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Flavylium based dual photochromism: addressing *cis–trans* isomerization and ring opening-closure by different light inputs†

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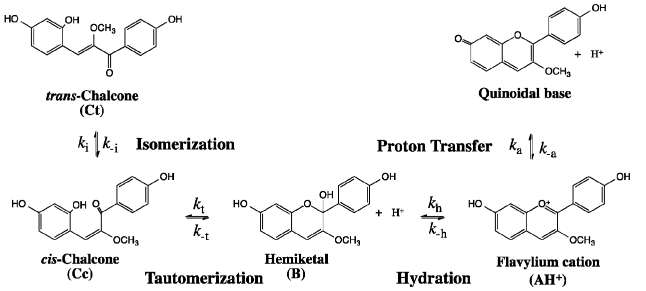
The multistate system of 4′,7-dihydroxy-3-methoxyflavylium is constituted by a multiequilibrium involving *trans*-chalcone, *cis*-chalcone, hemiketal, flavylium cation and quinoidal base. This system possesses two independently addressable inter-connected photochromic systems based on the *cis–trans* isomerization and ring opening-closure of the hemiketal.

Photochromic molecules are better known by the possibility of achieving reversible changes in the colour upon light absorption. However, they may also find many other applications such as switches, optical memory devices, sensors, or affecting the rheological properties of the materials containing these molecules.[1–6] The two main mechanisms to achieve photochromism are the *cis–trans* isomerization and the ring-opening closure, exemplified, respectively, by azobenzenes and stilbenes on one side and diarylethenes and spiropyrans on the other.

In this communication we describe a dual photochromic system based on *cis–trans* isomerization and ring opening-closure of 4′,7-dihydroxy-3-methoxyflavylium, a compound bio-inspired in anthocyanins, the dyes responsible for most of the red and blue colours of flowers and fruits.[7] Similarly to anthocyanins five species of this compound are reversibly interconverted by pH changes, Scheme 1.[8] The flavylium cation is the stable species in highly acidic solutions. Upon raising the pH the multistate system reaches a different equilibrium involving the other species of Scheme 1. The complex multistate system can be simplified considering a single acid base reaction involving the species **AH**$^+$ and its conjugate base **CB** defined as the sum of the other species **A**, **B**, **Cc** and **Ct**, eqn (1)

$$\mathbf{AH}^+ + H_2O \rightleftharpoons \mathbf{CB} + H_3O^+ \quad K_a' = K_a + K_h + K_hK_t + K_hK_tK_i \quad \text{with}$$
$$[\mathbf{CB}] = [\mathbf{A}] + [\mathbf{B}] + [\mathbf{Cc}] + [\mathbf{Ct}] \qquad (1)$$



Scheme 1 Multistate system of 4′,7-dihydroxy-3-methoxyflavylium in acid to neutral medium.

The mole fraction distribution of the conjugate base, **CB**, is dramatically dependent on the substitution pattern of the 2-phenylbenzopyrylium core. For example, 4′,7-dihydroxyflavylium possesses 90% of **Ct** and 10% of **A**, while anthocyanins have 70% of **B** and 4-methyl-7-hydroxyflavylium has almost 100% of **A**.[8]

The rate and equilibrium constants of the reactions shown in Scheme 1 can be conveniently studied by direct pH jumps defined as the addition of a base to equilibrated solutions sufficiently acidic to have **AH**$^+$ as the stable species, as well as by reversed pH jumps carried out by addition of acid to equilibrated solutions of **CB**. The chemical reactions reported in Scheme 1 exhibit different rates. Proton transfer is by far the fastest process and takes place during the mixing time of the stopped flow apparatus (*circa* 6 ms). Consequently, after a direct pH jump species **A** is immediately formed. Brouillard and Dubois[7] discovered that **A** is stable and its disappearance in moderately acidic solutions only occurs *via* the hydration of the flavylium cation (**AH**$^+$) to give hemiketal (**B**). The hydration is pH dependent and its rate decreases upon increasing the pH, ranging from several seconds to minutes. The tautomerization reaction (see Scheme 1) takes place in sub-seconds and can be better studied by reverse pH jumps. Finally the isomerization occurs in several hours or seconds according to the nature and position of the flavylium substituents. The rates of the kinetic processes of 4′,7-dihydroxy-3-methoxyflavylium are represented in Fig. 1A.

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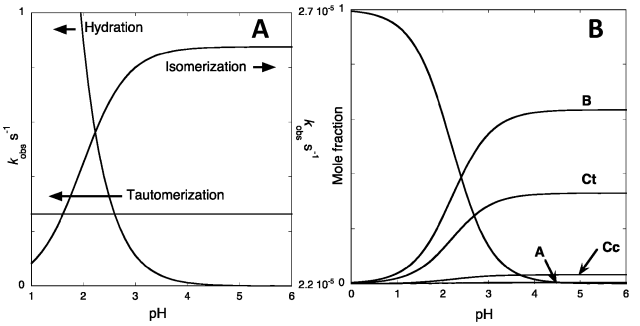


Fig. 1 (A) Rate constants of the several distinct kinetic processes. The acidic and basic catalytic effects on the tautomerization were neglected; (B) mole fraction distribution at the equilibrium of 4′,7-dihydroxy-3-methoxyflavylium.

