
30%:	2.2846e4	g/mol
50%:	2.9630e4	g/mol
70%:	3.8169e4	g/mol
90%:	5.2705e4	g/mol

Figure S2. Molecular weight analysis of C3 using GPC with tetrahydrofuran as the eluent.

OFET Devices Fabrication and Characterization

To fabricate the OFET devices, Si/SiO₂/Au substrates were cleaned using piranha mixture (2:1 18M H₂SO₄: 30% H₂O₂) for 20 minutes and copious rinsing with water. The cleaned and dried substrates were then modified with a thin layer of octadodecylsilane⁷ in a vacuum oven for 3 hours. The OTS treated surfaces were then rinsed in hexane, chloroform, and then dried with nitrogen air prior to use. The OFET devices were then fabricated by spin casting the 10 mg/mL solution at ambient. To eliminate any possible thermal history, the thin films were then annealed at 140 °C inside a N₂ glove box for 20 minutes. The films were then allowed to cool to ambient before OFET characterization. Charge carrier mobility measurements were then carried out using Keithley 4200 at ambient. OFET performances were obtained by applying a gate bias from -60 V to 6 V, with the potential gradient between the source and drain contacts kept at -60 V. The OFET channel width and length were kept at 1400 and 40 μm, respectively. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (WC_i / 2L)\mu(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is the threshold voltage.

