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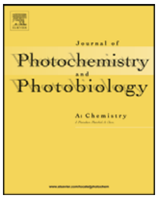

Solvent dependent excited state spectral properties of 4-hydroxyacridine: Evidence for only water mediated excited state proton transfer process

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ABSTRACT

The possibility of ground and excited state proton transfer reaction across the five member intramolecular hydrogen bonded ring in 4-hydroxyacridine (4-HA) has been investigated spectroscopically and the experimental results have been correlated with quantum chemical calculations. The difference in the emissive behaviour of 4-HA in different types of solvents is due to the presence of different species in the excited state. In non-polar solvents, the species present is non-fluorescing in nature, whereas 4-HA molecule shows normal emission from intramolecularly hydrogen bonded closed conformer in polar aprotic solvents. In polar protic solvents like MeOH, EtOH, etc. (except water), a single broad emission band is attributed to the hydrogen bonded solvated form of 4-HA. However, in case of water, fluorescence from the tautomeric form of 4-HA is observed apart from emission from the solvated form. Emission from the tautomeric form may arise due to double proton transfer via a single water molecule bonded to 4-HA. Evaluation of the potential energy surfaces by quantum chemical calculations using density functional theory (DFT) and time dependent density functional theory (TDDFT), however, points towards the possibility of proton transfer—both intrinsic intramolecular as well as water mediated in the first excited state of 4-HA.

1. Introduction

Inter- and intramolecular hydrogen bonding molecular systems have been studied extensively over the past decades due to their interesting photophysical and photochemical properties [1–13]. In particular, proton transfer processes in molecules containing bifunctional groups such as a proton donor and a proton acceptor site have been studied due to their relevance in living systems [7–13]. The types of systems studied for proton transfer reaction can be broadly classified into three categories. The first category comprises of systems with proton donor and acceptor sites within the same molecule having cyclic intramolecular hydrogen bonded (IMHB) ring in the ground state which facilitates proton transfer in the excited state. In this category, apart from the standard systems such as salicaldehyde, methyl salicylate and their derivatives [8,14–16] a number of other interesting systems such as 7-hydroxy-1-indanone (7HIN) [17,18], 3-hydroxy flavone and its derivatives [4,19–25] hydroxyl naphthyl pyrazoles [26,21] naphthaldehyde derivatives [7,9–13,27], etc. have been studied for excited state intramolecular proton transfer (ESIPT) process. The second category includes systems where double proton transfer occurs via a concerted process from one functional group to other as was reported in the case of double hydrogen-bonded dimers of 7-azaindole [28–30] or relayed by acyclic bridge of solvent molecules between two different groups such as in 7-hydroxyquinoline (7-HQ) [31–33]. The third category comprises of molecules such as 6-hydroxyquinoline (6-HQ) [34] where the bifunctional groups are far apart from each other and proton transfer is mediated by solvent water. In this case, water serves the purpose well due to its amphiprotonic nature.

This work describes a detailed insight into the emissive behaviour of 4-HA. The molecule acridine is one of the several aza-polycyclic aromatic hydrocarbons found in the partial combustion of fossils fuels and tobacco [35]. It is also detected in motor vehicle exhaust emissions, cigarette smoke, shale oil, coal tar and coal liquefaction products [35]. The molecule 4-HA is a substituted product of parent molecule acridine. This compound was chosen for the following reasons—firstly to explore the possibility of proton transfer process in five member hydrogen bonded ring system [4,36–39] which even till date is less studied one compared to six member hydrogen bonded ring systems. A similar type of system with a five member IMHB ring is 7-hydroxy-1-indanone [16–18] in which the tautomer state exists as a metastable state and the spectral properties are different compared to other studied related molecules having six member IMHB ring [11–13]. The five

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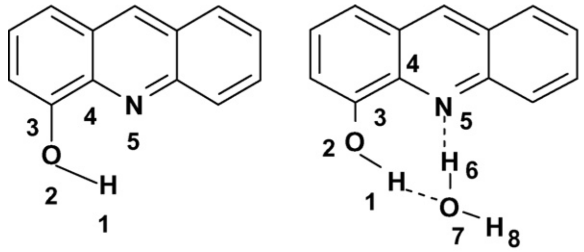


Scheme 1. Structure of 4-hydroxyacridine (4-HA) and its single water hydrated cluster with numbering of atoms at the hydrogen bonded site.

member ring in 7HIN imparts a strain to the hydrogen bonded site and hence, the hydrogen bond is weak in nature [16–18]. Therefore, 7HIN easily forms anion in protic solvents and in some polar aprotic solvents whereas other ESIPT systems with the six member IMHB do not form such anions under the same experimental condition [9,11–13]. Secondly, the photophysical study of 4-HA could be interesting as it is used in analytical chemistry as a good chelating agent. The cyclopalladated complex of 4-HA is known to have anticancer activity [40]. Metal complexes are known to serve as the intercalators for DNA [40]. Lastly, our interest is to investigate whether the change of chromophore from the basic quinoline unit to acridine unit can influence the photophysics. The molecule 4-HA has never been studied earlier for proton transfer reaction, though its naphthalene counterparts, 8-hydroxyquinoline (8-HQ) [36,37] and 8-mercaptoquinoline (8-MQ) [38,39] are well-studied compounds. We are interested to study the photophysics of 4-HA by a thorough analysis of ground and excited state properties in various solvents at different temperature and pH of the medium using absorption and emission spectroscopy. Furthermore, the structural calculations have been performed for the ground and excited states at DFT and TDDFT levels of theory. In particular, the potential energy curves (PECs) for intrinsic intramolecular proton transfer in the ground and excited states have been calculated along the proton transfer coordinate O_2–H_1 distance (Scheme 1) and PECs for water assisted proton transfer are calculated by simultaneous variation of O_2–H_1 and N_5–H_6 distance (Scheme 1) at the proton translocation site to correlate the theoretical findings with the experimental results. Presence of IMHB has been confirmed by analysis of the IR spectrum in solid as well as in solution phase.

