Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unraveling the enigma of ultrafast excited state relaxation in non-emissive aggregating conjugated polymers

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SUPPORTING INFORMATION

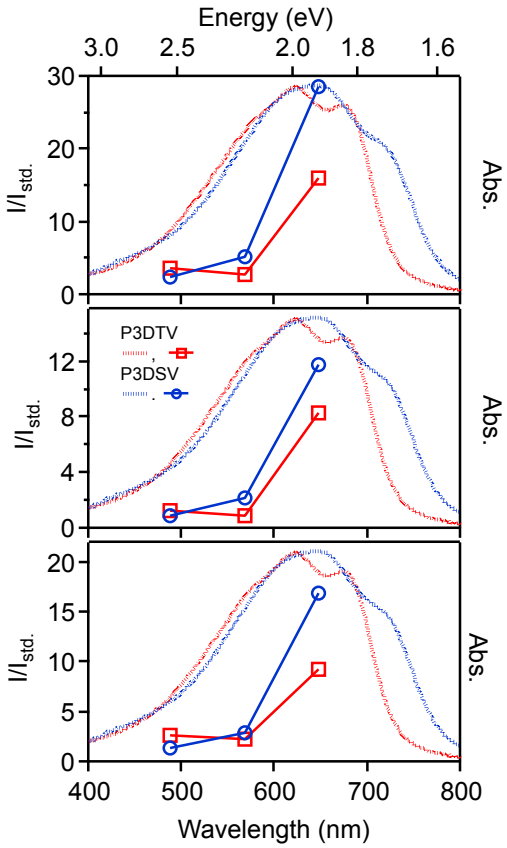

Figure S1. Relative Raman excitation profiles for P3DSV and P3DTV for the three largest displaced skeletal modes (estimated error ~20%).

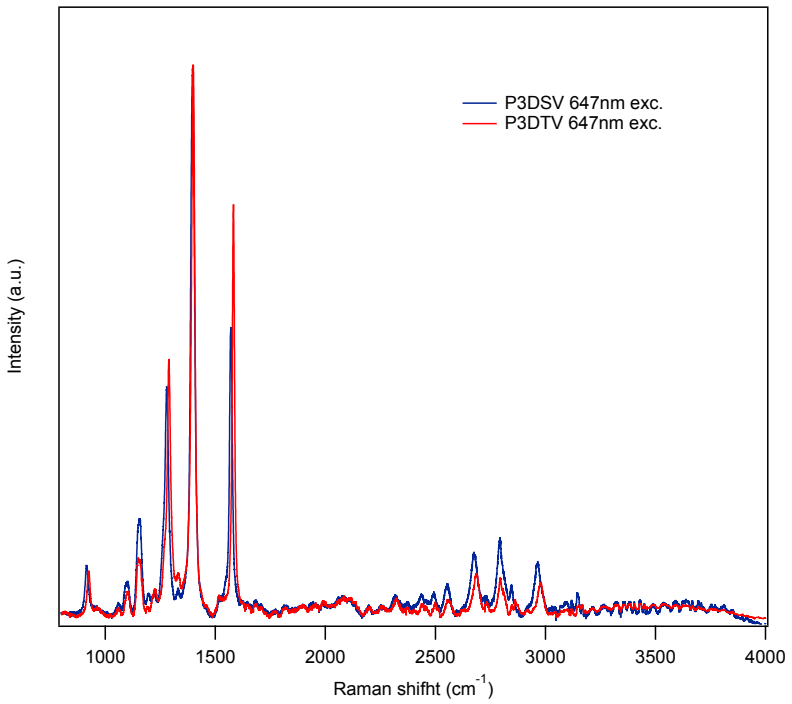

Figure S2. Resonance Raman spectra of P3DSV and P3DTV thin films excited at 647 nm.

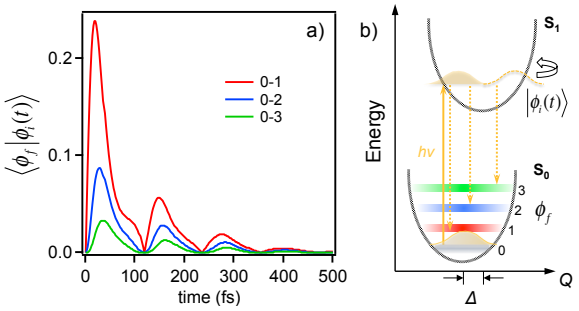

Figure S3. Cross-correlation overlap functions of the 1580 cm^{-1} mode for the fundamental (0-1) and higher overtone (0-2 and 0-3) transitions. b) Potential energy surface diagram illustrating resonance Raman processes in PTV systems.

Transient Absorption Spectroscopy (TAS) fitting:

Data analysis for pump probe experiments was conducted in Surface Xplorer V4.2 (Ultrafast Systems). All pump probe lifetimes were fit to Equation S1. The IRF is the instrument response which is collected independently from pure solvent and fit using the solvent response function. An average solvent response is then fixed into the algorithm.

$$\boldsymbol{y = e^{-\left(\frac{t-t_0}{t_p}\right)^2} + \Sigma_i A_i e^{t-t_0/t_i}}\ , \qquad \text{where } \boldsymbol{t_p = \frac{IRF}{2*ln2}} \qquad \text{Equation S1}$$

Principal component analysis was conducted by Singular Value Decomposition using the Surface Xplorer SVD function. The resulting kinetics were then fit independently using Equation S1.

