



## Acid–base behavior of 3-aminoquinoline in its ground and excited states

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### ABSTRACT

Electronic absorption and fluorescence spectroscopic techniques reveal that the  $pK_b$  for neutral form (N) of 3-aminoquinoline (3AQ) is 5–5.7, in the ground as well as the first electronically excited state. However, the case is quite different for the second  $pK_b$ , involving the monocation and the dication. The emissive state is found to be monocationic, even in highly acidic conditions and in nafion membrane, where the ground state of the molecule is predominantly dicationic. This indicates that the dication loses a proton in its electronically excited state, possibly due to the delocalization of the lone pair on the amino nitrogen atom over the ring, due to an intramolecular charge transfer. The  $pK_b$  values have been computed using density functional theory (DFT) for the equilibria of neutral  $\rightleftharpoons$  monocation and monocation  $\rightleftharpoons$  dication respectively and found to be reasonably in good agreement with the experimental observations.

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### 1. Introduction

Quinolines have been proposed to be potential fluorescent sensors and so, the study of their excited state properties are of significant interest [1–4]. Recently we have explored the solvent dependence of excited state dynamics of 3-aminoquinoline and have proposed that the flip-flop motion of the amino group is the principal reason for the unusually high nonradiative rates in non-polar solvents while in solvents of higher polarity such flip-flop motion is hindered due to the stabilization of the structure of the molecule in which the amino group is coplanar with the quinoline ring, as this structure facilitates intramolecular charge transfer (ICT). The unusually small nonradiative rates in protic solvents are rationalized in the light of further hindrance of the motion of the amino group due to hydrogen bonding with the solvent molecules [5]. The formation of monocation of 3AQ by the protonation of its ring nitrogen increases the electron-accepting ability of ring that stabilizes the intramolecular charge transfer (ICT) state and hinders the flip-flop motion of amino group even further, signaled by high fluorescence quantum yield and long lifetime [5].

In the present paper, the effect of the acidity of the medium on the photophysics of 3AQ is explored in detail. The study has been performed in aqueous solution of acid–base concentration in the range of  $H_0/pH$  –5 to 11 and in nafion membranes, made up of a fluorocarbon backbone with pendant-chains terminated with polar sulfonate ( $SO_3^-$ ) headgroups (Chart 1) [6,7]. Nafion is a superacidic membrane, due to the electron-withdrawing effect of the perflu-

orocarbon chain acting on the sulfonic acid group. Consequently, it is possible to subject guest molecules like 3AQ to a significantly high local acidity, in these membranes. Besides, the acidity can be regulated by performing simple cation exchange, which is known to affect acid–base equilibria of guest molecules to a significant extent [8,9]. The water content depends on the kind of cation that is incorporated in place of the hydronium ions. This is why the experiments have been performed in this membrane, so as to explore the effect of acidity and water content on the acid–base equilibria of 3AQ in ground and excited states. The emphasis here is to unravel the difference in the prototropism of the two basic centers in the molecule: the ring nitrogen atom and the amino nitrogen atom, in the light of our earlier report of ICT in polar solvents.

### 2. Materials and methods

#### 2.1. Experimental detail

3-Aminoquinoline from Lancaster, UK is used as received. Deionized water is distilled twice before being used as a solvent. The pH is adjusted by addition of NaOH and  $HClO_4$  solutions and is monitored by a pH meter (Toshniwal Inst. Mfg. Pvt. Ltd., Ajmer, India). 1–5 M solutions of  $HClO_4$  are also prepared from its stock solution (11.66 M) by proper dilution. Nafion-117 of thickness 0.007 in. and equivalent weight (EW) 1100, from Sigma–Aldrich, is washed with concentrated  $HNO_3$  till it becomes colorless and is then soaked in boiling double-distilled water. The ion ( $Na^+$  and  $Me_4N^+$ ) exchanged membranes, are prepared by soaking the nafion membrane in 1(M) solutions of NaOH and  $Me_4NCl$  (TMAC) respectively for nearly 24 h. The excess base remaining on the surface of the membrane is removed by washing the membrane

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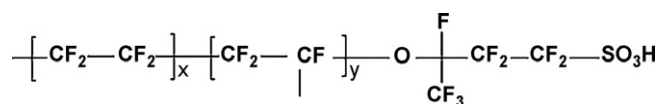
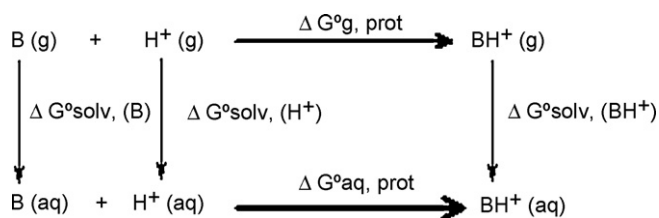


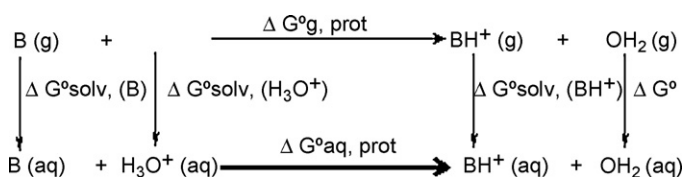
Chart 1.

