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ORIGINAL PAPER

Singlet Excited State Pyridinic Deprotonation of the N_9-methylbetacarboline Cations in Aqueous Sodium Hydroxide Solutions

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Abstract The singlet excited state pyridinic deprotonation of the 9-methyl-9H-pyrido[3,4-b]indole, MBC, cations has been studied in aqueous NaOH solutions by absorption, steady state and time resolved fluorescence measurements. This excited state reaction proceeds through a stepwise mechanism involving different ground and excited state hydrogen bonded MBC-$(water)_n$ complexes. Thus, in aqueous NaOH solutions of MBC above pH 8, two ground state hydrogen bonded MBC-water adducts, namely PC and PTC, coexist in equilibrium. Upon excitation, the PC behaves as an independent fluorophore, whereas the PTC reacts with water molecules during its excited state lifetime to give the intermediate CL*. This exciplex is the precursor of the excited state cation, C*. In almost all the pH range, C* is practically the only existing species in the singlet excited state of MBC. In concentrated NaOH solutions beyond the pH range, C* deprotonates giving CL* and PTC* species.

Keywords Betacarboline · Proton-transfer · Excited state · Deprotonation

Introduction

Photoacids/photobases are light-absorbing molecules that are more acid/basic in the excited than in the ground state. Therefore, after optical excitation, these molecules interact with the solvent, or other solutes, donating or accepting a proton, respectively. Because of its fundamental importance in chemistry and biology, these excited state proton transfer, ESPT, reactions have been thoroughly studied for many years [1–5]. In particular, due to the peculiar nature of water, the ESPT reactions in aqueous media are exceedingly complex [6–8]. Indeed, many molecular details regarding the dynamics and mechanism of the apparently simple water assisted ESPT reactions remain yet elusive.

Betacarbolines or pyrido-indoles, a class of naturally occurring alkaloids [9–11], constitute excellent prototypes of photobases. Thus, upon excitation, the pyridinic nitrogen atom of the betacarbolines becomes 6–7 pK_a units more basic than in the ground state [12]. During the last years we have thoroughly studied the ESPT reactions of 9-methyl-9H-pyrido[3,4-b]indole, MBC, and its 1-methyl derivative with alcohols in low polar aprotic solvents [13–17]. These studies revealed the stepwise nature of these proton transfer processes. The sequential formation of different MBC-$(alcohol)_n$ hydrogen bonded adducts and exciplexes modulates the gradual transfer of the proton from the donor to the acceptor.

More recently, we have demonstrated that a similar stepwise mechanism also operates in the water assisted ground and singlet excited state pyridinic protonation of MBC in water-N,N-dimethylformamide (DMF) mixtures [18]. Thus, as depicted in Scheme 1, upon increasing the water proportion of the water-DMF mixtures, a hydrogen bonded complex, HBC, its proton transfer tautomer, PTC, a pre-cationic complex, PC, and the pyridinic protonated cation, C, are sequentially formed in the ground state. The HBC and the PC behave as independent fluorophores in the excited state. Conversely, the PTC* reacts during its excited state lifetime with additional water molecules to give the intermediate CL*. This exciplex is the precursor of the excited state cation, C*. Therefore, C* can be formed

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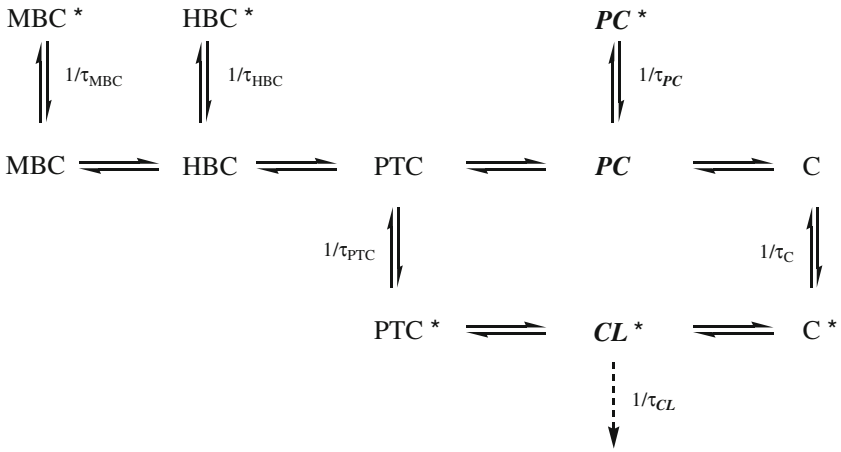
Scheme 1 Ground and excited state mechanisms of the water assisted MBC pyridinic protonation in water-DMF mixtures



trough two parallel pathways: the direct excitation of ground state cations C and the excited state reaction of the PTC. The tentative structures of the ground and excited state hydrogen bonded MBC-$(water)_n$ complexes involved in the MBC protonation mechanism are depicted in Scheme 2.

