Title: Supramolecular organization in oligomers of selected alkyl thiophene derivatives on HOPG by scanning tunneling microscopy

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ABSTRACT

Alkylthiophene oligomers are known as an interesting class of solution-processable electroactive compounds suitable for applications in optoelectronic devices i.e. field effect transistors. It is known that semiconducting properties of thin layers of such compounds, in general, and the charge carriers mobility, in particular, are very sensitive to several factors of molecular and supramolecular nature. Among them, the length of the oligomer chain and its regioregularity play a dominant role. In the light of this discussion questions of fundamental importance arise: how does supramolecular organization depend on these molecular factors? and what are its consequences on electronic properties of macroscopic layers?

This work concerns comparative study of two types of conjugated regioisomers, namely, oligomers of: 3,3”-dioctyl-2,2’:5’,2”-terthiophene (abbreviated as 3,3”DOTT) and 4,4”-dioctyl-2,2’:5’,2”-terthiophene (4,4”DOTT), which can be considered as model compounds for two isomeric polymers of significantly different electronic transport properties. The undertaken investigations included: (1) chromatographic purification and fractionation of organic material to monodispersed fractions, (2) microscopic investigations of structural properties of self-organized monolayers formed from monodispersed fractions (n-mers, n = 2-5) of both isomers (a main part of presented work), and (3) comparative studies of doping level and electrical properties of thin films in their undoped and doped states.

STM investigations performed at molecular resolution on series of monomolecular layers prepared on HOPG show evident structural differences between two isomeric oligomers of the same length. Moreover, the evolution of supramolecular organization with increasing oligomer length was different for both compounds. Presented dissimilarities have been explained by different alkyl chains interdigitation patters and by different nature of the intermolecular interactions caused by slightly different positions of the alkyl substituents in the two series of compounds.

Moreover, detailed investigations performed on thin layers by complementary techniques, i.e. gravimetry and conductivity, indicate strong impact of the type of regioregularity on the maximum doping level. In addition, the electrical conductivity changes were correlated with the evolution of the 2-D supramolecular organization specific for each regioisomer. I believe, that such studies may help to understand the fundamental properties of this family of organic semiconductors and doped conductors.