Scheme 1. The thermodynamic cycle used for the calculation of  $pK_b$  in method 1.

repeatedly with doubly distilled water. 3AQ is incorporated in the nafion membrane by keeping the membrane immersed for 24 h in aqueous 3AQ solution with absorbance nearly 0.01 at 338 nm. Again the excess 3AQ on the surface of the membrane is removed by thorough washing of membrane with double-distilled water. The absorbance of the loaded membrane is kept less than 0.2 at  $\lambda_{\text{abs}}^{\text{max}}$ . The steady state spectra are recorded on JASCO V530 spectrophotometer and Perkin Elmer LS55 fluorimeter. The excitation spectra are recorded keeping emission monochromator at 500 nm. The Multiple Component Analysis (MCA) coded in PhotochemCAD (computer-aided photochemistry) software has been performed in order to determine the relative abundance of the two forms of 3AQ [10]. The Flexible Simplex Method implemented in MCA finds the minimum least square value for a function with multiple variables. The decomposition of a two-component spectrum is performed by providing pure spectrum of neutral and cationic species of 3-aminoquinoline. The spectrum of 3AQ at pH 3 is assumed to be pure monocationic and at pH 11 pure, neutral. Time-resolved fluorescence measurements have been performed on an IBH picosecond time correlated single photon counting (TCSPC) spectrometer using excitation by 295 nm diode. FWHM of the instrument response function (IRF) = 750 ps. Decays are recorded at  $\lambda_{\text{em}} = 450$  nm with a resolution of 0.11 ns per channel [11]. The fluorescence decays have been collected with the emission polarizer at a magic angle of  $54.7^\circ$  and have been fitted to single or multiexponential functions after deconvolution of the IRF, using an iterative deconvolution method using IBH DAS 6.0 software.

## 2.2. Computational detail

The ground state geometries of different forms of 3AQ in gas phase and in water are optimized using the density functional theory method with the Becke3LYP functional [12,13] in conjugation with both double and triple-zeta basis sets having diffuse functions, namely, 6-31++G\*\* and 6-311++G\*\* respectively as implemented in the Gaussian 03 software package [14]. The polarized continuum solvent model (PCM) [15] is adopted for calculation of the standard free energy in water. The default options for the self-consistent field (SCF) convergence and threshold limits in the optimization are used. For calculations of the basicity constants ( $pK_b$ ) of a base B,

Scheme 2. The thermodynamic cycle used for the calculation of  $pK_b$  in method 2.

two methods have been adopted here. The thermodynamic cycles used for method 1 and 2 are shown in Schemes 1 and 2 respectively. The standard free energy of protonation of a base, B in water  $\Delta G_{\text{aq,prot}}^\circ(\text{B})$  is calculated using thermodynamic cycles 1 and 2 [16].

$$\Delta G_{\text{aq,prot}}^\circ(\text{B}) = \sum \Delta G^\circ[\text{Products}(\text{aq})] - \sum \Delta G^\circ[\text{Reactants}(\text{aq})] \quad (1)$$

$\Delta G^\circ[\text{BH}^+(\text{aq})]$ ,  $\Delta G^\circ[\text{B}(\text{aq})]$ ,  $\Delta G^\circ[\text{H}^+(\text{aq})]$ ,  $\Delta G^\circ[\text{H}_3\text{O}^+(\text{aq})]$  and  $\Delta G^\circ[\text{H}_2\text{O}(\text{aq})]$  are the standard free energies of  $\text{BH}^+$ , B,  $\text{H}^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  in water respectively. The standard free energy of a species (X),  $\Delta G^\circ[\text{X}(\text{aq})]$  in water can be written by the sum of the gas phase standard free energy,  $\Delta G^\circ[\text{X}(\text{g})]$  and the standard free energy of solvation in water,  $\Delta G_{\text{solv}}^\circ[\text{X}]$  (Scheme 1):

$$\Delta G^\circ[\text{X}(\text{aq})] = \Delta G^\circ[\text{X}(\text{g})] + \Delta G_{\text{solv}}^\circ[\text{X}] \quad (2)$$

