Excited state proton transfer in synthetic flavylium salts: 4-methyl-7-hydroxyflavylium and 4′,7-dihydroxyflavylium

Example of a four-level molecular device to invert the population of the excited state

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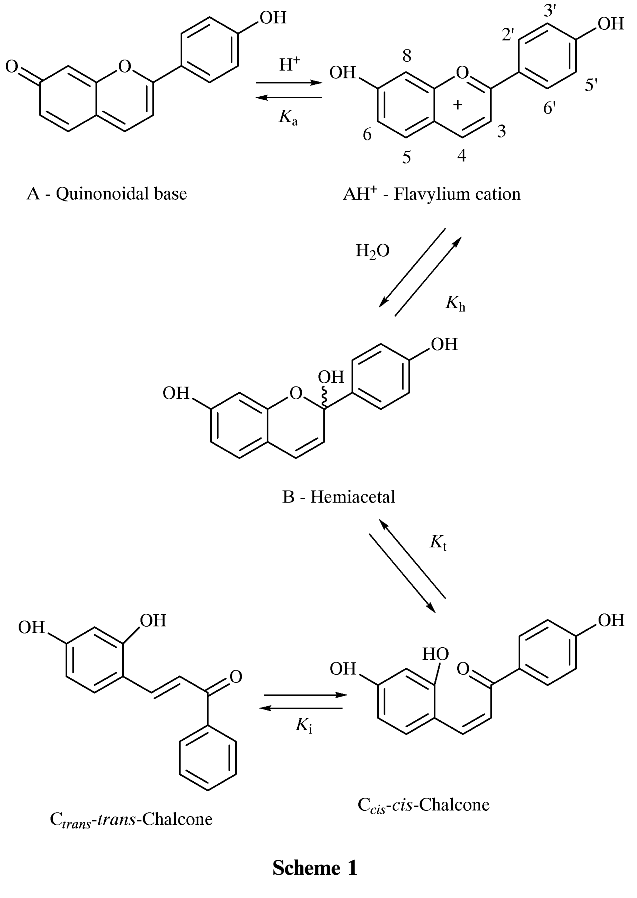
The excited state proton transfer (ESPT) observed in the compounds 4-methyl-7-hydroxyflavylium and 4′,7-dihydroxyflavylium is described, and the results are quantitatively interpreted on the basis of the Weller approach. ESPT is especially efficient in the case of 4-methyl-7-hydroxyflavylium. For pH > 2, proton recombination in the excited state does not occur and the yield of the adiabatic formation of excited base (A*) through the excited acid (AH^{+*}) is 0.93. This result compares with 0.45 for 4′,7-dihydroxyflavylium under identical conditions. The use of adiabatic proton transfer to obtain the inversion of the population of the excited state is discussed.

Excited state proton transfer (ESPT) is an interesting phenomenon that consists of a reversible adiabatic transfer of a proton between an excited acid and its conjugate base.[1–4] The excited state is a new chemical species whose properties are often different from those of the parent ground state, and for this reason large changes in its acidity can often be observed.[1–14] The differences in the acidity between the ground and the excited states can be detected experimentally by comparing the shape of the titration curves obtained by absorption and fluorescence spectroscopy. The inflection point of the titration curve obtained by steady state fluorescence emission gives the quantity[5] $pK^*_{ap} = -\log[(1 + k^*_a \tau_{AH^+})/k^*_{-a}\tau_A]$, where τ_{AH^+} and τ_A are the lifetimes of the acidic and basic species, respectively. Therefore, the observed inflection point (pK^*_{ap}) can be different from pK^*_a (the equivalent of the pK_a of the ground state applied to the equilibrium of the excited state) and the molecule may seem more acidic or more basic depending on the lifetime ratio. The differences in acidity strength between excited and ground states can thus be attributed to both thermodynamic and kinetic factors because (*i*) the electronic distribution generally changes from the ground to the excited state, leading to different acid-base equilibrium constants (pK_a different from pK^*_{ap}), and (*ii*) the observed pK^*_{ap} depends on the ratio between the lifetimes of the excited acidic and basic forms. ESPT was first observed by Weber[1] and then studied by Förster[2] and Weller.[3] It has been discussed in detail for a few families of compounds, namely phenols, in particular 2-naphthol,[3,5,6a,7–9] 1-naphthol[3,5,6b,7–9] and cyano-substituted 2-naphthols,[10] as well as benzophenones[11,12a] and hydroxyquinolines.[12b,13]

