Tuning the Photochromic Properties of a Flavylium Compound by pH

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We studied the intricate pH- and light-dependent network of the thermal and photochemical reactions of the 4′-(dimethylamino)-7-hydroxyflavylium ion by continuous irradiation, flash photolysis, ^{1}H NMR spectroscopy, and stopped flow analysis. The distribution of the various forms at the pH-dependent thermodynamic equilibrium and the rates of several interconversion processes were measured. The most interesting feature of this multistate/multifunctional system is related to the possibility of pH-tuning the colour change caused by photoirradiation, because the *cis*-chalcone isomer, obtained from the photoisomerization of the *trans*-chalcone form, is spontaneously transformed into coloured species (flavylium cation and quinoidal base) at low values of pH, but reverts back to the uncoloured *trans*-chalcone at high values of pH because of the low energy barrier between the *cis* and *trans* chalcone isomers.

Introduction

Synthetic flavylium compounds possess chemical structures very similar to that of anthocyanins, the ubiquitous water-soluble pigments responsible for the red and blue colours found in most flowers and fruits.[1−6] The intricate pH- and light-dependent network of chemical reactions involving synthetic flavylium compounds is, therefore, basically identical to that exhibited by anthocyanins in acidic and neutral media, as shown in Scheme 1 for a prototype of the flavylium compounds, 7-hydroxyflavylium.[7]

In the last few years, we have performed a systematic investigation on the photochemical and thermal reactions of synthetic flavylium compounds.[6−12] These compounds are interesting because their photochromic behaviour is interconnected with a more-or-less complex network of pH-dependent thermal reactions, yielding a number of species, each one of which exhibits its own properties. Therefore, flavylium compounds represent examples of multistate/multifunctional chemical systems[13−21] that can be used for information processing at the molecular level according to principles similar to those that govern information transfer in living organisms.[22] In particular, flavylium compounds can behave as optical memories and logic gates.[10−12]

As shown in Scheme 1, it is possible to distinguish five species for a flavylium compound in acidic and neutral aqueous solutions: a flavylium cation (**AH**$^+$); a quinoidal base (**A**), formed upon deprotonation of the flavylium cation; hemicetal (**B2**) obtained by hydration of the flavylium cation; *cis*-chalcone (**Cc**) obtained by tautomerization of the hemicetal; and *trans*-chalcone (**Ct**) resulting from isomerization of the *cis*-chalcone.[3−6] The equilibria among these five species can be represented by Equation (1)−(4):

$$\mathbf{AH}^+ \leftrightarrows \mathbf{A} + \mathrm{H}^+ \qquad K_\mathrm{a} \qquad (1)$$

$$\mathbf{AH}^+ + \mathrm{H_2O} \leftrightarrows \mathbf{B2} + \mathrm{H}^+ \qquad K_\mathrm{h} \qquad (2)$$

$$\mathbf{B2} \leftrightarrows \mathbf{Cc} \qquad K_\mathrm{t} \qquad (3)$$

$$\mathbf{Cc} \leftrightarrows \mathbf{Ct} \qquad K_\mathrm{i} \qquad (4)$$

These can be simplified in one single acid−base equilibrium, Equation (5), if the **A**, **B2**, **Cc**, and **Ct** species are represented together as one generic conjugate base **CB** (given by the sum of the species **A**, **B2**, **Cc** and **Ct**) that is in equilibrium with the acidic flavylium cation **AH**$^+$.[23]

$$\mathbf{AH}^+ \leftrightarrows \mathbf{CB} + \mathrm{H}^+ \qquad K'_\mathrm{a} = K_\mathrm{a} + K_\mathrm{h} + K_\mathrm{h}K_\mathrm{t} + K_\mathrm{h}K_\mathrm{t}K_\mathrm{i} \qquad (5)$$

At sufficiently acidic values of pH, the flavylium cation **AH**$^+$ is the only species present in solution, but upon increasing the pH it is replaced by **CB**, [Equation (5), Scheme 1]. An interesting feature of these systems is the possibility of obtaining very different ratios between the

