Effect of SDS micelles on the reactivity of 4′-methoxyflavylium ion: A stopped-flow and photochemical study

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Abstract

The network of chemical reactions of the compound 4′-methoxyflavylium was studied in the presence of SDS micelles, using stopped-flow, UV–vis absorption and flash photolysis techniques. The results were compared with analogous experiments carried out in water. The large stabilization of the flavylium cation onto the micelles was proven to be due to an increase in the rate of the dehydration reaction, rather than a decrease of the hydration reaction; the *cis–trans* isomerisation of the chalcone was not affected by the micelles. It is shown that SDS micelles can be considered as an external stimulus capable of changing the system from one state to another.
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1. Introduction

The design and construction of molecular-level electronic devices, mimicking the functions performed by macroscopic electronic components is of great interest in the emerging field of nanotechnology [1–8]. In this context, the investigation of molecules that can exist in two forms, interconvertible by an external input (switching), is of fundamental importance not only for basic studies, but also for innovative applications [5–9]. Typical examples of such molecules are the photochromic compounds where light has the role of the switching input [4b–9]. Very important are also the systems capable of existing in more than two forms (*multistate*) and that can be interconverted by more than one type of external stimuli (*multifunctional*) [10–14]. It is well known that flavylium-type ions, which have basically the chemical structure of natural anthocyanins [15] can undergo multiple structural transformations in aqueous solution that can be driven by light excitation and pH changes [16–21]. We have investigated the thermal and photochemical reactions of sev-

eral flavylium ions, emphasizing the multistate/multifunctional character of the chemistry of these compounds [22–34]. In particular, we have shown that flavylium-type systems with a large kinetic barrier for the isomerisation reaction (either forward or backward) can perform *write-lock–read–unlock–erase* cycles [30] thus exhibiting the properties required by optical memory devices with multiple storage and non-destructive readout capacity.

Among the various synthetic flavylium salts, 4′-methoxy-flavylium ion was probably the first whose chemical and photochemical behaviour was carefully investigated. In 1980, McClelland and Gedge, [18] by using pH-jump techniques, identified seven species that can be mutually interconverted depending on the experimental conditions (Fig. 1). This multistate system was able to perform *write-lock–read–unlock–erase* cycles [23], and was also explored in the mimicry of some elementary properties of neurons [24].

To extend our knowledge on this system, we investigate and report here the results on the effect of sodium dodecylsulfate (SDS) micelles on the pH and light induced interconversion of the 4′-methoxyflavylium cation 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.

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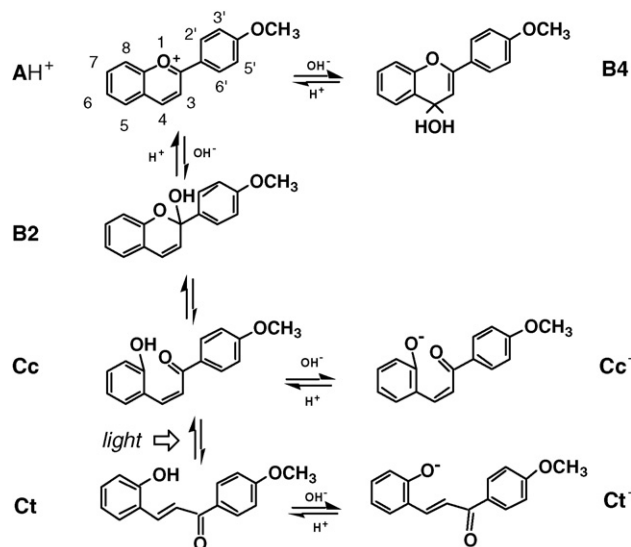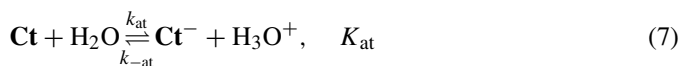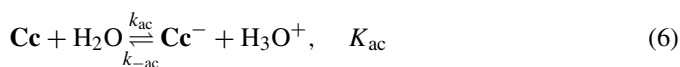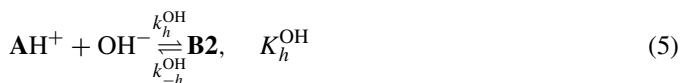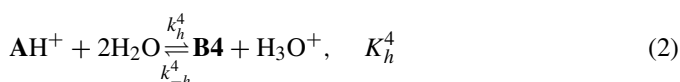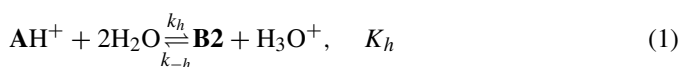mmaestri@ciam.unibo.it (M. Maestri).

Fig. 1. Species present in aqueous solutions of 4′-methoxyflavylium.

2. Results and discussion

2.1. Aqueous solution

Fig. 1 shows the species originated upon dissolution of 4′-methoxyflavylium perchlorate in aqueous solution as well as the reversible processes connecting them [18,23].

The complex network of species of Fig. 1 can be accounted for by the set of equilibria defined in Eqs. (1)–(7):

$$\mathbf{AH^+} + 2H_2O \underset{k_{-h}}{\overset{k_h}{\rightleftharpoons}} \mathbf{B2} + H_3O^+, \quad K_h \tag{1}$$

$$\mathbf{AH^+} + 2H_2O \underset{k_{-h}^4}{\overset{k_h^4}{\rightleftharpoons}} \mathbf{B4} + H_3O^+, \quad K_h^4 \tag{2}$$

$$\mathbf{B2} \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} \mathbf{Cc}, \quad K_t \tag{3}$$

$$\mathbf{Cc} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathbf{Ct}, \quad K_i \tag{4}$$

$$\mathbf{AH^+} + OH^- \underset{k_{-h}^{OH}}{\overset{k_h^{OH}}{\rightleftharpoons}} \mathbf{B2}, \quad K_h^{OH} \tag{5}$$

$$\mathbf{Cc} + H_2O \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftharpoons}} \mathbf{Cc^-} + H_3O^+, \quad K_{ac} \tag{6}$$

$$\mathbf{Ct} + H_2O \underset{k_{-at}}{\overset{k_{at}}{\rightleftharpoons}} \mathbf{Ct^-} + H_3O^+, \quad K_{at} \tag{7}$$

