Supplementary Information

Dynamic-structural-distortion of spheroidene activates a hidden $3A_g^-$ state mediating carotenoid-to-bacteriochlorophyll energy transfer in light-harvesting 2

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Contents:

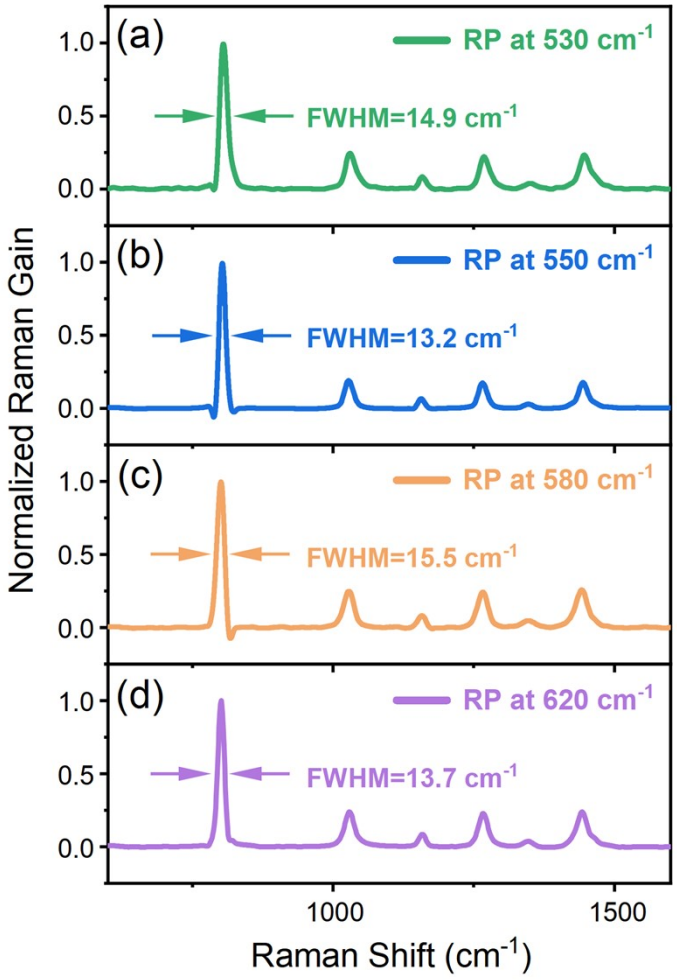

Figure S1. The ground state FSRS spectra of cyclohexane. **(a)** s-FSRS with 530 nm Raman pump, **(b)** s-FSRS with 550 nm Raman pump, **(c)** a-FSRS with 580 nm Raman pump and **(d)** a-FSRS with 620 nm Raman pump. The Full Width Half Maximum (FWHM) was determined to be 14.9 cm^{-1}, 13.2 cm^{-1}, 15.5 cm^{-1}, and 13.7 cm^{-1}, respectively. The FWHM indicates the spectral resolution of FSRS.

