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Supplementary information for Structure-function relations in diF-TES-ADT blend organic field effect transistors studied by scanning probe microscopy

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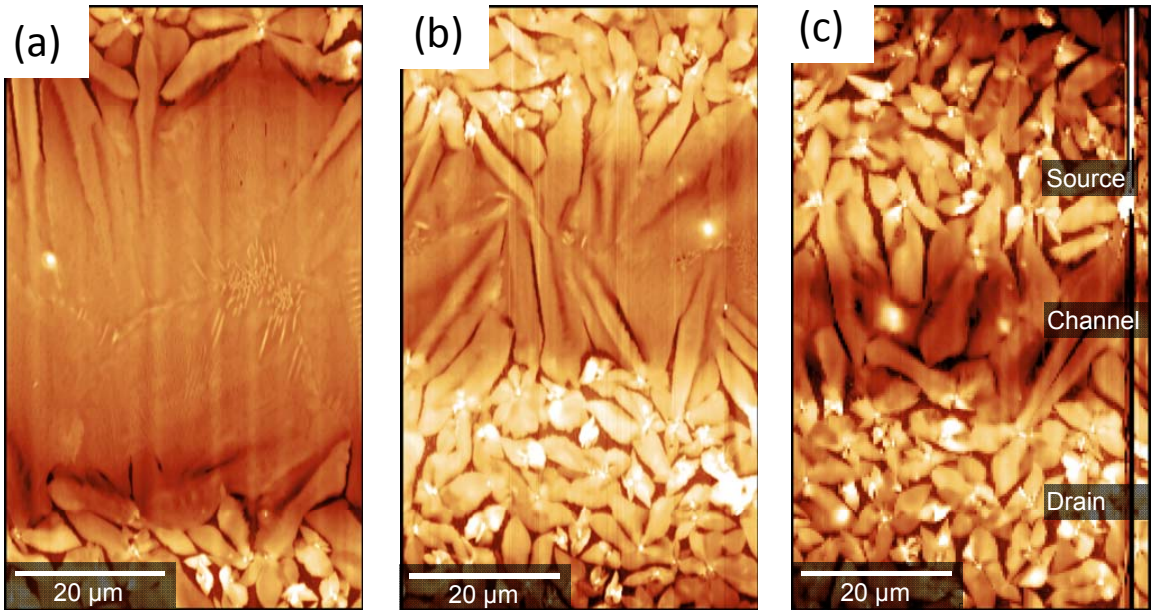

Figure S1 *AFM topography images of the channel region of different channel length devices with (a) L = 50 µm, (b) L = 20 µm and (c) L = 10 µm. In the L = 50 µm device, large domains form, resulting in a well-connected and nearly continuous film in the channel centre. In the shorter L devices much smaller domains are formed, with large boundaries between them. In the case of L= 10 µm in particular, the crystallites resemble those formed on top of the electrodes and are poorly connected across the channel. This poor connectivity and presence of large domain boundaries relative to the 50 µm devices likely play an important role in degrading the performance of the 20 and 10 µm devices.*