An interesting family of phenols, whose excited states can undergo dramatic changes in the acidity properties in comparison with the ground state, are synthetic flavylium salts.[14] These molecules are involved in structural transformations in aqueous solution[15–17] (Scheme 1 for the synthetic 4′,7-dihydroxyflavylium) that follow the same kinetic scheme as antho-



Scheme 1

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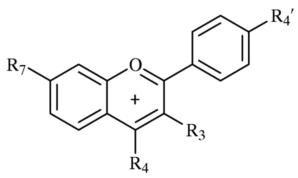
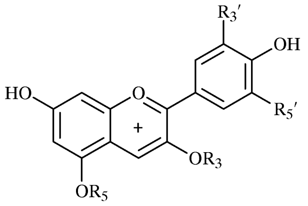
cyanins, an important family of natural compounds responsible for most of the color of flowers and fruits. The chemical structure of both families of compounds is very similar, as can be confirmed by comparing the most common anthocyanins (and anthocyanidins) and some synthetic flavylium salts.



Synthetic Flavylium[a]



Anthocyanin[b]

[a] R_4' and R_7 = H, OCH_3 or OH; R_3 = H, OCH_3, CH_3; R_4 = H, CH_3
[b] R_3' and R_5' = H, OCH_3 or OH; R_3 and R_5 = H or a glucoside

Synthetic flavylium salts have been used as model compounds for anthocyanins and their study has contributed to the elucidation of several aspects of the structural transformations observed in the ground state of both families.[15,16] Although most of the interest in the chemistry of these compounds has been motivated by their similarities with anthocyanins, it should be noted that synthetic flavylium salts present very interesting photochemical properties.[17,18] Such properties have been used to explore the possibility of designing molecular devices capable of undergoing write-lock-read-unlock-erase cycles,[17a] which could constitute the basis for an optical memory system with multiple storage and nondestructive readout capacity. In this paper we describe the quantitative aspects of ESPT of 4-methyl-7-hydroxyflavylium and 4′,7-dihydroxyflavylium, and the results are discussed on the basis of the Weller approach.[1,5] Use of the adiabatic proton transfer phenomenon to obtain a population inversion between the ground state and an excited state, a basic requirement for the laser effect, is also discussed.

Experimental

Materials and procedures

The synthetic flavylium salts were prepared according to the published procedure.[19,20] All other chemicals used were of analytical grade.

All measurements were carried out at 25 °C by using a Haake thermostated water bath.

The pH was measured with a Metrohm 713 pH meter. Calibration was performed with a set of Metrohm buffers of pH = 1, 4 and 7. Adjustment to the desired pH values was accomplished by addition of HCl or NaOH. Where pH values lower than 1 were used, namely in the fluorescence emission experiments, the negative logarithm of the analytical concentration of the added acid was used.

Absorption spectroscopy and fluorescence emission measurements

Absorption spectra were recorded on a Perkin–Elmer Lambda 6 spectrophotometer and fluorescence emission spectra were measured using a SPEX F111 Fluorolog spectrofluorimeter. The absorption and emission measurements were performed on 8 and 1.5×10^{-6} M solutions of 4-methyl-7-hydroxyflavylium, respectively (1×10^{-5} and 3×10^{-6} M for 4′,7-dihydroxyflavylium). For 4′,7-dihydroxyflavylium the solutions used were previously equilibrated in the dark.

Parameters were obtained from the fit of the theoretical equations to the experimental titration data by least-squares analysis using the bracketing technique.[5]

NMR spectroscopy

The compound was dissolved in DCl (approx. 0.1 M) to a final concentration of 0.5 mM. The pH was changed by the addition of small aliquots of 1 M NaOD or DCl. Quoted pH values are direct meter readings. Spectra were obtained in Bruker AMX300 or DRX500 spectrometers with presaturation of the water resonance for 3 s. For one-dimensional spectra the following conditions were used: 60° flip angle, 4.7 s total recycle time and 32 K acquisition data points. Spectra were processed with 0.2 Hz line broadening prior to Fourier transformation. COSY spectra were acquired with 4096 (t_2) × 512 (t_1) data points in the phase sensitive mode using standard pulse programs of the Bruker library. Chemical shifts are referenced to internal 3-(trimethylsilyl)-propanesulfonic acid sodium salt. All spectra were taken at 25 °C.

