

Thermal and photochemical properties of 4'-hydroxyflavylium in water–ionic liquid biphasic systems

Damián Fernández^a, A. Jorge Parola^a, Luís C. Branco^a,
Carlos. A.M. Afonso^b, Fernando Pina^{a,*}

^a REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal

^b CQFM, Departamento de Engenharia Química, Instituto Superior Técnico, 1049-001 Lisbon, Portugal

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Abstract

The multistate/multifunctional properties of 4'-hydroxyflavylium in a water/1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆]) biphasic system are described. The kinetics and thermodynamics of this flavylium salt have been fully characterised in aqueous solutions and compared to those obtained in [bmim][PF₆]. The *trans*-chalcone is thermally more stable in the ionic liquid but shows efficient photoisomerisation to the *cis*-chalcone, allowing to define *write–read–erase* cycles in this biphasic system.

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1. Introduction

Synthetic flavylium salts, can exist in different forms (multistate) that can be interconverted by different external *stimuli* (multifunctional) [1]. In particular, they respond to light and pH stimuli in a way that is similar to the behaviour of an optical memory, and in some cases are capable to mimicking, in a primitive way, some properties of neurons [1d].

In the framework of supramolecular chemistry, increasing of complexity can be viewed as a step further to the bottom-up approach. This approach should give rise to different properties and by consequence to new functions. Recently, this strategy was carried out by incorporating the 4',7-dihydroxyflavylium in water–ionic liquids biphasic systems [2]. Room temperature ionic liquids are thermally stable salts, constituted by an organic cation and either an organic or inorganic anion, and unlike traditional inorganic molten salts, present a high degree of asymmetry that inhibits crystallisation at room temperatures. In addition, they are air and water stable, exhibit a non-measurable vapour pressure and are able to solvate a variety of organic and inorganic compounds, and have found a variety of applications in catalysis [3], biocatalysis [4] and separation processes [5].

In this work, the multistate/multifunctional properties of 4'-hydroxyflavylium in a water/1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆]) biphasic system is described. This compound is very well characterised in aqueous solution [1c,6], and can thus be an interesting probe of some properties of the ionic liquid.

2. Results and discussion

Synthetic flavylium salts constitute a class of molecules possessing the same basic structure of anthocyanins, as well as the same sequence of structural transformations in aqueous solution, as shown in Scheme 1, for 4'-hydroxyflavylium in water [1c,6].

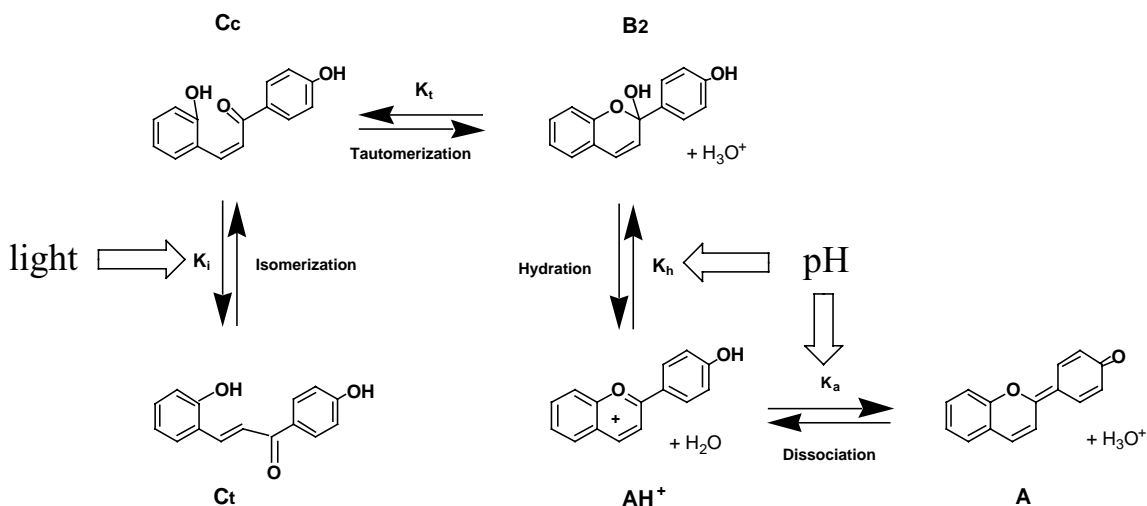
In acidic water, it is possible to distinguish five species of this compound: the flavylium cation (AH⁺); the quinoidal neutral base (A), formed upon deprotonation of AH⁺; the hemiketal (B2), obtained by hydration of AH⁺; the *cis*-chalcone (Cc), resulting from tautomerisation of B2; and the *trans*-chalcone (Ct), due to the isomerisation of Cc. In basic water, ionised *cis*- and *trans*-chalcones (Cc⁻, Cc²⁻, Ct⁻ and Ct²⁻), obtained by deprotonation of phenolic hydroxyl groups, can be observed in the equilibrium or as transient species.

