JOURNAL OF Materials CHEMISTRY

Micelle effect on the 'write–lock–read–unlock–erase' cycle of 4′-hydroxyflavylium ion

Ana Roque,[a] Fernando Pina,*[a] Sérgio Alves,[a] Roberto Ballardini,[b] Mauro Maestri*[c] and Vincenzo Balzani*[c]

[a]*Departamento de Química, Centro de Química Fina e Biotecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal E-mail: fjp@dq.fct.unl.pt*
[b]*Istituto FRAE-CNR, Via Gobetti 101, 40129 Bologna, Italy*
[c]*Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via Selmi 2, I-40126 Bologna, Italy. E-mail: mmaestri@ciam.unibo.it*

Received 8th April 1999, Accepted 20th May 1999

In aqueous solution the 4′-hydroxyflavylium ion ($\mathbf{AH^+}$) can be interconverted into several different neutral forms by light excitation and/or pH changes. All the observed processes are fully reversible and accompanied by strong changes in absorption and emission spectra. This system exhibits properties required by optical memory devices with multiple storage in two different memory levels and non-destructive readout capacity through a *write–lock–read–unlock–erase cycle*. The effect of micelles on the pH and light induced interconversion of $\mathbf{AH^+}$ and its neutral forms has been investigated. Negatively charged sodium dodecyl sulfate micelles stabilize $\mathbf{AH^+}$, whereas the positively charged cetyltrimethylammonium bromide and neutral polyoxyethylene(10) isooctyl phenyl ether (Triton X-100) micelles stabilize the uncharged (basic) forms. Besides affecting the molar fraction distribution of the various species, the presence of micelles also influences their interconversion rates. Addition of micelles can therefore be considered as a third external stimulus (besides light excitation and pH jump) capable of changing the state of this *multistate/multifunctional* molecular-level system. Particularly interesting is the possibility to change the autolock pH of the photochromic reaction by addition of micelles.

Introduction

Current computers are based on sets of components (wires, switches, transistors, *etc.*) constructed by the 'top down' approach. This approach, however, has arrived close to its intrinsic limitations. A necessary condition for further miniaturization to increase the power of information processing and computation is the 'bottom up' construction of molecular-level components able to perform the functions needed (chemical computer).[1,2] The possibility that future computers may be based on solution instead of on solid-state systems should also be taken into consideration.[3] In this context, the design and construction of molecular-level systems capable of existing in different forms that can be interconverted by external stimuli is a topic of great interest not only for basic studies, but also for innovative applications.[1–12]

Molecules that can exist in two forms, interconvertible by an external input, have been extensively investigated. Typical examples of such molecules are the photochromic compounds where the input causing the switching between the two forms is light.[12] Much less attention has been devoted to systems capable of existing in more than two forms (*multistate*) and that can be interconverted by more than one type of external stimulus (*multifunctional*).[13,14] It is well known that flavylium-type ions, which have basically the chemical structure as natural anthocyanins,[15] can undergo multiple structural transformations in aqueous solution.[16–21] In the case of 4′-hydroxyflavylium ion the most important species involved are shown in Scheme 1. All the observed processes are reversible and accompanied by strong changes in absorption and emission spectra. We have recently investigated the thermal and photochemical reactions of several flavylium ions and have emphasized the multistate/multifunctional character of the chemistry of these compounds.[22–28] In particular, we have shown that the 4′-hydroxyflavylium ion ($\mathbf{AH^+}$) exhibits properties required by optical memory devices with multiple storage in two different memory levels and non-destructive readout capacity through a *write–lock–read–unlock–erase cycle*.[25] We report here the results of an investigation on the effect of micelles on the pH and light induced interconversion of $\mathbf{AH^+}$ and its neutral forms. It is shown that micelles can be considered as a third external stimulus (besides light excitation and pH jump) capable of changing the state of this *multistate/multifunctional* molecular-level system.