Results and Discussion

Ground state

The structural transformations of synthetic flavylium salts in acidic and moderately acidic aqueous solutions are described in Scheme 1 for 4′,7-dihydroxyflavylium. Generally, it is possible to distinguish five species [see eqns. (1)–(4)]: (*i*) the flavylium cation (AH^+), (*ii*) the quinoidal base (A) obtained from AH^+ by proton dissociation, (*iii*) the hemiacetal (B), also obtained from AH^+ by a hydration reaction, (*iv*) the *cis*-chalcone (C_{cis}) formed from the hemiacetal through a tautomeric process, and (*v*) the *trans*-chalcone (C_{trans}) resulting from isomerization of the *cis*-chalcone.

$$AH^+ \xrightleftharpoons{K_a} A + H^+ \tag{1}$$

$$AH^+ \xrightleftharpoons{K_h} B + H^+ \tag{2}$$

$$B \xrightleftharpoons{K_t} C_{cis} \tag{3}$$

$$C_{cis} \xrightleftharpoons{K_i} C_{trans} \tag{4}$$

As shown previously,[14] the molar fraction distribution of the acidic form can be obtained through eqn. (5):

$$\frac{[AH^+]}{C_0} = \alpha = \frac{[H^+]}{[H^+] + K'_a} \tag{5}$$

where $C_0 = [AH^+] + [A] + [B] + [C_{cis}] + [C_{trans}]$ and K'_a is given by:

$$K'_a = K_a + K_h + K_h K_t + K_h K_t K_i \tag{6}$$

According to eqn. (5), the complex equilibria described by eqns. (1)–(4) are equivalent to a single acid-base equilibrium between the species AH^+ and its conjugate base, ‘CB’, with the acidity constant K'_a.

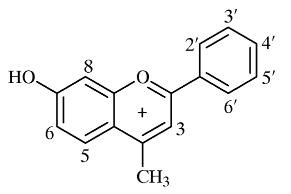
‘CB’ is thus the sum of the species $A + B + C_{cis} + C_{trans}$, and its molar fraction distribution is given by eqn. (7):

$$\frac{[A] + [B] + [C_{cis}] + [C_{trans}]}{C_0} = \beta = \frac{K'_a}{[H^+] + K'_a} = 1 - \alpha \tag{7}$$

The individual expressions of the molar fractions of each component of CB can also be easily calculated.[14] Depending on the substituents, it is possible to observe different compositions for the conjugate base, for example, detection of all four basic species in Malvin[15] or exclusive formation of *trans*-chalcone in 4′-methoxyflavylium.[16a]

The simplest situation: 4-methyl-7-hydroxyflavylium

NMR spectra. Proton NMR spectra of 4-methyl-7-hydroxyflavylium at different pH values are shown in Fig. 1. At pH = 1 the species present in solution is the flavylium cation. The assignment of the resonances in this spectrum was



4-methyl-7-hydroxyflavylium

straightforward and was based on the relative intensity of the resonances, the observed multiplet pattern due to spin-spin coupling and the COSY (correlation spectroscopy *via J* coupling) spectrum. Resonances centered at 8.362 and 7.724 ppm have intensities corresponding to two protons and the COSY spectrum shows strong cross-peaks between them; the resonance at 7.724 ppm shows a strong correlation also with the resonance at 7.831 ppm, whereas only a very weak correlation is detected between this resonance and that at 8.362 ppm. Therefore, resonances at 8.362, 7.724 and 7.831 ppm are assigned to $H_{2'6'}$, $H_{3'5'}$ and $H_{4'}$, respectively. The only singlet at 8.298 ppm is immediately assigned to H_3 and the remaining assignments follow from the connectivities between H_5 and H_2 observed in the COSY spectrum and the long-range coupling expected between H_6 and H_8. It was surprising that no resonance due to the methyl group at position 4 could be assigned in the spectra of solutions in D_2O; however, when the spectrum of the flavylium cation in 90% H_2O was run, a singlet with intensity corresponding to 3 protons was observed at 3.038 ppm. It was also verified that the protons of this methyl group are completely exchanged with deuterium within a few hours following the dissolution of the compound in D_2O at pH 2. At pH values lower than 2.6 the spectra do not change significantly, but upon a further increase in pH all the resonances shift to lower frequencies. No further significant change is observed at pH values higher than 5.4 (spectra not shown). The observed pH dependence of the resonance chemical shifts shows that there is an exchange between the species in solution that is fast on the NMR timescale. Therefore, at intermediate values of pH the chemical shifts observed are interpreted as being due to the weighted average of the chemical shifts of the protonated and unprotonated forms, AH^+ and A. The NMR parameters measured for each form are summarized in Table 1.

