

Surfactant Dependent pH Controlled “off-on”, “off-on-off” and “on-off” Fluorescent Switches Exhibited by N-Benzylidenenaphthalen-1-Amine

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Abstract N-benzylidenenaphthalen-1-amine (**L**) acts as pH dependent “off-on”, “off-on-off” and “on-off” fluorescent switch in 1:1 (v/v) CH₃CN:H₂O depending on the presence of anionic sodiumdodecyl sulphate (SDS), neutral triton X-100 (TX-100) and cationic cetyltrimethylammonium bromide (CTAB) surfactants respectively. DFT calculation shows the possibility of formation of L.H⁺ due to protonation at immine N and L.OH⁻ due to introduction of OH⁻ group at immine C. The relative stability of these two cationic and anionic species depends on the charge environment provided by surfactants. This influences the photoinduced electron transfer (PET) processes involved and results in different switch behaviour.

Keywords Benzylidenenaphthalen-1-amine · Fluorescence · Molecular switch · Off-on-off · Surfactant · DFT

Introduction

Chemically driven molecular switches are the small tools based on molecules or molecular systems which can transmit events occurring in molecular level to the macroscopic world [1]. Fluorescence molecular switches gained recent interest due to very high sensitivity and relatively low costs [2]. H⁺ in the form of pH as the stimulus is especially convenient because it causes mild perturbation, does not cause degradation of the system and its operation can be repeated at will [3].

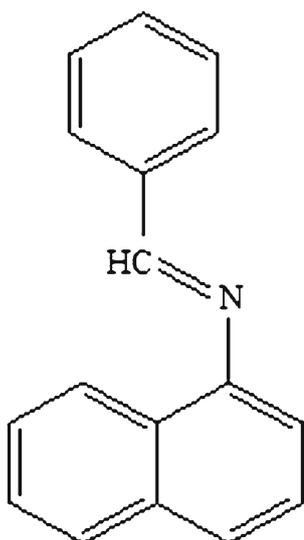
A number of pH responsive fluorescent “on-off” or “off-on” type switches have been reported. Anthracene as fluorophore joined to aromatic iminodiacetate as receptor through the spacer -CH₂- acts as “on-off” fluorescent pH switch [4]. Bis-azamacrocyclic anthracene having two 12-membered cyclic tetraamine connected through a 9,10-dimethylantracene spacer shows fluorescent “on” switch behaviour at pH < 7 and “off” behaviour at pH > 10 [5]. Polyamines bearing anthracene and benzophenone moiety at the two ends is another reported fluorescent “on-off” switch with “on” window between pH 2.0 to pH 9.0 [6]. Anthracene moiety attached to diethylenetriamine behaves as “off-on” switch for 416 nm emission and “on-off” switch for 510 nm emission when excited with wavelength of 402 nm [7]. When anthracene was replaced by pyrene it showed fluorescence “on-off” and “off-on” at emission wavelengths 376 and 480 nm respectively on excitation at 316 nm [8].

A three components systems comprising - Cu²⁺, a tetraaza ligand and the fluorophore Coumarin reported as “on-off-on” fluorescent switch [9]. A series of compounds synthesised by linking methylnaphthalene fragments at both ends of a variety of polyamine chains showed fluorescence “off-on-off” behaviour for fluorescence emission 418 nm on excitation wavelength of 287 nm [10]. pH dependent Fluorescent “off-on-off” switch is also reported for supramolecular system based on benzocrown ether [11]; natural products anabasin and coumarin [12]; dipod 1,2-bis(8-quinolinoxymethyl)benzene and tetrapod 1,2,4,5-tetrakis(8-quinolinoxymethyl)benzene [13] etc. Most of these switches involve complicated organic synthesis.

Fluorescent switch of “off-on-off” type involving surfactant sodium dodecyl sulfate (SDS) micelle, pyrene, poly(acrylic acid) (PAA) and Cu²⁺ reported [14]. The condensation product of salicylaldehyde and 2,4-di-nitrophenylhydrazine showed different fluorescent switching behaviour based on

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Scheme 1 N-benzylidenenaphthalen-1-amine (L)

cationic, neutral or anionic surfactant micelles present in the solution [15]. Charge nature of surfactant micelle was employed to influence the keto-enol tautomerism of salicylaldehyd-aniline condensation product and hence the pH dependent fluorescent switch behaviour [16].

In this paper we report that pH dependent fluorescent switch behaviour of N-benzylidenenaphthalen-1-amine is “off-on”, “off-on-off” and “on-off” type when anionic SDS, neutral TX-100 or cation CTAB surfactant molecules are present in the medium.

