Supporting Information for
Metallic Behaviour in Acid Doped Highly Conductive Polymers

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Polymer synthesis and parameters

The deposition and synthesis of PEDOT:OTf are described in the experimental section. The polymerization parameters were chosen according to previous work from Murphy et al.[1–4] The effects of the addition of PEG-PPG-PEG to the solvent have been widely described in their work. The polymerization occurs from temperature as low as 30 °C. However, such low temperatures result in low values of electrical conductivity and/or thicknesses. Figure S1 shows σ obtained for various polymerization temperatures from 40 °C to 90 °C. In the experimental conditions, the highest σ (1218 S cm^{-1}) is reached for a polymerization temperature of 70 °C.

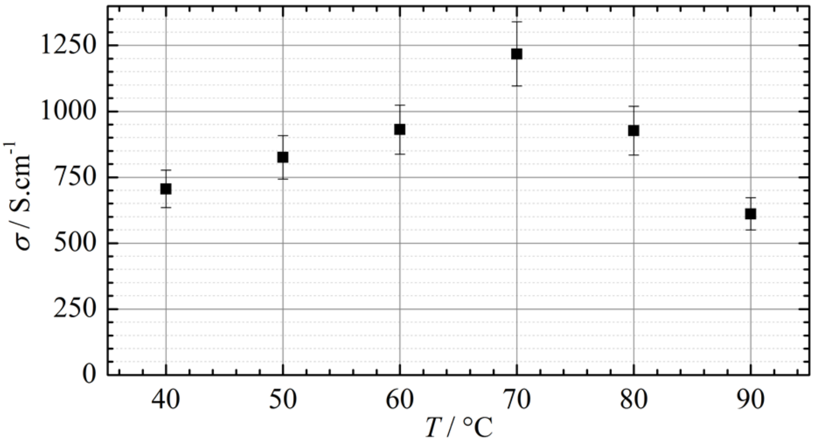

Figure S1. Conductivity of PEDOT:OTf thin films as a function of the polymerization temperature

UV-Vis-NIR spectrometry

The UV-Vis-NIR spectra of PEDOT:OTf layers treated with different acids are presented in figure S2. The treatment of PEDOT:OTf layers with H_2SO_4 or TfOH solutions (pH 1) results in an increase of the absorbance in the BP band and a slight decrease of absorbance in the RC band which is consistent with the enhancement of σ. Treating the layer with TsOH increases the absorbance of in the RC and in the BP bands whereas HCl and HNO_3 treatments decrease the absorbance in the BP band with an increase of the absorbance in the RC band. HCl and HNO_3 treatments also induce a downshift of σ consistently with the spectrometric data.

The inferred doping effect is the insertion of charge carriers in the polymer layer. Therefore the "de-doping" effect induced by HNO_3 and HCl is linked to a partial disappearance of these charge carriers achieved by removal of a fraction of the OTf anions initially located in the layer. Further experiments necessary to ascertain the actual reaction mechanism are beyond the scope of this communication.

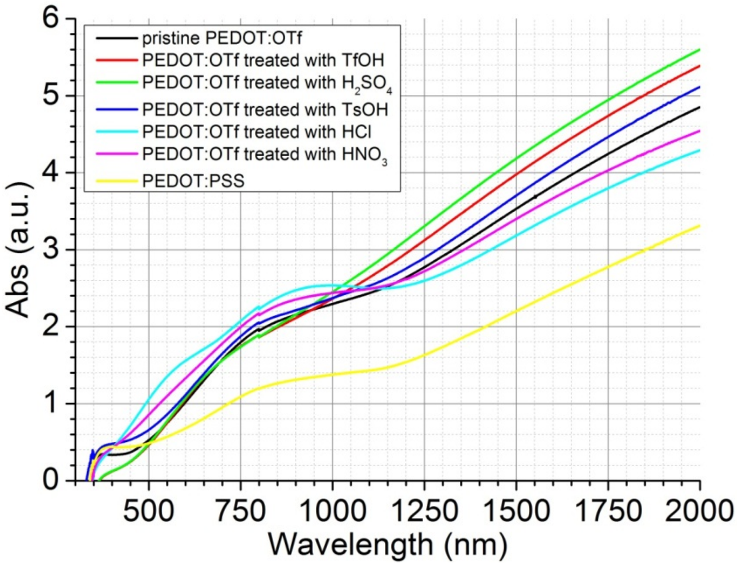

Figure S2. Absorption spectra of a PEDOT:PSS layer and several PEDOT:OTf layers treated with different species. Absorbance is divided by the thickness value of the layer.

