Supporting Information to Vibronic and excitonic dynamics in perylenediimide dimers and tetramer

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Steady state spectra

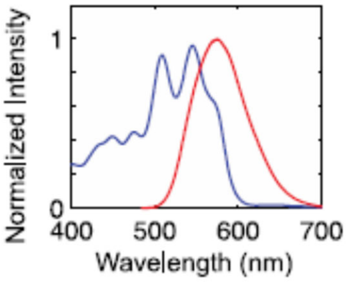

Figure S 1. Steady state absorption spectrum of PDI dimer A measured in dichloromethane (blue curve) and typical pulse spectrum (red curve).

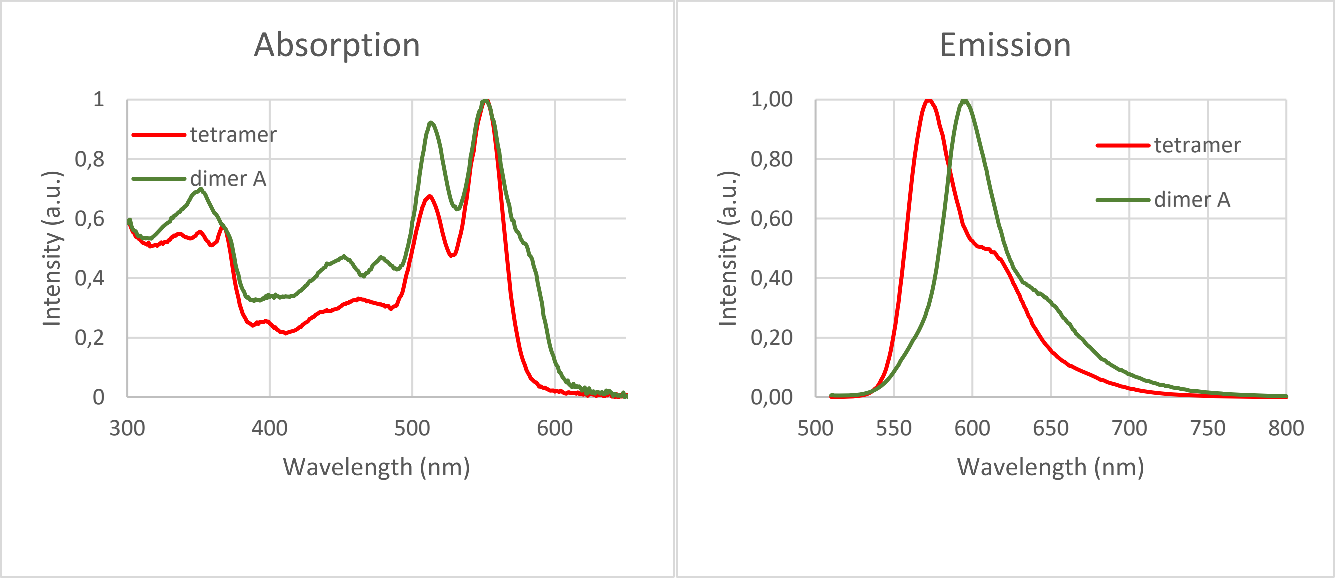

Figure S 2. Steady state absorption and emission spectrum of PDI dimer A and tetramer measured in chlorobenzene.

PDI compound	$\lambda_{max,em}$ (nm)
Dimer A	595
Tetramer	572.5

Table S 1. Maximum emission wavelength of PDI dimer A and tetramer measured in chlorobenzene.

Dimer B and tetramer

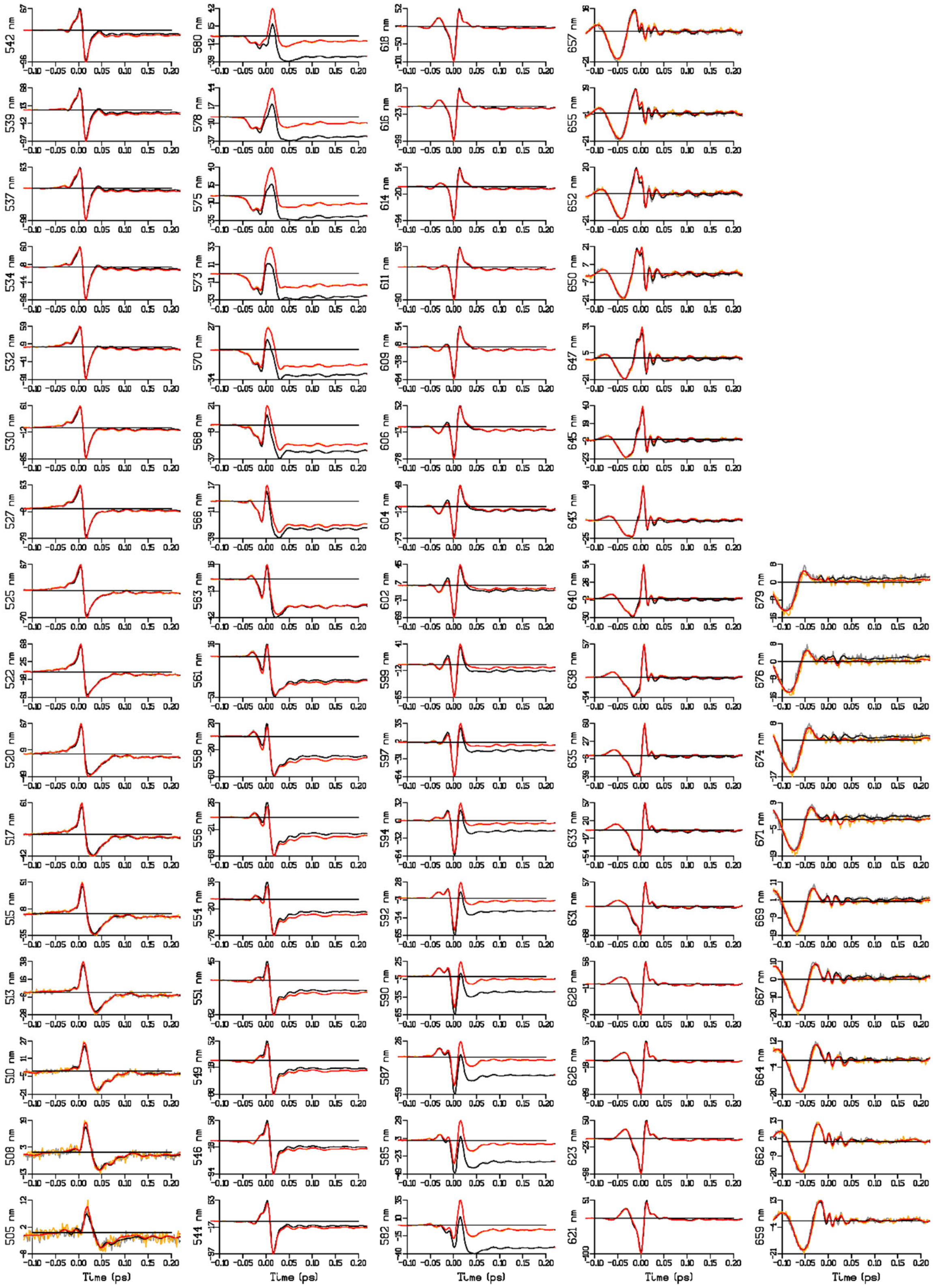

Figure S 3. Zoom from -0.1 to 0.2 ps of selected time traces of PDI dimer B in chlorobenzene data (in mOD, grey) and fit (black). Orange and red depict the tetramer data and fit. Wavelength is indicated in the ordinate label. Time zero corresponds to the location of the maximum of the IRF. Rms error of the fit was 0.60 mOD, thus the SNR is better than 100.