2. Materials and methods

2.1. Materials

The molecule 4-hydroxyacridine (Scheme 1) and Aerosol OT (AOT) were purchased from Aldrich Chemicals and used as supplied. The solvents methylcyclohexane (MCH), heptane (HEP), cyclohexane (CYC), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), acetonitrile (ACN), isopropanol (Iso-prop), ethanol (EtOH) and methanol (MeOH) were purchased from Spectrochem and the purity of solvents have been checked in the wavelength range used for spectroscopic study. Triple distilled water was used for the preparation of aqueous solutions. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl), acetic acid and triethylamine (TEA) from E-Merck were used as supplied. Analytical grade sodium hydroxide (NaOH) was used.

2.2. Steady state measurements

The absorption and emission spectra of 4-HA in solvents of varying polarity have been taken by Hitachi UV–Vis (Model U-3501) spectrophotometer and PerkinElmer (Model LS-50B) fluorimeter, respectively. In all measurements, the sample concentration has been maintained within the range 10^{-4}–10^{-5} mol/dm^3 in order to avoid aggregation and reabsorption effects. IR spectrum of the molecule in KBr pellets and in different solvents is measured by a PerkinElmer spectrophotometer (PerkinElmer Spectrum RXI FT-IR system serial no. 54350).

2.3. Time-resolved measurements

The fluorescence lifetime of the molecule has been measured by a picosecond time correlated single photon counting (TCSPC) set-up [41]. A picosecond diode laser is used as exciting light source (IBH, UK, NanoLED-07, s/n 03931, 408 nm). The fluorescence signal was detected in magic angle (54.7°) polarization using Hamamatsu MCP PMT (3809U). The typical system response of the laser system was 75 ps. The decays were analyzed using IBH DAS-6 decay analysis software.

2.4. Computational procedures

The computed ground state geometry of the neutral species (N-form), open form (O-form) and its monohydrate complex (SN-form in scheme 2 and 3) have been computed at DFT levels with B3LYP functional and 6-311++G** basis set using Gaussian 03 software [42]. For the calculation of excited states information, TDDFT method has been used with the same functional and basis set. Possibility of ground state intramolecular proton transfer (GSIPT) was explored by constructing the PEC with the variation of O_2–H_1 distance (Scheme 1). At different OH bond distances the geometry has been optimized to get the ground state potential energy curve. The excited state surface can be generated by different methods [43–46]. In general, similar to the ground state calculation the excited state optimization can be performed at different OH distances using CIS method [46]. However, information regarding ESIPT mechanism can be obtained by constructing the Franck–Condon curves by adding the TDDFT/6-311++G** vertical excitation energies to the corresponding GSIPT curves. Such methods are successfully implemented to evaluate the PECs for the ESIPT reaction in several studied systems [43–45]. The possibility of water assisted proton transfer in the monohydrate complex of 4-HA monomer was also studied for both the ground and excited states following the same procedure. Here, both O_2–H_1 and N_5–H_6 (Scheme 1) distances are simultaneously varied to construct the potential energy curves.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of 4-HA (Fig. 1) were measured in various types of solvents and the absorption band maxima are presented in Table 1. As seen in Fig. 1, the absorption spectra exhibit two bands in all solvents—one at ~285 nm and another broad band at ~385 nm. The spikes observed at ~340 and ~360 nm arise from the parent chromophore unit of acridine. Such types of spikes have been observed in the absorption spectra of some nitrogen containing polycyclic compounds studied earlier [47,48]. As we move from non-polar solvents to the polar ones, the band smoothens out indicating greater solute solvent interaction as was observed for numerous systems with IMHB in the ground state [9,12,13].

Addition of H_2SO_4 or acetic acid to methanolic solution of 4-HA leads to emergence of a new band at ~435 nm (Fig. 2a). Addition of TEA or NaOH results in generation of a band at ~450 nm (Fig. 2b). The same result was observed for the variation of pH in ACN solution as well as in water solution. The species formed on addition

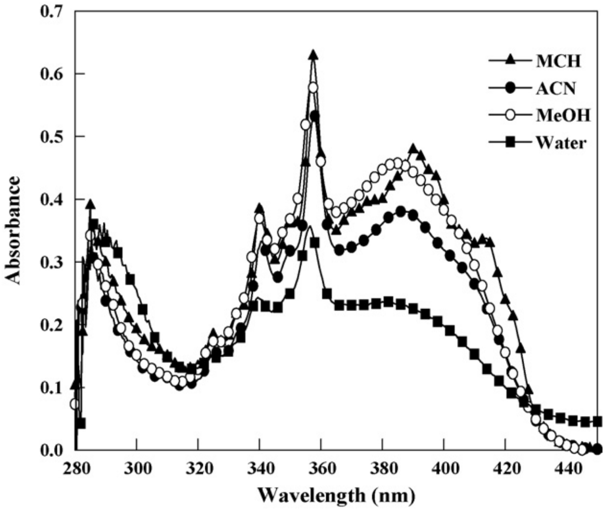


Fig. 1. Absorption spectra of 4-HA in different solvents at room temperature.

of acid which absorbs at ~435 nm can be undoubtedly assigned to the protonated or the cationic form of 4-HA (C-form of Scheme 2). In the case of 8-HQ, addition of concentrated H_2SO_4 results in the formation of the sulphonated product with entirely different fluorescence properties [36]. However, for 4-HA, the formation of the sulphonated product on addition of H_2SO_4 is ruled out as the band at ~435 nm is also observed on addition of acetic acid. Similarly, the species formed on addition of base is the anionic form of 4-HA which absorbs at ~450 nm (A-form of Scheme 2). As seen in Fig. 2a and b, gradual addition of both the acid or base results in the disappearance of the absorption band at ~385 nm with the emergence of the respective new bands with clear isobestic points indicating the formation of new bands corresponding to species generated from the same ground state species having absorption at ~385 nm. Comparing the absorption spectra of 8-HQ, the species absorbed at 385 nm in 4-HA in all solvents is assigned to the ground state lowest energy intramolecular H-bonded closed form (N-form of Scheme 2). The presence of intramolecular hydrogen bond in the ground state is further confirmed from the analysis of the IR spectrum of 4-HA in non-polar and polar aprotic solvents which shows a band with OH stretching frequency of 3399 cm^{-1}. This characteristic stretching frequency arises from hydrogen bonded OH group. Possibility of intermolecular hydrogen bonded species in the above mentioned solvents was absent as the IR-spectrum was independent of sample concentration. For 8-HQ, the OH stretching frequency in IR spectrum in dichloromethane, chloroform and carbon tetrachloride is located in the range 3410–3412 cm^{-1} which is ascribed to the presence of intramolecular H-bond in 8-HQ in these solvents. The anion and cation are generated from the closed conformer of 4-HA and the absorption bands of both the ions shifted

