Supplementary Information for

Substituent Effect on the MLCT Excited State Dynamics of Cu(I) Complexes Studied by Femtosecond Time-Resolved Absorption and Observation of Coherent Nuclear Wavepacket Motion

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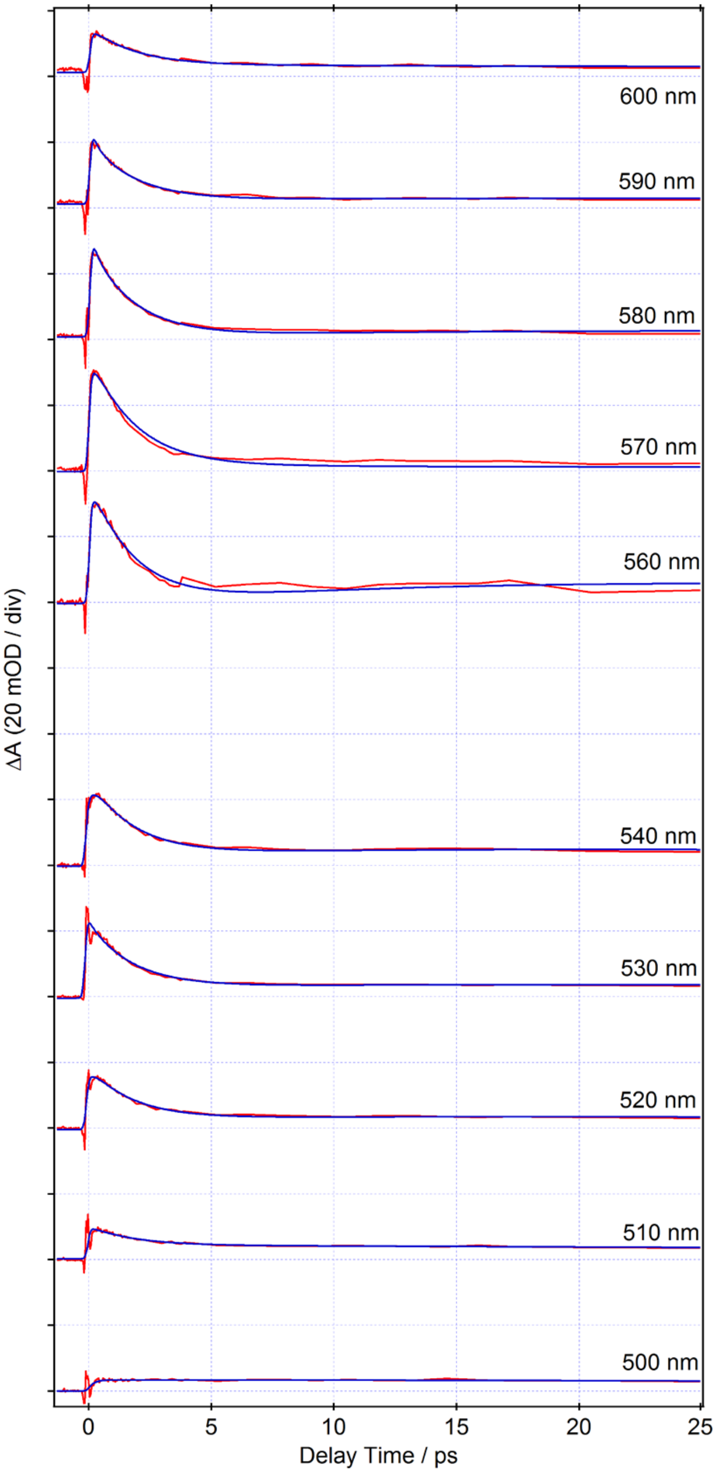
Contents

(1) Global fitting of the time-resolved absorption signal of $[Cu(phen)_2]^+$ in dichloromethane.



