Chlorophyll in chlorophyll-protein complexes: the major antenna complex of photosystem II, LHCII, as a paradigm.

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Chlorophyll (chl) molecules are bound to proteins in the chl-protein complexes that make up photosystems of plants and are responsible for their characteristic, lowest energy, Q_y absorption band (red region of the visible spectrum). They play an essential role in light harvesting and primary photochemistry (charge separation processes). The spectral characteristics of protein-bound chls are modulated by interactions with their protein environment, giving rise to spectroscopically different chl forms, or eigenstates, having different absorption transition energies. This structurally induced spreading of chl energy transitions and the mutual interactions present between the chromophores broaden and shift towards lower energies the Q_y absorption band of chl-protein complexes with respect to chl absorption band in solvents (e.g. Diethyl-ether). The complex chl vibronic structure and the intrinsic transition energy inhomogeneous broadening prevents the direct identification of all the energy levels characteristic of the chromophore arrays of chl-protein complexes. Moreover, interaction among chromophores within the array changes the distribution pattern of transition energies, giving rise to eigenstates that are, in principle, delocalized over a number of chromophores and with the dipole strengths being redistributed amongst them. This final picture is a function of both chl spatial organization and unperturbed chl site energy transitions, i.e. those transitions characteristic of chl sites in the absence of interactions among them.

Information concerning both the site transition energies and the chl mutual interacting energies are not directly accessible from the experimental data. Whereas X-ray crystal model analysis gives information on chl spatial arrangement, their mutual orientation and distances, allowing interaction energy estimation, information about the site specific chl transition energies is lacking. This information is essential to understand the optical properties of the chl-protein complexes as well as energy transfer in chl antenna-reaction center arrays. It becomes evident from the X-ray structure analysis of the chl-protein complexes, crystallized up to now, that a number of qualitatively different ligand-protein contacts are present. This induces different chl macrocycle deformations. Analysis of these chl deformations, using the chl atomic coordinates obtained by LHCII crystal model analysis, indicates that the Q_y energy transitions are strongly modified. On this basis, and taking into account the planar macrocycle conformation, chla Q_y absorption transition red shifts of up to about 17 nm were estimated. These are rather close to the experimental data. This transition energy modulation is suggested as being the principle source of chl spectral form generation (chlorophyll energy disorder).