

## Supporting information

### Ultrafast coherent dynamics reveals a reactive mode in the ring-opening reaction of fulgides

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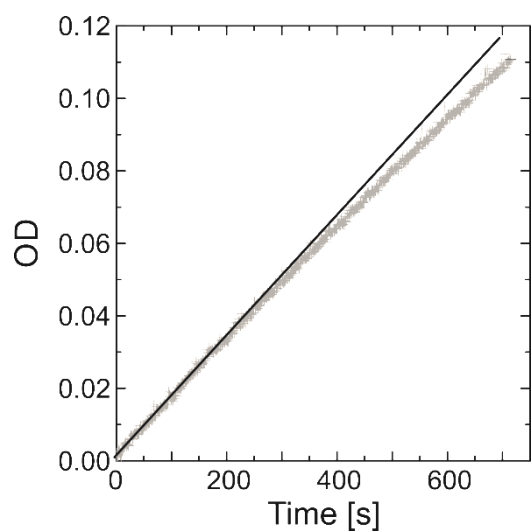
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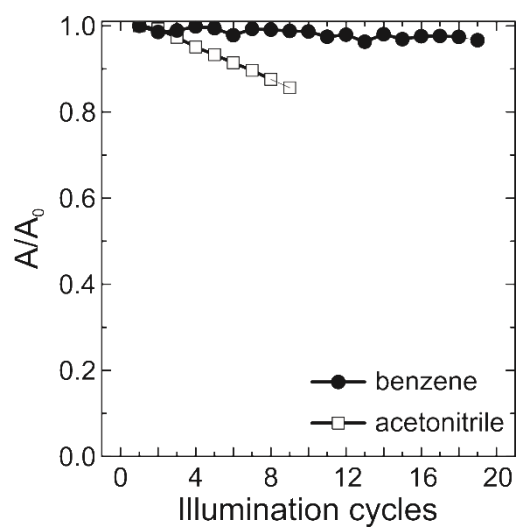
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**ABSTRACT:** The ultrafast ring-opening reaction of photochromic fulgides proceeds via conical intersections to the ground state isomers involving activation barriers in the excited state. The coherent oscillations observed in the femtosecond transient absorption signal of a methyl-substituted indolylfulgide were analysed in the framework of vibrational wavepackets to expose a dominant low-frequency mode at  $\sim 80\text{ cm}^{-1}$ . The quantum chemical calculations in the relaxed excited state geometry of this fulgide revealed that the experimentally observed vibrational normal mode has a dominant contribution to the relevant ring-opening reactive coordinate.