The standard Gibbs free energy in the gas phase is given by

$$\Delta G^\circ[\text{X}(\text{g})] = E_{0\text{K}}[\text{X}(\text{g})] + \text{ZPE}[\text{X}(\text{g})] + \Delta G_{0 \rightarrow 298}[\text{X}(\text{g})] \quad (3)$$

where  $E_{0\text{K}}$  is total electronic energy at 0K, ZPE is the zero point vibrational energy, and  $\Delta G_{0 \rightarrow 298}$  is the Gibbs free energy change from 0 to 298 K at 1 atm. The well-accepted value of standard free energy of the proton,  $\Delta G^\circ[\text{H}^+(\text{g})]$  is  $-6.28$  kcal/mol [16,17]. The standard free energy of a base, B in gas phase is calculated using the following equations:

$$\Delta G_{\text{g,prot}}^\circ(\text{B}) = \sum \Delta G^\circ[\text{Products}(\text{g})] - \sum \Delta G^\circ[\text{Reactants}(\text{g})]$$

The gas phase free energies ( $\Delta G_{\text{g}}^\circ$ ) are calculated at the standard state which is defined as 1 mol ideal gas at 1 atmospheric pressure whereas the calculated free energies of solvation ( $\Delta G_{\text{solv}}^\circ$ ) are defined as a transfer of a solute from its 1 M gas phase state into its 1 M solution phase state. Thus, the estimation of the solution phase free energy ( $\Delta G_{\text{aq}}^\circ$ ) needs a correction term ( $\Delta G^{\text{corr}}$ ) due to the reversible state change of 1 mol gas from 1 atm ( $24.47 \text{ L mol}^{-1}$ ) to 1 M ( $1 \text{ mol L}^{-1}$ ).

$$\begin{aligned} \Delta G^\circ[\text{X}(\text{aq})] &= \Delta G^\circ[\text{X}(\text{g})] + \Delta G_{\text{solv}}^\circ[\text{X}] \\ \Delta G^\circ[\text{X}(\text{aq})] &= \Delta G^\circ[\text{X}(\text{g})] + \Delta G_{\text{solv}}^\circ[\text{X}] + \Delta G^{\text{corr}} \\ \Delta G^{\text{corr}} &= RT \ln \frac{V_i}{V_f} = RT \ln(24.47) = 1.89 \text{ kcal/mol} \end{aligned} \quad (4)$$

**Method 1:**  $\Delta G_{\text{aq,prot}}^\circ(\text{B}) = \Delta G_{\text{g,prot}}^\circ(\text{B}) + (\Delta G_{\text{solv}}^*[\text{BH}^+] - \Delta G_{\text{solv}}^*[\text{B}] - \Delta G_{\text{solv}}^*[\text{H}^+] - \Delta G^{\text{corr}})$ . In this study, the value of  $\Delta G_{\text{solv}}^*[\text{H}^+]$  used is  $-267.9$  kcal/mol. The basis of accepting such value is that it provides a good match between theoretical and experimental results of amines [18].

**Method 2:**  $\Delta G_{\text{aq,prot}}^\circ(\text{B}) = \Delta G_{\text{g,prot}}^\circ(\text{B}) + (\Delta G_{\text{solv}}^*[\text{BH}^+] + \Delta G_{\text{solv}}^*[\text{H}_2\text{O}] - \Delta G_{\text{solv}}^*[\text{B}] - \Delta G_{\text{solv}}^*[\text{H}_3\text{O}^+])$ . In case of method 2 there is no need of any correction term since they will cancel each other. The basicity constants ( $pK_b$ ) [19] of a base B is then calculated using the equation given below:

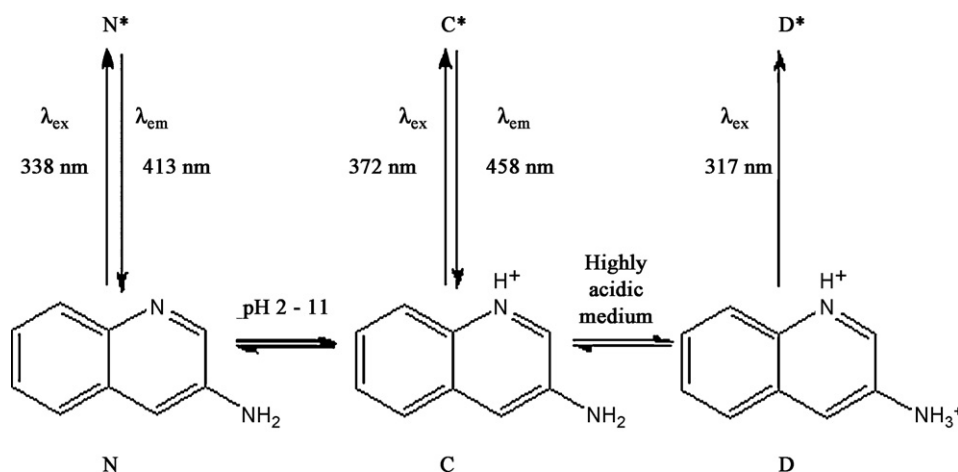
$$pK_b = \frac{\Delta G_{\text{aq,prot}}^\circ(\text{B})}{2.303 \times RT} \quad (5)$$

