

A Multiswitchable Acidichromic and Photochromic Bisdiarylethene. An Experimental and Theoretical Study

SI-2

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Photochemistry of *bis*DAE in CH₂Cl₂/CHCl₃ at 240 K

In order to reduce thermal processes by lowering temperature and improve the reproducibility of on-off cycles, photochemistry of *bis*DAE was also investigated in a CH₂Cl₂/CHCl₃ (1/1 v/v) mixture at 315, 240 and 90 K. However, the three-components rigid matrix (90 K) turned out to be unstable upon UV irradiation and no reliable measurement could be done at this temperature.

The results at 240 K are reported in the following. Photocoloration was investigated by exciting at 345 nm: a fairly intense band was formed peaked at 522 and 580 nm, isosbestic points were maintained at 345 and 417 nm up to attainment of the photostationary state, as shown by the spectral evolution and kinetics illustrated in Figure 1_SI2. From the figure the reaction appears clean from the maintenance of the isosbestic points and the mono-exponential trends of the kinetics.

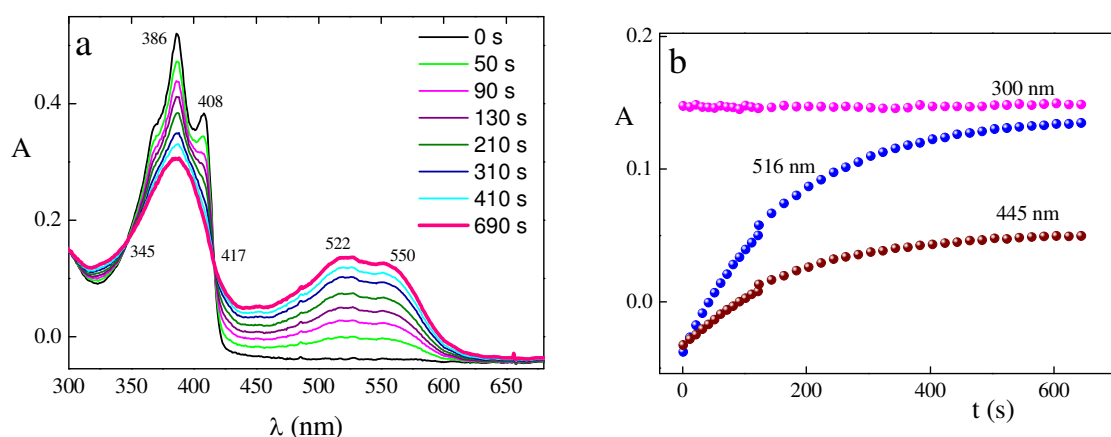


Figure 1_SI2. Spectral evolution (a) and kinetics (b) during the photocoloration of *bis*DAE 8.5×10^{-6} mol dm⁻³ in CH₂Cl₂/CHCl₃ (1/1 v/v) at 240 K, $\lambda_{\text{exc}} = 345$ nm.

The photodecoloration was promoted by exciting at 516 nm. The spectral evolution and kinetics are illustrated in Figure 2_SI2. The decoloration is not complete leading to a new spectrum with both the color band and the intense π, π^* band shifted to the red. Spectra and kinetics clearly show that the reaction is not clean generating a three (at least) components system.

By re-irradiating the partially decolored solution with 422 nm wavelength, which is only absorbed by the new photoproduct, coloration is again observed with further red shift and inversion of the relative intensities of the color band maxima. Spectral evolution and kinetics are shown in Figure 3_SI2. The reaction appears again clean: isosbestic points at 300, 366 and 437 nm.

