Supplementary

Inelastic relaxation inside PEDOT:PSS

The criterion of the conductivity profile in PEDOT:PSS is the positive temperature coefficient $\frac{\mathrm{d}\sigma_T}{\mathrm{d}T}$ of the conductivity. This profile is not to be mixed with a semiconductor-type transport based on thermal activation and an exponential decay with the exponent $\frac{E_\mathrm{a}}{kT}$, which would yield a dramatic drop in σ when $E_\mathrm{a} \ll kT$. This is obviously not the case in PEDOT:PSS (see figure 1C). The profile here is non-exponential - this is particularly visible as $T \longrightarrow 0$ (weak localization). PEDOT:PSS (ie. with 5% DMSO) can be understood as highly-doped semiconductor at the metallic side of the metal-to-insulator transition. In these metallic systems with a certain amount of disorder present *inelastic* scattering dominate the relaxation processes. Consequently the inelastic mean scattering path λ_ϵ exceeds the elastic mean scattering path λ.

$$\lambda_\epsilon \gg \lambda \tag{1}$$

Inelastic relaxation implies a positive coefficient as shown for similar metallic disordered systems such as amorphous metals, highly-doped metallic semiconductors and metallic polymers. At low T the system thereby approaches a conductivity minimum σ_min (Mott's minimum conductivity), which is defined as a T-independent point (with a consequent turn in the sign of the coefficient) with the situation that the elastic processes become dominant again. Directly at the minimum the mean free electron scattering length of inelastic and elastic processes are similar $\lambda_\epsilon = \lambda$.

From figure 1C we see a positive coefficient throughout the measured T-regime from 300 K to 1.8 K. We therefore cannot derive a concrete value for σ_{min}. This also implies, that the condition from equation 1 is valid in all our experimental data. We underline our statement in figure 3A by showing W ($= \frac{\mathrm{dln}\sigma}{\mathrm{dln}T}$) over T. We see a positive W(T) slope (further denoted as γ), which is regarded as signature for a metallic transport beyond the MIT. We fit W in the 5% DMSO PEDOT:PSS linearly according to

$$\log W = \text{constant} - \gamma \cdot \log T \tag{2}$$

where γ represents the mentioned W(T) slope with a positive value of 0.53 (figure S1). In the sample at the MIT (2% DMSO) we find $\gamma = 0.25$, which rather implies that we are close to the transition regime.

Addendum morphology

We added here the AFM topographies corresponding to the phase images in the body text.

The XRD-spectra in figure 2F show PEDOT:PSS grown at various DMSO concentrations. In order to help to assign the peaks - in partiuclar the ones emerging from π-stacking and PSS, respectively - we add the response of rr-P3HT (regio-regular poly(3-hexylthiophene) in the background. The stacking peak has a fingerprint response around 25 deg (indicated in the graph). This has to be separated in PEDOT:PSS from the halo emerging at 20 deg. We denote, that also because of the overlapping PSS and PEDOT peaks, it is difficult to read out parameters here.

References

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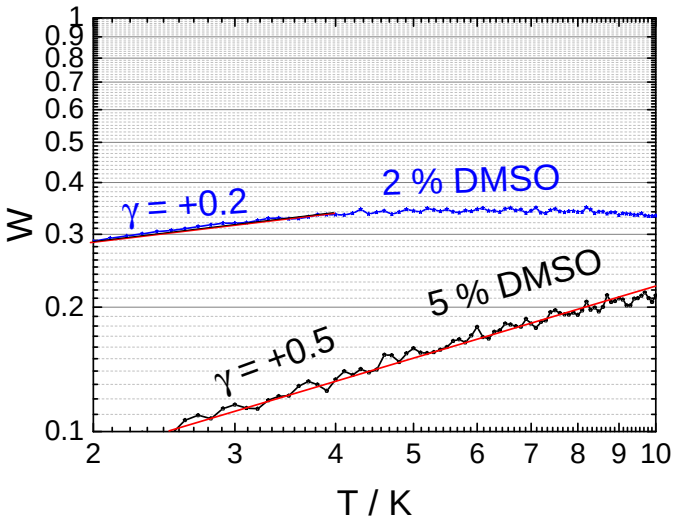

Figure 1: In addition to the results presented in figure 3A,B we add here the slope analysis of the W-plots without magnetic field to underline the metallic character of PEDOT:PSS with a positive exponent γ of 0.5 and 0.25 for the two representative samples.

