4,4'-Dimethylazobenzene as a Chemical Actinometer

Lorenzo Casimiro[1,*], Leonardo Andreoni[2,3], Jessica Groppi[3], Alberto Credi[3,4], Rémi Métivier[1] and Serena Silvi[2,3*]

[1]Université Paris Saclay, ENS Paris-Saclay, CNRS, PPSM – UMR 8531, 91190 Gif-sur-Yvette, France.

[2]Dipartimento di Chimica "G. Ciamician", Università di Bologna, 40126 Bologna, Italy.

[3]CLAN-Center for Light Activated Nanostructures, Istituto ISOF-CNR, via Gobetti 101, 40129 Bologna, Italy.

[4]Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, 40136 Bologna, Italy.

Supporting Information

1. Synthesis

Materials. 4-Nitrosotoluene was synthesized according to previously published procedures.[1] 4-aminotoluene was purchased from Merck in reagent-grade quality and was used without further purification. Solvents were dried according to literature procedures. The NMR spectra were recorded on a Varian Inova spectrometer operating at 500 MHz. Chemical shifts are quoted in ppm relative to tetramethylsilane using the residual solvent peak as a reference standard and all coupling constants (J) are expressed in Hertz (Hz).

4,4'-dimethylazobenzene (DMAB): A solution of 4-nitrosotoluene (0.57 g, 4.7 mmol) and 4-aminotoluene (0.50 g, 4.7 mmol) in acetic acid (about 25 mL) was stirred at room temperature for 12 h in the dark. Water was added to the reaction mixture to induce the precipitation an orange solid that was collected by filtration and washed with water. The product was purified by recrystallization from boiling EtOH, filtered, and washed with water. The product was an orange solid obtained in 41 % yield (0.40 g, 1.9 mmol) . ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.83 (d, *J* = 8.2 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 4 H), 2.44 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K): 150.9, 141.3, 129.8, 122.8, 21.6.

2. Absorption spectra

The absorption coefficient ε of *E*-**DMAB** was obtained from the absorption spectra of several solutions prepared independently. The absorption spectrum of *Z*-**DMAB** was extracted by the Fischer method[2] from the photostationary states obtained upon irradiation at 334 nm and 365 nm. The corresponding absorption coefficient is the average value on 42 combinations of PPS (6 at 334 nm and 7 at 365 nm).

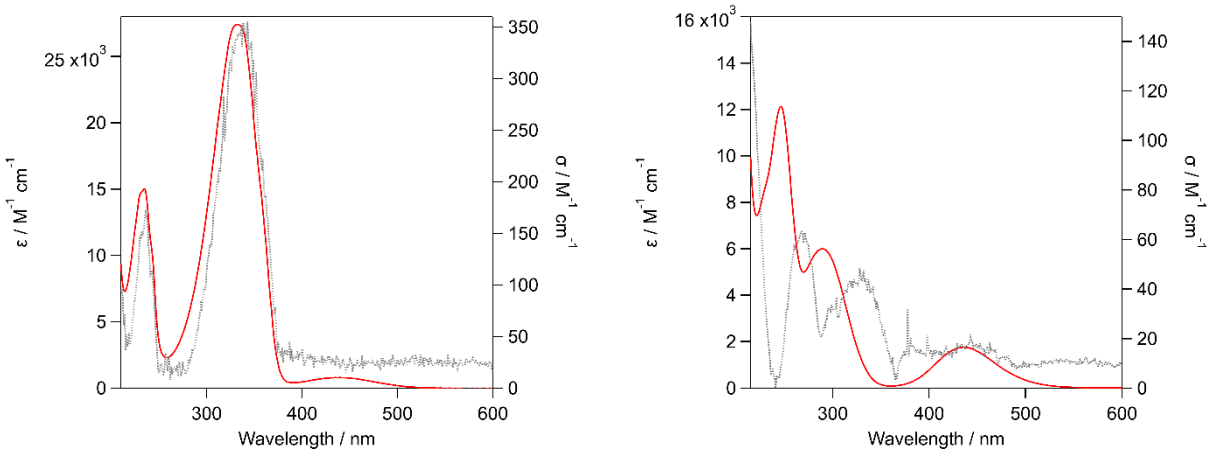

*Figure S1: Absorption spectra in MeCN (red lines) and standard deviation (σ, grey dotted lines) of the E- (left) and Z- (right) isomers of **DMAB**.*