An important aspect of synthetic flavylium salts is the fact that the chalcones exhibit photoinduced *cis–trans*

* Corresponding author. Tel.: +351-21-2948355;

fax: +351-21-2948385.

E-mail address: fjp@dq.fct.unl.pt (F. Pina).

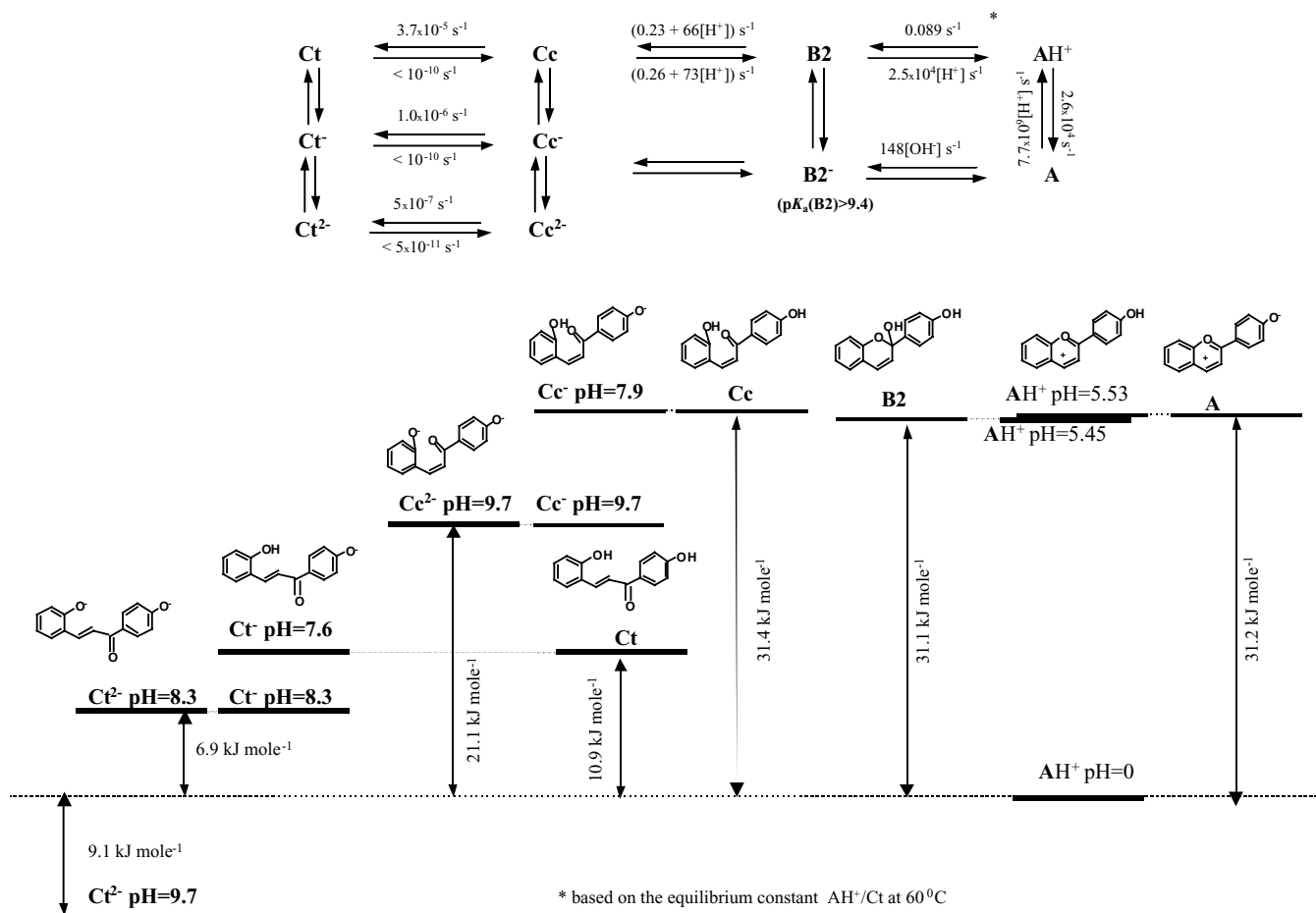


Scheme 1.

isomerisation. For example, the *trans*-chalcone can lead, upon irradiation, to the *cis*-chalcone or the flavylium cation, depending on pH.

The equilibrium and rate constants of the several processes occurring in 4'-hydroxyflavylium are shown in

Scheme 2. In a previous study [6], McClelland and McCall reported on the kinetics and thermodynamics of the several equilibria described in Scheme 1. Additional information on this system was obtained from the photochemical behaviour, in particular by flash photolysis [1c]. A thermal



barrier of 129 kJ mol^{-1} between the *cis*- and *trans*-chalcones was then determined. The existence of this barrier allows to obtain the *trans*-chalcone in a metastable state, in a pH range where the thermodynamically stable species is the flavylium cation, and prevents the back reaction of the photoproduct *cis*-chalcone, when it is obtained from irradiation of its *trans* isomer, write step, see below.

