Electronic Supplementary Information

Role of Thermal Excitation in Ultrafast Energy Transfer in Chlorosomes Revealed by Two-Dimensional Electronic Spectroscopy

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Principle of two-dimensional electronic spectroscopy

Two-dimensional electronic spectroscopy (2D-ES) is an optical analog of two-dimensional NMR technique and can probe the evolution of excitations and couplings between multiple chromophores with femtosecond time resolution. 2D-ES makes use of three coherent optical pulses to induce third-order polarization signal, $P^{(3)}$. The experimental setup for 2D-ES is schematically shown in Figure S1 with the time ordering of a sequence of the three pulses shown in the inset of Figure S1. The first pulse interacts with the sample system to create coherence between the ground and excited states. After a time delay, τ, called coherence time, the second pulse generates a population in the excited or ground states. Then, after a time delay, T, called population time (or waiting time), the third pulse brings the system back to

the coherence between the ground and excited states. After a time delay, t, called rephasing time, the third-order signal (called photon echo) is radiated in a phase-matched direction ($k_s = k_1 + k_2 - k_3$). The emitted signal is measured as a function of the three time delays (τ, T, and t), and the measured time-domain data $S_{2D}(\tau, T, t)$ is Fourier transformed with respect to τ and t into a complex-valued two-dimensional spectrum, $S_{2D}(\omega_\tau, T, \omega_t)$ for each T value. The real part of the 2D spectrum corresponds to transient changes in the absorption of the sample at a probe frequency ω_t induced by an excitation frequency ω_τ after the time period T. In contrast, the imaginary part describes transient changes in the refractive index of the sample. In other words, ω_τ and ω_t correspond to "absorption" and "emission" frequencies, respectively, at an instant T. The peaks on the diagonal correspond to linear absorption spectrum and the peaks off the diagonal (called cross peaks) at (ω_τ, ω_t) locations represent coupling and energy transfer between the states with the transition frequencies of ω_τ and ω_t. Therefore, we can reveal the dynamics of excitation energy transfer unambiguously by monitoring the time evolution of amplitudes of the diagonal and the cross peaks. The theory and experiment of 2D-ES are described in detail elsewhere.[1-3]

