



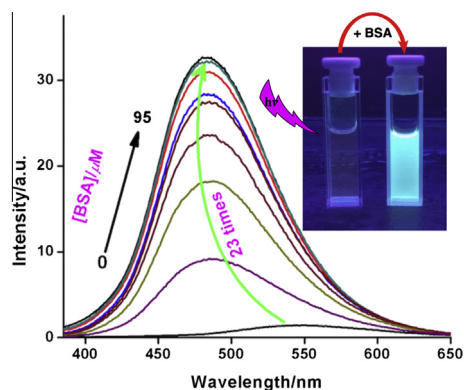
# Probing microenvironment of micelle and albumin using diethyl 6-(dimethylamino)naphthalene-2,3-dicarboxylate: An electroneutral solvatochromic fluorescent probe



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## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 October 2015  
Revised 8 December 2015  
Accepted 11 December 2015  
Available online 30 December 2015

### Keywords:

Naphthalimide dye  
Intramolecular charge transfer  
Fluorescence spectroscopy  
Solvatochromism  
Critical Micelle Concentration (CMC)  
Serum albumin

## ABSTRACT

Synthesis, single-crystal X-ray characterization, and spectroscopic investigation of small, non-charged diethyl 6-(dimethylamino)naphthalene-2,3-dicarboxylate (DMNDC) by UV–Visible, steady-state, and time-resolved fluorescence reveal a series of interesting photophysical properties originating from the intrinsic intramolecular charge transfer (ICT) state, leading to diverse applications. Stokes shift, lifetime, and emission maxima of DMNDC show a very good correlation with  $E_T(30)$  solvent polarity scale for a series of different polarity solvents, confirms that it has very good environment sensitivity. Furthermore, this dye has been found to be an exceptionally suitable probe for determining Critical Micelle Concentration (CMC) and probing self-organization processes of five different type of surfactant with structural diversity. A 20–60 nm blue shift in emission maxima accompanied by a large fluorescence lifetime enhancement (*ca.* 23 ns) was observed upon relocation of DMNDC into a hydrophobic microenvironment. Along with this, the small size, electroneutrality, pH stability, and excellent solvatochromic fluorescent properties are employed for deciphering the number of hydrophobic binding pockets with strong affinity and their local microenvironment present in Bovine Serum Albumin (BSA).

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## 1. Introduction

Fluorophores with environment sensing ability form a very important class of fluorophores, which shows distinctive

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fluorescence properties in different kind of environments [1–3]. They are very useful for probing diverse physical and biochemical events which includes detection of Critical Micelle Concentration (CMC) of surfactants [4–8], protein–protein interaction [9,10], protein–ligand interaction [11–13], conformational changes of the proteins [13], in medical diagnostics [14,15] supramolecular chemistry, and looking into the local hydrophobic interior of proteins [16]. This class of compounds are also known as solvatochromic fluorophore [17,18], since they exhibit differential fluorescence response towards different type of solvents [18]. Structural investigation reveals that these dyes belong to the class of ICT (intramolecular charge transfer) dyes, e.g., 2-propionyl-6-dimethylaminonaphthalene (PRODAN) [19,20], 6-*N,N*-dimethylamino-2,3-naphthalimide (6-DMN) [21,22], 4-*(N,N)*-dimethylamino phthalimide (4-DMAP) [23,24], dapoxyl sodium sulfonate (DSS) [25–27], 1-anilino-8-naphthalene sulfonate (ANS), etc. [26,28]. ICT dyes are composed of an electron rich moiety and an electron deficient moiety connected by a  $\pi$ -conjugated spacer. An efficient charge transfer from the electron rich (donor) and deficient (acceptor) moiety generates a high dipole moment in the molecule, both in the ground state and as well as in excited state [29]. Due to the presence of high dipole moment in the excited state, the fluorescence properties can be altered easily by changing the surrounding local environment [18,30]. Naphthalimide based dyes are a very well known class of environment sensitive ICT dyes with large Stokes shift, good stability and quantum yield [1,13,21,31]. 1,8-naphthalimide dyes are much more popular when compared to its other positional isomers, due to their relatively simpler synthetic procedure [32–34]. These dyes are well studied and used in various fields [35]. Recently, 2,3-naphthalimide derivatives are drawing much attention for its versatile use and the development of modern synthetic chemistry methods leading to easy synthesis with different functional groups. This class of dyes have been used widely in diverse fields like as sensors [35], intracellular biomarkers [31], fluorescence imaging [36], DNA photo cleaver [37], ratio metric pH sensor [38], ratiometric DNA detector [39], etc. Usually, ICT dyes shows a low fluorescence quantum yield in water, but significant enhancement has been observed when they are taken in organic solvents or relocated into a hydrophobic environment after attaching with proteins [21].

