Supporting information for manuscript:

The effect of drawing on the electrical, thermoelectrical and mechanical properties of wet-spun PEDOT:PSS fibers

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Details on self-heating technique for the measurement of the thermal conductivity

If a small current, I, flows through a wire of radius r and length L which is thermally grounded at temperature T_0 at its ends, the spatial (z) dependence of its temperature is governed by:

$$\frac{I^2\rho(T)}{\pi r^2} = 4\sigma\varepsilon(2\pi r){T_0}^3T - \kappa(\pi r^2)\frac{d^2T}{dz^2} \qquad \text{eq. S1}$$

Here ρ is the electrical resistivity, κ the thermal conductivity, σ the Stefan-Boltzman constant, and ε the (unknown) emissivity, and we assume that the sample is in vacuum. To second order in current, the local temperature will then be:

$$T(z) = T_0 + \frac{I^2R}{\kappa L\alpha^2\pi r^2}\left[1 - \frac{\cosh(\alpha z)}{\cosh\left(\frac{\alpha L}{2}\right)}\right] \qquad \text{eq. S2}$$

where $\alpha \equiv \left[8\sigma\varepsilon{T_0}^3/(\kappa r)\right]^{1/2}$ and $R \equiv L\rho(T_0)/(\pi r^2)$ is the resistance in the absence of Joule heating.

Then the change in the measured resistance will be:

$$\frac{dR}{dI^2} = R\frac{\frac{dR}{dT}}{8\sigma\varepsilon{T_0}^3\pi rL}\left[1 - \frac{\tanh\left(\frac{\alpha L}{2}\right)}{\frac{\alpha L}{2}}\right] \qquad \text{eq. S3}$$

Note that for negligible cooling by thermal radiation (small T_0 or $\varepsilon \to 0$), eq. S3 reduces to eq. 1 in the main text. For our samples at liquid nitrogen temperature, the differences in κ calculated with eq. S3 assuming maximum emissivity, $\varepsilon = 1$, and $\varepsilon = 0$ were < 6%.

The specimens were mounted for 4-probe resistance measurements, with inner contacts separated by L = 5-7 mm, on four indium pedestals on a sapphire substrate with small drops of melted indium. The resistances of the specimens were found to be stable and the contact resistances determined by comparison of measured 2-probe and 4-probe resistances, were generally < 1% of the resistance.

Eq. S1-S3 assume that there is negligible heating at the contacts and that the sample is thermally grounded at the contacts. To check for this, we compared values of dR/dI^2 measured with the normal 4-probe configuration, in which current is applied at the outer contacts and voltage measured at the inner, and an "inverted" configuration, in which current and voltage contacts are switched. If the inner contacts did not thermally ground the sample, the change in resistance would be smaller for the inverted configuration. However, we always obtained identical results within the noise for the two configurations, as shown for two samples in **Figure S1**.

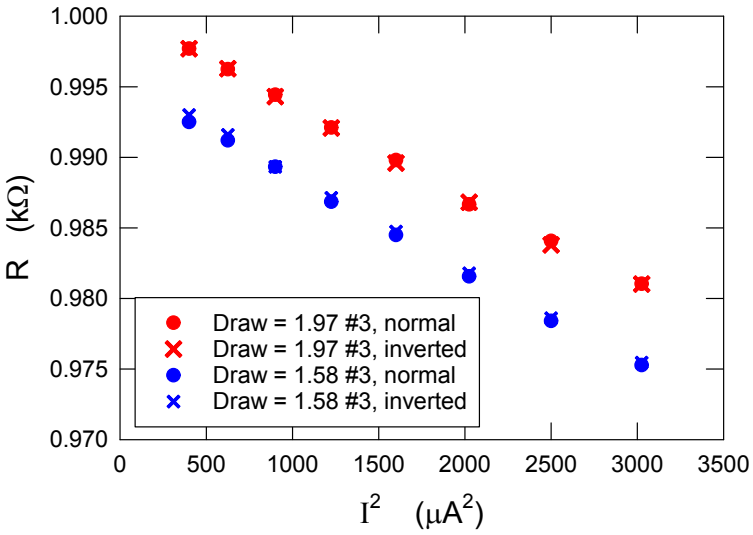

Figure S1. Comparison of the current dependence of the resistance of two specimens from different samples (total draw 1.58 and 1.97) with normal 4-probe contacts and inverted 4-probe contacts.

