Photochemistry of 2-(4-hydroxystyryl)-1-naphthopyrylium

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Supplementary material:

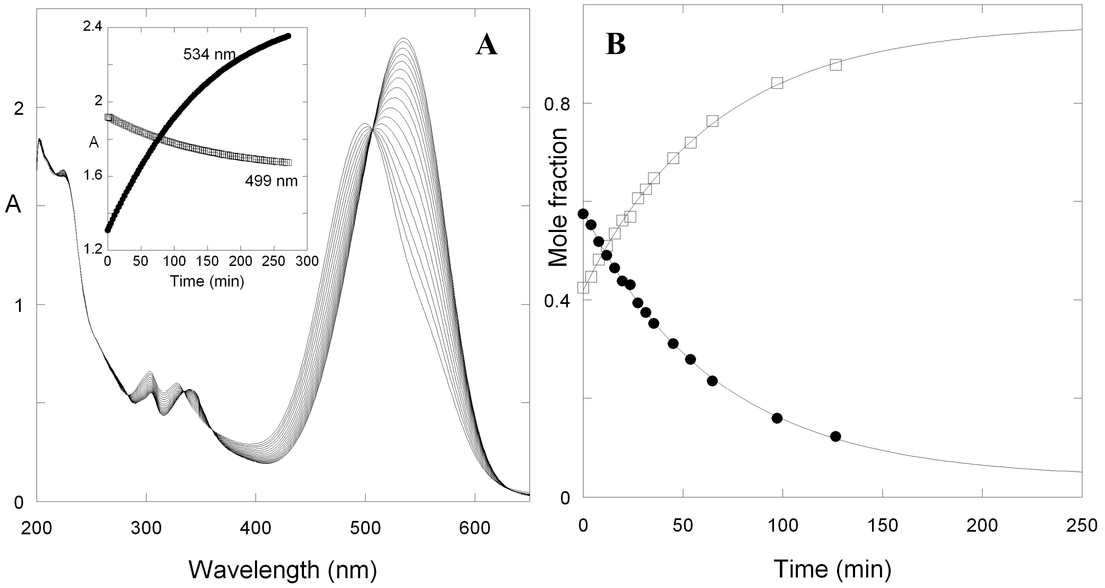


Figure S1. A- UV-vis kinetics of the conversion of 2-(4-acetoxystyryl)-1-naphthopyrylium (**V**) into 2-(4-hydroxystyryl)-1-naphthopyrylium (**IV**) in MeOH. [HCl] = 0.25 M, k_{obs}=1.1x10^{-4} s^{-1}. **B-** The same followed by ^{1}H NMR in CD3OD (pD<1) calculated from the integration of proton 4, k_{obs}=2.5x10^{-4} s^{-1}.

