SUPPORTING INFORMATION

Complete kinetic and photochemical characterization of the multi-step photochromic reaction of DASA

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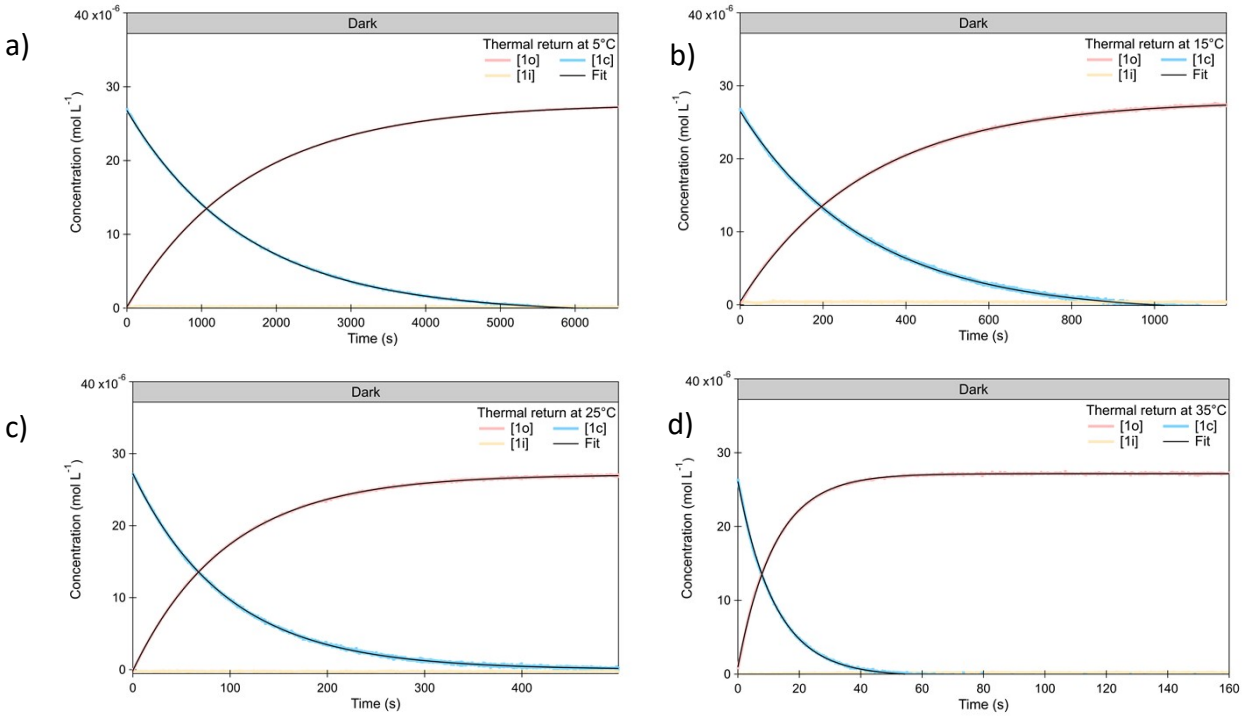


Figure S1. Concentration profiles of isomers **1o**, **1i** and **1c** during irradiation and thermal-back reactions, obtained at different temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C. Irradiation is set at 575 nm for 26 mW power.

