3.4 Supporting Information

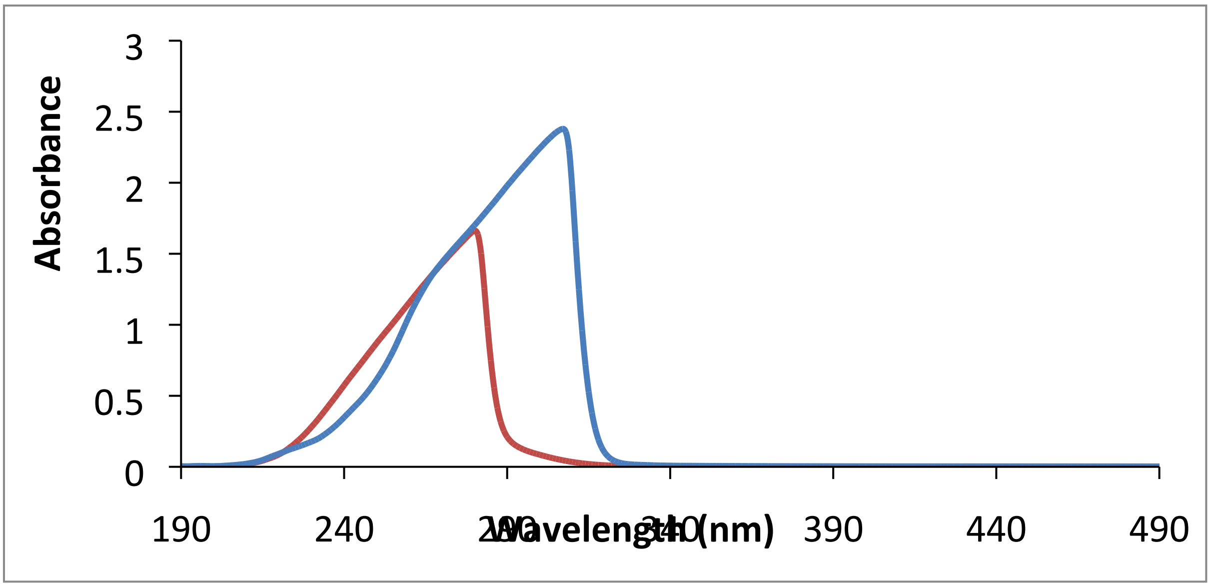
S1. Experimental

UV-Visible spectra were obtained using a Jasco V-670 spectrophotometer scanning samples at 1000 nm/min between 1500-300 nm. While Raman acquisitions between 3200-100 cm^{-1} were taken using a Renishaw inVia Raman microscope, stimulated by a 514 nm coherent green laser running at ~35.0 A, 0.362 W with a sample contact of 5-10 mW. Samples for both UV-Visible and Raman spectroscopy were prepared on glass substrates using the polymerisation techniques described above.

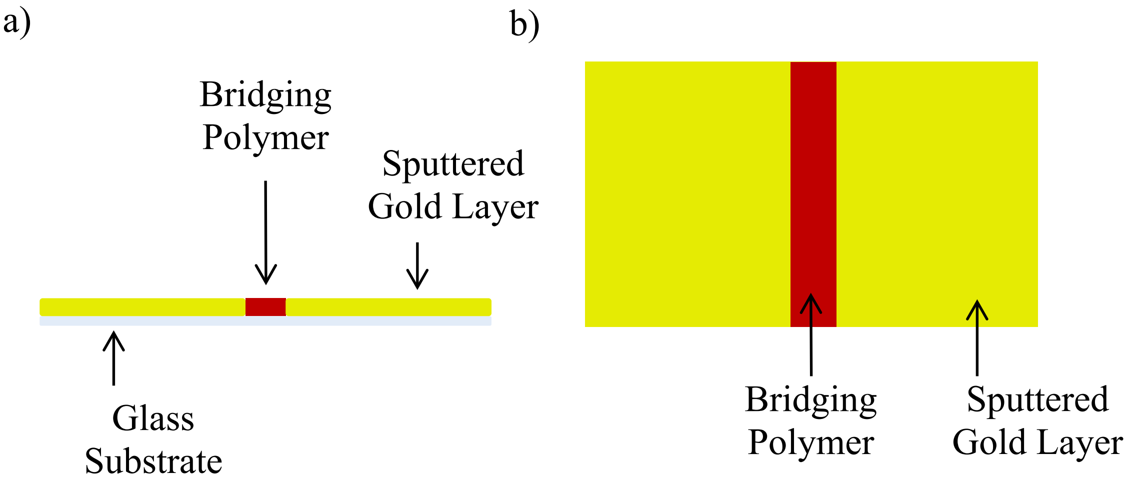
Chronoamperometry scans were used to measure the current at several potentials *via* a two-electrode setup to calculate the conductivities of each polymer. The scans were conducted step-wise on a glass substrate which was sputter coated with a gold layer. A 0.2 cm x 2.0 cm gap in the gold layer was bridged by a PTT or PDTT film synthesised *via* VPP shown in S3.

