Supporting Information:

Chlorophyll-Carotenoid Excitation Energy Transfer in High-Light-Exposed Thylakoid Membranes Investigated by Snapshot Transient Absorption Spectroscopy

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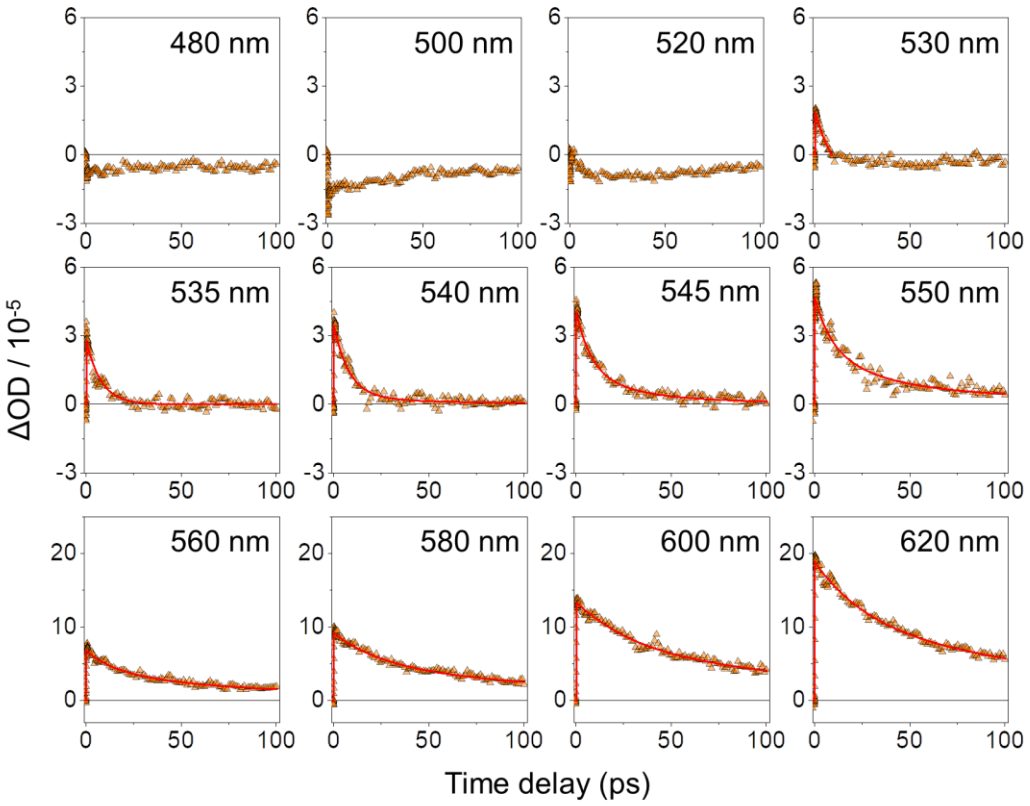

Figure S1. TA kinetic profiles of high-light-exposed thylakoid samples. Through global analysis, it was deduced that at least three lifetime components (τ_1=7.81 ps, τ_2=28.2 ps, and τ_3=160 ps) are required for fitting the ESA signal of the samples in the wavelength range of 530 ~ 620 nm. From the TA kinetic profile at 620 nm, the two longest lifetime components (τ_2=28.2 ps and τ_3=160 ps) mainly represent the contribution of Chl ESA. The probe wavelength is denoted in each panel.

