Supporting information

Dyad 1 in THF

The EADS for dyad **1** in THF are shown in figure S1. The spectra are very similar to the EADS of the measurement in toluene. After carotenoid excitation, the first EADS (gray, fixed at 100 fs) shows the S_2 spectrum. The second EADS (red, 547 fs) shows the signatures of the hot S1 state and the charge separated state. In the next spectrum (blue, 4.2 ps) the S1 excited state absorption has shifted towards the blue, indicating vibrational cooling.

The fourth (cyan, 11 ps) and fifth EADS (green, 666 ps, expanded 5x), show the signature of the charge separated state, like discussed for the dyad in toluene. According to the area under the DADS, 92% of the molecules recombine on an 11 ps timescale and 8% on a 666 ps timescale. No triplet was found for this dyad in THF, which can be explained by the fast decay rate of the vast majority of the molecules. The fluorescence excitation spectrum for this dyad in THF was similar to the spectra in toluene, indicating that energy transfer from the carotenoid to porphyrin is absent.

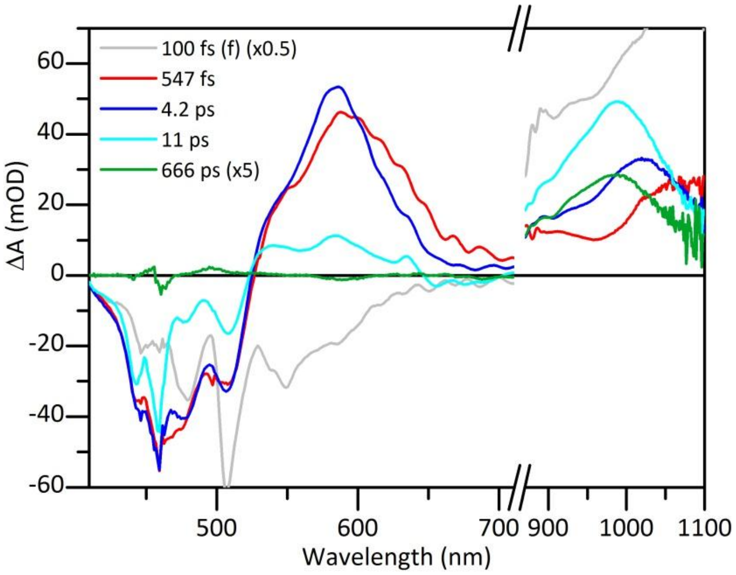

*Figure S1. EADS of dyad **1** in THF.*

Dyad 2 in THF

Figure S2a shows the EADS for dyad **2** in THF. The observed processes are similar to the measurements in toluene, but occur at faster rates. The carotenoid is excited to the S_2 state (gray EADS, fixed at 100 fs). Subsequently the second EADS (blue, 659 fs) shows the carotenoid S1 spectrum and carotenoid cation. In toluene the carotenoid S1 evolves into fullerene excited state and charge separation. Here, this also seems to be the case, but the two processes could not be distinguished, because the rate constants are too similar. The two processes are therefore fitted with one time constant. Figure S2b shows the time trace at the carotenoid ground state bleach. Again there is decay and increase of ground state bleach, but this is less profound than in toluene, suggesting that the fullerene excited state is occupied less.

The next two EADS (cyan and green) again show the typical charge separated state that decays with 4.5 ps and 42 ps time constants. In the toluene experiment, the last spectrum contained just the carotenoid triplet. In THF this spectrum contains both the triplet and a small band of the carotenoid ion, indicating that part of the molecules in which charge separation has taken place recombine at a very slow rate.