Experimental

All the chemicals were purchased from Loba, Chemie. Fluorescence spectra were recorded in Hitachi 2500 spectrophotometer at room temperature by using 1.0 cm quartz cuvette. pH values were measured using a Merck digital pH metre. NMR spectra were recorded on a Bruker Ultra shield 300 MHz spectrophotometer. FT-IR spectra were recorded on Perkin-Elmer spectrophotometer (RX1). High Resolution Mass Spectra were recorded in Agilent spectrometer using HPLC methanol as solvent.

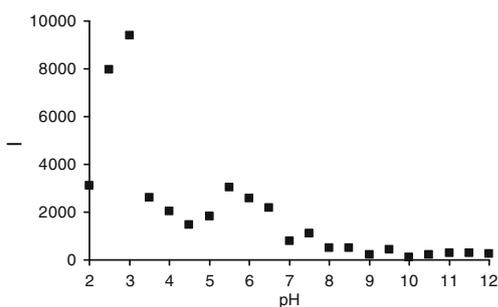


Fig. 1 Changes in fluorescent intensity I of L at different pH in 1:1 v/v $\text{CH}_3\text{CN}:\text{H}_2\text{O}$

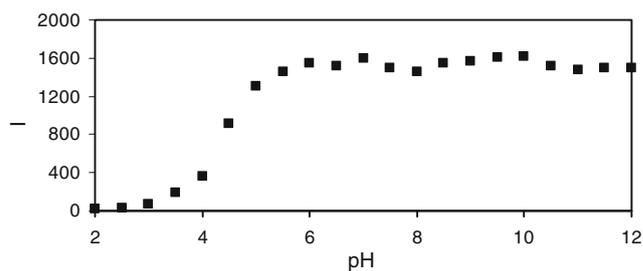


Fig. 2 Changes in fluorescent intensity I of L at different pH in 1:1 v/v $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ containing 3 % w/v SDS

Synthesis and Characterisation of N-Benzylidenenaphthalen-1-Amine (L)

L (Scheme 1) was already synthesised and reported as fluorescent sensor for Al^{3+} ion [17]. Briefly: 1-naphthylamine (0.136 g, 1.0 mmol) was dissolved in dichloromethane (20 mL). Benzaldehyde (0.106 g, 1.0 mmol) was added and the reaction mixture was refluxed for 10 h. After completion of reflux, the reaction mixture was diluted with dichloromethane and extracted successively with water and NaHCO_3 solution (10 % aqueous). The organic extracts collected were dried over anhydrous Na_2SO_4 and the solvent was evaporated to obtain a liquid product of brown colour. Yield: 70 %.

ESI-MS: $[\text{M}+\text{H}]^+$, m/z, 232.11 ($\text{C}_{17}\text{H}_{13}\text{N}$, 100 % abundance); FT-IR: (KBr, cm^{-1}): 1597.08 ($\nu_{\text{C}=\text{N}}$), 3045 ($\nu_{\text{C}-\text{H}}$), 1409 ($\nu_{\text{C}=\text{C}}$); ^1H NMR: (CDCl_3 , δ ppm, TMS): 8.57 (s, 1H); 8.38 (m, 1H); 8.06 (m, 2H); 7.89 (m, 1H); 7.76 (d, 1H, $J=8.4$); 7.57 (m, 6H); 7.06 (m, 1H); ^{13}C NMR: (CDCl_3 , δ ppm, TMS): 160.4, 149.2, 136.3, 133.8, 131.4, 128.9, 128.8, 128.5, 127.6, 126.3, 126.0, 123.9, 112.7.

DFT Optimisation Studies

DFT calculations were performed with the Gaussian 09 package [18]. The structure of L, L.H^+ and L.OH^- were optimised using Becke's three-parameter hybrid functional combined with the Lee-Yang-Parr correlation functional (B3LYP) [19, 20] level of DFT with 6-311G++ basis set for all calculations.

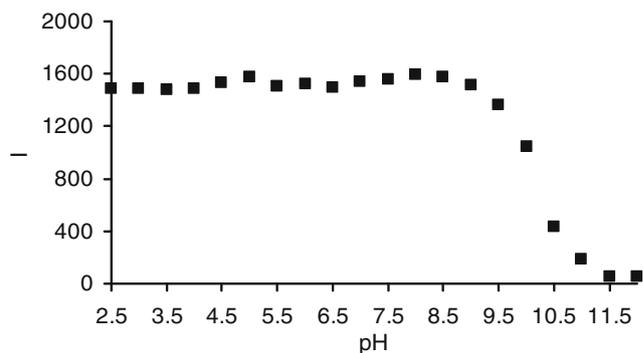


Fig. 3 Changes in fluorescent intensity I of L at different pH in 1:1 v/v $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ containing 3 % w/v CTAB

