Supplementary Materials for

Long-lived Electronic Coherence Transfer in Platinum(II) Molecular Assemblies Revealed by Two-Dimensional Electronic Spectroscopy

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Materials. 4H thin film studied in this work was synthesized and structurally characterized as described previously. The sample thickness in this study is 300 nm.

Setup of Two-Dimensional Electronic Spectroscopy. 2DES measurements were performed using an ytterbium-doped laser system (Pharos, Light Conversion) operating at a central wavelength of 1030 nm, with a repetition rate of 3.125 kHz, a pulse energy of 800 μJ, and a pulse duration of 190 fs. Two identical pulse replicas were generated using a low-group-delay-dispersion (low-GDD) 50/50 beam splitter and subsequently spectrally broadened through a DPMPC+MPC scheme. A short-pass filter with a cutoff wavelength of 980 nm was placed before the compression stage to remove the strongest spectral components at and above 1030 nm. This reduces the risk of optical damage to the subsequent components in the system. The resulting spectra of the broadened pulse replicas extended from 550 to 980 nm. Pulse compression was achieved using ten reflections from each chirped mirror pair. The compressed pulses exhibited a sub-5 fs full width at half maximum (FWHM) duration, which was characterized by polarization-gating frequency-resolved optical gating (PG-FROG, the results are shown in Figure~S3A-S3E). Following pulse compression, the beam was divided into pump and probe arms. In the pump arm, a CLIMBS system was employed to generate a pair of phase-stable pump pulses. The coherence time ($\Delta\tau$) between the two pump pulses was controlled by a nanopositioning linear translation stage (LS2430-V1, Nators). A laser-triggered mechanical chopper operating at half of the laser repetition rate (1.5625 kHz) was used for signal modulation. The excitation power was adjusted using a broadband half-wave plate in combination with a wire-grid polarizer. A motorized delay stage (DL325, Newport) in the probe arm was employed to control the waiting time (t_2). The pump and probe beams were focused onto the sample in a noncollinear geometry with an intersection angle of approximately 5^{o}. After transmission through the sample, the pump beams were blocked by a beam dump, while the probe beam carrying the transient signal was directed into a home-built spectrometer. The spectrometer employed prisms as dispersive elements for spectral dispersion. The dispersed signal was detected using a high-speed linear-array camera (Glaz Linescan-I-Gen2 equipped with an S12198-512Q CMOS sensor, Synertronic/Hamamatsu).

Central Line Slope Analysis. To quantify the spectral lineshape, a central line slope (CLS) analysis was performed. A selected range of detection wavelengths λ_{det} was first defined, and the peak intensity position along the excitation wavelength axis λ_{ex} was determined for each λ_{det}. The collection of these peak positions constituted the central line (CL) of the spectrum. Subsequently, the CL was fitted using a polynomial function, from which the slope was extracted. The corresponding tilt angle of the fitted line was then calculated and defined as the CLS angle.

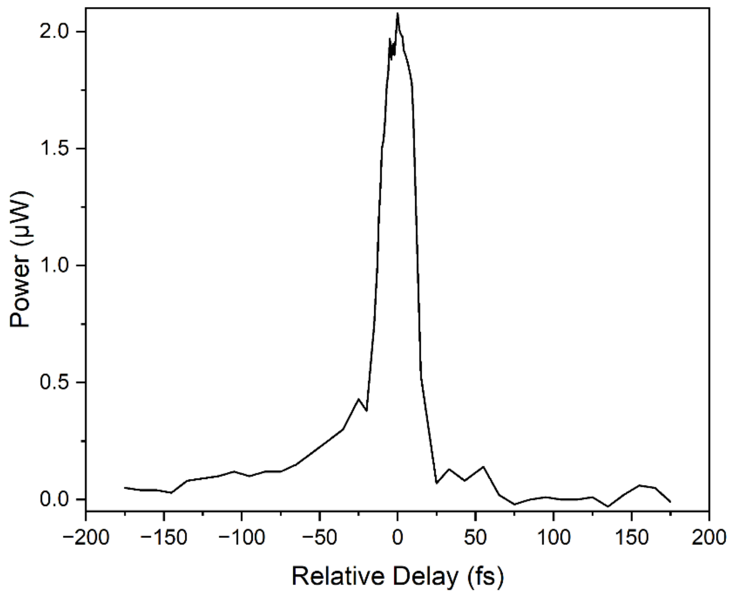

Figure S1. Determination of time zero in t_2 through Second Harmonic Generation (SHG).

