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Formation of a *leuco* Spirolactone from 4-(2-Carboxyphenyl)-7-diethylamino-4′-dimethylamino-1-benzopyrylium: Design of a Phase-Change Thermochromic System Based on a Flavylium Dye

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Abstract: A phase-change thermochromic system was designed through the reversible transformation of the 4-substituted flavylium dye 4-(2-carboxyphenyl)-7-diethylamino-4′-dimethylamino-1-benzopyrylium into its *leuco* form, in the presence of a developer (ethyldiisopropylamine) and a suitable solvent (e.g., acetonitrile, *n*-pentadecanonitrile). The *leuco* form of the flavylium-based dye is a spirolactone species whose ring opens at low temperature (below the solvent melting point) to form the blue flavylium cation. Decarboxylation of the lactone to give 4-phenyl-7-diethylamino-4′-dimethylamino-1-benzopyrylium was observed upon irradiation of the system with UV light, erasing the thermochromic effect.

Keywords: flavylium · lactone · photodecarboxylation · spiro compounds · thermochromism

Introduction

Flavylium compounds constitute an important family of molecules that comprises anthocyanins, the ubiquitous dyes which are found in flowers and fruit (Figure 1). According to the position and nature of the substituents on the flavylium ring system, a panoply of natural and synthetic flavylium derivatives has been reported in the literature.[1] Besides their fundamental role in coloring flowers and fruit, some synthetic analogues show very interesting pH dependences and photochromic properties leading to multistate systems operated by external stimuli such as pH and light.[1b,2,3] In particular, flavylium compounds have been claimed as models for optical memories[4] and even as being capable of mimicking some elementary properties of neurons.[5]

In spite of the fact that 4-substituted flavylium compounds were the first flavylium structures to be reported in literature after the pioneering work of Bülow at the beginning of the 20th century,[6] their chemistry has been less explored most probably because of their scarce abundance in Nature and by the fact that the synthetic analogues do not show relevant photochromic properties.

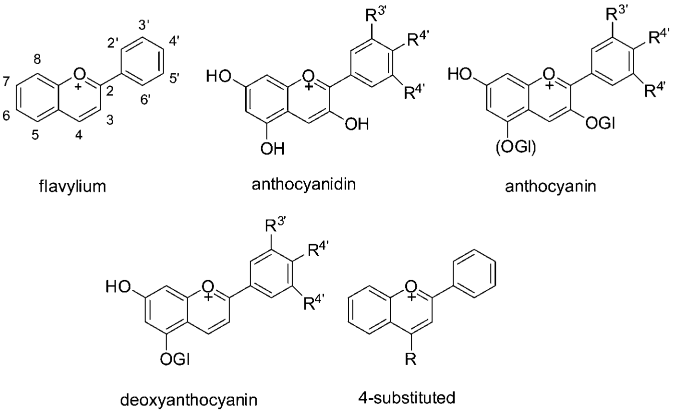

Figure 1.

It is well established that flavylium compounds are involved in a more or less complex network of chemical reactions as shown in Scheme 1.[1b,2,7,8] Flavylium cation (AH^+) is the stable species at low pH values. When the pH is raised, quinoidal base (**A**), or the hemiketal form (**B2**) can be obtained by deprotonation of the hydroxyl substituent or hydration at position 2, respectively. On the other hand, the hemiketal can open leading to the *cis*-chalcone (**Cc**) which can isomerize to form the *trans*-chalcone (**Ct**). Scheme 1 can thus be viewed as representing a multistate system where