The cyclic voltammetry used for characterisation was based upon Corrandini, A., *et al.* and used a 1 M $LiClO_4$/PC electrolyte[1, 2]. A platinum reference electrode was used however; it is known that platinum suffers from potential drift in organic electrolytes. To overcome this Ferrocene was added but was found to co-ordinate with the conducting polymers in-situ. Subsequently, a pseudo reference was obtained *via* a separately run CV containing Ferrocene vs platinum to obtain the Ferrocene (Fc^+/Fc) redox spectrum (0.64 V vs. SHE) relative to the cell setup. Subsequently, the Pt vs Fc/Fc pseudo reference electrode was used for the characterisation of the polymer samples.

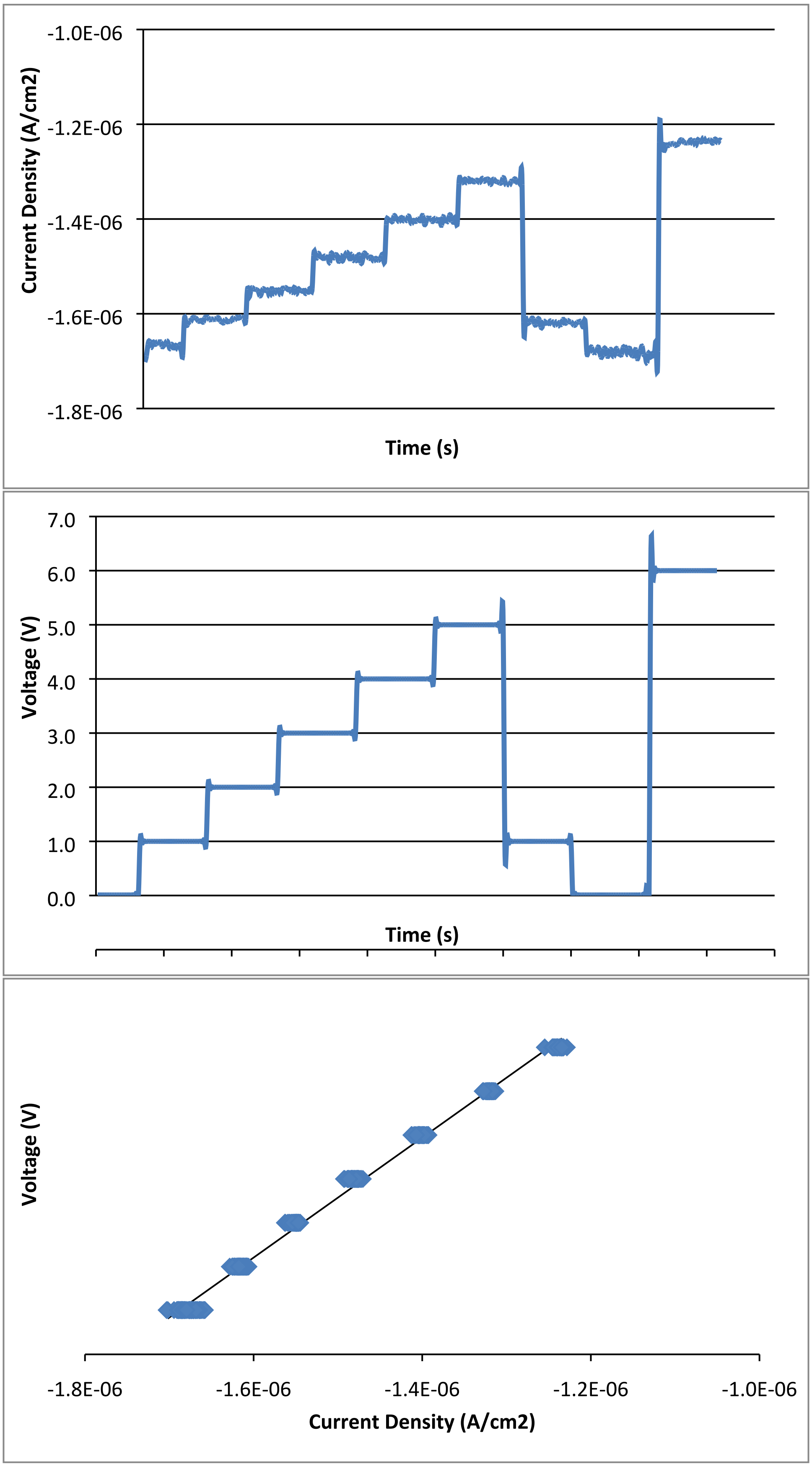
Scanning Electron Microscopy (SEM) imagery were taken to compare the surface morphologies achieved *via* the different polymerisation methods. Samples were polymerised on fluorine-doped tin oxide (FTO) substrates which were then coated with a thin layer of gold. SEM images were obtained using a JEOL 7100F Field Emission Gun SEM at 5 kV.