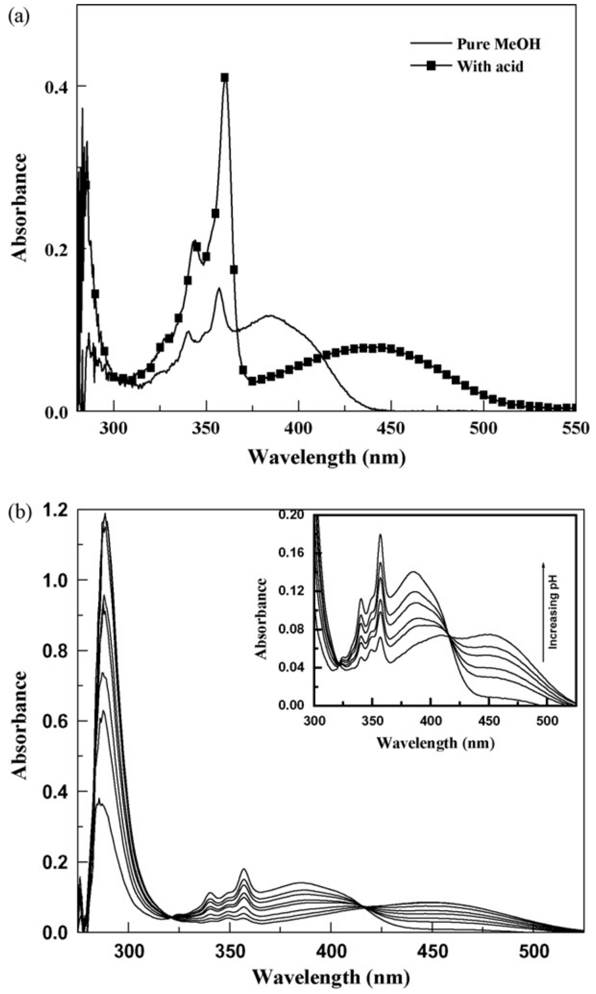


Fig. 2. Effect of addition of (a) sulphuric acid and (b) NaOH on the absorption spectra of 4-HA in MeOH.

Table 1
Spectroscopic parameters obtained from absorption and emission measurements of 4-HA at room temperature.

Solvent	Absorption band (nm)			Emission band (nm) $\lambda_{\text{ext.}} = 385$ nm	Quantum yields (Φ_f)
	λ_1	λ_2	λ_3		
CYC	285	390	–	–	–
HEP	285	391	–	–	–
MCH	285	390	–	–	–
$CHCl_3$	287	386	–	460	2.52×10^{-3}
CCl_4	286	385	–	462	2.13×10^{-3}
THF	289	389	–	465	3.52×10^{-3}
ACN	286	383		465	2.24×10^{-3}
$ACN+H^+$	286	350	435	–	–
Isopropanol	286	385	–	478	2.44×10^{-3}
$MeOH+OH^-$	285	385	–	482	2.52×10^{-3}
$MeOH+H^+$	285	350	430	–	–
$MeOH+OH^-$	285	–	450	–	–
EtOH	286	385	–	484	1.13×10^{-3}
H_2O	289	382	–	473, 534	1.015×10^{-3}
H_2O+H^+	290	350	430	–	–
H_2O+OH^-	290	–	450	–	–

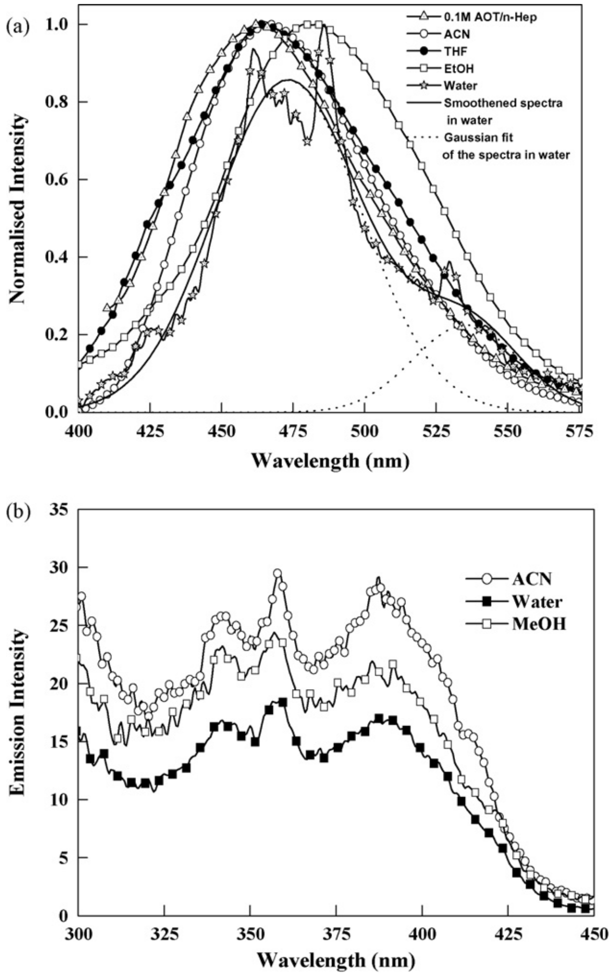


Fig. 3. (a) Fluorescence emission spectra of 4-HA in different solvents at room temperature ($\lambda_{\text{ext.}} = 385$ nm); (b) excitation spectra of 4-HA monitored at relevant emission band positions in different solvents at room temperature.

to red due to favourable resonance stabilization of the charge at the aromatic ring systems.

