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Spectroscopic and computational studies of 1,4-bis[β-(6-tertbutyl-2-benzoxazolyl)vinyl]benzene(BTBVB) laser dye

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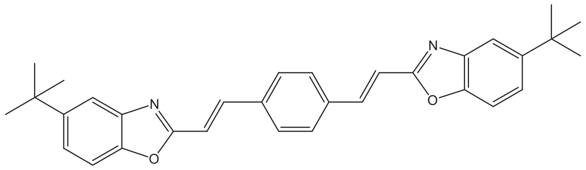
ABSTRACT

The electronic absorption, fluorescence spectra and photophysical parameters such as, molar absorptivity (ε), oscillator strength (f), transition dipole moment (μ_{12}), and fluorescence quantum yield (φ_f) of BTBVB were determined in different solvents and micelles. Both electronic absorption and emission spectra are less sensitive to medium polarity which indicates little change in the dipole moment of singlet (S_0) ground and excited state (S_1) of BTBVB molecule upon excitation. The quantum yield for photochemical transformation (Φ_c) of BTBVB was calculated in different organic solvents such as DMSO, DMF, EtOH and $CHCl_3$ at room temperature. The dye solutions in DMSO, DMF, $CHCl_3$ and EtOH give laser emission in the blue–green region upon excitation by a 337.1 nm nitrogen pulse. The tuning range, gain coefficient (α) and emission cross-section (σ_e) have been determined. Excitation energy transfer from BTBVB to rhodamine B was studied in *n*-butanol, methanol and ethylene glycol to improve the laser emission from RB dye when excited by nitrogen laser. Such an energy transfer dye laser system (ETDL) obeys a long range columbic energy transfer mechanism with a critical transfer distance, R_0, of 36 Å and k_{ET} equal $6 \times 10^{12}\ M^{-1}\ s^{-1}$. The density functional theory (DFT) was used to optimize the ground and excited state geometry of the dye, the computed peaks of absorption and emission spectra are in a reasonable agreement with the experimental results.

1. Introduction

Benzoxazole derivatives have applications in many areas. They have been used as fluorescent whitening agents [1,2] emitting in the blue–green region of visible spectrum, and several benzoxazole derivatives are also reported as good laser dyes of reasonable photostability [3–5]. Other applications are in electroluminescent devices [6,7], UV photostabilization of polymers [8], electrochromic displays and optical imaging devices [9]. Some benzoxazole derivatives act as antifungal and antibacterial agents [10].

In this paper we report the photophysical parameters in different media, photostability and laser activity of 1,4-bis[β-(6-tertbutyl-2-benzoxazolyl)vinyl]benzene(BTBVB). The excitation energy transfer from BTBVB to rhodamine B laser dye is also studied in ethanol.



BTBVB

2. Experimental

2.1. Materials and solvents

Rhodamine B (Aldrich) was used without further purification. Cetyltrimethyl ammonium bromide (BDH) was used to prepare cationic micelles and sodium dodecyl sulfate (Fluka) was used to prepare anionic micelles. All solvents used in this work were of spectroscopic grade and were checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges.

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2.2. Dye preparation

1,4-Bis [β-(6-tertbutyl-2-benzoxazolyl) vinyl] benzene (BTBVB) was prepared according to the general procedure reported for the preparation of this series of diolefinic compounds [11] as the following: A solution of 0.01 mol of terephthalaldehyde in the necessary amount of DMF (20 ml) was added in a dropwise manner to a stirred mixture of 0.03 mol of 2-methyl-6-tertiary butylbenzoxazole and 4.5 g of powdered potassium hydroxide in 30 ml of DMF, and the mixture was stirred at room temperature for 1 h. It was then cooled with ice and treated with 10% hydrochloric acid until it was slightly acidic. The resulting precipitate was removed by filtration, washed to neutrality with water, washed with 10 ml of methanol, and dried. The dye was recrystallized twice from dimethylformamide (DMF) with yield 97%, m.p. 285 °C. The structure of the synthesized dye was confirmed by elemental and spectral characteristics which include melting point, FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra. The material was then vacuum sublimed in the dark. Anal. Calc. For **$C_{32}H_{32}O_2N_2$**: C, 80.64; *H*, 6.77; N, 5.88. **Found:** C, 79.67; *H*, 6.61; N, 6.05. FT-IR (KBr) (cm^{-1}): $\upsilon = 1580–1500$ cm^{-1} (m, phenylene), 1620 (s, C=N group), 2920 (w, CH stretching of aliphatic), 3040 (w, CH stretching of aromatic). ^{1}H-NMR ($CDCl_3$): $\delta = 1.58$ (s, 18*H*, 6 CH_3 groups), 7.18–7.94 (m, 4*H* 2C=C of diolefine and 6*H*, of aromatic moieties). ^{13}C-NMR ($CDCl_3$): $\delta = 154.62$, 148.93, 146.02, 141.74, 136.05, 132.92, 128.12, 123.13, 119.34, 112.45, 37.85, 34.54 which were in accordance with the proposed structure. MS: *m*/*z*, (%) = 476.61 (M^{+1}, 100).

