

## Molecular Switches

# Thermal and Photochemical Properties of 4',7-Dihydroxyflavylium in Water–Ionic Liquid Biphasic Systems: A Write–Read–Erase Molecular Switch\*\*

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In the framework of supramolecular chemistry, synthetic flavylium salts can be envisaged as molecular systems that exist in different forms (multistate), which can be interconverted by different external stimuli (multifunctional).<sup>[1]</sup> Herein we explore a new dimension brought by ionic liquids to flavylium chemistry.

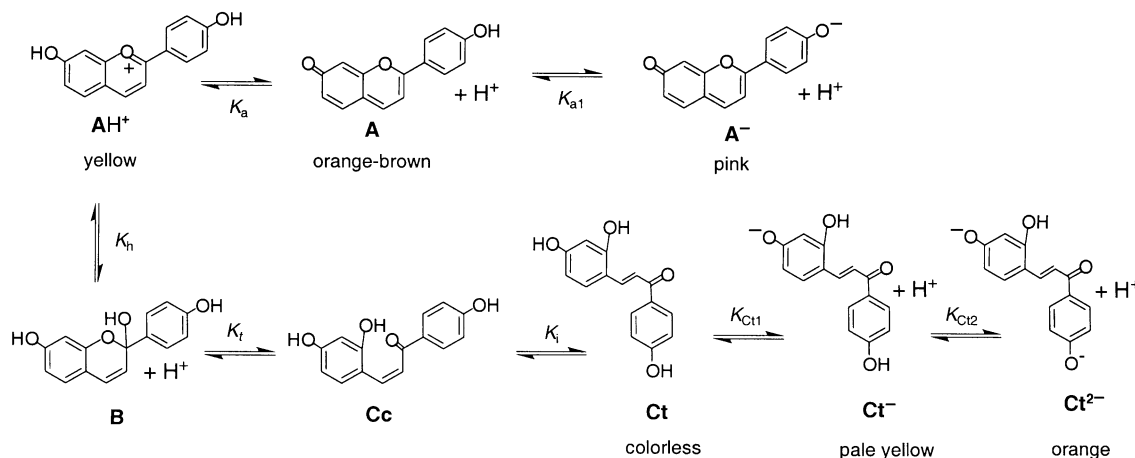
Room-temperature ionic liquids are thermally stable salts constituted by an organic cation and either an organic or inorganic anion. These liquids, unlike traditional inorganic molten salts, present a high degree of asymmetry that inhibits crystallization at room temperatures. They are air- and water-stable, exhibit a nonmeasurable vapor pressure, and solvate a variety of organic and inorganic compounds. For these reasons ionic liquids are emerging as alternative green solvents, that is, as reaction media in many transformations including catalysis,<sup>[2]</sup> biocatalysis,<sup>[3]</sup> and separation processes.<sup>[4]</sup>

In Scheme 1 the complex network of chemical reactions in which the compound 4',7-dihydroxyflavylium is involved is represented.<sup>[5]</sup> We selected this particular flavylium salt,

because: 1) it is stable over the whole pH range, 2) it exhibits a variety of colored species, which are easily identified and therefore a useful sensor to the “naked eye” in the ionic liquids, and 3) its thermal and photochemical behavior was previously characterized in water.<sup>[5–7]</sup>

In acidic water, five species of this compound can be distinguished: the flavylium cation ( $\text{AH}^+$ ); the quinoidal neutral base (**A**) formed upon deprotonation of  $\text{AH}^+$ ; the hemiketal (**B**) obtained by hydration of  $\text{AH}^+$ ; the *cis*-chalcone (**Cc**) resulting from tautomerization of **B**; and the *trans*-chalcone (**Ct**) owing to the isomerization of **Cc**. However, **B** and **Cc** are short-lived, transient species whose absorption spectra have not been observed experimentally.<sup>[5–7]</sup> In basic water, ionized quinoidal base ( $\text{A}^-$ ) and ionized *trans*-chalcones ( $\text{Ct}^-$  and  $\text{Ct}^{2-}$ ), obtained by deprotonation of the hydroxy groups, are found in equilibrium or as transient species.

