Multistate/Multifunctional Behaviour of 4′-Hydroxy-6-nitroflavylium: A Write-Lock/Read/Unlock/Enable-Erase/Erase Cycle Driven by Light and pH Stimulation

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Abstract: We have investigated the network of reactions observed for the photochromic 4′-hydroxy-6-nitroflavylium compound in aqueous solutions upon pH changes (including pH jump and stopped flow experiments) and light excitation. The changes observed in the NMR and UV/Vis spectra allowed identification of ten different forms in which this compound can be transformed depending on the experimental conditions. Equilibrium and kinetic constants have been determined. Compared with other members of the flavylium family, 4′-hydroxy-6-nitroflavylium is characterized by a large *cis*→*trans* isomerization barrier, and a very efficient hydration reaction. These peculiar features allow writing, reading, storing and erasing photonic information on 4′-hydroxy-6-nitroflavylium by a novel cyclic process that involves the following steps: write-lock/read/unlock/enable-erase/erase.

Keywords: flavylium salts · heterocycles · molecular devices · optical memories · supramolecular chemistry

Introduction

Great attention is currently devoted to the development of molecular-level devices.[1–9] Photochromic compounds and other systems exhibiting multistate/multifunctional behaviour have been proposed as switches and memory elements.[1,10–13]

In the last few years we have carried out a systematic investigation on the multistate/multifunctional properties of photochromic flavylium compounds capable of performing as molecular-level optical memories.[14,15] The complex network of reactions displayed in acidic medium by these compounds is illustrated in Scheme 1 for the case of the 4′-hydroxyflavylium species.[16]

This compound can perform a *write–lock–read–unlock–erase* process, that is, a cycle (Figure 1a) in which i) a bit of information is photochemically “written” on a molecule, ii) “locked” by a chemical input (+I), iii) “read” by light absorption, iv) “unlocked” by another chemical input (−I), and v) “erased” by a photon or thermal energy. This occurs because, i) the **Ct** form of the 4′-hydroxyflavylium compound can be photochemically converted into its **Cc** isomer, which ii) can be transformed by addition of acid into the stable $\mathbf{AH}^+$ species, and iii) is photostable and can thus be spectroscopically determined by UV/Vis spectroscopy (Figure 1b). When necessary, the reaction can be reverted: iv) addition of a base leads $\mathbf{AH}^+$ back to **Cc**, which v) can be reconverted to **Ct** by heating or light excitation.

A necessary requirement for performing the above-mentioned cycle is the presence of an energy barrier in order to prevent a fast *cis*→*trans* thermal isomerization. The lack of this barrier would in fact result in the immediate erasing of the information written by the *trans*→*cis* photochemical reaction.

Previous studies[14,16] have shown that a hydroxyl substituent in position 7 decreases the isomerization barrier, whereas a hydroxyl substituent in position 4′ has the opposite effect. In order to get more insight concerning the role played by substituents on the performance of this family of compounds, we have synthesized a flavylium species bearing an electron withdrawing nitro group in position 6 and a hydroxyl unit in position 4′. We have studied the interconver-

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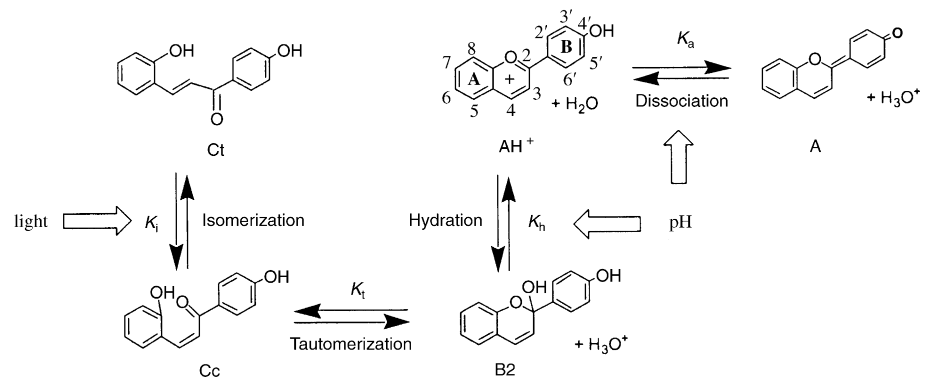


Scheme 1.