Our results on the water assisted ground and excited state pyridinic protonation of the MBC in water-DMF mixtures notably differ from those previously reported by other authors for the ESPT reactions of betacarbolines in aqueous solutions [19–22]. Concretely, these authors proposed that the betacarboline ESPT reactions in bulk water take place directly, in one single step, without the mediation of any type of adduct or exciplex. This discrepancy can be justified if we consider that these authors ignored the complexity of the betacarboline-water hydrogen bonding interactions. Indeed, without this information, it is really difficult to experimentally infer that in bulk water co-exist different betacarboline-$(water)_n$ complexes. Therefore, this fault possibly distorted the results and conclusions obtained in the previous studies on proton transfer reactions of the betacarbolines in aqueous media.

To check this hypothesis, we have studied the ESPT reaction of MBC in bulk water bearing in mind the results of our previous study on the MBC protonation in water-DMF mixtures. Because of its strong photobasicity, excited MBC molecules rapidly protonate in aqueous media. Thus, C* are practically the only excited state species existing in the MBC aqueous solutions within the pH range. The extremely fast nature of this ESPT process, in the pico- or femtosecond scale of time, makes very difficult its experimental study. Conversely, the relatively slow deprotonation reaction of the C* species results much more appropriate for its study by conventional spectroscopic techniques. Moreover, the study of the C* deprotonation process can provide basically the same information for our purpose, than that of the reverse protonation process. For this reason, in this paper we will study the excited state deprotonation of the MBC cations in NaOH aqueous solutions. The main goal of this study is to verify if, as in the water-DMF mixtures, this ESPT reaction in bulk water also accomplishes a stepwise mechanism similar to that depicted in Scheme 1.