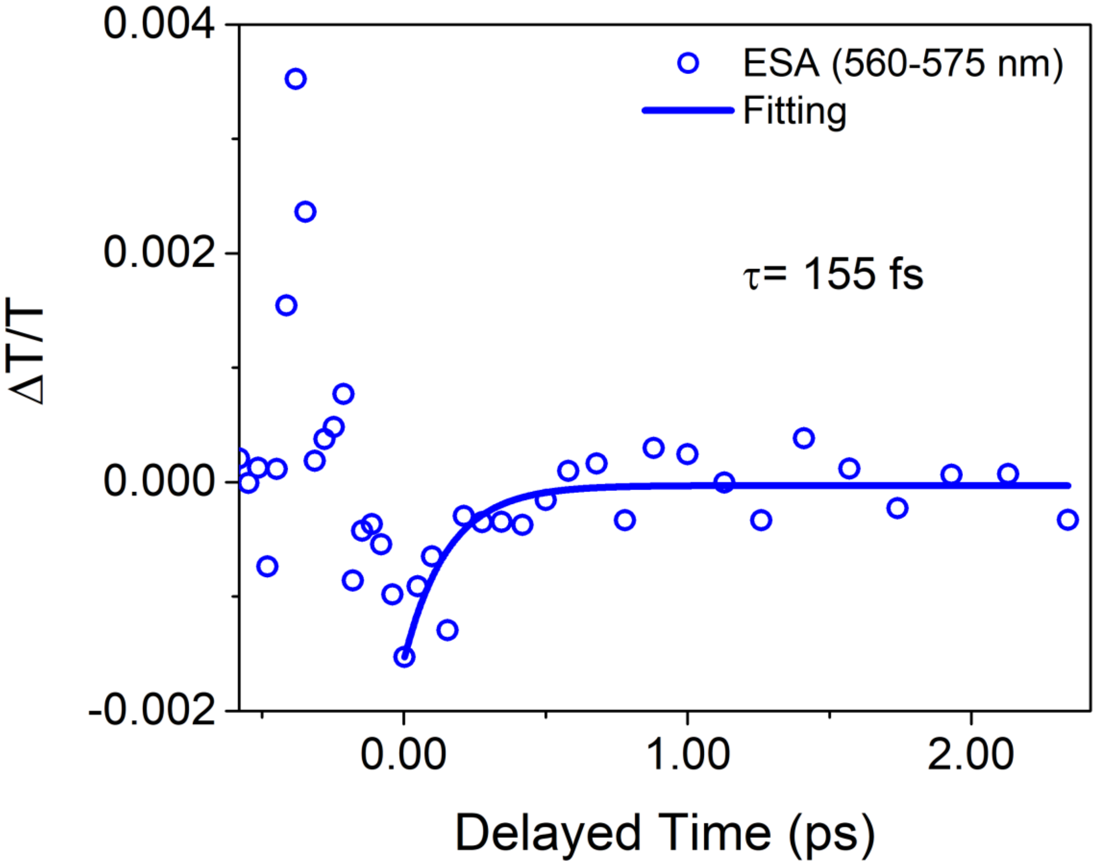

Figure S2. Averaged time trace of the singlet-state ESA (averaged range: 560–575 nm) from TA measurement. Here we use a single exponential function to obtain the decay lifetime, which shows 155 fs.