The flavylium cation $\mathbf{AH^+}$ is the stable form in strongly acidic solutions. In moderately acidic or neutral solutions, the thermodynamically stable form is the neutral *trans*-chalcone species, $\mathbf{Ct}$, which is formed from $\mathbf{AH^+}$ through the two intermediate compounds $\mathbf{B2}$ and $\mathbf{Cc}$. $\mathbf{B2}$ is a hemiketal species, obtained by hydration at position 2 of the flavylium cation (Eq. (1)), and $\mathbf{Cc}$ is a *cis*-chalcone, formed from the hemiketal $\mathbf{B2}$ through a tautomeric process (Eq. (3)). The $\mathbf{AH^+}$ form can also hydrate in

position 4 to give the $\mathbf{B4}$ species (Eq. (2)). At the equilibrium, this process leads to the formation of very small amounts of $\mathbf{B4}$ (always less than 1% of $\mathbf{B2}$) and can thus be neglected. However, the analysis of the kinetic processes should account for the transient formation of this species.

$\mathbf{Cc}$ and $\mathbf{Ct}$ can be thermally equilibrated (Eq. (4)) or photochemically interconverted. Moreover, the $\mathbf{Cc}$ and $\mathbf{Ct}$ forms can undergo deprotonation to give the respective monoanions (Eqs. (6) and (7), respectively) which, being *cis/trans* isomers, can in principle be also interconverted by light excitation.

The interesting feature of these systems is that the $\mathbf{AH^+}$ and $\mathbf{B2}$ forms can be reversibly interconverted by pH changes (Eq. (1)), [16–19] whereas $\mathbf{Cc}$ and $\mathbf{Ct}$ (often also $\mathbf{Cc^-}$ and $\mathbf{Ct^-}$) can be interconverted photochemically [20–34]. Since the $\mathbf{B2}$ and $\mathbf{Cc}$ forms are in tautomeric equilibrium (Eq. (3)), it follows that pH and light stimulations can be used to cause interconversion among all the species interconnected by the very intricate series of chemical reactions shown in Fig. 1.

As shown previously [35,36] the mole fraction of the acidic form $\mathbf{AH^+}$ can be obtained from Eq. (8):

$$\frac{[\mathbf{AH^+}]}{C_0} = \alpha = \frac{[H^+]}{[H^+] + K_a'} \tag{8}$$

where C_0 is the total concentration and K_a' is given by Eq. (9) (when Eq. (2) is ignored):

$$K_a' = K_h + K_h K_t + K_h K_t K_i \tag{9}$$

Eq. (8) accounts for the complex equilibria described by Eqs. (1), (3) and (4) in terms of a single acid–base equilibrium (Eq. (10)), between the acidic species $\mathbf{AH^+}$ and a conjugated base $\mathbf{CB}$ having a concentration equal to the sum of the concentrations of $\mathbf{B2}$, $\mathbf{Cc}$ and $\mathbf{Ct}$, and a mole fraction given by Eq. (10) [36]:

$$\mathbf{AH^+} \rightleftharpoons \mathbf{CB} + H^+, \quad K_a' \tag{10}$$

$$\frac{[\mathbf{CB}]}{C_0} = \frac{[\mathbf{B2}] + [\mathbf{Cc}] + [\mathbf{Ct}]}{C_0} = \beta = \frac{K_a'}{[H^+] + K_a'} = 1 - \alpha \tag{11}$$

The individual expressions of the mole fractions of each component of $\mathbf{CB}$ can be easily calculated [36]; if the pH is sufficiently high to consider all the compounds in the form of CB ($\beta = 1$), the relationships shown in Eq. (12) apply:

$$\frac{[\mathbf{B2}]}{C_0} = \frac{K_h}{K_a'}, \quad \frac{[\mathbf{Cc}]}{C_0} = \frac{K_h K_t}{K_a'}, \quad \frac{[\mathbf{Ct}]}{C_0} = \frac{K_h K_t K_i}{K_a'} \tag{12}$$

The global constant K_a' (defined in Eq. (9)) can be experimentally determined following the decrease of the absorbance of the flavylium cation (e.g., the mole fraction of $\mathbf{AH^+}$) as a function of pH. The remaining constants can be calculated measuring the mole fraction of each component of $\mathbf{CB}$ at the equilibrium, when $\mathbf{AH^+}$ is no longer present. This is not a trivial task, and in most cases NMR techniques must be used associated with pH jumps.

A useful approach is to consider the existence of a *pseudo-equilibrium state*, which is attained when all the species equilibrate, prior to the formation of the *trans*-chalcone, $\mathbf{Ct}$, Eq. (13). This approach is valid whenever a thermal barrier between
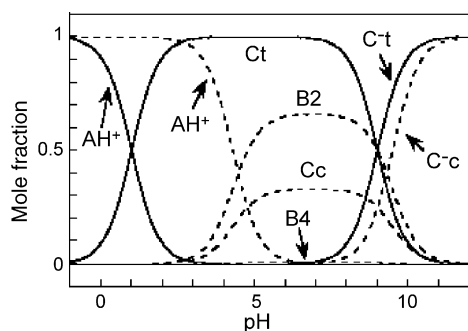
Fig. 2. Mole fraction distribution of the various species originated by the 4′-methoxyflavylium salt in aqueous solution at 25 °C as a function of pH, immediately after dissolution (- - -) and after final equilibration (—).

Fig. 3. Absorption spectra of the three main species originated by the 4′-methoxyflavylium salt in acidic conditions.

the *cis*, and *trans* chalcones occurs, as is the case with 4′-methoxyflavylium [18,23]. It is easy to show that in this case the *pseudo-equilibrium* constant is given by Eq. (14), and that its determination can also be obtained following the absorbance decrease of the flavylium cation as a function of pH, in these precise conditions [36]:

$$\mathbf{AH^+} \rightleftharpoons \mathbf{B2} + \mathbf{Cc} + \mathbf{H^+}, \quad \hat{K}_a \tag{13}$$
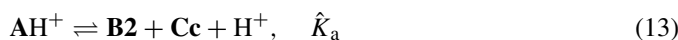
$$\hat{K}_a = K_h + K_h K_t \tag{14}$$

McClelland and Gedge determined the thermodynamic and the kinetic constants of almost all the processes involved in the neutral and acidic region [18]. Suitable elaboration [23] of the results obtained by McClelland and Gedge [18] leads to the plot of Fig. 2 that shows the mole fraction distribution of the various species in aqueous solution at 25 °C as a function of pH at both the pseudo-equilibrium and the final thermodynamic equilibrium.

