## Supporting Information

# Lycopene Crystalloids exhibit singlet exciton fission in tomatoes

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# Time Resolved Absorption Measurements

## Monomeric Lycopene

The photophysics of monomeric lycopene were obtained as a control for the aggregated and crystalloid lycopene. Figure S1 shows the dynamics obtained for lycopene dissolved in *n*-hexane upon 490 nm excitation. This set of data can be globally fitted to obtain a cascade of events 107 fs $\rightarrow$ 642fs$\rightarrow$ 4.8 ps. This is in general agreement with results in the literature, which gave the longest decay lifetime of around 5 ps in *n*-hexane [1]. Hence we may assign this cascade of events to the following sequence of excited states $S_2 \rightarrow S_1^* \rightarrow S_1 \rightarrow S_0$, with $S_1^*$ representing a non-relaxed (vibrationally "hot") $S_1$ state. The fast relaxation of the excited states of carotenoids following the depicted cascade events is characteristic for a wide range of (if not all) iso-propenoids, due to their electronic configuration [2].

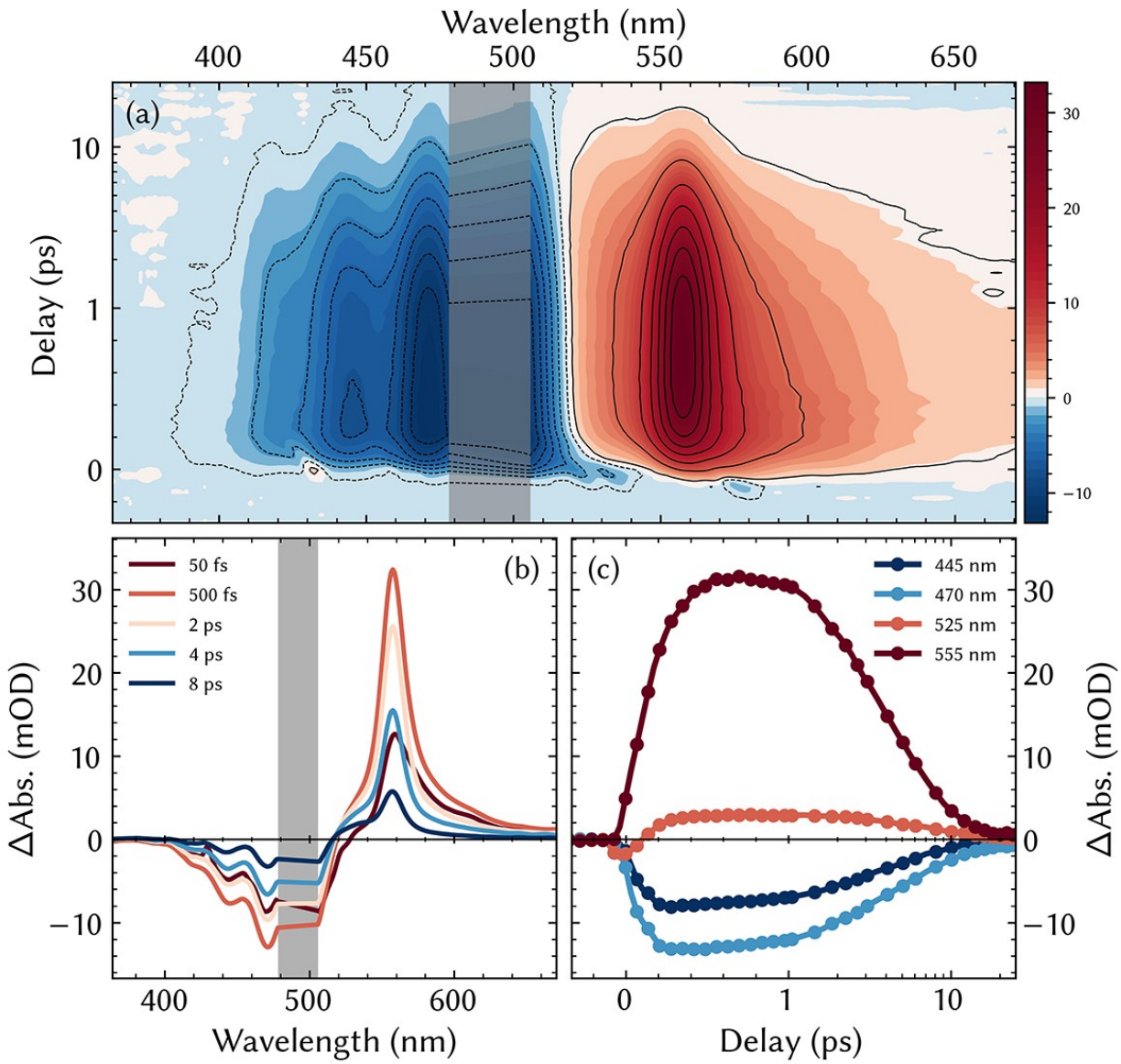


