Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Ultrafast excited-state dynamics in some spirooxazines and chromenes. Evidence for a dual relaxation pathway

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. Spectral and dynamic behaviour of SO-2

The slightly negative absorption signal initially detected for SO-2 upon 400 nm excitation in MeCN solution increased over the whole visible spectral region within 1-2 ps (Fig. 1-ESI a). Then, a decrease was observed on the wings of the spectral extension and an increase between 583 and 710 nm (isosbestic points), forming the typical merocyanine band centred at ~ 630 nm, with a rise time of ~ 20 ps, Fig. 1-ESI b. The spectrum corresponds to that obtained at the photostationary state upon continuous irradiation (Fig. 1b, inset).[28] A slower process in the same direction followed with rise time of ~ 170 ps. See below kinetics (Fig. 2-ESI) and kinetic parameters (Table 1-ESI).

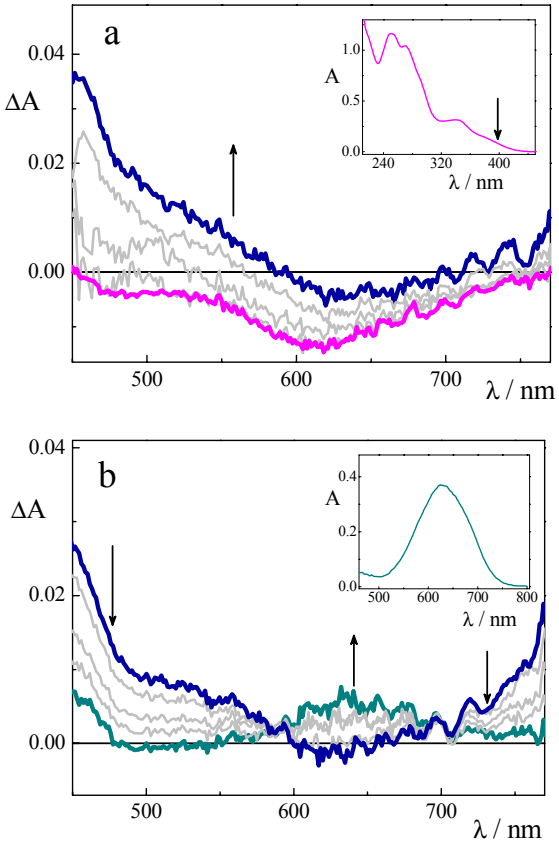

Fig. 1-ESI. Time-resolved absorption spectra of the transients obtained from SO-2 by 400 nm excitation in MeCN; vertical arrows indicate the direction of absorbance evolution a): 0-2 ps. Inset: absorption spectrum of SO-2 in MeCN, the arrow indicates the irradiation wavelength; b): 2-1345 ps. Inset: absorption spectrum of the PM in MeCN under stationary irradiation.

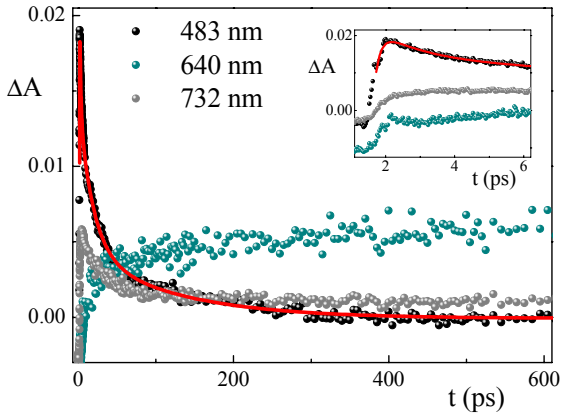

Fig. 2-ESI. Relaxation kinetics of the transients obtained from SO-2 by 400 nm excitation in MeCN at selected wavelengths. Inset shows the signals on shorter time scale. The interpolating functions (red lines) are superimposed to the experimental traces at 483 nm, as an example of the goodness of fit.

Table 1-ESI. Dynamics of relaxation of the transients from SO-2, excited at 400 nm and probed at selected wavelengths in MeCN (r, rise-time; d, decay-time). R^2 is the square correlation factor.

