Supporting Information

Ultrafast Triplet Generation and its Sensitization Drives Efficient Photoisomerization of tetra-*cis*-lycopene to all-*trans*-lycopene

*Kanchustambham Vijayalakshmi, Ajay Jha and Jyotishman Dasgupta**

*Email: dasgupta@tifr.res.in

Department of Chemical Sciences, Tata Institute of Fundamental Research, Mumbai-400005, India

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MATERIALS AND METHODS

Chemicals: Prolycopene was extracted from *Tangerine* tomato and tendersweet orange watermelon. Prolycopene was purified by high performance liquid chromatography (HPLC).The seeds and fruits of *Tangerine* tomato variety were kindly provided by Prof. Joseph Hirschberg, Hebrew University, Israel and the seeds of tendersweet orange watermelon were purchased from Wilding Woods, AR, United States. All-*trans*-lycopene was purchased from Carotenature, Switzerland and was used in experiments without further purification. HPLC grade solvents acetone, acetonitrile, methanol, ethyl acetate, n-hexane, petroleum ether, cyclohexane, toluene and chloroform were purchased from SD Fine-Chem. Pvt. Ltd., India. d_{12}-cyclohexane was purchased from Cambridge isotope Laboratories (CIL). Silica gel (200-400) mesh for column chromatography was purchased from SD Fine-Chem. Pvt. Ltd., India.

Steady state absorption measurements: All the absorption measurements were carried out using UV-Vis spectrophotometer (Specord 205, Analytic Jena).

Resonance Raman spectroscopy: We recorded resonance Raman spectra of all carotenoids using confocal Raman microscope (alpha300R, WITec, GmbH, Ulm, Germany). The system was equipped with a frequency doubled DPSS Nd: YAG laser (532 nm, 56.1 mW) and a lens based ultra-high throughput spectrometer (UHTS300) coupled to a back illumination CCD-camera (1024 x 128 pixels, Peltier cool to -65°C). Spectra were recorded with an integration time of 1s at a laser power of 0.9 mW using a 20x Zeiss microscope objective. The scattered light in the focal plane is collected through 100 μm core multimode fiber served as pinhole. The spectral resolution of ~ 2 cm^{-1} per CCD pixel was achieved on 1800 grooves/mm grating. All the carotene samples in toluene were measured under constant flow through 1 mm flow-cell to prevent photodamage upon long-term exposure to the laser pulses. The intermediates formed during photoisomerization of prolycopene were characterized with the time series module provided in the WITec control. The data was processed with the help of WITec project software and plotted using IGOR5 software.

Time-lapsed resonance Raman spectroscopy: The time-lapsed resonance Raman spectroscopy is used as an appropriate method to observe intermediates in real time about millisecond time scales of reaction. Prolycopene in toluene was maintained under inert conditions and kept under constant flow through the flow capillary. The *cis-trans* isomerization reaction was initiated by

light emitting diode (LED) of center wavelength 457 nm, photon flux 500 μmol m^{-2} s^{-1} and simultaneously spectra were recorded with an integration time of 100 ms at a laser power of 0.2 mW using a 20x Zeiss microscope objective.

Ultrafast transient absorption spectroscopy: Details of the pump-probe set up have been described elsewhere.[1] Femtosecond laser pulses were generated from the oscillator (Micra-5 mode-locked Ti: Sapphire operating at 80 MHz repetition rate) and amplified using a regenerative amplifier (Coherent Legend Elite) to produce ~30 fs amplified pulses at the repetition rate of 1 kHz with the energy of ~4 mJ/pulse. The amplified output was divided into two parts, one for the generation of the tunable actinic pump using an optical parametric amplifier (Coherent OPeraASolo Ultrafast Optical Parametric Amplifier system) and the second part was focused on to a 2 mm thick sapphire crystal to produce a white-light continuum (420 nm-700 nm) as probe. The pump (400 nm & 480 nm, 40-100 nJ) and probe pulses were focused and spatially overlapped on the sample inside a flow cuvette with 0.5 mm quartz window. The time delay between pump and probe pulses were controlled with a motorized translation stage with quadra-pass mirror assembly. The probe light was dispersed on to a multichannel detector provided by Ultrafast Systems, Sarasota USA. Any effect of rotational diffusion was corrected by adjusting the polarization between pump and probe to the magic angle (54.7°). The temporal resolution of the experiment was determined by performing a cross-correlation experiment on 1 mm glass using an optical Kerr-effect (OKE) arrangement. The temporal resolution of the experiment was ~90 fs with 400 nm pump pulse. Transient absorption measurements of prolycopene and all-trans lycopene were carried out in toluene. The sample was flowed continuously through quartz flow-cell with 1 mm path length, to prevent photo-degradation upon long-term exposure to the laser pulses. HPLC method was used to check sample integrity after the measurements (Figure S14). The decay kinetics was fitted with multi exponential kinetic model convoluted with the IRF using software IGOR 5 Pro. The singular value decomposition of the transient data was carried out by using the Surface Xplorer® software from Ultrafast Systems.

Kinetic data fitting procedure: Time resolved data were analyzed by multi-exponential fitting with the help of IGOR 5 wavemetrics software. Fitting equation consists of four exponential time constants in convolution with the instrument response function (IRF) which yields decay time

constants and the respective amplitudes. The instrument response function (IRF) is the full width half maximum (FWHM) of all the fits.

The equation used is given below:

$$
\begin{aligned}
y(t) = \quad & w_1\left[\left(w_2 e^{\frac{\left[k_0^2-4bk_0(t-w_9)\right]}{4b}}\right)\text{normdist}\left(\frac{2b(t-w_9)-k_0}{\sqrt{2b}}\right)\right. \\
& +\left(w_4 e^{\frac{\left[k_1^2-4bk_1(t-w_9)\right]}{4b}}\right)\text{normdist}\left(\frac{2b(t-w_9)-k_1}{\sqrt{2b}}\right) \\
& +\left(w_6 e^{\frac{\left[k_2^2-4bk_2(t-w_9)\right]}{4b}}\right)\text{normdist}\left(\frac{2b(t-w_9)-k_2}{\sqrt{2b}}\right) \\
& \left.+\left([-1-(w_4-w_6)]e^{\frac{\left[k_3^2-4bk_3(t-w_9)\right]}{4b}}\right)\text{normdist}\left(\frac{2b(t-w_9)-k_3}{\sqrt{2b}}\right)\right]
\end{aligned}
$$

Where,

$$b = \frac{4\ln 2}{w_0^2} \quad k_0 = \frac{1}{w_3} \quad k_1 = \frac{1}{w_5} \quad k_2 = \frac{1}{w_8}$$

w_0= IRF determined by the Optical Kerr experiment.

w_1= common scaling factor that scales the curve.

$w_2,\ w_4,\ w_6$ = amplitudes of the first, second, third exponentials.

$w_3,\ w_5,\ w_7,\ w_8$= Four time constants.

w_9= zero time, the offset of actual pump probe.