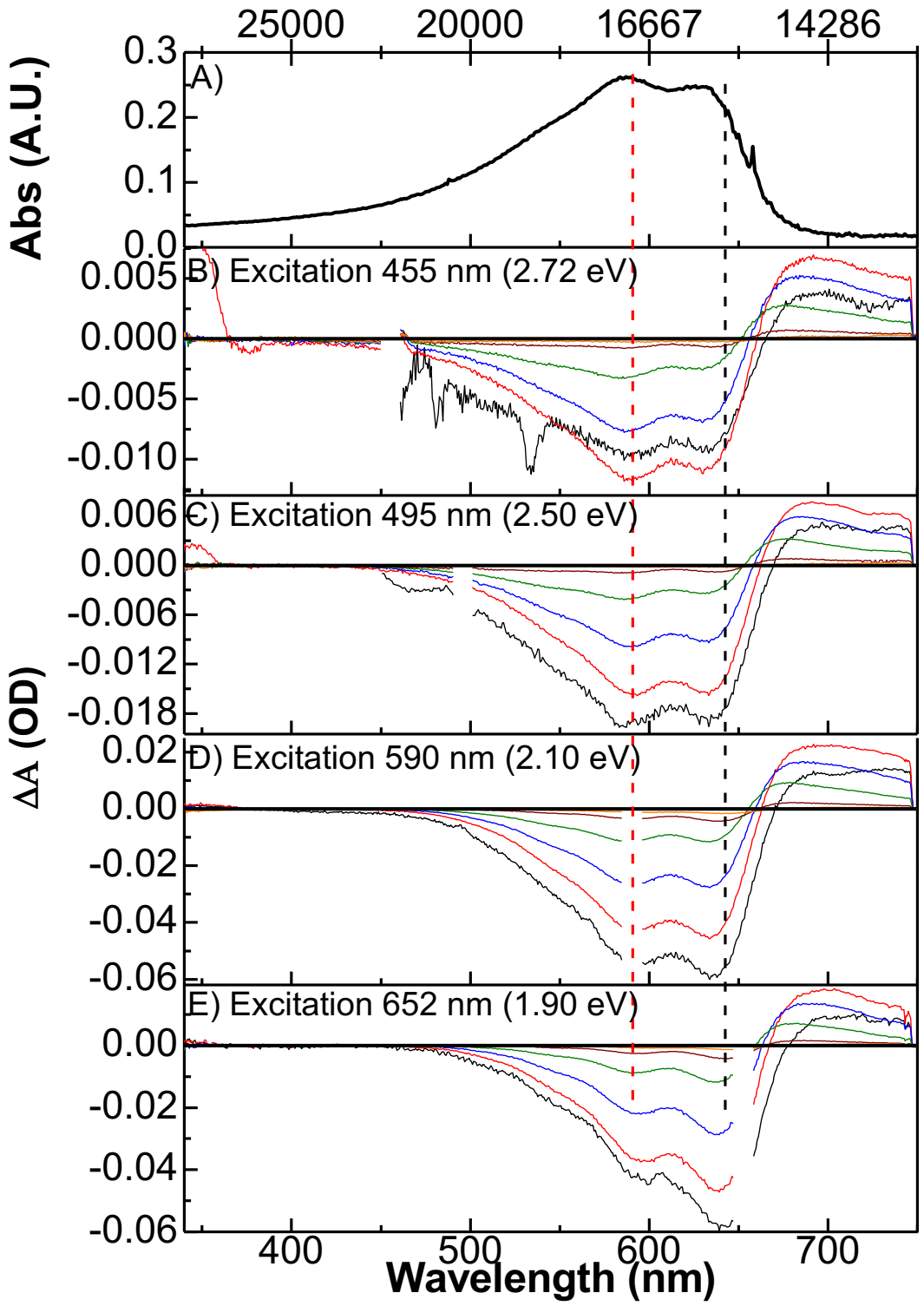

Figure S4. a) Electronic absorption spectrum for P3DTV 0.15 mg/L solution in chlorobenzene prepared under an Argon atmosphere. Transient absorption spectra collected at 0.3 ps (black), 0.75 ps (red), 1.5 ps (blue), 3 ps (green), 8 ps (brown), and 50 ps (orange) intervals with pump energies of b) 2.72 eV (455 nm), c) 2.50 eV (495 nm), d) 2.1 eV (590 nm), and e) 1.9 eV (652 nm).

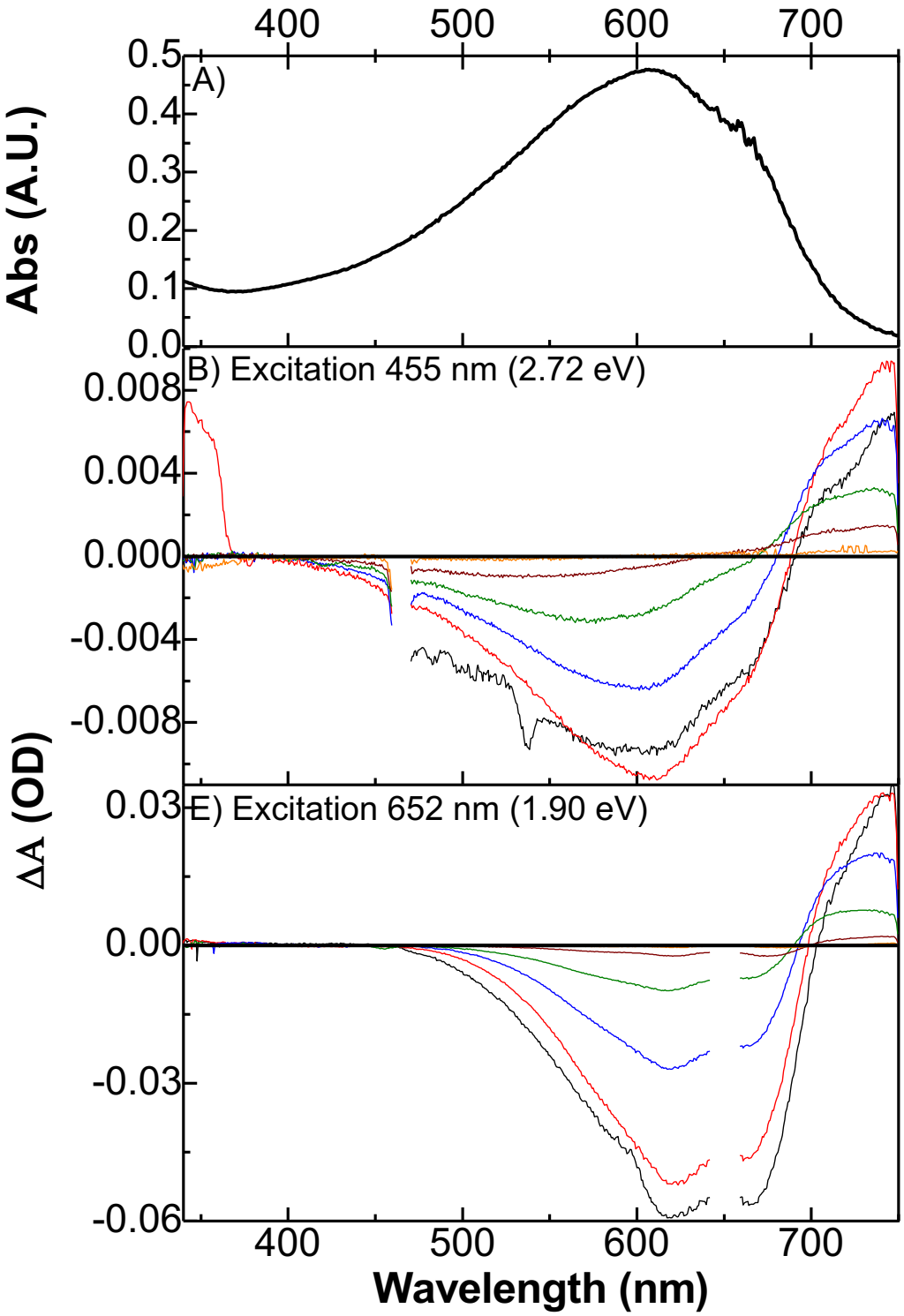

Figure S5. A) Electronic absorption spectrum for P3DSV 0.2 mg/L solution in chlorobenzene prepared under an Argon atmosphere. B) Transient Absorption Spectra collected at 0.3 ps (black), 0.75 ps (red), 1.5 ps (blue), 3 ps (green), 8 ps (brown), and 50 ps (orange) following a 455 nm excitation. C) Transient Absorption Spectra following a 652 nm excitation (time delays are the same as Figure S3).