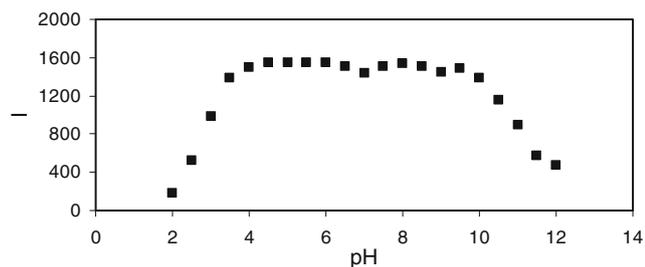


Fig. 4 Changes in fluorescent intensity *I* of **L** at different pH in 1:1 v/v CH₃CN:H₂O containing 3 % w/v TX-100

Preparation of Solutions

L was dissolved in 1:1 v/v CH₃CN:H₂O. Appropriate surfactant was added so that the final surfactant concentration is 3 % (w/v). The solutions were allowed to stand for 3 h before fluorescence spectra were recorded.

Result and Discussions

L in 1:1 v/v CH₃CN:H₂O showed fluorescence emission in the range 370 to 570 nm with λ_{max} at 430 nm when excited with wavelength 310 nm [17]. Figure 1 shows the fluorescence intensity (*I*) of **L** as a function of pH in 1:1 (v/v) CH₃CN:H₂O. A sharp increase in intensity was observed at pH *ca.* 3.0. Another hump in fluorescence intensity was observed at pH 5.6.

Figure 2 shows the fluorescence intensity of **L** as a function of pH when the solution contains 3 % (w/v) SDS. The fluorescence intensity increased from pH 3.0 and attained maximum at pH 6.0 resulting in fluorescent “off-on” switch. When the solution contained 3 % (w/v) CTAB fluorescence was “on” till pH 9.0 (Fig. 3). Further increase in pH led to decrease in fluorescence intensity attaining full “off” state at pH 11.0. Presence of 3 % (w/v) TX-100 in 1:1 v/v CH₃CN:H₂O solution of **L** resulted in fluorescent “off-on-off” switch behaviour (Fig. 4). The fluorescence intensity was found to increase from pH 2.0 till pH 4.0 and remained unchanged till

Scheme 2 PET process in **L.H**⁺ (at pH 2.0) and **L.OH**⁻ (at pH 12.0)

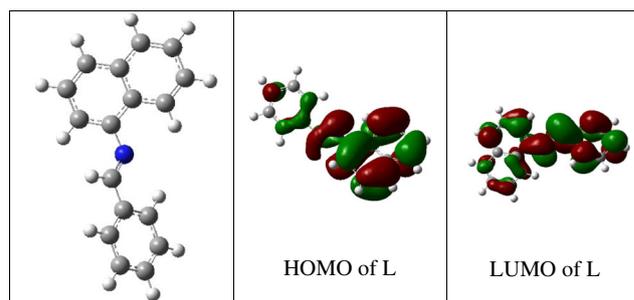
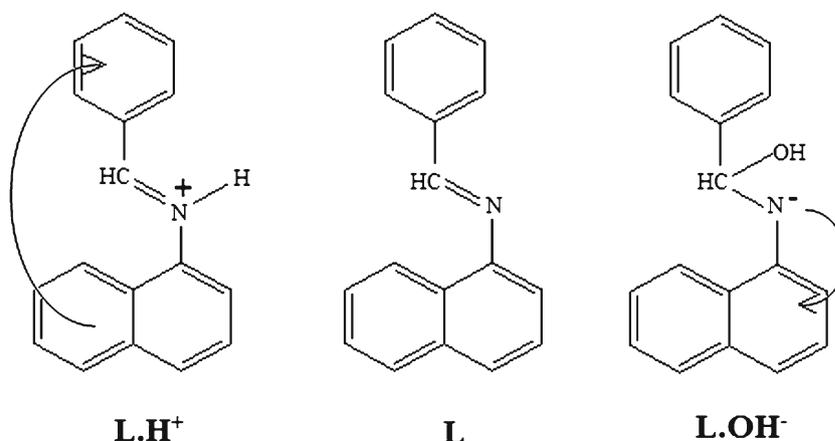


Fig. 5 DFT optimized structure of **L** and its HOMO and LUMO in singlet

pH 10.0 which started to decrease thereafter and became fully “off” at pH 12.0. Hence **L** in 1:1 v/v CH₃CN:H₂O behaves as a fluorescence “off-on” switch in presence of anionic surfactant SDS, “on-off” switch in presence of cationic surfactant CTAB and “off-on-off” when neutral surfactant TX-100 is present.