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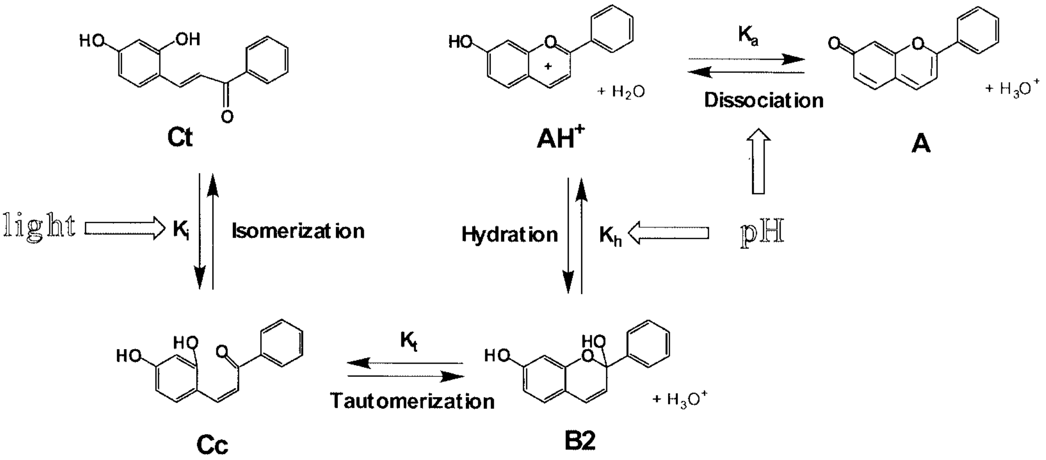
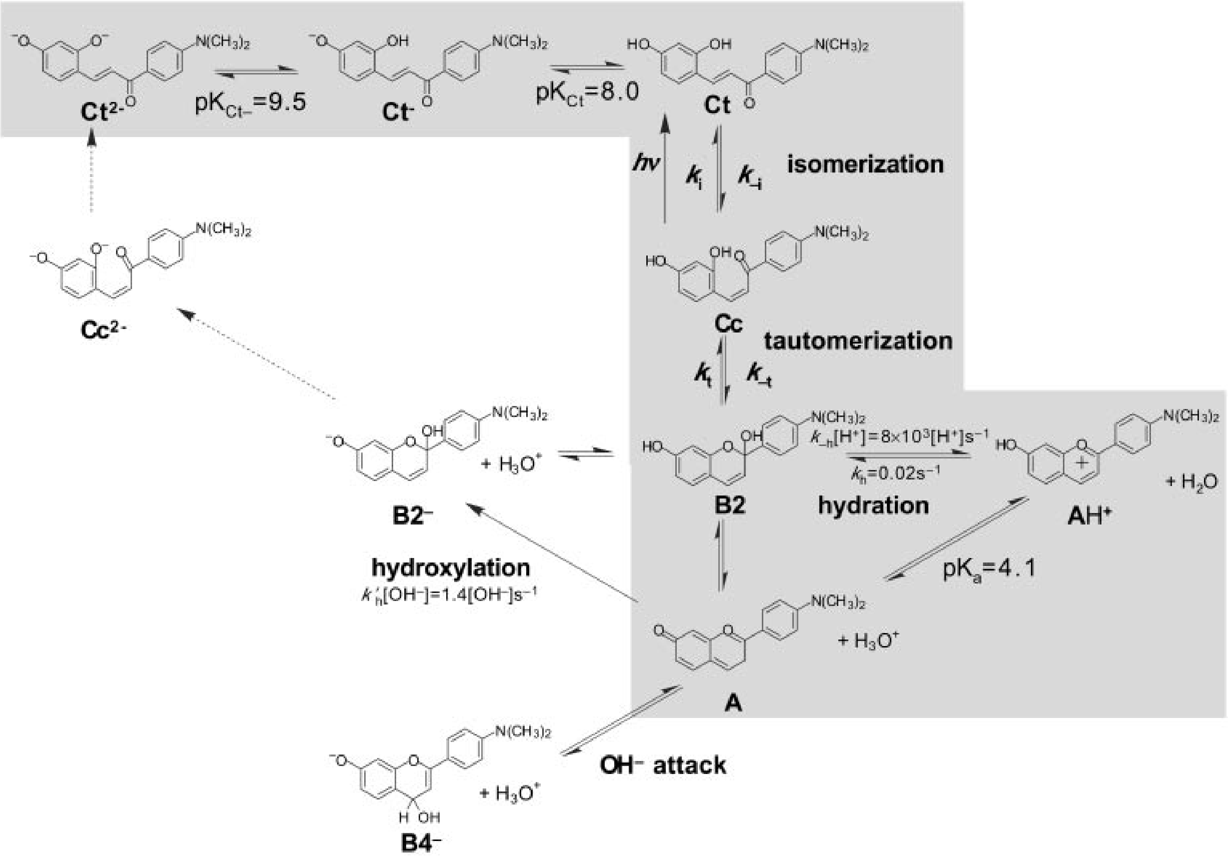


Scheme 1

concentrations of the various species constituting to **CB** (i.e., **A**, **B2**, **Cc**, and **Ct**) at the thermodynamic equilibrium, as well as different kinetic rates to reach the equilibrium depending on the nature and position of the substituents in the benzopyrylium ring. Furthermore, the nature of the substituent affects the photoisomerization quantum yields and the energy barrier (and, therefore, the rate) of the *cis−trans* thermal isomerization.

In this paper, we examine the behaviour, in acid, neutral and basic solutions, of the 4′-(dimethylamino)-7-hydroxyflavylium derivative to elucidate the effect of the electron-donating dimethylamino group in the 4′ position on the pH-tuning of the photochromic properties. Since we have extended the study to basic solution, the mono- and dianions of the *cis* and *trans* isomers are also expected to be involved, as shown in Scheme 2.

We have identified and characterized the species in the shadow area of the scheme, while **B2**$^-$, **B4**$^-$ and **Cc**$^{2-}$ are forms postulated to allow interpretation of the kinetic data obtained at basic values of pH. The equilibrium and rate



Scheme 2

constants obtained from the experiments described below are displayed in the scheme.

Results and Discussion

Thermodynamic Equilibrium

The absorption spectra of thermally equilibrated solutions of 4′-(dimethylamino)-7-hydroxyflavylium as a function of pH are represented in Figure 1.

In the pH range 1−6 (Figure 1, a), the absorption band intensity of the flavylium cation $\mathbf{AH^+}$ having its maximum at 457 nm decreases with increasing pH, accompanied by an increase of the near-UV absorption band (λ_{max} = 372 nm) characteristic of the *trans*-chalcone form **Ct**, as well as by a small absorption at longer wavelengths assigned to the quinoidal base, **A**. This pattern is similar to that previously found for other flavylium compounds possessing a hydroxy substituent in position 7.[7] From the absorbance variation at 457 nm, a value of pK'_a [Equation (5)] of 3.0 is obtained, similar to that (2.7) obtained for 7-hydroxyflavylium.[7]

Upon increasing the pH in the range 6−12 (Figure 2, b), the *trans*-chalcone form, in equilibrium with the quinoidal base, is converted into other species that exhibit absorption bands in the visible region. The lack of isosbestic points suggests that more than one species is formed.

Useful information on the species involved can be obtained by monitoring the absorption spectra immediately after a pH jump from 1 to the less acidic region (Figure 2, a). Inspection of Figure 2 clearly shows that, as expected, the species formed upon the pH jump is the quinoidal base, **A** (Scheme 2). From the pH dependence of the absorption spectra, a value of pK_a = 4.1 was obtained (Figure 2, a, inset).

