Understanding the relationship between structural organization at the nanometer scale and electronic properties represents a breakthrough for molecular and organic electronics. This is especially true in the case of regio-regular poly(3-alkylthiophene)s (P3ATs) which still stand as model semi-conducting polymers for their self-organization properties\(^1\) and their entailed high mobilities in field effect transistors (OFET) configuration\(^2\). Despite intensive research aimed at improving P3ATs OFETs performances, the origin of carrier mobility limitation in such nano-electronic devices is still unclear.

For such investigations, Scanning Tunnelling Microscopy (STM) and Spectroscopy (STS) are powerful tools, as they give access to local (sub nm scale) conformation and density of states of conducting and semi-conducting materials. However, so far few STS studies have been carried out on semi-conducting polymers monolayers\(^3\). To our knowledge, the electronic structure of P3ATs monolayers remains an open question.

In this communication we present STM/STS studies in the low current mode (LC-STM)\(^4\) of regio-regular poly(3-dodecylthiophene) sub-monolayers, self-assembled on Highly Oriented Pyrolitic Graphite (HOPG). Two dimensional spectroscopic images have been obtained with intra-chain resolution. Their contrast and extracted spectra are discussed and compared to simulations: a combination of ab initio and tight binding approaches is used to calculate the polymer DOS and STM I-V curves. The dependence of P3DDT semi-conducting bandgap on local conformation is investigated. The existence of a partially nucleated second layer, associated to an apparent increase of the bandgap, allows to debate hybridization effect on HOPG.


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