3. Photoisomerization and thermal back isomerization

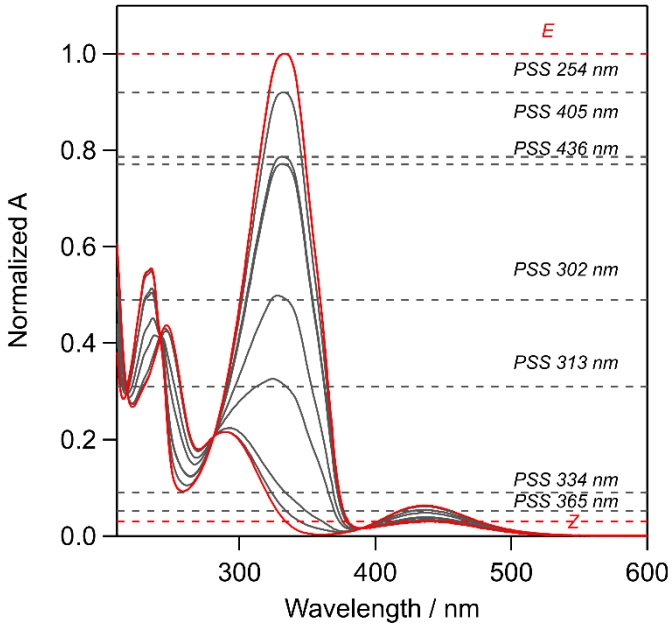

Figure S2: Normalized spectra of the photostationary states obtained by irradiation at 254 nm, 302 nm, 313 nm, 334 nm, 365 nm, 405 nm, 436 nm.

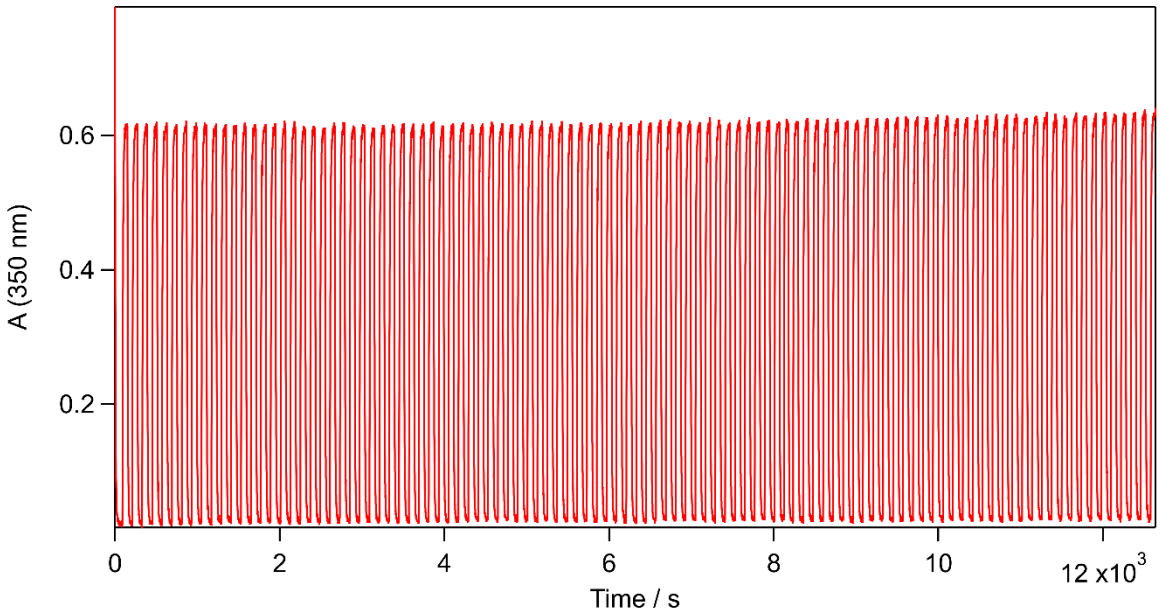

*Figure S3: Fatigue resistance of a 4.0×10^{-5} M solution of **DMAB** in MeCN, upon alternate irradiations at 365 nm and 436 nm. Throughout the irradiation, the increase of concentration is estimated to be 2%.*

