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Complexes of basic tricyclic dyes in their acid and basic forms with cucurbit[7]uril: Determination of pK_a and association constants in the ground and singlet excited state

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ABSTRACT

Cucurbituril having seven glycoluril units (CB[7]) forms strong host–guest complexes with tricyclic basic dyes in water. Depending on the pH of the aqueous solution, these dyes can be in their acidic or basic form. Typically, the basic form is present at pH values higher than 12. One part of this study deals with the difference in the association constants between the acid or basic forms of the dye with CB[7]. Other part of our study focus on the CB[7] complexation of the dyes in their excited states. Thus, for seven dyes (proflavine, acridine orange, pyronine, pyronine Y, oxonine, thionine and methylene blue) we have determined the association constants (K_B) of their acid and basic forms with CB[7], both in the ground and in the excited state, as well as the pK_a values of free and complexed dyes. As a general trend, we have observed that the pK_a values of the complexed dyes in the ground are about two units higher than the pK_a values of the free dyes. Also, we have found that the association constants in the excited state as well as those of the basic form are between one or two orders of magnitude smaller than the association constants of the ground state dye in the acid form.

1. Introduction

Cucurbiturils (CBs) are organic capsules whose structure is formed by cyclooligomerization of glycoluril units bridged by methylene groups [1–4]. The pumpkin-like shape of these capsules allows the formation of host–guest inclusion complexes provided that the molecular size of the guest is smaller than the dimension of the CB portals [1–14]. There is much current interest in determining the formation of the host–guest complexes with CBs in the ground state and the estimation of the corresponding binding constants [5–13,15,16]. Also, there has been ongoing interest in establishing the differences in the properties of the guest upon complexation [7–9,11–13,16,17].

In contrast to the wealth of reports dealing with complexation in the ground state [7–9,11–14,16–18], the number of precedents describing the influence of CB complexation on the properties of the excited states is considerably more limited [19,20]. In particular, an issue that deserves attention is to determine if the high binding constants often measured for the ground state are maintained for the complexes of CB in the electronic excited states. Also of interest is the measurement of the variations of the pK_a of CB complexes upon electron excitation of the guest. On the other hand, it has been recently reported that the pK_a of acridine orange (AO) changes two units when this dye is incorporated in CB[7] [21]. It is worth to determine if similar pK_a changes also occur for complexed singlet excited states.

In this work we report a set of binding constants for a series of tricyclic basic dyes complexed with CB[7] in their singlet excited state as well as pK_a values in the excited state either free or forming CB[7] complexes. The data obtained show that, in contrast to cyclodextrins (CDs) in which decomplexation of excited states has been observed, CB[7] binding constants for excited states are also very high, the complexes being strong in the singlet excited state. Also as a general trend, we have found that pK_a values of the complexed dyes in their singlet excited state increases about three pK_a units.

2. Results and discussion

Host–guest complexes of CBs are frequently compared to the inclusion complexes of other organic capsules and, particularly, CDs. For these capsules, Scaiano and other groups have shown that excitation of xanthone β-CD complexes in aqueous solutions produces decomplexation [22–25]. The dynamics of xanthone migration from β-CD to water occurs in the microsecond time scale and decomplexation can be assessed by transient spectroscopy

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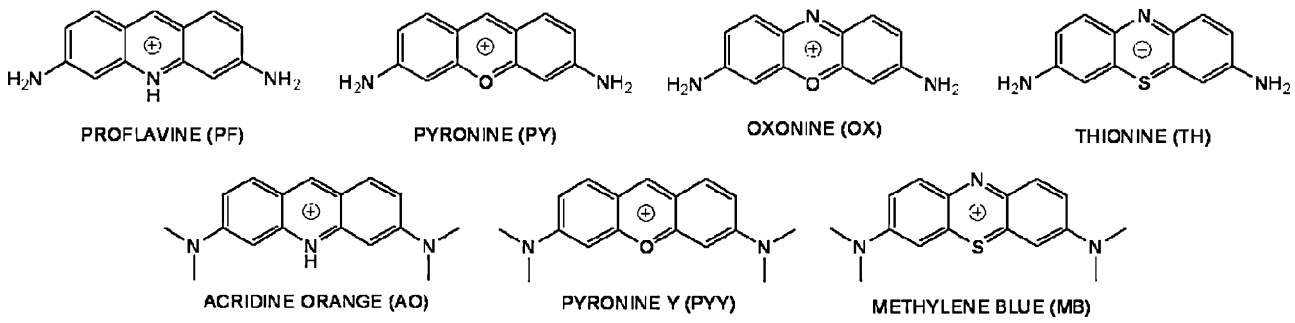