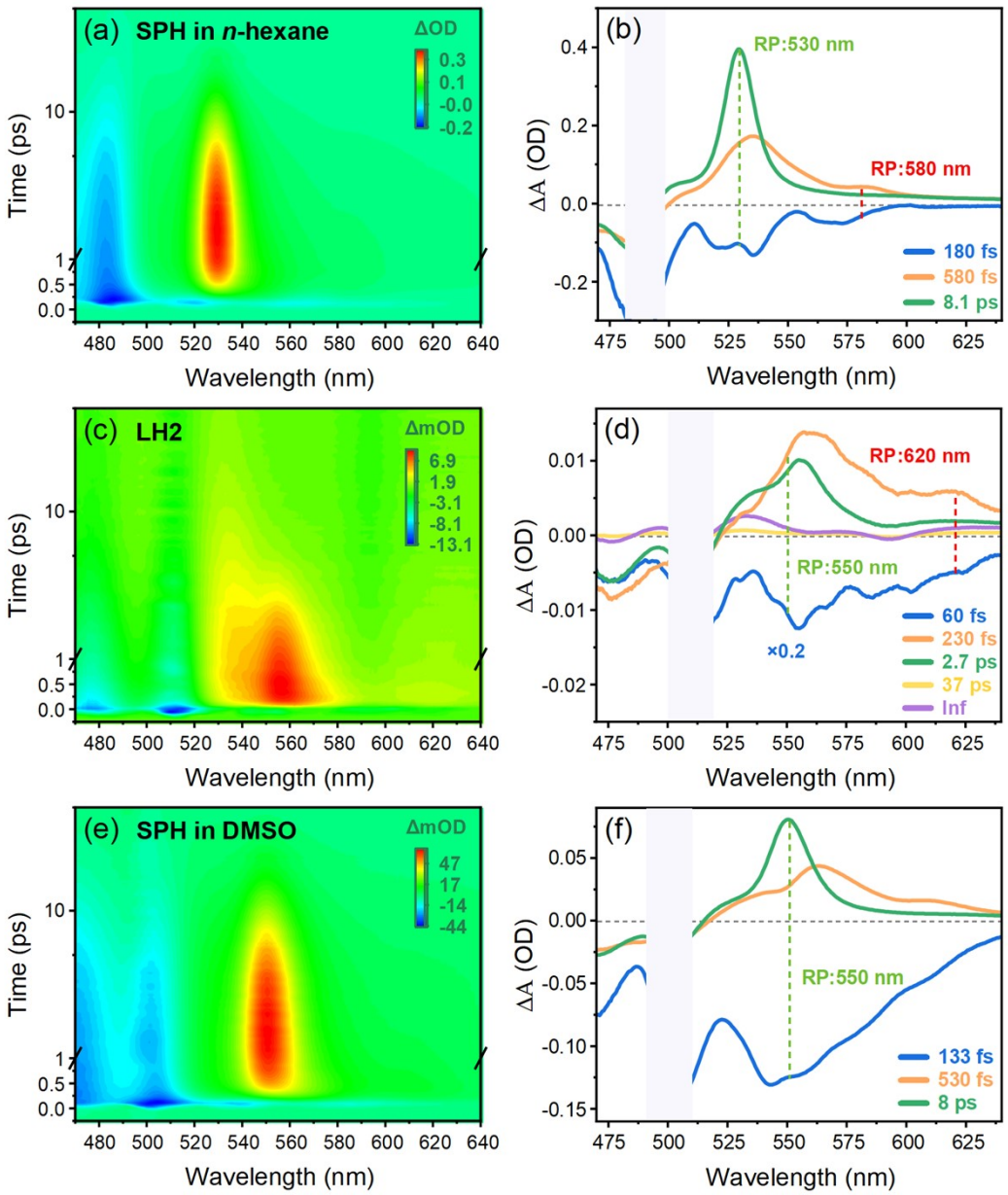

Figure S2. The 2D TA spectra of spheroidene (SPH) in **(a)** *n*-hexane, **(b)**LH2 complex, and **(c)** DMSO. Evolution-associated difference spectra (EADS) obtained using global analysis for TA spectra of SPH in **(b)** in *n*-hexane, **(d)**LH2 complex, and **(f)** DMSO; the Raman pump (RP) wavelengths in s-FSRS and a-FSRS experiments are indicated by green and red dotted lines, respectively.

