

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Continuous Melt-Drawing of Highly Aligned Flexible
and Stretchable Semiconducting Microfibers for Organic
Electronics

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Experimental details

Material preparation. DPP-C0 (3.3 mg/mL) and DPP-C5 (10 mg/mL) were dissolved in dichlorobenzene at 50 °C stirred overnight.

Polymer microfiber fabrication from melt-drawing. DPP-C5 solid material (~10mg) was placed onto silicon or glass substrate on a hot plate inside nitrogen filled glovebox. The temperatures used for melt-drawing are 160-180 °C for DPP-C5. After the material got fully liquefied, a needle was used to draw some material out from polymer melt surface and further drew out the long polymer microfiber continuously at different speed. With very fast speed (~50 cm/s), thin microfiber (5-10 μm) can be obtained. The very thick microfiber up to 250 μm was fabricated by slow speed (~1 cm/s) and bigger needle.

Characterization of physical properties of the polymer microfiber. The POM measurement was carried out using an Olympus BX-51 Optical Microscope. Polarized micro-reflection spectroscopy was carried out by a homemade setup in Prof. Libai Huang's group at Purdue University. GIXRD measurement was carried out in Argonne National Laboratory. For the 1D line-cut of GIXRD data, due to the missing wedge at out-of-plane direction, we cannot get the 1D data at φ around 0°. Therefore, data from φ around 5-10° was selected for 1D out-of-plane line-cut. The 1D in-plane line-cut data was from φ around 88-83°. The microribbon for all the measurement was prepared by pressing the microfiber between two glass slides or silicon wafers. To obtain thin ribbons, the microfibers can be pressed at temperature around 120 °C on hot plate. The stretchability was measured by ESM303 test stand with Series 5 force gauge. The Young's modulus E , was calculated by the following equation:

$$E = \frac{FL_0}{A_0\Delta L}$$

Where E is the Young's modulus, F is the force exerted on an object under tension, A_0 is the actual cross-sectional area through which the force is applied, ΔL is the amount by which the length of the object changes, L_0 is the original length of the object.

Optical characterization. In the polarized micro-reflection spectroscopy, the white light from a stabilized tungsten-halogen light source (Thorlabs) is focused on a pinhole with 10 μm diameter. It is then collimated and focused on the sample with a $50\times/\text{NA} = 0.95$ objective. The beam size of white light is about 3 μm. This small beam size allows us to measure the small piece of very thin ribbon (See Figure S3). The reflected light is collected with the same objective, dispersed with a monochromator (Andor Technology) and detected by a TE cooled charge coupled device (CCD) (Andor Technology).

FET device Fabrication and measurement. A heavily n-doped Si wafer with a 300 nm SiO₂ surface layer (capacitance of 11 nF/cm²) was employed as the substrate with Si wafer serving as the gate electrode and SiO₂ as the dielectric. The gold S/D electrodes were sputtered and patterned by photolithography technique. For the octadecyltrichlorosilane^[31] modification, the silicon wafers were first cleaned with hot piranha solution for 20 minutes. It was then washed with deionized (DI) water several times, and further subjected to sonication sequentially in DI water and acetone for 6 min each. After drying inside an oven, the silicon wafer was then put into a clean petri dish with a small drop of OTS. The dish was then covered and heated in a vacuum oven at 120 °C for 3 hours, resulting in the formation of an OTS self-assembled monolayer on the surface. The OTS modified substrates were rinsed successively with hexane, ethanol, and chloroform, and dried by nitrogen. For polymer microfiber/ribbon devices, the polymer microfiber was placed onto the channel area parallel or perpendicular to the electric field between S/D electrodes. The polymer microfiber was then pressed by another OTS-modified silicon wafer at 120 °C in glovebox to form good contact between semiconductor and electrodes. For devices with microfiber perpendicular to

electric field, the channel width is 1000 μm and channel length is 10 μm . For devices with microfiber parallel to electric field, interdigital electrode style was used to increase contact area to reduce measurement error. The channel length is 50 μm and channel width is the microribbon width measured by microscope.

Device characterization was carried out using Keithley 4200 in ambient environment. The field-effect mobility was calculated in the saturation regime by using the equation $I_{\text{DS}} = (\mu W C_i / 2L)(V_G - V_T)^2$, 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.