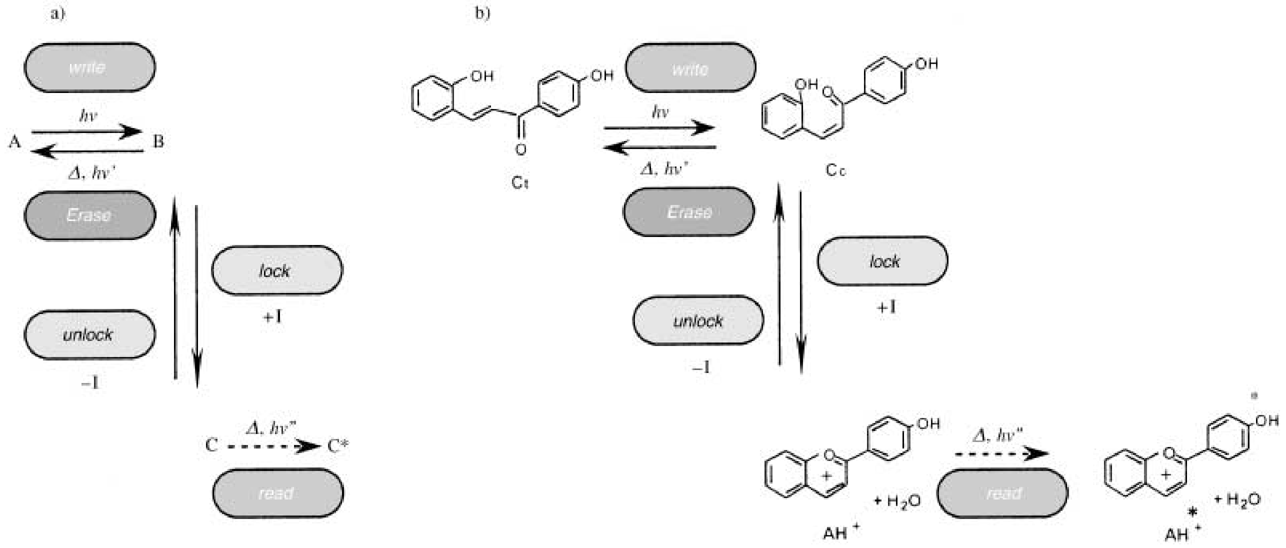


Figure 1. A write/lock/read/unlock/erase process in a generic photochromic compound (a) and in the 4′-hydroxyflavylium compound (b).

sion reactions among the various forms of the 4′-hydroxy-6-nitroflavylium compound in acid and basic media upon light excitation and changes in the pH of the solution (including pH jumps and stopped flow experiments) and we have found that it exhibits some peculiar properties. The complete pattern of processes occurring for this compound is represented in Scheme 2.

Results and Discussion

Acid media: In acid media, flavylium compounds bearing a hydroxyl in position 4′ can be present in five fundamental forms (Schemes 1 and 2), namely the flavylium cation $\mathbf{AH}^+$, the quinoidal base **A** formed upon deprotonation of the flavylium cation, the hemiketal species **B** obtained by hydration of the flavylium cation, the *cis*-chalcone form **Cc** obtained by tautomerisation of the hemiketal, and the *trans*-chalcone **Ct** form resulting from isomerization of the **Cc**.[16,2]

$$\mathbf{AH}^+ \rightleftharpoons \mathbf{A} + \mathrm{H}^+ \quad K_a \qquad (1)$$

$$\mathbf{AH}^+ \rightleftharpoons \mathbf{B} + \mathrm{H}^+ \quad K_h \qquad (2)$$

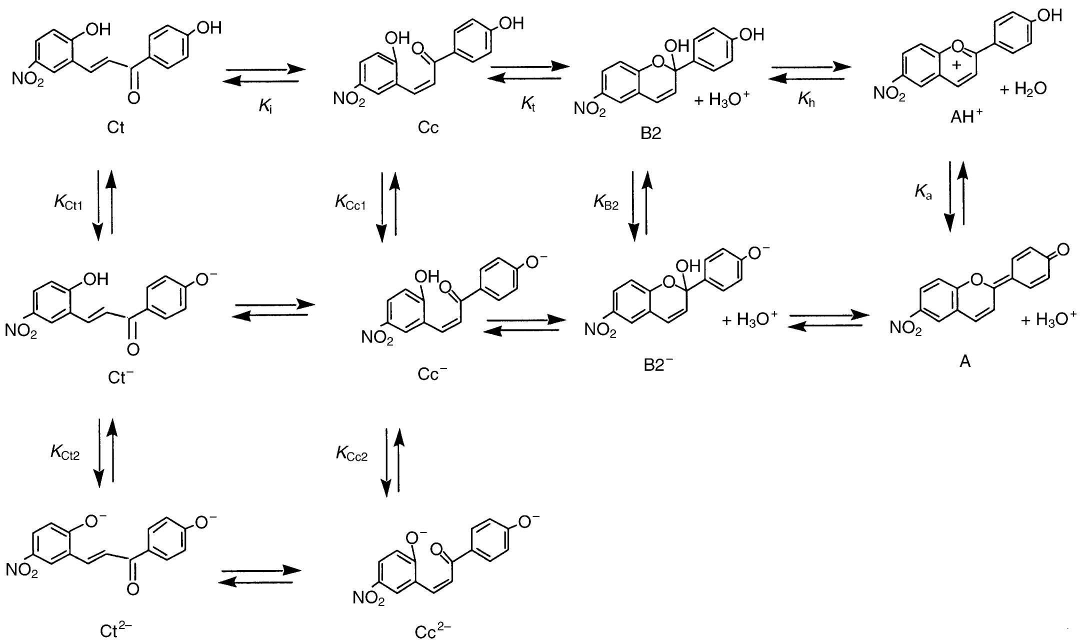
$$\mathbf{B} \rightleftharpoons \mathbf{Cc} \quad K_t \qquad (3)$$

$$\mathbf{Cc} \rightleftharpoons \mathbf{Ct} \quad K_i \qquad (4)$$

This set of equilibria can be simplified in one single acid–base equilibrium, Equation (5), if the **A**, **B**, **Cc**, and **Ct** species are represented together as a generic conjugate base **CB**, which is in equilibrium with the flavylium cation $\mathbf{AH}^+$:[14,15,21,22]

$$\mathbf{AH}^+ \rightleftharpoons \mathbf{CB} + \mathrm{H}^+ \quad K'_a = K_a + K_h + K_hK_t + K_hK_tK_i \qquad (5)$$