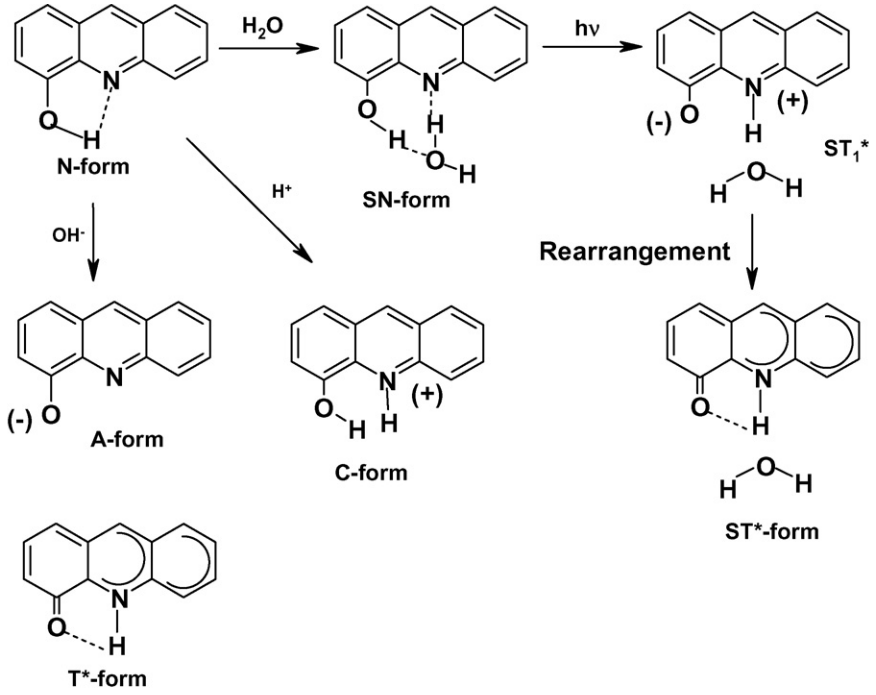
3.2. Emission spectra

The emissive behaviour of 4-HA is quite different in different category of solvents (Fig. 3a). Thus, spectral analysis in different solvents is used to characterize different species. In alkane type of solvents, practically no emission is observed for 4-HA molecule. However in 0.1 M AOT surfactant molecule in n-heptane, a band at ~465 nm is observed ($\lambda_{\text{ext.}} = 385$ nm). In polar aprotic solvents, excitation of the 385 nm band shows an emission band at ~465 nm. In alcoholic media, 4-HA shows a broad band with emission maxima at ~480 nm for the same excitation. In water, along with a broad emission band (473 nm), a prominent shoulder band is observed at the red side of the broad band. A Gaussian fit of the band shape shown in Fig. 3a indicates the presence of two bands—one at 473 nm and another at 534 nm.

These varied observations are due to the presence of different species in different solvents. Like 8-HQ, the lack of fluorescence in alkanes in the concentration range used for fluorescence measurements is due to formation of dimers which can undergo biprotonic transfer in the excited state [36]. This is confirmed when an emission band at ~465 nm is observed for 4-HA in 0.1 M AOT surfactant solution in *n*-heptane. In the organized medium of AOT, the dimer formation of 4-HA is hindered as the size of the dimer is higher than the AOT micelle cavity size and hence local emission from the bare molecule is observed at ~465 nm. As in case of AOT/*n*-heptane medium, in polar aprotic solvents like ACN, $CHCl_3$ and CCl_4 too, the emission band at ~465 nm is assigned to the normal emission from the excited N-form of 4-HA which is analogous to the case of 8-HQ in polar aprotic solvents [36]. In alcoholic media, a relatively intense and broad band with the emission maxima at ~480 nm is observed and is assigned to the emission from the excited solvated normal form (SN*-form) of 4-HA molecule (Scheme 2). Interestingly, in water, 4-HA shows two emission bands—one at 473 nm and another red sided band at 534 nm. Comparing the emission behaviour of 4-HA with 8-HQ in water, the emission band at 473 nm is assigned to the emission from the monohydrate complex of 4-HA with a single water molecule bridging the two functional groups (SN*-form). The most red-sided emission band at ~534 nm could be the emission from the excited tautomeric form (T*-form) of 4-HA generated after proton migration from donor to the acceptor site via a water molecule in the excited state (Scheme 2). However, the absence of tautomer emission in 8-HQ has been ascribed by considering quenching of fluorescence via non-radiative deactivation. Excitation spectra (Fig. 3b) of 4-HA in all solvents at the relevant emission band positions are found to be similar to the absorption spectra (Fig. 1). Thus, different bands in different solvents arise from the same ground state species which absorbs at ~385 nm.

Addition of H_2SO_4 or NaOH to aqueous or alcoholic solution leads to complete disappearance of the emission bands (Fig. 4). This indicates that the cation and anion of 4-HA are non-emissive in nature as was seen in case of 8-HQ molecule [36]. However, addition of acetic acid to ACN solution of 4-HA results in a blue shift of the emission band from ~465 nm to ~450 nm (Fig. 4c). This may be due to the formation of adduct of acetic acid molecule with 4-HA monomer having different emissive behaviour. It is found that addition of both acid and base in aqueous solution of 4-HA results in the disappearance of the ~473 nm band and only the band at 534 nm is observed which ultimately vanishes after addition of larger amounts of acid as well as base. This is because both the C*- and A*-forms of 4-HA (Scheme 2) are non-fluorescent in nature. Acid or base first easily breaks the weak intermolecular hydrogen bond of the SN-form and then ruptures the comparatively strong intramolecular hydrogen bond of the N-form. Furthermore, addition of acid or base leads to fluorescence quenching of 480 nm band in methanolic medium without emergence of the band at 534 nm as is observed in aqueous medium. The amphiprotonic nature of water plays a significant role here since emission from the T-form is observed more prominently only in aqueous medium. As proposed for 8-HQ, [36] the resulting tautomer of 4-HA must also have a ketonic structure (Scheme 2) rather than a zwitterionic structure. This is due to transfer of electronic charge from one ring to the other which removes the charge developed at the prototropic site. This zwitterionic structure may be the intermediate which finally gives rise to the ketonic form. Thus, the whole process is ascribed to water-assisted proton transfer reaction in the excited state. In case of 8-HQ, the tautomeric form undergoes rapid deactivation resulting in complete absence of fluorescence in water. In contrast to 8-HQ, presence of another aromatic ring in 4-HA, may provide additional stability to the tautomeric form due to the possible extensive delocalization of the electronic charge to the rings. Hence the large Stokes shifted fluorescence band at 534 nm is observed for T-form in aqueous medium. The lack of fluorescence from this T-form in other solvents indicate towards the possibility of only water assisted excited state proton transfer process in 4-HA.

