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Photochromism in Ionic Liquids. Theory and Applications

Fernando Pina and Luís C. Branco

REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica,
Portugal

1. Introduction

Research on photochromic compounds by itself is an important issue with great industrial impact from ophthalmic lens fabrication to the achievement of intelligent windows and displays.[1,2]Furthermore, the possibility of having photochromism in ionic liquids is an appealing objective due to the unique properties exhibited by these compounds. The research on this field is very recent and can be divided in two main categories: i) photochromic compounds dissolved in ionic liquids, ii) and more recently the preparation and study of intrinsically photochromic ionic liquids.
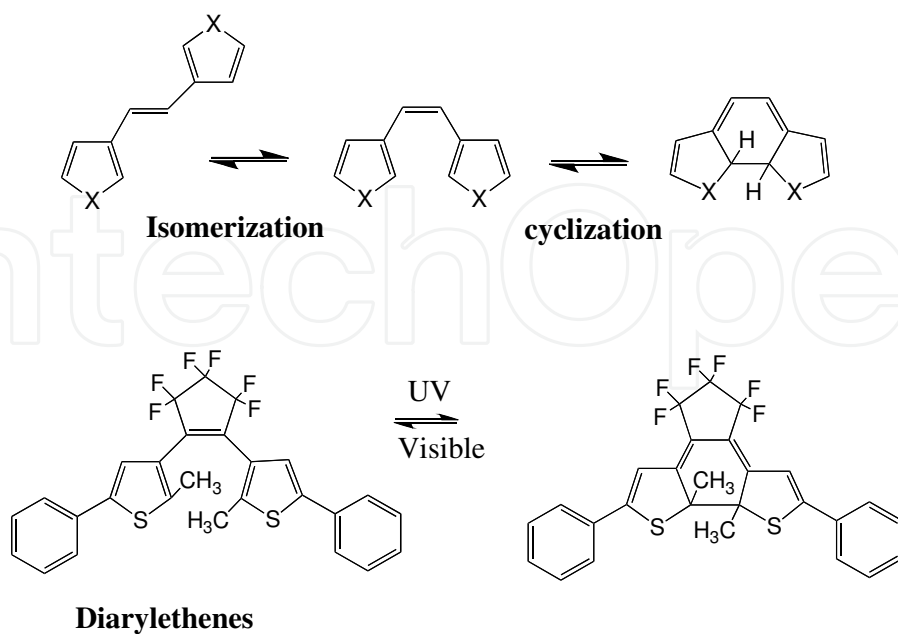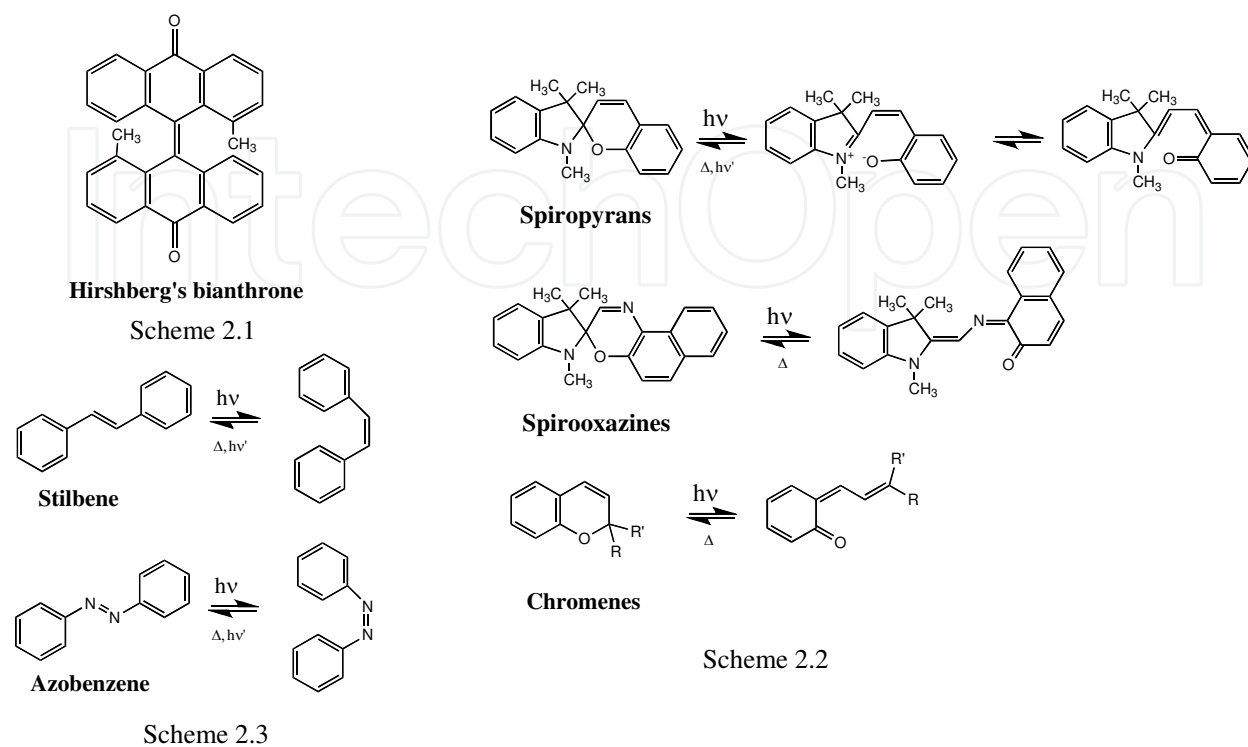
2. Photochromism in common solvents

The term photochromism was coined by Hirshberg in a series of papers appearing during the first years of the fifties of the last century.[3] Photochromism can be defined as a reversible photo-induced change of colour, the back reaction taking necessarily place through a thermal or a photochemical process.
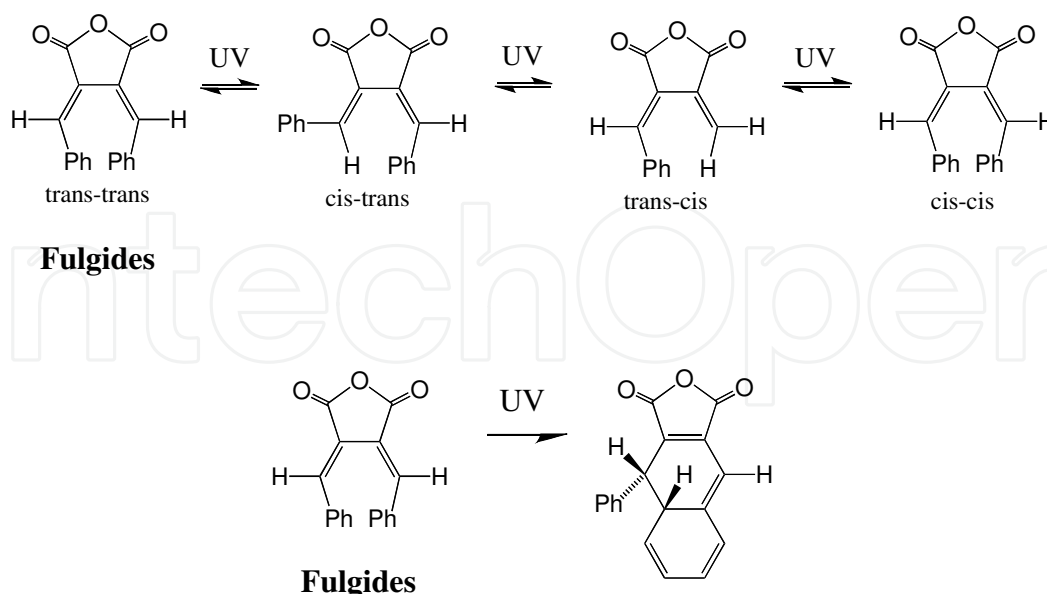
The photochromism early reported by Hirshberg and co-workers was observed in bianthrones (dianthraquinones), Scheme 2.1, and spiropyrans, Scheme 2.2. Through the years, photochromism of (a few) other families of compounds have been reported, the most relevant are described above.[2]

In order to achieve photochromism, a photo-induced reaction leading to a new species possessing different physical and chemical properties, in particular the absorption spectra, should occur. In the case of the spiropyrans, spirooxazines and chromenes, the initial photochemical step consists of the spirocarbon C-O bond cleavage followed by the rearrangement of the molecule, Scheme 2.2.

The other common photo-induced initial step is the *cis-trans* isomerisation as in the case of stilbenes and azobenzenes, Scheme 2.3. Other systems consist of two steps, a *cis-trans* isomerisation followed by cyclization, as in diarylethenes, Scheme 2.4, and fulgides, Scheme 2.5. In the case of diarylethenes the photoisomerisation step is avoided by "freezing" the compound in its *cis* configuration through an appropriate structural modification. This prevents the initial isomerisation process and the photochromism is only controlled by the cyclization reaction, Scheme 2.4, bottom.[4]

Hirshberg's bianthrone

Scheme 2.1

Stilbene

Azobenzene

Scheme 2.3

Spiropyrans

Spirooxazines

Chromenes

Scheme 2.2

Isomerization   **cyclization**

Diarylethenes

Scheme 2.4

Fulgides

Fulgides

Scheme 2.5

Quinones can also exhibit photochromism, which is caused by a reversible photoinduced migration of hydrogen, aryl or acyl groups. The following mechanism considering the formation of a δ complex was claimed, Scheme 2.6.[2]
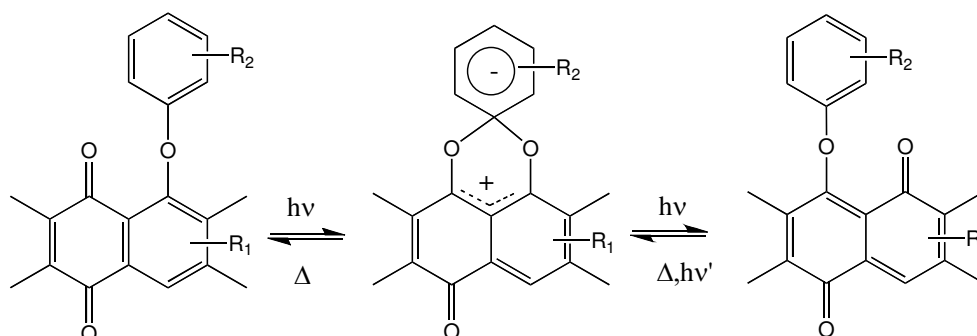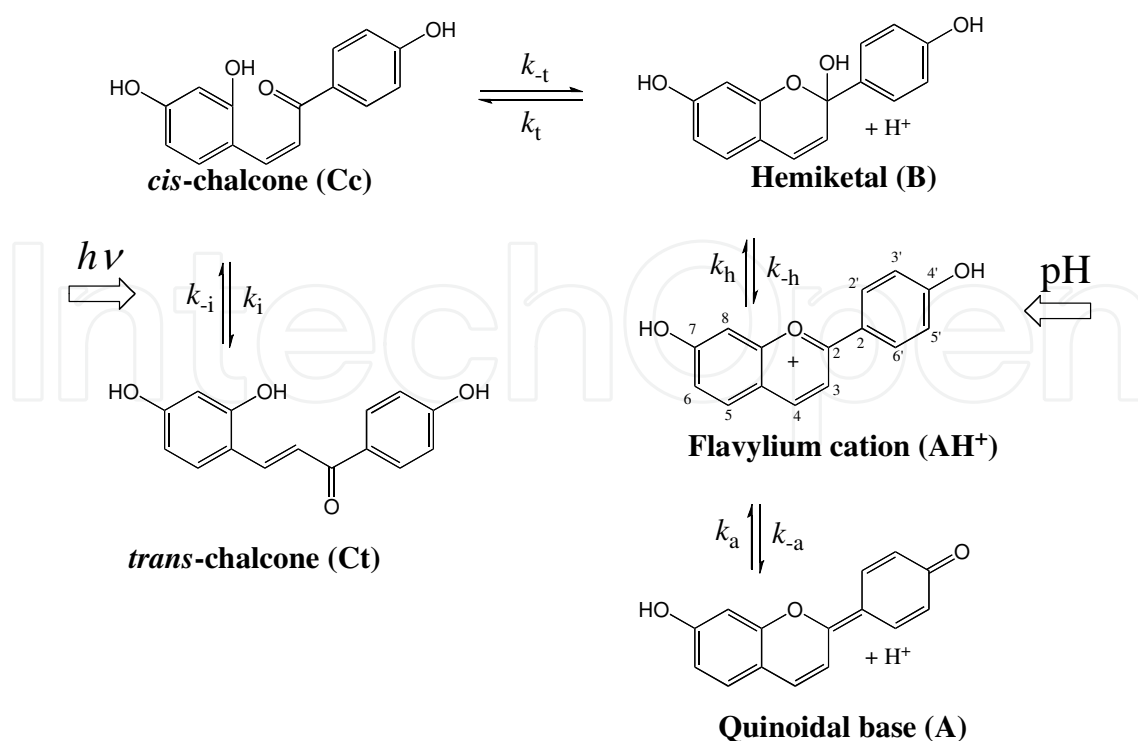

Scheme 2.6

2.1 The Flavylium network of chemical reactions. A new photochromic system.
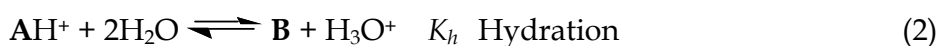
During the last decade the photochromism of flavylium derivatives has been the object of some attention.[5] This family of compounds comprises anthocyanins, the ubiquitous colorants of flowers and fruits. In spite of the fact that anthocyanins by themselves do not show significant photochromism, many synthetic[5] and also natural[6] flavylium derivatives exhibit a versatile photochemistry.

