

# Excited-State Phototautomerization of 8-amino-1-naphthol-3, 6-disulfonate in Polar and Acidic Solutions

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## Abstract

Excited-state photodynamics of 8-amino-1-naphthol-3,6-disulfonate (8-ANDS) in some polar solvents and aqueous acidic solutions has been studied by using steady-state fluorescence and picoseconds time-correlated single-photon counting techniques. 8-ANDS in protic solvents exhibits two conformers in the excited state namely, a neutral form and a zwitterion. At shorter wavelength, 8-ANDS decays exponentially due to a neutral form while at longer wavelength, it shows a bi-exponential decay due to an additional decay of the zwitterion. Fluorescence decays of 8-ANDS in the acetonitrile solutions and  $D_2O$  support a mechanism of solvent assisted proton hopping from  $-OH$  to  $-NH_2$  to form a zwitterion in the excited state. A bi-exponential decay is also observed in perchloric acid solutions due to a protonated form and the zwitterion.

**Keywords:** 8-amino-1-naphthol-3, 6-disulfonate, Phototautomerism, solvent effect, excited-state proton-transfer, fluorescence lifetime.

## Résumé

Nous avons étudié la photodynamique de l'état excité de 8-amino-1-naphthol-3,6-disulfonate (8-ANDS) dans certains solvants polaires et solutions aqueuses acides, grâce à la fluorescence état stationnaire et aux techniques de comptage en picosecondes corrélées dans le temps au photon unique. Le composé 8-ANDS dans les solvants protiques montre deux conformères dans l'état excité, soit une forme neutre et un zwitterion. Aux longueurs d'onde plus courtes, 8-ANDS se décompose exponentiellement à cause de la forme neutre, alors qu'aux longueurs d'onde plus grandes, il montre une décroissance bi-exponentielle

à cause de la décomposition additionnelle du zwitterion. La dégradation de la fluorescence de 8-ANDS dans les solutions d'acétonitrile et  $D_2O$  supporte l'idée d'un saut du proton assisté par le solvant, de  $-OH$  à  $-NH_2$ , pour former un zwitterion à l'état excité. La décroissance bi-exponentielle est aussi observée dans des solutions d'acide perchlorique à cause de la forme protonée et du zwitterion.

## Introduction

Fluorescence studies on aromatic molecules with mono-functional group or bi-functional groups have received much attention in the past due to their applicability in many chemical processes [1-6]. The photophysical and photochemical properties of the bi-functional aromatic molecules differ significantly from that of the mono-functional aromatic molecules. The acid-base properties of the functional groups and their relative positions to each other in the aromatic moiety are quite important to the fluorescence property of the aromatic molecule. If one functional group is an electron-donating group while the other is an electron-withdrawing group, the migration of the proton from one functional group to another takes place in the excited state due to phototautomerization. If functional groups are in the ortho-position to each other, the phototautomerization takes place through intramolecular hydrogen bond and if they are widely separated, the phototautomerization occurs mainly through a biprotic process [7].

Mehata and coworkers [4] have reported that the fluorescence decay of a 6-hydroxyquinoline in methanol shows a single exponential whereas in aqueous solution, it shows a dual fluorescence due to the excited-state proton-transfer because of proton rearrangement in methanol-water clusters. Chowdhury *et al.* [5] have also studied the excited-state prototropic activities of 2-hydroxy-1-naphthaldehyde in hydroxylic and hydrocarbon solvents.

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The probe exists in two ground-state conformers. The excitation of the closed conformer leads to intramolecular proton transfer to give an excited zwitterion in hydrocarbon solvents. The excitation of the open conformer in hydroxylic solvents leads to emission from the neutral conformer. Tolbert and Solntsev [3] have also discussed the role of solvent and the importance of the formation of the hydrogen-bonded complex with the probe and the solvent in the excited-state proton-transfer. Mallick *et al.* [6] have proposed that the fluorescence of 3-acetyl-4-oxo-6,7-dihydro-12H indolo-[2,3,-a] quinolizine originates from two states with a charge transfer state that lies above the lowest triplet state. It also occurred even in a very polar medium. Manoharan and Dogra [1] have also studied the solvents and pH dependent of the fluorescence emission of 2,3-diaminonaphthalene and reported that the two amino groups are twisted with respect to the naphthalene moiety.

Zeolites are solid acids and widely used in industry as catalysts. As the concentration and strength of the acid site on the surface of zeolite affects its catalytic performance, a number of techniques have been employed to measure the acidity of zeolites [8, 9]. Recently, El-Rayyes *et al.* [10] have used the excited-state proton-transfer between 1-naphthylamine and zeolites as a mechanistic tool to characterize the acidity of zeolites with different acid strengths. To further understand the surface acidities of catalysts, we have extended the study by using another possible probe, namely 8-amino-1-naphthol-3,6-disulfonate (8-ANDS). In this paper, we present the fluorescence emissions of 8-ANDS in both protic and aprotic solvents, and in aqueous medium with different acid strength at room temperature. 8-ANDS shows a single exponential decay originated from a neutral form at shorter wavelength and a departure from the exponential decay is observed at longer wavelength due to an additional fluorescence emission from a zwitterion.

