Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic supplementary information for

Unraveling Vertical Inhomogeneity in Vapour Phase Polymerized PEDOT:Tos Films

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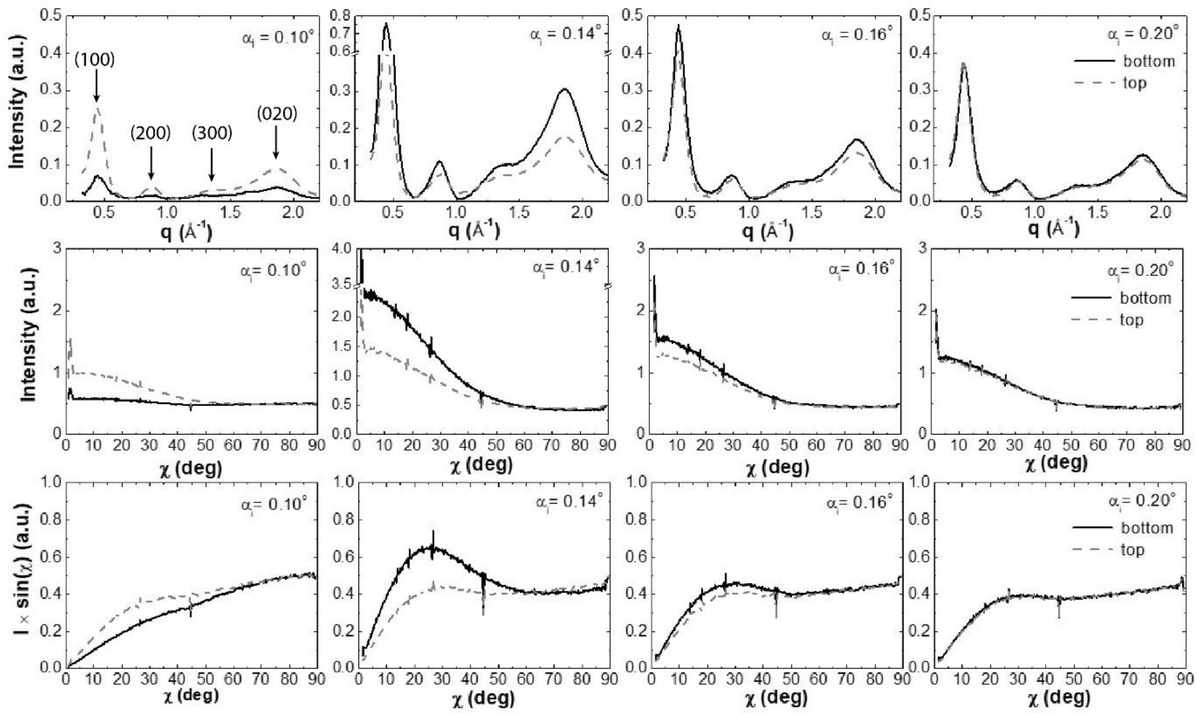

Figure S1 1D GIWAXS data acquired at the bottom (flipped sample) and top (original sample) surfaces of the VPP PEDOT:Tos films, at 0.10°, 0.14°, 0.16° and 0.20° angle of incidence. **First row:** the 1D scattering patterns calculated after radial integration of the corresponding 2D GIWAXS images. The diffraction peaks are indicated. **Second row:** the polar plots (Intensity *versus* polar angle χ) calculated at the (100) peak. **Third row:** the corresponding corrected I × sin(χ) *versus* χ plots. In all cases data are presented after background correction.

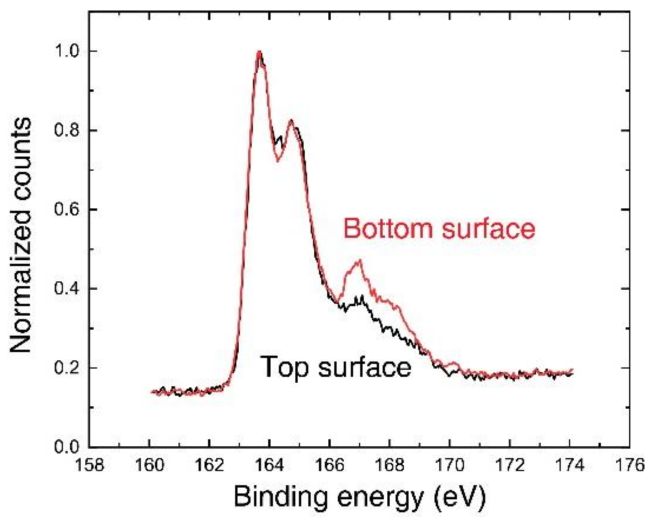

Figure S2 S(*2p*) XPS spectra for top (black curve) and bottom (red curve) surfaces of thin films without post-annealing step. The results indicate that the bottom surface has a higher oxidation level than the top surface.