Conducting microfibers fabrication and measurement. The DPP-C5 polymer microfiber was doped in FeCl_3 nitromethane solution (100 mg/mL) for 1 hour and dried in vacuum before use. The conductivity measurement was carried out using Keithley 4200 in ambient environment. For the demonstration with LED bulb (rated voltage: 4.5 V), 50 V voltage was used.

Table S1. DPP-C5 polymer microfiber diameter with different drawing speed and temperature.

Temperature	Drawing speed			
	1 cm/s	5 cm/s	25 cm/s	50 cm/s
160 $^{\circ}\text{C}$	$\sim 250 \mu\text{m}$	$\sim 190 \mu\text{m}$	$\sim 130 \mu\text{m}$	$\sim 25 \mu\text{m}$
180 $^{\circ}\text{C}$	$\sim 200 \mu\text{m}$	$\sim 160 \mu\text{m}$	$\sim 110 \mu\text{m}$	$\sim 10 \mu\text{m}$

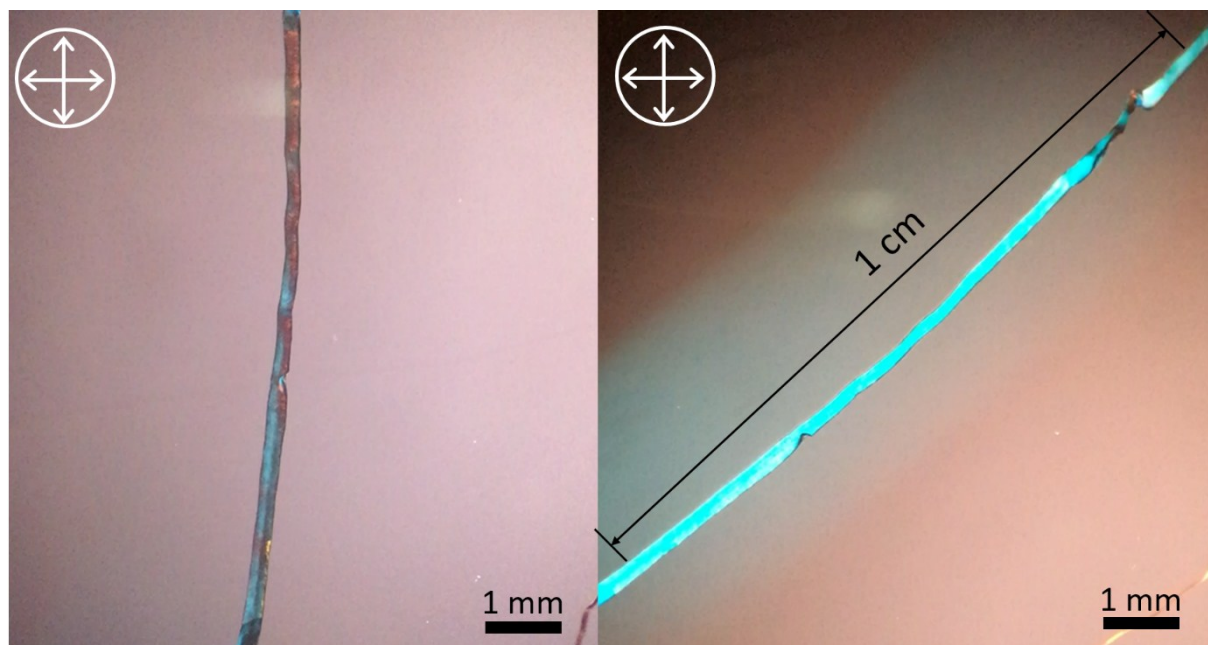


Figure S1. Long range uniformity of the microfiber made by this melt-drawing method. When rotated under cross-polarized light, this DPP-C5 polymer ribbon exhibited same color and behavior up to centimeter range scale.

