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| **Title** | **Identifying the molecular requirements for effective photoprotective mechanisms in light-harvesting complexes** | |
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| # months (min.3) | 4 | |

**Project description (2 page max):**

**State of the art**

Light-harvesting complexes play a crucial role in the photosynthetic process, as they capture photons and transfer their energy to the photosystems, where photons are converted into chemical energy. The efficiency of light harvesting depends on the ability to (i) maximize the cross-section for the solar radiation most available in the ecological niche of the parent organisms, and (ii) deliver the harvested energy to the reaction centers with minimal losses, while (iii) preventing the formation of dangerous reactive species.

The three criteria are inherently at odds, since increasing the antenna size and broadening the spectrum of the harvested light increases the light absorption but also tend to increase the time scale of excitation energy migration. In turn, this second effect can lead to increased photodamage. In fact, the probability of populating triplet states, and thus the associated formation of dangerous reactive oxygen species, increases with the lifetime of chlorophyll excited states.

In natural light-harvesting complexes, a fast response to the effects of excess illumination promoting energy dissipation is obtained via the mechanism of triplet–triplet energy transfer (TTET), in which carotenoid molecules quench chlorophyll’s triplets. There are still open questions concerning the molecular requirements fulfilled by the light-harvesting complexes to perform efficient of TTET. The subject is extremely relevant because elucidating the details of the photoprotective role played by Car in natural systems is fundamental for the design of artificial systems that not only efficiently harvest light but, likewise, either avoid the formation of 1O2 or scavenge it after sensitization. The construction of biomimetic systems aims at matching the ever-growing demand for renewable and sustainable energy sources.

**Spectroscopic investigation of natural complexes characterized by different pigmentations**

Advanced EPR have been extensively employed in the past to gain insight into the TTET mechanism in several light harvesting complexes, revealing some structural requirements for efficient Chl triplet quenching, and especially a short center-to-center distance between the excitation donor and acceptor [1]. Interestingly, microwave induced triplet-*minus*-singlet (T–S) absorption spectra of carotenoids in several light-harvesting complexes, obtained via absorption-detected magnetic resonance, have shown the presence of bands in the Qy region (i.e., the S0 → S1 electronic transition) of chlorophyll. Such bands have been attributed to a change in the interaction between chlorophyll and carotenoid as the latter accedes its triplet state, and its intensity has been related to the photoprotective Car-Chl interaction [2].

Therefore, during the project these powerful spectroscopic tools will be used to investigate light-harvesting complexes isolated from diverse photosystems, looking for organisms characterized by diverse pigmentations to better adapt to ecological niched characterized by different light availabilities. In particular, light-harvesting complexes isolated from organisms adapted to harvest far-red light (such as in caves and below the canopy) or blue-green light (shallow waters) will be compared [3-5] to understand how their widely different pigmentations influence their photoprotective performance.

**Computational determination of the chemical descriptors required to effective photoprotection**

The interpretation of the T–S spectra of pigment complexes in the Q*y*-band spectral region has been recently achieved by combining state-of-the-art time-dependent density functional theory (TDDFT) with analysis of the relationship between electronic properties and nuclear structure [6]. In this project, this approach will be adapted to the investigated systems. Furthermore, multiscale simulation approaches combining molecular dynamics with TDDFT analysis (or possibly real-time TDDFT) will be used to take into account the chemical environment of the chromophores under investigation and gain a dynamic picture of the excitation transfer.

Combining the information obtained by magnetic and opto-magnetic spectroscopies on the triplet states populated under illumination with quantum mechanical calculations, we expect to disentangle the contributions of individual properties of the interacting chromophores to the overall performance of the chlorophyll triplet quenching in different complexes. This analysis will be employed to guide implementations of biomimetic pigment complexes in artificial photosynthesis research.

**Application of the design principles to improve the photostability of an antenna model system**

In the second phase of the project, the design principles derived from the combined spectroscopic and theoretical characterization will be used to inform the design of light-harvesting complexes with altered pigment compositions (during the international secondment at the Vrije Universiteit Amsterdam). The main light-harvesting complex of plants will be employed as the protein architecture, since it proved to be able to accommodate different pigments while maintaining effective single-singlet and triplet-triplet energy transfer pathways [7]. The transferability of our findings to other systems will be revealed by reconstituting *in vitro* LHCII from higher plants with altered pigmentations that in other systems proved to be particularly effective in triplet quenching.

**References**

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