Table 1 Equilibrium constants of compound 4′,7-dihydroxy-3-methoxyflavylium[a]

pK'_a	$pK^{\wedge}_a$	pK_a	K_h/ M^{-1}	K_t	K_i
2.2	2.37	4.6	4×10^{-3}	0.05	10.4

[a] Estimated error 10%.

Additional information on the system can be achieved by NMR, see the ESI.†

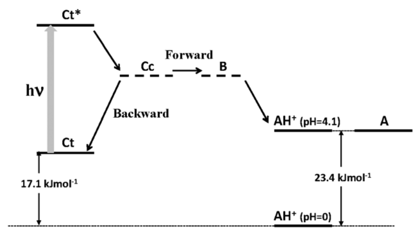
In previous work we reported a step by step procedure to obtain the rate and equilibrium constants of the flavylium based systems.[8] In the ESI† the complete set of experiments regarding direct and reverse pH jumps and the calculations of the rate and equilibrium constants here presented in Tables 1 and 2 and Fig. 1A are described. In particular using the data of Table 1, it is possible to represent the pH dependent mole fraction distribution of the multistate system species, Fig. 1B.

Another convenient way to represent the flavylium multistate system is the use of an energy level diagram, where for each chemical reaction the standard Gibbs free energy ΔG^0 is defined by the relation $\Delta G^0 = -RT\ln K$ where R is the gas constant, T the absolute temperature and K the equilibrium constant, as shown in Schemes 2 and 3.[7,11]

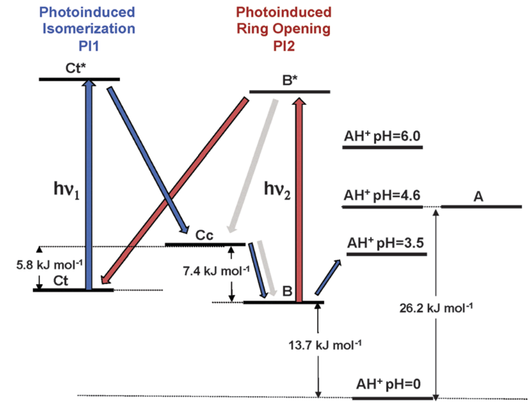
Table 2 Rate constants of compound 4′,7-dihydroxy-3-methoxyflavylium[a]

k_h (s^{-1})	k_{-h} (M^{-1} s^{-1})	k_t (s^{-1})	k_{-t} (s^{-1})	k_i (s^{-1})	k_{-i} (s^{-1})
0.3	75	1.25×10^{-2}	0.25	2.3×10^{-4}	2.2×10^{-5}

[a] Estimated error 15%.



Scheme 2 Energy level diagram of compound 3′,4′,7-trihydroxyflavylium at the equilibrium. Arrows of the excitation energy are not in scale.



Scheme 3 Energy level diagram of 4′,7-dihydroxy-3-methoxyflavylium at the equilibrium. Arrows of the excitation energy are not in scale.

The flavylium photochromic systems described up to now have been based on the *cis–trans* isomerization.[8] In most cases the mole fraction of **B** and **Cc** is very small and their energy level is higher than that of **Ct** and **A**, Scheme 2. For example, irradiation of **Ct** of 3′,4′,7-trihydroxyflavylium at pH = 4.1, Scheme 2, leads to **Cc**, which due to the relatively low *cis–trans* isomerization barrier, can spontaneously revert backward to **Ct** or forward to the flavylium cation/quinoidal base.[9] The competition backward/forward is dependent on the isomerization barrier and pH. When the barrier is very high, the backward reaction is negligible and models for optical memory devices capable of writing, reading and erasing can be conceived.[8,10]

The behaviour of 4′,7-dihydroxy-3-methoxyflavylium is different, due to the relative stability of species **B**, see Scheme 3. In Fig. 2 the spectral variations accompanying the light irradiation at 275 nm and 365 nm of this compound, at pH = 3.5, are shown. The most interesting feature of the photochemistry is the different behaviour at these two wavelengths: while at 275 nm **Ct** is formed essentially from the disappearance of **B** and some **AH$^+$**, at 365, **Ct** disappears to give **B** and **AH$^+$**. Considering that the contribution of **Cc** to the light absorption may be neglected (its mole fraction is only 3%) the appearance of **Ct** upon irradiation at 275 nm can only be explained from the excited state of **B**. Hemiketal, **B**, is a chromene and these species are known to open their ring upon light irradiation.[4,11,12]

