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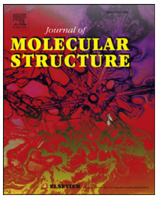

Photoinduced intramolecular charge transfer and photophysical characteristics of (2*Z*)-3-[4-(dimethylamino) phenyl]-2-(2-methylphenyl) prop-2-ene-nitrile (DPM) in different media

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ABSTRACT

A new fluorophore, (2*Z*)-3-[4-(dimethylamino) phenyl]-2-(2-methylphenyl) prop-2-ene-nitrile (DPM), was synthesized by knoevenagel condensation of 4-(dimethylamino) benzaldehyde and 2-methylbenzyl cyanide in ethanol using NaOH as base. The electronic absorption and emission characteristic of DPM was studied in different solvents. The X-ray crystallographic structure of DPM was also investigated. A crystalline solid of DPM gives a strong green emission at about 533 nm; these phenomena are important for the application of DPM dye in organic photo emitting diode. DPM exhibits a red shift in its emission spectrum as solvent polarity increases, indicating a large change in the dipole moment of dye molecule upon excitation due to intramolecular charge transfer in excited DPM*. The fluorescence quantum yield depends strongly on the properties of the solvents, which was attributed to positive and negative solvatokinetic effects. The DPM dye displays solubilization in cationic (CTAB) micelle and could be used as a probe to determine the critical micelle concentration (CMC) of CTAB.

1. Introduction

Stilbenes and its derivatives are well known photoreactive organic compounds, have been a great interest for researchers for many decades owing to their wide variety of applications in many areas of science. Upon photo excitation, stilbene-like molecules undergo various internal processes that make them as a model molecule for researchers in many branches of research. The properties of stilbene derivatives can be tuned, upon interaction with light, are the main theme for their exploitation in optoelectronic, optical storage devices and optical brighteners [1–5]. The substituent effect play a prominent role in the photophysics and photochemistry of stilbene derivatives, hence structurally modified stilbene based luminophores have become a subject of intense research in various aspects of science that interface with physics, materials chemistry, biology, and medical science.

Pi-conjugated organic compounds containing a donor and acceptor group at the opposite end separated by an ethenyl bridge show a phenomenon called intramolecular charge transfer (ICT) [6] upon photo excitation and therefore, most of the studies on these type of compounds are focused on the control or utilization of the ICT effect. Compounds of this class shows dual emission in polar solvents; one originated from their locally excited state and the other from the ICT state. The latter produce the large change in dipole moment that is sensitive to solvent polarity and hence provides a tool for the studies of the polarity and viscosity of media in the vicinity of a solute molecule [7–9]. However, instead of having an acceptor group at the opposite end of donor group; compounds containing an acceptor group in the α-position of ethylenic bond also exhibits ICT state and solvent sensitivity. Moreover these pi-conjugated molecules can be functionalized to improve their properties by chemical modification. This paper presents the synthesis, characterization and photophysical behavior of a cyano stilbene derivative, (2Z)-3-[4-(dimethylamino) phenyl]-2-(2-methylphenyl) prop-2-enenitrile (DPM) in different solvents as well as in cationic and anionic micelles. The pKa, pKa* and single crystal X-ray characterizations were also investigated.

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2. Experimental

2.1. Synthesis and characterization of DPM

(2*Z*)-3-[4-(dimethylamino) phenyl]-2-(2-methylphenyl) prop-2-ene-nitrile (DPM) was synthesized by reaction of 4-(dimethylamino)benzaldehyde with 2-methylbenzyl cyanide (Scheme 1). A solution of 4-(dimethylamino)benzaldehyde (1.5gm,0.010 mol) and 2-methylbenzyl cyanide (1.35gm.0.010 mol) in ethanolic solution of NaOH (2 g in 20 ml ethanol) was stirred for 3–4 h at 70–80 °C and was allowed to stand overnight. The solid product was collected by filtration, dried, and recrystallized from ethanol as light-orange solid (80–82% yield). The structure of the compound was confirmed by IR, ^{1}H NMR, ^{13}C NMR and X-ray crystallography.

Light-orange solid: yield: 82%; m.p. 182–190 °C; IR (KBr) ν_{max} cm^{-1}: 3010 (Ar–H), 2928 (C–H), 2242(C≡N), 1570(C=C); ^{1}H NMR (600 MHz, $CDCl_3$) (δ/ppm): 6.73 (d,2H,CH$_{aromatic}$ J = 1.8 Hz),6.71 (d,2H,CH$_{aromatic}$J = 1.8 Hz),6.87 (d,1H,CH$_{aromatic}$,J = 9 Hz),6.45 (d,1H,CH$_{aromatic}$,J = 9 Hz),7.25 (m,1H,CH $_{aromatic}$),7.85 (d,1H, CH$_{aromatic}$),2.47 (s,3H,CH$_3$ $_{aromatic}$),3.05 (s,6H, N(CH$_3$), 5.3 (s,1H,olefinic), ^{13}C NMR (150 MHz, $CDCl_3$) δ: 40.9,77.5111.6, 119.3, 121.6, 126.3, 126.8, 128.4, 129.5, 130.7, 130.09, 123.10, 131.6, 145.4, 147.1, 151.2, 151.7.