XPS spectrometry

Figure S3 shows the overview spectra of PEDOT:OTf, PEDOT:OTf doped with TfOH and PEDOT:Sulf. TfOH doping results in an increase of the F(1s) signal. Upon doping with H_2SO_4, the F(1s) signal disappears, thus showing that OTf ions are withdrawn from the layer.

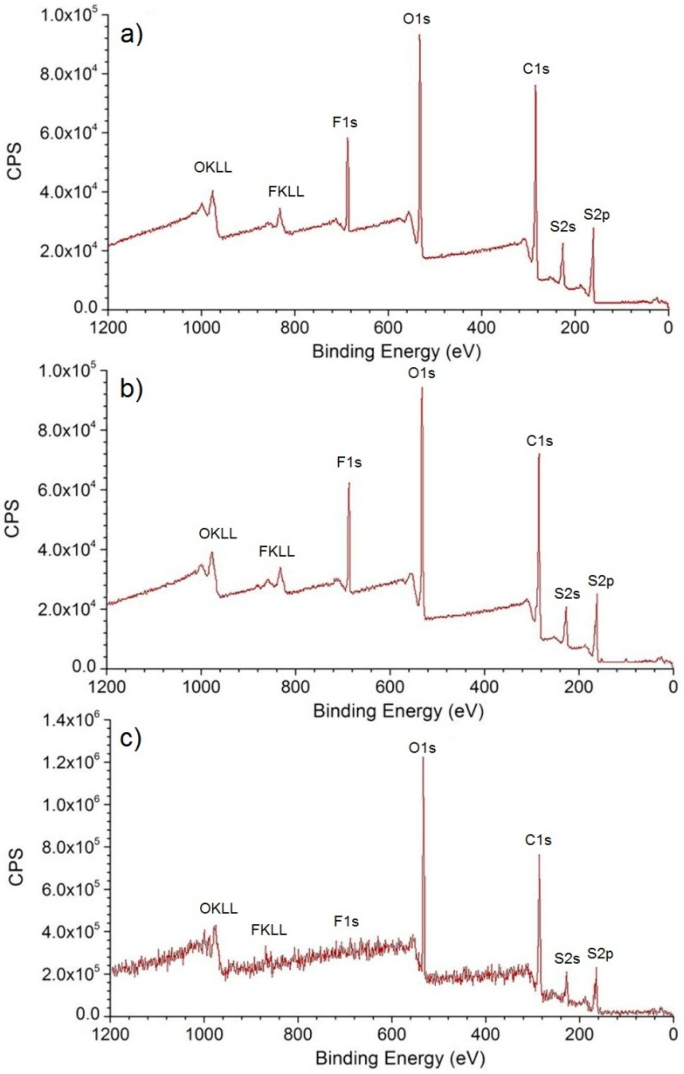

Figure S3. Overview Spectra of a) PEDOT:OTf ; b) PEDOT:OTf doped with TfOH; c) PEDOT:Sulf

SAXS measurements

The X-ray beam was collimated, and K_α/K_β filtered, using two (vertical and horizontal) Ni-coated focussing mirrors working at grazing incidence in condition of total reflection. The X-ray patterns were recorded on a large area (18 cm x 18 cm) multi-wire gas filled detector, with a sample-detector distance of 20 cm corresponding to a scattering vector range 5 x 10-2 $Å^{-1} < q < 2$ $Å^{-1}$ [$q = 4\pi \sin(\theta)/\lambda$, with θ the half-scattering angle and λ the wavelength]. As the X-ray patterns were isotropic, the diffraction patterns I(q) were obtained by reduction of the two dimensional data by radial integration of intensities from the centre of the direct beam after correction for background scatter recorded from the empty camera. The data were normalized for the incoming X-ray flux, the sample transmission, and the sample thickness. Silver behenate was used as a standard sample for q calibration. All samples had a thickness of typically 1 mm and were studied as freely suspended in the X-ray beam.