It can be seen that the thermodynamically stable form in the pH range 2–8 is the *trans*-chalcone, **Ct**, which, at higher pH values, is transformed into its anion, **Ct⁻** (Fig. 2, solid lines). In strongly acidic solutions, **AH⁺** becomes thermodynamically stable; however, **Ct** can hardly be converted to **AH⁺** because of the very large activation barrier (93 kJ mol^{-1}, pH 4.0, 30–65 °C temperature range) [23] involving isomerisation of **Ct** to the intermediate compound **Cc**. Furthermore, a solution of **AH⁺** is stable for several days at room temperature below pH 3. Under such conditions, a very large kinetic barrier prevents conversion of **AH⁺** to the thermodynamically stable **Ct** form via **B2** and species. At higher pH values, however, **AH⁺** is very reactive [18,23]. For example, starting from an aqueous solution of **AH⁺** at 25 °C and pH 1, a pH jump to pH 4.29 leads within a few seconds to a pseudo-equilibrium consisting of 50% **AH⁺**, 33.2% **B2**, 0.3% **B4** and 16.5% **Cc** (Fig. 2, dashed lines). A much slower reaction follows (half-life 19.7 h), resulting in complete conversion to the thermodynamically stable form **Ct**.

We have recently [23] studied the photochemical behaviour of the 4′-methoxyflavylium ion and we have found that the **Ct** and **Cc** forms are photochemically reactive and that the effect of irradiation (either continuous or pulsed) depends on the pH of the solution. In particular, continuous irradiation of aqueous solutions of **Ct** at pH 1.0 with 365 nm light converts **Ct** into **AH⁺**, without formation of measurable amounts of other products. At
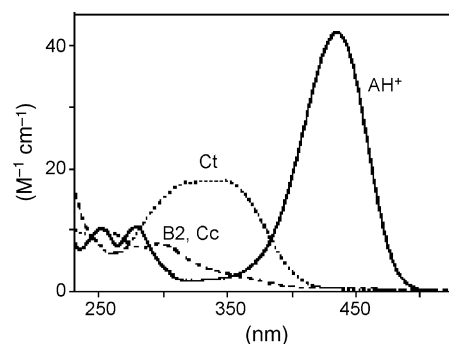
pH 1.0, no back reaction takes place and irradiation with 434 nm light, corresponding to the maximum of the absorption band of **AH⁺** (Fig. 3) causes no effect.

Irradiation of **Ct** at pH 4.0 leads to a mixture **AH⁺**, **Cc** and **B2**, but some thermal back reaction back to **Ct** was observed. At this pH, the rate of the back reaction is temperature dependent. At pH 7.0, in agreement with the data shown in Fig. 2, irradiation of **Ct** shows the formation of the pseudo-equilibrated mixture of open-closed, **Cc** and **B** forms. The thermal back reaction is fast, and complete disappearance of **Ct** cannot be observed. Flash excitation [23] of aqueous solutions of **Ct** at 25 °C causes the disappearance of **Ct**, and the formation of **Cc**; then, depending on pH, as Fig. 2 shows, **Cc** equilibrates with **B2** (4 < pH < 8) or leads to **AH⁺** through **B2** (pH ≤ 2), or gives an equilibrated mixture of the three forms **AH⁺**, **Cc** and **B** (2 < pH < 5). The rates of **AH⁺** and **B** formation can be thus determined by means of the proper transient spectroscopy. Finally, at pH > 3 the back reaction follows, turning the system to its initial situation (**Ct** form).

2.2. Effect of SDS micelles

Sodium dodecyl sulphate (SDS) gives rise to micelles when its concentration is higher than a critical value [37]. We have investigated the thermal and photochemical reactions of 4′-methoxyflavylium ion (ca. 5×10^{-5} M) in the presence of such micelles ([SDS] = 0.1 M) and we have found that they profoundly affect the thermodynamic and kinetic parameters of the system.

The absorption spectra of the four main species in acidic media (namely **AH⁺**, **B2**, **Cc** and **Ct**) in SDS are practically identical to the absorption spectra of the same forms in pure water (Fig. 3). Among these species, only the 4′-methoxyflavylium cation is strongly colored ($\lambda_{\max} = 449$ nm, $\varepsilon = 42,000$ M^{-1} cm^{-1}). The red-shift of the first singlet of **AH⁺**, on going from water (435 nm) to SDS is indicative of incorporation of the cationic chromophore into the anionic detergent micelles [38–40].

2.2.1. Steady state measurements

Fig. 4 shows the UV–vis absorption spectra of 4′-methoxyflavulium in SDS solutions at different pH values. The spectra were run immediately after a pH jump from a stock solu-
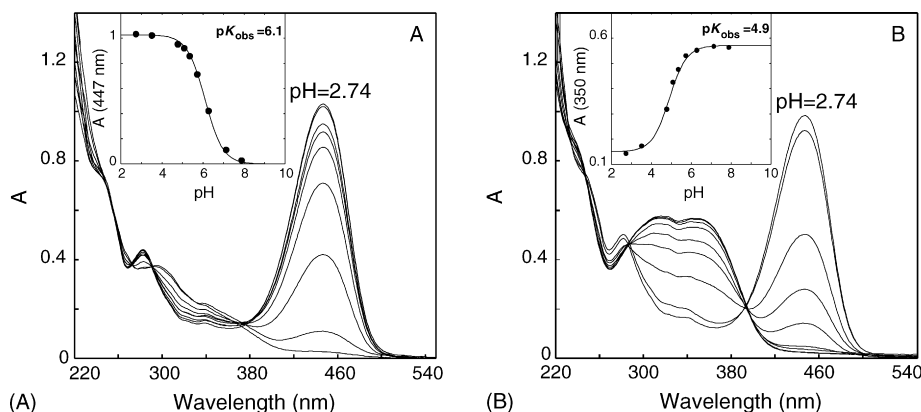
Fig. 4. Spectral changes of 2.4×10^{-5} M 4′-methoxyflavylium perchlorate in 0.1 M SDS solutions vs. pH, qt 25 °C; (A) immediately after the pH jump; (B) 7 days after the pH jump. pH values: 2.74, 3.51, 4.78, 5.09, 5.36, 5.73, 6.28, 7.14, 7.89.

tion at pH 1.0 to various acidic or neutral pH values (Fig. 4A) and 7 days later (Fig. 4B).

