Architecture and function of plant light-harvesting complexes II
Xiaowei Pan, Zhenfeng Liu, Mei Li and Wenrui Chang

The antenna system associated with plant photosystem II (PSII) comprises a series of light-harvesting complexes II (LHCII) which are supramolecular assemblies of chlorophylls, carotenoids, lipids and integral membrane proteins. These complexes not only function in capturing and transmitting light energy, but also have pivotal roles in photoprotection under high-light conditions through a mechanism known as non-photochemical quenching process. Among them, the most abundant major species (majLHCII) is located at the periphery of PSII and forms homo/hetero-trimers. Besides, three minor species, named CP29, CP26 and CP24, are adjacent to the PSII core, exist in monomeric form and bridge the majLHCII trimers with the core complex. Structural studies on majLHCII and CP29 have revealed the overall architecture of plant LHC family, the binding sites of pigment molecules and the distribution pattern of chromophores in three-dimensional space. The high-resolution structural data of LHCII s serve as fundamental bases for an improved understanding on the mechanisms of light harvesting, energy transfer and photoprotection processes in plants.

Addresses
National Laboratories of Biomacromolecules, Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, China

Corresponding authors: Liu, Zhenfeng (liuzf@sun5.ibp.ac.cn), Chang, Wenrui (wrchang@sun5.ibp.ac.cn)

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Introduction
Light-harvesting complexes (LHCs), a superfamily of chlorophyll (Chl) and carotenoid (Car) binding proteins present in eukaryotic photosynthetic organisms (plants and green algae), are responsible for the absorption of solar energy and transfer of excitation energy to the reaction centers. Under high-light conditions, the switch of LHCs from efficient light-harvesting state to a highly quenched state is vital for protecting plants against the damaging effect of excessive energy. Such a photoprotection mechanism is known as non-photochemical quenching (NPQ) or non-radiative dissipation (NRD) of excitation energy [1]. Around the plant photosystem II (PSII) core, the most abundant antenna complex is trimeric major LHCII (majLHCII) which contains three apoprotein subunits Lhcb1, Lhcb2 and Lhcb3, and form Lhcb(1)3, Lhcb(2)3 homotrimers or mixed Lhcb1/Lhcb2/Lhcb3 heterotrimers with variable stoichiometry of three subunits [2,3]. In addition, three minor antenna complexes of PSII are present as monomers and named CP29 (Lhcb4), CP26 (Lhcb5) and CP24 (Lhcb6) on the basis of the apparent molecular mass of their apoproteins [4].

The major and minor LHCII s are associated with the core complex of PSII to form PSII–LHCII supercomplex in green plants. The large C2S2M2 supercomplex observed by electron microscopy contains a dimeric core complex (C2), two strongly bound majLHCII trimers (S2), two moderately bound majLHCII (M2), two CP29, two CP24 and two CP26 (Figure 1a) [5,6,7*]. Besides the S2 and M2 majLHCII trimers, there are loosely bound majLHCII trimers (L) at peripheral region which can migrate between PSII and PSI to balance the excitation level of two photosystems in response to light fluctuations [8*]. The process involves reversible phosphorylation and dephosphorylation of majLHCII, a fundamental event of state transition mechanism [9,10]. Recently, stable plant PSI–LHCCI supercomplex has been isolated and electron microscopy analysis shows that majLHCII is bound to PSI at 1:1 ratio when it is phosphorylated during state transition (Figure 1b) [8*].

The following part of this review will focus on discussing the structure and function of the LHCCI complexes in detail.

