

Supplementary Information

to

Ring-opening reaction of a trifluorinated indolyfulgide: mode-specific photochemistry after pre-excitation

by

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Contributions to the signal

In this supplementary information the different transient absorption signals for the pump and probe wavelength of the 3-pulse experiment will be described and discussed in detail. As illustrated in Figure 1 the absorption maximum of *Z*-form ground state molecules is at 424 nm. Above 500 nm the *Z*-form has negligible absorption. In this wavelength range the *C*-form ground state has its absorption maximum (563 nm).

To obtain a better understanding of the ring-closure reaction we show in Figure S1 the transient absorption data for a pump pulse at 480 nm recorded with high temporal resolution (80 fs cross-correlation width) under magic angle conditions. The excited state of *Z*-form molecules decays with a time constant of about 0.3 ps (evident especially from long probing wavelengths). Additionally we observe absorption transients related to cooling dynamics on the 1 to 10 ps timescale of the vibrationally hot molecules in the *C*- and *Z*-form ground states. This is shown in detail in Figure S2 (left) at the probe wavelength 580 nm and in Figure S2 (right) at 630 nm. In the data shown in Figure 3 and 4 which was not recorded under magic angle conditions an additional slow process is visible due to rotational redistribution of the molecules.

The data shown in Figure S1 and S2 guided the selection of exciting and probing wavelengths for the 3-pulse experiment. Excitation: At the excitation wavelength of 630 nm we have

reasonable strong absorption of *C*-form molecules and no absorption of the ground state of the *Z*-form. Probing: At the probing wavelength of 580 nm, one finds a very strong absorption of the excited electronic state of the *C*-form. Thus the probing wavelength of 580 nm allows to monitor the decay of the excited state and the course of the ring-opening reaction.

In the 3-pulse experiment (in Figure 4a) we apply the pre-excitation pulse ($\lambda = 400$ nm) at a delay time of -6 ps. Exclusively *Z*-form molecules are excited by the pre-excitation pulse. As described above, the excited state of these *Z*-form molecules decays with a time constant of 0.3 ps. So in the time range between -5 ps and 0 ps only absorption of vibrationally hot molecules in the electronic ground states is observed at 580 nm. At a wavelength of 630 nm exclusively *C*-form molecules in their electronic ground state absorb. At the delay time 0 ps we apply the excitation pulse at 630 nm, which excites exclusively the newly formed *C*-form molecules. In the time-range between 0 ps and about 10 ps the excited state dynamics and the ring-opening reaction can be observed. After about 20 ps all molecules in the sample are in their electronic ground state. So after 20 ps only ground state absorption of *C*-form molecules can be monitored at 580 nm, because the *Z*-form ground state does not absorb here. After $t_2 > 20$ ps the 3-pulse data (circles) lies below the ring-closure data (line). This is due to reconversion of *C*-form molecules to the *Z*-form. The observed difference in absorption is connected to the quantum efficiency of the ring-opening reaction of vibrationally hot *C*-form molecules.

Similar to Figure 2a we plotted in Figure S3 a scheme where all appearing transient absorption signals are summarized.