where  $R$  is the gas constant and  $T$  is the temperature.

## 3. Results and discussion

### 3.1. The equilibrium between the neutral and the monocationic forms

3AQ is likely to exist in different states of the protonation depending upon the acidity of the medium; the neutral form (N), the monocation (C) and the dication (D) (Scheme 3). The ring nitrogen is expected to be more basic than the amino nitrogen



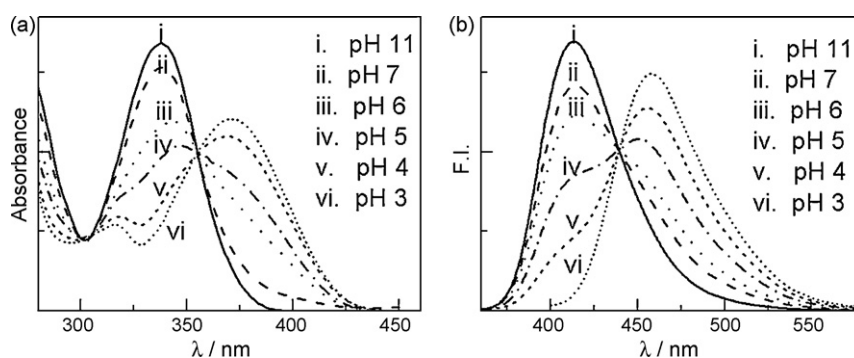
**Scheme 3.** Acid–base equilibria of 3AQ in ground and excited states. The excitation and emission wavelengths are also shown.

[19] as the lone pair in the ring nitrogen resides in an  $sp^2$ -hybrid orbital and hence is localized on the nitrogen atom. The lone pair on the amino nitrogen, however, is delocalized to some extent through resonance. Such delocalization is more pronounced in the excited state of the molecule, due to occurrence of ICT in polar media [5]. This contention finds support in earlier studies on aminopyridine [20] and hydroxyquinoline [21]. With this background, we assign the absorption with  $\lambda_{\max} = 338$  nm at pH 11 to the neutral (N) form of 3AQ. Upon decreasing the pH, a new spectrum emerges with  $\lambda_{\max} = 372$  nm. The spectra between pH 3 and 11 depicted in Fig. 1a are area-normalized spectra as the actual spectra do not pass through an isosbestic point, even though a two-state equilibrium exists. In a situation, where isosbestic zones appear rather than points, the area-normalization method can quantify the number of curve-crossing points which also serve as the indicators of equilibrium. These curve-crossing points are shifted in wavelength from their corresponding isosbestic points, called pseudo-isosbestic points [22,23]. The causes of appearance of isosbestic zones are the nonlinear behavior of absorption spectra and the fluctuation of the total concentration of the components in solution through their decomposition, specific interaction with solvents, or experimental error in sample preparation. In the pH dependent studies with 3AQ, an aliquot of probe solution was added to the solutions of different pH values of fixed volume to maintain the constant concentration of probe. However, a sharp point is not observed due to two likely reasons: experimental error and difference in ionic strengths. Upon area-normalization, we observe a pseudo-isosbestic point at 355 nm. The fluorescence spectra follow a similar trend of the pH dependence (Fig. 1b). The neutral and the cationic forms have maxima at 413 nm and 458 nm