Results and discussion

Aqueous solution

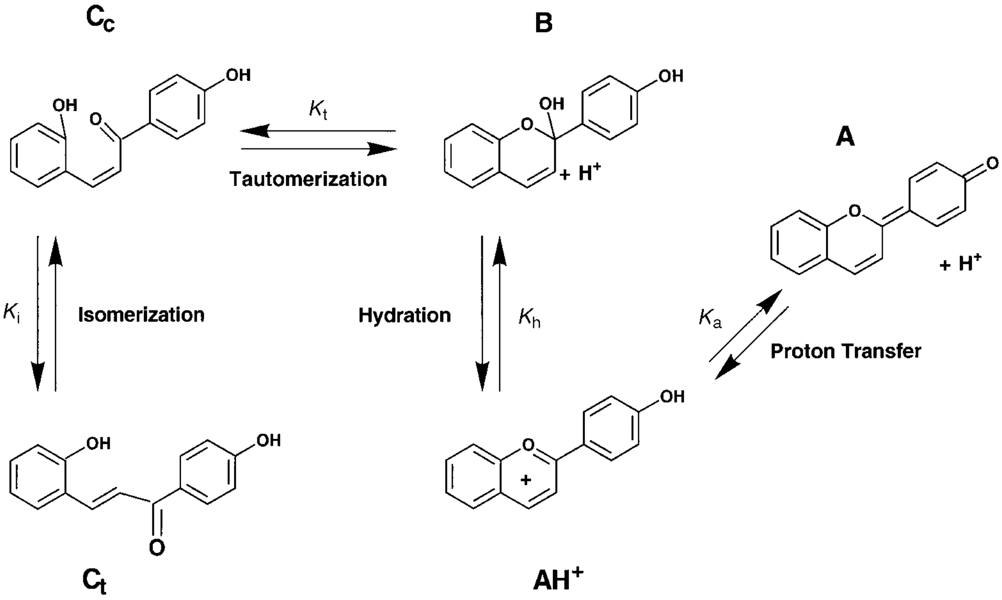
Before discussing the micelle effect on the structural transformations of 4′-hydroxyflavylium ion ($\mathbf{AH^+}$, Scheme 1), it is necessary to recall the main properties of this system.[25] In aqueous solution $\mathbf{AH^+}$ is thermodynamically stable only at $\mathrm{pH} < 1.0$. The behaviour of the system after a pH jump from $\mathrm{pH} < 1.0$ to less acidic or neutral media is governed by two pseudoequilibria and a thermodynamic equilibrium, schematically shown in eqns. (1)–(3),

$$\mathbf{AH^+} \rightleftharpoons \mathbf{A} + \mathrm{H^+} \qquad \mathrm{p}K_1 = 5.53 \text{ at } 25\,^{\circ}\mathrm{C} \qquad (1)$$

$$\mathbf{AH^+} \rightleftharpoons \mathbf{A} + \mathbf{B} + \mathbf{C_c} + \mathrm{H^+} \qquad \mathrm{p}K_2 = 4.4 \text{ at } 25\,^{\circ}\mathrm{C} \qquad (2)$$

$$\mathbf{AH^+} \rightleftharpoons \mathbf{C_t} + \mathrm{H^+} \qquad \mathrm{p}K_3 = 1.9 \text{ at } 60\,^{\circ}\mathrm{C} \qquad (3)$$

which are achieved in very different timescales. The first pseudoequilibrium (1) is due to a proton transfer reaction involving the flavylium cation and its quinoidal base **A**. This process occurs in the submillisecond timescale and its kinetics can only be measured by very fast techniques, such as temperature jumps. The second pseudoequilibrium (2), which is attained on the timescale of minutes, is generally controlled by the hydration reaction that leads from $\mathbf{AH^+}$ to **B** ($+\mathbf{C_c}$). The thermodynamic equilibrium (3) is reached only after a long time (from several minutes to days depending on temperature and pH) and leads to the stable (in neutral or slightly acidic solutions) $\mathbf{C_t}$ form.



Scheme 1 Structural transformations of the 4′-hydroxyflavylium ion. Only the most important forms are shown.

