

Mgr Joanna Zapala

Ph.D. dissertation written under supervision of:
Dr hab. Robert Nowakowski, Assoc. Prof. (IChF PAN),
and Dr hab. David Djurado (CNRS – CEA Grenoble)

Structural study of self-assembled monolayers and thin layers of semi-conducting organic molecules

Organic semiconductors are attracting great interest as new materials for applications in many optoelectronic devices, like solar cells, light emitting diodes, displays, sensors, and field effect transistors. The principal advantages of organic electroactive molecules consist of facile processability and the possibility of precise tuning their electronic and/or optoelectronic properties by chemical modification of molecular structure. However, the usefulness of these compounds in real applications is a complex issue, governed not only by the properties of an individual molecule, but also by supramolecular organization.

The main aim of this work was to establish correlations between chemical structure of the selected organic semiconductors and their self-assembly properties (in 2-D and 3-D). The studies were performed by means of two complementary methods, i.e., scanning tunneling microscopy (a powerful tool for imaging and local characterization of interfacial structures in monolayers) and X-ray diffraction methods (which enables providing information about molecular organization in various 3-D systems including single crystals, powders, and thin films).

Selected semiconductors (16 compounds) were comprehensively studied as logically designed five series of derivatives mutually differing in some structural elements. There are new molecules of complex electronic structure of a donor-acceptor-donor type from two families, i.e., arylene bisimide derivatives containing triarylamine or alkoxyphenyl substituents and alkyl derivatives of dithiophene with a centrally located electron-acceptor unit (thiadiazole or tetrazine). Comparison of results obtained for a series of compounds for each semiconductor type allowed determining the effect of different elements of molecular structure on supramolecular organization.

The obtained results indicate that supramolecular organization of such complex in electronic structure molecules is a hard to predict process which has to consider co-existence and competition of mutual interactions between segments of molecules of different electron affinity. Microscopic imaging performed at submolecular resolution under different conditions of electron tunneling (bias voltage) allowed to distinguish in the ordered monolayers the electron-donor and electron-acceptor parts of the molecules. The investigations clearly enabled determining influence on supramolecular organizations of several important structural elements of the molecules including extension and chemical structure of a conjugated unit as well as the type, location, and size of terminal substituents. Moreover, the comparative analyses of supramolecular organization in 2-D and 3-D systems were performed. The undertaken comparison clearly confirmed polymorphism for some of the

studied adsorbates yielding different organization in 3-D crystals, as compared to monomolecular layers.