## Unraveling the enigma of ultrafast excited state relaxation in nonemissive 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<sup>-1</sup> 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.

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

P3DTV ex 652	Principle Component 1	Principle Component 2	592 nm	640 nm	680 nm	725 nm
t <sub>0</sub>	0.28	-	0.29	0.26	0.35	0.29
IRF	0.15	-	0.15	0.15	0.15	0.15
A <sub>1</sub>		-			$-0.011 \pm 0.002e$	$-0.007 \pm 0.0007$
$\tau_1$		-			$0.54\pm0.10$	$0.18\pm0.03$
<b>A</b> 2	$-0.129 \pm 0.002$	-	$-0.0454 \pm 0.0009$	$-0.0594 \pm 0.0007$	$0.022\pm0.002$	$0.0193 \pm 0.0004$
τ2	$1.51\pm0.06$	-	$1.54\pm0.07$	$1.45\pm0.04$	$2.1 \pm 0.2$	$1.46\pm0.05$
<b>A</b> 3	$-0.006 \pm 0.002$		$-0.0018 \pm 0.0008$	$-0.0036 \pm 0.0007$	$0.0013 \pm 0.0007$	$0.0008 \pm 0.0001$
$ au_3$	$80 \pm 100$		$80\pm120$	$58 \pm 30$	$15.5 \pm 8$	$45 \pm 20$
P3DTV	Principle	Principle	586 nm	635 nm	676 nm	725 nm
ex590	Component 1	Component 2	500 mm	055 mm	070 IIII	725 1111
to	$0.248\pm0.008$	$0.139\pm0.003$	0.16	0.14	0.32	0.27
IRF	0.15	0.15	0.15	0.15	0.15	0.15
A <sub>1</sub>		$-0.6 \pm 0.2$	$0.019\pm0.002$	$0.024\pm0.005$	$-0.0106 \pm 0.0006$	$-0.0126 \pm 0.0005$
$\tau_1$		$2.1 \pm 0.2$	$0.28\pm0.05$	$0.38\pm0.09$	$0.40\pm0.03$	$0.2 \pm 0.02$
A <sub>2</sub>	$0.137\pm0.002$	$0.8 \pm 0.2$	$-0.063 \pm 0.002$	$-0.074 \pm 0.006$	$0.0236 \pm 0.0006$	$0.0283 \pm 0.0004$
$ au_2$	$1.56\pm0.05$	$1.1 \pm 0.1$	$1.35\pm0.05$	$1.19\pm0.07$	$2.4 \pm 0.1$	$1.36\pm0.03$
<b>A</b> 3	$0.007\pm0.002$	$4.8\pm0.9a$	$-0.0040 \pm 0.0004$	$-0.005 \pm 0.0004$	$0.0016 \pm 0.0003$	$0.0018 \pm 0.0001$
τ3	$60 \pm 35$	$0.075\pm0.004a$	$28 \pm 4$	$36 \pm 5$	$23 \pm 5$	$38 \pm 6$
D2DTV	Duinainla	D				
rspiv	Frincipie	Principle	595 nm	625 nm	676 nm	725 mm
ex495	Component 1	Component 2	585 nm	635 nm	676 nm	725 nm
ex495 t <sub>0</sub>	$\frac{\text{Component 1}}{0.12 \pm 0.01}$	$\frac{\text{Component 2}}{0.098 \pm 0.004}$	585 nm 0.13	635 nm 0.09	676 nm 0.27	<b>725 nm</b> 0.15
ex495 t <sub>0</sub> IRF	$\frac{\text{Component 1}}{0.12 \pm 0.01}$ $0.15$	$\frac{\text{Component 2}}{0.098 \pm 0.004}$ 0.15	0.13 0.15	635 nm 0.09 0.15	676 nm 0.27 0.15	0.15 0.15
t <sub>0</sub> IRF	$\frac{\text{Component 1}}{0.12 \pm 0.01}$ $0.15$	Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$	$ \begin{array}{r}     585 \text{ nm} \\     0.13 \\     0.15 \\     0.01 \pm 0.02 \end{array} $	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \end{array}$	0.27 0.15 -0.0069 ± 0.0003	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ -0.012 \pm 0.001 \end{array}$