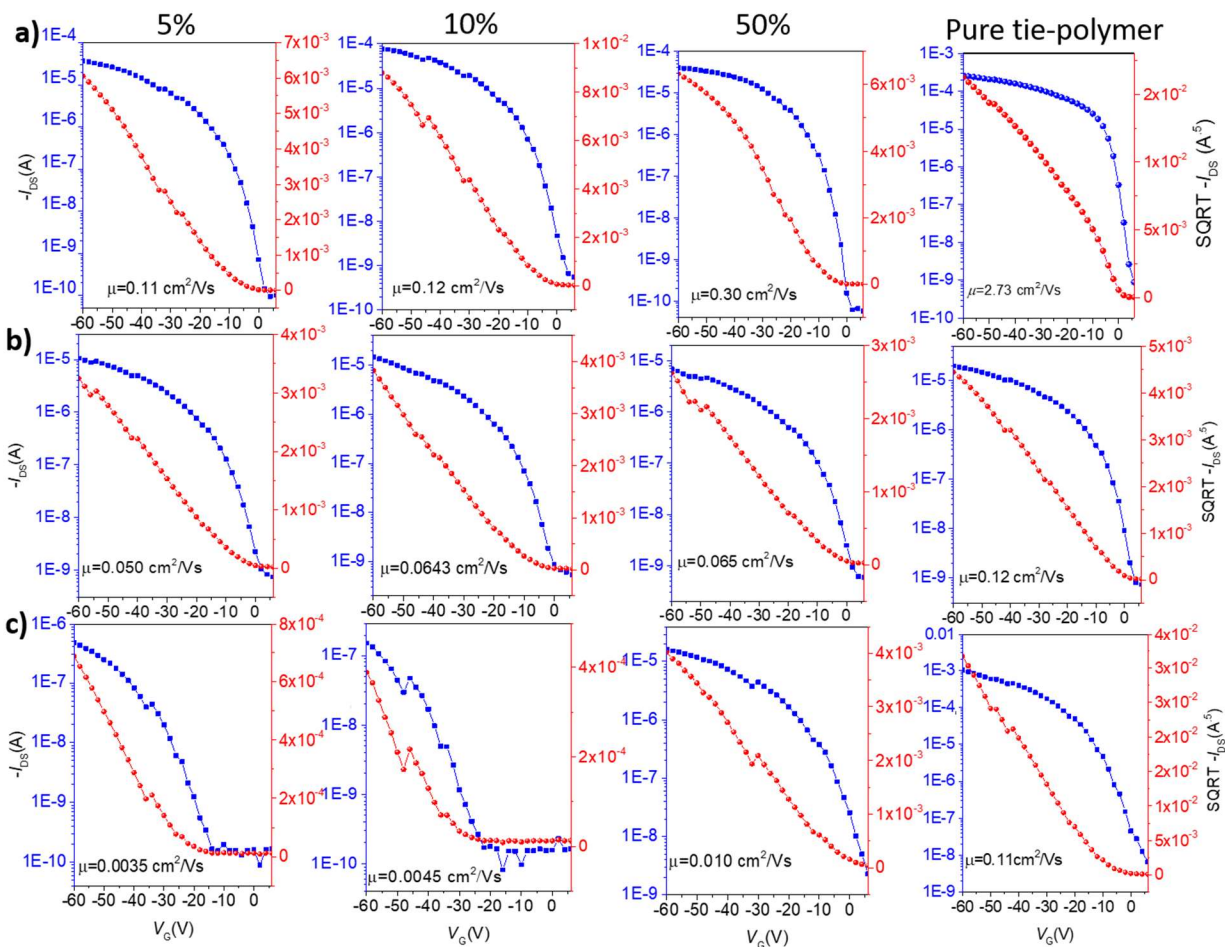


Figure S3. Transfer curves of OFET devices fabricated from representative blend solutions of C3 in a) P1, b) P2, and c) P3.

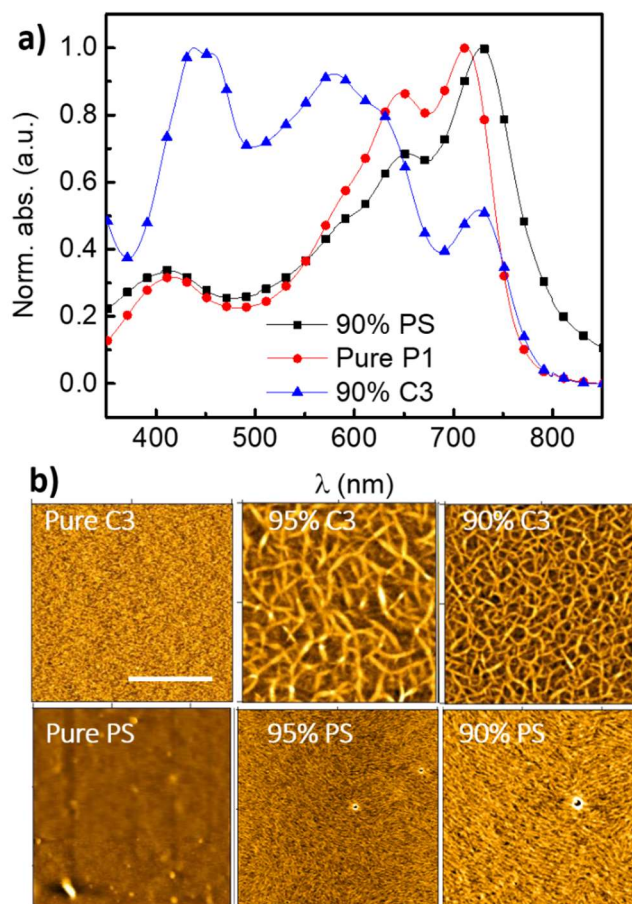


Figure S4. Comparative analysis between designed complementary blends and the common blends using insulating matrices (e.g. polystyrene). a) UV-Vis absorption spectra of thin-films of P1 blended with the studied matrix, C3, in comparison to polystyrene. The $0-0$ vibronic peak showed a significant red shift only in polystyrene-based blends, while the blends forming nanofibers showed no evidence of long-range aggregation of the tie chains. b) AFM height images of the pure matrices and corresponding blends revealing no formation of fibers when polystyrene is used.

Glass Transition Temperature (T_g) Measurement and Calculation

All thin films used for T_g calculations were prepared by spin coating (2000 rpm, 60s) of 10 mg/mL solution in chloroform. Temperature dependent UV-Vis absorption spectra were obtained using Agilent Cary 6000i UV-Vis-NIR Spectrophotometer. A Peltier temperature controller was used to regulate the temperature inside the chamber using liquid nitrogen as the coolant. Before each scan, the thin film temperature was allowed to stabilize for 2 minutes. The spectra were then used to extract T_g values in Python by the tools provided and detailed by Sam Root and colleagues.⁸ For comparison, oscillatory shear rheometry⁹ was utilized for P1 as previously reported.