Singular value decomposition (SVD)

SVD analysis of the transient absorption data was performed in order to obtain decay associated difference spectra, DADS using a mathematical tool "Surface Xplorer". The 3D transient absorption spectra obtained during measurement is the product of three matrices. These matrices were solved for the eigen vectors with their significance to the raw data that discerns the contribution of actual chemical processes from the experimental noise. The principal components obtained was used to construct the target model.

Laser flash photolysis: We measured transient absorption of long lived photo-intermediate during isomerization of prolycopene using laser flash photolysis (LP920, Edinburgh Photonics) as described earlier.[2] The transient absorption measurements were performed in 1 cm path length cuvette containing the degassed sample solution without stirring at room temperature. Prolycopene is excited by the third harmonic of the (10 Hz) Nd: YAG laser at 355 nm, 12 mJ per pulse. The triplet state spectra of carotenoids were probed by a pulsed 450 W Xenon lamp in a configuration perpendicular to the pump pulse at the sample. The temporal changes in the attenuated probe beam following the excitation, is dispersed on to a spectrograph containing 1800g/mm Czerny-Turner triple Grating (TMS300) and focused on to a charge coupled device (CCD). Data is acquired through a digital oscilloscope of bandwidth 100 MHz. The time resolution of the experiment (FWHM) is 6 ns and the transient spectra are averaged over 5 scans. The intermediates formed in the photoisomerization of prolycopene are monitored by the UV-Vis absorption spectra before and after every transient measurement (Figure S16).

Extraction and purification of prolycopene: The crude material from *Tangerine* tomato and tender sweet orange watermelon was extracted in to the acetone layer and partitioned against petroleum ether in 2:1 (v/v). The non-polar phase is separated out and dried under vacuum. The dried carotene mixture was dissolved in n-hexane and loaded on to the self-packed silica gel column equilibrated with increasing gradients of chloroform to isolate crude carotenoid fractions. The fractions containing prolycopene was purified by a Prominence series ultra-high performance liquid chromatography (model UFLC; Shimadzu, Columbia, MD) equipped with photodiode array detector (PDA). A semi-preparative HPLC system-I was developed using a reverse phase column C18 (Varian, 250 x 10 mm, 10 µm) maintained at 4°C. The solvent gradient established using mobile phase A (acetonitrile: water; 90:10 v/v) and the mobile phase B (ethyl acetate) with a flow rate of 1.2 ml/min. Further purification was carried out using HPLC system-II developed using column YMC carotenoid C30 S-3 µm, 150 x 4.6 mm I.D. maintained at 4°C and solvent gradient established using mobile phase A (methanol: *tert*-butyl-methyl ether: water; 5:1:1 v/v/v) and mobile phase B (methanol: *tert*-butyl-methyl ether; 1:3 v/v) with a flow rate of 0.8 ml/min.[3,4] Individual *cis*-carotenoids and prolycopene were resolved, identified and detected with a PDA detector. The collected fractions were dried under vacuum and maintained under N_2 atmosphere.

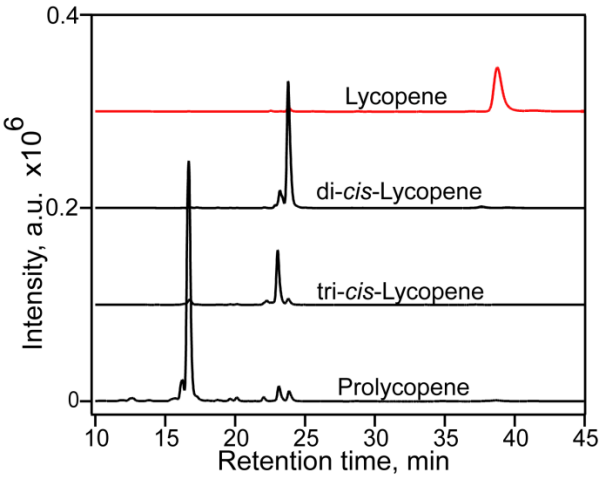


Figure S1: HPLC chromatograms of purified prolycopene (RT = 16.2 min), tri-*cis*-lycopene (RT = 22.5 min), di-*cis*-lycopene (RT = 23.2 min) and commercially obtained lycopene (RT = 37.5 min).

Matrix-assisted laser desorption/Ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of prolycopene: Prolycopene molecular mass is measured using MALDI-TOF mass spectrometer Bruker ultrafleXtreme^{TM} (Bruker Daltonics). Prolycopene molecular mass is analyzed by reflector positive mode in the mass range 500-3500 Da. Prolycopene in acetone and mixed with α-cyano-4-hydroxycinnamic acid (HCCA) matrix solution in 1:1 ratio. Prolycopene prepared in matrix is loaded on to a target of MALDI probe and the target plate is inserted under vacuum interlocked to the ion source after complet evaporation of solvent from prolycopene sample. Matrix containing prolycopene is irradiated by 337 nm laser and the ions produced are detected by time-of-flight mode. Prolycopene mass is confirmed at m/z 536.07$[M]^+$ and the mass at 537.07 $[M+H]^+$.[5]

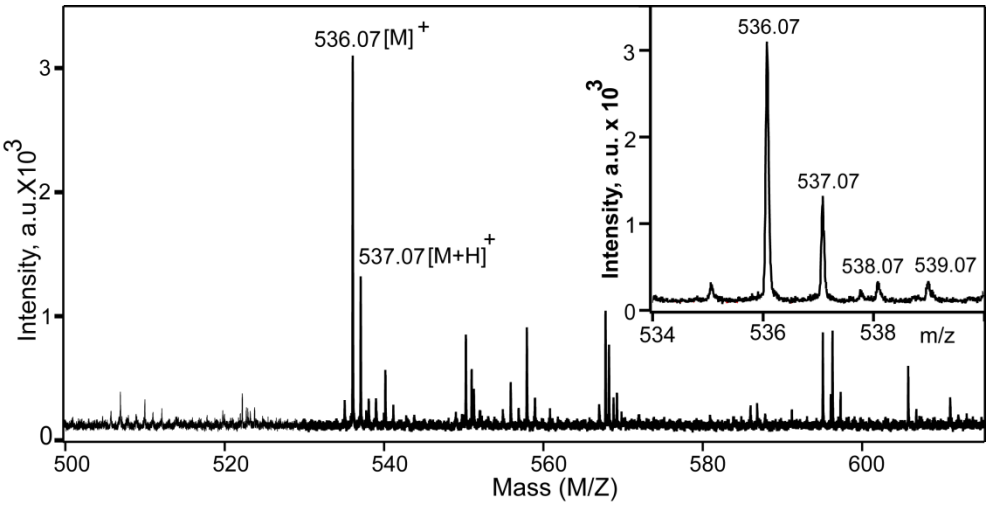


Figure S2: MALDI-TOF mass spectrum of prolycopene prepared in matrix α-cyano-4-hydroxycinnamic acid (HCCA) showing molecular mass at m/z 536.07 $[M]^+$and the mass at 537.07 $[M+H]^+$. Ions are generated using 337 nm laser and 25 kV source voltage, 22.35 kV extraction voltage are used.