The spectral changes in the presence of SDS micelles are qualitatively similar but quantitatively different from the behaviour in pure water. A higher pH is needed to obtain a complete conversion of $\mathbf{AH^+}$ into $\mathbf{B}$ and $\mathbf{Cc}$ (immediately after the pH jump) or $\mathbf{Ct}$ (after 7 days in the dark). The spectral changes of the bands at 450 nm ($\mathbf{AH^+}$ disappearance, Fig. 4A) or 350 nm ($\mathbf{Ct}$ formation, Fig. 4B) allow to plot the two insets of Fig. 4, whose fittings give, respectively, the pseudo-equilibrium constant, $\hat{K}_a = 7.9 \times 10^{-7}$, and the final equilibrium constant, $K'_a = 1.3 \times 10^{-5}$, to be compared with the analogous higher values 5.1×10^{-5} and 0.26 in pure water (see Table 1) [18].

These results are consistent with the data previously reported for other flavylium salts (natural [38,41] or synthetic [28,39]) as well as for other similarly charged systems [42]. In all cases, positive $\Delta pK'_a$ (i.e., a decrease of the equilibrium constant of Eq. (10)) were found on going from water to negatively charged micelles. This behaviour was explained on the basis of the main localization of the positively charged flavylium ion ($\mathbf{AH^+}$) on the negatively charged surface of the micelles where a concomitant preferential localisation of protons, with an effective concen-

tration higher than that in the bulk, leads to a stabilization of $\mathbf{AH^+}$.

A fact to emphasize on these results, however, is the value of $\Delta pK'_a = +4.3$ which is higher than the expected on the basis of previous results (usually $\Delta pK'_a \sim +2$) [28,30,38–42]. A possible explanation for this finding may be found on an overestimation of this equilibrium constant in water by McClelland and Gedge [18]. They obtained their value based on an upper limit of 0.02% for the $\mathbf{Cc}$ (or $\mathbf{B}$) concentration present at the final equilibrium with $\mathbf{Ct}$. This value, however, has large uncertainty due to the high energetic barrier to cis–trans isomerisation [23]. A more realistic estimation [32] of K_i leads to $\Delta pK'_a \sim +2.1$, in accordance with the values observed in similar systems.

2.2.2. Transient spectroscopy
2.2.2.1. The direct and reverse pH jumps and flash photolysis.
To study the effect of SDS on the kinetic parameters of the system, we performed a stopped-flow analysis of pH jumps either from stocked solutions at pH 1.0 to less acidic or basic pH values or from freshly prepared solutions at pH 8.0 to acidic pH values (reverse pH jumps).

From the steady state measurements (Fig. 4) it is clear that while in direct pH jumps (from 1 to higher pH's) the conversion of $\mathbf{AH^+}$ to $\mathbf{B}$ and $\mathbf{Cc}$ is expected to be observed, in the reverse pH jump experiments (from 8.0 to lower pH's), the conversion of the pseudo-equilibrated mixture of $\mathbf{B2}$ and $\mathbf{Cc}$ to $\mathbf{AH^+}$ is monitored (note that in this last case the experiments are carried out with no presence of $\mathbf{Ct}$, since its formation would require more time owing to the existence of the thermal barrier in the cis–trans isomerisation).

The changes in the absorbance at 449 nm versus time at five different final pH values, resulting from reverse pH jumps, are shown in Fig. 5. For pH ≥ 4.1, the curves exhibit a double exponential behaviour. The fastest component of these decays is the dehydration reaction which directly converts the $\mathbf{B2}$ species present at the pseudo-equilibrium at pH 8 into $\mathbf{AH^+}$, while the slowest one shows the conversion of the $\mathbf{Cc}$ species (also present at the pseudo-equilibrium at pH 8), into $\mathbf{B2}$ followed by fast formation of $\mathbf{AH^+}$. At the more acidic pH values ($1.5 \leq pH \leq 3.3$), the decays are better fitted with one exponential meaning that our experimental conditions hardly allow detection of the fastest

Table 1
Thermodynamic and kinetic constants for 4′-methoxyflavylium perchlorate in 0.1 M SDS and in water; $T = 25$ °C

	SDS[a]	H_2O[b]
K'_a	$(1.3 \pm 0.2) \times 10^{-5}$	0.26 (1.8×10^{-3})[c]
$\hat{K}_a$	$(7.93 \pm 0.9) \times 10^{-7}$	5.1×10^{-5}
K_h (M)	$(5.10 \pm 0.05) \times 10^{-7}$	3.4×10^{-5}
K_t	0.54 ± 0.04	0.5
K_i	44 ± 7	1.5×10^4 (ca. 100)[c]
k_h (s^{-1})	0.36 ± 0.04	0.47
k_{-h} (M^{-1} s^{-1})	$(7.0 \pm 0.04) \times 10^5$	1.4×10^4
k_h^4 (s^{-1})	0.16 ± 0.01	0.23
k_h^H (M^{-1} s^{-1})	500 ± 25	39
k_t^{OH} (M^{-1} s^{-1})	$(5.0 \pm 0.3) \times 10^8$	2×10^{10}
k_i (s^{-1})	$(10 \pm 1) \times 10^{-5}$	5.8×10^{-5}
k_{-i} (s^{-1})	$(2.0 \pm 0.3) \times 10^{-6}$	(5.9×10^{-7})[c]

[a] This work.
[b] Ref. [18].
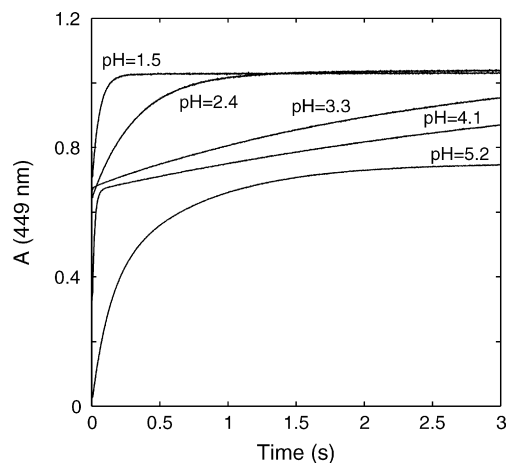[c] Based on a more realistic estimation of K_i, from Ref. [32].