Scheme 1. Structure, name and acronyms of the tricyclic basic dyes studied in this work.

monitoring the variation of the wavelength maxima of T–T absorption of xanthone triplets that undergoes a shift when moving from the interior to the cyclodextrin to the solution. Based on kinetic data, the association constant of xanthone triplet excited state with CD could be estimated [22–25]. In general, CBs form inclusion complexes with much higher binding constants than CDs [1–4,6,18,26]. In a previous study we and others have reported the binding constant (K_B) for the ground state of the series of basic dyes with CB[7] [10,15]. K_B in the ground state were experimentally determined by titration of dye solutions with CB[7] using optical or fluorescence spectroscopy and applying the Benesi–Hildebrand equation that correlates the intensity of absorption or emission with CB[7] concentration. The main reason for this higher stability of the CB complexes compared to those of CDs is frequently electrostatic interactions between positively charged guests and the polar carbonyl groups of the CB portals [1–3,18]. Considering this higher binding constant (typically in the range of $10^6\ M^{-1}$ for 1:1 complexes) for CB complexes, an important issue is to determine which are the K_B values for CB complexes in the singlet excited state to assess if, in contrast to CDs [22], complexes in the singlet excited state are also thermodynamically stable with respect to the individual components. To address this question, we have studied the complexes of CB[7] with a series of seven tricyclic basic dyes (see Scheme 1).

We envisioned a thermodynamic cycle from which knowing the binding constant in the ground state (K_B^{DH}) and the excitation energies of the free dye ($E_{0\text{-}0}^{DH}$) and the dye@CB[7] complex ($E_{0\text{-}0}^{DH@CB[7]}$) it is possible to estimate the binding constant for complexation in the singlet excited state energy potential surface (K_B^{*DH}). Scheme 2 illustrates the cycle used to estimate the binding constants of the dye excited state.

Our approach, based on Förster's cycle [27], considers that the free energy of excitation can be taken as the excitation energy of the 0–0 transition ($E_{0\text{-}0}$) and that the contribution of entropy changes to the free energy is negligible. The Förster cycle has been previously used for analogous calculations of the thermodynamic constants of excited states and herein we have applied this established methodology [27]. This assumption disregarding entropy variations assumes a similar geometry for the inclusion complex in the ground and excited states and the occurrence of minor changes in solvation due to the fact that the dye molecule is mainly *solvated* by the organic capsule. Experimental evidence to support minor changes in the dye@CB[7] complexes were obtained by laser flash photolysis studies in where destruction of the complex upon excitation is not observed. Also, structural reorganization of the host–guest complex in the excited state is typically reflected by a large Stokes shift (>60 nm). In this context, it has been reported that the Förster cycle should not be used for those cases in which a significant Stokes shift is observed. As it can be seen in Fig. 1 and in supplementary material, the Stokes shift for the tricyclic basic dyes encapsulated inside CB[7] is, in many cases, negligible and only for PR (50 nm) near the limit of application of the Förster cycle. This should be taken into account when considering the accuracy of our measurements.

$$\ln\left(\frac{K_B^{*DH}}{K_B^{DH}}\right) = \frac{hcN \times 10^9}{RT}\left(\frac{1}{\lambda_{0-0}^{DH}} - \frac{1}{\lambda_{0-0}^{DH@CB[7]}}\right) \quad (1)$$

Eq. (1) shows that following our approximation, the binding constant of the singlet excited state of the dyes and CB[7] (K_B^{*DH}) can be obtained from the measurements of the binding constant of the ground state (K_B^{DH}) and the 0–0 transition wavelength (λ_{0-0}^{DH}). Thus, the error of the values for the thermodynamic parameters in the excited state depends on the accuracy in which λ_{0-0} is determined. The 0–0 transition wavelengths for the acid form of the dye, free (λ_{0-0}^{DH}) and complexed with CB[7] ($\lambda_{0-0}^{DH@CB[7]}$), were obtained from the crossing of the absorption and emission spectra of the free dyes and the dyes complexed with CB[7]. Since tricyclic basic dyes are known to undergo aggregation in water and this phenomenon is reflected in changes in the absorption spectrum that could introduce inaccuracy in λ_{0-0}^{DH} measurements, in the present case we have performed the study at diluted dye concentration (10^{-6} M). In this concentration range, only the monomer of the dyes should be present. Controls using twice or one half this concentration do

