

Streszczenie w języku angielskim

This doctoral dissertation focuses on the study of new perimidine compounds as part of a perinone system in the electrooxidation process and the determination of subsequent addition/coupling reactions. The selection of the studied compounds aimed to verify the possibility of polymer formation through coupling, specifically the formation of ladder-like structures. The following bifunctional monomers were used: those possessing one or two types of terminal reactive groups, i.e., exclusively perimidine rings or perimidine along with carbazole/thiophene.

As part of the research, the optimization of electrodeposition processes for perimidine derivatives depositing on various substrates via electrooxidation was conducted. The research objectives were planned based on the use of electrochemical, spectroscopic, spectroelectrochemical (UV-Vis-NIR, IR, EPR, AFM) techniques, and quantum-chemical calculations using the DFT method.

The conducted studies demonstrated the ability to form covalent bonds between perimidine units in the examined perinone systems as a result of the electrooxidation process. The reactivity of perimidine compounds may also be influenced by intermolecular interactions in the precursor solution, which can either promote or hinder electrode processes (likely due to the specific orientation geometry of the substrate relative to the electrode surface). For example, different electrodeposition efficiencies were observed for solutions of phthaloperinone isomers derived from 4,4'-isopropylidenediphenyl. The efficiency of the addition process is also affected by competing processes associated with the formation of stable charged π -dimers (after the generation of monomeric radical cations or diradical cations), such as in the case of carbazolo[4,5]isoquino[2,1-*a*]perimidin-14-one. These processes can be limited through appropriate monomer structural design.

Ladder-like perimidine-perimidine linkages were obtained in low-molecular-weight products such as dimers, where enhanced interlayer interactions enabled the subsequent oxidation of bis-perimidine units initially connected by a single bond—such as in the case of phthaloperinone and phenanthroline-dione derivatives. However, the preferred bonding site was always the C1 position, leading to bond formation stabilized by hydrogen bonds involving the oxygen atom of the carbonyl group. This system is formally charged and exhibits a characteristic redox process at +0.1/-0.05 V (relative to Fc | Fc⁺). Electrooxidation of the perimidine derivative of phenanthroline-dione resulted in a product with disrupted π -conjugation due to the presence of stable protonated redox centers. The potential barrier between oxidation and reduction processes was found to be very low, at less than 0.5 eV.

It was also found that the electrooxidation product of the perimidine derivative of phenanthroline-dione was successfully applied as a solid contact in ion-selective membrane sensors. The perimidine unit may represent a new and interesting class of side groups for polymer systems, modifying the properties of classical linear π -conjugated polymers and influencing the chain planarity and macroscopic organization of the entire system (e.g., the thiophenocarbazo[4,5]isoquino[2,1-*a*]perimidin-14-one derivative).

Additionally, it was shown that the presence of carbonyl groups in perinone segments ensures the existence of reversible reduced states, while negative polarons are highly delocalized. It was also demonstrated that modification of the perylene monomer core enabled its dissolution and electrooxidation in solution, where electrocoupling was observed for the perimidine derivative in a bis-amidine system. In this case, due to weaker interlayer and hydrogen bonding interactions, ladder-like connections did not form efficiently, and coupling was dominated by a single deprotonated bis-perimidine bond. The product exhibited greater porosity due to the presence of additional phenoxy substituents in the perylene core, and the p- and n-doping processes were more potential-separated but demonstrated high reversibility.

The presented studies characterize a new class of conductive materials, describe methods for their synthesis, and highlight potential application directions. The obtained results represent a significant step toward the development of organic conductive materials with controlled electrochemical properties. Further work may focus on optimizing synthesis parameters and investigating the long-term electrochemical and functional stability of the obtained materials for technological applications.

Keywords: Perimidine, Electrochemistry of organic compounds, Conductive polymer