Competition between phase separation and structure confinement in P3HT/PCDTBT heterojunctions: Influence on nanoscale charge transport

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The structure and hole transport properties of P3HT/PCDTBT (1:1) heterojunctions are investigated as a function of film thickness using several complementary techniques. By Atomic Force Microscopy (AFM) we have investigated the blends morphology and by Scanning Transmission X-ray Spectro-Microscopy (STXM) and Grazing Incidence X-ray Scattering (GIWAXS) we have study the chemical composition and the internal structure (Fig. 1). We find that the P3HT/PCDTBT is an immiscible blend with lateral phase separation when spin-coated. The domain sizes of both components decrease as film thickness decreases. The P3HT/PCDTBT (1:1) thin films with a thickness of ~165 nm and thicker present a dense crystal needle-like morphology while no evidence of needle-like motifs appears in the thinnest thin film. In addition conductive-AFM (C-AFM), used to characterize the electrical properties at the nanoscale, clearly shows that thicker films present a fibrous network where the strongest current is measured (Fig 1). These results evidence that P3HT needle-like crystals grow from the P3HT domains acting as bridges through the PCDTBT domains. However the current image of the thinnest film does not show any fibrous network, nor evidence of needle-like motifs. This fact that can be explained by confinement inhibiting crystallization due to the very thin domains of P3HT of only 40 nm thickness. A strong impact of crystal morphology on hole mobility is evidenced.

Figure 1. a,b) STXM images of a P3HT/PCDTBT thin film, c,d) C-AFM images of P3HT/PCDTBT thin films with different thickness and e, f) GIWAXS patterns of corresponding P3HT/PCDTBT thin films.