^{1}H NMR chemical shifts of prolycopene in cyclohexane: ^{1}H NMR spectrum of HPLC purified prolycopene in cyclohexane were recorded on Varian 600 MHz. The assignment is based on previous published work on prolycopene structural elucidation.[6,7] The assignment is done by the assumption of quasi isolated spin systems like two spin H(7) and H(8), three spin H(10), H(11), H(12) and four spin H(14), H(14'), H(15), H(15').The couplings between subsystems is not determined in the present work. The chemical shift (δ ppm) values for protons in the olefinic range are H(2) 5.087, H(6) 6.098, 6.079, H (7) 6.302, 6.283, 6.264, H(8) 5.921, 5.902 H(10) 6.023, 6.005, H(11) 6.467, 6.448, 6.442, 6.423, H(12) 6.213, 6.188, H(14) 6.150, 6.137, H(15) 6.540, 6.527. The chemical shift of protons H(3) and H(4) are 2.07 and 2.09 but the peaks are broadened and indistinguishable from each other. The chemical shift values for protons in the methyl groups are H (16) 1.652, H(17) 1.558, H(18) 1.801, H(19) 1.953, H(20) 1.859. The couplings measured in the spectrum of prolycopene are $J_{6,7}$= 11.4 Hz, $J_{7,8}$ = 11.4 Hz, $J_{10,11}$= 10.8 Hz, $J_{11,12}$= 15 Hz and $J_{14,15}$= 7.8 Hz. The coupling consant $J_{7,8}$ = 11.4 Hz indicates C_7=C_8 double bond is hindered in *cis* while $J_{11,12}$ = 15 Hz shows C_{11}=C_{12} double bond is in *trans*-geometry. The residual solvent peaks from *tert*-butyl-methyl ether (TBME), acetone, methanol and cyclohexane are unassigned.

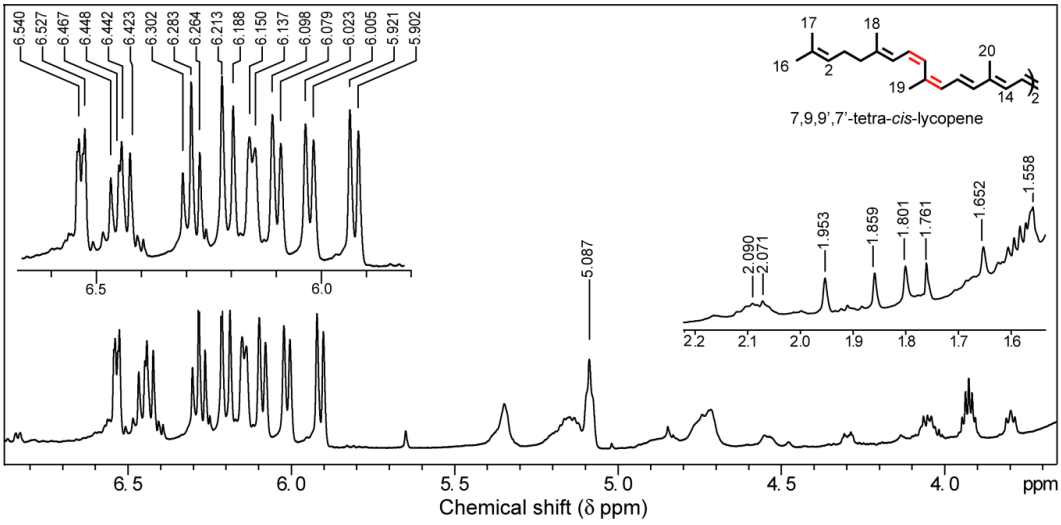


Figure S3: ^{1}HNMR chemical shifts of purified prolycopene in cyclohexane recorded on Varian 600 MHz. The residual solvent peaks from *tert*-butyl-methyl ether (TBME), acetone and methanol are unassigned.

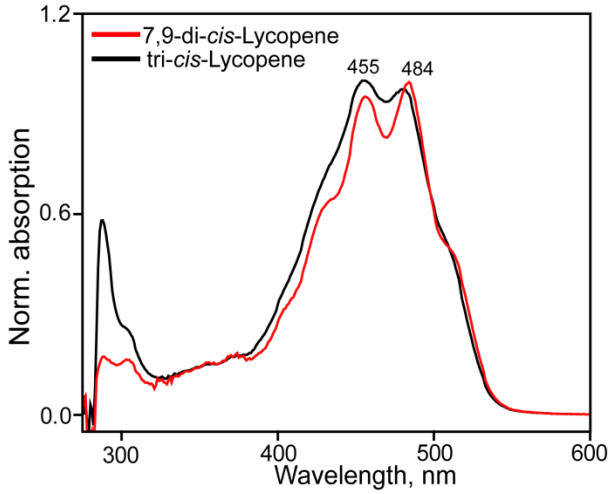


Figure S4: Normalized UV-Vis absorption spectra of tri-*cis*-lycopene (black) and di-*cis*-lycopene (red). Absorption peak at 287 nm is the solvent subtraction artifact represented in (*).

Solvatochromic shift of prolycopene and lycopene: Absorption spectra of prolycopene and lycopene are measured in methanol (n=1.328, R(n)= 0.203), *tert*-butylmethyl ether (n=1.369, R(n)= 0.225), ethyl acetate (n=1.372, R(n)= 0.227), *n*-hexane (n=1.375, R(n)= 0.229), cyclohexane (n=1.426, R(n)= 0.256), chloroform (n=1.446, R(n)= 0.266) and toluene (n=1.496, R(n)= 0.292). It is observed that absorprtion spectra shifts to longer wavelengths with increasing polarizability function R(n) of solvent where n is the refractive index. The spectral shift is linearly dependent on R(n) with some deviation observed in n-hexane and chloroform. It is explained previously that the observed solvent induced absorption spectral shift arises due to induced dipole-dipole interactions (dispersive interactions). [8-13]

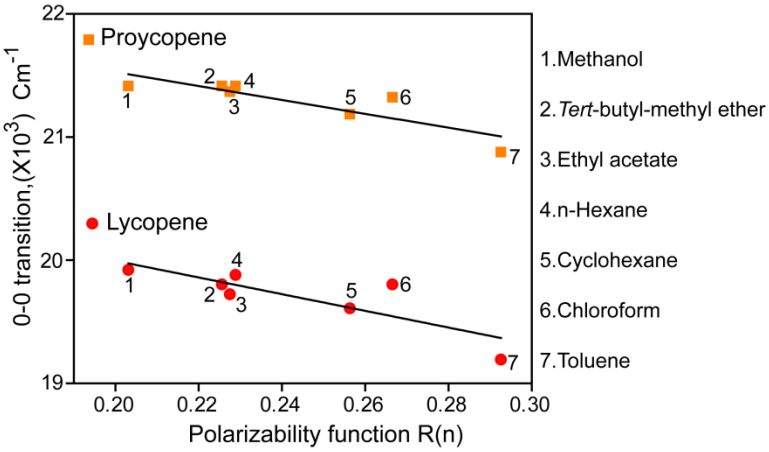


Figure S5: 0-0 transition (cm^{-1}) of prolycopene (squares) and lycopene (circles) plotted against polarizability function of solvent R (n) = (n^2-1)/ (n^2+2).

