Dissertation abstract

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„Characteristic of chemosensors based on anthraquinone signaling unit”

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The main goal of presented dissertation was to determine the physicochemical properties of effective molecular sensors based on the signaling system of anthraquinone. The literature and experimental studies presented herein are aimed at demonstrating which structural factors play fundamental role governing the spectroscopic, acid-base and electrochemical properties of the amine derivatives of anthraquinone. These features regulate the sensitivity of the signaling unit to the impact of the identified group.

The research subjects were three groups of aminoanthraquinone derivatives containing different types of detection groups, differing in both: structure and the connection with the signaling unit. The first series (A) were derivatives with a macrocyclic fragment based on 12-crown-4 attached to the anthraquinone molecule via the nitrogen atom in position 1. In the second group (B) the chromophore system was an integral part of the macrocycle. The signaling unit was connected to a coronal or cryptand group in positions 1 and 8 of anthraquinone. The third group (C) are derivatives in which the substituent was an amino acid residue attached to the anthraquinone via a piperazine ring.

This thesis provides a comprehensive and an insightful characterization of an interplay between the structure and the properties of this type of compounds. The structural aspects, such as: the type of the detection group and the way of its linkage with the signaling system, the number of amino groups and their distribution in the host unit, and the ordinariness of the nitrogen that bonds the basic elements of the chemosensor were thoroughly analyzed.

In order to obtain the intended goal, the number of studies allowing full characterization of anthraquinone derivatives were performed. Spectral analysis is provided on the basis of spectrophotometric measurements. Characteristic absorption bands and their molar absorption coefficients were determined, and moreover, their changes were attributed to the particular structural elements. Based on changes in the absorbance of compounds as a function of pH (in acetonitrile-methanol (9: 1) or solutions of acetonitrile or methanol), the values of acid dissociation constants were resolved, which allowed to verify the basicity of the tested compounds. The values of K_a constants were associated with the structural elements of the compounds and their behavior in the tested solutions. The infrared spectra of the AQ-ppz-Asp, AQ-ppz-Glu and AQ-ppz-pGlu derivatives as well as quantum-chemical simulations confirmed the existence of different types of structure stabilization by hydrogen bonds. The results of the cyclic voltammetry measurements are also presented. The redox potentials of the tested compounds were determined and the effects of strong methanesulfonic acid and tetrabutylammonium base were discussed. The study presents an analysis of the electrochemical changes and attributes them to the processes of protonation of the active redox forms of compounds or to the formation of hydrogen bonds.

The research conducted as a part of this doctoral thesis has broadened the scope of a utilizable knowledge necessary to design an effective chemosensor, based on the signaling unit of an anthraquinone. The analysis of the literature and experimental research collected in this dissertation presents the properties of an effective molecular receptor, and more importantly defines and systematizes structural features conditioning their existence.