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A novel water soluble solvatochromic probe as a micropolarity reporter for homogeneous and microheterogeneous media

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ABSTRACT

A new water soluble donor–acceptor dye, *sodium 4-(methyl((1E,3E)-3-(1-oxo-1H-inden-2(3H)-ylidene) prop-1-enyl)amino)benzoate* (DN3) has been synthesized. Optical response of the solvatochromic dye (DN3) has been studied in various homogeneous (neat and mixed binary solvents) and heterogeneous (SDS and CTAB homomicelle and β-cyclodextrin nanocavity) media. To get information regarding the change in the solvation interaction of the dye with the alteration in its microenvironment in different media, the photophysical properties of the dye have been monitored in various media using steady state and time resolved spectral analysis. Results obtained for mixed binary solvents containing water indicate that the solute is preferentially solvated by one of the component solvents and solvent–solvent interactions are also important in determining the preference. Effect of variation of pH in aqueous medium on the spectroscopic parameters of the dye has been studied and its *pKa* has been estimated. Studies in homomicelles (SDS and CTAB) reveal that the dye distributes itself between the aqueous and the micellar phase and the values of distribution coefficient have been estimated from the fluorescence parameters. The dye is encapsulated in β-cyclodextrin nanocavity and a 1:2 dye-β-cyclodextrin host–guest interaction is indicated. Semi-empirical quantum chemical calculations have been carried out to support the experimental results.

1. Introduction

Study of solvation in terms of solute–solvent and solvent–solvent interaction is a subject of current interest. Customarily the study is done by monitoring the physicochemical properties of a given solute (probe) in different media. Ketocyanine and structurally similar donor–acceptor dyes form an important class of probes used for the investigation of solvation interaction in various homogeneous and micro-heterogeneous media [1–10]. These dyes are characterized by solvent sensitive absorption and fluorescence bands. They possess donor (amino *N*) and acceptor (carbonyl *O*) groups separated by hydrophobic moieties. The presence of donor and acceptor groups within the dye molecule enables them to exhibit intramolecular charge transfer (ICT) transition within the molecule, which is responsible for their characteristic solvatochromism. Ketocyanine dyes have a fairly long solvatochromic range and can be used as a probe in both absorption and fluorescence modes [1,2]. Photophysical parameters of the dyes also exhibit solvent dependence. Thus, this class of compounds is very useful for probing biological systems. The presence of hydrophobic wing makes these dyes insoluble in water. Thus, inspite of the fact that these class of compounds are extremely useful in monitoring micropolarity and solvation interactions in non-aqueous media, studies in aqueous media using these dyes have been fraught with difficulty. The dyes are difficultly soluble in cyclodextrins and micellar media where the solvation studies could be made [4,7,9,11–13]. But one cannot study the onset of aggregation of surfactants in the aqueous solution. Again, the preferential solvation of these class of dyes in mixed binary solvents provides information about solute–solute and solvent–solvent interactions [2]. But the solvation interaction in aqueous binary mixture over the entire range of solvent composition cannot be studied using dyes insoluble in water. Thus it is instructive to look for a water soluble dye, structurally akin to a ketocyanine dye, which would provide information about the solvation interaction in different aqueous media by monitoring the photophysical properties like the energy of maximum fluorescence, Stokes shift, quantum yield and lifetime. To this end we have attempted the synthesis of a water soluble donor–acceptor dye, *sodium 4-(methyl((1E,3E)-3-(1-oxo-1H-inden-2(3H)-ylidene)prop-1-enyl)amino)benzoate* (henceforth termed as DN3) as shown in Fig. 1(a). Photophysical

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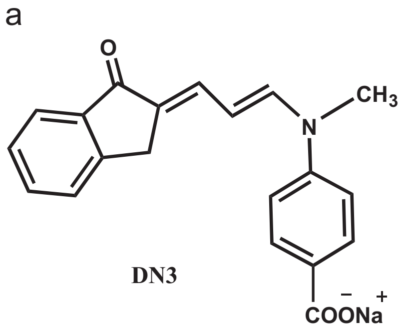


Fig. 1. The dyes DN3 (a) and DN2 (b) used in the present study.

properties of a structurally similar dye, DN2 (Fig. 1b), have been studied previously [4,14]. In the present work a systematic study of the optical response of the dye (DN3) has been made in 15 neat solvents and the results thus obtained have been used to analyze and explain the observations in mixed aqueous binary solvents, aqueous micellar media and β-cyclodextrin nanocavity. Steady state and time resolved electronic spectral methods have been used to get information about solvation interaction in the different media using a judicious analysis of the spectral data. Study of the spectroscopic parameters in different buffer solution provides the value of *pKa* of the dye.

