Supplementary data for *Phys. Chem. Chem. Phys.*

Spectroelectrochemical Responses of Thin Film Conducting Copolymers Prepared Electrochemically from Mixtures of 3,4-Ethylenedioxythiophene and 2,2-Bithiophene

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Supplementary XPS data:

XPS data for polymers prepared electrochemically from a mixture of octylthiophene (OT) and EDOT are presented in **Figure 1**. Similar data for polymers prepared from a mixture of terthiophene (TT) and EDOT are presented in **Figure 2**. The two systems in combination with EDOT show contrasting behaviour. In the case where octylthiophene (OT) is the other component of the binary mixture **Figure 1** shows that the spectra of the polymer films grown from mixtures weighted with OT *e.g.* X_{EDOT} = 0.1 (X_{OT} = 0.9), are almost indistinguishable from those of the pure PEDOT holompolymer (X_{EDOT} = 1.0). This indicates that very little (if any) OT is incoporated into a copolymer grown this way from a binary mixture with EDOT.

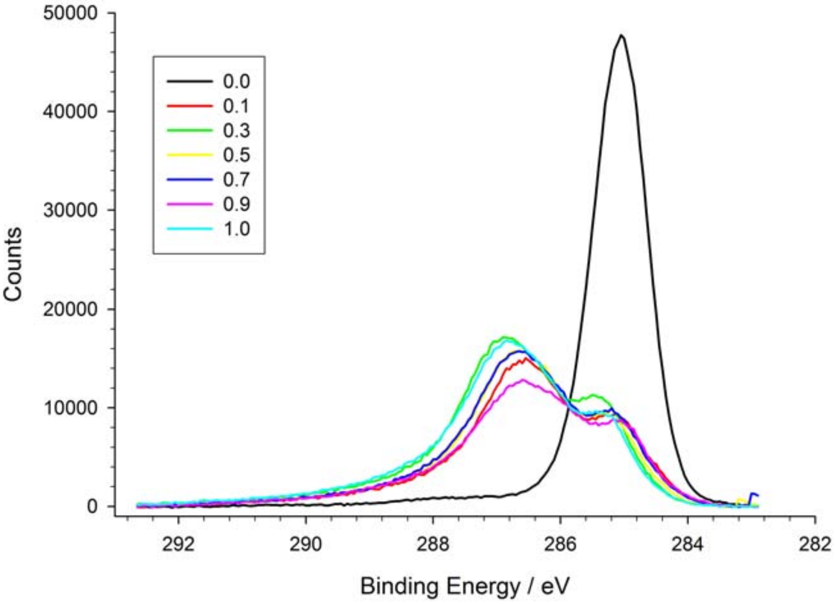

Fig. 1: XPS data, C(1s), for the series of polymers grown from solutions containing octylthiophene (OT) and EDOT. The legend refers to the mole fraction of EDOT, X_{EDOT}, in the solution from which the polymer was grown.

In contrast where terthiophene (TT) is the other component of the binary mixture **Figure 2** shows that the spectra of the polymer films grown from mixtures weighted with EDOT *e.g.* X_{EDOT} = 0.9 (X_{TT} = 0.1) are very similar to the pure homopolymer of TT.

In both of these cases it is clear that the reactivites of the two other components of the binary mixture (OT or TT) towards polymer formation are very different to that of EDOT such that in one case (OT) the film consist s mostly of EDOT whilst in the other (TT) EDOT is all but excluded.