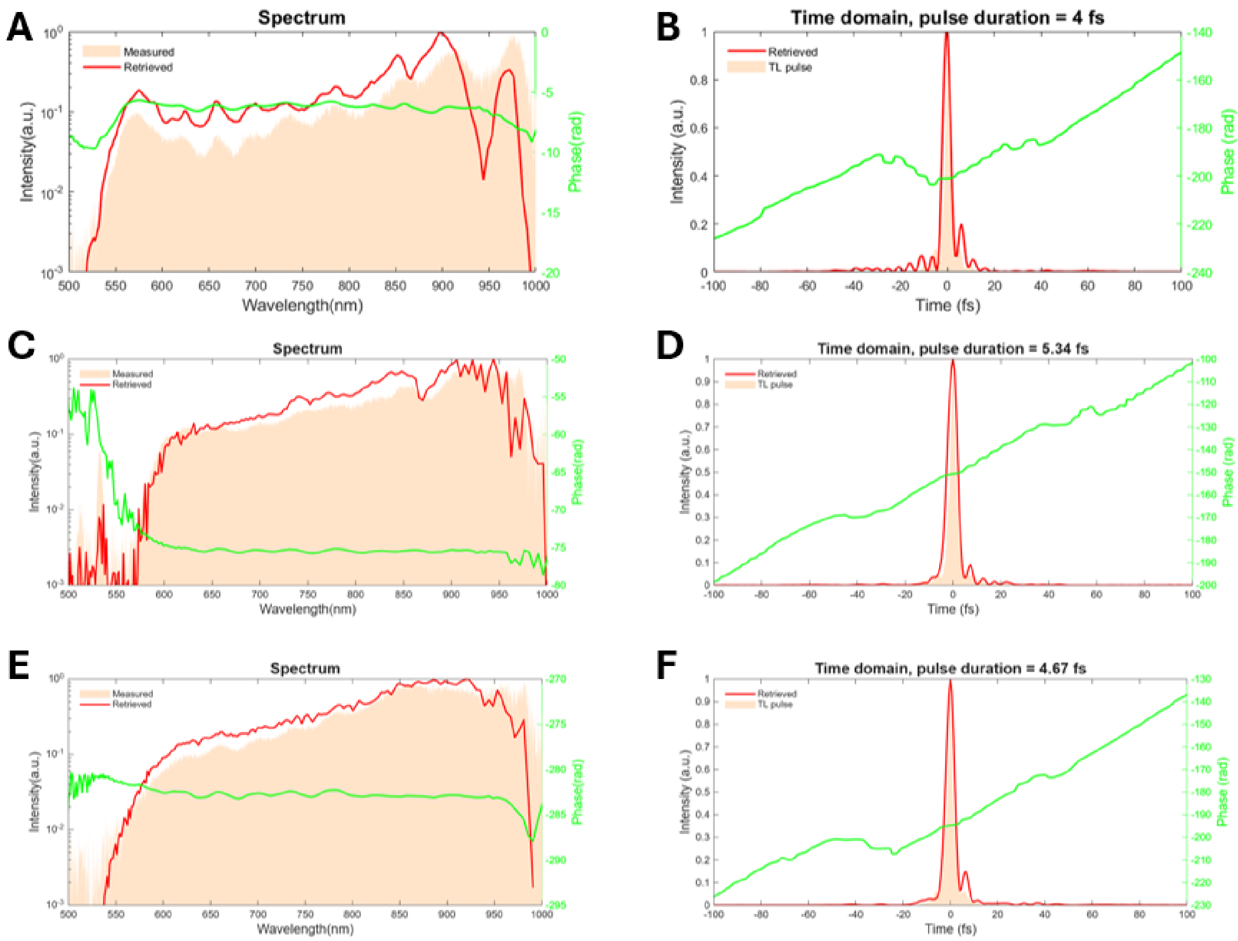

Figure S3. PG-FROG results of the pump 1, the pump 2 and the probe beams. A, C, E are measured (orange shaded area) and retrieved (red line) spectrums with retrieved phase (green line); B, D, F are transformed limited (TL, orange shaded area) and retrieved (red line) pulse shape in time domain with retrieved phase (green line).