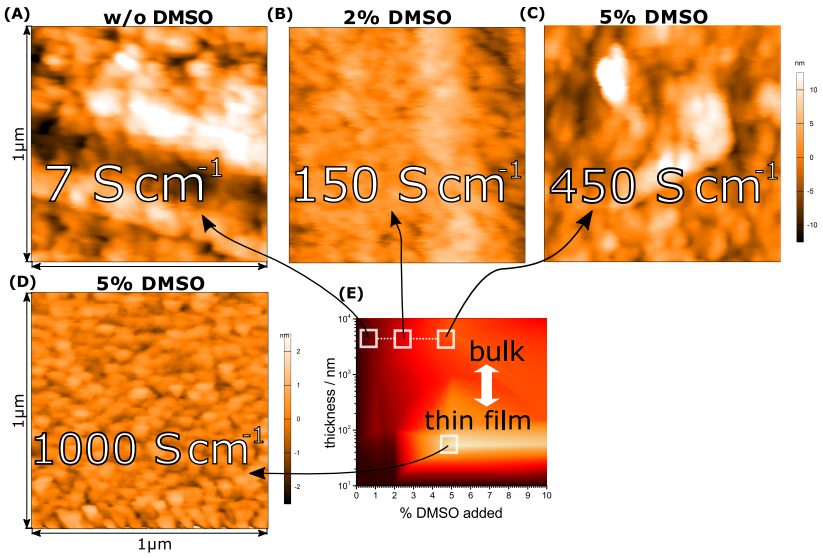

Figure 2: In the panels (A,B and C) the cross-section and surface (D),**(1)** morphologies by AFM of bulk-film PEDOT:PSS at **(ref)**, 2% **(4)** and 5% DMSO **(2)** are shown by their topographies (in addition to the phase images are in the figure 2).

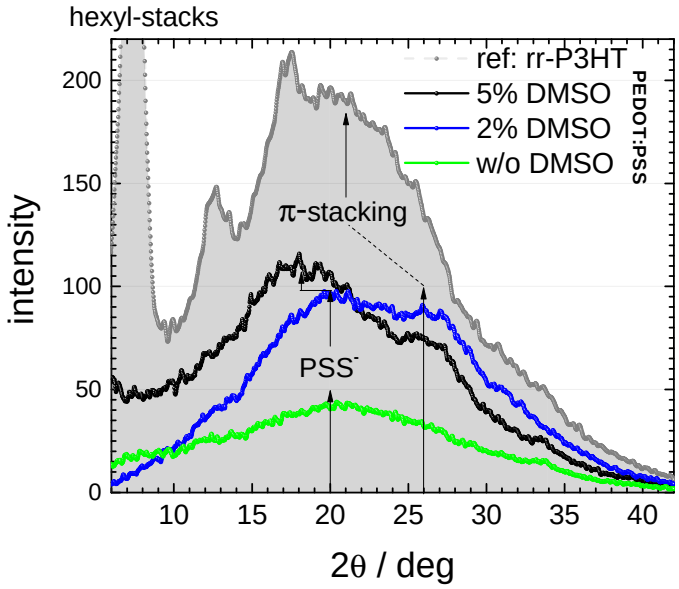

Figure 3: The XRD-spectra of PEDOT:PSS samples with different growth condictions in front of a rr-P3HT spectrum helping to separate between PSS halo and π-stacking.

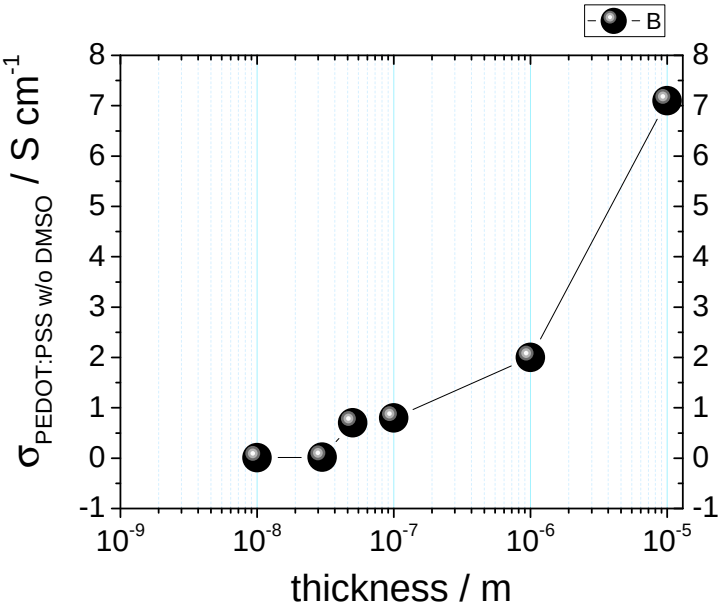

Figure 4: The conductivity of PEDOT:PSS without DMSO (**ref**) changes with the thickness. This profile is shown in the graph.