**Figure S1|** Room temperature transient absorption data of monomeric lycopene dissolved in n-hexane, excited at 490 nm. Panel (a): dataset showing the observed dynamics over the time range from femtoseconds to picoseconds. Panel (b): the femtosecond-to-nanosecond time-gated spectra at selected delay times. Panel (c): transient absorption kinetics of dataset shown in panel (a) at 445, 470, 525, and 555 nm probe wavelength. Greyed regions in panels (a) and (b) indicate areas omitted due to scattering of the pump pulse.

## Aggregated Lycopene

The full set of transient absorption signals acquired using 532 nm excitation (both fs and ns) are presented in figure S2. The initial femtosecond signals are dominated by contributions from non-aggregated lycopene molecules, and the measured spectra closely resemble those of monomeric lycopene in solution (figure S1). They clearly show that the sample contains both aggregated and isolated pigment molecules. When exciting these samples at 532 nm, the first several tens of picoseconds exhibit identical spectra as monomer lycopene. At longer delay times, however, the signals observed must arise from associated lycopene. For this associated lycopene, the time-resolved absorption signal comprises a weak induced absorption contribution below 520 nm, an additional peak at 560 nm and a broad negative band extending from 590 to beyond 750 nm. This spectrum decays within several microseconds, as can be observed from the kinetic trace measured at 620 nm (Fig S2, panel (d)).