ex495 t <sub>0</sub> IRF A <sub>1</sub> τ <sub>1</sub>	$\frac{\text{Component 1}}{0.12 \pm 0.01}$ 0.15	Ormetpie           Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$	$ \begin{array}{c}     585 \text{ nm} \\     0.13 \\     0.15 \\     0.01 \pm 0.02 \\     0.7 \pm 0.5 \\ \end{array} $	$ \begin{array}{r}     635 \text{ nm} \\     0.09 \\     0.15 \\     0.013 \pm 0.008 \\     0.5 \pm 0.2 \\ \end{array} $	$\begin{array}{c} 676 \text{ nm} \\ \hline 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \end{array}$	$\begin{array}{c} & 0.15 \\ & 0.15 \\ -0.012 \pm 0.001 \\ & 0.2 \pm 0.03 \end{array}$
ex495 t <sub>0</sub> IRF A <sub>1</sub> τ <sub>1</sub> A <sub>2</sub>	$\begin{array}{c} \text{Component 1} \\ 0.12 \pm 0.01 \\ 0.15 \\ \end{array}$	Ormetpie $Component 2$ $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$	$     \begin{array}{r}       585 \text{ nm} \\       0.13 \\       0.15 \\       0.01 \pm 0.02 \\       0.7 \pm 0.5 \\       -0.029 \pm 0.026 \\     \end{array} $	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \end{array}$	$\begin{array}{c} \textbf{676 nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \end{array}$	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ -0.012 \pm 0.001 \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \end{array}$
rsDTv           ex495           t₀           IRF           A₁           τ₁           A₂           τ₂	$\begin{array}{r} \text{Principle} \\ \hline \text{Component 1} \\ \hline 0.12 \pm 0.01 \\ 0.15 \\ \hline 0.146 \pm 0.002 \\ \hline 1.64 \pm 0.05 \end{array}$	Ormetpie           Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$	$ \begin{array}{c}       585 \text{ nm} \\       0.13 \\       0.15 \\       0.01 \pm 0.02 \\       0.7 \pm 0.5 \\       -0.029 \pm 0.026 \\       1.2 \pm 0.4 \\   \end{array} $	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ \end{array}$	$\begin{array}{c} \textbf{676 nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \end{array}$	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ \textbf{-0.012} \pm 0.001 \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \\ 1.4 \pm 0.1 \end{array}$
rsDTv           ex495           t₀           IRF           A₁           τ₁           A₂           τ₂           A₃	$\begin{array}{c} \text{Component 1} \\ \hline 0.12 \pm 0.01 \\ 0.15 \\ \hline 0.146 \pm 0.002 \\ 1.64 \pm 0.05 \\ \hline 0.004 \pm 0.002 \end{array}$	Ormetpie $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$	$\begin{array}{c} 585 \text{ nm} \\ 0.13 \\ 0.15 \\ 0.01 \pm 0.02 \\ 0.7 \pm 0.5 \\ -0.029 \pm 0.026 \\ 1.2 \pm 0.4 \\ -0.0013 \pm \\ 0.0004 \end{array}$	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ \hline 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \end{array}$	$\begin{array}{c} \textbf{676 nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \end{array}$	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ \textbf{-0.012 \pm 0.001} \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \\ 1.4 \pm 0.1 \\ 0.0006 \pm 0.0002 \end{array}$