An important characteristic of the structural changes of the 4′-hydroxyflavylium ion is the presence of a large kinetic barrier that makes difficult the thermal *cis–trans* isomerization reaction between $\mathbf{C_c}$ and $\mathbf{C_t}$. This is the reason why it is possible to obtain pseudo-stable solutions far from the thermodynamic equilibrium. For example, $\mathbf{C_t}$ can be stored in the dark at pH 2 and room temperature for a long period of time. The situation can be visualized using an energy level diagram such as that shown in Fig. 1. At pH 0, $\mathbf{AH^+}$ is the thermodynamically stable species. Upon a jump to pH 5.5 equal quantities of $\mathbf{AH^+}$ and **A** are present. Then, a pseudoequilibrium state is reached involving the species $\mathbf{AH^+}$, **A**, $\mathbf{C_c}$ and **B**, eqn. (2). On a longer timescale, the thermodynamic equilibrium of all the species is attained with formation of $\mathbf{C_t}$, eqn. (3). The pH dependent molar fraction distributions of the five species in the thermodynamic equilibrium (solid lines) and in the pseudoequilibrium (dashed lines) states are shown in Fig. 2.

Another important property is that irradiation of the thermodynamically equilibrated system [eqn. (3)] at pH > 3, where the almost exclusive component is $\mathbf{C_t}$, leads to $\mathbf{C_c}$ and therefore gives rise to the pseudoequilibrium described by eqn. (2). With reference to Fig. 2, we can say that light excitation changes the molar fraction distribution from the solid lines to the dotted lines.

Since the $\mathbf{C_t}$ and $\mathbf{C_c}$ forms can be interconverted by means of light excitation, a write–lock–read–unlock–erase cycle can be performed starting from $\mathbf{C_t}$, as in Scheme 2.[25] The *writing* step is carried out by irradiation of the $\mathbf{C_t}$ species, for example

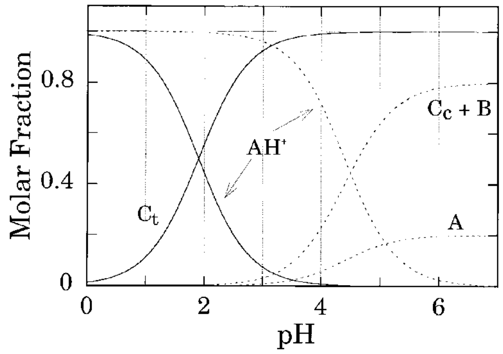


Fig. 2 Molar fraction distribution of the various species in aqueous solution at 25 °C as a function of pH for the 4′-hydroxyflavylium ion. Solid lines refer to the species obtained at the thermodynamic equilibrium. Dashed lines refer to the pseudoequilibrium reached in the minute timescale.

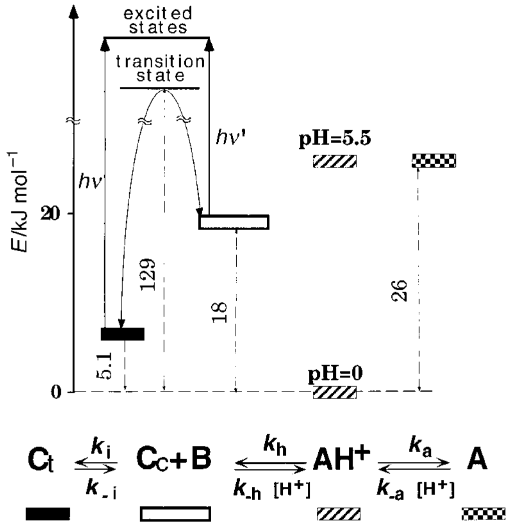
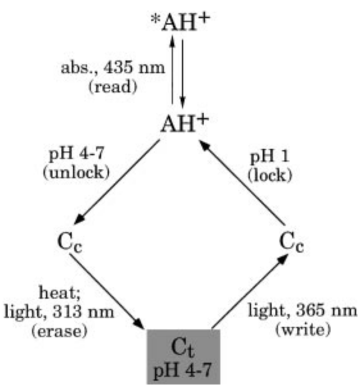


Fig. 1 Energy level diagram for the species involved in the pH jump and flash-photolysis experiments carried out on the 4′-hydroxyflavylium ion. The ratio between the molar fractions of $\mathbf{C_c}$ and **B** is *ca.* 1 : 1. For simplicity these two species are represented by the same energy level.



