

Two coupled photochromic systems of 3',4'-(methylenedioxy)flavylium: kinetic and thermodynamic characterization†

Damián Fernández, Filipe Folgosa, A. Jorge Parola and Fernando Pina*

REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal. E-mail: fjp@dq.fct.unl.pt

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The chemistry and photochemistry of 3',4'-(methylenedioxy)flavylium was studied by means of UV–Vis spectrophotometry, ^1H NMR, stopped flow, and continuous irradiation, in acidic and basic aqueous solutions. Six species were identified: the flavylium cation, AH^+ ; the hemiketal, **B**; the *cis*- and the *trans*-chalcones, **Cc** and **Ct**, and their ionized forms, Cc^- and Ct^- . These species define a multiequilibria network whose kinetics and thermodynamics were completely characterized. The two pairs of chalcones define two coupled photochromic systems, respectively in acidic and basic media, both allowing cycles capable of writing, reading and erasing to be defined.

Introduction

One important feature of photochromic compounds is their capacity to switch, by the action of light, between two different states exhibiting different molecular shapes and electronic configurations.^{1,2} A photon is simultaneously a bit of information and a quantum of energy. In Nature, the information of the light captured by a photochromic compound is transferred and amplified by the complex machinery of the living organisms, leading, for example, to vision, phototropism or photo-movements.

In recent years, the photochromic properties of synthetic flavylium compounds, in particular their multistate/multifunctional properties, have been the object of a systematic study.^{3,4} The most important feature of these photochromic compounds is their pH dependent photoresponse. This behaviour permits one to obtain different states exhibiting different properties according to sequences of pH and light stimuli.

Another interesting aspect of synthetic flavylium compounds is the possibility of tuning their thermal and photochemical properties, by changing the nature and position of the substituents. In the present work, the multistate/multifunctional behaviour of the 2-aryl-substituted benzo[*b*]pyrylium salt 3',4'-(methylenedioxy)flavylium tetrafluoroborate is reported. It was observed that this compound shows a network of chemical equilibria similar to those observed for other reported flavylium salts,^{3–8} Scheme 1. However, the presence of two kinetic barriers between the two pairs of chalcones confers great novelty on this system, with the possibility of defining two pH coupled write–read–erase cycles.

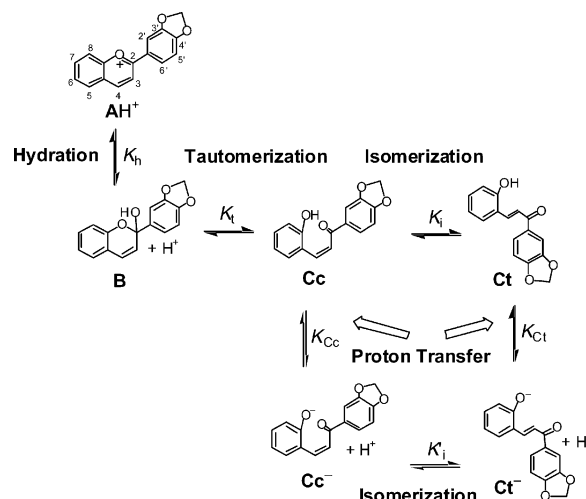
In acidic aqueous solution, it is possible to distinguish four species for this compound: the flavylium cation (AH^+); the hemiketal (**B**), obtained by hydration of AH^+ ; the *cis*-chalcone (**Cc**), resulting from tautomerization of **B**; and the *trans*-chalcone (**Ct**), due to the *cis*–*trans* isomerization of **Cc**. In basic aqueous solutions, ionized *cis*- and *trans*-chalcones (Cc^- and Ct^-), obtained by deprotonation of the hydroxyl group, can be observed in the equilibrium or as transient species. Accord-

ing to Scheme 1, AH^+ should be the prevalent species in very acidic solutions; **B**, **Cc** and **Ct** are present at intermediate pH values and, Cc^- and Ct^- , at more basic pH values. In terms of the kinetics of conversion between the aforementioned species, deprotonation is the fastest process whose rate can not be followed by stopped flow methods. On the other hand, tautomerization and hydration can be easily followed by this last technique. Finally, the thermal *cis*–*trans* isomerizations are slow enough to be monitored by a standard UV–Vis spectrophotometer.

