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## Study on intramolecular charge transfer fluorescence properties of trans-4-[4'-(N,N'-dimethylamino)styryl]pyridine: Effect of solvent and pH

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## ABSTRACT

Photophysical characterization of a molecule, trans-4-[4'-(N,N'-dimethylamino)styryl]pyridine (4-DMASP) containing donor and acceptor moieties has been done experimentally as well as theoretically. Upon single excitation a charge-transfer state with high dipole moment is formed through rapid relaxation of a locally excited (LE) state in polar medium. A complete charge transfer process occurs as a result of twisting of donor group with respect to the acceptor part of the molecule resulting in the highly stabilized twisted state in polar medium giving fluorescence from LE state as well as from twisted state. However, in a nonpolar solvent emission occurs explicitly from a LE state. Hydrogen bond donor ability of solvents rather than dipolar interactions contributes more to the stability of ground state. However, dipolar interactions have greater contribution towards the stability of an excited state. All such interactions have higher contribution towards the stability of excited state than that of ground state. Very low fluorescence quantum yield in water is because of high rate of nonradiative processes as a result of high degree of stabilization of charge transfer state thereby making closer proximity of this state to triplet as well as ground charge transfer states. Monocation of 4-DMASP formed due to the protonation of pyridine nitrogen atom is more stable than neutral and dication species at ground as well as excited states because of greater extent of flow of charge from donor to acceptor part in monocation. Basicity of pyridine nitrogen atom being greater at excited state than that in ground state results in higher extent of pulling of charge from donor to acceptor part of monocation at excited state. Theoretical calculations suggest donor twisting as a possible path for creation of a charge transfer state rather than acceptor twisting. Excited state dipole moment value obtained from theoretical calculation corroborates well with the value determined experimentally. Theoretical calculation suggests no cis–trans photoisomerization in the ground state as well as excited state at room temperature.

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## 1. Introduction

From the time the dual fluorescence of dimethylaminobenzonitrile (DMABN) in polar solvents reported by Rotkiewicz and Grabowski [1,2] for its twisted intramolecular charge transfer (TICT) phenomenon, the molecular systems with similar charge transfer fluorescence properties have found their potential applications in photoelectronic devices [2], chemical sensor [3], nonlinear optical properties [4], probing molecule induced nanotubular suprastructures [5] and photobiological process [6]. Upon excitation, molecular systems with donor and acceptor connected by a single bond may exist as intramolecular charge transfer (ICT) or

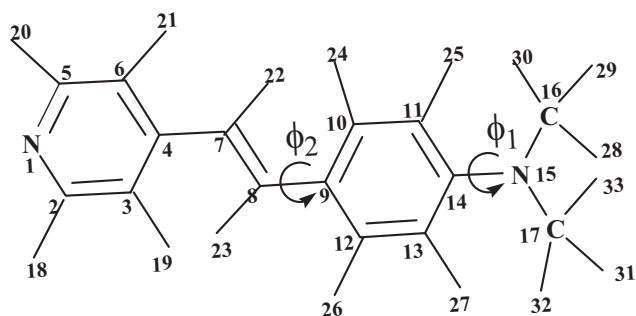
TICT state [7–12]. Many such molecules show dual fluorescence where a short wavelength emission arises from the locally excited (LE) state whereas the ICT state is responsible for the emission at longer wavelength in polar and/or viscous medium [1,7–12]. In many cases complete charge transfer occurs as a result of twisting of donor with respect to the acceptor part of the molecule resulting in the highly stabilized TICT state in polar medium giving fluorescence from LE as well as TICT state upon single excitation [8,9,13].

Among the different TICT molecules reported so far, pyridine derivatives deserves important role in wide areas such as in the determination of cell microviscosity [14], chemiluminescence [15], fluorescent sensor [4], and silane sol–gel transition studies [16] to name a few.

Bruni et al. [17] studied the solvatochromism of trans-4-[4'-(N,N'-dimethylamino)styryl]pyridine (4-DMASP) [Scheme 1] and dimethylamino-1,10-phenanthroline (DAPHEN) to determine the

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Scheme 1. Structure of 4-DMASP.

quadratic hyperpolarizability,  $\beta$  of dipolar molecules. In their paper they reported the charge transfer behavior of 4-DMASP to rationalize the more polar excited state than the ground state. In addition, Wang et al. [18], reported excited state deprotonation (ESDP) process of 4-DMASP by analyzing the behavior of it in chloroform in different acidic concentrations. They proposed intramolecular charge transfer (ICT) character for a red shift in emission spectra with an increase of solvent polarity. As this molecule is having dimethylamine group which is connected with a styrylpyridine with a single bond, it can very well act as donor–acceptor system. Sensitivity of fluorescence properties of a derivative of 4-DMASP towards viscosity of medium has made it useful as a fluorescent probe for cell microviscosity [14].