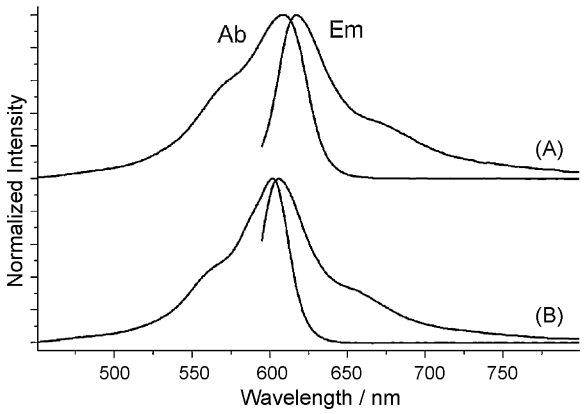
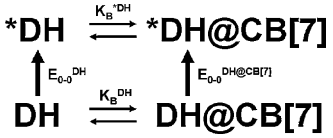


Fig. 1. Visible absorption (Ab) and emission (Em) spectra recorded for 10^{-6} M aqueous solutions of TH free (A) or complexed with CB[7] (10^{-4} M) (B). The emission spectra have been recorded upon excitation at 450 nm for the free and complexed dyes.



Scheme 2. Thermodynamic cycle used to estimate the binding constants in the singlet excited states (K_B^{*DH}) for the acid form of the dyes.

Table 1
Wavelength of the 0–0 transition for the free and complexed dye and values of the association constants in the ground and singlet excited state.

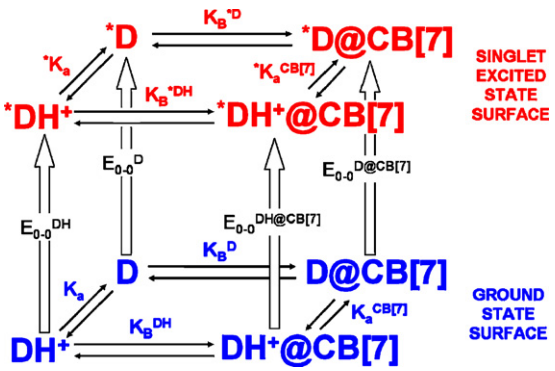
Dye	λ_{0-0}^{DH} (nm)	$\lambda_{0-0}^{DH@CB[7]}$ (nm)	$K_B^{DH} \times 10^{-7}$ (M^{-1})[a]	$K_B^{*DH} \times 10^{-6}$ (M^{-1})
PR	480 ± 2	465 ± 2	1.7 ± 0.25	0.9 ± 0.1
AO	512 ± 2	499 ± 2	0.31 ± 0.05	0.30 ± 0.05
PY	510 ± 2	510 ± 2	1.47 ± 0.48	14.7 ± 4.8
PYY	558 ± 2	552 ± 2	0.46 ± 0.01	1.75 ± 0.04
OX	593 ± 2	589 ± 2	1.21 ± 0.16	6.9 ± 0.9
TH	614 ± 2	604 ± 2	1.35 ± 0.10	3.6 ± 0.3
MB	679 ± 2	670 ± 2	1.26 ± 0.28	4.8 ± 1.0

[a] Taken from Ref. [15].

not show any change in the absorption spectrum besides variation of the band intensity. This lack of spectrum variation indicates that no aggregation of the free dyes is occurring. Fig. 1 shows an illustrative example of the shifts in λ_{0-0} that occur upon complexation of the basic dyes in CB[7]. A full set of absorption and emission spectra from which λ_{0-0} were measured is provided in supplementary material. This procedure to obtain the 0–0 energy has been widely use in the literature [27]. Alternatively, values of E_{0-0} were also obtained by averaging the wavelength of the longest absorption and the shortest emission peaks [28]. Both methods to determine λ_{0-0} were in good agreement and the values with their corresponding errors are listed in Table 1.