Determination of Effective conjugation length of prolycopene:

The steady state absorption spectrum of prolycopene is blue shifted by ~35 nm compared to that of all-*trans*-lycopene. The observed spectral shift is dependent on the effective conjugation length of the carotenoid molecule which is sensitive to the configuration of the isomer.[14] The effective conjugation length of prolycopene was calculated using the empirical relations described in the reference.[15] The state energies in solution were expressed as linear function of 1/ (2N+1), where N is the conjugation length of the molecule.

$E(1^1Bu^+) = 143105x\frac{1}{2N+1} + 13501\ cm^{-1}$ …….(1)

$E(1^1Bu^-) = 394797x\frac{1}{2N+1} - 1012\ cm^{-1}$ ……(2)

$E(2A_g^-) = 219137x\frac{1}{2N+1} + 3764\ cm^{-1}$ ……...(3)

Energy of S_2 (1^1Bu^+) state was obtained from the steady state absorption spectrum. The observed solvatochromic shift of 0-0 transition of prolycopene and lycopene showed a perfect linear dependence of solvent polarizability function, R(n). In figure S5, a linear fit provided us the following expressions for both prolycopene and lycopene in different solvents.

Lycopene: $\tilde{\nu} = 21348 - 6770 \times R(n)$ [± 500 cm^{-1}] ……..... (4)

Prolycopene: $\tilde{\nu} = 22654 - 5640 \times R(n)$ [± 500 cm^{-1}] …….. (5)

Where $R(n) = (n^2-1) / (n^2+2)$, is the solvent polarizability function and "n" is the refractive index of the solvent.

For lycopene in toluene with R(n) = 0.29, we get $\tilde{\nu}$ = 19385 ± 500 cm^{-1} OR 2.4 ± 0.06 eV
Prolycopene in toluene, we get $\tilde{\nu}$ = 21018 ± 500 cm^{-1} OR 2.6 ± 0.06 eV

Substituting the energy of S_2 state of prolycopene and lycopene in equation 1,
The effective conjugation length of prolycopene N_{eff} is estimated to be 9.1 ± 0.5 while N_{eff} is 11.6 ± 0.5 for all-*trans*-lycopene.

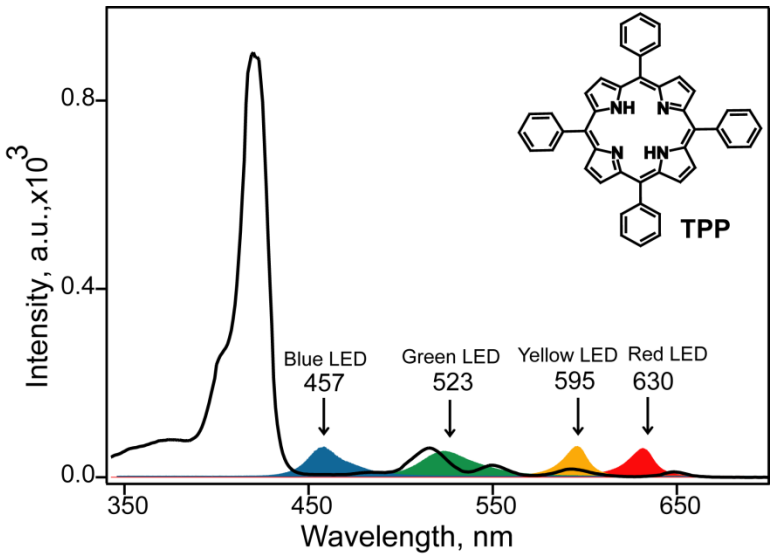


Figure S6: UV-Vis absorption spectrum of *meso*-tetraphenylporphyrin (TPP) and the spectra of different excitation source light emitting diodes used in the photo-isomerisation of prolycopene. These excitation wavelenths correspend to the $S_0 \rightarrow S_2$ transition in prolycopene in toluene (451 nm) and Q-band transitions of TPP (515 nm, 550 nm, 593 nm and 650 nm).

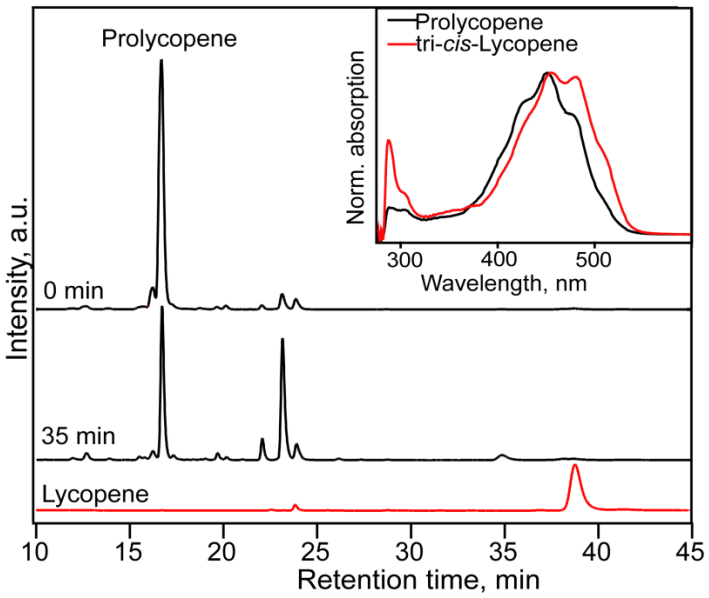


Figure S7: HPLC chromatogram of prolycopene before and after the time-lapsed resonance Raman spectroscopy measurements. *Inset.* UV-Vis absorption spectra of tri-*cis*-lycopene and prolycopene.