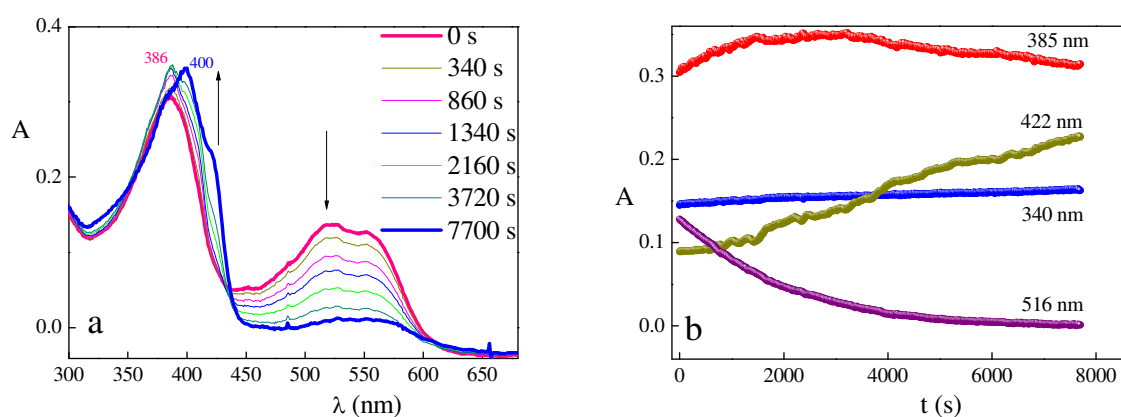


Figure 2_SI2. Spectral evolution (a) and kinetics (b) during the photocoloration of *bis*DAE $8.5 \times 10^{-6} \text{ mol dm}^{-3}$ in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ (1/1 v/v) at 240 K, $\lambda_{\text{exc}} = 516 \text{ nm}$.

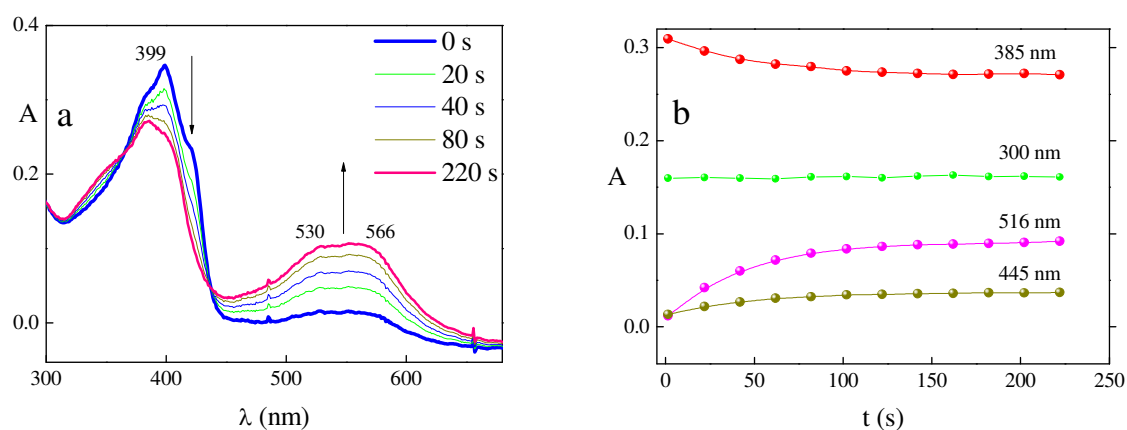


Figure 3_SI2. Spectral evolution (a) and kinetics (b) during the photocoloration with 422 nm excitation at 240 K of the *bis*DAE solution $8.5 \times 10^{-6} \text{ mol dm}^{-3}$ in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ (1/1 v/v) previously photocolorized ($\lambda_{\text{exc}} = 345 \text{ nm}$) and photo-decolored ($\lambda_{\text{exc}} = 516 \text{ nm}$).

A graphical abstract of these results at 240 K is illustrated in Figure 4_SI2.