rsDTv           ex495           t₀           IRF           A1           τ1           A2           τ2           A3           τ3	$\begin{array}{c} \text{Principle} \\ \hline \text{Component 1} \\ \hline 0.12 \pm 0.01 \\ 0.15 \\ \hline 0.146 \pm 0.002 \\ \hline 1.64 \pm 0.005 \\ \hline 0.004 \pm 0.002 \\ \hline 60 \pm 70 \\ \end{array}$	Ormetiple           Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$	$\begin{array}{c} 585 \text{ nm} \\ 0.13 \\ 0.15 \\ 0.01 \pm 0.02 \\ 0.7 \pm 0.5 \\ -0.029 \pm 0.026 \\ 1.2 \pm 0.4 \\ -0.0013 \pm \\ 0.0004 \\ 17.0 \pm 6 \end{array}$	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \\ 26 \pm 6 \end{array}$	$\begin{array}{c} 676 \text{ nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \\ 31 \pm 18 \end{array}$	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ \textbf{-0.012 \pm 0.001} \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \\ 1.4 \pm 0.1 \\ 0.0006 \pm 0.0002 \\ 25 \pm 13 \end{array}$
rsb1v           ex495           t₀           IRF           A₁           τ₁           A₂           τ₂           A₃           τ₃	$\begin{array}{c} \text{Component 1} \\ \hline 0.12 \pm 0.01 \\ 0.15 \\ \hline 0.146 \pm 0.002 \\ 1.64 \pm 0.05 \\ 0.004 \pm 0.002 \\ \hline 60 \pm 70 \\ \hline \end{array}$	Ormetpie           Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$	$\begin{array}{c} 585 \text{ nm} \\ 0.13 \\ 0.15 \\ 0.01 \pm 0.02 \\ 0.7 \pm 0.5 \\ -0.029 \pm 0.026 \\ 1.2 \pm 0.4 \\ -0.0013 \pm \\ 0.0004 \\ 17.0 \pm 6 \end{array}$	$\begin{array}{c} 635 \text{ nm} \\ \hline 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \\ 26 \pm 6 \end{array}$	$\begin{array}{c} 676 \text{ nm} \\ \hline 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \\ 31 \pm 18 \end{array}$	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ \textbf{-0.012 \pm 0.001} \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \\ 1.4 \pm 0.1 \\ 0.0006 \pm 0.0002 \\ 25 \pm 13 \end{array}$
ex495 t <sub>0</sub> IRF A <sub>1</sub> τ <sub>1</sub> A <sub>2</sub> τ <sub>2</sub> A <sub>3</sub> τ <sub>3</sub> P3DTV	$\begin{array}{r} \text{Principle} \\ \hline \text{Component 1} \\ 0.12 \pm 0.01 \\ 0.15 \\ \hline \end{array}$ $\begin{array}{r} 0.146 \pm 0.002 \\ 1.64 \pm 0.05 \\ 0.004 \pm 0.002 \\ \hline 60 \pm 70 \\ \hline \end{array}$ $\begin{array}{r} \text{Principle} \end{array}$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle	585  nm 0.13 0.15 0.01 ± 0.02 0.7 ± 0.5 -0.029 ± 0.026 1.2 ± 0.4 -0.0013 ± 0.0004 17.0 ± 6 588 pm	$635 \text{ nm}$ $0.09$ $0.15$ $0.013 \pm 0.008$ $0.5 \pm 0.2$ $-0.033 \pm 0.009$ $1.1 \pm 0.1$ $-0.0011 \pm$ $0.0002$ $26 \pm 6$	$\begin{array}{c} 676 \text{ nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \\ 31 \pm 18 \end{array}$	$725 \text{ nm}$ 0.15 0.15 -0.012 $\pm$ 0.001 0.2 $\pm$ 0.03 0.0096 $\pm$ 0.0005 1.4 $\pm$ 0.1 0.0006 $\pm$ 0.0002 25 $\pm$ 13