The photochromic behaviour of synthetic flavylium compounds, more properly the one of the *trans*-chalcone species, only recently was perceived as a new photochromic system with many potentialities.[7] In spite of its apparent complexity is a simple sequence of three well known elementary steps: i) photo induced isomerisation ii) cyclization and iii) dehydration to give the coloured product, the flavylium cation, (or the very coloured quinoidal base, depending on pH), Scheme 2.7.
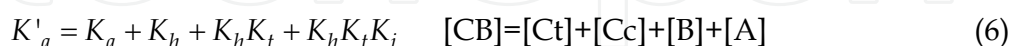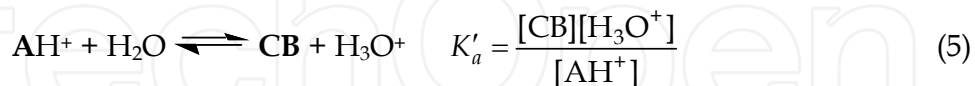
Scheme 2.7

The network of flavylium compounds in water (acid to moderately acid) is easily accounted for by eq.(1) to eq.(4)[8,9]

$$AH^+ + H_2O \rightleftharpoons A + H_3O^+ \quad K_a \quad \text{Proton transfer} \tag{1}$$

$$AH^+ + 2H_2O \rightleftharpoons B + H_3O^+ \quad K_h \quad \text{Hydration} \tag{2}$$

$$B \rightleftharpoons Cc \quad K_t \quad \text{Tautomerization} \tag{3}$$

$$Cc \rightleftharpoons Ct \quad K_i \quad \text{Isomerization} \tag{4}$$

Equations (1) to (4) can be substituted by a single acid-base equilibrium

$$AH^+ + H_2O \rightleftharpoons CB + H_3O^+ \quad K'_a = \frac{[CB][H_3O^+]}{[AH^+]} \tag{5}$$

$$K'_a = K_a + K_h + K_h K_t + K_h K_t K_i \quad [CB] = [Ct] + [Cc] + [B] + [A] \tag{6}$$

The mole fraction distribution of the different species is calculated as follows:

$$\chi_{AH^+} = \frac{[H^+]}{[H^+] + K'_a} \; ; \; \chi_A = \frac{K_a}{[H^+] + K'_a} \; ; \; \chi_B = \frac{K_h}{[H^+] + K'_a} \; ; \; \chi_{Cc} = \frac{K_h K_t}{[H^+] + K'_a} \; ; \; \chi_{Ct} = \frac{K_h K_t K_i}{[H^+] + K'_a} \tag{7}$$

In practical terms, it is now well established a routine procedure based on pH dependent UV-visible spectroscopy, NMR spectroscopy and stopped flow measurements that permits the calculation of the kinetic and equilibrium constants of the flavylium network.[9,10] Using these constants, the mole fraction distribution of the several species at the equilibrium

can be calculated, see Figure 2.1 a) for 7,4'-dihydroxyflavylium: flavylium is the dominant species at very low pH values and the respective "bases" **CB**, at moderately acid to neutral, their relative amounts being dependent on the nature and position of the substituents. A convenient way to represent the flavylium network is the use of an energy level diagram where the Gibbs free energy, ΔG^{o}, of the different equilibria is represented at different pH values, Figure 2.1 b).[11]
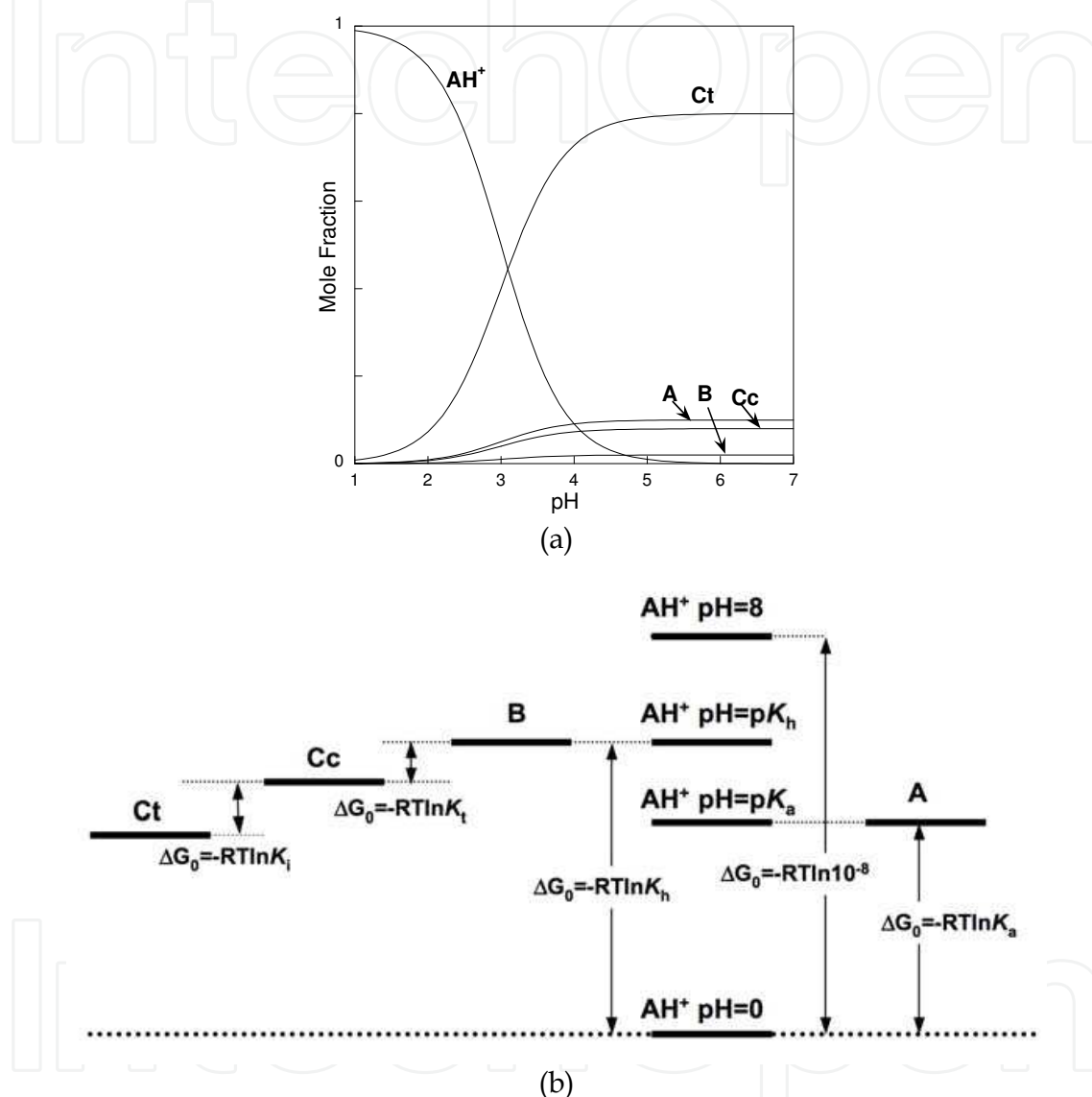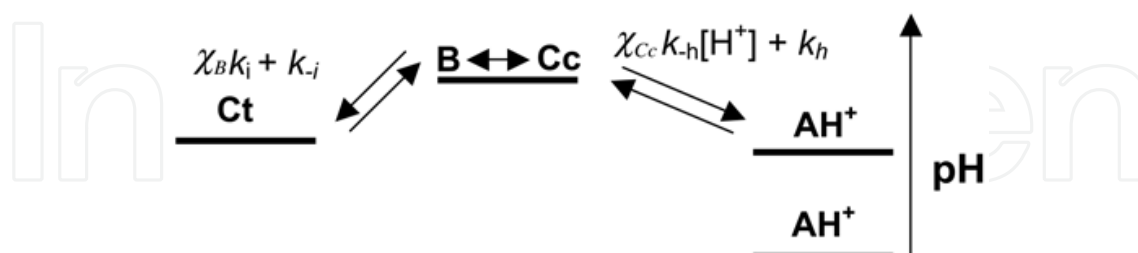

(a)

(b)

Fig. 2.1. a) Mole fraction distribution of the compound 7,4'-dihydroxyflavylium: b) Energy level diagram of the species involved in a flavylium network.

The photochemical performance and in particular the presence or absence of a thermal *cis-trans* isomerisation barrier as well as the flavylium (and base) colour, is dramatically dependent on the nature and position of the substituents, making the system particularly versatile. For example, hydroxyl substituents at position 4' of the flavylium backbone lead to a network exhibiting the barrier, while at position 7 its absence is favoured.[12] In the case of the flavylium network lacking of the *cis-trans* isomerisation barrier, the appearance of the colour upon irradiation of the **Ct**, is a balance between the back reaction that restores **Ct**

from **Cc**, and the sequence of reactions, cyclization and dehydration, leading to **AH⁺**. Due to the fact that usually the isomerisation (timescale of seconds to hours) and the dehydration (timescale of seconds to minutes) are slower than cyclization (subseconds) the network of reactions can be approximately described as in Scheme 2.8, the meaning of the symbols being reported above.

$$\chi_B k_i + k_{-i} \qquad \mathbf{B} \longleftrightarrow \mathbf{Cc} \qquad \chi_{Cc} k_{-h}[H^+] + k_h$$

Ct   **AH⁺**

                                          AH⁺   pH

Scheme 2.8

The system is equivalent to two competitive parallel reactions with the particularity that one of them is dependent on pH. The best pH value to observe the colour contrast is thus the result of two opposite effects that follow immediately the irradiation: by one hand higher proton concentration favours the appearance of the flavylium cation, by the other hand the proton concentration should not be excessive otherwise flavylium cation is the most stable specie (colour exists prior to the irradiation). Once the coloured species are formed, flavylium or quinoidal base, the system reverts completely back to the equilibrium according to eq.(8).[7] In other words, the bleaching of **Ct** due to the irradiation is recovered in two steps: i) faster one from **Cc** in competition with the hydration that leads to the coloured species, ii) slower one from the coloured species via hydration followed by ring opening and isomerisation, eq.(8).

$$k_{obs} = \left(\frac{\dfrac{[H^+]}{[H^+] + K_a} K_h K_t K_i + [H^+]}{\dfrac{K_t K_i}{k_{-h}} + \dfrac{[H^+]}{k_{-i}}} \right) \tag{8}$$

A limiting situation occurs at sufficiently high pH values: **Cc** (in equilibrium with **B**) is formed upon irradiation, but reverts completely back to **Ct** in a few seconds and no coloured species are formed.

The network of chemical reactions can be extended to the basic medium. One example of a complete flavylium network (in water) lacking of the thermal barrier is the compound 7,4′-dihydroxyflavylium, presented in Scheme 2.9 and used above as a probe for biphasic systems water/IL.[13]

At pH=1 the yellow flavylium, **AH⁺**, is the dominant species and the solution is yellow. When the pH is raised, (direct pH jump) the orange quinoidal base, **A**, is immediately formed around pH=4-6 and the pink ionized base, **A⁻**, at higher pH values. However these are transient species: when **A** is formed disappears in several minutes (depends on pH) to give the most stable species and only slightly coloured *trans*-chalcone, **Ct**; when **A⁻** is formed reverts to the ionized chalcones **Ct⁻** or **Ct²⁻**, depending on pH with a rate which is also dependent on pH. At pH>12 the **A⁻** is transformed in **Ct²⁻** in a few minutes. If now the stable **Ct²⁻** at pH=12 suffers a pH jump to acidic (reverse pH jump), the protonated chalcones are
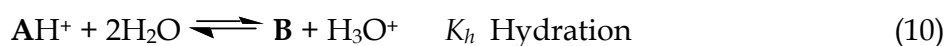
immediately formed, because proton transfer is the fastest reaction occurring in the network. The chalcones are the equilibrium species up to pH *circa* 4.[14] If the final pH of the reverse pH jump is lower than 4 (pH= 1 for example), **Ct** is immediately formed but after some minutes gives the yellow flavylium, **AH⁺**, the stable species at this pH value.
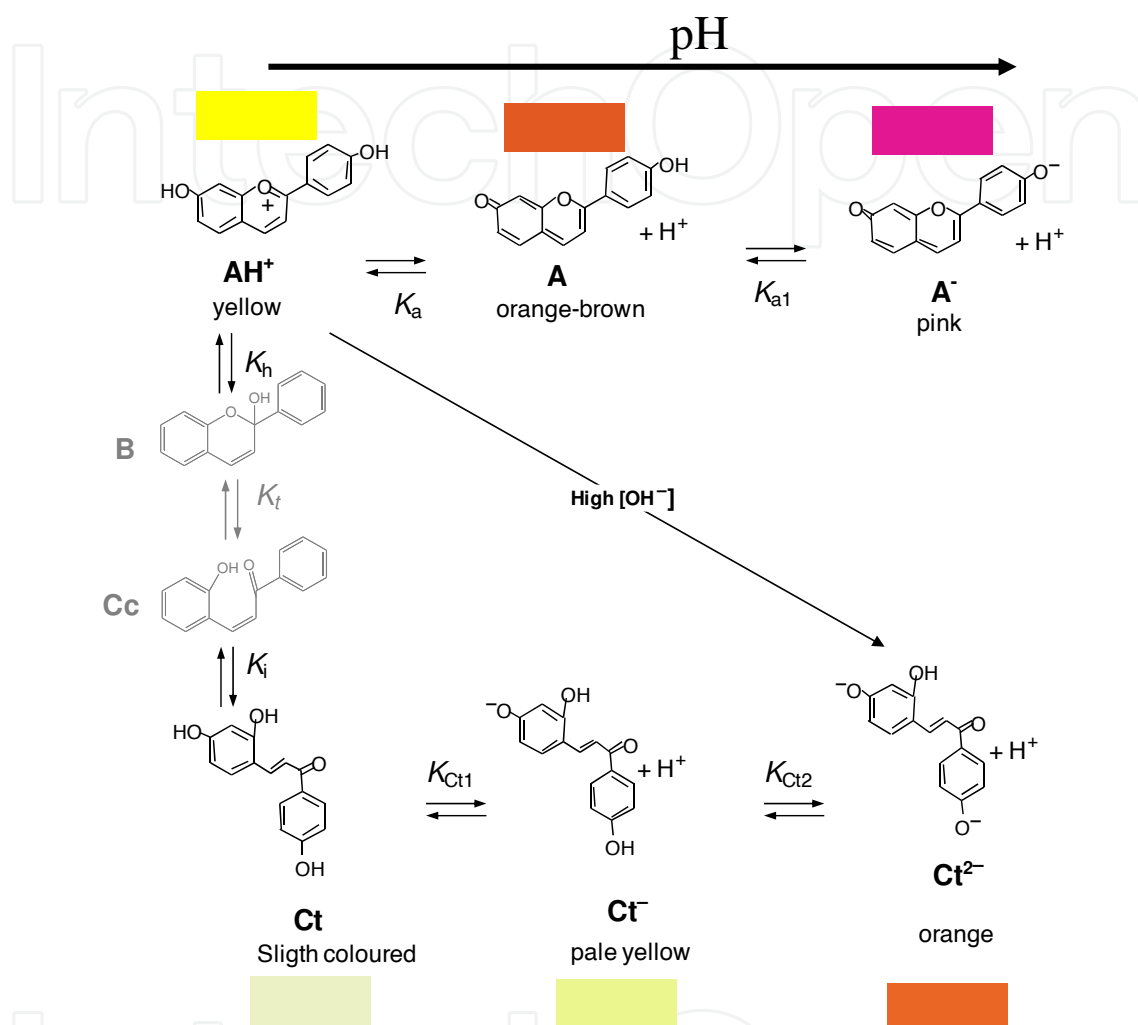

Scheme 2.9

Irradiation of **Ct** (pH=4 for example) photo-induces the isomerisation as shown in Scheme 2.8. In spite of the competition between the direct recovery of **Ct** from **Cc**, part of **Cc** leads the photoproducts **AH⁺ (A)** which are thus accumulate under irradiation. The photostationary state is reached when the thermal rate of **AH⁺ (A)** disappearance equals the rate of its photochemical production.