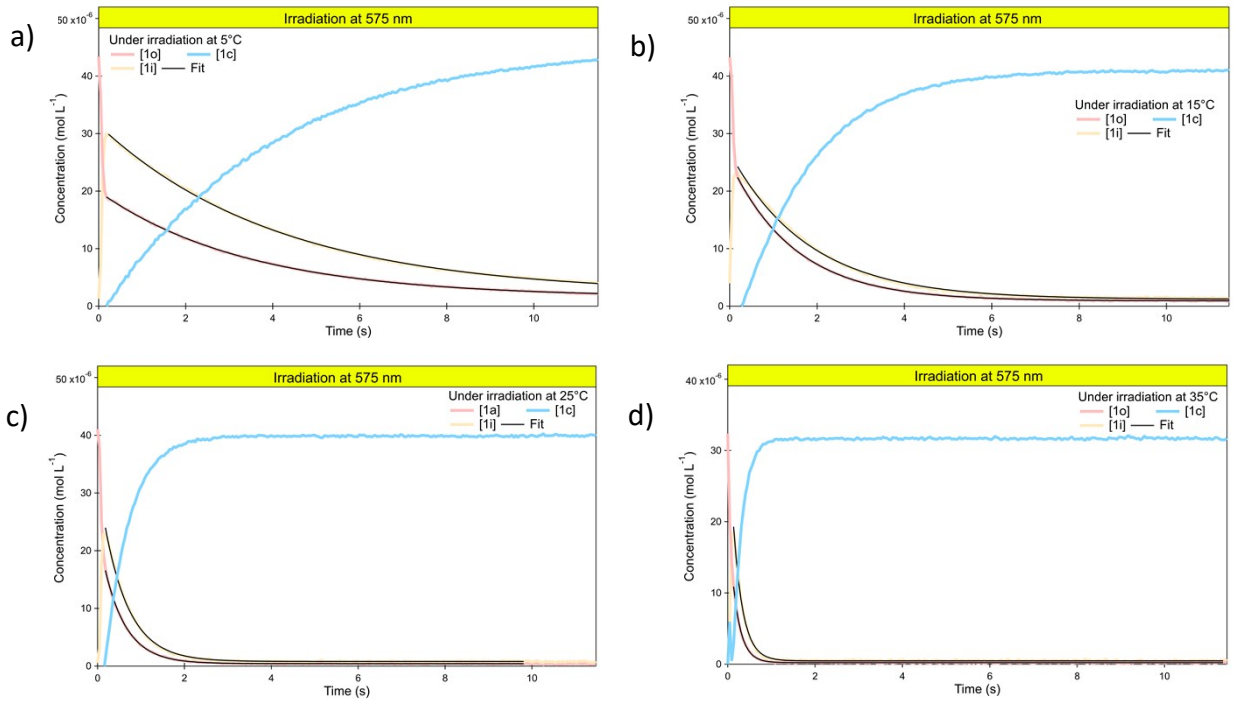


Figure S2. Concentration profiles of isomers **1o**, **1i** and **1c** during the first 10 sec of irradiation, obtained at different temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C. Irradiation is set at 575 nm for 26 mW power.