P3DTV ex495 to IRF A1 T1 A2 T2 A3 T3 P3DTV ex450	Omega $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$	Principle         Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$	$     \begin{array}{r}       585 \text{ nm} \\       0.13 \\       0.15 \\       0.01 \pm 0.02 \\       0.7 \pm 0.5 \\       -0.029 \pm 0.026 \\       1.2 \pm 0.4 \\       -0.0013 \pm \\       0.0004 \\       17.0 \pm 6 \\       \hline       588 \text{ nm}     \end{array} $	$\begin{array}{c} 635 \text{ nm} \\ 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \\ 26 \pm 6 \end{array}$	$\begin{array}{c} 676 \text{ nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \\ 31 \pm 18 \end{array}$	$725 \text{ nm}$ $0.15$ $0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$
rsDTV           ex495           t₀           IRF           A1           τ1           A2           τ2           A3           τ3           P3DTV           ex450           t₀	Omponent 1 $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle Component 1 $0.232 \pm 0.006$	Principle           Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle           Component 2 $0.027 \pm 0.011$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$	$\begin{array}{c} 635 \text{ nm} \\ 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \\ 26 \pm 6 \\ \hline \\ 645 \text{ nm} \\ 0.10 \\ \end{array}$	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09	725  nm 0.15 0.15 -0.012 ± 0.001 0.2 ± 0.03 0.0096 ± 0.0005 1.4 ± 0.1 0.0006 ± 0.0002 25 ± 13 725 nm 0.12
rsb1v           ex495           t₀           IRF           A₁           τ₁           A₂           τ₂           A₃           τ₃           P3DTV           ex450           t₀           IRF	Principle         Component 1 $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15	$     \begin{array}{r}       585 \text{ nm} \\       0.13 \\       0.15 \\       0.01 \pm 0.02 \\       0.7 \pm 0.5 \\       -0.029 \pm 0.026 \\       1.2 \pm 0.4 \\       -0.0013 \pm \\       0.0004 \\       17.0 \pm 6 \\       \hline       588 \text{ nm} \\       0.19 \\       0.15 \\     \end{array} $	$\begin{array}{c} 635 \text{ nm} \\ 0.09 \\ 0.15 \\ 0.013 \pm 0.008 \\ 0.5 \pm 0.2 \\ -0.033 \pm 0.009 \\ 1.1 \pm 0.1 \\ -0.0011 \pm \\ 0.0002 \\ 26 \pm 6 \\ \hline \\ \hline \\ 645 \text{ nm} \\ 0.10 \\ 0.15 \\ \end{array}$	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15	$\begin{array}{c} \textbf{725 nm} \\ 0.15 \\ 0.15 \\ -0.012 \pm 0.001 \\ 0.2 \pm 0.03 \\ 0.0096 \pm 0.0005 \\ 1.4 \pm 0.1 \\ 0.0006 \pm 0.0002 \\ 25 \pm 13 \\ \hline \textbf{725 nm} \\ 0.12 \\ 0.15 \\ \end{array}$