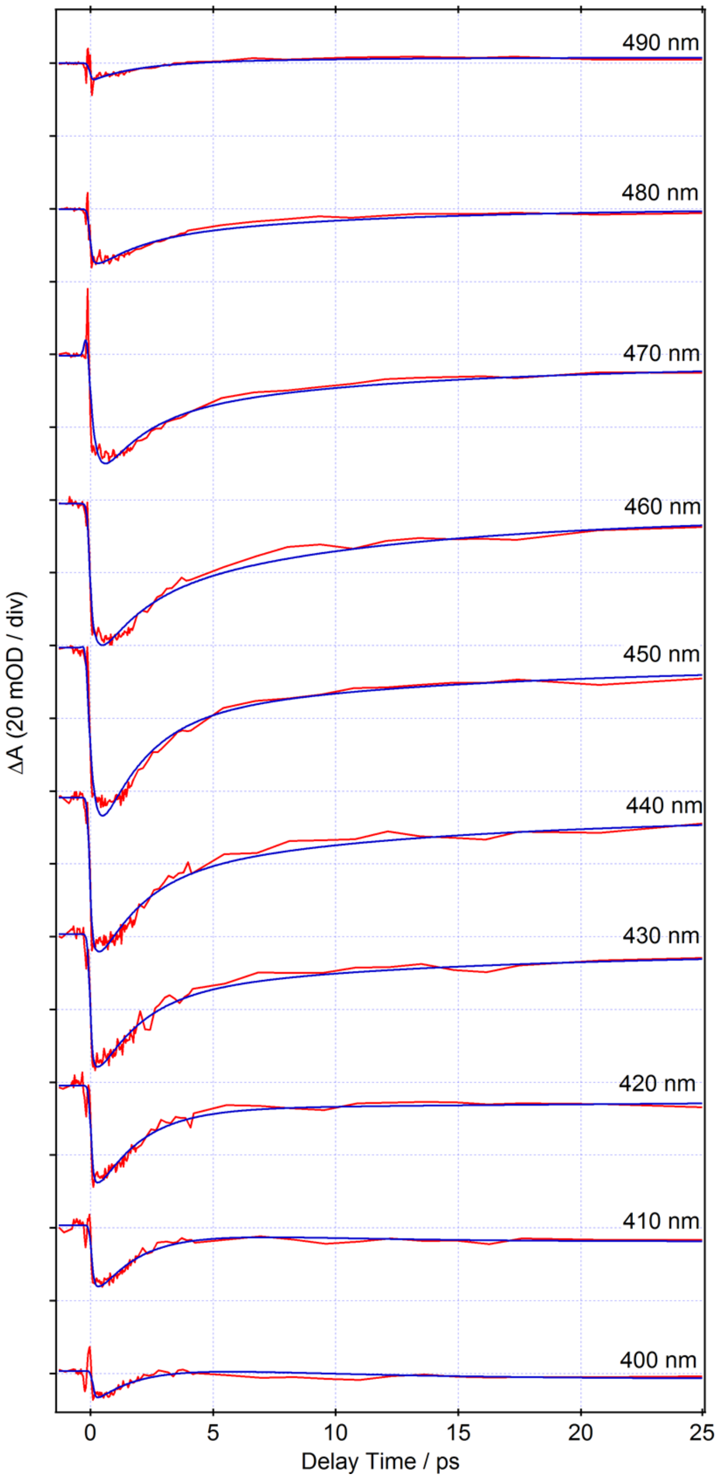


Figure S1. Global fitting of the time-resolved absorption signals of $[\mathrm{Cu(phen)_2}]^+$ in dichloromethane observed at various wavelengths. The experimental data and the best-fit curves are plotted in red and blue, respectively. (Pump 550 nm; 2×10^{-3} mol/dm^3)

(2) Time-resolved absorption data of [Cu(phen)$_2$]$^+$ in acetonitrile.

