Supporting Information

Light-switchable hemithioindigo-hemistilbene containing peptides: Ultrafast spectroscopy of the Z to E isomerization of the chromophore and the structural dynamics of the peptide moiety

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Characterization of the Photostationary States

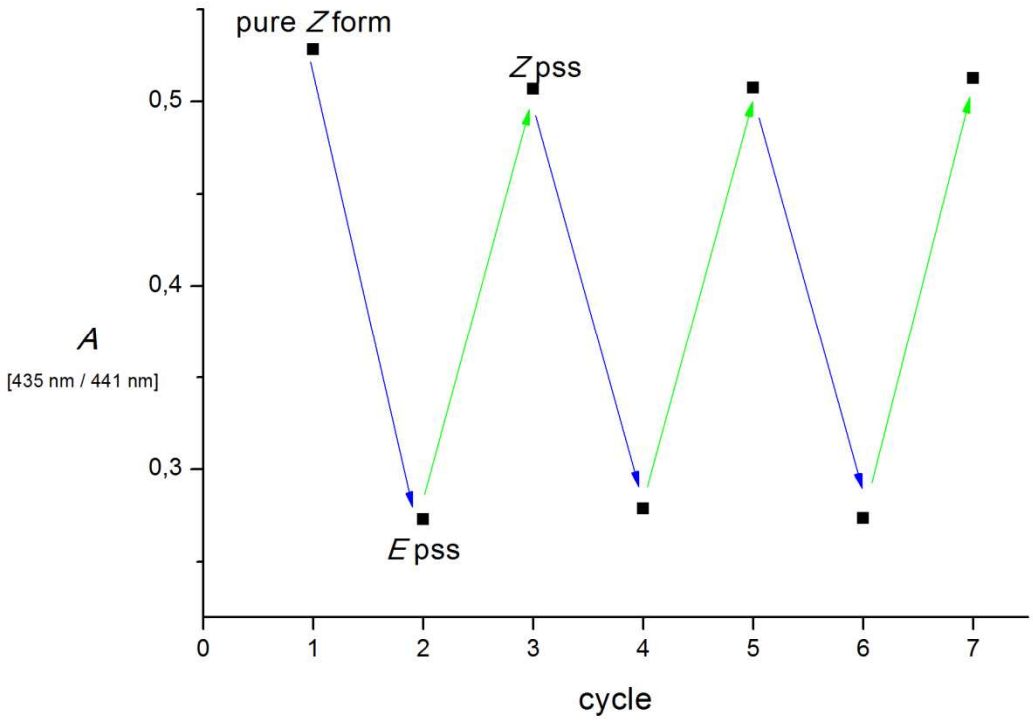

Fig. SI-1: UV/Vis absorbance at 435 nm and 441 nm upon of Peptide II after repetitive illumination to the photostationary state pss by UV light at 415 nm (E_{pss}) and visible light at 514 nm (Z_{pss}). The data evaluation shows a high stability of the HTI molecules even after different illumination cycles.