r3DTV         ex495         t0         IRF         A1         τ1         A2         τ2         A3         τ3         P3DTV         ex450         t0         IRF         A1	Principle $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$	Principle         Component 2 $0.098 \pm 0.004$ $0.15$ $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ $0.15$ $1.4 \pm 1.6$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.19$ $0.15$ $0.0145 \pm 0.0008$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 6 645 nm 0.10 0.15 0.023 ± 0.001	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15 -0.0127 ± 0.0009	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.12$ $0.15$ $-0.02 \pm 0.01$
r3DTV         ex495         t0         IRF         A1         τ1         A2         τ2         A3         τ3         P3DTV         ex450         t0         IRF         A1         τ1	Principle $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15 $1.4 \pm 1.6$ $0.66 \pm 0.63$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.15$ $0.0145 \pm 0.0008$ $0.20 \pm 0.02$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 645 nm 0.10 0.15 0.023 ± 0.001 0.20 ± 0.02	$\begin{array}{c} 676 \text{ nm} \\ 0.27 \\ 0.15 \\ -0.0069 \pm \\ 0.0003 \\ 0.2 \pm 0.02 \\ 0.0078 \pm 0.0001 \\ 2.7 \pm 0.1 \\ 0.0004 \pm 0.0001 \\ 31 \pm 18 \\ \hline \\ 686 \text{ nm} \\ \hline \\ 0.09 \\ 0.15 \\ -0.0127 \pm \\ 0.0009 \\ 0.37 \pm 0.04 \\ \end{array}$	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.12$ $0.15$ $-0.02 \pm 0.01$ $0.5 \pm 0.1$
$\begin{array}{c} r_{3} r_{3} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{2} \\ r_{3} \\ r_{3} \\ \hline \\ r_{3} \\ \hline \\ r_{3} \\ \hline \\ r_{3} \\ \hline \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{2} \\ r_{3} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{2} \\ r_{3} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{4} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{4} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{1} \\ r_{2} \\ r_{4} \\ r_{1} \\ r_{1} \\ r_{2} \\ r$	$\frac{\text{Component 1}}{0.12 \pm 0.01}$ $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.002$ $60 \pm 70$ $\frac{\text{Principle}}{\text{Component 1}}$ $0.232 \pm 0.006$ $0.15$ $-0.124 \pm 0.004$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15 $1.4 \pm 1.6$ $0.66 \pm 0.63$ $-1 \pm 5.6$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.19$ $0.15$ $0.0145 \pm 0.0008$ $0.20 \pm 0.02$ $-0.0182 \pm$ $0.0008$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 6 645 nm 0.10 0.15 0.023 ± 0.001 0.20 ± 0.02 -0.019 ± 0.001	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15 -0.0127 ± 0.0009 0.37 ± 0.04 0.0113 ± 0.0010	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.12$ $0.15$ $-0.02 \pm 0.01$ $0.5 \pm 0.1$ $0.02 \pm 0.01$