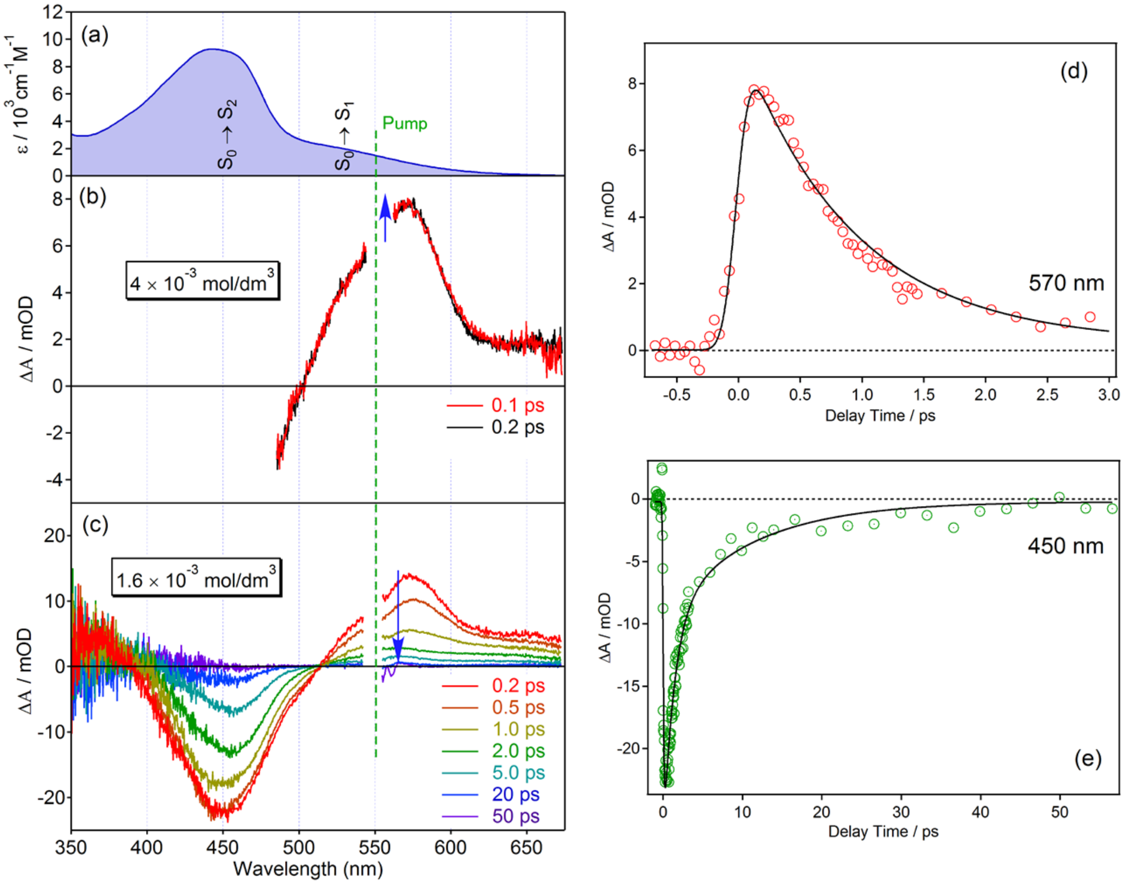
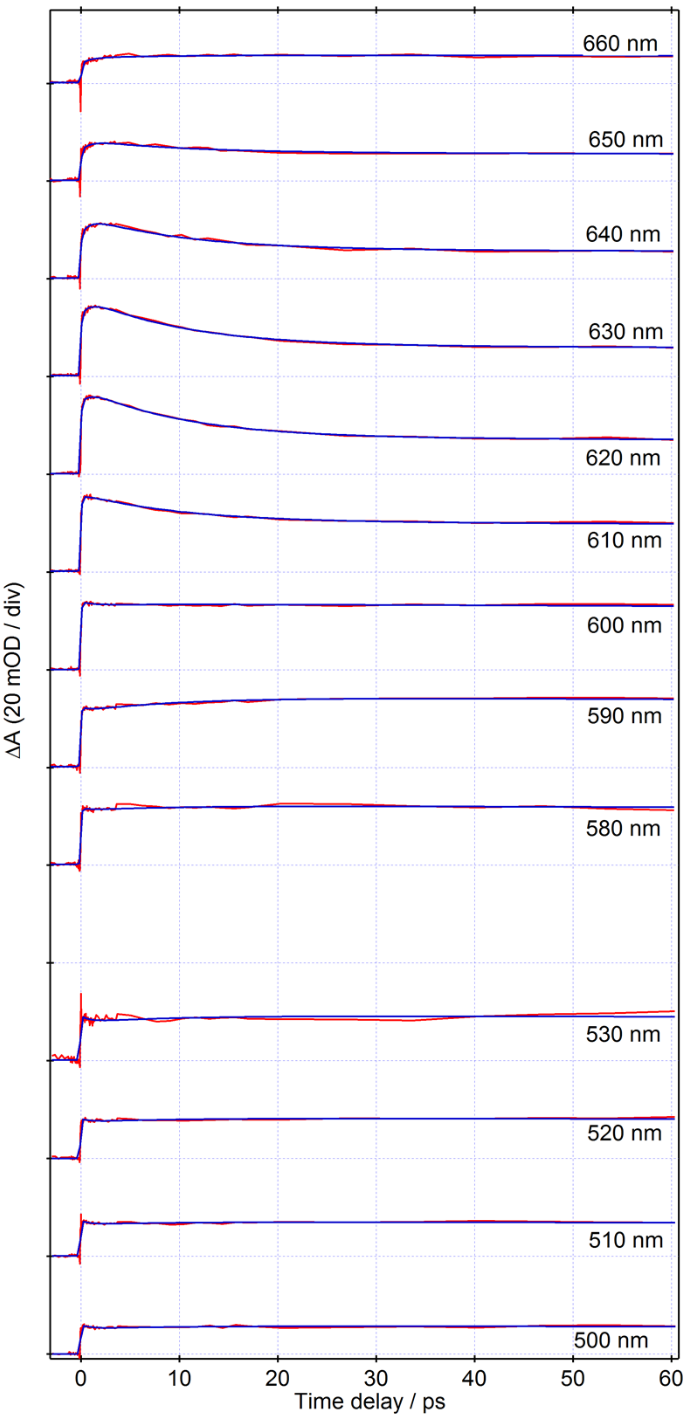