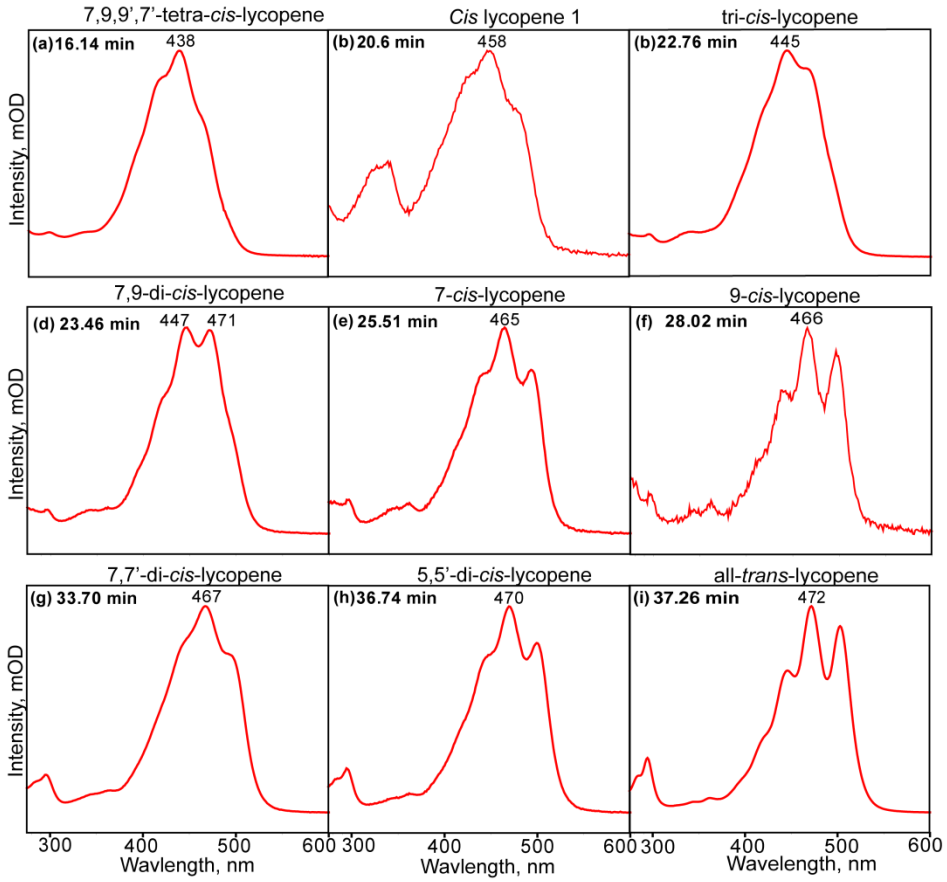


Figure S8: UV-Vis absorption spectra of prolycopene and "on pathway" *cis*-isomers of lycopene formed in the photo-isomerization of prolycopene monitored in HPLC: (a) Prolycopene (RT = 16.14 min); (b) *cis*-lycopene 1 (RT = 20.6 min); (c) tri-*cis*-lycopene (RT = 22.76 min); (d) 7,9-di-*cis*-lycopene (RT = 23.46 min); (e) 7-*cis*-lycopene (RT = 25.51 min); (f) 9-*cis*-lycopene (RT = 28.02 min) (g) 7,7'-di-*cis*-lycopene (RT = 33.70 min); (h) 5,5'-di-*cis*-lycopene (RT = 36.74 min); and (i) all-*trans*-lycopene (RT = 37.26 min).

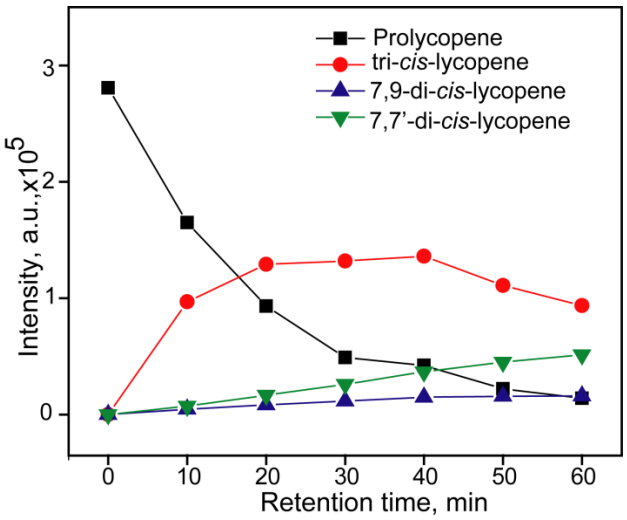


Figure S9: Population kinetics of *cis*-isomers formed on pathway of photoisomerization reaction, prolycopene (black), tri-*cis*-lycopene (red), 7,9-di-*cis*-lycopene (blue), 7,7'-di-*cis*-lycopene (green).

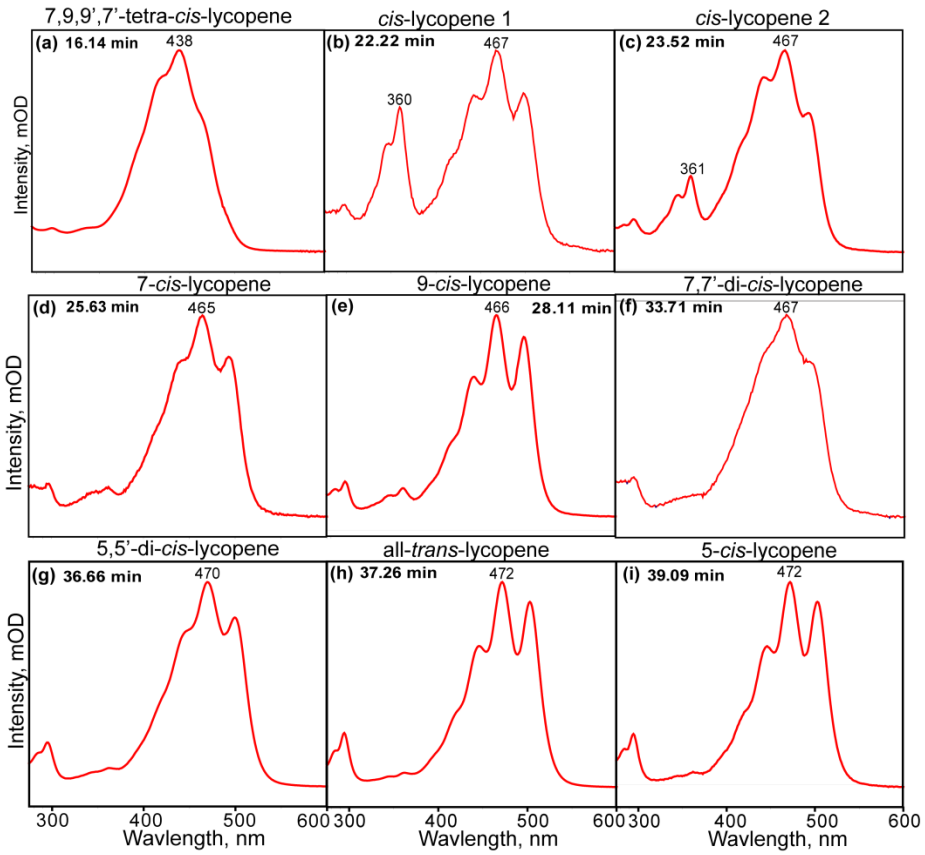


Figure S10: UV-Vis absorption spectra of prolycopene and "on pathway" *cis* isomers of lycopene formed during photo-isomerization carried out in the presence of 10 eqv. of *meso*-tetraphenyl porphyrin (TPP) and monitored via HPLC: (a) Prolycopene (RT = 16.14 min) ; (b) *cis*-lycopene 1 (RT = 22.22 min); (c) *cis*-lycopene 2 (RT = 23.52 min); (d) 7-*cis*-lycopene (RT = 25.63 min); (e) 9-*cis*-lycopene (RT = 28.11 min); (g) 5,5'-di-*cis*-lycopene (RT = 36.66 min); (h) all-*trans*-lycopene (RT = 37.26 min); and (i) 5-*cis*-lycopene (RT = 39.09 min).

