ABSTRACT

Photoactive organic molecules studied by time-resolved fluorescence spectroscopy.

This thesis describes time-resolved fluorescence spectroscopy and stationary fluorescence and absorption spectroscopy techniques and their use in study of selected group of photoactive molecules. A great deal of effort has been also put into developing custom experimental setup operating on the basis of the time correlated single photon counting technique. The specificity of the investigated by this tool processes necessitated the use of a tunable source of excitation and single photon detector capable to detect photons in the upper range of visible and in the lower range of near-infrared light. Commercially available measurement systems that implement time correlated single photon counting technique are not usually able to meet all these requirements. To overcome this limitation, a custom experimental setup was built and together with the method of analysis of the data obtained with its use are described herein.

Photoactive molecules are defined as those in which light absorption initiates useful physical processes or chemical reactions. Photosensitizers, which are used in photodynamic therapy of cancer and bacterial or viral infections are one of the most interesting group of photoactive organic molecules. Photodynamic therapy is therapeutic procedure that can exert a selective photoactivity toward a certain type of cells. The procedure involves administration of a photosensitizing agent followed by irradiation at a wavelength corresponding to photosensitizer absorption band. Photosensitizer is then transformed to its excited electronic states, also responsible for the generation of reactive oxygen species directly destroying unwanted cells. The majority of the latest generation photosensitizers used in medical practice are aromatic macrocyclic compounds that are mainly analogues of naturally-occurring porphyrins. Surprisingly, phthalocyanines were initially used mainly as dyes in the textile and paper industry, and have recently made their way into photodynamic therapy as photosensitizing agent. Synthetic analogues of phthalocyanine seem to be much more promising photosensitizers due to their high molar absorption coefficient over the range of wavelengths that are well transmitted by human skin. The key aspect of efficient photodynamic therapy operation is the ability to efficiently deliver a photosensitizer to a selected place in the body. Tailoring of phthalocyanines' properties in order to assure efficient and selective distribution is attempted through the introduction of bulky substituents. However, the substitution may cause an aromatic plane distortion which affects the electronic structure, lowers aromatici-

ty and increases basicity, making molecules more prone to protonation. Moreover, bulky substituents might also significantly modify the susceptibility to aggregation. Both protonation and aggregation are undesirable effects because they can lower the photosensitivity of the photosensitizer, by reducing the efficiency of photodynamic therapy. Unfortunately, the photophysical properties of aggregated and protonated metallophthalocyanines are rarely studied together and the literature lacks side-by-side comparisons of the effects caused by each phenomena. This work tries to fill this gap and report on systematic spectroscopic studies of protonation and aggregation of metallophthalocyanines bearing the same substituent in all non-peripheral positions. The obtained results will allow to design better photosensitizers by taking into account the studied effects.

To be precise, protonation of three pairs of two types of metallophthalocyanines (zinc and magnesium) non-peripherally substituted with eight 1,4,7-trioxanonyl, *n*-butoxy or *i*-propoxy moieties was studied by steady-state and time-resolved optical spectroscopy. Each compound is easily protonated in organic solvents, but the central metal ion strongly affects the character of this process. In particular, the magnesium derivatives form the *cis*-diprotonated isomers, which was observed for the first time in metallophthalocyanines, in contrast to its zinc counterparts which form the typical and widely observed *trans*-diprotonated isomer. In addition, studies performed on metallophthalocyanines substituted with any listed groups at their non-peripheral positions indicated that the formation of the *cis*-diprotonated forms is a more common feature of alkoxy-substituted magnesium metallophthalocyanines, in contrast to derivatives with zinc ion. The *cis*-diprotonated forms of the magnesium derivatives are formed at much lower proton concentrations than the *trans*-diprotonated forms of their zinc counterparts. The *cis*-isomers were also found to have more advantageous photophysical properties for photoactive applications than the *trans*-isomers. Aggregation studies of the 1,4,7-trioxanonyl metalophthalocyanines revealed that the magnesium derivative aggregates much more easily in non-coordinating solvents than its zinc counterpart. Both the derivatives form fluorescent aggregates, which is typically attributed to the presence of oxygen-to-metal intermolecular coordination preventing formation of non-fluorescent H-aggregates. These results indicate that the oxygen-to-metal coordination plays a significant role in the studied systems and that the stronger oxygen-coordination ability of magnesium ions compared to zinc ions may underlie the observed differences between the metallated phthalocyanines. The determined fluorescence decay times of the basic and protonated forms investigated metalophthalocyanines are a function of the degree of protonation, but the shape of this dependence is different depending on the metal ion. Fluorescence decay times determined for 1,4,7-trioxanonyl zinc metalophthalocyanine are in the close correlation with the Stokes shift and with the Q band position where magnesium derivative

retains only correlation with the Stokes shift. The following observations may indicate that the emission properties of the *cis*-diprotonated magnesium derivatives of phthalocyanine are defined not only by the energy gap law but also by another phenomenon able to compensate this fundamental rule.