Estimation of the bulk density of the fibers

The single-filament test system FAVIMAT+ from Textechno used to perform the tensile tests can also measure the average linear density of each filament by using a vibration method. In this method the resonance frequency of the filament is measured at constant gauge length and known pre-tension. The linear density can then be calculated using:

$$LD = \frac{T}{4f^2L^2} \qquad \text{eq. S4}$$

where LD is the linear density, T is the applied pre-tension, f is the fundamental resonant frequency and L is the gauge length. The linear density is related to the bulk density by:

$$LD = \rho_{fiber}A \qquad \text{eq. S5}$$

where A is the cross-sectional area of the fibers. Thus, from the slope of **Figure S2** we can extract the estimated bulk density of the fibers.

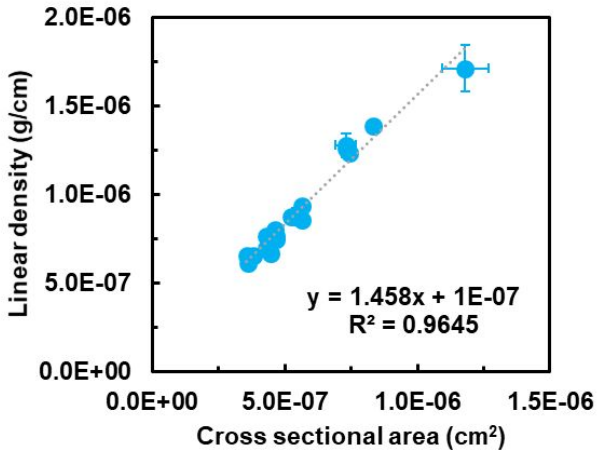

Figure S2. Linear density versus the average cross-sectional area for all samples.

Details on the removal of PSS from the fibers in the DMSO stretch bath

Post-treatment of PEDOT:PSS films to remove excess PSS is a common practice in the literature. Thus, we studied the possible removal of PSS from the fiber in the short time (average of 5 seconds) that the fibers spent in the DMSO bath during fabrication.

X-ray photoelectron spectroscopy (XPS) of a bundle of coagulation bath fibers and a bundle of DMSO stretched fibers was performed. **Figure S3** shows the S2p binding energies showing the increase in relative intensity of the peaks corresponding to PEDOT at the filament surface indicating partial removal of PSS in the DMSO bath. The surface PEDOT to PSS weight ratio of the DMSO stretched fibers is estimated at 1:1.95 (33.9 wt.% PEDOT).

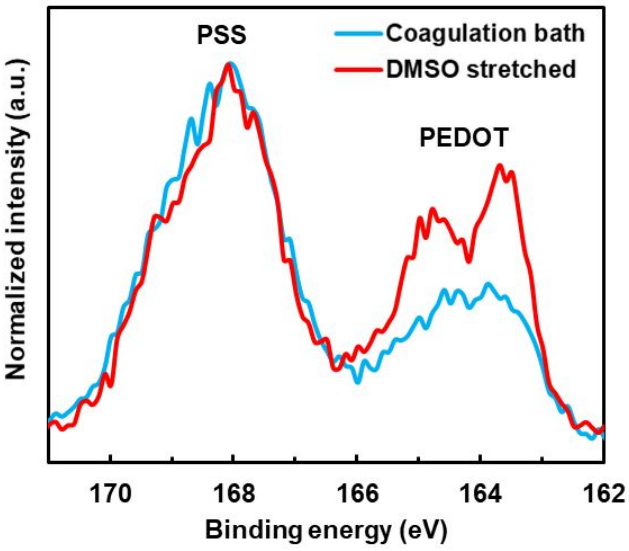

Figure S3. Comparison between the XPS S2p of coagulation bath fibers and DMSO stretched fibers.