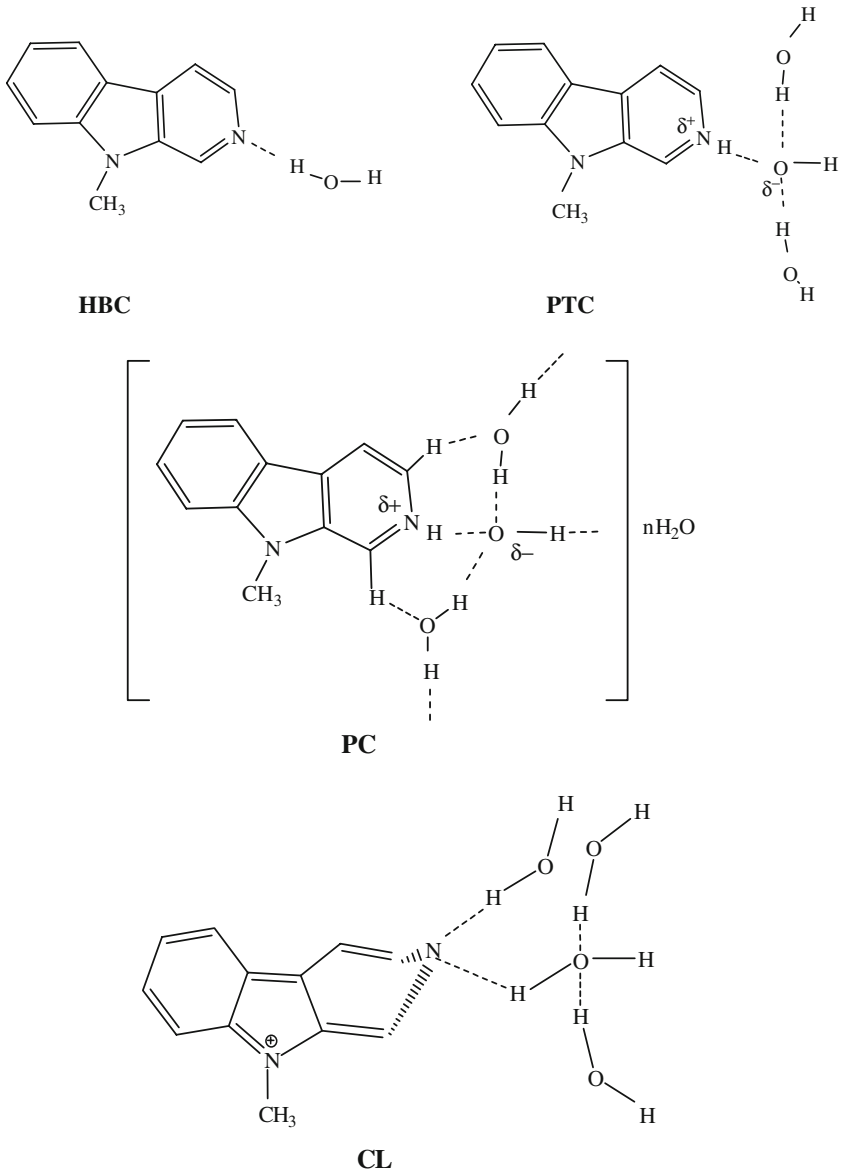
Experimental

The MBC sample, the instruments and the methods used to carry out the spectroscopic measurements were basically the same as in the preceding paper [18]. Doubly distilled water was used thoroughly. The pHs of the diluted NaOH aqueous solutions were measured with a Radiometer Copenhagen PMH80 pH-meter and a Teknokroma Single Pore Glass P/N 238160 electrode of very low alkaline error. Solutions for spectroscopic measurements were freshly prepared and kept in the dark to avoid photodecomposition. Because the quenching by molecular oxygen was checked to be negligible, the measurements were carried out with non-degassed solutions under temperature-controlled conditions, 25.0±0.1 °C.

The UV-vis absorption spectra were recorded on a Cary 100 spectrophotometer and stationary fluorescence measurements in a Hitachi F-2500 spectrofluorometer using Spectrosil quartz cells of 1 cm path length. Dilute solutions of MBC (≈10^{-5} M) were used to avoid inner filter effects and re-absorption phenomena. The Peak Fit© Jandel Scientific Program was used to deconvolute the fluorescence spectra of MBC into their individual components. The emission bands were fitted to the logistic asymmetric function:

$$y = a_0(1+\exp X)^{-(a_3+1)}a_3^{-a_3}(a_3+1)^{(a_3+1)}\exp X \qquad (1)$$

Scheme 2 Tentative structures of the ground and excited state hydrogen bonded MBC-(water)$_n$ complexes



with

$$X = -\frac{(x + a_2 \ln a_3 - a_1)}{a_2} \quad (2)$$

The amplitudes, a_0, centres, a_1, widths, a_2, and shapes, a_3 of the convoluted bands were optimised with the Marquardt algorithm. The goodness of the fits was judged by the correlation coefficient and the visual inspection of the residuals.

The excitation spectra were recorded in a Perkin-Elmer spectrofluorometer 650–40 equipped with a data processor 650–0178. The spectra were corrected by measuring the instrumental response on the excitation side (rhodamine B) and on the emission side (cell diffuser). The time-resolved fluorescence measurements were performed with the time-correlated single photon counting FL900CD and Mini-τ spectrofluorimeters of Edinburgh Analytical Instruments. These instruments used as the excitation sources a hydrogen flash lamp and a picosecond laser diode, respectively. The fluorescence decay curves were acquired to (1–2) 10^4 counts in the peak and were fitted, by re-convolution analysis with the instrumental response function, to a sum of exponential functions with amplitudes, α_i, and lifetimes, τ_i.

$$I(t) = \Sigma \alpha_i \exp(-t/\tau_i) \quad (3)$$

The quality of the fits was analysed by the randomness of the residuals and the reduced chi-squares (χ^2). Global analyses of the fluorescence decays were performed using

the standard program Level 2 based on the tried and tested Marquardt-Levenberg algorithm, supplied by Edinburgh Analytical Instruments.

Results and discussion

The influence of the pH in the absorption spectra of MBC is depicted in Fig. 1. In the NaOH aqueous solutions above pH 8, the MBC absorption spectrum shows the structured band at long wavelengths with maxima at 348 nm and 362 nm, typical of the neutral MBC species. This spectrum does not practically change as the NaOH concentration of the aqueous MBC solutions increases up to 2 M, Fig. 2. Conversely, upon acidification, the intensity of this band diminishes and, concomitantly, the broad red shifted band around 390 nm, typical of the MBC cations, grows up.

Since these spectral changes present an isosbestic point at 368 nm, we assumed that, in these media, C and N species coexist in equilibrium in the MBC ground state. The ground state pK_a obtained from these spectrophotometric data for the MBC pyridinic cation was 6.91±0.05. This pK_a value is entirely similar to that obtained for the non-methylated betacarboline, 6.85±0.03 [12]. Therefore, the methylation of the pyrrolic nitrogen of the betacarboline has not appreciable effect on the basicity of its pyridinic nitrogen atom.