λ_{anal} / nm	τ_1 /ps	τ_2 /ps (r)	τ_3 /ps	τ_4 /ps	R^2
430	0.10 ± 0.01	1.9 ± 0.4	24 ± 1 d	205 ± 25	0.99
453	0.099 ± 0.004	1.14 ± 0.06	20.6 ± 0.6 d	165 ± 10	0.99
483	0.16 ± 0.01	1.4 ± 0.1	18 ± 1 d	125± 10	0.99
519	0.102 ± 0.006	1.4 ± 0.1	16.2 ± 0.9 d	146 ± 10	0.99
640	---	2.0 ± 0.7	14 ± 3 r	265 ± 39	0.97
732	0.17 ± 0.05	0.9 ± 0.1 d	24 ± 2 r	121 ± 41	0.98
749	0.12 ± 0.04	0.8 ± 0.1	24 ± 2 d	188 ± 30	0.99
average	$\tau_1 < 0.15$	1.4	~ 20	~ 170	

2. Spectral and dynamic behaviour of NP-1

The time evolution of the transients obtained from NP-1 upon 400 nm excitation in MeCN is shown in Fig. 3-ESI; kinetic parameters are reported in Table 2-ESI and examples of relaxation dynamics at selected wavelengths are illustrated in Fig. 4-ESI. Immediately after excitation, a broad absorption increases that covers the entire visible wavelength range, with an unpronounced maximum around 600 nm. The rise time ($\tau_1 < 0.15$ ps) is of the order of magnitude as the laser pulse and therefore has no significant meaning from the numerical point of view, but testifies that a

very fast process is simultaneously occurring with the excitation pulse (Fig. 3-ESI a). Further evolution causes a shift of the maximum to shorter wavelength (compare spectra at 1.7 and 4.3 ps in Fig. 3-ESI b), accompanied by vibrational relaxation in the long wavelength side within a few picoseconds (τ_2 ~ 2 ps). Then, conversion to the stable merocyanine isomer takes place, which is characterized by an absorption with two maxima at 496 and 584 nm, as observed in the steady state experiments (see inset of Fig. 3-ESI b).[28]

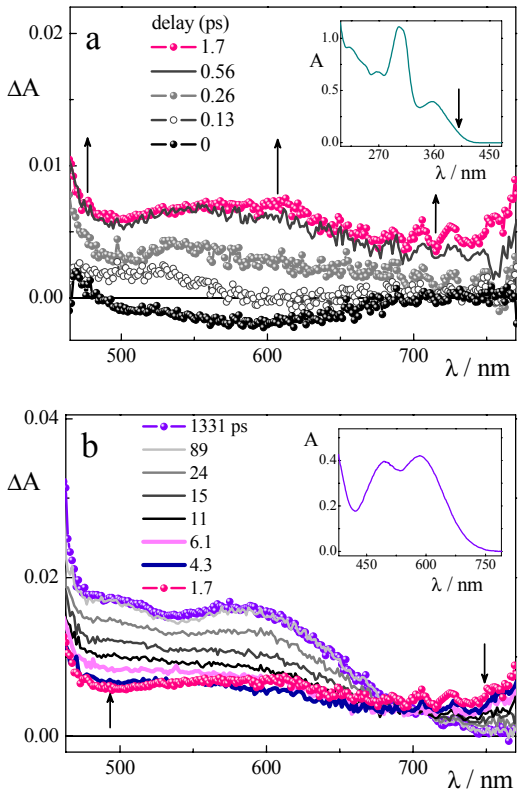

Fig. 3-ESI. Time-resolved absorption spectra of the transients obtained from NP-1 by 400 nm excitation in MeCN; vertical arrows indicate the direction of absorbance evolution Insets: a) absorption spectrum of NP-1 in MeCN, the arrow indicates the irradiation wavelength; b) absorption spectrum of the PM in MeCN recorded under stationary irradiation.

