Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION:
DECOUPLING ORDER AND CONDUCTIVITY IN DOPED CONDUCTING POLYMERS

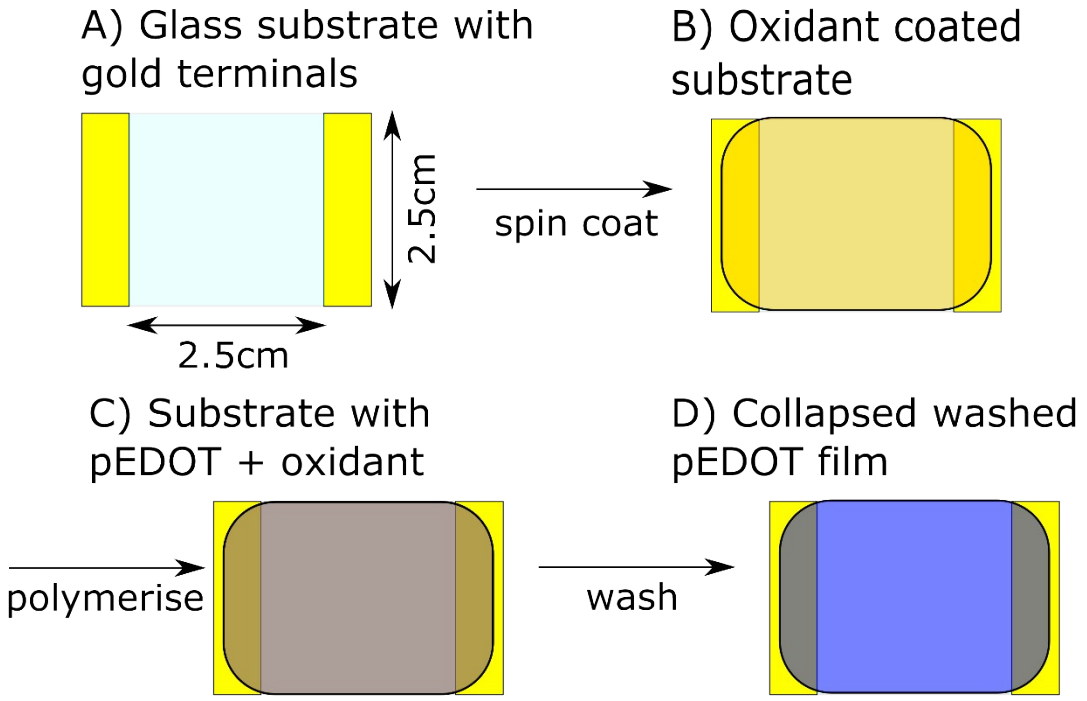

Figure S1 – A schematic of the manufacturing process for pEDOT. It is demonstrated in Figure 1 of the main text that π-stacking and edge stacking only occur at stage D of the process.

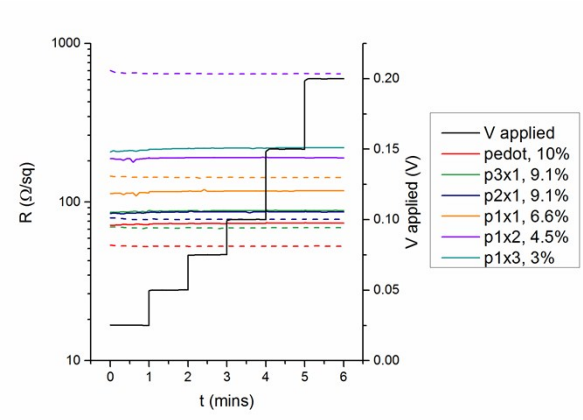

Figure S2 – Resistance before and after ordering for cast samples. This figure is the raw data for Figure 3 of the main text. In this case the data reported is that of the **MOLAR** ratio pEDOT to oxidant (x) in the disordered state of the film as well as in % Vol pEDOT in the unwashed film. Solid lines are the ordered state and dashed lines are in the disordered state.

The raw data for the resistance of samples made by the casting method is shown in Figure S2, molar ratios of pEDOT:oxidant are reported for ease of reproducibility by readers. Figure S2 shows a trend,

where for disordered systems with higher quantities of pEDOT in the film; the film has a lower resistance in the disordered state than the ordered state. However, for lower pEDOT:oxidant ratios, interchain interaction becomes a contributing factor to resistance, in the disordered state.