The fluorescence emission spectra of MBC in NaOH aqueous solutions of different pHs are reported in Fig. 3. Because of the strong photobasicity of the MBC, the singlet excited state deprotonation of the MBC cations, C*, takes place in much more basic media than in the ground state. Indeed, C* are practically the only MBC emitting species in almost all the 0–12 pH range. The C* emission around 455 nm can be still observed in the NaOH solutions far beyond this pH range. As expected, the corrected excitation spectra of MBC in these solutions are emission wavelength dependent, Fig. 2. Noteworthy, whereas the excitation spectrum obtained monitoring the emission at 380 nm is close to the absorption spectrum, that obtained monitoring the cationic emission at 490 nm show small, but significant differences. Thus, as Fig. 2 shows, the high-energy band in this excitation spectrum is slightly blue shifted with respect to that in the absorption spectrum. Moreover, this excitation spectrum does not show the long tail at the longest wavelengths observed in the absorption spectrum and in the excitation spectrum monitored at 380 nm.

In the NaOH basic solutions beyond pH 12, the quenching of the C* emission and the appearance of a

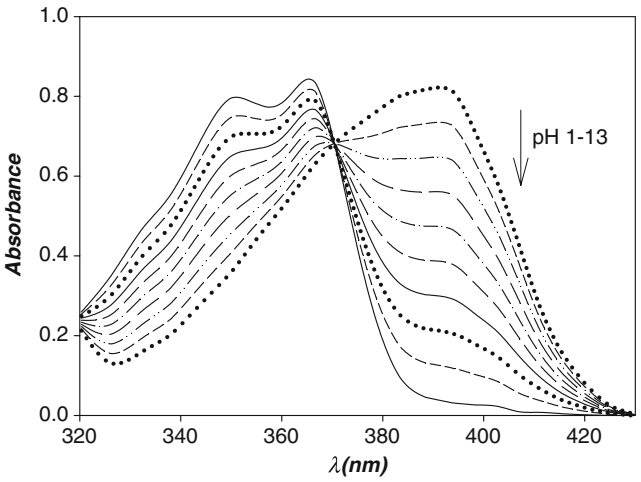


Fig. 1 Absorption spectra of MBC (1 10^{-3} M) in aqueous solutions of different pHs. The *arrow* indicates the spectroscopic changes with the increase of the pH from 1 to 13

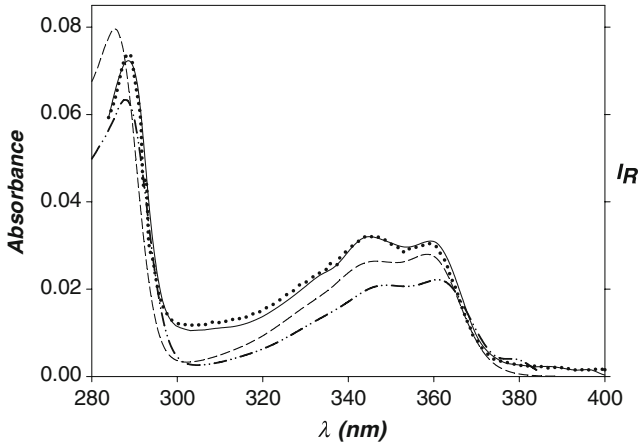


Fig. 2 Absorption spectra of MBC in 0.1 M (···) and 2 M (—) NaOH solutions and excitation spectra of MBC in 0.1 M NaOH solution monitored at 380 nm (–··–) and 490 nm (—) emission wavelengths

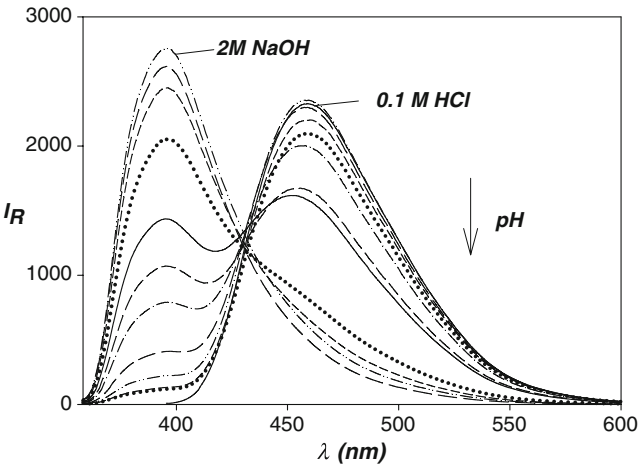


Fig. 3 Fluorescence emission spectra of MBC (5 10^{-5} M) in aqueous solutions of different pHs obtained by exciting the samples at the isosbestic point, 368 nm, of the absorption spectra. The *arrow* indicates the spectroscopic changes with the increase of the pH from 0.1 M HCl to 2 M NaOH solutions