Figure S2. Steady-state and femtosecond time-resolved absorption data of [Cu(phen)$_2$]$^+$ in acetonitrile. (a) Steady-state absorption spectrum. (b) Time-resolved absorption spectra measured with 550-nm excitation at the delay times of 0.1 and 0.2 ps. In this experiment, the concentrated sample solution (4 × 10^{-3} mol/dm^3) was used to reduce coherent spikes observed around the time zero. This allowed us to properly measure the early-time dynamics of the excited-state absorption around 570 nm, but it was difficult to measure in the short wavelength region (350 – 480 nm) because the probe pulse was strongly absorbed by the sample. (c) Time-resolved absorption spectra of a more dilute solution (1.6 × 10^{-3} mol/dm^3) measured with 550-nm excitation in the delay time range of 0.2 – 50 ps. (d) Time-resolved absorption trace of the concentrated solution (4 × 10^{-3} mol/dm^3) observed at 570 nm (red circle) and the calculated best-fit curve (black curve). (e) Time-resolved absorption trace of a dilute solution (1.6 × 10^{-3} mol/dm^3) observed at 450 nm (green circle) and the calculated best-fit curve (black curve). We note that the bleaching recovery at 450 nm is well reproduced with the time constant of 1.4 ps but the time constant obtained at 570 nm is slightly shorter.

(3) Global fitting of the time-resolved absorption signal of $[Cu(dpphen)_2]^+$ in dichloromethane.