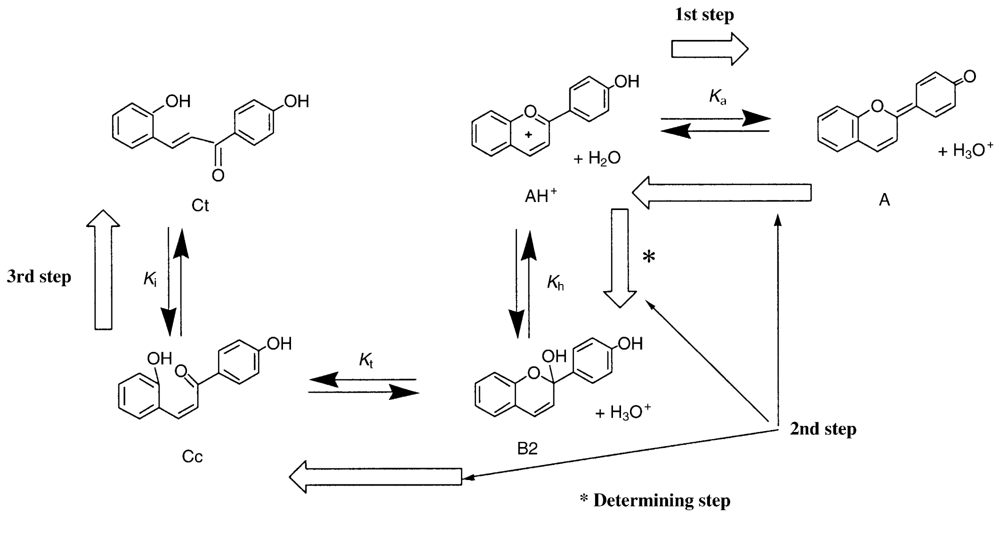
According to Equation (5), $\mathbf{AH}^+$ is the stable form for pH $< \mathrm{p}K'_a$ and the set of species **CB** are stable for pH $> \mathrm{p}K'_a$, (however, as we shall see below, in basic medium other forms can be obtained, see Scheme 2). A useful way to obtain information on the network of reactions is to perform pH jump experiments from pH $< \mathrm{p}K'_a$ to pH $> \mathrm{p}K'_a$, and to monitor the spectral variations that take place as a function of time.



Scheme 2.

With a few exceptions, and we will see that the 4′-hydroxy-6-nitroflavylium compound is indeed one of them, the kinetic processes that occur upon such pH jumps can be described as follows (Scheme 3): 1) a very fast deprotonation reaction leads to the complete or partial disappearance of the flavylium cation AH^+ with formation of the quinoidal base **A** as a transient product; 2) the hemiketal **B** and *cis*-chalcone **Cc** species (which are in very fast equilibrium) are formed through the hydration of the flavylium cation as the rate determining step; when there is a kinetic barrier to the *cis*→*trans* isomerization, a pseudo equilibrium is reached at this stage; 3) on a longer time scale, the *cis*→*trans* isomerization reaction leads to the thermodynamic equilibrium, with formation of **Ct**.

The pH dependent absorption spectra of dark equilibrated solutions (two months in the dark at room temperature) in the case of 4′-hydroxy-6-nitroflavylium are displayed in Figure 2a. Inspection of this Figure shows that on increasing pH the absorption band of the flavylium cation (λ_{max} = 450 nm) decreases; additionally an absorption band arises with shape and energy which are characteristic of the chalcone.[14,15] A further investigation has shown that at this stage about 97% of the *trans*-chalcone form is present. From the absorbance variation at 450 nm, a value of −0.6 was obtained for the overall pK'_a [Eq. (5)]. This value can be compared with pK'_a 1.9 for the parent 4′-hydroxyflavylium cation,[16] showing that the 6-nitro substituent has a considerable destabilization effect on the cationic form with re-



Scheme 3.

