

Oligothiophene-based Semi-Conducting Nanostructures: from Solution to Solid-State Aggregates

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Introduction

Nanoscale and mesoscale order in π -conjugated systems is a topic of utmost importance because it determines the performance of the materials when used as components in organic electro-optical devices such as solar cells [1], light emitting diodes (LEDs) [2] and field effect transistors (FETs) [3,4]. Well-defined π -conjugated oligomers play an important role in this field because their precise chemical structure and conjugation length gives rise to well-defined functional properties and facilitates control over their supramolecular organization.

The control of molecular assembly to give well-defined structures on the nanoscale can be carried out via different complementary approaches: (i) self-assembly can take place in solution; (ii) because conjugated oligomers can be sublimed, it is also possible to follow their assembly as they form thin deposits on surfaces from individual molecules in the vapor phase; (iii) another possibility is to generate thin deposits from conjugated compounds molecularly dispersed in a solution; aggregation takes place during the deposition and then depends on the interplay between the conjugated molecules, the solvent and the substrate surface.

Oligomers and polymers based on α,α' -linked thiophenes are at the forefront of organic semiconductor materials with potential for applications in FETs and related structures [5]. The formation of supramolecular interactions via hydrogen bonding arrays in combination with π - π stacking has also been used to self-assemble oligothiophenes into one-dimensional arrays on surfaces, generating a material with remarkable high charge carrier mobility [6]. In fact, the self-organization of conjugated building blocks in solution or on surfaces, leading to the construction of nanoscopic and mesoscopic (10-1000 nm) architectures, can represent a starting point for the construction of molecular electronics or even circuits [7], through surface patterning with nanometer-sized objects [8]. In other words, these investigations constitute a step forward towards organic nanoelectronics. In the present work, we focus on the supramolecular organization of thin deposits made from assembly of thiophene-based oligomers starting from aggregates formed in solution or from molecularly dissolved solutions.

Experimental

Materials. In this study, we have considered quinquethiophene, sextithiophene, and heptathiophene molecules (5T, 6T, and 7T, respectively), end-capped at the α terminal positions by one or two short, flexible, and strongly hydrophilic segments of poly(ethylene oxide) (PEO) or an alkyl chain. The details of the synthesis of the compounds are described in Refs 9-12.

Sample preparation. The samples for AFM were prepared by casting thin films on to substrates from THF, toluene or *n*-butanol solutions. The substrates were freshly cleaved muscovite mica, silicon wafer, or HOPG. The solvent was allowed to evaporate slowly at room temperature in air or a solvent-saturated atmosphere.

Atomic Force Microscopy. Tapping-Mode Atomic Force Microscopy was performed with a Nanoscope IIIa microscope from Digital Instruments/Veeco (operating in air at room temperature).

Results and discussion

The study of the self-assembly of oligothiophenes having oligo(ethylene oxide) tails that takes place in solution provides important information on the aggregation behavior. From our results, it appears that the self-assembly process is governed by the substitution on the conjugated backbone, the nature of the solvent and the temperature. In particular, the collected data indicate that the evolution between molecular dissolution and aggregation in solution is a subtle function of solvent polarity, with aggregation occurring in non-polar and strongly polar solvents and molecular dissolution prevailing in slightly polar solvents. When generating thin solid-state deposits from conjugated compounds molecularly dispersed in solution, upon slow evaporation, all three types of interactions (molecule-molecule, molecule-solvent, molecule-surface) are at play, which provides additional tenability for the controlled formation of conjugated nanostructures with one dimension (fibrils) and two dimensions (platelets). Even though the structural information obtained from the AFM data is quite qualitative, it is nevertheless important because the transport processes in organic FETs take place in a very thin region in contact with the dielectric. Information on the molecular orientation within that region is therefore essential for the understanding of the device performances. Clearly, the presence of a stereocenter in the molecule induces the formation of chiral assemblies in the solid state. Molecular Mechanics and Dynamics calculations provide pertinent information to corroborate these results.

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