Scheme 2 Write–lock–read–unlock–erase cycle starting from the $\mathbf{C_t}$ form of the 4′-hydroxyflavylium compound. For simplicity the **B** form, which is in a *ca.* 1 : 1 molar ratio with $\mathbf{C_c}$, is not shown.

at pH 7, giving rise to $\mathbf{C_c}$ and **B** (these two species are in fast equilibrium and in an approximate 1:1 molar ratio). As mentioned above, in the case of the 4′-hydroxyflavylium ion there is a large kinetic barrier that prevents the thermal, back isomerization reaction (this is not the case for other flavylium ions).[28] In spite of its thermal stability, $\mathbf{C_c}$ cannot be optically detected without being destroyed because the photoisomerization reaction is reversible. In order to overcome this difficulty, it is necessary to transform $\mathbf{C_c}$ (and **B**) into $\mathbf{AH^+}$. This *locking* step can be performed by a pH jump to a more acidic medium (Scheme 2). When the initial pH is sufficiently low, the system undergoes *autolocking*. Since $\mathbf{AH^+}$ is stable under light excitation the system can then be *read* without being erased. When necessary, the system can be *unlocked* by a jump to higher pH values, with formation of $\mathbf{C_c}$ and **B**, and finally *erased* by light or high temperature.

From the kinetic viewpoint, writing (by flash photolysis) is a fast process, locking and unlocking occur in the second timescale, and thermal erasing requires days even at high temperature (hours at the autolock pH).

As we have seen above, in the write–lock–read–unlock–erase cycle autolocking takes place when an appropriate pH value is chosen. The most suitable pH value for autolocking results from a compromise between the needs to have the largest amount of $\mathbf{C_t}$ at the thermodynamic equilibrium described by eqn. (1), and the largest amount of $\mathbf{AH^+}$ in the pseudoequilibrium described by eqn. (2). This is the pH where the solid line representing the molar fraction of $\mathbf{C_t}$ crosses the dotted line representing the molar fraction of $\mathbf{AH^+}$ (pH 3.1, Fig. 2).

Effect of micelles

Molar fraction distribution. It is well known that in aqueous solution cetyltrimethylammonium bromide (CTAB), polyoxyethylene(10) isooctyl phenyl ether (Triton X-100), and sodium dodecyl sulfate (SDS) give rise to micelles when their concentration is higher than a critical value.[29] We have investigated the thermal and photochemical reactions of 4′-hydroxyflavylium ion (5×10^{-5} M) in the presence of such micelles (5×10^{-2} M) and found that they profoundly affect the thermodynamic and kinetic parameters of the system.

The p*K* values for the equilibria (1)–(3) in the absence and in the presence of micelles are gathered in Table 1. The three equilibria refer to the acid dissociation of $\mathbf{AH^+}$ to yield neutral species. The results obtained show that: (i) the negatively charged SDS micelles stabilize $\mathbf{AH^+}$; (ii) the positively charged CTAB, and to a minor extent, the neutral Triton X micelles destabilize $\mathbf{AH^+}$; (iii) the effect of a micelle on the three equilibria is qualitatively the same, but quantitatively different.

The observed effect is consistent with the results reported for similar systems. For example, in an elegant set of experiments Fernández and Fromherz[30] studied the fluorescence of aminocoumarin and hydroxycoumarin located at the surface of micelles and found that the magnitude and direction of the ΔpK_a values were related to the charge of the micelle (negative and positive shift, respectively, for positively and negatively charged micelles). They also observed a negative shift in the case of neutral micelles and attributed it to the reduction of the polarity at the micelle surface. The ΔpK_a values they reported are similar to those obtained for our systems. Such a similarity suggests that the flavylium species tend to be located at the micelle surface.

Table 1 Effect of micelles on the equilibria involving 4′-hydroxyflavylium, eqns. (1)–(3)[a]

	CTAB	Triton X-100	Water	SDS
pK^{I}	3.1	3.7	5.5	6.7
pK^{II}	2.2	2.8	4.4	6.4
pK^{III}	1.3	2.0	1.9[b]	3.9

[a] Aqueous solution at 25 °C, unless otherwise noted. [b] At 60 °C.

More recently, Maçanita *et al.*[31] observed that in SDS micelles the pH domain of the red color of the flavylium cation of the natural anthocyanin Malvin is shifted to higher pH values.