## Experimental

8-ANDS, ethanol of HPLC grade, methanol, ethylene glycol, acetonitrile and dimethyl sulfoxide (DMSO) were obtained from Aldrich and used as received. Deionized water was used for sample preparation, and deuterium oxide (99.8%) was purchased from Fluka. Perchloric acid ( $\text{HClO}_4$ ) was used to prepare aqueous acidic solutions. Stock solutions of 8-ANDS were initially prepared in different solvents and by dilution, sample solutions were then prepared by keeping the concentration of 8-ANDS

at  $10^{-5}$  M. Aqueous solutions of 8-ANDS with the same concentration of the probe were also prepared at different pH, and in 1 M and 6 M perchloric acid.

Absorption spectra of all samples were recorded by a Lambda-5 UV/Vis (Perkin Elmer) Spectrophotometer and fluorescence emission spectra were measured by a SPF-500 Spectrofluorometer from SLM Instruments, Inc. Excitation spectra were taken for some samples. The cavity-dumped synchronously pumped Rhodamine 6G dye laser with a mode-locked Nd: YAG laser system was used as an excitation source. The details of the laser system were mentioned elsewhere [11]. The excitation wavelength was set at 300 nm and the fluorescence lifetimes of 8-ANDS were measured by a Time-Correlated Single-Photon Counting Spectrometer from Spectra Physics.

## Results and Discussion

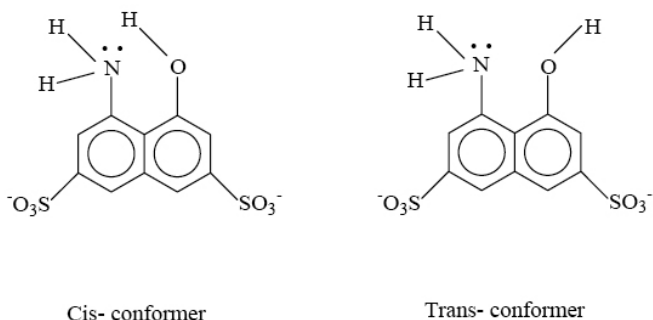
### Solvent effect

#### Absorption

8-ANDS has a  $-\text{OH}$  and a  $-\text{NH}_2$  functional group in its C-1 and C-8 positions. Two possible structures of a neutral 8-ANDS in the ground state are presented in scheme 1. In the ground state, 8-ANDS exists mainly in a cis-form in solution [12]. Absorption spectra of 8-ANDS in water, acidic solution (pH 2) and basic solution (pH 10) are shown in Fig. 1. The absorption maxima in water appear at 340 and 360 nm. As can be seen from Fig. 1, both  $-\text{OH}$  and  $-\text{NH}_2$  functional groups in their first excited state cause a red shift and blue shift in the absorption spectra of 8-ANDS when deprotonated and protonated. The absorption of 8-ANDS in dimethyl sulfoxide, ethanol, ethylene glycol, and methanol is very much alike to the one in water as the position and shape of the absorption band do not change with the polarity of the solvent. This indicates the absence of a solvent-solute (8-ANDS) interaction in the ground state.

#### Steady-state fluorescence

Figure 2 shows the fluorescence spectra of 8-ANDS in dimethyl sulfoxide, ethanol, ethylene glycol, methanol and water respectively. The fluorescence emission of 8-ANDS is blue shifted in dimethyl sulfoxide, which is a polar aprotic solvent. This observed blue shift is attributed to the formation of an intramolecular hydrogen bond in the excited state between the amino and hydroxyl groups of 8-ANDS due to their enhanced basicity and acidity following excitation. In contrast, a red shifted is



Scheme 1.

observed with the rest of the protic solvents. The broadness of fluorescence emission band with increasing polarity of the protic solvent suggests the development of a specific solvent-solute interaction that favors an intermolecular hydrogen bond between 8-ANDS and the protic solvent in the excited state. Water, having higher hydrogen bond donor ability among the solvents used, caused a larger red shift to emission as shown in Fig.2.