Results and discussion

Thermodynamic equilibrium

In the pH range 1–4, the spectral modifications observed for 3',4'-(methylenedioxy)flavylium are reported in Fig. 1a. At pH = 1.0, the dominant species is the flavylium cation, whose absorption decreases with increasing pH, leading to the



Scheme 1

† Electronic supplementary information (ESI) available: experimental data. See <http://www.rsc.org/suppdata/nj/b4/b405346j/>

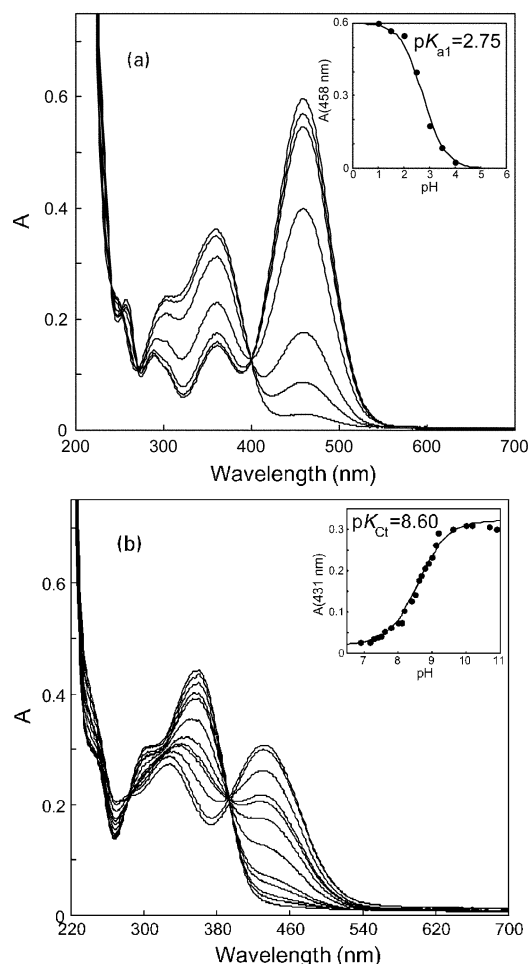
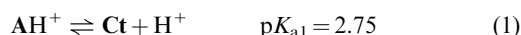
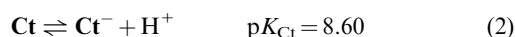


Fig. 1 Spectral variations of 3',4'-(methylenedioxy)flavylium 2.0×10^{-5} M at the equilibrium: a) pH range 1 to 4, AH^+ transforming into Ct; b) pH range 7 to 11, Ct ionizing to Ct^- .

characteristic spectrum of the *trans*-chalcone at pH = 4.0, see eqn. (1).



The *trans*-chalcone can be deprotonated at higher pH values, as reported in Fig. 1b, according to eqn. (2).



At the thermodynamic equilibrium, only three species AH^+ (pH < 1), Ct (4 < pH < 7) and, Ct^- (pH > 10) are observed. These results were confirmed by ^1H NMR. At pH = 1.0, the ^1H NMR spectrum is compatible with the existence of a single species that corresponds to the flavylium cation (see ESI†). At basic pH values, by dissolving 3',4'-(methylenedioxy)flavylium at pH = 11, a ^1H NMR spectrum is initially obtained that is compatible with the presence of Ct^- , as shown by the value of $^3J_{\text{H3-H4}} = 12.4$ Hz, characteristic of ionized *cis*-chalcones (see ESI).⁶ This solution, either by heating at 60 °C (see below, Fig. 3b) or irradiating at 313 nm (see below, Fig. 7c), leads to the formation of a new species that is assigned to Ct on the basis of the large scalar coupling constant between protons 3 and 4, $^3J_{\text{H3-H4}} = 15.7$ Hz, characteristic of conjugated *trans* double bonds (see ESI).^{5,6}

Pseudo equilibrium

In Fig. 2, the spectral variations obtained immediately upon preparation of a set of solutions at different pH values are shown. In the pH range up to pH = 6, the spectra clearly show that the characteristic absorption band of flavylium cation