In the case of flavylium networks possessing a high *cis-trans* isomerisation barrier, as 4'-methoxyflavylium[9] no significant back reaction takes place immediately after the irradiation (**Ct** recovered from **Cc**) and a pseudo-equilibrium can be assumed. The pseudo-equilibrium is mathematically treated by means of the following expressions:

$$\mathbf{A}\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \mathbf{A} + \text{H}_3\text{O}^+ \qquad K_a \text{ Proton transfer} \tag{9}$$

$$\mathbf{A}\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons \mathbf{B} + \text{H}_3\text{O}^+ \qquad K_h \text{ Hydration} \tag{10}$$

$$\mathbf{B} \rightleftharpoons \mathbf{Cc} \qquad K_t \quad \text{Tautomerization} \tag{11}$$

$$\mathbf{Cc} \rightleftharpoons \mathbf{Ct} \qquad K_i \quad \text{Isomerization} \tag{12}$$

Equations (9) to (12) can be substituted by a single acid-base equilibrium

$$\mathbf{AH^+} + H_2O \rightleftharpoons \mathbf{CB^\wedge} + H_3O^+ \qquad K_a^\wedge = \frac{[CB^\wedge][H_3O^+]}{[AH^+]} \tag{13}$$
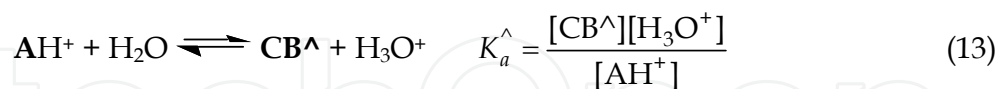
$$K_a^\wedge = K_a + K_h + K_h K_t \qquad [CB^\wedge] = [Cc] + [B] + [A] \tag{14}$$

The mole fraction distribution of the different species can be written as follows:

$$\chi^\wedge{}_{AH^+} = \frac{[H^+]}{[H^+] + K_a^\wedge} ; \chi^\wedge{}_A = \frac{K_a}{[H^+] + K_a^\wedge} ; \chi^\wedge{}_B = \frac{K_h}{[H^+] + K_a^\wedge} ; \chi^\wedge{}_{Cc} = \frac{K_h K_t}{[H^+] + K_a^\wedge} \tag{15}$$

In order to select the best pH value to obtain the great colour contrast, it is very convenient to represent the mole fraction distribution of the equilibrium together with the one of the pseudo-equilibrium, the distribution reached if complete photo-conversion of **Ct** takes place, Figure 2.2.
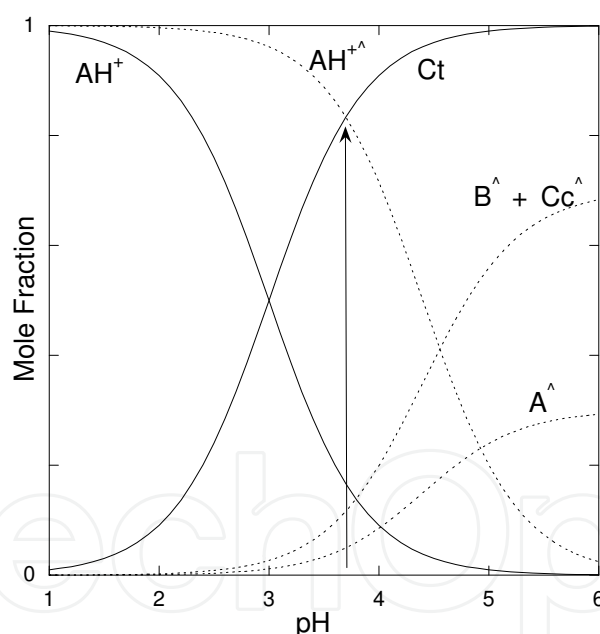

Fig. 2.2 Mole fraction distribution of the equilibrium (full line) and pseudo-equilibrium (traced line) of a flavylium network.

In this case the pH should not be too high because the fraction of flavylium cation after the irradiation (that corresponds to the one of the pseudo-equilibrium) becomes lower. Conversely, it can not be too low otherwise the flavylium is the dominant species before irradiation. In some cases the mole fraction of the base at the pseudo-equilibrium is high enough to see colour, and profit can be taken from irradiation at higher pH values.

In the case of flavylium systems possessing the *cis-trans* isomerization barrier, they are special useful to illustrate the concept of optical memory, Scheme 2.10.[15]
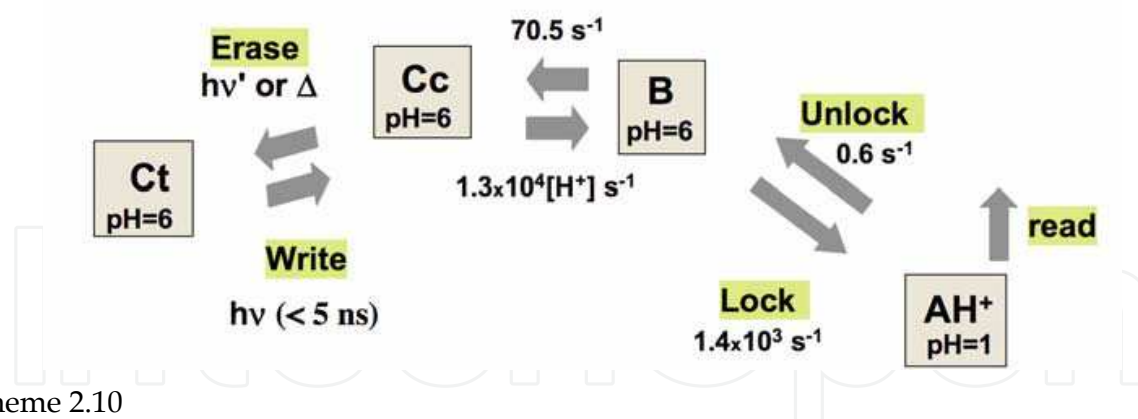
Scheme 2.10

The write step consists on the formation of **Cc** in equilibrium with **B**. This photochemical reaction is not interesting for the scope of an optical model memory by two essential motives: i) the colour contrast is small, ii) using an optical detection of the signal, irradiation of **Cc** produces **Ct**, a common effect in *cis-trans* systems. The present system allows the introduction of a lock step, by acidifying the solution. When this is done, **B** (and **Cc** through **B**) is spontaneously converted into **AH+**, see also the thermodynamic Scheme in Figure 2.1. **AH+** is stable at low pH and the information (its colour) can be read without being erased. To erase the system, it is necessary to add base that converts the flavylium cation into **Cc** and **B** and heat the solution or use light. One drawback of this system is the need of adding acid and base. Some attempts to use light to change the pH of the solution without adding mass have been undertaken.[16]
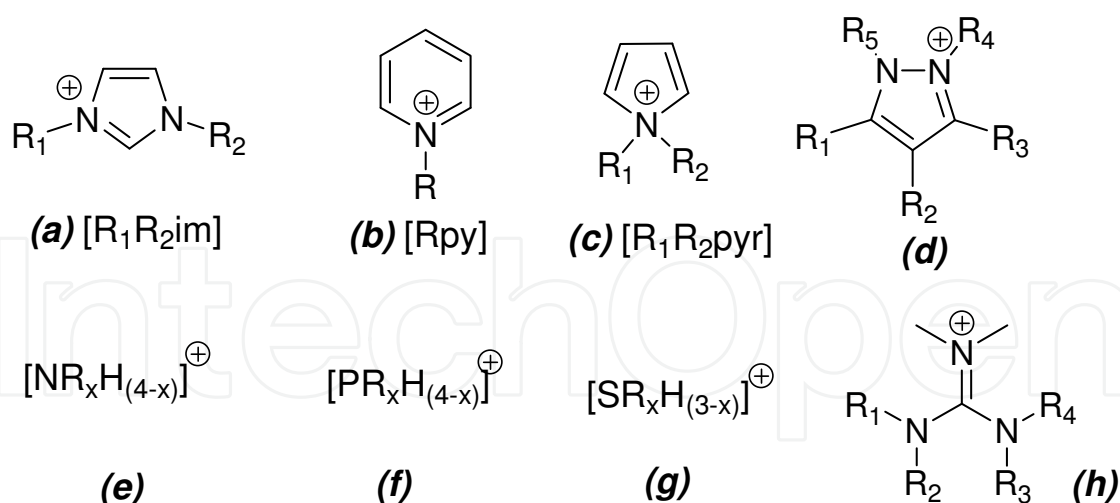
3. Properties of ionic liquids

Ionic Liquids (ILs) can be defined as organic salts with a melting point below than 100ºC.[17]

This class of compounds have received much attention mainly due their peculiar physico-chemical properties[18] such as high chemical and thermal stability, negligible vapour pressure, high ionic conductivity and a large electrochemical window.

Generally, ILs mainly comprise bulk organic cations with low symmetry based on (a) 1,3-dialkylimidazolium[19], (b) N-alkylpyridinium[20], (c) N,N-dialkylpyrrolidinium[21], (d) N,N,-dialkylpyrazolium[22], N,N-dialkyltriazolium[23], (e) tetra-alkylammonium[24], (f) tetra-alkylphosphonium[25], (g) trialkylsulphonium[26] and (h) tetra-alkyldimethylguanidinium[27] structures, among others. All of these organic cations have been combined with several inorganic or organic anions such as halides (e.g. chloride, bromide, iodide), hexafluorophosphate, tetrafluoroborate, hexafluoroantimonate, dicyanamide, triflate, bistrifluoromethanesulfonylimide, tiocyanate, trifluoroacetate, among others.

Some of the cations that have been used in order to prepare ILs are described in scheme 3.1. All organic salts that have a melting point lower than ambient temperature are called as room temperature ionic liquids (RTILs). Wilkes et al.[28] firstly reported a RTIL based on the 1-alkyl-3-methylimidazolium cation in 1982. Then, many other ILs containing a variety of cations and anions of different sizes have been synthesized to provide specific characteristics.

(a) [R$_1$R$_2$im]   (b) [Rpy]   (c) [R$_1$R$_2$pyr]   (d)

[NR$_x$H$_{(4-x)}$]$^{\oplus}$ [PR$_x$H$_{(4-x)}$]$^{\oplus}$ [SR$_x$H$_{(3-x)}$]$^{\oplus}$

(e)   (f)   (g)   (h)

Scheme 3.1.

Depending on the anion and type of organic cation, the ILs can solubilise organic compounds (e.g. carbonyl compounds, alcohols, alkyl halides) as well as inorganic or organometallic complexes and polymeric materials.[29] Furthermore, they can have low miscibility with dialkyl ethers, alkanes, water and can be insoluble in supercritical CO_2 (scCO$_2$). Particularly relevant the behaviour of ILs in the presence of scCO$_2$ which is soluble into ILs, but the different types of ILs are insoluble in scCO$_2$. This peculiar solubility property can be useful for specific applications related with separation and extraction processes.

In this context the ILs can be called as "designer solvents"[30] because their physical properties (such as melting point, viscosity, density and hydrophobicity) can be modified according to the nature of the desired application by modification of their cations and anions. The range of available anion and cation combinations could provide up to 10^{18} different ILs.

Applications of ILs include their use as solvents or co-catalysts in many catalytic and non-catalytic synthetic methodologies and separations, polymerizations processes such as extraction with organic solvent and scCO$_2$, pervaporation, and as supporting membranes. More recent, ILs have found useful application in solar cells, batteries, sensors, lubricants, and dissolution of bio- and nanomaterials. Novel ILs based on a specific organic cation and/or anion for several potential applications have been also described. Particularly relevant are the examples of chiral ionic liquids (using natural or synthesized chiral units) for asymmetric catalytic transformations, enantioselective resolution or separation processes; pharmaceutical ionic liquids (called API-ILs incorporating an active principle ingredient as cation or anion); magnetic ionic liquids (based on FeCl$_4$ anions) for efficient separation processes and others ionic liquids as intrinsically functional materials (for example luminescent, photochemical or electrochemical ILs).

Attending the recent applications of ILs, one of the most relevant parameters is related with the purity of ILs. Several studies have been reported about the significant impact of impurities such as halogen or water content, in some values of density, viscosity and conductivity of ILs. For similar ILs is possible to find discrepancies in terms of these physico-chemical properties. Also, the electrochemical and thermal stability and solubility parameters can be completely changed according with the final purity of ILs.

Nowadays, the possibility to develop alternative synthetic and purification methodologies in order to improve the final purity of ILs is one of the most important issues for further technological and industrial applications.

4. Photochromic compounds dissolved in ionic liquids

Ionic liquids due to their peculiar properties are very appealing as solvent to study photochromic molecules. Two main objectives can be achieved in these studies: the influence of ionic liquids in the performance of the photochromic compounds and the information about the properties of the ILs themselves. The ionic liquid can influence the photo-induced step that gives the photoproduct or the thermal back reaction.