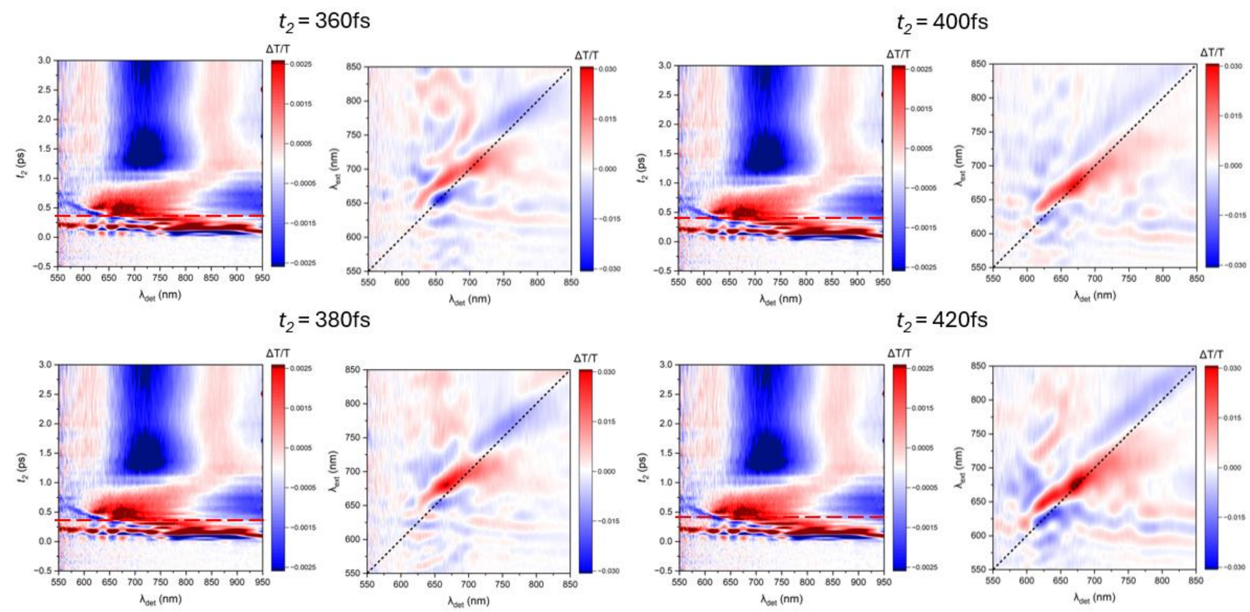

Figure S4. 2DES maps from 360fs - 420fs. The red dash line indicates the corresponding t_2 at the TA map.

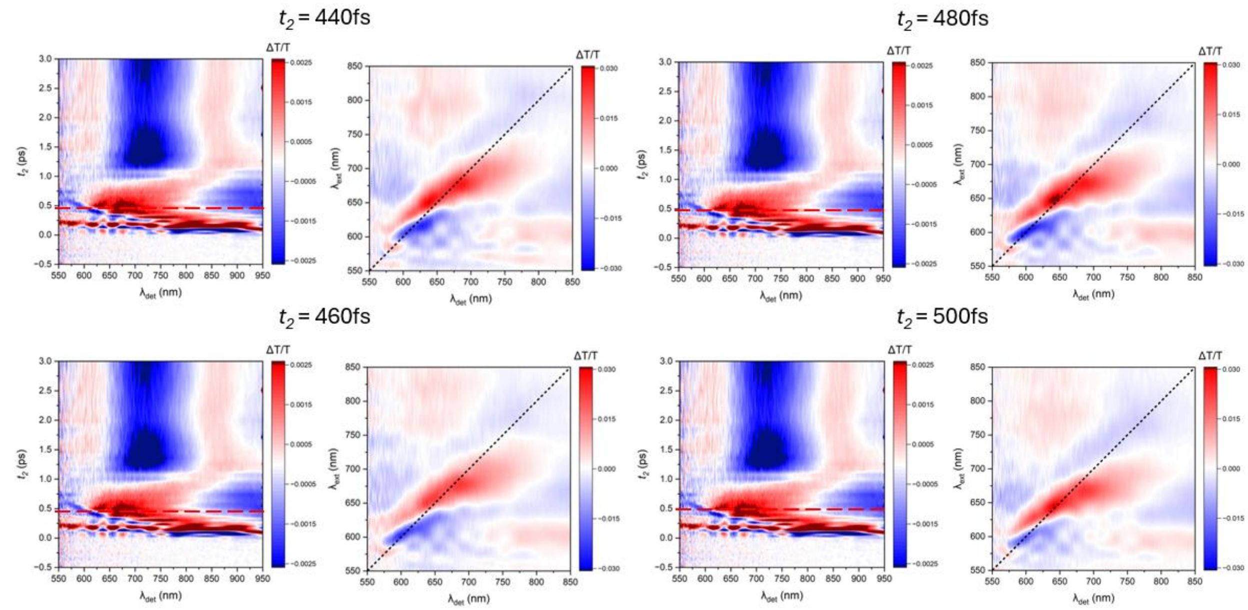

Figure S5. 2DES maps from 440fs - 500fs. The red dash line indicates the corresponding t_2 at the TA map.