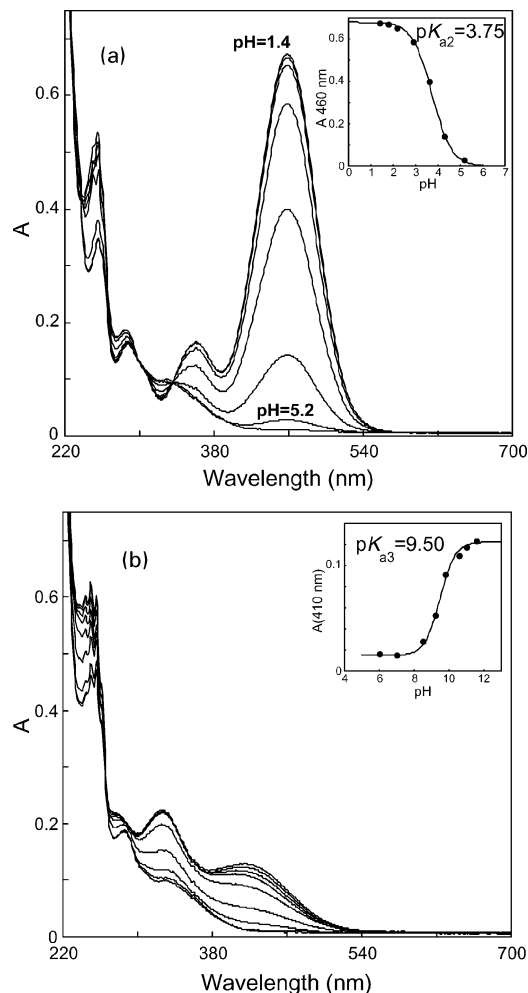


Fig. 2 Spectral variations of 3',4'-(methylenedioxy)flavylium 2.0×10^{-5} M in the pseudo equilibrium: a) pH range 1 to 6, AH^+ transforming into B + Cc; b) pH range 7 to 12, Cc ionizing to Cc^- .

decreases with increasing pH, with the concomitant appearance of a new absorption band which can be assigned to the *cis*-chalcone, in equilibrium with the hemiketal, see Fig. 2a.

When higher pH values are considered, Fig. 2b, the absorption spectra of *cis*-chalcone leads to another absorption band whose characteristics clearly indicate that the ionized *cis*-chalcone is forming. This assignment was confirmed by ^1H NMR, as referred to above.

The absorption spectra shown in Fig. 2 can be maintained without major modifications for a fairly long period of time at room temperature. This is due to the existence of large kinetic barriers between Cc and Ct at intermediate pH values and, Cc^- and Ct^- at basic pH values. This situation also permits consideration of a pseudo equilibrium, described by eqns. (3) and (4), which is very useful to fully characterize the system.



Thermal kinetics

Fig. 3 shows the spectral modifications corresponding to the conversion of the pseudo equilibrium into the final equilibrium. At pH = 6.3, the Cc species is converted into the Ct species. In order to confirm that the conversion was almost complete, a pH jump on the final Ct solution to pH = 1.0 was carried out. No significant spectral modifications were observed, showing that the amount of Cc at the equilibrium at pH = 6.3 is negligible (otherwise Cc would rapidly be converted

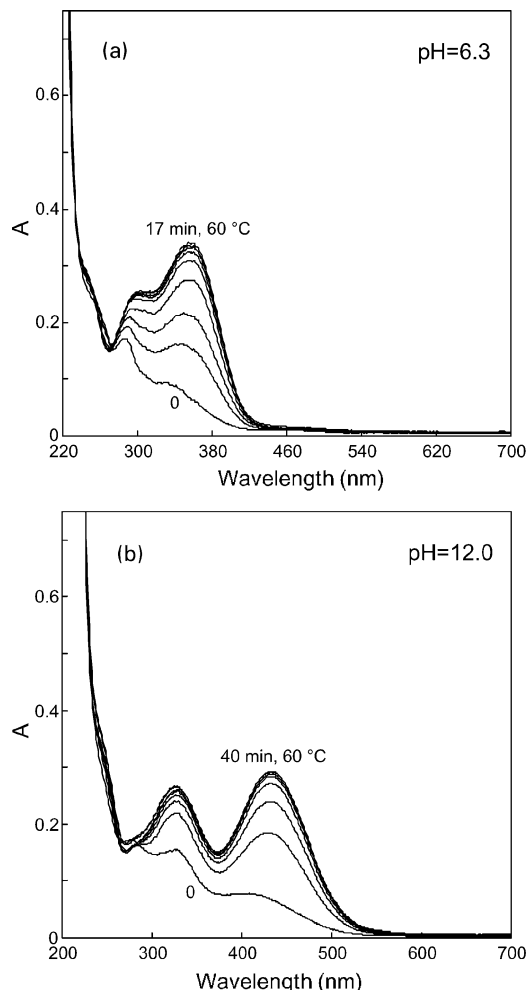


Fig. 3 Spectral modifications of 3',4'-(methylenedioxy)flavylum 2.0×10^{-5} M, showing the conversion of species at pseudo equilibrium to the final equilibrium: a) Cc isomerizes to Ct in *ca.* 17 min, at pH=6.3 and 60 °C; b) Cc^- isomerizes to Ct^- in *ca.* 40 min, at pH=12.0 and 60 °C.

into AH^+). At room temperature, the conversion of the Ct species at pH=1.0 into the thermodynamically stable AH^+ takes several days to be completed.

An identical process can be observed at pH=12.0. In this case, the Cc^- species obtained during the pseudo equilibrium is converted into its Ct^- isomer. Acidification to pH 1 of this solution leads to the absorption spectrum of Ct without formation of any AH^+ , which indicates that the thermal conversion from Cc^- to Ct^- is also complete in these conditions.