4.1 Monophasic systems
4.1.1 Photoinduced process
The photoisomerization of *trans*-stilbene, Scheme 2.3, was investigated in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$].[31] Steady state irradiation followed by UV absorption confirms that formation of the *cis*-isomer takes place in the ionic liquid, is spite of its very high viscosity. Moreover, from the lifetime of the fluorescence decay of *trans*-stilbene in [BMIM][PF$_6$], 138 ps, the isomerisation rate constant, k_{iso}= 6.6x10^9 s^{-1}, was calculated. This value lays in the some order of magnitude of the isomerisation rate constants found for stilbene in alcohols and is more or less in agreement with the expected polarity of [BMIM][PF$_6$], obtained through the E$_T$(30) value (which is also close to those of the alcohols). However, when the isomerisation rate constant in alcohols is extrapolate to the viscosity of [BMIM][PF$_6$], 312 cP at 303 K,[32] a much lower value, k_{iso}= 9.7x10^8 s^{-1}, is predicted. Viscosity cannot to be the controlling parameter for the isomerisation of this molecule at least in [BMIM][PF$_6$]. This was interpreted as an evidence of the intriguing nature of ionic liquids and the problems that arise in the conventional framework of polarity and viscosity parameters.[31]

An opposite behaviour regarding the effect of the viscosity was reported by Sarkar and co-workers[33] on the study of the photoisomerization of 3,3'-diethyloxadicarbocyanine iodide (DODCI) in [BMIM][PF$_6$], Scheme 4.1. They found that photoisomerization of DODCI in the ionic liquid is 36 times slower when compared with the isopolar conventional solvent (methanol) and also slower than in water. The results were interpreted as a consequence of the high viscosity of the ionic liquid that inhibits the twisting motion about the conjugated double bonds of DODCI.

The photoisomerization of DODCI and another cyanine derivative, MC 540, Scheme 4.1, was investigated in the IL [BMIM][PF$_6$] and aqueous glycerol (90% wt glycerol:3% wt water).[34] In the case of DODCI, it was observed that the non-radiative rate constant, which represent the rates of photoisomerization, are almost identical in the ionic liquid and aqueous glycerol at a given temperature, confirming that the viscosity governs the photoisomerization of this compound. In contrast, the photoisomerization rate constant of MC 540 is higher by a factor of 2 in aqueous glycerol when compared to the IL. The stabilization of the twisted state (due to the zwiterionic character of MC 540) by the solute-solvent hydrogen bonding interactions in aqueous glycerol explains the lowering of the isomerisation barrier and the consequent increasing of the isomerisation rate.

DODCI cation

MC 540 anion
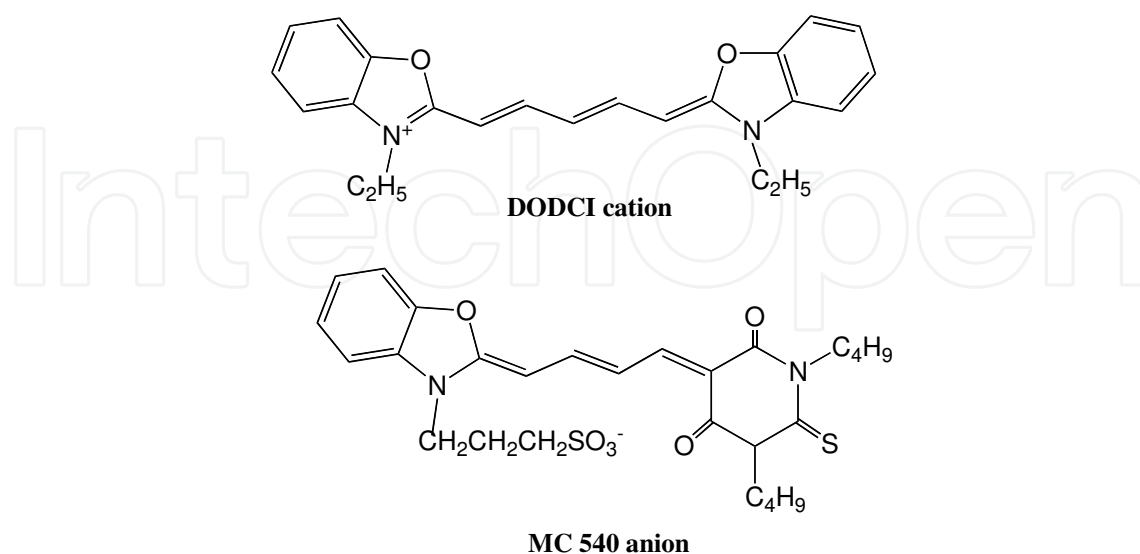
Scheme 4.1

4.1.2 The thermal back reaction

4.1.2.1 Spiropyran

Nitrobenzospiropyran and its derivatives are up to now the photochromic system most studied in ILs, see Table 1. These compounds have been widely reported in molecular solvents and it is well established that the back thermal reaction decreases with increasing the polarity of the solvent. This is due to the zwiterionic character of merocyanine, stabilized in polar solvents, differently from the closed form, stabilized in non-polar solvents.

The photo and solvatochromic properties of nitrobenzopyran was studied in ILs: i) containing the same bistrifluoromethanesulfonylimide $[NTf_2]^-$ anion and several cations, entries 10 to 15 in Table 1, set A in Scheme 4.2,[35] ii) possessing the same phosphonium $[P_{6,6,6,14}]$ and $[P_{1,4,4,4}]$ cations and different anions, entries 16 to 20 in Table 1, set B in Scheme 4.2[36] and iii) having the same anion $[NTf_2]^-$ and 1-alkyl-3-methylimidazolium $[C_nMIM]$ cation, with different chains,[37] entries 21 to 26, Table 1, set C in Scheme 4.2. Similarly to the behaviour in molecular solvents, irradiation of BSP-NO$_2$ in these ILs leads to the merocyanine (MC). In a few cases the merocyanine is more stable and negative photochromism is observed, *i.e.*, formation of the spiropyran from the merocyanine. The rates of the thermal recovery are dependent on the IL cation and anion. No linear relation seems to occur between the logarithm of the rate constants and the polarity parameter $E_T(30)$, as observed in molecular solvents,[38] see Figure 4.1. In general, the rate constant in ILs is lower than the one in molecular solvents of the same $E_T(30)$ polarity: from 2.1×10^{-4} s^{-1} for [EMIM][NTf$_2$][35] to 2.5×10^{-3} s^{-1} for $[P_{6,6,6,14}][DCA]$,[36] that compare with polar solvents like ethanol and acetonitrile, but not with non-polar solvents like *n*-hexane 47.4×10^{-3} s^{-1}.[39]

	Solvent	K_e (x10²)	$K_{recovery}$(s⁻¹)	$E_T(30)$ (Kcal mol⁻¹)	E_a (kJmol⁻¹)	Π*	α	β
1	Acetonitrile	3.85	8.4x10⁻⁴ [a] 8.8x10⁻⁴ [b]* 2.92x10⁻³ [d] 4.61x10⁻³ [p] (31°C)	45.5[a] 45.6[i] 46.4 [e]	102.4 [d]	0.79 [e]	0.42 [e] 0.35 [g]	0.37 [e]
2	Ethanol	4.57[a]	1.91 x10⁻⁴ [a] 0.612x10⁻³ [d] 0.5x10⁻³ [k] 1.59x10⁻³ [p] (31°C)	51.8 [a] 51.9[f] 52.1[e]	102.2 [d] 102.01[k]	0.63 [e] 0.54 [h]	0.90 [e] 0.83 [h]	0.72 [e] 0.77 [h]
3	Methanol			55.4[e)f]		0.71 [e] 0.73 [h]	1.06 [e] 1.05 [h]	0.62 [e] 0.61 [h]
4	Dichloromethane	0.51[a]	7.0 x10⁻³ [a]	40.6 [a] 40.7[i]				
5	Hexane		47.7x10⁻³ [m]		76.4[d]			
6	Benzene		66.2 x10⁻³ [m]		70.6 [d]			
7	1,4-Dioxane		56.6 x10⁻³ [m]		77.4 [d]			
8	Acetone		7.28 x10⁻³ [d] 5.3x10⁻³ [k] 1.07x10⁻³ [p] (31°C)	42.5 [e]	101 [d] 104.5 [k]	0.67 [e] 0.70 [h]	0.25 [e] 0.20 [h]	0.57 [e] 0.54 [h]
9	DMF		1.55 x10⁻³ [m]		96.2 [d]			
10	[C₃MPYR][NTf₂] [b]	4.16[b]	6.90 x10⁻⁴ [b] *	48.9 [b]				
11	[C₄MPYR][NTf₂] [b]	3.85 [b]	7.80 x10⁻⁴ [b]*	48.1 [b] 48.3 [l]				
12	[P₆,₆,₆,₁₄][NTf₂] [b), e]	1.15 [b]	8.50 x10⁻⁴ [b]*	47.97 [b] 46.1[e]		0.83 [e]	0.37 [e]	0.27 [e]
13	[EMIM][NTf₂] [b]	4.57[b]	2.10 x10⁻⁴ [b]*	53.3 [b] 53.1[i]				
14	[EDMIM][NTf₂] [b]	3.24[b]	3.90 x10⁻⁴ [b]*	51.79 [b]				
15	[N₁,₈,₈,₈][NTf₂] [b), e]	4.16 [b]	4.00 x10⁻⁴ [b]*	49.13 [b] 45.9 [e]		0.87 [e]	0.33 [e]	0.23 [e]
16	[P₆,₆,₆,₁₄][DSBA] [a]	1.45 [a]	8.12 x10⁻⁴ [a]	46.6[a]	88[a]			
17	[P₆,₆,₆,₁₄][DCA] [a]	0.57 [a]	25.03 x10⁻⁴ [a]	46.1[a]	75 [a]			
18	[P₆,₆,₆,₁₄][NTf₂] [a]	1.16 [a]	6.5 x10⁻⁴ [a]	47.9 [a] (47.97)	90 [a]			
19	[P₁,₄,₄,₄][TOS] [a]	1.74 [a]	5.19 x10⁻⁴ [a]	48.2[a]	71 [a]			
20	[P₆,₆,₆,₁₄][FAP] [a]	1.16 [a]	7.31 x10⁻⁴ [a]	48[a]	76 [a]			

	Solvent	K_e (x10²)	$K_{recovery}$ (s⁻¹)	E_T(30) (Kcal mol⁻¹)	E_a (kJmol⁻¹)	Π*	α	β
21	[C₂MIM] [NTf₂] [j),k]	0.866[k]	1.2 x10⁻³ [k]	52.6[k),i]	106.69[k]			
22	[C₄MIM] [NTf₂] [j]	0.702 [k]	1.0 x10⁻³ [j]	52.4 [j] 51.6[i]	96.93 [j),k]			
23	[C₆MIM] [NTf₂] [j]	0.116 [k]	1.0 x10⁻³ [j]	53.3 [j] 51.9[i]	98.84 [j),k]			
24	[C₈MIM] [NTf₂] [j]	0.53 [k]	1.7 x10⁻³ [j]	51.2 [j] 51.1[i]	103.34 [j),k]			
25	[C₁₀MIM] [NTf₂] [j]	0.794 [k]	1.8 x10⁻³ [j]	51.6 [j] 51.0[i]	106.68 [j).k]			
26	[C₁₂MIM] [NTf₂] [j]	0.763 [k]	2.0 x10⁻³ [j]	51.2 [j]	105.27 [j),k]			
27	[BMIM][BF₄] [c),d]	4.62 [d]	0.396 x10⁻³ [d]	52.4 [l]	73.8 [d]	1.05 [c]	0.63 [c]	0.38 [c]
28	[BMIM][PF₆] [c),d]	1.88 [d]	0.792 x10⁻³ [d]	51.1 [l]	70.6 [d]	1.03 [c]	0.63 [c]	0.21 [c]
29	[BMIM][TfO] [c]			51.1 [l]		1.00 [c]	0.62 [c]	0.46 [c]
30	[BMMIM][BF₄] [d]	1.48 [d]	0.107 x10⁻³ [d]	49.4 [d]	90.9 [d]			
31	[EMIM][BF₄] [d]	3.76 [d]	0.232 x10⁻³ [d]		70.9 [d]			
32	[EMIM][DCA] [d]	6.78 [d]	0.382 x10⁻³ [d]		96.1 [d]			
33	[HOEMIM][PF₆] [d]	15.24 [d)#]	0.0237 x10⁻³ [d]		97.0 [d]			
34	[HOEMIM][NO₃] [d]	4.69 [d]	0.407 x10⁻³ [d]	61.7 [d]	-			
35	[BMMIM][DCA] [d]	4.23 [d]	0.404 x10⁻³ [d]		81.5 [d]			
36	[EMIM][CH₃SO₃] [d]	3.64 [d]	0.336 x10⁻³ [d]		75.9 [d]			
37	[BMIM][NO₃] [d]	2.64 [d]	0.498 x10⁻³ [d]		88.5 [d]			

*In the original paper these values are 100 times greater, but this should be an error in their table. See values for the solvents. # negative photochromism

References indicated on Table 1: a) R. Byrne, S. Coleman, K. J. Fraser, A. Raduta, D. R. McFarlane, D. Diamond, *Phys. Chem. Chem. Phys.*, **2009**, *11*, 7286-7291. b) R. Byrne, K. J. Fraser, E. Izgorodina, D. R. MacFarlane, M. Forsyth D. Diamond, *Phys. Chem. Chem. Phys.*, **2008**,*10*, 5919-5924. c) Y. Wu, T. Sakaki, K. Kazusi, T. Seo, K. Sakurai, *J. Phys. Chem. B*, **2008**, *112*, 7530-7536. d) S. Zhang, Q. Zhang, B. Ye, X. Li, X. Zhang, Y. Deng, *J. Phys. Chem. B*, **2009**, *113*, 6012-6019. e) S. Coleman, R. Byrne, S. Minkovska, D. Diamond, *Phys. Chem. Chem. Phys.*, **2009**, *11*, 5608-5614. f) K. Iwata, M. Kabita, H. Hamaguchi, J. Chem. Phys. B, 2007, 111, 4914-4919. g) Book *"Photochromism: Molecules and systems"*, Ed. by H. Dürr, H. Bouas-Laurent, Elsevier B. V., 2003. h) A. K. Burrel, R. E. D. Sesto, S. N. Backer, T. M. McCleskey, G. A. Backer, *Green Chemistry,*, **2007**, *9*, 449-454. i) C. Reichardt, *Green Chemistry*, **2005**, *7*, 339-351; *Chem. Rev.* **1994**, *94*, 2319-2358. j) S. Coleman, R. Byrne, N. Alhshimy, K. J. Fraser, D. R. MacFarlane, D. Diamond, *Phys. Chem. Chem. Phys.*, **2010**, *12*, 7009-7017. k) S. Coleman, R. Byrne, S. Minkovska, D. Diamond, J. *Phys. Chem. B*, **2009**, *113*, 15589-15596. l)L. Crowhurst, P.R. Mawdsley, J. M. Perez-Arlandis, P.A. Salter, T. Welton, *Phys. Chem. Chem. Phys.*, **2003**, *5*, 2790-2794. m) Y. Sueishi, M. Ohcho, N. Nishimura, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2608-2613. n) J. Figueras, *J. Am. Chem. Soc.,* **1971**, *93*, 3255-3263. o) R. Byrne, S. Coleman, S. Gallagher, D. diamond, Phys. Chem. Chem..Phys., **2010**, *12*, 1895-1904. p) X. Song, J. Zhou, Y. Li, Y. Tang, J. Photochem. Photobiology A, **1955**, *92*, 99-103.

