Multistate/Multifunctional Molecular-Level Systems: Light and pH Switching between the Various Forms of a Synthetic Flavylium Salt

Fernando Pina,* Ana Roque, Maria João Melo, Mauro Maestri,* Livia Belladelli, Vincenzo Balzani*

Abstract: The photochromic properties of the 4′-hydroxyflavylium ion (**AH**$^+$) have been investigated in aqueous solution. This system can be interconverted between as many as ten different forms by light excitation and/or pH changes. In neutral or moderately acidic solution the thermodynamically stable form of this compound is *trans*-2,4′-dihydroxychalcone (**Ct**). Light excitation of **Ct** in acidic or neutral solution gives rise to *cis*-chalcone **Cc** ($\Phi = 0.04$ at 365 nm), which undergoes slow equilibration with three other forms, namely hemiacetal **B**, flavylium cation **AH**$^+$, and quinoidal base **A**. The relative amounts of the photoproducts depend on pH. At pH < 3 the only product is the colored **AH**$^+$. In neutral and moderately acidic solutions, the four photoproducts revert back to **Ct** by a slow thermal reaction ($k = 4.0 \times 10^{-5}$ s^{-1}, half-life 27 hours at 25 °C, pH = 3), whose rate can be accelerated by increasing the temperature ($k = 1.8 \times 10^{-2}$ s^{-1} at 75 °C, pH = 3), and by exploiting the photochemical conversion of **Cc** to **Ct** ($\Phi > 0.16$ at 313 nm). At pH < 1, **AH**$^+$ is the thermodynamically stable form of the system. A pH jump from 1 to 12 causes the complete conversion of **AH**$^+$ to the **Cc**$^{2-}$ dianion. This species is relatively stable (half-life 400 hours at pH 12 and 25 °C). Its thermal and photochemical reactions ($\Phi = 0.17$ at 313 nm) lead to **Ct**$^{2-}$, which is the thermodynamically stable form of the system in basic solution. **Ct**$^{2-}$ does not undergo any photochemical reaction. All the observed processes are fully reversible and accompanied by large changes in the absorption and emission spectra. The flavylium salt investigated represents a *multistate/multifunctional* molecular-level system. It has properties required by optical memory devices with multiple storage in two different memory levels and nondestructive readout capacity through a *write–lock–read–unlock–erase cycle*. Its light- and/or pH-induced transformations can be taken as a basis for simple logic operations and create an intricate network of chemical processes.

Keywords: flavylium salts · information storage · logic gates · molecular devices · photochromism

Introduction

Much effort is currently being devoted to the design of molecular-level switching devices. By reducing the switching elements to molecular size, the memory density of computers could be increased by several orders of magnitude and the power input decreased significantly.[1] Although computation at the molecular level appears to be far off,[2] the design and construction of molecular-level systems capable of existing in different forms interconvertible by external stimuli is of great interest in both basic and applied research.[3–9]

Molecules that can exist in two forms interconvertible by an external input are rather common. Typical examples are photochromic compounds, where the input causing the switching between the two (stable) species is light.[10] From a logic viewpoint,[5, 8, 11, 12] such simple systems perform YES/NO logic functions. Systems capable of existing in more than two forms (*multistate*) and that can be interconverted by more than one type of external stimulus (*multifunctional*), on the other hand, are less common.[13, 14] Such multistate/multifunctional systems can behave as complex logic devices. Chemical systems capable of performing AND,[11] OR,[11] XOR,[9a] and XNOR[9b] logic operations have been recently reported.

Like anthocyanins, which are one of the most important sources of color in flowers and fruits, synthetic flavylium salts undergo structural transformations in aqueous solution that follow a previously discussed general scheme.[15–19] Some of the structural transformations of the 4′-hydroxyflavylium ion are illustrated in Scheme 1. Several reports concerning the thermodynamic as well as the kinetic aspects of the thermal reactions of flavylium-type compounds have appeared in the literature.[15–19] Much less attention has been paid to the

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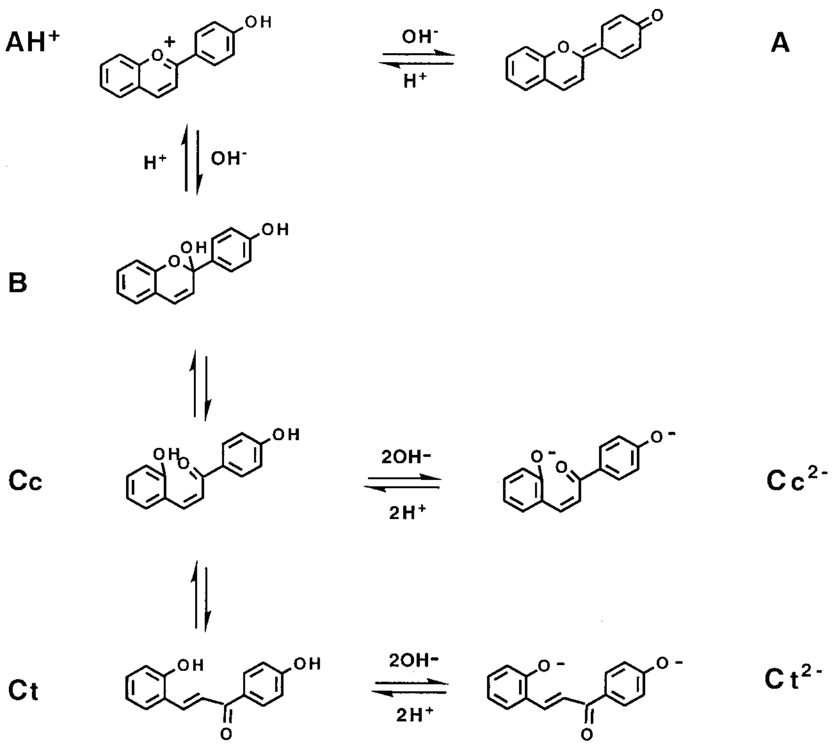