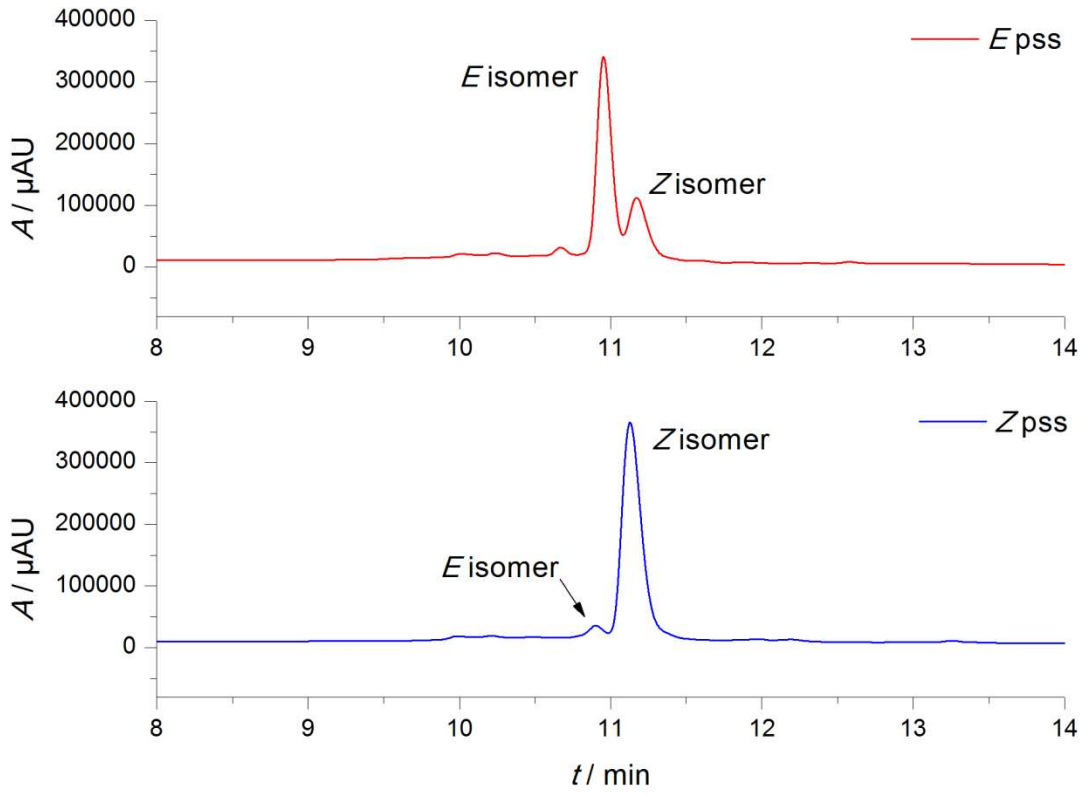

Fig. SI-2: Isomer ratios of Peptide II in the photostationary states (E_{pss} and Z_{pss}) reached after 415 nm (top, 72% E content in E_{pss}), and 545 nm (bottom, 97% Z content in Z_{pss}) illumination determined by RP-HPLC.

Stationary IR-Spectra of different mHTI-peptides

IR absorption spectra recorded for the different photostationary states of Peptide II and a related Peptide IIa (where Phe close to the Gly Asp Gly turn region was replaced by a Tyr) are used to identify the structural differences of the peptide moiety between the Z and the E-form. There are strong indications for the disruption of the anti-parallel β-structure when the mHTI chromophore is switched to the E-form. Absorption decrease (see Fig. SI-3 and SI-4) found at 1645 cm^{-1} is due to the disappearance of strong inter-strand hydrogen bonds. Negative absorption changes at 1684 cm^{-1} can be used to support this interpretation. The absorption differences Peptide IIa (see Fig. SI-5) between the Z and the E-forms

around 1563 cm^{-1} point to changes at the region of the Glu (see Scheme 1) in the center of the hairpin strand connected with strong changes of the structure. The similarities of the Asp (1582 cm^{-1}) and Typ (1515 cm^{-1}) absorption bands of Z and E-forms indicated that the Gly Asp Gly turn region, where the two amino acids are located do not experience considerable structural changes.

From the IR absorption spectral one may conclude that the isomerization of the mHTI chromophore leads to structural changes over a considerable part of the hairpin structure with a strong decrease in inter-strand hydrogen bonds and an opening of the hairpin structure. These interpretations are supported by NMR spectroscopy of Peptide II in DMSO where the changes in the positions of the C_α and the amino hydrogens are investigated (Rück-Braun, personal information).