Increasing of temperature results in a blue shift of the 465 nm emission band in ACN and 480 nm emission band in MeOH (Fig. 5a



Scheme 2. Possible ground and excited state species of 4-HA.

and b) with decrease in intensity. However the decrease of intensity in case of MeOH solution (Fig. 5b) is more prominent than in case of ACN (Fig. 5a). Increase of temperature assists non-radiative channels in both solvents. However, rupture of intermolecular hydrogen bonds with MeOH solvent decreases the intensity to a greater extent in methanol solvent.

3.3. Fluorescence quantum yield and lifetime

The molecule 4-HA shows very low quantum yield in almost all types of solvents, (Table 1) and no fluorescence in alkane solvents. Fluorescence decay is monitored in ACN ($\lambda_{mon.} = 465\,nm$) and in MeOH ($\lambda_{mon.} = 482\,nm$) solvent using $\lambda_{ext.} = 408\,nm$ (Fig. 6). Lack of fluorescence in alkanes and very fast excited state decay kinetics in water made lifetime measurements impossible in these solvents. All the decays were fitted to single exponential and the lifetime in ACN ($\alpha = 0.033$, $\iota = 12.48\,ns$, $\chi^2 = 1.05$) and MeOH ($\alpha = 0.157$, $\iota = 0.327\,ns$, $\chi^2 = 1.26$) are in nanosecond scale but in case of ACN solution, a small fast component was present which was beyond the resolution limit of the instrument (75 ps). The fluorescence lifetime for the local emission of 4-HA molecule in ACN solvent is larger than fluorescence lifetime of the hydrogen bonded clusters of 4-HA with MeOH solvent. This is because hydrogen bonding insists non-radiative deactivation path.

3.4. Computational details

The first insight into the electronic reorganization during the process of proton transfer-both intramolecular as well as water assisted proton transfer is achieved by the determination of the structure of 4-HA for both the ground and excited states. Calculated geometries for the N-form, solvated form and O-form were performed at DFT (B3LYP/6-311++G**) level (Scheme 3). Excited state calculations were performed using TDDFT method. Though geometry optimization was not possible in the excited state by this method, the values obtained were good enough to support our experimental findings. The relevant structural parameters of the fully optimized geometries for the ground state of N-, T-, SN- and ST-forms (Scheme 3) at B3LYP/6-311++G** are tabulated in Table 2. The energies of the ground state optimized structures for the different possible forms of 4-HA and the dipole moments are presented in Scheme 3. From the calculated results it is found that in the ground state the N-form is far more stable than the O-form and the SN- form is again more stable than the N-form (Scheme 3). The strength of the intramolecular H-bond in the ground state estimated from the energy difference between the N-form and the O-form is ~8.28 kcal/mol. The energy of the T-form (in absence of water molecule) is ~14.07 kcal/mol higher in energy (B3LYP/6-311++G**) than the intramolecularly H-bonded closed form (N-form) of 4-HA. Therefore, calculations show the existence of N-form and solvated SN-form in the ground state and rule out the existence of T-form in the ground state.

Table 2
Relevant structural parameters for the ground state optimized geometry of different possible species of 4-HA at DFT level using B3lYP/6-311++G** basis set.

Parameters	N-form	T-form	SN-form	ST-form
O_2–H_1	0.975	2.064	0.981	1.674
O_2–C_3	1.350	1.259	1.3441	1.270
C_3–C_4	1.439	1.469	1.447	1.466
C_4–N_5	1.336	1.341	1.344	1.352
N_5–H_1	2.077	1.031	–	1.037
O_2–N_5	2.6700	2.611	–	1.794
$\angle H_1$–O_2–C_3	105.77	86.31	–	0.995
$\angle N_5$–H_1–O_2	117.46	110.52	–	–
N_5–H_6	–	–	1.841	1.037
H_6–O_7	–	–	0.985	1.794
O_7–H_1	–	–	1.784	0.995
$\angle O_2$–H_1–O_7	–	–	176.09	157.96
$\angle O_7$–H_6–N_5	–	–	156.70	175.51
$\angle H_1$–O_2–C_3	–	–	115.31	132.43
$\angle H_1$–O_7–H_6	–	–	76.64	75.90
$\angle H_1$–O_7–H_8	–	–	116.09	106.35
$\angle O_2$–H_1–O_7–H_6	–	–	−111.46	−4.43
$\angle C_4$–N_5–H_6–O_7	–	–	17.63	38.45
$\angle C_3$–O_2–H_1–O_7	–	–	112.59	6.92