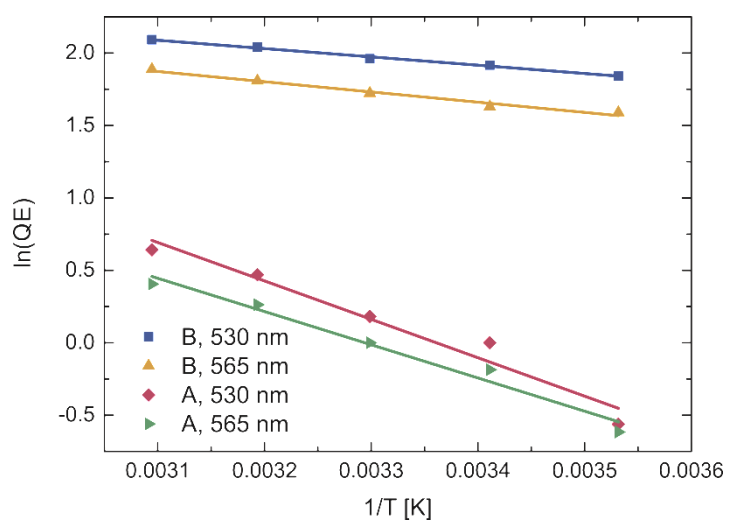
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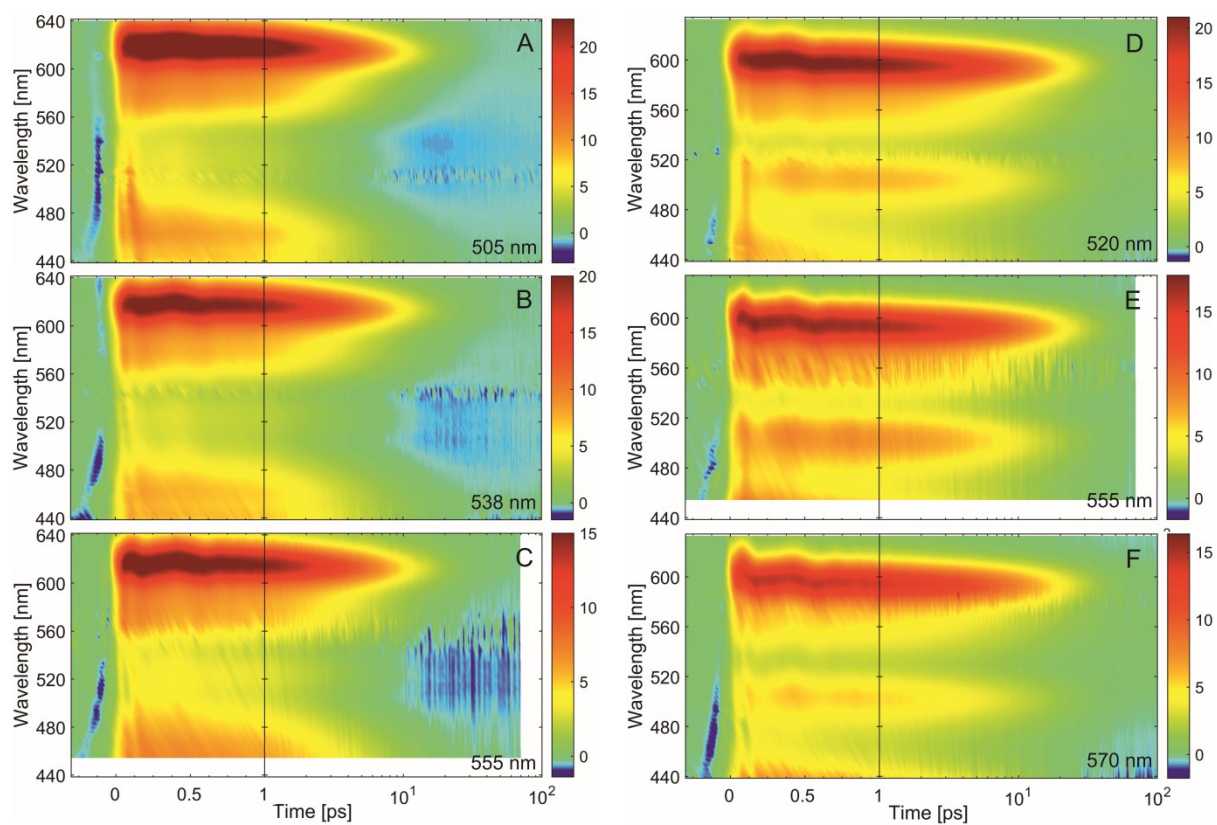
**Fig. S1.** Linear dependence of absorbance changes and number of absorbed photons during the initial stage of illumination. The slope of this linear range is used in the calculation of the reaction quantum efficiency.