When the pH-jump experiments are extended to the basic region (full lines in Figure 2, b), up to pH = 8, the absorption spectrum is that of the quinoidal base **A**, but a new species is formed for pH values higher than 8. To characterize this new species, the solutions resulting from the pH jumps from 1 to the basic region were immediately reverted back to pH = 1.0 (Figure 2, b, dashed lines). The results obtained show that while the sequence pH = 1 to pH < 8 to pH = 1 leads back to the flavylium cation $\mathbf{AH^+}$, the sequence pH = 1 to pH > 8 to pH = 1 gives rise to a percentage of *trans*-chalcone, **Ct** (100% **Ct** at pH = 11.5). This process allows us to conclude that the species obtained

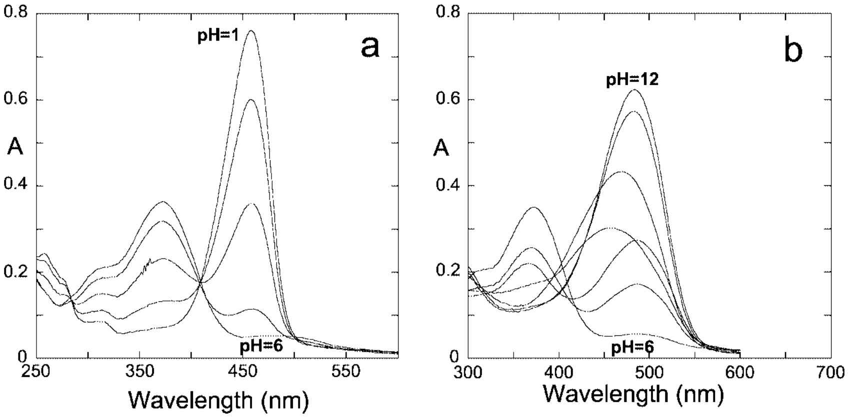


Figure 1. Absorption spectra of an aqueous solution of 4′-(dimethylamino)-7-hydroxyflavylium (1.2×10^{-5} M) in the pH ranges (a) 1−6 and (b) 6−12

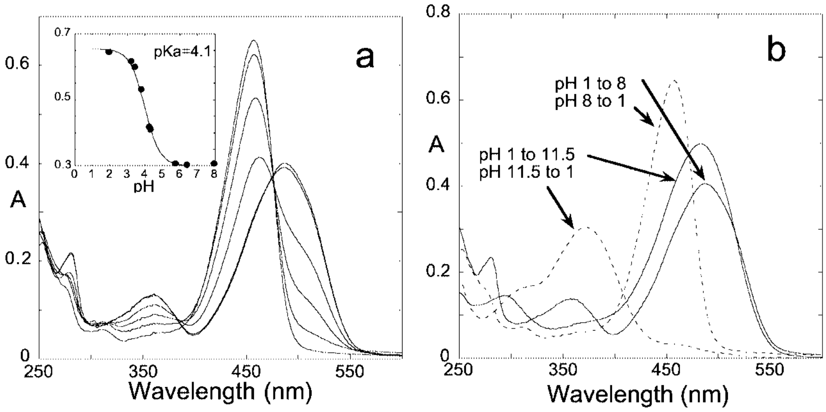


Figure 2. Spectral variations observed for an aqueous solution of 4′-(dimethylamino)-7-hydroxyflavylium (1.0×10^{-5} M) immediately after a pH jump (a) from 1 to the acidic region ($\mathbf{AH^+/A}$ pseudo-equilibrium) and (b) to the basic region (full lines) followed by another pH jump back to pH = 1 (dashed lines)

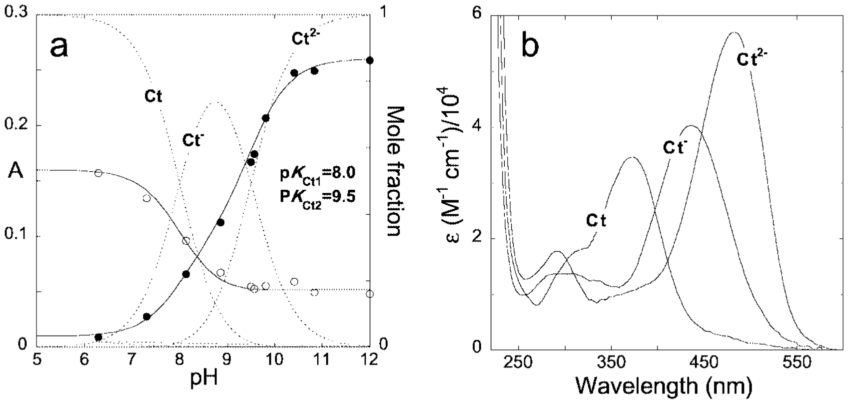


Figure 3. (a) Absorbance changes at 483 nm (full circles) and 372 nm (open circles) used to obtain the mole fraction distribution of the three chalcones. (b) Absorption spectra of the three species. The spectrum of **Ct**$^-$ was obtained upon subtraction of the contributions from **Ct** and **Ct**$^{2-}$ because there is no value of pH at which **Ct**$^-$ is the only absorbing form

at pH = 11.5 (Figure 2, b) is an anionic *trans*-chalcone form. To establish if it is a monoanionic (**Ct**$^-$) or a dianionic (**Ct**$^{2-}$) species, the solution at pH = 11.5, which is stable for several days in the dark, was subjected to pH jumps to less-basic and acidic media. When the final pH was lower than 6, the spectrum of **Ct** was obtained, but at higher values of pH, two species, most likely **Ct**$^-$ and **Ct**$^{2-}$, were clearly present, as shown by the lack of isosbestic points (see Figure 3, a).

An interesting feature of this system is the formation of **Ct**$^{2-}$ (or **Ct**$^-$) immediately after a pH jump to pH > 8, with a consequent decrease of the quinoidal base **A**. At neutral or moderately basic values of pH, the species **A** reacts slowly to give the thermodynamic equilibrium distribution, but on increasing the hydroxide concentration, the ionized **Ct**$^-$ and **Ct**$^{2-}$ forms appear immediately even though the concentration of flavylium cation is practically zero. This process can happen only as a consequence of a hydration reaction of the quinoidal base **A** upon OH$^-$ attack, a process that is discussed below in the section on stopped-flow experiments.

