SINGLET OXYGEN GENERATION BY NANOASSEMBLIES CONTAINING PORPHYRIN MACROCYCLES: STERIC AND SCREENING EFFECTS, ENERGY TRANSFER AND COMPETING PROCESSES

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To date, it is well documented that molecular oxygen, O_2, being a unique and fascinating molecule plays the significant role in many processes occurring on earth. Correspondingly, the study of oxygen and oxygen-dependent processes continues to be of scientific and practical interest. Especially within last fifty years and up to now the related scientific activity was connected with the photo-induced generation of cytotoxic forms of O_2, investigation of their emission, photophysical and redox properties as well as to search their practical applications.

Here, we discuss some principal aspects which should be taken into account upon quantitative analysis of the interaction with O_2 and the singlet oxygen ($^1O_2$ or $^1\Delta_g$) generation by various tetrapyrrolic photosensitizers (including monomers, chemical dimers, triads, pentads and organic-inorganic nanoassemblies). In all cases, the direct experimental measurements of $^1O_2$ emission at λ_{max}=1.27 μm need to be corrected to the solvent influence (refractive indexes, molecular polarizability) on the rate constant of the radiative transition $^1\Delta_g \rightarrow {}^3\Sigma^-_g$ in a $^1O_2$ molecule. For porphyrin and chlorin chemical dimers, T_1 states quenching by O_2 followed by $^1O_2$ generation depends on donor-acceptor interactions between the dimer halves, extra-ligation effects as well as on the spacer flexibility. In the case of self-assembled triads and pentads containing Zn-porphyrin dimers and pyridyl substituted porphyrin free bases (H_2P) as extra-ligands, quenching rate constants of H_2P T_1 states by O_2 are smaller compared to those found for individual monomeric H_2P molecules which is explained by the spatial screening influence of a strongly quenched Zn-porphyrin dimer in multiporphyrin complexes. Finally, at 293 K for nanoassemblies of two types (semiconductor quantum dots CdSe/ZnS + coordinative linked tetra-pyridyl porphyrins, and semiconductor negatively charged quantum dots AgInS/ZnS + positively charged porphyrin molecules) it was quantitatively shown that non-radiative energy transfer FRET quantum dot→porphyrin (competing with electron tunneling under conditions of quantum confinement) is only responsible for the singlet oxygen $^1O_2$ generation by nanoassemblies.

These studies demonstrate that the combination of experimental techniques and molecular-level insight into quantum dot (QD) morphology may increase our molecular-level understanding of the surface chemistry and photophysical events in QD-porphyrin nanoassemblies. In addition, the attachment of photoactive porphyrin macrocycles with biocompatible water-soluble AIS/ZnS/GSH QDs may solve such urgent problems in the photodynamic therapy (PDT) as the photosesitizer toxicity, undesirable aggregation, prolonged release and also developing new carriers for safe photosesitizer delivery to the target site. AIS/ZnS/GSH QDs contain no toxic elements, have excellent optical and electronic properties (depending on pH and local polarity), and can be applied in cancer diagnosis and PDT Basic results being obtained and discussed here, may be useful in the directed formation of new nanoscale organic-inorganic building blocks and offer significant advantages in a wide areas of applications including the photodynamic therapy.

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