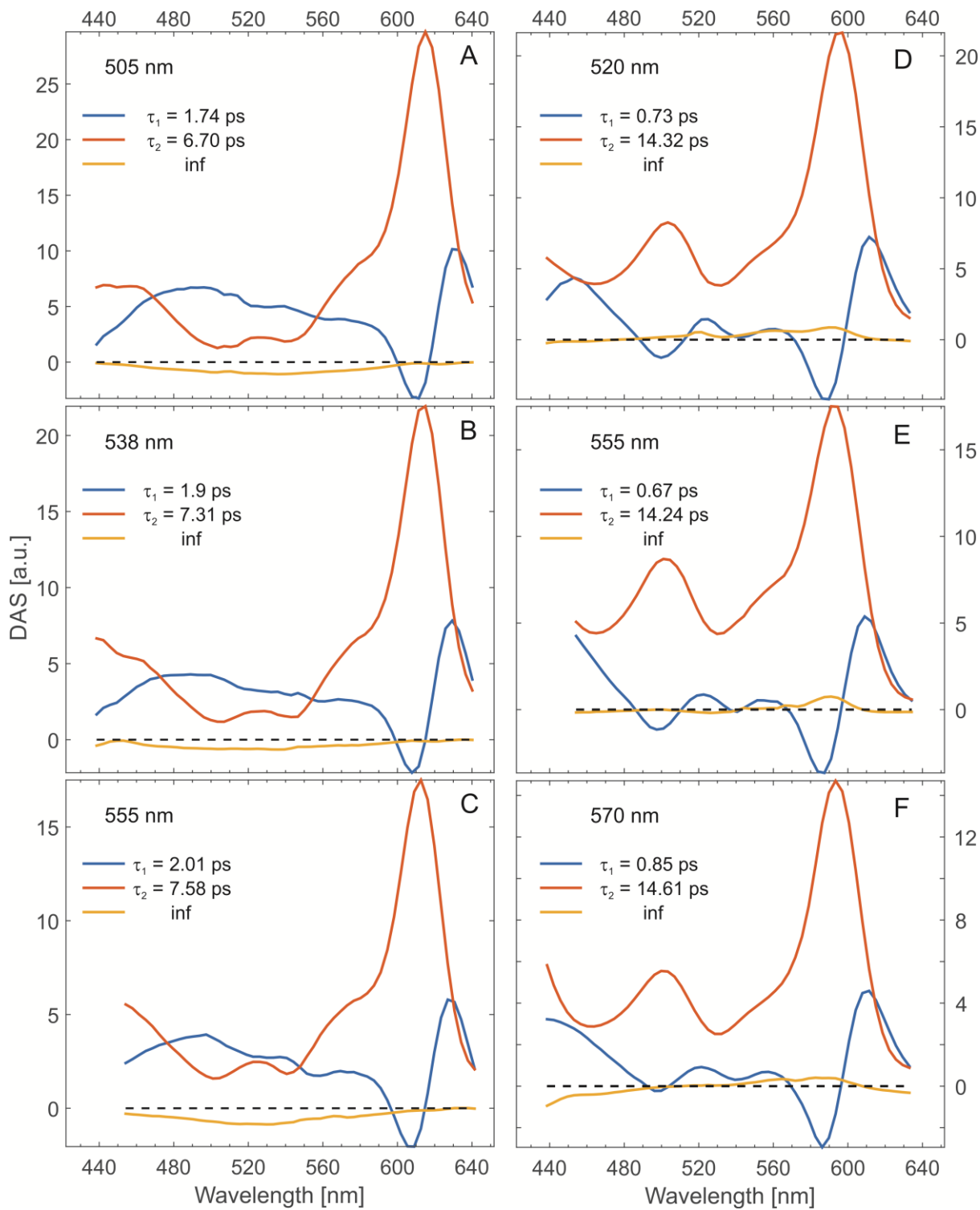
**Fig. S2.** Photostability of the studied compound in benzene and acetonitrile.