References

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3. J. Kim, V. M. Huxter, C. Curutchet and G. D. Scholes, *J. Phys. Chem. A*, 2009, **113**, 12122-12133.
4. S. Park, K. Kwak and M. D. Fayer, *Laser Phys. Lett.*, 2007, **4**, 704.
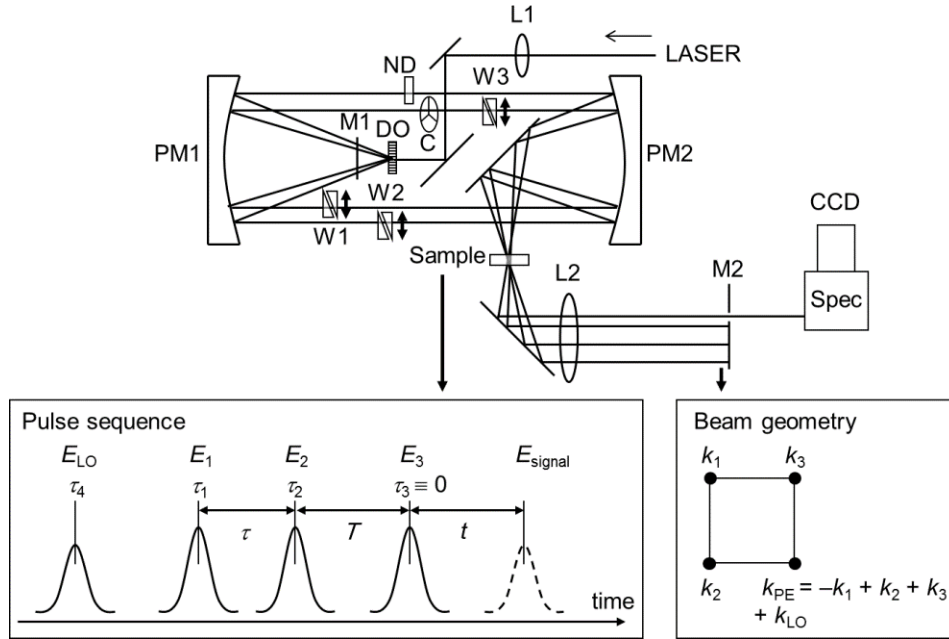
Figure S1. Experimental setup for two-dimensional electronic spectroscopy. A beam of optical pulse is focused onto a diffractive optic (DO) by a 50 cm focal length (f.l.) concave spherical mirror (L1) to generate four beams of pulses, E_1, E_2, E_3, and E_{LO}, diffracted at first order. The four beams transmitted through the mask (M1) are collimated and focused onto the sample by a pair of 25 cm f.l. paraboloid mirrors (PM1, PM2). The E_1, E_2, E_3, and E_{LO} pulses are incident on the sample with k_1, k_2, k_3, and k_{LO} wavevectors at τ_1, τ_2, τ_3, and τ_4 arrival times, respectively. Time zero is defined at the center of the pulse 3, i.e. $\tau_3 = 0$. The third-order signal (k_s) is radiated in the direction of $-k_1 + k_2 + k_3$, which is the same direction as k_{LO} in the four-beam BOXCARS geometry. The LO pulse is attenuated by a factor of 10^3 using a neutral density filter (ND) and always precedes the E_3 pulse by the time delay, τ_4, that was set to be $\tau_4 \sim -500$ fs. The time delays between the three pulses and the signal, τ, T, and t, are varied with interferometric precision by moving one of each glass wedge pair (W1, W2, and W3) inserted into the E_1, E_2, and E_3 optical beams. After being collimated by a 25 cm f.l. concave spherical mirror (L2), the heterodyned signal is detected as a spectral interferogram along ω_t axis by a combination of spectrograph and CCD array detector.
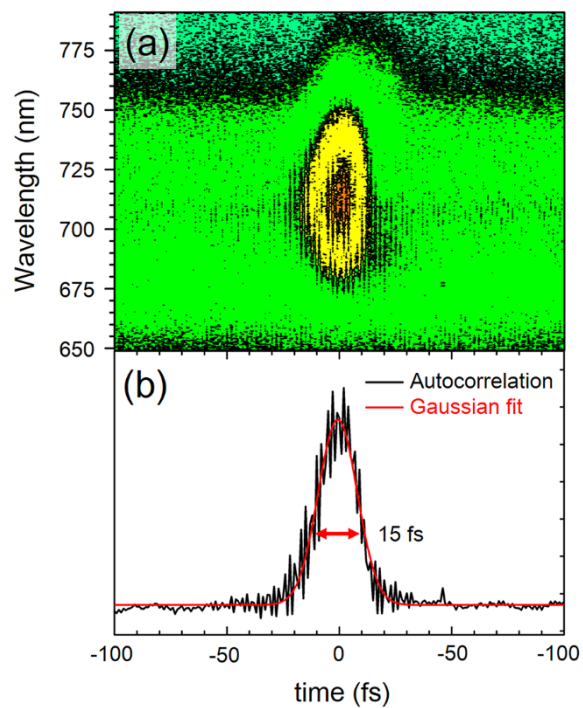
Figure S2. (a) Temporal and spectral profile of the laser pulse characterized by non-resonant transient grating measurement of pure solvent (carbon tetrachloride). (b) Temporal profile of the laser pulse obtained by projecting the profile in (a) onto the time axis. The temporal profile was fitted by a Gaussian function of 15 fs FWHM.

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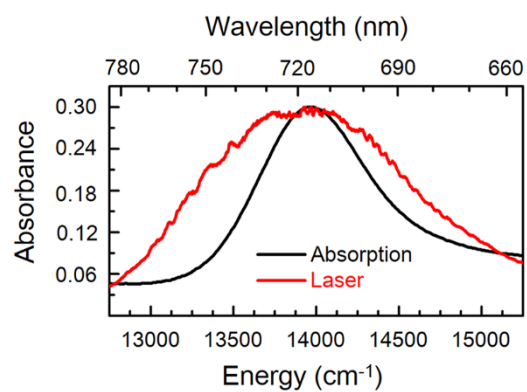
Figure S3. Absorption spectrum of chlorosomes and spectral profile of the laser pulse. The absorption spectrum (black) of chlorosomes from *Cba. limnaeum* measured at room temperature and the spectral profile of the laser pulse (red). The absorption band in the 650 – 800 nm region is ascribed to the Q_y transition of chlorosomes.

