

## Transport at grain boundaries in polymeric and small molecule organic semiconductors

Alberto Salleo,<sup>1</sup> Leslie H. Jimison,<sup>1</sup> Jonathan Rivnay,<sup>1</sup> Ludwig J. Goris,<sup>1</sup> Michael F. Toney,<sup>2</sup> Antonio Facchetti,<sup>3,4</sup> Tobin J. Marks,<sup>4</sup> Iain McCulloch<sup>5</sup> and Martin Heeney.<sup>6</sup>

<sup>1</sup> Department of Materials Science and Engineering, Stanford University, Stanford CA, USA.

<sup>2</sup> Stanford Synchrotron Radiation Lightsource, Menlo Park CA, USA

<sup>3</sup> Polyera Corp., Skokie IL, USA

<sup>4</sup> Department of Chemistry and Materials Research Center, Northwestern University, Evanston IL, USA

<sup>5</sup> Department of Chemistry, Imperial College, London, UK

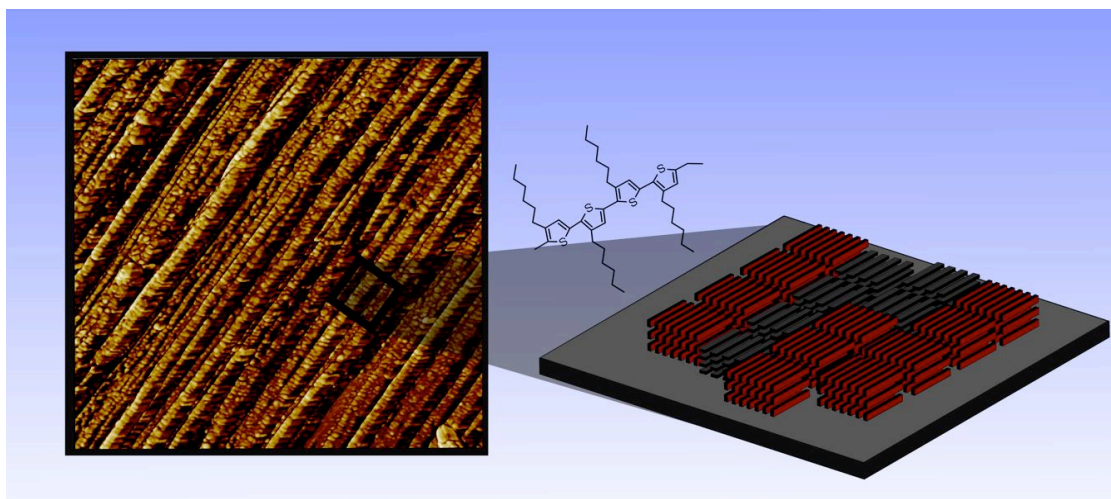
<sup>6</sup> Department of Materials Science and Engineering, Queen Mary University, London, UK.

As organic semiconductors approach commercialization, there is a need to better understand the relationship between charge transport and microstructure, in particular to identify the inherent bottlenecks to charge transport. A commonly accepted materials design rule is to synthesize molecular structures that promote the formation of large crystals. Thus, the highest field-effect mobility is found in semicrystalline polymers and in solubilized small molecules that crystallize readily. No consistent correlation however is found between grain size and mobility. This observation suggests the importance of the role of intergrain charge transport in semicrystalline and polycrystalline organic thin films.

In semicrystalline polymeric semiconductors, the importance of grain bridging has been suggested. For instance, in low  $M_w$  P3HT, chains are too short to efficiently bridge well-formed crystallites thereby reducing the hole mobility. In order to study grain bridging, P3HT films were processed by directional crystallization to produce well-defined grain-boundaries. The directionally-crystallized films have a fiber-like morphology where the P3HT backbones are oriented along the long axis of the fibers (see figure). The crystallinity of the films as well as the in-plane anisotropy of crystallite orientations was verified by X-ray diffraction. AFM confirms the existence of clearly defined grain-boundaries across the fibers. As a result of the directionality of the films, grain-boundaries across the fibers can be bridged by relatively straight polymer chains while the fiber-to-fiber grain-boundaries would force bridging chains to exhibit severe twists. TFT measurements along and across fiber directions confirm that fiber-to-fiber grain-boundaries, where grain bridging is unlikely, hinder transport more than the grain-boundaries located within the fibers. Indeed, TFT mobility measured along the fibers exceeds  $10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$  while that measured across the fibers is of the order of  $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ , with a minimum anisotropy factor of 20. This experiment clearly highlights the importance of grain-bridging by polymer chains in semicrystalline polymeric semiconductors.

The bridging mechanism previously described cannot exist in small molecule films. As the characteristic microstructural length-scales of the semiconducting film approach those of the device size, transistor performance can vary widely, making it difficult to reproducibly control the electronic properties of these films. Indeed, in this

case the effects of just a few grain-boundaries may govern the overall device performance. We determined that the local structure of grain-boundaries can greatly affect the electronic performance of these materials. Thin films of a high mobility, solution processable, n-type small molecule semiconductor, *N,N'*-bis(*n*-octyl)-(1,7&1,6)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI8-CN<sub>2</sub>) are produced with engineered microstructures by promoting the growth of elongated and oriented crystallites. The crystalline structure and the packing of the molecules is verified by a combination of X-ray diffraction, AFM characterization and first principles DFT calculations. The types of grain-boundaries in the film is essentially reduced to two: one low-angle type and one high-angle type. In high-angle grain-boundaries, the molecular orientation across the grain-boundary is such as to reduce the intermolecular transfer integral compared to low-angle grain-boundaries. TFTs are made to separately measure transport across low-angle and high-angle grain-boundaries. It is found that the mobility of devices where the current flows across low-angle grain-boundaries ( $\mu \sim 2 \times 10^{-2} \text{ cm}^2/\text{V.s}$ ) is two orders of magnitude higher than that of devices where the current flows across high-angle grain-boundaries ( $\mu \sim 10^{-4} \text{ cm}^2/\text{V.s}$ ). These findings are important in order to design small molecule materials that are relatively insensitive to grain-boundary orientation.



AFM of a directionally oriented P3HT film (left) and orientation of the crystallites as determined by X-ray diffraction (right). The P3HT chains are parallel to the fibers' long axes.