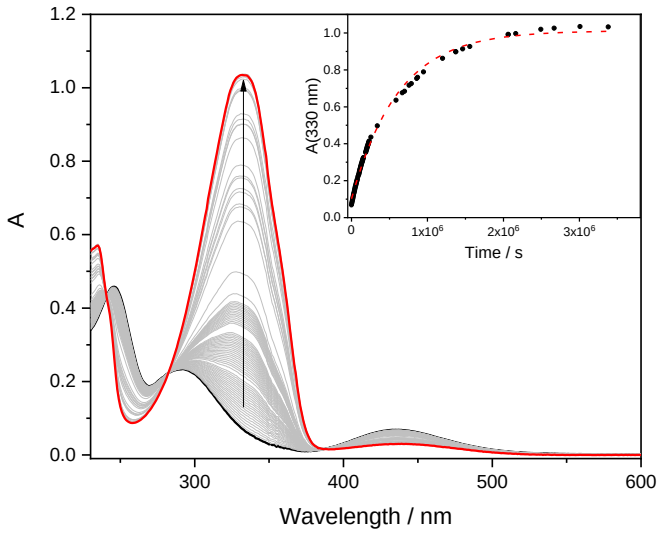

*Figure S4: Time-dependent absorption spectra showing the thermal Z→E isomerization of a 3.8 × 10^{-5} M solution of **DMAB** in MeCN at 298 K, previously irradiated to the photostationary state at 365 nm (black line). The last spectrum (red line) matches with the one of E-**DMAB**. The inset shows the absorption at 330 nm in time (black dots) and the fitting of the data with a first order kinetic model (dashed red line).*

4. Actinometric procedure

To test the DMAB actinometer, we compared the values of photon flux of a medium-pressure mercury lamp at 365 nm measured with the potassium ferrioxalate actinometer and with the **DMAB** actinometer following procedures **A** and **B**.

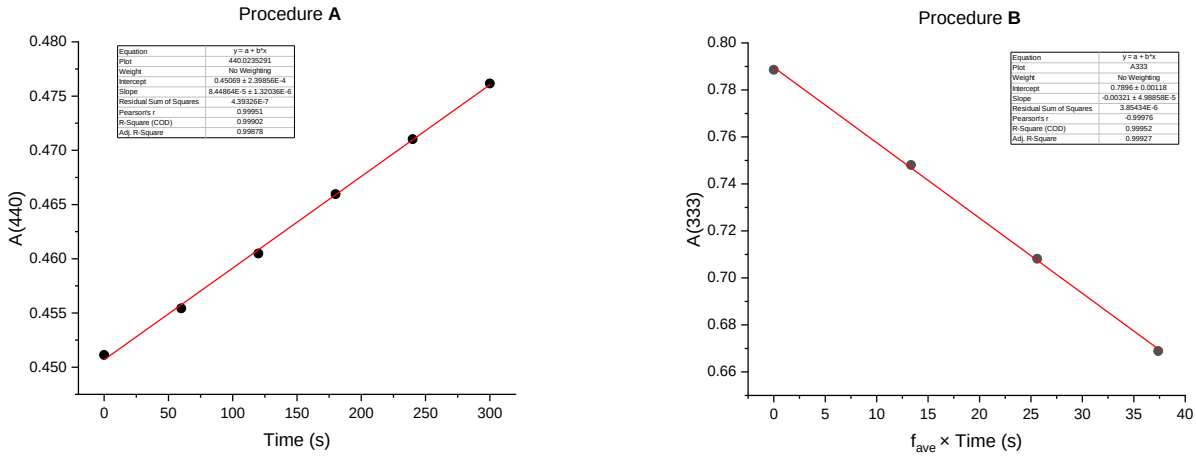

*Figure S5: Left: Absorption at 440 nm in time (black dots) upon irradiation at 365 nm of a 5.7 × 10^{-4} M solution of **DMAB** in MeCN and linear fit of the data (red line). Right: Absorption at 333 nm as function of irradiation time × f_{ave} (black dots) upon irradiation at 365 nm of a 3.0 × 10^{-5} M solution of **DMAB** in MeCN and linear fit of the data (red line).*

In total absorption regime (figure S5, left), the value of photon flux q_0 obtained from the slope is 1.49 × 10^{-9} mol s^{-1} and the one determined with the potassium ferrioxalate actinometer is 1.46 × 10^{-9} mol s^{-1}. In intermediate absorption regime (figure S5, right), the value of flux obtained from the slope is 2.02 × 10^{-9} mol s^{-1} and the one determined with the potassium ferrioxalate actinometer is 2.01 × 10^{-9} mol s^{-1}.

References

1. Defoin A., Simple Preparation of Nitroso Benzenes and Nitro Benzenes by Oxidation of Anilines with H_2O_2 Catalysed with Molybdenum Salts, *Synthesis* **5**, 706-710 (2004).

2. Fischer, E. Calculation of photostationary states in systems A ⇄ B when only A is known. *J. Phys. Chem.* **71**, 3704–3706 (1967).