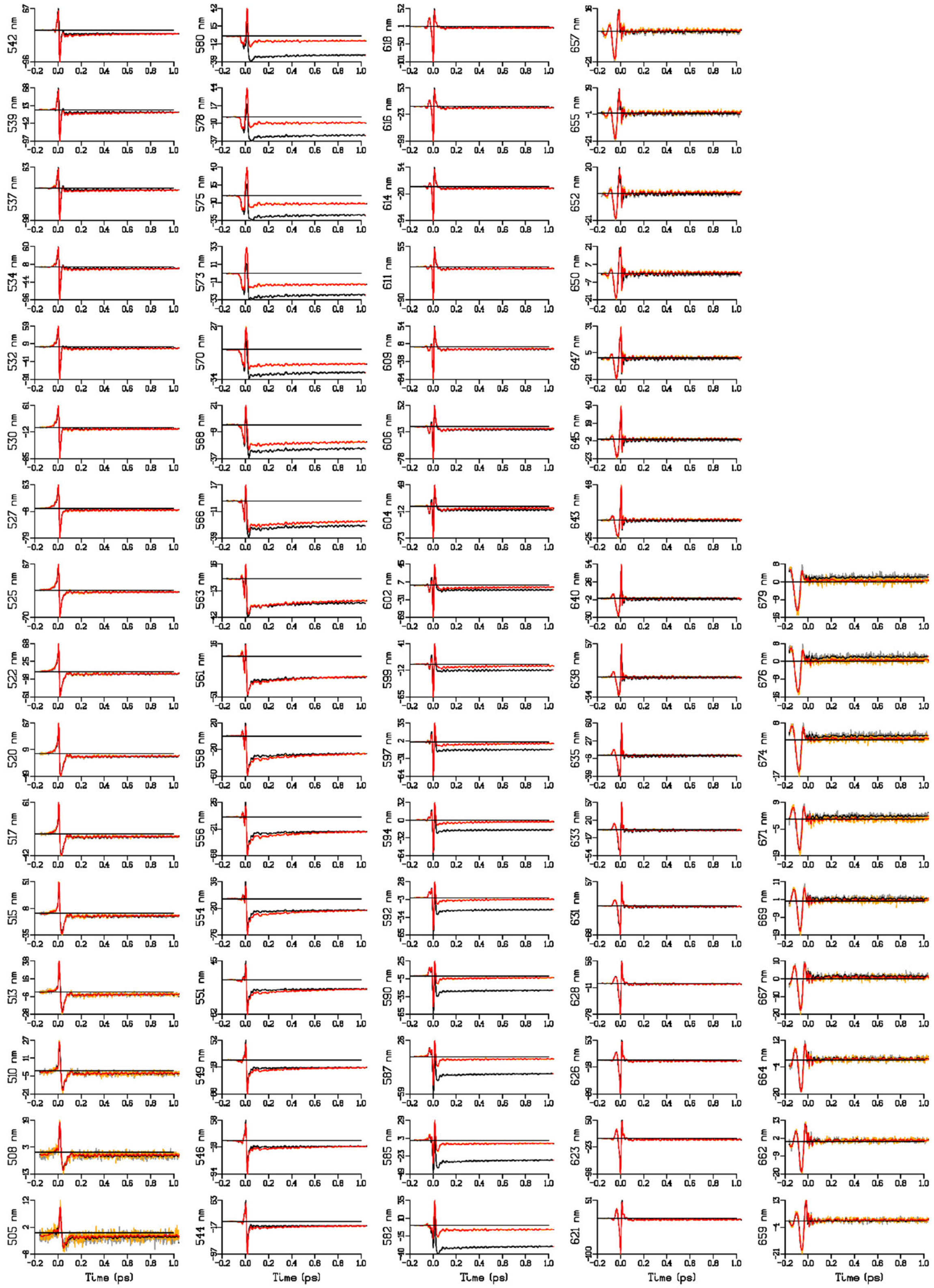

Figure S 4. Full time range of selected time traces of PDI dimer B in chlorobenzene data (in mOD, grey) and fit (black). Orange and red depict the tetramer data and fit. Wavelength is indicated in the ordinate label. Time zero corresponds to the location of the maximum of the IRF. Rms error of the fit was 0.60 mOD, thus the SNR is better than 100.

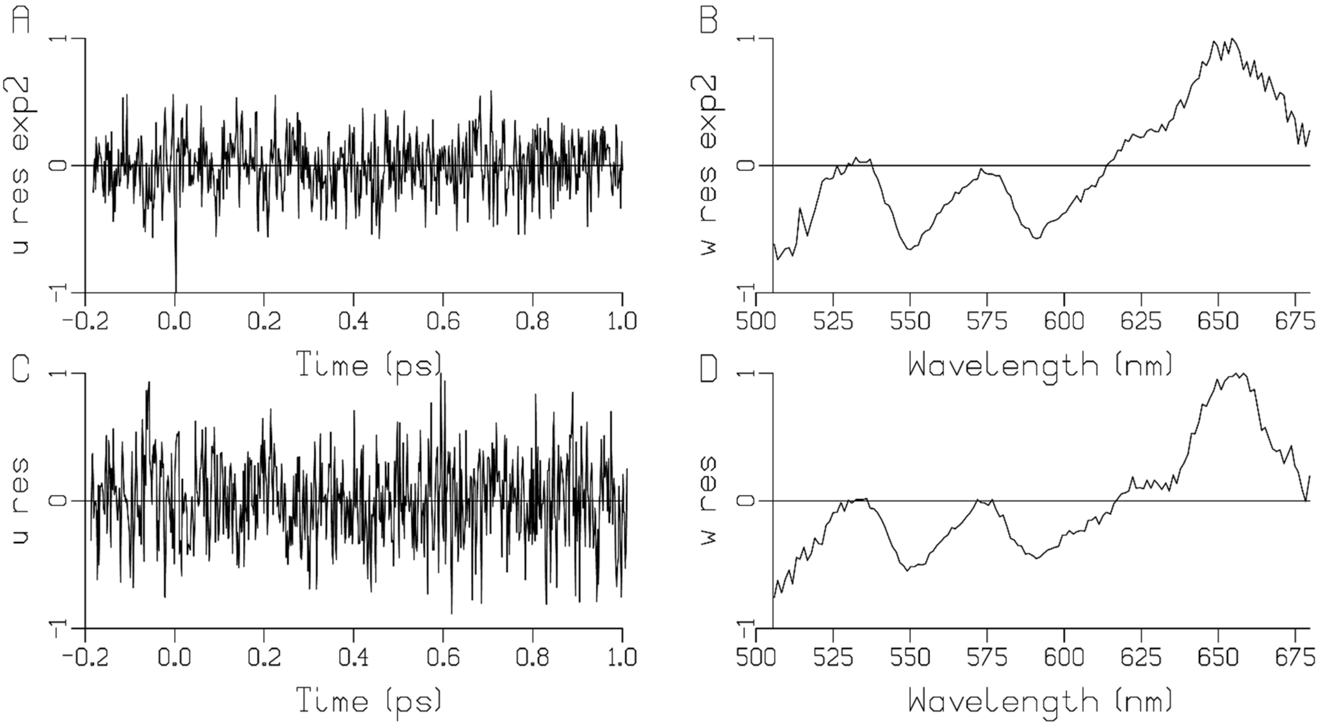

Figure S 5. Residual properties after fitting the damped oscillations with the PDI tetramer (panels A,B) and dimer B (panels C,D) in chlorobenzene data. First left (u res, A,C, time zero corresponds to the location of the maximum of the IRF) and right (w res, B,D) singular vectors of the residual matrix.