Table 1 also includes binding constants estimated based on Eq. (1) for complexation of CB[7] with the dyes in their singlet excited state. As it can be seen in Table 1, variations between the binding constant in the ground and singlet excited state arise from variations in λ_{0-0} for the free and complexed form of the dye. These differences in λ_{0-0} for DH and DH@CB[7] can vary from 0 to 17 nm, for PY and PR, respectively.

Although the experimental errors and the assumptions made in the thermodynamic cycle shown in Scheme 2 produces some uncertainty in the determination of the binding constant in the singlet excited state, the estimated values are all notably high (in the range of 10^6 M^{-1}) indicating that, in contrast to the case of aqueous solutions of xanthone in CDs, destruction of the complexes should not occur for CB[7] and the singlet excited dyes under consideration. However, we notice that except for PY, the estimated binding constants in the singlet excited state are consistently smaller than K_B in the ground state. Although the most frequent ratio between K_B^{DH} and K_B^{*DH} is about 3, in the most extreme case corresponding to PR a 20-fold decrease of the binding constant for the excited state was estimated. These lower binding constants, smaller than for the ground state complex, indicate that the interaction of the tricyclic basic dyes with CB[7] is weaker in the excited state. This decrease in the binding constants probably reflects a larger charge delocalization in the excited state as compared to the ground state of the dye.



Scheme 3. Relationship between the dyes in their acid (DH) and basic (D) forms either free or forming CB[7] complexes in their ground and singlet excited state.

Continuing with the determination of properties of tricyclic dyes@CB[7] complexes in the excited state, we wanted to know the variations of the pK_a values for both, free and CB[7] complexes in the excited state as well as the binding constants for the basic form of the dyes in the excited state. In order to estimate all these set of values, we proceeded to obtain the data for the ground state from which by means of a thermodynamic cycle, we could determine the constants for the excited state. Scheme 3 shows the relationship between the different species involved in the cycle, and the thermodynamic parameters involved in the transformation of each couple.

Thus, in the first place, we measured pK_a values in the ground state for free and CB[7] complex of the basic dyes. These pK_a data were obtained from optical spectroscopy by recording the visible spectrum of the dye at different pH values. To illustrate the changes observed, Fig. 2 shows the variations in the optical spectrum of TH at different pH values in the absence and in the presence of an excess of CB[7]. We notice that for the TH titration there is not a consistent isosbestic point. This lack of accurate isosbestic point can be responsible for the fact that the titration curve shown in the inset of Fig. 2 left does not exhibit an abrupt change at pH 11.2 compared to the host–guest TH@CB[7] complex (Fig. 2, right). One of the possible reasons for this could be the lower solubility of TH basic form as compared to the solubility of TH at acid pH values.

Considering the high binding constants, we assume that the variation of the spectra recorded at increasing pH using an excess of CB[7] (Fig. 2, right) are due to the deprotonation of the complex dye@CB[7]. By plotting the intensity of the λ_{max} for the dye versus the pH of the solution, a titration plot is obtained (see inset of Fig. 2) from which the pK_a values in the ground state were obtained from the inflection point of the curve. We noticed that the shape of the titration plots for TH and TH@CB[7] is different, the later changing

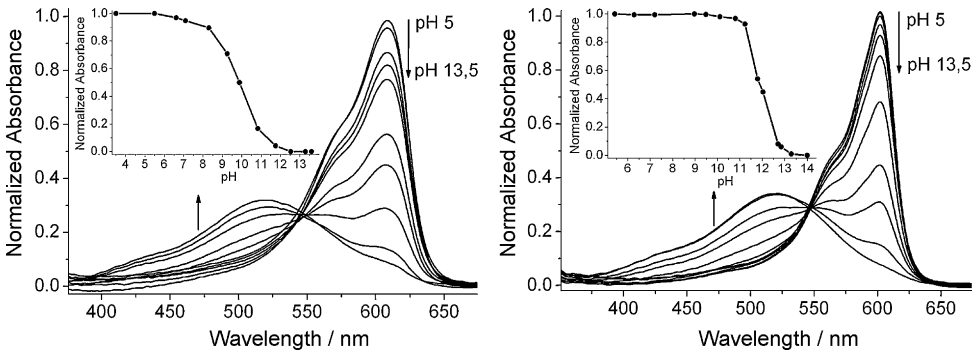
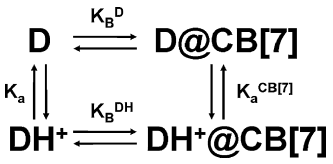


Fig. 2. Optical spectra of aqueous solutions (10^{-6} M) of TH (left) and TH@CB[7] (right) at different pHs in the range 4.5–13.7. The inset shows the normalized variation of the intensity of λ_{max} (608 nm for TH and 602 nm for TH@CB[7]) as a function of the pH. The continuous line corresponds to an extrapolation of the experimental data point and the arrows indicate the relative variation of the bands as the pH increases.



