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Electronic Energy Relaxation Processes in Chlorophyll and its Analogs: From Concentrated Solutions to Structurally-Organized Nanoassemblies

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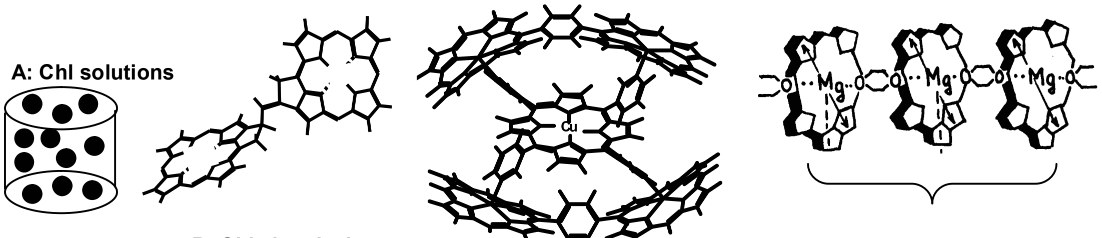
The seminal importance of chlorophylls as Nature's chief light absorbers has elicited vast studies encompassing biology, chemistry, and physics. Chlorophylls along with heme and bacteriochlorophylls are the most abundant members of the so-called "pigments of life", which constitute a subset of the large class of tetrapyrrole macrocycles. The investigations of the primary light-harvesting reactions in natural photosynthetic systems have improved appreciably our understanding of the mechanisms involved in the transfer and trapping of solar energy. Nevetheless, up to now the interpretation of the spectral-kinetic parameters of *in vivo* photosynthetic light-harvesting systems and reaction centers is met with considerable difficulties due to the combined effects of the pigment–pigment and pigment–protein interactions taking place in natural objects. In this respect, the formation of artificial complexes containing chlorophyll and other tetrapyrrolic compounds followed by comprehensive analysis of mechanisms of photoinduced relaxation processes seems to be considered as a necessary and important step in order to understand detailed pathways and specificity of natural photoprocesses taking place in living systems.

This review talk presents main results being obtained by Byelorussian scientific school of academician G.P. Gurinovich and his followers devoted to the study of spectral-kinetic properties and photonics of pigment-pigment interactions for chlorophyll and its immediate analogs *in vitro* (from highly concentrated solutions to structurally-organized heterogeneous nanoassemblies of various morphology, see Figure below). The combination of modern experimental spectroscopic approaches has been used in this study in a temperature range of 4.2 ÷300 K: steady-state and time-resolved (ns-ps-fs) spectroscopy, optical activity and polarization measurements, fluorescence line narrowing and spectral hole burning, etc. The adequacy was validated for various theoretical models describing the primary processes of photosynthesis (the electronic excitation energy transfer and the photoinduced charge transport) at small interchromophore distances subject to surrounding properties the conformational dynamics of interacting subunits.



B: Chl chemical

D: Polymeric ordered Chl

C: self-assembled multiporphyrin complexes

Application-oriented aspects were considered concerning the use of multicomponent nanostructures based on photostable tetrapyrrolic compounds with controllable electron-transport properties and conformation mobility for the development of elemental base in molecular electronics, photonics, medicine and nanobiotechnology. Here, we review possible strategies for designing nanoscale light-harvesting systems based on tetrapyrrolic pigments and nanoassemblies on their basis. In fact, understanding the evolutionary constraints imposed on bioenergetic systems is not only an intellectual pursuit but may be a key to unlock our energy future.