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Probing Film Morphology and Surface Microstructure of Semiconducting Polymers with GIWAXS and NEXAFS

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In making organic electronics a reality, donor-acceptor based semiconducting polymers will play a pivotal role. The molecular packing, orientation and crystallinity of semiconducting polymer thin-films strongly influence the performance of organic electronic devices. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) collected at the SAXS/WAXS beamline has been used to probe the molecular packing and relative crystallinity of polymer thin films; while Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the soft X-ray beamline has been used to probe the microstructure and molecular orientation of film-surfaces. A novel polymer **BFS4** is studied, which is based on a dithienyl-benzo[1,2-b':4,5-b']dithiophene as a donor-unit and 5-fluoro-2,1,3-benzothiadiazole as an acceptor-unit. GIWAXS reveals that the crystallites are in a mixture of orientations where the in-plane alkyl-chain stacking distance is 2.17 ± 0.01 nm and out-of-plane -stacking distance is 0.385 ± 0.005 nm. Coherence lengths are measured to be 15 ± 2 nm and 2.6 ± 0.2 nm respectively. Two different types of solution processing methods show differing crystallinity, which can be correlated directly to their respective transistor charge transport properties. NEXAFS reveals a mixture of edge-on and face-on orientations of the molecular planes, and the same orientational preference is confirmed. NEXAFS additionally reveals the relative orientation of the donor and acceptor units of the backbone of this novel polymer, probing backbone planarity directly.

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