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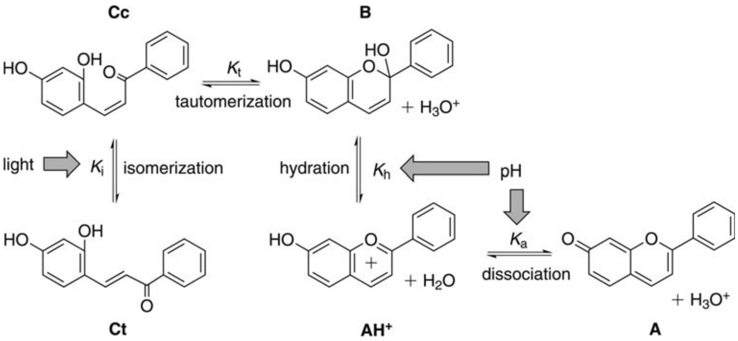
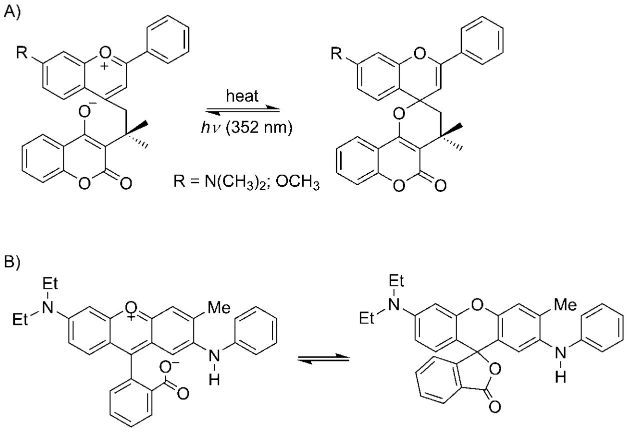


Scheme 1.



Scheme 2.

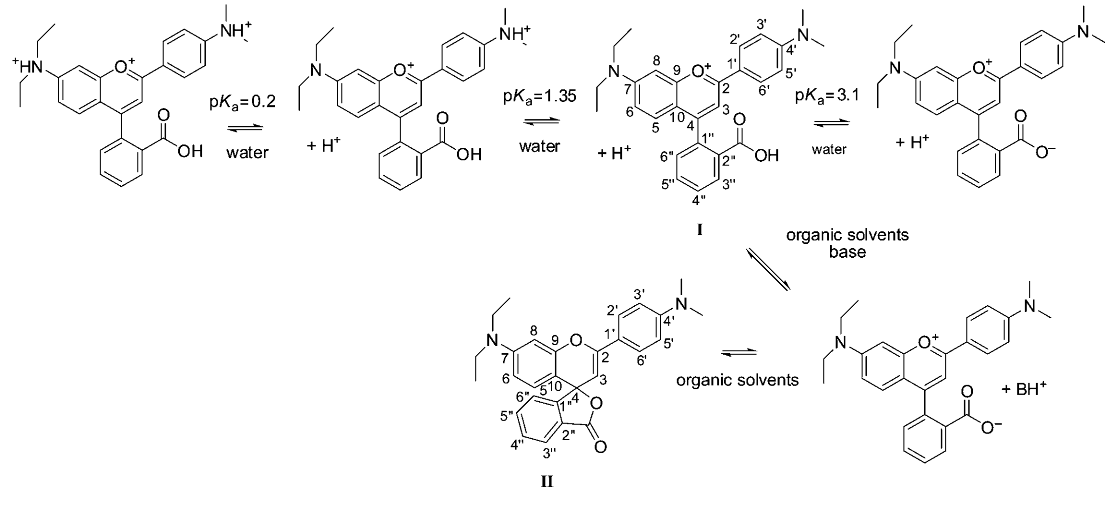
the different states can be reached by external stimuli, such as light and pH.

Previous work carried out in 4-substituted flavylium compounds has shown that they are not easily hydrated in aqueous solutions to give the hemiketal and the subsequent species according to Scheme 1. For example, in the case of the compound 4-methyl-7-hydroxyflavylium,[9] only $\mathbf{AH^+}$ and **A** can be detected in the pH range from 1 to 8. However, 4-substituted flavylium compounds bearing more elaborated substituents, in particular aromatic rings with a nucleophilic group at the α position, can give rise to the formation of spiropyran derivatives. Some examples were recently reported: a flavylium compound with an attached phenolate[10,11] (Scheme 2A),[10] and a dibenzo-fused pyrylium with an attached benzoic acid that forms a lactone (Scheme 2B).[12]

In this work, we report on a strategy to obtain a *leuco* spiropyranlactone (compound **II**) from a flavylium cation bearing a 4-(2-carboxyphenyl) substituent (compound **I**), using an organic amine in a suitable organic solvent to deprotonate the carboxylic acid and promote lactonization (Scheme 3). This conversion can then be controlled by using temperatures below the solvent melting point, which again induces the formation of the colored flavylium species. This process is reversible and thus enables the design of a thermochromic system based on flavylium compounds.