#### Fluorescence decay

As reported in Table 1, 8-ANDS decays exponentially at shorter wavelength with a lifetime ( $\tau_1$ ) of about 2.5 ns due to its neutral form in the solvents. The exponential decay of 8-ANDS in  $D_2O$  solvent with the same lifetime supports the earlier presumption of the solvent-solute interaction in the excited state due to an intermolecular hydrogen bonding of solvent to 8-ANDS. However, the

fluorescence decay of 8-ANDS at longer wavelength shows a bi-exponential with the two time constants  $\tau_1$  and  $\tau_2$ , where  $\tau_2$  varies with the solvents. It is expected that the specific solvent-solute interaction in which the solvent water is intermolecularly hydrogen bonded to 8-ANDS finally leads to the formation of a zwitterion in the excited state that has a lifetime ( $\tau_2$ ) of 4.2 ns in the aqueous solution.

The difference of  $\tau_2$  in ethanol and ethylene glycol explains the dependence of  $\tau_2$  on the nature of the solvent such as the polarity, the hydrogen bond donor ability (acidity), hydrogen bond acceptor ability (basicity) and the solvation of the zwitterion in the solution [13]. Ethanol has lower polarity compared to that of water and ethylene glycol. Due to poor solvation of the zwitterion in the ethanol solution, the  $\tau_2$  has a shorter lifetime of 1.6 ns. Although the polarity of ethylene glycol is not very much different from that of water, its hydrogen bond acceptor ability is believed to strengthen the solvation of the zwitterion, causing  $\tau_2$  to be longer in ethylene glycol.

#### Steady-state fluorescence and fluorescence decay in acetonitrile

As shown in Fig. 3, 8-ANDS shows the emission maximum around 380 nm in acetonitrile. Likewise in other used solvents, the fluorescence decay of 8-ANDS is a single exponential decay in acetonitrile with a lifetime of 2.1 ns. When a small amount of water, i.e. 1% by vol-

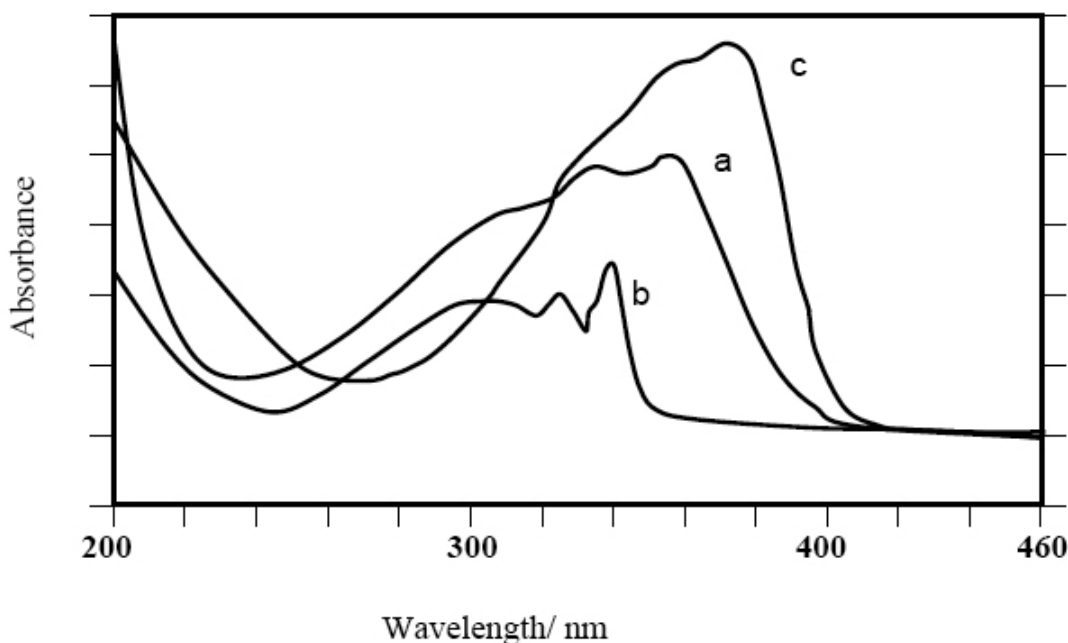


Figure 1. Absorbance spectra of 8-ANDS in (a) water and in the aqueous solutions of (b) pH 2 and (c) pH 10.

