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Photoinduced intramolecular charge transfer in methyl ester of *N*,*N*′-Dimethylaminonaphthyl-(acrylic)-acid: Spectroscopic measurement and quantum chemical calculations

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Abstract

The excited state intramolecular charge transfer process of a synthesized donor–acceptor naphthalene chromophoric system methyl ester of *N*,*N*′-Dimethylaminonaphthyl-(acrylic)-acid (MDMANA) has been investigated spectroscopically in combination with quantum chemical calculation. Apart from the local emission the molecule shows a solvent polarity dependent low energy emission from the charge transfer excited state. In polar protic solvents ground state hydrogen bonded clusters of MDMANA are formed which also shows low energy emission. Structural calculation and potential energy surfaces along both the donor and acceptor twist coordinates by considering twisted intramolecular charge transfer (TICT) model at density functional theory (DFT) level predict that a stabilized twisting geometry is responsible for charge transfer emission. The solvent polarity effect on the emission spectra has been explored using time-dependent density functional theory-polarizable continuum model (TDDFT-PCM) which correlates well with the experimental spectral data.

Keywords: *N*,*N*′-Dimethylaminonaphthyl-(acrylic)-acid methyl ester (MDMANA); Dual fluorescence; Twisted intramolecular charge transfer; Density functional theory

1. Introduction

In the realm of photochemistry, the formation of the charge transfer (CT) state is one of the fundamental processes [1–6]. Research interest was directed towards the CT phenomenon after the first observation of dual fluorescence from 4-(*N*,*N*′-dimethylamino) benzonitrle (DMABN) in polar solvents in 1959 by Lippert et al. [1]. Since then, a variety of systems have been studied to explore the mechanistic insight of dual emission in donor–acceptor CT molecules [1–13]. Apart from the normal fluorescence band (L_b), the origin of the longer wavelength ‘anomalous’ (L_a) fluorescence band of DMABN was assigned to the formation of the charge transfer state [14]. This process involves relaxation of the solvent dipoles around the fluorophore and the formation of the CT state depends on the dielectric relaxation rate. Grabowski and co-workers proposed twisted intramolecular charge transfer (TICT) model and explain dual emission in a number of systems, e.g. 4-dialkylamino derivates of benzonitrile, benzaldehyde, pyrimidines, pyridine, etc. [15,16]. According to this model, the formation of CT state from the complete decoupling of the donor and acceptor groups is best achieved when the two groups are perpendicular to each other. In this twisted conformation, the dipole moment is greatly enhanced and this leads to greater stability of the CT state with increasing solvent polarity. An alternative planarised intramolecular charge transfer model for the longer wavelength band was put forward by Zachariasse and co-workers in 1993 [17]. According to them, the dual emission of DMABN is originated from the coupling of the NMe_2 group with the quinoid like benzene π system. Apart from the experimental investigation on the charge transfer phenomenon of a number of donor–acceptor systems, theoretical approaches to this problem have also been suggested by many groups [6,18–20]. Ab initio and DFT methods have been applied to explore the potential energy surfaces along the twisting co-ordinates in absence as well as in presence of solvents to throw light on

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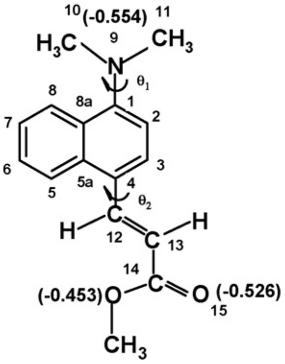
the mechanistic path of ICT process [9–12,18–20]. Though different schools put forward different theoretical models, the most accepted one is the TICT model advocated by Grabowski et al. [2,3].