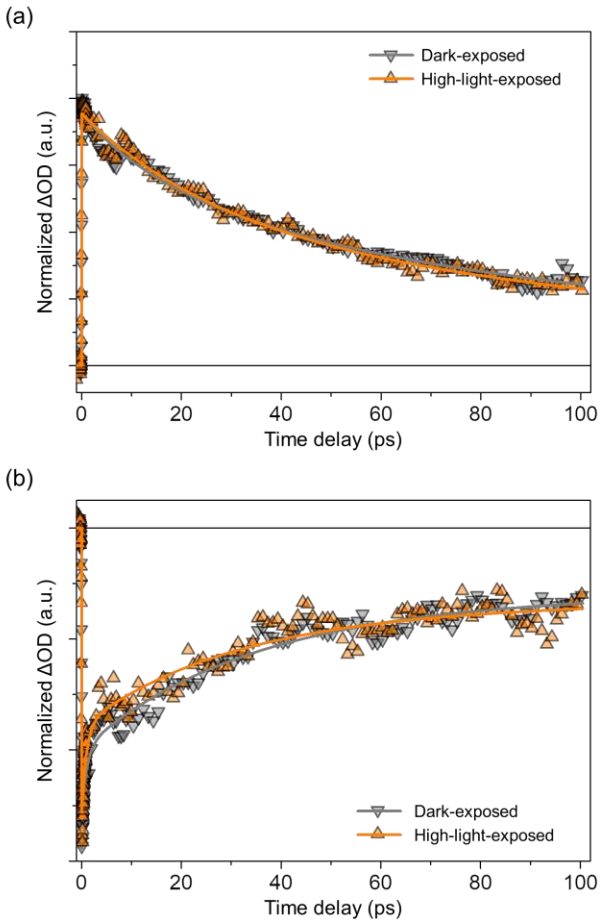

Figure S2. Transient absorption kinetics of spinach thylakoid membranes under dark-exposed (gray, down triangle) and high-light-exposed (orange, up triangle) conditions. Samples were excited at 650 nm and probed at (a) 620 nm and (b) 680 nm.

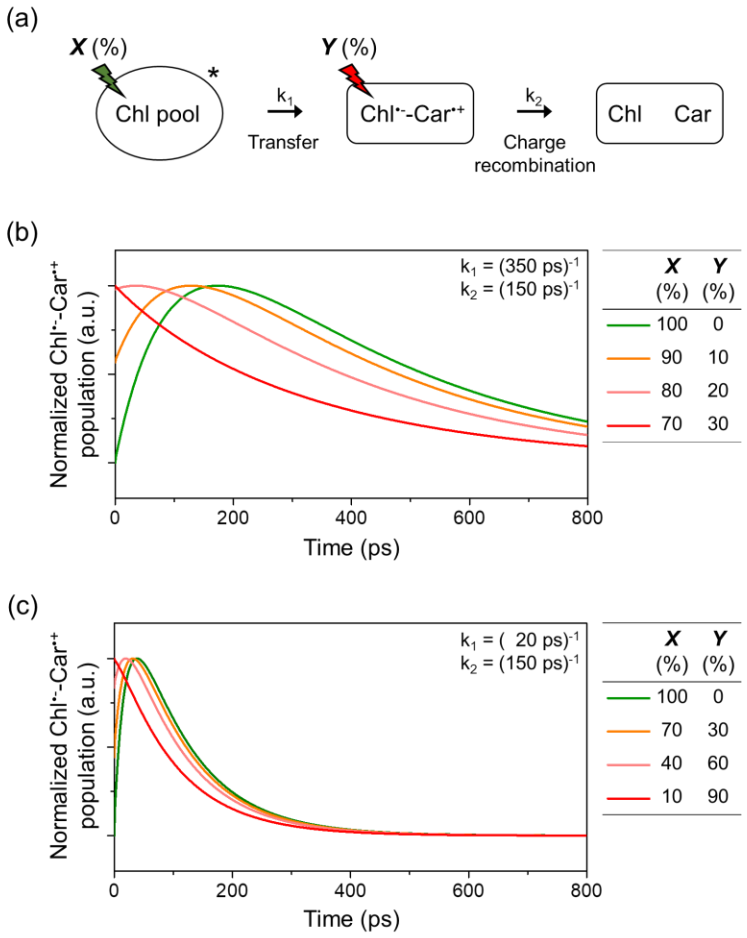

Figure S3. (a) Kinetic scheme for the CT quenching mechanism in light-exposed thylakoid membranes. Relative percentages of Chl excitations between Chl pool and a Chl adjacent to Car are denoted as ***X*** and ***Y***, respectively. (b, c) Dynamics of the charge-transfer (CT) state population calculated with various initial excitation populations at the bulk Chl pool vs. Chl close to Car. The scheme uses a slower de-excitation (charge recombination) rate ($k_2 \cong (150\ ps)^{-1}$) at quenching sites. The rate constant k_1 can vary as the PSII antenna structure changes during light exposure, so calculation was performed with two different values. (b) The k_1 was assumed to be $(350\ ps)^{-1}$ based on the bulk Chl fluorescence lifetime in quenched state (Figure 5a). (c) The k_1 was assumed to be $(20\ ps)^{-1}$ based on previous literature.[S1] In both cases, due to the slower charge recombination (k_2), rise components exist in the simulated dynamics even after significant initial population (~ 20% and ~ 60% for (b) and (c), respectively) is placed on the ***Y*** group (a).

