

## ORGANIC SEMICONDUCTING NANOSTRUCTURES VIA CONJUGATED (CO)POLYMER SELF-ASSEMBLY

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It is well known that the arrangement of conjugated polymer or oligomer molecules in the solid state has a major influence on the absorption, luminescence, and charge transport properties. This comes as a consequence of the  $\pi$ - $\pi$  interactions between conjugated segments on adjacent chains. Here we illustrate how those intermolecular interactions can be controlled by modifying the molecular architecture and the chain assembly in the solid state. As a test case, we study a series of fluorene-based polymers, either as homopolymers, random copolymers or as block copolymers with a non-conjugated chain. Block copolymers are expected to phase separate into chemically pure domains on the nanometer scale. This process can be exploited to generate well-defined morphologies that emerge from competing interactions (e.g., the assembly of the conjugated segments vs. the crystallization of the non conjugated chains). For this study, we combine theoretical modeling of chain assembly, as investigated with force-field molecular mechanics and dynamics, and the experimental observation of the thin film microstructure with Atomic Force Microscopy (AFM). We show how the formation of fibrillar structures can be controlled via the one-dimensional assembly of conjugated segments via  $\pi$ -stacking.

The formation of the fibrillar structures leads to a clear red shift in the luminescence spectrum, probably as a result of both cofacial packing of the conjugated segments and easy exciton diffusion to oxidized sites along the chains. In terms of electrical properties, such morphology leads to increased charge mobility. In contrast, when  $\pi$ -stacking is prevented via the modification of the side groups or the block copolymer architecture, the formation of the microfibrils is impeded, the blue luminescence is preserved but charge mobility is reduced.

Finally, we describe an orientation method suitable for conjugated polymers, which provides efficient orientation with precise control of the spatial localization of the oriented regions with a nanometric resolution. This method combines template growth and nano-rubbing. Upon rubbing amorphous polymer surfaces, we have observed on the surface the formation of crystalline aggregates, perfectly aligned along the sliding direction. These aggregates then act as a template to propagate the chains orientation towards the bulk when the polymer is annealed. This approach has been applied to poly(3-hexylthiophene); we have investigated the influence of the polymer regioregularity and the rubbing conditions on the optical and electrical properties on the micrometer scale.