MS43-P4 Polymorphic phases of an organic semiconductor: a combined raman and grazing incidence X-ray diffraction study

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There is currently a great interest in solution-processable organic molecular semiconductors due to their potential to produce cheap, efficient and flexible organic devices. Polymorphism has already been observed in several molecular semiconductors, notably pentacene, and this can have an effect on the key physicals properties of these materials, such as the charge transport mobility. Understanding the structure of these systems when coated onto a gate dielectric is therefore of prime importance, especially as charge transport has been shown to primarily occur in the first molecular layers at the interface with the dielectric, meaning knowledge of the molecular arrangement in this region is essential. Excellent charge transport mobilities of up to 43 cm^2 V^{-1} s^{-1} have been observed for solution processed films from the family of alkylated [1]benzothieno[3,2-b]benzothiophenes (BTBT),[1] making them of importance for the future production of high performance organic devices. Here, we present structural investigations of the BTBT derivative, 2,7-dioctyloxy-BTBT (C_8O-BTBT-OC_8). Unusually, C_8O-BTBT-OC_8 shows a different polymorphic phase to that of the single crystal structure when spin-coated as a thin film (herringbone packing in films vs. layered π-π stacking in the single crystal).[2] This type of polymorphic phase, which is only observed in thin films, is termed a substrate-induced phase (SIP) and understanding the formation and structure of such phases is an important challenge when dealing with organic semiconductor thin films. The phase behaviour of C_8O-BTBT-OC_8 in single crystals and also thin and thick films has been investigated extensively by X-ray diffraction (specular and grazing incidence), Raman spectroscopy and AFM. The temperature dependent phase behaviour is also investigated, revealing new polymorphic phases, while solvent vapour annealing and aging of the films is also shown to alter the phase which is present. The structure and origins of these different phases of an organic semiconductor with a rich polymorphic landscape will be discussed, with the implications for the control of film structure and morphology highlighted.

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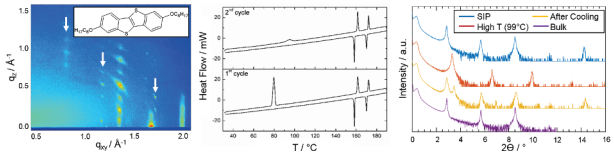

Figure 1. Left: Reciprocal space map from a film of C_8O-BTBT-OC_8 with structure inset; white arrows show peaks belonging to the bulk, other peaks correspond to the SIP. Centre: DSC measurement of bulk C_8O-BTBT-OC_8. Right: Specular X-ray diffraction of the different phases in films of C_8O-BTBT-OC_8.

Keywords: Organic semiconductors, thin films, polymorphism, substrate-induced phase.