Fig. 3 shows the molar fraction distribution of the various species in the presence of CTAB micelles. Comparison with Fig. 2 shows that the pH domain of all the species is shifted to more acidic regions. It can also be noticed that the molar fraction distribution of the species involved in eqn. (2) is modified, with a significant decrease in the concentration of the quinoidal base **A**. Under such conditions, a write–lock–read–unlock–erase cycle can again be performed, but with different characteristics compared with the system in the absence of CTAB micelles. In particular, the autolock pH in the presence of CTAB micelles is 1.9, and at this pH 25% of the species at thermodynamic equilibrium are already present as $\mathbf{AH^+}$, so that only 75% conversion of $\mathbf{C_t}$ can take place. In the presence of Triton X micelles a quite similar behavior is observed.

In the case of the negatively charged SDS micelles, the pH domain of all the species is shifted to higher values (Fig. 4). The molar fraction distribution of the quinoidal base **A** at the basic plateau is much higher than in water. The autolock pH is around 5.5, and the maximum conversion of $\mathbf{C_t}$ is *ca.* 90%.

Steady state irradiation. Fig. 5 shows the spectral variations observed upon continuous irradiation of an aqueous solution of the $\mathbf{C_t}$ form of 4′-hydroxyflavylium ion with 365 nm light in the presence of CTAB micelles at the autolock pH value (1.9). As in the case of solutions not containing micelles,[25] the decrease of the $\mathbf{C_t}$ absorption band with $\lambda_{max} = 350$ nm is accompanied by an increase of the $\mathbf{AH^+}$ absorption band with $\lambda_{max} = 436$ nm. For the other two micelles the qualitative behaviour at the autolock pH value is quite similar. The values

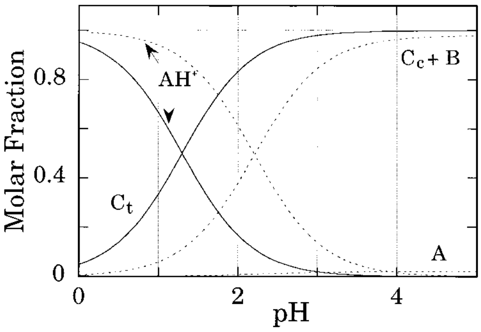


Fig. 3 Molar fraction distribution of the various species in CTAB micelles solution at 25 °C as a function of pH for the 4′-hydroxyflavylium ion. Details as in Fig. 2.

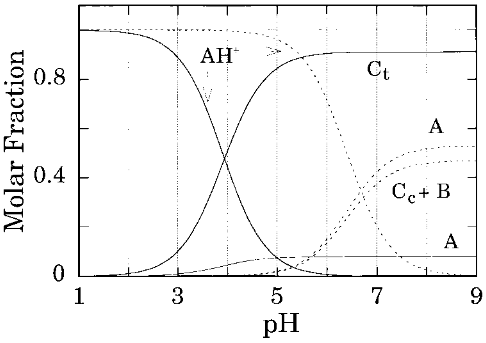


Fig. 4 Molar fraction distribution of the various species in SDS micelles solution at 25 °C as a function of pH for the 4′-hydroxyflavylium ion. Details as in Fig. 2.

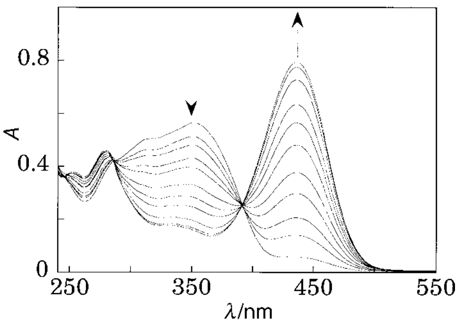


Fig. 5 Spectral changes caused by continuous irradiation of an aqueous solutions of the C_t form of 4′-hydroxyflavylium ion with 365 nm light in the presence of CTAB micelles at the autolock pH value (1.9); $[C_t] = 5 \times 10^{-5}$ M. The curves correspond to the following irradiation times: 0; 0.25; 0.5; 0.75; 1; 1.5; 2; 3; 4; 5; 10 min.

of the quantum yield of the $C_t \rightarrow C_c$ photoisomerization reaction at the autolock pH value for the solutions containing micelles is about twice that obtained in the absence of micelles (Table 2).