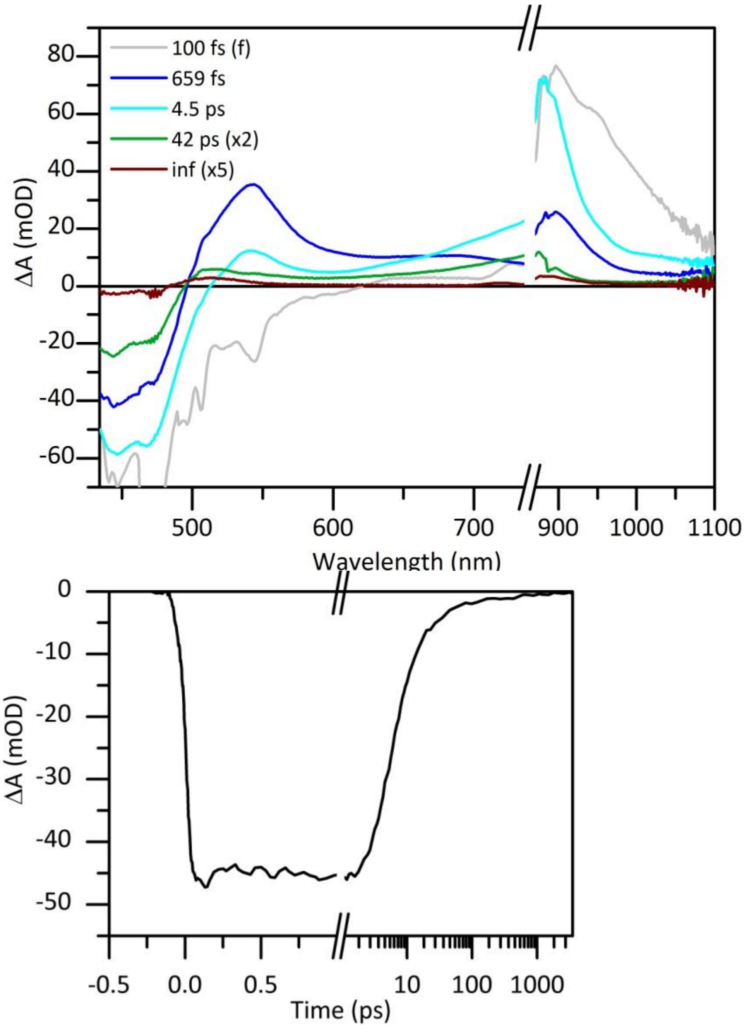

Figure S2. a) EADS of dyad ***2*** *in THF. b) Time trace of dyad* ***2*** *in THF at 457 nm.*

Decay associated difference spectra (DADS)

As described in the methods section, the transient absorption data is analyzed globally. Figure S3-S6 show the decay associated difference spectra (DADS) that follow from this analysis. The DADS, which show the spectral changes with the given time constants, show the same processes as the EADS, but highlight different subtleties. In the DADS of dyad **1** in toluene for example, there are differences between the charge recombination processes on the 261 ps (magenta) and 907 ps (green) timescale.

In the DADS, the fast recombination process has maximal Q-band bleach at 654 nm, whereas this band is found at 658 nm for the slow recombination process. Furthermore the triplet, which is expected to be formed predominantly from those molecules that recombine most slowly, shows Q-band bleaching at 664 nm. Likewise, the Soret band is found at 459 nm, 462 nm and 464 nm for the fast, slow and triplet curves. The shift of position of the observed bleach peaks can be caused by a shift in ground state absorption itself or a shift in the excited state absorption that overlaps with this band. In either case, the peak shift shows that there is heterogeneity in the sample, for example multiple conformational states or dyad aggregation.