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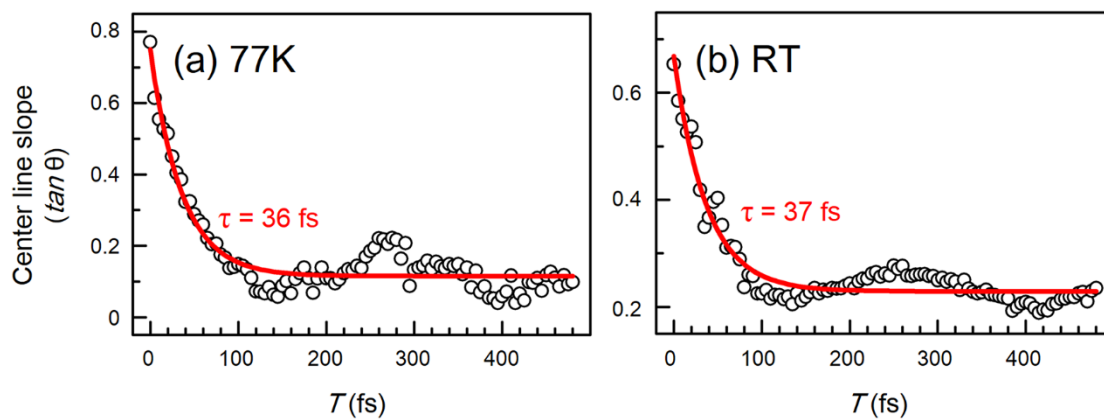
Figure S4. Time evolution of the centre line slope of 2D spectra at (a) 77 K and (b) RT. The center line slope was determined using a method in ref. [4]. Each time trace of the centre line slope was fitted with a single exponential and we obtained the time constant of 36 fs at 77 K and 37 fs at RT.
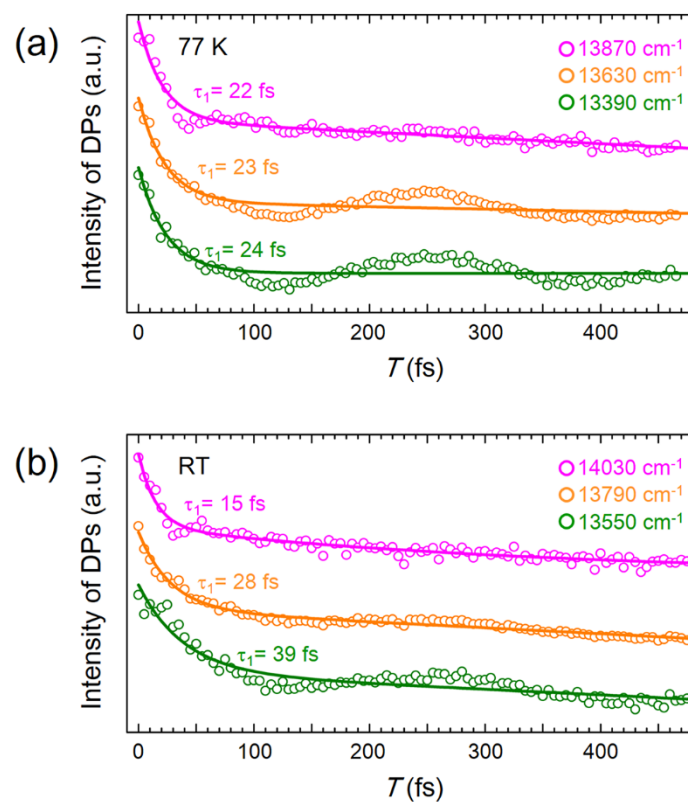
Figure S5. Time traces of the 2D-ES signal amplitude in the population time range up to 480 fs at three selected diagonal points at (a) 77 K (magenta: $\omega_\tau = \omega_t = 13870$ cm^{-1}, orange: $\omega_\tau = \omega_t = 13630$ cm^{-1}, green: $\omega_\tau = \omega_t = 13390$ cm^{-1}) and (b) RT (magenta: $\omega_\tau = \omega_t = 14030$ cm^{-1}, orange: $\omega_\tau = \omega_t = 13790$ cm^{-1}, green: $\omega_\tau = \omega_t = 13550$ cm^{-1}).