Studies of the photophysics of highly fluorescent Red Mega 480 laser dye in solutions: Steady state spectroscopy
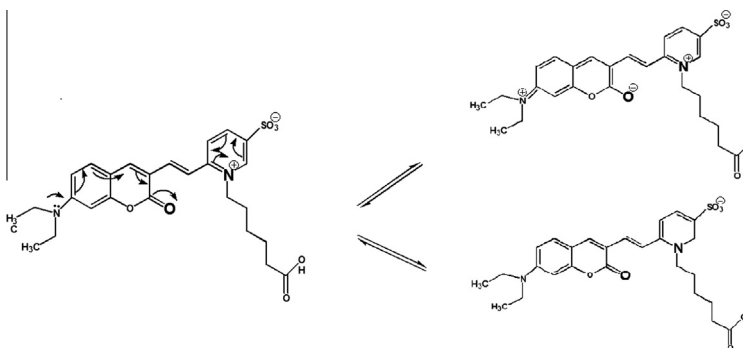
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HIGHLIGHTS

- Solvent effect on absorption and fluorescence spectra of highly fluorescent Red Mega 480 laser dye studied.
- Bathochromic shift is observed with increasing polarity.
- Excited state dipole moments are larger than the ground state due to high polarity in excited state.
- Dipole moments are calculated by various methods.
- Linear solvation energy relationships are studied on the dye in reference to degree of solvation strength.

GRAPHICAL ABSTRACT

ABSTRACT

The absorption and fluorescence spectra of highly fluorescent industrially useful medium sized Red Mega 480 dye have been studied in various solvents at 298 K. The solute photophysical behavior depends strongly on the solute–solvent interactions. In order to understand the effect of inter molecular interactions on spectral behaviors of the dye in different solvents extent of this behavior can be analyzed by linear solvation energy relationships. In addition, ground and excited state dipole moments were evaluated by various methods. It is observed that excited state dipole moment (μ_e) is larger than the ground state (μ_g), absorption spectra show a bathochromic shift with increasing polarity indicating that transition involved is $\pi \rightarrow \pi^*$ and Onsager cavity radius is determined by atomic increment method.

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Introduction

The effects of solvent environment on absorption and fluorescence spectra of highly fluorescent organic compounds has been the subject of several great motivating [1,2] investigations. Effects are complex, and are due several factors that affect the absorption and fluorescence emission spectra and quantum yields like solvent polarity, rate of solvent relaxation, probe conformational changes, rigidity of the local environment, internal charge transfer, intermolecular charge transfer, proton transfer and excited state reactions, probe–probe interactions and changes in radiative and non-radiative decay rates.

These multiple effects provide many opportunities to investigate the effect of local environment on a fluorophore [1]. However, it is difficult to know which effect is dominant in a particular experimental system, and predictably more than one

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effect will simultaneously affect the fluorophore. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can lead to an increase or decrease of dipole moment of the excited state as compared to the ground state.

A dipole moment represents a direct measure of electron distribution in a molecule of known geometry [3]. It is a physical constant which can be obtained by many experimental and theoretical techniques. A number of excellent texts, monographs, and reviews devoted to dipole moments are available and contain a detailed discussion on the theory of dipole moments. It seems worthwhile to point out here that, dipole moments convey most important sources of structural information about organic molecules in ground and excited states [2].

Knowledge of the dipole moment in the ground and excited state reflects the charge distribution in the molecule and helps to assess the efficiencies of the quantum chemical derivations, electronic and geometrical structure of the molecule in short-lived state, course of photochemical transformation, electron correlation treatments and for calculating the electron density distribution in the singlet and triplet state. It has been useful in the extraction of parameters like molecular polarizability in nonlinear optical materials using electro optic methods [5]. An excellent overview of the solvatochromic method by Koutek [5] has shown to facilitate satisfactory results. The statistical analysis performed using various expressions in the process of identifying the best parameters were based on the bulk solvent properties such as refractive index (n) and dielectric constant (ε). Out of the various expressions chosen a few have been identified which could afford satisfactory results for our selected Red Mega 480 dye compound. The best expression identified by Koutek [4] was used earlier by Kawski [4,6], Bakshiev [7], Chamma–Viallet [8], Lippert [9] and Suppan [10] several reports are available in the literature in which the above methods have been used independently or with other methods to evaluate the excited state dipole moments. Several organic compounds such as coumarin 6, coumarin 7, coumarin 30 and coumarin 337 have been widely studied by U.S. Raikar et al. [11–16], apart from the above mentioned methods there have been other authors who have used various solvent parameters in order to relate the spectral shifts. One of the well used parameter is the $E_T(30)$ scale put forward by Reichardt [2]. Other parameters are also taken into consideration by Katritzky et al. [17] in our present work.

