Impact of xanthophyll pigments on molecular organization and photophysical properties of pigment-protein complex LHCII

The largest light harvesting pigment-protein complex of Photosystem II (LHCII) is the major photosynthetic antenna protein which involves more than half of chlorophyll molecules in biosphere. The main role of antenna complexes (in normal light condition) is solar energy collection and excitation energy transfer towards to the photosynthetic reaction center where charge separation takes place. In light stress condition, overexcitation of photosynthetic apparatus can lead to their oxidative damage. This phenomenon is the result of singlet excited states to the triplet excitation conversion within chlorophylls. In triplet state chlorophyll plays a role of photosensitizer. Reactions between this form of chlorophyll and molecular oxygen can lead to the formation of harmful, highly reactive singlet excited oxygen. Fortunately, during the evolution, plants developed different mechanisms preventing photodamage. One of the most efficient photoprotective solution is binding carotenoid pigments in photosynthetic complexes. Xanthophylls are able to dissipate energy excited chlorophyll triplet via heat emission.

In addition to photoprotective function, it is considered that xanthophyll pigments take part in molecular organization of photosynthetic antenna. All the pigment-protein complexes in the photosynthetic apparatus of plants are located within the thylakoid membranes. One of the remarkable features of the thylakoid membranes is extremely high concentration of protein with respect to lipids. The protein fraction in the chloroplast grana region may reach even 70 % of the thylakoid membrane surface. Close distances between pigment-protein complexes in densely-packed membranes ensures efficient energy transfer, but on the other hand, such a high molecular crowding would induce aggregation of complexes. These forms of molecular organization pigment-protein complexes are able to quench electronic excitations by turning them into heat. It is very important to find and understand mechanism which allow efficient transfer and quenching to coexist in the same system. One of mechanisms would be formation supramolecular structures with xanthophylls pigments which are present in lipid phase of the thylakoid membrane. In such structures xanthophylls would play a role of the linkers complexes, and at the same time, spacers preventing their aggregation.

The main objections of research were explanation the impact of additional exogenous xanthophyll pigments on the lamellar organization of the LHCII complex and understanding mechanisms involving these pigments in regulation energy transfer within antenna complexes.

The study was performed in artificial and natural system. The objects of measurements were monolayers: LHCII, LHCII with additional xanthophylls and intact leaves of *Delonix regia* and *Arabidopsis Thaliana*. The measurements were carried out using a variety of techniques: Langmuir-Blodget, structural (AFM) and spectroscopic (steady state and time resolves fluorescence, Infrared and UV-VIS absorption).

The results indicate that xanthophylls are involved in photoprotective mechanism connected with quenching higher excited states of chlorophylls via energy transfer to the exciton levels. Exciton states are formed in the presence of supramolecular structures of proteins and xanthophylls. Such structures under physiological illumination condition determine efficient excitation energy transfer.

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