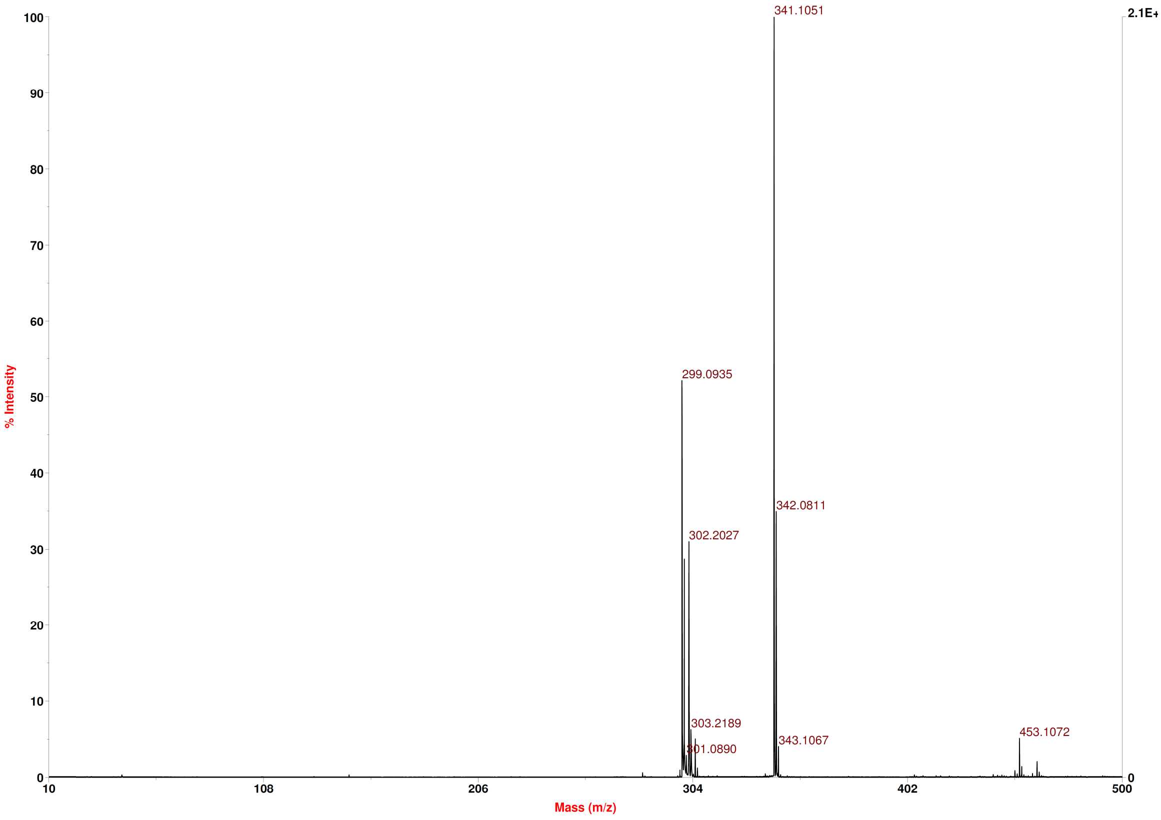


Figure S2. MALTI-TOF MS spectrum (positive mode) of a fresh solution of the solid obtained from obtained from the synthesis in methanol ([HCl] = 0.1 M).

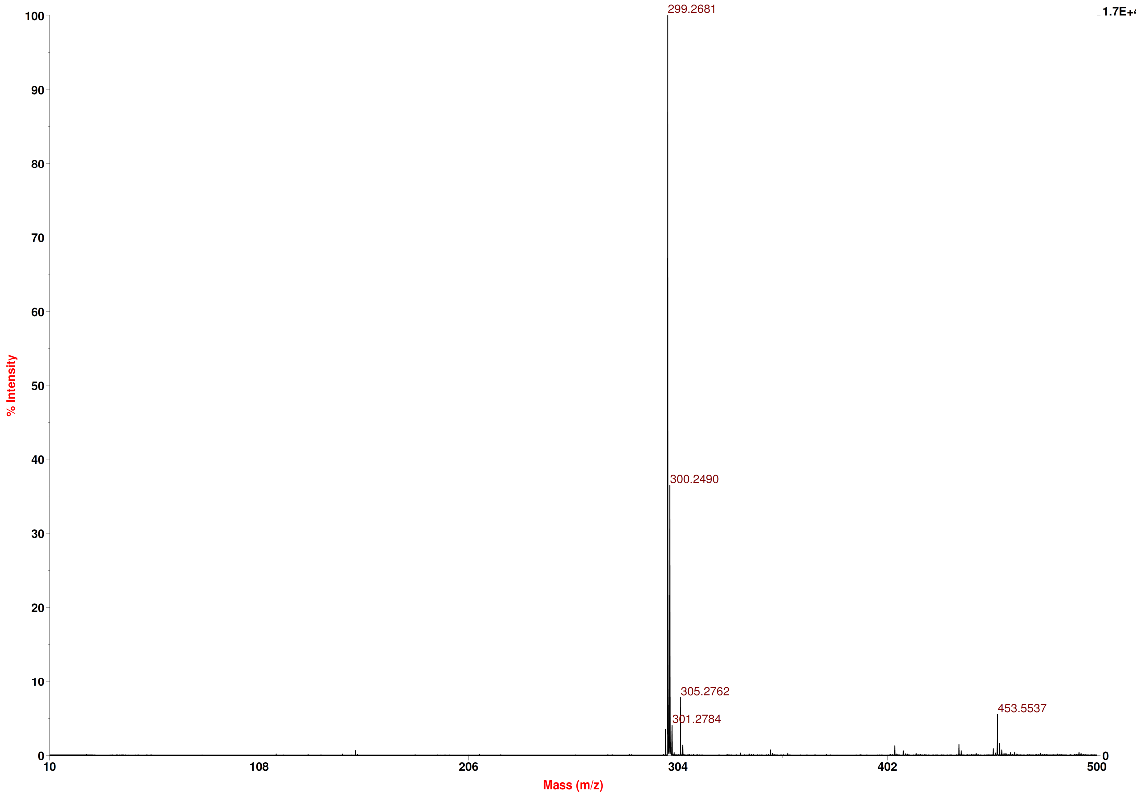


Figure S3. MALTI-TOF MS spectrum (positive mode) of the same sample of Fig. S2 after two days.

