

## Impact of competing crystallization processes on the structure of all-conjugated donor-acceptor block copolymers P3HT-*b*-PNDIT2 in highly oriented thin films

Martin Brinkmann<sup>1\*</sup>, Viktoriia Untilova<sup>1</sup>, Fritz Nübling<sup>2</sup>, Laure Biniek<sup>1</sup> and Michael Sommer<sup>2,3</sup>

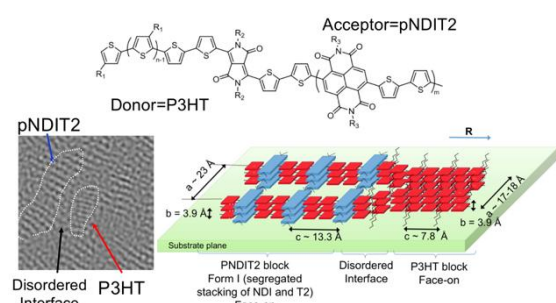
<sup>1</sup> Institut Charles Sadron, CNRS-Université de Strasbourg, 23 rue du Loess, Strasbourg, 67034, France

\*[martin.brinkmann@ics-cnrs.unistra.fr](mailto:martin.brinkmann@ics-cnrs.unistra.fr)

<sup>2</sup> Makromolekulare Chemie und Freiburger Materialforschungszentrum, Universität Freiburg, Stefan-Maier-Straße 21, 79014 Freiburg, Germany

<sup>3</sup> Institut für Chemie, Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany

Mastering orientation and crystallization of all-crystalline, all-conjugated donor-acceptor diblock copolymers is of high interest for photovoltaic applications, as electronically beneficial nanostructuring of thermodynamically stable bulk heterojunctions can be achieved. Diblock copolymers composed of a regioregular poly(3-hexylthiophene) (P3HT) as donor and PNDIT2 as acceptor block were crystallized and oriented by epitaxy and high-temperature (HT) rubbing. The resulting highly oriented thin film structures were investigated in detail by transmission electron microscopy (electron diffraction and high resolution) and temperature-dependent polarized UV-vis absorption spectroscopy. Epitaxy and HT rubbing allow for selective crystallization and orientation of the blocks to obtain structures not accessible by standard spin coating and annealing processes. Epitaxy on trichlorobenzene allows for orientation and crystallization of P3HT, whereas additional annealing is necessary to crystallize the PNDIT2 block also. By contrast, HT rubbing aligns both blocks. The rubbing temperature controls the polymorphism (form I *versus* form II of PNDIT2), the orientation and the contact plane (edge-on *versus* face-on) of the backbones on the substrate. Crystallization of PNDIT2 constraints stacking of P3HT and modifies its unit cell parameters especially along the alkyl side chain direction. The lattice mismatch between the P3HT and PNDIT2 blocks hampers the growth of long-range highly ordered lamellar domains and results in highly disordered interfaces at the block junction. Overall, this study underlines the necessity to adapt layer spacings along alkyl side chains between donor and acceptor blocks to minimize unit cell mismatches and to enhance long range self-assembly into ordered lamellar donor-acceptor phases.<sup>1</sup>



**Figure 1.** Molecular structure of all crystalline all conjugated copolymer PNDIT2-*b*-P3HT, HR-TEM image showing the molecular arrangement and schematic illustration of the copolymer structure at the block junction.

**Référence.** V. Untilova et al. ACS Appl. Polymer Materials, DOI 10.1021/acspapm.9b00220