Supporting Information

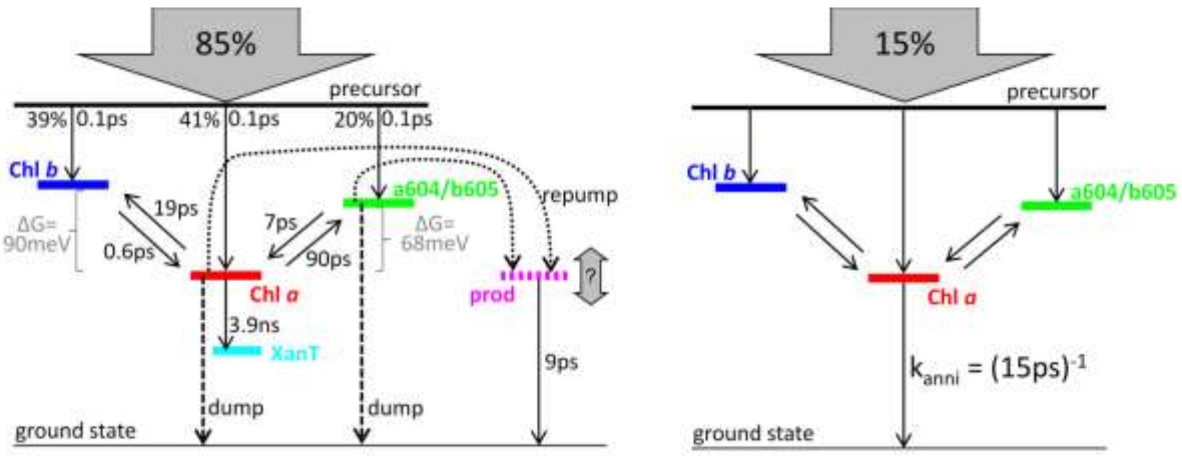
Full target model including annihilation

The PP and PDRP' data sets were fitted simultaneously in a global target analysis, using the kinetic target model shown in Supplementary Scheme 1. The model consists of two parallel branches. The left branch describes the principle kinetics, and the right branch the singlet-singlet annihilation process. The spectra, rates, and branching ratios are constrained to equality in both branches, except for the dumping/repumping related parameters which are only present in the left branch, and the annihilation rate which is only present in the right branch.

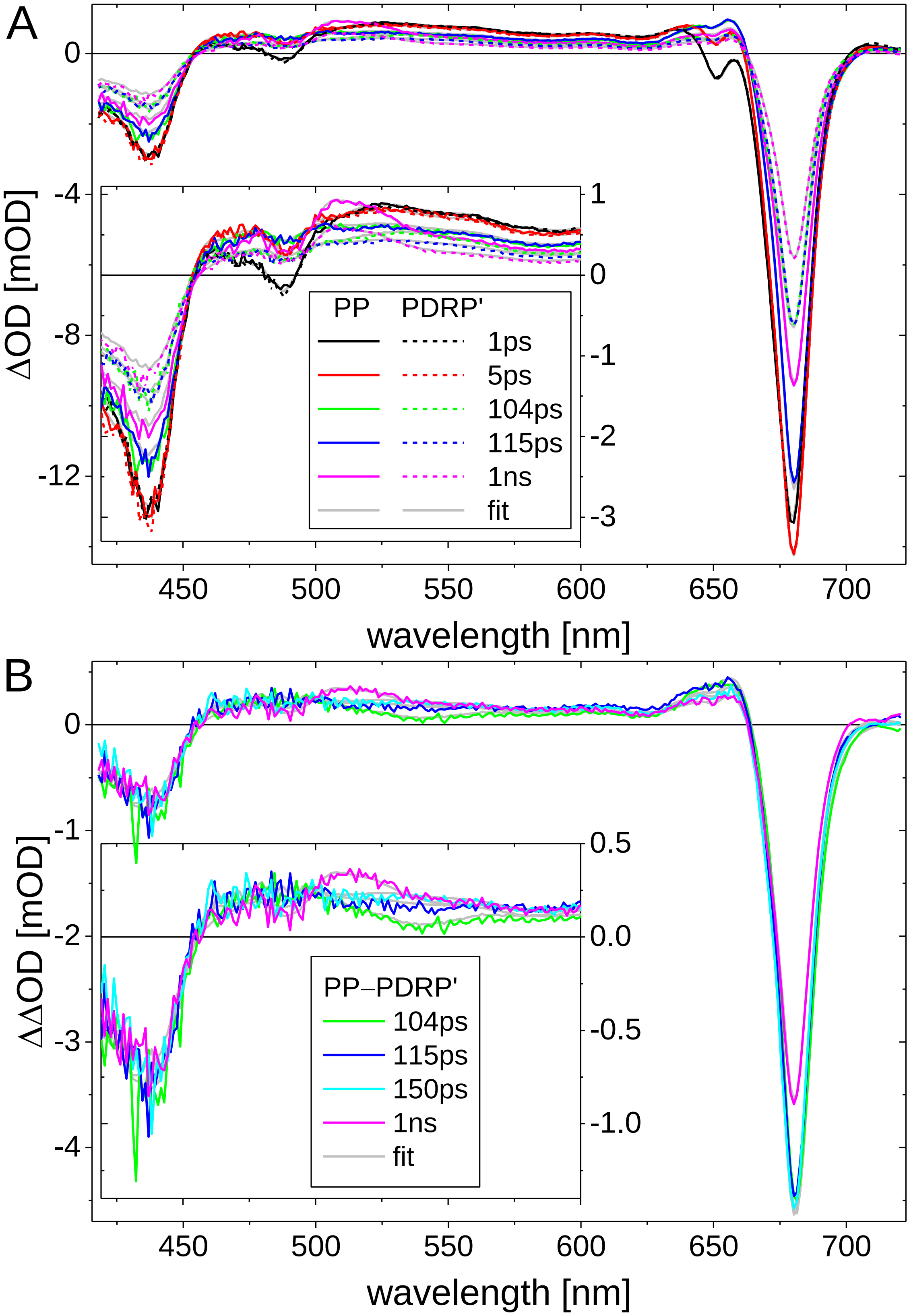
Annihilation is modeled as a monoexponential depopulation of the lowest energy Chl excited state compartment ("Chl *a*"), which contains most of the population. Strictly speaking, annihilation does not follow mono-exponential kinetics[1], but for low fractions of annihilation the mono-exponential approximation is valid.[1,2] The fit yielded a partition ratio of 85:15 between the left and right branches, so 15% of the excitations are lost through annihilation. The fitted annihilation rate of $(15\ \text{ps})^{-1}$ is in good agreement with previously reported values (e.g., refs 2–4) and the result of the sequential fit (Figure 4 of the main text).