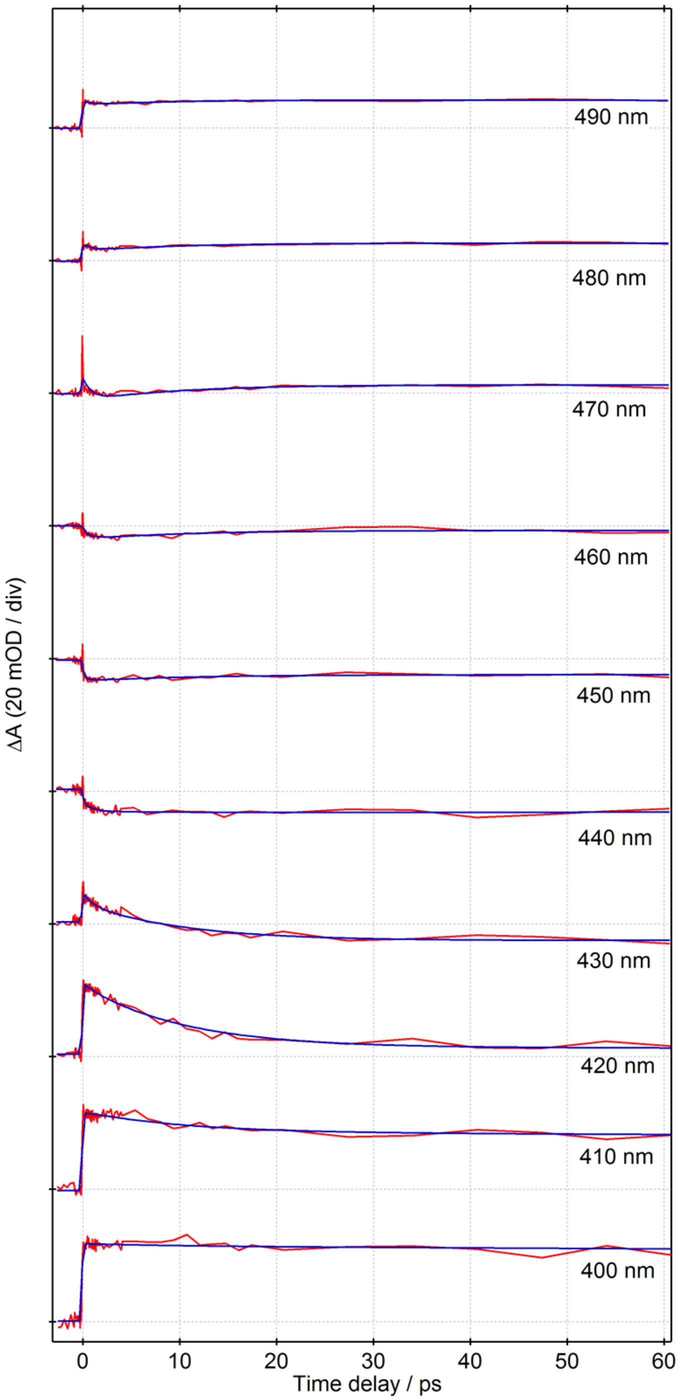


Figure S3. Global fitting of the time-resolved absorption signals of $[Cu(dpphen)_2]^+$ in dichloromethane observed at various wavelengths. The experimental data and the best-fit curves are plotted in red and blue, respectively. (Pump 550 nm; 2×10^{-3} mol/dm^3)

(4) Time-resolved absorption data of $[Cu(dpphen)_2]^+$ in acetonitrile.