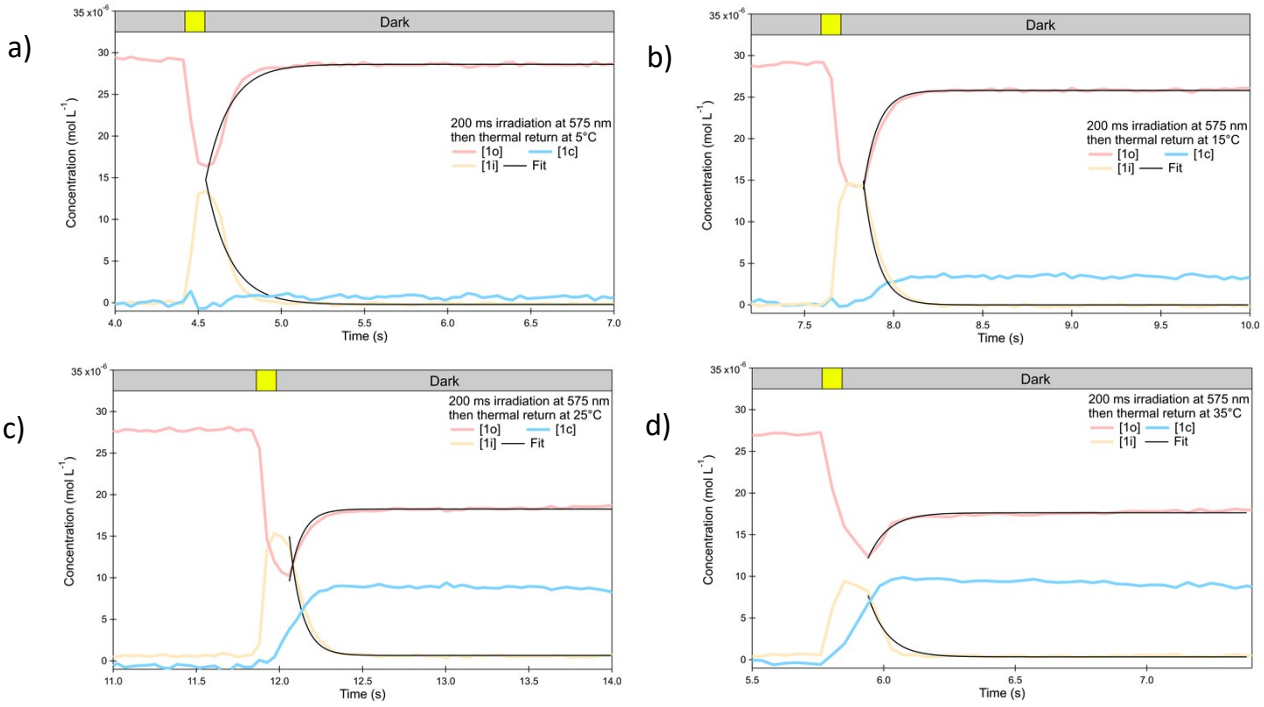


Figure S3. Concentration profiles of isomers **1o**, **1i** and **1c** after a short pulse of 200 ms of irradiation, obtained at different temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C. Irradiation is set at 575 nm for 26 mW power.

a)

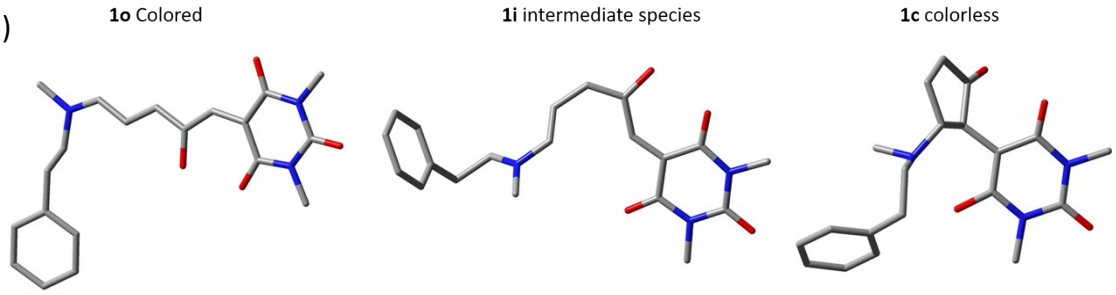
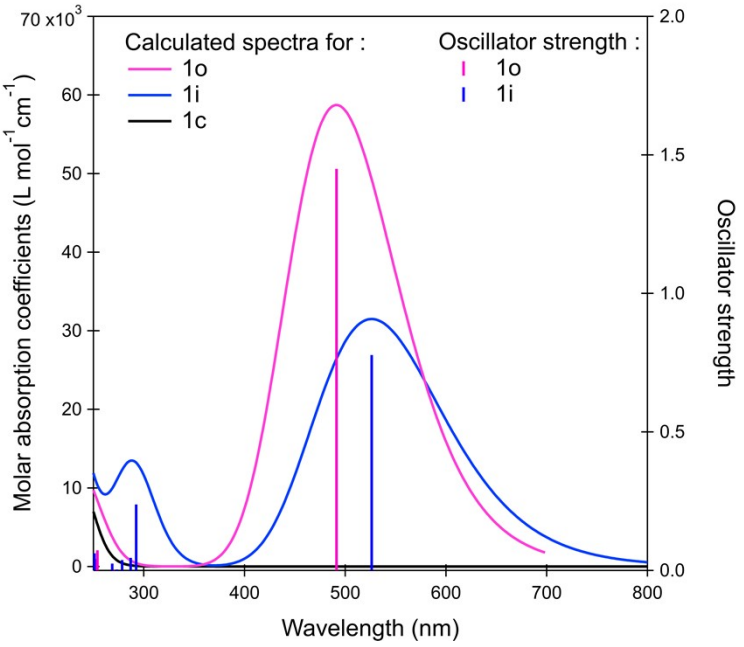


Figure S4. a) Calculated geometry of the **1o**, **1i** and **1c** forms and b) the calculated absorption spectra and oscillator strength for the three isomers obtained by DFT and TD-DFT calculations with the hybrid functional M06-2X and the base 6-31G+(d,p).

b)



