Supporting Information

Concentration-Dependent Aggregation of Methylene Blue Acting as a Photoredox Catalyst

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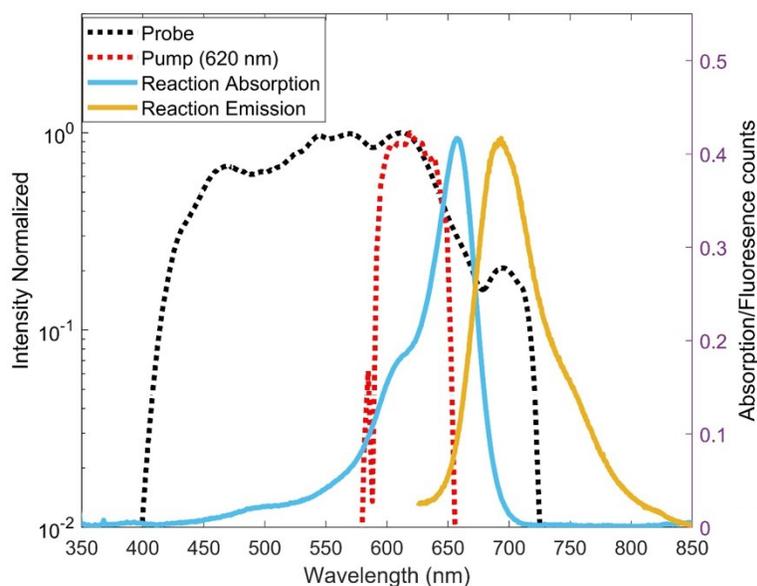
Steady-State Spectra

Figure S1. Normalized laser spectra for the pump and the probe as well as absorption and fluorescence spectra of 0.7 M methylene blue in the presence of DIPEA (0.3 M) and phenylboronic acid (0.06M) in a 1:4 water:acetonitrile solution.

Figure S1 presents the normalized laser spectrum for the pump and the probe used for the transient absorption measurements presented here. The broadband probe spectra was generated through the optical Kerr effect by slowly focusing (f=2 m) approximately 2 W of 800 nm light (2 mJ, 100 fs and 1 kHz repetition rate via Coherent Libra regenerative amplifier) into an argon medium (sapphire entrance/exit ports and argon gas at 15 psi). The chirp of the broadband probe was compensated for using paired chirped mirrors (Laser Quantum, DCM9). The pump pulse was also generated from the broadband source and was set to a central wavelength of 620 nm with a full width half max of 50 nm using an acousto-optic modulator (DAZZLER). The center wavelength was chosen to be resonant with both the methylene blue monomer and the dimer. Absorption and fluorescence spectra for methylene blue in the presence of DIPEA (0.3 M) and phenylboronic acid (0.06 M) are also presented in Figure S1. The absorption trace was collected using a 100 µm pathlength and the fluorescence was collected using a 2 mm pathlength H-cell.
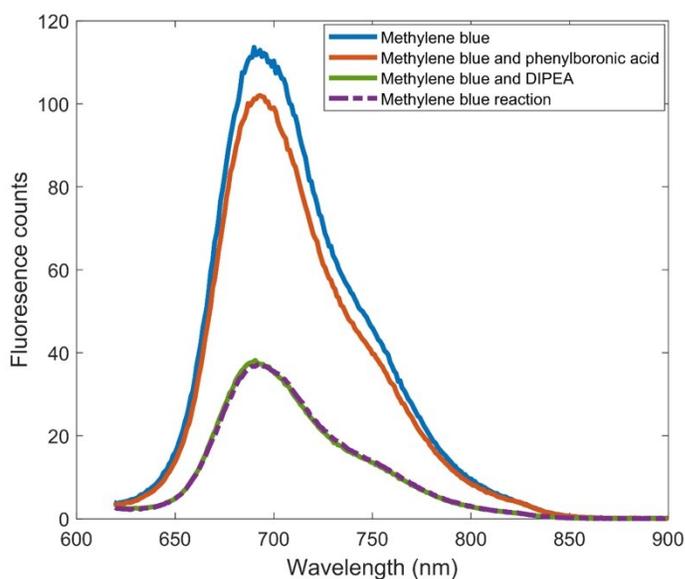
Figure S2. Fluorescence spectra for methylene blue at high concentration (0.7 mM) alone (blue), in the presence of phenylboronic acid (0.06 M, red), in the presence of DIPEA (0.3 M, green), and in the presence of phenylboronic acid (0.06 M) and DIPEA (0.3 M) (purple dashed) in a 1:4 water:acetonitrile solution.