Table 1. Photochromism and polarity parameters for nitrospiropyran

BSP-NO₂ ⇌ (hν / Δ, hν') **MC**
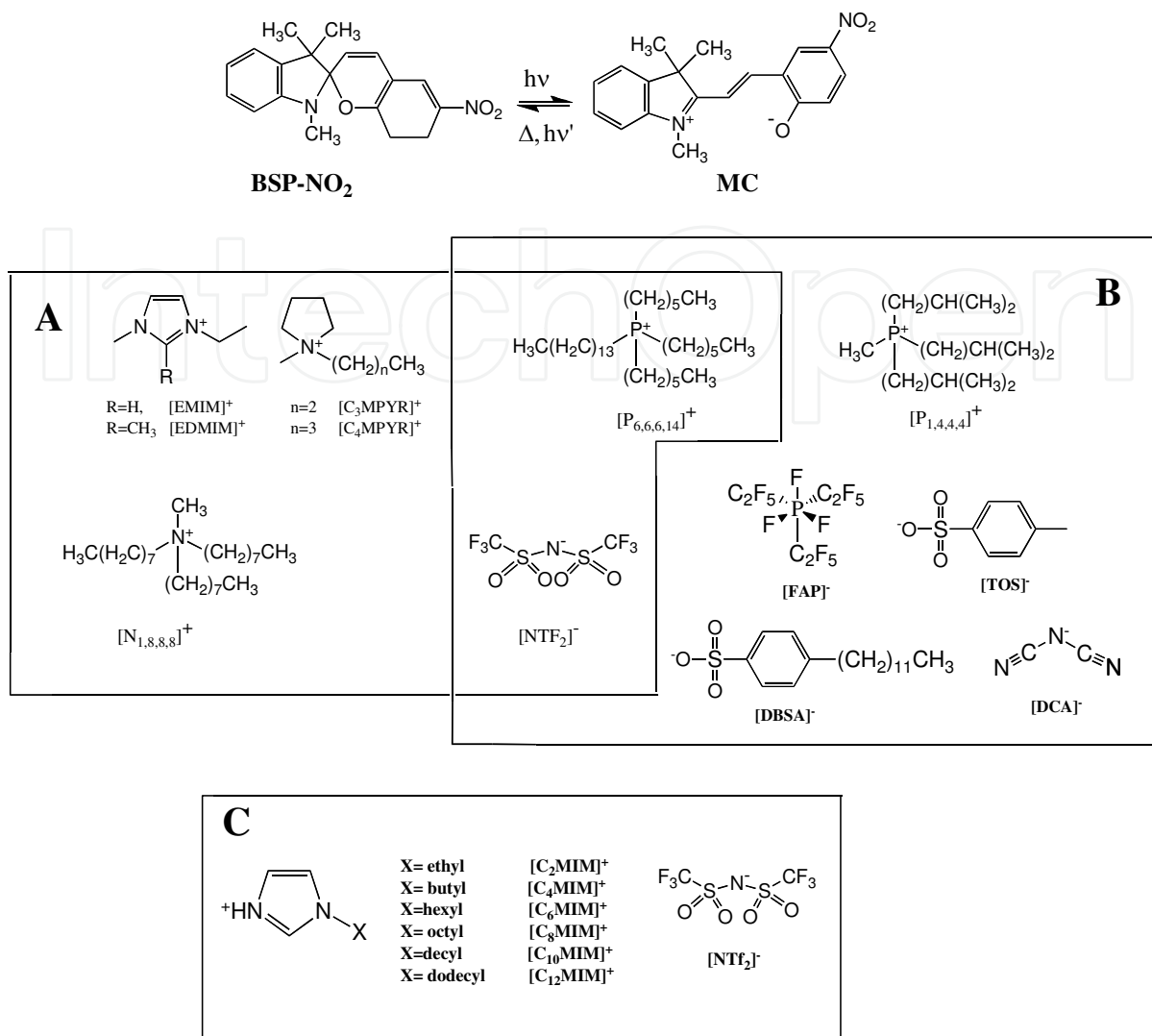
Scheme 4.2

A similar system regarding the photochromism of nitrospiropyran derivatives in a series of ionic liquids was independently reported, Scheme 4.3.[40] The overall solvent polarity was characterized by the Reichardt's dye $E_T(30)$, as well as by 4-nitroaniline and *N,N'*-diethyl-4-nitroaniline for the Kamlet-Taft parameters (α- hydrogen bond donor, β- hydrogen bond acceptor, and π^*-dipolarity/polarizability). The ionic liquids were divided into 3 categories: **A** (strong hydrogen bond basicity), $\alpha < 0.9 < \beta$; **B** (moderate hydrogen bond acidity and basicity), α and $\beta < 0.9$; **C** (strong hydrogen bond acidity), $\beta < 0.9 < \alpha$. In group **A** only the spiropyrans forms are observed at the (dark) equilibrium and no evident change of colour takes place upon irradiation (no *trans* merocyanine was detected) possibly due to the stabilization of the *cis*-isomers of the merocyanine by the ionic liquid.[41] Solutions of the spiropyrans in ionic liquids of group **B** show a small fraction of merocyanine at the (dark) equilibrium, which is increased upon irradiation at 365 nm (positive photochromism). In solvents of group **C**, the *trans*-merocyanine is formed at the (dark) equilibrium and irradiation leads to the formation of the spiropyran form at the expenses of the *trans*-merocyanine. The system reverts back to the equilibrium in the dark (negative photochromism).
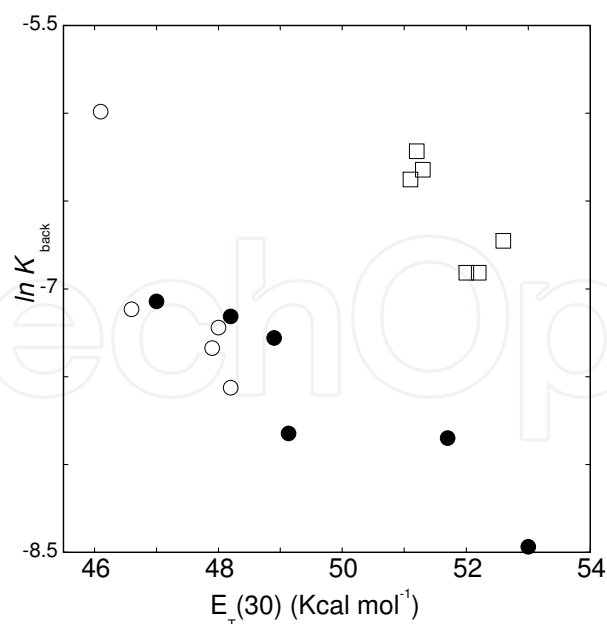
Fig. 4.1. Comparison of the logarithm of the rate constants of the back thermal reaction of the nitrobenzospiropyran: in the ionic liquids based on the [NTf₂] anion (black circles), set A in Scheme 4.2;[35] in ionic liquids based on [P$_{6,6,6,14}$], [P$_{1,4,4,4}$][36] cations (open circles) set B in Scheme 4.2, and same anion [NTf₂] together with 1-alkyl-3-methylimidazolium [C$_n$MIM] cation, with different chains[37] (open squares) set C in Scheme 4.2.
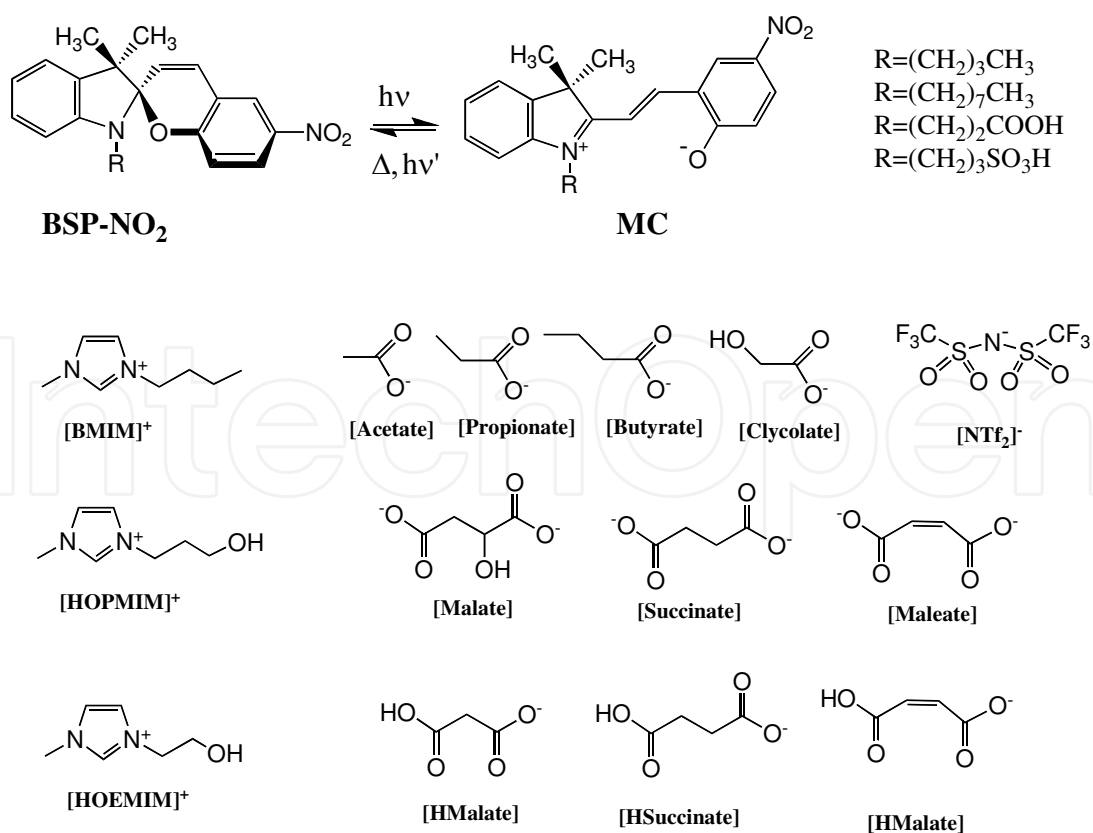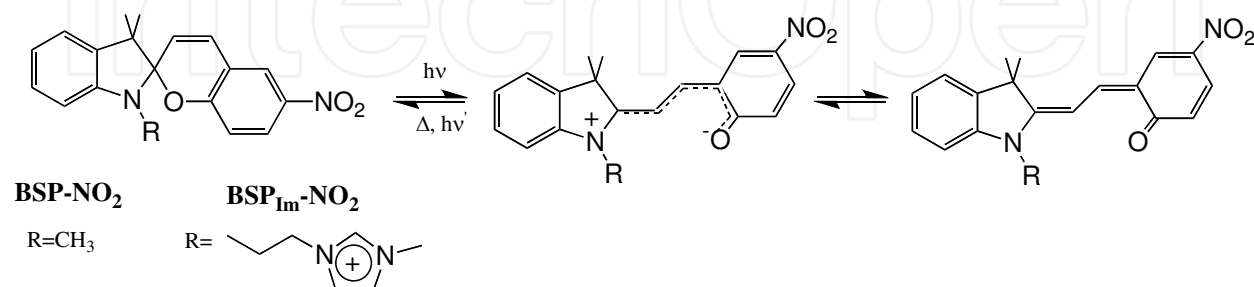