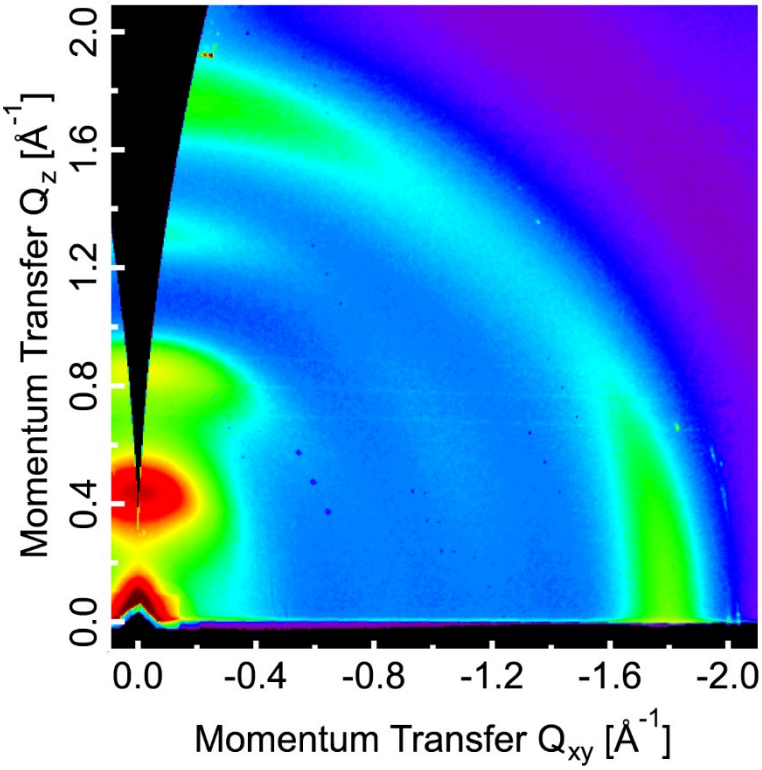

Figure S3 - GIWAXS of ordered cast pEDOT exhibiting the same ordering as that of the VPP samples.

The same ordering is exhibited using the VPP method is also observed when using the casting method.

Table S1 – A table of the calculation of the number of electrons conducted across during resistance test for a the film manufactured by VPP

Electrons moved		
Coulombs	Mols	
0.490	5.08×10^{-6}	
	V of film	
	0.025	m
	0.025	m
	2.2×10^{-7}	m
	1.38×10^{-10}	m^3
Density	1	g/cm^{-3}
mass pEDOT	1.38×10^{-7}	kg
MW EDOT	142	g/mol
Mol EDOT	$9.7E \times 10^{-7}$	mol
Mol oxidant	2.18×10^{-6}	mol
Sum of mol oxidant + EDOT		
	3.15×10^{-6}	mol

Currents are steady during the measurement at each voltage step indicating that no polarization is occurring, demonstrating that the current measured is electronic rather than ionic. The calculation in Table S1 of the amount of charge moved across the film relative to the amount of EDOT and oxidant within the film was made. It was found that for a 0.20 micron film of pEDOT a total of ~ 5×10^{-6} mol of electrons was moved across the film over the 5 minutes. The total amount of EDOT that comprises this film is ~ 0.9×10^{-7} mol. Assuming that the oxidant is fully reacted, the film also has ~2.25* $\times 0.9 \times 10^{-7}$ mol of reacted oxidant. Given that the total amount of oxidant and monomer units that comprises the film is less than the number of electrons that were transferred across the film, over the 5 minute period, it can be concluded that electrical conduction (and not ionic conduction) occurred.

A question to address is whether the electrical measurements themselves affect the film. We suggest that, based on the calculation above where over the period of 5 minutes more moles of electrons are moved across the film than there are moles of Fe-ions + EDOT units in the film in both the washed and unwashed state, that it is not possible for the conduction to affect the film. If indeed this were the case, the film's conductivity would vary drastically during each individual conductivity measurement.

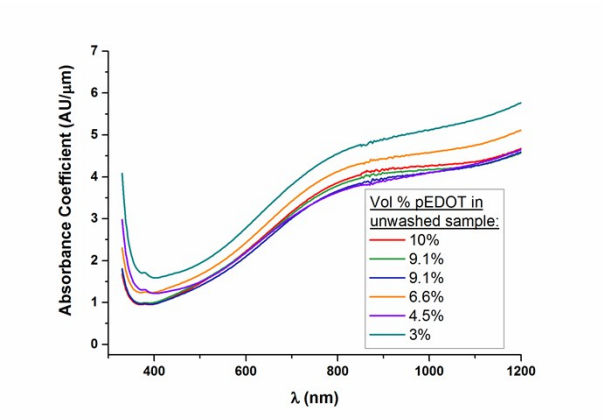

Figure S4 – Absorbance coefficient of ordered cast pEDOT as a function of Vol % pEDOT in the unwashed disordered state.

Upon washing, and consequentially ordering the pEDOT, the absorbance coefficient for all samples made by the casting method, irrespective of the amount of pEDOT manufactured is indistinguishable.

* It is expected that for every 2 Fe(III) PTS 1 monomer of EDOT can be polymerised, it has been measured that some of the oxidant is used up in oxidising the polymer; in particular this results in a 1:2.25 ratio between EDOT units and oxidant[1]

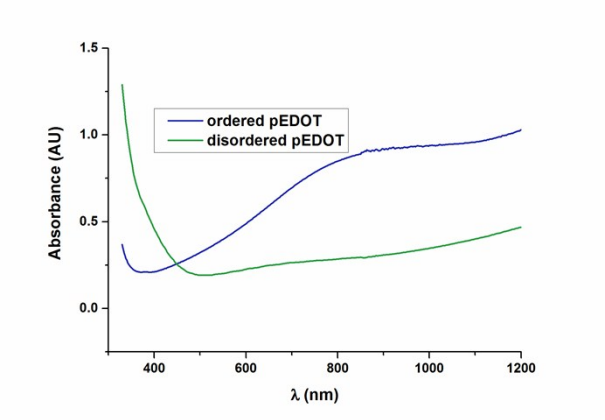

Figure S5 – The optical absorbance before and after ordering for cast pEDOT.

The optical absorbance of pEDOT, manufactured via the casting method shows identical absorbance character to that which is manufactured by VPP as seen in Figure 3 of the main text.

REFERENCES:

1. Aasmundtveit, K. E. *et al.* Structure of thin films of poly(3,4-ethylenedioxythiophene). *Synth. Met.* **101,** 561–564 (1999).