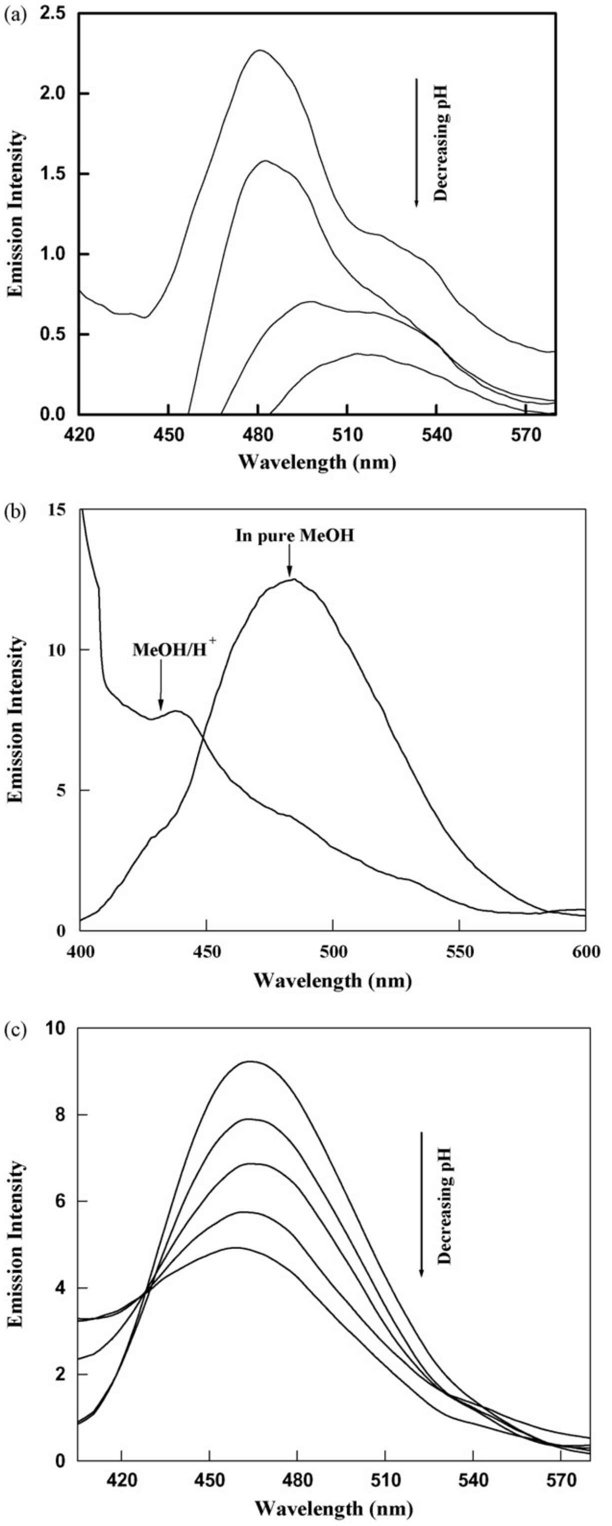


Fig. 4. Effect of addition of sulphuric acid on the emission spectra of 4-HA in (a) water, (b) MeOH and (c) effect of addition of acetic acid on the emission spectra of 4-HA in ACN ($\lambda_{ext.}$ = 385 nm).

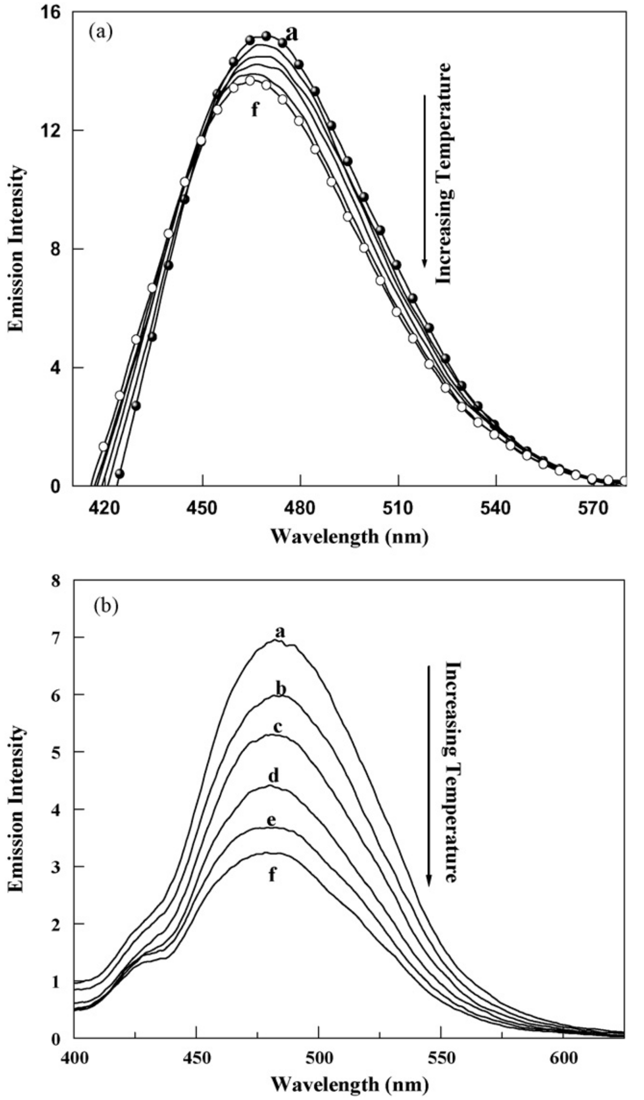
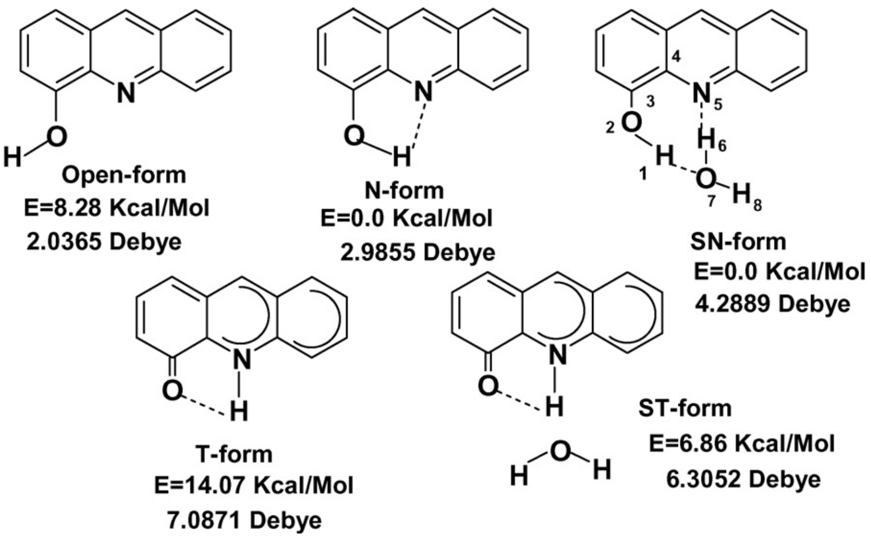


Fig. 5. Effect of increasing temperature on the emission spectra of 4-HA in (a) ACN and (b) MeOH ($\lambda_{ext.}$ = 385 nm) (a—273 K, b—283 K, c—293 K, d—303 K, e—313 K and f—323 K).