Results and Discussion

In Figure 2 the titration of the compound 4-(2-carboxyphenyl)-7-diethylamino-4′-dimethylamino-1-benzopyrylium (**I**) in aqueous solution followed by absorption (A) and emission spectroscopy (B) is shown. In the case of the absorption, the experimental results allow to detect unequivocally an acid–base equilibrium with a $pK_{a2} = 1.35$, as well as a second one at $pK_{a1} \approx 0.2$. These pK_a values are compatible with three flavylium species, bearing two and one protonated amines, as well as the non-protonated flavylium cation. The absorption of both (mono and bis) amino-protonated flavylium species are blueshifted in comparison with the non-protonated flavylium cation. Similar results have been found for other amino-substituted flavylium compounds,[13–15] confirming that the two observed pK_a values involve protonation of the amino groups. The value of 1.35 (mono-protonation)



Scheme 3.

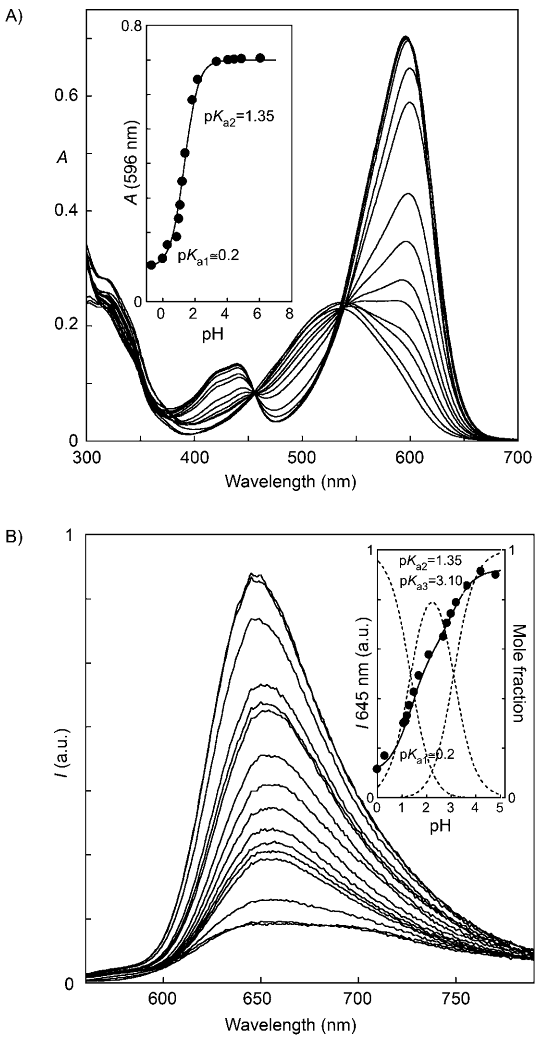


Figure 2. A) Absorption spectra of compound **I**, 1.0×10^{-5} M in water/ethanol 9:1 as a function of pH. B) Fluorescence emission spectra of the same compound 1.0×10^{-6} M, $\lambda_{exc}=540$ nm. Insets: fittings of the absorbance and of the emission intensity at specific wavelengths to obtain pK_a values.

compares with p$K_a=-0.4$ for 4′-aminoflavylium,[15] p$K_a=-0.6$ for 4′-dimethylaminoflavylium,[13] and p$K_a=-0.67$ for 7-(*N,N*-diethylamino)-4′-hydroxyflavylium.[14] There is no clear evidence of which of the *N,N*-dialkylamino groups, the 7 or the 4′, is protonated first; in principle it should be the one in position 4′, because the protonated amine in position 7 in the case of the compound 7-(*N,N*-diethylamino)-4′-hydroxyflavylium is more acidic than the protonated amine in position 4′ of the compound 4′-aminoflavylium, in spite of the donor effect of the hydroxyl in the former. On the other hand, the acid–base process of the carboxylic acid, expected to occur below pH 5, could not be observed by changes in absorption spectra suggesting that the aromatic carboxylic acid in position 4 does not conjugate substantially with the π system of the 2-phenyl-1-benzopyrylium moiety.

Analysis of the data of the spectrofluorimetric titration in Figure 2B is also compatible with the protonation of both amines, the first one observed by changes in the fluorescence emission intensity, and the second one detected through an analysis of the Stokes shifts (see Supporting Information, Figure S1). Moreover, another inflection at p$K_{a3}=3.1$ is now clearly detected in the fluorescence emission intensity, and is attributed to the deprotonation of the benzoic acid moiety. This behavior also suggests that in contrary to the ground state, the benzoic acid substituent is in resonance with the benzopyrylium system in the excited state. Therefore a full characterization of the acid–base equilibria is achieved within this set of experiments.