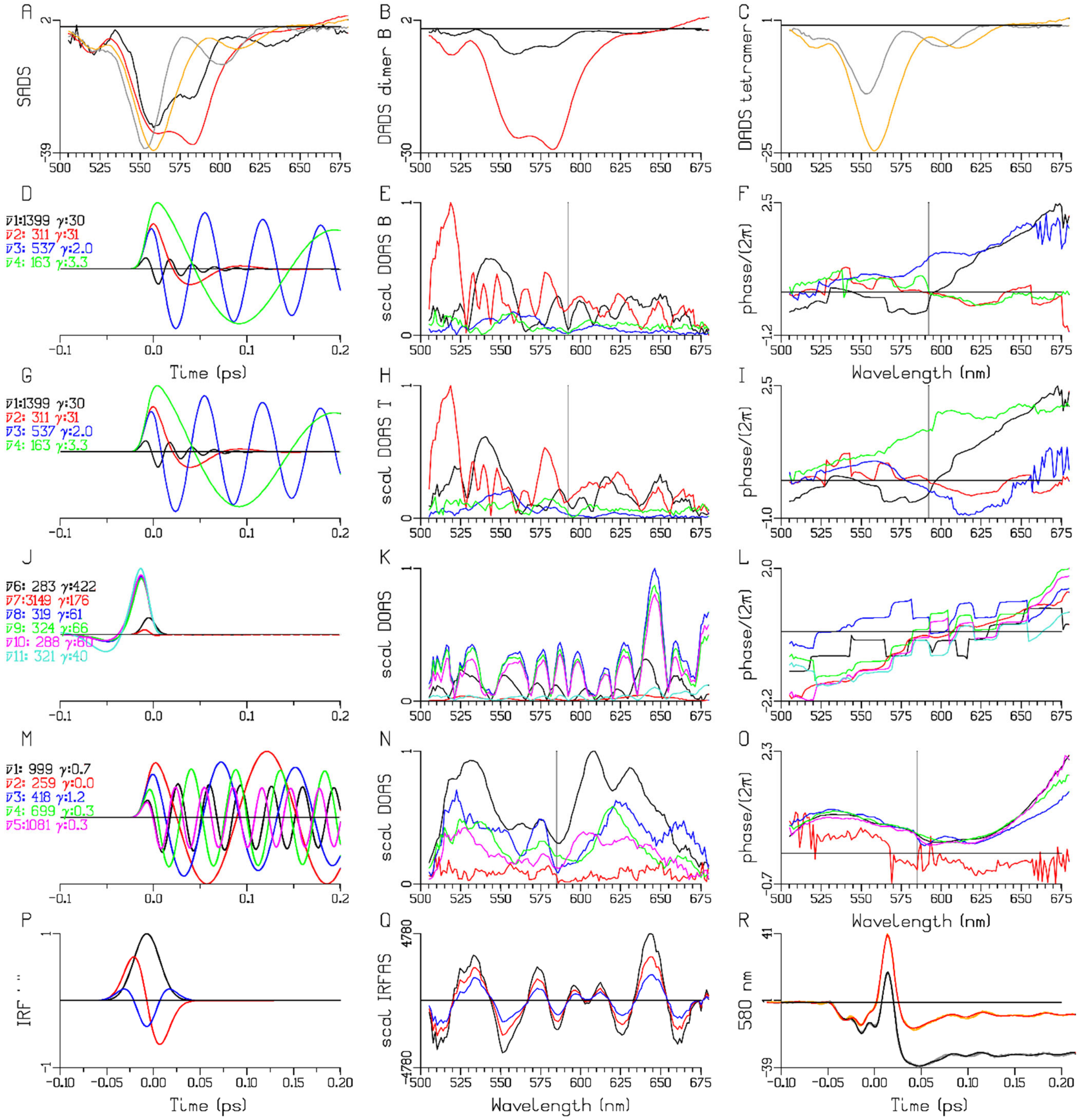

Figure S 6. Simultaneous DOAS analysis of PDI dimer B and the PDI tetramer in chlorobenzene excited with a 15-fs pulse centered at 580 nm and probed with an attenuated pulse. (A) Estimated SADS and DADS (B, C). Key A-C: 313 fs (black), and long lived (red), 478 fs (grey), and long lived (orange). Panels D-F belong to dimer B, whereas panels G-I belong to the tetramer, panels J-Q are common to dimer B and the tetramer.

Overview of the estimated DOAS and phases. (D,G,J,M) Cosine oscillations with frequencies $\bar{\nu}n$ (in cm^{-1}) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (E,H,K,N) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (F,I,L,O) Estimated phase profiles of the DOAS. The grey vertical lines at 592 nm in panels E,F,H,I and at 585 nm in panels N and O are discussed in the text.

(P) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (Q) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (R) Zoom from -0.1 ps to 0.2 ps (after the maximum of the IRF) of the 580 nm data (in mOD, grey, dimer B) and the fit (black, dimer B). Orange and red curves depict the tetramer data and fit.

