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Mechanical Rubbing Changes the Molecular Packing and Orientation of a Conjugated Semiconducting Polymer

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In making organic electronics a reality, donor-acceptor based conjugated semiconducting polymers are playing a pivotal role. However, the molecular packing, crystallinity and the disorder of the polymer matrix in the thin-films typically result in low charge transport mobilities. To this end, mechanical rubbing with velvet cloths is used to mediate the chain assembly and directional alignment of the polymer, poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']-dithiophen-2-yl)-[1,2,5]-thiadiazolo-[3,4-c]-pyridine], (PCDTPT). Intrinsic mobility and the charge transport properties of the PCDTPT thin-films are characterized by Organic Field Effect Transistors (OFETs), molecular packing and relative crystallinity are probed by the Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) and the surface molecular orientations are probed by the Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. Top-Gated OFET mobility of the spin-coated films is found very high, $\sim 2.8 \pm 0.2 \text{ cm}^2/\text{VS}$. GIWAXS reveals that mechanical rubbing introduces a face-on orientation of the crystallites, a stark contrast to the spin-coated films with edge-on orientation. In both the samples, the pi-pi stacking distance is $0.355 \pm 0.005 \text{ nm}$ and the alkyl-chain stacking distance is $2.50 \pm 0.05 \text{ nm}$. Likewise, C- and N-edge NEXAFS experiments confirm that the crystallites at the top-surfaces of the rubbed-films are indeed packed in a face-on fashion, but they adapt an edge-on orientation in the spin-coated films.

Keywords

Semiconducting polymers, Molecular Packing, Crystallinity, Orientation, Morphology, Mobility, Organic electronics

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