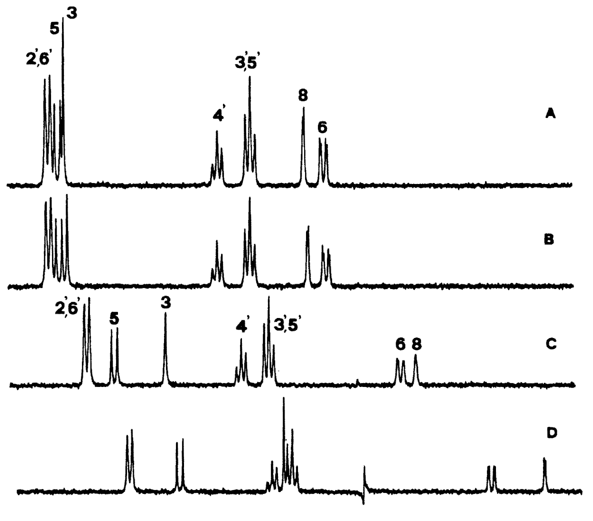


Fig. 1 ^1H NMR (300 MHz) spectra of 0.5 mM 4-methyl-7-hydroxyflavylium chloride in D_2O at 298 K at pH (A) 1, (B) 2.6, (C) 4.3, (D) 5.4

Table 1 Proton chemical shifts (δ) of the resonances of 4-methyl-7-hydroxyflavylium chloride detected in D_2O at 25 °C

	δ (AH^+)[a]	A
$H_{4'}$	7.831	7.685
$H_{3'5'}$	7.724	7.620
$H_{2'6'}$	8.362	8.141
H_3	8.298	7.647
H_5	8.331	7.980
H_6	7.476	6.984
H_8	7.528	6.816

[a] Coupling constants for the protonated form are: $H_{2'6'}$–$H_{3',5'}$, 7.9 Hz; H_5–H_6, 9.3 Hz; H_6–H_8, 2.3 Hz; $H_{3'5'}$–H_4, 7.6 Hz. Similar coupling constants were measured for the unprotonated form.

Absorption and Steady State Fluorescence emission. The situation described above simplifies the study of the acid-base equilibrium in both ground and excited states, because we only have to deal with an acid (AH^+) and its conjugate base (A), leading to the situation in which $K_a' = K_a$ [eqn. (6)]. In Fig. 2 the variation of the absorption spectrum of 4-methyl-7-hydroxyflavylium is shown as a function of pH. The molar fraction of the acidic species is given by eqn. (8):[14]

$$\alpha = \frac{(A'/A_0') - C'}{1 - C'} \tag{8}$$

where A' is the pH dependent absorbance at the chosen wavelength, A_0' is the absorbance at a sufficiently acidic pH value to consider the flavylium cation as the sole species present in solution, and the factor C' is a constant obtained experimentally at a pH value sufficiently high that $\alpha = 0$[5a] (C' is the ratio A'/A_0' when $\alpha = 0$). Fitting of the experimental α function by means of eqn. (5) allows us to calculate the acidity constant $pK_a = 4.40 \pm 0.05$ as shown in the inset of Fig. 2. This result is in agreement with the pK_a calculated from the chemical shifts of Fig. 1.

In Fig. 3 the steady state fluorescence emission spectra at $pH = -0.56$ and 6.65 are shown. In phenols the fluorescence emission from the basic species is red-shifted in comparison with the emission from the acidic one, and the excited state is more acidic than the ground state[4a,b,5a]. Therefore, at pH 6.65 the observed emission spectrum is assigned to the basic form. At $pH = -0.56$ the low emission band centered at *ca.* 475 nm

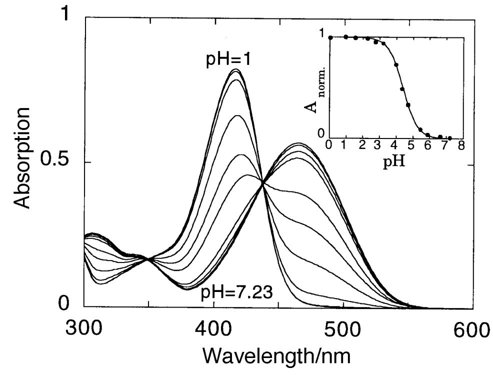


Fig. 2 Absorption spectra of 4-methyl-7-hydroxyflavylium as a function of pH, from pH = 0.96 to pH = 6.65. Insert: (●) Normalized absorption at 416 nm; (——) fitted curve with an α function, eqns. (8) and (5), with $pK_a = 7.23$