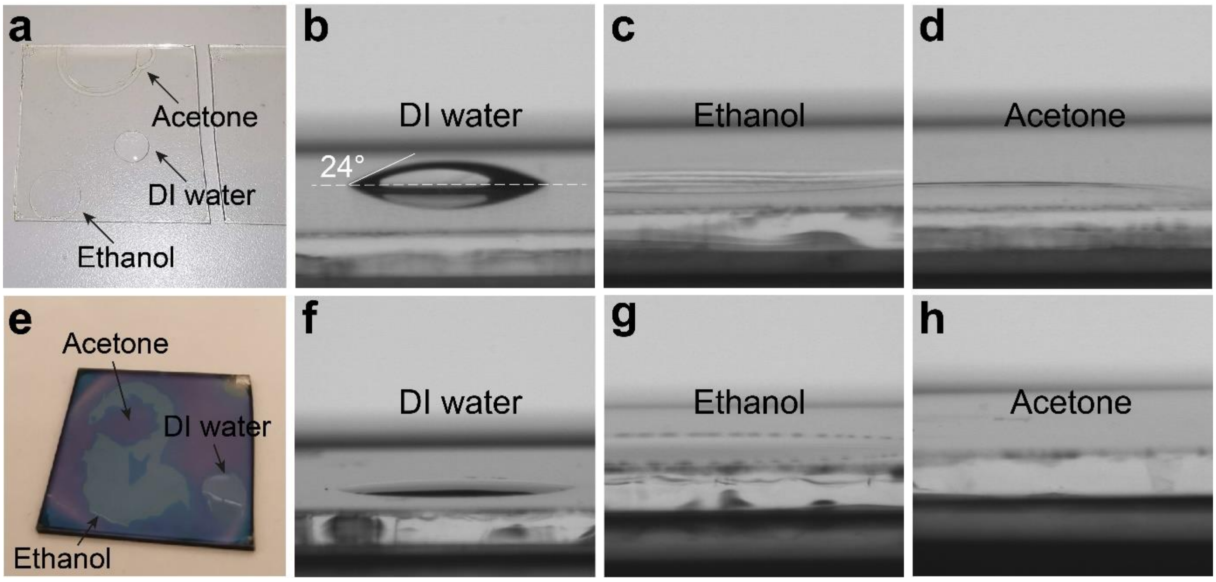

Figure S3 Contact angle measurements of oxidant (**a-d**) and PEDOT films (**e-h**). Image of de-ionized (DI) water, ethanol, and acetone droplets on oxidant (**a**) and PEDOT films (**e**). Ethanol and acetone can dissolve the oxidant film and evaporate rapidly on PEDOT film. **b-d**, Contact angle measurement of oxidant film with DI water (**b**), ethanol (**c**), and acetone (**d**) droplets. The contact angle of DI water on oxidant film is 24°. **f-h,** Contact angle measurement of PEDOT film with DI water (**f**), ethanol (**g**), and acetone (**h**) droplets. The small contact angle of DI water on PEDOT film can hardly be calculated.

Calculation of estimated X-ray penetration depth in PEDOT:Tos thin film

In order to provide estimates of the layer thicknesses probed at the 4 angles of incidences studied herein, we calculate below the X-ray penetration depth as a function of the angle of incidence, α_i . The penetration depth, Λ, is defined as the depth at which the intensity is reduced by 1/e. We follow the formalism reported by Parratt[1]. For a medium with X-ray refractive index $n = 1 - \delta - i\beta$ (δ and β parameters are the dispersion and absorption components of the complex refractive index), the penetration depth is:

$$\Lambda = \frac{\lambda}{4\pi B} = \frac{\lambda}{4\pi}\frac{\sqrt{2}}{\sqrt{\sqrt{({\alpha_i}^2 - {\alpha_c}^2)^2 + 4\beta^2} - {\alpha_i}^2 + {\alpha_c}^2}}$$

Where λ is the X-ray wavelength and α_c is the critical angle of the medium, with $\alpha_c = \sqrt{2\delta}$. Assuming homogeneous PEDOT:Tos with typical oxidation level of 33 %[2], the penetration depth of a beam with λ = 0.98 Å evolves as shown in **Figure S4** (the results are only slightly dependent on the oxidation level). At α_i = 0.10° less than 10 nm principally contribute to scattering, while at α_i = 0.20° the whole thickness of the film (that is 150 nm) contributes. At α_i = 0.16° the calculated penetration depth is larger than the actual thickness of the film, however the experimental data recorded at this angle for the original and the flipped films do not collapse (as is the case at α_i = 0.20°), showing that in reality the thickness that is probed is less than the total thickness of the film.

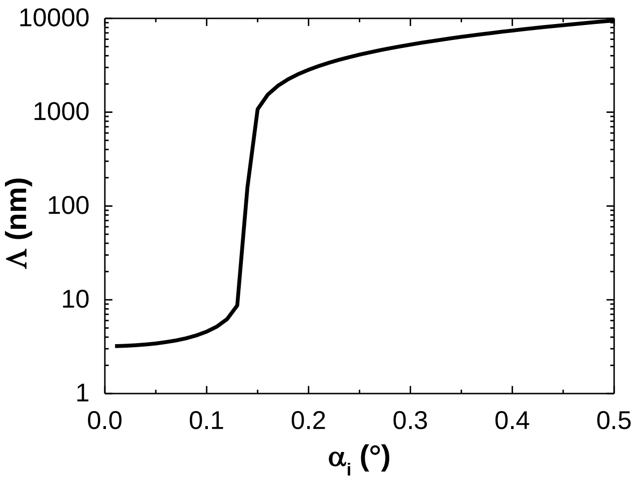

Figure S4 Penetration depth as a function of the angle of incidence, calculated for a X-ray beam of λ = 0.98 Å that probes a homogeneous PEDOT:Tos at the grazing geometry.

References

1. L. G. Parratt, *Physical review*, 1954, **95**, 359.
2. D. Kim and I. V. Zozoulenko, *The Journal of Physical Chemistry B*, 2019.