The determination of the activation energies for the two kinetic barriers, between Cc and Ct in moderately acidic media and, between Cc^- and Ct^- in basic media, was carried out through Arrhenius plots, leading to values of 97 kJ mol^{-1} and 106 kJ mol^{-1} , respectively.

Stopped flow experiments

In order to characterize the kinetic processes occurring in the present system, a series of pH jumps were performed and the respective variations of the absorbance followed by stopped flow methods. A solution of the compound freshly prepared at pH=6.0 (containing B and Cc at equilibrium) was submitted to pH jumps to lower pH values, Fig. 4a. When the final pH is lower than *ca.* 2.5, two different processes can be identified, both following first order kinetic laws: i) one of the processes is slightly dependent on the final pH, with a rate constant of 0.84 s^{-1} at pH=2.1 and 1.5 s^{-1} at pH=1.6; ii) the other process varies linearly with proton concentration (Fig. 4b) with a slope

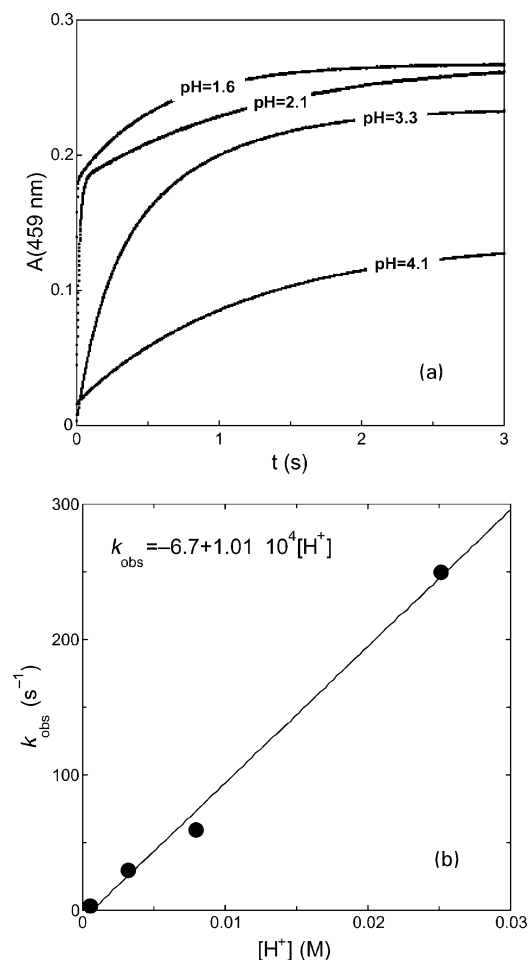


Fig. 4 a) Traces of the absorbance measured at 459 nm (AH^+ absorption) obtained upon a pH jump from solutions freshly prepared at pH=6.0 to more acidic values; b) representation of the pH dependent process as a function of proton concentration.

of $1.01 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. As pointed out by McClelland and Gedge,⁹ these results can be interpreted by considering B in fast exchange with Cc at the pseudo equilibrium (pH=6.0). On this basis, the more strongly pH dependent process (ii) can be attributed to the hydration–dehydration reaction ($\text{AH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}^+$), whose rate is $k_h + k_{-h}[\text{H}^+]$ and, by consequence $k_{-h} = 1.01 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Unfortunately, k_h can not be calculated with accuracy from this experiment, but a value of $k_h = 1.2 \text{ s}^{-1}$ can be obtained from the thermodynamic equilibrium constant, $K_h = k_h/k_{-h}$, see below. On the other hand, the slightly pH dependent kinetic process (i) should be due to the tautomerization reaction ($\text{B} \rightleftharpoons \text{Cc}$). At higher pH values, the hydration–dehydration reaction becomes the rate determining step of the global process and consequently only one pH dependent trace, corresponding to a first order kinetic process, is observed. Inspection of Fig. 4a clearly shows that at pH=1.6 and pH=2.2, the amplitude of the faster process (hydration–dehydration) is practically the same, as expected if all the B species is consumed to give AH^+ . In addition, the formation of different final plateaus in the slow process is a consequence of the decrease of the AH^+ species at the final pseudo equilibrium, with increasing pH, according to the data reported in Fig. 2a. One important aspect of Fig. 4a is that the amplitudes of the traces of both processes reported at pH=1.6 and 2.1, allow calculation of the pseudo equilibrium constant between B and Cc , $K_t = 0.49$. McClelland and Gedge observed that in the case of 2-(phenyl)benzo[*b*]pyrylium (unsubstituted flavylum) and the parent compounds substituted in position 4' with methoxy or methyl groups, the tautomerization rate is constituted by one term which is pH independent, 1.78 s^{-1} ,