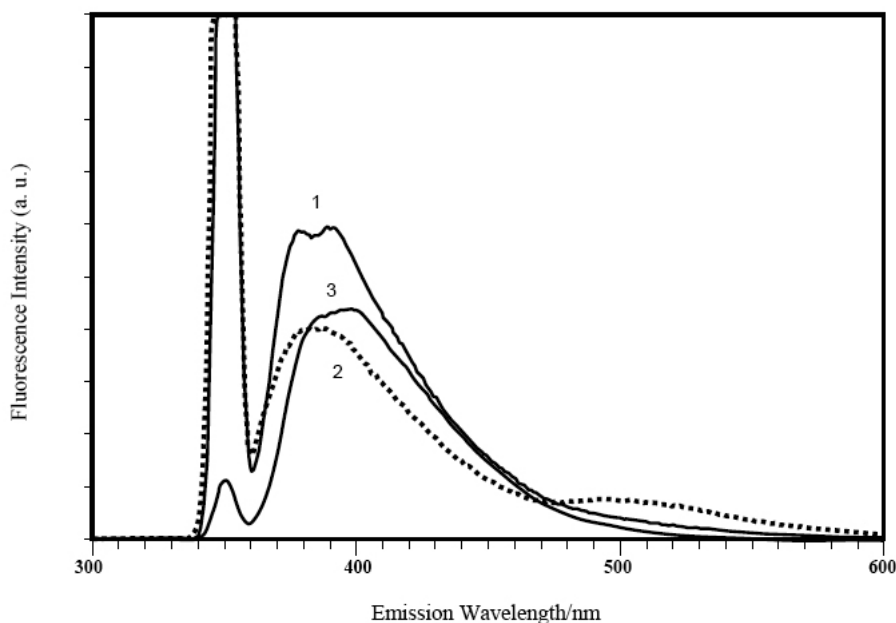


Figure 2. Steady-state fluorescence spectra of 8-ANDS in (1) dimethyl sulfoxide (2) ethanol (3) ethylene glycol (4) methanol and (5) water.

Table 1. Fluorescence decay of 8-ANDS in some polar solvents at 25°C ( $\lambda_{exc} = 300$  nm).

Solvent	$\lambda_{em}$ (nm)	$A_1$ (%)	$\tau_1$ (ns)	$A_2$ (%)	$\tau_2$ (ns)	$\chi^2$
Water	430	100	2.7	-	-	1.0
	530	82	2.8	18	4.6	1.0
Ethanol	370	100	2.6	-	-	1.0
	470	57	2.9	43	1.6	1.2
Ethylene glycol	410	100	2.4	-	-	1.0
	500	96	2.5	4	8.5	1.1
Methanol	410	100	2.4	-	-	1.0
D <sub>2</sub> O	430	100	2.8	-	-	1.0
Acetonitrile	370	100	2.1	-	-	1.1
Acetonitrile (1% in water)	370	50	2.3	50	4.2	1.1
Acetonitrile	370	100	3.3	-	-	1.1

ume, is added into the acetonitrile solution, a broad emission band emerges at 500 nm. Although the addition of 1% of water is too small to affect the refractive index and dielectric constant of the acetonitrile solution, it causes a substantially red shift from 380 to 500 nm. Adding 5% water or more also results in the same spectral shift in the acetonitrile solution. In fact, the entire spectral shift is produced only by about 1% of water. Therefore, the observed red shift supports the existence of an intermolecular hydrogen bond between 8-ANDS and water in the excited state. A bi-exponential fluorescence decay of 8-ANDS in 1% water solution further supports the formation of a zwitterion in the acetonitrile solution as the decay has shown two time constants with  $\tau_1 = 2.3$  ns

and  $\tau_2 = 4.2$  ns, where  $\tau_2$  is identical to that in water.

In 5% water, it seems that not only the hydrogen bonding effect is observed in the 1% water solution but also general solvent effects contribute to stabilization of the zwitterion due to a higher polarity of the solution. It is possible that the fluorescence emission and solvent relaxation occur at comparable rates in 5% water solution and thus, only a single lifetime of 3 ns which is comparable to the spectral relaxation time, was observed.

#### Photodynamics in aqueous acidic solutions

The absorption of 8-ANDS is sensitive to the pH of the aqueous solution. In pure water, the absorption is due to the neutral form. However, the absorption shifts