Scheme 1. Structural transformations of the 4′-hydroxyflavylium ion (**AH**$^+$). For the sake of simplicity, the monoanionic forms **B**$^-$, **Cc**$^-$, and **Ct**$^-$, which play a marginal role in the experiments dealt with in this paper, are not represented.

photochemical and photophysical behavior of these compounds except for an interesting paper by von Sperling et al. on the *trans–cis* photoisomerization of some flavylium ions[20] and the excited-state twisting of flavylium ions and its consequences on their fluorescent behavior.[21] We and others have recently undertaken a systematic investigation in this field.[22] In a previous paper[13i] we illustrated the possibility of using a photochromic flavylium ion as the basis for an optical memory device with multiple storage and nondestructive readout capacity through a *write–lock–read–unlock–erase* cycle. Here we report the results of an investigation on the photochromic behavior of another flavylium compound, namely the 4′-hydroxyflavylium ion, which can exist in four different thermodynamically stable forms depending on the pH of the solution and can be interconverted between as many as ten forms by using light excitation or changes in pH.

Experimental Section

Materials: Synthetic 4′-hydroxyflavylium (**AH**$^+$) perchlorate was prepared according to a published procedure.[23] A useful procedure for preparing a stock solution of **Ct** is to dissolve a solid sample of 4′-hydroxyflavylium in NaOH (0.01N). Under these conditions, **AH**$^+$ is completely converted into **Ct**$^{2-}$ within a few days at 60 °C. Solutions of **Ct** at the desired pH are then obtained by addition of the necessary amount of $HClO_4$ and a buffer (citrate or phosphate buffer, 0.01M). A solution of **Ct** at ca. pH 7 was also obtained by dissolving **AH**$^+$ perchlorate at this pH value and keeping the solution at room temperature for 7 days. The transformation of **AH**$^+$ into **Ct** was followed by UV/Vis absorption spectroscopy. The molar fraction distribution of the various species as a function of pH was calculated as reported in refs. [22a,b].

Photochemical experiments: In continuous irradiation experiments, light excitation was performed by a medium-pressure mercury lamp. Interference filters (Oriel) were used to select a narrow spectral range with λ_{max} 365 and 313 nm. The irradiated solution was contained in a 3 mL spectrophotometric cell. The intensity of the incident light (2.4×10^{-7} einstein/min at 365 nm and 1.2×10^{-7} einstein/min at 313 nm) was measured with a ferrioxalate actinometer.[24] The estimated uncertainty in the quantum yields of the photochemical reactions is 10%. Flash photolysis experiments were performed according to the procedure described elsewhere.[22c]

Results and Discussion

Synthetic flavylium salts in aqueous solution undergo a series of complex structural transformations that can be driven by pH changes and light excitation. These complex transformations follow a general scheme previously discussed for the compounds which carry a methyl or methoxy group in the 4′ position.[15–18] In the case of the 4′-hydroxyflavylium ion, the scheme is further complicated by the presence of the hydroxyl substituent and the consequent formation of a quinoidal base. Altogether, as many as ten different forms are involved and connected by a network of processes. As far as the present study is concerned, the species playing an important role are the seven shown in Scheme 1. The three species not directly involved in our discussion, and therefore not shown in the scheme, are the monoanionic **Ct**$^-$, **Cc**$^-$, and **B**$^-$ forms. As described below, the thermodynamically stable species are **AH**$^+$, **Ct**, **Ct**$^-$, and **Ct**$^{2-}$, depending on the pH of the solution. The other species can be transiently obtained by pH jump or flash photolysis. Their half-lives vary from submilliseconds to months, depending on the specific species and the experimental conditions.

Thermal reactions: The thermal reactions of the 4′-hydroxyflavylium ion have been investigated in great detail by McClelland and McGall.[19] We re-examined several aspects of the thermal behavior of this system; our results agree substantially with those reported by those authors, except for the values of a pK_a and a molar absorption coefficient (vide infra).

In strongly acidic solution (pH = 1), the 4′-hydroxyflavylium ion (**AH**$^+$) is the thermodynamically stable form of the system (Scheme 1). This species is yellow, its absorption spectrum showing an intense band with $\lambda_{max} = 435$ nm ($\varepsilon = 41\,000\,\text{M}^{-1}\text{cm}^{-1}$). In moderately acidic or neutral solution (pH 3–7) the thermodynamically stable form is the neutral, colorless *trans*-2,4′-dihydroxychalcone (**Ct**), which exhibits a moderately intense broad band with $\lambda_{max} = 350$ nm ($\varepsilon = 21\,000\,\text{M}^{-1}\text{cm}^{-1}$). In basic solution (pH = 12) the thermodynamically stable form is the pale yellow *trans*-2,4′-dihydroxychalcone dianion (**Ct**$^{2-}$) ($\lambda_{max} = 428$ nm, $\varepsilon = 22\,600\,\text{M}^{-1}\text{cm}^{-1}$). The absorption spectra of **AH**$^+$, **Ct**, and **Ct**$^{2-}$ are shown in Figure 1a. Since we will discuss the behavior of the system at

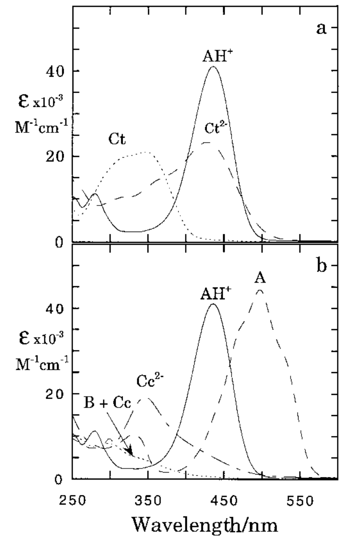

Figure 1. Absorption spectra of the species derived from 4′-hydroxyflavylium ion in aqueous solution at 25 °C: a) $\mathbf{AH^+}$, **Ct**, and $\mathbf{Ct^{2-}}$; b) **A**, $\mathbf{AH^+}$, $\mathbf{Cc^{2-}}$, and **B** and **Cc** mixture at pH = 7.

pH 1–7 and 12, the spectrum of $\mathbf{Ct^-}$, the most stable form around pH = 8, is not relevant to our discussion.