In Figure 3 (a), the changes in absorbance at 483 nm (maximum of the **Ct**$^{2-}$ band) and 372 nm (maximum of the **Ct** band) are reported as a function of pH. From these titration curves, the two values of pK_a of *trans*-chalcone were obtained. In Figure 3 (b), the absorption spectrum of the three species is shown.

$$\mathbf{Ct} \rightleftarrows \mathbf{Ct}^- + H^+ \qquad pK_{Ct1} = 8.0 \tag{6}$$

$$\mathbf{Ct}^- \rightleftarrows \mathbf{Ct}^{2-} + H^+ \qquad pK_{Ct2} = 9.5 \tag{7}$$

As we will see below, these values are in fair agreement with those obtained by ^{1}H NMR spectroscopic titration.

^{1}H NMR Experiments

We have also performed ^{1}H NMR spectroscopy experiments to establish the nature of the species present in solution at various values of pH. The results obtained are summarized in Table 1.

Table 1. ^{1}H NMR spectroscopic chemical shifts (δ/ppm) and scalar couplings (*J*/Hz) of several forms of 4′-(dimethylamino)-7-hydroxyflavylium perchlorate in D_2O at 301.0 ± 0.5 K

	AH$^{+[a]}$		**A**$^{[b]}$		**Ct** $^{[b]}$		**Ct**$^{2-}$ $^{[c]}$	
Proton	δ	*J*	δ	*J*	δ	*J*	δ	*J*
H2′ + H6′	8.26	8.9	8.04	8.9	7.92	8.9	7.82	8.9
H3′ + H5′	7.11	8.9	7.05	8.9	6.98	8.9	6.95	8.9
H3	8.09	8.9	7.44	8.1	7.53	14.9	7.13	14.9
H4	8.89	8.9	8.30	8.1	7.87	14.9	8.11	14.9
H5	7.97	8.9	7.80	9.3	7.52	8.9	7.35	8.9
H6	7.29	8.9, 2.0	6.82	9.3, 2.4	6.41	8.9, 2.4	5.86	8.9, 2.4
H8	7.37	2.0	6.68	2.4	6.34	2.4	5.68	2.4
$N(CH_3)_2$	3.84	–	3.80	–	3.78	–	3.76	–

[a] pD = 1.47. [b] pD = 5.92; **A** evolved to **Ct** over time. [c] pD = 11.31.

The spectrum of favylium cation, **AH**$^+$, was obtained at pD = 1.47, where it is the only species present in solution. A singlet at δ = 3.84 ppm, which integrates for six protons, is assigned to the two methyl groups of the amine. The two doublets at δ = 8.26 and 7.11 ppm, which integrate for two protons each, are assigned to ring **B** protons H2′/H6′ and H3′/H5′, respectively, by comparison with similar flavylium salts.[24] The doublet at δ = 7.37 ppm is assigned to the proton H8 on the basis of the small *meta* scalar coupling constant, $^4J_{H8,H6}$ = 2 Hz. This feature allows the assignment of the double doublet peak at δ = 7.29 ppm to be proton H6. One-proton doublets at δ = 8.89 and 8.09 ppm are assigned to ring C protons H4 and H3, respectively, by comparison with similar flavylium salts.[25] The remaining doublet at δ = 7.97 ppm can be attributed only to proton H5.

To obtain the spectra of **A** and **Ct**, a solution having pH in the range 4.5–7.5 was prepared and examined as a function of time. The initially formed quinoidal base, **A**, evolves to **Ct**, depending on the value of pH. At pD = 5.92, for instance, the ratio [**A**]/[**Ct**] was 79:21 after 9 h, 55:45 after

20 h, and 1:99 (i.e., almost exclusively **Ct**) after 5 days. The assignment of peaks for **A** was made on similar grounds as for $\mathbf{AH}^+$. The assignment of the second species as **Ct** was based on the high value (14.9 Hz) observed for the coupling constant between H3 and H4.

Dissolving the flavylium salt in NaOD ($\approx$ 0.01 M) leads to the fast formation of $\mathbf{Ct}^{2-}$. Titration with DCl allowed us to obtain values of $pK_{Ct1} = 7.7$ and $pK_{Ct2} = 9.2$ that are in reasonable agreement with the values obtained from spectrophotometric data [see Equations (6) and (7)]. A detailed comparison of the titration curves of protons H6 and H8 showed that the first (pK_{ct1}) and second (pK_{ct2}) deprotonations concern the hydroxy groups of **Ct** in positions 7 and 9, respectively.

The absorption spectra of the five species observed in the pH range 1−12 are reported in Figure 4. The spectrum of the flavylium cation, $\mathbf{AH}^+$, was obtained at pH = 1.0; that of the quinoidal base, **A**, was obtained immediately after a pH jump to pH = 6; the spectrum *trans*-chalcone forms were obtained as described above.

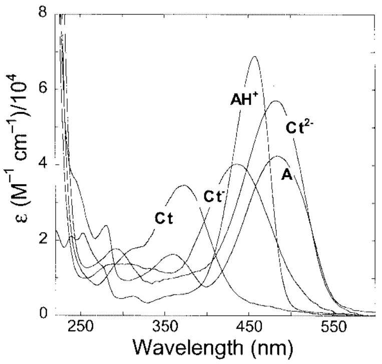


Figure 4. Absorption spectra of the five species observed in the pH range from 1 to 12

Kinetic Aspects

pH Jump Experiments

A series of pH jump experiments were performed on dark-equilibrated solutions, from pH = 1 ($\mathbf{AH}^+$) to the pH range 2−6, and from pH = 12 ($\mathbf{Ct}^{2-}$) to the acidic region (Figure 5). First-order kinetic laws were obeyed in both cases. In the first case, the flavylium cation, which is in a fast equilibrium with the quinoidal base formed immediately upon the pH jump, is transformed into the *trans*-chalcone, while in the second case the **Ct** species ($\mathbf{Ct}^{2-}$) formed immediately upon effecting the pH jump leads to the flavylium cation $\mathbf{AH}^+$, or to a mixture of **Ct** and **A**, depending on the value of pH.