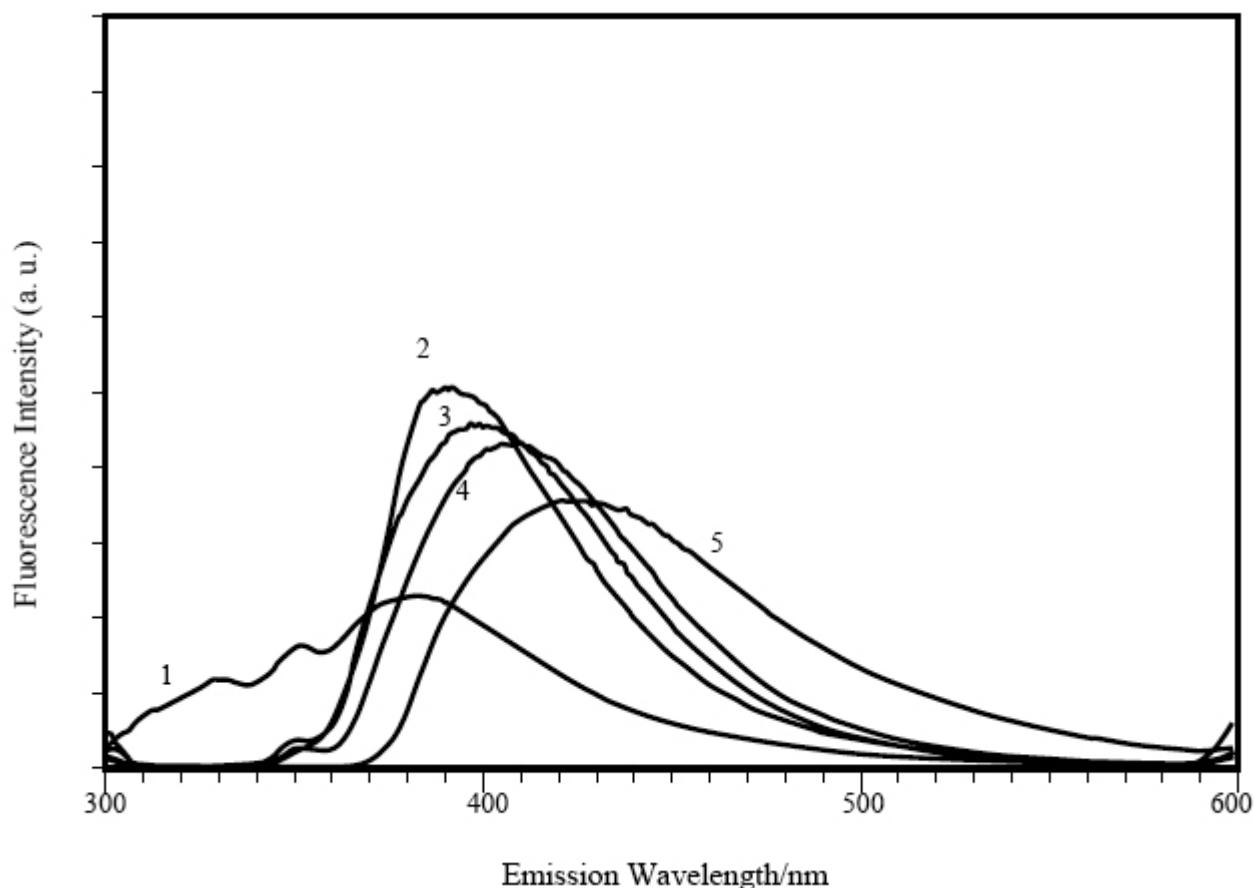


Figure 3. Fluorescence spectra of 8-ANDS in acetonitrile solutions with (1) no water (2) 1% water and (3) 5% water (by volume). Note that the fluorescence intensities of emission spectra (1) and (2) are increased by tenfold compared to that of the emission spectrum (3).

to shorter wavelength with decreasing pH of the solution, indicating the existence of a protonated form in the ground state in addition to the neutral form.

The fluorescence intensities of the emission spectra shown in Fig. 4 are increased by a hundredfold. The fluorescence emission 8-ANDS in acidic solutions shows mainly in two forms, a protonated and zwitterion in the excited state. In neutral solution, 8-ANDS shows a single emission band at 430 nm due to its neutral form. With decreasing pH of the solution, the fluorescence emission, however, shifts to a longer wavelength. This opposite sequences of spectral shifts of absorption and fluorescence shifts with changing pH implies the occurrence of phototautomerization in the excited state [7]. In addition, pH dependence of the fluorescence emission of 8-ANDS indicates that the phototautomerization occurs via an intermolecular proton transfer process. Therefore, we believe that the solvent, which is water in this case, does assist the proton hopping from  $-\text{OH}$  to  $-\text{NH}_2$  (either simultaneously or in stepwise manner) to form the zwitterion. Under very high acidic condi-

tions, the fluorescence emission from a protonated form appears at 360 nm as the fluorescence intensity of the zwitterions at 500 nm is quenched to the neutral. The Stern-Volmer quenching constant turns out to be  $1.84 \text{ M}^{-1}$  when the fluorescence intensity of the zwitterion is fit to the normal Stern-Volmer equation [14]. Based on the experimental data, the phototautomerization of 8-ANDS is proposed in scheme 2.