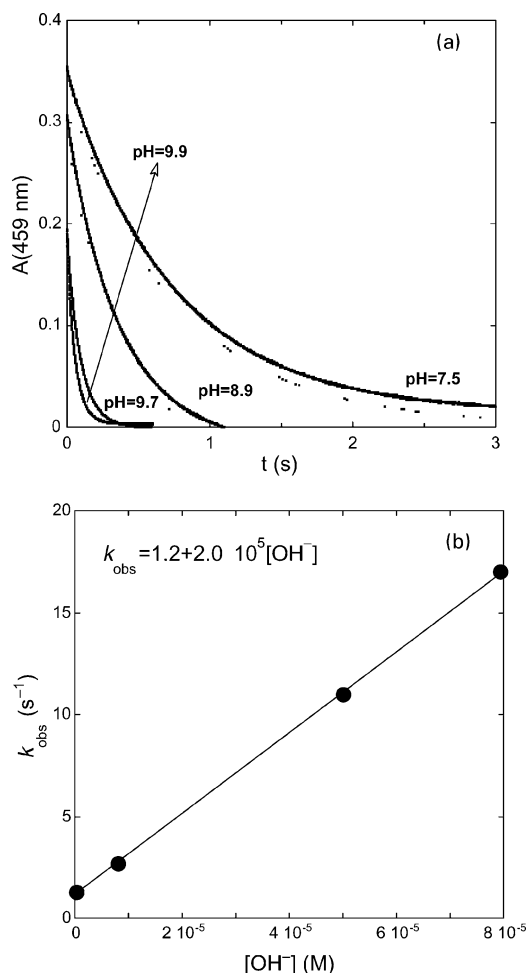


Fig. 5 a) Traces of the absorbance measured at 459 nm (AH^+ absorption) obtained upon a pH jump from solutions freshly prepared at pH=1.0 to the basic pH region; b) representation of the pH dependent process as a function of the hydroxide concentration.

0.96 s^{-1} and 0.46 s^{-1} , respectively, and another one which increases linearly with increasing proton concentration, 42, 39 and $44 \text{ M}^{-1}\text{s}^{-1}$.⁹ In the present system, we obtained for the pH independent term 0.54 s^{-1} , and for the other term, $38 \text{ M}^{-1}\text{s}^{-1}$. Taking into account that in our experiment the equilibrium between **Cc** and **B** is not reached, since **B** is immediately consumed to give AH^+ , k_{-1} should be equal to 0.54 s^{-1} , leading to $k_1 = 0.26 \text{ s}^{-1}$, from the tautomeric equilibrium constant, K_t , determined above, see Table 2.

Another series of pH jumps from equilibrated solutions at pH=1.0 to less acidic pH values was also performed. For example, if the final pH after the pH jump is 2.9, a single first order process with rate constant equal to 0.90 s^{-1} was measured. At this pH value, k_{obs} for the hydration–dehydration reaction is predicted to be *ca.* $1.2 + 1.01 \times 10^4 \times 10^{-2.9} = 14 \text{ s}^{-1}$. Consequently, the rate determining step of the global process is the tautomerization reaction, whose calculated rate is $0.26 + (0.54 + 38 \times 10^{-2.9}) = 0.85 \text{ s}^{-1}$, in good agreement with the experimental value. Finally, the traces of the pH jumps from solutions at pH=1.0 (AH^+) to basic pH values, Fig. 5a, can be fitted according to a first order kinetic process, with rates that are linearly dependent on the hydroxyl concentration, with a slope of $2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and an intercept of 1.2 s^{-1} , see Fig. 5b. These constants compare well with those previously reported for the compound 4'-methoxyflavylium,⁹ $1.8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and 1.38 s^{-1} , respectively. The value of the intercept should reflect the hydration reaction due to water attack, and as expected it is coincident with k_h .

Table 1 Equilibrium constants for 3',4'-(methylenedioxy)flavylium in aqueous solutions, at 23.0°C

K_h	K_t	K_i	K_{Cc}	K_{Ct}	K'_i
$1.2 \times 10^{-4} \text{ M}$	0.49	30	$9.6 \times 10^{-10} \text{ M}$	$2.5 \times 10^{-9} \text{ M}$	75

Energy level diagram and mole fraction distribution

To completely characterize the network of reactions represented in Scheme 1, equilibrium constants for each process must be evaluated. Taking into account reactions (1)–(4) and the fast equilibrium between **B** and **Cc**, it is easy to demonstrate (see ESI†) that the fittings on the insets of Figs. 1 and 2, together with the value of $K_t = 0.49$ calculated from the stopped flow experiments, allows us to obtain all the relevant thermodynamic data for the system, Table 1.

The self consistency of the data can be tested by calculating the value of the equilibrium constant $\text{p}K_{\text{a}1} = 2.71$ from the data of Table 1, which compares well with the experimental value of 2.75.

