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## Spectral properties of a simple azine Schiff base and its sensing ability towards protic environment through hydrogen bonding interaction



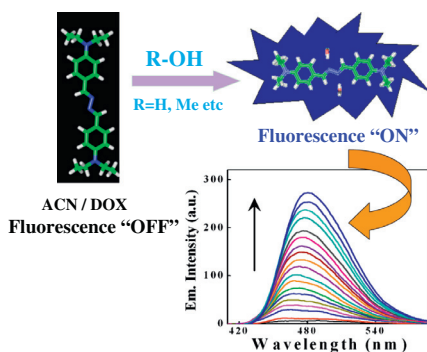
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### HIGHLIGHTS

- Fluorosensor for protic solvents by a simple azine linkage containing Schiff base.
- “Fluorescent off” in aprotic solvents and “Fluorescence on” in protic solvents.
- Intermolecular hydrogen bonding interaction is responsible for sensing behaviour.
- Spectroscopic findings well corroborate with DFT and NBO results.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A simple azine linkage containing Schiff base p-N,N-diethylaminobenzaldazine (PDEAB) has been synthesized and its spectroscopic properties have been investigated using steady state absorption and fluorescence measurement. Both the absorption and emission studies indicate that the compound PDEAB forms intermolecular hydrogen bond with protic solvents. The formation of intermolecular hydrogen bond between PDEAB and protic solvents is further verified by Quantum chemical calculation using Density Functional Theory (DFT) (B3LYP/6-31++G(d,p)) and Natural Bond Orbital (NBO) analysis. The non-fluorescent nature (fluorescence off) of PDEAB in aprotic environment can be switched over to a fluorescent system (fluorescence on) in presence of protic solvents and hence this molecule can be used as highly sensitive fluorosensor for protic solvent in aprotic medium like ACN or DOX.

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### Introduction

The most common and severe problem in the chemistry laboratory is the contamination of organic solvents by water. It is very important and essential to detect and quantify the presence of minute quantity of unwanted water in these solvents. Detection of trace amount of water in chemical, petroleum, food, and textile industries is absolutely necessary [1–4]. A number of methods are available in the literature for the detection of contaminating water.

These are the very well established Karl Fischer method [5], chromatography [6] and different spectroscopic techniques [7,8]. However, the most desirable technique would be one which is simpler and which entails least effort. One such way is the spectroscopic technique using an optical sensor which changes its spectral properties like absorbance or fluorescence upon interacting with the species (which is to be detected) of interest. Different merocyanine dyes [9], flavone derivatives [10] and optical-fibre sensors employing acridine [11] orange and various osmium(II) [12] and ruthenium(II) [13,14] complexes etc. have been successfully used as optical sensors for the spectroscopic detection of trace amount of water in organic solvents.

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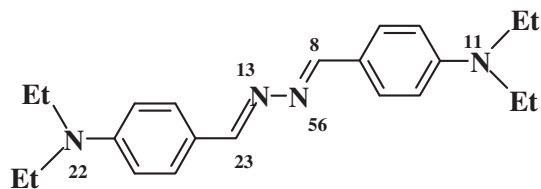
In the present work we have chosen a simple azine Schiff base molecule p-N,N-diethylaminobenzaldazine (PDEAB), a potential chemosensor for  $\text{Hg}^{2+}$  ion [15], as a good sensor of protic environment (including water) in aprotic organic solvents such as acetonitrile (ACN) and dioxane (DOX) by “fluorescence on” mechanism. Detection technique based on the “fluorescence on” mechanism is more reliable and much favoured over the “fluorescence off” mechanism because the latter can be brought about by the presence of any external impurities through collisional quenching mechanism. In 1986, Habashy et al. reported some acyclic azines namely o-hydroxybenzaldazine, p-N,N-dimethylaminobenzaldazine and 2-hydroxy-1-naphthaldazine which fluoresce very weakly at room temperature [16], but fluorescence intensities of these Schiff bases are observable at low temperature (77 K). They also interpreted that the rotation around the N–N single bond is practically responsible for their weak fluorescent property at room temperature. They suggested that fluorescence intensity as well as fluorescence quantum yield of these molecules may be enhanced by restricting this single bond rotation.

In this paper we describe the spectral properties of PDEAB, a very simple azine Schiff base, based on the steady state absorption and emission measurement. Besides the general solvent effects like polarisability, polarity, and refractive indices the hydrogen bonding interactions may also influence the photophysical properties of PDEAB. The preferential spectral signature of PDEAB in protic solvents through hydrogen bonding interaction over any other aprotic solvent makes it as a protic solvent sensor in the aprotic medium. It is well known that both intra- and intermolecular hydrogen bonding are site specific interactions between the hydrogen donor and acceptor molecules. There are numerous reports available in the literature regarding the non-covalent intermolecular hydrogen bonding interaction among various Schiff base molecules with other molecular systems [17–19]. In the present case the intermolecular hydrogen bonding interaction with the protic solvents plays the most crucial role in the fluorescent behaviour of PDEAB in protic solvents. Intermolecular hydrogen bonding interaction in the ground and excited states has been investigated spectroscopically. Furthermore, theoretical calculations have also been performed using Density Functional Theory (DFT) level of theory and Natural Bond Orbital (NBO) analysis to correlate the experimental findings.

