PHOTOSENSITIZER $TPPS_4$ AGGREGATION AND AGGREGATE TYPE SPECTROSCOPIC STUDIES IN NEUTRAL AND HIGHLY ACIDIC PH ENVIRONMENTS

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Cancer development in patients is at an utmost high. A progressive cancer treatment is photodynamic therapy (PDT), that utilizes photosensitizer, light and molecular oxygen to initiate selective cancer cells death by singlet oxygen, produced by the long lived triplet state of the photosensitizer.

The absorption spectra changes of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$), a photosensitizer proposed for PDT, were measured with Varian Cary 50 spectrophotometer in spectral region 350 nm - 750 nm, in deionized water at different pH (achieved by adding into the aqueous solution HCl (1M) and NaOH(1M)) and different concentrations ($1x10^{-2}$M - $1x10^{-6}$M). It is well known that in acidic environment $TPPS_4$ molecules can form J-aggregates, that exhibit characteristic absorption bands at 490 nm and 709 nm. These aggregates are formed because negatively charged SO_3^- group interacts with the positively charged core of protonated porphyrin ring [1]. At neutral pH, the $TPPS_4$ core is neutral, therefore J-aggregates are unable to form, but spectral changes were detected at high $TPPS_4$ concentrations. A significant Red-shift of Q_1 and Q_4 absorption bands and the intensity redistribution of central Q_2 and Q_3 bands show a new type of aggregate, possibly face-to-face, formation.

At very acidic pH=-1 all SO_3^- are protonated, therefore there are no electrostatic interactions of the positively charged core of porphyrin ring and neutral SO_3^-, but, with increasing $TPPS_4$ concentration, absorption spectrum changes were detected, which are slightly similar to J-aggregate formation. Our studies have shown that, regardless of the pH of the solution, $TPPS_4$ form aggregates at high concentrations, that are characterized by a lower quantum efficiency of singlet oxygen generation, therefore it is necessary to control the concentration of TPPS-based photodrugs, injected into the patient, because a too high dose of a photosensitizer can lead to aggregation and, as a result, the decrease in singlet oxygen generation, which will determine the lower efficiency of PDT.

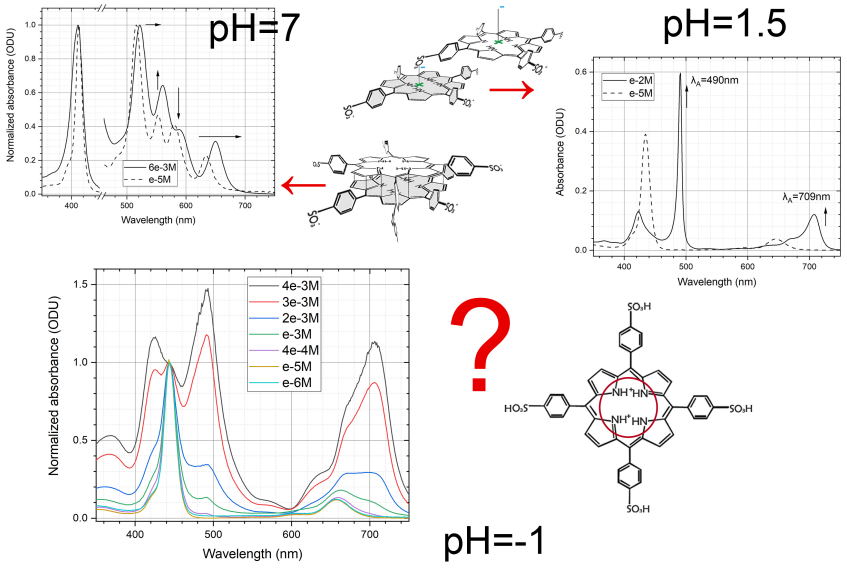

Fig. 1. $TPPS_4$ aggregation and aggregate types in different pH environments.

[1] Rotomskis R, Augulis R, Snitka V, Valiokas R, Liedberg B, Hierarchical Structure of $TPPS_4$ J-Aggregates on Substrate Revealed by Atomic Force Microscopy, J. Phys. Chem. B 2004 108(9), 2833-2838. DOI: 10.1021/jp036128v