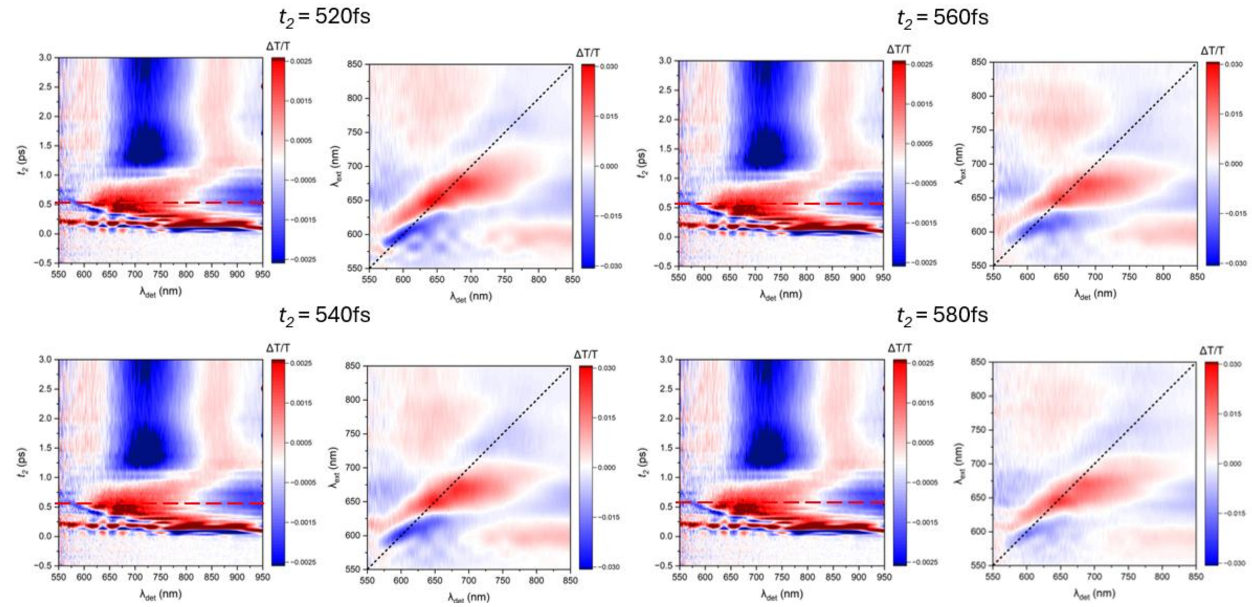

Figure S6. 2DES maps from 520fs - 580fs. The red dash line indicates the corresponding t_2 at the TA map.

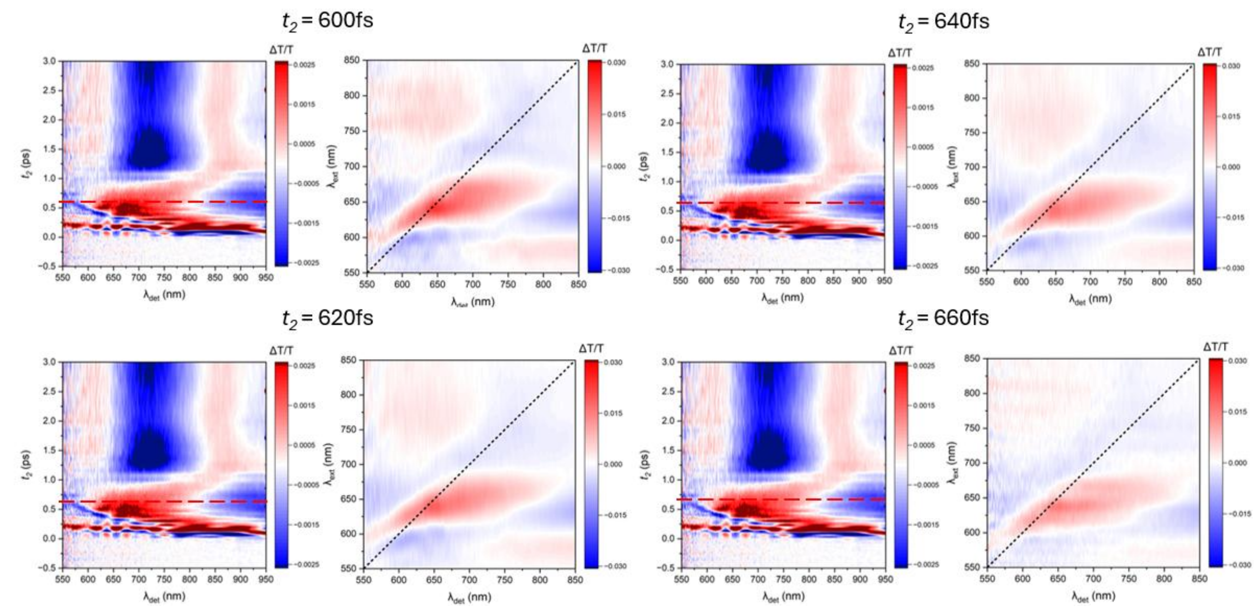

Figure S7. 2DES maps from 600fs - 660fs. The red dash line indicates the corresponding t_2 at the TA map.

