Abstract

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Title of diploma thesis: Modulation of pK_a of the recognition moiety of azaphthalocyanine sensors II.

Our research group recently developed the sensors based on azaphthalocyanine (AzaPc) core containing one or two phenolic groups as recognition moiety and because of them, the AzaPcs can be utilized as fluorescent sensors. The fluorescent state of the molecule depends on the pH of the environment and the pK_a of the recognition moiety. The latter can be modified by altering the substituents on phenol.

The formation of AzaPcs was initiated by the synthesis of their precursors. In most of the cases, the starting material was 4-hydroxyacetophenon that was modified by electrophilic substitution. The products were oxidized to corresponding vicinal ketoaldehydes using selenium dioxide and immediately condensed with diaminomaleonitrile to substituted pyrazine-2,3-dicarbonitriles. Synthesis were completed by the cyclotetramerization reaction of this dicarbonitrile with 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile using magnesium butoxide as initiator.

Six different congeners were obtained by this reaction from which the required congener with one asymmetric part was isolated by the column chromatography. Some of the synthetized AzaPcs in the form of magnesium complex were converted to metal-free derivatives and subsequently to zinc complexes. Finally, fluorescence and absorbance were measured. In acidic environment, AzaPcs had intensive red fluorescence which was turned off after ionization at higher pH. Based on the fluorescence changes, the pK_a value of recognition moiety was determined for each molecule. The values ranged from 5 to 10.5. Unlike AzaPcs, pyrazine precursors showed intense changes in absorption spectra visible to the naked eye