Upon addition of base to a solution of $\mathbf{AH^+}$ at pH 1, $\mathbf{AH^+}$ is converted into **Ct**, $\mathbf{Ct^-}$, or $\mathbf{Ct^{2-}}$. As is apparent from the formulae shown in Scheme 1, such a conversion can only occur through a complex reaction sequence involving the formation of intermediate species, whose spectra and rate constants for formation/disappearance can be obtained by pH-jump, temperature-jump, and/or flash photolysis techniques.

Acidic and neutral solutions: When an aqueous $\mathbf{AH^+}$ solution is subjected to a pH jump from pH 1 to pH 7, the first spectral change observed is a decrease in absorbance at 435 nm and an increase at 500 nm. This process, assigned[19] to deprotonation to form quinoidal base **A** (Scheme 1), is so rapid that its rate cannot be measured by stopped-flow analysis. It can, however, be measured by the technique of temperature jump.[19] The p*K* of the equilibrium $\mathbf{AH^+} \rightleftharpoons \mathbf{A} + \mathrm{H^+}$, hereafter indicated by pK^{I}, is 5.53.[19] Therefore at pH 7 practically 100% of the flavylium cation is converted to the quinoidal base in the first step. The immediate formation of **A** is accompanied by a slower process, readily observable on the stopped-flow time scale (Figure 2). This process is attributed[19] to the equilibration of **A** with species **B** and $\mathbf{C_c}$ via $\mathbf{AH^+}$. Extrapolation of the absorbance changes to $t = 0$ provides the spectrum of **A** shown in Figure 1b ($\lambda_{max} = 500$ nm, $\varepsilon = 44\,000\,\mathrm{M^{-1}cm^{-1}}$).[25] The spectrum of the equilibrated mixture of **B** and **Cc** at pH 7 (30 min after the pH jump) is also shown in Figure 1b. As is always the case for aromatic derivatives of ethylene,[26] the absorption spectrum of **Cc** must be less intense and slightly blue-shifted relative to that of **Ct**. Compound **B** has a structure similar to **Cc** and is therefore expected to exhibit a similar spectrum.

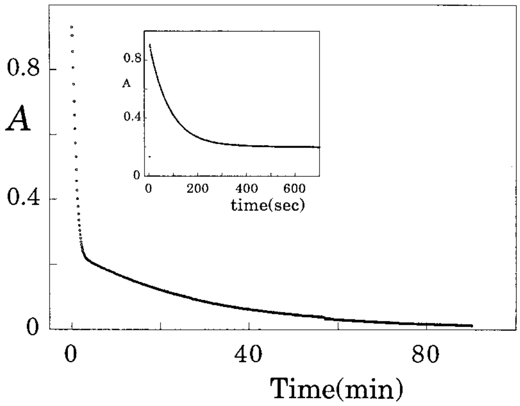

Figure 2. Decay of the absorbance at 500 nm after a pH jump of 4′-hydroxyflavylium ($\mathbf{AH^+}$) from pH = 1 to pH = 7 in aqueous solution at 55 °C. The inset shows the first part of the decay for a solution at 25 °C.

On a much longer time scale (half-life 10 hours at pH 7) the system undergoes a third process, leading to **Ct**, the thermodynamically stable product at this pH value. Figure 2, which displays the absorbance changes at 500 nm for a solution at 55 °C, clearly shows two consecutive decay processes following the immediate formation of **A**.

Upon a pH jump from 1 to 4, the fast deprotonation of $\mathbf{AH^+}$ to give the quinoidal base **A** is incomplete and leaves a mixture of both compounds, which, on the minute time scale, equilibrates with **B** and **Cc**. This process is then followed by the slow reaction leading to the thermodynamically stable product at pH 4, **Ct**. Similar behavior is observed throughout the acidic pH range. Figure 3 shows the absorption spectra obtained 30 minutes after a pH jump from 1 to a series of final pH values. These spectra are due to the presence of the four species $\mathbf{AH^+}$, **A**, **B**, and **Cc**, whose relative amounts depend on the final pH of the solution. The inset of Figure 3 shows the molar fraction of $\mathbf{AH^+}$ as a function of pH, calculated from the absorbance at 435 nm. A best-fitting procedure on this plot gives a p*K*, hereafter indicated by pK^{II}, of 4.4 for the dissociation equilibrium of $\mathbf{AH^+}$ to give **A**, **B**, and **Cc**. This value is somewhat different from that (5.0) reported by McClelland.[19]

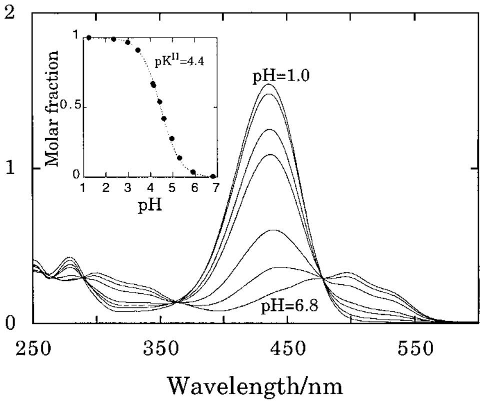

Figure 3. Absorption spectra recorded after 30 min for 4′-hydroxyflavylium ($\mathbf{AH^+}$) aqueous solution upon a series of pH jumps from pH = 1 to different pH values. The inset shows the molar fraction of $\mathbf{AH^+}$ as a function of pH.