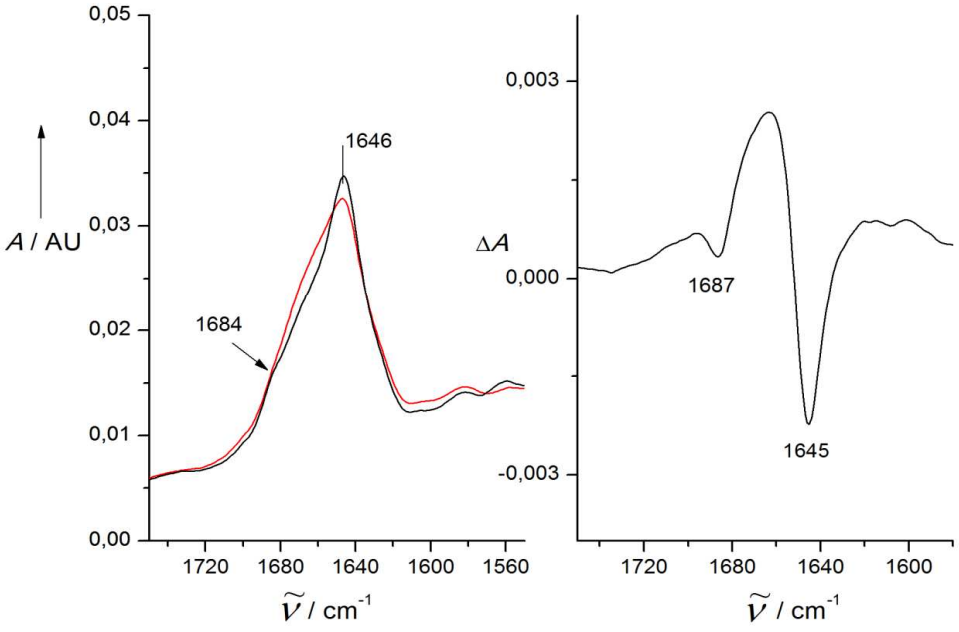

Fig. SI-3: FTIR spectra of peptide II in d_4-MeOH; left: pure Z form (black) and E form in the pss (red); right: E-Z difference spectra.

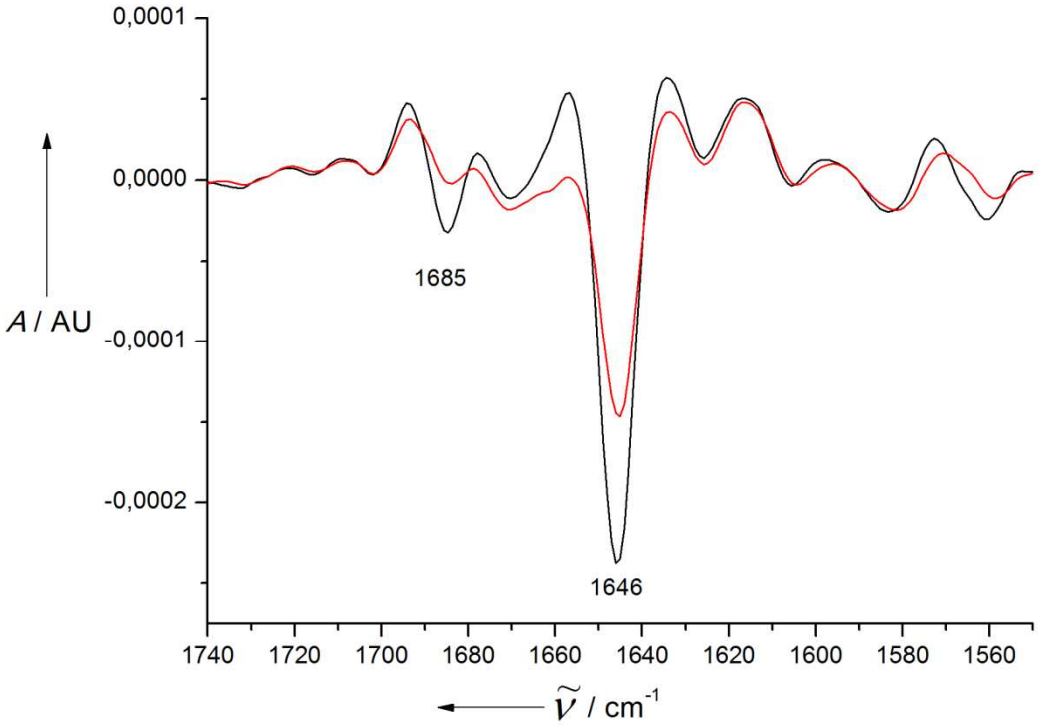

Fig. SI-4: Second derivative spectra for peak positioning of the IR bands of peptide II in the two samples shown in Fig. SI-3.