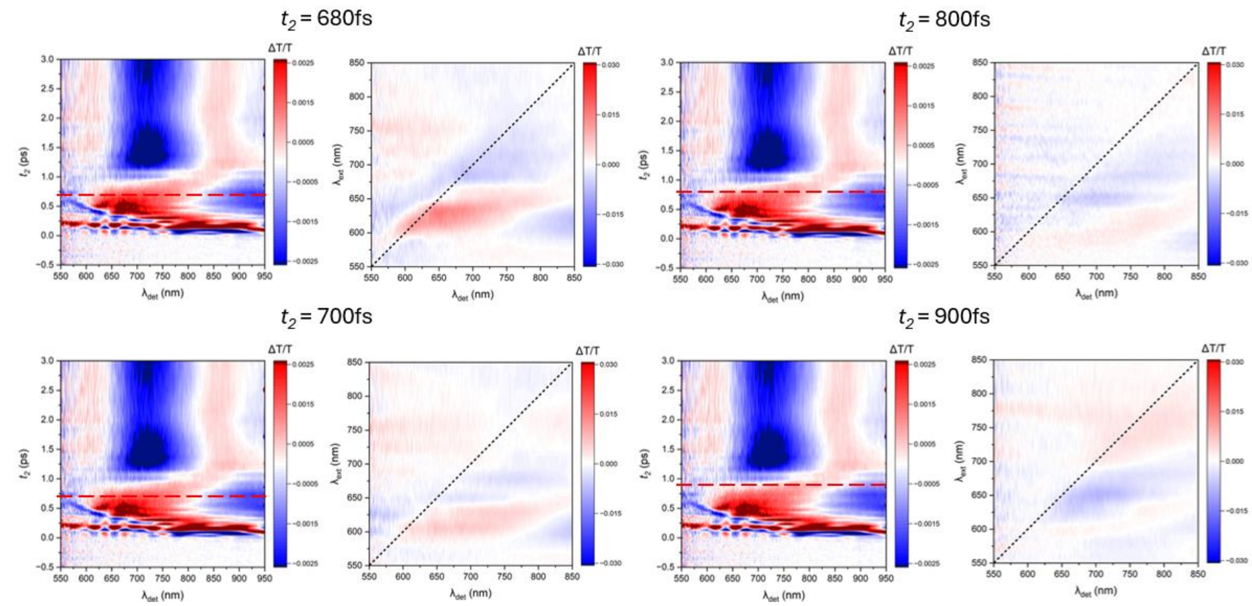

Figure S8. 2DES maps from 680fs – 900fs. The red dash line indicates the corresponding t_2 at the TA map.

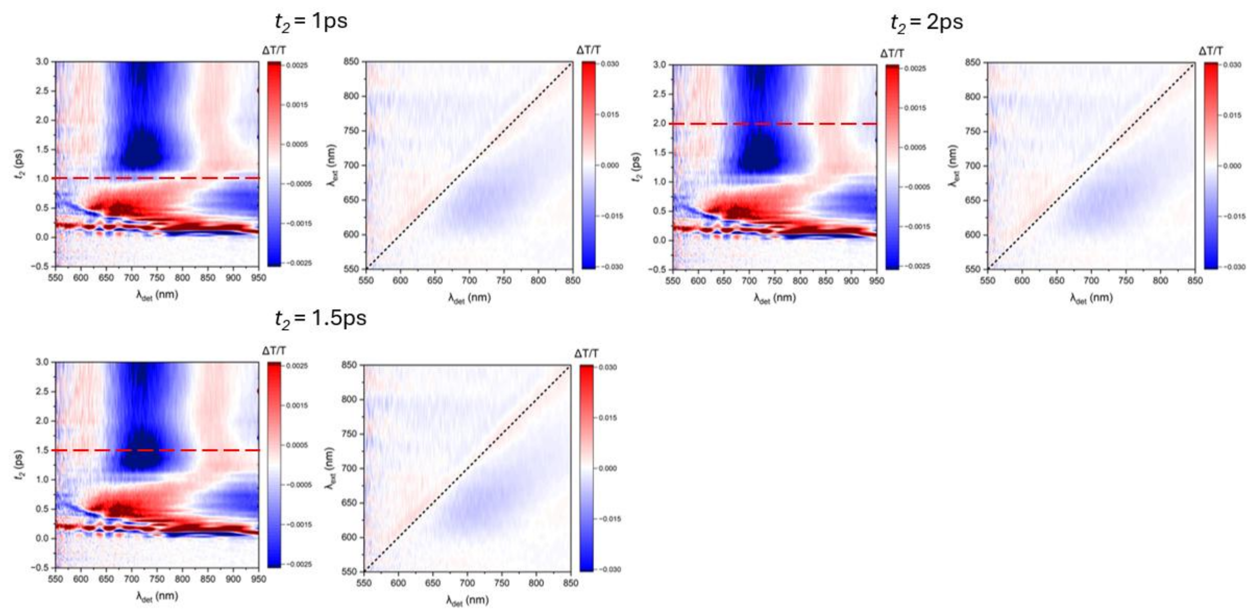

Figure S9. 2DES maps from 1 – 2ps. The red dash line indicates the corresponding t_2 at the TA map.