r3DTV         ex495         t0         IRF         A1         τ1         A2         τ2         A3         τ3         P3DTV         ex450         t0         IRF         A1         τ1         A2         τ2         A3         τ3	Principle $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15 $1.4 \pm 1.6$ $0.66 \pm 0.63$ $-1 \pm 5.6$ $1 \pm 1.1$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.19$ $0.15$ $0.0145 \pm 0.0008$ $0.20 \pm 0.02$ $-0.0182 \pm$ $0.0008$ $1.27 \pm 0.10$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 6 645 nm 0.10 0.15 0.023 ± 0.001 0.20 ± 0.02 -0.019 ± 0.001 0.90 ± 0.07	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15 -0.0127 ± 0.0009 0.37 ± 0.04 0.0113 ± 0.0010 1.6 ± 0.2	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.15$ $-0.02 \pm 0.01$ $0.5 \pm 0.1$ $0.02 \pm 0.01$ $1.0 \pm 0.3$
r3DTV         ex495         t0         IRF         A1         τ1         A2         τ2         A3         τ3    P3DTV ex450        t0         IRF         A1         τ1         A2         τ2         A3         τ3	Principle $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$ -0.124 $\pm 0.004$ $1.8 \pm 0.1$ -0.0036 $\pm 0.0036$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15 $1.4 \pm 1.6$ $0.66 \pm 0.63$ $-1 \pm 5.6$ $1 \pm 1.1$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.19$ $0.15$ $0.0145 \pm 0.0008$ $0.20 \pm 0.02$ $-0.0182 \pm$ $0.0008$ $1.27 \pm 0.10$ $-0.0014 \pm$ $0.0004$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 6 645 nm 0.10 0.15 0.023 ± 0.001 0.20 ± 0.02 -0.019 ± 0.001 0.90 ± 0.07 -0.0006 ± 0.0002	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15 -0.0127 ± 0.0009 0.37 ± 0.04 0.0113 ± 0.0010 1.6 ± 0.2 0.0003 ± 0.0008	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.12$ $0.15$ $-0.02 \pm 0.01$ $0.5 \pm 0.1$ $0.02 \pm 0.01$ $1.0 \pm 0.3$ $0.0008 \pm 0.0003$
r3DTV         ex495         t0         IRF         A1         T1         A2         T2         A3         T3    P3DTV ex450        t0         IRF         A1         T1         A2         T2         A3         T3	Principle $0.12 \pm 0.01$ $0.15$ $0.146 \pm 0.002$ $1.64 \pm 0.05$ $0.004 \pm 0.002$ $60 \pm 70$ Principle         Component 1 $0.232 \pm 0.006$ $0.15$ -0.124 $\pm 0.004$ $1.8 \pm 0.1$ -0.0036 $\pm 0.0036$ 110 $\pm 420$	Principle Component 2 $0.098 \pm 0.004$ 0.15 $1.0 \pm 0.1$ $0.16 \pm 0.02$ $0.4 \pm 0.1$ $1.0 \pm 0.4$ $-0.3 \pm 0.2$ $2.6 \pm 0.6$ Principle Component 2 $0.027 \pm 0.011$ 0.15 $1.4 \pm 1.6$ $0.66 \pm 0.63$ $-1 \pm 5.6$ $1 \pm 1.1$	$\frac{585 \text{ nm}}{0.13}$ $0.13$ $0.15$ $0.01 \pm 0.02$ $0.7 \pm 0.5$ $-0.029 \pm 0.026$ $1.2 \pm 0.4$ $-0.0013 \pm$ $0.0004$ $17.0 \pm 6$ $\frac{588 \text{ nm}}{0.19}$ $0.19$ $0.15$ $0.0145 \pm 0.0008$ $0.20 \pm 0.02$ $-0.0182 \pm$ $0.0008$ $1.27 \pm 0.10$ $-0.0014 \pm$ $0.0004$ $17 \pm 7$	635  nm 0.09 0.15 0.013 ± 0.008 0.5 ± 0.2 -0.033 ± 0.009 1.1 ± 0.1 -0.0011 ± 0.0002 26 ± 6 6 645 nm 0.10 0.15 0.023 ± 0.001 0.20 ± 0.02 -0.019 ± 0.001 0.90 ± 0.07 -0.0006 ± 0.0002 50 ± 38	676  nm 0.27 0.15 -0.0069 ± 0.0003 0.2 ± 0.02 0.0078 ± 0.0001 2.7 ± 0.1 0.0004 ± 0.0001 31 ± 18 686 nm 0.09 0.15 -0.0127 ± 0.0009 0.37 ± 0.04 0.0113 ± 0.0010 1.6 ± 0.2 0.0003 ± 0.0008 22 ± 8	725 nm $0.15$ $0.15$ $-0.012 \pm 0.001$ $0.2 \pm 0.03$ $0.0096 \pm 0.0005$ $1.4 \pm 0.1$ $0.0006 \pm 0.0002$ $25 \pm 13$ 725 nm $0.12$ $0.12$ $0.15$ $-0.02 \pm 0.01$ $0.5 \pm 0.1$ $0.02 \pm 0.01$ $1.0 \pm 0.3$ $0.0008 \pm 0.0003$ $21 \pm 12$

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

P3DSV ex650	Principle Component 1	Principle Component 2	619 nm	670 nm	703 nm	735 nm
to	$0.047\pm0.005$	$0.257\pm0.008$	$0.262\pm0.007$	$0.24\pm0.01$	$0.07\pm0.01$	$0.281 \pm 0.005$
IRF	0.15	0.15	0.15	0.15	0.15	0.15
$A_1$	$1.0 \pm 0.2$				$-0.033 \pm 0.004$	
$ au_1$	$0.7 \pm 0.2$				$0.60\pm0.07$	
$A_2$	$-0.6 \pm 0.2$	$-0.147 \pm 0.003$	$-0.071 \pm 0.001$	$-0.064 \pm 0.001$	$0.025\pm0.005$	$0.0389 \pm 0.0005$
$ au_2$	$1.8 \pm 0.4$		$1.21\pm0.05$	$1.05\pm0.06$	$2.0 \pm 2.0$	$1.58\pm0.05$
<b>A</b> 3	$0.014\pm0.008$		$-0.002 \pm 0.001$	$-0.002 \pm 0.001$	$-0.0003 \pm 0.0003$	$0.0011 \pm 0.0006$
τ3	$43 \pm 36$		$30 \pm 25$	$37 \pm 36$	$94 \pm 220$	$42 \pm 35$
P3DSV	Principle	Principle	550 nm	604 nm	703 nm	736 nm
P3DSV ex455nm	Principle Component 1	Principle Component 2	550 nm	604 nm	703 nm	736 nm
P3DSV ex455nm t <sub>0</sub>	Principle Component 1 0.22	Principle Component 2 -0.01	550 nm 0.206 ± 0.003	604  nm $0.235 \pm 0.006$	703 nm 0.02	736 nm 0.06
P3DSV ex455nm to IRF	Principle Component 1 0.22 0.15	Principle Component 2 -0.01 0.15	550 nm 0.206 ± 0.003 0.15	$604 \text{ nm} \\ 0.235 \pm 0.006 \\ 0.15$	703 nm 0.02 0.15	736 nm 0.06 0.15
P3DSV ex455nm to IRF A1	Principle Component 1 0.22 0.15	Principle Component 2 -0.01 0.15	$550 \text{ nm}$ $0.206 \pm 0.003$ $0.15$ $-0.007 \pm 0.001$	<b>604 nm</b> 0.235 ± 0.006 0.15	703 nm 0.02 0.15 -0.009 ± 0.001	736 nm 0.06 0.15 -0.017 ± 0.001
P3DSV ex455nm t0 IRF A1 τ1	Principle Component 1 0.22 0.15	Principle Component 2 -0.01 0.15	$550 \text{ nm}$ $0.206 \pm 0.003$ $0.15$ $-0.007 \pm 0.001$ $1.2 \pm 0.2$	<b>604 nm</b> 0.235 ± 0.006 0.15	703 nm           0.02           0.15           -0.009 ± 0.001           0.49 ± 0.08	$\begin{array}{c} \textbf{736 nm} \\ 0.06 \\ 0.15 \\ \textbf{-0.017} \pm 0.001 \\ 0.29 \pm 0.04 \end{array}$
P3DSV ex455nm t0 IRF A1 τ1 A2	$\begin{array}{c} \mbox{Principle}\\ \hline \mbox{Component 1}\\ 0.22\\ 0.15\\ \end{array}$	Principle Component 2 -0.01 0.15 -0.51 ± 0.05	$550 \text{ nm}$ $0.206 \pm 0.003$ $0.15$ $-0.007 \pm 0.001$ $1.2 \pm 0.2$ $-0.003 \pm 0.001$	604  nm 0.235 ± 0.006 0.15 -0.0138 ± 0.0004	$\begin{array}{c} \textbf{703 nm} \\ 0.02 \\ 0.15 \\ -0.009 \pm 0.001 \\ 0.49 \pm 0.08 \\ 0.007 \pm 0.001 \end{array}$	$\begin{array}{c} \textbf{736 nm} \\ 0.06 \\ 0.15 \\ \textbf{-0.017} \pm 0.001 \\ 0.29 \pm 0.04 \\ 0.015 \pm 0.001 \end{array}$