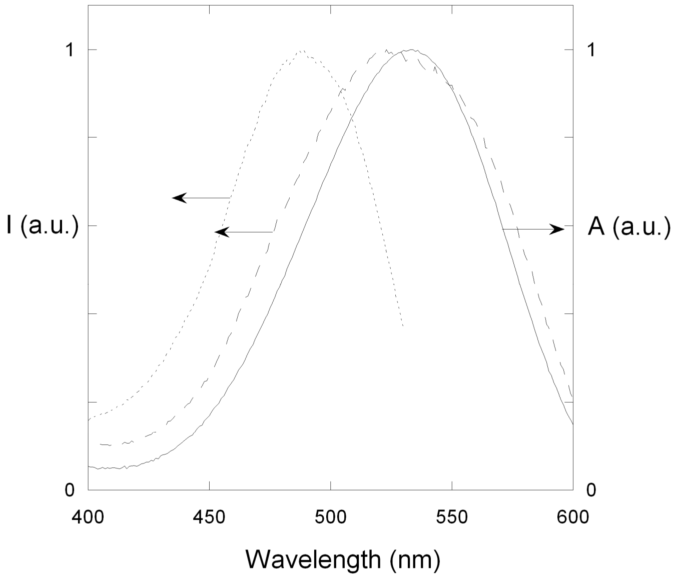


Figure S4. Absorption (full line) and excitation spectra at $\lambda_{em} = 685$ nm (dashed line) and $\lambda_{em} = 540$ nm (pointed line) of a equilibrated solution of the solid obtained from the synthesis in water:ethanol (1:1, pH < 1, 4.0×10^{-6} M).

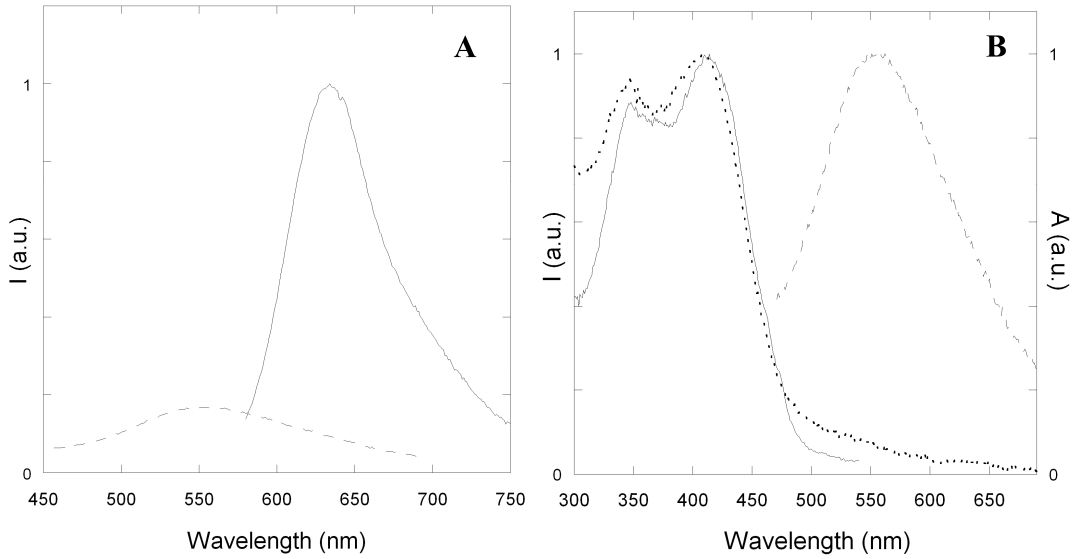


Figure S5. **A-** Corrected fluorescence spectra in water:ethanol (1:1) of the flavylium cation ([HCl] = 0.25 M, $\lambda_{exc} = 565$ nm, full line) and the *trans*-chalcone (pH = 5.6, $\lambda_{exc} = 380$ nm, dashed line) of 2-(4-hydroxystyryl)-1-naphthopyrylium. **B-** Normalized absorption (pointed line), excitation ($\lambda_{em} = 550$ nm, full line) and emission ($\lambda_{exc} = 380$ nm, dashed line) spectra of the *trans*-chalcone (water:ethanol (1:1), pH = 5.6).