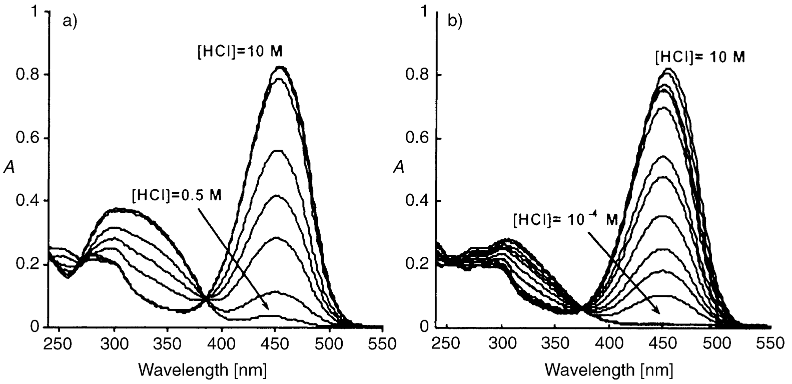
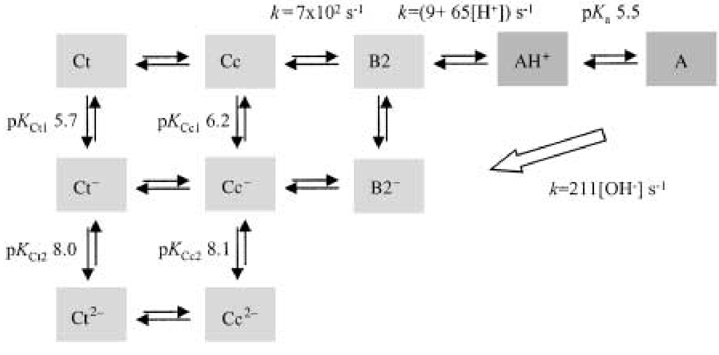


Figure 2. Absorption spectra of dark equilibrated (a) and immediately prepared (b) aqueous solutions of 4′-hydroxy-6-nitroflavylium, 2.0×10^{-5} M, as a function of proton concentration.

spect to the **CB** species. This behaviour is due to the very efficient hydration reaction, see below.

The pH dependence of the absorption spectra was also examined immediately after the preparation of the solutions (Figure 2b). The flavylium cation absorption decreases again with increasing pH, but comparison with Figure 2a shows that **Ct**, whose absorption is higher than that of **Cc** below 400 nm,[14–16] is not formed; this indicates the existence of a *cis→trans* isomerization barrier at room temperature. This barrier was determined to be 90.4 kJ mol^{-1}, on the basis of a van't Hoff plot. Immediately after the pH jump, the flavylium cation is involved in a pseudo-equilibrium with **Cc** and eventually **B2**, an interpretation that was confirmed by ^{1}H NMR spectroscopy, see below.

An interesting feature of the present system (see stopped flow measurements below) is that no quinoidal base **A** is formed, unless the final pH of the jump is higher than 4. In this case the formation of **B2** through the hydration reaction of AH^+ takes place at a pH value *lower* than the pK_a of the AH^+/**A** acid–base reaction. In other words, the first step upon a pH jump from very acidic solutions (pH < 0) to pH < 4 is no longer the deprotonation, as usually observed for other flavylium compounds, but the formation of **B2** and **Cc**, (Scheme 4). The quinoidal base, **A**, is formed only in less acidic or basic media and disappears by a new channel, which corresponds to the attack of OH$^-$ to position 2 (or 4) leading to **B2**$^-$ (or **B4**$^-$) and **Cc**, **Cc**$^-$ or **Cc**$^{2-}$ depending on pH, see below.



Scheme 4.

In conclusion, in freshly prepared solutions at pH < 4, where **A** and **Ct** are not present, the overall constant, usually called $K^{\wedge}_{a}$, can be written as $K^{\wedge}_{a} = K_h + K_hK_t = 0.125$. On the contrary, in solutions at the final equilibrium, where **A** is not present, $K'_a = K_h + K_hK_t + K_hK_tK_i = 3.98$. From the difference between the two equilibrium constants (K'_a and $K^{\wedge}_{a}$), the mole fraction distribution of **Ct** at the final equilibrium, given by the ratio $K_hK_tK_i/K'_a = 0.97$ can be calculated.[23]

Basic media: We have also studied the behaviour of 4′-hydroxy-6-nitroflavylium in basic media. A pH jump from pH 0.7 to 12 causes the immediate formation of the quinoidal base **A** (see stopped flow data below). **A** is then transformed (several days) into an anionic form of *cis*-chalcone.

Acid titration of the *cis*-chalcone form obtained immediately after a pH jump to 12 leads to the spectral changes reported in Figure 3a and c. Identical titrations, Figure 3b and d, can be carried out on the *trans*-chalcone species obtained either several days after a pH jump to 12 or by irradiation of the *cis*-chalcone at the same pH, see photochemical experiments. The titration data show that for both *cis* and *trans* isomers, two novel species can be obtained on decreasing pH, leading to the conclusion that at pH 12 the *cis* and