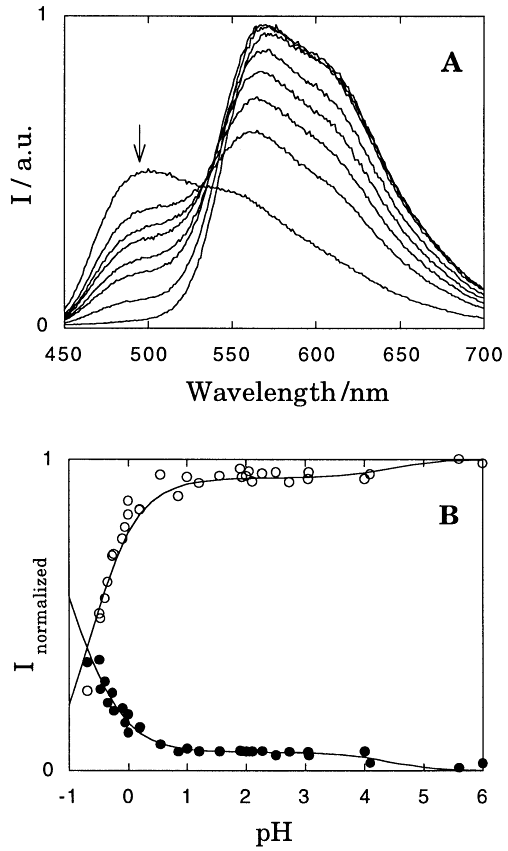
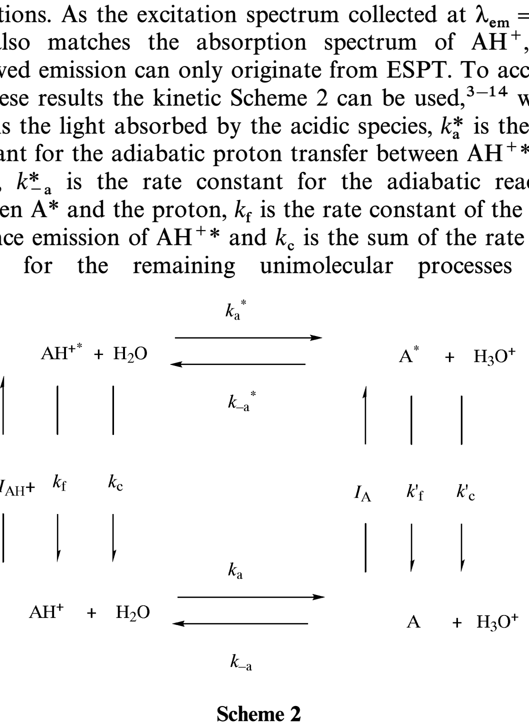


Fig. 3 (A) Fluorescence emission spectra of 4-methyl-7-hydroxyflavylium at the excitation wavelength of 438 nm (isosbestic point): between pH = −0.56 and pH = 6.65. (B) Normalized fluorescence emission curves: (●) emission from acidic species ($\lambda_e = 493$ nm), (○) emission from acidic species ($\lambda_e = 603$ nm). The best (lines) [eqns. (9) and (10)] is obtained with values of $pK_{ap}^* = -1 \pm 0.3$ and $\eta_A^* = 0.93 \pm 0.02$

can be attributed to the flavylium cation, confirmed through the excitation spectrum obtained by collecting the light at $\lambda_{em} = 484$ nm, which matches the absorption spectrum of AH^+. However, inspection of Fig. 3(A) indicates that the emission from the basic form is still present even under these acid conditions. As the excitation spectrum collected at $\lambda_{em} = 605$ nm also matches the absorption spectrum of AH^+, the observed emission can only originate from ESPT. To account for these results the kinetic Scheme 2 can be used,[3–14] where I_{AH^+} is the light absorbed by the acidic species, k_a^* is the rate constant for the adiabatic proton transfer between AH^{+*} and water, k_{-a}^* is the rate constant for the adiabatic reaction between A^* and the proton, k_f is the rate constant of the fluorescence emission of AH^{+*} and k_c is the sum of the rate constants for the remaining unimolecular processes that deactivate the AH^{+*} excited state. For the basic species (′) the symbols have an equivalent meaning.