S2. Monomer UV-Vis spectra both dissolved in BuOH in a quartz cell, thieno[3,2-b]thiophene (TT) (red) and dithieno[3,2-b:2',3'-d]thiophene (DTT) (blue).



S3. a) Side view and b) top view of the working electrode setup for the two-electrode step-wise conductivity measurements.



S4. a) CA of PTT_{VPP} held at various potentials, b) applied potential at arbitrary time intervals and c) current output vs applied voltage to calculate resistance from Ohm's law.

S5. <u>Calculating conductivity of PTT$_{VPP}$</u>

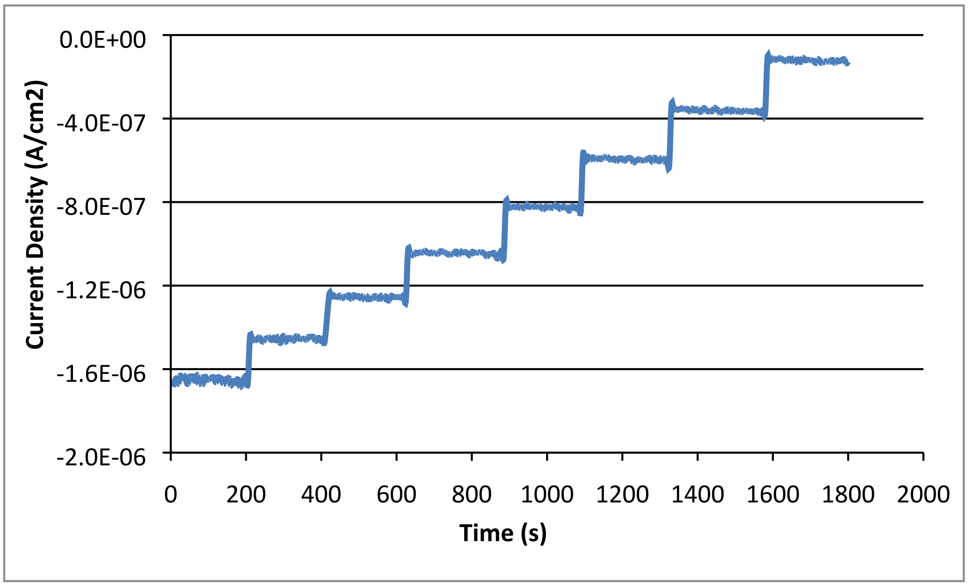
Resistance = 13671365.4 Ωcm

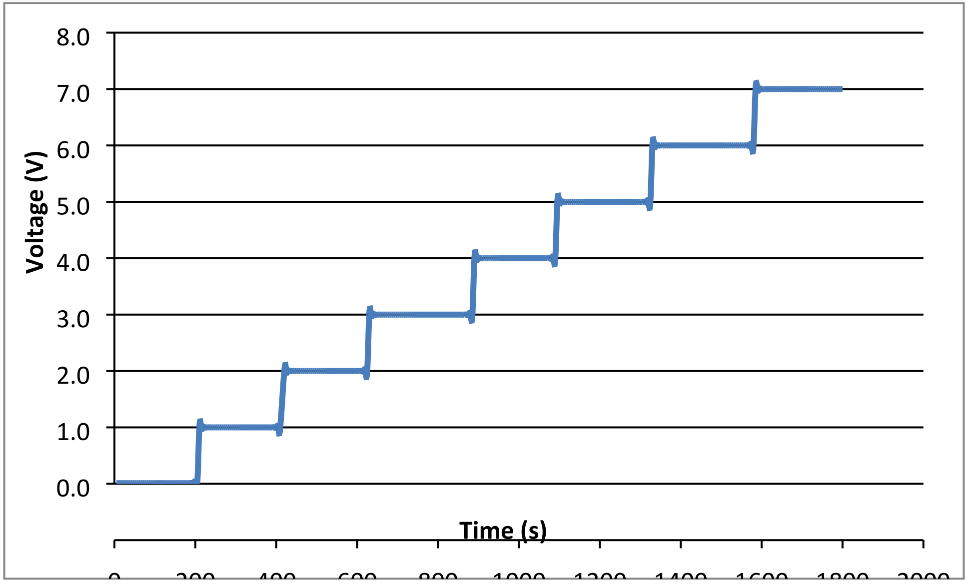
Film thickness = 9.23 x 10^{-5} cm

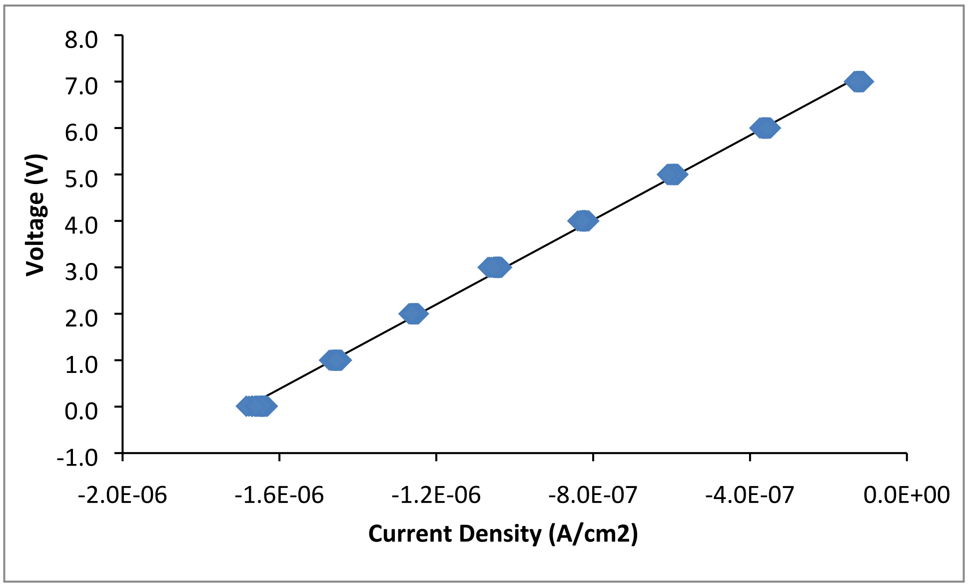
Film length = 2.0 cm

Film width = 0.2 cm

Conductivity = 7.9 x 10^{-5} S/cm







S6. a) CA of $PDTT_{VPP}$ held at various potentials, b) applied potential at arbitrary time intervals and c) current output vs applied voltage to calculate resistance from Ohm's law.

S7. Calculating conductivity of $PDTT_{VPP}$

Resistance = 4552304.1 Ωcm

Film thickness = 1.16×10^{-4} cm

Film length = 2.1 cm

Film width = 0.2 cm

Conductivity = 1.8×10^{-4} S/cm

3.5 References

1. R. Danieli, C. Taliani, R. Zamboni, G. Giro, M. Biserni, M. Mastragostino and A. Testoni, *Synthetic Metals*, 1986, **13**, 325-328.
2. A. Corradini, M. Mastragostino, A. S. Panero, P. Prosperi and B. Scrosati, *Synthetic Metals*, 1987, **18**, 625-630.