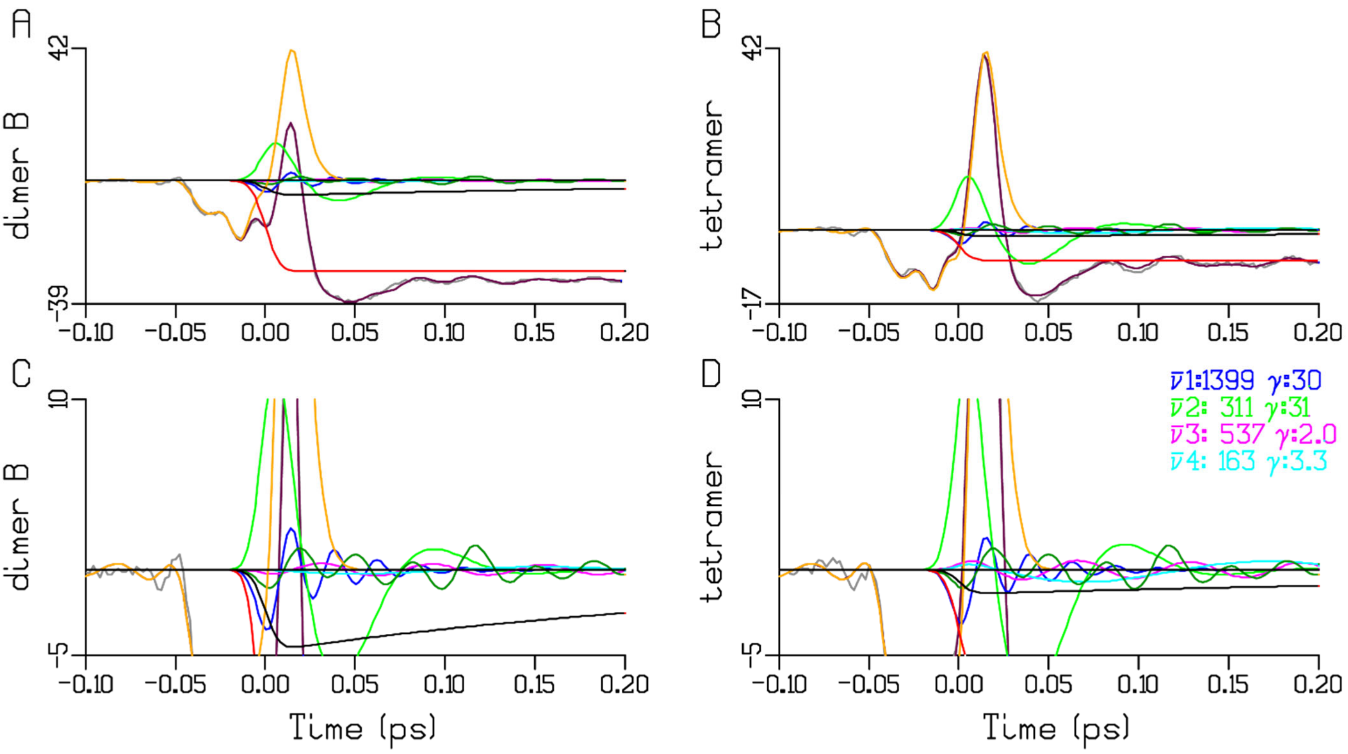

Figure S 7. Decomposition of the 580 dimer B (A) and tetramer (B) data (in mOD, grey, and the fit, maroon), with zoom ins in panels C and D. Key: black A,C: 313 fs (dimer B) and B,D: 478 fs (tetramer), red: long lived. Dark green is the superposition of the solvent ISRS. Orange is the superposition of the CA related signals (IRF and its derivatives, DOAS #6,7,8,9,10,11). The strongly damped DOAS #1,2 are in blue and green, and the weakly damped DOAS #3,4 are in magenta and cyan, with a legend in panel D.

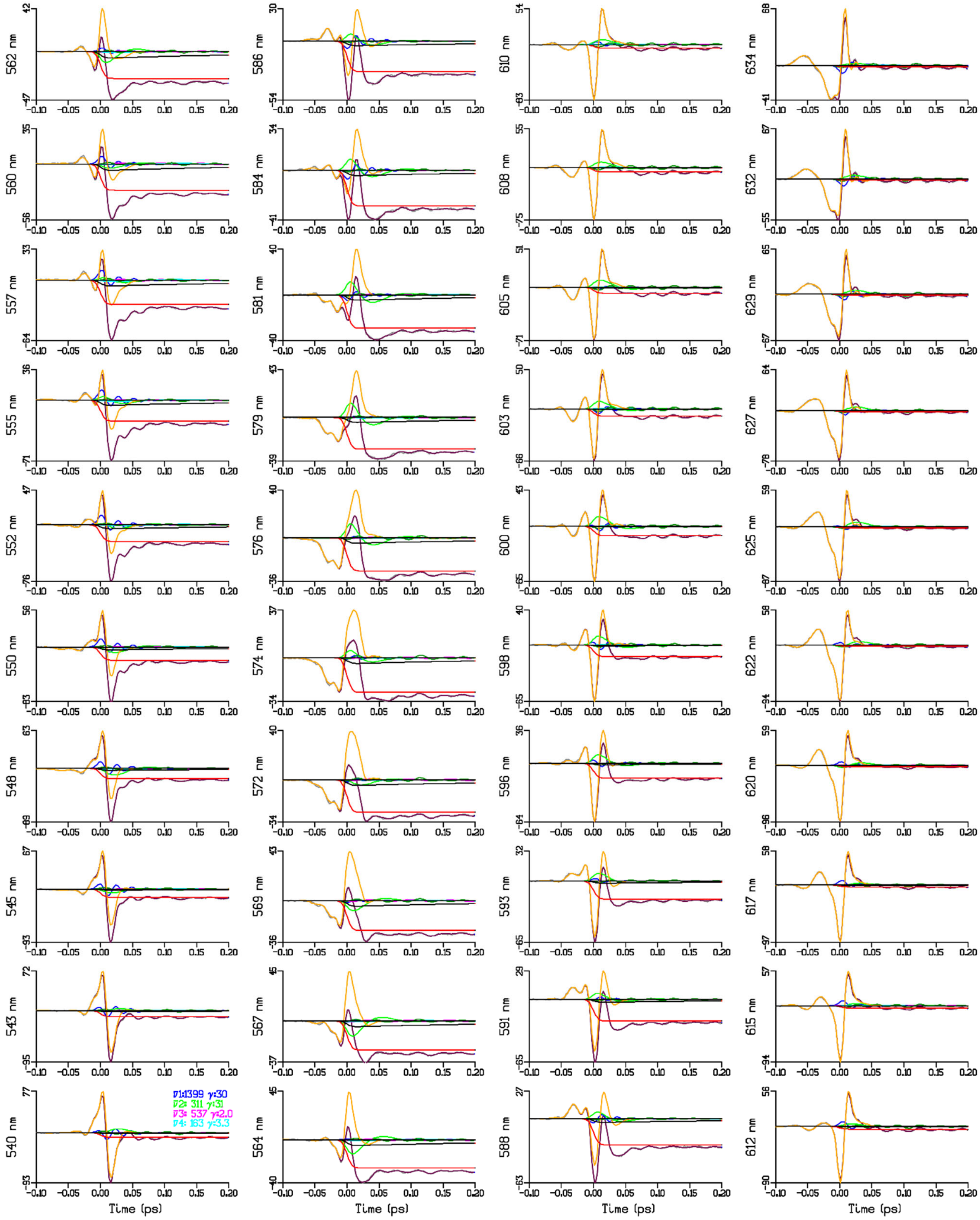

Figure S 8. Decomposition of selected time traces of PDI dimer B in chlorobenzene data (in mOD, grey, and the fit, maroon). Key: black 313 fs and red: long lived. Dark green is the superposition of the solvent ISRS. Orange is the superposition of the CA related signals (IRF and its derivatives, DOAS #6,7,8,9,10,11). The strongly damped DOAS #1,2 are in blue and green, and the weakly damped DOAS #3,4 are in magenta and cyan, with a legend in the lower left panel.