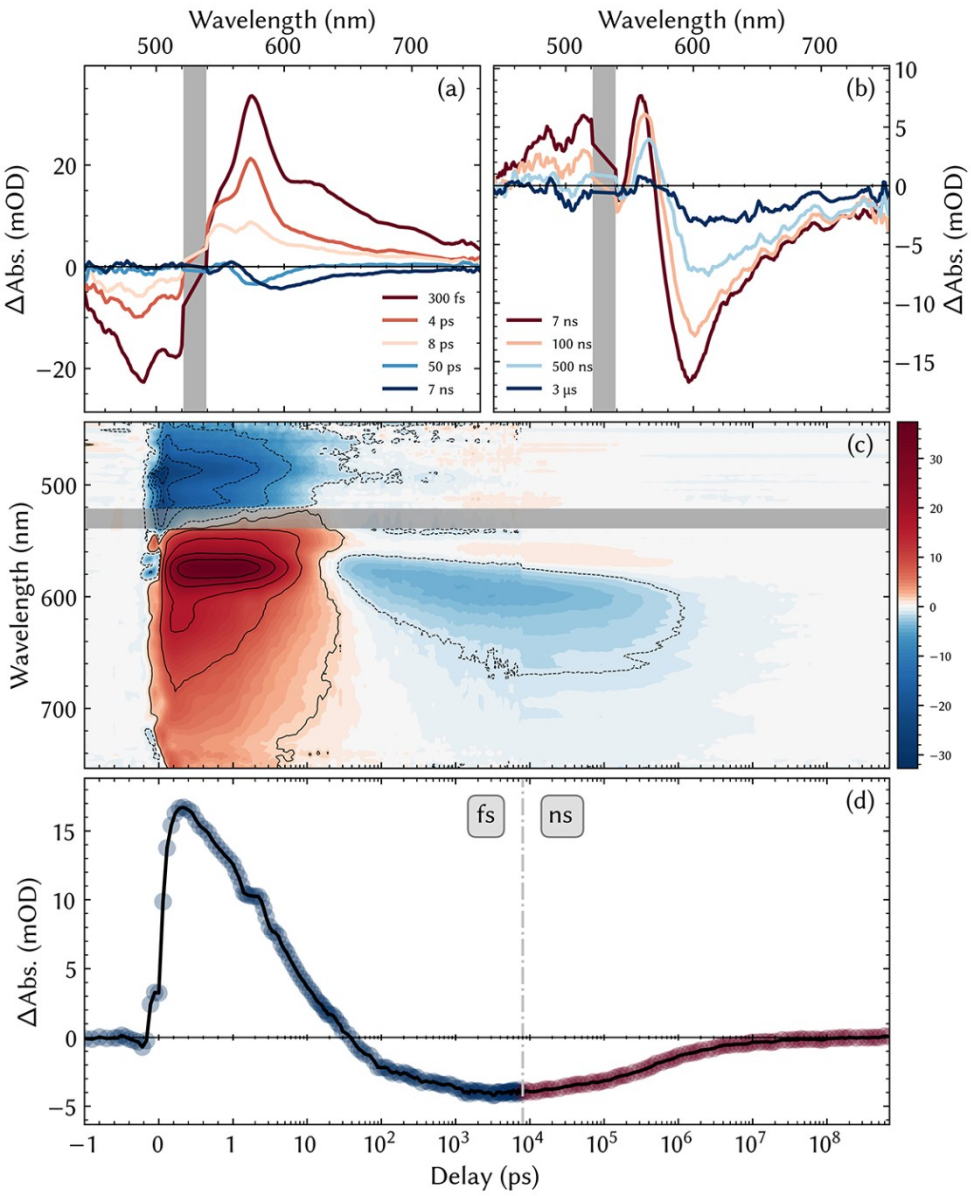


**Figure S2|** Transient absorption measurements in lycopene aggregates. Panel (a): Femtosecond-to-nanosecond TA spectra at selected delays measured in lycopene aggregates excited at 532 nm. Panel (b): Nanosecond-to-microsecond TA dynamics of the same sample. Panel (c): Overview of the entire spectral dynamics (datasets of a and b stitched together) in femtosecond-microsecond time range. d: Kinetic trace measured at 605 nm wavelength.

The dynamics for lycopene aggregates were globally fitted using the estimate that when the excitation wavelength is 532 nm, about 87% of photons are absorbed by monomeric lycopene and the remaining 13% of the photons are absorbed by the lycopene aggregates. This estimate was established by comparing the ground-state bleaching signal when $S_1$ is present (1 ps) to the bleaching which remains after the monomeric lycopene has completely returned to the ground state (200 ps). We made the assumption that the absorption of lycopene aggregates is similar in intensity to that of lycopene monomer. In general, the transition dipole of an aggregate should increase; however, this increase is likely to be balanced out by the fact that the spectrum shifts to the red upon aggregation, and 480 nm represents the maximum absorption of the monomer. Therefore, it can be reasonably expected that the order of magnitude of monomer and aggregate absorption at this position are correctly estimated. The characteristic dynamics for monomeric lycopene 107 fs $\rightarrow$ 642 fs $\rightarrow$ 4.8 fs ($S_2 \rightarrow S_1^* \rightarrow S_1 \rightarrow S_0$) were used to fit the signal from associated lycopene to these species. Then, the dynamics of lycopene aggregates span a wide timescale and require at least five lifetimes for an adequate fit. This reveals a cascade of five exited states to return to the ground state, 28 ps $\rightarrow$ 405 ps $\rightarrow$ 11.6 ps $\rightarrow$ 350 nm $\rightarrow$ 6.5 μs ($A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4 \rightarrow A_5 \rightarrow S_0$).