#### *Fluorescence decay in 1M and 6M perchloric acid solutions*

As reported in Table 2, the fluorescence decay of 8-ANDS is a bi-exponential in both 1M and 6M perchloric acid solutions. The mole fraction of undissociated  $\text{HClO}_4$  in 1M and 6M perchloric acids is about 0.018 and 0.13, respectively [15]. Thus, more of 8-ANDS is in its protonated form in 1M perchloric acid than in 6M perchloric acid. Within experimental limit, a lifetime of the protonated form ( $\tau_3$ ) is found to be about 500 ps while the lifetime of the zwitterion ( $\tau_4$ ) is about 6 ns at longer wavelengths. In 6M perchloric acid solution,

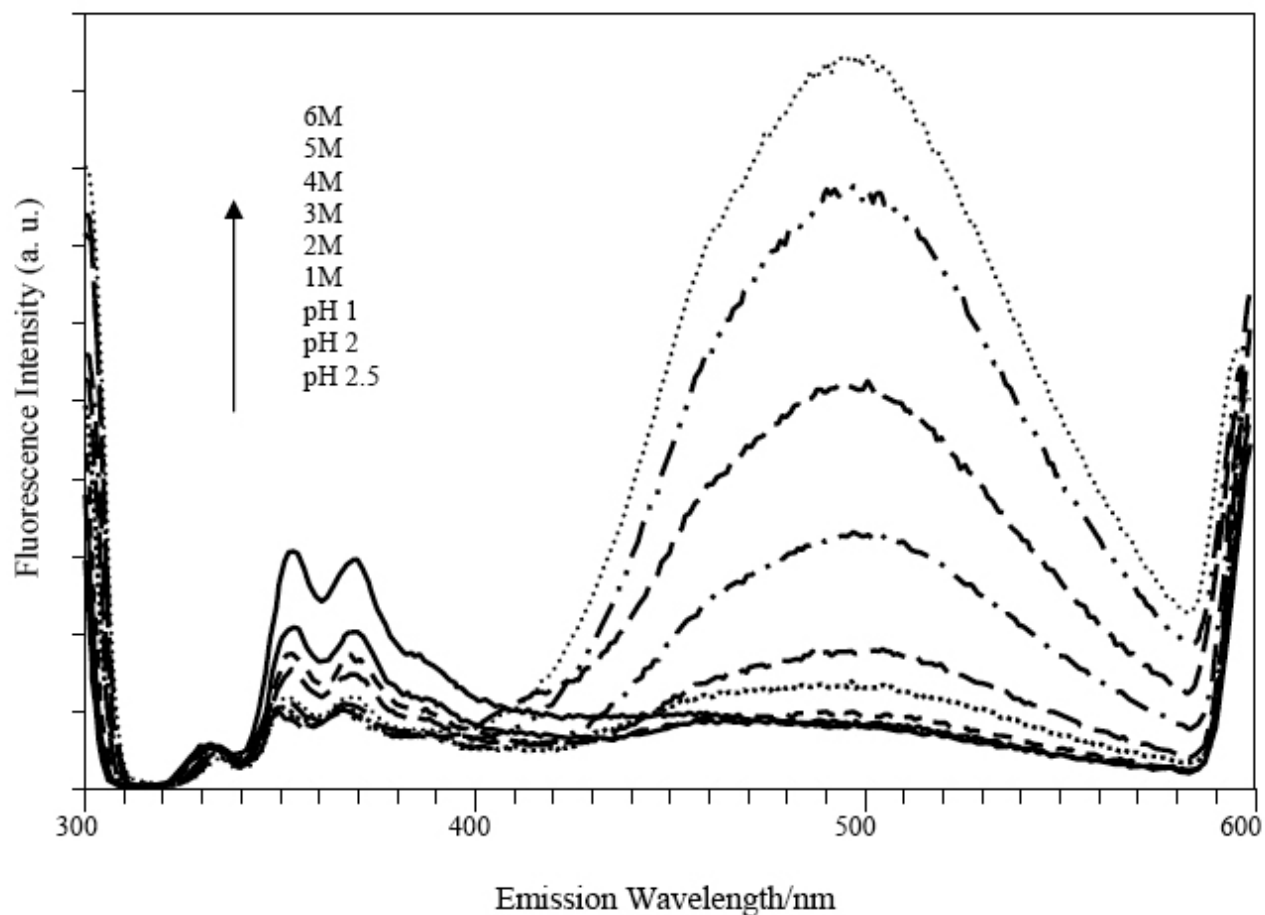
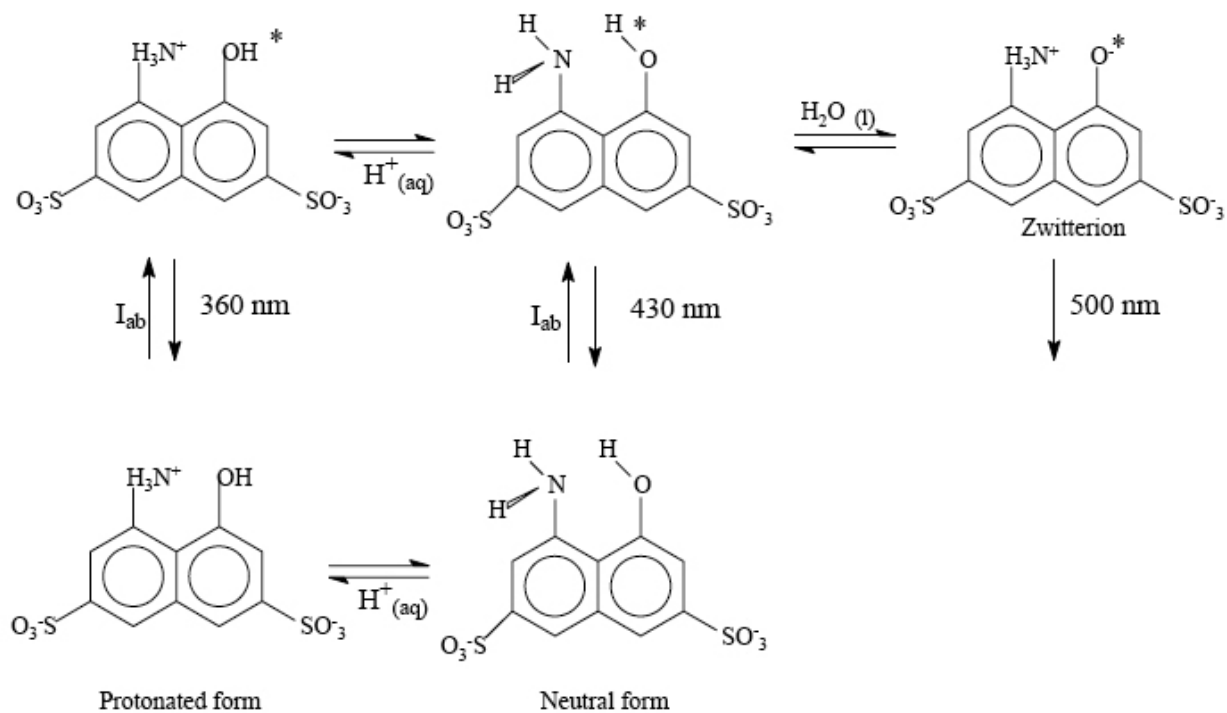