new emission band at shorter wavelengths are simultaneously observed in the MBC fluorescence spectra, Fig. 3. The intensity of this new emission band increases as the concentration of the NaOH solutions increases and it reaches its maximum intensity in a 2 M NaOH solution. However, contrarily to that it would be expected for a direct C*→N* transformation, isoemissive points are not observed in the fluorescence spectra even when the MBC solutions are excited at the isosbestic point in the absorption spectra. It must also be noted that the fluorescence spectra of the species resulting from the MBC deprotonation have not the vibrational structure typically observed for other neutral betacarboline derivatives in methanol, a polar protic solvent similar to water [23]. Therefore, these results point out to a more complex C* deprotonation mechanism.

The time resolved measurements of the MBC fluorescence in these aqueous NaOH solutions provide the definitive proof that corroborates the complexity of the C* deprotonation mechanism. Thus, whereas for an elementary one-step C*→N* transformation bi-exponentials decays would be expected, in these media the MBC fluorescence decays multi-exponentially. This result points out that the MBC hydrogen-bonded hydrates previously observed in the water-DMF mixtures could also play a role in the C* deprotonation mechanism. In this case, the experimental fluorescence spectra of MBC in NaOH solutions should be composite of the different emissions of the water-MBC adducts depicted in Schemes 1 and 2.

To check this hypothesis we probed to reproduce the experimental MBC emission spectra in the aqueous NaOH solutions by re-convoluting the typical emission spectra of the PTC*, PC*, CL* and C* species previously observed in the water-DMF mixtures [18]. The HBC species were not used for the re-convolutions since, as the results of the water-DMF system suggest, in bulk water these species would be completely converted into its PTC tautomer.

This spectral analysis plentifully confirmed our predictions. Thus, as Fig. 4 typically shows, the MBC emission spectra in the aqueous NaOH solutions could be nicely reproduced by this re-convolution procedure. The re-convolution analysis also showed that, as expected, the relative contributions of the different water-MBC adducts to the fluorescence spectra, measured as the areas under their de-convolved emission bands, vary with the NaOH concentration Thus, as Fig. 5 shows, upon increasing the NaOH concentration the PTC*, PC* and CL* contributions smoothly increase, whereas that of C* progressively diminishes becoming practically zero in the concentrated NaOH solutions.

Therefore, to account for the pyridinic deprotonation of the excited state MBC cations, the general mechanism in Scheme 1 can be modified as depicted in Scheme 3.

According to this mechanism, two different ground state MBC species are present in the aqueous NaOH solutions: the PTC and the PC hydrogen bonded adducts. The perusal of the spectra in Fig. 2 indicates that these species possess very close absorption spectra. The more prominent difference between the PTC and PC absorption spectra is a weak absorption tail at the long wavelengths in the PC spectrum. Thus, this spectral feature is absent in the excitation spectrum obtained by selectively monitoring the C* emission at 490 nm. At this point, it must be recalled that, according to the proposed mechanism, this spectrum corresponds to the absorption spectrum of the PTC, i. e. the ground state precursor of C*. Conversely, the absorption tail can be observed in the MBC excitation spectrum monitored at 380 nm, where both the PTC and the PC emit. Therefore, these results conclusively show that the weak tail observed at the long wavelengths in the absorption spectrum of the MBC aqueous NaOH solutions is due to the PC absorption. This weak absorption tail in the PC absorption spectrum possibly envelops a charge transfer band. In fact, this spectral feature is typical of certain

