ENERGY TRANSFER AND SINGLET OXYGEN GENERATION IN "SEMICONDUCTOR QUANTUM DOT – PORPHYRIN" NANOASSEMBLIES

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A "bottom-up" strategy was used for the directed formation of two types of sel-organized nanoassemblies based on colloidal semiconductor quantum dots (QDs) and porphyrins: i) TOPO-capped CdSe/ZnS QDs attached via coordination interactions with tetra-pyridylporphyrins, $H_2P(3'\text{-}Py)_4$, in toluene, and ii) AgInS/ZnS QDs stabilized by glutathione (GSH) electrostatically coupled with positively charged porphyrin molecules $H_2P(4'\text{-}MePy+)_4$ via Coulomb attraction in water. Based on experimental and theoretical analysis it was argued that the QD photoluminescence (PL) quenching in QD-porphyrin nanoassemblies is caused by two main competing non-radiative PL processes: i) non-radiative energy transfer QD → porphyrin of Foerster type (FRET); ii) non-FRET processes including electron tunneling beyond the QD core under conditions of quantum confinement. Depending on QD type, FRET efficiency is Φ = 10-15% (CdSe/ZnS) and achieves Φ = 70% (AgInS/ZnS).

For "CdSe/ZnS QD-Porphyrin" nanoassemblies, using direct measurements of near-IR photoluminescence measurements of singlet oxygen $^1\Delta_g$ emission (λ_{max} = 1.27 μm) it was shown that efficiencies of $^1\Delta_g$ generation by QD-porphyrin nanoassemblies are in a good coincidence with FRET efficiencies Φ_{FRET} obtained from the direct sensitization data for porphyrin fluorescence. In the case of "AIS/ZnS/GSH QD-porphyrin" nanoassemblies, the generation of $^1\Delta_g$ was detected indirectly using an alternative method for the oxidation of specific substrates (pyridoxine molecules) that readily react with singlet oxygen. For nanoassemblies of both types it was shown, that upon excitation of QD singlet oxygen $^1\Delta_g$ generation is realized by triplet excited porphyrin molecules formed after FRET QD → porphyrin presumably. These results together with a specific dependence of spectral-kinetic parameters of AIS/ZnS/GSH QDs on pH and local polarity, studied by us recently, make these nanoobjects perspective in various biomedical applications (drug delivery carriers, the distant testing the local pH, the photodynamic therapy of cancer cells, etc.).

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