In recent years, we introduced a simple energy level diagram which can be constructed from the equilibrium constants of the complex network of chemical reactions, as shown in Scheme 2 (bottom) [1]. Such a diagram is very useful to understand the response of the system to the light and pH impulses, and can be complemented with a second scheme detailing the kinetic processes of the network, see Scheme 2 (top). This scheme was elaborated by recasting the data originally reported in [1c] and [6].

Scheme 2 can be used to illustrate the write–read–erase properties of the system. Solutions of the flavylium cation at pH = 1.0 are very stable and can be stored during long periods of time. Taking a solution of the compound at pH = 1.0 and performing a pH jump, for example, to 12, the following kinetic process take place: (i) formation of A with a lifetime of $38 \mu\text{s}$; (ii) hydroxylation of A leading to B2 (eventually B2^-), with lifetime of 0.7 s, followed by a faster process (not observable) that gives Cc^{2-} ; (iii) Ct^{2-} can be obtained from irradiation of Cc^{2-} or at high temperature in several minutes; (iv) a pH jump back to pH = 1.0 leads to the Ct species in a metastable state; (v) irradiation of Ct leads to Cc which in 69 ms forms B2 (*write step*); (vi) B2 in 0.4 ms gives rise to the final product, AH^+ ; (vii) AH^+ constitutes the signal, the response of the system, and because it is thermal and photochemically stable, the information can be *read* without being erased; (viii) in order to prepare the system for another cycle, the information should

be *erased*. This operation can be carried out through steps (i) to (iv).

