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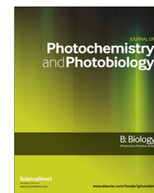

Short Review

# Dissipative pathways in the photosystem-II antenna in plants

Christopher D.P. Duffy, Alexander V. Ruban *

*School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK*

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The antenna of photosystem II in plants possesses a remarkable functional flexibility, allowing for the photoprotective regulation of light-harvesting in the face of rapid fluctuations in light intensity. Central to this adaptability is the reversible formation of dissipative energy transfer pathways within the antenna that protect the reaction centres from a potentially damaging excess of excitation energy. The exact molecular nature of these pathways and the mechanism by which they form are still open questions within the field of photosynthesis research. We present a review of current knowledge on the subject. We discuss the multi-scale nature of these pathways, how intrinsic structural and electronic changes within individual antenna proteins are coupled to large scale changes in the structure and energetic connectivity of the membrane as a whole. We review the physical properties and likely validity of current competing models of the dissipation mechanism before discussing a recently studied general property of the dissipative pathways — the slow and economic nature of the NPQ quencher. This property reflects the finely-tuned nature of the quenching pathway, i.e., its ability to offer protection to the photosynthetic machinery without compromising normal photosynthetic function.

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## 1. Introduction

The energy required by the biosphere is almost exclusively supplied by photosynthesis which in turn relies upon a continuous and sufficient input of solar energy. In the aquatic environment where photosynthetic life evolved the most pressing challenge faced by photosynthetic organisms was a paucity of available light energy. This challenge was overcome by the evolution of the photosynthetic antenna. The ‘division of labour’ between the small subset of photochemically active chlorophyll (Chl) pigments in the reaction centre (RC) and the vast pool of antenna pigments ensures that continuous and sufficient energy input into the photosynthetic reactions is maintained even under poor illumination. Despite considerable biodiversity in RC/antenna structure the essential *design principles* are universal [1]. The large majority of the chlorophyll pigments (along with secondary photosynthetic pigments) are housed in a large, modular assembly of light-harvesting antenna proteins, termed light-harvesting pigment-protein complexes or LHCs, that vastly enhance the spatial and spectral *cross-section* of the RC chlorophylls. The LHC proteins function as a *programmed solvent*, binding a densely-packed and specifically-oriented pigment complement. By controlling the separation and relative orientation of the light-harvesting pigments

*Abbreviations:* NPQ, non-photochemical quenching; PSII, photosystem II; RC, reaction centre; Chl, chlorophyll.

* Corresponding author.
*E-mail address:* a.ruban@qmul.ac.uk (A.V. Ruban).

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this programmed solvent ensures not only a broad and environmentally-tuned absorption profile, but highly efficient pathways for the transfer of excitation energy from the antenna to the RC complexes.

We will focus on the light-harvesting system associated with photosystem-II (PSII) in plants, due not only to its exemplary efficiency but to its highly flexible and adaptable nature [2–5]. This adaptability arises from the need to regulate light harvesting in a fluctuating light environment. The antenna of PSII is highly efficient, with ~85% of the photo-induced excitation being delivered to the RC and undergoing photosynthetic charge separation [1]. In low light this efficiency ensures an optimal rate of energy delivery to the PSII RCs. In high light, however, a highly efficient antenna can lead to saturation of the RCs and an accumulation of excitation energy within the antenna, potentially leading to photodamage to the delicate photosynthetic *machinery*. Such damage, known as *photoinhibition* [6], can take several hours to reverse [7], and could potentially impact on the viability of the organism (for a discussion of the complex relationship between light, photoinhibition and productivity the reader is directed to [8]). However, evolution has endowed plants with the ability to cope with intense illumination through the collective action of many adaptive mechanisms. For the most rapid fluctuations in light intensity the rate of photoinhibition is down regulated via the regulation of the energy transfer pathways within the PSII antenna. A sudden elevation in illumination results in the formation of *dissipative pathways* that lead to an enhancement of the rate of non-radiative decay of excitation energy in the antenna, thereby relieving the *excitation pressure* on the over-burdened RCs via the thermal dissipation of excess excitation energy, in a process that manifests itself as the non-photochemical quenching (NPQ) of chlorophyll fluorescence [7–12]. The essence of the photoprotective process is that a sudden, potentially detrimental increase in illumination leads to the formation of excitation-quenching pathways within the PSII antenna, in which excitation energy is transferred to *trap sites* that dissipate it through some non-radiative process(es). Despite the wealth of experimental and theoretical information concerning the NPQ mechanism there is still no consensus regarding the molecular nature of the excitation-trapping sites, their precise location within the PSII antenna, or the intra-inter-protein mechanisms that lead to their formation in high light or their relaxation in the dark. What is known is that there is a causal association between pNPQ and three molecular factors: the development of a strong transmembrane pH gradient ($\Delta$pH) due to a high rate of photosynthetic charge separation [13–16]; the light-induced, enzymatic conversion of the antenna-associated xanthophyll violaxanthin to zeaxanthin (part of the *xanthophyll cycle*) [15,17–27]; and the presence of the PsbS protein within the photosynthetic (thylakoid) membrane [28–37]. For a comprehensive review of these aspects of the photoprotective process the reader is directed to a recent a review by Ruban and co-workers [2].