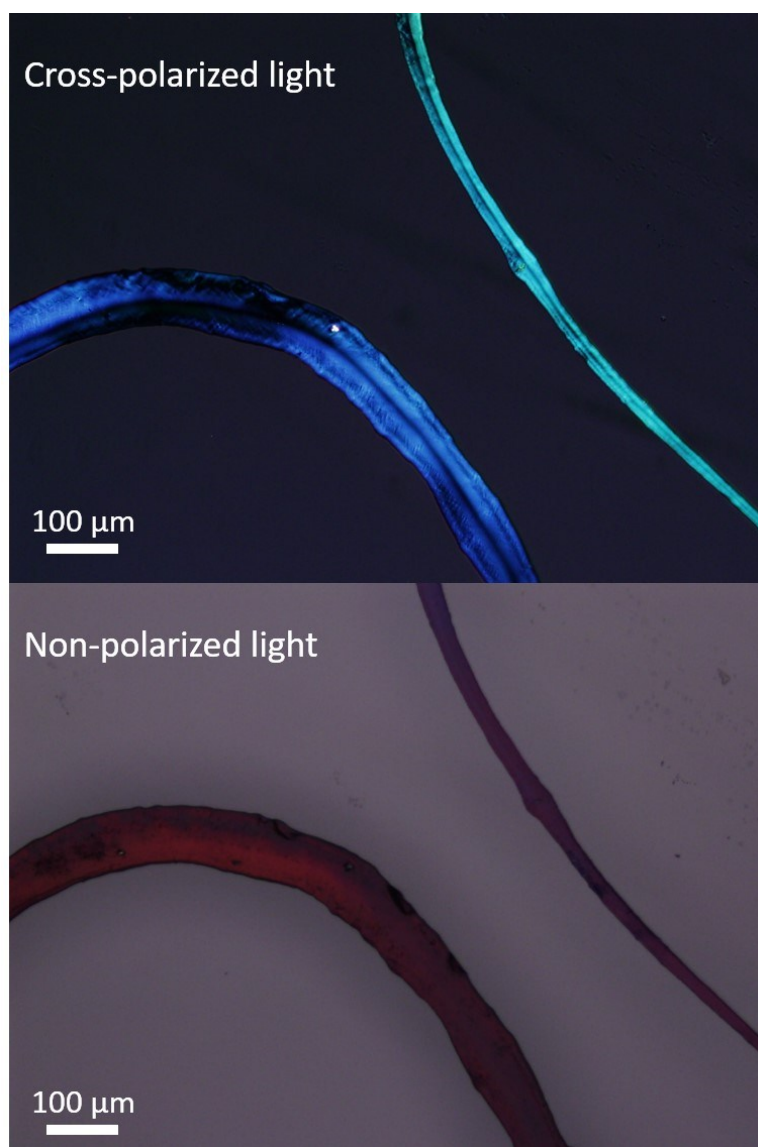


Figure S2. DPP-C5 ribbon under cross-polarized light and non-polarized light. Clear dark line in the center of the ribbons can be observed under cross-polarized light. However, the ribbons look smooth under non-polarized light. This proves that the dark line in the center of the ribbons is due to polymer chains packing/alignment. One possible explanation is the crystallization of the polymer melt started from the low temperature surface to the center. The polymer chains at the center are loosely assembled and less crystalline, resulting in this dark center under cross-polarized light.