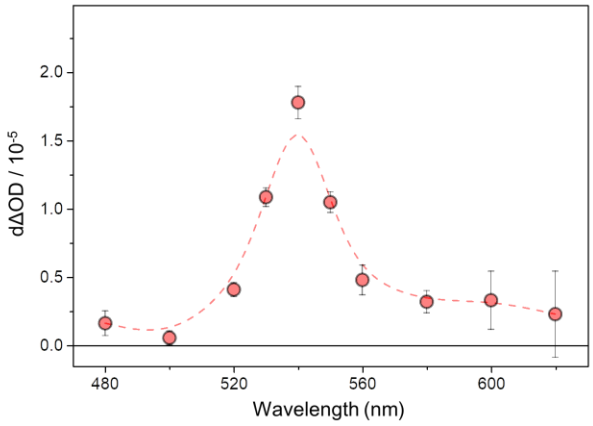

Figure S4. Difference TA spectrum reconstructed by subtracting the dark-exposed signal from the high-light-exposed signal. The dΔOD spectrum was reconstructed using the following equation:

$$d\Delta OD_{Car\ S_1}(\lambda) = \Delta OD_{at\ 1\ ps}(\lambda, light) - \Delta OD_{at\ 1\ ps}(\lambda, dark) \times \left(\frac{\Delta OD_{at\ 40\ ps}(\lambda, light)}{\Delta OD_{at\ 40\ ps}(\lambda, dark)}\right)$$

where λ is the probe wavelength. Data are presented as the mean ±SE (n=5). The dashed line represents a b-spline interpolation among the experimental data points.

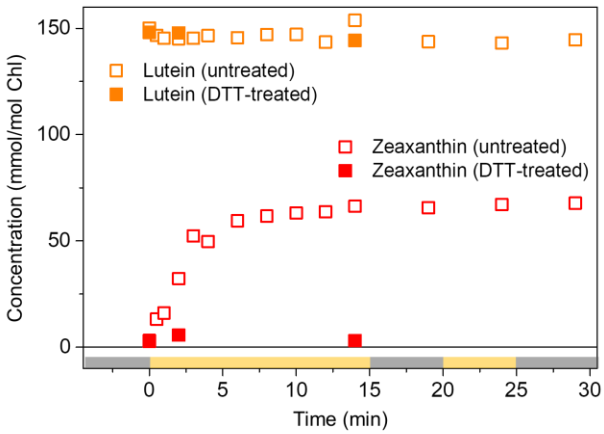

Figure S5. Concentrations of zeaxanthin and lutein in untreated and DTT-treated thylakoid membranes determined by time-resolved high-performance liquid chromatography measurements. The accumulation of zeaxanthin in this figure originally published in S. Park et al., *J. Phys. Chem. Lett.* 2017, 8 (22), 5548–5554 (ref 17).

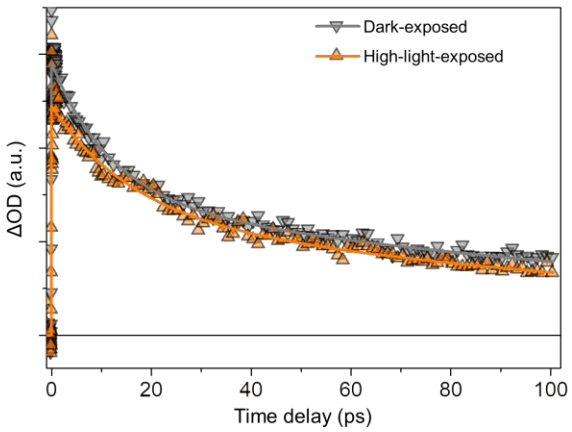

Figure S6. Transient absorption kinetics of DTT-treated spinach thylakoid membranes under dark-exposed (gray, down triangle) and high-light-exposed (orange, up triangle) conditions. Samples were excited and probed at 650 nm and 540 nm, respectively.

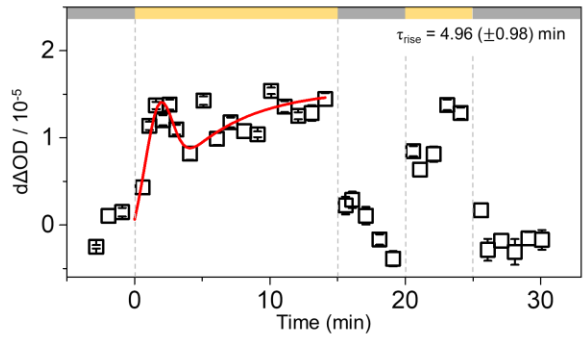

Figure S7. Snapshot TA data of untreated thylakoid samples with curve fit (red) in the first high-light-exposure period. Curve fittings use a combined single exponential rise and Gaussian peak function. The Gaussian peak function with a center at 1.9 min was included to account for the sharp rise and fall of the data which is likely a result of the sharp spike in ΔpH following high-light exposure. The time constants of the single exponential rise component are denoted.

References

(S1) Cheng, Y. C.; Ahn, T. K.; Avenson, T. J.; Zigmantas, D.; Niyogi, K. K.; Ballottari, M.; Bassi, R.; Fleming, G. R. Kinetic Modeling of Charge-Transfer Quenching in the CP29 Minor Complex. *J. Phys. Chem. B* **2008**, *112* (42), 13418–13423.