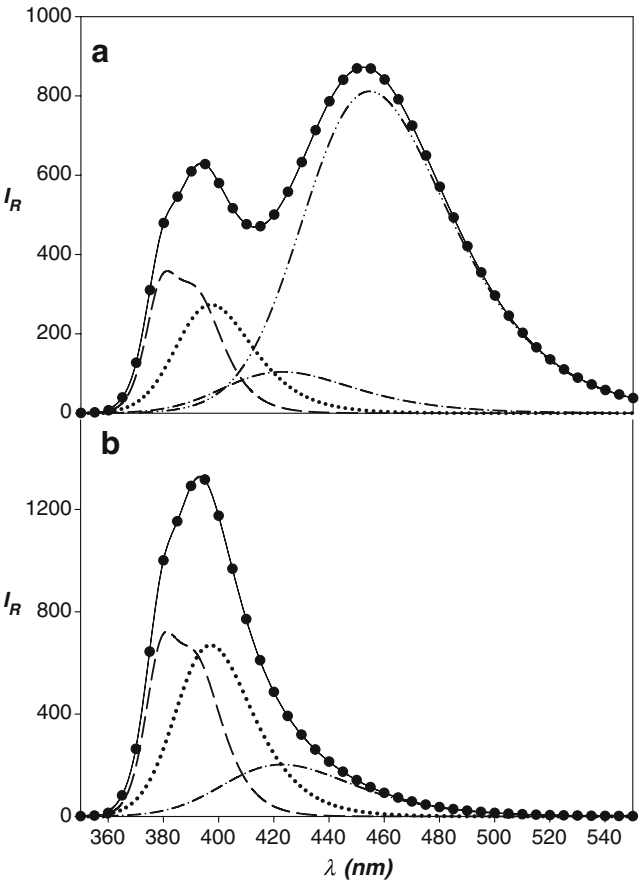


Fig. 4 Comparison of the experimental MBC emission spectra, λ_{exc}= 325 nm, in 0.05 M (**a**) and 2 M (**b**) NaOH solutions (*dash lines*) with those reconstructed (*dotted lines*) by re-convoluting the PTC* (—), PC* (····), CL* (-·-·-) and C* (-··-) emission spectra

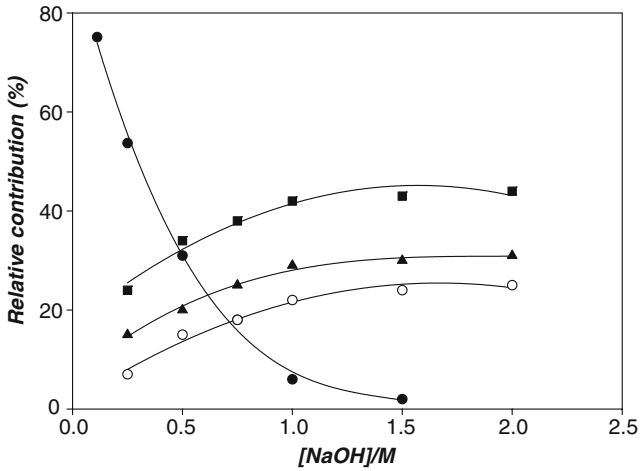
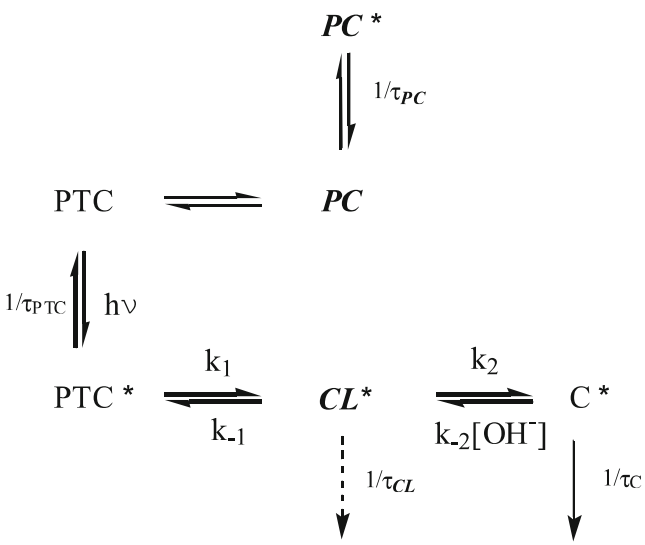


Fig. 5 Percentage of the relative contributions of the PTC* (○), PC* (■), CL* (▲) and C* (●) species to the MBC fluorescence spectra as a function of NaOH concentration

betacarboline derivatives where internal charge transfer processes play an important role [24–26].