Scheme 4.3

The BSP-NO_2 was studied in some ILs reported in Scheme 4.4, entries 27 to 37 in Table 1.[42] The authors obtained an excellent linear correlation between the logarithm of the thermal reversion as a function of the parameter E_{sp} defined as $28591/\lambda_{max}$(nm) where λ_{max} represents the maximum absorption of the merocyanin form. Moreover, a direct proportionality between the activation energy for the thermal reversion as a function of the activation entropy (ΔS^*) was observed.
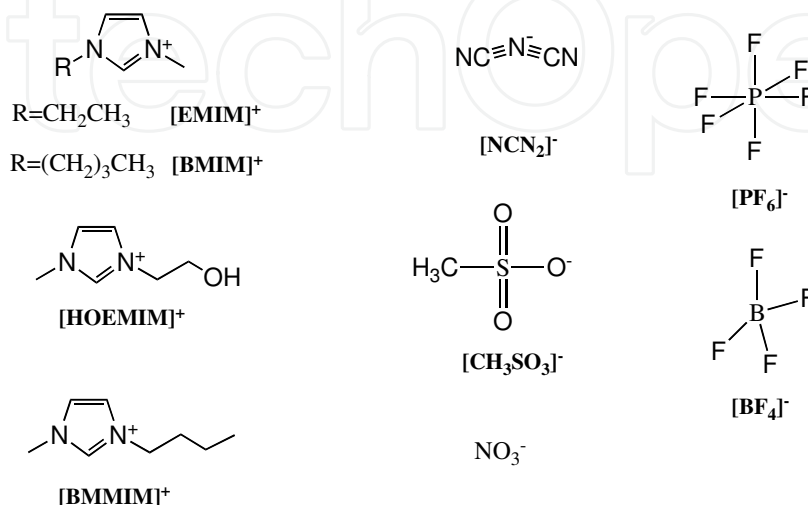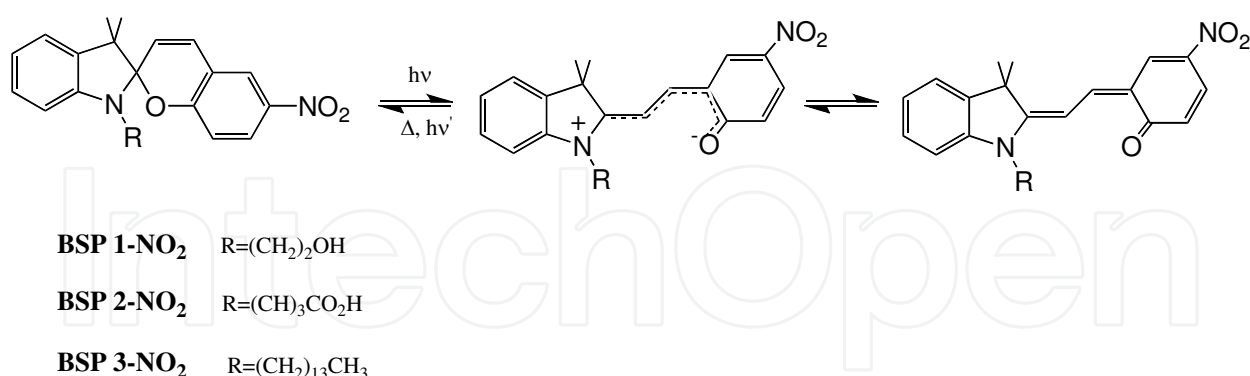

Scheme 4.4

Diamond and co-workers extended their previous work by attaching an imidazolium cation to the spiropyran, Scheme 4.5.[43] The new compound BSP_{Im}-NO_2 was studied in several ILs based on derivatives of the benzimidazolium cation and [NTf$_2$] anion, set C in Scheme 4.2. The rate of thermal recovery of BSP_{im}-NO_2 was found to be 14 times faster than the reference compound BSP-NO_2 in [C_6MIM][NTf$_2$]. In addition, the BSP_{Im}-NO_2 equilibrium is shifted towards the closed form. The authors considered that the IL forms nano-structured domains of polar and non-polar nature. The side group of BSP_{im}-NO_2 would interact with the polar domain, while the photoswitchable part of the molecule would be accommodate in the non-polar domain. The compound would be unable to move to more polar regions capable of stabilizing the open form. In contrast, unbound BSP is relatively free to migrate from one domain to the other.

Scheme 4.5

The same system was further investigated using three nitrobenzopyrans BSP 1-NO_2, R=(CH$_2$)$_2$OH; BSP 2-NO_2, R=(CH$_2$)$_3$CO$_2$H and BSP 3-NO_2, R=(CH$_2$)$_{13}$CH$_3$, Scheme 4.6, based on the ILs from set B, Scheme 4.2.[44]

BSP 1-NO$_2$ R=(CH$_2$)$_2$OH

BSP 2-NO$_2$ R=(CH)$_3$CO$_2$H

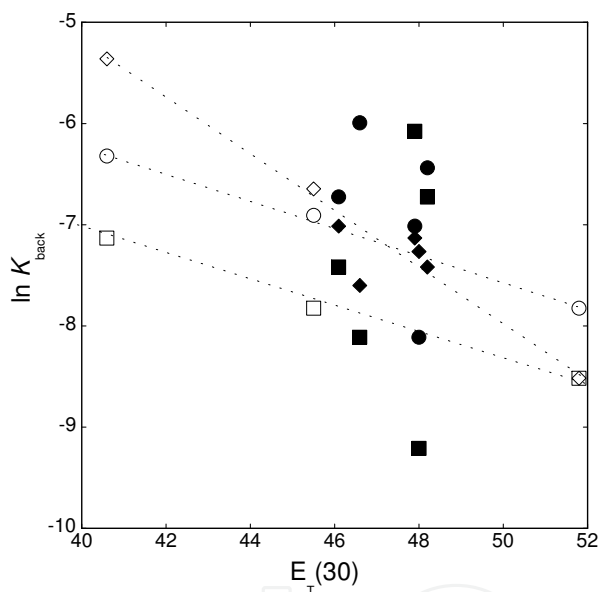**BSP 3-NO$_2$** R=(CH$_2$)$_{13}$CH$_3$

Scheme 4.6

Fig. 4.2. Representation of the logarithm of the rate constants for BSP 1-NO$_2$ (●),BSP 1-NO$_2$ (■), BSP 1-NO$_2$ (♦) in the ILs from set B, Scheme 4.2. The same for the solvents ethanol, acetonitrile and dichloromethane (equivalent open symbols)[44]

Clearly the E$_T$(30) still gives a linear relation with the logarithm of the rate constant in molecular solvents, but fails of significance in ILs.

Hydroxyl ILs were compared with non-hydroxyl analogs, Scheme 4.7.[45] The E$_T$(30) parameter is lower (51.6-52.4) Kcal.mol^{-1} for non-hydroxyl than for hydroxyl ILs (55.5-62.0) Kcal mol^{-1}. Positive photochromism takes place only for the lower E$_T$(30) values (< 56.2), while negative photochromism occurs for higher E$_T$(30) values (>60.1); ILs based on [HOEMIM]$^+$ and the anions [PF$_6$]$^-$, [NTf$_2$]$^-$ and [ClO$_4$]$^-$. This is in accordance with a stabilization of the merocyanine form in polar solvents. No linear correlation was obtained for the back thermal reaction with the E$_T$(30) value.

[EMIM]+ [Cl-] [Acetate] [NO₃-]

[HOEMIM]+ [DCA]- [ClO₄-]

[HOPMIM]+ [NTf₂]- [PF₆-]
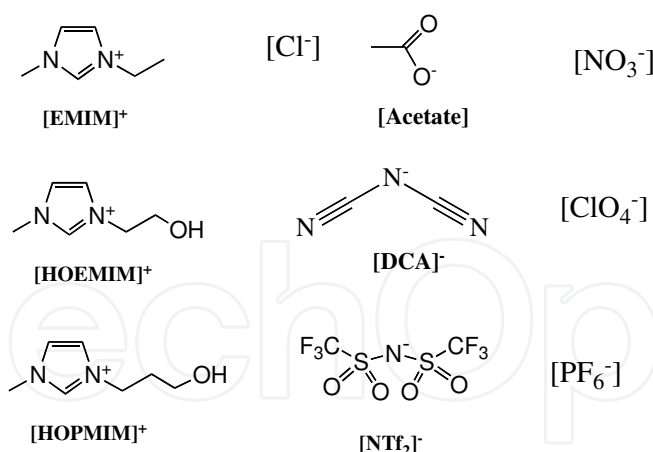
Scheme 4.7

4.1.2.2-Spirooxazines

Spirooxazine Scheme 4.8 was also studied in the presence of the ILs, Set C, Scheme 4.2.[37] The effect of the increasing of the side chain length of ILs based on imidazolium cations of different lengths and [NTf₂]- was found to have only minor effects on the rate of the thermal recovery of the merocyanine form in spirooxazines as well as in nitrobenzospiropyran.
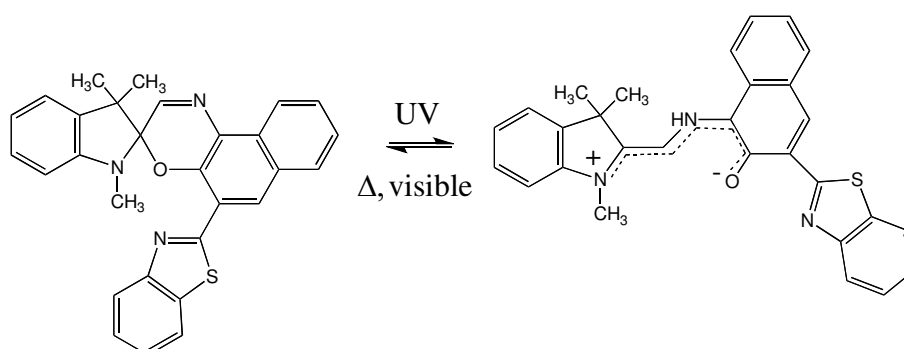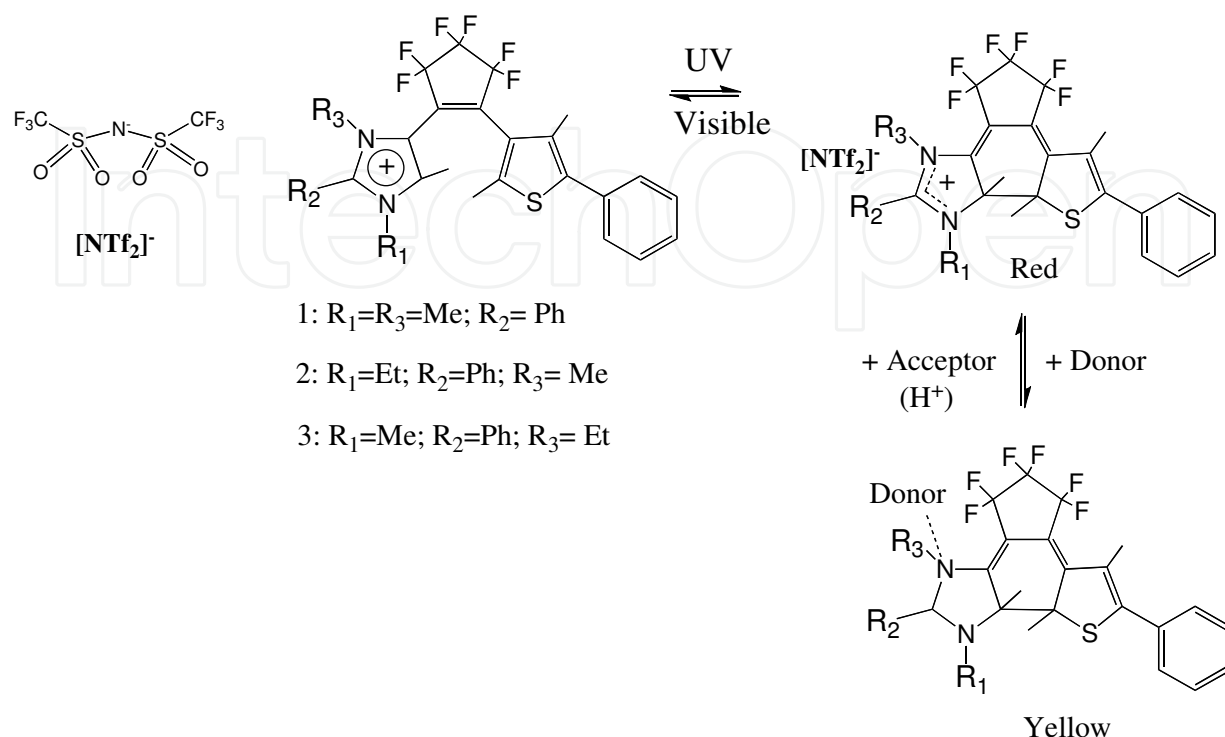

Scheme 4.8

The thermal reversion of spirooxazine, Scheme 4.7 was also studied in the ILs of set A in Scheme 4.2.[46] The recovery is slower in ionic liquids than in molecular solvents with similar polarity, indicating a greater degree of interaction between ILs and MC$_{(SO)}$, lifetime of 90.9 s in [P$_{6,6,6,1}$][NTf₂] that compares with 19.6 s in acetonitrile. The thermal back reaction MC$_{(SO)}$ to BSP is more dependent on the temperature in polar protic ILs like [BMIM]+ than in aprotic ILs as [P$_{,6,6,6,14}$]+.

4.1.2.3-Diarylethenes

Cationic diarylethenes were synthesized by appending an imidazolium directly connected to the central ethane unit as an aryl group in order to participate in the photochromic hexatriene-cyclohexadiene reaction, Scheme 4.9.[47] At least one of these compounds (1-open form) is described in the experimental part as being an oil, and probably is an intrinsically photochromic ionic liquid, see below.[48] The solvatochromic behaviour of 1 was studied in two ionic liquids, [EMIM][NTf₂] and [EMIM][EtSO₄], as well as in some common solvents. The closed ring form shows different absorption spectra depending on the anion of the IL. The red form is stabilized in [EMIM][EtSO₄] while the yellow form in

[EMIM][NTf$_2$]. The changes in colour were attributed to the different donor-acceptor properties of the solvents.

1: R$_1$=R$_3$=Me; R$_2$= Ph

2: R$_1$=Et; R$_2$=Ph; R$_3$= Me

3: R$_1$=Me; R$_2$=Ph; R$_3$= Et

Scheme 4.9

4.1.3 Photochromism in magnetic ionic liquids.

The photochromism of azobenzene, Scheme 2.3, was investigated in a greenish paste of equimolar quantities of the magnetic IL constituted by [BMIM][Fe^{III}Cl$_4$] and the photochromic compound.[49] Before irradiation, the mixture showed a paramagnetic linear response similar to the pure IL. Irradiation of the system gives rise to an increase of the magnetic moment tending asymptotically to a limit. The photochromic system is reversible, but the magnetic transformation is irreversible. This irreversibility was explained by the formation of aggregates of the iron chloride complex.

4.2 Biphasic systems

Some ILs are not miscible with water giving rise to biphasic systems, as for example [BMIM][PF$_6$] and water. The question is how the existence of these two phases can influence the photochromism. The flavylium photochromic system is very adequate to carry out these kind of studies due to the existence of a network of species exhibiting different properties, in particular colour, and reversibly reached through pH, light and thermal inputs and the possibility of switching from one phase to another.