Structures of majLHCII and CP29
A long journey toward high-resolution structures of plant LHCII s
Through progressive refinement of two-dimensional crystal samples of the majLHCII from pea, Kühbrandt and coworkers obtained a three-dimensional model of majLHCII at 3.4 Å resolution using electron crystallography [11,12**,13,14]. In this structure, three membrane-spanning κ helices, a small amphipathic helix in the C-terminal region, and the backbones of 12 chlorophyll (Chl) and two lutein (Lut) molecules were resolved. Because of the limit of resolution along the direction of membrane normal, important information relevant to the function of majLHCII remained undefined such as the assignment of Chla or Chlb (the difference being methyl or formyl at the C7 position of tetrapyrrole ring), the head and tail groups of each individual Chl (important for the determination of transition dipole moment of Chl), the binding sites for two other carotenoid molecules, namely

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neoxanthin (Neo) and violaxanthin (Vio, a xanthophyll-cycle carotenoid), and the detailed interactions between protein and pigment molecules. For an accurate and quantitative analysis of the energy absorption and transmission process, as well as the mechanism of photoprotection involving LHCIIIs, it is indispensable to solve their high-resolution structures with complete assignment of each individual chromophores. To this end, the structure of spinach majLHClII was solved at 2.72 Å by X-ray crystallography in 2004, which provided an unprecedented high-resolution view of the entire complex [15**]. A year later, the X-ray structure of pea majLHClII was reported [16] and is essentially identical to the spinach majLHClII structure except that they were solved in different crystal forms. Subsequently, the crystal structure of a minor LHC, CP29 from spinach, was solved at 2.8 Å resolution [17**]. With the high-resolution structures of majLHClII and CP29, it becomes possible to gain detailed insights into the mechanism of light energy harvesting and regulation processes.

Major LHCII and CP29 have similar apoprotein structures but different oligomeric states

The apoproteins of majLHClII and CP29 both contain three membrane-spanning α-helices, named helices A, B and C, as well as two short amphipathic helices (D and E) located at their luminal surfaces. The amino termini are located at the stromal side and the carboxyl termini are on the luminal side (Figure 2a–d). Helices A and B intertwine in the middle of membrane and form a left-handed supercoil. Two conserved inter-helix ionic pairs (Glu65-Arg185 and Arg70-Glu180 in majLHClII, or Glu96-Arg202 and Arg101-Glu197 in CP29) contribute to the stability of the central supercoil (helices A and B) (Figure 2e). A pseudo-C$_2$ axis runs through the core region of each monomer and relates helices A–D to helices B–E. The helix C runs nearly perpendicular to the membrane plane and does not abide to the internal pseudo-C$_2$ axis. It contains a conserved intra-helix ionic pair (Glu139-Arg142 in majLHClII or Glu159-Arg162 in CP29). Despite overall similarity of apoprotein folds, significant differences between majLHClII and CP29 are present.
The overall structures of majLHCII and CP29. (a) The overall structure of majLHCII viewed in parallel with the membrane plane. For comparison with CP29, only one monomer of majLHCII is shown as cartoon model, while the rest two monomers are shown as transparent surface presentation. (b) majLHCII viewed from the stromal side along the three fold axis. (c, d) The overall structure of CP29 viewed in parallel with the membrane plane (c) and along the membrane normal from stromal side (d). The transmembrane and amphipathic helices in majLHCII monomer and CP29 are labeled as ‘A–E’. The cofactors in each complex are shown as ball-and-stick models. For clarity, the phytol tails of chlorophyll molecules are omitted. Color code: green, chlorophyll a (Chla); blue, chlorophyll b (Chlb); cyan, Chl a/b610 in CP29; magenta, lutein (Lut); yellow, violaxanthin (Vio); orange, neoxanthin (Neo); pink, phosphatidyl glycerol (PG) in majLHCII; pale-blue, digalactosyl diacylglycerol (DGDG) in majLHCII; wheat, glyceraldehyde 3-phosphate (G3P) in CP29. (e) Superposition of majLHCII apoprotein (blue) with that of CP29 (yellow). (f) The interfacial region important for trimerization of majLHCII. The key parts are highlighted as colored ball-and-stick models.

The helices A and B of CP29 are both slightly shorter than the corresponding helices in majLHCII. The amphipathic helix D of CP29 moves closer toward the hydrophobic core. The A–C, B–E and E–C loops of CP29 are all shorter than those of majLHCII (Figure 2c). The Val119 in the E–C loop of majLHCII, whose carbonyl oxygen serves as the central ligand of Chl b605, does not find its counterpart in CP29.