When aqueous solutions of 4'-hydroxyflavylium are mixed with the ionic liquid 1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆], the two solutions are not miscible and several interesting phenomena take place. Fig. 1 shows one sequence of steps that allows to describe a cycle exhibiting the function of *write–read–erase*. In a typical experiment, an aqueous solution of the compound 4'-hydroxyflavylium perchlorate, at pH = 1.0, was added to a similar volume of the ionic liquid. Moderate shaking leads to complete transfer of all the flavylium cation into the ionic liquid, in its orange-brown quinoidal base form, A. However, upon ca. 1 min of vigorous shaking, the bottom ionic liquid solution becomes yellow, indicating that A was protonated to form the AH^+ species. The system is now ready for a write–read–erase cycle.

2.1. Cycle to write–read–erase

Flavylium cation, AH^+ , dissolved in the ionic liquid is the starting and arriving point of the proposed cycle. Fig. 1c–f show four stages obtained upon a pH jump from 1 to 12 carried out in the aqueous phase. The final equilibrium in this step is obtained with the Ct^{2-} species completely dissolved into the aqueous phase, Fig. 1f.

The absorption spectra of the several species in [bmim][PF₆] are shown in Fig. 2, in accordance with the colours displayed in Fig. 1. Trace b is the initial absorption spectra of the flavylium cation and, trace h its final spectrum after the cycle. Traces a, d and e show the progressive transformation of the base A, with its typical vibrational resolution, into the $\text{Cc}^{2-}/\text{Ct}^{2-}$ species, which are more soluble in the aqueous phase (not shown).

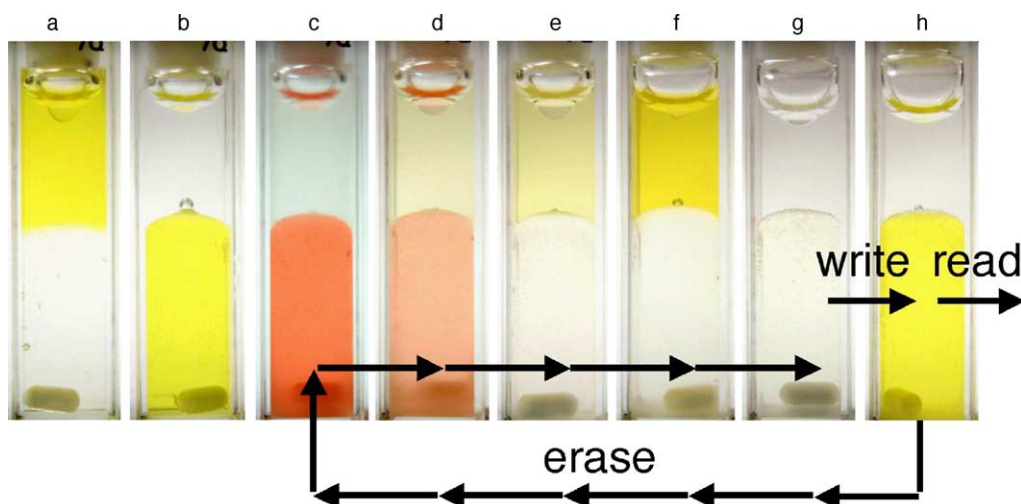


Fig. 1. (a) [bmim][PF₆] (bottom phase) and 4'-hydroxyflavylium perchlorate in 0.01 M HCl (upper phase); (b) after strong shaking of both solutions; (c) after alkaline pH jump (pH 12) with minimum shaking; (d) after medium shaking; (e) after strong shaking; (f) after several minutes at room temperature or upon irradiation of the aqueous phase; (g) after reacidification of the aqueous phase (pH 1) and strong shaking; (h) after irradiation of the ionic liquid phase.

