Photochromism of 7-(*N,N*-diethylamino)-4′-hydroxyflavylium in a water–ionic liquid biphasic system

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Photochromism of *trans*-4-(*N,N*-diethylamino)-2,4′-dihydroxychalcone, with formation of the photoproduct 7-(*N,N*-diethylamino)-4′-hydroxyflavylium, is promoted in the ionic liquid phase of a water/[bmim][PF6] biphasic system.

Ionic liquids have been claimed to possess a large potential for new chemical technologies, in particular as green solvents,[1,2] because of their extremely low vapour pressure at room temperature. Moreover, ionic liquids can be distilled at low pressure avoiding decomposition, opening up the possibility of obtaining these solvents with high purity through recycling processes.[3] The aim of this work is to present a new dimension of ionic liquids: their ability to improve the photochromism of flavylium compounds.

The interaction of synthetic flavylium compounds with water/ionic liquid biphasic systems was recently reported.[4] In particular, it was shown that a low kinetic barrier for the *trans–cis* isomerization 7,4′-dihydroxyflavylium in water, at room temperature, is increased in ionic liquids, allowing one to define systems that behave as memory models able to perform write–read–erase cycles,[4] and also taking advantage of the solute residing between the water and ionic liquid. Herein, we explore the unique photochromic properties of *trans*-4-(*N,N*-diethylamino)-2,4′-dihydroxychalcone, at equilibrium with 7-(*N,N*-diethylamino)-4′-hydroxyflavylium, in a biphasic system constituted by the ionic liquid 1-*n*-butyl-3-methylimidazolium hexaflurophosphate ([bmim][PF6]) and water.[5]

Synthetic flavylium salts can be envisaged as molecular systems that exist in different forms (multistate), which can be interconverted by different external stimuli (multifunctional), for example pH changes and light.[6] The flavylium compound 7-(*N,N*-diethylamino)-4′-hydroxyflavylium gives rise to the following network of chemical reactions in water.[7] In moderately acidic media, five species of this compound can be distinguished: 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 tautomerization of B2; and the *trans*-chalcone (Ct) owing to the isomerization of Cc. For this compound, there is no significant *cis–trans* isomerization barrier.[7] In basic aqueous solutions, ionized *trans*-chalcones (Ct^- and Ct^{2-}), obtained by deprotonation of the hydroxyl groups, are formed, while in extremely acidic media ($[H^+] > 2$ M) protonated flavylium (AH_2^{2+}) and *trans*-chalcone (CtH^+; $pH < 4$) have been observed. According to Scheme 1, a one directional cycle can be performed starting from the red AH^+ species at pH = 1, as follows: (i) pH jump to 12 leading in a few minutes to the orange Ct^{2-}; (ii) pH jump back to acid forms the yellow CtH^+, that is spontaneously transformed into AH^+, in a time scale of minutes, depending on pH. On the other hand, if a pH jump from, for example, 1 to *ca.* 7 is carried out, the blue base A is formed. The base is transformed in the thermodynamically more stable species, Ct. However if this pH jump is immediately followed by another one back to pH = 1 (avoiding Ct formation), the flavylium is completely and immediately restored (proton transfer is very fast). As observed in other amino substituted flavylium compounds, no photochemistry of the *trans*-chalcones of the present compound was observed in water.[8]

Fig. 1 presents a sequence of photos showing how 7-(*N,N*-diethylamino)-4′-hydroxyflavylium is partitioned in the biphasic system constituted by water and the ionic liquid [bmim][PF_6]. Aqueous solutions of 7-(*N,N*-diethylamino)-4′-hydroxyflavylium at pH = 1.0 contain exclusively the flavylium cation, AH^+, that only very slowly diffuses to the ionic liquid phase, remaining at the upper aqueous phase, Fig. 1a. When the system is vigorously shaken and the two phases allowed to separate, the flavylium cation completely dissolves into the ionic liquid phase, Fig. 1b. The upper aqueous phase can be made basic by addition of NaOH (or by substitution of the acidic phase by a basic solution), followed by vigorous shaking of the mixture. When the two phases separate it is possible to see a blue colour in the ionic liquid phase due to the base, A, Fig. 1c. The blue color is not stable and leads to chalcones or ionized chalcones with a rate and protonation stage that are pH dependent. An interesting feature is that at moderately basic pH values of the aqueous solution, it is possible to have the yellow chalcone completely dissolved in the ionic liquid phase (not shown in Fig. 1). On the other hand, high hydroxyl concentrations favor the formation of orange Ct^{2-} that is transferred to the aqueous phase, Fig. 1d. Acidification of this last solution followed by immediate shaking of the two phases, leads to dissolution of Ct/CtH^+ into the ionic liquid, Fig. 1e. The thermal stability of this species in the ionic liquid depends on the amount of proton added. High proton concentrations lead to spontaneous formation of AH^+, while lower proton concentrations allow to obtain the Ct species as the thermodynamic product. In conclusion, neutral and mono-charged species will reside preferentially into ionic liquid, while double charged species prefer water.