The most notable difference between majLHCII and CP29 is the oligomeric state change from trimer (majLHCII) to monomer (CP29). The trimerization regions of majLHCII involve the N-terminal and C-terminal domains, the stromal end of helix B, several hydrophobic residues from helix C as well as the pigment and lipid molecules bound to these areas (Figure 2f). The amino acid sequence WYXXXR in position 16–21 of majLHCII was indicated to be essential for trimer formation [18]. This motif is conserved among Lhcb1, Lhcb2, Lhcb3 and CP26, but not in CP29 or CP24. In the majorLHCII structure, the WYXXXR motif not only directly contributes to the binding of a phosphatidyl glycerol (PG) molecule at the trimerization interface, but also stabilizes the local structure of the N-terminal domain that is essential for binding and positioning of the PG molecule and a Chlb (Chl b601) at the interface (Figure 2f). Biochemical studies have shown that both the N-terminal domain and PG are vital for the stability of majLHCII trimer [19,20]. In addition to the N-terminal domain, the C-terminal region of majLHCII also contributes to the stability of its trimeric state [21]. The bulky side chain of Trp222 in this region intercalates at the monomer–monomer interface and serves as a stabilizer for the interactions between adjacent monomers. In the case of CP29 monomer, its N-terminal domain was partially degraded in the process of crystallization, suggesting it is relatively flexible or contains a disordered region that is amenable to protease digestion. The final structural model of CP29 does not cover the first 87 residues of the polypeptide chain. A moiety shaped like a glyceraldehyde
3-phosphate (G3P) molecule occupies the corresponding position of the polar head group of PG in majLHCII. The tentatively assigned G3P is sandwiched between Chls \( a_{611} \) and \( a_{615} \), and coordinated to the central magnesium atoms of both Chls through its phosphate group (Figure 2c, d). Moreover, the C-terminal region of CP29 becomes six residues shorter than that of majLHCII and the Trp222 residue of majLHCII has been replaced by Leu239 in CP29 (Figure 2e). Essentially, nearly all the major elements critical for trimerization are absent in CP29, thus explaining why it exists as a monomer.

**Chlorophyll binding sites and their arrangement pattern**

Chlorophylls are the major light-harvesting molecules in LHCII complexes. As shown in Figure 3a, b, each majLHCII monomer contains 14 chlorophyll molecules including eight Chls \( a \) and six Chls \( b \). In comparison, the CP29 monomer contains 13 chlorophyll molecules, including eight Chls \( a \), four Chls \( b \) and a Chl \( ab \) mixed binding at the 610 site (Figure 3c, d). The central magnesium atoms of chlorophyll molecules are coordinated by the side chains of amino acid residues, the backbone carbonyl groups, water or lipid molecules (Table 1). Besides direct coordination through the central Mg atoms, these coordinating entities also act as bridges between adjacent Chls within each layer of majLHCII monomer or CP29 (Figure 3a, b, c, d).

Arrangement of pigment molecules within majLHCII trimer and CP29 monomer. (a, b) The pigment molecules within majLHCII trimer in the layers close to the stromal (a) and the luminal surfaces (b), respectively. (c, d) The pigment molecules of CP29 within the stromal (c) and the luminal layers (d), respectively. The adjacent Chls within each layer of majLHCII monomer or CP29 are connected with dark dashed lines, and the distances (\( \AA \)) between their central Mg atoms are labeled with red digital numbers.
magnesium, some Chl$a$ and Chl$b$ molecules are additionally attached to the protein through hydrogen bonds formed with the C13'-keto group of Chl$a$ or the C7-formyl group of Chl$b$. Most of the chlorophyll binding sites in majLHCII and CP29 overlap except that Chls $b_{601}$ and $b_{605}$ (both coordinated by the backbone carbonyls) in majLHCII are absent in CP29, whereas Chl $a_{615}$ in CP29 has no counterpart in majLHCII. The conserved 609 and 614 sites are, respectively, occupied by Chl$b$ and Chl$a$ in majLHCII, but by Chl$a$ and Chl$b$ in CP29 instead. The selective binding of Chl $b/a$ on these sites is mainly due to the presence/absence of hydrogen-bond donor for the binding of C7-formyl group of Chl$b$ molecule. For example, in the case of 609 site, the side-chain amide group of Gln131 in majLHCII serves as the hydrogen-bond donors for the C7-formyl groups of Chls $b_{607}$ and $b_{609}$ at the same time, while in CP29, this site is replaced by a Glu residue (Glu151) which contains only one hydrogen-bond donor available for the binding of Chl $b_{607}$ but not for the one at 609 site. As for the 614 site in CP29, the NH group of Trp226 indole ring serves as the hydrogen-bond donor for the C7-formyl group of Chl $b_{614}$, whereas in majLHCII, the residue on the equivalent position is replaced by Leu209 whose apolar side chain is more favorable for the binding the C7-methyl group of a Chl$a$ molecule.