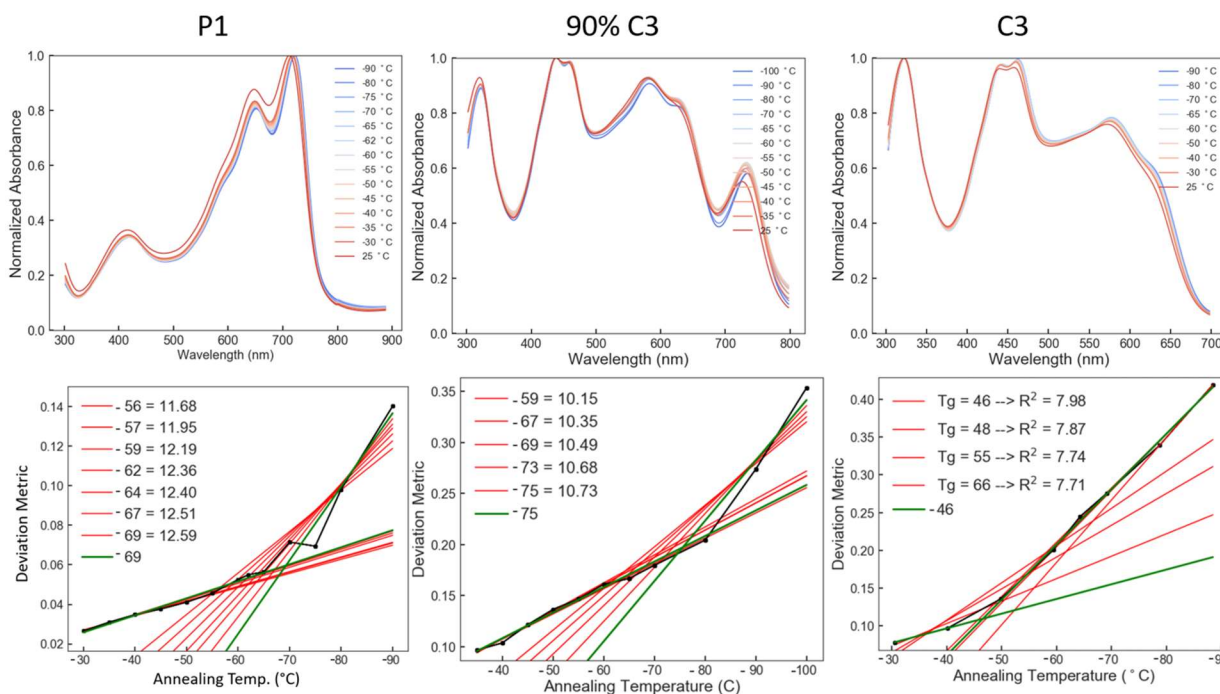


Figure S5. Temperature-dependent thin-film UV-Vis spectra used for T_g calculation and T_g-extraction by double-linear regression of the deviation metric.

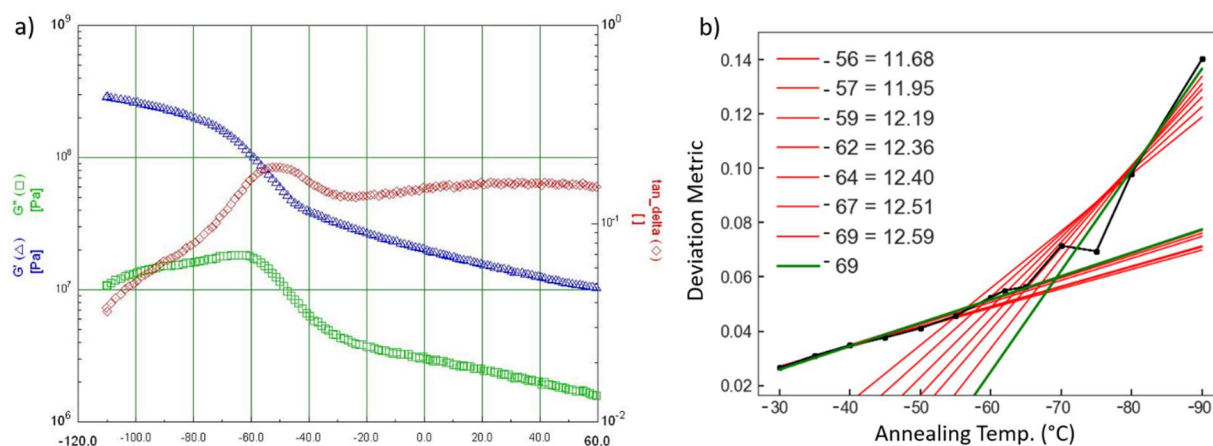


Figure S6. Extraction of T_g of polymer P1 using a) rheology, b) UV-Vis absorption method. The change in molecular segmental motion can be observed when the polymer material is cooled to as low as -60 °C.