A 2 mm path length cuvette (quartz, H-cell) was used for fluorescence measurements collected with a Cary Eclipse (Agilent) spectrophotometer presented in Figure S2. In the presence of phenylboronic acid there is a slight decrease in overall fluorescence, and for DIPEA and the full reaction mixture (DIPEA and phenylboronic acid) the fluorescence is quenched by approximately a factor of three.
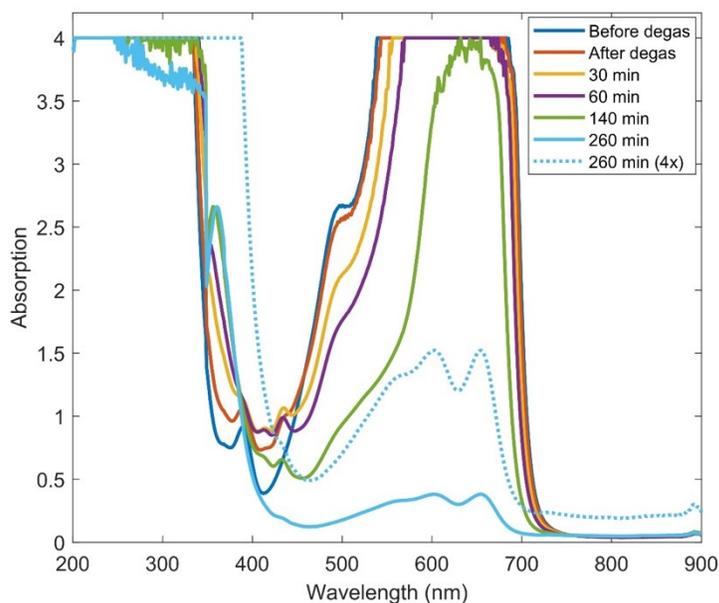
Figure S3. Steady state absorption measurements of methylene blue (0.7 mM) in an oxygen-free environment under laser exposure (620 nm) in a 1:4 water:acetonitrile solution. Recorded in a 1 cm pathlength cuvette. The times listed in the legend correspond to amount of time the cuvette has been exposed to laser light after an initial degas via freeze-pump-thaw. Final trace is 4x the 260 min trace to show the absorption of the dimer at 608 nm is similar to that of the monomer at 658 nm.

Freeze pump thaw was used to degas a mixture of methylene blue (0.7 mM). The degassed mixture was transferred via Schlenk line to a 1 cm cuvette before being placed after an optical parametric amplifier (TOPAS, Coherent) set to 620 nm for time periods listed in the legend of Figure S3. After each exposure time, the absorption was recorded. The monomer is consumed rapidly as the reaction proceeds as shown by the drop in absorption near 658 nm, generating the colorless leuco-methylene blue. Since there is no oxygen present, leuco-methylene blue cannot be oxidized back to the methylene blue cation. Additionally, the decrease in the absorption of the monomer is greater than for the dimer.

Transient Absorption Spectra of Methylene Blue with DIPEA

Transient absorption spectra were collected for methylene blue (0.7 mM) in the presence of DIPEA (0.3 M). The data for these measurements is presented in Figures S4-S6.
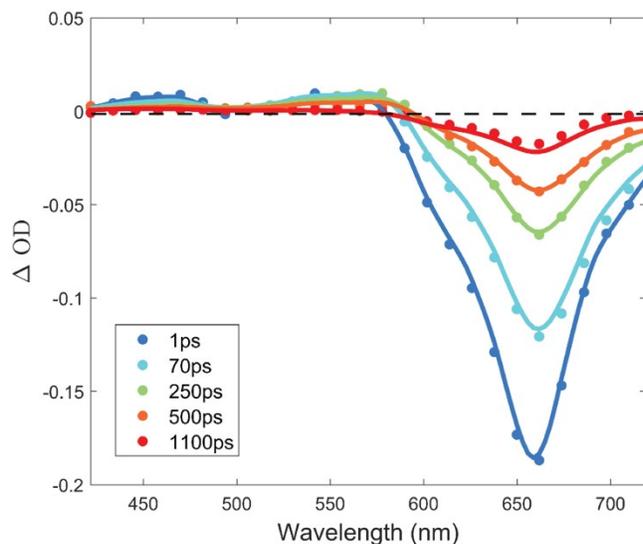