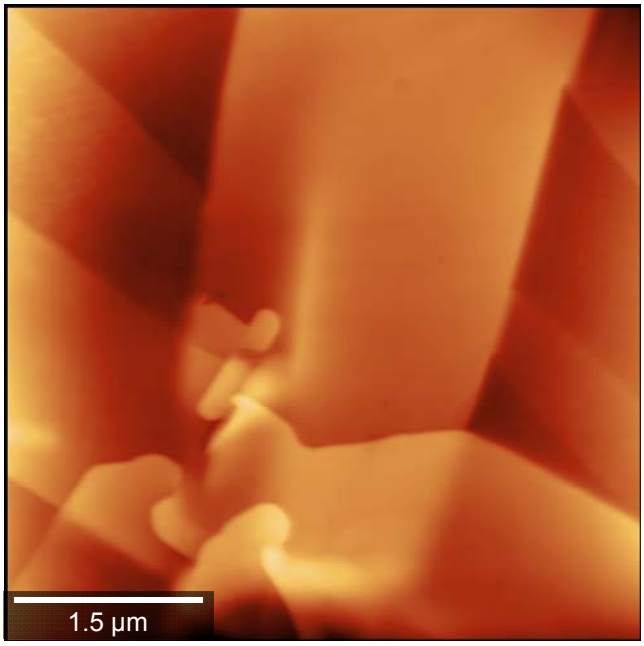

Figure S2 *Reference devices using TIPS-PEN as the small molecule semiconductor were fabricated in exactly the same manner as the diF-TES-ADT devices. The figure is an AFM topography image of a region atop the electrode. Long lathe-like TIPS-PEN crystals were observed extending from the source/drain electrodes. Unlike the petal-like diF-TES-ADT crystallites that can be seen in an analogous region in Figure 5, these crystallites are much narrower and no obvious nucleation centre can be discerned.*

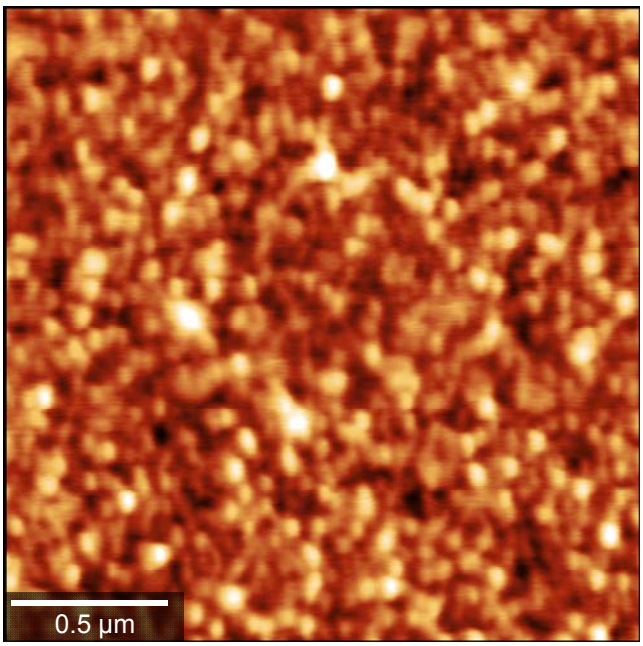

Figure S3 *AFM topography image of the polycrystalline Ag electrode deposited on the dielectric. Small crystallites can be seen to decorate the majority of the image and have a number density of 70* μm^{-2}.