Scheme 4. Thermodynamic cycle used to determine the binding constants for the basic form of the dye.

more abruptly the intensity with the pH. This is a reflection of the different basic strength and nature of the TH and TH@CB[7] species. These pK_a values, combined with the association constant of the acid form of the dye (K_B^{DH}) and according to Scheme 4, allowed determining the binding constant for the basic form of the dye (K_B^D) by applying

$$\frac{K_B^D}{K_B^{DH}} = \frac{K_a^{CB[7]}}{K_a} \quad (2)$$

Table 2 contains a full set of pK_a and K_B data for the dyes under study. AO is the only dye of this table for which the p$K_a^{CB[7]}$ has been previously measured [29]. The value of p$K_a^{CB[7]}$ for AO estimated by us agrees very well with that previously reported in the literature (see footnote b in Table 2). It has to be commented that the association constants for the basic form of some of the dyes cannot been obtained directly from variations in the optical spectra at basic pH values. This is due to the fact that either the basic form of some of them are *leuco* forms devoid of color and spectrum in the visible region (PY, OX and MB) or there are very minor spectral changes upon titration of the dye with CB[7] (PR, AO, PYY and TH).

From the data in Table 2, it can be seen that as a general trend, complexation with CB[7] increases up to two units the pK_a, indicating that the dyes become less acidic when included inside the host. Also, the binding constants for the basic form of the dye are in general one or two orders of magnitude lower than those of the acid form of the dye. These facts can be easily rationalized considering that CBs form strong complexes with positively charged species and, in the case of the dyes under study, this positive charge is lost upon deprotonation. Also, deprotonation to form the basic species of the dye should be less favourable when the positive charge of the acid form is stabilized by the CB[7] host.

With the ground state pK_a and K_B data for the acid and the basic forms of the dyes, and determining the E_{0-0} energy of the excited state of the four species involved (acid and basic forms, free and complexed), it is possible to build thermodynamic cycles that allows to estimate the pK_a and K_B values in the excited state energy surface. To obtain these data in the singlet excited state, we have to follow the cycles shown in Scheme 3 and apply Eq. (1) for the corresponding ground and singlet excited state species involved. In this way, it has been possible to estimate the *pK_a and $^*K_D$ data shown in Table 3.

Table 2
pK_a values for the free and CB[7] complex of dyes and association constants for the basic form of the dyes (K_B^D according to Scheme 4). The numbers in brackets correspond to those pK_a values previously reported in the literature [29,30].

Dye	pK_a	p$K_a^{CB[7]}$	$K_B^D \times 10^{-6}$ (M^{-1})
PR	9.6 ± 0.2 (9.6)[a]	11.6 ± 0.1	2.35 ± 0.57
AO	9.9 ± 0.1 (9.8)[b]	11.9 ± 0.1 (11.7)[b]	0.42 ± 0.07
PY	10.5 ± 0.3	12.0 ± 0.2	3.40 ± 1.41
PYY	12.0 ± 0.2	12.5 ± 0.1	2.01 ± 0.34
OX	11.2 ± 0.1 (11.27)[a]	12.0 ± 0.1	5.44 ± 0.72
TH	11.2 ± 0.3 (11.0)[a]	12.7 ± 0.2	3.05 ± 0.53
MB	>14	>14	–[c]

[a] Ref. [30].
[b] Ref. [21].
[c] Not determined due to the impossibility to obtain the basic form in aqueous solutions.

Table 3
Association constants and pK_a values in the singlet excited state potential energy surface for some of the dyes under study. For the meaning of K_B and pK_a parameters see Scheme 3.

Dye	$^*K_B^D \times 10^{-5}$ (M^{-1})	*pK_a	*p$K_a^{CB[7]}$
PR	4.6 ± 1.1	12.2 ± 0.2	13.3 ± 0.1
AO	1.0 ± 0.1	13.3 ± 0.1	14.7 ± 0.1
PYY	14.5 ± 2.5	23.9 ± 0.2	24 ± 0.1
TH	4.3 ± 0.8	12.6 ± 0.3	13.5 ± 0.2
MB	–[a]	>18	>18

[a] Not determined because the basic form does not exist in aqueous solution.

