Bis(2,2'-bithienyl)methane-derived functional monomers: from molecular recognition to sensing applications

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Abstract

The present Ph.D. thesis is focused on development of a systematic approach to fabrication of chemosensors for selective determination of several different biorelevant analytes, such as adrenaline (neurotransmitter), adenosine-5'-triphosphate (nucleotide), 5-fluorouracil (chemotherapeutic drug), nitroaromatic compounds (explosives), and nicotine (toxin). Stability of pre-polymerization complexes of analytes with dedicated functional monomers was first estimated. For that, the Gibbs free energy gains due to complex formation was calculated using quantum chemistry computing with the density functional theory (DFT) at different levels of basis sets. Next, the UV-vis spectroscopy and fluorescence titrations were used to determine stoichiometry and stability constants of these complexes in solutions. The latter titration was possible because the bis(2,2'-bithienyl)methane moiety of the functional monomers is a fluorophore. If complexes in solutions appeared to be sufficiently stable, they were transferred onto surfaces of different electrodes including the Pt disk electrode, Au-coated glass slide, or Au-coated quartz crystal resonator (Au-QCR), by potentiodynamic electropolymerization. In effect, molecularly imprinted polymer (MIP) films were deposited, as clearly imaged by AFM. At this stage, the analytes played the role of templates. The presence of templates in MIPs, and then extraction of these templates from the MIPs was confirmed by measurements using different techniques. Among them, the most powerful was XPS. Therefore, it was preferred in our research. For determination of the analytes, different methods were used to reach

sensitivity, detectability, and selectivity as high as possible. Differential pulse voltammetry (DPV) revealed the lowest limit of detection (LOD). However, the DPV transducer was not preferred because its applicability was restricted to batch working conditions. The capacitive impedimetry (CI) signal was very stable with respect to the double-layer capacity. However, selectivity reached by CI was low because this capacity varied with absorption of any analyte or interference. Piezoelectric microgravimetry (PM) was our favorite transduction platform to evaluate sensitivity and selectivity as well as the imprinting factor of the (MIP film)-coated Au-QCR. Moreover, the first ever "hyphenated" procedure of simultaneous PM and chronoamperometry (CA) determination of electroactive analytes, such as nitroaromatic explosives and nicotine, were developed to allow for dual analyte determination.