The most interesting feature of this system is however its photochemistry. When the ionic liquid phase containing Ct at

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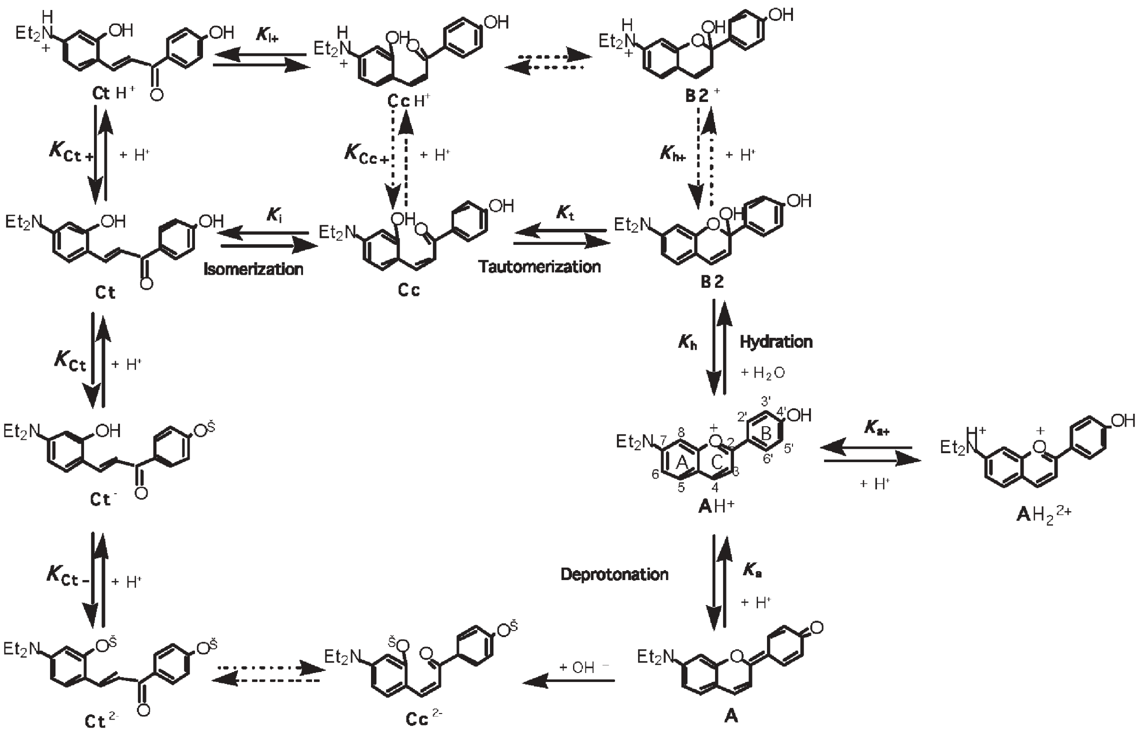

Scheme 1

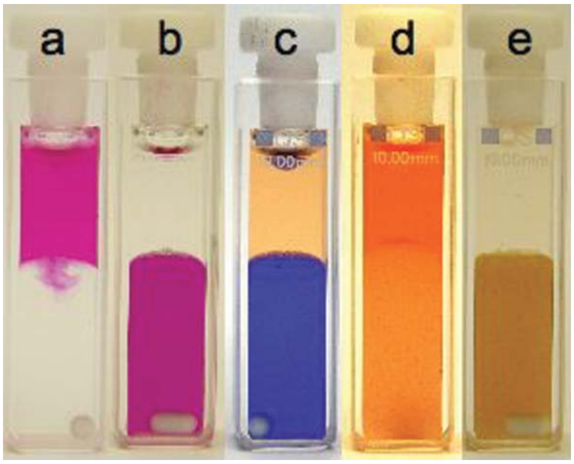

Fig. 1 Behaviour of 7-(*N,N*-diethylamino)-4′-hydroxyflavylium tetrafluoroborate in biphasic systems constituted by aqueous solution (upper phase) and 1-*n*-butyl-3-methyl-imidazolium hexaflurophosphate, [bmim][PF$_6$] (lower phase), upon pH jumps in the aqueous phase. (a) pH = 1.0 in the aqueous phase, AH$^+$ species, before shaking; (b) after shaking, AH$^+$ completely transfers to the ionic liquid; (c) upon addition of base and shaking for two minutes; (d) upon 10 minutes (shaking); (e) upon addition of acid and shaking.