Evaluation of the GSIPT curve for intrinsic intramolecular proton transfer is done by optimizing the geometry at B3LYP/6-311++G** level for a number of structures of 4-HA with O_2–H_1 distance varying in the range 0.87–2.06 Å. The ESIPT curves are obtained by adding the vertical excitation energy to the GSIPT curve. Fig. 7 shows the plot of variation of potential energy of 4-HA with the variation of O_2–H_1 bond length. It is found that the energy of the S_0 state increases with the increase of O_2–H_1 bond length. It is also seen that the N-form is the global minimum on the S_0 surface. As seen in Fig. 7, the existence of the T-form in the S_0 state is completely ruled out as T-form is quite a high-energy structure on the S_0 surface. But, the S_1 state represents an asymmetric double well potential along the reaction coordinate (O_2–H_1 bond length) with two minima at N* and T* forms. In the S_1 state, the T*-form is far more stable than the N*-form and the transition from N* to T*-form is accompanied by a small energy barrier of ~5.49 kcal/mol. Same is observed for S_2 state too (picture not given). However excitation to S_2 surface will require far more energy than that for S_1 surface, hence this possibility is ruled out. Theoretically intrinsic proton transfer is only possible if the excited N*-form can cross over this barrier to form the T*-form which can give rise to the red shifted emission for the proton transfer form.

Similarly, the GSPT curve for water assisted proton transfer in 4-HA monomer (Scheme 2) is computed using the energies of the optimized geometry for different structures by varying the O_2–H_1 and N_5–H_6 distances, simultaneously. Fig. 8a and b shows the 3D



Scheme 3. Possible species in the ground state of 4-HA and their dipole moment and energy with respect to the lowest energy form calculated at DFT(B3LYP/6-311++G**) level.

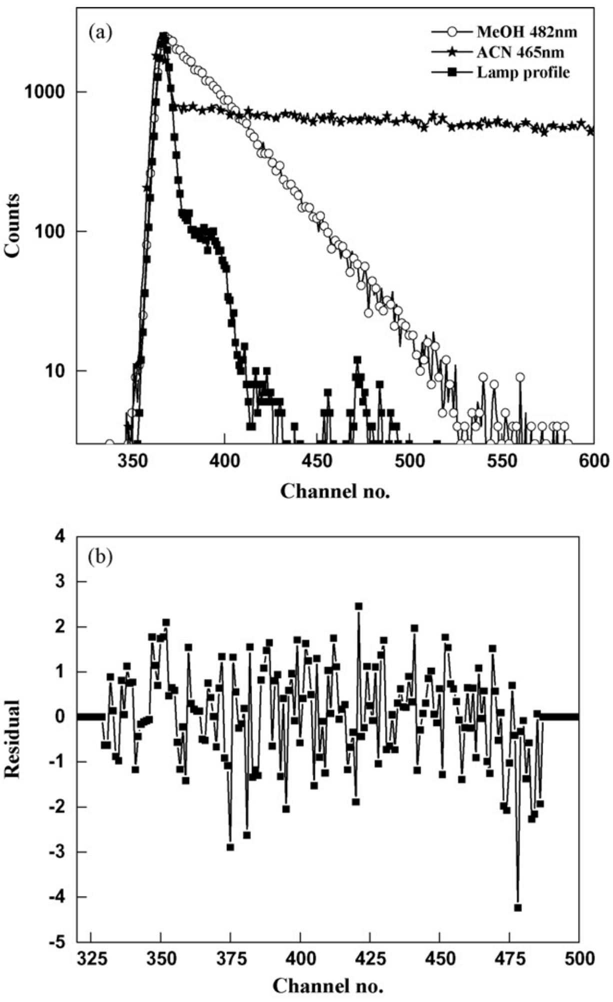


Fig. 6. (a) Fluorescence decay profiles of 4-HA in MeOH ($\lambda_{mon.}$ = 482 nm) and in acetonitrile ($\lambda_{mon.}$ = 465 nm) at 298 K. The curves represent the best fit of the experimental points to a single exponential decay ($\lambda_{ext.}$ = 408 nm, the lamp profile is given); (b) residual plot for decay curve of 4-HA in MeOH.

potential energy surfaces for S_0 and S_1 states with variation of O_2–H_1 and N_5–H_6 distance in the 4-HA monomer complexed with a water molecule (SN-form). As is evident from the figure that the process of water assisted ESIPT in 4-HA is a barrierless process whereas the excited state intramolecular proton transfer in bare molecule of 4-HA involves a small barrier (Fig. 7). Theoretically single water molecule assisted concerted proton transfer process leads to the possibility of a red shifted emission form the ST*-form. As seen in Fig. 8, the transformation from SN-form to ST-form in the S_0 surface goes through a transition state (TS) with high barrier energy. On the other hand, on the S_1 surface the transition from SN* to ST* is a barrierless process. Therefore, theoretically single water molecule assisted proton transfer is supportive to the experimental findings.

Nagaoka and Nagashima proposed the nodal plane concept of π-system molecular orbital to rationalize the phenomenon of ESIPT in 1-hydroxy-2-acetophenone [49]. They divided the systems under study into three parts—the hydroxyl part, the carbonyl part and the benzene part. Considering only the benzene part, the electronic excitation from HOMO to LUMO produced biradicals with nodal

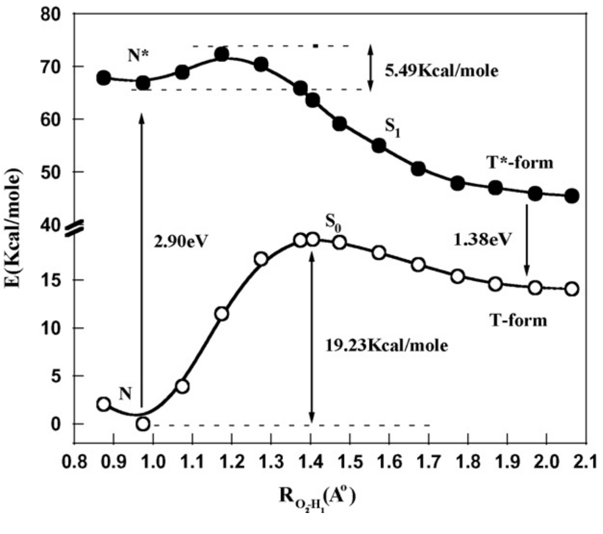


Fig. 7. Potential energy curves for the ground (S_0) and first excited state (S_1) of 4-HA with variation of O_2–H_1 distance using B3LYP functional and 6-311++G** basis set.