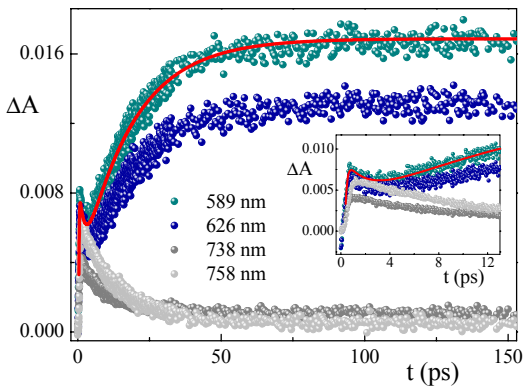

Fig. 4-ESI. Kinetics of the transients obtained from NP-1 in MeCN excited at 400 nm and probed at selected wavelengths. Inset: signals on shorter time scale. The interpolating functions (red lines) are superimposed to the experimental traces at 589 nm, as an example of the goodness of fit.

Table 2-ESI. Dynamics of the transients obtained from NP-1 in MeCN by 400 nm excitation and probed at selected wavelengths (r, rise-time; d, decay-time). R^2 is the square correlation factor.

λ_{anal} /nm	τ_1 /ps	τ_2 /ps	τ_3 /ps	R^2
502	---	1.1 ± 0.3 r	17.5 ± 0.2 r	0.99
589	0.14 ± 0.03 r	1.8 ± 0.1 d	17.8 ± 0.2 r	0.98
626.5	0.09 ± 0.02 r	2.0 ± 0.2 d	19.0 ± 0.3 r	0.98
738.5	0.18 ± 0.02 r	4.0 ± 0.8 d	14 ± 1 d	0.96
average	$\tau_1 < 0.15$	~ 2	~ 17	

3. Spectral and dynamic behaviour of NP-2

A first transient, produced within about 1 ps from the end of the pump (rise-time, τ_1 ~ 400 fs), exhibited a well- pronounced absorption maximum at about 550 nm and an extended and intense absorption region towards the red (Fig. 5-ESI a). This transient had a lifetime of about 2 ps (Fig. 5-ESI b). The flat spectrum (no maximum detectable), observed after 15 ps from the pump pulse (Fig. 5-ESI c), corresponds to a ground-state merocyanine isomer.

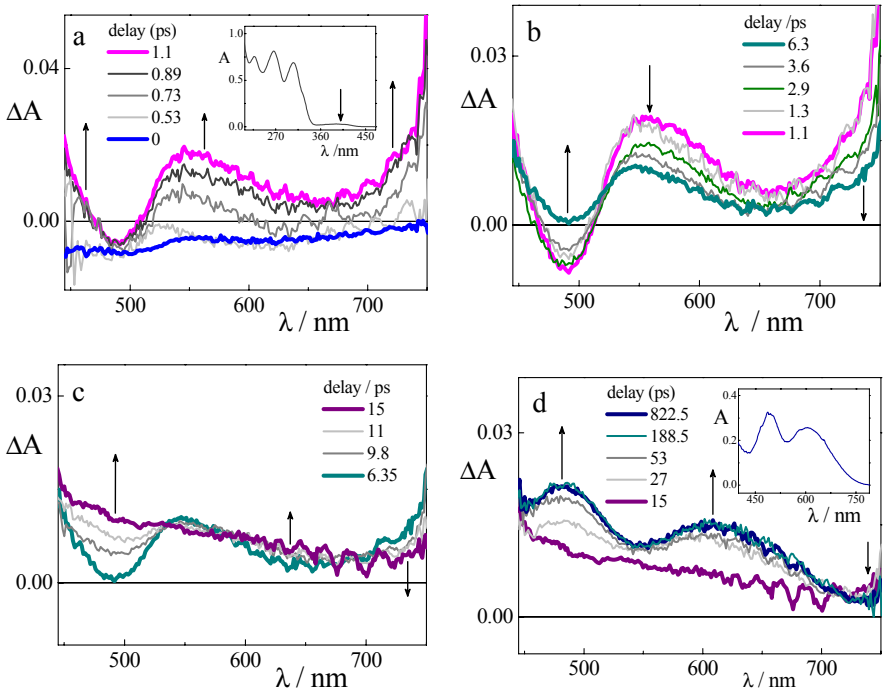

Fig. 5-ESI. Time-phases of the spectral evolution of NP-2 with 400 nm excitation in MeCN; vertical arrows indicate the direction of absorbance evolution. Insets: a) absorption spectrum of NP-2 in MeCN, the arrow indicates the irradiation wavelength; d) absorption spectrum of the MP obtained under continuous irradiation.