The pH-dependent mole-fraction distribution of the species reported in Scheme 1 are represented in Figure 1, at equilibrium (red solid lines, bottom color bars), or as transient forms obtained immediately upon a pH stimulus (blue dotted lines, top color bars). From these data, it can be concluded that equilibrated solutions of 4',7-dihydroxyflavylium are yellow at  $\text{pH} < 2$ , slightly orange-brown at  $\text{pH} 4\text{--}8$ , pale brown-pink at around  $\text{pH} 9$ , and orange at  $\text{pH} > 11$ . On the other hand, immediately upon a “direct” pH jump from  $\text{pH} 1$  (yellow  $\text{AH}^+$ ) to  $\text{pH} 6$  or  $\text{pH} 10$ , **A** (orange-brown) and  $\text{A}^-$  (pink), respectively, are formed (Figure 1a). In the case of “reverse” pH jumps, from  $\approx \text{pH} 12$  (orange  $\text{Ct}^{2-}$ ), the transient species  $\text{Ct}^-$  (pale yellow) and **Ct** (colorless) can be detected (Figure 1b). In all pH jumps, the final equilibrium is



**Scheme 1.** Network of reactions involving 4',7-dihydroxyflavylium in water.

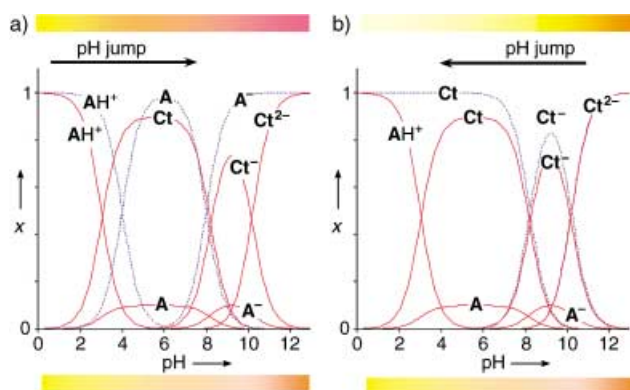
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reached after several minutes, depending on pH and temperature.

The photochemistry of 4',7-dihydroxyflavylium in water is based on the efficient *trans*–*cis* photoisomerization of the chalcone.<sup>[6–7]</sup> In a typical photochemical experiment, a solution previously equilibrated in the pH range 3–6 and containing  $\approx 90\%$  **Ct** and  $\approx 10\%$  **A** is irradiated. Depending on the specific pH value, the formation of  $\text{AH}^+$  (yellow) or **A** (orange-brown) is observed. However, these species spontaneously revert back to the initial equilibrium concentrations;



**Figure 1.** Mole-fraction distribution of the several species of 4',7-dihydroxyflavylium in water, and color bars representing the corresponding color of the solution; a) pH jumps from pH 1 (yellow  $\text{AH}^+$ ) to less acidic or basic pH values lead to transient mole-fraction distributions immediately after the jump (blue dotted lines and top color bar) that evolve in time to reach a thermodynamic equilibrium (red solid lines and bottom color bar); b) "reverse" pH jumps from pH 12 (orange  $\text{Ct}^{2-}$ ) to less basic or acidic solutions lead to transient mole-fraction distributions immediately after the jump (blue dotted lines and top color bar) that evolve in time to reach a thermodynamic equilibrium (red solid lines and bottom color bar).

the process takes only several minutes. More information on the kinetics of the reaction network can be achieved by flash photolysis.<sup>[6,7]</sup> When the  $\text{Ct}$  species is submitted to a pulse of light, its absorption is bleached during the lifetime of the flash, but partial recovery of the absorbance occurs on a timescale of seconds. These results clearly indicate the lack of thermal barrier between the two chalcone species. On the other hand, the absorption of  $\text{AH}^+$  (or  $\text{A}$ ) species increases, indicating that not all the photoproducts ( $\text{Ct}$ ) revert back to  $\text{Ct}$ , but some go forward to form  $\text{AH}^+$  (or  $\text{A}$ ) (Scheme 1). The process is complete when photochemically produced  $\text{AH}^+$  (or  $\text{A}$ ) reverts spontaneously to  $\text{Ct}$  (timescale of minutes at room temperature at pH 3.5–5.5; see Figure 3S in the Supporting Information).