Charge carriers properties

The properties of the charge carriers are measured in an organic electrochemical transistor (OECT) accordingly to the method described by Ishida et al.[5]. This consists in fabricating a thin-film transistor using the polymer as channel and an ionic gel for the gate. Source and drain gold electrodes (50 nm thick) are sputtered through a shadow mask. The conductive polymer layer is spin-coated upon the electrodes (directly from the Clevios PH1000 for PEDOT:PSS and from the precursor solution, then polymerized at 70 °C and washed with ethanol for PEDOT:OTf) then trimmed to fit the drain/source dimensions. A silver paste droplet is cast and dried in the vicinity of the channel to serve as gate electrode contact. The ion gel is fabricated as reported by Frisbie et al. by mixing poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) with 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl) amide ([EMIM][TFSI]) in acetone, then drop casting the resulting solution on a glass substrate.[6] Once dried overnight in an oven under vacuum at 80 °C the dried ion gel is trimmed to fit the channel dimension and put across the gate electrode and the polymer channel. A picture of the OECT and a schematic are presented in figure S4. Pictures of the device in ON and OFF states are shown in the insets a) and b). The bluish coloration upon reduction is characteristic of neutral polymer chains as discussed with the UV-Vis-NIR spectra (NC band around 600 nm). The OECT channel length is 100 µm, its width is 10 000 µm and its thickness is 50 nm. The transfer curves obtained for the OECT with a PEDOT:PSS channel, a PEDOT:OTf channel and a PEDOT:Sulf channel are presented in figure S5. The mobility values extracted from these data in the article are an average value over 5 measurements.

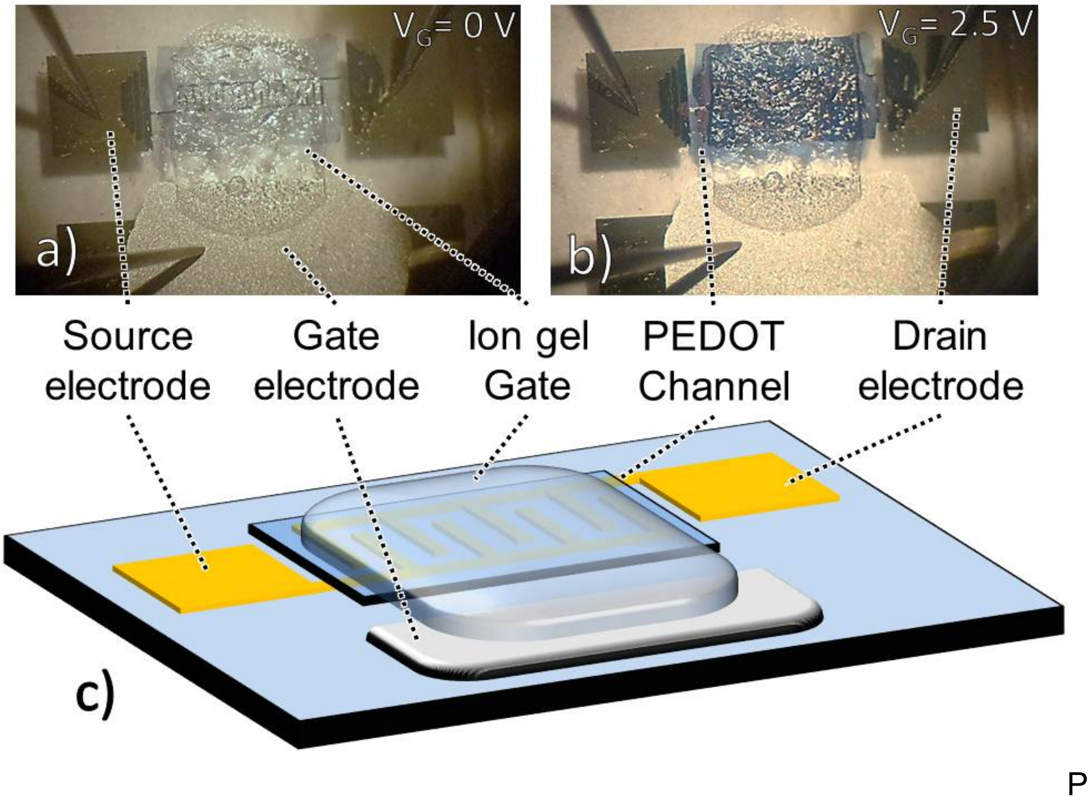

Figure S4. Pictures of the OECT device with a gate voltage of a) 0 V b) 2.5 V. c) Schematic of the device