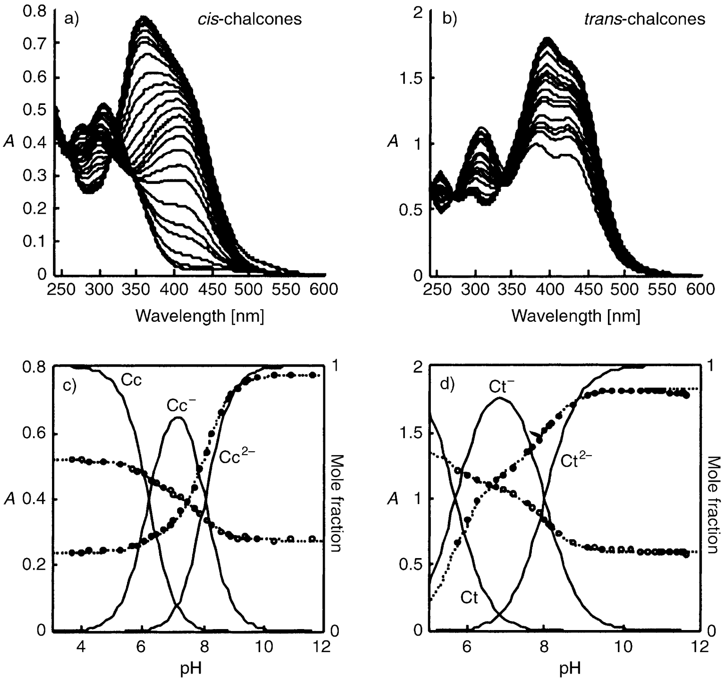


Figure 3. Absorption spectra of 4.0×10^{-5} M solutions of **Cc** (a) and **Ct** (b) at different pH values; absorbance changes at 354 (●) and 303 nm (○) for **Cc** (c) and at 395 (●) and 304 nm (○) for **Ct** (d).

trans isomers are present in their dianionic forms. From the fitting of the plots of Figure 3c and d, the values of the equilibrium constants for the two consecutive acid dissociation processes of **Cc** and **Ct** can be obtained:

$$\mathbf{Cc} \rightleftharpoons \mathbf{Cc}^- + H^+ \quad pK_{Cc1} = 6.2 \qquad (6)$$

$$\mathbf{Cc}^- \rightleftharpoons \mathbf{Cc}^{2-} + H^+ \quad pK_{Cc2} = 8.1 \qquad (7)$$

$$\mathbf{Ct} \rightleftharpoons \mathbf{Ct}^- + H^+ \quad pK_{Ct1} = 5.7 \qquad (8)$$

$$\mathbf{Ct}^- \rightleftharpoons \mathbf{Ct}^{2-} + H^+ \quad pK_{Ct2} = 8.0 \qquad (9)$$

^{1}H NMR studies: A ^{1}H NMR study was carried out on the system in order to characterize and confirm the assignment of species in solution at different pH values. The data are summarized in Table 1.

Table 1. ^{1}H NMR chemical shifts δ [ppm] and scalar J couplings [Hz] of several forms of 4′-hydroxy-6-nitroflavylium tetrafluoroborate in D_2O solutions at $T = 301.0 \pm 0.5$ K.

	AH^{+}[a]	$\mathbf{Cc}^{2-}$[b]	$\mathbf{Ct}^{2-}$[b,c]			
Proton	δ	J	δ	J	δ	J
$H_{2'}$+$H_{6'}$	8.20	9.3	7.55[d]	8.9	7.79	8.9
$H_{3'}$+$H_{5'}$	6.83	9.3	6.26[d]	8.9	6.46	8.9
H_3	8.24	9.3	6.36[d]	12.5	7.7[e]	[e]
H_4	8.83	9.3	6.95[d]	12.5	7.7[e]	[e]
H_5	8.72	2.4	7.7[e]	[e]	8.38	2.8
H_7	8.50	9.3, 2.4	7.7[e]	[e]	7.86	9.3, 2.8
H_8	7.99	9.3	6.25[e]	[e]	6.41	9.3

[a] pD = −0.80; [b] pD ~ 12; [c] after irradiatian of $\mathbf{Cc}^{2-}$ at 366 nm; [d] tentative assignment; [e] overlapped peak.

Dissolution of 4′-hydroxy-6-nitroflavylium tetrafluoroborate in 20% (*w*/*w*) DCl (pD −0.80) gave a single set of peaks that must be due, under this acid conditions, to the flavylium cation, $\mathbf{AH}^+$. The two doublets at 8.20 and 6.83 ppm, integrating for two protons each, are assigned to protons $H_{2'}+H_{6'}$ and $H_{3'}+H_{5'}$, respectively, by comparison with similar flavylium compounds.[16,23,24] The doublet at 8.72 ppm is assigned to proton H_8 on the basis of the small *meta* scalar coupling constant, $^4J_{H5,H7} = 2.4$ Hz. This allows the assignment of the double doublet peak at 8.50 Hz as proton H7. Irradiation of this proton allows to assign the doublet at 7.99 ppm to proton H8. The two remaining doublets at 8.83 and 8.24 ppm must be assigned to ring C protons H4 and H3, the lower field doublet corresponding to proton H4 by comparison with similar flavylium salts.[16,23,24]

On increasing pD in the range $-0.80 < pD < 2.2$, a single set of peaks is maintained with an overall shift of the spectrum to higher field values (further increase of pD to values in the neutral region leads to strong precipitation of a slightly orange solid that prevents NMR spectra to be obtained). This shift is compatible with the presence of a fast equilibrium between $\mathbf{AH}^+$ and **B2**+**Cc** in the ^{1}H NMR time scale (ca. 10^{-2}–10^{-4} s^{-1}), which is in accordance with the high values of the rate constants for hydration/dehydration and tautomerization equilibria, observed in stopped flow experiments.

