Project B1: Graphene-induced crystallization of semi-crystalline conjugated polymers

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Current state of the research. Surface-induced crystallization of polymers has been studied in many instances. Understanding how semi-crystalline polymers with stiff conjugated backbones self-assemble on solid supports is of great interest for organic electronic devices. Graphene is an emerging material for such devices that is often combined with semi-crystalline conjugated polymers like poly(3-hexylthiophene). For these applications, the interaction of crystallizable conjugated polymer chains with such two-dimensional carbon sheets will be crucial for electronic processes such as charge transfer, first detected as photoluminescence quenching. Considering that face-on stacking of various aromatic, planarizable chromophores is observed on graphite, graphene could also be an efficient agent for inducing crystallization in such materials.

Contributions of the principal investigators. M. Brinkmann has a strong expertise in orientation, epitaxial crystallization and structural analysis of semi-conducting polymer thin films and single crystals using Transmission Electron Microscopy. P. Samori has a strong expertise in the use of scanning probe techniques to study electrical and electronic properties of individual supramolecular nanostructures, in the tailoring of interfaces of organic electronic devices, and in the fabrication and characterization of multifunctional supramolecular devices such as field-effect transistors. M. Sommer has a strong expertise in the synthesis and self-assembly of conjugated polymers via a variety of polymerization techniques.

Research project and collaborations. This project studies graphene-induced crystallization of regioregular polythiophenes (P3HT, P3EHT, PDAPT, see Fig. *a*) having various side chains to elucidate the dependence of chain planarizability, and side chain pattern on the crystallization behaviour on graphene. Here the question of chain orientation (face-on or edge-on, Figure *b*) with respect to the graphene plane is of central importance. It can be envisioned that for efficient charge injection face-on orientation of the polymer is needed, a stacking mode found for poly(3-alkylthiophenes) on graphite. However, the situation can be different for P3EHT and PDAPT due to the side chain pattern, and edge-on orientation might occur. Several experimental approaches will be applied to investigate crystallization: *i*) bulk experiments (calorimetry, X-ray scattering, shear) to explore crystallization as a function of the amount of graphene and cooling rate, *ii*) experiments in solution with graphene as a seed to grow polythiophene single crystals. The single crystals will then be deposited onto solid substrates and analyzed by AFM, TEM, UV-vis and conductive AFM to study crystal size, chain orientation, and anisotropic electronic properties.

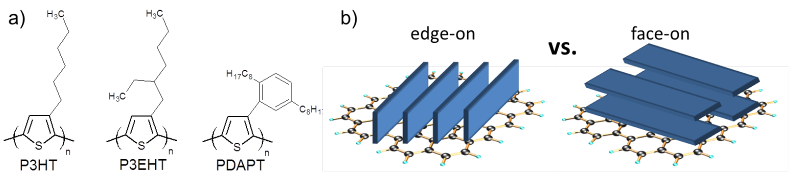

Figure: a) Regioregular semicrystalline polythiophenes: poly(3-hexylthiophene), poly(3-ethylhexylthiophene), and poly(dioctylphenylthiophene). b) Edge-on and face-on orientation of a planarized polymer backbone (blue bar) on graphene.

Work plan. The PhD projects consists of the following tasks: *i*) Synthesis of P3EHT of various molecular weights. P3HT, PDAPT and graphene dispersions will be provided from other sources. *ii*) Bulk crystallization experiments with different amounts of graphene and cooling rates. *iii*) Graphene-seeded crystallization in solution and structural analysis by optical microscopy, atomic force microscopy and TEM. *iv*) Electronic characterization of deposited crystals by conductive AFM and field-effect measurements.