Single crystal of DPM suitable for X-ray analysis was obtained at room temperature by slow evaporation of $CHCl_3$ solution. One crystal of DPM (orange 0.30 × 0.17 × 0.05 mm) was mounted on Agilent Supernova (Dual source) Agilent Technologies Diffract meter, equipped with a graphite-monochromatic CuKα radiation (λ = 1.54184 Ặ), to collect diffraction data using CrysAlisPro software at 296 K. The structure solution was achieved through SHELXS–97 [10] and refined by full–matrix least–squares methods on F^2 using SHELXL–97, in-built with X-Seed [11]. All the C–H hydrogen atoms were positioned geometrically and treated as riding atoms with C$_{aromatic}$–H = 0.93 Å, C$_{methyl}$–H0.96 Å and refined using a riding model with Uiso(H) = 1.5 Ueq(C) for methyl and Uiso(H) = 1.2 Ueq(C) for all other carbon atoms. CCDC 971329 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

2.2. Spectral measurements

All solvents used in this work were of spectroscopic grade and checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. UV–Vis electronic absorption spectra was recorded on a Shimadzu UV–Vis 1650-PC spectrophotometer, and steady state fluorescence spectra were recorded on a Shimadzu RF 5300 spectrofluorophotometer using a rectangular quartz cell of 0.2 cm path length to minimize the re-absorption of emitted photons; emissions were monitored at right angle. The fluorescence quantum yield (Φ_f) was measured using an optically diluted solution to avoid re-absorption effect (absorbance at excitation wavelength ≤ 0.1), relative method with a solution of quinine sulfate in 0.5 mol dm^{-3} H_2SO_4 (Φ_f = 0.55) reference standard [12–14]. The following relation has applied to calculate the fluorescence quantum yield (1) [15–17].

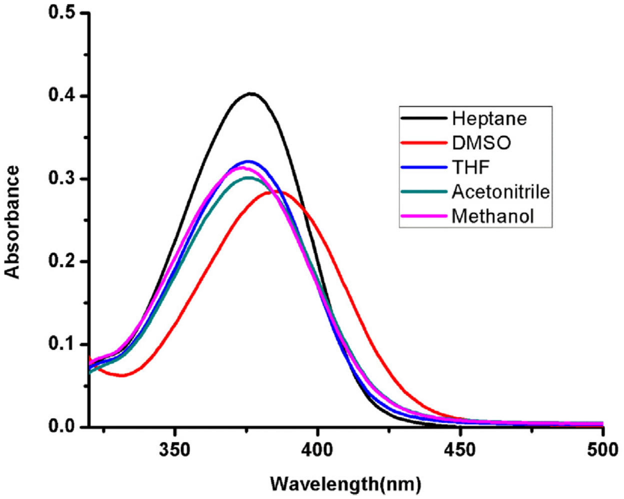


Fig. 1. Electronic absorption spectra of 1 × 10^{-5} mol dm^{-3} of DPM in different solvents.

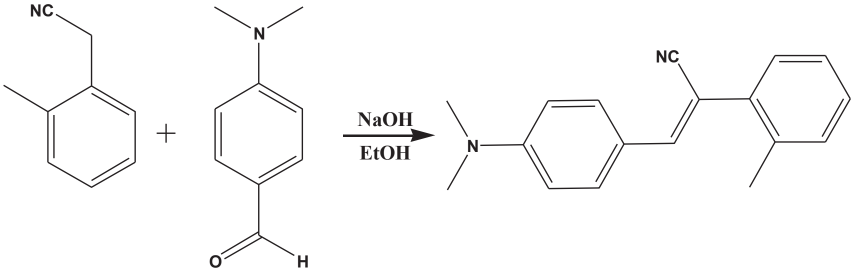
$$\Phi = \Phi_r \frac{I\ x\ A_r\ x\ n^2}{I_r\ \ x\ A\ x\ n_r^2} \qquad (1)$$

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.

3. Results and discussion

3.1. Spectral behavior of DPM in different solvents

The absorption and fluorescence spectra of 1 × 10^{-5} mol dm^{-3} DPM recorded in solvents of different polarity are shown in Figs. 1 and 2, and the corresponding spectral data in detail are summarized in Table 1. As observed in Fig. 1, polarity of solvent has only slight effect on the absorption maxima, indicating the weak polar character of DPM in the ground state. However, the emission spectra became broad and red shifted (Fig. 2) as the solvent polarity increases. The emission peak situated at around 410 nm corresponds to the locally excited singlet (LE) state and the other band at around 460 nm is the emission from intramolecular charge transfer (ICT) state, which shows a large red shift characteristic for the



Scheme 1. Synthetic route of DPM.