The chlorophyll molecules in majLHCII and CP29 arrange into two layers in parallel with the membrane plane. The layer close to the stromal surface contains eight chlorophyll molecules (five Chls $a$ and three Chls $b$ in each majLHCII monomer, or six Chls $a$, one Chl$b$ and one mixture of Chl$b/a$ in CP29) which form an elliptical ring surrounding the central helices A and B (Figure 3a, c). The remaining chlorophyll molecules are located in the layer close to the luminal surface and form two separate clusters, namely Chls $a_{604}$-$b_{605}$-$b_{606}$-$b_{607}$ and $a_{613}$-$a_{614}$ in the majLHCII monomer, or Chls $a_{604}$-$b_{606}$-$b_{607}$ and $a_{613}$-$b_{614}$ in CP29 (Figure 3b, d). Interestingly, most of Chl$a$ molecules are around the core helices A and B, while nearly all Chl$b$ molecules are enriched in the vicinity of helix C or at the interface regions of majLHCII trimer, or at the peripheral region of CP29 complex. The apparent mosaic pattern of Chl $a/b$ arrangement in majLHCII trimer might contribute to efficient energy equilibration within the trimer, while the peripheral localization of Chls $b$ in CP29 monomer indicates that they might serve as interfacial chlorophyll

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### Table 1

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<sup>a</sup> Water molecule hydrogen bonded to the C7-formyl group of Chl $b_{606}$ and also serving as the central ligand of Chl $b_{607}$ in both majLHC-II and CP29.

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molecules between CP29 and the ‘M’ type majLHCII (Figure 1a) and facilitate inter-complex energy transfer.

**Carotenoids as close neighbors of chlorophyll molecules**

There are four carotenoid binding sites observed in majLHCII, named as L1, L2, N1 and V1 sites (Figure 3b). In the case of CP29, only L1, L2 and N1 sites are detected in the structure (Figure 3d). The central L1 and L2 sites in majLHCII or CP29 contain two carotenoid molecules with all-trans configurations (Figure 4a, b). They are firmly bound in the two elongated hydrophobic cavities formed by helices A and B. From a structural view, these rigid molecules provide a strong cross-brace support for the two central helices and stabilize the complex. The L1 sites in both majLHCII and CP29 bind a lutein (Lut620) molecule whose β-cyclohexenyl ring is located near the luminal surface and the ε-cyclohexenyl ring is positioned close to the stromal surface. The β-cyclohexenyl ring of Lut620 in CP29 is pushed more inward toward the core region by the bulky side chain of Trp226 (Figure 4a). The steric hindrance and van der Waals forces in the vicinity of the ε-cyclohexenyl ring of Lut620 in CP29 result in its slightly flexural polypeptide chain in comparison to that of majLHCII.

On the L2 site, majLHCII also accommodates a lutein molecule (Lut621), whereas CP29 binds a violaxanthin molecule (Vio, an epoxidated form of xanthophyll-cycle carotenoid) (Figure 4b). In majLHCII, the L2 site is located near the trimeric core making it a stable site for Lut621 binding. The highly crowded environment exerts van der Waals repulsion force on the polypeptide chain of Lut621 on both ends, making it more twisted than that of Lut620 (L1) within the same complex. In CP29, the L2 site is apparently much more open than that of majLHCII since it is exposed on one side of the monomer surface. It is occupied by a Vio molecule instead and the open feature of L2 site in CP29 allows the exchange of Vio with zeaxanthin (Zea, a de-epoxidated form of xanthophyll-cycle carotenoid) which is involved in the regulation of light harvesting efficiency through charge-transfer quenching mechanism [22].