2.3. Instrumentation

Melting points reported for the monomers are determined on a Gallen-kamp Melting Point apparatus. Elemental analyses (C, H, N) were carried out on CHN Rapid analyzer. FT-IR spectrum was recorded on a Perkin-Elmar 100 series (Beaconsfield, Bucks, and UK) within the range of 4000 − 400 cm^{-1} using KBr pellet technique. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Advance 600 MHz using $CDCl_3$ as solvent. UV–vis electronic absorption spectra were recorded on a Shimadzu UV–vis 1650-PC spectrophotometer and steady state fluorescence spectra were recorded on a Shimadzu RF 5300 specrofluorophotometer using a rectangular quartz cell of 10 mm path length, emissions were monitored at right angles. The fluorescence quantum yield (Φ_f) was measured using the optically diluted solution to avoid the reabsorption effect (absorbance at excitation wavelength ≤ 0.1), relative method with a solution of quinine sulfate in 0.5 mol dm^{-3}H_2SO_4 ($\Phi_f = 0.55$) as reference standard [12–14]. The following relation was used to calculate the fluorescence quantum yield (Eq. (1)) [15–17]

$$\Phi = \Phi_r \frac{I \times A_r \times n^2}{I_r \times A \times n^2{}_r} \tag{1}$$

where Φ is the quantum yield, *I* is the integrated emission intensity, *A* is the absorbance at excitation wavelength, and *n* is the refractive index of the solvent. The subscript *r* refers to the reference fluorophore of known quantum yield. The oscillator strength (*f*) of electronic transition and the transition dipole moment (μ_{12}) from ground to excited state was calculated in different solvents using Eqs. (2) and (3)[18]:

$$\begin{gathered} f = 4.32 \times 10^{-9} \int \varepsilon(\tilde{\nu}) d\tilde{\nu} \\ \text{or } f = 4.32 \times 10^{-9} \Delta\tilde{\nu}_{1/2} \varepsilon_{\max} \end{gathered} \tag{2}$$

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} E_{\max}} \tag{3}$$

where $\varepsilon(\tilde{\nu})$the numerical value for the molar extinction coefficient is measured in dm^3 mol^{-1} cm^{-1}, $\tilde{\nu}$ is the wavenumber value in cm^{-1} and $E_{\max}$ is the energy maximum of the absorption band in cm^{-1}.

Light intensity was measured by using ferrioxalate actinometery [19]. Photochemical quantum yields (Φ_c) were measured using a method that accounted for the decrease in absorbance at the excitation wavelength as the photoreaction proceeded [20].

The lasing action was monitored at a dye laser (GL-302 Dye laser PTI) pumped by a nitrogen laser (GL-3300 Nitrogen laser, PTI). The pump laser ($\lambda_{ex} = 337.1$ nm) was operated at a repetition of 3 Hz with a pulse energy of 1.48 mJ and pulse duration of 800 ps. The narrow band output of the dye laser was measured with a pyroelectric Joule meter(ED 100, Gen-Tec). The energy of the pump laser was measured with a second pyroelectric Joulemeter (ED 200, Gen-Tec).

3. Results and discussion

3.1. Spectral characteristics of BTBVB in different solvents

The electronic absorption and emission spectra of BTBVB were measured in solvents of different polarity at room temperature. As shown in Figs. 1 and 2, the solvent polarity has only a slight effect on the electronic absorption and emission maxima (ca. 6 nm for absorption and ca. 10 nm for emission). The small shifts in the position of the absorption and emission spectra indicate a small change in the charges distribution on BTBVB molecule upon excitation; this means little change of polarity of BTBVB molecule upon excitation. There is also a mirror image relationship between the absorption and fluorescence spectra and a coincidence between absorption and excitation maxima. These facts together with the higher molar absorptivities and oscillator strength of electronic transition of dye is consistent with a strongly allowed transition $^1(\pi–\pi*)$ with small geometry change between electronic ground and excited state. In non-polar solvents, however, e.g. *n*-heptane the emission spectra exhibit more fine structure relative to polar-protic solvents such as ethylene glycol. This could be due to a specific solvent–solute interaction (e.g. hydrogen bonding with excited dye molecules). However, in two solvents of the same polarities for example methanol ($\Delta f = 0.39$) and ethylene glycol ($\Delta f = 0.38$), the emission maximum are shifted from 456 to 468 nm and Stocks′ shift are 65 and 81 nm for methanol and ethylene glycol respectively. The role of medium viscosity in causing bathochromic shift in emission spectra is explained in terms of the influence of the medium cage in maintaining molecular planarity in electronically excited states with a

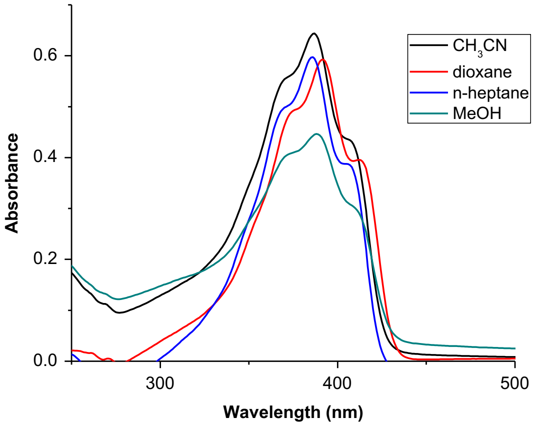

Fig. 1. Electronic absorption spectrum of 1 × 10^{-5} mol dm^{-3} of BTBVB in different solvents.