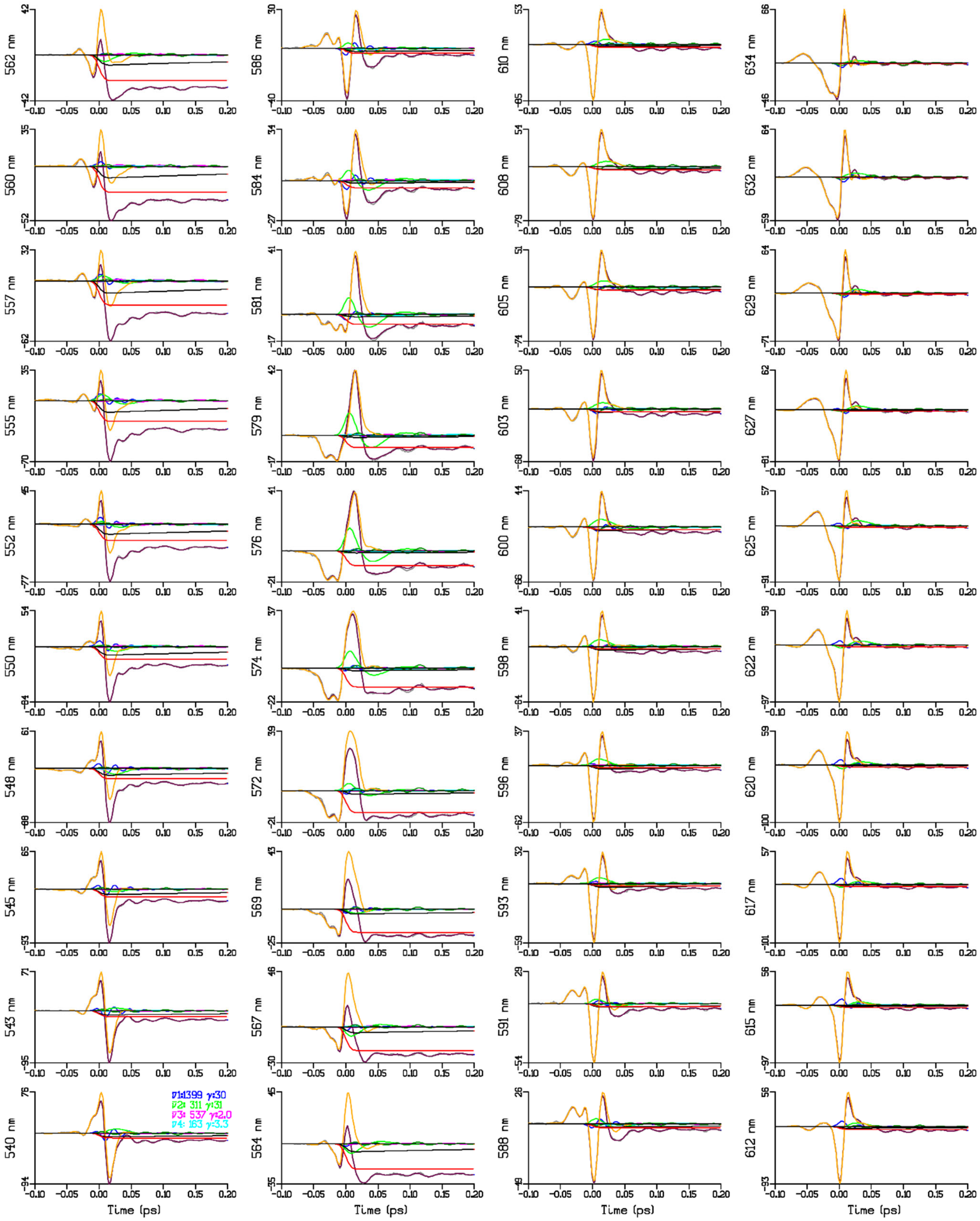

Figure S 9. Decomposition of selected time traces of PDI tetramer in chlorobenzene data (in mOD, grey, and the fit, maroon). Key: black 478 fs, red: long lived. Dark green is the superposition of the solvent ISRS. Orange is the superposition of the CA related signals (IRF and its derivatives, DOAS #6,7,8,9,10,11). The strongly damped DOAS #1,2 are in blue and green, and the weakly damped DOAS #3,4 are in magenta and cyan, with a legend in the lower left panel.

Dimer A

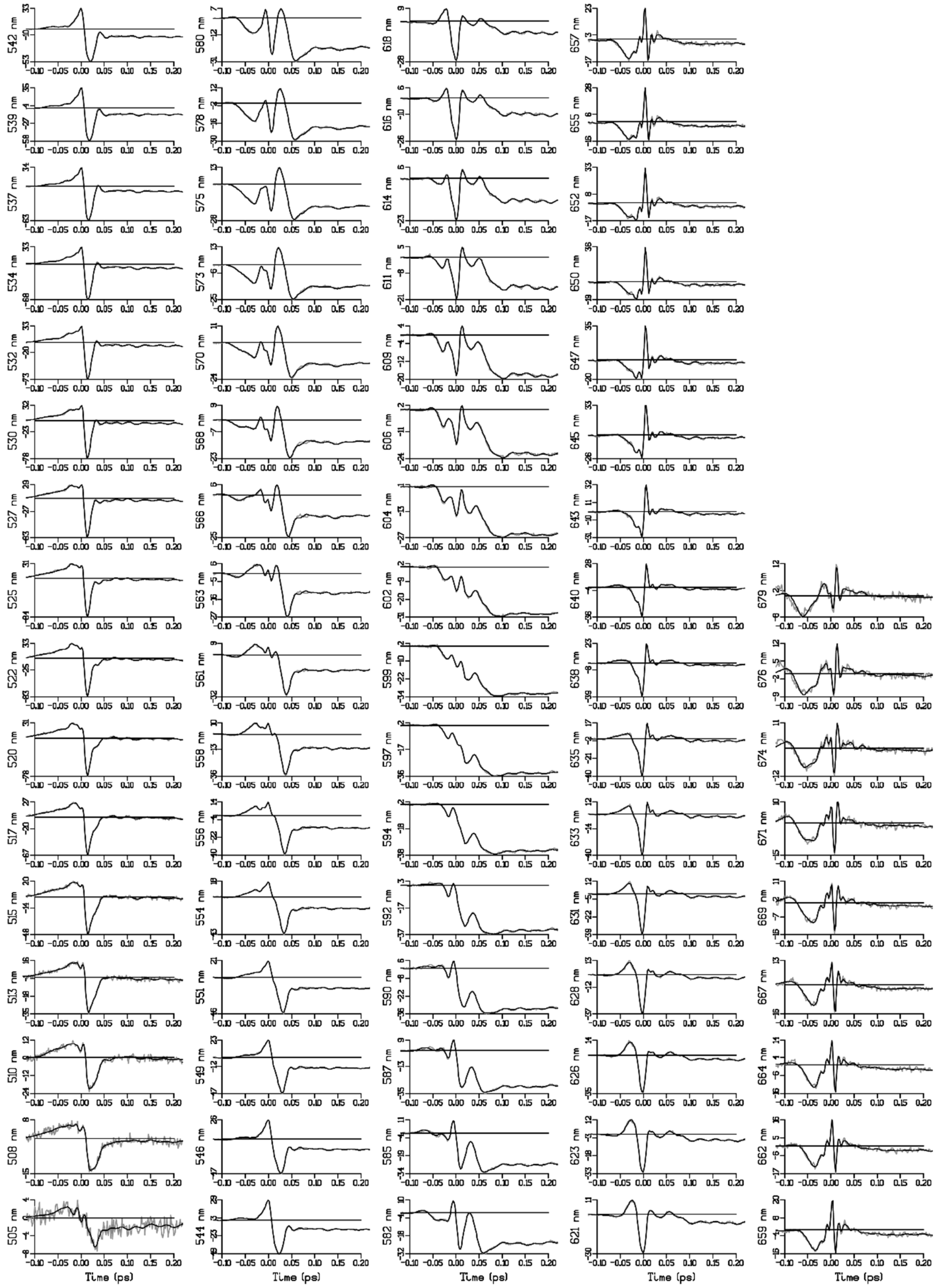

Figure S 10. Zoom from -0.1 to 0.2 ps of selected time traces of PDI dimer A in chlorobenzene data (in mOD, grey) and fit (black). Wavelength is indicated in the ordinate label. Time zero corresponds to the location of the maximum of the IRF. Rms error of the fit was 0.62 mOD, thus the SNR is better than 100.