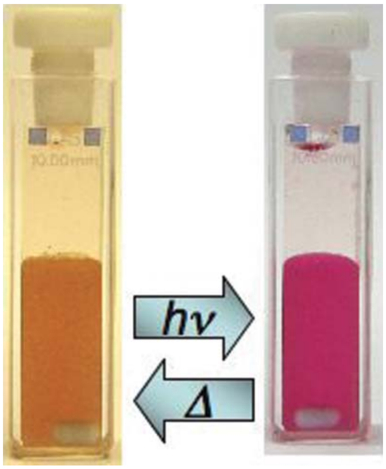

Fig. 2 Photochromic behaviour of 7-(*N,N*-diethylamino)-4′-hydroxyflavylium in water/ionic liquid [bmim][PF6] biphasic systems.

pH = 6.8 (measured in the upper aqueous phase) is irradiated, the photochemical product AH$^+$ appears. More interestingly, the system reverts back to Ct after *ca.* 11 h in the dark, at 22 °C. This constitutes, according to our knowledge, the first description on the use of ionic liquids to induce photochromic behaviour in potentially photochromic systems, Fig. 2.

In order to get more insight, flash photolysis experiments[9] were carried out by irradiating Ct on the bottom phase and following the transient absorption at 450 nm (where Ct absorbs) and at 510 nm (where AH$^+$ absorption spectrum peaks). A depletion of Ct is immediately observed, while AH$^+$ appears in a concomitant way. Both flash photolysis traces follow a first order kinetics at pH values between 5 and 8.5, the range where Ct is found on the ionic liquid phase (see Fig. 3). The recovery is not complete, and in fact a small but significant offset is observed, which increases with decreasing pH. The rate constant is pH independent within this range and is equal to 0.58 s^{-1}.

The appearance of an offset explains the photochemical behaviour depicted on Fig. 2. The chalcone should be preferentially solvated by the [bmim] organic cation. As Cc is formed by photoisomerization of Ct, it is either readily converted back to Ct

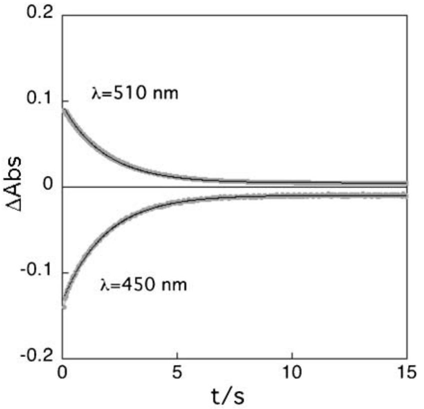

Fig. 3 Flash photolysis traces taken in the ionic liquid phase, after shaking with the aqueous phase at pH 7.13, and waiting *ca.* 30 min to obtain a good transparency of the ionic liquid solution.

(the back isomerization reaction) or to B2 and AH^+. Afterwards, AH^+ in the ionic liquid can be preferentially solvated by the anion and probably by the water molecules present on the water-saturated ionic liquid phase. Therefore, the photochemical production of net AH^+ in water/ionic liquids biphasic systems for this chalcone could be explained by the existence of a microheterogeneous structure,[10] where the flavylium cations would be stabilized by hydrogen bonding and electrostatic interactions with the anions into the water domains.[11]

In conclusion, the ionic liquid phase permits the existence of a reversible photochromic system, not possible in water, which opens up new possibilities for the use of ionic liquids in photochromic devices. Ionic liquids have been used by us to increase the kinetic barrier for *trans–cis* isomerization of chalcones, allowing to use the respective flavylium salt systems as models for optical memories. We have now shown that ionic liquids can also induce photochromism in chalcones that are not photochromic in water.

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11 One referee suggested that the observed photochemistry would be due to less vibrational deexcitation of the Ct excited state in the ionic liquid leading to the formation of Cc; in water, such vibrational deexcitation would be promoted by the O–H vibrator, preventing the isomerization.