Such a pH-dependent kinetic behaviour, which has been observed previously in the case of other 7-hydroxy-substituted flavylium compounds,[9] can be accounted for by Equations (1) and (8), where **X** stands for **B2** and **Cc** (Scheme 2), which are in rapid equilibrium.

$$\mathbf{AH}^+ \underset{k_{-h}[\mathrm{H}^+]}{\overset{k_h}{\rightleftharpoons}} \mathbf{X} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathbf{Ct} \qquad (8)$$

Because **X** does not accumulate, its formation must be slower than its disappearance. This situation is possible if formation of $\mathbf{AH}^+$ and **A** from **Ct** is controlled by the *trans* → *cis* isomerization reaction and the reverse reaction (formation of **Ct** from $\mathbf{A}/\mathbf{AH}^+$) by the hydration reaction. In other words, $k_h << k_{-h}[H^+]$ and $k_{-i} << k_i$. A kinetic treatment of this simplified scheme, based on the steady-state approximation for the intermediate **X** and considering that the equilibrium in Equation (1) is by far the fastest process, gives the following expression for the observed rate constant[6,9]

$$k_{obs} = \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K_a} \cdot \frac{k_i \cdot k_h}{k_i + k_{-h} \cdot [\mathrm{H}^+]} + \frac{k_i \cdot k_{-h} \cdot [\mathrm{H}^+]}{k_i + k_{-h} \cdot [\mathrm{H}^+]} \qquad (9)$$

Representation of Equation (9) as a function of pH leads to a bell-type curve (Figure 6) from which the rate constants can, in principle, be evaluated by a fitting procedure. Fortunately, k_{-h} and k_i can be measured accurately by flash photolysis, as we will see below. Therefore, we first obtained values of k_{-h} and k_i and then, by a fitting procedure to Equation (9), values of k_{-i} and/or k_h.

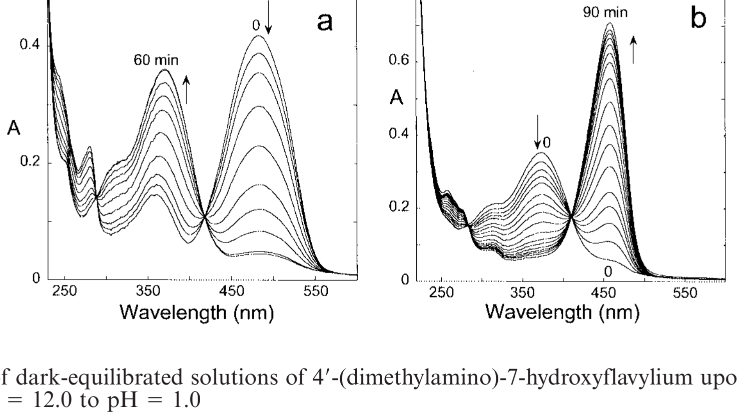


Figure 5. Spectral variations of dark-equilibrated solutions of 4′-(dimethylamino)-7-hydroxyflavylium upon a pH jump (a) from pH = 1 to pH = 5.3 and (b) from pH = 12.0 to pH = 1.0

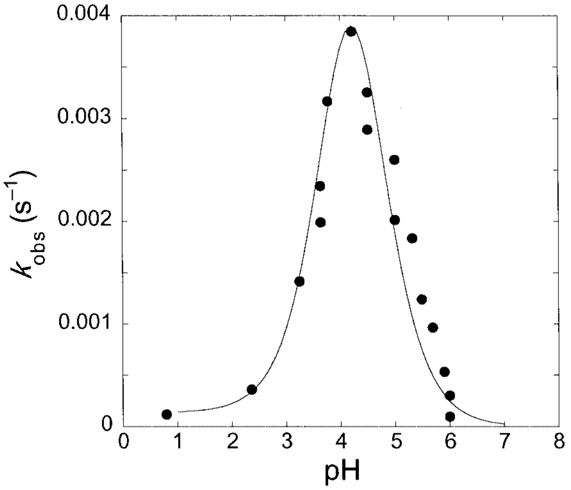


Figure 6. Representation of Equation (9) for the pH jump experiments

Stopped-Flow Experiments

The kinetic behaviour of the system in the basic region was studied by stopped-flow experiments. A solution of the compound was subjected to a pH jump from pH = 1 to a basic value of pH. When the final pH is 7.4 (Figure 7, a), the quinoidal species **A** is formed immediately and the absorption spectrum remains constant for a long time (hours). The species **A**, however, is thermodynamically unstable and, on a longer timescale, decays to the **Ct** species, as shown before. When the jump goes from pH = 1.0 to pH = 13.2 (Figure 7, b and c), the final product is, as shown previously, **Ct**$^{2-}$, which is formed by two distinct processes. Taking advantage of the fact that the quinoidal base is long-lived (several hours in the neutral region), a series of pH jumps starting from freshly prepared solutions at pH = 7.2 to the basic region were also carried out. The kinetic behaviour is the same, independent of whether the initial pH is 1.0 or 7.2, which indicates that the first process is the deprotonation of the flavylium cation **AH**$^+$ (occurring during the mixing time of the stopped flow) that leads to the quinoidal base, **A**. The two observable kinetic processes (Figure 7, c), which have rate constants of 9.1 and 0.22 s^{-1}, can be accounted for by two parallel reactions of **A**. The slower process clearly corresponds to the transformation of **A** into **Ct**$^{2-}$ (Figure 7, b and c) and its rate constant is directly proportional to the hydroxy concentration (1.4 × [OH^-] s^{-1}), which suggests that the attack of OH^- to the species **A** to give **B2**$^-$ is the rate-determining step of this process. The fastest process (Figure 7, c) shows a decrease of the absorbance at 480 nm and follows a first-order kinetic law with a rate constant equal to 9.1 s^{-1}; this process can be attributed to the formation of a second hydroxylation product, **B4**$^-$, resulting from the attack of OH^- on **A**. This reaction is only visible at values of pH > 12, and **B4**$^-$ can be considered as a kinetic product in a rapid equilibrium with **A**. According to this interpretation, **B4**$^-$ disappears at