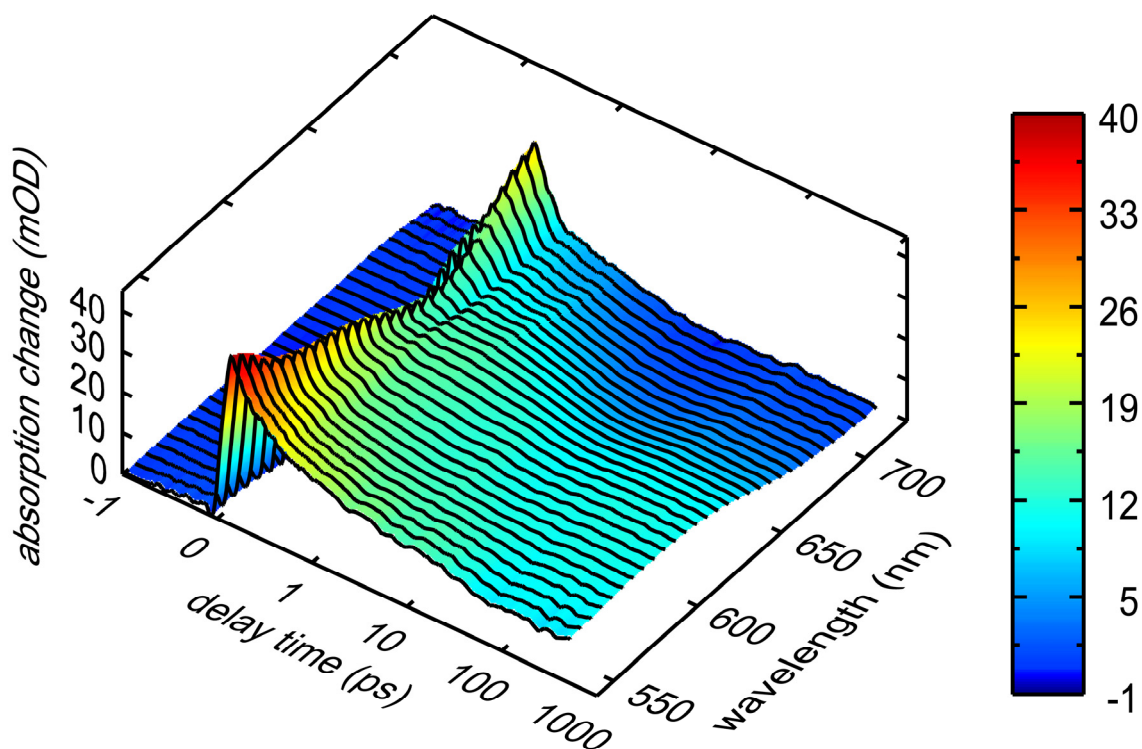


Figure S1. Dynamics of the ring-closure reaction of a trifluorinated indolylfulgide sample in PSS-435. Standard pump-probe absorption change with excitation at 480 nm, under magic angle conditions. The time scale is linear up to 1 ps and logarithmic afterwards.

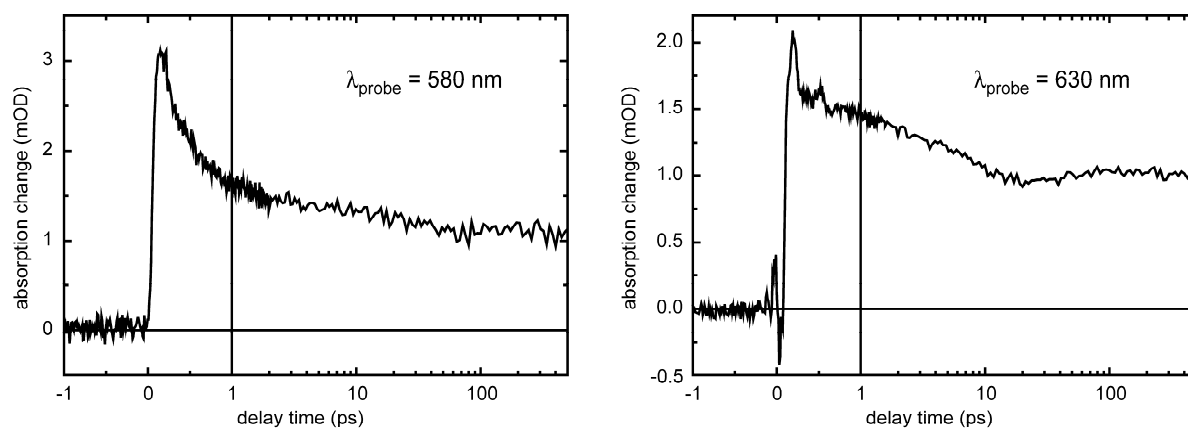


Figure S2. Dynamics of the ring-closure reaction of a trifluorinated indolylfulgide sample in PSS-435. Standard pump-probe absorption change with excitation at 480 nm, probed at 580 nm (left) and 630 nm (right) under magic angle conditions. The time scale is linear up to 1 ps and logarithmic afterwards.

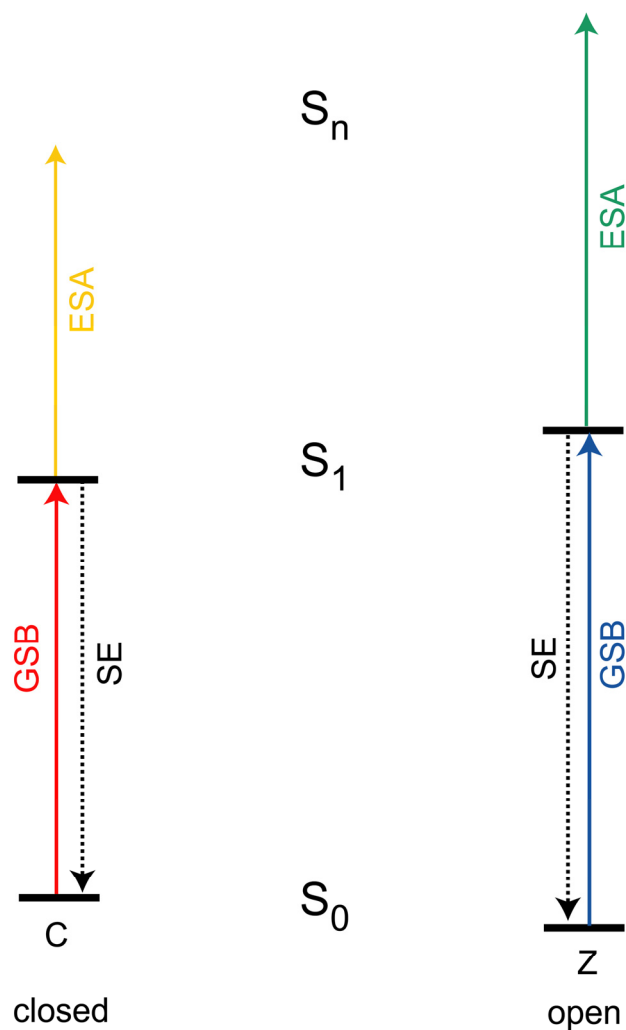


Figure S3. Extended energy level scheme including the optical transitions used for probing. Ground state bleach (GSB), excited state absorption (ESA) and stimulated emission (SE) are depicted.