This annihilation rate results in complete depopulation of the "right branch" at the time of the dump/repump pulse (100 ps), so the presence of annihilation does not affect the dumping and repumping processes. Lower excitation power would reduce the fraction of annihilation, but also the excited state population, with which the dump/repump pulse interacts. Thus there is a trade-off between the signal intensity and low amount of annihilation. The currently used excitation power allowed for simple mono-exponential description of annihilation, while maintaining high signal intensity.

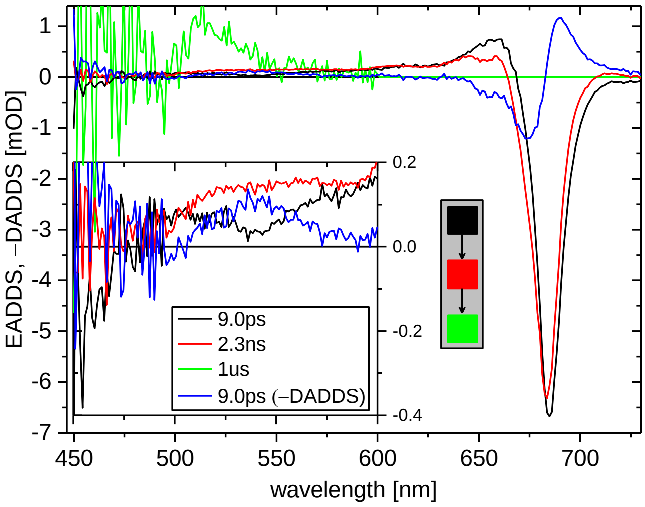
The SADS of XanT was constrained to zero above 575 nm, and for Chl *b* above 670 nm.



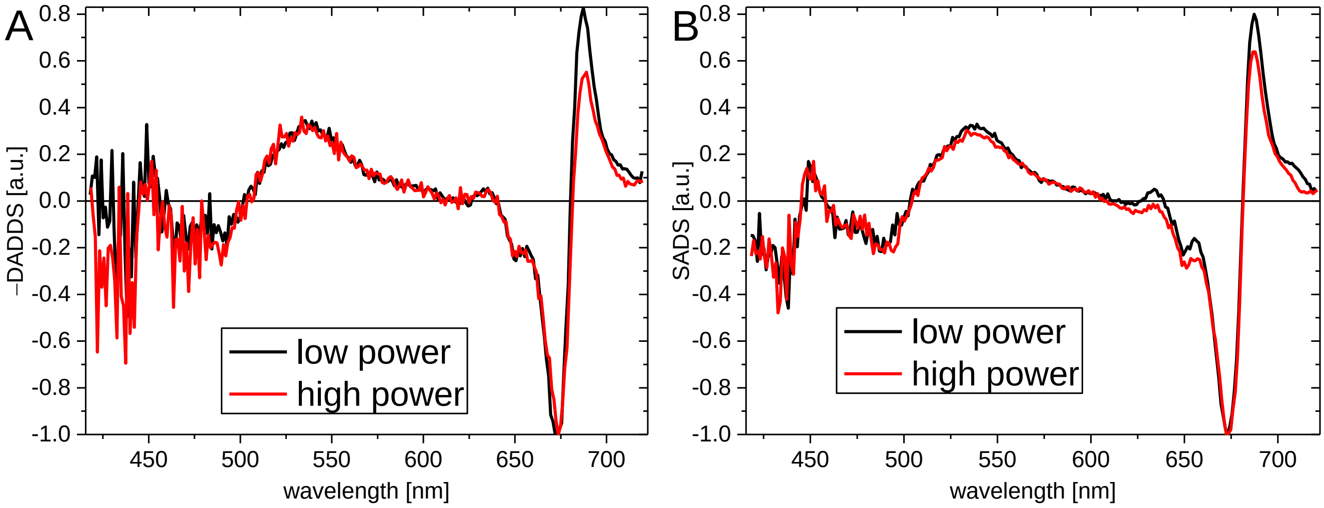
Supplementary Scheme 1. Target model used for simultaneous fitting of PP and PDRP' data sets. Branching ratios, energy transfer rates and relaxation/decay rates are identical in the left and right branches, and are indicated in the left branch. Annihilation (right branch) occurs from the lowest energy Chl*, with a rate of $(15\ \text{ps})^{-1}$. The initial relative populations of the left and right branch are 85% and 15%, respectively.