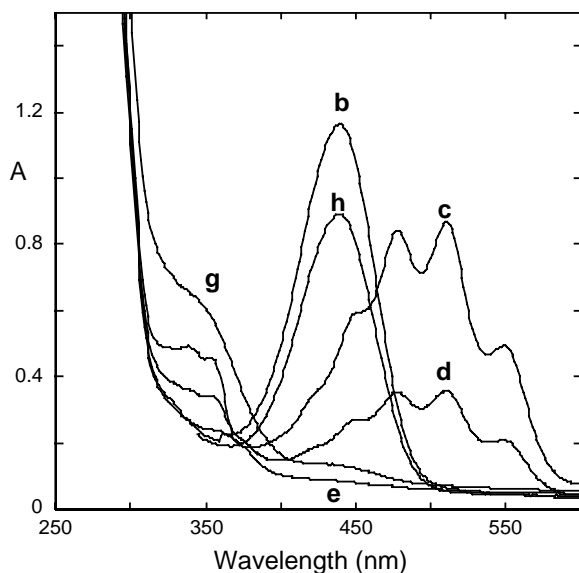


Fig. 2. Absorption spectra of the several species of 4'-hydroxyflavylium in [bmim][PF₆]. Labels correspond to those in Fig. 1.

The next step of the cycle consists into a pH jump in the aqueous phase, back to pH = 1.0, followed by vigorous mixing of the two phases. This procedure allows the Ct species formed in the aqueous phase to completely dissolve in the ionic liquid, Fig. 1g and trace g of Fig. 2. The Ct species in the ionic liquid is relatively stable, with a lifetime of 9.7 days at room temperature, in the dark, see Fig. 3. This value compares with the shorter lifetime of 0.3 days in aqueous solutions obtained under similar conditions [6].

In contrast with the high thermal stability of the Ct species in the ionic liquid, efficient formation of AH⁺ occurs when Ct is irradiated with near UV light, allowing a *write* step to be executed.

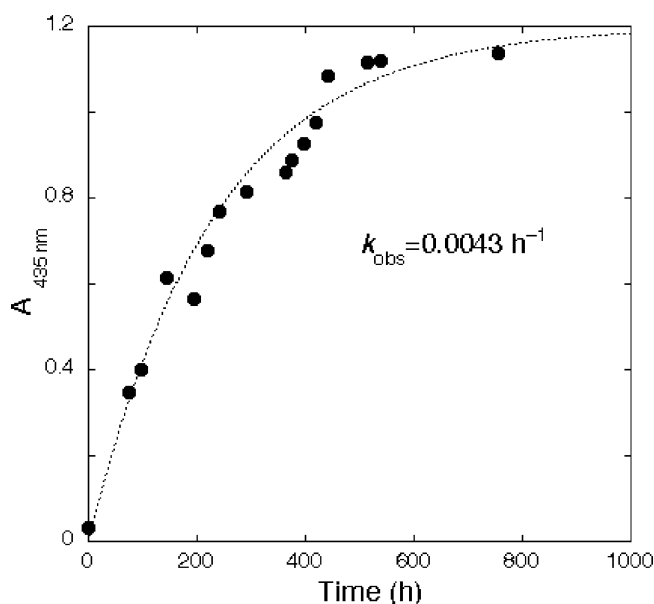


Fig. 3. Kinetics of the formation of AH⁺ from Ct in [bmim][PF₆], with a lifetime of 9.7 days. The solution was maintained in the dark, at room temperature.

The spectral variations occurring upon steady-state irradiation at 365 nm of the Ct species dissolved into the ionic liquid are qualitatively similar to those previously reported for the 4'-dihydroxyflavylium in pure water. Flash photolysis measurements are reported in Fig. 4. Two processes that follow the light pulse can be individuated. The first one corresponds to the bleaching of the solution at 340 nm occurring during the lifetime of the flash, Fig. 4B. This process can be assigned to the *trans-cis* isomerisation. The second one is the formation of AH⁺ from Cc, with $k_{\text{obs}} = 0.2 \text{ s}^{-1}$, clearly shown by the increasing absorption at 440 nm, Fig. 4A. According to the traces of Fig. 4, neither recovery of the