Figure S4. Transient absorption spectra of methylene blue (0.7 mM) in the presence of DIPEA (0.3 M) in a 1:4 water:acetonitrile solution. Points are data and lines are fits generated using a custom target analysis developed using the KiMoPack python global analysis package.[1]

The transient absorption data of methylene blue with DIPEA shown in Figure S4 has similar features to methylene blue alone including the ground state bleach at 665 nm, an excited state absorption near 581 nm and an excited state absorption near 455 nm. The decay is faster than methylene blue alone due to quenching by the tertiary amine, DIPEA. This faster decay is seen in any solution that contains DIPEA including the reaction mixture with DIPEA and phenyl boronic acid. In Figure S5, we see the same trends found in Figure 3 (b), but with a faster decay due to amine quenching. Figure S6 shows the species associated spectra (SAS) for the global analysis model. The model is the same as used for methylene blue alone at high concentration, where SAS1-SAS3 are monomer contributions and SAS4 and SAS5 are dimer contributions. SAS1 through SAS3 primarily include the negative contribution associated with the ground state bleach of the monomer and with the relaxation of the monomer through the singlet state. SAS3, associated with the triplet decay, has a peak near the excited state absorption maxima at 581 nm. The two dimer contributions show a stronger shoulder near 611 nm. SAS1, the vibrational decay of the excited singlet state, is fit to 4.3±0.6 ps, SAS2, the singlet decay and the intersystem crossing from the monomer singlet to the monomer triplet is fit to 424±43 ps and 210±29 ps respectively, while SAS3 is the long triplet decay of the monomer set to 1 microsecond. In the decay pathway of the dimer, SAS4 is the vibrational relaxation of the upper optically accessible state, set to 865±65 fs, while the final decay to the ground state is 6.3±0.7 ps and associated with SAS5.
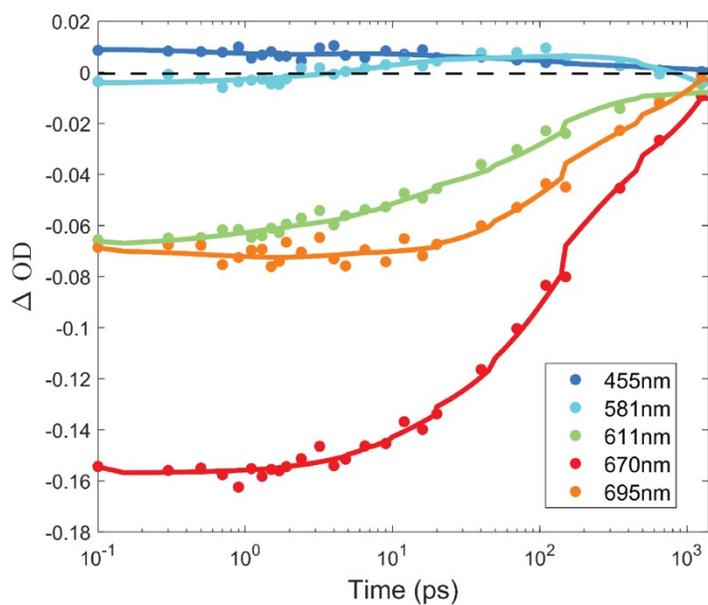
Figure S5. Transient absorption measurements methylene blue (0.7 mM) in the presence of DIPEA (0.3 M) in a 1:4 water:acetonitrile solution at specific wavelengths. 455 nm and 581 nm monitor the amplitudes of the excited state absorptions, 611 nm monitors the dimer related shoulder, 670 nm monitors the ground state bleach.
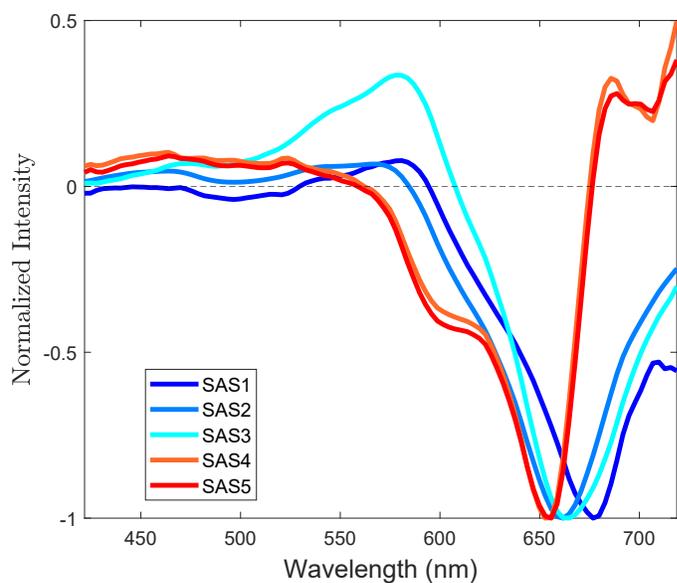
Figure S6. Species associated spectra for the kinetic scheme used to fit the transient absorption data for methylene blue (0.7 mM) in the presence of DIPEA (0.3 M) in a 1:4 water:acetonitrile solution. It utilizes the same decay scheme as methylene blue alone at high concentration, found in Figure 3.