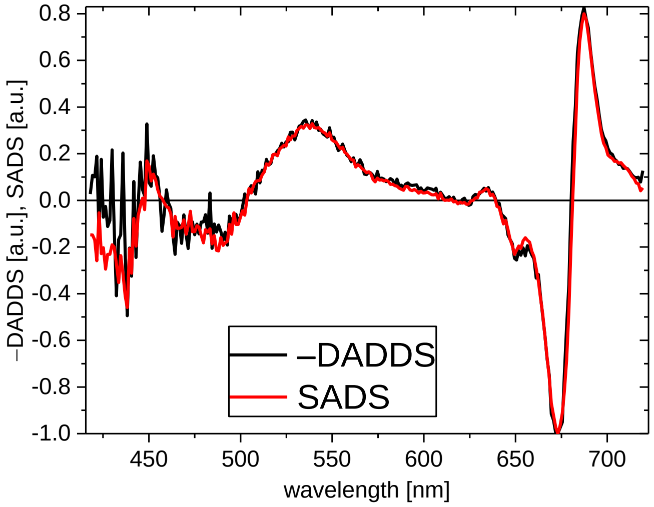
Supplementary Figure 1. Time-gated spectra of (A) PP and PDRP’ and (B) ΔΔOD≡PP−PDRP’ of trimeric LHCII at room temperature upon excitation at 630 nm and dump/repump at 760nm. Fit results of the target analysis (Supplementary Scheme 1 and Figure 6 in the main text) are in gray. For PP−PDRP’ this is the difference between the fit curves of PP and PDRP’. The insets show magnified views up to 600 nm. The legend indicates the probe times. The corresponding kinetic traces are presented in Figure 3 of the main text.



Supplementary Figure 2. EADDS and DADDS (blue) of ΔΔOD of monomeric LHCII at room temperature upon excitation at 630 nm and dump/repump at 760 nm. The inset shows a magnified view up to 600 nm. The grasy box shows the kinetic scheme for EADDS (for DADDS this is a parallel scheme). ΔΔOD contains contributions from both dumping (D in Figure 1) and photoproducts formed upon repumping (R in Figure 1). The dumping appears as a difference spectrum that evolves with the same kinetics as the undumped species. The photoproducts appear as difference spectra with inversed sign. The analysis for trimeric LHCII is shown in Figure 5 of the main text.



Supplementary Figure 3 (A) Comparison of –DADDS1 from global fits of ΔΔOD with high (red) and low (black) amounts of annihilation. (B) Same for the product SADSes from the target fit. Spectra are scaled to −1 at the negative peak around 675nm.



Supplementary Figure 4. Comparison of –DADDS1 from a global fit of ΔΔOD (red) and SADS from the target fit of simultaneously PP and PDRP (black). Spectra are scaled to −1 at the negative peak around 675nm.

Supplementary References

(1) Van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific Publishing: Singapore, 2000.

(2) Barzda, V.; Gulbinas, V.; Kananavicius, R.; Cervinskas, V.; van Amerongen, H.; van Grondelle, R.; Valkunas, L. Singlet-Singlet Annihilation Kinetics in Aggregates and Trimers of LHCII. *Biophys. J.* **2001**, *80*, 2409–2421.

(3) Gradinaru, C. C.; van Stokkum, I. H. M.; Pascal, A. A.; van Grondelle, R.; van Amerongen, H. Identifying the Pathways of Energy Transfer between Carotenoids and Chlorophylls in LHCII and CP29. A Multicolor, Femtosecond Pump-Probe Study. *J. Phys. Chem. B* **2000**, *104*, 9330–9342.

(4) Stahl, A. D.; Di Donato, M.; van Stokkum, I.; van Grondelle, R.; Groot, M. L. A Femtosecond Visible/Visible and Visible/Mid-Infrared Transient Absorption Study of the Light Harvesting Complex II. *Biophys. J.* **2009**, *97*, 3215–3223.