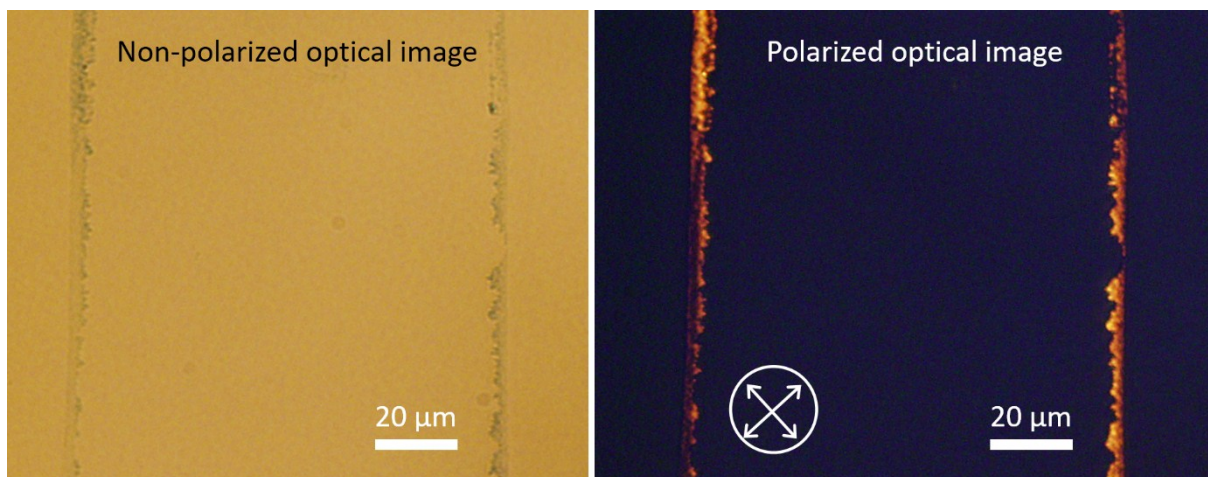


Figure S3. The Non-polarized optical image (left) and polarized optical image of polymer microribbon for polarized micro-reflection spectroscopy measurement. For this sample, the microribbon was peeled off with only very thin edge left.

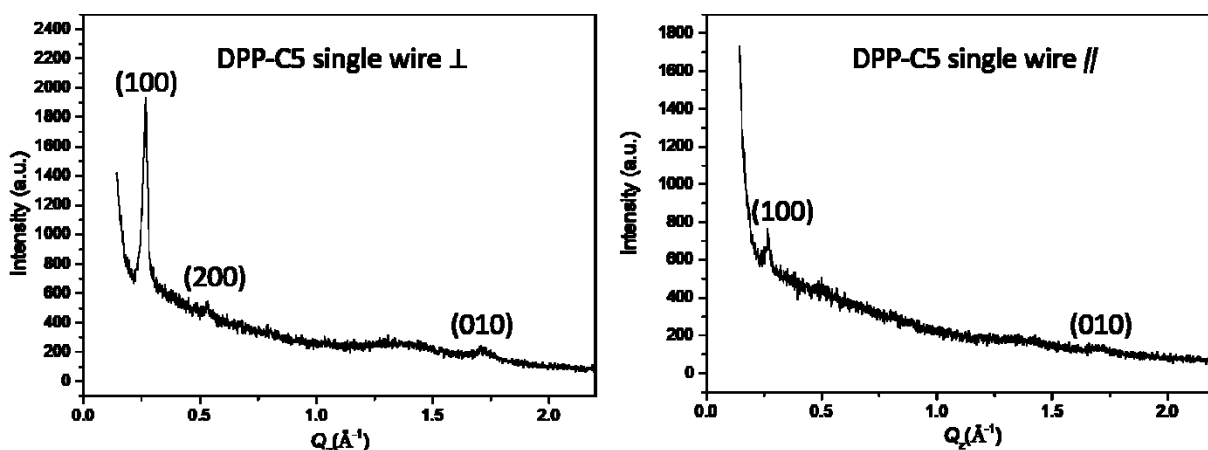


Figure S4. DPP-C5 single fiber out-of-plane 1D XRD results.