Fig. 5. Absorbance changes at 449 nm of 0.1 M SDS solutions of 2.4×10^{-5} M 4′-methoxyflavylium perchlorate vs. time after a reverse pH jump from 8.0 to five different lower pH values; all the solutions were kept only a few minutes at pH 8.0 to avoid the presence of **Ct**; $T = 25\,^{\circ}$C.

Fig. 6. Absorption changes at 449 nm of 4′-methoxyflavylium in 0.1 M SDS at pH 6.28 vs. time after a flash of white light; $T = 25\,^{\circ}$C.

process in this pH range. At each pH value, fitting of the data with one or the sum of two exponentials allowed to evaluate the kinetic constants of the two processes (see Fig. 7 and Supplementary material).

The curves of Fig. 5 also provide thermodynamic information besides the kinetic one. In fact, looking at the curves where the two processes are well separated in time, the ratio between the initial and the final (residual) absorbance recovery at 449 nm corresponds to the ratio between the concentrations of **B2** and **Cc** present at the pseudo equilibrium at pH 8.0. It is thus possible to evaluate the equilibrium constant of reaction (2), $K_t = [\mathbf{Cc}]/[\mathbf{B2}] = 0.54$. Using this value, the values of $\hat{K}_a$ and K'_a obtained from the data in Fig. 4, and Eqs. (9) and (14), the values of $K_h = 5.1 \times 10^{-7}$ and $K_i = 44$ could be obtained. Table 1 reports these values as well as those obtained in water, [18,23,32] for comparison purposes.

Assuming the value of $K_i \approx 100$ in water [23,32] as discussed above, it can be concluded that both the tautomerisation and the isomerisation equilibrium constants are not significantly affected by the SDS micelles. In contrast, the hydration reaction is strongly affected by the presence of these micelles (K_h decreases ca. two orders of magnitude). This can be interpreted by the effective concentration of protons in the surface of the micelle, i.e., the product $k_{-h} [\mathrm{H}^+]$ should increase in the presence of the SDS.

We have shown previously [22] that flash photolysis (ca. 0.1 s time resolution) in the slowest process can complement the information obtained by stopped-flow measurements. Flashes on a solution of **Ct** in the presence of 0.1 M SDS (prepared from a stable stock solution of **Ct$^-$**) at the desired pH, cause absorbance changes compatible with the formation of **AH$^+$**, Fig. 6. Since **B2** is not present in the equilibrated solution, its direct (and fast) dehydration to form **AH$^+$** is not possible; **AH$^+$** can only be formed upon dehydration of the **B2** species, which is formed at the expenses of the **Cc** species. This last species is obtained in the photochemical isomerisation of **Ct** occurred during the time of the flash. Therefore, the rate determining step for the
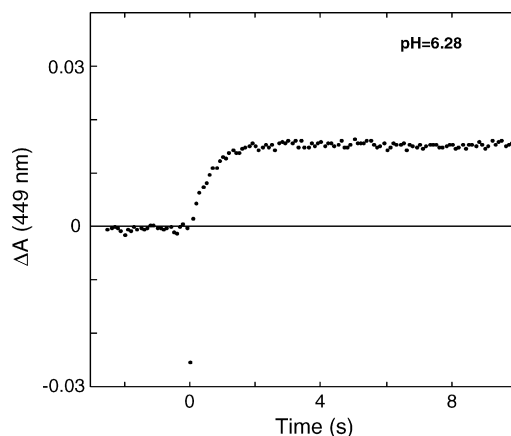
photochemical formation of **AH$^+$** is the tautomerisation process that converts **Cc** into **B2** and, the related kinetic constant has to be compared with the kinetic constant resulting from the slow process in the stopped-flow experiments upon reverse pH jumps. Stopped-flow and flash photolysis results obtained by pH jumps (direct and reverse) and photochemical measurements are reported in Fig. 7.

In the pH range $1 < \mathrm{pH} < 5$ of Fig. 7, the reverse pH jumps show a faster process (open squares) followed by a slower one (open circles). The observed rate constants represented by the open squares should be assigned to the dehydration/hydration processes while the open circles to the closure/opening of the pyrylium ring (tautomerisation). In which concerns the flash photolysis measurements (full circles), the rate determining step for **AH$^+$** formation is the tautomerisation process, by the reasons reported above. On the other hand, at basic pH values, the black
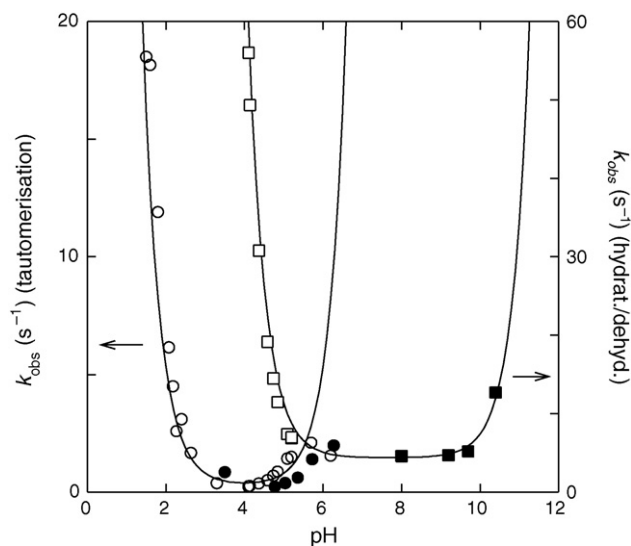

Fig. 7. pH dependence of the observed rate constants for tautomerisation (○ and ●) and hydration/dehydration (□ and ■); the rate constants were obtained by flash photolysis (●), and by stopped-flow experiments upon direct pH jumps (■) and reverse pH jumps (□ and ○); $T = 25\,^{\circ}$C.

squares have been previously [18,23] attributed to the attack of the hydroxide to position 2 of the flavylium.