P3DSV ex455nm to IRF A1 τ1 A2 τ2	$\begin{tabular}{ c c c c } \hline Principle \\ \hline Component 1 \\ \hline 0.22 \\ 0.15 \\ \hline 0.135 \pm 0.005 \\ \hline 1.6 \pm 0.1 \\ \hline \end{tabular}$	$\frac{\text{Principle}}{\text{Component 2}} \\ -0.01 \\ 0.15 \\ -0.51 \pm 0.05 \\ 0.6 \pm 0.1 \\ \end{array}$	$550 \text{ nm}$ $0.206 \pm 0.003$ $0.15$ $-0.007 \pm 0.001$ $1.2 \pm 0.2$ $-0.003 \pm 0.001$ $4.7 \pm 2.0$	$604 \text{ nm}$ $0.235 \pm 0.006$ $0.15$ $-0.0138 \pm$ $0.0004$ $1.7 \pm 0.1$	$\begin{array}{c} \textbf{703 nm} \\ 0.02 \\ 0.15 \\ \textbf{-0.009 \pm 0.001} \\ 0.49 \pm 0.08 \\ 0.007 \pm 0.001 \\ 2.1 \pm 0.4 \end{array}$	$\begin{array}{c} \textbf{736 nm} \\ \hline 0.06 \\ 0.15 \\ \textbf{-0.017 \pm 0.001} \\ 0.29 \pm 0.04 \\ 0.015 \pm 0.001 \\ 1.4 \pm 0.2 \end{array}$
P3DSV ex455nm to IRF A1 τ1 A2 τ2 A3	$\begin{array}{c} \mbox{Principle} \\ \hline \mbox{Component 1} \\ 0.22 \\ 0.15 \\ \hline \\ 0.135 \pm 0.005 \\ 1.6 \pm 0.1 \\ 0.007 \pm 0.005 \\ \end{array}$	$\begin{array}{c} \text{Principle} \\ \text{Component 2} \\ \hline -0.01 \\ 0.15 \\ \hline \\ -0.51 \pm 0.05 \\ \hline \\ 0.6 \pm 0.1 \\ 0.21 \pm 0.05 \end{array}$	$550 \text{ nm}$ $0.206 \pm 0.003$ $0.15$ $-0.007 \pm 0.001$ $1.2 \pm 0.2$ $-0.003 \pm 0.001$ $4.7 \pm 2.0$ $-0.0005 \pm 0.0003$	$\begin{array}{c} \textbf{604 nm} \\ \hline 0.235 \pm 0.006 \\ 0.15 \\ \hline \\ 0.0004 \\ 1.7 \pm 0.1 \\ -0.0002 \pm \\ 0.0004 \\ \hline \end{array}$	$\begin{array}{c} \textbf{703 nm} \\ 0.02 \\ 0.15 \\ \textbf{-0.009 \pm 0.001} \\ 0.49 \pm 0.08 \\ 0.007 \pm 0.001 \\ 2.1 \pm 0.4 \\ 0.0010 \pm 0.0002 \end{array}$	736 nm $0.06$ $0.15$ $-0.017 \pm 0.001$ $0.29 \pm 0.04$ $0.015 \pm 0.001$ $1.4 \pm 0.2$ $0.0017 \pm 0.0002$



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.

P3DTV ex 652	900	1100	1200
to	0.24	0.30	0.29
IRF	0.15	0.15	0.15
$\mathbf{A}_{1}$	$0.0392 \pm 0.0005$	$0.0302 \pm 0.0004$	$0.0182 \pm 0.0002$
$ au_1$	$\textbf{0.97} \pm \textbf{0.03}$	$\textbf{0.94} \pm \textbf{0.03}$	$\textbf{0.84} \pm \textbf{0.03}$
$A_2$	$0.0009 \pm 0.0004$	$0.0002 \pm 0.0002$	$0.0006 \pm 0.0002$
$ au_2$	$70\pm120$	$700\pm24000$	$32\pm25$

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

PSV	900.53	1101.31	1200.39
to	0.24	0.29	0.28
IRF	0.15	0.15	0.15
A <sub>1</sub>	$0.0037 \pm 0.0009$	$\textbf{0.110} \pm \textbf{0.003}$	$\textbf{0.070} \pm \textbf{0.002}$
τ1	$19\pm15$	$\textbf{0.45} \pm \textbf{0.02}$	$\textbf{0.43} \pm \textbf{0.02}$
A <sub>2</sub>	$\textbf{0.123} \pm \textbf{0.002}$	$\textbf{0.0007} \pm \textbf{0.0007}$	$0.0009 \pm 0.0005$
$ au_2$	$\textbf{0.49} \pm \textbf{0.02}$	$50\pm240$	$22\pm 45$