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## **The investigations of electrochemical and spectroelectrochemical properties of aryl imides and s-tetrazine derivatives**

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### **ABSTRACT**

The significance of organic compounds in such fields as electronics and photonics has been growing rapidly since the electrical conductivity of doped polyacetylene had been discovered. Despite the continuous development of organic electronics, there is still a problem with the stability of such systems, especially these which are based on electron transporting (n-doped) materials due to their low stability in the presence of oxygen and water.

This doctoral dissertation concerns the electrochemical and spectroelectrochemical investigations of compounds with potential applications in (opto)electronics as acceptors or ambipolar materials (materials showing both: electron and hole conductivity). The study involve two groups of compounds: aryl imide and s-tetrazine derivatives. The aim of this work is to determine the effect of the chemical structure on the electrochemical and spectroelectrochemical properties of these derivatives. Based on the conducted measurements it is possible to estimate the value of electron affinity (EA) and, in the case of bipolar structures, ionization energy (EI). The impact of type of core and substitution pattern of diimide (N- and core-substitution) on these properties and parameters are evaluated. Investigations of s-tetrazine derivatives are intended to the characterization the influence of substituents on the electrochemical reduction of 3,6-disubstituted derivatives. The second part of studies of this group of compounds relates to the donor-acceptor-donor (D-A-D) structures. Here, the impact of the linker between the donor and acceptor units of molecules on their properties, including activity in the electrochemical polymerization is investigated.

All the studied compounds undergo reversible or *quasi*-reversible electrochemical reduction. Reduction of naphthalene and perylene diimide derivatives proceed as a two-step process. During the first stage the radical anions are generated, which transit to dianions as an effect of the second step. Bipolar compounds undergo also electrochemical oxidation. In the

case of N-substituted diimide derivatives the interactions between the diimide core and N-substituents are not observed, which results in lack of (or negligible) influence of substituents on the reduction process. In the contrast, in the case of core-substituted derivatives a clear effect of the donor part on the reduction process is observed due to the conjugation between the donor and acceptor part of molecules.

The investigations of 3,6-disubstituted-*s*-tetrazine derivatives indicate a huge impact of the nature of substituents on the reduction potential of this compounds. Electron accepting substituents increase, whereas electron donating decrease potential of this process. The spin density in radical anions which are generated during reduction of *s*-tetrazine derivatives is localized only on the *s*-tetrazine ring. The compound with two *s*-tetrazine rings undergo two-step reduction. The first step leads to formation of radical anion which localizes only on one ring, the second stage involves the other *s*-tetrazine ring.

Some of investigated compounds are active in electrochemical polymerization. Obtained by this process polymers (oligomers) based on perylene diimide derivatives are more stable than layers obtained via electropolymerization of naphthalene imide derivatives. Electropolymerization of D-A-D *s*-tetrazine derivatives is strongly dependent on the monomer structure. The derivative with thienyl linker is not active in this process due to delocalization of generated diradical dication to the  $\pi$ -linker. The compound with an oxygen atom as a linker undergo electrochemical polymerization most easily. The increase of conjugation between donor and acceptor moieties in monomers effects also on properties of obtained polymeric films. Nevertheless, all polymerized layers exhibit unusual electrochemical properties related to charge trapping phenomena.