

ABSTRACT

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Title of the Thesis: **Influence of structural aspects on photophysical properties at phthalocyanines**

Phthalocyanines (Pc) and their aza-analogues tetrapyrroloporphyrins (TPyzPz) are macrocyclic compounds with 18 delocalized π -electrons. The large conjugated system of double bonds imparts them unique spectral, photophysical and electronic properties which can be tuned by peripheral substitution or/and central metal cation. They found their use in several areas such as photodynamic therapy, catalyst, liquid crystals and solar cells.

The first part of this doctoral thesis describes the influence of structural aspects on effectiveness of intramolecular charge transfer (ICT) at TPyzPz. ICT is responsible for considerable decrease of photophysical parameters of TPyzPz – quantum yields of singlet oxygen (Φ_{Δ}) and fluorescence (Φ_F). At first, we focused on the effect of the electronic properties of peripheral substituents attached on macrocycle core on ICT efficiency in TPyzPz. The series of TPyzPz with various peripheral substituents was designed and prepared. Peripheral substituents were chosen with the respect to their electronic effect described by Hammett substituent constant σ_p . We have found out that the effectiveness of the ICT significantly depended on the electron-accepting properties of the core. Increase of ICT efficiency was directly proportional to electron-withdrawing character of the substituents. Simultaneously, it was disclosed that the basicity of azomethine nitrogen can be affected by character of the peripheral substitution. Significant suppression of photophysical properties was observed after protonization of azomethine. In the following study, we prepared series of TPyzPzs with *N,N*-dimethylamino group attached to the core via π -conjugated linker of different length. In this study, we described the influence of a distance between donor and acceptor for ICT on its efficiency. Obviously, increasing length of linker between donor and acceptor moiety caused the suppression of ICT. Based on this, we designed pH indicators

operating through unique OFF-ON-OFF principle based on combination of two different quenching principles. Sensing properties of novel indicators were studied in organic as well as in water medium after incorporation to liposomes.

Second part of my doctoral thesis is focused on the investigation of the structure relationship in non-peripherally substituted Pc. Non-peripherally substituted Pc with sterically hindered *tert*-butylsulfanyl substituents showed unexpected hypsochromic shift of Q-band in comparison with others Pcs in the studied series. Moreover, substantial effect of substituents nature on basicity of azomethine nitrogens was observed. Finally, the series of non-peripherally and peripherally substituted Pcs was prepared and studied from acido-basic point of view. The influence of position and type of substituent attached to macrocyclic core on azomethine basicity based on determined $\log K_1$ was described