Kinetic effects. Table 2 shows the effect of micelles on the rate constants of the write and erase processes at the autolock pH value. As far as the writing step is concerned the four systems exhibit the same qualitative behavior, illustrated in Fig. 6 for a solution containing CTAB micelles. After flash excitation of C_t two absorbance changes can be detected. The first one, observed only at 310 nm where C_t shows a strong absorption band, is finished during the lifetime of the flash (several microseconds). It corresponds to the formation of C_c and **B** at the expense of C_t. No flavylium cation is formed in this step. The second process takes place according to first order kinetics with the same rate constant at 310 and 450 nm. It corresponds to the disappearance of C_c and **B** (which exhibit a moderate absorption at 310 nm) with formation of AH^+ ($\lambda_{max} = 436$ nm).

Table 2 Kinetic effect of micelles at the auto-lock pH[a]

	Autolock pH	Φ [b]	k_{write}/ s^{-1} [c]	$10^5\ k_{erase}$/ s^{-1} [d]
CTAB	1.9	0.08	0.09	12.0
Triton X-100	2.4	0.10	0.06	8.3
SDS	5.5	0.09	2.3[e]	18.0
Water	3.2	0.04	0.7	7.8

[a] Aqueous solution at 25 °C. [b] Quantum yield of the $C_t \rightarrow C_c$ photoisomerization reaction. [c] Rate constant of the 'writing' reaction $C_c(\mathbf{B}) \rightarrow AH^+$. [d] Rate constant of the 'erasing' reaction $AH^+ \rightarrow C_t$ at 60 °C. [e] In the flash photolysis detection limit.

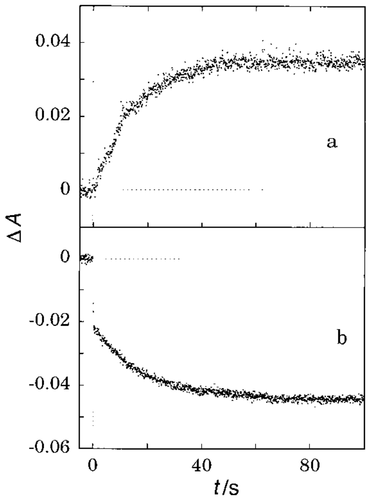


Fig. 6 Changes in absorbance observed after flash light excitation of an aqueous C_t (5×10^{-5} M) solution containing CTAB micelles. (a) Absorbance increase at 450 nm; (b) absorbance decrease at 310 nm.

The efficiency of the writing step at the autolock pH value depends on the photoisomerization quantum yield as well as on the rate of conversion of C_c and **B** into AH^+. As mentioned above, the presence of micelles increases the quantum yield in all cases, whereas the rate of conversion of C_c and **B** into AH^+ depends on the specific system. The rate of the erasing process is also slightly different for the various systems (Table 2). In SDS we observe the highest writing and erasing rates.

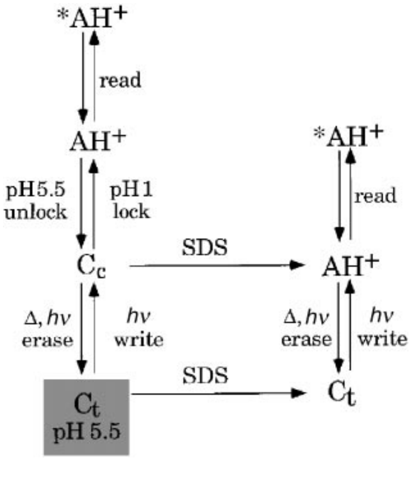
Micelles as an input

Network of chemical processes. In a previous investigation we showed that interconversion of the various forms of the system based on the 4′-hydroxyflavylium ion can be governed by two different external inputs, namely light excitation and changes in pH. The results obtained in this study show that the state of the system can also be changed by another external stimulus, namely addition of micelles. This adds a new dimension to the already complex network of processes[25] that can be obtained with this system. For example, starting from a C_t solution at pH 5.5, besides the previously described write–lock–read–unlock–erase cycle, an alternative cycle can be designed based on addition of SDS micelles and exploiting the autolocking and thermal erasing processes of this system (Scheme 3).