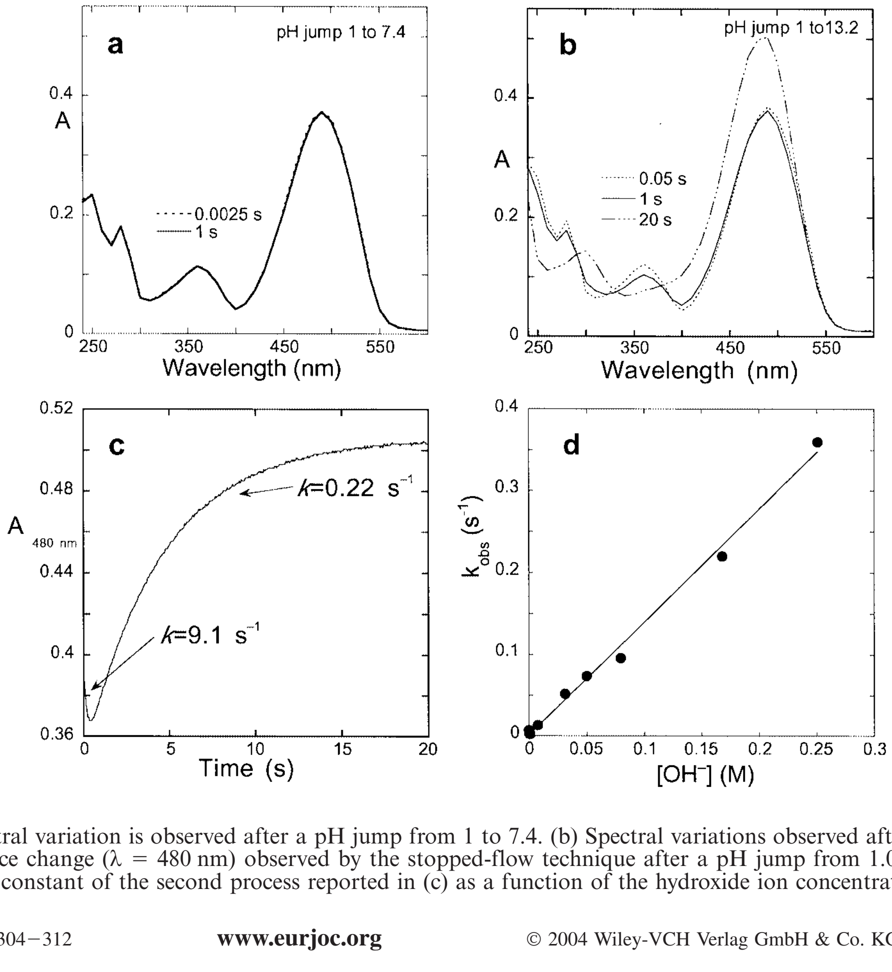


Figure 7. (a) No spectral variation is observed after a pH jump from 1 to 7.4. (b) Spectral variations observed after a pH jump from 1.0 to 13.2. (c) Absorbance change (λ = 480 nm) observed by the stopped-flow technique after a pH jump from 1.0 to 13.2. (d) Variation of the first-order rate constant of the second process reported in (c) as a function of the hydroxide ion concentration

the same time as **A** during the second and slower process to give the final product **Cc**$^{2-}$.

The formation of two hydration products, **B2** and **B4** from **AH**$^+$ is a common process that is observed in many other synthetic flavylium cations.[4,11] In the case of the 4′-methoxyflavylium compound, McClelland and Gedge reported the formation of **B4** and **Cc**$^-$ at pH = 12.[4]

Photochemical Experiments

Continuous Irradiation

A series of photochemical experiments were performed by irradiating dark-equilibrated solutions of 4′-(dimethylamino)-7-hydroxyflavylium at 365 nm in the pH range 3−6. As observed for many synthetic flavylium compounds, irradiation of the *trans* chalcone form **Ct** leads to the *cis* isomer, **Cc**, which, depending on pH, thermally evolves to **AH**$^+$ or **A** (see Figure 8, a) at pH = 3.3. The photochemical products, **AH**$^+$/**A**, go back to **Ct** because of the lack of a kinetic barrier to the isomerization reaction. The final equilibrated state is reached following the same kinetics of the pH jump at the same final value of pH. An important feature of the reaction quantum yield is its dramatic dependence on the proton concentration (Figure 8, b). This behaviour can be readily explained on the basis of the flash photolysis studies described below.

The *trans*-to-*cis* photoisomerization is not observed at pH = 12. If long irradiation times are used, however, decomposition of the **Ct**$^{2-}$ form occurs.

Flash Photolysis

Other interesting information was obtained by flash photolysis experiments performed on the **Ct** form.[9] The results obtained at pH = 5 are reported in Figure 9.

