Singlet Energy Dissipation in the Photosystem II Light-Harvesting Complex Does Not Involve Energy Transfer to Carotenoids


The energy dissipation mechanism in oligomers of the major light-harvesting complex II (LHC II) from Arabidopsis thaliana mutants npq1 and npq2, zeaxanthin-deficient and zeaxanthin-enriched, respectively, has been studied by femtosecond transient absorption. The kinetics obtained at different excitation intensities are compared and the implications of singlet–singlet annihilation are discussed. Under conditions where annihilation is absent, the two types of LHC II oligomers show distributive biexponential (bimodal) kinetics with lifetimes of \( \approx 5–20 \) ps and \( \approx 200–400 \) ps having transient spectra typical for chlorophyll excited states. The data can be described kinetically by a two-state compartment model involving only chlorophyll excited states. Evidence is provided that neither carotenoid excited nor carotenoid radical states are involved in the quenching mechanism at variance with earlier proposals. We propose instead that a chlorophyll–chlorophyll charge-transfer state is formed in LHC II oligomers which is an intermediate in the quenching process. The relevance to non-photochemical quenching in vivo is discussed.