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ScienceDirect

Journal of Luminescence 128 (2008) 1421–1430

JOURNAL OF LUMINESCENCE

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Spectroscopic and theoretical evidence for the photoinduced twisted intramolecular charge transfer state formation in *N*,*N*-dimethylaminonaphthyl-(acrylo)-nitrile

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Received 2 November 2007; received in revised form 18 January 2008; accepted 23 January 2008
Available online 7 February 2008

Abstract

The phenomenon of excited state twisted intramolecular charge transfer (TICT) process in *N*,*N*-dimethylaminonaphthyl-(acrylo)-nitrile (DMANAN) has been reported on the basis of steady-state absorption and fluorescence spectroscopy in combination with quantum chemical calculations. The absorption and fluorescence characteristics of DMANAN in solvents of different polarity reveal the presence of a single species in the ground state which forms the intramolecular charge transfer state upon photoexcitation. The observed dual fluorescence is assigned to a high-energy emission from the locally excited or the Franck–Condon state and the red-shifted emission from the charge transfer (CT) state. In polar protic solvents, hydrogen-bonding interaction on CT emission has been established from the linear dependency of the position of the low-energy emission maxima on hydrogen-bonding parameter (α). The experimental findings have been correlated with the theoretical results based on TICT model obtained at density functional theory (DFT) level. The theoretical potential energy surface for the first excited state along both the donor and acceptor twist coordinates in the gas phase obtained by time dependent density functional theory (TDDFT) method and in polar solvent by time dependent density functional theory-polarized continuum model (TDDFT-PCM) method predicts well the experimental spectral properties.

Keywords: *N*, *N*-dimethylaminonaphthyl-(acrylo)-nitrile; TICT; Absorption; Fluorescence; Density functional theory

1. Introduction

The basic process involved in the excited state intramolecular charge transfer (ICT) reactions is an interesting arena for researchers in the field of physical chemistry and chemical physics. Even after decades of the discovery of dual fluorescence in 4-*N*,*N*-dimethylaminobenzonitrile (DMABN) by Lippert et al. [1], new molecules are being designed for the possibility of photoinduced ICT reaction [2–15]. The need for new donor–acceptor charge transfer (CT) molecules crops up due to their vast applications in the field of pure and applied sciences such as pH and ion detectors, sensors for free volume in polymers, study of micro-heterogeneous environments, etc. to mention a few [16,17]. The need and interest for new molecules multiplied when it became clear that photoinduced ICT may play a crucial role in biological light-harvesting processes such as photosynthesis [18]. The dual fluorescence of the benchmark molecule DMABN has been studied from experimental and theoretical perspectives for describing ICT process over the past few decades [19–23]. In DMABN, the higher energy band from L_b state arises due to normal fluorescence, whereas the lower energy (LE) band from L_a state is described as the "anomalous" fluorescence band from the CT state. The past years have however witnessed the rise of different schools, which did not agree in their views of the ICT state. Broadly classifying, three different theoretical models have been described to explain the observed anomalous emission of the molecules exhibiting ICT process. These are mainly (i) twisted intramolecular

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0022-2313/$ - see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jlumin.2008.01.015

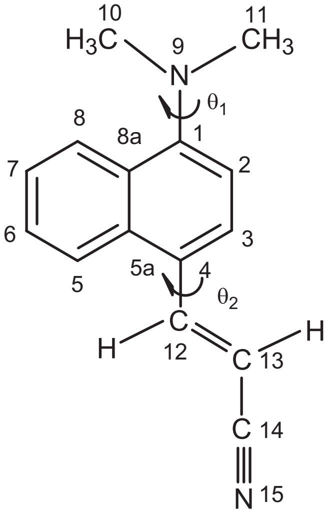
charge transfer (TICT) [24–26], (ii) planarized intramolecular charge transfer (PICT) [27] and (iii) rehybridized intramolecular charge transfer [28]. Out of these models, the concept of TICT has been put to maximum use while explaining the ICT process in most cases. However, the PICT model put forward by Zachariasse and co-workers in a number of papers has also gained importance since 1993 [29,30]. In the concept of TICT, it is stated that in the twisted conformation the donor-NMe_2 group of DMABN is twisted 90° out of plane and hence completely decoupled from the acceptor nitrile group [24–26]. Under this condition, complete CT takes place and the L_a band is thought to be responsible for CT emission from this twisted conformer.