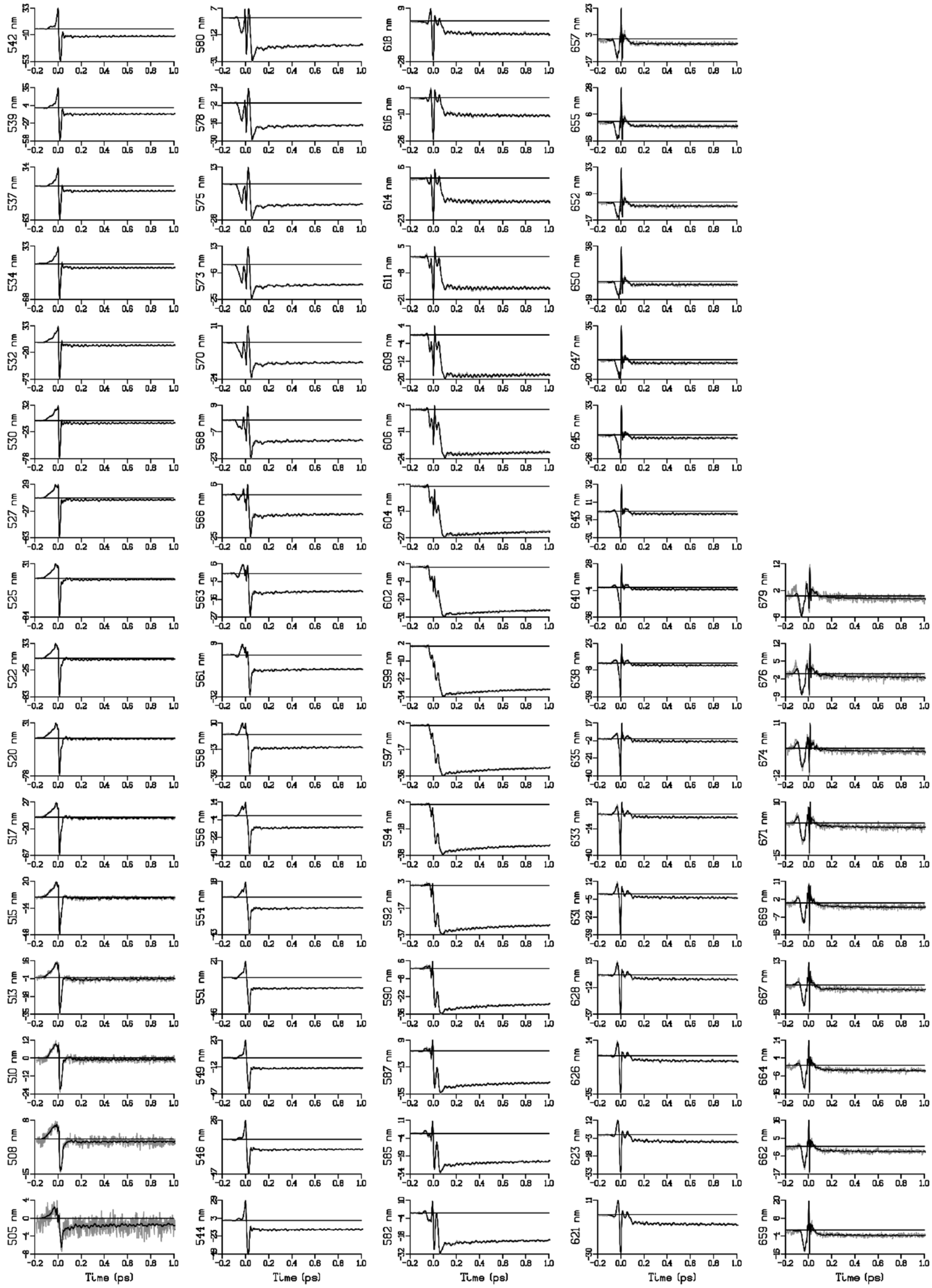

Figure S 11. Full time range of selected time traces of PDI dimer A in chlorobenzene data (in mOD, grey) and fit (black). Wavelength is indicated in the ordinate label. Time zero corresponds to the location of the maximum of the IRF. Rms error of the fit was 0.62 mOD, thus the SNR is better than 100.

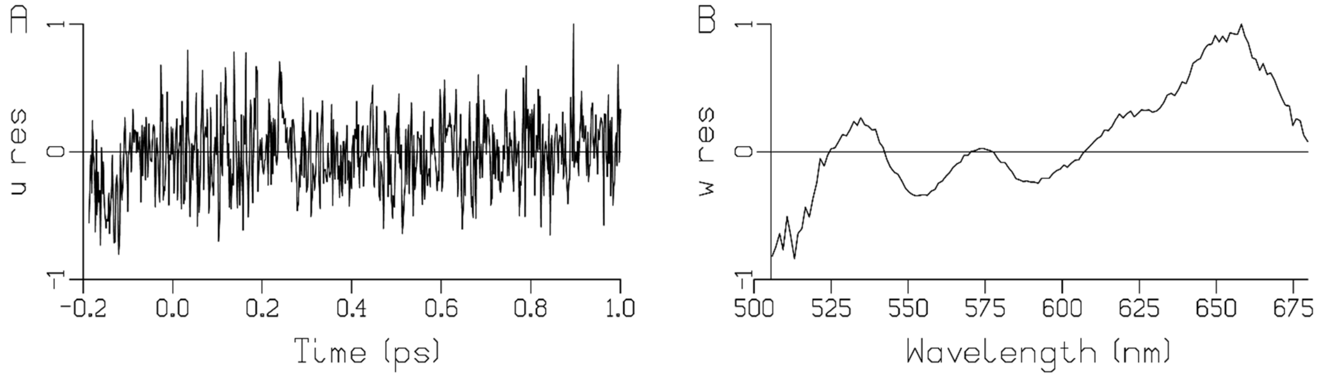

Figure S 12. Residual properties after fitting the damped oscillations. First left (u res, A, time zero corresponds to the location of the maximum of the IRF) and right (w res, B) singular vectors of the residual matrix.