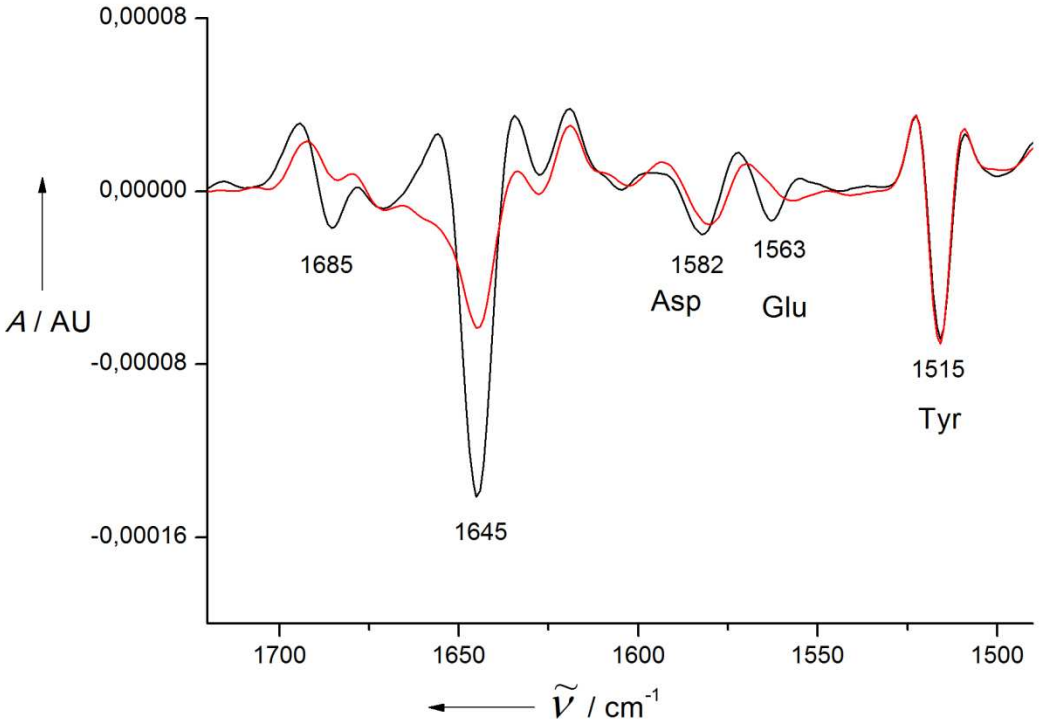

Fig. SI-5: Second derivative spectra for peak positioning of the IR bands of Peptide IIa.

Ultrafast Absorption Experiments

Some traces for the time dependence of the absorption change at certain delay times are given in Fig. SI-6 showing clearly the different reaction dynamics.