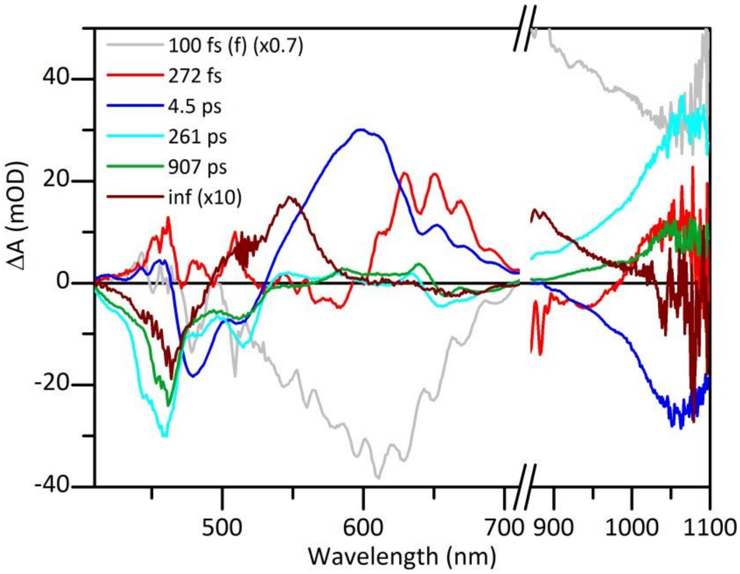

*Figure S3. DADS of dyad **1** in toluene.*

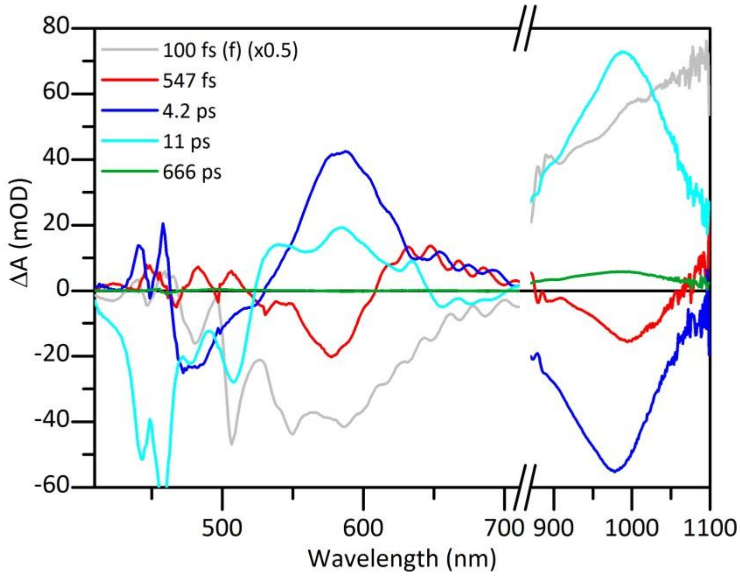

*Figure S4. DADS of dyad **1** in THF.*

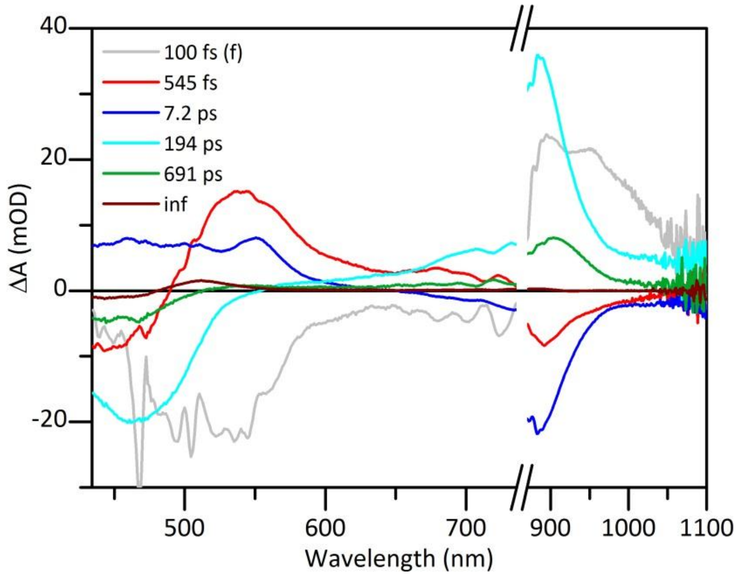

*Figure S5. DADS of dyad **2** in toluene.*

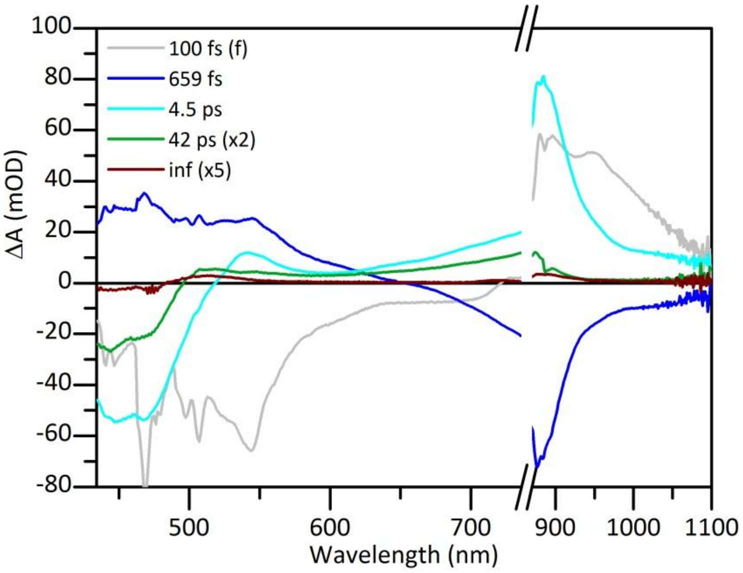

*Figure S6. DADS of dyad **2** in THF.*

Time traces

In figures S7-S10 we present time traces of the transient absorption data (black lines) together with the fit that results from analysis (red lines). It can be seen that the fits agree well with the measured data for dyad **1**. For dyad **2** the fit of the measurement in THF (figure S10) deviates from the data (see discussion of figure S2).