The equilibrium constants of Table 1 can be combined (i) with the data from the stopped flow analysis to obtain rate constants for the hydration–dehydration and tautomerization processes and, (ii) with the data from thermal *cis*–*trans* isomerization kinetics to obtain rate constants for the two *cis*–*trans* isomerizations. The kinetic data are collected in Table 2.

As reported previously for other flavylium salts, the data shown in Table 1 allow an energy level diagram of the network to be obtained, Scheme 2.³ In this particular case, the scheme was extended to species existing at basic pH values. This type of representation allows to visualize which species should be predicted for a given pH value at the equilibrium, as well as at the pseudo equilibrium. Another alternative to visualise the system is the representation of the mole fraction distribution of the equilibrium and pseudo equilibrium, shown in Fig. 6. In this figure, the full lines represent the mole fraction distribution at the equilibrium, while the dotted lines the same for the pseudo equilibrium. If, for instance, the compound is dissolved at pH=6, the system evolves from a mixture of *ca.* 65% **B** + 35% **Cc** at the pseudo equilibrium to a final equilibrium containing only **Ct**.

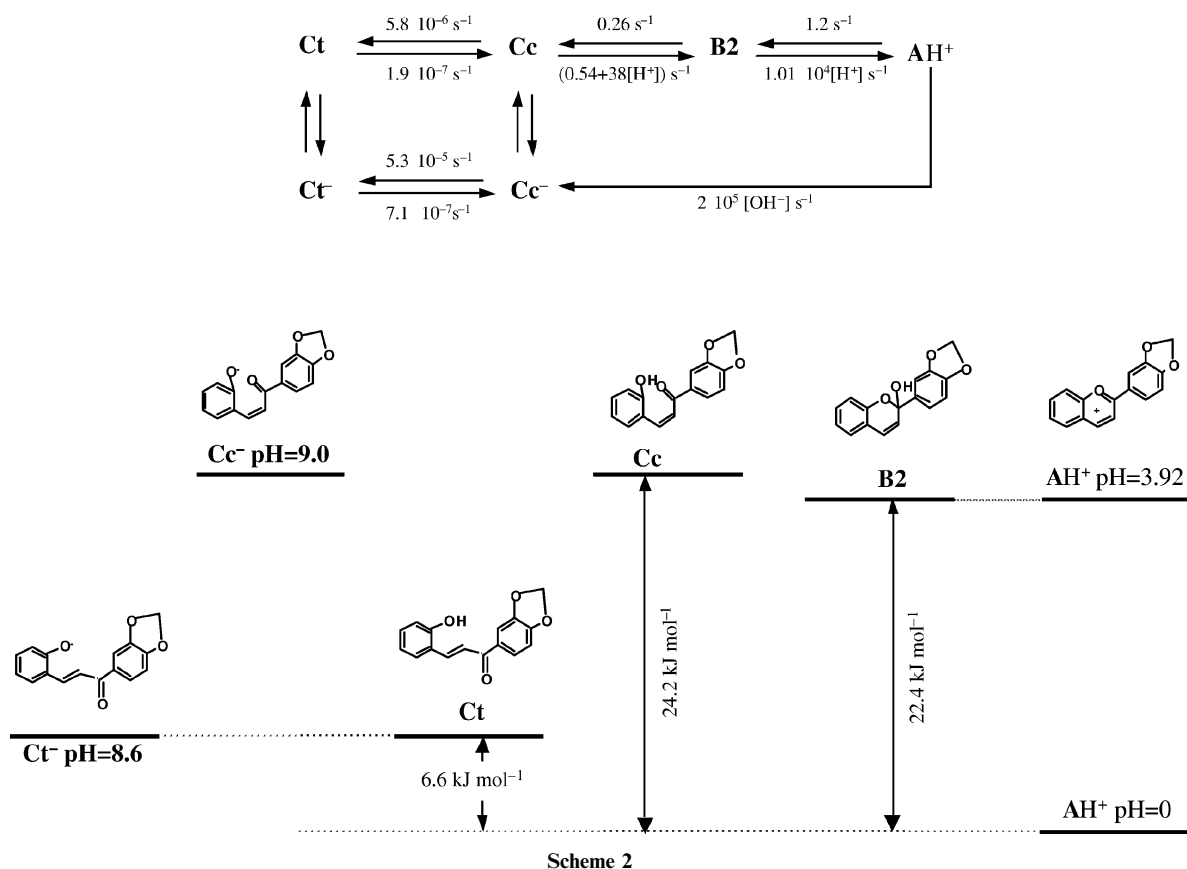
Photochemistry

The compound 3',4'-(methylenedioxy)flavylium presents two photochromic systems depending on pH, *i.e.*, $\text{Cc} \rightleftharpoons \text{Ct}$ (System I), and $\text{Cc}^- \rightleftharpoons \text{Ct}^-$ (System II), each one exhibiting a different behaviour. The photochemistry of System I is reported in Figs. 7a and 7b. As mentioned above, the thermal barrier permits the **Ct** form to be obtained in a metastable situation, even in very acidic solutions. However, irradiation at 313 nm of the **Ct** species (pH=1.3) leads to the formation of AH^+ , the thermodynamically stable species at this pH value, with a quantum yield of $\Phi = 0.02$. On the other hand, irradiation at 313 nm and pH=6.3 of the **B** + **Cc** species (pseudo equilibrium) leads to the formation of a photostationary state between **Cc** and the **Ct** species, since acidification to pH=1.0 of the photostationary state gives rise to the formation of some flavylium cation. The amount of flavylium cation permits calculation of the ratio $\text{Cc}/\text{Ct} = 0.27$ at the photostationary state. The quantum yield of the photochemical conversion of **Cc** into **Ct**, calculated from the