Turning now to the dynamics of the MBC excited state, the mechanism in Scheme 3 implies that, in addition to the kinetically uncoupled PC*, there are three kinetically coupled species in the excited state, namely PTC*, CL* and C*. In general, this should lead to tetra-exponential decays that become tri-exponential at the long wavelength emissions where the PC* does not emit. Under these experimental conditions, the time evolution of the three-coupled species is given by the third order equation:

$$d/dt\begin{bmatrix} PTC^* \\ CL^* \\ C^* \end{bmatrix} = \begin{bmatrix} -X & k_{-1} & 0 \\ k_1 & -Y & k_{-2}[OH^-] \\ 0 & k_2 & -Z \end{bmatrix}\begin{bmatrix} PTC^* \\ CL^* \\ C^* \end{bmatrix} \quad (4)$$



Scheme 3 Pyridinic deprotonation mechanism of the excited state MBC cations in NaOH solutions

with

$$X = k_1 + 1/\tau_{PTC} \quad (5)$$

$$Y = k_{-1} + k_2 + 1/\tau_{CL} \quad (6)$$

$$Z = k_{-2}[OH^-] + 1/\tau_C \quad (7)$$

Equation 4 predicts tri-exponential time-dependent functions for the three species PTC*, CL* and C*, whose reciprocal decay times, λ_i, are the roots of the third order equation:

$$\begin{bmatrix} \lambda_1 - X & k_{-1} & 0 \\ k_1 & \lambda_2 - Y & k_{-2}[OH^-] \\ 0 & k_2 & \lambda_3 - Z \end{bmatrix} = 0 \quad (8)$$

where k_1 and k_2 are the pseudo unimolecular rate constants of the water assisted formation of CL* and C*, respectively.

The resolution of Eq. 8 can be considerably simplified under certain limit conditions. Thus, at very low NaOH concentrations (k_1 and $k_2 >> k_{-1}$ and $k_{-2}[OH^-]$) the roots of Eq. 8 can be approximated as:

$$\lambda_1 = 1/\tau_1 = X = k_1 + 1/\tau_{PTC} \quad (9)$$

$$\lambda_2 = 1/\tau_2 = Y \approx k_2 + 1/\tau_{CL} \quad (10)$$

$$\lambda_3 = 1/\tau_3 = Z = k_{-2}[OH^-] + 1/\tau_C \quad (11)$$

As it is well known, the resolution of multiexponential decays becomes more difficult as the number of decay times increases [27]. Thus, because of the correlation among the parameters of the fit, the actual uncertainties in the recovered lifetimes are usually very large. The problem is even greater when the decay times have disparate contributions to the emission signal. In such cases, the global analysis of a set of experimentally related decays substantially improves the resolution of the lifetimes. Therefore, to check the validity of the theoretical predictions, we probed to globally fit the experimental decay data, obtained under the aforemen-

Table 1 The τ_3 lifetimes and their pre-exponential factors (in brackets) extracted from the three-exponential global fit $\left(\chi_g^2 = 1.291\right)$ of the MBC fluorescence decays at 454 nm in diluted NaOH solutions (λ_{exc}=348 nm) performed linking the τ_1 and τ_2 lifetimes

[NaOH]/M	τ_3/ ns	χ^2
0.0030	23.14±0.03 (0.140)	1.218
0.0126	22.60±0.06 (0.133)	1.148
0.0234	22.01±0.05 (0.125)	1.020
0.0525	20.14±0.06 (0.109)	1.203
0.0794	19.08±0.04 (0.113)	1.183

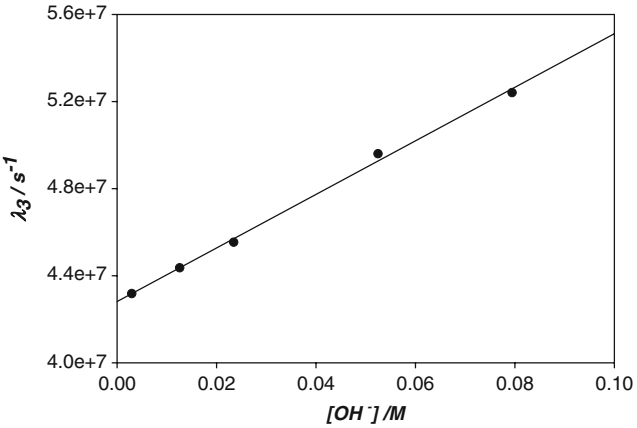


Fig. 6 Plot of λ_3 against [NaOH]

tioned experimental conditions, to a tri-exponential function with two linked life times, τ_1 and τ_2, and a third free life time, τ_3.