The percentage of $\mathbf{AH^+}$ present at the final (thermodynamic) equilibrium allowed us to calculate the equilibrium constant between $\mathbf{AH^+}$ and **Ct** ($pK^{III} = 1.9$ at 60 °C). As shown in Figure 4, the measurements performed in the pH range 4–7 showed a linear dependence of the rate constant of the reaction leading to **Ct** on the molar fraction of **Cc**. This confirms that the rate-determining step of the conversion of $\mathbf{AH^+}$ after the pH jump is the isomerization reaction $\mathbf{Cc} \rightarrow \mathbf{Ct}$.

All the observed reactions follow first-order (or pseudo-first-order) kinetics. At pH = 4 activation energies of 29 and 129 kJ mol⁻¹ were obtained from the Arrhenius plots for the

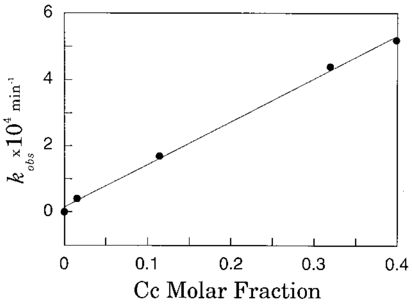

Figure 4. Plot of the first-order rate constant of the reaction leading from $\mathbf{AH^+}$/**A** to **Ct** as a function of the molar fraction distribution of **Cc**.

equilibration of $\mathbf{AH^+}$ with **A**, **B**, and **Cc** and the transformation of $\mathbf{AH^+}$ into **Ct**, respectively. The experiments at $pH < 3$ were carried out only at high temperature because of the relative inertness of the flavylium cation.

In conclusion, starting from a solution at $pH = 1$, where the only species present is $\mathbf{AH^+}$, and jumping to less acidic or neutral media, complex behavior is observed due to the presence of three equilibria [more properly, two pseudoequilibria and one real equilibrium, Eqs. (1), (2), and (3)] which are well separated in time allowing the determination of their pK values.

$$\mathbf{AH^+} \rightleftharpoons \mathbf{A} + H^+ \qquad pK^{I} = 5.53 \text{ at } 25\,^\circ C \tag{1}$$

$$\mathbf{AH^+} \rightleftharpoons \mathbf{A} + \mathbf{B} + \mathbf{Cc} + H^+ \qquad pK^{II} = 4.4 \text{ at } 25\,^\circ C \tag{2}$$

$$\mathbf{AH^+} \rightleftharpoons \mathbf{Ct} + H^+ \qquad pK^{III} = 1.9 \text{ at } 60\,^\circ C \tag{3}$$

Making the reasonable assumption that the value of pK^{III} is not appreciably temperature-dependent, we calculated the molar fractions of the five species $\mathbf{AH^+}$, **A, Ct**, **Cc**, and **B** in the pH range 0–7 under the pseudoequilibrium and equilibrium situations at 25 °C from the above pK values (Figure 5). The thermodynamically stable species are $\mathbf{AH^+}$ at $pH < 1$ and **Ct** at $pH > 3$, while **A**, **Cc**, and **B** (always present in a 1:2:2 ratio)[19] are transient species.

The behavior of the system under the above experimental conditions is illustrated in Figure 6, where the relative energy levels of the species involved (including those pertinent to the experiments in basic solution, vide infra) are indicated.

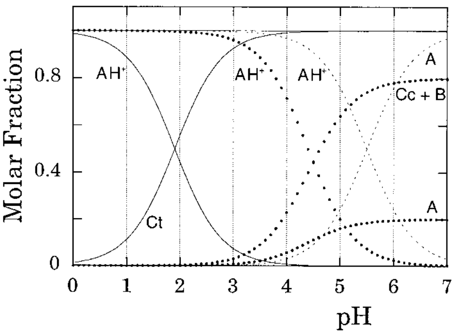

Figure 5. Molar fraction distribution in aqueous solution at 25 °C as a function of pH. Solid lines refer to the species obtained at the thermodynamic equilibrium. Thick dotted lines refer to the pseudoequilibrium reached in the minute time scale after a pH jump on $\mathbf{AH^+}$ solution or flash photolysis of **Ct** solutions. Dashed lines refer to the pseudoequilibrium reached in the submillisecond time scale after a pH jump on $\mathbf{AH^+}$ solutions.

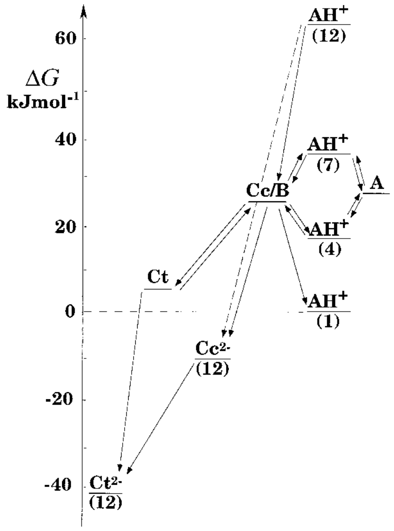

Figure 6. Energy-level diagram for the species involved in the pH-jump and flash-photolysis experiments. pH values are indicated in brackets. For the sake of simplicity the species **Cc** and **B** are represented by the same energy level. The ratio between the concentrations of **Cc** and **B** is ≈ 1.[20]

The technique of pH jump can also be applied in the reverse direction.[16, 18, 19] Starting from a solution at $pH = 7$ at its pseudoequilibrium (i.e., when the species present are **A, B,** and **Cc**) a reverse pH jump to $pH = 1$ shows a very fast process due to the protonation of the quinoidal base **A**, a fast process corresponding to the formation of $\mathbf{AH^+}$ from **B**, and a slower process in which more $\mathbf{AH^+}$ appears from the conversion of **Cc** through **B**.