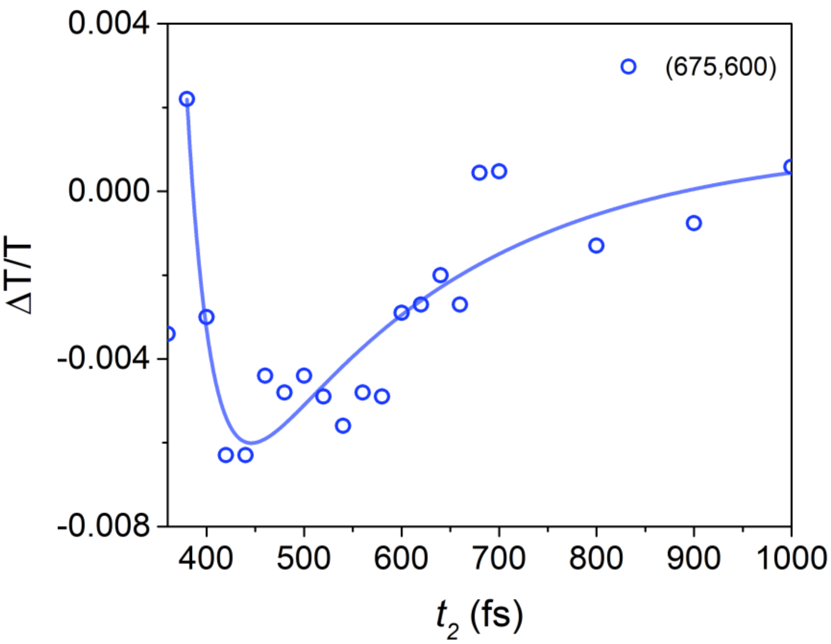

Figure S10. Temporal dynamics of the 2DES signal integrated over the excitation axis for selected regions of (675±10 nm, 600±10 nm). The fitted line is the biexponential function with the lifetimes of 25 fs and 228 fs.

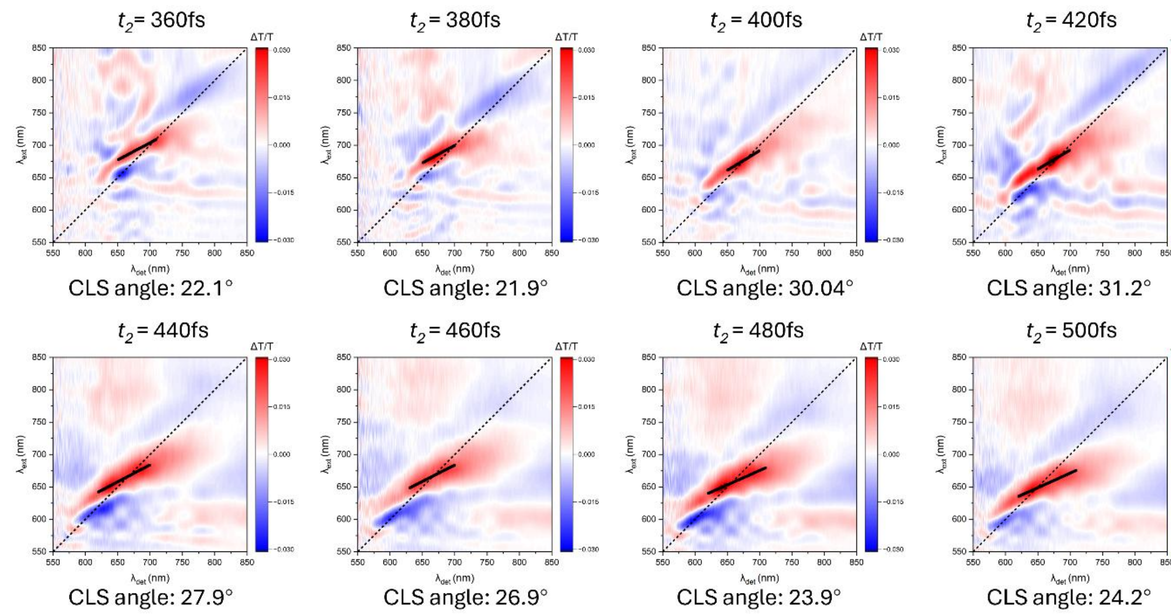

Figure S11. Central line slope analysis results from 360fs - 500fs with the corresponding CLS angle.