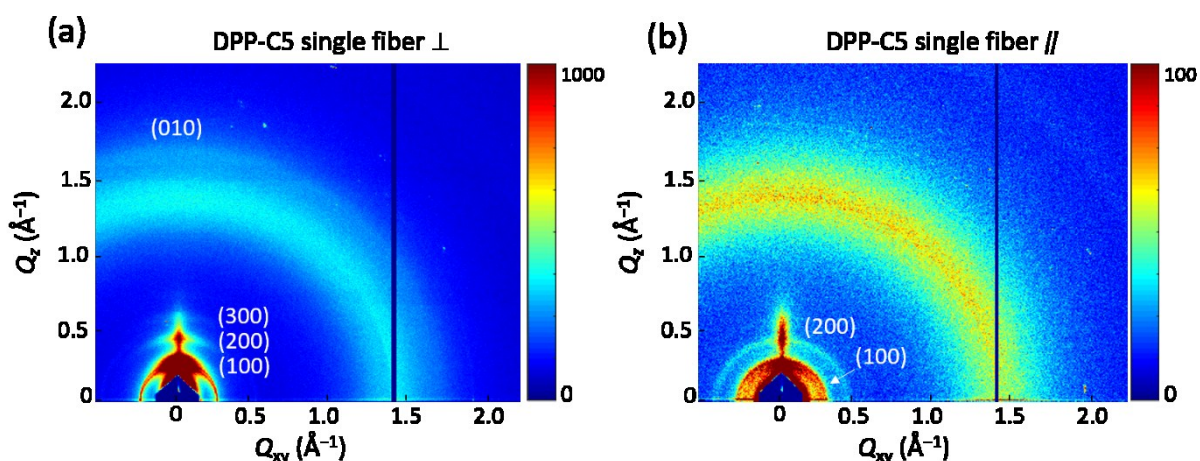


Figure S5. DPP-C5 single fiber GIXRD results. The results are similar to multiple fiber/ribbon GIXRD in Figure 3, but the intensity is much weaker.

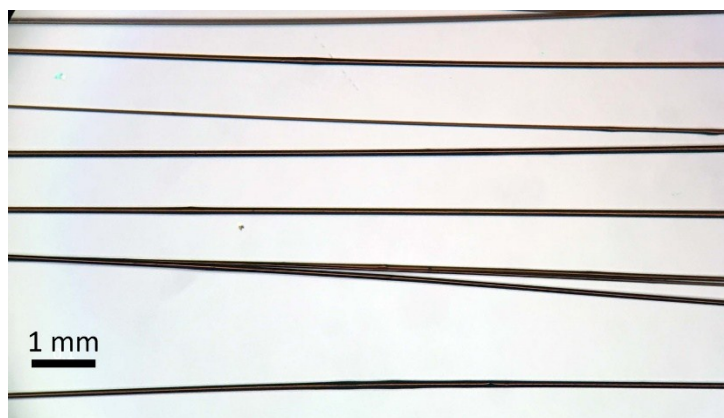


Figure S6. Aligned polymer microfibers for GIXRD measurement.

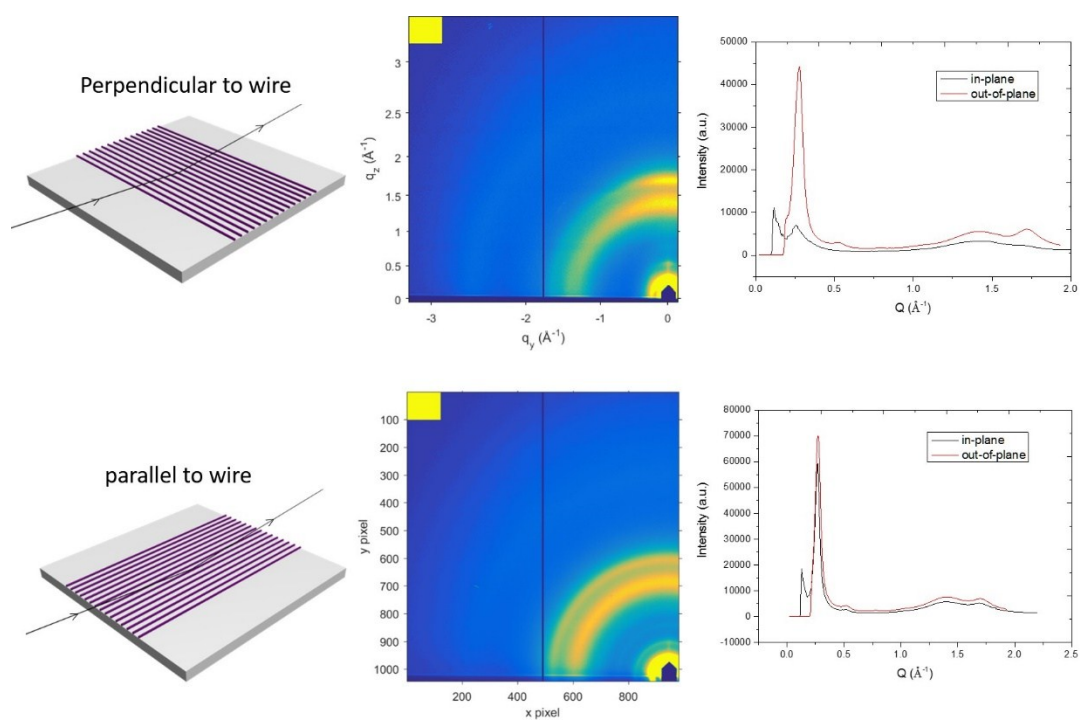


Figure S7. GIXRD of DPP-C5 multiple microfibers.

