Supporting Information

Alkyl Chain Assisted Thin Film Growth of 2,7-Dioctyloxy-Benzothienobenzothiophene

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Atomic force microscopy images of thin films grown at elevated temperatures and at low deposition rates are shown in Figure S1. The micrographs (Fig. S1 a – d) are given in combination with their height distribution functions (Fig. S1 e - f). The terrace like morphology is clearly visible in the micrographs, while an average height of the step edges of 3 nm is determined from the height distribution functions. An atomic force microscopy image of a 5 nm thick film prepared at elevated temperatures and low deposition rate is depicted in Figure S2. The coverage of the substrate surface of the different terrace levels is determined to be 94% for A, 63% for B, 6% for D and 2% for E.

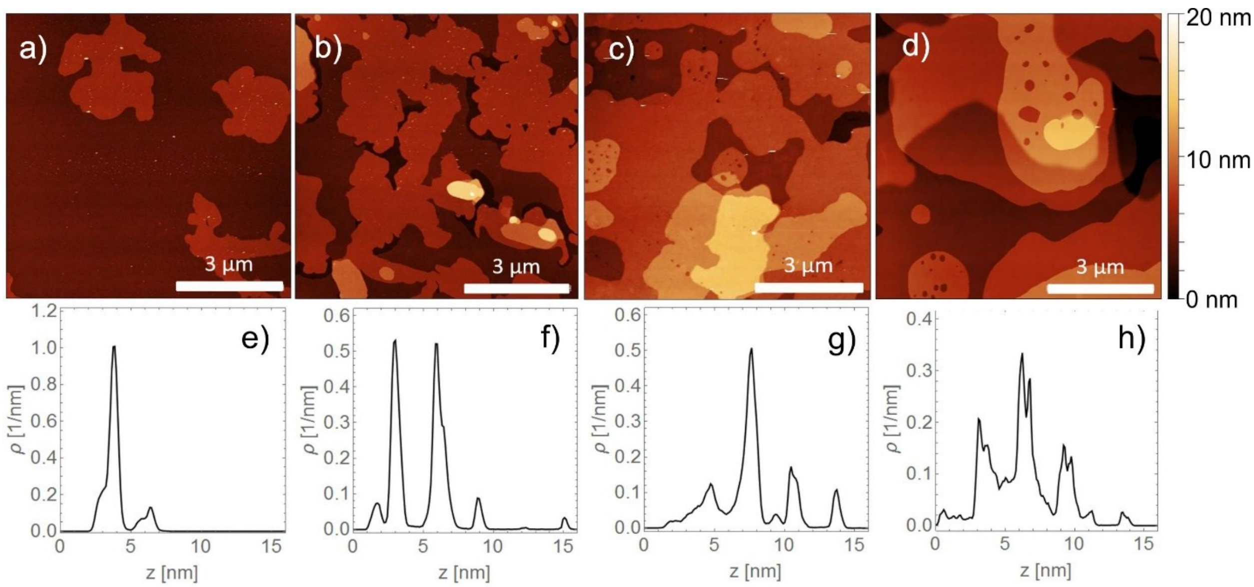

Figure S1: Atomic force microscopy images and height distribution functions of C8O-BTBT-OC8 films prepared at a substrate temperature of 75°C and at low deposition rates (0.15 nm/min) with different nominal thicknesses of a,e) 3.3 nm (1.1 monolayers), b,f) 5 nm (1.6 monolayers), c,g) 13 nm (4.3 monolayers) and d,h) 99 nm (33 monolayers). The z-scale of the images a–d is 20 nm.

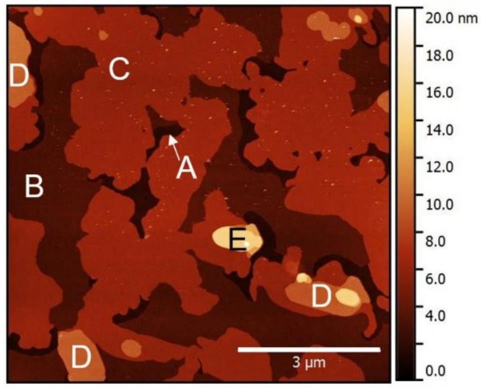

Figure S2: Atomic force microscopy of a 5 nm thick sample prepared at a substrate temperature of 75°C and at low deposition rate (0.15 nm/min). The different height levels are denoted with capital letters A, B, C, D and E.

X-ray reflectivity curves are presented for three samples with different thicknesses of 2.3 nm, 13 nm, and 99 nm. The result of a submonolayer film with a coverage of 77% (nominal thickness of 2.3 nm) is presented in Figure S3. The atomic force microscope image is depicted in Fig. S3a. The X-ray reflectivity curve together with the fit of the experimental data (Fig. S3b) reveals the electron density distribution across the thin film (Fig. S3c). The result of atomic force microscopy is plotted for comparison considering two different electron densities of the alkyl chains and of the aromatic core of the molecule, as discussed in the main text. The fit is performed by the software *Stochfit*.[1]

The results for the films with thicknesses of 13 nm and 99 nm are plotted in Figure S4 and Figure S5, respectively. These films are too thick to use *Stochfit* so the fits were performed using the X'Pert Reflectivity software package (PANalytical). Unlike *Stochfit*, this fitting procedure is model based with the model derived from a simplification of the electron density modulation from the crystal structure (shown in both figures). This model is a gross simplification of true electron density variation since it splits the structure up into slabs of aromatic and aliphatic regions. As a result, the simulated reflectivity curves do not match the experimental data perfectly. This does mean that our conclusions about the film thicknesses have some uncertainty, but the fits are enough to give us a reasonable estimate of the film thicknesses.