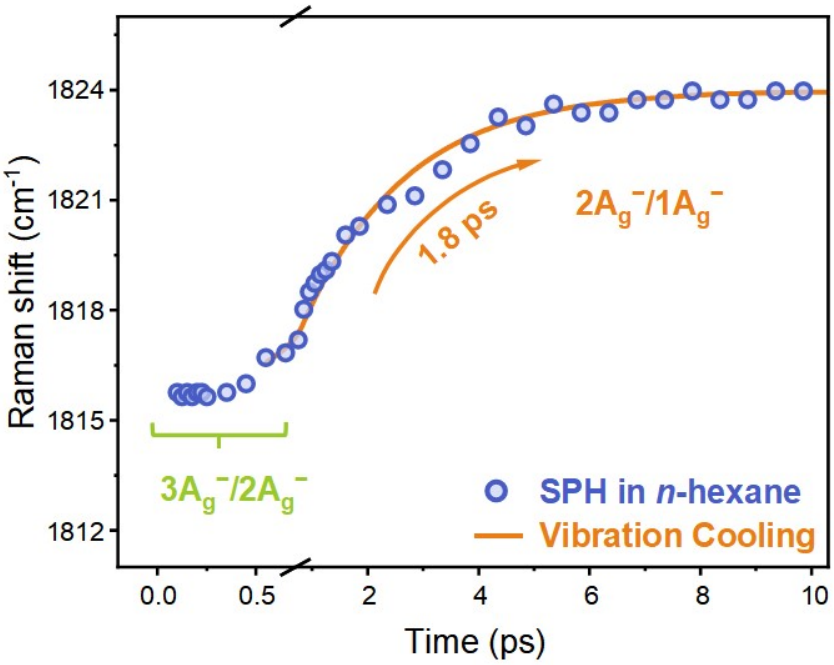

Figure S3. Transient Raman frequency shift of the A_g^--related vibronic coupling C=C stretching mode of spheroidene (SPH) in *n*-hexane. The 1.8 ps time constant can be attributed to the combined effect of a vibrational cooling within the S_1 state and a spectral overlap between the S_X and S_1 state at the early delay time.

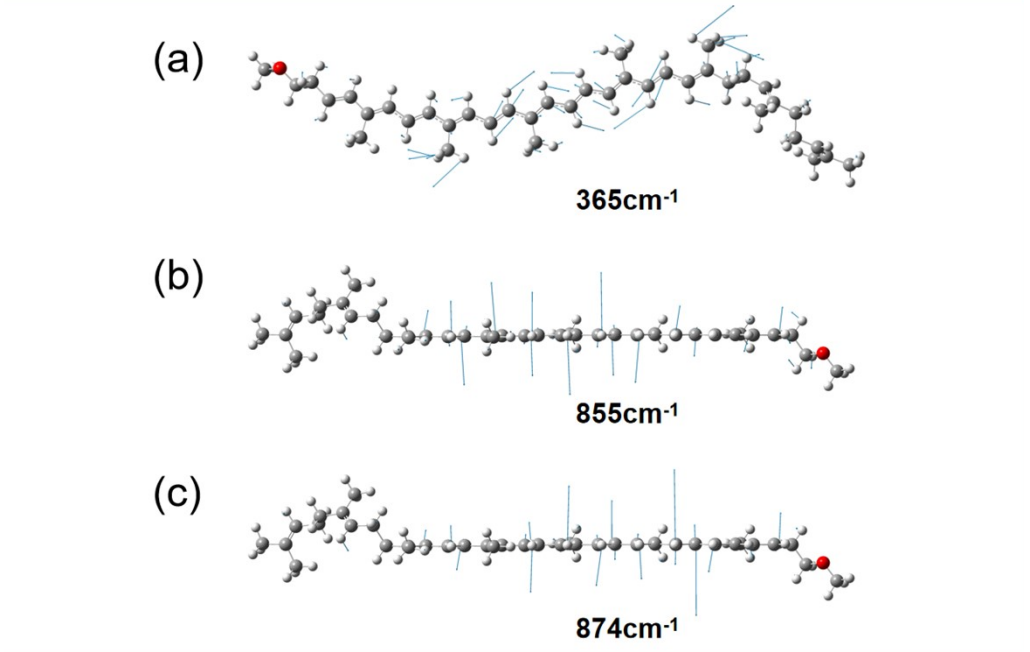

Figure S4. DFT calculation of spheroidene shows polyene chain in-plane skeletal bending mode at **(a)** 365 cm^{-1}, HOOP modes at **(b)** 855 cm^{-1}, and **(c)** 874 cm^{-1}.