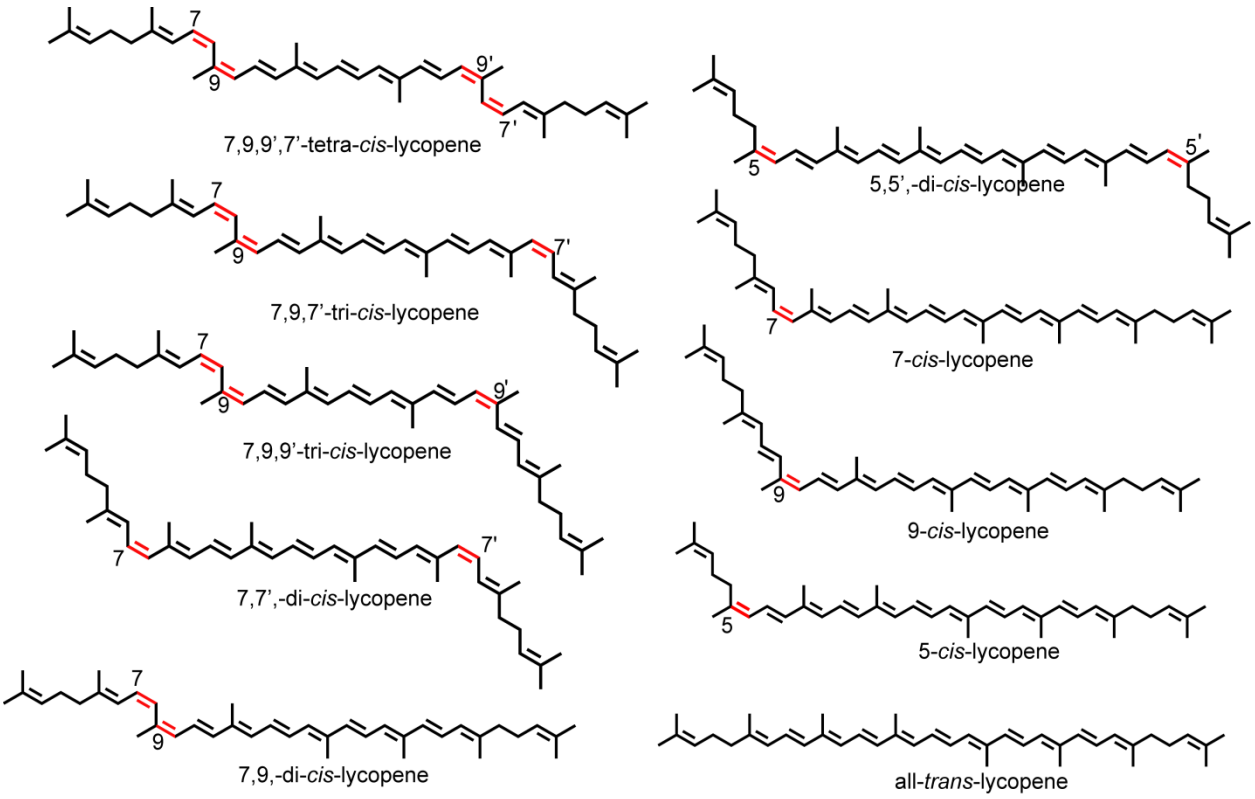


Figure S11: Structures of prolycopene, lycopene and *cis*-intermediates formed in the photoisomerisation of prolycopene in solution.

Quantum yield of photoisomerisation in the presence and absence of triplet sensitizer (TPP): Prolycopene in toluene is degassed for 15 min and injected on to the HPLC column before and after irradiation with blue LED of centred wavelength 457 nm and photon flux 500 μmol m^{-2} s^{-1}. The quantum yield of isomerisation is calculated for 10 minute reaction where prolycopene shows significant transormation to tri-*cis*-intermediate.The quantum yield of tri-*cis*-lycopene formation is 0.15 and for all-*trans*-lycopene formation is 0.003 calculated for 60 minute reaction (see Figure S14a). For sensitization experiment, prolycopene and triplet sensitizer TPP in toluene is degassed for 15 min and injected on to the HPLC column before and after irradiation with green LED of centred wavelength 520 nm and photon flux 500 μmol m^{-2} s^{-1}. The photoisomerisation reaction studied for 10 minutes and quantum yield of all-*trans*-lycopene formation increased by three orders of magnitude ~0.61(see Figure S14b).

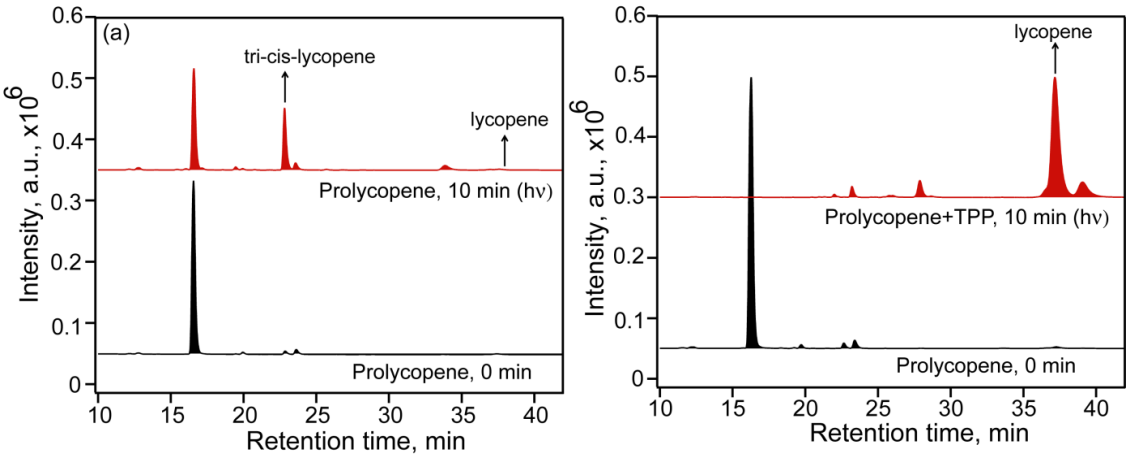


Figure S12: HPLC chromatogram depicting the time course of photo-isomerisation of prolycopene in (a) absence of triplet sensitizer TPP; (b) presence of triplet sensitizer TPP.