From the viewpoint of logic operations,[6,26,32,33] it can be noticed that starting from C_t at pH 5.5 and taking the formation of the AH^+ absorption at 436 or 450 nm as an output, the 'truth' table for the effect of the three inputs (pH jump to 1.0, addition of SDS, light excitation) shows a peculiar (Table 3) pattern corresponding to an OR function which is activated only in the presence of the third input (enabled OR).

Conclusion

We have investigated the effect of micelles on pH and light induced processes that can be observed for the 4′-hydroxyflavylium ion. It has been shown that both the thermodynamic and kinetic parameters of these processes are affected by the presence of micelles. In particular, negatively charged (SDS) and positively charged (CTAB) micelles have the opposite effect on the acid/base equilibria present in this



Scheme 3 Write–lock–read–unlock–erase cycles starting from the C_t form at pH 5.5. Left-hand side: light and pH jump inputs in the absence of micelles. This part is equivalent to the cycle in Scheme 2. Right-hand side: light input at the autolocking pH in the presence of SDS micelles.

Table 3 Logic behaviour of the system starting from $\mathbf{C}_t$ at pH 5.5

Inputs			
I pH jump→1	II SDS micelle	III $h\nu$ (365 nm)	Output A (450 nm)
1	0	0	0
0	1	0	0
1	1	0	0
0	0	0	0
1	0	1	1
0	1	1	1
1	1	1	1
0	0	1	0

system. This adds a new dimension to the already complex network of processes shown by this *multistate/multifunctional* molecular-level system.

Experimental

The 4′-hydroxyflavylium chloride was prepared according to a published procedure.[34] All other chemicals used were of analytical grade. The experiments were carried out in water at 25 °C. The pH of the solutions was adjusted by addition of $HClO_4$ (pH<2) or Universal buffer Theorell-Stenhagen (0.04 M) and measured by a Metrohom 713 pH meter. Flash photolysis experiments were performed as previously described.[22] Absorption spectra were recorded on a Perkin-Elmer lambda 6 spectrophotometer. Photoexcitation in continuous irradiation experiments was performed by using a medium pressure mercury lamp, and interference filters (Oriel) to isolate the excitation bands. The incident light intensity was measured by ferrioxalate actinometry.[35] The estimated error on quantum yield values is ±10%.

Acknowledgements

This work was supported in Portugal by Programa Plurianual CQFB and Project 2/2.1/QUI/56/96, in Italy by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Supramolecular Devices project) and University of Bologna (Funds for Selected Research Topics) and by a joint program between Consiglio Nazionale delle Ricerche (Italy) and ICCTI (Instituto de Cooperacao Cientifica e Tecnologica Internacional) (Portugal) n.423/CNR. A. Roque is grateful for grant BD 13330 97/PRAXIS XXI/FCT.

References

1 *Molecular Electronic Devices*, ed. F. L. Carter, R. E. Siatkowsky and H. Woltjien, Elsevier, Amsterdam, 1988; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; *Molecular Electronics*, ed. J. Jortner and M. Ratner, Blackwell, Oxford, 1997.

2 D. Rouvray, *Chem. Br.*, 1998, **34**, 26.

3 P. Ball and L. Garvin, *Nature* (*London*), 1992, **355**, 761; D. Bradley, *Science*, 1993, **259**, 890.

4 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.

5 L. B. Feringa, W. F. Jager and B. de Lange, *Tetrahedron*, 1993, **49**, 8267.

6 A. P. de Silva and C. P. McCoy, *Chem. Ind.*, 1994, 992.

7 L. Fabbrizzi and A. Poggi, *Chem. Soc. Rev.*, 1995, **24**, 197.

8 V. Balzani and F. Scandola, in *Comprehensive Supramolecular Chemistry*, ed. D. N. Reinhoudt, Pergamon, Oxford, 1996, vol. 10, p. 687.

9 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.

10 V. Balzani, A. Credi and F. Scandola, *Chim. Ind. (Milan)*, 1997, **79**, 751.

11 *Chemosensors for Ion and Molecular Recognition*, eds. A. W. Czarnik and J.-P. Desvergne, Kluwer, Dordrecht, 1997.

12 *Photochromism—Molecules and Systems*, eds. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.