Dissolution of 4′-hydroxy-6-nitroflavylium tetrafluoroborate in basic D_2O solutions leads to a single set of peaks that is assigned to the $\mathbf{Cc}^{2-}$ species, since a jump to strongly acidic solutions, gives the ^{1}H NMR spectrum of $\mathbf{AH}^+$. The peaks on the spectrum of $\mathbf{Cc}^{2-}$ were assigned on the basis of COSY spectra. Irradiation of a freshly prepared $\mathbf{Cc}^{2-}$ solution at 366 nm, followed by UV/Vis spectroscopy until stabilization, leads to a solution that shows a ^{1}H NMR spectrum whose peaks can be assigned to $\mathbf{Ct}^{2-}$ on the basis of COSY spectra and by comparison with the spectrum of similar ionized chalcones.[16]

The studies in acid and basic media together with the assignment through ^{1}H NMR spectroscopy are summarized in Table 2 where the main species are characterized by their absorption maxima and respective molar absorptivities.

Table 2. Absorption maxima and molar absorptivities of the main species present in aqueous solutions of 4′-hydroxy-6-nitroflavylium tetrafluoroborate.

	$\mathbf{AH}^+$	$\mathbf{Cc}$	$\mathbf{Cc}^-$	$\mathbf{Cc}^{2-}$	$\mathbf{Ct}$	$\mathbf{Ct}^-$	$\mathbf{Ct}^{2-}$
λ_{max} [nm]	450	308	407	361	314	388	397
ε [mol^{-1}dm^{3}cm^{-1}]	28900	13400	13700	20700	23700	20100	28700

Stopped flow experiments: The stopped flow analysis of a series of pH jumps was carried out as shown in Figure 4. Below pH 4, the species observable immediately after the dead time of the stopped flow apparatus is still the flavylium cation. In a second process, which follows a first-order kinetics, with a rate constant of 9 s^{-1}, $\mathbf{AH}^+$ disappears to give **Cc** in equilibrium with **B2**. On the contrary, a pH jump to 13.2 immediately leads to the quinoidal base **A** (see the absorption band at 500 nm) that evolves to the $\mathbf{Cc}^{2-}$ species according to a first-order process with a rate constant of 38 s^{-1}.

The results obtained for the pH jumps to neutral or moderately acidic media can be interpreted considering that the process with rate constant 9 s^{-1} should correspond (Scheme 2) to the hydration reaction (global rate constant equal to $k_h + k_{-h}[H^+]$).[16,25] The pK_a 5.5 of Equation (1) was also determined from the plot of the pH dependent absorbance (500 nm) of the species **A** immediately formed upon a series of pH jumps from pH 0.7 to >4.

After pH jumps at basic pH values, the rate constant of **A** disappearance depends linearly on the hydroxyl concentration (Figure 5); this suggests that the quinoidal base **A**, formed during the dead time of the stopped flow apparatus, undergoes a hydroxyl attack, most probably leading to $\mathbf{B2}^-$ and then, depending on pH, to $\mathbf{Cc}^-$ or $\mathbf{Cc}^{2-}$ through a fast ring opening. The occurrence of the quinoidal base attack

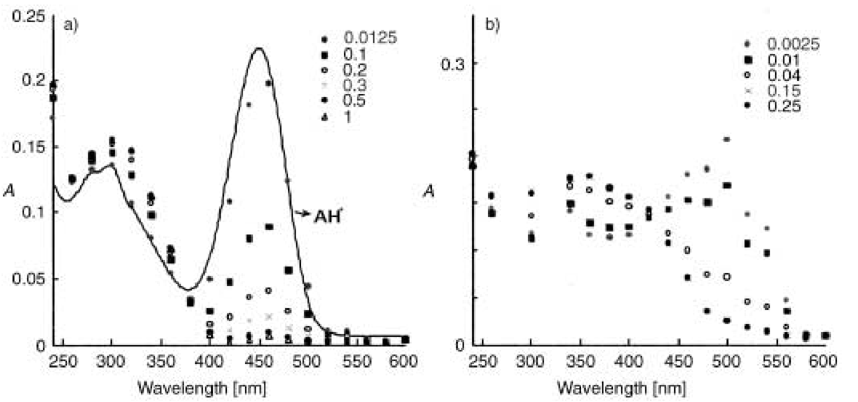


Figure 4. Spectral variations observed in stopped flow experiments upon pH jumps from pH 0.7 to: a) pH 4, b) pH 13.2; *t* [s].

by the hydroxyl group opens a new reaction channel as illustrated in Scheme 4 (see also Scheme 2).