Vibrational relaxation (12 ps) is followed by intramolecular rotation to the equilibrium ratio of two isomers, as shown by the change in the relative intensities of the two bands (λ_{max} = 492 and 604 nm, Fig. 5-ESI d) that characterize the spectrum obtained through continuous irradiation[28] (Fig. 5-ESI d, inset). The process was completed within about 100 ps. Kinetic parameters are reported in Table 3.

Table 3-ESI. Dynamics of relaxation of NP-2 in MeCN excited with 400 nm pulsed wavelength and probed at selected wavelengths (r, rise-time; d, decay-time). R^2 is the square correlation factor.

$\lambda_{analysis}$/nm	τ_1/ps	τ_2 /ps	τ_3 /ps	τ_4 /ps	R^2
489			12.8 ± 0.2 r		0.99
550	~ 0.4				
547		2.7 ± 0.2 d		22 ±3 r	0.88
618		1.8 ± 0.2 d		20 ±1 r	0.92
747		1.9 ± 0.3 d	11.0 ± 0.2 d		0.95
Average	~ 0.4	~ 2	12	21	

4. Details on the spectral and dynamic behaviour of SO-1

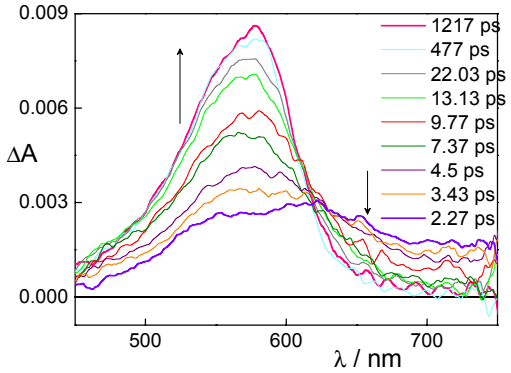

Fig. 6-ESI. Steps of spectral evolution of SO-1 after 267 nm excitation in 3-MP. Vertical arrows indicate the signal evolution.

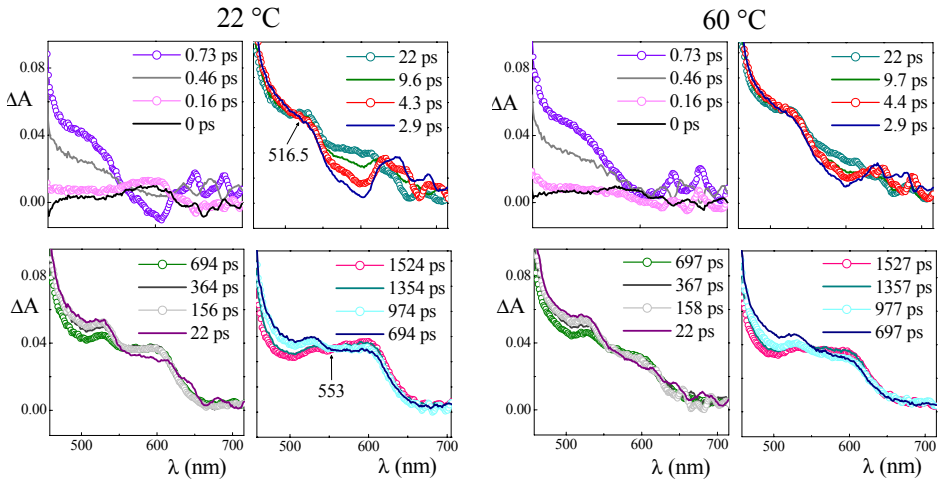

Fig. 7-ESI. Comparison of absorbance time courses upon 267 nm excitation of SO-1 at 22 °C and 60 °C in MeCN.