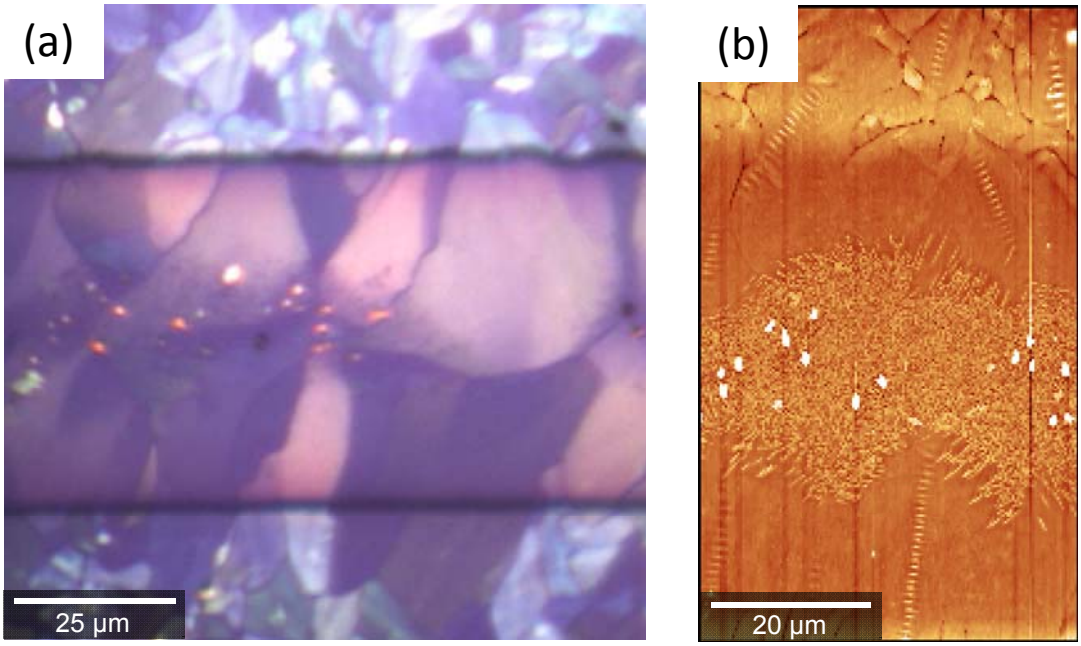

Figure S4 (a) *Polarised optical micrograph of the channel region of a device prepared without PFBT treatment of the Ag electrodes. (b) AFM topography image of a similar region. Relative to the PFBT-treated devices, a much larger band of needle-like crystallites can be seen along the channel centre, consistent with the diminishment of the birefringence in that can be seen in the optical micrograph. A number of 3D crystals corresponding to region D of Figure 4 can also be seen along the channel centre.*

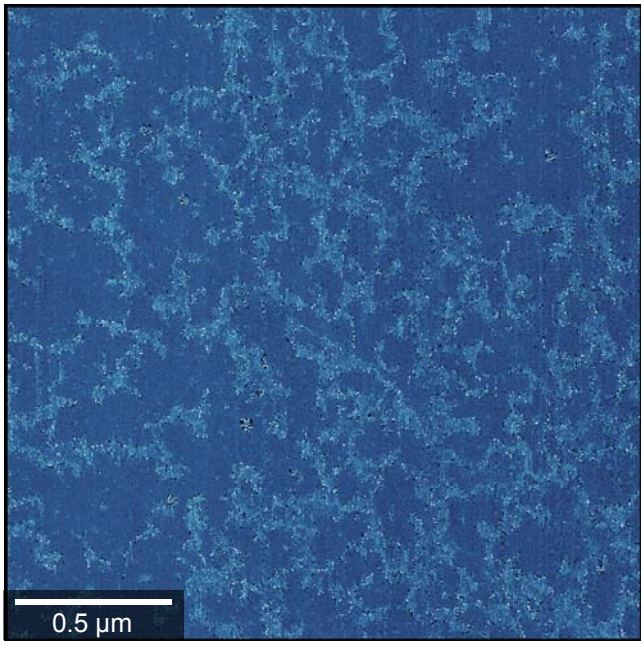

Figure S5 *AFM phase corresponding to the topography in Figure 6a. No contrast can be seen between the layers indicating that the chemical composition of each exposed plane is similar.*

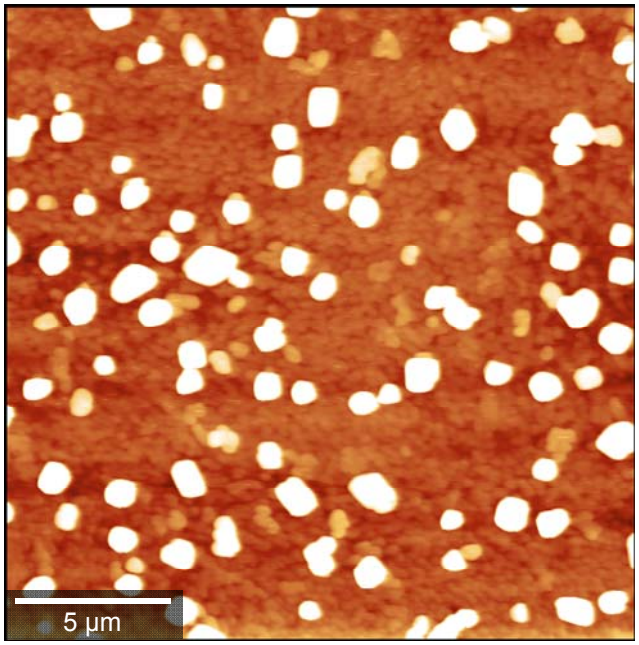

Figure S6 *AFM topography of a sample fabricated without electrodes. The thin film and 3D crystals regime analogous to region D of Figure 4 can be seen. These crystals extend up to approximately 280 nm above the surface of the film. The presence of this regime in the absence of the electrodes strongly*