4.2.1 Flavylium compound with cis-trans isomerisation thermal barrier

A simple example of this behaviour is the biphasic system involving 4′-hydroxyflavylium in water/[BMIM][PF$_6$],[50] Figure 4.3. Similarly to Scheme 2.9, in acidic water solutions of 4′-hydroxyflavylium, it is possible to distinguish the usual species, flavylium cation (**AH$^+$**),

quinoidal neutral base (**A**), hemiketal (**B**), *cis*-chalcone (**Cc**), and *trans*-chalcone (**Ct**). 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. The thermal barrier between the *cis*-chalcone and *trans*-chalcone in water was calculated, 129 kJ mol⁻¹. One interesting feature of this system in water is the transformation of the flavylium cation, **AH⁺** (pH=1) into **Cc²⁻** upon a pH jump to pH=12, for example. The ionized *cis*-chalcone takes more or less 1 day to be transformed into the thermodynamic product, **Ct²**. In other words, the *cis-trans* isomerisation thermal barrier is also observed for the di-ionized chalcones. A faster conversion takes place if the solution is irradiated. This is in contrast with the analogous 7′4′-dihydroxyflavylium behaviour where the appearance of **Ct²⁻** from **AH⁺** at the same pH takes only a few minutes. The practical result is the possibility of isolating in the aqueous solution the species **Cc²⁻**, see Figure 4.3.

Fig. 4.3 - See from left side: 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 alkalinisation of the aqueous phase (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.

When an aqueous solution of the compound 4′-hydroxyflavylium perchlorate, at pH=1.0, is added to a similar volume of the ionic liquid, the diffusion to the IL is slow and the photo in Fig. 4.3a can be obtained. However, after *ca.* 1 minute of vigorous shaking, the bottom IL solution becomes yellow, indicating that the **AH⁺** species was transferred to the IL phase Fig. 4.3b. Figs. 4.3c – 4.3f show four stages obtained upon a pH jump from 1 to 12 carried out in the aqueous phase. A few seconds shaking makes basic the IL phase and by consequence the orange base, A, is formed. The base, A, is transformed in to the ionized **Cc²⁻**, that is more stable in the water phase and goes up. In Figure 4.3e this species is already almost completely transferred into the water phase. As mentioned, **Cc²⁻** gives **Ct²⁻** slowly, but the respective conversion can be accelerated by light or heating. The final equilibrium in this step is obtained with the **Ct²⁻** species completely dissolved into the aqueous phase, Fig. 4.3f. A further step of the cycle consists into a pH jump in the aqueous phase, back to pH=1.0,

followed by vigorous shaking of the two phases. This procedure allows the **Ct** species formed in the aqueous phase to be completely transferred into the IL, Fig. 4.3g. At this pH value, **AH⁺** is the thermodynamic species at the equilibrium (in water and in IL), but due to the isomerisation barrier the **Ct** species in the IL is relatively stable, with a lifetime of 9.7 days at room temperature, in the dark. This value compares with the shorter lifetime of 0.3 days in aqueous solutions obtained under similar conditions.[51] The much lower back reaction to reach the equilibrium in ILs is in agreement with behaviour observed in section 3.3.2. The flash photolysis of the compound in the IL is similar to water, with two processes taking place after the light pulse: the first one corresponds to the bleaching of the solution at 340 nm occurring during the lifetime of the flash, Fig. 4.4b, assigned to the *trans-cis* isomerisation that his faster than *circa* 5 ns (the limit of flash photolysis apparatus); the second one is the formation of **AH⁺** from **Cc**, with k_{obs}=0.2 s⁻¹, clearly shown by the increasing absorption at 440 nm, Fig. 4.4a. In aqueous solution, at pH 1 flavylium is formed from the meta-stable state in 7.6 s⁻¹. In the ionic liquid, the equivalent process occurs with a rate constant of 0.2 s⁻¹, Fig. 4.4a. The lowering of the rate constant in the IL could be due to its peculiar structure or reflect the expected lower proton concentration in the ionic liquid phase.
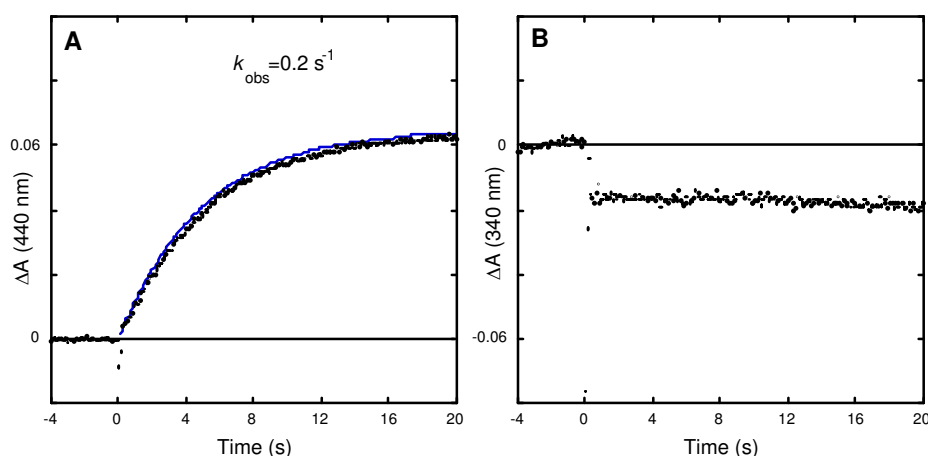

Fig. 4.4 - Flash photolysis of the **Ct** species in [BMIM][PF₆], in contact with an aqueous solution at pH=1: A) kinetics of **AH⁺** formation; B) kinetics of **Ct** disappearance.

The system allows to concept a write–read-erase cycle as shown in Figure 4.3: 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 3.

4.2.2 Flavylium compound lacking of the cis-trans isomerisation thermal barrier

In the case of the compound 7′4′-dihydroxyflavylium in the same biphasic system water/[BMIM][PF₆] the situation is similar but due to the existence of one more hydroxyl substituent an ionized quinoidal base, A⁻, can be formed, and in water no cis-trans isomerisation barrier exists.[13]
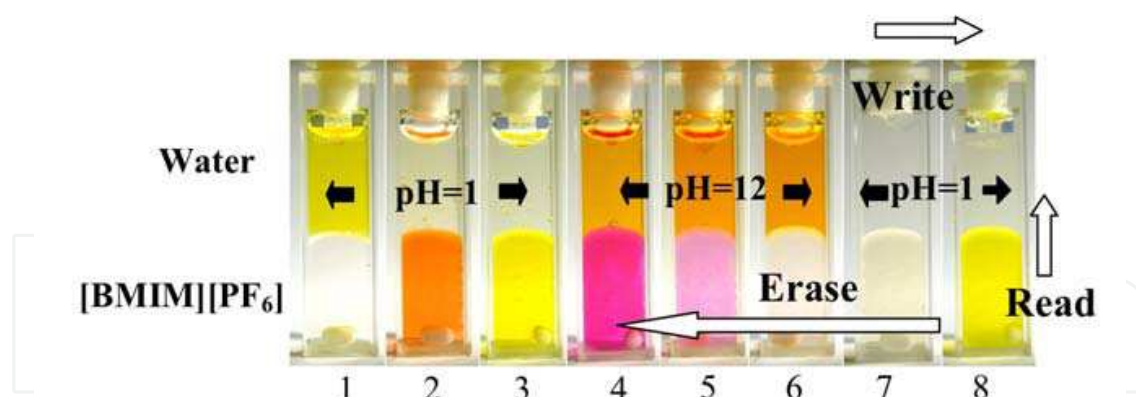
Fig. 4.5. A cycle involving the compound 7´4'-dihydroxyflavylium[13]

The solution of the flavylium compound was dissolved in water at pH=1.0 (flavylium cation) and poured in a cell previously filled with the ionic liquid (1). The diffusion of the flavylium compound from the water to the ionic liquid is very slow and shows two bands (like a chromatographic separation) the front band being orange (quinoidal base) and the back band yellow flavylium cation (not shown). This effect can also be observed if the mixture is shaken only a few seconds (2) or vigorously shaken for 1-2 minutes (3) before allow separation of the two phases. Assuming the polar and non-polar nano-domains of the ionic liquid, these results seem to indicate that diffusion to the non-polar domain is faster than diffusion to the polar domain, probably because in this last there is a competition with water. Apart the existence of the **A⁻** species, this system is similar to the previous one and a cycle to write-read-erase can also be performed. This is possible because contrary to water the **Ct** form is metastable in the IL phase (after 1 hour at 40 ºC less than 2% of flavylium cation was formed).
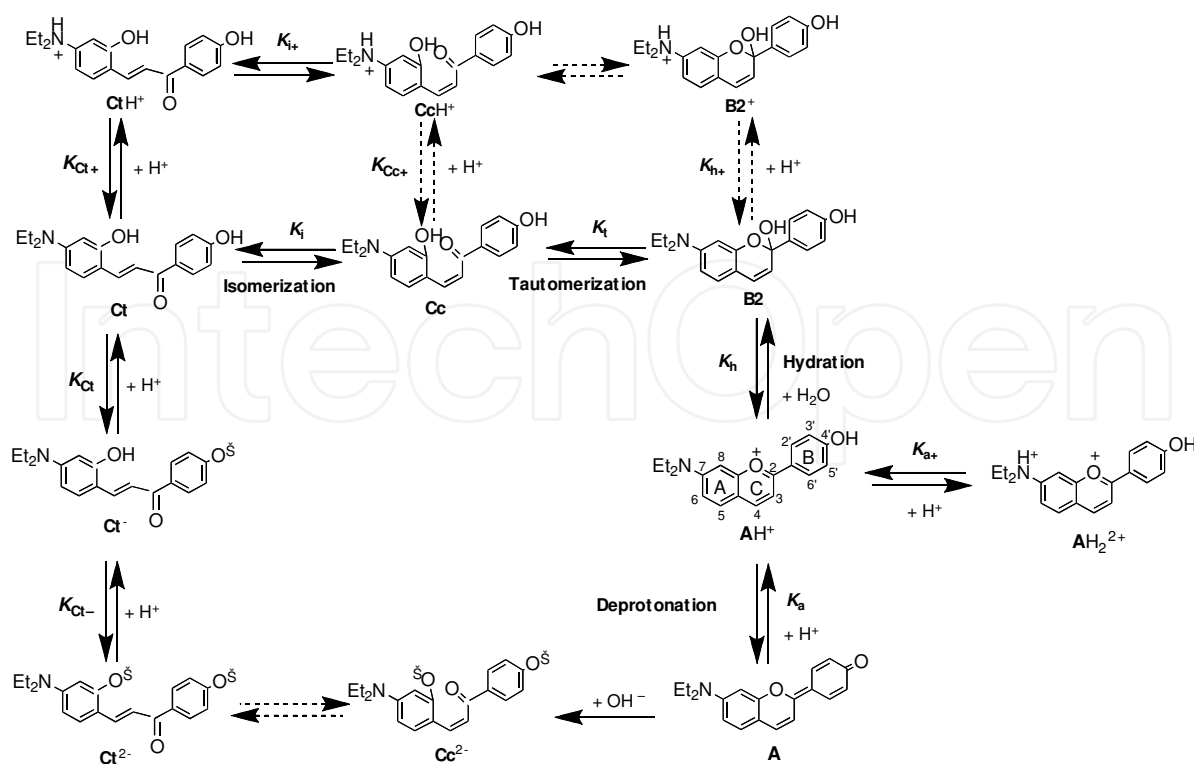
Scheme 4.10

A beautiful palette of colours is achieved when amine substituents are introduced in the flavylium backbone. In the case of the compound *trans*-4-(*N*,*N*-diethylamino)-2,4'-dihydroxychalcone, the network is once more similar to the previous compounds, Scheme 4.10.[52]

The presence of the amine not only permits to achieve red and blue colours but also introduces some peculiarities to the system, due to the possibility of the amine protonation. It is worth noting the formation of the species CtH+ that is spontaneously transformed into AH+, in a time scale of minutes, depending on pH. For this compound, as for those bearing amines substituents in general, there is no significant *cis-trans* isomerization barrier and no photochromic activity was detected in water[53]
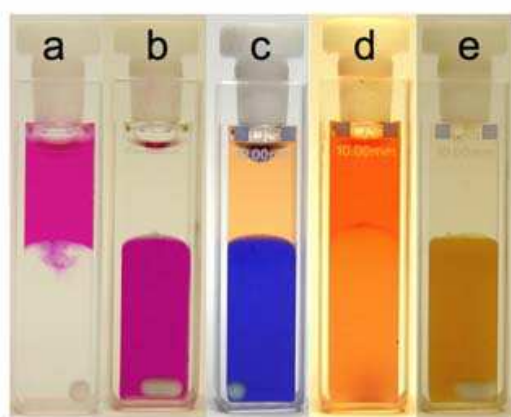

Fig. 4.6 Behaviour of 7-(*N*,*N*-diethylamino)-4'-hydroxyflavylium tetrafluoroborate in biphasic systems constituted by aqueous solution (upper phase) and 1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF$_6$] (lower phase), upon pH jumps in the aqueous phase. a) pH=1.0 in the aqueous phase, 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. 4.6 presents a sequence of photos showing how 7-(*N*,*N*-diethylamino)-4'-hydroxyflavylium is partitioned in the biphasic system constituted by water and [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. 4.6a. When the system is vigorously shaken and the two phases allowed to separate, the flavylium cation completely dissolves into the ionic liquid phase, Fig. 4.6b. 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 are separated, it is possible to see a blue colour in the ionic liquid phase due to the base, **A**, Fig. 4.6c. The blue colour 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. 4.6). On the other hand, high hydroxyl concentrations favour the formation of orange **Ct²⁻** that is transferred to the aqueous phase, Fig. 4.6d. Acidification of this last solution followed by immediate shaking of the two phases, leads to dissolution of **Ct/CtH+** into the ionic liquid, Fig. 4.6e. 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+, (because **Ct+** is formed) while at lower proton concentrations the **Ct** species is the thermodynamic product. In conclusion, as in the previous examples 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 in the IL phase, in contrast with its absence in water. When the ionic liquid phase containing **Ct** at pH=6.8 (measured in the upper aqueous phase) is irradiated, the photochemical product **AH+** appears. The system reverts back to **Ct** after ca. 11 hours in the dark, at 22 °C, Fig. 4.7.
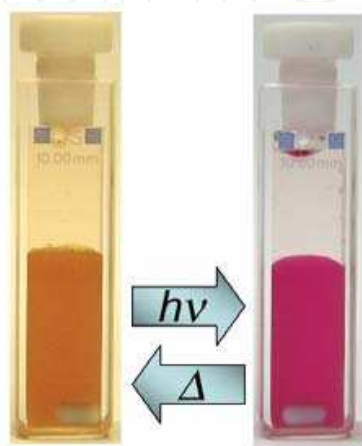

Fig. 4.7 Photochromic system of 7-(*N,N*-diethylamino)-4′-hydroxyflavylium in the IL phase of water/ionic liquid [BMIM][PF$_6$] biphasic systems.