Figure 4. Fluorescence spectra of 8-ANDS in the acidic solutions. (The fluorescence intensities of all emission spectra are increased by a hundredfold)



Scheme 2

Table 2. Fluorescence decay of 8-ANDS in a 1M HClO<sub>4</sub> and 6 M HClO<sub>4</sub> acid solutions at 25°C ( $\lambda_{exc}=300$  nm).

Emission Wavelength (nm)	1 M HClO <sub>4</sub> (aq)		6 M HClO <sub>4</sub> (aq)	
	$\tau_3$ (nm)	$\tau_4$ (nm)	$\tau'_3$ (nm)	$\tau'_4$ (nm)
410	0.70 (96%)	6.0 (4%)	1.4 (85%)	6.6 (15%)
450	0.50 (99%)	6.0 (1%)	1.4 (80%)	6.6 (20%)
510	0.40 (99%)	5.8 (1%)	1.4 (85%)	6.6 (15%)

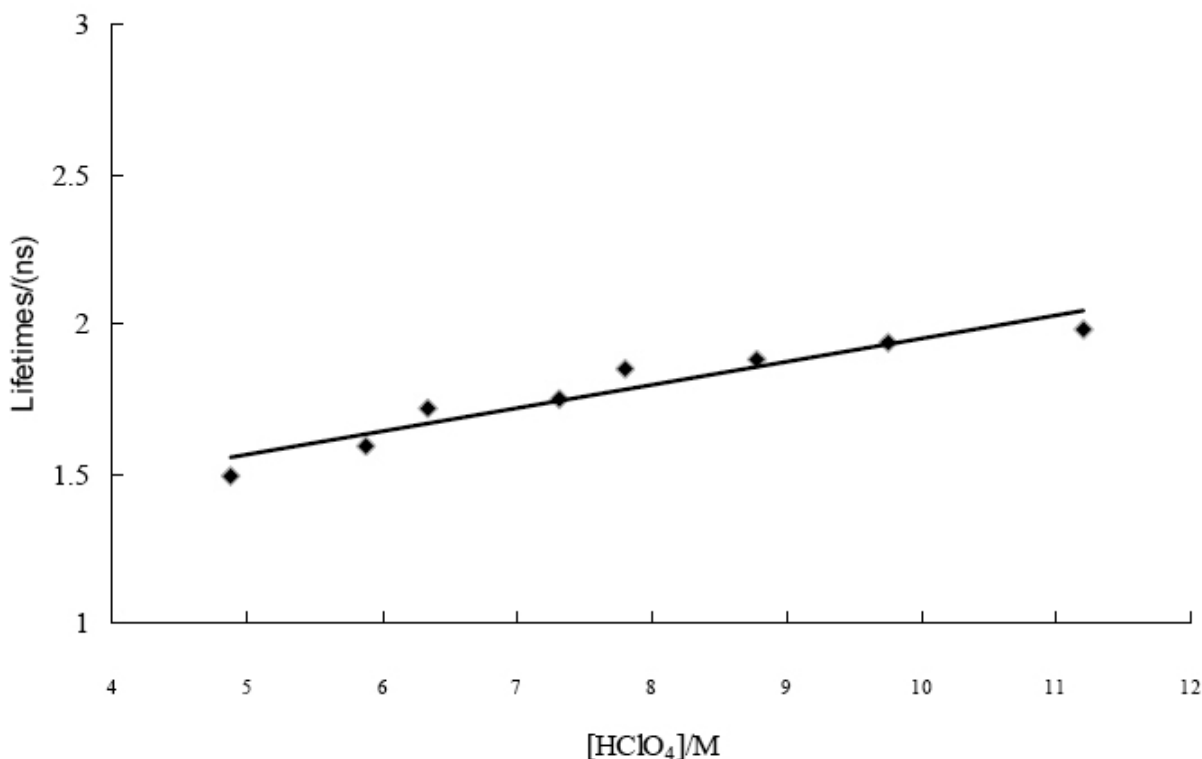


Figure 5 Fluorescence lifetime of protonated naphthylamine as a function of the perchloric acid concentration (Taken from Ref. 15).

the lifetime of the protonated form ( $\tau'_3$ ) is about 1.4 ns showing the relative stability of the protonated form as a result of lesser dissociation of the proton from the protonated form. El-Rayyes *et al.* [15] has also reported the lifetime of the protonated naphthylamine as 1.6 ns in 6M perchloric acid solution and the increase of the lifetime linearly with the concentration of perchloric acid up to 10 M perchloric acid solution (Figure 5). The trend of  $\tau'_4$  across the emission wavelengths is the same as that of  $\tau_4$ .

## Conclusion

Steady-state fluorescence and fluorescence decay of 8-ANDS in protic solvents and acidic solutions strongly imply the formation of a zwitterion in the excited state from a neutral form. We have explained the formation of

the zwitterion by adopting a proton hopping mechanism from the hydroxyl group to the amino group of 8-ANDS with solvent participation. The fluorescence decays of 8-ANDS in acetonitrile and D<sub>2</sub>O solutions further support a proposed mechanism of solvent-assisted intermolecular proton transfer process for the formation of zwitterion in the excited state.