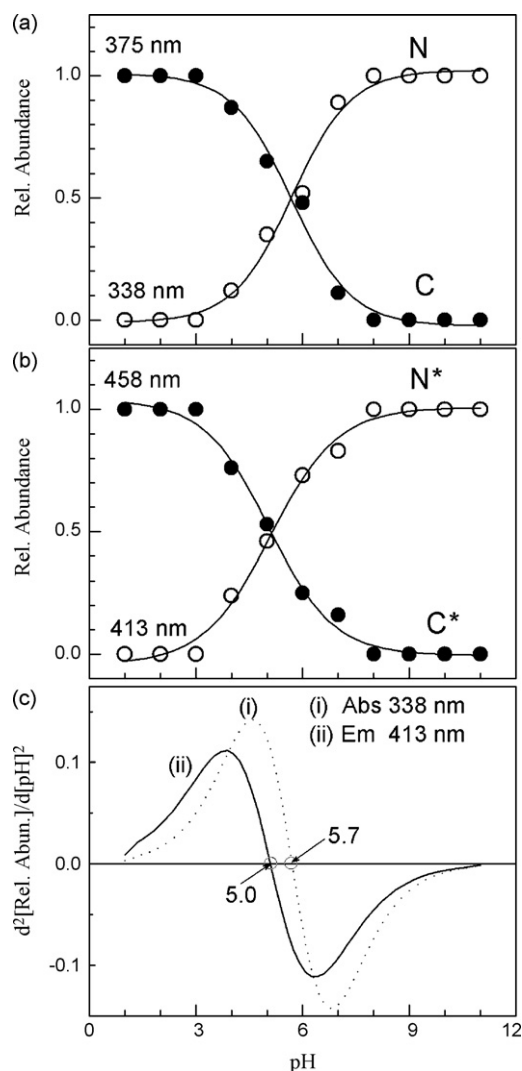
respectively. A pseudo-isoemissive point is observed at 439 nm. The plots of relative abundance vs. pH in both ground state and in lowest excited singlet state are sigmoidal in nature (Fig. 2a and b). The plot of double derivative of relative abundance with pH is constructed for calculation of ground state  $pK_b$  and excited state  $pK_b^*$  of 3AQ and consequent zero-crossing points are at 5.7 and 5.0 respectively (Fig. 2c) which are in close agreement with the computed value of 4.93 as is discussed later (Table 3). The  $pK_b$  is in agreement with the values for quinoline and the first  $pK_a$  of 3-aminopyridine, which are 4.94 and 5.98 respectively. This is in line with the contention that the ring nitrogen is more basic than the amino nitrogen. The miniscule change between  $pK_b$  and  $pK_b^*$  is rationalized by the absence of the coupling between the lone pair on the ring nitrogen atom and the  $\pi$ -electron system on the ring. So, a  $\pi$ - $\pi^*$  transition does not affect the availability of the lone pair on the ring nitrogen and thus, has no effect the first  $pK_b$ , which involved the ring nitrogen. However, the second  $pK_b$  may be expected to be affected significantly by electronic excitation, as it involves the amino nitrogen which is known to participate in ICT in the excited state [5]. Such a charge transfer would decrease the availability of the lone pair of the amino nitrogen and should cause it to be a weaker base in the excited state. In other words, the dicaton may be expected to lose a proton upon excitation, giving rise to the electronically excited monocation in the process. This contention is verified by the absorption and fluorescence studies at very high acid concentration.

### 3.2. 3AQ in highly acidic media

The absorption spectra of 3AQ in acidity range  $H_0 -5$  to  $-1$  at 25 °C is shown in Fig. 3a (upper panel). The dication exhibits