L shows both *cis* and *trans* isomers out of which the *trans* form is the stable one [21]. The pK_a of free naphthylamine and benzaldehyde are 3.92 and 14.9 respectively. In TX-100 when pH was decreased from pH 7.0 the fluorescence intensity started to decrease at pH 4.0 and becomes minimum at pH 2.0. This is due to protonation of the imine N atom and due to this protonation the electron density at the benzaldehyde ring decreases and secondary PET generated from naphthylamine ring to benzaldehyde ring as shown in Scheme 2. Such type of PET processes as well reported [22]. On the other hand when we increased pH from pH 7.0 the fluorescence intensity started to decrease from pH 9.8 and attained minimum at pH 12.0. The OH⁻ attacks the imine C atom forming an anion with negative charge on the N atom. This negative charge on N will be involved in PET process from it into the naphthylamine ring as shown in Scheme 1. Hence fluorescence intensity decreases at pH 9.8 and above. Thus we obtained a bell-shaped fluorescence intensity versus pH profile leading to fluorescent “off-on-off” switch behaviour in TX-100.

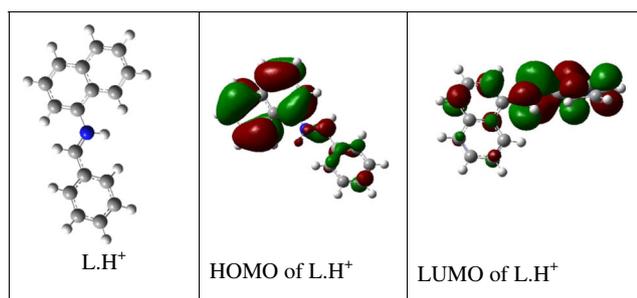


Fig. 6 DFT optimised structure of $L.H^+$ and its HOMO and LUMO in singlet

In SDS medium the protonation of immine N takes place and at a relatively higher pH compared to that in TX-100 because being anionic SDS shall facilitate formation of the protonated cation of **L** that is $L.H^+$. The anion formed due to OH^- attack on **L** is prevented by anionic SDS and therefore the fluorescence intensity remains in “on” state in case of SDS. Thus we obtained a pH dependent fluorescent “off-on” molecular switch for **L** in SDS. When cationic CTAB is present in the solution the protonation of immine N does not take place due to electrostatic reason and we get “on” state even at low pH. On the other hand in cationic CTAB the anionic state of **L** due to OH^- attack is well favoured. Fluorescence intensity starts to decrease at pH 8.5 attaining minimum at pH 11.0 due to PET from negative charge on N to the naphthalene ring. Being cationic CTAB can stabilise the anion more compared to that in neutral TX-100 leading to start of the “off” state at comparatively lower pH.

We have performed DFT calculations to check the possibility of protonation at immine N and addition of OH^- ion at immine C atom. Figure 5 shows the DFT optimised structure of **L** in the trans or E form and the shape of the HOMO and LUMO orbitals. DFT calculation shows that protonation at the immine N of **L** is quite favourable and Fig. 6 shows the structure of $L.H^+$ together with the shape of their HOMO and LUMO. DFT calculation also confirmed that OH^- can get associated with the immine C atom (Fig. 7).

In conclusion, N-benzylidenenaphthalen-1-amine (**L**) in 1:1 v/v $CH_3CN:H_2O$ can be tuned to show “off-on”, “off-on-off” or “on-off” fluorescent switch behaviour by introducing anionic SDS, neutral TX-100 or cationic CTAB into the solution. These could be explained on the basis of – (i) different

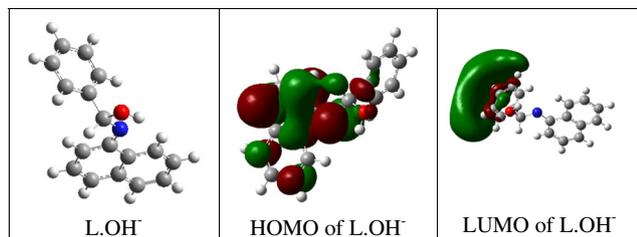


Fig. 7 DFT optimised structure of $L.OH^-$ and its HOMO and LUMO in singlet

stability of $L.H^+$ and $L.OH^-$ in presence of surfactant of different charges and (ii) Presence of secondary PET from naphthylene ring to benzaldehyde ring in $L.H^+$ and primary PET from negative charge of immine N to naphthylene ring in $L.OH^-$.

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