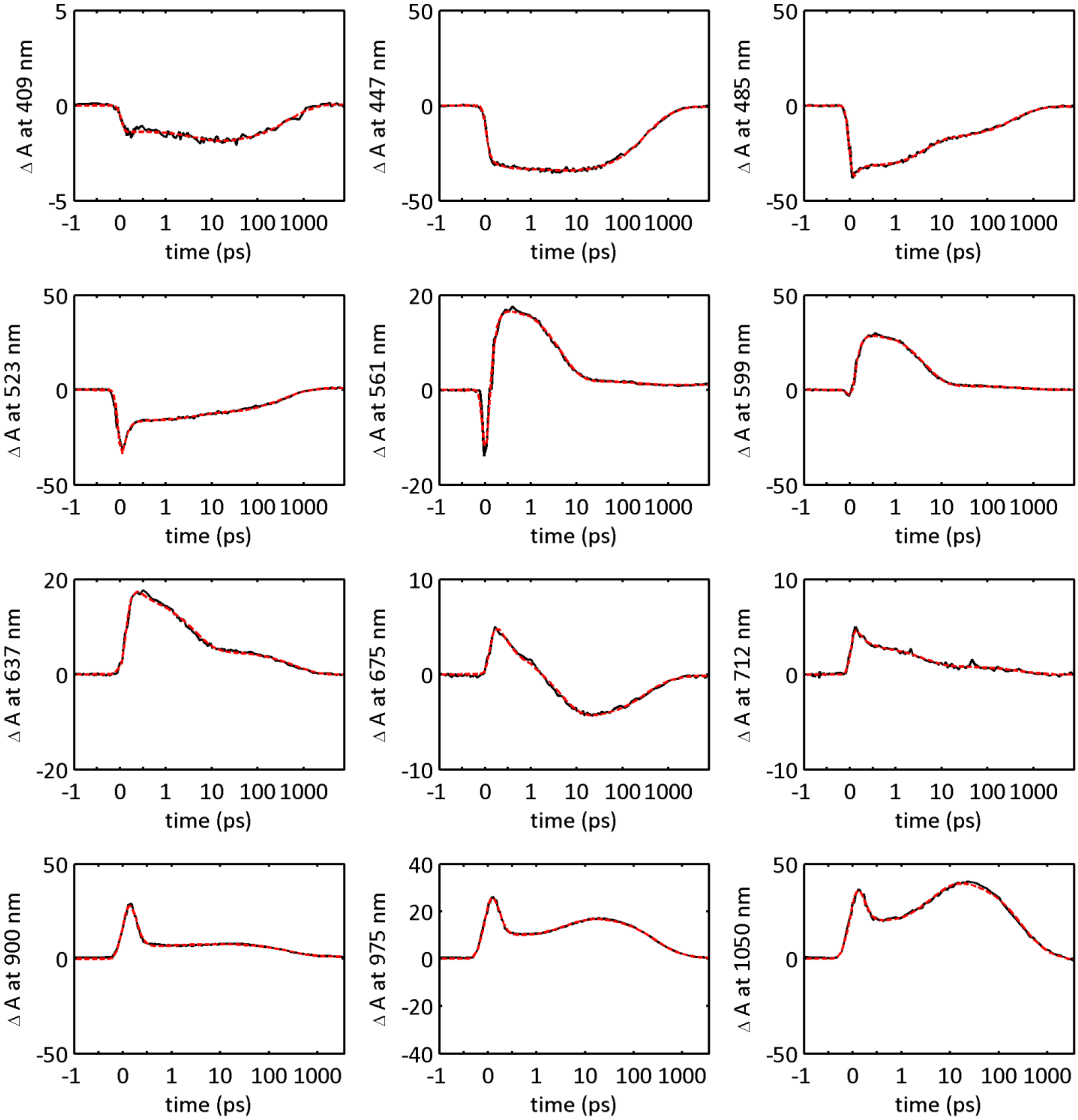

*Figure S7. Time traces of dyad **1** in toluene. Black: raw data. Red: fit of the data.*