When the system was monitored at 470 nm, formation of **AH**$^+$ or **A** (depending on pH) was observed (Figure 9, a). On the other hand, if a wavelength of 380 nm was used (Figure 9, b), fast bleaching occurs (within the lifetime of the flash), indicating that **Ct** was consumed to lead to **Cc** whose absorption at this wavelength is known to be lower. After the bleaching, the absorption is partially recovered in a process that exhibits the same rate constant as the **AH**$^+$/**A** formation. This last process corresponds to partial recovery of the **Ct** form. The recuperation is not complete because of the fraction of **Ct** that is consumed in the formation of **AH**$^+$/**A**.

$$k_{\text{obsd.}}(\text{flash}) = k_i + k_{-h}[\text{H}^+] \qquad (10)$$

According to Equation (10), a representation of the observed rate constant as a function of proton concentration leads to a linear relation from which the values of k_i and

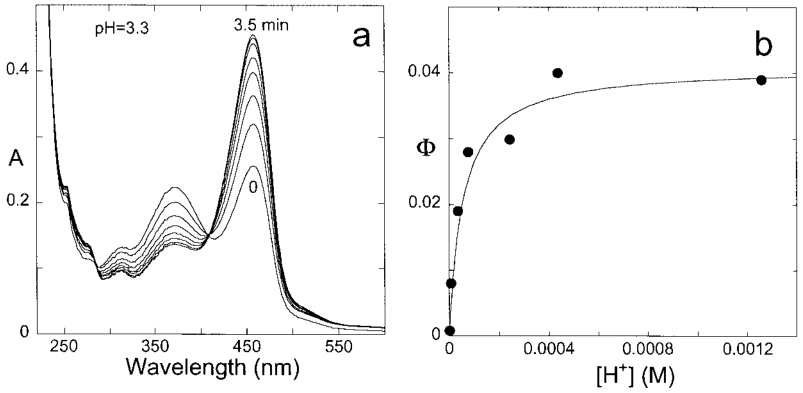


Figure 8. (a) Spectral changes observed upon irradiation at 365 nm of 4′-(dimethylamino)-7-hydroxyflavylium at pH = 3.3 (0, 0.5, 1, 1.5, 2, 2.5, 3, and 3.5 min). (b) Dependence of the quantum yield of the photoreaction on the proton concentration

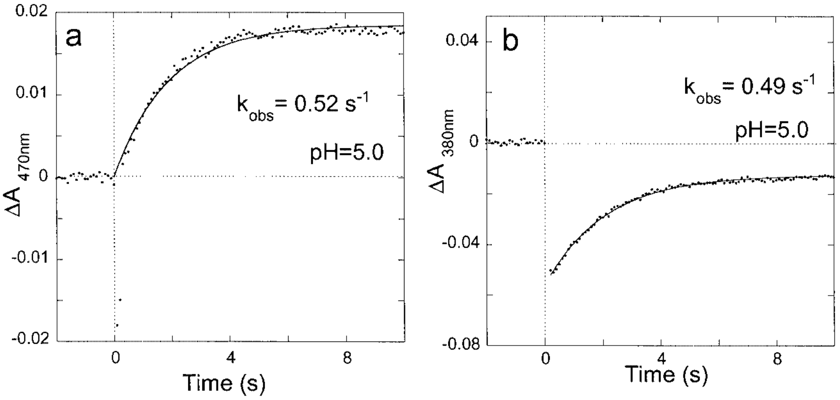


Figure 9. (a) Variation of the absorbance at 470 nm (**AH**$^+$/**A**) upon a flash; pH = 5.0. (b) The same experiment conducted at 380 nm (**Ct**/**Cc** absorption)

Table 2. Equilibrium and rate constants for 4′-(dimethylamino)-7-hydroxyflavylium in aqueous solution at 25 °C

K'_a	K_a	k_h/s^{-1}	$k_{-h}/s^{-1}\ M^{-1}$	k_i/s^{-1}	k_{-i}/s^{-1}	K_{Ct1}	K_{Ct2}
$(1.00 \pm 0.09) \times 10^{-3}$	$(8 \pm 1) \times 10^{-5}$	$(2.0 \pm 0.3) \times 10^{-2}$	$(8.0 \pm 0.4) \times 10^{3}$	0.40 ± 0.04	$< 1 \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-8}$	$(3.2 \pm 0.3) \times 10^{-10}$

k_{-h} can be calculated and further used to obtain k_{-i} and k_h from Equation (9) (Table 2).

When the proton concentration is sufficiently low, pH > 6.5, no quinoidal base is formed. Under such conditions, excitation of **Ct** with light leads only to **Cc**, which, in the dark, is converted back to **Ct** by a first-order process having a rate constant k_i, Equation (10).

The data reported in Table 2 allow us to construct an energy level diagram that can be used to summarise the behaviour of the examined system (Figure 10).[6] At very acidic values of pH, the flavylium cation is the most-stable species. Raising the pH to 4.1 causes an immediate distribution of the compound into equal amounts of AH^+ and **A**. This state is not the final one, however, because **Ct** is lower in energy, so most of the AH^+ and **A** species (ca. 90%), which are in fast equilibrium, are transformed into **Ct**. This process corresponds to the kinetics described by the bell-shaped curve of Figure 6. The scheme can also be useful to describe the photochemical behaviour. For example a dark-equilibrated solution at pH = 4.1 contains ca. 90% **Ct**, which is transformed by excitation with light into **Cc** that undergoes two parallel processes in the dark, one leading back to **Ct** and the other leading to equal amounts of AH^+ and **A**. This competition accounts for the proton dependence of the observed quantum yield of AH^+ formation, $\Phi_{obsd.}$, which can be expressed by Equation (11).

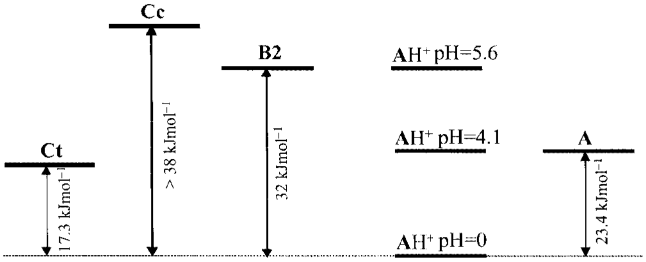


Figure 10. Energy level diagram for the 4′-(dimethylamino)-7-hydroxyflavylium compound.

$$\Phi_{obs} = \Phi_0 \frac{k_{-h}\cdot[H^+]}{k_i + k_{-h}\cdot[H^+]} \tag{11}$$

where Φ_o is the photoisomerization quantum yield (independent of pH). The fitting of the data in Figure 8 (b) was made using the constants listed in Table 1, leading to a photoisomerization quantum yield of ca. 0.04.

