Supplementary information

Quantum coherence controls the charge separation in a prototypical organic photovoltaic system

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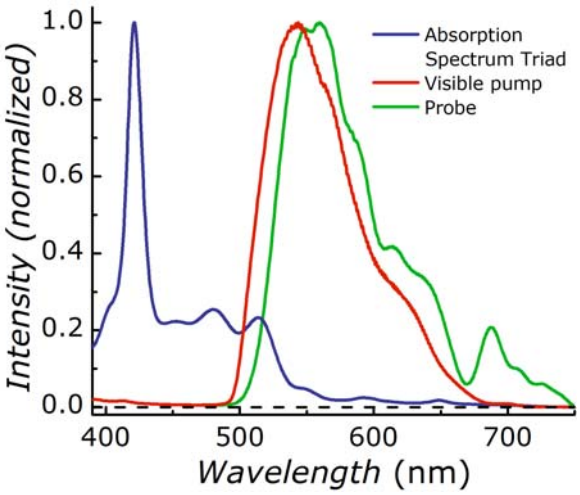
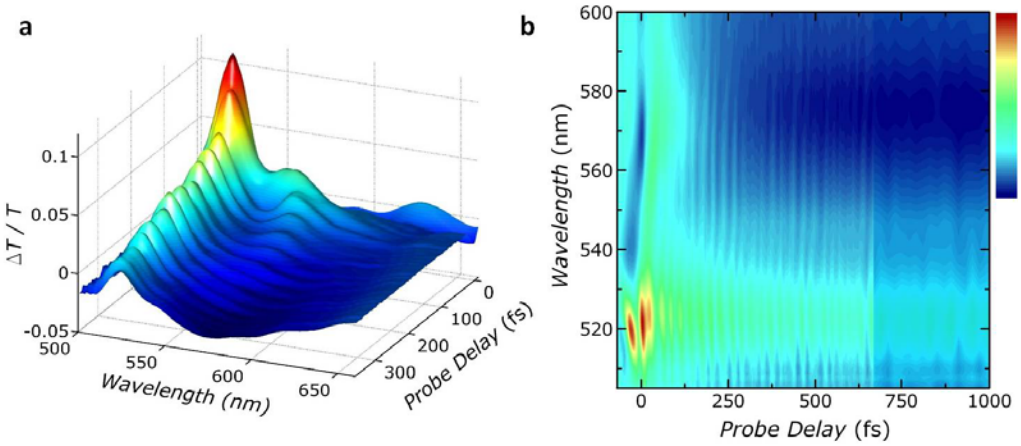
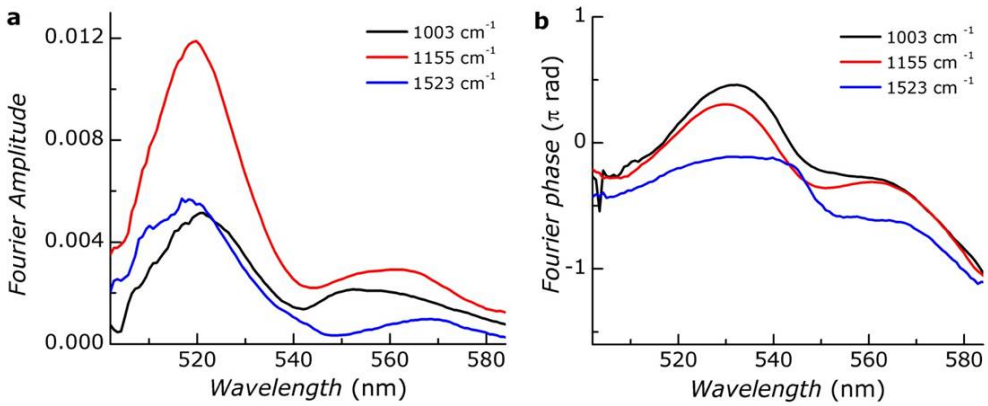


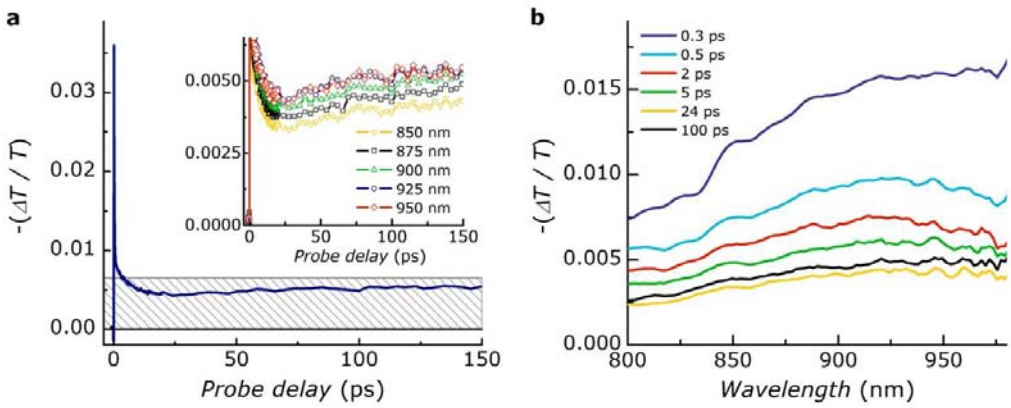
Supplementary Figure S1. Spectra of the pump (red line) and probe laser (green line) pulses and absorption spectrum (blue line) of the carotene-porphyrin-fullerene triad in toluene solution.