initial points, is $\Phi = 0.19$. From this value and the molar absorption coefficients of both species at 313 nm, the quantum yield of the reverse photoreaction $\text{Ct} \rightarrow \text{Cc}$ is calculated as $\Phi = 0.02$, in total agreement with the value obtained for the same photoreaction at pH=1.3. At basic pH values, photochromic system 2 (Fig. 7c) is characterized by a $\text{Cc}^- \rightarrow \text{Ct}^-$ quantum yield of 0.10 (pH=12). This

Table 2 Rate constants for 3',4'-(methylenedioxy)flavylium in aqueous solution

$k_h/s^{-1}M^{-1a}$	k_{-h}/s^{-1a}	k_t/s^{-1a}	k_{-t}/s^{-1a}	k_i/s^{-1b}	k_{-i}/s^{-1b}	k'_i/s^{-1c}	k'_{-i}/s^{-1c}
1.2	1.01×10^4	0.26	0.54	5.8×10^{-6}	1.9×10^{-7}	5.3×10^{-5}	7.1×10^{-7}

^a At 23 °C. ^b At 40 °C, assuming that the equilibrium constant is the same as the one determined at 23 °C and pH = 6.0. ^c The same as b) at pH = 11.8.



photoreaction proceeds to completion, since acidification of the final irradiated solution to pH = 1.0 shows no presence of flavylium.

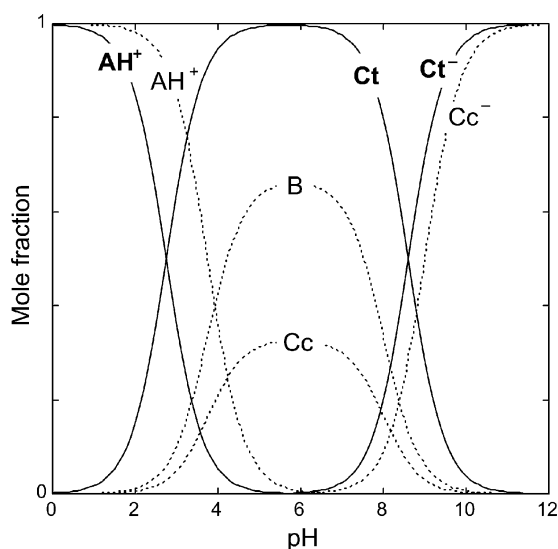


Fig. 6 Mole fraction distribution of the several species of the compound 3',4'-(methylenedioxy)flavylium as a function of pH: full lines: thermodynamic equilibrium; dotted lines: pseudo equilibrium.

Two coupled photochromic systems

The network of thermal and photochemical reactions of the compound 3',4'-(methylenedioxy)flavylium is shown in Fig. 8. In the pH range 1 to 6, a cycle capable of write–read–erase can be conceived. The starting point is the metastable **Ct** species at pH = 1.0. Using near-UV light, **Ct** is converted into **AH⁺**. The system can be erased by a pH jump to pH = 6.0 in order to produce **Cc** (in equilibrium with **B**), which is thermally reconverted into **Ct**. To prepare the system for a new cycle, a second pH jump to 1 should be performed. The other photochromic system is eventually more interesting because there is the possibility of two consecutive write steps. Starting for example with **Cc⁻** at pH = 11, the first write step consists of the irradiation of this species that totally converts into **Ct⁻**. The system can be erased through a pH jump to 1 leading to the metastable **Ct** species. At this point a second write step (the same as the previous cycle) is available, converting the system into **AH⁺**. This last reaction can also be carried out thermally. Finally, the system should be submitted to a second pH jump to the starting pH value, so that **Cc⁻** species is recovered.