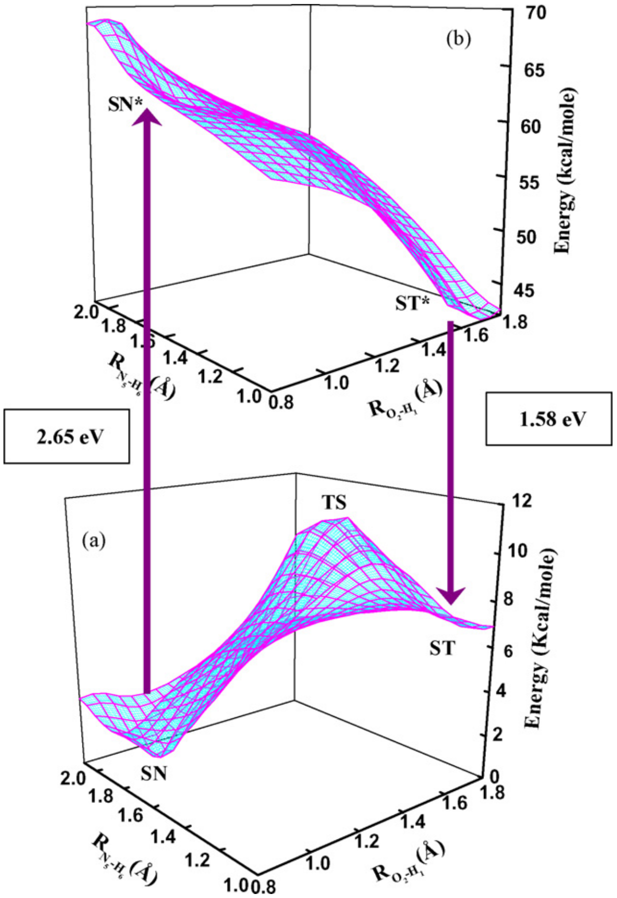


Fig. 8. 3D plot of potential energy variation for the transformation from SN form to ST form in the (a) S_0 and (b) S_1 states of 4-HA-water monohydrate with variation of O_2–H_1 and N_5–H_6 distances using B3LYP functional and 6-311++G** basis set.

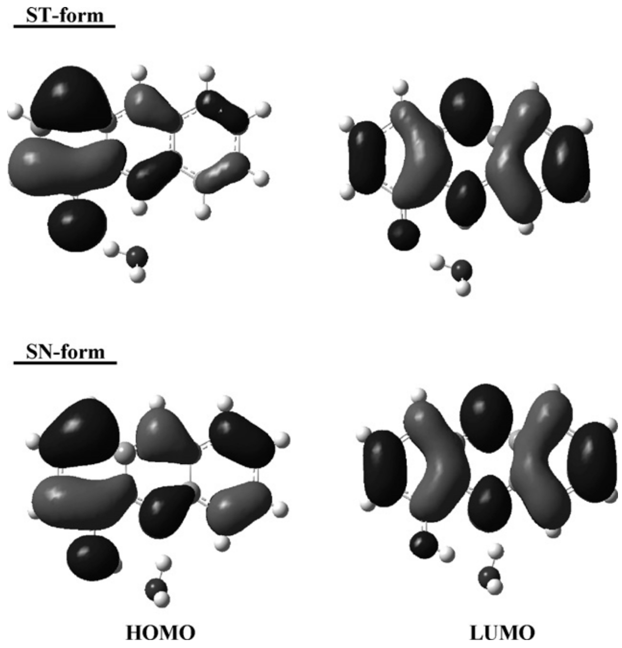


Fig. 9. Molecular orbital pictures of SN and ST forms of 4-HA computed at B3LYP/6-311++G** level.

plane running perpendicular to the benzene ring. Analysis of the HOMO and LUMO shows that the HOMO is a π-orbital with bonding character primarily along C_3–C_4 bond and anti-bonding character along C_3–O_2 and C_4–N_5 bonds for both SN and ST forms. As seen in Fig. 9, HOMO of both SN and ST forms has a large electron density on the O_2 atom with bonding character along $O_a\cdots N_5$. Thus, transfer of proton in the ground state does not lead to any further stabilization through electronic redistribution. Whereas, the LUMO is of π^* character and excitation of electron from HOMO to LUMO in the SN-form leads to specific localization of the π-electron density over the IMHB ring with anti-bonding character along C_3–O_2 and C_4–N_5 bond sites. Transfer of proton in the excited state produces a LUMO where the electron density increases over O_2 atom. The presence of nodal planes between C_3–O_2 and C_4–N_5 prevents electron delocalisation in the benzene ring thus preventing the reversal of proton transfer in the excited state.

4. Conclusion

From the spectroscopic and theoretical analysis of 4-HA carried out in this work, it has been established that 4-HA behaves differently in different type of solvents. After a thorough analysis of the variation of the absorption and emission spectra with the nature of solvents, effect of pH and temperature of the medium it is established that the molecule in the ground state exists as intramolecular hydrogen bonded closed conformer and intermolecular hydrogen bonded solvated clusters in protic solvents. The molecule 4-HA does not show fluorescence in non-polar solvents due to the formation of non-fluorescent dimer. In polar aprotic solvents and in AOT micelles, local emission is observed from the closed conformer of 4-HA. Hydrogen bonding solvents methanol and ethanol form solvated clusters which shows low energy emission. In water, the molecule shows in addition to the local emission from the hydrogen bonded clusters, a low energy emission, which is ascribed to emission from proton transfer keto form. Presence of additional aromatic ring in 4-HA may be responsible for such transformation in the excited state compared to that of 8-HQ. Such keto tautomer of 4-HA may be formed due to water mediated double proton transfer on the excited state potential energy surface at the intermolecular hydrogen bonded network site. Theoretical calculations at DFT and TDDFT levels support a low barrier intramolecular proton transfer in the bare molecule and a barrierless single water assisted proton transfer in the first excited state of 4-HA.

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