In the present work, we have investigated the ground and excited state properties of *N*,*N*-dimethylaminonaphthyl-(acrylo)-nitrile (DMANAN) spectroscopically. Till date, most of the systems studied for excited state TICT reaction consisted of donor and acceptor groups connected to benzene chromophore [5,12–15]. There are examples where substances other than benzene chromophore have been used to study ICT reaction for donor–acceptor systems. We have tried to explore the possibility of ICT process in naphthalene ring-containing systems for which there are very few examples [31,32]. Very recently, we have investigated donor–acceptor excited state CT reaction in naphthalene systems such as methyl ester of *N*,*N*-dimethylaminonaphthyl-(acrylic)-acid (MDMANA) and ethyl ester of *N*,*N*-dimethylaminonaphthyl-(acrylic)-acid (EDMANA) [33,34]. The title molecule has been synthesized, and the absorption and fluorescence spectroscopy have been used to study its photophysical behaviour. Theoretical calculations for the ground state structure have been performed at density functional theory (DFT) level using B3LYP functional and 6–31G** basis set. Exploration of the ground and excited state potential energy curves (PECs) along the donor and acceptor coordinates in vacuo at DFT level further reinforced the idea of TICT process in DMANAN. The PECs with inclusion of solvent effect have been evaluated using time dependent density functional theory-polarized continuum model (TDDFT-PCM) method to correlate the observed spectral properties and solvent polarity dependent red-shifted emission band.

2. Materials and methods

2.1. Materials

The molecule DMANAN was prepared from *p*-(dimethylamino) naphthaldehyde by standard procedure . In brief, *p*-(dimethylamino) naphthaldehyde and triphenylphosphoranylideneacetonitrile in dry dichloromethane were stirred at room temperature for several hours. After the solvent was removed over vacuum, the crude compound was purified by silica gel column chromatography and repeated crystallization with a minimum amount of methanol done to get pure product DMANAN (Scheme 1),



Scheme 1. Structure of DMANAN with numbering of atoms, θ_1 and θ_2 are donor and acceptor twist angles, respectively.

^{1}HNMR (400 MHz, $CHCl_3$): δ 3.02 (s, 6 H, $-NMe_2$), 5.87 (d, $J = 16.32$ Hz, 1H), 7.10 (m, 1H), 7.56–7.64 (m, 3H), 8.03 (m, 1H), 8.16 (d, $J = 16.33$ Hz, 1H), and 8.34 (m, 1H).

Spectroscopic grade hexane (HEX), cyclohexane (CYC), *n*-heptane (HEP), methylcyclohexane (MCH), tetrahydrofuran (THF), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), dioxane (DOX), methanol (MeOH), ethanol (EtOH), isopropanol (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. In all measurements, the sample concentration has been maintained within the range 10^{-4}–10^{-5} mol dm^{-3} in order to avoid aggregation and reabsorption effects.

The fluorescence quantum yields of the CT species of DMANAN in solvents of different polarity are measured relative to recrystallized β-naphthol ($\Phi_f = 0.23$ in MCH) as the secondary standard (Table 1) and calculated on the basis of the following equation:

$$\Phi_f = \Phi_f^{\circ} \frac{n_o^2 A^{\circ} \int I_f(\lambda_f)\, d\lambda_f}{n^2 A \int I_f^{\circ}(\lambda_f)\, d\lambda_f}$$

where n_o and n are the refractive indices of the solvents, A^o and A are the absorbances, Φ_f^o and Φ_f are the quantum yields, and the integrals denote the area of the fluorescence bands for the standard and the sample, respectively.

2.2. Steady-state measurements

The absorption and emission measurements were done by Hitachi UV–vis U-3501 spectrophotometer and Perkin Elmer LS-50B fluorimeter, respectively. In all measurements, the sample concentration was maintained within the range 10^{-4}–10^{-5} mol dm^{-3}. All measurements were done at room temperature if not otherwise mentioned.