Additionally, the linear density of the fiber can also reflect the removal of PSS. Indeed, the linear density of the fibers can be found by applying a mass balance to the wet-spinning system and is given by:

$$LD = \frac{Q\rho_{dope}C_{PEDOT:PSS}}{v_{take-up}} \qquad \text{eq. S6}$$

where Q is the flow rate (constant at 0.25 mL/h in this work), ρ_{dope} is the dope density (assumed ~ 1 g/cm^3), $C_{PEDOT:PSS}$ is the PEDOT:PSS concentration in the dope (2.5 wt.% in this work) and $v_{take-up}$ is the take-up speed that varies with draw. **Figure S4** shows the linear density of the fibers as a function of the take-up speed. The solid line is the calculated linear density values using eq. S6 assuming no filament mass is lost to the baths (removal of PSS). The dashed line is the calculated linear density values if PSS loss occurs such that the final PEDOT to PSS ratio is 1:1.95, as obtained from the XPS results. On one hand, as can be observed the linear density of the coagulation bath samples (lowest take-up speed) are close to the calculated values assuming no removal of PSS (with exception of one of the samples that showed an unusually high linear density that we attribute to some unnoticed experimental deviation during processing). On the other hand, DMSO stretched samples deviate from the solid line and the linear density values are closer to those calculated assuming a final PEDOT:PSS weight ratio of 1:1.95, further supporting the XPS observations.

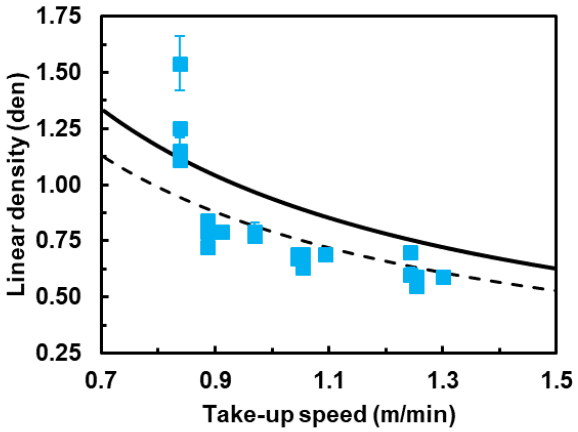

Figure S4. Average values of linear density as a function of take-up speed. Linear density is given in denier (grams fiber per 9000 meters of fiber). The solid line is calculated using eq. S6 assuming no loss of PSS while dashed line is calculated assuming loss of PSS to match the final PEDOT:PSS weight ratio of 1:1.95 obtained from the XPS analysis.

Effect of DMSO removal on the electrical conductivity

In order to decouple the effects that PSS removal and drawing have in the electrical conductivity of the fibers, we performed a post-treatment that consisted in the immersion of a spool of coagulation bath fibers in DMSO for a certain amount of time (1, 5, 10, 30 and 60 min) followed by water rinsing and drying at 140 ºC for 10 min. The linear density of the different samples is shown in **Figure S5a**. The linear density of the DMSO washed samples decreased to values between 0.7-0.8 denier presumably due to the removal of PSS. These values correspond with a PEDOT content of around 40 wt.% by comparison with the calculated linear density obtained from the mass balance and is similar to values obtained from fibers drawn through the DMSO bath.

The electrical conductivity of the different samples is shown in **Figure S5b**. Despite the PSS removal during the washing treatment, the electrical conductivity of the washed fibers was found

to be similar to that of the coagulation bath fibers. This result contrasts with the increase in electrical conductivity observed when the fibers where drawn through the DMSO bath and supports that the increase in electrical conductivity is not solely due to PSS removal but due to chain orientation during drawing or a combination of both. The fact that the electrical conductivity remains the same despite the removal of PSS could also be an indication of chain relaxation when the fibers are washed in DMSO without any tension applied. However, the intention of this work is to study the effect of drawing of PEDOT:PSS fibers fabricated in a continuous manner and thus further study of the washed samples is out of the scope of this work.