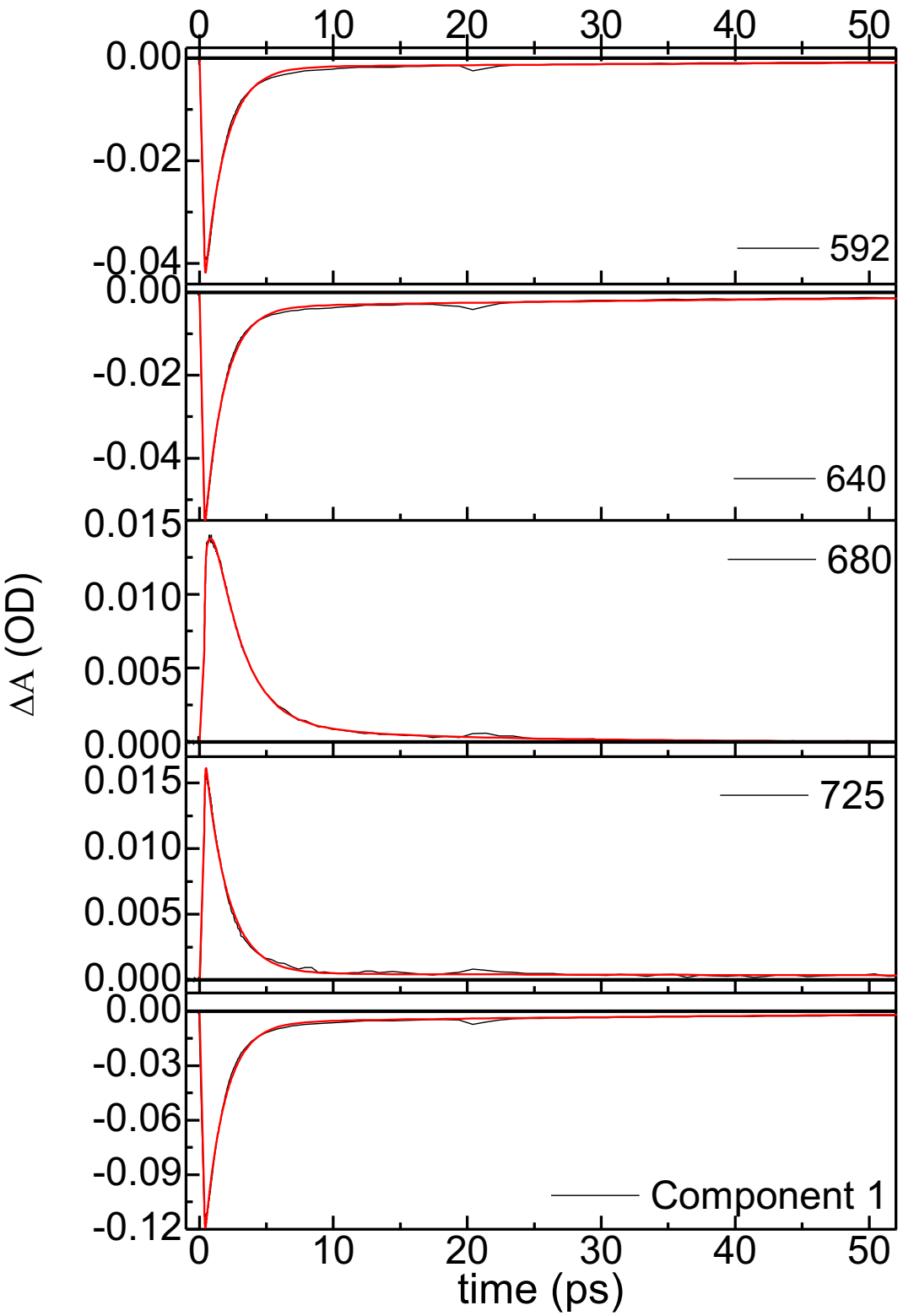

Figure S6. Single wavelength and global fitting kinetics of P3DTV in argon purged chlorobenzene post excitation at 652 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S1.