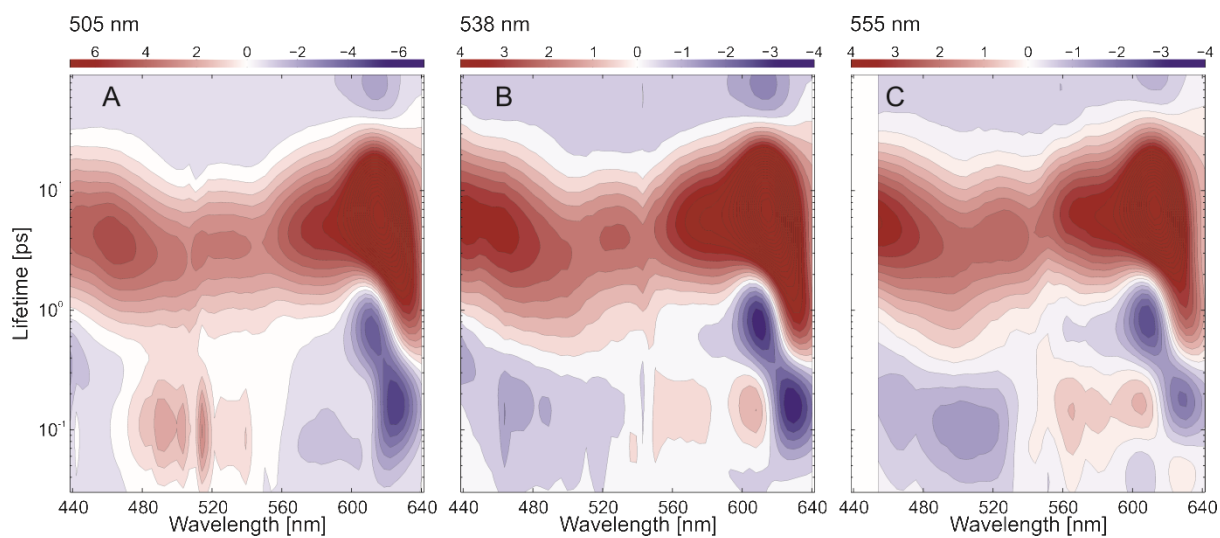
**Fig. S3.** Excitation wavelength dependence of the Arrhenius plots for the ring-opening reaction in different solvents (A – acetonitrile, B -benzene)



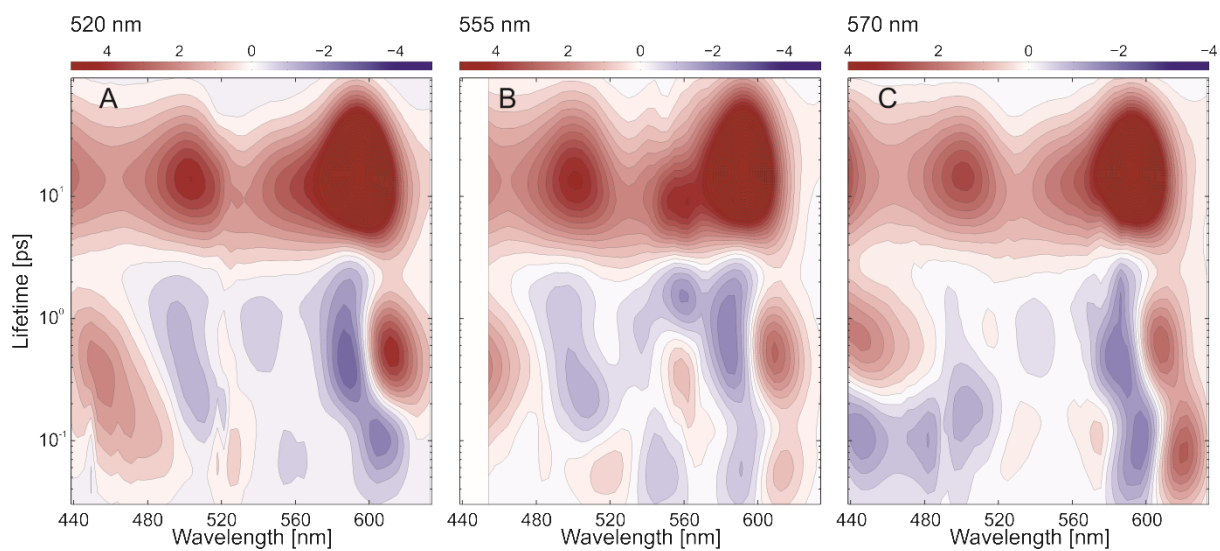
**Fig. S4.** Wavelength dependence of the transient absorption data of methyl indolylfulgide C-form in A-C) benzene and D-F) acetonitrile. The excitation wavelengths are given in the lower-right corner of the plots.