In Fig. 7, the open and black circles that correspond to the tautomerisation reaction rate constants, obtained respectively from the stopped-flow and flash photolysis experiments, can be fitted with the following equation: $0.3 + 500\,[H^+] + 5 \times 10^8\,[OH^-]$. In water, McClelland and Gedge, for the same compound, obtained a similar expression: $0.46 + 39\,[H^+] + 2 \times 10^{10}\,[OH^-]$ [18]. As shown by McClelland and Gedge [18] the independent term corresponds to the rate constant k_{-t}, because in the stopped-flow experiments upon reverse pH jumps (from a higher pH to lower pH value), **B2** is not accumulated (it leads rapidly to **AH$^+$**) and thus no significant reversibility occurs ($k_{-t} + k_t \approx k_{-t}$). On this basis, the rate constant k_t can be measured from the equilibrium constant K_t, see Table 1. When values obtained in water and in SDS solutions are compared, the following observations are pertinent: (i) the observed rate constant for tautomerisation, as well as the tautomerisation equilibrium constant, are practically not affected by the presence of the micelles; (ii) in contrast, the acidic and basic catalysis, i.e., the terms depending on $[H^+]$ and $[OH^-]$, are quite affected, the acidic catalysis being increased, while the basic catalysis decreases. These results can be interpreted again by the effective concentration of protons on the surface of the micelle, and the consequent decrease on effective hydroxide concentration.

In a similar way, the rate constants due to the hydration reaction, represented in Fig. 7 by the black and open squares, can be fitted by the following equation: $4.4 + 7 \times 10^5\,[H^+] + 3 \times 10^4\,[OH^-]$. In this case, the expression obtained by McClelland and Gedge for water was: $1.38 + 1.38 \times 10^4\,[H^+] + 1.8 \times 10^5\,[OH^-]$ [18]. The independent term is the sum of the contributions of the rate constants involved in the equilibrium leading to **B2**, as well as the one leading to **B4**. In other words, as shown by McClelland and Gedge, the value 1.38 obtained in water is basically the sum of k_h (Eq. (1)) to give **B2** and k_h^4 (Eq. (2)) leading to **B4**. Taking into account that the equilibrium constant $K_h = k_h/k_{-h}$ is already known (see above) as well as the fact that the term dependent on $[H^+]$ should be assigned to k_{-h}, it is possible to obtain all of these rate constants, see Table 1. Inspection of this table permits to conclude that the great effect of the SDS micelles in the decreasing of the hydration equilibrium constant of 4′-methoxyflavylium occurs in the dehydration reaction, since the hydration is only slightly affected. Once more, the effect of the proton concentration on the micelle surface can explain this result, as well as the decrease of the hydroxylation reaction on going from water ($1.8 \times 10^5\,M^{-1}\,s^{-1}$) to SDS micelles ($3 \times 10^4\,M^{-1}\,s^{-1}$). On the other hand, the formation of **B4**, k_h^4, is very much increased in the presence of micelles. This suggests that the flavylium cation may seat on the micelle surface with the oxygen of the pyrylium ring pointing to the inner space of the micelle, thus rendering attack to position 4 less sterically hindered relative to the attack on position 2.

2.2.2.2. The cis–trans isomerisation. In neutral aqueous solutions, McClelland and Gedge observed a *cis–trans* isomerisation constant equal to $1.95 \times 10^{-5}\,s^{-1}$ [18]. The actual
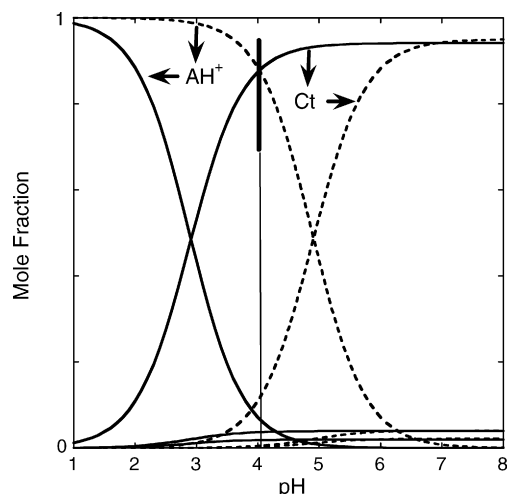

Fig. 8. Mole fraction distribution of the several species of 4′-methoxyflavylium as a function of pH in water (traced lines) and in the presence of 0.1 M SDS (solid lines), at 25 °C.

observed rate constant should be divided by the mole fraction of the **Cc** form ($K_h K_t / \hat{K}_a = 0.33$, Eq. (12)), leading to a value of $5.9 \times 10^{-5}\,s^{-1}$. In reality, this value should be the sum of $k_i + k_{-i}$; and assuming our estimation for the equilibrium constant $K_i \approx 100$, [32] allows to calculate $K_i = 5.8 \times 10^{-5}\,s^{-1}$, in accordance with the reported value,[18] and $k_{-i} = 5.9 \times 10^{-7}\,s^{-1}$ In the presence of micelles, we observed a net isomerisation constant equal to $3.4 \times 10^{-5}\,s^{-1}$ at pH 8.0, where flavylium cation does not interfere ($\beta = 1$, Eq. (11)) and **Ct** is the final product, according to the shape of the absorption spectra at the end of the experiment. Taking into account that the mole fraction of **Cc** in the presence of SDS micelles is 0.35, the actual value of the global process is $9.7 \times 10^{-5}\,s^{-1}$ and by consequence $k_i = 1 \times 10^{-4}\,s^{-1}$, and $k_{-i} = 2 \times 10^{-6}\,s^{-1}$. In conclusion, the SDS micelles do not significantly affect the *cis–trans* isomerisation process.