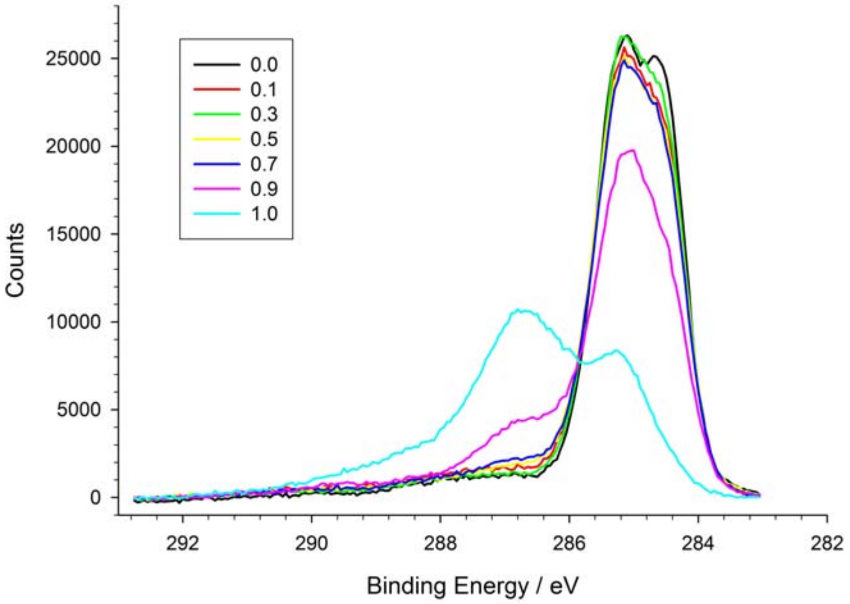

Fig. 2: XPS data, C(1s), for the series of polymers grown from solutions containing terthiophene (TT) and EDOT. The legend refers to the mole fraction of EDOT, X_{EDOT}, in the solution from which the polymer was grown.

An intermediate scenario is observed for bithiophene (BT) EDOT mixtures that is described in the main manuscript.

Supplementary AFM data:

The thicknesses of polymer films and underlying gold metal was quantified using high resolution taping mode AFM measurements. Typically the gold thickness was measured by lifting a portion of the gold surface from the substrate with adhesive tape and then measuring the step height. The polymer thickness was measured in a similar way by scoring of the polymer. On occasion it was possible to quantify the thickness of both gold and polymer on the substrate using AFM techniques and a single line trace from such a determination is shown in **Figure 3**. Here the gold step is *ca.* 25-30 nm above the quartz substrate and the polymer deposit is *ca.* 70 nm above the gold. This dual measurement was to some extent facilitated by the thin polymer. Of additional interest here is the roughness of the polymer at the edge; this is considerably greater than at the bulk surface of the polymer. Here it is likely that during the action of scoring (surface scratching) the polymer surface (to make a measurement step-edge) particulate material and high energy polymer fragments have remained adhered to the surface.

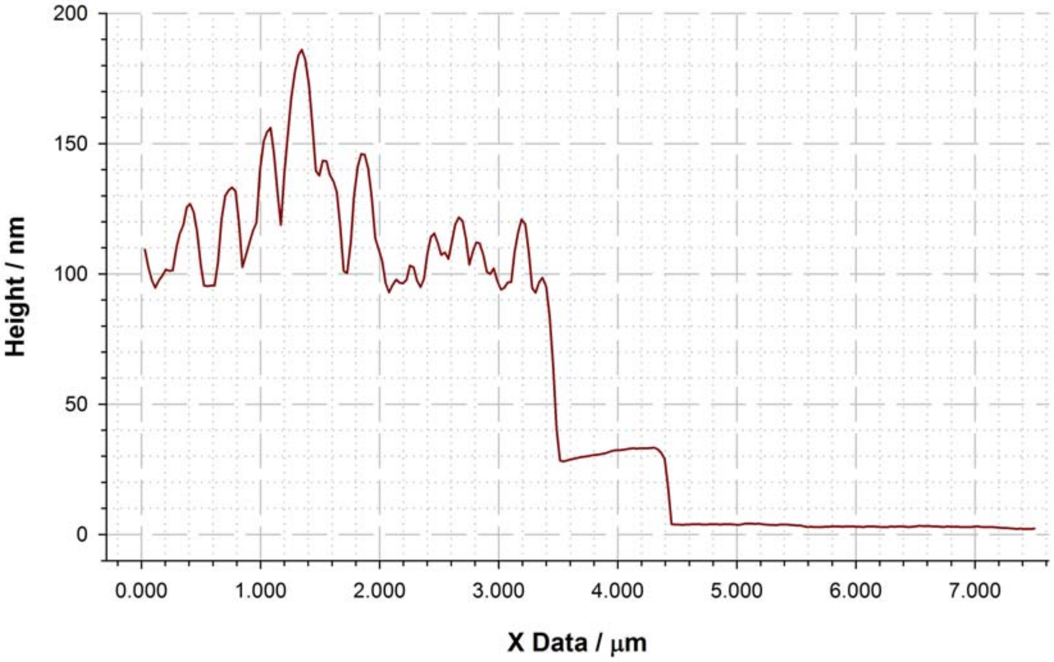

Fig. 3: Homopolymer of PEDOT deposited on a Au layer evaporated onto a quartz substrate. The line trace was recorded as part of an image on a Veeco Nanoscope IV, Dimension 3100 AFM instrument operated in tapping mode.