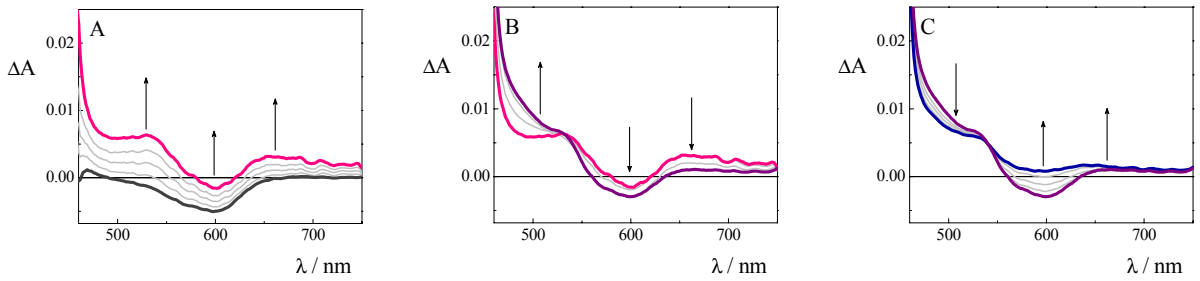

Fig. 8-ESI. Steps of spectral evolution of SO-1 upon 400 nm pulsed excitation in MeCN: (A) 0-1 ps; (B) 1-9.4 ps; (C) 9.4-1280 ps. Vertical arrows indicate the direction of absorbance evolution.

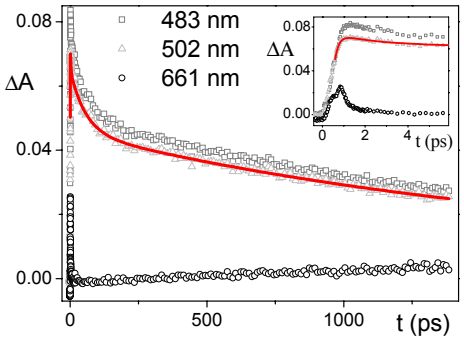

Fig. 9-ESI. Relaxation dynamics of SO-1 in MeCN excited by 400 nm and probed at selected wavelengths. Inset shows the signals on shorter time scale. The interpolating functions (red lines) are superimposed to the experimental traces at 502 nm, as an example of the goodness of fit.

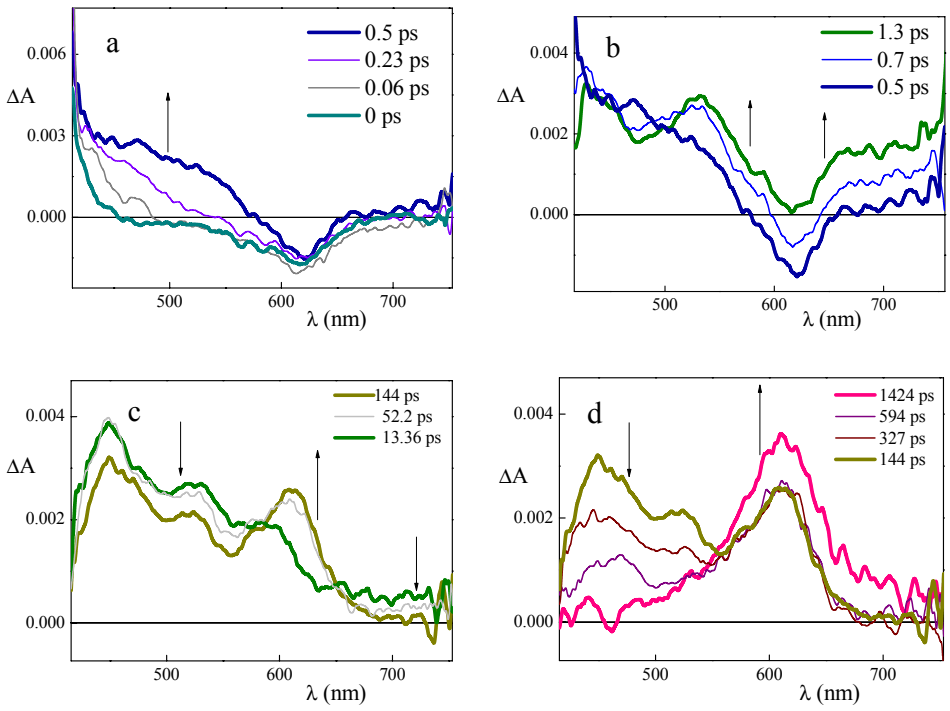

Fig. 10-ESI. Subsequent steps of spectral evolution of SO-1 upon 267 nm excitation in EtOH. Vertical arrows indicate the direction of absorbance evolution.