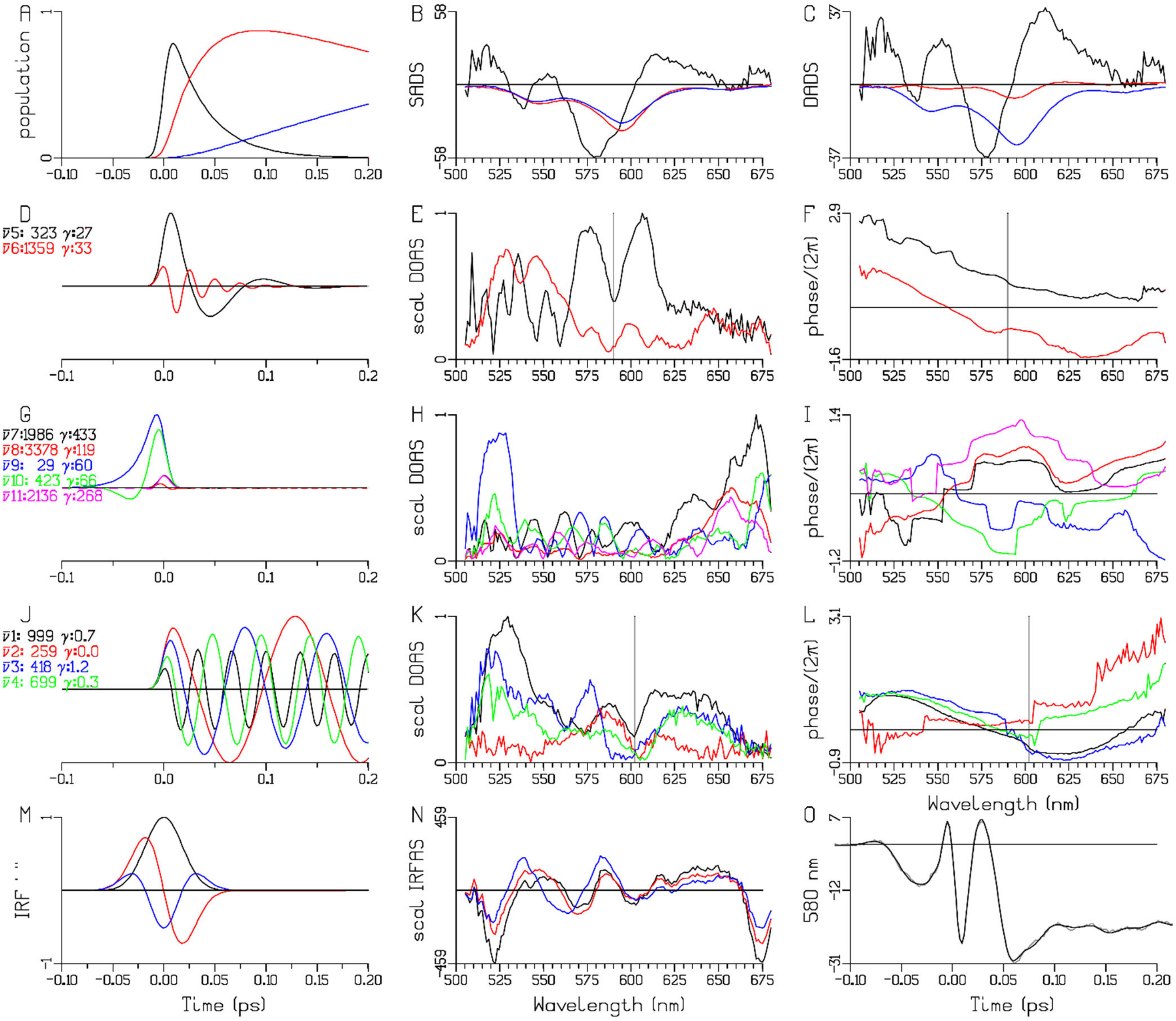

Figure S 13. DOAS analysis of PDI dimer A in chlorobenzene excited with a 15 fs pulse centered at 580 nm and probed with an attenuated pulse. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 35 (black), 402 fs (red), and long lived (blue).

Overview of the estimated DOAS and phases. (D,G,J) Cosine oscillations with frequencies $\bar{\nu}n$ (in cm^{-1}) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (E,H,K) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (F,I,L) Estimated phase profiles of the DOAS. The grey vertical lines at 590 nm in panels E and F and at 602 nm in panels K and L are discussed in the text.

(M) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (N) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (O) Zoom from -0.1 ps to 0.2 ps (after the maximum of the IRF) of the 580 nm data (in mOD, grey) and the fit (black).

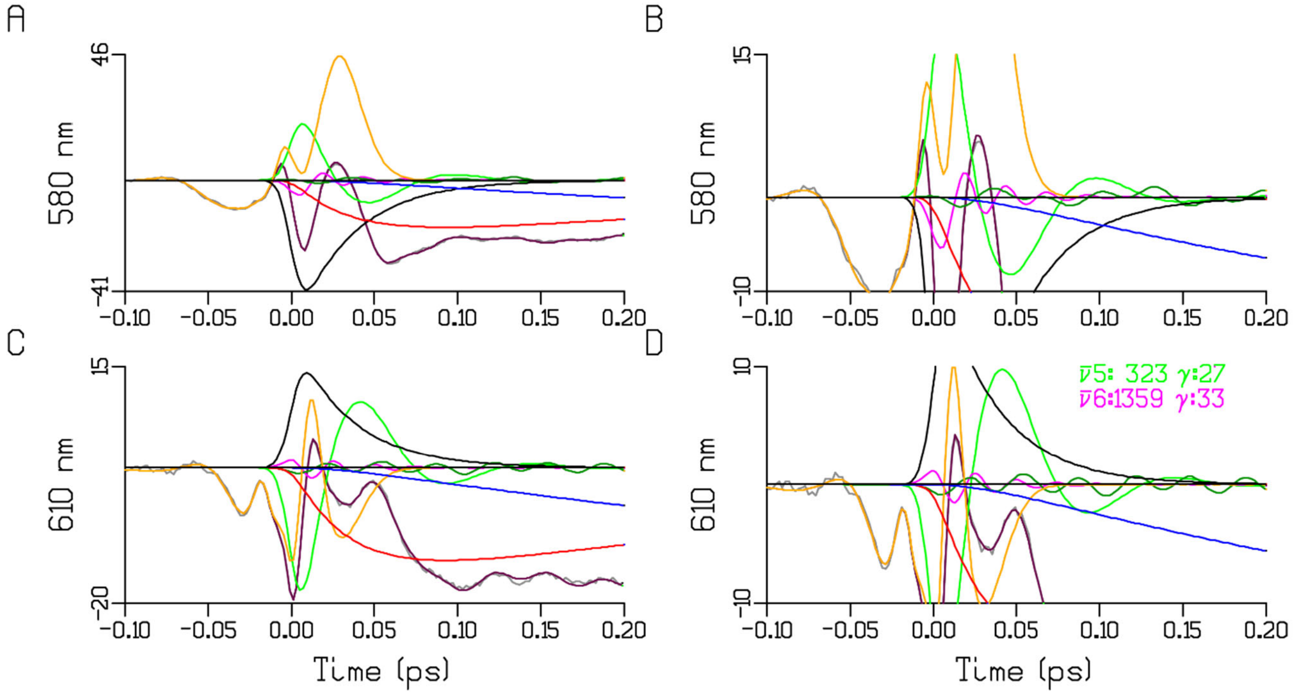

Figure S 14. Decomposition of the 580 and 610 nm PDI dimer A data (in mOD, grey, and the fit, maroon), with zoom ins in panels B and D. Key: 35 (black), 402 fs (red), and long lived (blue). Dark green is the superposition of the solvent ISRS (DOAS #1,2,3,4). Orange is the superposition of the CA related signals (IRF and its derivatives, DOAS #7,8,9,10,11). The strongly damped DOAS #5,6 are in green and magenta with a legend in panel D.

Decomposition of the SADS and steady state spectra for the tetramer and the monomer

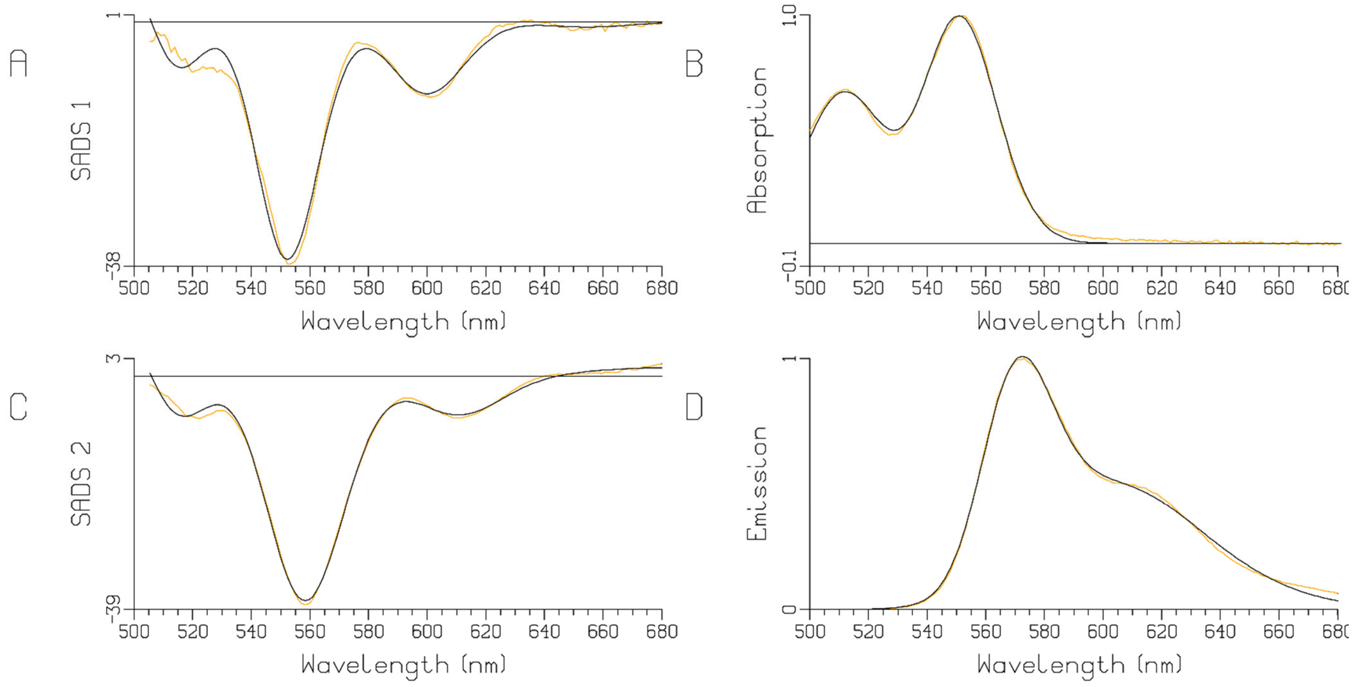

Figure S 15. Spectral decomposition fit of the estimated SADS and the steady state spectra (orange lines) for the tetramer in chlorobenzene. The spectra (cf. the ordinate labels) are fitted with a sum of Gaussian bands (black lines) of which the parameters are collated in Table 2.