In this paper, we have reported effect of solvent and hydrogen ion concentration on fluorescence emission properties of 4-DMASP. Dependence of large Stokes shifted fluorescence band on the polarity of medium supports emission from ICT state. To investigate the origin of charge transfer state, quantum chemical AM1-SCI (singly excited configuration interaction) calculations have been carried out. Recently, Chakraborty et al. [19] have reported dual fluorescence of a donor–acceptor system, trans-3-(4-monomethylamino-phenyl)-acrylic acid (*t*-MMPAA) giving normal fluorescence from LE state and large Stokes shifted fluorescence from twisted excited state of charge transfer character. The theoretical calculations performed on the molecule raised the possibility of having stable twisted excited state through two twisting coordinates: one along donor and other along the acceptor twisting path. However, their molecular orbital calculation showing HOMO as localized nitrogen lone pair orbital suggested occurrence of TICT state through donor–twisting path. Present calculation on 4-DMASP suggests that charge-transfer state is created through the relaxation of LE state in polar medium only after twisting of donor part of the molecule with respect to acceptor part. High dipole moment of twisted conformation results in stabilization of TICT state in polar solvents giving highly Stokes shifted fluorescence bands.

Wang et al. [18] have reported basicity difference between the excited state and the ground state ( $\Delta pK_a$ ) of neutral and monocation species of 4-DMASP using Förster cycle method. In the present work, we have determined ground state acidity constant ( $pK_a$ ) of dication–monocation equilibrium and have shown that excited state equilibrium between the same species cannot exist because of faster rate of emissions of species compared to the rate of proton transfer between them.

Although, charge-transfer nature of fluorescence emissions of 4-DMASP and its derivatives in various types of polar solvents (protic and aprotic) have been indicated by different groups [14,18], but present study find out the individual contribution of dipole–dipole interactions, hydrogen bond donor ability and acceptor ability of solvents towards the stability of ground state as well as excited state of the molecule by the solvatochromic comparison method (SCM) proposed by Kamlet et al. [20].

## 2. Experimental

### 2.1. Materials and methods

4-DMASP was procured from Sigma–Aldrich chemical company, WI, USA and was recrystallized three times from a mixture of ethanol and a small percentage of n-hexane. All the solvents used were of spectroscopic grade and procured from Spectrochem Company, India. Triple distilled water was used for the preparation of the aqueous solutions. Dilute sulfuric acid and sodium hydroxide solutions were used to adjust the pH of the prepared aqueous solutions. A stock solution of 4-DMASP ( $5 \times 10^{-4}$  M) was prepared in pure methanol to record the UV–visible absorption and fluorescence spectra of it in pure solvents; 0.1 mL of this solution was poured in a 10 mL volumetric flask and left for a few hours for complete evaporation of methanol and then the compound was dissolved in respective solvents to make final volume of 10 mL. The concentration of 4-DMASP in all the experimental solutions used for spectroscopic measurements was  $5 \times 10^{-6}$  M. The fluorescence quantum yields were determined with respect to that of quinine sulfate in 0.1N  $H_2SO_4$  (0.55). The absorption spectra were recorded using a Hitachi U-2900 UV–visible spectrophotometer. Fluorescence measurements were performed using Horiba Jobin Yvon Fluoromax-4 scanning spectrofluorimeter. Eutech PC 510 pH meter was used to adjust the pH of aqueous solutions. All spectroscopic measurements were done at room temperature,  $25 \pm 1$  °C.

#### 2.1.1. Solvatochromic comparison method (SCM)

This method was proposed by Kamlet et al. [20] provides information about the individual contribution of different solvent effects. This multiparametric approach separates the dielectric effects of solvents ( $\pi^*$ ), hydrogen-bond donor ability ( $\alpha$ ), and hydrogen-bond acceptor ability ( $\beta$ ) of the solvents on the spectral properties. The equation describing these effects is:

$$E = E^0 + c\pi^* + a\alpha + b\beta \quad (1)$$

where  $a$ ,  $b$  and  $c$  are the coefficients and  $E^0$  is the spectral maxima independent of solvent effects. The values of  $\pi^*$ ,  $\alpha$  and  $\beta$  of different solvents have been taken from the report of Kamlet et al. [20]. The values of  $E$  are absorption/fluorescence band maxima in terms of  $cm^{-1}$ .

#### 2.1.2. Quantum chemical calculations

Hyperchem package Version 6.01 (Hypercube Inc., Canada) has been used for the theoretical calculations. The ground state ( $S_0$ ) geometry of the compound was optimized by AM1 method [21–24]. AM1-SCI was performed to get the energy ( $E_g$ ) and dipole moment in the ground state, the transition energies ( $\Delta E_{i \rightarrow j}$ ), and dipole moments of different excited states. We have taken care of all the singly excited configurations within an energy window of 10.5 eV from the ground state.  $\Delta E_{i \rightarrow j}$  corresponds to the excitation of an electron from the orbital  $\varphi_i$  (occupied in the ground state) to the orbital  $\varphi_j$  (unoccupied in the excited state). The total energy of the excited state ( $E_j$ ) was then calculated as  $E_j = E_g + \Delta E_{i \rightarrow j}$ . The CI wavefunction has been used to generate  $g$  orbitals and one-electron density matrices, which were used to calculate the dipole moments of the excited states of the compound. The stabilization of different states due to solvation has been calculated from the solvation energies based on Onsager's theory [25]. Assuming that the solute molecule having a dipole  $\mu_i$  in the  $i$ th electronic state is fully solvated, the solvation energy is given by

$$\Delta E_{\text{solv}} = \frac{2\mu_i^2(\epsilon - 1)}{a^3(2\epsilon + 1)} \quad (2)$$

where  $\epsilon$  is the relative permittivity of the solvent and  $a$  is the cavity radius.

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