A pH jump from an acidic solution of compound **I** in water/ethanol (9:1) to the basic region leads to the formation of poor absorbing species compatible with less conjugated structures such as the hemiketal or a spirolactone involving the carboxylate moiety (compound **II** in Scheme 3). The system returns to the flavylium cation when a reverse pH jump back to the acidic region is carried out. However, if the basic solutions are left for some days, a slow evolution of the absorption spectra is observed and the system no longer reverts totally back to the flavylium cation, indicating that some decomposition product is formed.[16]

In order to observe the possibility of the spirolactone formation upon deprotonation of the carboxylic acid and considering that water is not an appropriate solvent to stabilize this neutral species due to its protic character, acetonitrile solutions of **I** were treated with an organic amine base. The absorption and fluorescence emission spectra of compound **I** in dry acetonitrile were monitored as a function of added ethyldiisopropylamine (EDIPA; Figure 3).

Addition of the base leads to the disappearance of the visible color with formation of a new band absorbing in the UV region, with $\lambda_{max}=313$ nm (and $\lambda_{max}{}^{em}=348$ nm, see Supporting Information, Figure S2). Representation of the absorbance as a function of the equivalents of added base shows that one equivalent of base is enough to the removal of the benzoic proton and formation of the new species. This is corroborated by the emission of the flavylium species (Figure 3B). The deprotonation reaction was also followed by ^{1}H NMR spectroscopy (Figure 4). The most affected proton is H3, followed by protons H3″, H8 and H5 (see Supporting Information for δ/ppm vs. equiv EDIPA plots, Figures S3, S4) which suggests that the new UV absorbing species is spirolactone **II**. This was confirmed by full assignment of ^{1}H and ^{13}C NMR spectra (see Supporting Information, Tables S1, S2). In particular, the δ ^{13}C value for C2 at 159.4 ppm is characteristic of the spirolactone and is not compatible with the formation of a hemiketal species, expected to be at ~100 ppm. However, formation of this last species in strongly basic aqueous solutions of **I** can not be excluded.

The *leuco* product was isolated by treating a solution of **I** in ethyl acetate/EDIPA 1:1, washing with water and moderately basic water in order to remove the amine, and drying. Evaporation of the solvent yielded a solid composed mostly by the spirolactone derivative (around 90% mol by ^{1}H NMR analysis, the remaining 10% mol was mainly EDIPA). Comparison between the IR spectra of this prod-

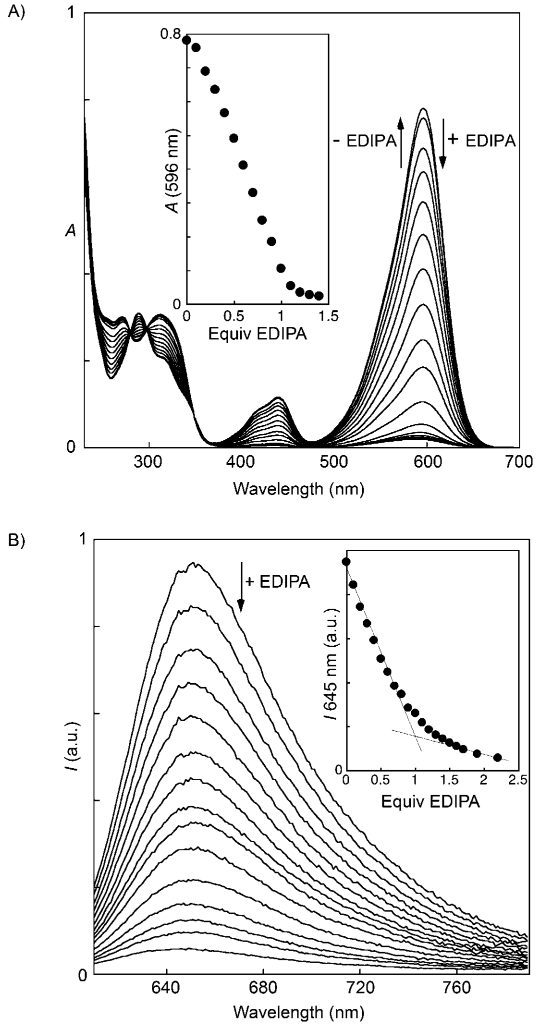


Figure 3. A) Absorption spectra of compound **I**, 1.0×10^{-5} M in acetonitrile, as a function of added ethyldiisopropylamine (EDIPA). B) The same followed by fluorescence emission spectra, 1.0×10^{-6} M, $\lambda_{exc}=596$ nm. Insets: mole ratio plots.

