

Supporting information

Study of the photo-switching of a Fe(II) chiral complex through linear and nonlinear ultrafast spectroscopy

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S1. Data analysis

S1.1 Fit of the time resolved absorption data for complexes in solution

To fit the data, we have numerically integrated the following set of differential equations for the fractional populations $P_i = N_i/N_T$ of the different excited states.

$$\begin{aligned}\frac{dP_1}{dt} &= \frac{\sigma_p I_{p0}}{\sqrt{\pi} \tau_p} \exp\left(-\frac{(t-t_0)^2}{\tau_p^2}\right) - \frac{P_1}{\tau_1}, \\ \frac{dP_2}{dt} &= \frac{P_1}{\tau_1} - \frac{P_2}{\tau_2}, \\ \frac{dP_3}{dt} &= \frac{P_2}{\tau_2} - \frac{P_3}{\tau_3},\end{aligned}$$

where I_{p0} , t_0 and τ_p are the intensity, the peak position of a Gaussian shaped pulse and the duration of the pump pulse, respectively. This set of partial differential equations is supplemented with the following boundary conditions: for $t=0$, $P_0=1$, $P_1=P_2=P_3=0$ with $P_0+P_1+P_2+P_3=1$. The initial integration was performed with a given pulse duration and an initial set of relaxation times. This makes it possible to compute the evolution of the fractional population N_i of the different state of the complexes. Since, at the used probe wavelength, our experiment is mainly sensitive to the change in the population of the excited states, we computed the quantity $S(t)=A*(P_1(t)+P_2(t)+P_3(t))$ where A is an adjustable parameter that modulate the change in the optical density and t is the delay between the pump and the probe pulses. However, if the relaxation time constants are such that $\tau_1 \ll \tau_2 \ll \tau_3$, it is mainly the longer relaxation time which will contribute to the quantity $S(t)$. Hence, since we have already shown that $\tau_1 \ll \tau_2 \ll \tau_3$ for the $[\text{Fe}(\text{phen})_3]^{2+}$ complexes in solution, once the pulse duration is fixed, one needs only to adjust the parameters A and τ_3 . To fit the data presented in Fig 1, we solved the set of differential equations with the following initial parameters $A=0.03$, $\tau_p=\tau_1=\tau_2=0.3$ ps and $\tau_3=1000$ ps. Then, the parameters A and τ_3 were optimized using a $\chi^{(2)}$ square minimizing procedure. The evolution of the fractional populations used to plot the fitted data in Fig. 1 is displayed in Fig. S1.

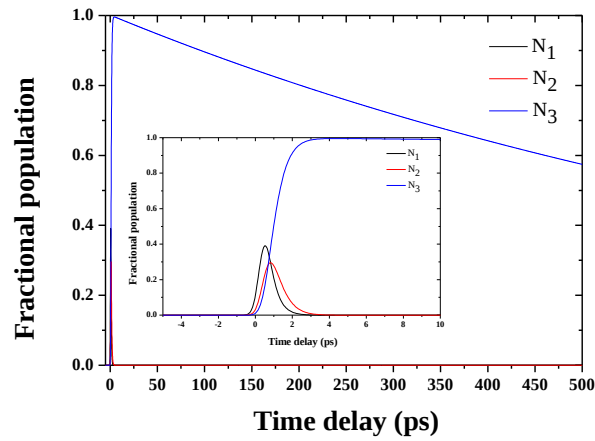


Figure S1 :

S2 Fit of the time resolved absorption data for complexes in the bulk

Using the procedure we just described, we first fitted the data displayed in Fig 2a adjusting the amplitude of A but keeping the same time constant used to fit the data presented in Fig. 1. As can be noticed in Fig. S2 (red solid line), the fit correctly reproduces the data on the long time scale, but a clear shift appears on the small time scale ($0 < \text{delay} < 50$ ps). To correct for this shift, we considered that the time constant τ_2 is also an adjustable parameters. The result of the optimized fit considering that the parameters A, τ_2 and τ_3 are adjustable is displayed on Fig. S2 (a) (blue solid line). As expected, the introduction of a new free parameter corrects for the discrepancy we had between the fitting curve and the experimental data. The evolution of the fractional populations used to plot the fitted data in Fig. 2a is displayed in Fig. S2b.

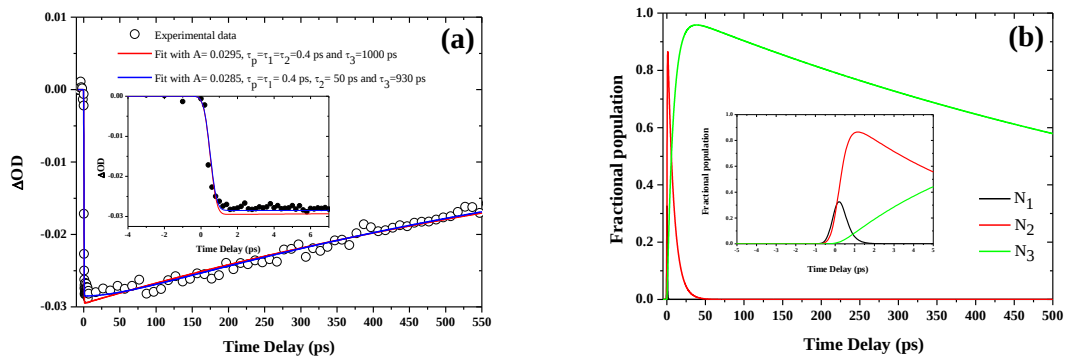


Figure S2 :