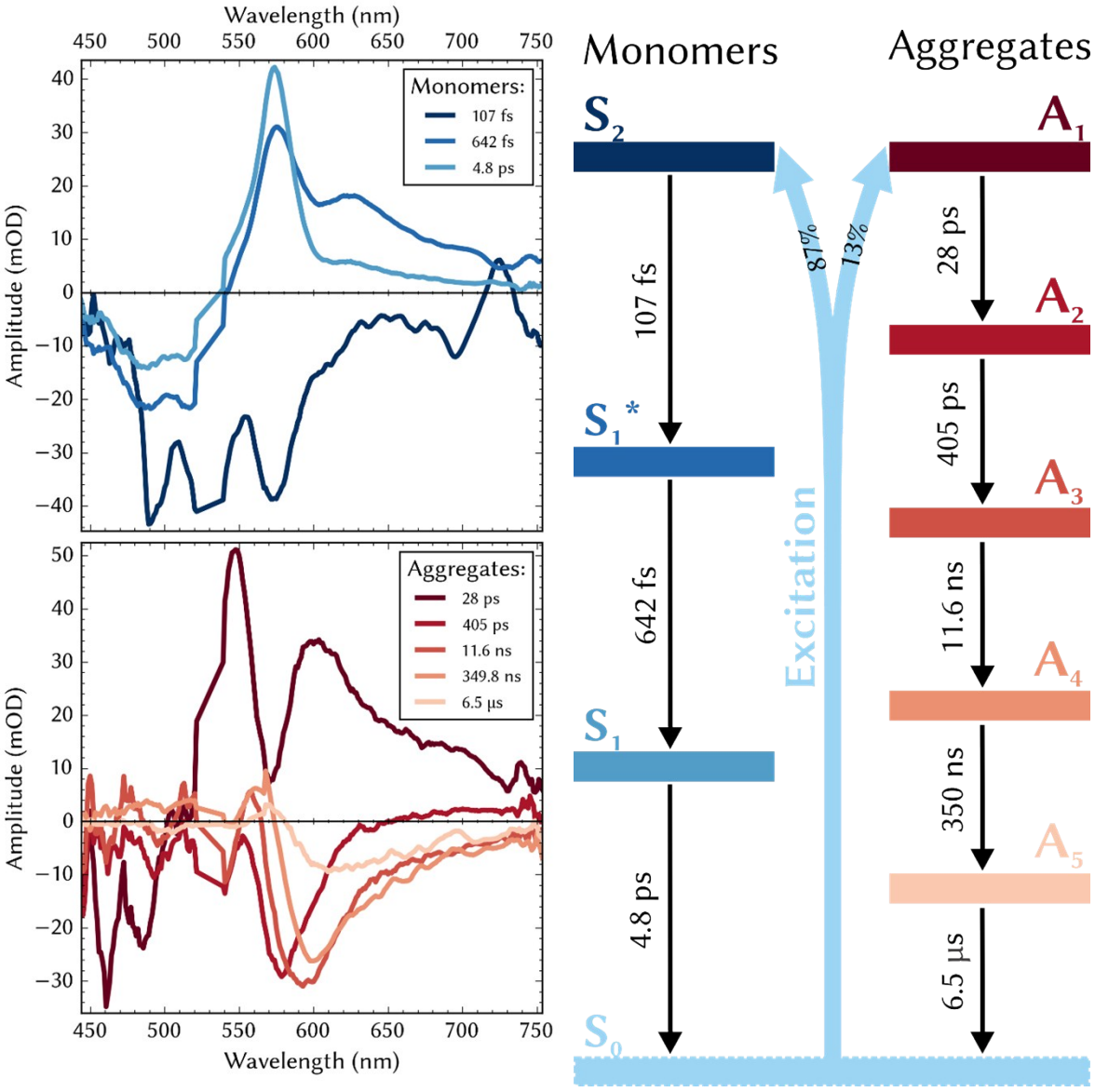


**Figure S3| Left:** Species-associated difference absorption spectra resulting from the global analysis of the transient absorption data on lycopene aggregates. **Right:** model describing two subpopulations (monomeric and aggregated lycopene) decaying in parallel. The estimated lifetimes of different states are shown next to the arrows.