13 For seminal examples concerning photochromic systems, see: J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely and K. M. Rapp, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1494; T. Iyoda, T. Saika, K. Honda and T. Shimidzu, *Tetrahedron Lett.*, 1989, **30**, 5429; J. Daub, C. Fischer, J. Salbeck and K. Ulrich, *Adv. Mater.*, 1990, **8**, 366; Y. Yokoyama, T. Ymamane and Y. Kurita, *J. Chem. Soc., Chem. Commun.*, 1991, 1722; K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1993, **115**, 6442; M. Irie, *Mol. Cryst. Liq. Cryst.*, 1993, **227**, 263; T. Saika, T. Iyoda, K. Honda and T. Shimidzu, *J. Chem. Soc., Perkin Trans 2*, 1993, 1181; M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894; M. J. Preigh, F.-T. Lin, K. Z. Ismail and S. G. Weber, *J. Chem. Soc. Chem. Commun.*, 1995, 2091; S. H. Kawai, S. L. Gilat, R. Posinet and J.-M. Lehn, *Chem. Eur. J.*, 1995, **1**, 285; G. M. Tsivgoulis and J.-M. Lehn, *Chem. Eur. J.*, 1996, **2**, 1399; M. Inouye, K. Akamatsu and H. Nakazumi, *J. Am. Chem. Soc.*, 1997, **119**, 9160.

14 For multiplexing optical systems based on mixtures of photochromic compounds, see: G. M. Tsivgoulis and J.-M. Lehn, *Adv. Mater.*, 1997, **9**, 627.

15 R. Brouillard, In *The Flavonoids, Advances in Research*, ed. J. B. Harborne, Chapman and Hall, London, 1988, p. 525; in *Anthocyanins as Food Colors*, ed. P. Markakis, Academic Press, New York, 1982, Ch. 1.

16 R. Brouillard and J. E. Dubois, *J. Am. Chem. Soc.*, 1977, **99**, 1359.

17 R. Brouillard and J. Delaporte, *J. Am. Chem. Soc.*, 1977, **99**, 8461.

18 R. A. McClelland and S. Gedge, *J. Am. Chem. Soc.*, 1980, **102**, 5838.

19 R. A. McClelland and G. H. McGall, *J. Org. Chem.*, 1982, **47**, 3730.

20 G. Haucke, P. Czerney, C. Igney and H. Hartmann, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 805; G. Haucke, P. Czerney, D. Steen, W. Rettig and H. Hartmann, *Ber. Bunsenges. Phys. Chem.*, 1993, **97**, 561.

21 R. Matsushima and M. Suzuki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 39; R. Matsushima, H. Mizuno and A. Kajiura, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1762; R. Matsushima, H. Mizuno and H. Itoh, *J. Photochem. Photobiol. A*, 1995, **89**, 251.

22 F. Pina, M. J. Melo, L. Flamigni, R. Ballardini and M. Maestri, *New. J. Chem.*, 1997, **21**, 969.

23 F. Pina, M. J. Melo, M. Maestri, R. Ballardini and V. Balzani, *J. Am. Chem. Soc.*, 1997, **119**, 5556.

24 F. Pina, M. J. Melo, M. H. Santos, J. C. Lima, I. Abreu, R. Ballardini and M. Maestri, *New J. Chem.*, 1998, 1093.

25 F. Pina, A. Roque, M. J. Melo, M. Maestri, L. Belladelli and V. Balzani, *Chem. Eur. J.*, 1998, **4**, 1182.

26 F. Pina, M. J. Melo, A. J. Parola, M. Maestri and V. Balzani, *Chem. Eur. J.*, 1998, **4**, 2001.

27 F. Pina, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2109.

28 F. Pina, M. Maestri and V. Balzani, *Chem. Commun.*, 1999, 107.

29 J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.

30 M. Fernández and P. Fromherz, *J. Phys. Chem.*, 1977, **31**, 1755.

31 A. L. Maçanita *et al.*, unpublished work.

32 A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Nature* (*London*), 1993, **364**, 42; A. P. de Silva, T. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell and T. E. Rice, *J. Am. Chem. Soc.*, 1999, **121**, 1393.

33 A. Credi, V. Balzani, S. J. Langford and J. F. Stoddart, *J. Am. Chem. Soc.*, 1997, **119**, 2679.

34 C. Michaelis and R. Wizinger, *Helv. Chim. Acta*, 1951, **34**, 1761.

35 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.

Paper 9/02805F