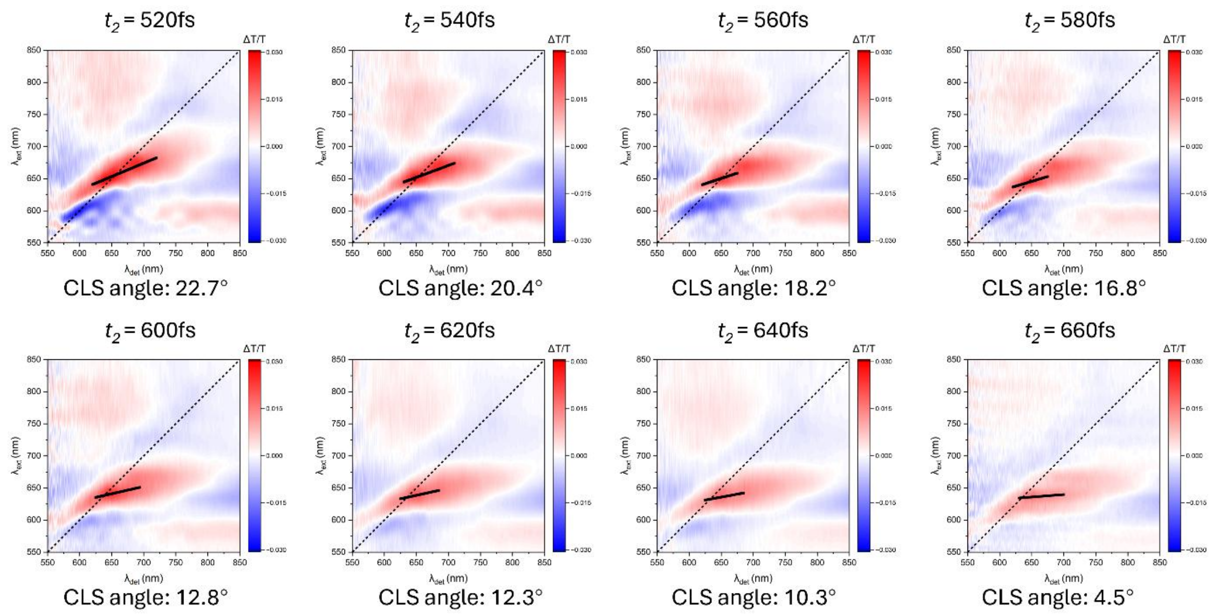

Figure S12. Central line slope analysis results from 520fs - 660fs with the corresponding CLS angle.

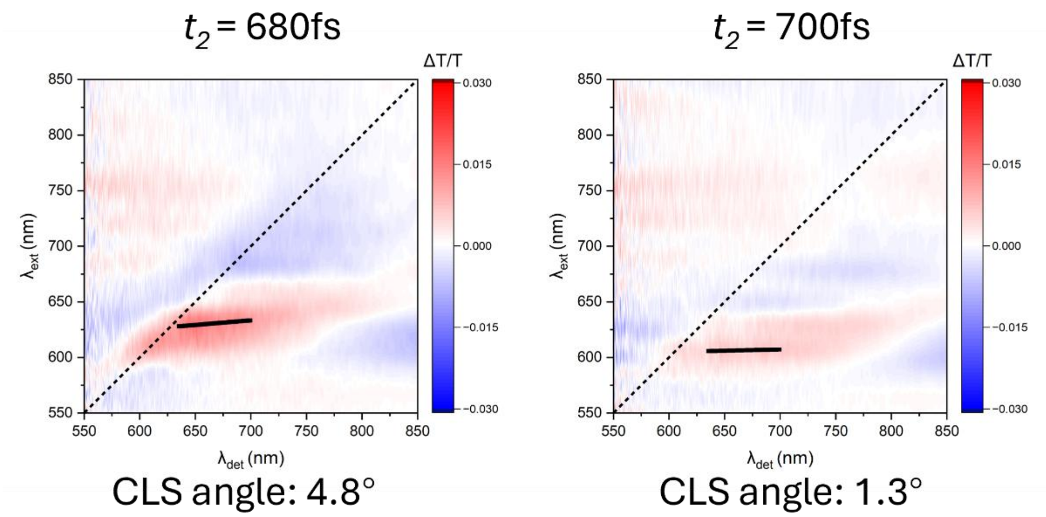

Figure S13. Central line slope analysis results from 680fs - 700fs with the corresponding CLS angle.