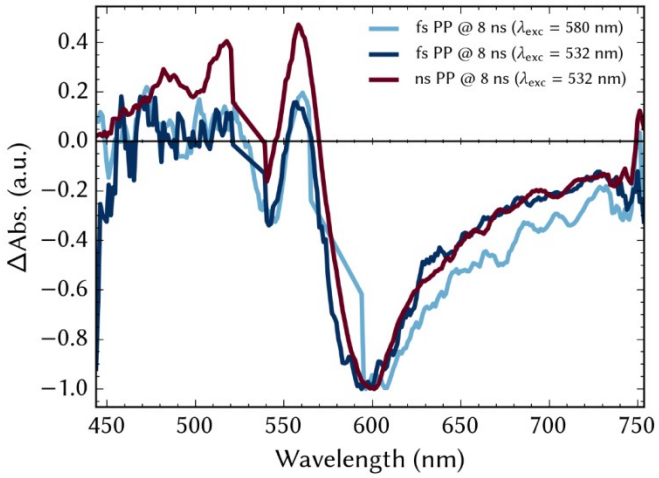


**Figure S4|** Comparison of normalized transient absorption spectra measured at 8 ns using different experimental conditions: femtosecond pulse excitation at 580 nm, nanosecond pulse excitation at 532 nm and femtosecond pulse excitation at 532 nm.

## Power- Resolved Resonance Raman

Power-resolved resonance Raman spectroscopy consists in dynamically accumulating the transient excited state(s) in the sample, by increasing the laser excitation used to produce the Raman signal [3, 4]. Figure S5 displays the $\nu_1$ region (~1500 $cm^{-1}$, C=C stretching modes) of resonance Raman spectra of aggregated lycopene recorded at 180 K, upon 514.5 nm exitation. The blue spectrum is obtained at low excitation power (< 0.01 mW), corresponding to the $\nu_1$ of ground-state lycopene aggregates at 1520.8 $cm^{-1}$. When the intensity of the laser increases, long-lived excited states can be populated. The red spectrum depicts the signal obtained in the same conditions but with an incident excitation power higher than 100 mW, so that the signal obtained is a mixture of the ground and exited states. We observe a downshift of the C=C stretching mode to 1516 $cm^{-1}$, as previously described for carotenoid triplet excited states [3, 4].

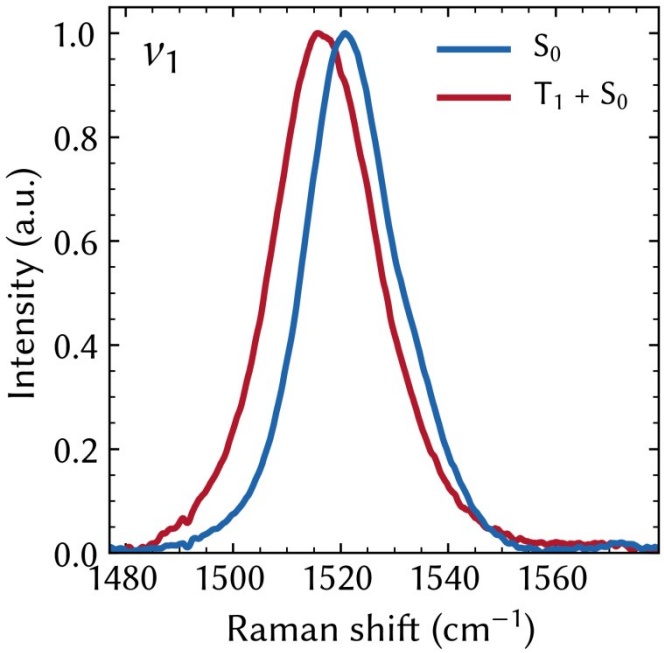


**Figure S5|** 180 K resonance Raman spectra in the $\nu_1$ region of lycopene aggregates, using 514.5 nm excitation at low and high power (blue, dark red respectively).

## References

1. Hörvin Billsten, H., et al., *Dynamics of vibrational relaxation in the S1 state of carotenoids having 11 conjugated C=C bonds.* Chemical Physics Letters, 2002. **355**(5–6): p. 465-470.
2. Frank, H.A., et al., *The Photochemistry of Carotenoids*. 1999, Kluwer Academic Publishing.
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