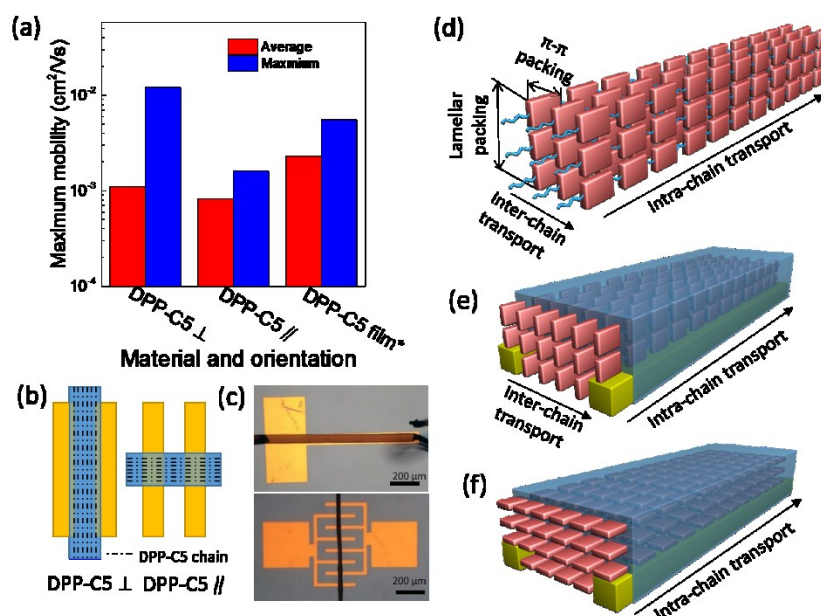


Figure S8. (a) Charge carrier mobility from fiber OFETs measurement. (b) Schematic illustration of devices and charge carriers transport pathway in DPP-C5 $\perp$ and $\parallel$ polymer microfiber/ribbon (black lines and dots denote π - π stacks and flexible spacers). (c) Optical images of polymer microribbon OFETs. (d) Molecular structure of DPP-C5 and the schematic illustration of DPP-C5 packing. (e) Edge-on and (f) face-on packing mode in DPP-C5 $\perp$ polymer microfiber/ribbon. * DPP-C5 thin film OFETs results are from previous work ref. 30.