## Experimental section

### Materials

PDEAB (Scheme 1) was synthesized according to the literature procedure [15]. Spectroscopic grade solvents such as n-hexane (n-HEX), acetonitrile (ACN), dioxane (DOX), n-butanol (BuOH), isopropanol (iPrOH), methanol (MeOH), ethanol (EtOH) and trifluoroethanol (TFE) were purchased from Spectrochem (India) and were used after proper distillation whenever required. Triply-distilled water was used for the preparation of solutions. Trifluoroacetic



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**Scheme 1.** Chemical structure of p-N,N-diethylaminobenzaldazine with numbering of some atoms with respect to the optimized structure.

acid (TFA) from Spectrochem was used as supplied. Urea was purchased from Merck and was used after proper recrystallisation.

### Instrumentation and procedure

Absorption and emission measurements were carried out using a Hitachi UV-Vis U-3501 spectrophotometer and Perkin-Elmer LS-55 fluorimeter, respectively. In all measurements the sample (PDEAB) concentration was maintained in the range  $\sim 10^{-7}$ – $10^{-8}$  M in order to avoid aggregation and reabsorption effects. Only freshly prepared solutions were used for spectroscopic study and all experiments were carried out at room temperature (300 K).

Fluorescence quantum yield ( $\Phi_f$ ) was determined using the following equation where Quinine Sulphate is used as secondary standard ( $\Phi_r = 0.577$ ).

$$\frac{\Phi_s}{\Phi_r} = \frac{A_s}{A_r} \times \frac{(Abs)_r}{(Abs)_s} \times \frac{n_s^2}{n_r^2} \quad (1)$$

where 'A' indicates the fluorescence area under the curve, 'Abs' is absorbance,  $n$  is the refractive index of the medium and  $\Phi$  is the fluorescence quantum yield, and subscripts 's' and 'r' denote the studied and reference samples, respectively.

### Theoretical calculations

The ground state structural calculations for the isolated PDEAB and PDEAB–( $\text{H}_2\text{O}$ )<sub>2</sub> cluster were computed using Density Functional Theory (DFT) at B3LYP/6-31++G(d,p) level using GAUSSIAN 03W suite of programmes [20]. The Time Dependent Density Functional Theory (TDDFT) method at the same level has been used to calculate the oscillator strength ( $f$ ) of the system. Long-range effects induced by solvent polarity were taken into account by means of dielectric continuum approach using Polarizable Continuum Model (PCM) [21,22].

The stabilisation energies ( $\Delta E_{\text{stab}}$ ) of PDEAB–( $\text{H}_2\text{O}$ )<sub>2</sub> cluster have been calculated using the following equation [23].

$$\Delta E_{\text{stab}} = E_{\text{complex}} - (E_{\text{PDEAB}} + 2E_{\text{water}}) \quad (2)$$

where  $E_{\text{complex}}$ ,  $E_{\text{PDEAB}}$  and  $E_{\text{water}}$  are the calculated energies of the PDEAB–( $\text{H}_2\text{O}$ )<sub>2</sub> complex, PDEAB and one water molecule, respectively. The stabilization energy was corrected for basis set superposition error (BSSE) using the method of Boys and Bernardi [24]. So the corrected stabilization energy of the complex is:

$$\Delta E_{\text{stab}}(\text{corrected}) = \Delta E_{\text{stab}} + \text{BSSE} \quad (2a)$$

The Natural Bond Orbital (NBO) second order perturbation energy has been calculated as follows: [25–27]

$$\Delta E_2 = \Delta E_{ij} = \frac{|\langle \Phi_i | \hat{F} | \Phi_j \rangle|^2}{(\epsilon_i - \epsilon_j)} \quad (3)$$

$\hat{F}$  is the Fock operator and  $\epsilon_i$  and  $\epsilon_j$  corresponds to the energy eigen values of the donor molecular orbital  $\Phi_i$  and the acceptor molecular orbital  $\Phi_j$ , respectively.

## Results and discussions

### Absorption spectra

The absorption spectra of PDEAB have been recorded in different non-polar, polar aprotic and protic organic solvents at room temperature (Fig. 1) and the corresponding spectroscopic parameters are summarised in Table 1. The main absorption band of PDEAB is found to be centered at  $\sim 390$  nm along with a higher energy hump at  $\sim 325$  nm. In non-polar solvents like n-hexane the

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