suggests that it occurs independent of the heteronucleation and growth induced by the PFBT-treated electrodes.

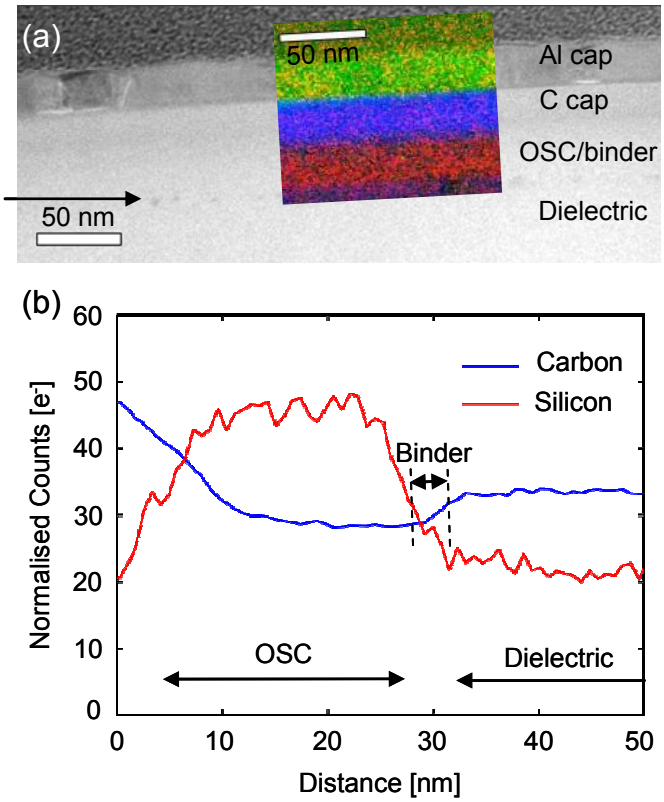

Figure S7 *(a) Bright field cross-sectional TEM image of an area just outside the gate electrode, with (inset) a composite EFTEM map showing the location of the Si-rich OSC. Ag nanoparticles (indicated by an arrow) can be seen the bright field image and are approximately 3 – 6 nm in diamaeter. (c) Normalised intensity profile showing the phase separation of OSC/polymer blend, with the step in C intensity between OSC and dielectric taken to be the binder.*

The TEM cross-section was made after protection by capping layers of C then Al. The bright field (BF) TEM image yields little contrast between the OSC and dielectric since there is little difference in atomic mass or density, However, the cross-section was taken just outside the evaporated electrodes, which taper-off to a thin layer of silver nanoparticles (indicated by an arrow) that form useful fiducial markers for the boundary. The false-coloured inset in (a) is a composite of energy filtered transmission electron microscopy (EFTEM) maps with red, blue and green depicting Si, C and Al respectively. Measuring the thickness of the combined carbon coat and active layers from the BF-

TEM image (54.9 nm) and subtracting from this the measured thicknesses of the carbon cap and the silicon-rich OSC layers leaves 3.3 nm as the thickness of the layer of polymer binder. The thicknesses of the C cap and semiconductor layers were measured as the full width half maximum (FWHM) from profiles of the EFTEM data, giving values of 28.5 nm and 23.1 nm, respectively. An intensity profile across the semiconductor, binder and dielectric layers is shown in Figure S7b; note that this corresponds to only a fraction of the length of the EFTEM image in Figure S7a in order to clearly display the region of interest: the OSC-binder interface.