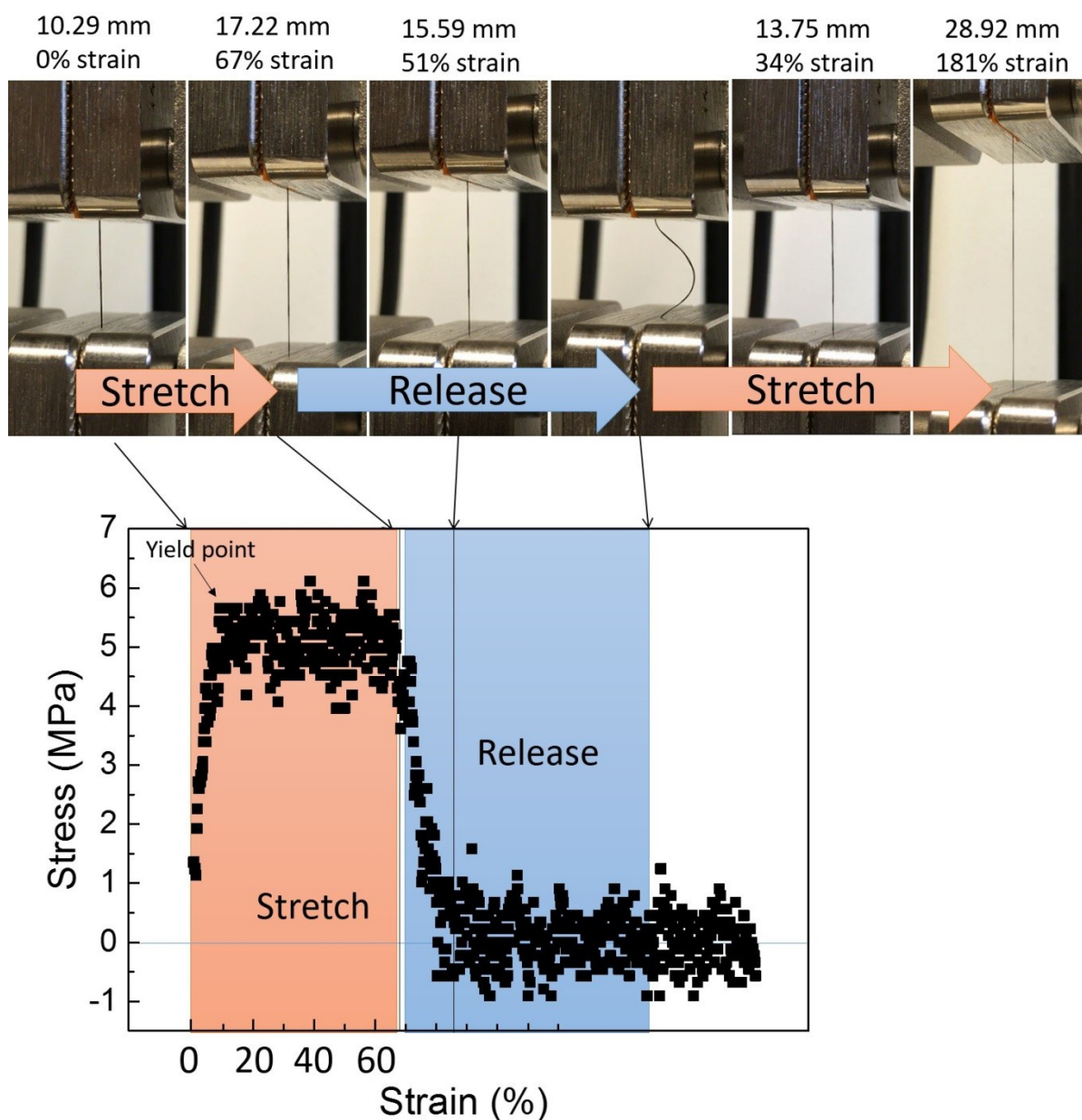


Figure S9. Optical images (top) and their strain-stress plot (bottom) of stretch-recovery measurement after yield point. A 10.29 mm long and 150 μm thick DPP-C5 polymer microfiber was chosen to this measurement. The microfiber was first stretched to 17.22 mm (67% strain), and then released directly. Upon releasing, the microfiber remained straight until 15.59 mm (51% strain) and after that, the microfiber curved. After 70 seconds, the microfiber recovered to 13.75 mm (34% strain). The microfiber was stretched up to 28.92 mm (181% strain) before breaking. Please see video SI.

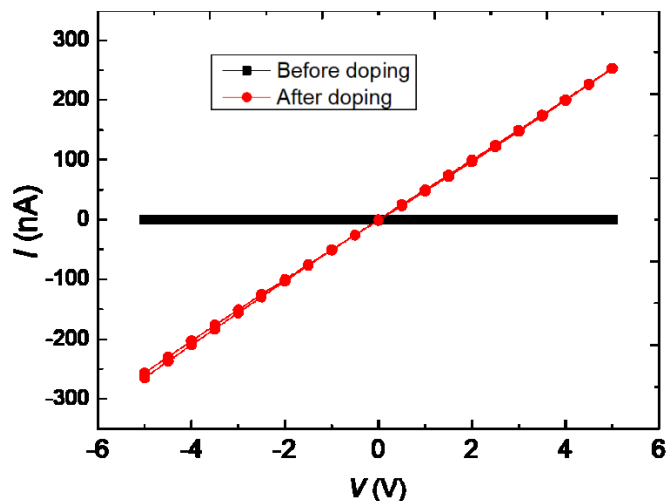


Figure S10. Two-probe conductivity measurement of the doped DPP-C5 polymer microfibers. The polymer microfibers were doped in FeCl_3 solution (100 mg/mL in nitromethane) for 1 h. Before measuring, the microfibers were dried under vacuum. The distance between two probes is 4 mm, diameter of the fiber is 95 μm , and the calculated conductivity is 8.9 S/cm. Four-probe measurement was also carried out and the measured conductivity agrees very well with two-probe measurement.