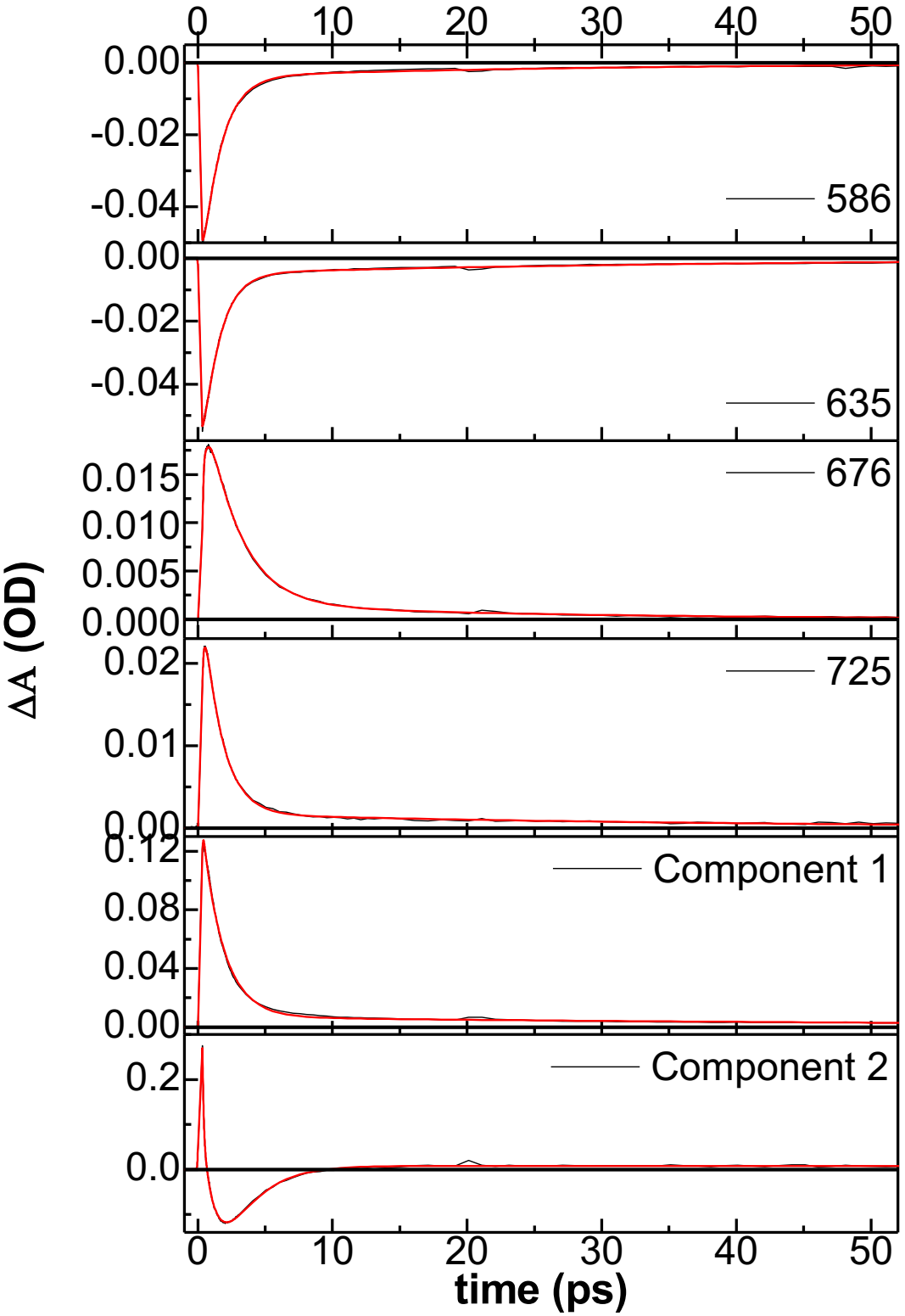

Figure S7. Single wavelength and global fitting kinetics of P3DTV in argon purged chlorobenzene post excitation at 590 nm. The experimental data is presented in black with the corresponding fit in red. Fitting results are presented in Table S1

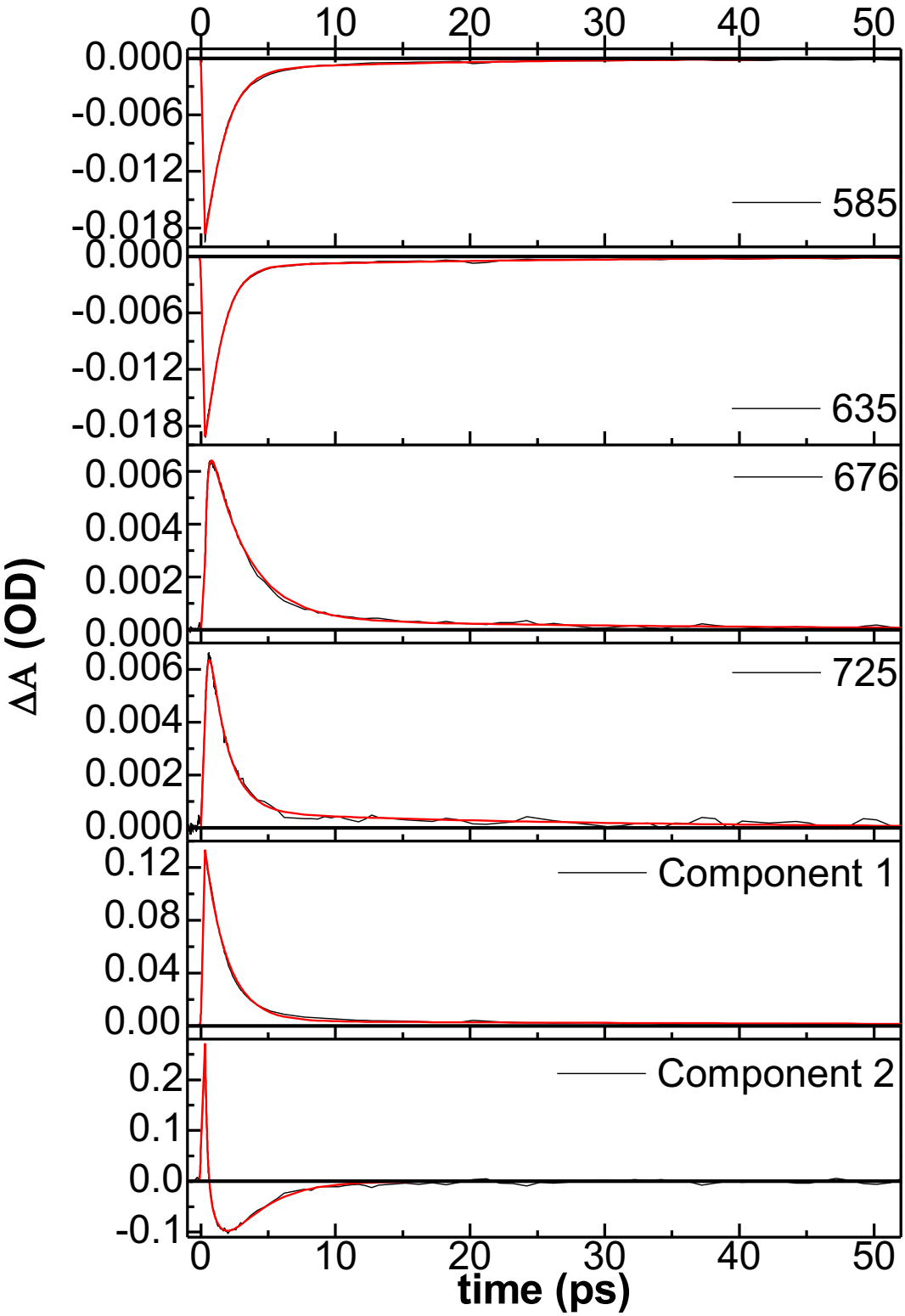

Figure S8. Single wavelength and global fitting kinetics of P3DTV in argon purged chlorobenzene post excitation at 495 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S1.