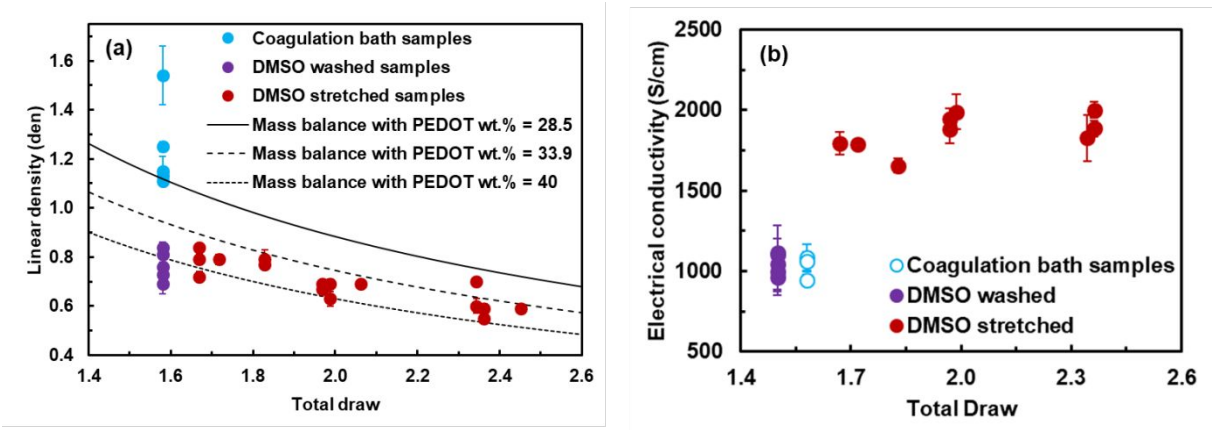

Figure S5. **(a)** Linear density as a function of total draw. **(b)** Electrical conductivity as a function of total draw. In **(b)** coagulation bath samples that were washed in DMSO are plotted at total draw of 1.5 instead of 1.58 to avoid overlap of the symbols and increase clarity.

Electrical conductivity-strain curve

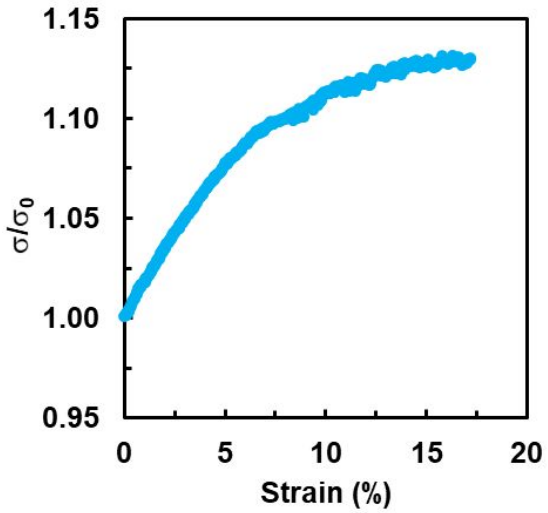

Figure S6. Electrical conductivity (standardized to the initial electrical conductivity) as a function of strain for a coagulation bath sample spun into 10 vol.% DMSO in IPA. For this test the resistance as a function of strain was measured, and then, the electrical conductivity at each strain was calculated assuming constant specimen volume. Values presented are average of 3 specimens.

Stress-strain curves

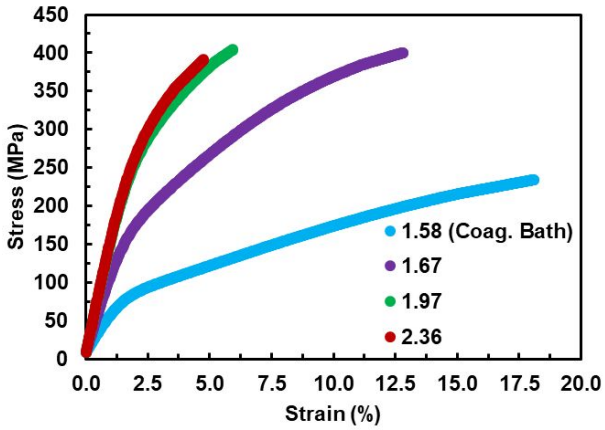

Figure S7. Typical stress-strain curves in uniaxial tension of fibers spun into 10 vol.% DMSO in IPA at different draw ratios from 1.58 to 2.36.