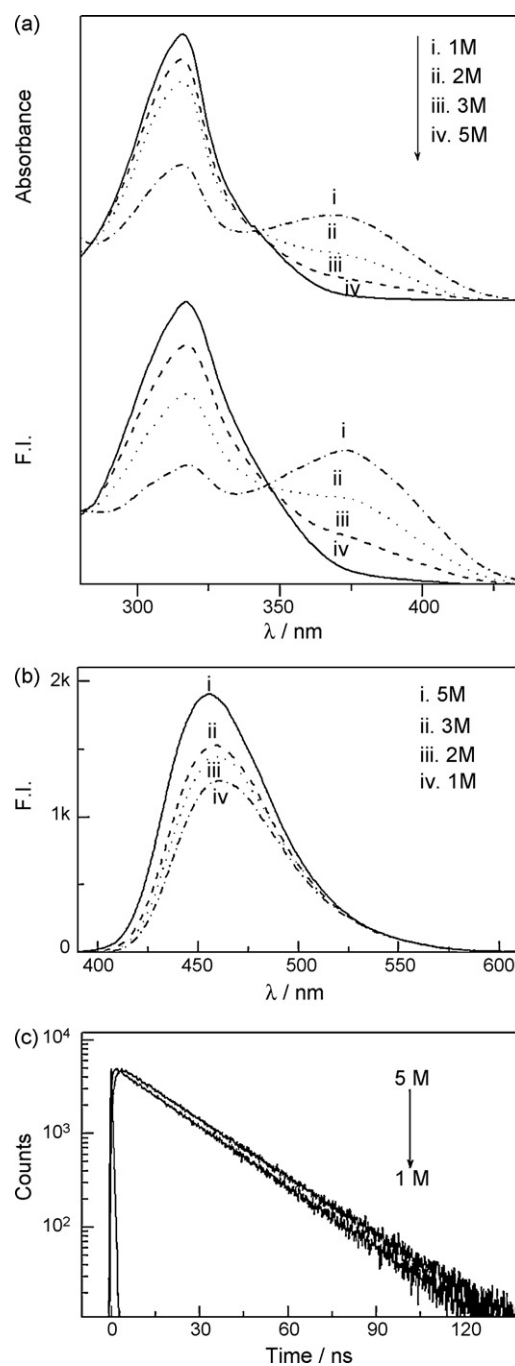


**Fig. 1.** (a) Area-normalized absorption spectra and (b) area-normalized emission spectra of 3AQ at various pH: (i) pH 11, (ii) pH 7, (iii) pH 6, (iv) pH 5, (v) pH 4, and (vi) pH 3. Pseudo-isosbestic point and pseudo-isoemissive point are at 355 nm and 439 nm respectively.



**Fig. 2.** pH dependence of (a) relative abundance in ground state at 338 nm and 375 nm, (b) relative abundance in lowest excited state at 413 nm and 458 nm, and (c) point of inflexion in ground and lowest excited singlet state.

absorption maximum at 317 nm whereas the monocation absorbs at 370 nm (Fig. 3a). The excitation spectra of 3AQ recorded at  $\lambda_{em} = 500$  nm resemble to the absorption spectra (Fig. 3a, lower panel). With increase in acid strength, the intensity of the peak corresponding to monocation gradually decreases. Fluorescence of 3AQ in various  $H_0$  values collected keeping excitation wavelength at 317 nm is shown in Fig. 3b. With increase in acid strength a blue-shift of 5 nm and increase in fluorescence intensity are observed. Neither isoemissive nor pseudo-isoemissive points are observed on superposition of the spectra. The emission window in high acid strength at excitation of 317 nm is close to that of monocation, which indicates that all the emission is from monocation, which is in line with the agreement proposed in the previous section. The contention is bolstered from time-resolved fluorescence measurements. The fluorescence decays are single exponential (Fig. 3c) and the fluorescence lifetimes of 3AQ measured in the high acid strengths are 20–21 ns, which is the same as that of the monocation (Table 1). The observed red shift of 5 nm in fluorescence and small change in fluorescence lifetime can be attributed in terms of the change in polarity of the medium. The point emerges from the study in homogeneous solution is that in excited state, monocation ( $C^*$ ) is formed from the dication ( $D^*$ ). With this background we



**Fig. 3.** (a) Absorption spectra (upper panel) and excitation spectra (lower panel) recorded keeping emission monochromator at 500 nm, and (b) emission spectra of 3AQ in different concentration of  $HClO_4$  ( $\lambda_{ex} = 317$  nm). (c) Time-resolved fluorescence decays of 3AQ in 1 and 5 M  $HClO_4$  ( $\lambda_{ex} = 295$  nm;  $\lambda_{em} = 450$  nm).

**Table 1**  
Fluorescence decay parameters of 3-aminoquinoline in 1–5 M  $HClO_4$  and in ion exchanged solid nafion membrane ( $\lambda_{ex} = 295$  nm;  $\lambda_{em} = 450$  nm).