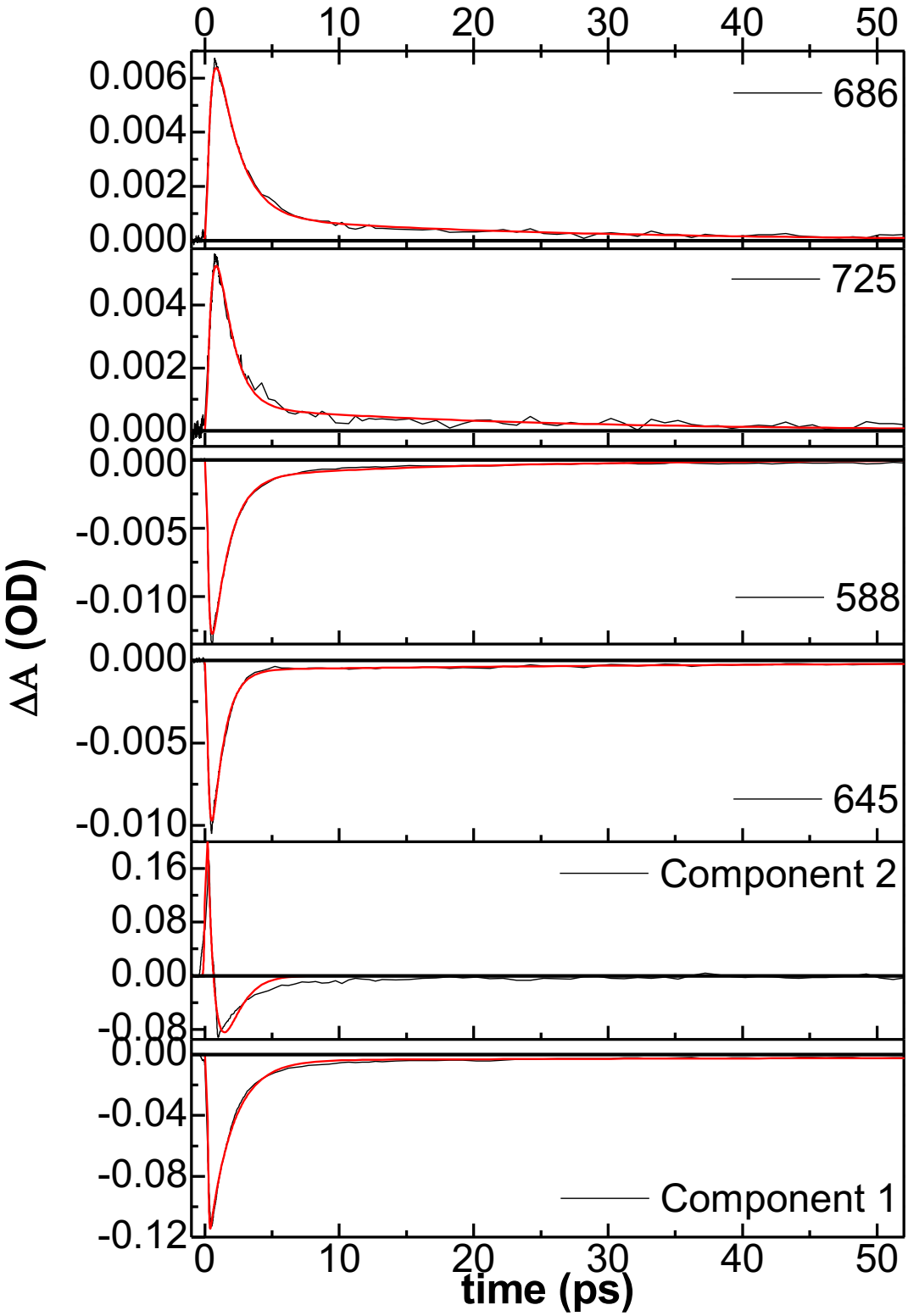

Figure S9. Single wavelength and global fitting kinetics of P3DTV in argon purged chlorobenzene post excitation at 455 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S1.

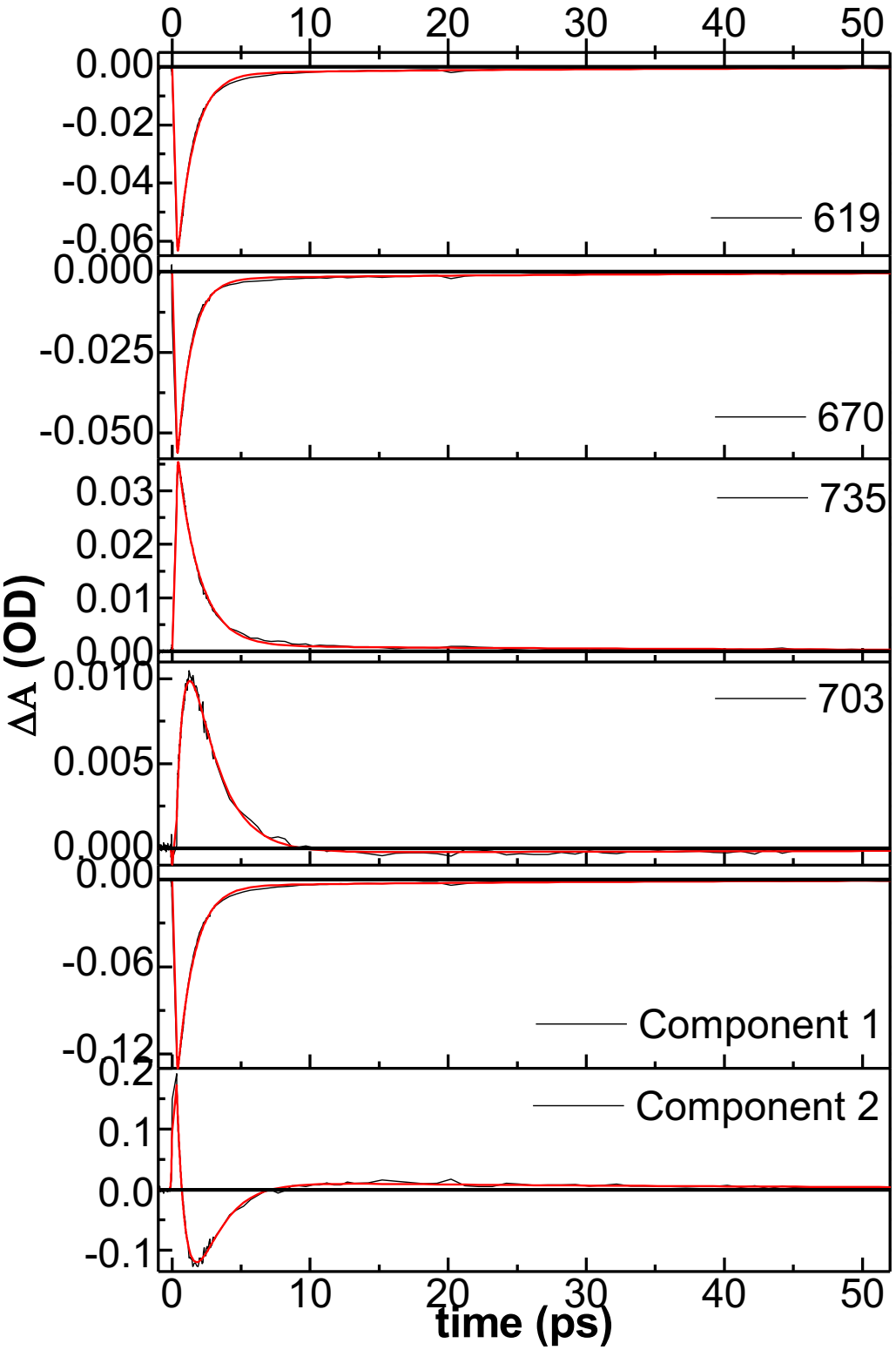

Figure S10. Single wavelength and global fitting kinetics of P3DSV in argon purged chlorobenzene post excitation at 650 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S1.