This particular behaviour allows us to use pH to control the photochemical formation of coloured species AH^+ and **A**.

Tuning the Photochromic Properties by pH: a Photoswitch System Controlled by pH

The pH dependence of the photochemical behaviour of 7-hydroxy-4′-(dimethylamino)flavylium can be illustrated by Figure 11. At high values of pH, e.g., pH = 6, the system is OFF because **Cc** reverts back to **Ct** and there is practi-

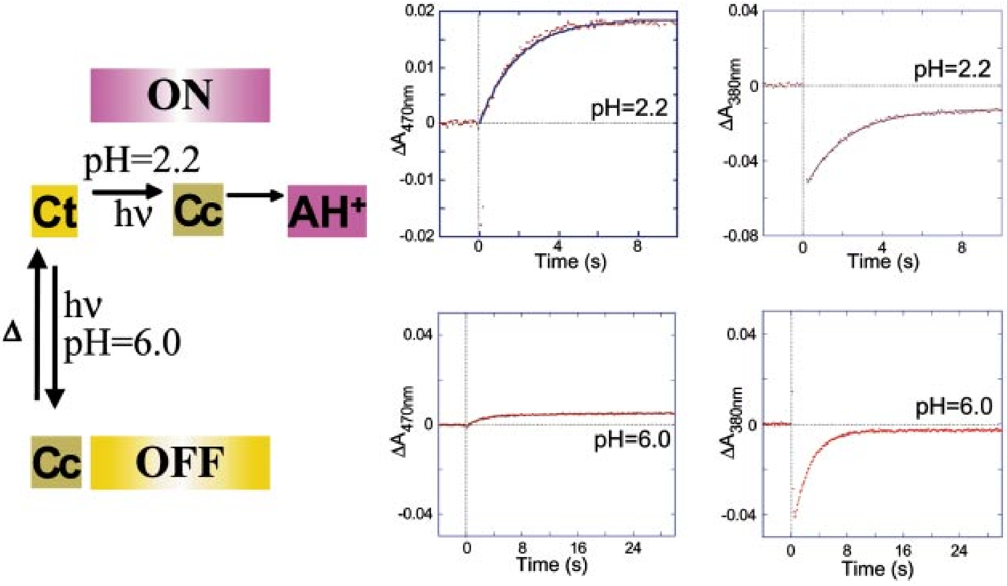


Figure 11. Photoswitch based on 4′-(dimethylamino)-7-hydroxyflavylium. At pH 6, the photoproduct **Cc** reverts back to the *trans* isomer; the system is **OFF**. At pH = 2.2, the photoproduct leads to the flavylium cation, producing the signal (appearance of the colour); the system is **ON**

cally no formation of coloured AH^+ species. At low values of pH, e.g., at pH = 2.2, the system is ON because the **Cc** isomer formed upon irradiation converts to AH^+. Additionally, it should be noted that the signal (i.e., the colour intensity) cannot only be switched ON/OFF, but can be modulated to any desired intermediate value also by adjusting the pH of the solution.

Experimental Section

4′-(Dimethylamino)-7-hydroxyflavylium perchlorate was prepared[26] from the condensation of 4′-dimethylaminoacetophenone (0.70 g, 5 mmol) and 2,4-dihydroxybenzaldehyde (0.81 g, 5 mmol) by dissolving the reagents in formic acid (10 mL) and bubbling HCl (produced in situ) through the mixture for 5 h. The red solid that precipitated was recrystallised by dissolving it in 3% (v/v) $HClO_4$ and then adding concentrated $HClO_4$, which allowed us to isolate the product (1.02 g, 56%). M.p. 216 °C (dec.). $C_{17}H_{16}O_2NClO_4{\cdot}6.5H_2O$ (482.9): calcd. C 42.29, H 6.05, N 2.90; found C 42.12, H 4.75, N 3.03. ^1H NMR: see Table 1.

All other chemicals were of analytical grade. The experiments were carried out in aqueous solutions. The pH was adjusted by addition of HCl and NaOH, or buffer, and was measured using a Metrohm 713 pH meter.

UV/Vis absorption spectra were recorded using either a Perkin−Elmer lambda 6 or Shimadzu UV2501-PC spectrophotometer. Light excitation was carried out using a medium-pressure mercury arc lamp, and the mercury lines were isolated with interference filters (Oriel). The intensity of the incident light was measured by ferrioxalate actinometry.[27] The flash photolysis experiments were performed as described previously.[7] ^1H NMR spectra were recorded using a Bruker ARX-400 spectrometer operating at 400.13 MHz. In solutions having acidic or basic values of pH, the perchlorate salt of the flavylium ion dissolves well enough to allow spectra to be obtained within a reasonable number of scans (< 64). In the pH range 4−8, a precipitate forms when starting either from acidic (red precipitate, **A**) or basic values of pH (orange precipitate, **Ct**), leaving solutions with concentrations of ca. 5×10^{-5} M. This phenomenon meant that solutions in this pH region had to be filtered and their ^1H NMR spectra accumulated with a high number of scans (0.5−3 k). The reported values of pD are direct readings of the pH meter, which can be corrected for the isotope effect through the equation pD = pH + 0.4.[28,29]

Reaction profiles were collected on an SX 18 MV stopped-flow spectrophotometer (Applied Photophysics) interfaced to a computer for data collection and analysis. The standard flow tube has an observation path length of 1 cm. The driving ram for the mixing system was operated to the recommended pressure of 8.5 bar. Under these conditions, the time required to fill the 1-cm cell was determined experimentally to be 1.35 ms (based on a test reaction).

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