Ultra-high Charge Carrier Mobility in an Organic Semiconductor by Vertical Chain Alignment

The control of the electronic and optical properties of conjugated polymer thin films is of great interest for building more efficient solution processed organic electronic devices, e.g. photovoltaic (OPV) and light emitting (OLED) devices. The crystallinity and the chain orientation in the polymer film has been shown to strongly influence both optical and electronic properties, with a faster charge transport along the chain backbone. In both OPVs and OLEDs, charges must be transport efficiently in the out-of-plane (vertical) direction inside the polymer film. Polythiophene polymers, e.g. poly(3-hexylthiophene) (P3HT), have been among the most studied materials due to their strong optical absorbance and ease of processing from solution. However, until now the vertical charge carrier mobility (μ) of P3HT was still too low with values of $\mu \sim 10^{-3}$ - 10^{-2} $cm^2/V.s$, to produce fast charge transport and devices.

One of the main issues that needed to be addressed in order to enhance charge transport in semiconducting polymers was to find a way to align chains vertically and crystallize them in the most efficient orientation for fast vertical charge transport. A method to do so was demonstrated, and which produces highly efficient long-range out-of-plane charge transport in P3HT reaching record high average mobilities above 3.1 $cm^2\ V^{-1}\ s^{-1}$. These mobilities rival that of inorganic materials, and may open up the possibility to produce more efficient organic electronic devices with vertical charge transport (e.g. OPV, OLED, etc.).

In this study a team of physicists, chemists and materials scientists, led by Prof. D. R. Barbero joined forces to understand the mechanism of charge mobility enhancement in a patterned semiconducting polymer film. In the fields of polymer science and organic electronics, it is customary to chemically modify, or dope, molecules in order to enhance their charge transport capabilities. However, in this study, a method was demonstrated where charge transport is strongly enhanced solely by controlled chain and crystallite orientation, without any doping.

The charge transport was measured in a diode configuration by two different methods, one capacitive measurement with macroscopic electrodes, and one nanoscopic measurement using a conducting Atomic Force Microscope. These measurements were performed independently both in Umeå University, Sweden, and in Groningen University, Netherlands, and gave very similar values of mobility, with values as high as 10.6 $cm^2/V.s$. This value comes close to the theoretical mobility estimated in P3HT by density functional theory and by an acoustic deformation potential model, and also to that measured along the backbone of a chain by terahertz-probe spectroscopy.

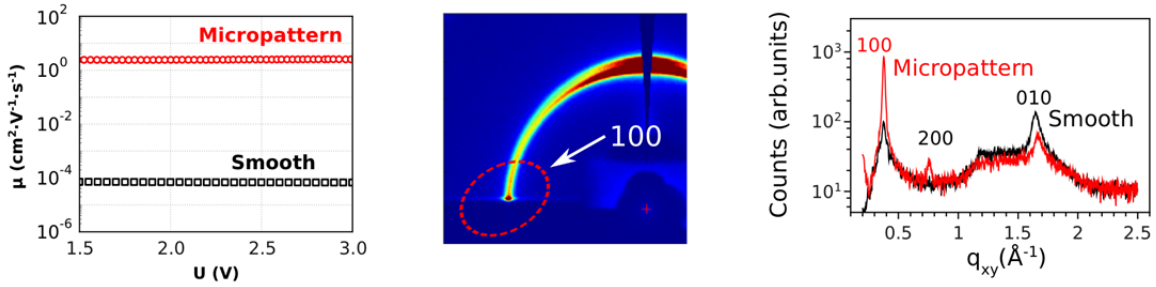

Figure 1. High mobility in an organic semiconducting polymer by controlled crystallite orientation in a micropatterned film, and compared to a smooth (not structured) film.

These high mobilities were assigned to the re-orientation of the polymer chains and subsequent favorable chain-on crystallite formation, during processing of the viscous polymer melt by nanoimprinting, as characterized in detail by synchrotron x-ray diffraction at SSRL by D. R. Barbero and his team in collaboration with Dr. Mike Toney, on Beam Lines 11-3 and 2-1. The high quality of the instrumentation, as well as the precise set-up of the stations, offered at SSRL was crucial in providing the final piece of data necessary to understand the mechanism by which the high mobility was produced. The vertical chain orientation measured by synchrotron x-ray diffraction was moreover later confirmed by polarized microscopy. This favorable chain backbone orientation is explained by the shearing imposed on the viscous P3HT melt along the molds cavity during nanoimprinting which produces vertical chain alignment, and leads to high mobility in this direction.

The vertical chain alignment produced by the method shown is very versatile due to the possibility to change the processing parameters (shearing, viscosity, time, molds material, etc.) over a large range of experimental conditions. In particular, this method could be used with many different types of structures and different polymers in order to enhance vertical charge transport for a specific application.

The results open up the route to producing high mobility conjugated polymer films without chemical modification of the polymer, and they may also help better design more efficient electronic devices with vertical charge transport, e.g. OLEDs and OPVs.

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