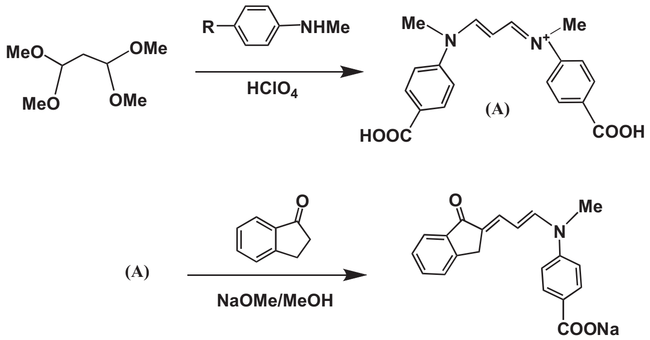
2. Materials and methods

2.1. Synthesis of the dye

The dye, DN3, has been prepared according to Scheme 1. 1,1,3,3-tetramethoxy propane (25 mmol,) and 4-(methylamino) benzoic acid (50 mmol,) were mixed in ethanol and then perchloric acid (60%) solution was added to it. The mixture was kept at 50 °C for 1 h to produce brownish yellow intermediate compound (A) which was stored overnight in a refrigerator. This was then added to a solution of sodium methoxide and indanone (14 mmol) and the mixture was then refluxed for 2 h. The mixture was cooled and acidified with dilute hydrochloric acid when a red precipitate was obtained which was washed several times with dry diethyl ether. The product, which is the acid form of DN3, was purified by repeated crystallization from ethanol and dried in vacuum. Purity of the compound was checked by C, H, N analysis (observed: C 71.14%, H 5.67%, N 4.22%; calculated: C 75.24%, H 5.33%, N 4.39%). DN3 was obtained by the reaction of crystallized product with aqueous sodium hydroxide solution. The purity of the dye was further checked using Thin Layer Chromatography. Characterization was done using Mass spectroscopic and NMR studies: MS (m/e, relative intensity) 342.18 [100, M–H]$^+$ (calculated mass = 341.34); (^{1}H NMR 500 MHz, d$_6$-DMSO, δ in ppm): 7.61–7.93(8H, aromatic proton); 7.42(*d*, 1H,C$^\beta$ alkene proton); 7.25 (*d*, 1H, C$^\delta$ alkene proton); 5.88(d, 1H,C$^\gamma$ alkene proton); 3.58(*s*, 2H, indanone –CH$_2$); 3.39 (*s*, 3H, N–Me).

2.2. Reagents and solvents

1,1,3,3-tetramethoxy propane and 4-(methylamino) benzoic acid used for the synthesis were procured from Sigma-Aldrich. β-cyclodextrin and the surfactants used in the study, namely, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich and were used as received. All solvents (except ethanol) were of spectroscopic grade and obtained from Sigma-Aldrich. Ethanol, obtained from Jiangsu Huaxi International was purified by standard procedures [15,16]. Solvents were dried by refluxing with calcium hydride followed by distillation prior to use. Triple distilled water has been used for preparing aqueous solutions.



Scheme 1. Reaction Schematics to show the synthesis of DN3.

2.3. Steady state spectral measurements

Absorption (UV–Vis) measurements were performed on a Cary 300 Bio UV–Visible spectrophotometer. Fluorimetric measurements were done on a Perkin-Elmer LS55 and a Horiba Jobin Yvon Fluoromax-3 spectrofluorimeters. The concentration of dye in solution was in the range 10^{-5}–10^{-6} M. The energies (E) of maximum fluorescence and absorption were calculated from the wavelength (λ_m) of maximum fluorescence and absorbance using the following relation.

$$E/\text{kcal mol}^{-1} = \frac{28,590}{\lambda_m/\text{nm}} \tag{1}$$

The $E_T(30)$ values used were obtained from literature [17,18]. Quantum yield (φ) was calculated using the following equation.

$$\varphi = \varphi_R \left(\frac{I}{I_R}\right)\left(\frac{A_R}{A}\right)\left(\frac{n^Z}{n_R^Z}\right) \tag{2}$$

where I, A, and n denote respectively integrated intensity of fluorescence, absorbance and refractive index. The subscript R indicates reference. Solution of fluorescein (Sigma-Aldrich) in 0.1 M NaOH was used as standard references (φ_R=0.95) for quantum yield measurements.

The fluorescence anisotropy at a particular wavelength has been determined by Eq. (3) [19].

$$r_{em}(\lambda) = \frac{[I_{VV}(\lambda) - G(\lambda)I_{VH}(\lambda)]}{[I_{VV}(\lambda) + 2G(\lambda)I_{VH}(\lambda)]} \tag{3}$$

where $I(\lambda)$ denotes the fluorescence intensity at a particular wavelength, λ and the first and second subscripts (H,V) respectively refer to the setting of excitation and emission polarizers. $G(\lambda)$ is an instrumental factor representing the polarization