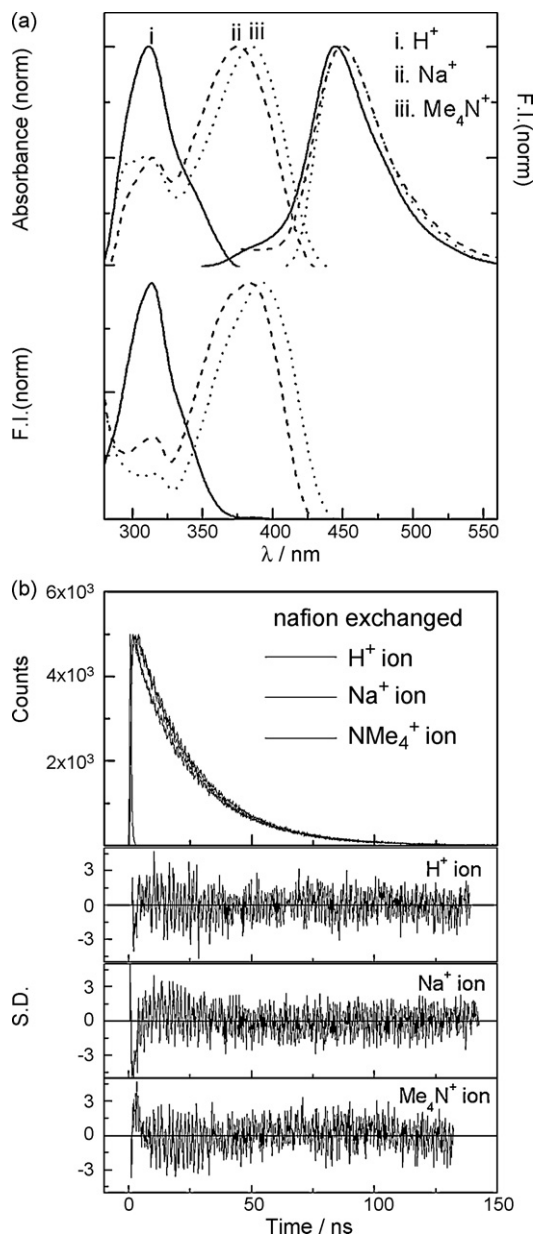
	Molarity (M)	$\tau$ (ns)	$\chi^2$
HClO <sub>4</sub>	1	19.98	1.16
	2	20.42	1.14
	3	20.66	1.13
	4	20.94	1.14
	5	21.07	1.15
Nafion	Acid-washed	22.89	1.28
	Na <sup>+</sup> ion exchanged	23.90	1.54
	Me <sub>4</sub> N <sup>+</sup> ion exchanged	23.77	1.40

**Table 2**Calculated free energy of solvation,  $\Delta G_{\text{solv}}^*$  (kcal/mol) of various protonated forms of 3AQ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ .

	Basis set	Base (N)	Cation (C)	Dication (D)	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$
$^a \Delta G_{\text{solv}}^*$	6-31++G(d,p)	-7.88	-53.04	-191.87	-112.41	-7.06
	6-311++G(d,p)	-7.98	-52.89	-190.39 <sup>b</sup>	-112.23	-6.81 <sup>c</sup>

<sup>a</sup> Geometry reoptimization in the aqueous phase.<sup>b</sup> Single-point calculations in the aqueous phase on the geometry optimized in gas phase.<sup>c</sup> The reported value  $\Delta G_{\text{solv}}^*[\text{H}_2\text{O}(\text{aq})] = -63.2$  kcal/mol (Ref. [24]).

have studied such excited state switching between cationic species in microheterogeneous media of nafion membrane. The motivation of this study is to perceive the role of microheterogeneous media towards regulation of such dynamics.



**Fig. 4.** (a) Peak-normalized absorption spectra (left panel) and peak-normalized fluorescence spectra (right panel) of 3AQ in ion exchanged nafion membrane: (i)  $\text{H}^+$  ion, (ii)  $\text{Na}^+$  ion, and (iii) ( $\text{Me}_4\text{N}^+$ ) ion. For native nafion,  $\lambda_{\text{ex}} = 317$  nm,  $\text{Na}^+$ -exchanged,  $\lambda_{\text{ex}} = 330$  nm, and  $\text{Me}_4\text{N}^+$ -exchanged membrane,  $\lambda_{\text{ex}} = 330$  nm. The excitation spectra of 3AQ in membranes are shown in lower panel ( $\lambda_{\text{em}} = 500$  nm). The spectra are peak-normalized for the sake of comparison. (b) Time-resolved fluorescence decays of 3AQ in nafion membrane ( $\lambda_{\text{ex}} = 295$  nm;  $\lambda_{\text{em}} = 450$  nm).