- *Determination of the quantum yield for photoconversion of the trans-chalcone into the flavylium cation / quinoidal base of 2-(4-hydroxystyryl)-1-naphthopyrylium **(IV)***

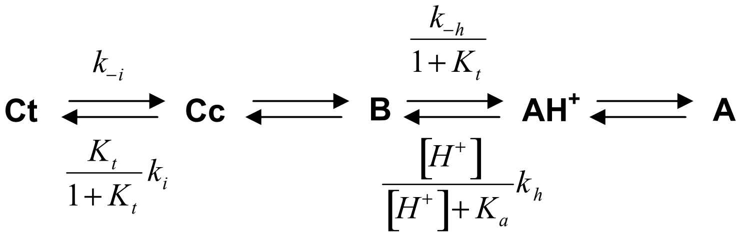
3 mL of an equilibrated solution at the corresponding pH value were irradiated at 365 nm with a xenon/medium pressure mercury arc lamp and the variations in absorbance measured at consecutive time intervals. The quantum yield was calculated through the equation:

$$\phi = \frac{\dfrac{\Delta Abs(AH^+/A,530nm)}{\varepsilon(AH^+/A,530nm)}V_{irr}}{I_{365nm}(1-10^{-A(Ct,365nm)})} \qquad \text{(S1)}$$

Where ΔAbs (AH^+/A, 530 nm) was determined as the slope of the linear increment of the photoproduct absorbance (AH^+ or a mixture AH^+/A, depending on pH) at 530 nm, occurring during the first seconds of irradiation; ε (AH^+/A, 530 nm) corresponds to the molar extinction coefficient of the photoproduct at 530 nm; V_{irr} is the volume of irradiated solution; I_{365nm} is the intensity of the light source at 365 nm (measured by ferrioxalate actinometry);[1] and A(Ct, 365 nm) corresponds to the average absorbance of the trans-chalcone at 365 nm during the first seconds of irradiation.

Appendix 1. The bell shaped curve.

B and **Cc** are considered in fast equilibrium, as well as the pair **AH^+** and **A**, as shown in the Scheme



Reporting to the Scheme

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[1] C. G. Hatchard and C. A. Parker, A new sensitive chemical actinometer. 2. Potassium ferrioxalate as a standard actinometer, *Proc. R. Soc. (London), Ser. A*, 1956, **235**, 518-536.

$$-\frac{d[Cc+B]}{dt}=\frac{K_t}{1+K_t}k_i[Cc+B]+\frac{k_{-h}}{1+K_t}[H^+][Cc+B]-k_{-i}[Ct]-\frac{[H^+]}{[H^+]+K_a}k_h[AH^++A]$$

(S2)

Assuming a steady state for **Cc** in equilibrium with **B**

$$[Cc+B]=\frac{k_{-i}}{\frac{K_t}{1+K_t}k_i+\frac{k_{-h}[H^+]}{1+K_t}}[Ct]+\frac{\frac{[H^+]}{[H^+]+K_a}k_h}{\frac{K_t}{1+K_t}k_i+\frac{k_{-h}[H^+]}{1+K_t}}[AH^++A]$$

(S3)

$$\frac{d[AH^++A]}{dt}=-\frac{[H^+]}{[H^+]+K_a}k_h[AH^++A]+\frac{1}{1+K_t}k_{-h}[H^+][B+Cc]$$

(S4)

Rearranging eq.(S4)

$$\frac{d[AH^++A]}{dt}=-\frac{[H^+]}{[H^+]+K_a}\left(\frac{k_hK_tk_i}{K_tk_i+k_{-h}[H^+]}\right)[AH^++A]+\frac{k_{-i}k_{-h}[H^+]}{K_tk_i+k_{-h}[H^+]}[Ct]$$

(S5)

The kinetic process between **AH$^+$/A** in fast equilibrium and **Ct** can be reduced to a forward and reverse reaction both of first order for each pH value.
The observed rate constant is thus given by eq.(S6)

$$k_{obs}=\frac{[H^+]}{[H^+]+K_a}\left(\frac{k_hK_tk_i}{K_tk_i+k_{-h}[H^+]}\right)+\frac{k_{-i}k_{-h}[H^+]}{K_tk_i+k_{-h}[H^+]}$$

(S6)

or rearranged as in eq.(S7) to use the product of the equilibrium constants $K_hK_tK_i$

$$k_{obs} = \left(\frac{\frac{[H^+]}{[H^+]+K_a} K_h K_t K_i + [H^+]}{\frac{K_t K_i}{k_{-h}} + \frac{[H^+]}{k_{-i}}} \right)$$

(S7)

or

$$k_{obs} = \left(\frac{\frac{[H^+]}{[H^+]+K_a} K_h K_t k_i + k_{-i}[H^+]}{\frac{K_t k_i}{k_{-h}} + [H^+]} \right)$$

(S8)

as used through the article.

Representation of eq.(S7) or (S8) as a function of pH gives a bell shape curve with $k_{\text{-i}}$ as a limit for low pH and zero as upper limit for high pH.