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Synthesis of new 2,2'-bisbithienylmethane and fullerene derivatives, and their application as functional monomers for preparation of recognition polymer films of chemosensors for selective determination of biologically significant compounds

The present Ph.D. thesis focuses on the designing and synthesizing of new functional monomers (FMs) and their use for the preparation of chemical sensors for biologically significant substances. One of the synthesised monomers was used for the preparation of a chemical sensor capable of selective determination of oligonucleotide of the nucleobase sequence characteristic for the HIV virus. For that, the FM bearing the biotin moiety was potentiodynamically electropolymerized on the surface of an electrode. On top of the resulting films, neutravidin was irreversibly immobilized by the complexation of the biotin moieties of the polymer. Finally, the recognizing biotinylated oligonucleotide was immobilized on top of the thus prepared structure by complexing the surface-immobilized neutravidin. This layer-by-layer assembly served for the determination of the target oligonucleotide. Electrochemical impedance spectroscopy (EIS) and piezoelectric microgravimetry (PM) were used for signal transduction. Analytical parameters of EIS and PM chemosensors, including the limit of detection, linear dynamic concentration range, and selectivity, were 50 nM and 0.5 pM, from 50 to 600 nM and from 0.5 pM to 30 μ M, respectively. The developed method of surface modification with neutravidin was utilized for the preparation of molecularly imprinted polymer (MIP) chemosensor for the determination of myoglobin. Prepared EIS chemosensor was characterized by linear dynamic concentration range of 10 to 500 ng/mL.

Moreover, eighteen functional monomers were designed and synthesised. Sixteen of them were derivatives of (2,2'-bisbithienyl)methane and two others were [C60]fullerene derivatives. The presence of the thiophene or fullerene moiety assured polymer film formation via oxidative or reductive electropolymerization, respectively. Each FM contained a recognizing moiety in order to interact with various template molecules. Those interactions included ionic interactions, hydrogen bondings, π-π interactions, van der Waals interactions, and weak dispersion interactions.

After FM preparation, their binding capabilities were assessed via quantum-chemical calculations. For that, structures of pre-polymerization complexes of FMs with selected templates were optimized using the DFT method. Then, the energy gain of complex formation was calculated. Apparently, the synthesised FMs formed stable complexes with certain classes of templates and, therefore, could be used for the preparation of MIP films. These films then served as recognition units of the chemical sensors fabricated.

Some of the synthesized FMs were used for the preparation of chemosensors for important analytes such as 6-thiogunanine (chemotherapeutic drug), nicotine (toxin), and nitroaromatic compounds (explosives). Moreover, the MIP chemosensor for melamine, previously studied and described by the Group of Molecular Films of IPC PAS, was prepared in order to evaluate its capability to determine melamine in real samples of pet feed as well as to assess the feasibility of a new transduction platform, namely, surface plasmon resonance spectroscopy, in MIP chemosensing.