Both majLHCII and CP29 contain a 9′-cis neoxanthin (Neo) molecule at the N1 site near the helix C. The Neo is stabilized by a hydrogen bond between its epoxidated cyclohexane ring and the side chain of a conserved Tyr residue. Around the N1 site of CP29, Tyr157 and Ile158 on one side of Neo polypeptide chain replace the Ala137 and Val138 respectively in majLHCII. The relative larger side chains give rise to strong van der Waals repulsion force, rendering the polypeptide chain of Neo in CP29 more bended and tilted outward into lipid bilayer region (Figure 4c).

Carotenoid binding sites in majLHCII and CP29. (a) L1 sites in majLHCII and CP29 are both occupied by lutein molecules with different conformations. Lut in majLHCII is shown in magenta, while that of CP29 is in light-pink. (b) The L2 sites in majLHCII and CP29 are occupied by Lut (magenta) and Vio (yellow), respectively. (c) The N1 sites of majLHCII and CP29 are both occupied by neoxanthin molecules with different conformations. Neo from majLHCII is shown in orange, while that of CP29 is in lemon color. (d) A Vio molecule (yellow) binds at the V1 site in majLHCII. No equivalent site is found in CP29. All four panels are viewed approximately in parallel with the membrane plane from different angles. Only the chlorophyll molecules that are in close interactions with carotenoids (with the shortest π–π distances less than 5 Å) are shown. The chlorophylls from majLHCII are in blue, while those of CP29 are in wheat.

Carotenoids function as accessory light-harvesting pigments in antenna complexes and are also essential for photoprotection [23]. The ultrafast singlet energy transfer between individual carotenoid and their surrounding chlorophyll molecules, as well as the effective roles of carotenoids in quenching triplet Chlβ to prevent the formation of singlet oxygen, are dependent on the close π–π interaction of carotenoid and chlorophyll molecules, and the optimal mutual orientation between the two conjugated π systems. The arrangement of chlorophyll molecules around L1, L2 and N1 sites in majLHCII and CP29 share the similar pattern as shown in Figure 4a–c. Such pigment arrangement is consistent with the previous spectroscopic studies on majLHCII and CP29 which discovered that the singlet excitation energy of Lut in their L1 site is transferred exclusively to Chlβ, whereas
the carotenoids at their L2 sites (Lut in majLHCII or Vio in CP29) are transferred not only to Chls but also to Chlb [24,25]. The slight rotation of Neo within CP29 in respect to that of majLHCII may be responsible for their different behavior in transferring energy to Chls. It was reported that Neo in majLHCII only transfers energy to Chlb [25], whereas the Neo in CP29 is able to transfer energy to both Chla and Chlb [24]. The majLHCII contains a fourth carotenoid binding site V1 occupied by a violaxanthin (Vio) molecule which is absent in CP29. This site is located at the monomer-monomer interface and contributes to trimerization of majLHCII (Figure 2f). The V1 site in majLHCII was believed to serve as a reservoir site storing and provide Vio molecules for the operation of xanthophyll cycle [26]. The arrangement of chlorophyll molecules (b601 and a614) (Figure 4d) around the V1 site is not favorable for efficient energy transfer between chlorophyll and carotenoid [23,26].

**Insights into the energy transfer pathways between chlorophylls**

The chlorophyll concentration within majLHCII or CP29 is around 0.5 M. To avoid severe concentration quenching effect observed in the chlorophyll solution [27], the pigment molecules are positioned and oriented precisely within the LHCs, so as to prevent the formation of random energy trap that will quench excitation energy. Meanwhile, interactions between each individual chlorophyll molecule and their specific binding environments lead to the formation of discrete site energy of individual chlorophyll. The high-resolution structural data of majLHCII have promoted quantitative studies of their spectroscopic features and simulation of their energy transfer properties [28,29,30**]. These followup studies aimed to determine the specific site energy of individual chlorophyll molecules and gain a comprehensive picture of the energy transfer pathways within the majLHCII trimer.