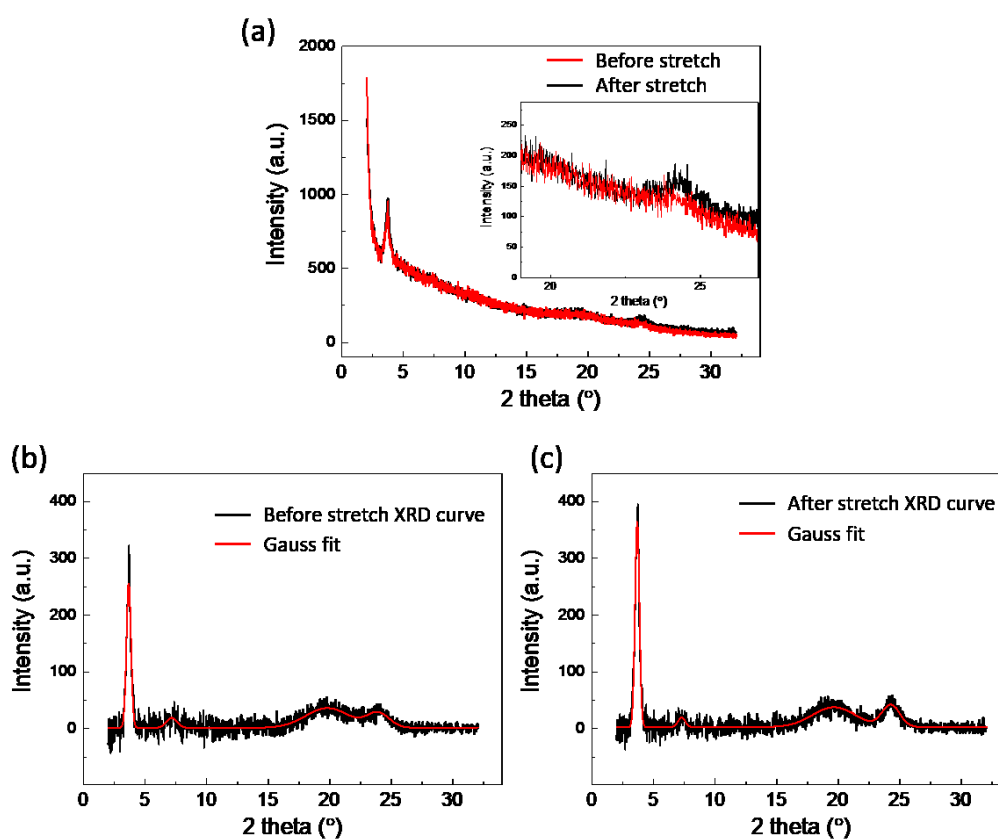


Figure S11. (a) The raw data of XRD measurement for DPP-C5 single microfiber before and after stretching (20% strain). (b) and (c), The XRD data after baseline correction and its Gauss fitting curve for DPP-C5 microfiber before and after stretching, respectively.

Table. S2. The parameter of DPP-C5 single microfiber XRD measurement before and after stretching.

	Before stretching		After stretching	
	Peak position (°)	FWHM	Peak position (°)	FWHM
Lamellar packing	3.6826	0.4309	3.6851	0.4177
Amorphous peak	19.827	4.163	19.656	4.0721
π - π packing	23.944	2.146	24.285	1.7097

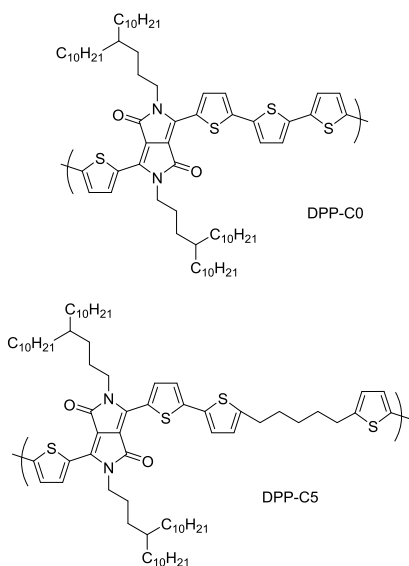


Figure S12. Molecular structures of DPP-C0 and DPP-C5