Concerning Table 3, it has to be noted that no data are presented for PY and OX. These lack of data is due to the fact that the basic forms of PY and OX do not have absorption spectrum in the visible, either free or complexed with CB[7]. For this reason, it is not possible to estimate the E_{0-0} transition energy for the basic forms of these two dyes and, therefore, the thermodynamic cycle cannot be established. Also in Table 3 we notice that the $^*K_B$ data for the association constant of the basic forms of MB and CB[7] is missing. The reason for this is that the pK_a values in the ground and the excited state are unknown because they are larger than the pK_a range that can be determined in water. In other words, in contrast to the other dyes, MB neither in the ground nor excited state has basic form in water.

From Table 3 and even considering the necessary caution due to the uncertainty of the calculated values, some general trends can be observed. Thus, the *pK_a values of the dyes in the excited state are about one or two units higher both for the free and complexed form than the ground state. This lower acidity of the singlet excited states reflects the higher relative stability of the acid form of the dyes in this energy surface probably due to larger charge delocalization. Concerning the association constants of the basic form of the dye and CB[7], the available data indicates that there is not much difference of $^*K_B^D$ in the excited state and in the ground state.

Overall, the present work provides a comprehensive set of thermodynamic data for the host–guest inclusion complexes of CB[7] with tricyclic dyes in the ground state or in their singlet excited state for the acid and basic forms. The results have shown that complexation decreases the acidity of the dyes. On the other hand, the basic forms of the dyes exhibit lower binding constants with CB[7] than the acid form. The same trend is maintained for the singlet excited state surface, the electronic excitation increasing the pK_a values of the dyes and decreasing the association constants. To put this set of data into context, they have to be compared with those reported for CDs complexes. In this regard, the same trend is observed for host–guest complexes in CB and CDs, i.e., association constants for CDs are lower for the excited states [22–25]. However, even in the excited state, the absolute values of $^*K_B$ for CBs still remain much higher than those reported for CDs in the ground state. For this reason, and in contrast with the known behaviour of some CD complexes that are unstable in the excited state, the guest exiting from the CD capsule to the solution, in the case of CBs singlet excited state complexes are still thermodynamically more stable than the free dye in solution. Although our data are thermodynamic constants that serve to calculate the concentration of the complexes in the equilibrium, they indicate that the kinetics of the dethreading rate of the complex in the excited state should be favoured with respect to the situation in the ground state.

3. Experimental

PF, AO, PYY, TH, MB and CB[7] were commercial samples from Aldrich and used as received. PY and OX were synthesized according to the procedures reported in the literature [31]. After purification

by column chromatography, spectroscopic data of synthesized PY and OX coincide with the data reported in the literature [31]. In all cases, the water used for the measurements was milli-Q grade in the absence of any buffer, even in the pK_a values determination. Measurements were performed at room temperature (24 °C). Optical spectra were recorded in a Shimadzu PC4140 spectrophotometer using a 1 cm × 1 cm quartz cell and 10^{-6} M aqueous solutions of the corresponding dye, free or complexed with CB[7]. The accuracy of wavelength measurement was below 1 nm as determined using the reported wavelength of pyrene in ethanol. The CB[7] concentration used to form the complexes was 10^{-4} M. All the pH titrations were obtained at room temperature by adding a small volume of a 10^{-2} M aqueous solution of NaOH. In order to minimize volume changes upon the addition of NaOH, to the corresponding solution containing the dye, in its free or complexed form, at 10^{-6} M concentration. Otherwise, these volume changes can cause the lack of observation of true isosbestic points. The poor solubility of the basic forms of the dyes causes some turbidity that can cause some artifact in the optical spectra. Emission spectra were recorded on a PTI LPS-220B spectrofluorimeter having excitation and detection Czerny–Turner monochromators and a slit of 1 mm. According to the manufacturer specifications, the error in the wavelength is below 1 nm. Excitation was carried out at the λ_{max} of the corresponding absorption spectra and the emission was recorded from 450 nm up to 800 nm. The pH of the aqueous solutions was measured with a metroOhm pHmeter.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.02.019.

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