Mechanical Properties Measured by Buckling Method.

All polymers were dissolved in the chloroform with the concentration of 10 mg/mL. The solutions were stirred at 50 °C overnight to completely dissolve the materials. The solutions of the blends were prepared by mixing the solution of P1 and the matrices with different ratios. PDMS was prepared by mixing the base and the curing agent at a ratio of 10:1 (by mass). After degassing in the vacuum, the PDMS was heated to 60 °C for 2 hours. The PDMS was then cut into strips with the size of 1 cm × 7 cm × 2 mm. The modulus of PDMS was measured by stretching stage (ESM303, Mark-10) and force gauge (Series 5, Mark-10) by plotting the strain-stress curve. The modulus of the PDMS curing at the temperature of 60 °C for 2 hours was ~ 1 MPa; after annealing the PDMS at the temperature of 140 °C for 10 minutes, the modulus increased to ~ 1.6 MPa. The cover glass (thickness ~ 220 μm) was cut into the size of 1 cm × 1 cm. Before spin coating process (1500 rpm, 30 s), the glass wafers were treated with uv-ozone for 30 minutes. The wafers with the semiconducting polymer layer on top were placed face down on the pre-strained (5% strain) PDMS, which were then immersed in water. As the wafer was hydrophilic and the PDMS was hydrophobic, water would move into the interface between the polymer and the glass wafer to separate them apart. As a result, the film would be transferred onto the PDMS. The whole transfer process took about 30 minutes. The transferred film was left in the air for 2 hours for the evaporation of the water on the sample surface. After the strain applied on the PDMS was released, the buckles could form on the semiconducting polymer simultaneously. Optical microscope images were used to extract the buckles periodicity using MATLAB. The film thicknesses were measured by AFM after making a cut in different regions of the film and imaging the step edge. Film thickness of 100 nm ($\pm$ 12.0 nm) could be cast and transferred onto PDMS slabs.