Basic solutions: McClelland and McGall[19] have shown that upon a pH jump in an aqueous solution of $\mathbf{AH^+}$ from $pH = 1$ to $pH = 12$, the behavior is much simpler (Figure 6) because the deprotonation of $\mathbf{AH^+}$ and subsequent disappearance of **A** are very fast processes. Only one intermediate state is observed (half-life 400 hours at $pH = 12$), consisting of mono- or di-ionized species of *cis*-chalcone (pK_a 7.9 and 9.7, respectively).[19] The thermodynamically stable products are the mono- and dianionic *trans*-chalcones, which we have found to have pK_a 7.6 and 8.3, respectively. The absorption spectra of the relevant basic forms, the colored *trans*-2,4′-dihydroxychalcone dianion ($\mathbf{Ct^{2-}}$) and the colorless *cis*-2,4′-dihydroxychalcone dianion ($\mathbf{Cc^{2-}}$) ($\lambda_{max} = 347$ nm, $\varepsilon = 19\,000$ $M^{-1}cm^{-1}$) are shown in Figure 1.

Photochemical reactions: We found that $\mathbf{AH^+}$ and $\mathbf{Ct^{2-}}$are not photosensitive, whereas **Ct** shows interesting photochemical behavior. The transient species **Cc** and $\mathbf{Cc^{2-}}$are also photosensitive.

Continuous irradiation: Continuous irradiation of **Ct** with 365 nm light causes spectral variations at all pH values in the range 1–7. Figure 7 shows the absorbance changes obtained at pH 4 and 7. These spectral changes are exactly the reverse of those observed in the thermal reactions following the pH

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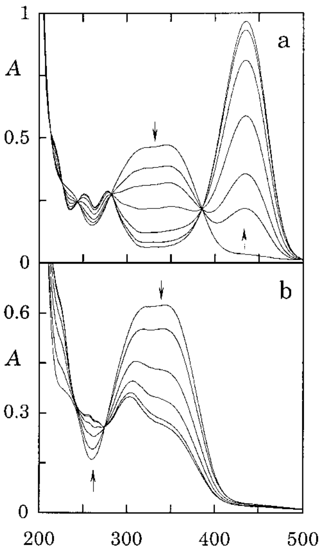

Figure 7. Spectral changes observed by continuous irradiation with 365 nm light of **Ct** aqueous solutions. a) pH = 4 and 2.4×10^{-5} M; b) pH = 7 and 2.9×10^{-5} M.

jumps of $\mathbf{AH^+}$ solutions from pH = 1 to the same pH of the irradiated solution.

As shown by the flash photolysis experiments described below, the primary product of the photochemical reaction of **Ct** is **Cc** (Scheme 1), which then undergoes the previously discussed thermal reactions leading on a short time scale (minutes) to its pseudoequilibrium with **B**, $\mathbf{AH^+}$, and **A**. The relative amounts of the photoproducts **Cc**, **B**, $\mathbf{AH^+}$, and **A** are determined by the pH of the solution (Figure 5, dotted lines). At pH < 3, the only photoproduct is $\mathbf{AH^+}$. At pH = 4, $\mathbf{AH^+}$ is still the main photoproduct, but small amounts of **A**, **B**, and **Cc** are also formed. At pH 5 and 6 a mixture of $\mathbf{AH^+}$, **A**, **B**, and **Cc** is obtained, while at pH = 7 no $\mathbf{AH^+}$ is present in the mixture. As in the thermal reactions described above, the photochemical products revert to **Ct** on a long time scale (hours). At pH < 3, when the thermal back reaction is negligibly slow and the only photoproduct is $\mathbf{AH^+}$, the quantum yield of $\mathbf{AH^+}$ formation is 0.04. This, of course, is also the quantum yield of the photoisomerization $\mathbf{Ct} \rightarrow \mathbf{Cc}$.

As stated above, a pH jump experiment from 1 to 7 on an $\mathbf{AH^+}$ solution at pH = 7 after 30 minutes leads to an equilibrated mixture of **A**, **B**, and **Cc** that can be maintained for a time period sufficiently long to allow the study of its photochemical behavior. Continuous irradiation of this equilibrated mixture at 313 nm causes an absorbance increase at 350 nm, indicating the formation of **Ct**. The apparent photochemical quantum yield for this reaction, based on the total light absorbed by the mixture, is ca. 0.16. From the formulae of the three components of the mixture (Scheme 1), it is clear that the only species responsible for the photoreaction leading to **Ct** is **Cc**. Since at pH = 7 **Cc** constitutes about 40% of the mixture and presumably absorbs a comparable fraction of the total absorbed light, it follows that the quantum yield of the *cis* → *trans* photoisomerization is probably close to 0.4.

A pH jump from 1 to 12 on a solution containing $\mathbf{AH^+}$ was found to give an absorption spectrum (Figure 8) identical to that reported by McClelland and McGall for $\mathbf{Cc^{2-}}$.[19] Continuous irradiation of this solution at 313 (or 365) nm caused the spectral changes shown in Figure 8. The final spectrum is identical to the spectrum of $\mathbf{Ct^{2-}}$ obtained by a pH jump to 12 on a solution of **Ct**. The initial quantum yield of the $\mathbf{Cc^{2-}} \rightarrow \mathbf{Ct^{2-}}$ photochemical conversion is 0.17 at 313 nm. Irradiation at 436, 365, or 313 nm of the final irradiated solution (or of a **Ct** solution after pH jump to pH = 12) does not cause any spectral changes.

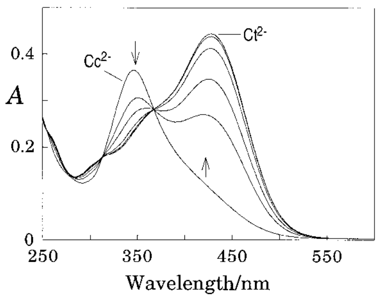

Figure 8. Spectral changes caused by continuous irradiation with 313 nm light of a 2.0×10^{-5} M aqueous solution of $\mathbf{Cc^{2-}}$ at pH = 12.