Scheme 2

On the basis of this scheme, since the excited flavylium is much more acidic than the ground state (see below), if the excitation is carried out at the isosbestic point, a set of simple mathematical expressions based on Weller's interpretation of ESPT can be deduced:[5] eqns. (9) and (10). In these equations $I(AH^+)$ and $I(A)$ refer to the intensity of the steady state fluorescence emission, from the acidic and basic forms, respectively, $I(AH^+)_0$ is the maximum emission intensity of the acidic form and $I(A)_0$ is the same for the basic species.[5,21]

$$\frac{I(AH^+)}{I(AH^+)_0} = \alpha \cdot \alpha'^* \tag{9}$$

$$\frac{I(A)}{I(A)_0} = 1 - \alpha\alpha'^* = \beta + \alpha\beta'^* \tag{10}$$

In eqns. (9) and (10) α and β functions are the pH dependent molar fractions of the ground state, previously described in eqns. (5) and (7), respectively, and $\alpha'^* = 1 - \beta'^*$ with

$$\beta'^* = \eta_A^*\left(\frac{K_{ap}^*}{[H^+] + K_{ap}^*}\right) = \eta_A^* \beta^* \tag{11}$$

where

$$K_{ap}^* = \frac{k_a^* \tau_{AH^+}}{k_{-a}^* \tau_A} \cdot \frac{1}{\eta_A^*} = \frac{1 + k_a^* \tau_{AH^+}}{k_{-a}^* \tau_A} \tag{12}$$

$\tau_A[\equiv(k'_c + k'_f)^{-1}]$ and $\tau_{AH^+}[\equiv(k_c + k_f)^{-1}]$ are the lifetimes of the basic and acidic species and η_A^* is the proton transfer efficiency in the excited state defined by eqn. (13):

$$\eta_A^* = \frac{k_a^*}{k_a^* + k_c + k_f} \tag{13}$$

In general in the case of synthetic flavylium salts, and in particular in 4-methyl-7-hydroxyflavylium, the maximum emission intensity of the acidic species $[I(AH^+)_0]$ is not accessible experimentally. This is due to the fact that, not only is the pK_{ap}^* very low, but also there is the possibility of quenching by protons.[3,5,6]. However, with the additional condition that the sum of eqns. (9) and (10) must be equal to unity,[3,4b,5] it is possible to obtain $I(AH^+)_0$. Using this strategy, the parameters $\eta_{A*} = 0.93 \pm 0.02$ and $pK_{ap}^* = -1 \pm 0.3$ can be calculated by a simultaneous fitting of eqns. (9) and (10), [see Fig. 3(B)]. As discussed elsewhere,[5] the parameter K_{ap}^* defines the inflection point of the titration curve, while η_A^* defines the position of the first plateau that is reached when the adiabatic transfer of the proton to the excited base is negligible. In effect, η_A^* is a measure of the efficiency of proton 'injection' from the excited acidic species. For 4-methyl-7-hydroxyflavylium, 93% of the excitation energy absorbed by the acidic form can be adiabatically transferred to the base. According to recent measurements[22] the lifetime of the acidic form is 130 ps, which gives a value of 1.4×10^{11} s^{-1} ($k_a^* \tau_{AH^+} = 13.3$) for the rate constant k_a^* of the ESPT process. This value is higher than the values reported for the ESPT process in the case of 1-naphthol[5] (5×10^9 s^{-1}), 2-naphthol[5] (7×10^7 s^{-1}), 5-cyano-2-naphthol[10a] (8×10^{10} s^{-1}) and compares with the value[9] of 1.4×10^{11} s^{-1} for the proton transfer reaction: $H_3O_{aq}^+ + OH_{aq}^- \rightarrow 2\ H_2O_l$. In spite of the errors that are associated with our calculations, we can assess that the adiabatic ESPT exhibited by 4-methyl-7-hydroxyflavylium is not only very efficient but also one of the fastest rates of proton transfer to water reported in the literature. Moreover, as pK_{ap}^* is coincident with pK_a^* $(\tau_{AH^+} \approx \tau_A)^{22}$ within experimental error, a very large enhancement of the acidity of the excited state in comparison with the ground state is observed.