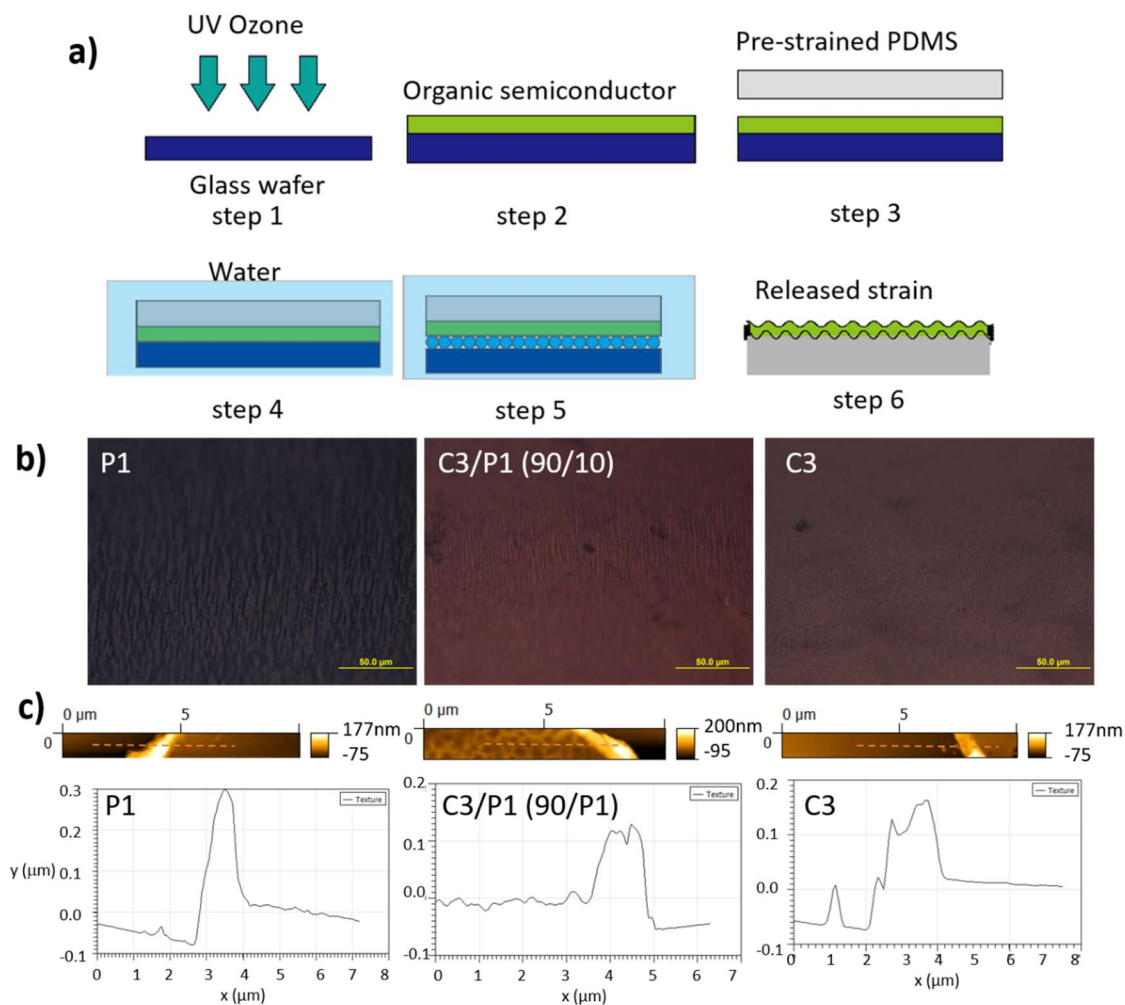


Figure S7. a) Illustration of buckling method, b) typical optical microscope images of formed buckles upon strain release and c) the AFM-extracted film thickness.

Crack-on-Set Strain Analysis and Electrical Measurement

For the OFET devices studied under strain, the film transfer was achieved as previously described for crack-on-set analysis on PDMS slabs. The PDMS/polymer assembly was left inside a vacuum oven to remove any residual water. The dried assembly was then carefully laminated and taped onto OTS-treated substrates with the corresponding strain applied. The representative OFET hole mobilities for devices obtained by applying strain parallel to the electrodes are summarized in Table S1.