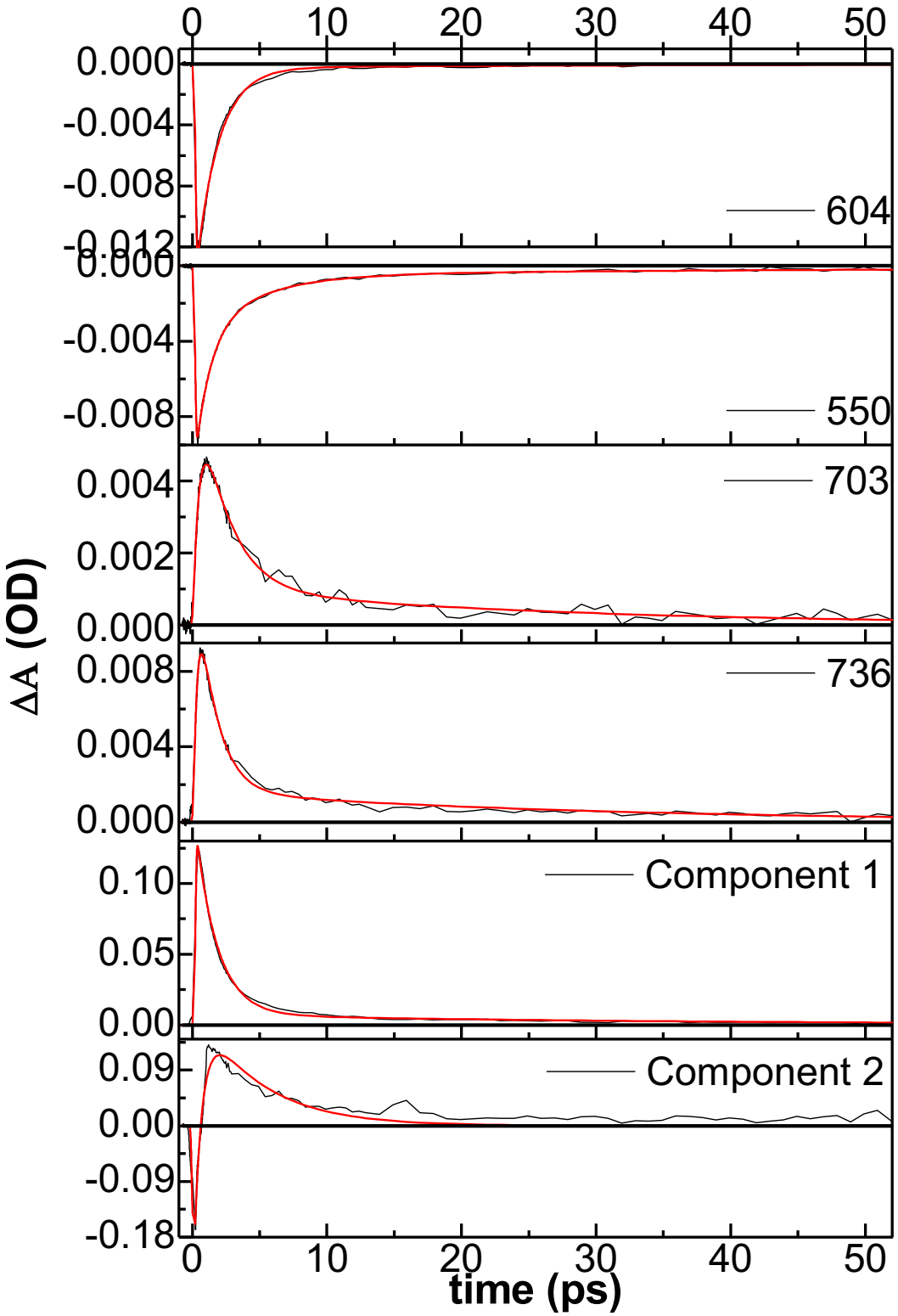

Figure S11. Single wavelength and global fitting kinetics of P3DSV in argon purged chlorobenzene post excitation at 445 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S1.

Table S1. Kinetic fitting parameters for all pump probe visible experiments.

P3DTV ex 652	Principle Component 1	Principle Component 2	592 nm	640 nm	680 nm	725 nm
t_0	0.28	-	0.29	0.26	0.35	0.29
IRF	0.15	-	0.15	0.15	0.15	0.15
A_1		-			-0.011 ± 0.002e	-0.007 ± 0.0007
τ_1		-			0.54 ± 0.10	0.18 ± 0.03
A_2	-0.129 ± 0.002	-	-0.0454 ± 0.0009	-0.0594 ± 0.0007	0.022 ± 0.002	0.0193 ± 0.0004
τ_2	1.51 ± 0.06	-	1.54 ± 0.07	1.45 ± 0.04	2.1 ± 0.2	1.46 ± 0.05
A_3	-0.006 ± 0.002		-0.0018 ± 0.0008	-0.0036 ± 0.0007	0.0013 ± 0.0007	0.0008 ± 0.0001
τ_3	80 ± 100		80 ± 120	58 ± 30	15.5 ± 8	45 ± 20

P3DTV ex590	Principle Component 1	Principle Component 2	586 nm	635 nm	676 nm	725 nm
t_0	0.248 ± 0.008	0.139 ± 0.003	0.16	0.14	0.32	0.27
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A_1		-0.6 ± 0.2	0.019 ± 0.002	0.024 ± 0.005	-0.0106 ± 0.0006	-0.0126 ± 0.0005
τ_1		2.1 ± 0.2	0.28 ± 0.05	0.38 ± 0.09	0.40 ± 0.03	0.2 ± 0.02
A_2	0.137 ± 0.002	0.8 ± 0.2	-0.063 ± 0.002	-0.074 ± 0.006	0.0236 ± 0.0006	0.0283 ± 0.0004
τ_2	1.56 ± 0.05	1.1 ± 0.1	1.35 ± 0.05	1.19 ± 0.07	2.4 ± 0.1	1.36 ± 0.03
A_3	0.007 ± 0.002	4.8 ± 0.9a	-0.0040 ± 0.0004	-0.005 ± 0.0004	0.0016 ± 0.0003	0.0018 ± 0.0001
τ_3	60 ± 35	0.075 ± 0.004a	28 ± 4	36 ± 5	23 ± 5	38 ± 6