Supplementary Figure S2. (a) Differential transmission spectra $\Delta T / T(\lambda, \tau)$ of the triad in toluene solution after excitation with 10-fs pulses centered at 550 nm. The spectra of the corresponding pump- and probe-pulses are shown in Supplementary Figure S1. **(b)** $\Delta T / T$ map of the photoinduced CPF triad dynamics during the first picosecond. The $\Delta T / T$ values are plotted on a linear color scale extending from -0.05 to 0.12. Among the most prominent features are (i) a slowly rising and long-lived photoinduced absorption peaking at around 575 nm, (ii) a long-lived photobleaching band centered around 523 nm, and (iii) a short-lived increased transmission band extending from 540 to 580 nm. Pronounced oscillatory features are superimposed on all of these resonances, reflecting impulsively excited wave packet dynamics of the triad supramolecule.

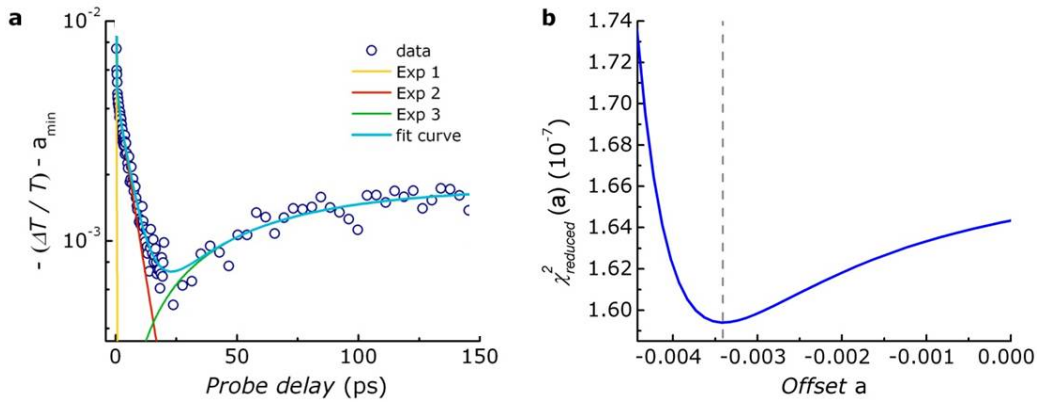


Supplementary Figure S3. Simulated Fourier amplitude (a) and phase (b) spectra of the three dominant β-carotene ground-state vibrational modes (1003 cm^{-1}, 1155 cm^{-1} and 1523 cm^{-1}) observed in differential transmission data of the triad. Following earlier work[24,25], the oscillatory pattern $f(\tau)$ seen on the different transmission data has been modeled as $f(\tau)=\sum_{i=1}^{3} A_i \cos(\omega_i \tau+\varphi_i)\exp(-\gamma_i \tau)$, with real Fourier amplitudes A_i, vibrational frequencies ω_i, phases φ_i and damping times $\gamma_i \approx 1\,\mathrm{ps}^{-1}$. The data analysis was restricted to probe delay times τ between 172 and 672 fs to avoid contributions from short-lived excited state vibrational wavepacket motion. The deduced vibrational frequencies correspond to the methyl rocking mode, the symmetric C-C stretch mode and the symmetric C=C stretch mode, respectively[26]. The analysis allows for an accurate determination of the displacement of ground and excited state oscillators as well as for a chirp analysis of the broadband probe pulses[24]. We have used this data analysis to subtract coherent oscillations $f(\tau)$ from the differential transmission data in Supplementary Figure S2 to generate the differential transmission data displayed in Figure 2 of our manuscript.

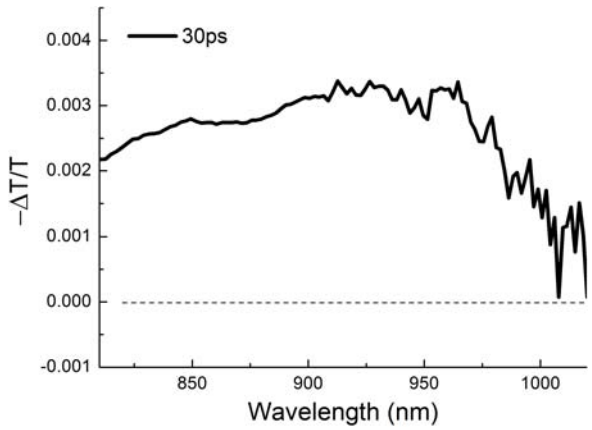


Supplementary Figure S4. (a) Transient *ΔT* / *T* dynamics of the supramolecular triad in toluene solution probed at 925 nm upon excitation centered at 550 nm. Inset: Transient *ΔT* / *T* dynamics at different probe wavelengths between 850 and 950 nm. Displayed is a zoom into the region marked with a gray rectangle in **(a)**. **(b)** Representative *ΔT* / *T* spectra at different time delays.