In agreement with the theoretical predictions, the fluorescence decays of the MBC at the long emission wavelengths where PC* does not emit and PTC*, CL* and C* co-exist in the excited state can be globally fitted to the tri-exponential function predicted by the theoretical model (χ^2=1.291). The linked lifetimes τ_1 and τ_2 extracted from this global fit were a rise time of 0.3±0.2 ns, almost in the resolution limit of our single photon counting apparatus, and a decay time of 1.1±0.2 ns. A similar rise time of 0.4± 0.2 ns was also previously observed for the MBC in the water-DMF mixtures with more than 90% *v/v* of water [18]. Since at the long emission wavelengths where the decays were obtained the PTC* does not emit, the rise time of 0.3±0.2 ns would be unambiguously assigned to τ_1 and, consequently, the decay time of 1.1±0.2 to τ_2. The short value of the rise time observed for the PTC* indicates that the PTC*→CL* reaction very efficiently competes with the PTC* radiative deactivation. On the other hand, the τ_3 lifetimes extracted from the global fit, Table 1, were decay times close to that of 23.61±0.02 ns measured for the MBC excited cations in 0.1 M HCl solutions. Moreover, as Eq. 11 theoretically predicts, the reciprocals of these long decay times linearly increase with the increasing of the NaOH concentration, Fig. 6.

Therefore, using the τ_1 and τ_2 values obtained from the global analysis of the decay data, and those of τ_{PTC}=5 ns and τ_{CL}=14 ns obtained in the previous work [18], Eqs. 9 and 10 allowed to roughly estimate the values of k_1 and k_2 as 3 10^9 s^{-1} and 1 10^9 s^{-1}, respectively. Similarly, using Eq. 11, a value of (1.23±0.04) 10^8 M^{-1} s^{-1} can be obtained for k_{-2} from the slope of the plot of λ_3 against [NaOH] shown in Fig. 6. Worthing to note, the value of 23±1 ns obtained for τ_C from the intercept of this plot is in excellent agreement with that of 23.61±0.02 ns experimentally determined for the lifetime of the MBC cationic species in 0.1 M HCl.

In more concentrated NaOH solutions, once C* is not present in the MBC singlet excited state, PTC* and CL* remain kinetically coupled, while PC* behaves as an independent fluorophore. In agreement with the predictions, under these experimental conditions, the MBC fluorescence decays at 396 nm, λ_{exc}=348 nm, can be globally fitted to tri-exponential functions. As reported in Table 2, the global fit of the decays performed by fixing the lifetime of the PC* to 7.5 ns [18], gives a decay time component around 12–14 ns close to that typical of the CL* exciplex, and a very short rise time component. Unfortunately, the great errors affecting the rise times precluded the quantitative analysis of these results.

Conclusions

The results of the present study support our initial hypothesis on the stepwise nature of the ESPT reactions of the betacarbolines in bulk water. This hypothesis, contrarily to that previously proposed by other authors, implies that in bulk water the ESPT process of the betacarbolines are modulated by different ground and excited state hydrogen bonded hydrates, namely PTC, PC and CL. Thus, the changes observed in the MBC emission spectra upon increasing the NaOH concentration of the aqueous solutions, can be nicely reproduced by re-convoluting the emission spectra of the PTC*, PC*, CL* and C* species described in a previous paper [18]. On the basis of these results, the mechanism in Scheme 3 has been proposed for the excited state deprotonation of the MBC cations.

Table 2 Three-exponential global fit $\left(\chi_g^2 = 1.271\right)$ of the MBC fluorescence decays at 396 nm in concentrated NaOH solutions (λ_{exc}=348 nm) performed fixing the PC* lifetime, τ_4, to 7.5 ns [18]. The numbers in brackets are the pre-exponential factors of the decay time components

[NaOH]/M	τ_1/ns	τ_2/ns	τ_4=7.5ns	χ^2
0.5	0.2±0.1 (−0.060)	13.95±0.06 (0.072)	(0.003)	1.201
1.0	0.3±0.2 (−0.053)	13.76±0.09 (0.071)	(0.004)	1.190
1.5	0.4±0.2 (−0.069)	12.33±0.06 (0.072)	(0.004)	1.214
2.0	0.2±0.1 (−0.064)	11.95±0.07 (0.073)	(0.004)	1.290

According to this mechanism, in bulk water, three different species can be present in the ground state of MBC. The pyridinic protonated cation, C, and the neutral hydrogen bonded water-MBC adducts PTC and PC. Upon light absorption, the basicity of the MBC pyridinic nitrogen atom strongly increases. Therefore, the singlet excited state cations, C*, are stable in a wider range of NaOH solutions than in the ground state. In fact, in almost all the pH range, C* is practically the only existing species in the MBC singlet excited state. However, in concentrated NaOH solutions, C* deprotonates to give, as depicted in Scheme 3, CL* and PTC* adducts.

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