### 3.3. 3AQ in nafion membrane

The peak-normalized absorption spectra of 3AQ loaded in nafion membranes are shown in Fig. 4a. The  $\lambda_{\text{max}}^{\text{abs}}$  in acid-washed nafion film occurs at 316 nm. This is similar to the  $\lambda_{\text{max}}^{\text{abs}}$  of the dication in aqueous solution of acid strength  $\text{H}_0 = -5$ . It may be mentioned here that nafion is known to have a high concentration of  $\text{H}_3\text{O}^+$  ion. Consequently the molecules incorporated in this membrane often get protonated to the maximum possible extent [8]. On performing cation exchange by  $\text{Na}^+$  ion, the absorption peak is shifted to 375 nm, resembling that of monocation, C at pH 3. This is in line with the fact that cation exchange increases the pH as  $\text{H}_3\text{O}^+$  ions are replaced by  $\text{Na}^+$  or  $\text{Me}_4\text{N}^+$  ions. Notably, the spectral changes are similar for the cations, which is in contrast to our earlier observation with 2-(2'-pyridyl)benzimidazole [8]. This implies that the water content does not have a significant role to play in the present case. Fluorescence spectra of all nafion membranes are shown in Fig. 4a (left panel). The peaks are normalized for clarity. In the acid-washed film, the emission peak occurs at 445 nm, while in case of cation exchange membranes, the peak is shifted to 450 nm. Once again, the emission occurs only from the monocation for the acidic as well as ion exchanged membrane, even though the monocation is not present to a significant extent in the ground state in the acidic membrane. The excitation spectra of 3AQ in nafion membranes recorded at  $\lambda_{\text{em}} = 500$  nm are superimposable with the absorption spectra (Fig. 4a, lower panel). The fluorescence decays at 450 nm are single exponential (Fig. 4b and Table 1). The time constants for 3AQ loaded acid-washed membrane is 23 ns while that for  $\text{Na}^+$  and  $\text{NMe}_4^+$ -exchanged membranes are 24 ns. These time constants are close to that measured in highly acidic homogeneous media which again fortifies that emission observed in all the film comes from monocation. Thus, even, in nafion films, the dication loses a proton in the excited state before emission takes place.

### 3.4. Calculation of $\text{pK}_b$

The solvation free energy ( $\Delta G_{\text{solv}}^\circ$ ) of neutral and cationic forms of 3AQ, gas phase protonation free energy ( $\Delta G_{\text{g,prot}}^\circ$ ) and  $\text{pK}_b$  values for neutral and monocationic form of 3AQ are tabulated in Tables 2 and 3. It should be pointed out here that the issue on the absolute values of  $\Delta G_{\text{solv}}^*[\text{H}^+(\text{aq})]$ ,  $\Delta G_{\text{solv}}^*[\text{H}_3\text{O}^+(\text{aq})]$  and  $\Delta G_{\text{solv}}^*[\text{H}_2\text{O}(\text{aq})]$  is controversial [24,25]. The computed values of  $\Delta G^*[\text{H}_3\text{O}^+(\text{aq})]$  is  $-112$  kcal/mol which is much lower than the value ( $-110.2$  kcal/mol) reported by Pliego and Riveros [26]. However, the calculated  $\Delta G_{\text{solv}}^*[\text{H}_2\text{O}(\text{aq})]$  is in good agreement with reported values (Table 2) [27]. The reason for emphasizing on this point is that the change of 2 kcal/mol in solvation energy of proton/hydronium ion results in a significant shift on computed  $\text{pK}_b$  values. However, the observation of dependency of  $\text{pK}_b$  values on basis set is commensurate with the observation of other groups [28]. The experimentally observed first  $\text{pK}_b$  of 3AQ is 5.7 whereas the computed value of  $\text{pK}_b^{\text{N} \rightarrow \text{C}}$  is 4.93, which confirms that ring nitrogen as the first protonation site. The results also reveal that the amino group of 3AQ is less susceptible towards protonation and its dication is a very weak base, which are in accordance with

**Table 3**Calculated ground state  $pK_b$  values of 3-aminoquinoline.

Step	${}^a \Delta G_{g,prot}^*$				$pK_b$			
	6-31++G(d,p)		6-311++G(d,p)		6-31++G(d,p)		6-311++G(d,p)	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
N → C	-216.70	-53.47	-216.27	-54.32	3.04	4.93	3.54	4.54
C → D	-102.65	60.58	-101.81	60.14	17.98	19.86	19.57	20.57

<sup>a</sup> ZPE and thermal corrections from B3LYP/6-31G(d,p).  $\Delta G_{solv}^*[H^+] = -267.9$  kcal/mol (Ref. [17]).

experimental findings. It can be mentioned here that the method 2 where all the  $\Delta G^*$ (aq) parameters have been computed provides better agreement towards experimental results than in comparison to method 1.

#### 4. Conclusion

3AQ resides in three forms neutral (N), monocation (C) and dication (D), depending on the pH of the medium. The first  $pK_b$  has a value of 5–5.7 for the ground state as well as the excited state of 3AQ. This is rationalized in the light of the absence of the coupling of the ring nitrogen atom with the  $\pi$ -electron system in the ring. In solutions of high acidity and in acid-washed nafion membrane, the fluorophore exists as a dication (D). Even in these media, the emissive state is found to be monocationic, as the monocation–dication equilibrium involves the amino group, whose lone pair is strongly coupled with the  $\pi$ -electron system in the ring in the excited state, due to an ICT process that is operative in polar media. Consequently, the amino group gets deprotonated in the excited state, even very highly acidic media. The computed  $pK_b$  values for protonation of 3AQ are in reasonably good agreement with the experimental observations.

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