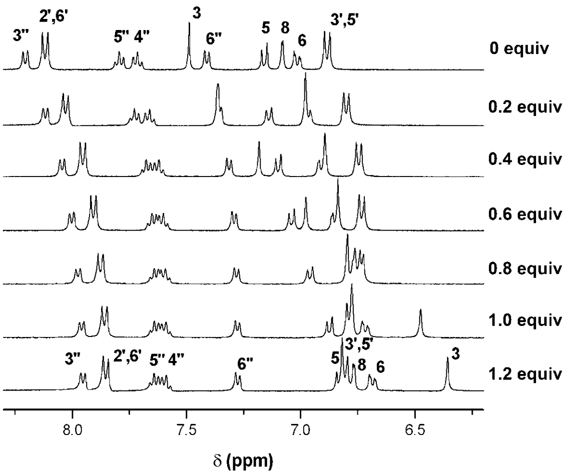


Figure 4. Titration of **I** with ethyldiisopropylamine (EDIPA) in CD_3CN. Refer to Scheme 3 for the assignment of the chemical shifts in the range comprised between 8.5 and 6 ppm.

uct with that of flavylium **I** (see Supporting Information, Figure S5), shows the disappearance of the band at 3462 cm^{-1} (COO–H stretching) and the shifting of the carbonyl stretching frequency from 1700 to 1751 cm^{-1}.

Thermochromism: Some molecules exhibit the property of changing the color according to the temperature. These molecules comprise spiroheterocyclic compounds,[11,17–19] salicyl-Schiff bases,[20–23] overcrowded ethylenes[24–26] and phase-change thermochromic materials (PCTM, organic thermochromic mixtures) that include crystal violet lactone and related compounds.[27–31] Thermochromism involving the present flavylium compound is a PCTM sample and was achieved by using EDIPA as a color developer, and different solvents, namely acetonitrile and *n*-pentadecanonitrile (Figure 5).

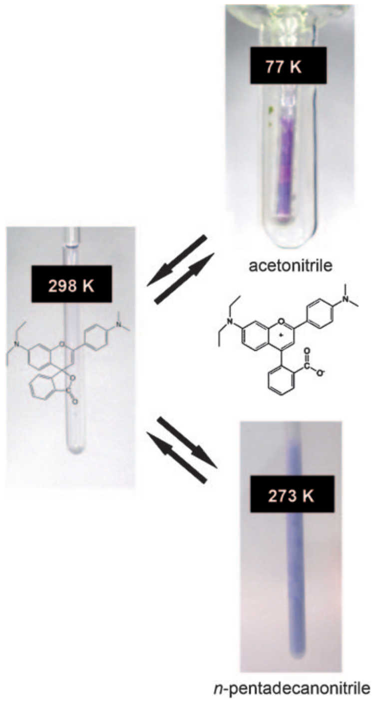


Figure 5. Thermochromic behavior of compound **I**.

Changes in the absorption spectra of the system **I**/EDIPA in *n*-pentadecanonitrile (containing 10% acetonitrile) were monitored as a function of temperature (Figure 6). At temperatures above the melting point of the solvent mixture (ca. 16°C) the characteristic spectra of the spirolactone **II** is observed, but as the temperature decreases, with the concomitant solidification of the solvent mixture, absorption spectra resembling that of the flavylium cation **I** appear. The increase in the flavylium-type absorption is more important immediately after freezing (around 16°C) and then continues in a slighter way with the reduction of temperature. Interestingly, the main absorption band of the flavylium species in the 480–680 nm range contains two shoulders (around 560 and 605 nm, respectively). In the case of acetonitrile, the change in color occurs at about −41 ± 1 °C, the freezing temperature of the mixture containing **I** dissolved in acetonitrile and 1.2 equiv of EDIPA (the melting point of acetonitrile is −45.7 °C).