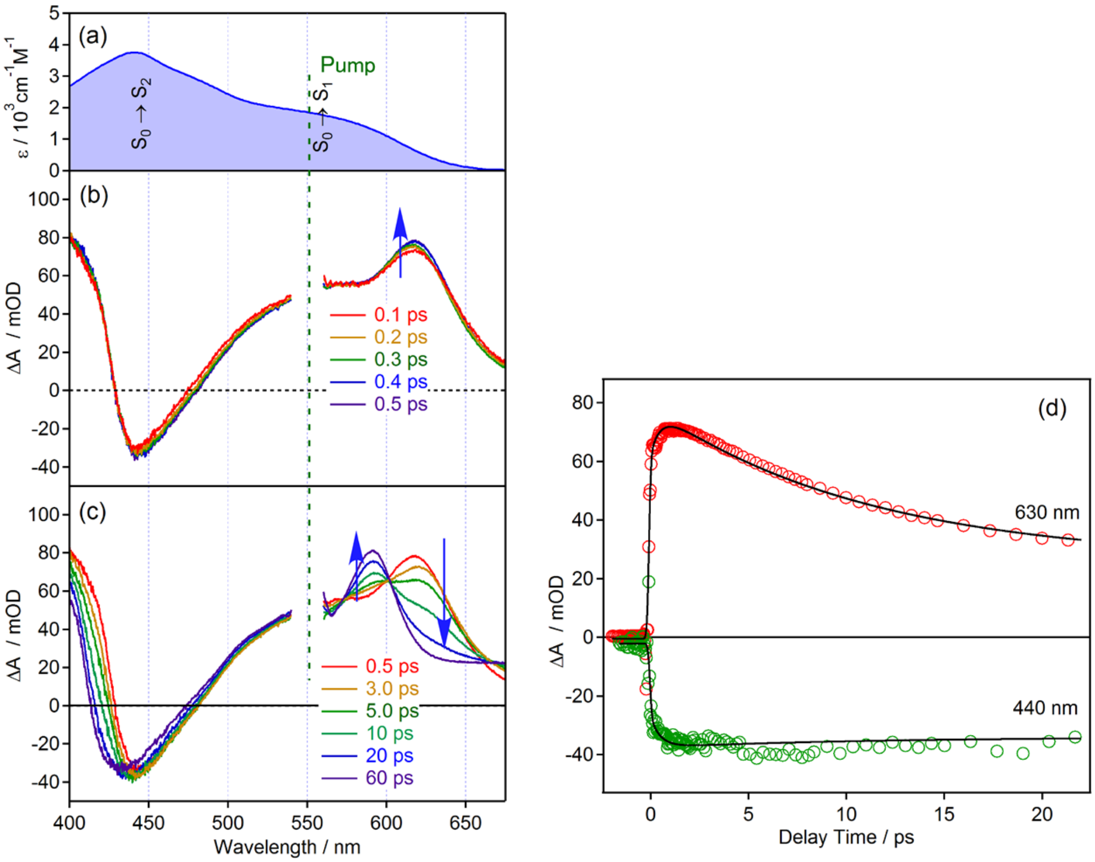


Figure S4. Steady-state and femtosecond time-resolved absorption data of $[Cu(dpphen)_2]^+$ in acetonitrile. (a) Steady-state absorption spectrum. (b) Time-resolved absorption spectra of a 2×10^{-3} mol/dm^3 solution measured with 550-nm excitation in the delay time range of 0.1 – 0.5 ps. (c) Time-resolved absorption spectra of a 2×10^{-3} mol/dm^3 solution measured with 550-nm excitation in the delay time range of 0.5 – 60 ps. (d) Time-resolved absorption traces observed at 440 nm (green circle) and 630 nm (red circle), shown with the calculated best-fit curve for each signal (black curve).

(5) Procedure of extracting the oscillatory component of the S_1 state of $[Cu(phen)_2]^+$ in dichloromethane.

The oscillatory signal observed in dichloromethane involves substantial contributions due to the solvent bands at 286 cm^{-1} and 700 cm^{-1}, in addition to those due to the S_1 state of $[Cu(phen)_2]^+$. We removed the solvent contributions and obtained the oscillatory component purely due to the S_1 state by the following procedure described below.

First, the oscillatory signal (Figure S5(a), red), which is obtained by subtracting the population component from the raw pump-probe trace, was multiplied with a sine-type window function (Figure S5(b), green) to suppress the spiky features around the time zero, and then it was converted into the frequency space by Fourier transformation (FT). In the resultant FT magnitude spectrum (Figure S5(c), black), the solvent bands are recognized as two predominant peaks at 286 cm^{-1} and 700 cm^{-1}. We fit a gaussian function to each of the solvent bands, as shown by blue dotted curves, and subtracted the best-fit calculated solvent bands from the FT magnitude spectrum. We left the phase of the FT spectrum intact. Then, the FT magnitude spectrum after subtraction of the solvent contributions (Figure S5(c), shaded in gray), together with the FT phase spectrum, was converted back to the time domain by inverse FT (Figure S5(b), blue). Lastly, the temporal trace obtained by the inverse FT was divided by the same window function to obtain the oscillation component that is free from the solvent contributions, as shown by the blue curve in Figure S5(a).