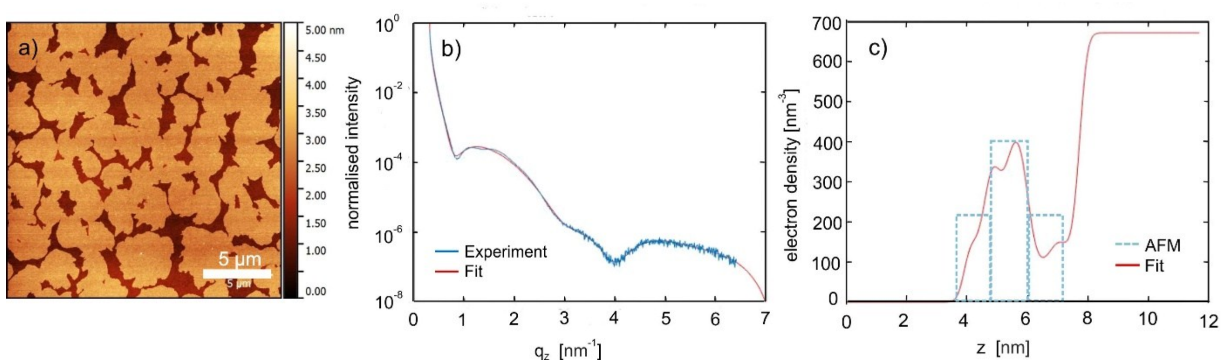

Figure S3: a) Morphology study of a thin film with a nominal thickness of 2.3 nm (0.77 monolayers). a) Atomic force microscopy image, b) X-ray reflectivity curve together with a fit to determine the electron density profile c) electron density distribution across the thin film as obtained by the fit of the X-ray reflectivity curve together with a direct comparison with results of the atomic force microscopy studies.

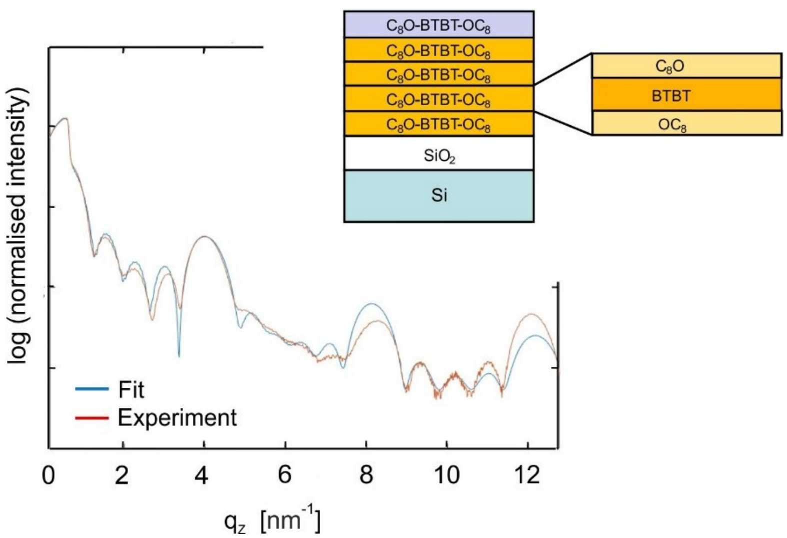

Figure S4: X-ray reflectivity data and fit of a 13 nm thick film. The model for the fit is presented in the inset composed by five molecular layers where the top layer was fitted only with a partial coverage of 64%. Each layer is divided into an aromatic core of the benzothienobenzothiophene units (BTBT) and aliphatic chains (C8O, OC8) with individual thicknesses and electron densities.

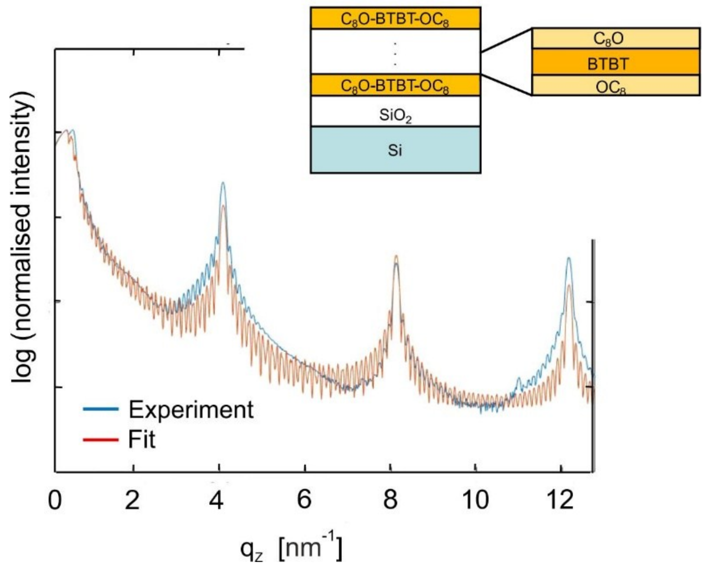

Figure S5: X-ray reflectivity data and fit of a 99 nm thick film. The model for the fit is presented in the inset. In total, 33 layers of upright-standing C8O-BTBT-OC8 molecules were used to fit the data. Each layer is divided into an aromatic core of the benzothienobenzothiophene units (BTBT) and aliphatic chains (C8O, OC8) with their individual thicknesses and electron densities.

1 S. M. Danauskas, D. Li, M. Meron, B. Lin, K. Y. C. Lee, *J. Appl. Crystallogr.,* 2008, **41,** 1187.