S3 Fit of the time resolved SHG data

Here also, we fitted the data integrating numerically a set of differential equations accounting for the evolution the fractional populations $P_i = N_i/N_T$ of the different excited states. But, according to our model and contrary to the TRA absorption, the TRSHG signal recorded by our experimental set-up writes:

$$S_{SHG}(t) = \sum_i A_i P_i.$$

This means we have much more parameters to play with. The procedure we used consisted in minimizing the numbers of parameters to adjust. Our experimental data clearly stresses that at least a set of two differential equations is needed. In other words, a mono-exponential decay cannot account for our experimental data. Therefore, we started considering the set of the following differential equations:

$$\begin{aligned} \frac{dP_1}{dt} &= \frac{\sigma_p I_{p0}}{\sqrt{\pi} \tau_p} \exp\left(-\frac{(t-t_0)^2}{\tau_p^2}\right) - \frac{P_1}{\tau_1'} \\ \frac{dP_2}{dt} &= \frac{P_1}{\tau_1'} - \frac{P_2}{\tau_2'} \end{aligned}$$

with the following boundary conditions: for $t=0$, $P_0=1$, $P_1=P_2=0$ with $P_0+P_1+P_2=1$.

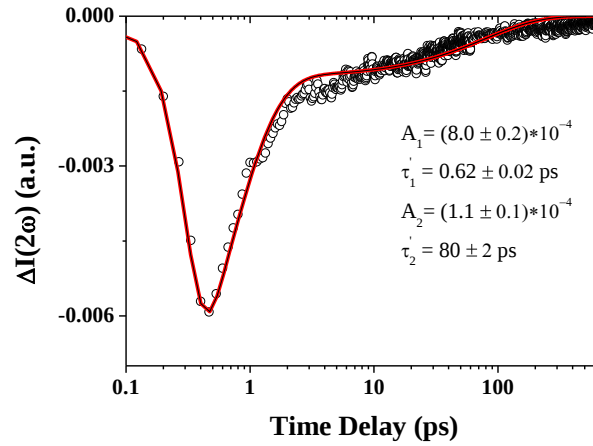


Figure S3

Here, considering $\tau_p=150$ fs, we numerically integrated our set of differential equations using a set of initial parameters and optimized the parameter through a $\chi^{(2)}$ square minimizing procedure. The results of these computations are displayed in Fig. S3. One can notice on both short and long time delays that this set of differential equations is not able to properly account for our data. As for the TRA experiment, we then considered a similar set of three differential

equations for the evolution the fractional populations, integrated them with a set of initial parameters that we optimized through a $\chi^{(2)}$ square minimizing procedure. The results are displayed in Fig. S4.

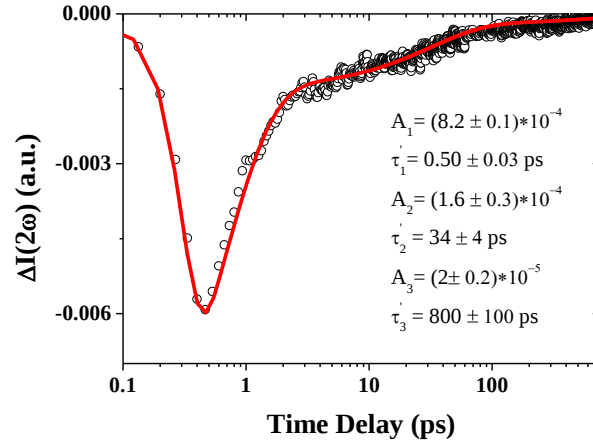


Figure S4

With such a set of differential equations, we were able to properly fit our experimental data. One can however notice a small shift between experimental and numerical data during the early relaxation time. It is to correct for this latter shift that we finally considered the set of four differential equations for the evolution the fractional populations.

$$\begin{aligned}\frac{dP_1}{dt} &= \frac{\sigma_p I_{p0}}{\sqrt{\pi} \tau_p} \exp\left(-\frac{(t-t_0)^2}{\tau_p^2}\right) - \frac{P_1}{\tau'_1}, \\ \frac{dP_2}{dt} &= \frac{P_1}{\tau'_1} - \frac{P_2}{\tau'_2}, \\ \frac{dP_3^*}{dt} &= \frac{P_2}{\tau'_2} - \frac{P_3^*}{\tau'_3}, \\ \frac{dP_3}{dt} &= \frac{P_3^*}{\tau'_3} - \frac{P_3}{\tau'_4}\end{aligned}$$

As expected and as shown in Fig. S5, with a larger set of free parameters, we were able to reproduce very nicely our experimental data. But more importantly, we also found a better agreement with two of the main time constants we deduced from the TRA experiment.

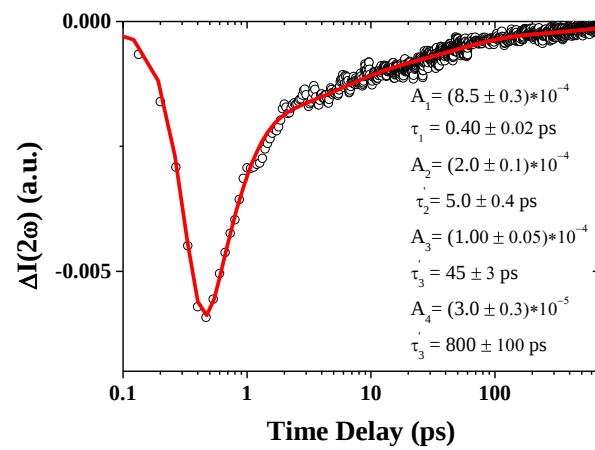


Figure S5