In a typical "optical memory", the write step consists of the use of light to irradiate the  $\text{Ct}$  species, which should give the  $\text{AH}^+$  (or  $\text{A}$ ) form, whose color formation is the output of the system, its signal. To read this signal, a wavelength at which  $\text{Ct}$  does not absorb must be used, which can easily be selected as the flavylium species exhibits a red-shifted absorption band relative to the chalcones and is photochemically stable. The existence of a *cis-trans* thermal barrier that prevents the back reaction is required for the operation of such an "optical memory", otherwise the written information is erased before it can be read. The erasing of the "memory" and preparation for a new cycle can be achieved by a pH jump to basic medium, leading to  $\text{Ct}^{2-}$ , followed by a "reverse" pH jump to regain the  $\text{Ct}$  species. Some synthetic flavylium salts, namely those with a single substituent such as an hydroxy or methoxy group in the 4' position, exhibit these properties in water and have been used as models for "optical memories".<sup>[1]</sup> The lack of the *cis-trans* isomerization barrier of 4',7-dihydroxyflavylium in aqueous solutions immediately excludes this compound for these purposes.

When aqueous solutions of 4',7-dihydroxyflavylium are combined with the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{bmim}][\text{PF}_6]$ ), the two solutions are not miscible, and several interesting phenomena take place. Figure 2 describes one sequence of steps that allows a



**Figure 2.** a) 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate,  $[\text{bmim}][\text{PF}_6]$  (lower phase), 4',7-dihydroxyflavylium perchlorate in 0.01 M HCl,  $\text{AH}^+$  species (upper phase); b) after moderate shaking,  $\text{A}$  species (lower phase); c) after vigorous shaking,  $\text{AH}^+$  species (lower phase); d) after making the aqueous phase alkaline (pH 12) with minimum shaking,  $\text{A}^-$  (lower phase),  $\text{Ct}^{2-}$  (upper phase); e) after moderate shaking; f) after vigorous shaking,  $\text{Ct}^{2-}$  species (upper phase); g) after reacidification of the aqueous phase and vigorous shaking,  $\text{Ct}$  species (lower phase); h) after irradiation of the ionic-liquid phase at 366 nm,  $\text{AH}^+$  species.

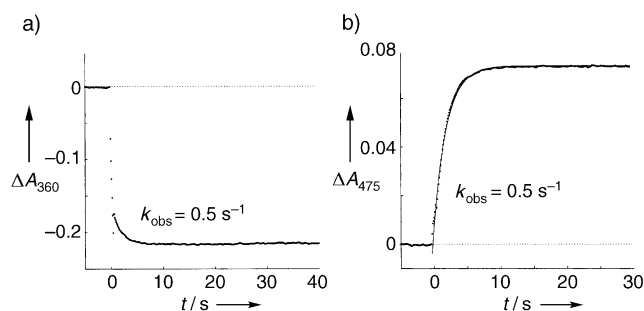
description of a *write-read-erase* cycle and provides information on the ionic-liquid properties. In a typical experiment, an aqueous solution of 4',7-dihydroxyflavylium perchlorate ( $2 \times 10^{-5}$  M, 2 mL) at pH 1.0 was added to the ionic liquid (2 mL). Moderate shaking leads to the dissolution of all the flavylium cation in the ionic liquid in its orange-brown quinoidal base form,  $\text{A}$ . However, after shaking vigorously for approximately 1 minute, the bottom ionic-liquid solution becomes yellow, indicating that  $\text{A}$  was protonated to form the  $\text{AH}^+$  species.

The flavylium cation,  $\text{AH}^+$ , dissolved in the ionic liquid is the starting and finishing point of the proposed cycle. Figures 2d,e, and f show three stages obtained upon a jump from pH 1 to pH 12 in the aqueous phase. The final equilibrium in this step is obtained with the  $\text{Ct}^{2-}$  species completely dissolved in the aqueous phase (Figure 2f). The next step of the cycle consists of a pH jump in the aqueous phase back to pH 1, followed by vigorous mixing of the two phases. This procedure allows the  $\text{Ct}$  species formed in the aqueous phase to dissolve completely in the ionic liquid. The equilibrium species at this pH value ( $\text{AH}^+$ ) is formed at a slow rate, (after 1 hour at 40 °C, less than 2 % of flavylium cation was formed) showing that, in contrast to the behavior in water, the  $\text{Ct}$  species in the ionic liquid exhibits a very large kinetic barrier that prevents rapid *cis-trans* isomerization, a requirement for a "memory" model.