The results obtained through this work permit to conclude that the largest effect observed on the stabilization of the flavylium cation in the presence of SDS micelles is not due to the protection from hydration, but is a result of the increasing rate of dehydration, in agreement with a similar effect previously reported by Maçanita and co-workers, in the case of malvidin-3-glucoside in the presence of SDS micelles [38].

The change in K_a' introduced by the addition of SDS to aqueous solutions of 4′-methoxyflavylium can be explored in the context of multistate/multifunctional systems [28,41]. Fig. 8 illustrates the use of micelles as an input, besides pH and light, to move the system from one state of the network to another. At pH 4, in the absence of micelles, the system is equilibrated with ca. 90% of **Ct**. Addition of SDS in concentrations above CMC gives rise to a shift in the equilibrium where **Ct** accounts now for 10% of the mixture, the rest being **AH$^+$**, with the appearance of the respective yellow colour. In practical terms, an effect similar to a pH jump from pH 4 to ≈ 2 is observed.

3. Experimental

$4'$-Methoxyflavylium perchlorate was prepared as reported in the literature [43]. All experiments were carried out at $25\,^\circ$C, in 0.1 M sodium dodecyl sulfate aqueous solutions. The flavylium salt had final concentrations in the range $(1–5) \times 10^{-5}$ M. The pH was adjusted by addition of HCl, NaOH or buffer, and was measured in a Meterlab pHM240 pH meter from Radiometer Copenhagen.

pH jumps were done by adding a certain volume of a stock solution of the flavylium salt in 0.1 M HCl to a $10\,cm^3$ flask containing an equivalent amount of NaOH to neutralize the HCl, $5\,cm^3$ of 0.2 M SDS, and $1\,cm^3$ of 0.1 M universal buffer of Theorell and Stenhagen [44] at the desired final pH followed by addition of water to the final volume. This defines the ionic strength as 0.1 M (it is controlled by the NaCl concentration resulting from the neutralization). Reverse pH jumps involved a second pH jump to a lower pH value, by addition of HCl.

UV–vis absorption spectra were recorded in a Shimadzu UV2501-PC spectrophotometer.

Flash photolysis experiments were carried out as described in Ref. [22].

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 flow rate.

The decays were fitted either manually using the Solver feature of the Excel or using predefined fitting equations of Origin® 7.0 SR0 v.7.0220 for Windows.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.photochem.2006.07.001.

References

[1] D. Rouvray, Chem. Br. 34 (1998) 26.
[2] (a) P. Ball, L. Garvin, Nature 355 (1992) 761;
    (b) D. Bradley, Science 259 (1993) 890.
[3] (a) V. Balzani, F. Scandola, in: D.N. Reinhoudt (Ed.), Comprehensive Supramolecular Chemistry, vol. 10, Pergamon Press, Oxford, England, 1996, p. 687;
    (b) V. Balzani, A. Credi, M. Venturi, Molecular Devices and Machines. A Journey into the Nanoworld, Wiley–VCH, Weinheim, 2003.
[4] (a) L.B. Feringa, W.F. Jager, B. de Lange, Tetrahedron 49 (1993) 8267;
    (b) L.B. Feringa (Ed.), Molecular Switches, Wiley–VCH, Weinheim, 2001.
[5] (a) A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515;
    (b) A.P. de Silva, N.D. McClenaghan, Chem. Eur. J. 8 (2002) 1;
    (c) A.P. de Silva, N.D. McClenaghan, C.P. McCoy, in: V. Balzani (Ed.), Electron Transfer in Chemistry, vol. 5, Wiley–VCH, Weinheim, 2001, p. 156.
[6] (a) A.N. Shipway, I. Willner, Acc. Chem. Res. 34 (2001) 421;
    (b) J.-P. Sauvage (Ed.), Struct. Bond. Molecular Machines and Motors, 2001, p. 99 (Special volume);
    (c) F.M. Raymo, Adv. Mater. 14 (2002) 401;
    (d) Y. Luo, C.P. Collier, J.O. Jeppesen, K.A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J.F. Stoddart, J.R. Heath, Chem. Phys. Chem. 3 (2002) 519.
[7] L. Fabbrizzi, A. Poggi, Chem. Soc. Rev. 24 (1995) 197.
[8] A.W. Czarnik, J.-P. Desvergne (Eds.), Chemosensors for Ion and Molecular Recognition, Kluwer, Dordrecht, 1997.
[9] H. Dürr, H. Bouas-Laurent (Eds.), Photochromism-Molecules and Systems, Elsevier, Amsterdam, 1990.
[10] For seminal examples concerning photochromic systems, see;
    (a) J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely, K.M. Rapp, Angew Chem. Int. Ed. Eng. 28 (1989) 1494;
    (b) Y. Yokoyama, T. Ymamane, Y. Kurita, J. Chem. Soc. Chem. Commun. (1991) 1722;
    (c) K. Uchida, M. Irie, J. Am. Chem. Soc. 115 (1993) 6442;
    (d) T. Saika, T. Iyoda, K. Honda, T. Shimidzu, J. Chem. Soc. Perkin Trans. 2 (1993) 1181;
    (e) M. Irie, O. Miyatake, K. Uchida, T. Eriguchi, J. Am. Chem. Soc. 116 (1994) 9894;
    (f) M.J. Preigh, F.-T. Lin, K.Z. Ismail, S.G. Weber, J. Chem. Soc. Chem. Commun. (1995) 2091;
    (g) S.H. Kawai, S.L. Gilat, R. Posinet, J.-M. Lehn, Chem. Eur. J. 1 (1995) 285;
    (h) M. Inouye, K. Akamatsu, H. Nakazumi, J. Am. Chem. Soc. 119 (1997) 9160.
[11] (a) M. Irie (Ed.), Chem. Rev. Photochromism: Memories and Switches, 2000, p. 100 (Special issue);
    (b) M. Irie, in: B.L. Feringa (Ed.), Molecular Switches, Wiley–VCH, 2001, p. 37;
    (c) M. Irie, K. Matsuda, in: V. Balzani (Ed.), Electron Transfer in Chemistry, vol. 5, Wiley–VCH, Weinheim, 2001, p. 215.
[12] (a) H. Bouas-Laurent, H. Dürr, Pure Appl. Chem. 73 (2001) 639;
    (b) H. Bouas-Laurent, A. Castellan, J-P. Desvergne, R. Lapouyade, Chem. Soc. Rev. 29 (2000) 43.
[13] B.L. Feringa, R.A. van Delden, R.A. Koumura, E.M. Geertsema, Chem. Rev. 100 (2000) 1789.
[14] For multiplexing optical systems based on mixtures of photochromic compounds, see;
    G.M. Tsivgoulis, J.-M. Lehn, Adv. Mater. 9 (1997) 627.
[15] (a) R. Brouillard, in: J. Harborne (Ed.), The Flavonoids, Advances in Research, Chapman and Hall, London, 1988, p. 525;
    (b) R. Brouillard, in: P. Markakis (Ed.), Anthocyanins as Food Colors, Academic Press, New York, 1982 (Chapter 1).
[16] R. Brouillard, J.E. Dubois, J. Am. Chem. Soc. 99 (1979) 1359.
[17] R. Brouillard, J. Delaporte, J. Am. Chem. Soc. 99 (1979) 8461.
[18] R.A. McClelland, S. Gedge, J. Am. Chem. Soc. 102 (1980) 5838.
[19] R.A. McClelland, G.H. McGall, J. Org. Chem. 47 (1982) 3730.
[20] (a) von W. Sperling, F.C. Werner, H. Kuhn, Ber. Bunsenges. Phys. Chem. 70 (1966) 530;
    (b) G. Haucke, P. Czerney, C. Igney, H. Hartmann, Ber. Bunsenges. Phys. Chem. 93 (1989) 805;
    (c) G. Haucke, P. Czerney, D. Steen, W. Rettig, H. Hartmann, Ber. Bunsenges. Phys. Chem. 97 (1993) 561.
[21] (a) R. Matsushima, M. Suzuki, Bull. Chem. Soc. Jpn. 65 (1992) 39;
    (b) R. Matsushima, H. Mizuno, A. Kajiura, Bull Chem. Soc. Jpn 67 (1994) 1762;
    (c) R. Matsushima, H. Mizuno, H. Itoh, J. Photochem. Photobiol. A: Chem. 89 (1995) 251.
[22] M. Maestri, R. Ballardini, F. Pina, M.J. Melo, J. Chem. Educ. 74 (1997) 1314.
[23] F. Pina, M.J. Melo, M. Maestri, R. Ballardini, V. Balzani, J. Am. Chem. Soc. 119 (1997) 5556.