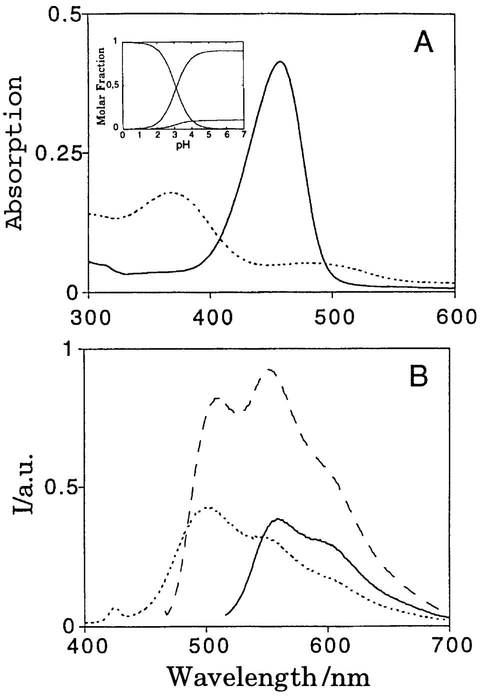


Fig. 4 (A) Absorption spectra of the compound 4′,7-dihydroxyflavylium at pH = 1.0 (full line) and pH = 6.0 (dotted line). Insert: Molar fraction distribution of the species as a function of pH. (B) Steady state fluorescence emission spectra at pH = 1.0 and $\lambda_{exc} = 458$ nm (dashed line), pH = 6.0 and $\lambda_{exc} = 370$ nm (dotted line), pH = 6.0 and $\lambda_{exc} = 500$ nm (full line)

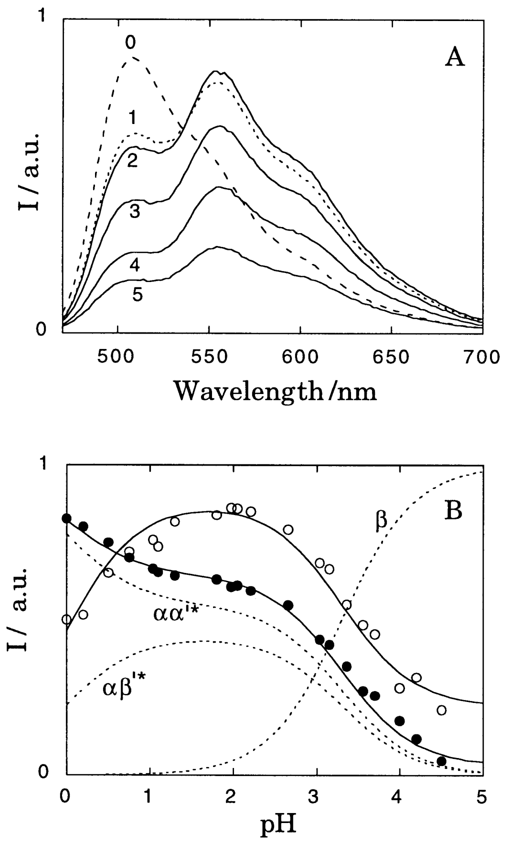


Fig. 5 (A) Steady state fluorescence emission spectra of 4′,7-dihydroxyflavylium at an excitation wavelength of 458 nm, for the following pH values: 0.2, 1.3, 2, 3.0, 3.5, 4. (B) Normalized fluorescence emission at $\lambda_e = 520$ nm (●) and 560 nm (○) simultaneously fitted to eqn. (14) with values of $pK^*_{ap} = 0.0 \pm 0.5$ and $\eta^*_A = 0.45 \pm 0.02$ ($C_1 = 1$, $C_2 = 0.21$, $C_3 = 0.03$ at 520 nm and $C_1 = 0.05$, $C_2 = 1.9$, $C_3 = 0.22$ at 560 nm)

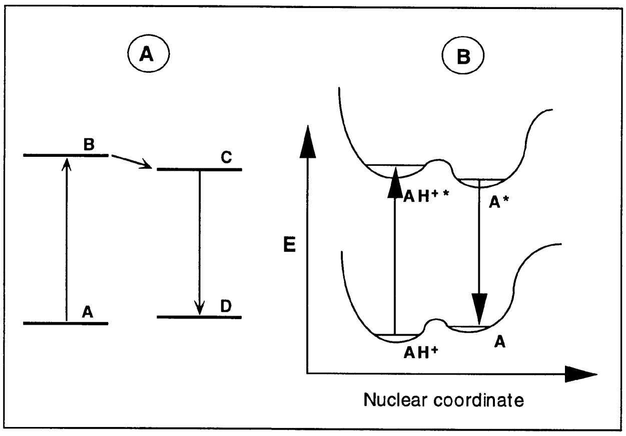


Fig. 6 (A) Four-level system for amplified spontaneous emission. (B) Population inversion in a molecular system based on ESPT occurring in an acid-base system