A bi-exponential decay observed in perchloric acid solutions is due to the emission from the protonated form and zwitterion. Of course, an instrument with a better time resolution is required to explore further on the specific solvent-solute interaction observed in acetonitrile solutions.

### Acknowledgement

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### References

1. R. Manoharan and S. K. Dogra, *J. Phys. Chem.*, **92**, 5282 (1988).
2. J. C. Penedo, M. Mosquera, and F. Rodríguez-Prieto, *J. Phys. Chem. A.*, **104**, 7429 (2000).
3. L. M. Tolbert, and K. M. Solntsev, *Acc. Chem. Res.*, **35**, 19 (2002).
4. M.S. Mehata, H. C. Joshi, H. B. Tripathi, *Chem. Phys. Lett.*, **359**, 314 (2002).
5. P. Chowdhury, S. Panja and S. Chakravoti, *J. Phys. Chem. A*, **107**, 83 (2003).
6. A. Mallick, S. Maiti, B. Haldar, P. Purkayastha and N. Chattopadhyay, *Chem. Phys. Lett.*, **371**, 688 (2003).
7. S. G. Schulman, "Fluorescence and Phosphorescence Spectroscopy: Physicochemical Principles and Practice" Pergamon Press Ltd, England, UK, 1977, p.95.
8. A. Corrna, *Chem. Rev.* **97**, 2373 (1997).
9. A. Corrna, M. S. Grande, V. Gonzales Alfaro and A. V. Orchilles, *J. Catal.* **159**, 375 (1996).
10. A. A. El-Rayyes, H. P. Perzanowski, U. K. A. Klein and S. A. I. Barri, *Catal. Lett.*, **78**, 161 (2002).
11. M. T. Htun, A. Suwaiyan, U. K. A. Klein, *Chem. Phys. Lett.*, **243**, 71 (1995).
12. A. A. El-Rayyes and T. Htun, *J. Mol. Structure (Theochem)*, **681**, 9 (2004).
13. K. A. Connors, "Chemical Kinetics, The study of reaction rates in solution" John Wiley & Sons, Inc., USA, 1990, p. 385.
14. B. Valeur, "Molecular Fluorescence: Principles and Applications", Wiley-VCH Verlag GmbH, Germany, 2002, p. 72.
15. A. A. El-Rayyes, H. P. Perzanowski, S. A. Barri and U. K. A. Klein, *J. Phys. Chem. A*, **105**, 10169 (2001).