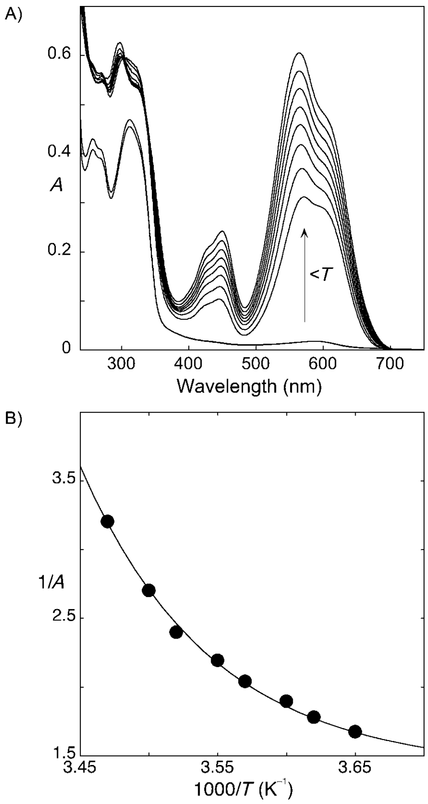


Figure 6. A) Absorption spectra of the system **I** (1.0×10^{-4} M)/EDIPA (1.2×10^{-4} M) in the solvent mixture *n*-pentadecanonitrile/acetonitrile 9:1, as a function of temperature. The spectra were acquired at the following temperatures: 20.0, 17.9, 14.9, 12.9, 10.9, 8.9, 6.9, 4.9, 2.9 and 0.9 °C. B) van′ t Hoff plot (A measured at 570 nm) according to Equation (3).

Considering a very simple scheme, where $\mathbf{AH^+}$ is **I** and **L** refers to **II**:

$$\mathrm{AH^+ + EDIPA} \overset{K}{\rightleftarrows} \mathrm{L + EDIPAH^+} \qquad (1)$$

In the case where $c^{+}_{\mathrm{AH}} \approx c_{\mathrm{EDIPA}}$, which is close to the conditions of the experiment described in Figure 6, it can be easily demonstrated (see Supporting Information, Section 5) that:

$$[\mathrm{AH^+}] = \frac{c_{\mathrm{AH^+}}}{1+\sqrt{K}} \qquad (2)$$

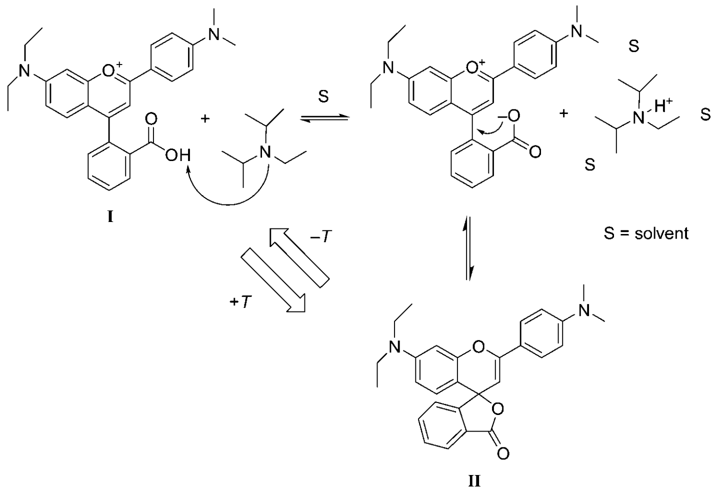
And therefore

$$\frac{1}{A} = \frac{1}{\varepsilon_{\mathrm{AH^+}}c_{\mathrm{AH^+}}}\left(1+\sqrt{K}\right) = \frac{1}{\varepsilon_{\mathrm{AH^+}}c_{\mathrm{AH^+}}}\left(1+\sqrt{e^{\frac{\Delta S}{R}}e^{-\frac{\Delta H}{RT}}}\right) \qquad (3)$$

A plot of $1/A$ versus $1/T$ should enable the determination of ΔH and ΔS of the flavylium/lactone conversion.