It is known that ionic liquids based on the imidazolium cation (im) have an organized layer-by-layer structure and are not an ensemble of statistical aggregates of anions and cations.<sup>[8]</sup> In line with reported strong interactions between ionic liquids and solutes capable of  $\pi$ - $\pi$ ,  $n$ - $\pi$ , or hydrogen bonding,<sup>[4c,9]</sup> a strong interaction of the  $\text{Ct}$  form with the ionic liquid is expected. The large kinetic barrier of *cis-trans* isomerization in the ionic liquid can be explained by this more rigid and stable distribution of  $\text{Ct}$  in the ionic liquid that needs

to be disrupted during the thermal isomerization owing to the formation of less-planar intermediates, as well as by the large viscosity of the ionic liquid.

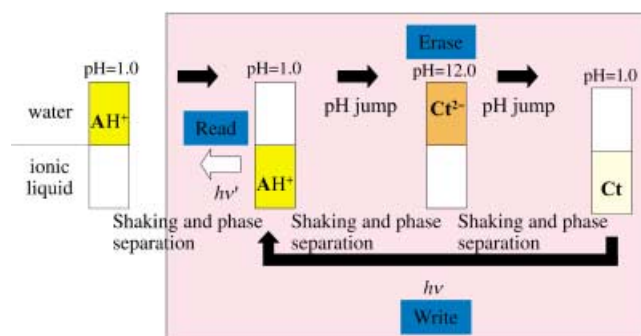
The spectral variations that occur upon steady-state irradiation at 365 nm of the **Ct** species dissolved in the ionic liquid are qualitatively similar to those previously reported for the 4',7-dihydroxyflavylium in pure water (see Supporting Information).<sup>[6,7]</sup> Flash photolysis measurements are reported in Figure 3. Two processes that follow the light pulse were



**Figure 3.** Flash photolysis of the **Ct** species in the ionic liquid, measured at: a) 360 nm (**Ct** absorption); b) 475 nm (**AH**<sup>+</sup>/**A** absorption).

identified. The first corresponds to the bleaching of the solution at 360 nm, which occurs during the lifetime of the flash. This process can be assigned to the *cis*–*trans* isomerization. The second process is the formation of **AH**<sup>+</sup> from **Cc** ( $k = 0.5 \text{ s}^{-1}$ ) clearly shown by the increasing absorption at 475 nm. According to the traces in Figure 3, neither recovery of the **Ct** absorption (Figure 3a) nor a decrease in **AH**<sup>+</sup> absorption (Figure 3b) was observed, confirming the existence of the thermal barrier.<sup>[10]</sup>

In conclusion, the following write–read–erase cycle can be proposed:<sup>[11]</sup> 1) the *write* step consists of the irradiation of the **Ct** species dissolved in the ionic liquid, with formation of flavylium cation, **AH**<sup>+</sup>; 2) the information thus obtained can be *read* at a wavelength at which the **AH**<sup>+</sup> (or **A**) absorbs but the **Ct** species does not, e.g. 475 nm; 3) to *erase* the system and prepare it for a new cycle, a sequence of operations need to be carried out: a jump to pH 12 and vigorous shaking to extract the compound from the ionic liquid into water in its **Ct**<sup>2–</sup> form, followed by a second jump back to pH 1.0 and vigorous shaking to dissolve the **Ct** species in the ionic liquid (Scheme 2).



**Scheme 2.** Write–read–erase cycle of 4',7-dihydroxyflavylium in a biphasic water/[bmim][PF<sub>6</sub>] system.

The advantage of the present cycle is that no significant mass variation occurs in the ionic liquid. Moreover, the top aqueous solutions or even the synthetic flavylium salt can be removed from the ionic liquid and substituted if necessary. Ionic liquids extend the possibility of using synthetic flavylium salts that lack a **Ct**→**Cc** thermal barrier, e.g. 4',7-dihydroxyflavylium, as models for “optical memories”.

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**Keywords:** ionic liquids · molecular switches · optical memory · photochemistry

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- [10] Compare with Figure 3S in the Supporting Information.
- [11] An identical cycle was performed with [bmim][NTf<sub>2</sub>] (Tf = trifluoromethanesulfonyl). In this case, the ionic-liquid phase is more turbid, thus making spectrophotometric measurements difficult.