PHOTOINDUCED ELECTRON TRANSFER IN NANOASSEMBLIES CONTAINING PORPHYRIN MACROCYCLES: PATHWAYS AND MECHANISMS

E. I. Zenkevich[1,2], **C. von Borczyskowski**[3]

[1]Belarussian National Technical University, Minsk, Belarus
[2]Research Center for Materials, Architectures and Integration of Nanomembranes, Chemnitz University of Technology, Chemnitz, Germany
[3]Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany

Today it is well documented that tetrapyrrole macrocycles displaying an impressive variety of electronic and optical properties, connected partly with various central metals, are considered as pigments of life in nature, performing different functions in living systems depending on the bound metal ion. Thus, it’s not surprising that a huge range of tetrapyrrole compounds as well multiporphyrin arrays has been investigated, with the goal of synthetizing efficient bioinspired molecular systems for light harvesting (energy transfer events), charge separation (photoinduced electron/hole transfer), photocatalytic processes, nanoelectronics and biomedicine. It was evidently shown that self-assembly is promising for construction of a wide variety of multiporphyrin nanoassemblies, whose 1D/2D/3D structures are typically relevant to their functions. In-depth understanding of their structure-function correlations is essential for rational design and development of functional multiporphyrin nanoassemblies. Given the potential applications and the need for better theoretical frameworks, the design and construction of novel multiporphyrin architectures by self-assembly and self-organization continues to be an active research area.

Here, taking into account our recent results (including experimental findings and theoretical calculations we would like to present quantitative comprehensive analysis of the reasons of luminescence quenching due to competing non-radiative relaxation processes paying an especial attention to the analysis of some peculiarities of photoinduced electron transfer (PET) presumably. Using the combination of spectral static and time-resolved experimental data together with theoretical calculations in the frames of the corresponding models, the dynamics of competing non-radiative relaxation processes was quantitatively studied for various nanoassemblies containing porphyrin macrocycles (meso-nitro-phenyl-octaethylporphyrins and their chemical dimers; Zn-porphyrin chemical dimers covalently linked with electron acceptor of non-porphyrin nature; self-assembled porphyrin triads with covalently linked electron acceptors) upon variation of properties of surrounding. Especial attention was paid to the analysis of some peculiarities of the photoinduced electron transfer (PET) in few unusual and rare cases: i) the direct PET “through-space” mechanism. with participation of S_1 and T_1 states in the conditions of strong steric interactions between bulky C_2H_5 substituents in β-positions of pyrrole rings and NO_2 group; ii) the competition of PET and energy migration in Zn-porphyrin chemical dimers with covalently linked electron acceptor; iii) in self-assembled porphyrin triads, the extra-ligand S_1 state quenching via hole transfer “extra-ligand → dimer” followed by the efficient formation of the locally excited T_1 state of porphyrin free base; iv) realization of low-temperature PET in triads containing fluorinated porphyrin as electron acceptor; v) the extra-ligand S_1 state quenching via long-range superexchange PET to covalently linked electron acceptor in triads.

The issues raised herein seem to be of interest in research concerning the development and studies of synthetic multiporphyrin arrays modelling light-harvesting and charge-transfer phenomena *in vivo* as well as for the rational design and application of multimolecular devices for nanophotonics and nanoelectronics.

This work was supported by BSPSR program “Photonics and Electronics for Innovations (Belarus, 2021–2025)”, European Union Grant Agreement 732482 (Bio4Comp 2021 in the framework of a Training Period, and Visiting Scholar Program of TU Chemnitz, Germany (2020–2021).