We found that $\mathbf{AH^+}$ and $\mathbf{Ct^{2-}}$ show fluorescence emission (Figure 9) with maxima at 515 and 615 nm, respectively, and comparable quantum yields (5×10^{-4}). This is an important result since $\mathbf{AH^+}$ and $\mathbf{Ct^{2-}}$, which absorb in the same spectral region, can be distinguished by fluorescence measurements (vide infra). The reason why $\mathbf{AH^+}$ exhibits a Stokes shift much smaller than $\mathbf{Ct^{2-}}$ is probably related to the rigidity of the former structure.

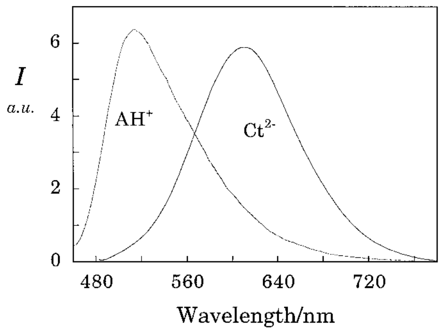

Figure 9. Fluorescence emission spectra of $\mathbf{AH^+}$ (pH = 1) and $\mathbf{Ct^{2-}}$ (pH = 12) aqueous solutions at 25 °C ($\lambda_{exc} = 435$ nm).

Flash photolysis: Previous investigations[13i, 22d] have revealed that important kinetic information on the conversion of the various forms of flavylium ions can be obtained by means of a simple flash photolysis apparatus.[22c]

Flash photolysis experiments were performed on aqueous solutions of **Ct** at 25 °C and pH = 4.0 and 7.0. After flash excitation, absorbance vs. time traces like those depicted in the insets of Figures 10 and 11 were recorded at several wavelengths in the spectral region 250–500 nm. From these traces, the difference spectra at pH = 4.0 and 7.0 shown in Figures 10 and 11 were obtained. At pH = 4, the absorbance changes occurred during the flash (Figure 10, bleaching at 350 nm and no absorption at 435 nm for the zero-time extrapolation) and are consistent with the formation of **Cc**. A subsequent process is observed (rate constant 0.22 s^{-1}) that causes an increase in absorption at $\lambda > 400$ nm as expected for the formation of $\mathbf{AH^+}$ and **A** (Figure 1). This process is attributed to the conversion $\mathbf{Cc} \rightarrow \mathbf{B}$, known from the pH jump experiments to be the rate-determining step (rate constant 0.27 s^{-1})[19] of the process $\mathbf{Cc} \rightarrow \mathbf{AH^+} + \mathbf{A}$. On a longer time

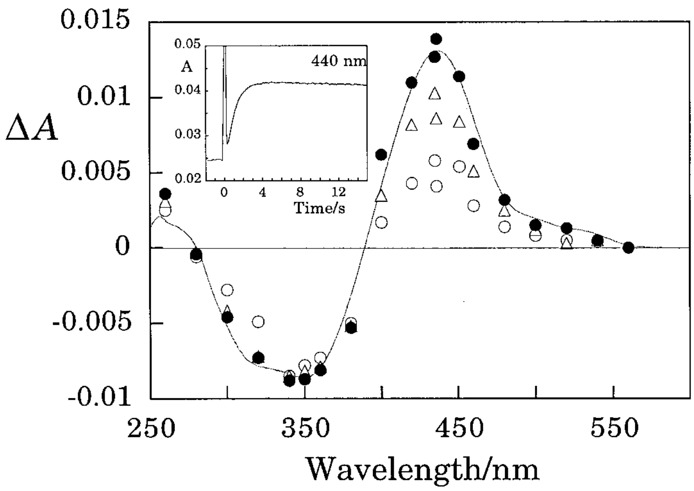

Figure 10. Difference spectra obtained after flash excitation of a aqueous solution of **Ct** (6×10^{-5} M) at pH = 4. The delay times are 1 s (○), 2 s (△), and 5 s (●). The unbroken line is the final difference spectrum obtained after continuous irradiation. The inset shows the absorbance vs. time trace obtained at $\lambda = 435$ nm (where **Ct** shows a minimum and **AH**$^+$ a maximum).

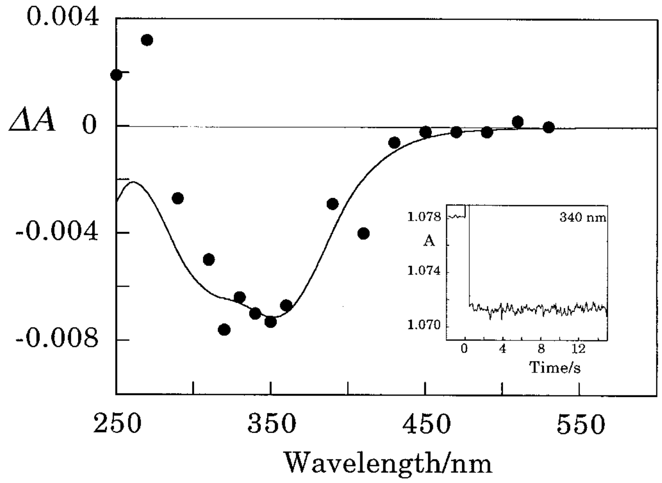

Figure 11. Difference spectrum obtained 1 s after flash excitation of a solution of **Ct** (6×10^{-5} M) at pH = 7. No further spectral change was observed in the second time scale. The unbroken line is the final difference spectrum obtained after continuous irradiation. The inset shows the absorbance vs. time traces obtained at 350 nm (where **Ct** shows a maximum and **AH**$^+$ a minimum).

scale, back reaction to **Ct** takes place, as in the pH jump experiments.

In the flash experiments at pH 7.0 (Figure 11) a fast process exhibiting the same characteristics discussed above takes place within the time scale of the flash. This process is again assigned to the photochemical conversion of **Ct** to **Cc**. A second, much slower, process (rate constant 0.0026 s^{-1}), not discernible in Figure 11, follows. The spectral changes indicate that this second process leads to the quinoidal base **A**. These results are again in full agreement with those obtained by McClelland from pH jump experiments[19] which showed that, at pH 7, the rate-determining step for formation of **A** from **Cc** is the reaction **B** → **AH**$^+$ (rate constant 0.0025 s^{-1}).