The resulting van′ t Hoff plot at 570 nm (Figure 6 B) gives rise to $\Delta H = 180\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S = 630\ \mathrm{J\,K^{-1}\,mol^{-1}}$. It can be seen that the entropic contribution is rather large, favoring the lactone form, but the enthalpic contribution is positive and induces the formation of flavylium cation. This means that at low temperatures, due to enthalpic reasons, the flavylium cation predominates. The reasons for a large entropy change in the flavylium/lactone reaction could be that the colored species is much more polar than the *leuco* species, and therefore the reaction demands a greater dipolar solvation organization. Similar results for the enthalpy and entropy were obtained with the parent dye rhodamine B in alcohol solutions.[32] The present values are nevertheless quite large, which could be due to the fact that cationic species are involved on a low dielectric constant environment (and therefore reorganization of ion pairs may play an important role), but also due to EDIPA that contributes to the equilibrium, and the fact that the solvent is in the solid state.

As mentioned above, phase-change thermochromic materials are constituted by a three-component system: dye/developer/solvent. In the present case, the deprotonation of the carboxylic acid is the key step for the lactone formation (see Scheme 4). Addition of the EDIPA base is thus a necessary requirement and this component plays the role of a developer.[31,33] The formation of the colored species from the lactone occurs upon the phase transition of the solvent. This implies that the protonated amine is less stabilized in the solid structure, which is a predicted effect taking into account that the solvation entropy increases in the liquid state favoring the deprotonation of the carboxylic moiety.



Scheme 4.

Photochemistry: Irradiation of the spirolactone **II** at 254 nm (prepared by titrating compound **I** with EDIPA in acetonitrile) gives rise to the appearance of an absorption band in the visible region as shown in Figure 7. The system is not thermally reversible even if more EDIPA is added suggesting that the flavylium type absorption comes from a new

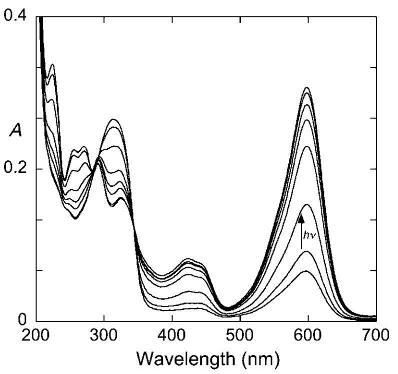
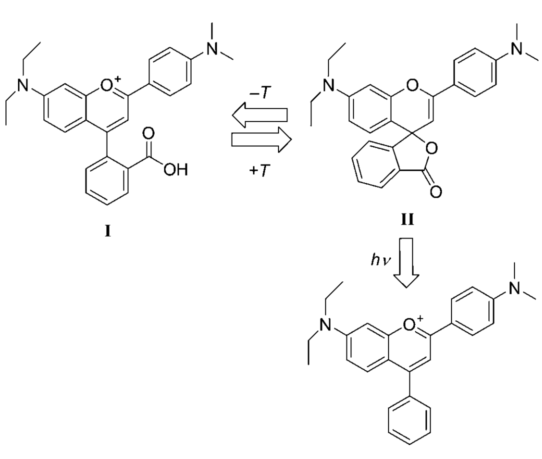


Figure 7. Spectral variations accompanying the irradiation at 254 nm of the mixture composed by **I** (1.0×10^{-5} M) and EDIPA (1.2×10^{-5} M), at 25 °C in CH_3CN, for the following irradiation times: 0, 30, 60, 130, 275, 390, 505, 635, 750 min ($I_0=1.58\times10^{-7}$ Einstein min^{-1}).

species. The $\lambda_{max}=598$ nm for this species is also slightly different from that of flavylium **I** (596 nm). MALDI-TOF mass spectra is compatible with a decarboxylated product (see Supporting Information, Figures S6, S7). Supporting this idea, the UV/Vis spectrum of the spirolactone **II** shows a band at 224 nm that is present as well in the spectrum of **I** (225 nm). This band is likely assigned to the presence of a carbonyl group in the structure[34] and disappears after irradiation (see Supporting Information, Figure S8). The determined quantum yield for this photoreaction is 5×10^{-4}.[35] Several examples of the photodecarboxylation of lactones have been reported in the literature and a better efficiency of this photoreaction seems to require a benzyl ester functionality (which is the case of spirolactone **II**, see Scheme 3) that cleaves through the COO−CAr bond to form a carboxy radical upon excitation (Scheme 5).[36] It is worth to note that no photochemistry was observed upon irradiation at 310 nm. Likewise, no reaction was detected when compound **I** (without EDIPA) was irradiated in the same conditions.



Scheme 5.