**Figure 5**

Energy transfer pathways within majLHCII. (a) Energy transfer within and between the three Chl clusters located at the stromal layer. The red star highlights the likely red-most a610 as a potential terminal emitter and the red arrow shows the estimated outward flow direction of excitation energy. (b) Energy transfer within and between the two chlorophyll clusters at the luminal layer. The purple/blue arrows indicate the directions of energy transfer between two chlorophyll molecules or clusters. The relaxation/migration time constants (at units of ps or fs) taken from reference [30**] are labeled above the arrows. The chlorophyll molecules are simplified as three-atom models with the nitrogen atoms of Chla in yellow and those of Chlb in cyan. The clusters are defined within the oval rings.
According to the latest results [28,30**, the chlorophyll molecules within majLHCII are grouped into five clusters, three at the stromal layer (Chls a602-a603, a610-a611-a612 and b601'-b608-b609) and two at the luminal layer (Chls b606-b607-b605-a604 and a613-a614). The major pathways of intra-monomeric and inter-monomeric energy transfers within majLHCII are shown in Figure 5. At the stromal layer of the majLHCII monomer, the Redfield-type relaxation within clusters a610-a611-a612 and b601'-b608-b609 is ultrafast at about 50 fs, while the relaxation within a602-a603 takes 425 fs. Migration rates between stromal clusters are mainly at sub-ps time constants (290–800 fs), including a fast energy transfer from Chl b cluster b601'-b608-b609 to Chl a cluster a602-a603 (at 290 fs) (Figure 5a). At the luminal side, the energy of b606-b607-b605-a604 is populated on b605 and a604 since they are relatively inefficient in transferring their energy to downstream chlorophylls (Figure 5b). Therefore, these two Chls are called ‘bottleneck’ sites in Chl b → a and a → a transfer events. Energy transfers between luminal clusters are slow at 33–140 ps. Between stromal and luminal layers, the energy transfers between a613-a614 and a602-a603/a610-a611-a612 clusters are mostly 9–45 ps events, while it takes about 7 ps for the energy to transfer from b606-b607-b605-a604 heterotetramer to b601'-b608-b609 trimer (Figure 5c).

The two adjacent majLHCII subunits within the trimer are connected by exciton-coupling Chl b601'-b608-b609 cluster at stromal side, so the efficient energy transfer at sub-ps time constant between adjacent subunits becomes possible. Final equilibration within the trimer occurs via slow (6–140 ps) migration between the Chl a clusters located on different monomeric subunits, either within the same layers (such as a602-a603 to a602''-a603'' in Figure 5a) or between layers (such as between a613-a614 and a602''-a603'' in Figure 5b, shown as blue arrows). In equilibrium, the energy is predominantly populated on the a610-a611-a612 cluster and the a610 was assigned as the red-most site [30**], suggesting it may serve as the terminal emitter (red star and arrow in Figure 5a). The location of Chl a610-a611-a612 cluster at the periphery of the majLHCII trimer supports its role as the connector chlorophylls at the interfaces with adjacent antenna complexes such as CP29, CP26, CP43, CP47 or other majLHCII trimers.

**Figure 6**

A schematic diagram showing the possible mechanisms of NPQ. Under high-light conditions, the NPQ process is triggered by the increased proton gradient (ΔpH) across the thylakoid membrane, following the de-epoxidation of violaxanthin into zeaxanthin. M'-type majLHCII, CP29 and CP24 are dissociated from the PSII supercomplex, leading to the reorganization and aggregation of antenna complexes [35]. One type of possible quenching centers (oval shaped red stars) is attributed to the random and tightly interacting pigment molecules exposed on the outer surface of the majLHCII. Other two alternative quenching centers are Chls a610-a611-a612-Lut (rainbow ellipsoids) located around the L1 site in both major and minor LHCII via energy transfer, and Chls a603-a609-Zea (four-pointed stars) located around the L2 site in the minor LHCII via charge transfer. Under high-light condition, the essential subunit, PabS interacts with majLHCII and CP29, and triggers the conformational changes within majLHCII and CP29, which may lead to the formation of quenching centers within or between the LHCII complexes.
The energy transfer within CP29 was studied using a crude structural model before the crystal structure was available [24,31]. It is highly anticipated in the near future that a more accurate analysis of the energy transfer pathways within CP29 based on the newly available crystal structure [17**] will provide new insights into these processes.