Transient Absorption Spectra of Methylene Blue with Phenylboronic Acid

Transient absorption spectra of methylene blue (0.7 mM) in the presence of phenylboronic acid (0.06 M) is presented in Figures S7-S9. Similar to the data for methylene blue alone, we observe a ground state bleach at 665 nm, an excited state absorption near 581 nm and an excited state absorption near 455 nm. The recovery of the bleach is the same as for methylene blue alone. In Figure S7, we see similar trends to that found in Figure 3 (b). Figure S8 shows the SAS for the global analysis model, which is the same as used for methylene blue alone at high concentration where SAS1-SAS3 are monomer contributions and SAS4 and SAS5 are dimer contributions. SAS1 through SAS3 primarily include the negative contribution associated with the ground state bleach of the monomer. The relaxation through the singlet state of the monomer, SAS1, is red shifted as seen in Figure S4. SAS3, the triplet decay, peaks near the excited state absorption maxima at 581 nm. The two dimer contributions show a stronger shoulder near the region of dimer absorption at 611 nm. SAS1, the vibrational decay of the excited singlet state, is fit to 9.3±1.2 ps, SAS2, the singlet decay and the intersystem crossing from the singlet to triplet states of the monomer is fit to 862±81 ps and 155±24 ps respectively, while SAS3 is the long triplet decay of the monomer set to 1 microsecond. For the relaxation of the dimer, SAS4 is the vibrational relaxation of upper optically accessible state, 800±158 fs, while the final decay of the dimer to the ground state is 13±1.7 ps and associated with SAS5.
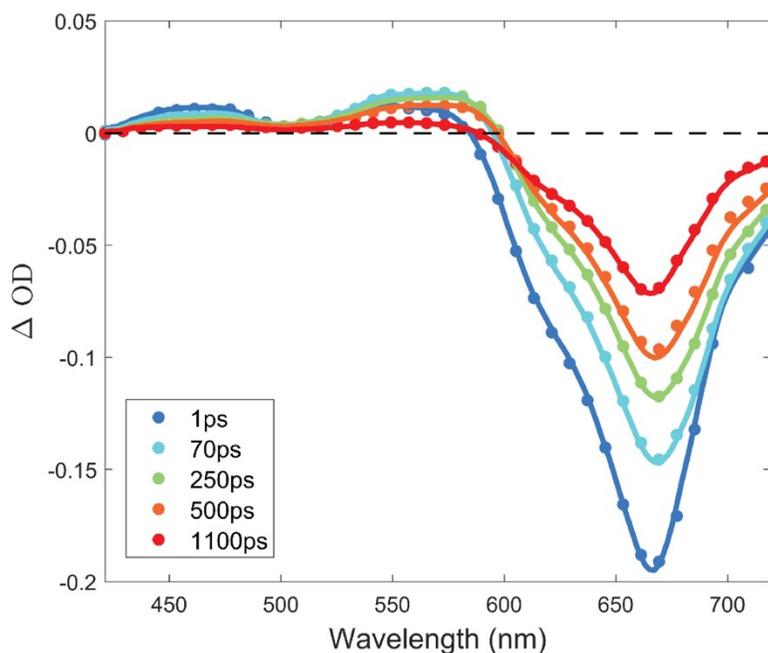