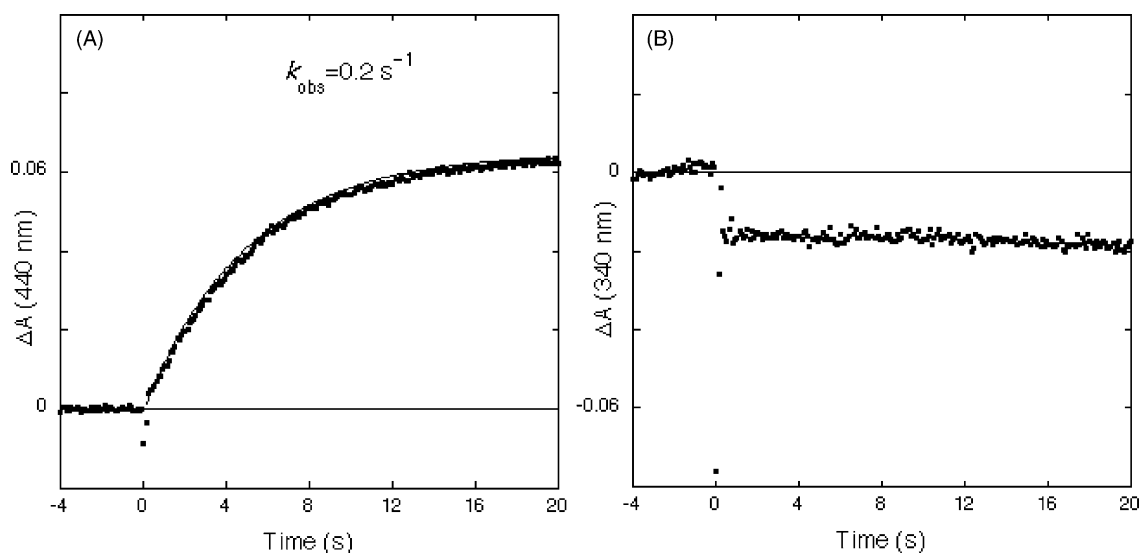


Fig. 4. Flash photolysis of the Ct species in [bmim][PF₆], in contact with an aqueous solution at pH = 1: (A) kinetics of AH⁺ formation; (B) kinetics of Ct disappearance.

Ct absorption, Fig. 4B, nor decreasing of AH⁺ absorption, Fig. 4A, is observed, confirming the existence of the thermal barrier [1,2]. According to Scheme 2, the rate determining step at pH 1, in aqueous solutions should be the tautomerisation reaction, with a rate constant of 7.6 s⁻¹ (0.26 s⁻¹ + 73 × 0.1 s⁻¹). In the ionic liquid, the equivalent process occurs with a rate constant of 0.2 s⁻¹, Fig. 4A. Taking into account that the reported pH values are always measured in the aqueous phase upon strong shaking, this lower value could reflect the expected lower proton concentration in the ionic liquid phase.

In conclusion, the following *write-read-erase* cycle can be proposed: (i) the *write* step consists on the irradiation of the Ct species dissolved in the ionic liquid, with formation of flavylium cation, AH⁺, (ii) the information thus obtained can be *read* at a wavelength where the AH⁺ (or A) absorbs but the Ct species does not, e.g. 440 nm, (iii) to *erase* the system and prepare it for a new cycle, a sequence of operations should be carried out: pH jump to 12 and vigorous shaking in order to extract the compound from the ionic liquid to water in its Ct²⁻ form, followed by a second pH jump back to 1.0 and vigorous shaking in order to dissolve the Ct species in the ionic liquid, see Scheme 2.

3. Experimental

4'-Hydroxyflavylium perchlorate was available from previous studies [1c]. 1-*n*-Butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆]) was prepared following general reported procedure [7]. The ionic liquid was further purified by flash column chromatography on silica gel and charcoal using dichloromethane as eluent. All other chemicals were of analytical grade.

The pH of the aqueous solutions was adjusted by addition of HCl and NaOH, and measured in a Metrohm 713 pH meter.

UV-Vis absorption spectra were recorded in a Perkin Elmer lambda 6 or Shimadzu UV2501-PC spectrophotometers. The flash photolysis experiments were performed as previously described [8].

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