P3DTV ex495	Principle Component 1	Principle Component 2	585 nm	635 nm	676 nm	725 nm
t_0	0.12 ± 0.01	0.098 ± 0.004	0.13	0.09	0.27	0.15
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A_1		1.0 ± 0.1	0.01 ± 0.02	0.013 ± 0.008	-0.0069 ± 0.0003	-0.012 ± 0.001
τ_1		0.16 ± 0.02	0.7 ± 0.5	0.5 ± 0.2	0.2 ± 0.02	0.2 ± 0.03
A_2	0.146 ± 0.002	0.4 ± 0.1	-0.029 ± 0.026	-0.033 ± 0.009	0.0078 ± 0.0001	0.0096 ± 0.0005
τ_2	1.64 ± 0.05	1.0 ± 0.4	1.2 ±.0.4	1.1 ± 0.1	2.7 ± 0.1	1.4 ± 0.1
A_3	0.004 ± 0.002	-0.3 ± 0.2	-0.0013 ± 0.0004	-0.0011 ± 0.0002	0.0004 ± 0.0001	0.0006 ± 0.0002
τ_3	60 ± 70	2.6 ± 0.6	17.0 ± 6	26 ± 6	31 ± 18	25 ± 13

P3DTV ex450	Principle Component 1	Principle Component 2	588 nm	645 nm	686 nm	725 nm
t_0	0.232 ± 0.006	0.027 ± 0.011	0.19	0.10	0.09	0.12
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A_1		1.4 ± 1.6	0.0145 ± 0.0008	0.023 ± 0.001	-0.0127 ± 0.0009	-0.02 ± 0.01
τ_1		0.66 ± 0.63	0.20 ± 0.02	0.20 ± 0.02	0.37 ± 0.04	0.5 ± 0.1
A_2	-0.124 ± 0.004	-1 ± 5.6	-0.0182 ± 0.0008	-0.019 ± 0.001	0.0113 ± 0.0010	0.02 ± 0.01
τ_2	1.8 ± 0.1	1 ± 1.1	1.27 ± 0.10	0.90 ± 0.07	1.6 ± 0.2	1.0 ± 0.3
A_3	-0.0036 ±0.0036		-0.0014 ± 0.0004	-0.0006 ± 0.0002	0.0003 ± 0.0008	0.0008 ± 0.0003
τ_3	110 ± 420		17 ± 7	50 ± 38	22 ± 8	21 ± 12

P3DSV ex650	Principle Component 1	Principle Component 2	619 nm	670 nm	703 nm	735 nm
t_0	0.047 ± 0.005	0.257 ± 0.008	0.262 ± 0.007	0.24 ± 0.01	0.07 ± 0.01	0.281 ± 0.005
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A_1	1.0 ± 0.2				-0.033 ± 0.004	
τ_1	0.7 ± 0.2				0.60 ± 0.07	
A_2	-0.6 ± 0.2	-0.147 ± 0.003	-0.071 ± 0.001	-0.064 ± 0.001	0.025 ± 0.005	0.0389 ± 0.0005
τ_2	1.8 ± 0.4		1.21 ± 0.05	1.05 ± 0.06	2.0 ± 2.0	1.58 ± 0.05
A_3	0.014 ± 0.008		-0.002 ± 0.001	-0.002 ± 0.001	-0.0003 ± 0.0003	0.0011 ± 0.0006
τ_3	43 ± 36		30 ± 25	37 ± 36	94 ± 220	42 ± 35

P3DSV ex455nm	Principle Component 1	Principle Component 2	550 nm	604 nm	703 nm	736 nm
t_0	0.22	-0.01	0.206 ± 0.003	0.235 ± 0.006	0.02	0.06
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A_1			-0.007 ± 0.001		-0.009 ± 0.001	-0.017 ± 0.001
τ_1			1.2 ± 0.2		0.49 ± 0.08	0.29 ± 0.04
A_2	0.135 ± 0.005	-0.51 ± 0.05	-0.003 ± 0.001	-0.0138 ± 0.0004	0.007 ±.0.001	0.015 ± 0.001
τ_2	1.6 ± 0.1	0.6 ± 0.1	4.7 ± 2.0	1.7 ± 0.1	2.1 ± 0.4	1.4 ± 0.2
A_3	0.007 ± 0.005	0.21 ± 0.05	-0.0005 ±0.0003	-0.0002 ± 0.0004	0.0010 ± 0.0002	0.0017 ± 0.0002
τ_3	35 ± 36	4.6 ± 1.5	64 ± 60	40 ± 115	26 ± 8	29 ± 7