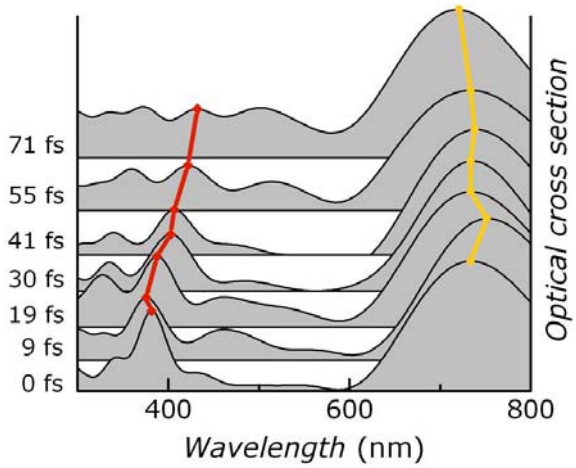
At all probe wavelengths the *ΔT* / *T* traces show a pronounced, pulsewidth-limited initial photoinduced absorption, *ΔT* < 0, which initially displays a rapid exponential decay with a time constant of $\tau_1 =$ 140 fs (amplitude $b_1 = 0.03$). This strong photoinduced absorption signal is well known from earlier studies of carotenoids[22] and reflects the transient absorption from the S_2 state and a possible intermediate state in the carotene moiety. The time constant of 140 fs then reflects the internal conversion from those states to the carotene S_1 state. After a few 100 fs, the *ΔT* / *T* signal has decayed to less than 20% of its maximum value and then remains almost constant for about 150 ps until it decays with a time constant of $\tau_4 = 0.7$ ns. The decay time was estimated from measurements performed for time delays of up to 400 ps. A closer inspection (s. inset in Fig. S4a) of the dynamics within the first 150 ps reveals, on top of a pronounced signal offset with an amplitude of $a \approx 0.004$, a partial initial decay with $\tau_2 =$ 7ps and $b_2 = 0.005$ and a slower partial rise with $\tau_3 =$ 40 ps and $b_3 = 0.002$. The transient dynamics are similar at all probe wavelengths and are well represented by a multi-exponential decay model $\Delta T / T(t) = \left(a + \sum_{i=1}^{2} b_i \, \mathrm{e}^{-t/\tau_i} + b_3 (1 - e^{-t/\tau_3}) \right) \mathrm{e}^{-t/\tau_4}$. All retrieved time constants are independent of the probe wavelength. The decay component with lifetime τ_2 = 7 ps might reflect residual absorption from the carotene S_1 state, known to decay on a few ps time scale[22].



Supplementary Figure S5. (a) Comparison of the experimental $\Delta T / T$ data at a probe wavelength of 925 nm and the multi-exponential decay model described in Supplementary Figure S4. The data are presented on a logarithmic intensity scale after subtracting a constant offset $a_{\min}$ from both curves. The three exponential components of Eq. (3) are indicated. **(b)** Reduced chi-square parameter $\chi^2_{reduced}$ as a function of the offset parameter a. The dashed gray line gives the optimum value $a_{\min} = 0.0375$.



Supplementary Figure S6. Transient $\Delta T / T$ spectrum of the supramolecular triad in toluene solution recorded at a delay of 30 ps for pulsed excitation at 550 nm. The data show a peak at around 950 nm, likely reflecting transient absorption of the carotene cation of the C^{+}-P-C_{60}^{-} biradical[28].



Supplementary Figure S7. Time resolved photoabsorption cross sections as calculated by TDDFT simulations in the case of freely moving ions at given time delays $\tau_i = 0,\ 9,\ 19,\ 30,\ 41,\ 55,$ and *71* fs after excitation. To deduce these spectra, additional TDDFT simulations are performed, impulsively re-exciting the system at the chosen delay time τ_i and computing the propagation for an additional 18.6 fs at time steps of 1.7 as. These spectra are calculated by taking as an initial condition not only the nuclear geometry at time τ_i, but also the excited-state electronic charge density $n(\mathbf{r},\tau_i)$ reached by the molecule during its initial, free time evolution.

These calculations are distinctly different from ground state simulations performed on a set of non-equilibrium geometries. They contain a much richer physics originating from the coupling of the electronic and ionic excited states. In particular, the spectra show pronounced temporal oscillations and a clear red shift in the porphyrin peaks around 400 and 440 nm (red lines). These spectral shifts are absent on the carotene resonance around 720 nm (solid yellow line), which instead display an oscillatory behavior both in frequency and in amplitude.