In order to get more insight on the system, a freshly prepared solution at pH 0.7 (AH^+ form) was submitted to a pH jump to 3.2, attaining the pseudo equilibrium, and subsequently to a pH jump to pH 0. The last step, that leads again to AH^+ formation, was followed by stopped flow technique, Figure 6. The decrease in absorbance (Figure 6b) at 320 nm shows two consecutive processes; the faster one ($k > 7\times10^2\,s^{-1}$) cannot be observed with sufficient accuracy because it is masked by the dead time of the apparatus; while the second, monitored either at 320 nm (decrease of **Cc** absorption) or at 470 nm (increase of AH^+ absorption), follows first-order kinetics with rate constant of $65\,s^{-1}$.

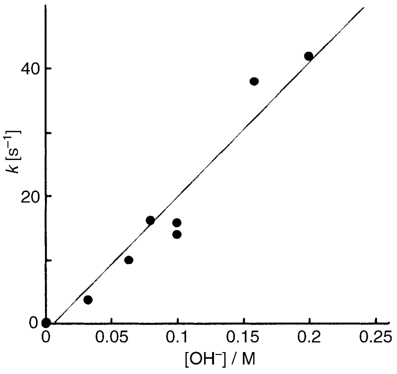


Figure 5. Dependence on the hydroxyl concentration of the first order rate constant of the process that takes place upon a pH jump from 0.7 to the basic region.

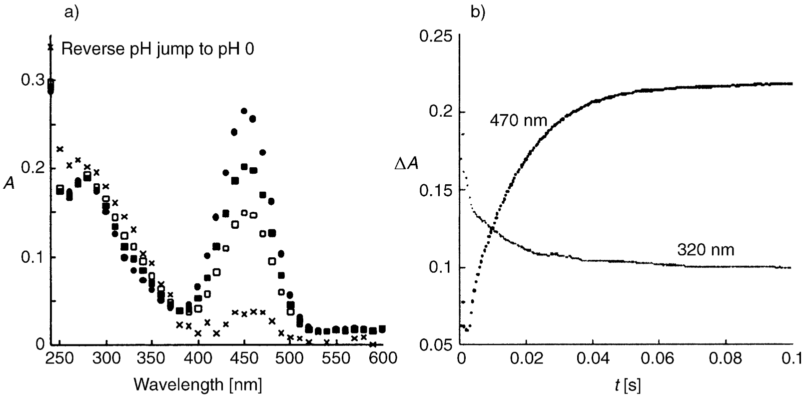


Figure 6. pH Jump from a pseudo-equilibrated solution at pH 3.2 to pH 0, followed by stopped flow: a) spectral changes × 0.001, □ 0.01, ■ 0.02, ○ 0.1, ● 0.2; b) kinetic plots at 320 and 470 nm.

This behaviour can be interpreted by considering that, at pH 3.2, **Cc** is the main species and the faster process is the tautomerization reaction (global rate $= k_t + k_{-t}$) that leads to **B2** (Scheme 2). The second and slower process can thus be identified as the dehydration reaction that forms the flavylium cation AH^+ (global rate $= k_h + k_{-h}[H^+]$). From the data of the direct and reverse pH jumps, it can be obtained $k_h = 9\,s^{-1}$ and $k_{-h} = 65\,s^{-1}$.

Photochemistry: Irradiation of the 4′-hydroxy-6-nitroflavylium compound at pH 12 (Cc^{2-} form) was carried out at 366 nm (see Figure 7). The final photoproduct is Ct^{2-}, since its acidification leads to **Ct**.

Irradiation of the **Ct** isomer in very acidic (4 M HCl) medium leads spectral changes compatible with the formation of AH^+, with a quantum yield of 0.02. At pH 2.99, a photostationary state involving the **Ct** and **Cc** species is attained with a similar quantum yield ($\Phi = 0.03$). Formation of AH^+ occurs only in very acid media (4 M HCl), because of the extremely low $pK^{\wedge}_a$ of this compound (Figure 8).

Multistate/multifunctional processes: As mentioned in the Introduction, the 4′-hydroxyflavylium species can perform as a molecular-level optical memory by a write–lock–read–unlock–erase cycle (Figure 1b) in which i) a photonic bit of information is "written" in the photochemical conversion of **Ct** into **Cc**, ii) "locked" into AH^+ by an acid input, iii) "read" in the photostable AH^+ species by light absorption, iv) "unlocked" to **Cc** by a base input, and v) "erased" by a photon that reconverts **Cc** into **Ct**.

Compared with other members of the flavylium family, this compound is characterized by a large *cis→trans* isomerization barrier together with a narrow pH domain of stability of the AH^+ species. This compound performs like an optical memory by means of a different cyclic process that involves

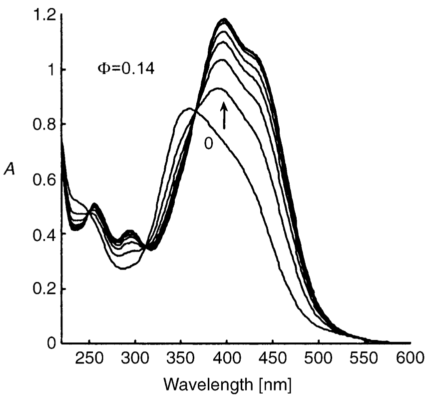


Figure 7. Irradiation at 313 nm of the *cis*-chalcone ($\mathbf{Cc}^{2-}$) of 4′-hydroxy-6-nitroflavylium 1.25×10^{-5} M at pH 12; from t = 0, 2.5, 5, 7.5, 10, 15, 20, 30, 40 min.