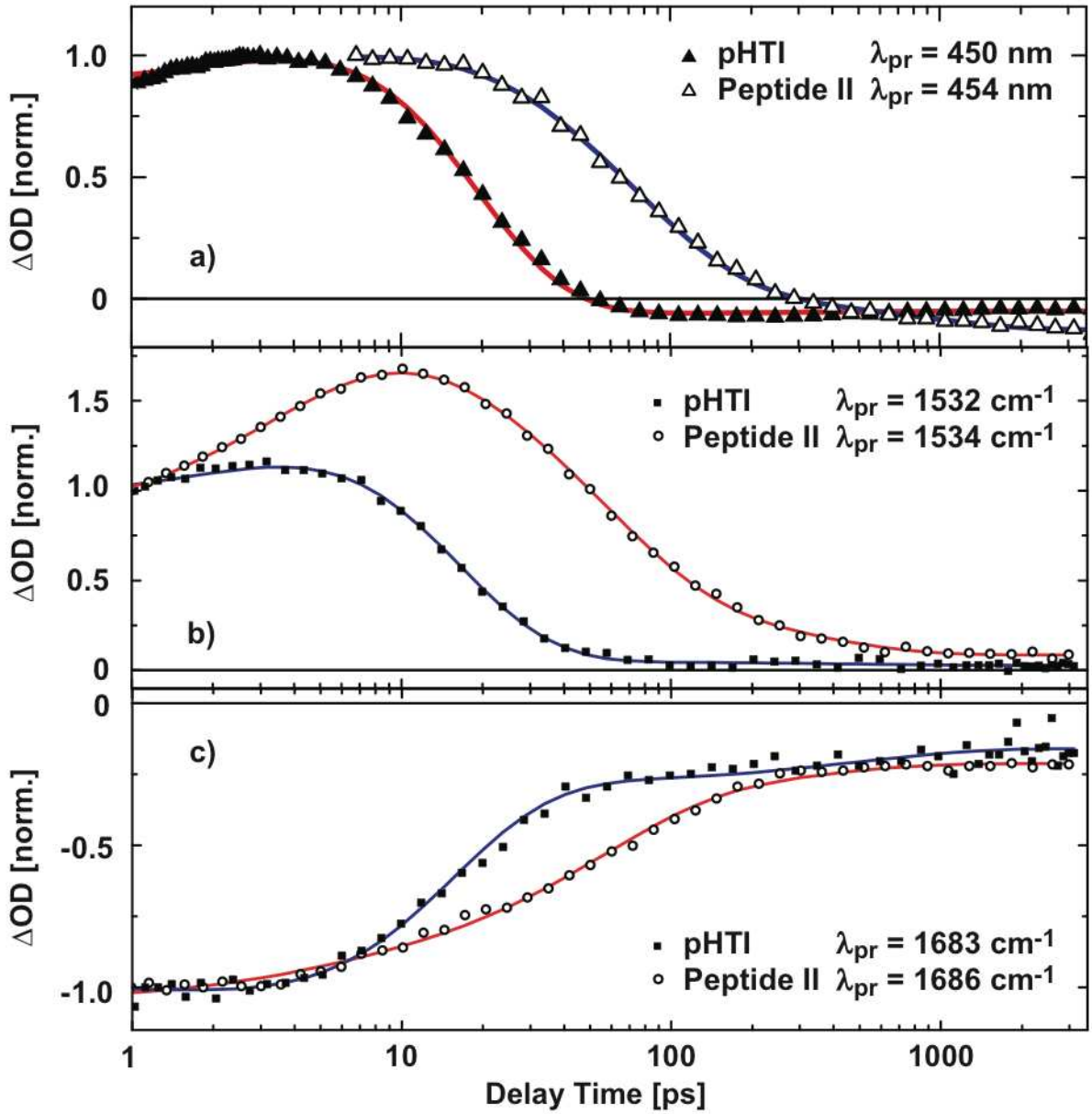

Fig. SI-6: Typical examples of the time dependence of the absorption changes recorded at different probing wavelengths.

Decay Associated Spectra of the Transient IR-Data

The decay associated spectra (DAS) of the time-resolved IR experiments are given in Fig. SI-7 to 10 for the different HTI samples. The DAS shown here reflect the fitting amplitudes related to the different time constants given in the legend. For Peptide II a further (weak) kinetic component was visible with a time constant of 210 ps, tentatively assigned to strucutral changes due to a partial relaxation of the strain between the switching chromophore and the unrelaxed peptide.

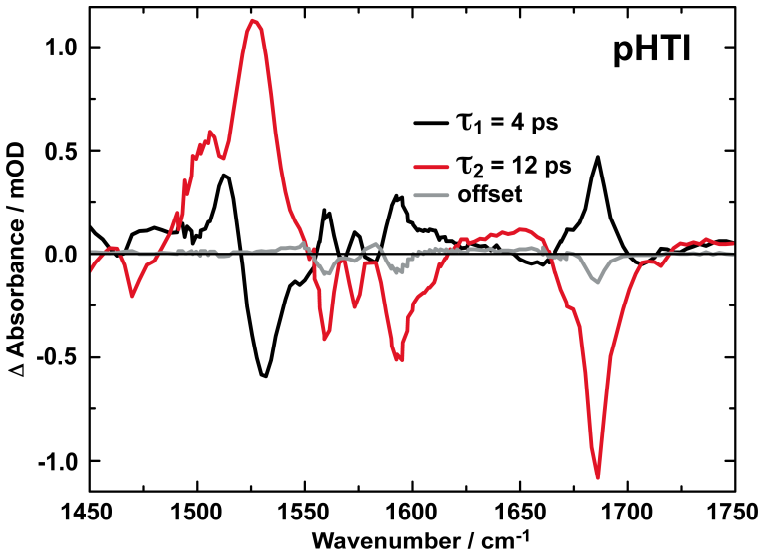

Fig. SI-7: DAS of the pHTI obtained from a multiexponential fit of the transient IR data.