In conclusion, light excitation of **Ct** causes a *trans* → *cis* photoisomerization that is followed by thermal equilibration of **Cc** to form **B**, **AH**$^+$, and **A**. In other words, light excitation of *trans*-chalcone converts the system from the thermodynamic equilibrium indicated by the full lines in Figure 5 to the pseudoequilibrium situation indicated by the dotted lines. This pseudoequilibrium is maintained for a length of time which depends on temperature, pH, and light excitation of the **Cc** form. At 25 °C and pH 7 in the absence of light, the recovery of **Ct** occurs with a half-life of 22 hours. However, as can be understood from Figure 6, the products of the **Ct** → **Cc** photoreaction can be a) frozen indefinitely as **AH**$^+$ by lowering the pH to 1, b) rapidly back-converted to **Ct** by increasing the temperature and/or by irradiation with 313 nm light, c) temporarily converted to **Cc**$^{2-}$ by increasing the pH to 12. In turn, **Cc**$^{2-}$ can be thermally or photochemically converted to the stable **Ct**$^{2-}$ form, which can be converted back to the starting **Ct** species by lowering the pH to 4.

Properties of the network of chemical processes: As mentioned in the introduction, molecular or supramolecular systems capable of existing in different forms (*multistate*) that can be interconverted by different external stimuli (*multifunctional*) are interesting for both basic and practical reasons. The system examined in this paper can exist as four different thermodynamically stable species depending on the pH of the solution and can be interconverted between a number of different forms by two different inputs, namely light (three reactions can be light-driven) or changes in pH. In the following discussion on the interconversion processes, the transient products **B** and **A** have been neglected for the sake of simplicity since they are always in equilibrium with **Cc**.

A write–lock–read–unlock–erase cycle: It is well known that photochromic systems represent potential molecular-level memory devices.[10, 13, 14] A number of problems, however, must be solved for practical applications. A particular challenge is to find systems with multiple storage and nondestructive readout capacity, that is, where the record can be erased when necessary, but is not destroyed by the readout. The 4′-hydroxyflavylium ion investigated in this paper can be taken as the basis for an optical memory system with multiple storage and nondestructive readout capacity through a write–lock–read–unlock–erase cycle similar to that previously described for another flavylium derivative.[13i] This behavior can be described with reference to Figures 6 and 12:

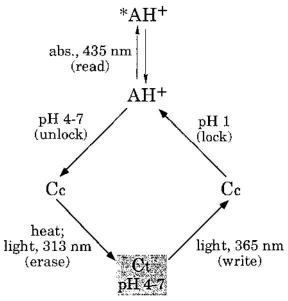

Figure 12. Write–lock–read–unlock–erase cycle starting from the **Ct** form.

a) At pH 4–7, the stable or kinetically inert (depending on pH) colorless species **Ct** can be photochemically converted (365 nm light) into the thermodynamically unstable, but relatively inert, form **Cc** (*write*);
b) by a second stimulus (addition of acid), **Cc** can be converted into the kinetically inert or thermodynamically

stable (depending on pH) $\mathbf{AH}^+$ form (*lock*); if the initial pH is 1, **Cc** autolocks as $\mathbf{AH}^+$;

c) $\mathbf{AH}^+$ is photochemically inactive and shows an absorption spectrum clearly distinct from that of **Ct** (Figure 1), so that it can be optically detected (*read*);

d) by addition of base, $\mathbf{AH}^+$ can be reconverted into **Cc** (*unlock*);

e) **Cc** can be reconverted to the initial **Ct** form by a thermal or a photochemical reaction (*erase*).

Reading without writing in a write–lock–read–unlock–erase cycle: A generally overlooked difficulty with photochromic systems is that the starting form (**Ct** in the above discussion) is the photoreactive one, so that it cannot be read by absorption spectroscopy without writing. In our system, this difficulty can be overcome starting from $\mathbf{AH}^+$, which is the thermodynamically stable form at pH = 1 (Figures 6 and 13). Since this form is not photosensitive, it can be read by light excitation (that is, by recording its absorption spectrum) without writing. It can then be unlocked by a pH jump, which yields the metastable $\mathbf{Cc}^{2-}$ form. At this stage, one can write the optical information obtaining the stable (locked) $\mathbf{Ct}^{2-}$ form that can then be read. When necessary, the information stored into $\mathbf{Ct}^{2-}$ can be unlocked by a pH jump yielding **Ct** and can then be erased by light excitation. The same performance can be obtained starting from $\mathbf{Ct}^{2-}$.

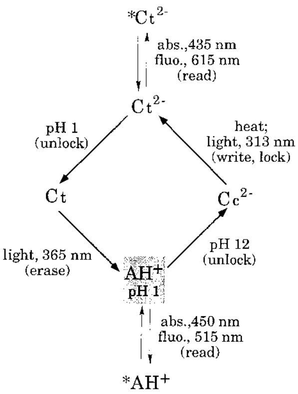

Figure 13. Read–write–lock–read–unlock–erase cycle starting from the $\mathbf{AH}^+$ form.

Permanent and temporary memories: The human brain contains shallow and deep memory forms.[27] The network of processes interconverting the various species (Scheme 1 and Figure 6) allows the presence of different levels of memory. Once the permanent (deep) $\mathbf{AH}^+$ form of memory has been obtained (*write* and *lock*, Figure 14), a jump to pH 12 leads to the formation of a temporary (shallow) memory state, $\mathbf{Cc}^{2-}$, whose spontaneous slow erasure to give the deep $\mathbf{Ct}^{2-}$ memory can be accelerated by light. Reset can then be accomplished by a back pH jump to pH 4.

