

DEACTIVATION OF EXCITED STATES IN NANOSTRUCTURES CONTAINING Cu-PORPHYRIN MACROCYCLES

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At present, supramolecular chemistry presents itself a highly interdisciplinary field of nanotechnology covering the chemical, physical, and biological features of chemical species held together and organized by means of intermolecular binding interactions of various nature. The most important source of inspiration for self-assembly strategies is natural photosynthesis in which the generation of complex, multicomponent three-dimensional structures involve intramolecular, as well as intermolecular and interfacial interactions. It is clear that for any given multicomponent nanostructure the main problem is the understanding presumably of how the multiple components by various nature and composition may interact and function as a whole in order to predict its possible applications. It should be noted that the photochemistry of hybrid nanoassemblies having tetrapyrroles with central paramagnetic metal ions, for instance Cu(II), is rather complex because of presence of unpaired d-electron in central metal.

Thus, keeping in mind the above peculiarity, in this report we discuss some relatively rare relaxation processes in multicomponent nanostructures including Cu containing tetrapyrrolic macrocycles namely which make these nanoassemblies more special. This discussion is based on steady-state, picosecond time-resolved measurements and single objects detection at 77-293 K. The important question is: what happens with excited states of nanoassembly subunits of various nature and morphology being coupled with adjacent Cu-porphyrins. Correspondingly, the systems under discussion are: porphyrin chemical dimers, self-organized porphyrin pentads and larger complexes, polymeric ordered aggregates of chlorophyll and protochlorophyll as well as nanoassemblies “Semiconductor CdSe/ZnS quantum dots (QD) + tetra-*meso*-pyridyl substituted Cu-porphyrins”.

It has been evaluated that the excitation energy relaxation in Cu-porphyrin containing hybrid chemical dimers are caused by few reasons: i) the increase of the non-radiative deactivation of excited states for the dimer half not containing central Cu ion (due to exchange d- π effects); ii) the energy transfer from 2T_1 and 4T_1 states of Cu-porphyrin to the excited T_1 state of porphyrin free base; iii) the formation of short-lived radical ion pair via the photoinduced electron transfer; iv) exchange resonance T-T energy transfer. In porphyrin pentads, long-distant exchange d- π effects manifest themselves in an additional fluorescence quenching of two chemical dimers (ZnOEP) $_2$ Ph. In the case of ordered protochlorophyll aggregates containing Cu-pheophytin (at small molar ratios PChl:Cu-Pheo = 1000:100), we showed that a fluorescence strong quenching is definitely connected with exchange d- π effects influence on the neighboring PChl *a* molecules in the close vicinity of Cu-Pheo subunit in mixed aggregates. Finally, using the combination of ensemble and single QD experiments together with low-temperature experiments and PL decay analysis for “QD+Cu-porphyrin” nanoassemblies, we showed for the first time that already one attached Cu-porphyrin molecule on QD surface causes not only QD PL quenching but also manifests itself in a low-temperature reconstruction of TOPO capping layer (“phase transition”) accompanied by significant changes of the QD electronic surface states in the energy scale.