4′,7-Dihydroxyflavylium

As reported in previous work,[17b,c] the conjugate base for 4′,7-dihydroxyflavylium is composed of the quinoidal base minor species (*ca.* 10%) and the *trans*-chalcone major species (*ca.* 90%). In Fig. 4(A) is represented the absorption spectra of the flavylium species at pH = 1.0 as well as that of *trans*-chalcone (absorption band centered at *ca.* 370 nm) plus quinoidal base (absorption band centered at *ca.* 500 nm) at pH = 6.0. The $pK'_a = 3.1 \pm 0.2$ value was determined in a previous work[17c] by means of eqn. (8) and the resulting molar fraction distribution is shown in the inset of this figure.

In Fig. 4(B) the steady state fluorescence emission spectra of 4′,7-dihydroxyflavylium solutions are shown. At pH = 1.0 the only species present in solution is the flavylium cation and for this reason the monitored spectrum represents the emission of this species as well as the emission of the quinoidal base due to ESPT (see below). At pH = 6.0, depending on the excitation wavelength, the emission from *trans*-chalcone (exc. at 370 nm) or that from quinoidal base (exc. at 500 nm) can be observed.

In order to account for the experimental data, a slight modification in eqns. (9) and (10) must be introduced, because one more species emits and separation of the emission from the three species becomes more complex. We verified that ESPT is not observed upon excitation of *trans*-chalcone. Under these conditions the total intensity of the fluorescence emission (not normalized), monitored at any pair of excitation and emission wavelengths, is the sum of three components:

$$I_\lambda = I(AH^+) + I(A) + I(C_{trans}) = c_1\,\alpha\alpha'^* + c_2\,\alpha\beta'^* + c_3\,\beta \qquad (14)$$

where the constants c_n are dependent on the geometric factor, fluorescence emission quantum yield and fraction of the total excitation light absorbed by the species.

The fluorescence emission at the excitation wavelength of 458 nm (flavylium absorption maximum) as a function of pH is shown in Fig. 5(A), and the intensities at the emission wavelengths of 520 nm (mainly from flavylium) and 560 nm (mainly from quinoidal base and *trans*-chalcone) were fitted by means of eqn. (14) in Fig. 5(B). The best fit was obtained for $\eta^*_A = 0.45 \pm 0.02$ and pK^*_{ap} *ca.* 0.[23]

In conclusion, the most impressive result of this study is that in the case of 4-methyl-7-hydroxyflavylium the yield of adiabatic formation of excited basic species (A*) through the excited acidic species (AH^{+*}) is 0.93, constituting one of the most efficient ESPT processes reported in the literature.[1–14] For example, the previously described examples of 1-naphthol and 2-naphthol have transfer yields of 0.69 and 0.36, respectively.

Inversion of population and laser effect

A basic requirement to obtain the laser effect is the inversion of the population of the excited state in comparison with the ground state.[24,25] A common approach to obtain this population inversion makes use of a four-level system, as for example in dye lasers. In this case the levels C and D are initially unpopulated and there is no need for a large fraction of A to be excited to B to produce an inversion of population between C and D Fig. 6(A). One interesting application of this type of amplified spontaneous emission was described for 3-hydroxyflavone.[25a] In this molecule the ESPT consists of the formation of an excited tautomer due to the adiabatic intramolecular transfer of the phenolic proton in position 3 to the carbonyl group in position 4. Our system is similar, with formation of the excited basic species instead of the excited tautomer [Fig. 6(B)]. However, not all molecules exhibiting ESPT, as for example hydroxyquinolines[13] and naphthols,[3,10] are suitable for this purpose. Hydroxyquinolines cannot be used to produce a laser effect since their basic form deactivates mainly *via* a nonradiative process.[13] In contrast, naphthols, especially cyano-substituted 2-naphthols, and 4-methyl-7-hydroxyflavylium are good candidates for this purpose. Nevertheless, 4-methyl-7-hydroxyflavylium present some advantages compared with naphthols: (*i*) it absorbs in the visible region, (*ii*) the ESPT is very efficient and (*iii*) its stability under the experimental conditions (very acidic solutions) is very good; no spectral variations were detected over a period of months.

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