In 2012, Ruban and co-workers established a conceptual description of the photoprotective process, stating that the full photoprotective *scenario* is comprised of four aspects: the *trigger*, the *site*, the *mechanism*, and the *quencher* [2]. The *trigger* is the primary event that induces the conformational change in the PSII antenna that brings about the formation of the dissipative pathways. There is now extensive evidence that $\Delta$pH constitutes the primary trigger [2,9,21,38–40]. The trigger acts upon the *site* which is now known to be the PSII antenna, with evidence that both the minor antenna [41–43] and LHCII [41,44] interact with membrane-sequestered protons that form the pH-gradient. High light is therefore 'sensed' via the action of the proton trigger upon the site of the dissipative pathways: the PSII antenna. The mechanism is the physical change occurring in the PSII antenna that brings about the formation of the *quencher*, i.e., the molecular state (or states) that accept and dissipate excess excitation energy. More so than for the trigger and site, the exact molecular natures of both the mechanism and the quencher have still not been unambiguously established [2]. These features of the dissipative pathways, their exact nature and the manner of their formation, form the main focus of this review. As we will discuss both the formation of the dissipative pathways and their operating principles once established are *multi-scale* in nature, involving processes at both the individual protein level and the level of the photosynthetic membrane as a whole. We will begin by discussing what we know about the dissipative pathways within individual light-harvesting antenna pigment-protein complexes.

## 2. Light-harvesting Complexes as Dissipative Switches

The formation of the quenchers occurs within the PSII antenna. Ultimately, the dissipation of excitation energy must occur via some inter-molecular state. The exact nature of this molecular state (or possibly states) is unclear but ultimately must result from interactions at the bound pigment level.

In the early 1990s Horton and co-workers proposed the aggregation model of quenching. It was found that the aggregation of detergent-solubilised LHCII trimers, induced by detergent removal, results in a transition from a fluorescent to a highly quenched state and this aggregation-induced quenching resembles the transition to the in vivo dissipative state [45–49]. The essence of the aggregation model is that the proton-trigger results in in-membrane aggregation of LHCII which is linked to some internal change within the complexes that brings about the formation of the quencher. The idea that aggregation is linked to the quenching state is further supported by the fact that the crystals from which the structure of LHCII was obtained [50] possess a fluorescence lifetime (~0.89 ns) significantly shorter than that of isolated trimers [51]. Additionally, in 1991 Jennings et al. demonstrated that laminar, microcrystalline sheets of isolated LHCII trimer display reversible, light-induced quenching with many of the spectral characteristics of in vivo quenching [52].

Recently, evidence has suggested that aggregation is not per se essential to the formation of the quenching state. This evidence suggests that *switching* between a light-harvesting and a photoprotective, dissipative state is an intrinsic property of individual LHCII trimers. Van Amerongen and co-workers showed that application of hydrostatic pressure was sufficient to induce strong quenching in LHCII trimer in the absence of aggregation [53]. This *pressure-quenching* possessed many spectroscopic similarities with aggregation induced quenching [45,49,54]. Additionally, LHCII trimers immobilised in polyacrylamide gel also displayed quenching of an identical spectral and biochemical character to that seen in aggregates [55]. Most recently, the single molecule fluorescence spectroscopy work of Krüger and co-workers has shown that spatially isolated LHCII trimers exhibit *fluorescence intermittency*, i.e., switching between highly fluorescent and highly quenched states [56–58]. Moreover, this intermittency was found to be sensitive to acidity and therefore shares mechanistic similarities with the in vivo quenching mechanism [56]. Theoretical modelling of this *blinking* indicates that it can be explained by a switching between two distinct conformational states, one fluorescent (or light-harvesting) and one dark (dissipative) [59].

The idea of a protein conformational change being central to the NPQ switch was a contentious point. Barros and co-workers instead proposed that the rigidity of LHCII precluded any conformational flexibility, instead contending that quenching interactions arise from interactions between trimers during aggregation or crystallization [60]. They therefore propose that the crystal structure of LHCII corresponds to a light-harvesting rather than a

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