The bases for non-photochemical quenching mechanism

Under high-light conditions, when the rate of the energy-converting process within the reaction centers becomes insufficient to process the amount of harvested photons, the antenna complexes are able to switch to a protective function by dissipating the excess energy as heat through NPQ mechanism [32,33]. The NPQ process is triggered by the increased proton gradient (ΔpH) across the thylakoid membrane which causes protonation of protein surfaces exposed in the lumen, as well as de-epoxidation of violaxanthin into zeaxanthin catalyzed by the violaxanthin deepoxidase [34]. The PSII antenna complexes are reorganized and a hetero-oligomeric antenna supercomplex containing ‘M'-majLHCII, CP24 and CP29 dissociates and detaches from the PSII core during NPQ [35]. The reorganization of antenna complexes may lead to aggregation of majLHCII which was known to be highly quenched [36] (Figure 6). It was proposed that the quenching centers in the majLHCII arose from random and tightly interacting pigment molecules exposed on the outer surface of the complex [37]. An alternative mechanism of NPQ suggested that the excitation energy is transferred from Chls a610-a611-a612 to a low-lying lutein molecule in the L1 site of majLHCII (Figure 3a), and the dissipative state was associated with a twisted configuration of the neoxanthin [38,39]. The domain composed of Chls a610-a611-a612 and Lut 620 in L1 site is conserved in both majLHCII and CP29 structures (Figure 3a, c), suggesting that a similar mechanism may also be present in CP29. Moreover, spectroscopic and biochemical studies revealed that such a putative quenching site is conserved in all LHCIIIs including majLHCII, CP29, CP26 and CP24 [40]. Meanwhile, it was found that Zea radical cation forms within isolated minor antenna complexes, supporting another NPQ model which suggests a charge-transfer mechanism occurs between chlorophyll and carotenoid [41]. The Chl a603-a609 dimer and Zea located in the L2 site of CP29 (Figure 3c) was believed to be responsible for the charge-transfer quenching mechanism [22]. More recently, it has been shown that a radical cation can also form in CP29 and CP24 when a lutein molecule binds at the L2 site [42]. Furthermore, the energy-dependent quenching of Chl fluorescence (qE), a major portion of NPQ, was shown to be dependent on the PsbS subunit which is also a member of LHC II superfamily [43,44*]. PsbS forms a dimer at neutral pH and dissociates into monomers at low pH when qE occurs [45]. It was proposed that the role of PsbS was independent of Zea [46] and it may interact with majLHCII and CP29 [47]. The role of PsbS in NPQ might be acting as a pH-dependent trigger/regulator of conformational changes within the LHCIIIs, leading to the formation of quenching center within or between the LHCIIIs. The various models of NPQ and potential quenching sites discussed above are summarized in Figure 6.

Summary

The LHCII are crucial to plants and green algae in utilizing solar energy under fluctuating light conditions. The high resolution structures of these protein–pigment complexes have revealed a delicate design of supramolecular assembly that can function both as an efficient harvester of solar energy and effective quencher of excess energy under high-light conditions. In spite of extensive efforts in the field, it remains elusive how they are able to switch from an efficient light harvesting state to a highly dissipative state. From a structural point of view, future studies should focus on obtaining and analyzing the structures of each individual type of the LHCII complexes at fluorescing or quenched states for direct comparison. Moreover, the structures of PsbS with or without bound pigments and PsbS in complex with LHCIIIs will prove to be valuable for an improved understanding on the essential role of PsbS in NPQ.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest


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It was shown for the first time that an intrinsic protein subunit of PSII, named PsbS, is essential for the operation of non-photochemical quenching. The Arabidopsis psbs deletion mutant (npq4) has impaired function in NPO.