[24] F. Pina, M.J. Melo, M. Maestri, P. Passaniti, V. Balzani, J. Am. Chem. Soc. 122 (2000) 4496.

[25] F. Pina, M.J. Melo, A.J. Parola, M. Maestri, V. Balzani, Chem. Eur. J. 4 (1998) 2001.

[26] F. Pina, A. Roque, M.J. Melo, M. Maestri, L. Belladelli, V. Balzani, Chem. Eur. J. 4 (1998) 1184.

[27] F. Pina, M.J. Melo, P. Passaniti, N. Camaioni, M. Maestri, V. Balzani, Eur. J. Org. Chem. 11 (1999) 3199.

[28] A. Roque, F. Pina, S. Alves, R. Ballardini, M. Maestri, V. Balzani, J. Mater. Chem. 9 (1999) 2265.

[29] F. Pina, M. Maestri, V. Balzani, Chem. Commun. (1999) 107.

[30] F. Pina, M.J. Melo, S. Alves, R. Ballardini, M. Maestri, P. Passaniti, New J. Chem. 25 (2001) 747.

[31] M. Maestri, F. Pina, V. Balzani, in: L.B. Feringa (Ed.), Molecular Switches, Wiley–VCH, Weinheim, 2001, p. 339.

[32] F. Pina, M. Maestri, V. Balzani, in: H.S. Nalwa (Ed.), Handbook of Photochemistry and Photobiology, vol. 3, American Scientific Publishers, CA, USA, 2003, p. 412.

[33] A. Roque, C. Lodeiro, F. Pina, M. Maestri, S. Dumas, P. Passaniti, V. Balzani, J. Am. Chem. Soc. 125 (2003) 987.

[34] M.C. Moncada, A.J. Parola, C. Lodeiro, F. Pina, M. Maestri, V. Balzani, Chem. Eur. J. 10 (2004) 1519.

[35] P. Figueiredo, J.C. Lima, H. Santos, M.-C. Wigand, R. Brouillard, F. Pina, J. Am. Chem. Soc. 116 (1994) 1249.

[36] F. Pina, L. Benedito, M.J. Melo, A.J. Parola, M.A. Bernardo, J. Chem. Soc. Faraday Trans. 92 (1996) 1693.

[37] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975.

[38] J.C. Lima, C. Vautier-Giongo, C.A. Lopes, E. Melo, F.H. Quina, A.L. Maçanita, J. Phys. Chem. A 106 (2002) 5851.

[39] C. Vautier-Giongo, C. Yihwa, P.F. Moreira Jr., J.C. Lima, A.A. Freitas, M. Alves, F.H. Quina, A.L. Maçanita, Langmuir 18 (2002) 10109.

[40] R. Rodrigues, C. Vautier-Giongo, P.F. Silva, A.C. Fernandes, R. Cruz, A.L. Maçanita, F.H. Quina, Langmuir 22 (2006) 933.

[41] M.J. Melo, S. Moura, M. Maestri, F. Pina, J. Mol. Struct. 612 (2002) 245.

[42] M. Fernandez, P. Fromherz, J. Phys. Chem. 81 (1977) 1755.

[43] C. Michaelis, R. Wizinger, Helv. Chim. Acta 34 (1761) 1951.

[44] F.W. Küster, A. Thiel, Tabelle per le Analisi Chimiche e Chmico-Fisiche, 12th ed., Hoepli, Milano, 1982, pp. 157–160.