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Investigating the excited electronic states of carotenoids in the main plant light-harvesting complex (LHCII) via femtosecond pump-probe spectroscopy

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Abstract content
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Natural photosynthesis is the chief energy storing process on earth. The photosynthetic light-harvesting apparatus of a plant switches rapidly between a highly efficient light-harvesting function and a very efficient photoprotective state. The natural photosynthetic apparatus consists of a complex network of membrane-bound pigment-protein complexes. In the main plant light-harvesting complex (LHCII), the protein-bound pigments (viz. chlorophylls and carotenoids) capture the solar photons and transfer the electronic excitation energy (on an ultrafast timescale) to neighbouring complexes and eventually to the reaction centre, where a charge separation is initiated. These ultrafast processes form the basis of the high efficiency of light harvesting and temporal storage of the harvested energy. Plants are self-protected against the adverse effects of over-illumination by activating a number of processes that collectively give rise to non-photochemical quenching (NPQ). The role of carotenoids in NPQ is not fully understood. Investigations of the excited-state dynamics of LHCII carotenoids in spinach leaves were conducted upon intensity-dependent, selective carotenoid excitation at 489 nm (primarily Lutein1 and Neoxanthin) and 506 nm (mainly Lutein2 and Violaxanthin), using femtosecond transient absorption (TA) pump-probe spectroscopy. A robust analysis technique, known as Global and Target Analysis, was applied on the TA spectra to resolve the transfer rates and decay lifetimes of the various transiently induced photoproducts. Differences in the excitation kinetics due to experimental variations (i.e. different pump wavelengths and intensities) will be discussed in the context of the carotenoids' involvement with NPQ.

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