Quantum yield of tri-*cis*-lycopene formation:

$$\Phi = \frac{\text{Number of moles of tri} - cis - \text{lycopene formed}}{\text{Number of moles of photons absorbed by prolycopene/unit time/ unit area}}$$

$$\Phi = \frac{\text{Area under tri} - cis - \text{lycopene peak} * \text{volume injected}}{\text{molecular extinction coefficient} * \text{optical pathlength} * \text{mean fraction of photons absorbed}}$$

$$\Phi = \frac{23080 * 20 * 10^{-6}\ \text{L}}{116000\ \text{L} * \text{mol}^{-1} * \text{cm}^{-1} * 1\ \text{cm} * 500 * 10^{-6}\text{mol} * 10^{-4}\text{cm}^{-2} * \text{s}^{-1} * 600\ \text{s} * 0.86\ \text{cm}^2}$$

$$\boldsymbol{\Phi = 0.154}$$

Quantum yield of all-*trans*-lycopene formation:

$$\Phi = \frac{\text{Number of moles of all} - trans - \text{lycopene formed}}{\text{Number of moles of photons absorbed by prolycopene/unit time/ unit area}}$$

$$\Phi = \frac{5208 * 20 * 10^{-6}\ \text{L}}{185000\ \text{L} * \text{mol}^{-1} * \text{cm}^{-1} * 1\ \text{cm} * 500 * 10^{-6}\text{mol} * 10^{-4}\text{cm}^{-2} * \text{s}^{-1} * 600\ \text{s} * 0.86\ \text{cm}^2}$$

$$\boldsymbol{\Phi = 0.003}$$

Quantum yield of all-*trans*-lycopene formation in the presence of triplet sensitizer TPP:

$$\Phi = \frac{\text{Number of moles of all} - trans - \text{lycopene formed per mole of sensitizer}}{\text{Number of prolycopene triplets generated by TPP sensitization}}$$

$$\Phi = \frac{\text{Number of moles of all} - trans - \text{lycopene formed per mole of sensitizer}}{\text{Number of moles of photons absorbed by TPP/unit time/unit area} * \text{Quantum yield of } {}^3_{\text{TPP}}}$$

$$\Phi = \frac{(120390) * (14880\ \text{L} * \text{mol}^{-1} * \text{cm}^{-1} * 1\ \text{cm}) * 20 * 10^{-6}\ \text{L}}{(185000\ \text{L} * \text{mol}^{-1} * \text{cm}^{-1} * 1\ \text{cm}) * (15505) * 500 * 10^{-6}\text{mol} * 10^{-4}\text{cm}^{-2} * \text{s}^{-1} * 600\ \text{s} * 0.86\ \text{cm}^2 * 0.82}$$

$$\boldsymbol{\Phi = 0.58}$$

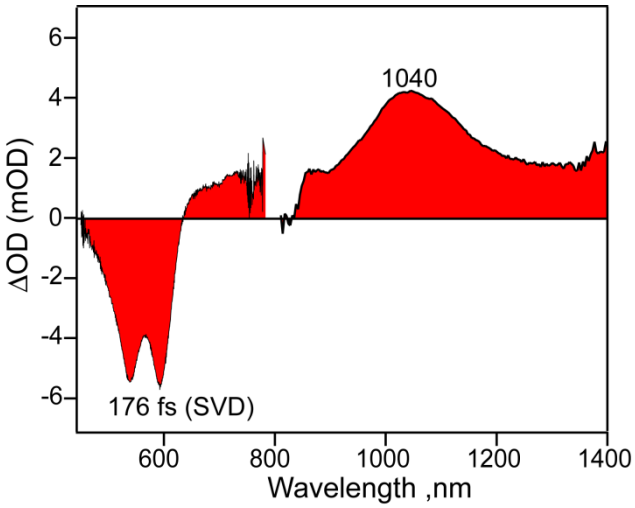


Figure S13: Near-IR transient absorption of prolycopene in toluene subsequent to excitation at 480 nm. The 176 fs component obtained from SVD analysis of pump-probe data in the visible range has been plotted along with the NIR transient.

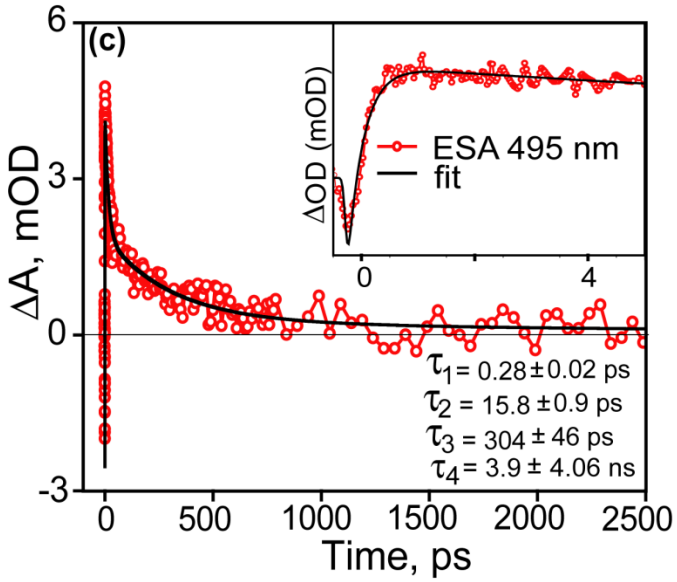
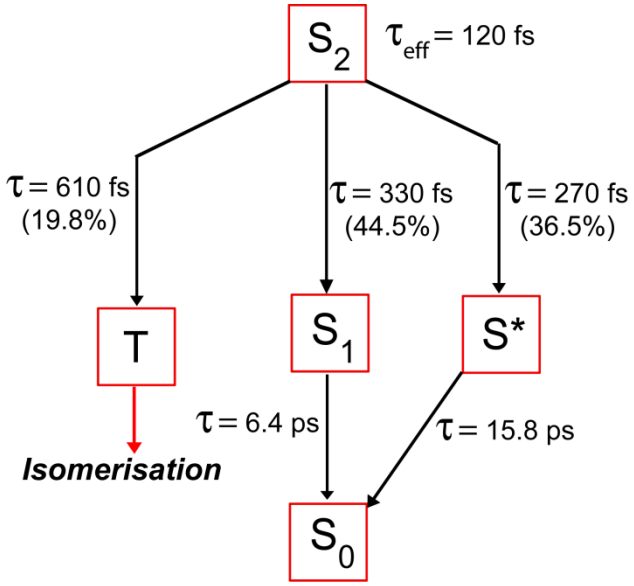


Figure S14: Multi-exponential single point kinetic analysis of prolycopene excited state dynamics at 495 nm subsequent to 400 nm excitation.