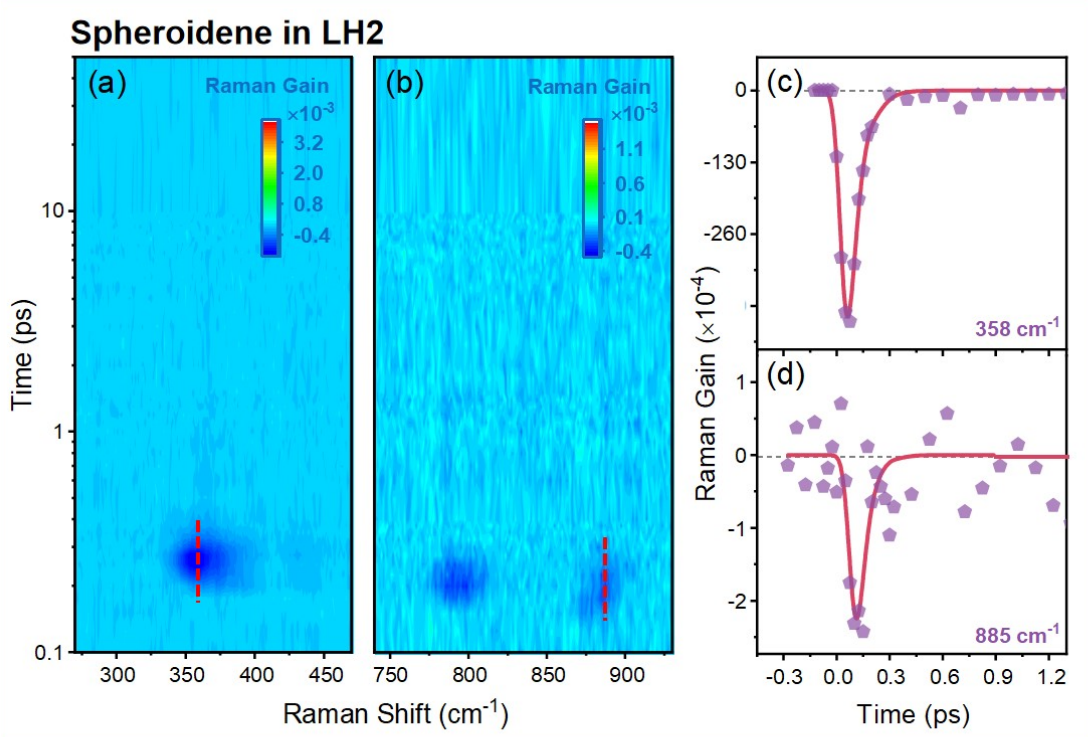

Figure S5. The 2D contour plots of the a-FSRS signals from spheroidene in the LH2 complex in the frequency range of (a) 270-470 cm^{-1} and (b) 740-930 cm^{-1}. Transient kinetic traces of Raman mode at (c) 358 cm^{-1}, (d) 885 cm^{-1}.