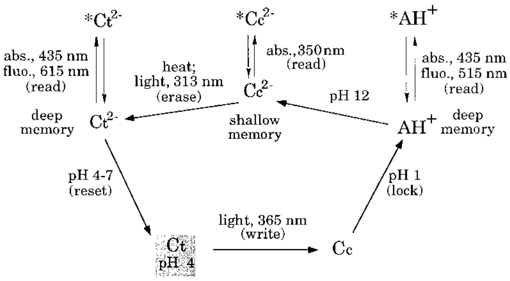

Figure 14. A write–lock–read–unlock–erase cycle with two memory levels.

Oscillating absorbance patterns: Another feature of the investigated system should be emphasized. Starting from $\mathbf{AH}^+$, alternation of pH jump and light excitation causes oscillation patterns of absorbance at different wavelengths, as shown in Figure 15. Such patterns may be of interest for signal generation purposes.

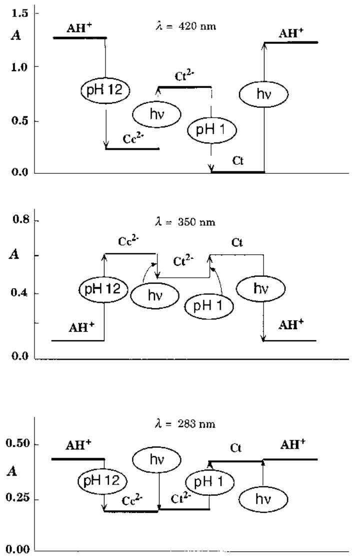

Figure 15. Absorbance oscillations caused by alternate pH jump and light excitation of a 3.3×10^{-5} M aqueous solution starting from $\mathbf{AH}^+$ at pH = 1.

Logic operations: Multistate/multifunctional molecular-level systems can be taken as bases for logic operations.[5, 8, 9, 11, 12] In the present system light excitation and pH jumps can be taken as inputs, and absorbance or fluorescence as outputs. Starting from the nonemitting **Ct** and taking the emission of $\mathbf{AH}^+$ at 515 nm as output signal, a jump to pH = 1 or light excitation alone cannot generate the output, whereas when these two imputs are applied in series, the output is obtained (AND logic function).

Multiple reaction patterns: Some of the species studied in this work are interconnected by multiple reaction patterns. For example, in order to go from $\mathbf{AH}^+$ to **Ct** three different routes can be chosen, as represented pictorially in Figure 16: i) jump to pH 12 with formation of $\mathbf{Cc}^{2-}$, followed by excitation with 313 nm light to obtain $\mathbf{Ct}^{2-}$, and by a jump to pH = 6; ii) jump to pH = 6 to form **Cc**; at this stage, one can choose between two sub-routes, namely iia) light excitation with 313 nm light, or iib) jump to pH 12 to merge into the preceding path which goes via $\mathbf{Cc}^{2-}$ and $\mathbf{Ct}^{2-}$. Once **Ct** has been obtained, one can go back to $\mathbf{AH}^+$ by two different routes: iii) light excitation at

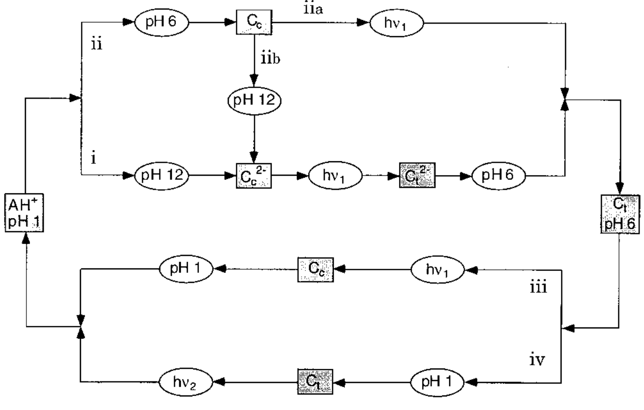

Figure 16. The network of processes caused by pH jumps and light excitations interconnecting the $\mathbf{AH}^+$ and **Ct** forms of the investigated system.

365 nm to obtain **Cc** and subsequent jump to pH = 1, or vice versa: iv) jump to pH = 1 and subsequent light excitation at 365 nm. Interestingly, in some cases, for example starting from **Ct** at pH 6, one obtains the same result (**AH**$^+$) regardless of the order in which light excitation (365 nm) and pH jump (pH = 1) are applied. In other cases, however, this is not true. For example (not shown in Figure 16), starting from **AH**$^+$ at pH = 1, light excitation followed by pH jump to 12 leads to **Cc**$^{2-}$, whereas when the two inputs are applied in the reverse order one gets **Ct**$^{2-}$. Since **Cc**$^{2-}$ and **Ct**$^{2-}$ exhibit very different spectroscopic properties (for example, **Ct**$^{2-}$ exhibits fluorescence whereas **Cc**$^{2-}$ does not), from the state of the system after the two inputs one can establish in which sequence the two inputs were applied.

Conclusions

We have described the properties of a chemical system that can exist in several forms (*multistate*) that can be interconverted by more than one type of external stimulus (*multifunctional*). Such a system exhibits properties required by optical memory devices, with multiple storage in two different memory levels and nondestructive readout capacity through a *write–lock–read–unlock–erase cycle*. Its light- and/or pH-induced transformations, which are accompanied by changes in the absorption and emission spectra, can be taken as a basis for simple logic operations and create an intricate network of chemical processes.

In the brain, neurons store, exchange, and retrieve information by extremely complicated chemical processes. Simple multistate/multifunctional systems may play the role of models for an initial understanding of the chemical basis of complex biological processes. It is by no means clear whether wet artificial systems can find real applications, for example in molecular-scale computers.[2] We point out, however, that the design and construction of molecular or supramolecular species capable of existing in different forms that can be interconverted by external stimuli introduces new concepts in the field of chemistry and stimulates the ingenuity of researchers engaged in the bottom-up approach to nanotechnology.

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