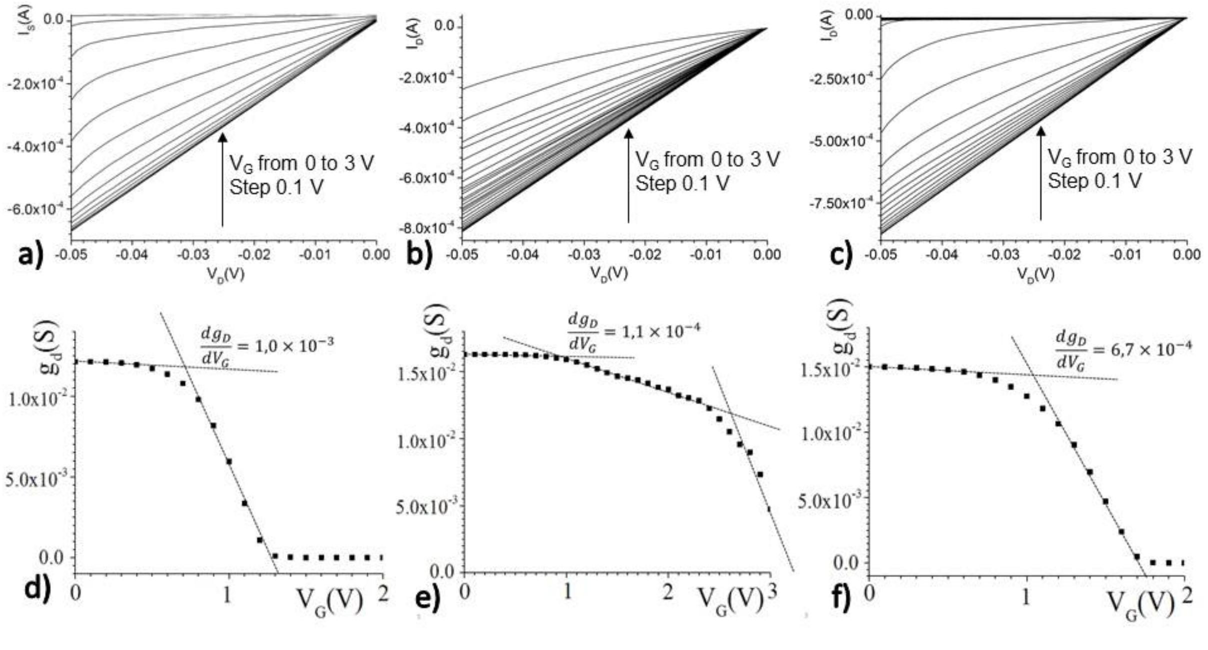

Figure S5. Output curves of OECT with different channel materials a) PEDOT:PSS ; b) PEDOT:OTf ; c) PEDOT:Sulf; conductance as a function of gate voltage for OECT with different channel materials ; d) PEDOT:PSS ; e) PEDOT:OTf ; f) PEDOT:Sulf

Electrical conductivity from 3 K to 325 K

Due to the relatively high value of σ for these materials, the resistance of the samples are small (typ. a few tens of Ohms). As a result, for accurate measurements, several precautions have been taken into account:

- The current has to be sufficiently high to detect a clear voltage drop;
- However, the current must stay as low as possible in order not to modify the sample temperature by Joule heating. In our case, the temperature variation due to this heating was checked to stay below 0.05 K during each measurement at all temperatures;

We measured σ by using the Current-Reversal Method in order to cancel any possible thermoelectric voltage contribution.

References:

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