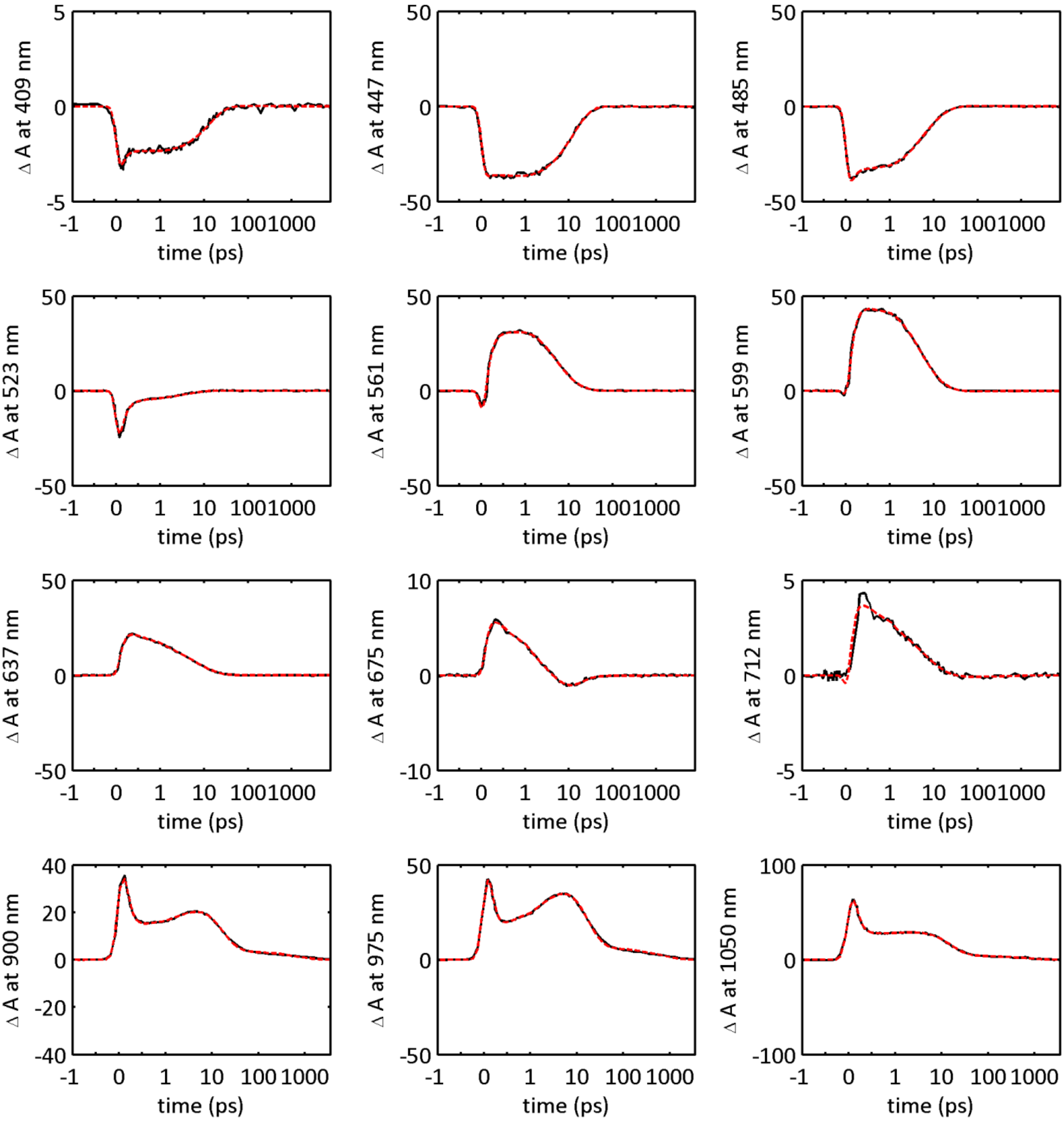

*Figure S8. Time traces of dyad **1** in THF. Black: raw data. Red: fit of the data.*