We have newly developed Red Mega 480 laser dye, whose dipole moments presented in the present work is of our great interest. Photophysics of a dye is an active field of research because of very much importance as laser material, strong absorption cross section and high florescence quantum yield makes it an excellent laser dye for the green–red region. Its fluorescence properties are dependent on the surrounding environments. That is why; it is widely used as a laser dye, daylight fluorescent pigment, lithography, microlithography, biomolecular labelling, direct conversion of excitation light into emission without using a FRET (Forster Resonance Energy Transfer) mechanism, variety of possible applications including DNA sequencing and FISH (Fluorescence InSitu Hybridization) microscopy, also used for multiwavelength backward photo acoustic scanner for 3D imaging of soft tissues to depths of several millimetres with a spatial resolution [18], biosensors, printing technology, imaging of biological tissues and lipophilic fluorescent probe for biochemical and medicinal investigations [16,17].

Solvent effects play a key role in many chemical and physical processes in solutions [1,2], this effect is closely related to the nature and the degree of the solute dipole moment changing in the process of solute–solvent interactions, solvent polarity, internal charge transfer and therefore it has been of the highest interest in developing quantitative measurement of the dipole moment and

solute–solvent interactions [3,4,6]. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes [19] in the excited state.

A number of experimental methods like microwave conductivity [20], electric dichroism [21], electric polarization of fluorescence and stark splitting [22] are available to determine the dipoles moment more precisely, but application have been limited to instrument intensive and restricted to small organic molecules. Solvatochromic method offers the simplest technique to determine the dipole moments and is based on the shift of absorption and fluorescence maxima in different solvents [23,24].

These studies have gained much importance due to the progress in photo science of dyes in recent and past. The accurate dipole moment values give the information about the optical aspects of a material. The improved estimation of the dipole moments means a better understanding of the electron charge distribution as these estimated values give insight into photochemical reaction or quantum yield of a highly applicative dye.

To establish the dipole moment in excited state (μ_e) with the solvatochromic method and also to compare the values which are obtained, several approaches have been used by Lippert [9,15], Bakhshiev [7,15], Kawski–Chamma–Viallet [6,13], Suppan [10,13], Ravi et al. [25], McRae [26] and these will be employed in this study.

The solvent dependency of Stokes shift can originate from dielectric constant and specific (hydrogen bonding) solute–solvent interactions. Further solvent effect can be analyzed by solvatochromic parameters and solvent polarity [17,15,27,28]. Stokes shift can be used to explain the multiparameter solvent polarity scales for solute–solvent interactions. Effect of solvent polarity on the spectral features of the solute can be interpreted by means of linear solvation energy relationship (LSER), a concept that can be formulated by Kamlet–Abboud–Taft (KAT) and Katritzky (KTZ) parameters [17,27,28].

In this paper, detailed calculations of dipole moments both in ground state and excited state of Red Mega 480 laser dye by various methods and in respect to solvent polarities are discussed in depth.

Materials and methodology

Red Mega 480 was purchased from Sigma Aldrich and was used without further purification. The Molecular structure for this highly fluorescent laser dye is given in Fig. 1. All the solvents viz., methanol, ethanol, propanol, butanol, nonanol, decanol, DMSO, and acetonitrile are of spectroscopic grade. Electronic absorption spectra are recorded on Ocean Optics spectrophotometer at 298 K.

Theory: determination of dipole moments

The independent equations used for the estimation of ground and excited state dipole moments of Red Mega 480 laser dye is as follows:
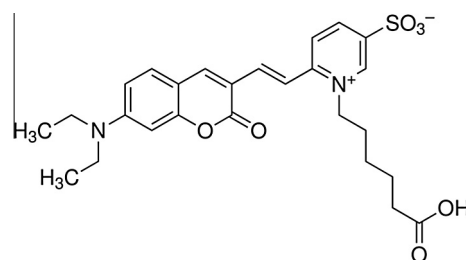

Fig. 1. Molecular structure and IUPAC name of Red Mega 480. Molecular formula: $C_{26}H_{30}N_2O_7S$ (Red Mega 480). IUPAC Name: 1-(5-carboxypentyl)-6-{2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]ethenyl}pyridinium-3-sulfonate.