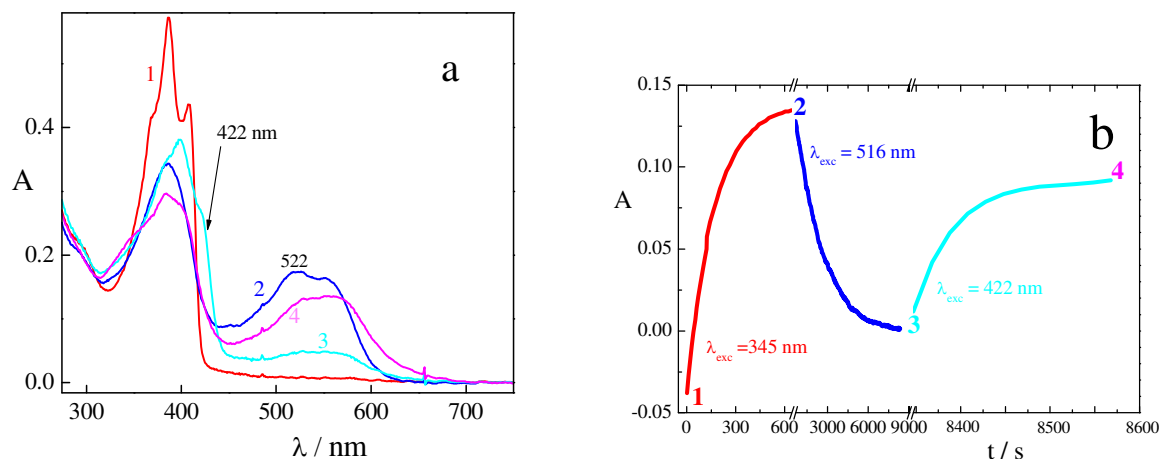


Figure 4_SI2. Photochromic cycle of the *bis*DAE solution $8.5 \times 10^{-6} \text{ mol dm}^{-3}$ in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ (1/1 v/v) at 240 K.

(a): (1) spectrum before irradiation; (2) spectrum at the photostationary state upon irradiation at 340 nm; (3) spectrum after photodecoloration with $\lambda_{\text{exc}} = 516 \text{ nm}$; (4) spectrum of the new colored form obtained upon irradiation of solution 3 with $\lambda_{\text{exc}} = 422 \text{ nm}$.

(b): Kinetics: 1→2 photocoloration at $\lambda_{\text{exc}} = 345 \text{ nm}$; 2→3 photodecoloration at $\lambda_{\text{exc}} = 516 \text{ nm}$; 3→4 photocoloration at $\lambda_{\text{exc}} = 422 \text{ nm}$. Note the break in the abscissa scale which was necessary to report the kinetic profiles on the same graph, being decoloration much more slower than coloration.

By using the kinetic equations previously reported, and assuming that the molar absorption coefficient of the colored form is the same as in dioxane, that is independent of the solvent, the photoreaction quantum yields of photocoloration ($\Phi_{\text{O} \rightarrow \text{C}}$) and photodecoloration ($\Phi_{\text{C} \rightarrow \text{O}}$) were calculated with reasonable approximation and are reported in Table 1-SI2.

Table 1-SI2: Photoreaction quantum yields of photocoloration ($\Phi_{O\rightarrow C}$) and photodecoloration ($\Phi_{C\rightarrow O}$) of the *bis*DAE in CH₂Cl₂/CHCl₃ (1/1 v/v) solution at 315 and 240 K

T / K	$\Phi_{O\rightarrow C}$	$\Phi_{C\rightarrow O}$
315	0.58	0.06
240	0.63	0.05

From the above experimental data and those reported in the article it results that the solvent plays an important role in determining the photobehavior of this molecule. It can be reasonably hypothesize that interaction with the solvent may lead to formation of adducts which alter the spectral features without suppressing the photochromic activity. Thus, alternated UV-visible irradiations make the system to evolve through different photoproducts. Such photoproducts have spectra of both the open and closed forms shifted to the red. Photocolorations appear clean (Figures 1_SI2 and 3_SI2), suggesting that such interactions occur during irradiation with visible light.

The scant solubility in most of organic solvents precludes the possibility to explore this effect over a wide set of media. A suggestion is to introduce some “pendants” which were able to increase its solubility in the molecular structure of *bis*DAE.