Experimental

3',4'-(Methylenedioxy)flavylium tetrafluoroborate was prepared from condensation of 3',4'-methylenedioxyacetophenone (0.49 g, 3 mmol) and salicylaldehyde (0.37 g, 3 mmol), on the basis of a method described by Katritzky for similar

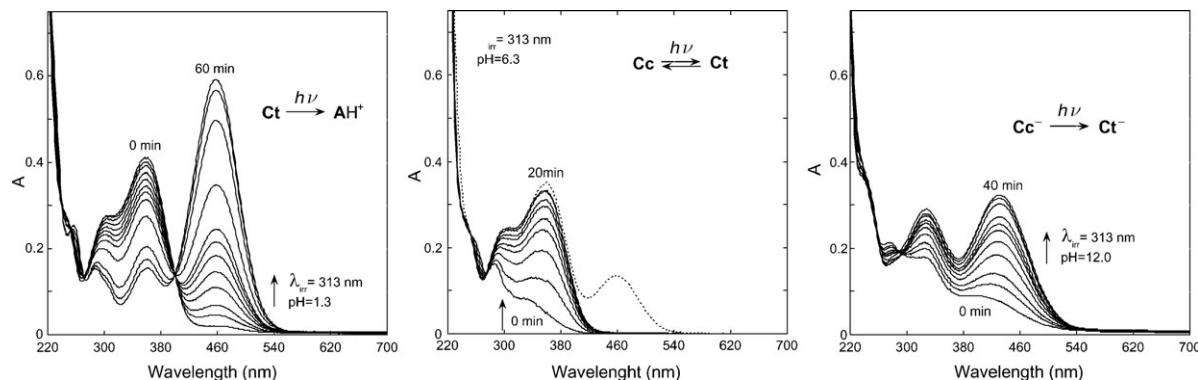


Fig. 7 Spectral variations upon irradiation at 313 nm of 3',4'-(methylenedioxy)flavylium 2.0×10^{-5} M: a) Ct form at pH = 1.3; b) B + Cc species at pH = 6.3; c) Cc⁻ species at pH = 12.0. Acidification to pH = 1.0 at the end of the photochemical reaction leads to the formation of some AH⁺ in the case of b) (trace line) but not in the case of c) (not shown).

compounds.¹⁰ The reagents were dissolved in acetic acid (5 mL) and tetrafluoroboric acid (1 mL) was added. Acetic anhydride (4 mL) was then added, keeping the temperature below 60 °C (~10 min). The solution was stirred overnight. The red solid that precipitated was filtered, washed with ethyl acetate, and dried under vacuum; 0.27 g (27%). Elemental analysis (Thermo Finnigan–CE Instruments EA 1112): found (calc. for C₁₆H₁₁BF₄O₃) %C 56.4 (56.8), %H 2.9 (3.2). ¹H NMR: see ESI.†

All experiments were carried out in aqueous solutions. The pH was adjusted by addition of HCl and NaOH, or buffer, and was measured using a Meterlab pHM240 pH meter from Radiometer Copenhagen.

UV–Vis absorption spectra were recorded on a Shimadzu UV2501-PC spectrophotometer.

Light excitation was carried out using a medium-pressure mercury arc lamp (Helius), and the excitation bands were isolated with interference filters (Oriel). The incident light intensity was measured by ferrioxalate actinometry.¹¹

The stopped flow experiments were collected in a SFM-300 spectrophotometer, controlled by a MPS-60 unit (Bio-Logic) and the data were collected by a TIDAS diode array (J&M), with wavelength range between 300 and 1100 nm, all connected to a computer. The standard cuvette has an observation path length of 1 cm. For this experiments the dead time of each shot was previously determined to be 6.4 ms with a 7 mL s⁻¹ flow rate.

Acknowledgements

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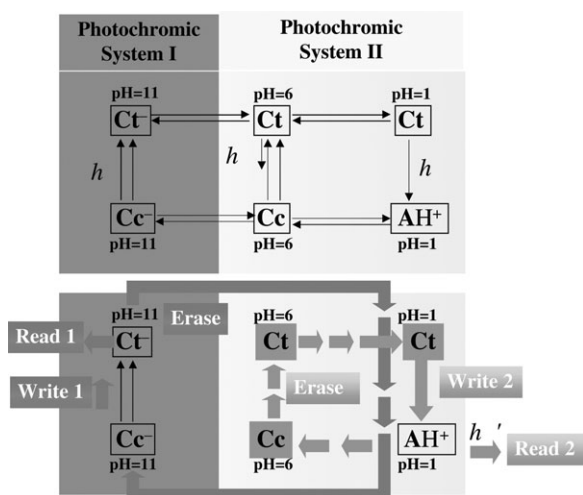


Fig. 8 The network of thermal and photochemical reactions of the compound 3',4'-(methylenedioxy)flavylium allows two write–read–erase cycles to be defined.