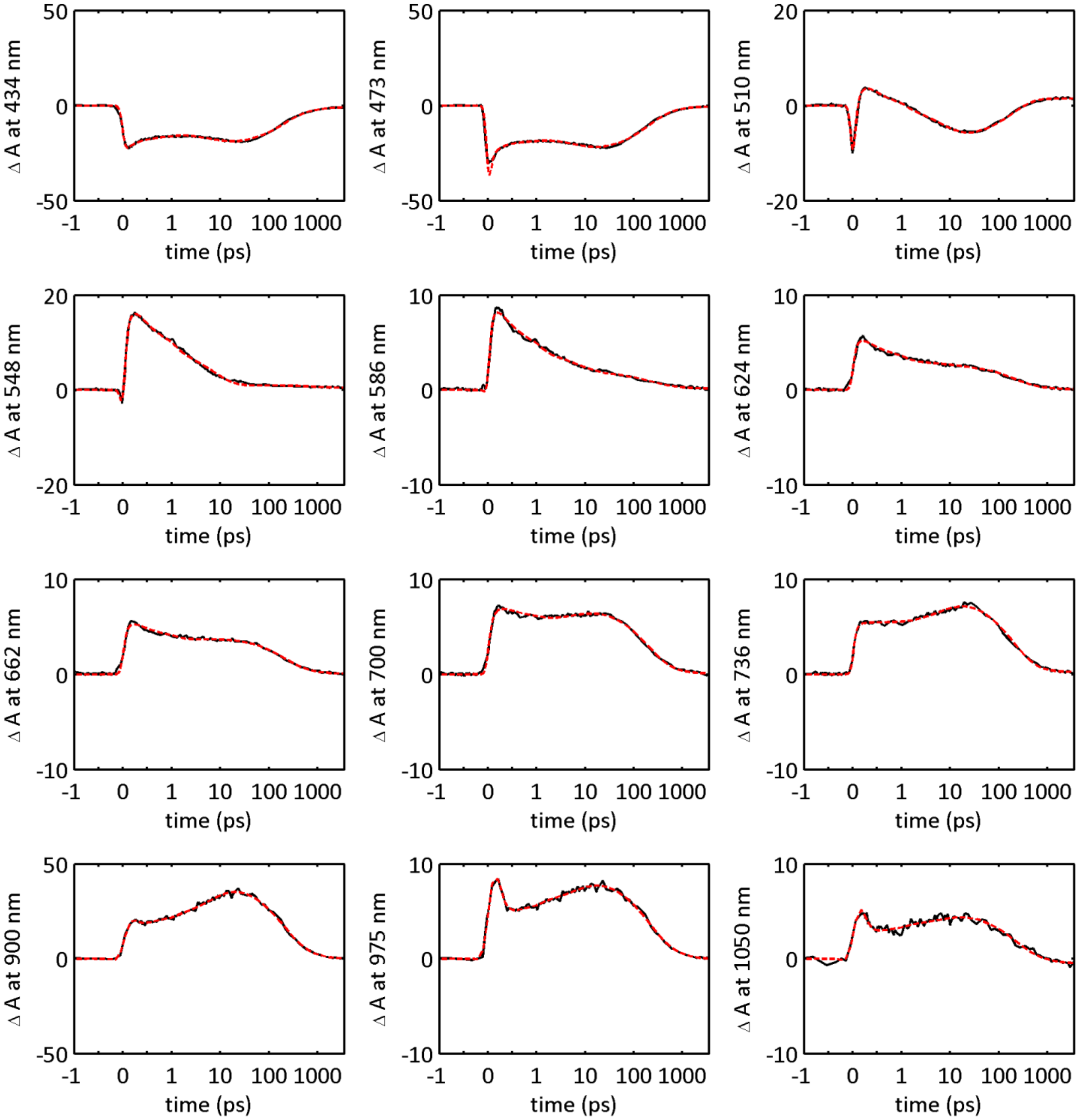

Figure S9. Time traces of dyad ***2*** *in toluene. Black: raw data. Red: fit of the data.*