The lack of the carboxylic moiety prevents formation of the lactone and explains the absence of the reversibility of the system. This behavior can also be used to illustrate the concept of an irreversible switch OFF thermochromic system. The thermochromic system under the absence of UV light changes its color form blue to colorless. As long as it is irradiated with UV, formation of a new 4-substituted flavylium cation lacking the carboxylate substituent is observed. The new flavylium cation can not form the lactone and thus the thermochromic properties disappear.

Conclusion

The flavylium based network of chemical reactions constitutes a versatile multistate system where different forms (states) exhibiting different properties can be interconverted by means of external stimuli, as protons, electrons and light. The composition, thermodynamics and kinetics of the network is dramatically dependent on the substituents attached to the flavylium backbone. In this work we have shown that using the appropriate design it is possible to achieve a flavylium compound that is also the basis of a thermochromic system. An interesting feature of the system is that its thermochromic ability can be cancelled by photo-decarboxylation.

Experimental Section

All reagents and solvents used were of analytical grade. Acetonitrile was dried over CaH_2.

Synthesis: The synthesis of the compound 4-(2-carboxyphenyl)-7-diethylamino-4′-dimethylamino-1-benzopyrylium was performed according to the literature.[37] ^{1}H NMR (400.13 MHz, 298 K, CD_3CN): δ = 8.20 (d, 1H, ^3J = 7.8 Hz), 8.12 (d, 2H, $^3J=9.2$ Hz), 7.79 (t, 1H, $^3J_1=7.6$, $^3J_2=6.6$ Hz), 7.72 (t, 1H, $^3J_1=7.6$, $^3J_1=7.6$ Hz), 7.49 (s, 1H), 7.41 (d, 1H, $^3J=7.4$ Hz), 7.16 (d, 1H, $^3J=9.4$ Hz), 7.08 (d, 1H, $^4J=2.3$ Hz), 7.01 (dd, 1H, $^3J=9.4$, $^4J=2.3$ Hz), 6.88 (d, 1H, $^3J=9.3$ Hz), 3.59 (q, 2H, $^3J=7.1$ Hz), 3.16 (s, 3H), 1.25 ppm (t, 3H, $^3J=7.1$ Hz); ^{13}C NMR (100 MHz, 298 K, CD_3CN): δ = 167.9, 167.0, 162.4, 159.0, 156.2, 155.5, 137.5, 133.8, 132.1, 131.7, 131.1, 130.7, 130.2, 130.1, 116.6, 116.1, 115.6, 113.5, 109.6, 97.2, 46.4, 40.6, 12.7 ppm; IR (solid): $\tilde{\nu}$ = 3462, 1700 cm^{-1}; MALDI-TOF MS: *m*/*z* (%): calcd for $C_{28}H_{29}N_2O_3^+$: 441.2; found: 441.7 [M^+] (100).

NMR: The NMR spectra at 298.0 K were obtained on a Bruker AMX400 operating at 400.13 MHz (^{1}H) and 100 MHz (^{13}C). The characterization of the compounds was made by running ^{1}H, ^{13}C, COSY, HMQC and HMBC spectra. Signals of the deuterated solvent was used as an internal reference.

UV/Vis absorption and emission: The measurements were made in a mixture water/ethanol 9:1 or in acetonitrile. To control the pH in the aqueous solutions, acidified (HCl) water and universal buffer was used.[38] Absorption spectra were run on a CARY 100Bio and fluorescence spectra on a Jobin Yvon Spex, Fluorolog FL3-22.

Thermochromic studies: The spectra were recorded on a Cary 5000i coupled to a Varian peltier temperature controller. A quartz cuvette with a 2 mm optical pathway was used in order to obtain suitable absorptions from the solid samples.

MALDI-TOF-MS: Analyses were performed with the positive reflector mode. The apparatus used is a Voyager-DETM PROBiospectrometry

Workstation model (Applied Biosytems) and data were analysed with Voyager V5.1 software.

Photochemical studies: Irradiation experiments were carried out with a Xe lamp (450 W) using a monochromator to select the 254±7 nm window. Light intensity was measured by ferrioxalate actinometry.[39]

IR spectroscopy: Infrared analyses were carried out using a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope (15× objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, in 50–100 μm areas; resolutions setting 4 cm^{-1} and 128 or 256 scans, using a Thermo diamond anvil compression cell.

Acknowledgements

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