ABSTRACT

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Doctoral Thesis: **Study of recognition moieties of sensoric azaphthalocyanines**

Azaphthalocyanines (AzaPcs) are planar macrocyclic compounds with unique photophysical properties like absorption and emission over 650 nm and high quantum yields of fluorescence. Alkylamine substituted AzaPcs have been shown to undergo an ultrafast intramolecular charge transfer (ICT) which is responsible for efficient quenching of excited states (nonfluorescent OFF state). ICT occurs between donor (peripheral amine) and acceptor (macrocyclic core). Blocking of ICT leads to restoration of high fluorescence emission (fluorescent ON state) which is the competitive relaxation pathway. There are two known possible ways how to block ICT in AzaPcs sofar: By protonation of donor in pH sensitive AzaPc sensors or by coordination of metal cation into the recognition moiety resulting in cation sensitive AzaPc sensors. Above-mentioned properties predestinate AzaPcs to become new fluorescent sensors with good brightness and advantageous absorption and emission of red light deep penetrating into the tissues thank low interference with endogenous chromophores.

The topic of my dissertation was focused on the study of the recognition moiety of sensoric AzaPcs sensitive to metal cations with the aim to disclose structural key factors influencing sensor selectivity and sensitivity, and to prepare a sensor highly selective and sensitive to a desired analyte. My work began with the project studying the effect of the size of aza-crown recognition moiety on the sensor selectivity. It was clearly demonstrated that the size of aza-crown is the key factor for selective binding of alkali metal cations but not for alkaline earth metal cations probably due to the higher electron density given by their divalent character. Second project dealt with the introduction of two aza-crowns in a specific arrangement called tweezer. Such an increase of rigidity of recognition moiety resulted in significant improvement of the both sensor selectivity and sensitivity to desired analyte with almost no-cross sensitivity to other analytes tested. The main drawback of this series, i.e. low fluorescence quantum yields in ON state of sensor due to the necessity of blocking the both donor centers, was overcome in the third project combining knowledge obtained in the first two projects. These sensors had just one donor center whereas increased rigidity was achieved by the attachment of an either lariat ether or an additional crown. As a result, AzaPc sensors highly selective to K$^+$

with 3,2× higher fluorescence quantum yields in ON state in comparison with tweezer-like sensors were developed.

The possibility to use pH-sensitive AzaPcs in development of new CO_2 sensors was investigated during my research stay in the group of Assoc. Prof. Sergey Borisov at Graz University of Technology (Graz, Austria). Firstly, the method for immobilization of AzaPc to a support foil was successfully developped. It was followed by the study of the possibility to use new alternative matrices based on polyurethane elastomers with different content of water uptake (5-25 %). Then, we focused on the tuning of the sensor sensitivity to pCO_2 by the choice of the base from the group of tetraalkylammonium hydroxides differing in the length of alkyl chain. Finally, the foil containing AzaPc indicator was inserted on the tip of glass fiber and used in an experiment demonstrating the possibility to use such device in real application (e.g. for monitoring CO_2 in breathe).