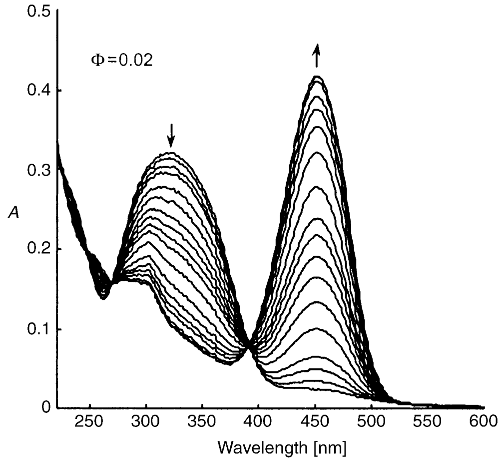
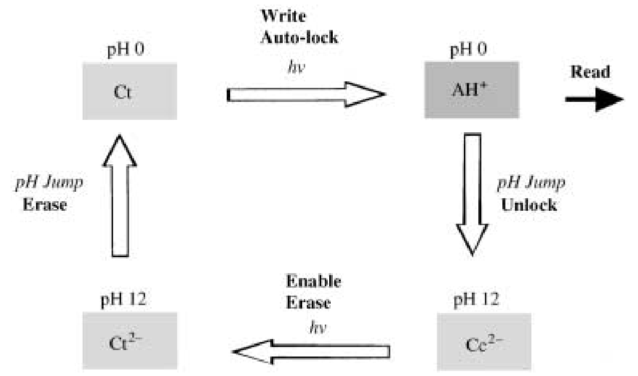


Figure 8. Spectral changes observed on irradiation at 313 nm of **Ct** 1.25×10^{-5} M in [HCl]=4 M; t = 0, 1, 3, 5, 10, 15, 20, 25, 30, 45, 60, 75, 90, 105, 135, 165, and 195 min.

the following steps: write-lock/read/unlock/enable-erase/erase (Scheme 5): i) starting with the **Ct** form at pH 0, light excitation causes the isomerization to **Cc** (write) that spontaneously converts (auto-lock) to $\mathbf{AH}^+$ because of the acidity of the solution; ii) $\mathbf{AH}^+$ is photostable and can thus be examined by UV/Vis absorption spectroscopy (read) without being erased; iii) when the information has to be erased, $\mathbf{AH}^+$ can be converted into $\mathbf{Cc}^{2-}$ by a pH jump to pH 12 (unlock); iv) $\mathbf{Cc}^{2-}$ can then be isomerized by light excitation to $\mathbf{Ct}^{2-}$, a process (enable-erase) that finally allows formation of the original **Ct** species by a pH jump to pH 0 (erase).

Experimental Section

4′-Hydroxy-6-nitroflavylium tetrafluoroborate was prepared by condensation of 4′-hydroxyacetophenone (0.34 g, 2.5 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.42 g, 2.5 mmol), on the basis of a method described by Katritzky for similar compounds.[26] The reagents were dissolved in acetic acid (3 mL) and tetrafluoroboric acid (0.6 mL) was added. Acetic anhydride (2.5 mL) was then added, keeping the temperature below 60 °C (~10 min). The solution was stirred overnight. The orange solid which precipitated was filtered, washed with ethyl acetate, and dried in vacuum (0.26 g, 28.5 %). It may be recrystallized from acetic acid. Elemental analysis calcd (%) for $C_{15}H_{10}BF_4NO_4$: C 50.74, H 2.84, N 3.94; C 51.46, H 2.81, N 3.71; MS-FAB(+): m/z (%): 269 [M+H]‘; ^{1}H NMR: see Table 1.



Scheme 5.

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

UV/Vis absorption spectra were recorded in a Perkin–Elmer lambda 6 or Shimadzu UV2501-PC spectrophotometers.

Light excitation was carried out using a medium-pressure mercury arc lamp, and the excitation bands were isolated with interference filters (Oriel). The incident light intensity was measured by ferrioxalate actinometry.[27] The flash photolysis experiments were performed as previously described.[28]

The ^{1}H NMR experiments were recorded in a Bruker ARX-400 spectrometer operating at 400.13 MHz. The tetrafluoroborate salt of the flavylium was dissolved in D_2O, acidified with 20 % (*w*/*w*) DCl, or basified with 40 % (*w*/*w*) NaOD. The reported pD values are direct readings of the pH meter which can be corrected for the isotope effect through the equation pD = pH+0.4.[29]

Reaction profiles were collected on a SX 18 MV stopped flow (Applied Photophysics) spectrophotometer 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 experimentally determined to be 1.35 ms (based on a test reaction).

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