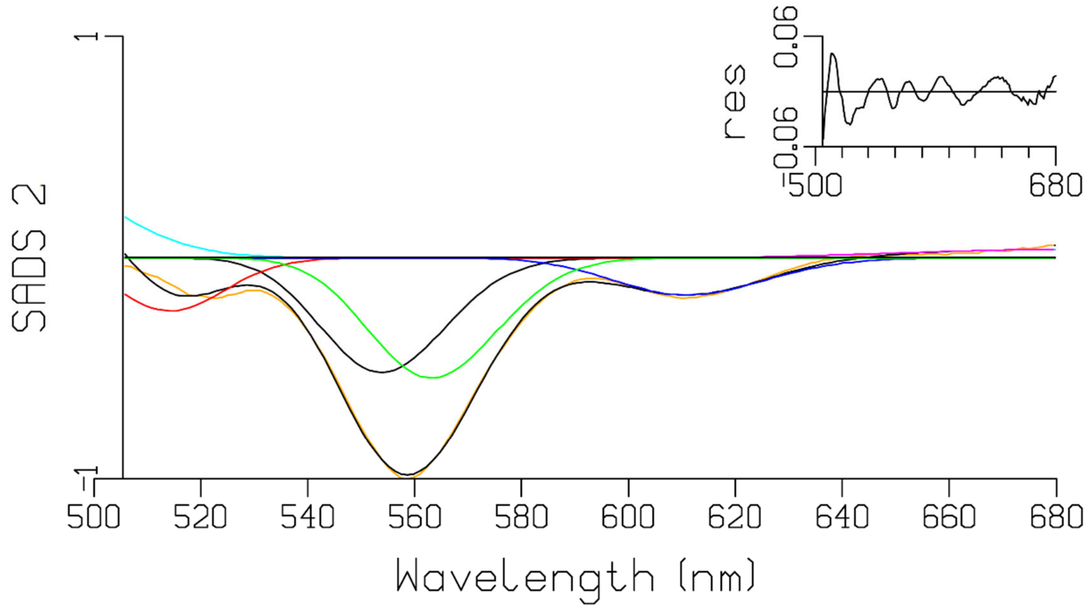

Figure S 16. Spectral decomposition details of the fit (black line) of the estimated SADS 2 (orange line) for the tetramer in chlorobenzene. The contributions of the different Gaussian bands of which the parameters are collated in Table 2 are indicated with different colors. Key (from low to high energy) magenta: ESA; blue: vibrational band of SE, shifted by 1395 cm^{-1} from the main band; green: main band of SE; black: main band of bleach; red: vibrational band of bleach, shifted by 1395 cm^{-1} from the main band; cyan: ESA. Inset shows the residuals of the fit.

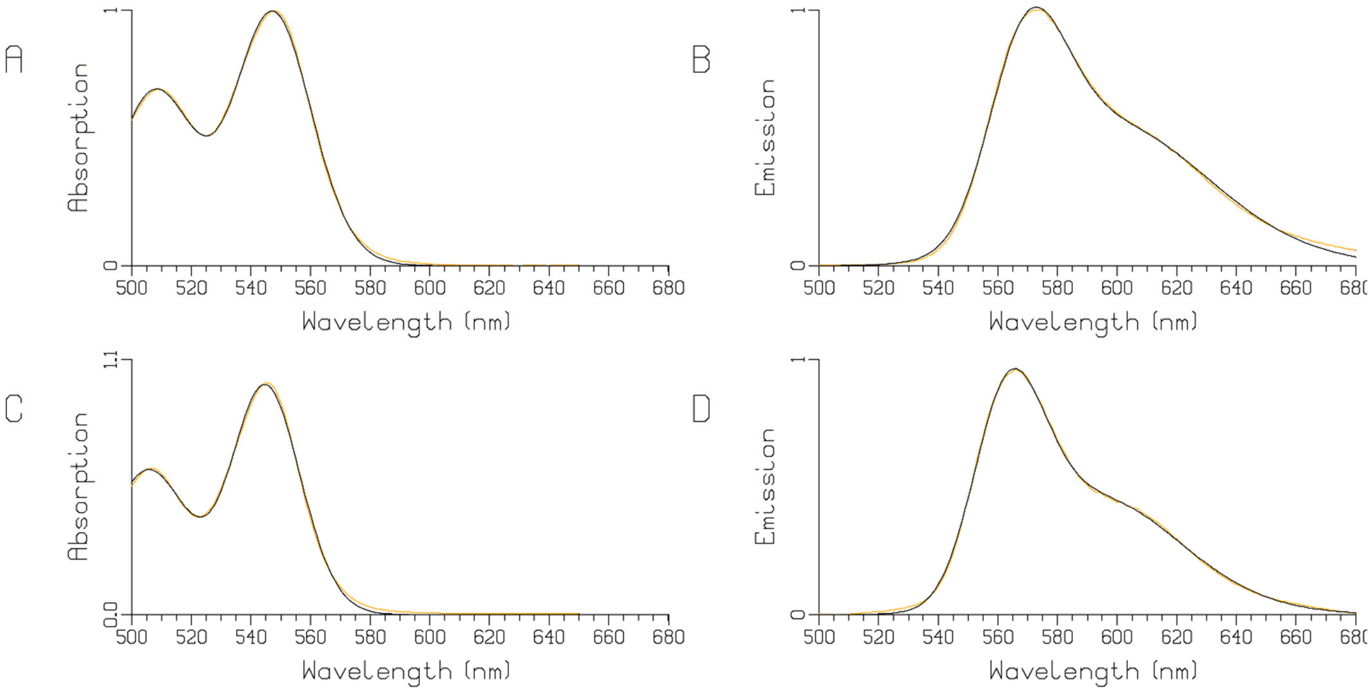

Figure S 17. Spectral decomposition fit of the steady state spectra (orange lines) for the tetramer (B,D) and the monomer (A,C) in dichloromethane. The spectra (cf. the ordinate labels) are fitted with a sum of Gaussian bands (black lines) of which the parameters are collated in Table S 2.

Spectrum	$\bar{\nu}_{\max}(cm^{-1})$	$\Delta\bar{\nu}(cm^{-1})$
tetramer		
Absorption	19645	1244
Absorption	**18250**	**981**
Emission	**17503**	**933**
Emission	16440	1964
monomer		
Absorption	19739	1197
Absorption	**18344**	**903**
Emission	**17706**	**876**
Emission	16651	1758

Table S 2. Location of the maximum $\bar{\nu}_{\max}(cm^{-1})$ and Full width at half maximum $\Delta\bar{\nu}(cm^{-1})$ of the Gaussian bands used to fit the steady state spectra of the tetramer and the monomer in dichloromethane. Main bands in bold.