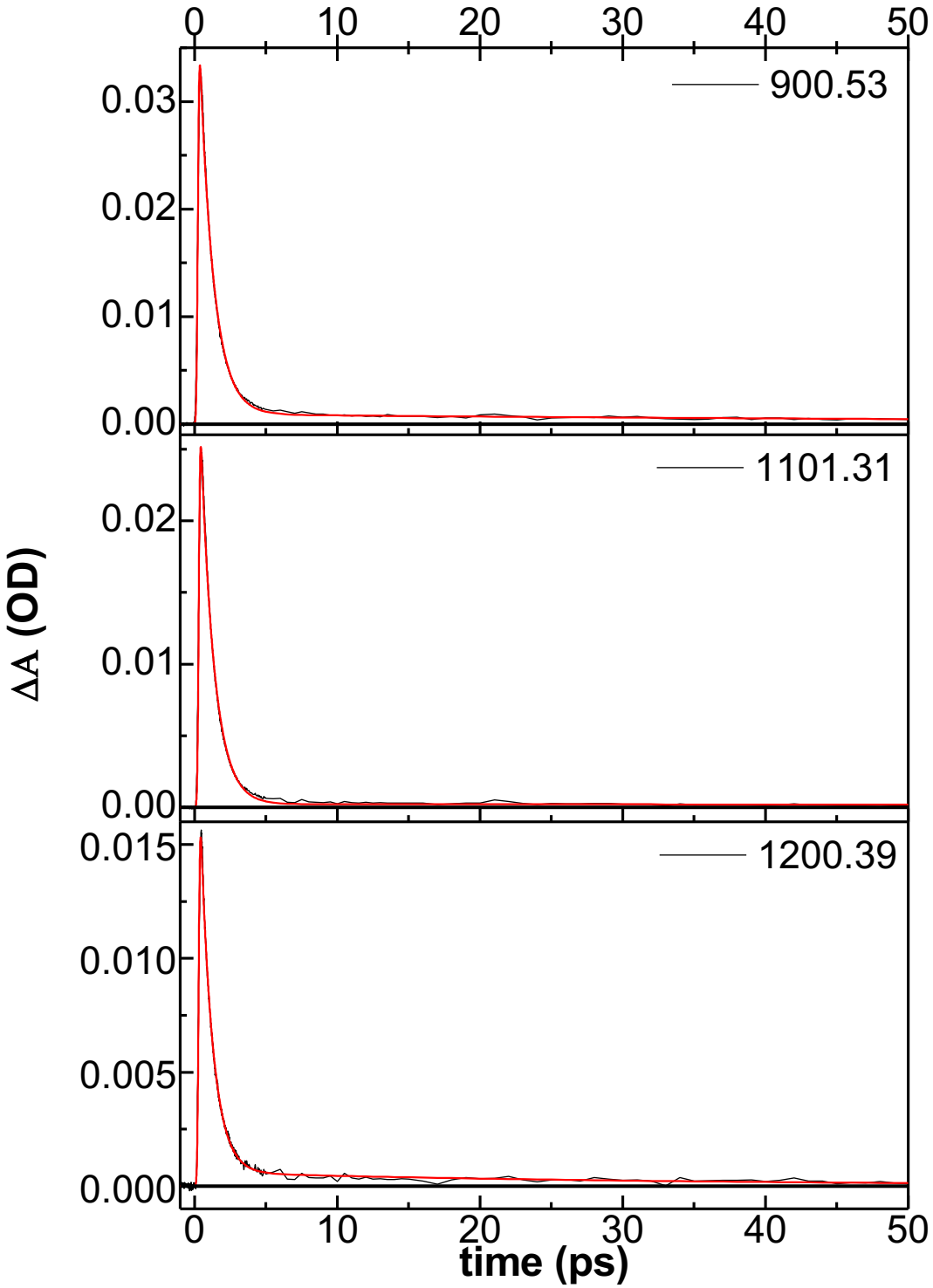

Figure S12. Single wavelength fitting kinetics of P3DTV in argon purged chlorobenzene post excitation at 652 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S2.

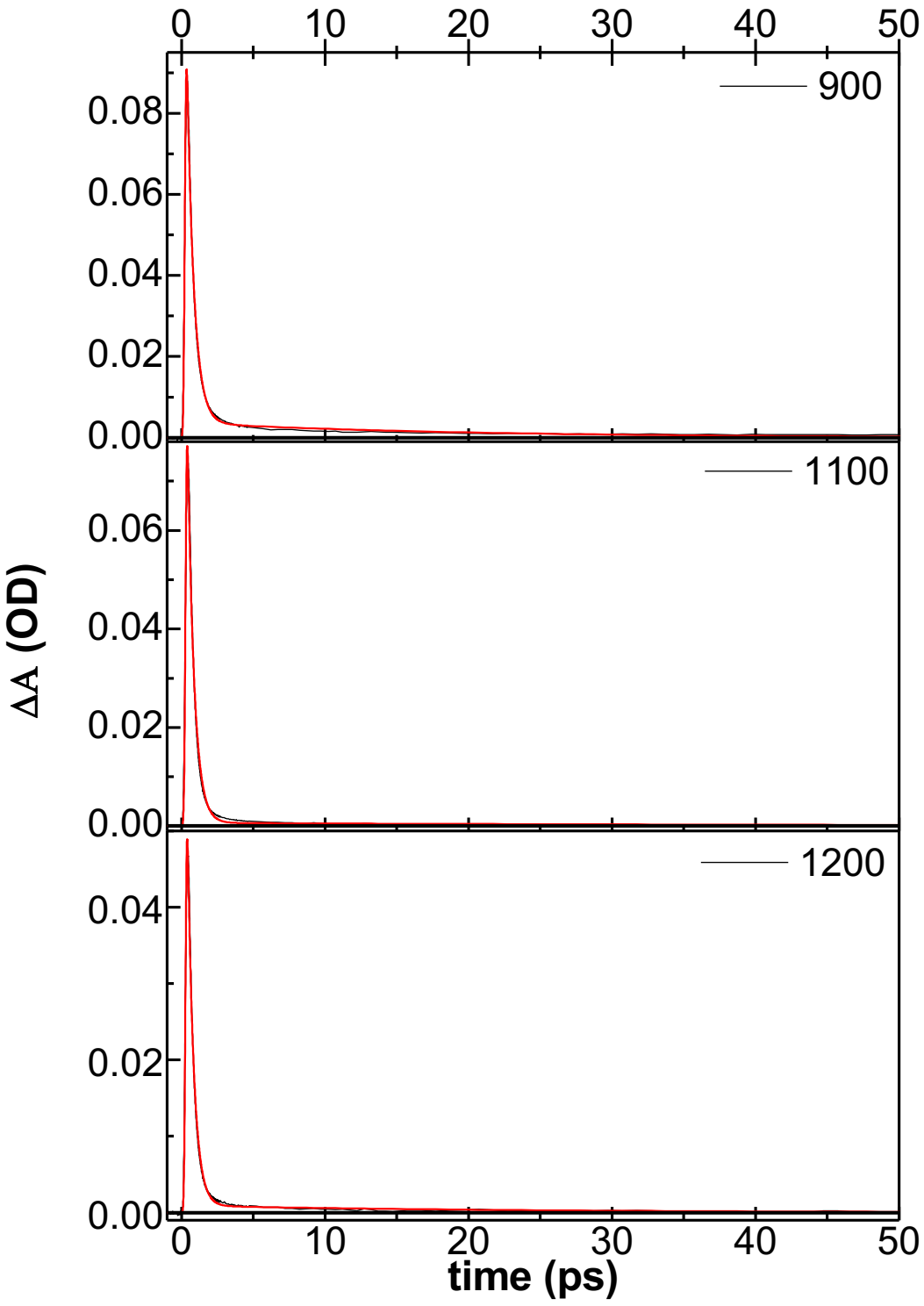

Figure S13. Single wavelength fitting kinetics of P3DSV in argon purged chlorobenzene post excitation at 650 nm. The experimental data is presented in black with the corresponding fitting in red. Fit parameters are presented in Table S2.

Table S2. Kinetic fitting parameters for all pump probe NIR experiments.

P3DTV ex 652	900	1100	1200
t_0	0.24	0.30	0.29
IRF	0.15	0.15	0.15
A_1	0.0392 ± 0.0005	0.0302 ± 0.0004	0.0182 ± 0.0002
τ_1	0.97 ± 0.03	0.94 ± 0.03	0.84 ± 0.03
A_2	0.0009 ± 0.0004	0.0002 ± 0.0002	0.0006 ± 0.0002
τ_2	70 ± 120	700 ± 24000	32 ± 25

PSV	900.53	1101.31	1200.39
t_0	0.24	0.29	0.28
IRF	0.15	0.15	0.15
A_1	0.0037 ± 0.0009	0.110 ± 0.003	0.070 ± 0.002
τ_1	19 ± 15	0.45 ± 0.02	0.43 ± 0.02
A_2	0.123 ± 0.002	0.0007 ± 0.0007	0.0009 ± 0.0005
τ_2	0.49 ± 0.02	50 ± 240	22 ± 45