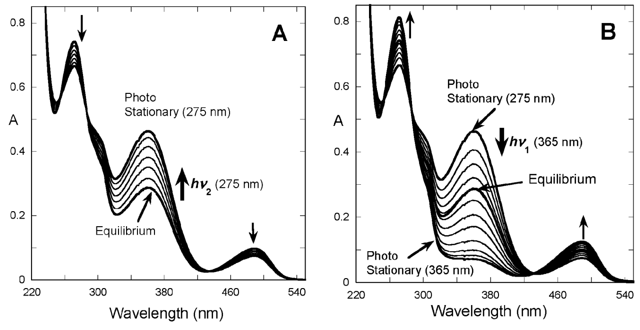


Fig. 2 (A) Spectral modifications upon irradiation of equilibrated solutions of compound 4′,7-dihydroxy-3-methoxyflavylium, 9.2×10^{-5} M pH = 3.5 at 275 nm and (B) irradiation of the solution at 365 nm after reaching the photo-stationary state at 275 nm.

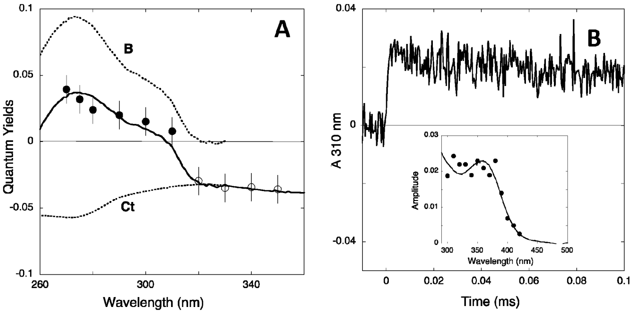


Fig. 3 (A) Quantum yields for the disappearance (open circles) and appearance (black circles) of **Ct**, 5.4×10^{-5} M at pH = 6.0; (B) nanosecond laser flash photolysis at an excitation wavelength of 266 nm pH = 6.0 trace obtained at 310 nm; inset-representation of the amplitude immediately after the flash fitted with the **Ct** absorption.

According to the literature there are two pathways for the photochemical reaction of a chromene: to produce **Cc** and/or **Ct**. The formation of both chalcones through a conical intersection resulting from the excitation of the hemiketal present in anthocyanins was recently reported by Macanita and coworkers.[11] The photochemical ring opening leads to the ground state formation of both isomers, *i.e.*, all the **Ct** is photochemically formed from the reaction of the excited state of **B** and not by the ground state isomerization of **Cc**, which takes hours. The photoproduct is thermally reversible, defining a new photochromic process in the flavylium multistate system.

In Fig. 2B the photo-stationary state obtained in Fig. 2A was irradiated at 365 nm, a wavelength at which **Ct** absorbs. The fact that the absorption of **Ct** at the equilibrium is reached during the first stages of the irradiation at this wavelength, but continues to decrease up to a new photo-stationary state is worthy of note. In other words the absorption of **Ct** can oscillate around the equilibrium absorption by means of two different light inputs.

More evidence for the new photochromic system based on irradiation of **B** was achieved by representing the quantum yields of the disappearance and formation of **Ct**, as a function of the irradiation wavelength, Fig. 3A. At an irradiation wavelength higher than 320 nm only **Ct** absorbs and the quantum yield for the formation of **B** is constant within the error as expected. On the other hand below 320 nm the quantum yield is roughly proportional to the absorption of **B** minus a fraction of the absorption of **Ct**. Further experimental evidence was obtained by the traces of nano-second flash photolysis under a pulse laser at 266 nm. Representation of the initial amplitude of these traces as a function of the monitoring wavelength can be fitted with the absorption spectrum of **Ct**, supporting that the last species is formed directly from the excited state of **B**.

The results described here can be rationalized by means of the energy level diagram of the compound 4′,7-dihydroxy-3-methoxyflavylium, Scheme 3.

Irradiation at 365 nm pumps **Ct** to **Cc**, which spontaneously gives **B** (blue arrows). Differently, irradiation at 275 nm excites species **B**, which forms directly **Ct** (red arrows). The disappearance of **B** drags also the disappearance of some **AH$^+$**. Conversely the appearance of **B** equilibrates with a small fraction of **AH$^+$**. **Cc** formed from the excited state of **B** reverts back to the ground state of **B** in sub-seconds and is not used to form **Ct** (grey arrows).

As far as we know this is the first clear demonstration of a photochromic system based on the *cis–trans* isomerization connected with ring opening-closure, both addressed using light of different wavelengths. The dual photochromic system is also pH dependent and as a consequence the system is able to respond to three stimuli. This example together with many others reported in the literature during the last few years show the potentialities of this family of compounds, bio-inspired in anthocyanins, as versatile photochromic systems.

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