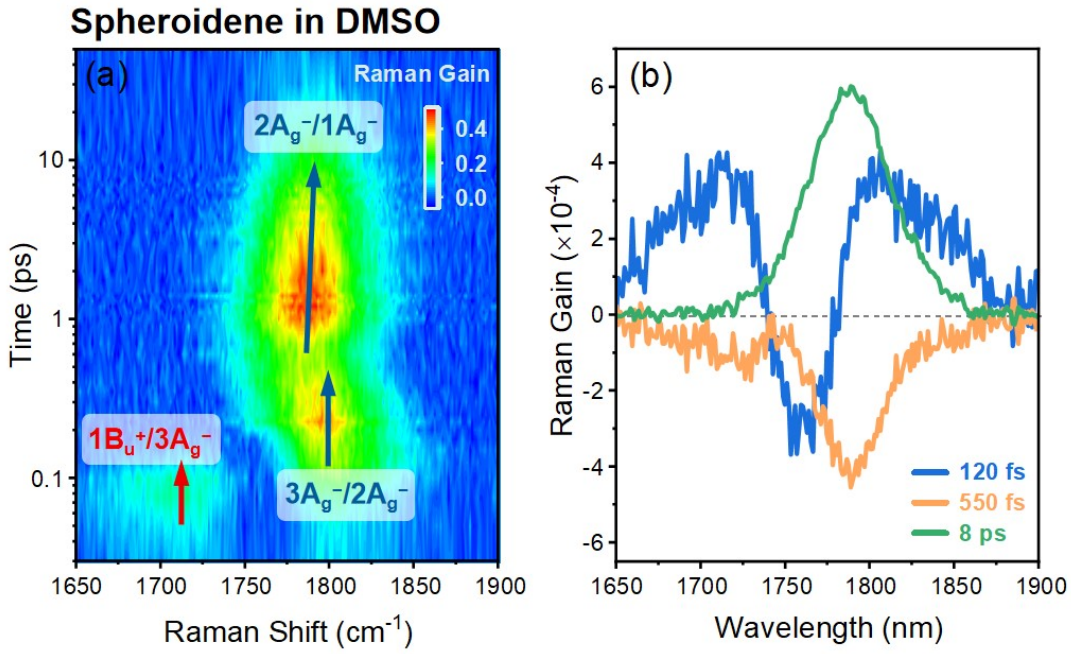

Figure S6. The 2D contour plots of the s-FSRS signals from free spheroidene in DMSO in the frequency range of (a)1650-1900 cm^{-1}. (b) DADS spectra of s-FSRS spectra in the Raman frequency range of 1650-1900 cm^{-1}.

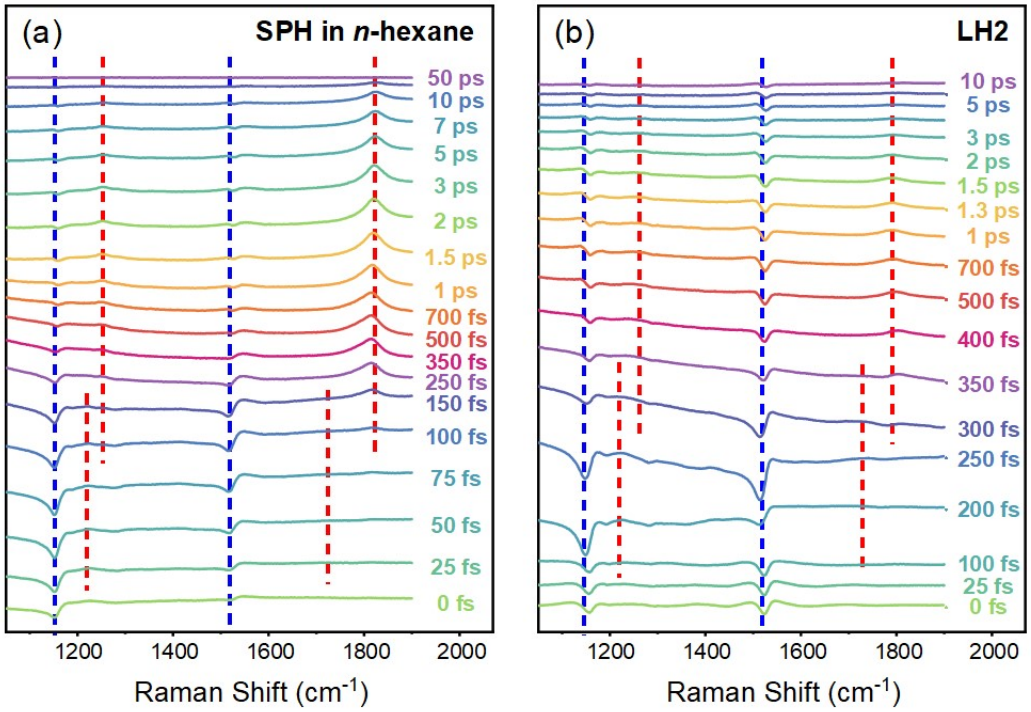

Figure S7. s-FSRS raw data of **(a)** spheroidene (SPH) in *n*-hexane and **(b)** LH2 complex at selected time points. Blue and red dashed lines show the position of ground state bleaching signals and excited state gain signals, respectively.