Flash photolysis was carried out in the Ct species on the bottom phase and the transient absorptions at 450 nm (where Ct absorbs) and at 510 nm (where AH+ absorption spectrum peaks) were monitored. 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. 4.8). The recovery is very extensive but not complete, and in fact a small but significant offset is observed, which increases with decreasing pH. The rate constant is pH independent within the pH range of Ct, and is equal to 0.58 s^{-1}.

The appearance of an offset explains why net photochemistry is observed in the IL, in spite of an efficient back reaction, Fig. 4.7. The chalcone should be preferentially solvated by the [BMIM] organic cation rather than water. As **Cc** is formed by photoisomerization of **Ct**, it is either readily converted back to **Ct** (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, where a small fraction of the flavylium cations would be stabilized by hydrogen bonding and electrostatic interactions with the anions into the polar domains that contain water.[54]

In conclusion, the IL phase permits the existence of photochromism in chalcones that are not photochromic in water. Moreover, ILs can be used to increase the kinetic barrier for *trans-cis* isomerization of chalcones, allowing the use their respective network as models for optical memories.
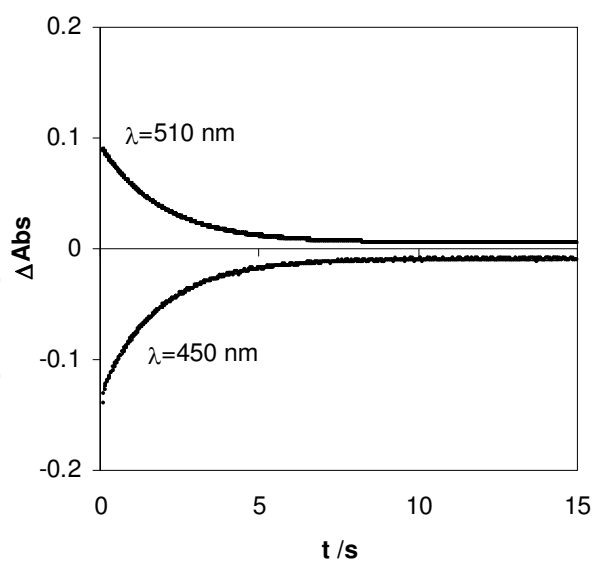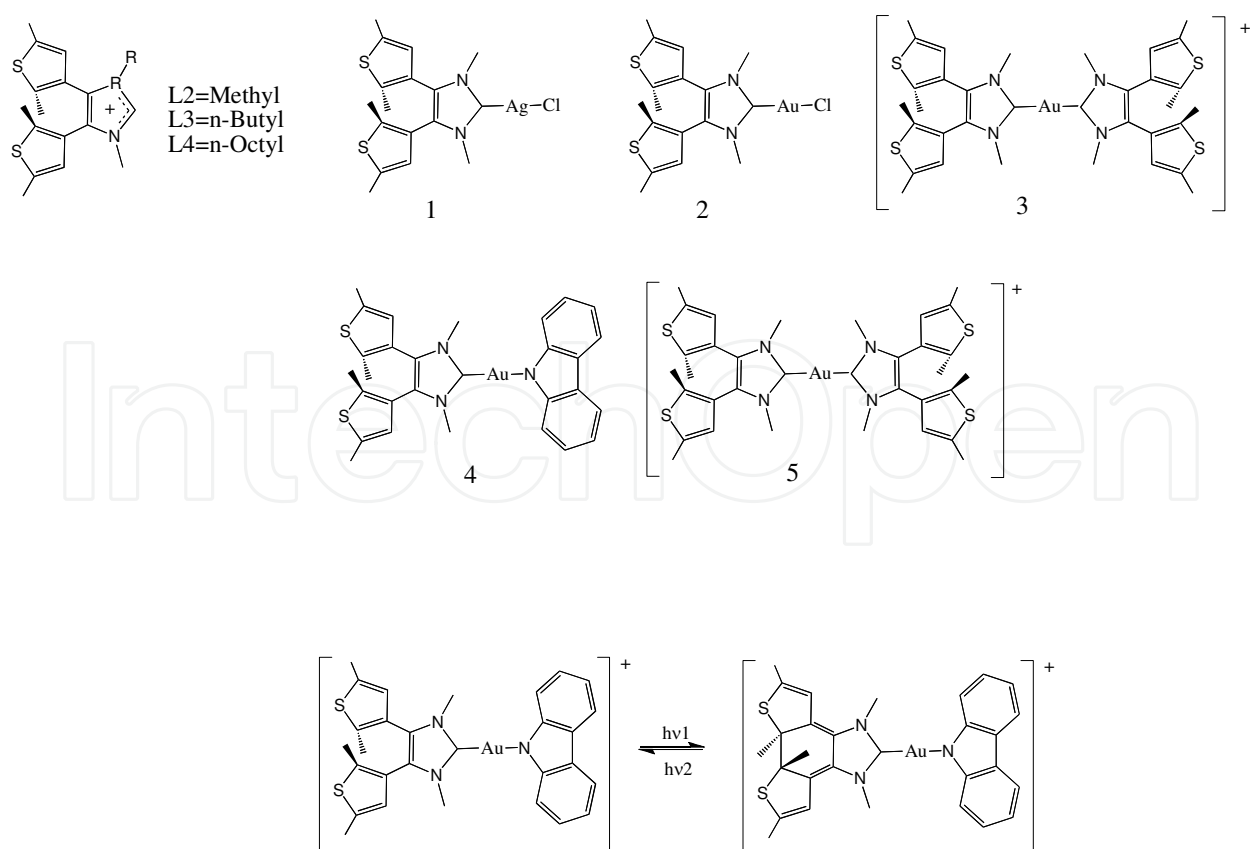
Fig. 4.8 Flash photolysis traces taken in the ionic liquid phase, after shaking with the aqueous phase at pH 6, and waiting *ca*. 30 minutes to obtain a good transparency of the ionic liquid solution.
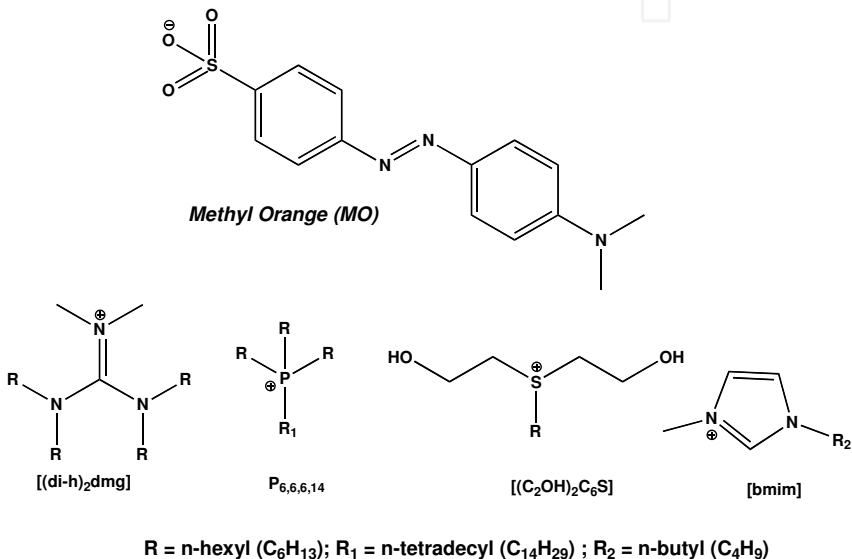
5. Intrinsically photochromic ionic liquids.

A series of diarylethene containing N-heterocyclic carbenes was reported.[55]

Scheme 5.1.

The quantum yields of photocyclization and cycloreversion as well as the half life of the closed forms of L2-PF$_6$, L3-PF$_6$, L4-PF$_6$ 1, 2, 3, 4, Scheme 5.1, were presented in the supplementary material of ref.[55]. The compound [L3][NTf$_2$] is the only one presenting the melting point below 100 °C (<20 °C) and thus the only behaving as a RTIL. The authors claim that the RTIL [L3][NTf$_2$] is also photochromic but no further experimental data is available in the communication or in the supplementary material.

The first claim of the term intrinsically photochromic IL regards the use of methyl orange and the appropriate organic cations in order to render the assemble liquid, Scheme 5.2.[56] In particular the guanidinium has a low melting point (48 °C) and the sulfonium, phosphonium are RTILs, Table 2.

Methyl Orange (MO)

[(di-h)$_2$dmg]   P$_{6,6,6,14}$ [(C$_2$OH)$_2$C$_6$S]   [bmim]

R = n-hexyl (C$_6$H$_{13}$); R$_1$ = n-tetradecyl (C$_{14}$H$_{29}$) ; R$_2$ = n-butyl (C$_4$H$_9$)

Scheme 5.2.

The photochromism of these ILs was studied in ethanol, in matrixes of a Polaroid B72 polymer or in tin films obtained by pressing the ionic liquid between two lamellas of quartz. This last experiment allows the study of the ionic liquids without any additional solvent or polymeric matrix. The *trans* form of the methyl orange ILs (the stable one in the dark) was irradiated with a light flash and the kinetics of the back *cis-trans* isomerisation monitored. The results are summarized in Table 2.
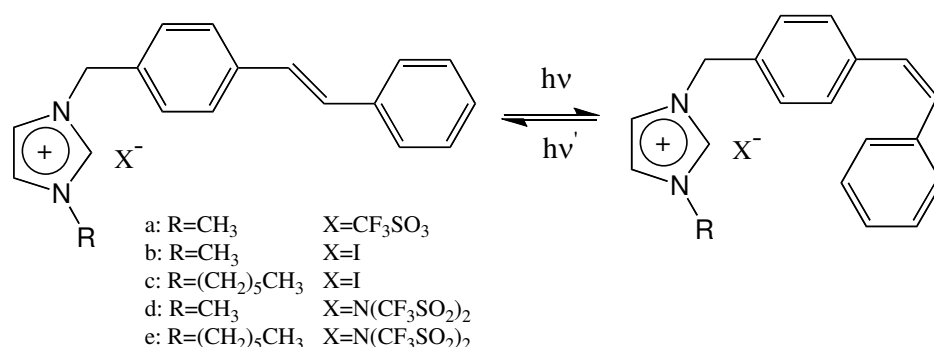
Photochromic Salt	Mp (Tg)[a] / °C	k_{back} (s^{-1}) 25 °C
Na MO	> 300	0.2 (Ethanol)
[BMIM][MO]	85 (-42)	1.2(Ethanol)/[b]/[b]
[(di-H)$_2$DMG][MO]	48(-41)	0.3 (Ethanol)/[c]/0.003(PB72)
[(C$_2$OH)$_2$C$_6$S][MO]	RTIL	2 (Ethanol)/0.3 (film)/ 0.1(PB72)
[P$_{6,6,6,14}$][MO]	RTIL	42.6 (Ethanol) / 2.1 (film)/[d]

a) Melting point (glass transition); b) Solid at room temperature; c) Films not stable (very hygroscopic); d) no mixing

Table 2. Ionic liquids form methyl orange[56]

The thermal back reaction in ethanol depends strongly on the cation. Regarding the two RTILs, the slower process corresponds to the sufonium cation, which is highly viscous and the only one able to form hydrogen bonds with methyl orange. Dissolution of the ILs in the polymer or in the films decreases the absolute rate of isomerisation, but the trend observed in ethanol is the same. The more rigid structure of the polymer is expected to introduce some constrains in the isomerisation process. In the case of the ILs films, the structural organization of the ILs, in particular its higher viscosity also renders the isomerisation slower.

A strategy to obtain photochromic ionic liquids was reported by Arai and co-workers and consists on appending an imidazolium substituent to a stilbene, Scheme 5.3.[57] The *cis* isomers are RTILs except for b) and the *trans* analogs are solids except for d) and e) which while being IL are not RTILs. Moreover, while the *trans* isomers are moderately emissive with quantum yields around 0.02, the *cis* analogs practically do not show fluorescence. This permits the authors to claim the possibility of switching photochemically from solid to liquid as well as from emissive to non-emissive systems.

a: R=CH$_3$ X=CF$_3$SO$_3$
b: R=CH$_3$ X=I
c: R=(CH$_2$)$_5$CH$_3$ X=I
d: R=CH$_3$ X=N(CF$_3$SO$_2$)$_2$
e: R=(CH$_2$)$_5$CH$_3$ X=N(CF$_3$SO$_2$)$_2$

Scheme 5.3

Another strategy to obtain photochromic ILs is represented in Scheme 5.4,[58] (melting point 50 °C). The photochromism of this compound was studied in organic solvents and ILs. *Trans-cis* isomerisation takes place by irradiation and the system is thermally reversible. The quantum yield of isomerisation decrease only slightly with the increasing viscosity of the solvent, from 0.12 in [BMIM][PF$_6$], (η=241 cP), to 0.19 in toluene (η<1 cP). No solvent dependence was observed for Arrhenius parameters of the thermal back reaction. No information is given about its behaviour as pure solvent.
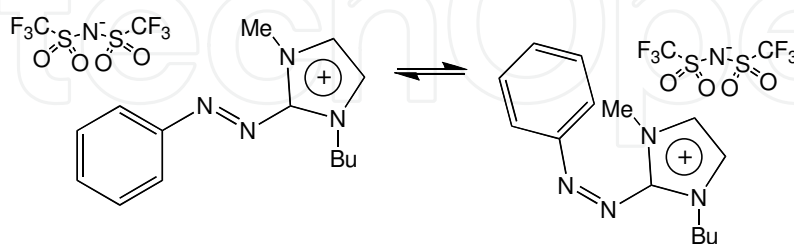
Scheme 5.4

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