Figure S7. Transient absorption spectra of methylene blue (0.7 mM) with phenylboronic acid (0.06 M) in a 1:4 water:acetonitrile solution. Points are data and lines are fits generated via the KiMoPack[1] global analysis package.
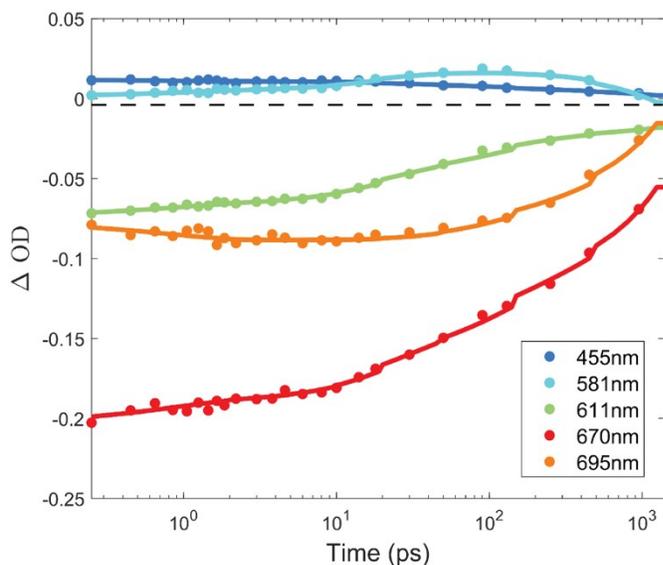
Figure S8. Transient absorption data of methylene blue (0.7 mM) in the presence of phenylboronic acid (0.06 M) with associated fits at specific wavelengths. 455 nm and 581 nm monitor the amplitudes of the excited state absorptions, 611 nm monitors the dimer related shoulder, 670 monitors the ground state bleach.
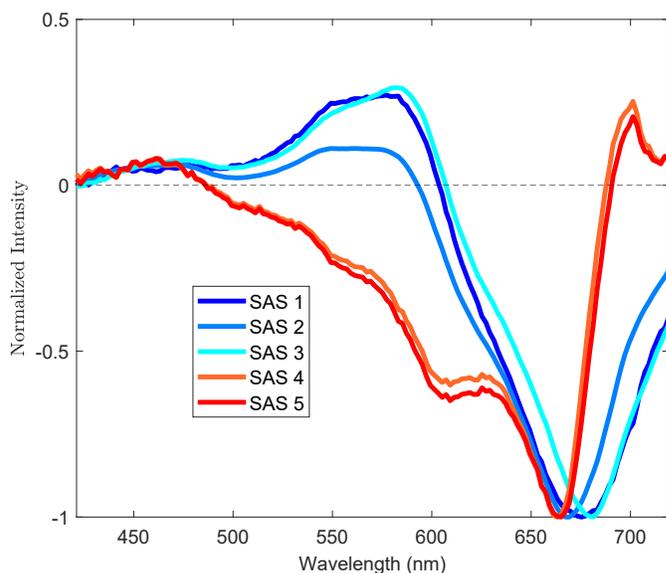

Figure S9. Species associated spectra for the global target analysis model used to fit the transient absorption data for methylene blue (0.7 mM) in the presence of phenylboronic acid (0.06 M). It utilizes the same decay scheme as methylene blue alone at high concentration, found in Figure 3.

Transient Absorption Spectra for Low Concentration Methylene Blue in Water-Acetonitrile Solution
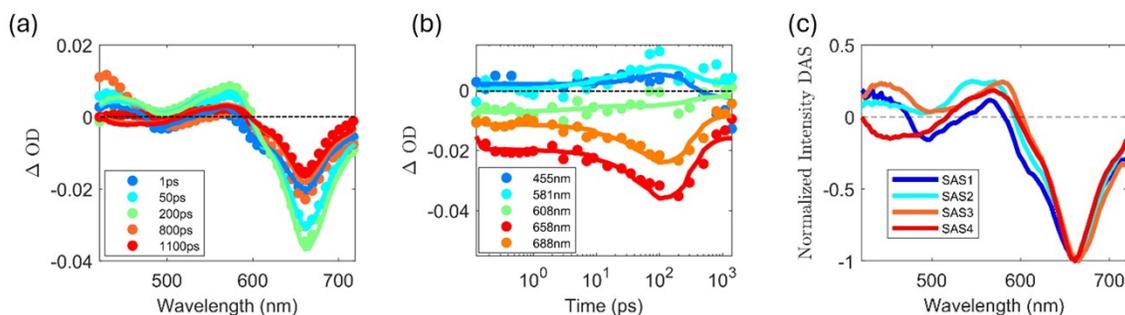