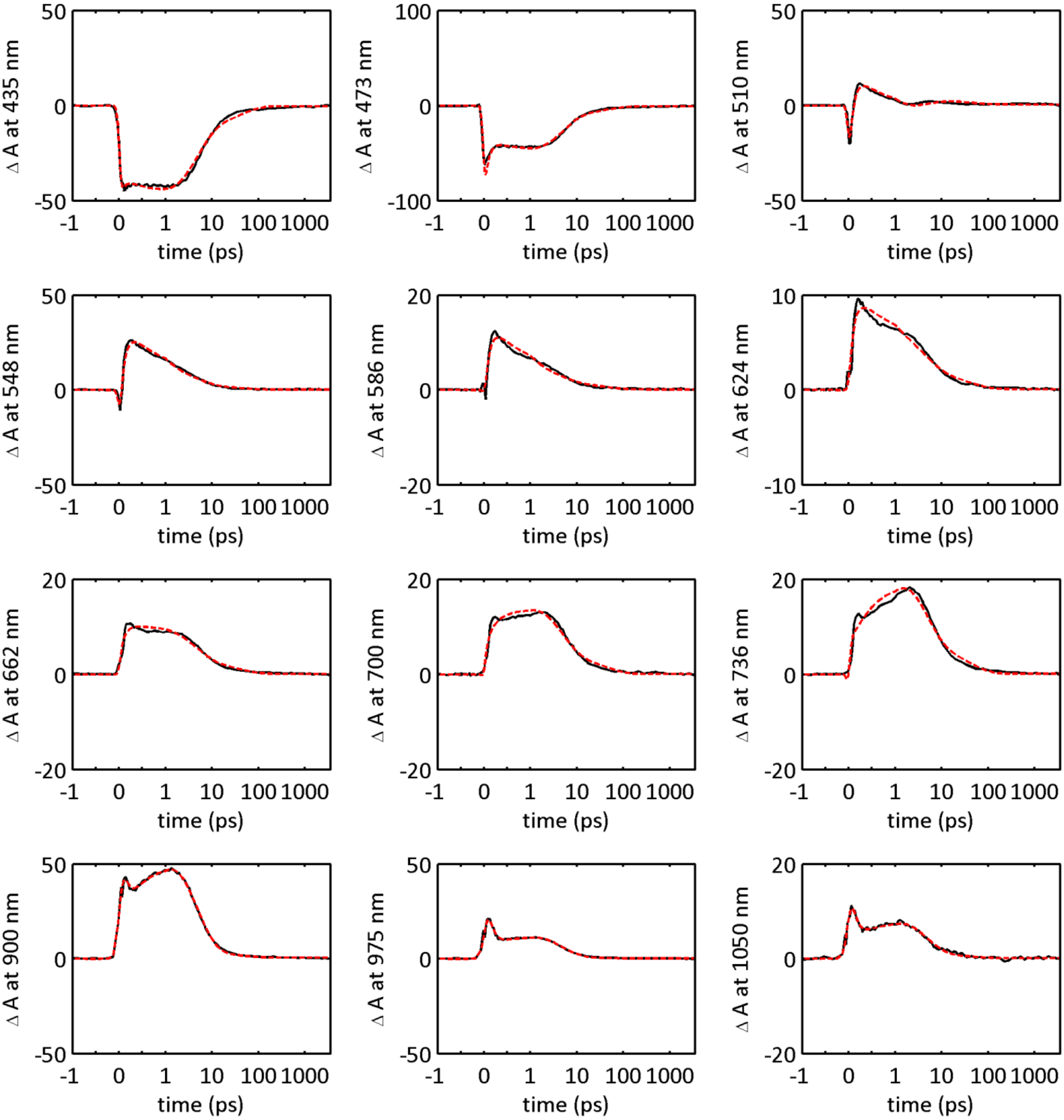

*Figure S10. Time traces of dyad **2** in THF. Black: raw data. Red: fit of the data.*