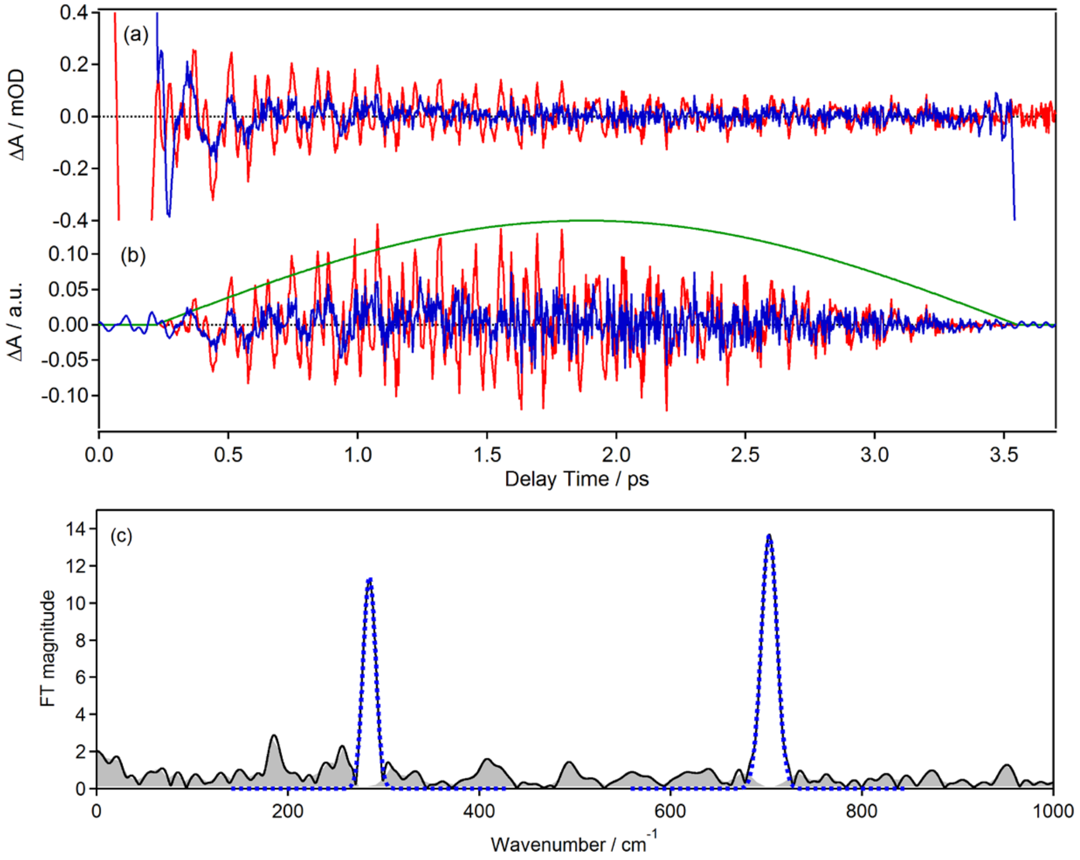


Figure S5. Procedure of extracting the oscillatory component due to the S_1 state of $[Cu(phen)_2]^+$ in dichloromethane. (a) Experimentally observed oscillatory signal, which is obtained by subtracting the population component from the raw pump-probe trace (red), and the oscillatory component after subtraction of the solvent contributions (blue). (b) Window function used in the analysis (green) and the oscillatory signal multiplied with the window function (red). Temporal trace obtained by the inverse Fourier transformation (blue). (c) Fourier transform magnitude spectra before (black curve) and after (shaded in gray) subtraction of the solvent bands. The best fit functions to the two solvent bands are shown by blue dotted curves.