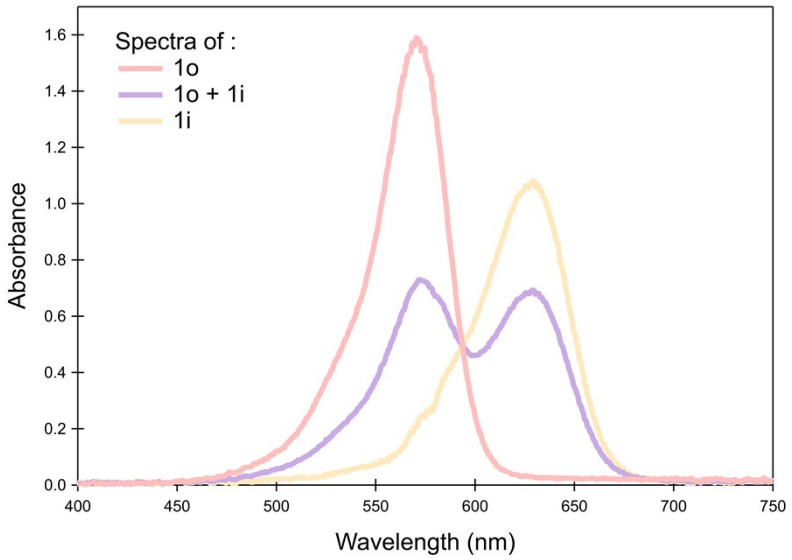


Figure S5. Absorption spectra of the isomers **1o** (before irradiation), a mixture of **1o** and **1i** (after irradiation), and the isomer **1i** (obtained by deconvolution, see below) of the DASA molecule in toluene at $4{,}5 \times 10^{-5}$ mol L^{-1}.

The spectra of **1o** and the mixture of **1o**+**1i**, and their corresponding concentrations, were obtained from the data shown in Figure S2a, at two different experimental time: t_0 which corresponds to the beginning of the experiment before irradiation and t_{mix} which corresponds to the experimental time right after the beginning of the irradiation (t_{mix}=180 ms) where the **1i** species reaches its maximum molar fraction (before its decreasing). The following equations can then be defined to deduce the absorption spectrum of **1i**:

At t_0

$C_{total} = C_{1o}(t_0) + C_{1i}(t_0) + C_{1c}(t_0)$ eq. S1

Assuming that all molecules are in the **1o** isomer state at the beginning of the experiment:

$Abs(t_0) = Abs_{1o} = \varepsilon_{1o} * C_{total} * l$ eq. S2

At t_{mix}

$C_{total} = C_{1o}(t_{mix}) + C_{1i}(t_{mix}) + C_{1c}(t_{mix})$

$Abs(t_{mix}) = \varepsilon_{1o} * C_{1o}(t_{mix}) * l + \varepsilon_{1i} * C_{1i}(t_{mix}) * l + \varepsilon_{1c} * C_{1c}(t_{mix}) * l$

Since $\varepsilon_{1c} = 0$ in the visible range, it can be simplified:

$Abs(t_{mix}) = \varepsilon_{1o} * C_{1o}(t_{mix}) * l + \varepsilon_{1i} * C_{1i}(t_{mix}) * l$ eq. S3

Combining eq. S2 and S3:

$Abs(t_{mix}) = Abs(t_0) * (C_{1o}(t_{mix})/C_{total}) + \varepsilon_{1i} * C_{1i}(t_{mix}) * l$ eq. S4

Thus, Abs_{1i} spectrum can be obtained from the two other experimental spectra, using the equation:

$Abs_{1i} = \varepsilon_{1i} * C_{1i}(t_{mix}) * l = Abs(t_{mix}) - Abs(t_0) * (C_{1o}(t_{mix})/C_{total})$ eq. S5

Precision concerning the errors about the photophysical constants:

For the kinetic constants k_{nm} and the activation energy E_{nm}, the error values have been obtained by the exponential and linear numerical fitting of experimental values, performed on the Igor Pro software (Wavemetrics).

Concerning the photochromic quantum yields Φ_{nm}, the errors have been estimated considering different experimental errors on the irradiation power measurements, the kinetic constants obtained previously, and the molar absorption coefficients obtained by the Beer-Lambert law (for **1o**) or oscillator strengths ratio (for **1i**).