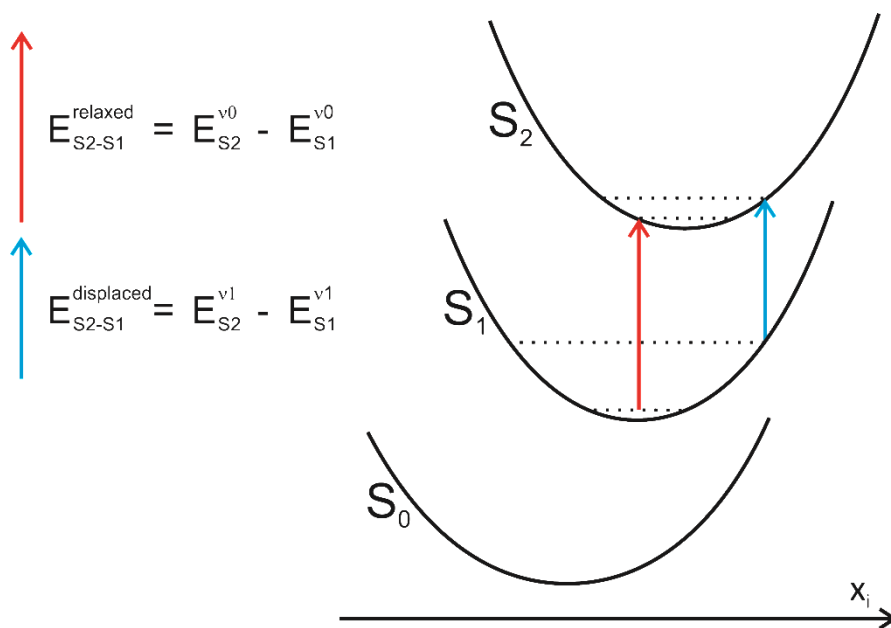
**Fig. S5.** Global lifetime analysis results from the wavelength dependence of the transient absorption data of methyl-indolylfulgide C-form in A-C) benzene and D-F) acetonitrile.



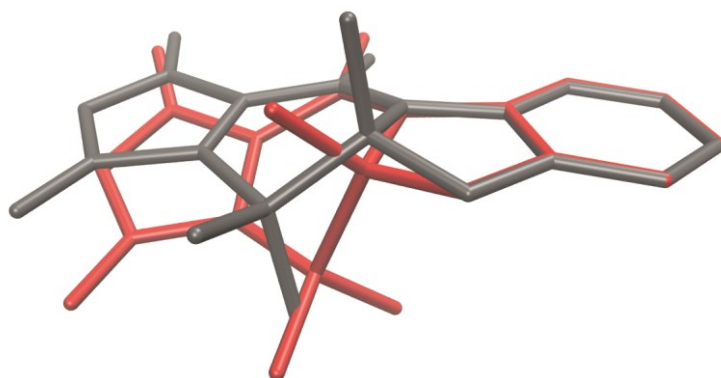
**Fig. S6.** Lifetime density analysis results from the wavelength dependence of the transient absorption data of methylindolyfulgide C-form in benzene.



**Fig. S7.** Lifetime density analysis results from the wavelength dependence of the transient absorption data of methylindolyfulgide C-form in acetonitrile.



**Fig. S8.** Schematic representation of the electronic states used in the calculation for estimating the contribution of the different normal modes to the shift in the excited state absorption associated with the coherent oscillations observed in the transient absorption data.



**Fig. S9.** Distortions of the structure of methyl-indolyfulgide caused by the  $80 \text{ cm}^{-1}$  normal mode.