Imperiali and co-workers for the first time reported the synthesis and application of 6-*N,N*-dimethylamino-2,3-naphthalimide (6-DMN) by attaching it to a peptide chain to investigate protein–protein interaction [21,40]. Later, Qian and co-workers published a brief and scalable synthesis of an anhydride precursor of 6-DMN and its derivatives [41,42]. Importantly, the diester compound, diethyl 6-(dimethylamino)naphthalene-2,3-dicarboxylate (DMNDC) (Fig. 1a, Scheme 1), which is obtained via the synthetic route employed for making 6-DMN, has potential for novel

fluorescence properties but its photophysical properties and applications have not been explored yet.

DMNDC contains a *N,N*-dimethylamine unit (electron rich donor part) and it is connected with two ester units (electron withdrawing acceptor part) through conjugation via a naphthalene unit (Fig. 1). An intramolecular charge transfer process occurs (Fig. 1c), due to the movement of lone-pair of nitrogen towards ester groups via the naphthalene linker. Hence, we consider its prominence to serve as a “push–pull” chromophoric dye with excellent solvatochromic fluorescence properties, but as far as our knowledge the spectroscopic properties of this compound is still not been explored as a potential ICT dye.

After successfully synthesizing, following the protocol available in the literature [21], and obtaining the crystal structure of DMNDC (Fig. 1b), we have investigated the solvent dependent photophysical properties of this fluorophore using steady-state and time-resolved spectroscopic techniques. Then, we explored its potential to probe self-assembling process and micro-environments of five structurally different micelles, (see Chart 1 in ESI for their structure) consisting of charged and non-charged surfactants and to determine their CMC and hydrophobic pockets of Bovine Serum Albumin (BSA).

## 2. Experimental section

### 2.1. Materials

Adogen 464, Taurocholic acid sodium salt, sodium dodecyl sulfate (SDS), Cetyltrimethylammonium bromide (CTAB), Bovine Serum Albumin (BSA), and Tris buffer (pH 7.2) were purchased from Sigma Aldrich (India), Triton X-100 (TX-100) was purchased from Spectrochem (India), NaOH and HCl were purchased from SD-Fine (India) and Rankem (India) respectively. All chemicals were used as received without any further purification. The solvents used for spectroscopic measurements were of spectroscopic grade; methanol, DMSO, THF, DMF, acetonitrile, isopropanol were purchased from Sigma Aldrich (India), benzene, *n*-hexane, cyclohexane, toluene, octanol, dichloromethane, DMA, and ethyl acetate were purchased from Sisco Research Laboratories (India) and no further purification was performed. Ethylene glycol was purchased from spectrochem (India). The experiments in water was carried out using Mili-Q grade water using Milipore water purification set up from Merck with resistivity 18.2 M $\Omega$  cm. pH of water solutions were adjusted by using HCl and NaOH solutions. All the experiments with surfactants were performed at the pH 7.0–7.2. The experiments with BSA were carried out at pH 7.2 using 5 mM Tris buffer solution. Ethanol was dried over magnesium metal overnight, followed by distillation under nitrogen atmosphere. All the experiments were carried out at (298  $\pm$  2) K.

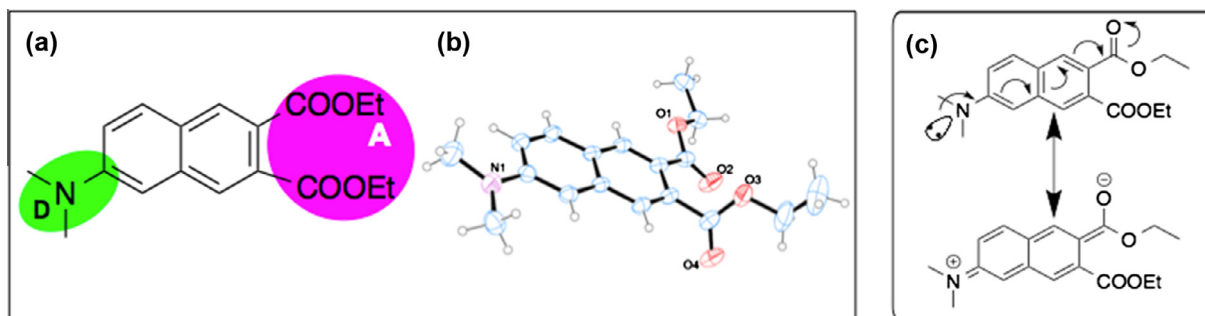


Fig. 1. (a) Structure of DMNDC (here D denotes electron donor part and A denotes electron acceptor part), (b) crystal structure of DMNDC (ORTEP diagram), and (c) excited-state intramolecular charge-transfer process in DMNDC.

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