Apart from the basic scientific interest on photoinduced ICT process of donor–acceptor charge transfer systems, the applications of ICT molecules as fluorescence probe are interesting and demanding [21–23]. The sensitivity of the longer wavelength band on local polarity and local viscosity of the surroundings makes the charge transfer chromophore a good fluorescent reporter of the surrounding microenvironment [21–23]. The need and interest for new molecules multiplied due to their vast application in the field of pure and applied sciences such as pH and ion detectors, etc. [24]. The photoinduced ICT process may also play a crucial role in biological light harvesting processes such as photosynthesis [25]. In the present work, we have studied the photophysical properties of the newly designed and synthesized donor–acceptor system methyl ester of *N*,*N*′-Dimethylaminonaphthyl-(acrylic)-acid (MDMANA) containing naphthalene chromophore. The ground and excited state properties of MDMANA have been explored by absorption and emission spectroscopy. Theoretical calculations at DFT level with B3LYP functional and 6-31G basis set were performed to study ground and excited state properties of MDMANA. The potential energy surfaces with respect to twist coordinates for the ground and first two excited singlet states indicates the formation of CT state in the first excited singlet state. The potential energy curves (PEC) with inclusion of solvent effect has been explored in acetonitrile solvent using DFT-PCM and TDDFT-PCM model for the ground and excited states, respectively, to correlate the experimental finding with theoretical results.

2. Materials and methods

2.1. Materials

Methyl ester of *N*,*N*′-Dimethylaminonaphthyl-(acrylic)-acid (Scheme 1) was prepared by stirring a mixture of 4-dimethylaminonaphaldehyde and methyl (triphenylphosphoraxylidene) acetate in dry dichloromethane at room temperature for about 24 h. After the solvent was removed over vacuum, the crude compound was purified on silica gel column chromatography and repeated crystallization in minimum amount of methanol to get pure product of MDMANA, ^{1}H NMR (400 MHz, $CHCl_3$): δ 2.96 (S, 6H, –NMe_2), 3.84 (S, 3H, OMe), 6.46 (d, J = 21 Hz, 1H), 7.07 (d, J = 10.6 Hz, 1H), 7.25–7.58 (m, 2H), 7.72 (d, J = 10.6 Hz, 1H), 8.18–8.21 (m, 1H), 8.26–8.29 (m, 1H), 8.49 (d, J = 21 Hz, 1H).



Scheme 1. Structure of MDMANA with atom numbering, θ_1 and θ_2 are donor and acceptor twist angles, respectively. Calculated charge densities are given in parenthesis.

Spectroscopic grade solvents such as hexane (HEX), *n*-heptane (HEP), cylohexane (CYC), methylcyclohexane (MCH), tetrahydrofuran (THF), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), dioxane (DOX), methanol (MeOH), ethanol (EtOH), *iso*-propanol (*iso*-pr) and acetonitrile (ACN) solvents were purchased from Spectrochem and were used after proper distillation. Sulphuric acid from E-Merck was used after proper vacuum distillation. Triple distilled water was used for the preparation of aqueous solutions.

2.2. Steady state and time-resolved measurements

The absorption and emission spectra were measured by Hitachi UV-VIS U-3501 spectrophotometer and Perkin-Elmer LS-50B spectrophotometer, respectively. In all measurements, the sample concentration was maintained within the range 10^{-4} to 10^{-5} mol/dm^3 in order to avoid aggregation and reabsorption effects.

2.3. Computational procedures

The theoretical global minimum structure of MDMANA and its molecular properties have been calculated using Gaussion 03W software [26]. Structural optimization has been done at DFT level with B3LYP functional and 6-31G basis set. The theoretical potential energy curves (PEC) for the ground and first two excited singlet states have been explored following the twisted intramolecular charge transfer model as proposed by Grabowski et al. [2,3]. So far there are different ways to calculate the ground and excited state surfaces for the donor–acceptor CT systems [27–37]. In our case during the evaluation of the potential energy surface, both in vacuo and in acetonitrile solvent, the structural parameters have been kept frozen to that of optimized geometry of the ground state for all the points and all the states investigated; the only parameter varied is the twisting angle θ_1 for donor group and θ_2 for acceptor group (Scheme 1). The PECs for the first two excited singlet states have been obtained using time-dependent density functional theory (TDDFT). The PECs with inclusion of solvent effect is also constructed using TDDFT-PCM method for the above mentioned basis set. The TDDFT method of calculation using Gaussian 03W does not implement analytical gradients within TDDFT and hence it fails to optimize the geometries for the excited states. Though TDDFT method of calculation fails to optimize the geometries for the excited states, results obtained using this method correlates well with the experimental data [9–12,27–31].