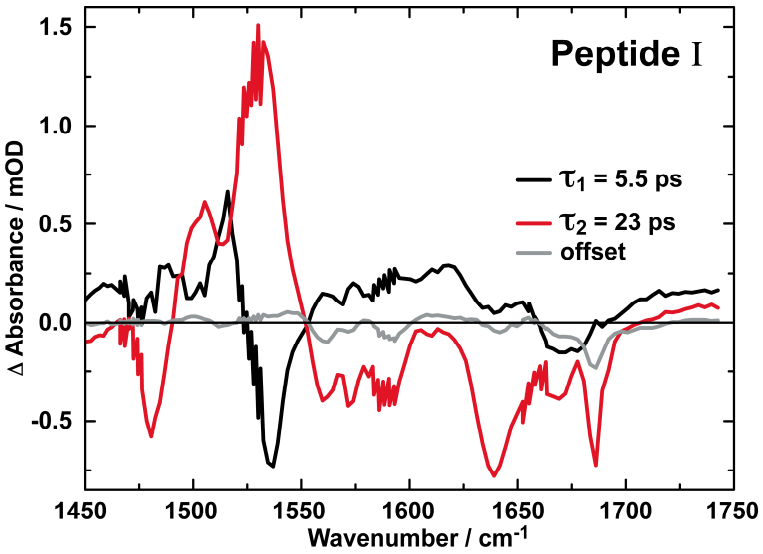

Fig. SI-8: DAS of Peptide I obtained from a multiexponential fit of the transient IR data.

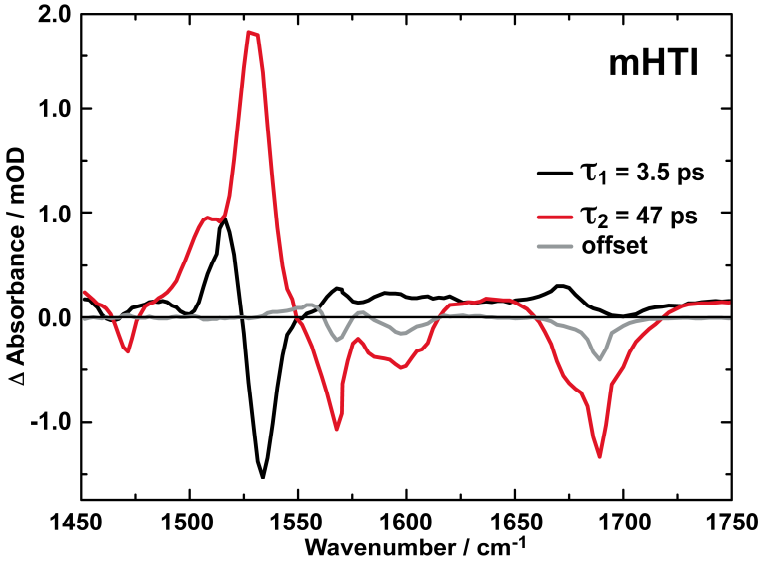

Fig. SI-9: DAS of mHTI obtained from a multiexponential fit of the transient IR absorption data.

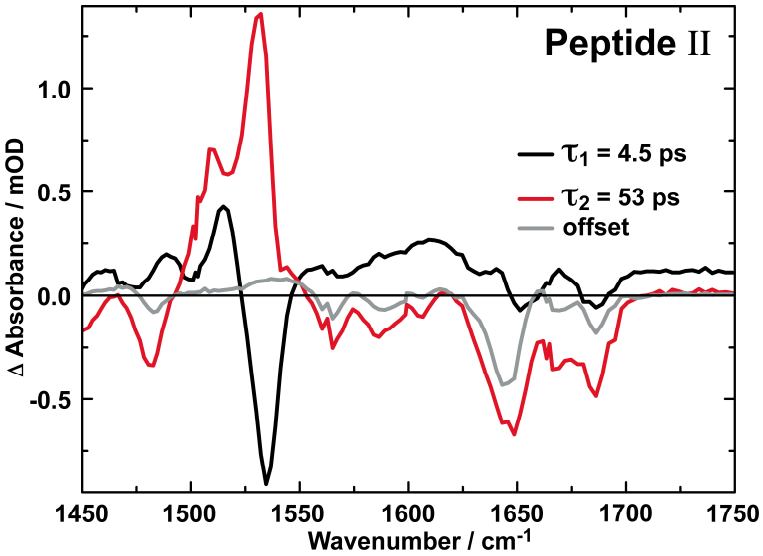

Fig. SI-10: DAS of Peptide II obtained from a multiexponential fit of the transient IR absorption data.