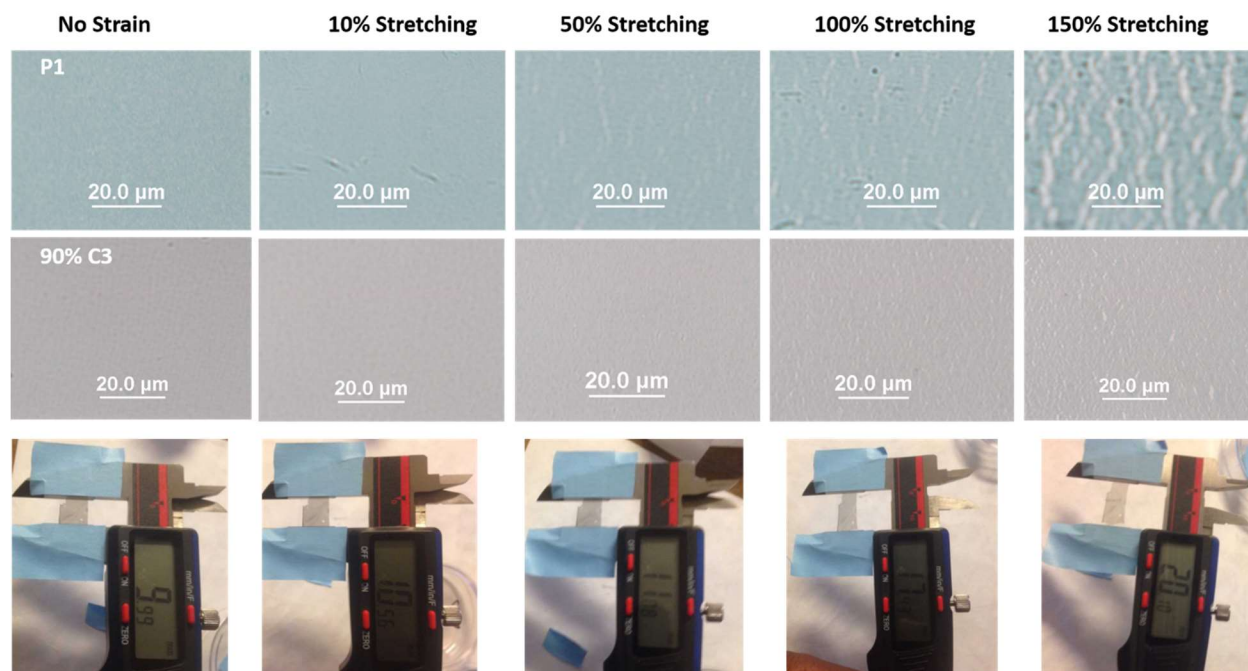
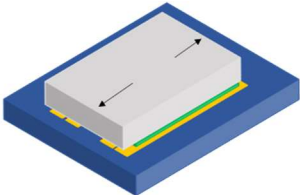
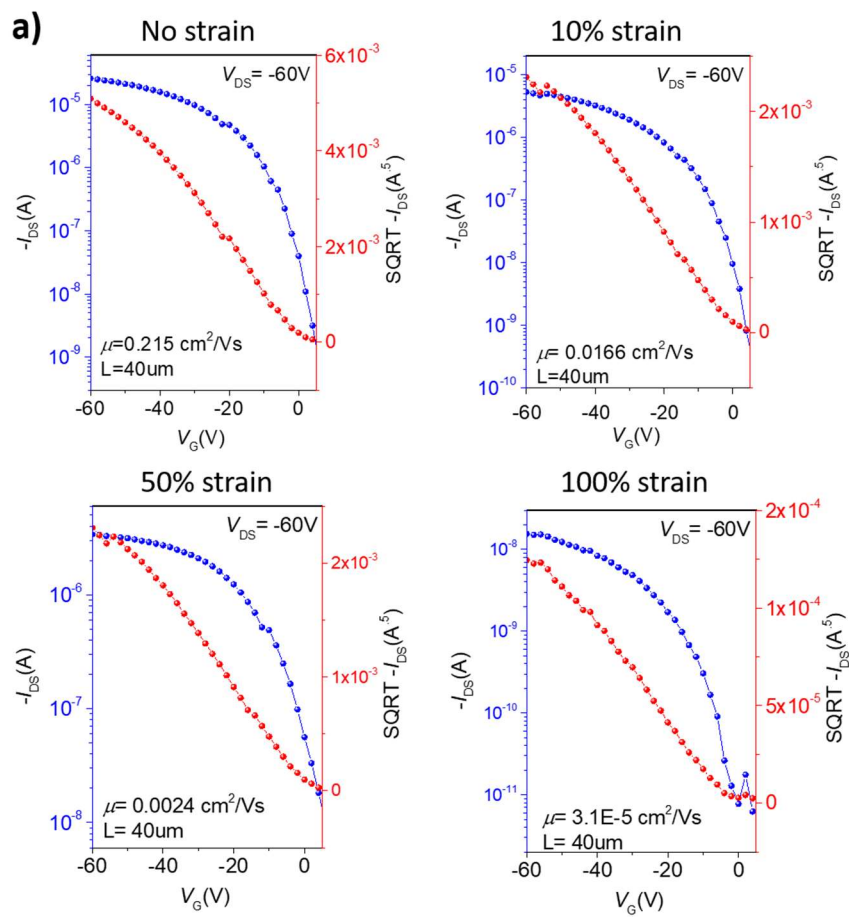


Figure S8. Crack-on-set analysis of the studied thin films on PDMS substrates. Optical microscopy was used to image the formation of microcracks in the thin films as strain was increased. The films based on nanofiber networks showed mechanical stability beyond 50% strain. Readings on the ruler: 9.99 (no strain), 10.56 (10% stretching), 11.08 (50% stretching), 17.43 (100% stretching), 20.10 (150% stretching).

Table S1. Summarized average hole mobilities of devices studied by parallel lamination under different strain levels.



	No strain	10% strain	50% strain	100% strain
	$\mu_{\text{max}}/\mu_{\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{ s}^{-1}$)	$\mu_{\text{max}}/\mu_{\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{ s}^{-1}$)	$\mu_{\text{max}}/\mu_{\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{ s}^{-1}$)	$\mu_{\text{max}}/\mu_{\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{ s}^{-1}$)
P1	0.21/0.10	0.15/0.11	2.1E-3/5.2E-5	<1E-7
90% C3	0.015/1E-3	0.012/1.4E-3	4.5E-3/3.3E-4	1.7E-4/3.1E-5
C3	2.0E-3/1.1E-3	1.7E-3/5E-4	8.4E-4/2.6E-5	5.1E-6/6.5E-7



