

Abstract

In this dissertation first-principles quantum mechanical calculations are applied to study prototype organic semiconductors and their interaction with inorganic materials. Materials studied are widely used in devices of the organic electronics (OE) technology.

At first, the structural details of molecular crystals formed by organic semiconductors are examined. In particular, different state-of-the-art Density Functional Theory (DFT) based approaches were used to relax the crystal structures of electron donor and acceptor materials, such as members of the oligo-acenes family (i.e. naphthalene, anthracene, tetracene and pentacene), the polymer P3HT, C₆₀ fullerene and its derivative PC₆₀BM. In addition, the electronic and optical properties of the stable structures were calculated. Regarding the oligo-acenes, the relation between the length of the molecule's long-axis and the electronic band gap (E_g) is found using calculations based on both the GGA and the PBE0 hybrid functionals. In addition, the structural details of different structural phases of the molecular crystal of pentacene (polymorphs) were presented and their opto-electronic properties were associated with the specific structural features.

It is well known that C₆₀ fullerenes at room temperature adopt an FCC lattice. On the other hand PC₆₀BM's crystal structure is still not known. Calculations showed that PC₆₀BM's stable molecular crystal structure is the simple cubic (SC), just slightly more favorable than the body-centered cubic (BCC). In contrast, the face-centered cubic (FCC) structure has significantly higher total energy and is thus less stable. The enhanced stability of the SC and the BCC lattice is associated with the presence of a hydrogen bond between neighboring molecules, whereas such bond is absent from the FCC configuration. P3HT is known to form well-defined crystals and using available experimental findings the structure was modeled and the optical and electronics properties were calculated. Strong optical anisotropy along the lattice vectors was found. In particular, strong absorption peaks are found along the polythiophene backbone, while along the direction of the alkyl side-chains the absorption begins for energies higher than 4 eV.

Next, continuous transformations on the molecular crystals of C₆₀ and PC₆₀BM were applied. These transformations can change molecular crystals continuously from a BCC to an FCC lattice, or from a BCC to an FCC through a SC configuration.

Regarding the molecular crystal of C_{60} , the atomic-scale details of polymerization are analyzed, and the ideal strength is obtained. Also, metastable crystalline polymorphs are identified, and their electronic properties are characterized. For $PC_{60}BM$ in particular, several local energy-minimum structures that differ significantly in terms of molecular conformations and electronic properties are identified.

Another major part of this thesis deals with the electronic effects introduced by prototype impurities (i.e. oxygen and water) on the properties of organic semiconductors. The resulting structures from the incorporation of oxygen in $PC_{60}BM$ and P3HT crystals are presented. Specifically, several different types of configurations are shown that range from intact molecules in crystalline voids to oxidized organic molecules. Furthermore, a number of impurity configurations are found to create states within the energy band gaps of the materials, creating thus shallow and deep carrier traps on both $PC_{60}BM$ and P3HT. Water molecules, on the other hand, are found to adsorb only intact in both semiconductors and are associated with a shallow acceptor-like trap in $PC_{60}BM$ and minimal effects in P3HT. Moreover, the vibrational properties of defective pentacene crystal configurations are studied. The impurity-related frequencies of the vibrations are obtained and the respective trends are shown giving a way for the identification of the defects and the association with the specific defective structures in experiments.

The last part of this thesis deals with the interactions between organic semiconductors $PC_{60}BM$ and P3HT and inorganic metal surface of silver and gold. $PC_{60}BM$ can adsorb on silver with different orientations, but slightly prefers to adsorb with the C_{60} part towards the surface. At the same time, the work function modification is found to depend strongly on the tail position. Specifically, the favorable configuration increases the work function, while for adsorption with the functional 'tail' of $PC_{60}BM$ towards the surface lower the work function. Adsorption on silver with the 'tail' lying parallel to the surface, practically doesn't change the work function, while adsorption on gold with the similar structural details, lowers gold's work function. Attachment on the gold surface for both $PC_{60}BM$ and P3HT was found to be stronger. Finally, P3HT adsorption on either surface, leads to a decrease of the work function, which is found larger the case of gold.