AZULENE DERIVATIVES AS BUILDING BLOCKS FOR THE CONSTRUCTION OF SELECTIVE ANION RECEPTORS

MSC DAWID LICHOSYT

SUPERVISOR: PROF. DR JANUSZ JURCZAK

The aim of this Ph.D. thesis was the synthesis and investigation of anion binding properties of new classes of anion receptors with a macrocyclic structure. These receptors are built of azulene units equipped with amide hydrogen bond donors. The azulene skeleton has been chosen as a building block due to its unique properties: geometry, internal dipole moment and a built-in chromophore. All these elements so far have not been fully exploited in the supramolecular chemistry of anions. The research carried out as part of the doctoral thesis was specifically aimed at: (i) designing effective classes of receptors using the potential of azulene; (ii) development of convenient synthetic methods that enable for an easy access to model receptors and their further generations; (iii) a detailed evaluation of the complex forming properties of receptors with model anions, by studying receptor-anion complexes in solution as well as in the solid phase. Considering that the designed receptors contain the binding sites of different geometries, the study gives insight the relationship between the structure of the designed compounds and the effectivity and selectivity of anion complexation. Morevover, the azulene moiety is a strong chromophore, therefore the next research task was to evaluate its potential in the construction of optical sensors for anions, allowing for their quick and easy detection.

The results presented in the own research section showed correlations of the binding site geometry with the efficiency and the selectivity of complexation of the model receptors. These studies demonstrate that, despite their structural similarity, the designed receptors offer varied properties in terms of their selectivity and affinity for anion binding, depending on the azulene building blocks used. Receptors containing the "broad" building block – that is, 1,3-diamide derivatives of azulene – selectively bind to large phosphate anions, while receptors containing the "narrow" building block – that is, 5,7-diamide derivatives of azulene – selectively bind to small chloride anions. These conclusions were supported by detailed studies of receptors, both in solution and in the solid phase. The results of these studies provided the detailed insight into the mechanisms of anion recognition, commonly occurring in biological systems and numerous processes involving anionic individuals in chemistry, which was the overarching goal of the doctoral dissertation. The acquired knowledge enables to design new generations of anion receptors with target efficiency and selectivity, required for practical applications. In a broader context, the research carried out contributes to the rational design of more advanced supramolecular systems.