Figure S10. Transient absorption data and global target analysis fits for lower concentration methylene blue (0.035 mM) in a 1:4 water:acetonitrile solution. (a) Spectrally-resolved transient absorption traces at different delay times. The points are data and the lines are fits generated from global analysis using a target analysis model. (b) Time-resolved transient absorption traces at selected wavelengths presented on a semi-log scale showing the dynamics in different spectral regions. (c) SAS spectra generated from the global target analysis for the data presented in (a) and (b).

Figures S10 presents transient absorption data and fits from global target analysis generated using KiMoPack[1] for methylene blue alone in an 4:1 v:v acetonitrile:water solution at low concentration (0.035 mM). The primary features in the transient absorptions presented in Figure S10 (a) are the bleach centered at 658 nm and the excited state absorptions at 581 nm and 455 nm. The bleach is narrower as compared to what we have seen with the high concentration methylene blue data, this is likely due to the absence of signal contributions from the dimer centered at 608 nm. Figure S10 (b) shows the corresponding time-resolved transient traces at specific wavelengths. There is significantly less signal at 608 nm as compared to high concentration. This is due to the lack of contributions from the dimer. The signal that is present is associated with overlap with the ground state bleach of the monomer.

The target analysis model used for the global analysis of the low concentration transient absorption data is the same as presented in Figure 3 with one additional decay. As shown in Figure S10 (c), SAS1 has a timescale of 9.3±1.2 ps and is associated with vibrational relaxation on the excited singlet state of the monomer. From here it decays with a timescale of 211±42 ps associated with SAS2, which is on the same order of magnitude as the decay time previously found to be associated with polarization anisotropy in this system.[2] The vibrationally relaxed singlet excited state decays in parallel either to its ground state or undergoes intersystem crossing to the monomer triplet corresponding to SAS3 of 866±126 ps and 155±34 ps, respectively. The final triplet decay back to the ground state, associated with SAS4, is fixed at 1 μs.
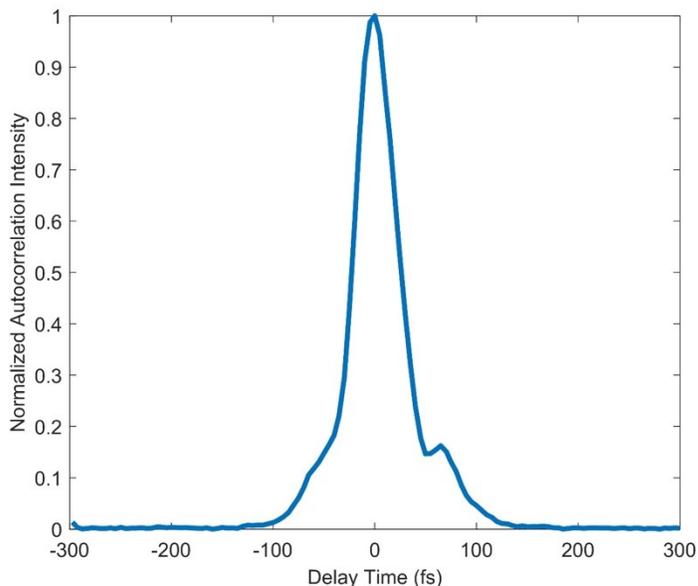
Pulse Characterization

Figure S11. Temporal pulse width of 35 fs recorded via cross-correlation measurement with BBO crystal.

The temporal pulse width was recorded by cross correlation measurement via a 1 mm BBO detected via a silicon photodiode (Thorlabs-Det10A2) connected to a lock-in amplifier. The measured full width half max of the cross-correlation was approximately 50 fs resulting in a 35 fs pulse width assuming a Gaussian pulse.

1.   C. Müller, T. Pascher, A. Eriksson, P. Chabera and J. Uhlig, *The Journal of Physical Chemistry A*, 2022, **126**, 4087-4099.
2.   J. C. Dean, D. G. Oblinsky, S. R. Rather and G. D. Scholes, *The Journal of Physical Chemistry B*, 2016, **120**, 440-454.