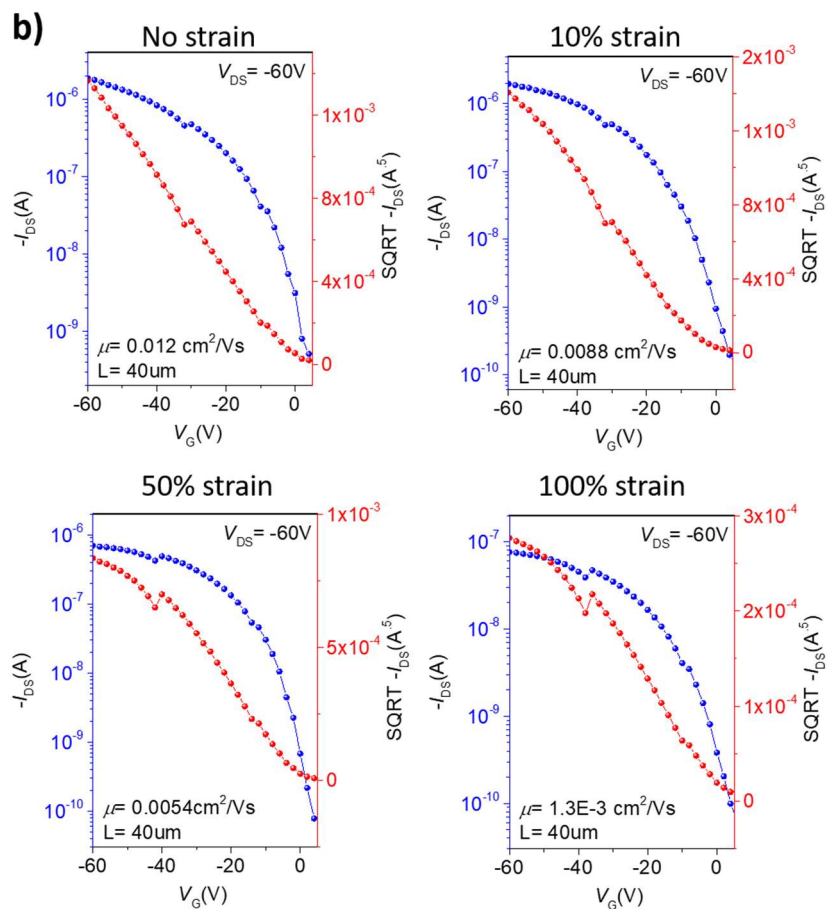


Figure S9. Representative transfer curves of representative OFET devices based on a) pure P1 and b) 90% C3 blend under various strain levels perpendicularly to the electrodes.

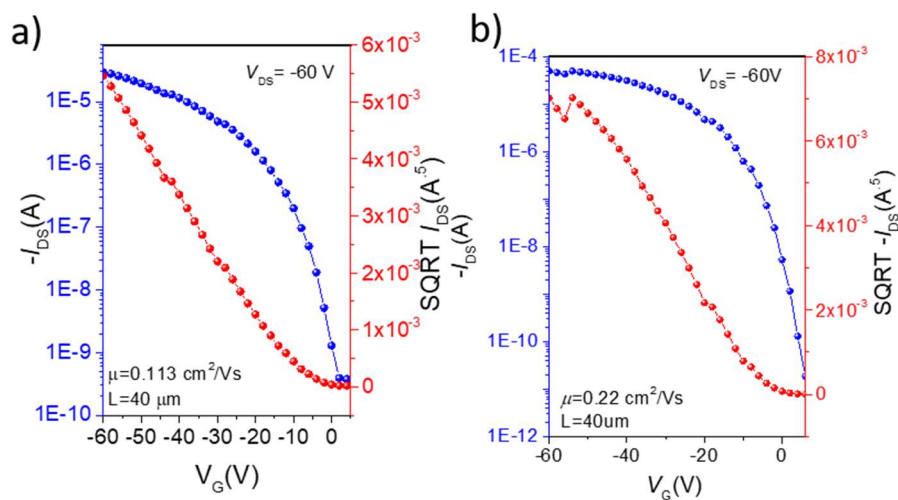


Figure S10. Representative transfer curves of the best performing OFET devices based on 90% C3 blend a) before and b) after blade shearing.

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