Quantum yield of prolycopene triplet formation:



Scheme S1: Branching of excited states from optically allowed S_2 state upon photoexcitation

$$\frac{1}{\tau_{S2}} = \frac{1}{\tau_{S1}} + \frac{1}{\tau_{S*}} + \frac{1}{\tau_{Triplet}}$$

$$\frac{1}{120\ \text{fs}} = \frac{1}{330\ \text{fs}} + \frac{1}{270\ \text{fs}} + \frac{1}{\tau_{Triplet}}$$

$$\tau_{Triplet} = 610\ \text{fs}$$

$$\Phi = \frac{\text{Number of moles of triplet formed}}{\text{Number of moles of photons absorbed by prolycopene}}$$

$$\Phi = \frac{k_{ISC}}{k_{ISC} + k_{IC\ to\ S*} + k_{IC\ to\ S1}}$$

$$\Phi = \frac{0.0016}{0.0016 + 0.0037 + 0.003}$$

$$\Phi = 0.19$$

Table ST1. Parameters obtained from multi-exponential fitting of kinetic traces of prolycopene excited state absorption probed in visible and near IR range subsequent to excitation at 400 nm and 480 nm respectively. Instrument response function, IRF was determined using optical kerr experiment.

Excitation wavelength	**IRF**	**1040 nm**	**590 nm**	**540 nm**	**495 nm**	**S_2branching ratio (error ± 1%)**
400 nm 480 nm (S_2 dynamics)	90 fs	120 fs (τ_{eff}) 330 fs (S_1) 270 fs (S*) 610 fs (T)	330 fs (50.1%) 6.4 ps (49.9%)	270 fs (50.4%) 5.2 ps (32.8%) 19 ps (16.8%)	280 fs (67.5%) 15.8 ps (19.1%) 304 ps (11.4%) > 1 ns (2%)	36.5% (S_1/S_2) 44.7% (S^*/S_2) 19.8% (T/S_2)

Triplet state spectra using nanosecond transient absorption. Direct excitation of prolycopene at 355 nm resulted in the formation of long-lived triplet state. Figure S15b shows the time-resolved absorption spectrum probed in the spectral range 350-600 nm, at 10 ns after averaging over 5 laser shots. The nanosecond transient spectrum (in Figure S15b) shows bleach signal in between 430-470 nm along with two absorption features at 490 nm and 515 nm respectively. Based on a comparison with the non-decaying component in the femtosecond transient experiments (Figure S15a), we assign the portion of 490 nm to the remnant triplet of the prolycopene molecule while the 515 nm to arise from a convoluted contributions of prolycopene and singly isomerized tri-*cis*-lycopene. The presence of the tri-*cis*-lycopene and other *cis*-isomers was confirmed using steady state absorption spectrum (Figure S16) These observations thus unequivocally show that triplet state forms the reactive surface for the first C=C isomerization reaction and a careful time-resolved description should emerge from nanosecond transient measurements in future.

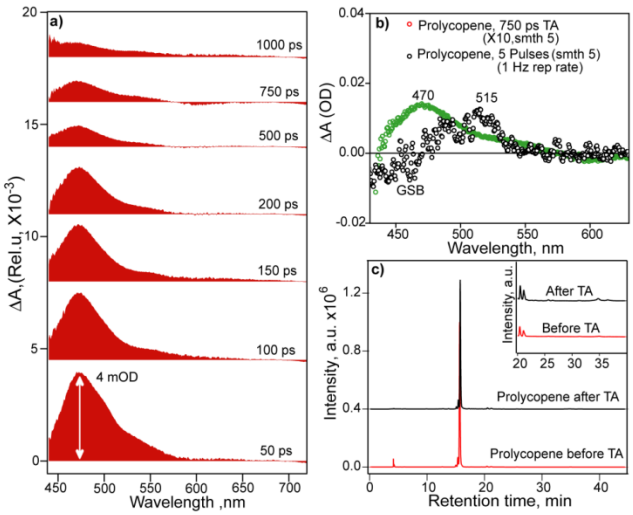


Figure S15: (a) Temporal evolution of the Triplet state from S_2 state of prolycopene in toluene followed by the excitation at 400 nm. The selected transient absorption traces are shown with the pump-probe time delays from 50 ps to 1000 ps. 5-point Savitzky-Golay smoothening was applied for the 750 ps and 1 ns points after scaling them by 2 times and 5 times respectively. (b) Overlay of the femtosecond transient absorption spectra of prolycopene in toluene at time point 750 ps (green) with the nanosecond spectrum obtained after 5 shots (black). (c) Stacked HPLC chromatogram of prolycopene analyzed before and after femtosecond transient absorption menasurements.

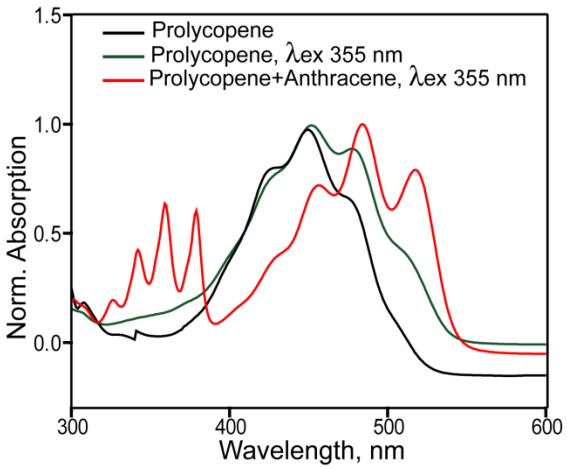


Figure S16: UV-Vis absorption spectra of prolycopene in toluene pre (black) and post (green) flash photolysis experiment. Post-measurement absorption spectrum of prolycopene in presence of triplet sensitizer anthracene (red) shows photoconversion to all-*trans*-lycopene.

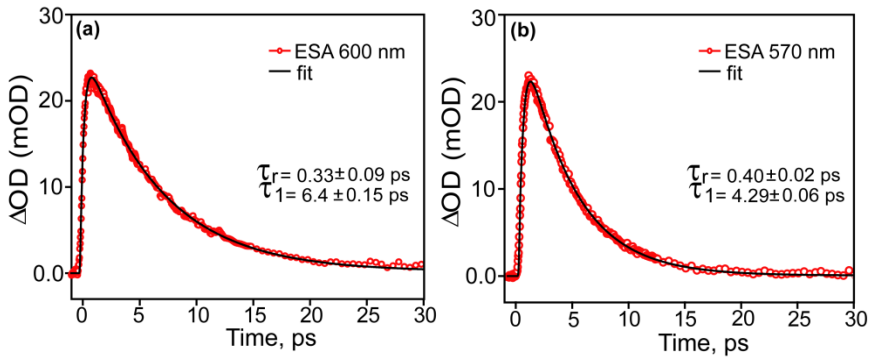


Figure S17: Multi-exponential kinetic analysis of excited state dynamics of prolycopene and lycopene in toluene subsequent to 400 nm excitation. Kinetics for (a) 600 nm; (b) 570 nm.

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