



Theoretical study on the intramolecular charge transfer induced twisting of the nitro and dimethylamino groups



Jiarui Xia^a, Meng Zhou^b, Shaowu Sun^b, Guan Wang^b, Peng Song^{b,*}, Meihua Ge^{c,*}

^a School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

^b Department of Physics and Chemistry, Liaoning University, Shenyang 110036, PR China

^c School of Physics, Shandong University, Jinan 250100, PR China

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ABSTRACT

The ground-state and excited-state electronic structures, relaxation dynamics as well as photophysical properties of the donor– π –acceptor compound 2-dimethylamino-7-nitrofluorene (DMANF) have been theoretically investigated using density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The calculated absorption and fluorescence spectrum agree well with the experimental results. The qualitative potential energy curves of twisting either donor or acceptor group favor the excited state intramolecular charge-transfer (ICT) relaxation process. However, the frontier molecular orbital picture supports that the twisting along the donor part is responsible for the fluorescence of the excited state. Further investigation of the strong dipolar stabilization with different structures indicates that two processes are involved in the whole twist and charge transfer dynamics: first, charge transfer is rapidly caused by the excitation to the first singlet state; second, charge transfer goes on slowly together with the twist motion. For strong dipolar stabilization, induced by twisting of the dimethylamino group, the charge transfer excited state corresponds to a more stable state with the twisted structure. Which results in these kinds of D– π –A compounds do not twist in nonpolar solvent. In the twisting charge transfer process, the nitrogen lone pair electrons play an important role.

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1. Introduction

In view of the key role of the photoinduced intramolecular charge-transfer (ICT) in the photophysics processes of donor–acceptor π -conjugated (D– π –A) compounds, the interest in molecular donor–acceptor [1] and different position substituted [2] systems has increased significantly, and they have been widely used in organic photo-voltaic (OPV) cells [3], fluorescence sensors [4] and as components for high-sensitivity optical analytical technique [5–7]. Since the first observation of the dual fluorescence phenomenon of 4-(N,N-dimethylamino) benzonitrile (DMABN) in polar solvents by Lippert et al. [8], numerous spectroscopic, thermodynamics and quantum chemical studies have been performed on ICT reactions and various models are explored to get an in depth understanding of the ICT state [9–15]. Up to now, two main models have been proposed to explain the mechanism in interpreting the essential of ICT state through analyzing the conformational relaxation accompanying with the ICT reaction, named twisted intramolecular charge transfer (TICT) and planar intramolecular charge

transfer (PICT) [13,14]. But the characterization of the ICT states (e.g., electronic nature and molecular geometry) is far from straightforward, even for a simple molecule such as DMABN. Just as Rappoport et al. have mentioned “the TICT–PICT controversy has emerged not from different experimental results, but from disagreement on how to interpret them” [15].

The requirement to further understand the nature of the ICT state has triggered a large number of theoretical and experimental studies. And the derivatives of DMABN by changing its different part (donor or/and acceptor) have been widely developed, of which the different ICT characters were shown. For example, Zhao et al. demonstrated that the intermolecular hydrogen bond $C\equiv N \cdots H-O$ formed between DMABN and MeOH can induce the $C\equiv N$ stretching mode shift to the blue in both the ground state and the TICT state of DMABN. It gives a new mechanism for explaining the time-resolved infrared (TRIR) absorption spectra of DMABN in MeOH solvent. According to the calculated results, it also revealed that the $C\equiv N \cdots H-O$ bond is significantly strengthened in the TICT state, which can facilitate the deactivation of the excited state via internal conversion (IC), and thus account for the fluorescence quenching of DMABN in protic solvents [10]. The photophysical properties of 4-(2-

* Corresponding authors. Tel.: +86 24 62202306; fax: +86 24 62202304.

E-mail addresses: songpeng@lnu.edu.cn (P. Song), mhge@sdu.edu.cn (M. Ge).

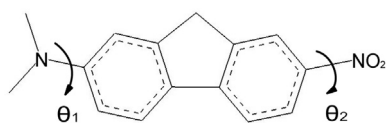


Fig. 1. Molecular structure of DMANF.

dimethylaminoethoxy)-N-octadecyl-1,8-naphthalimide were investigated in different solutions. Changing from a non-polar to a polar solvent increased the solvent interaction and both the excitation and emission spectra were shifted to longer wavelength and intensity decreased through taking advantage of TICT process. The theoretical calculations and spectral analyses revealed that such fluorophores were capable of sensing protons by intramolecular charge transfer. According to our previous theoretical studies, the N,N-diphenylaminophenyl-2,2':6',2'-terpyridine can be initially excited to the unrelaxed locally excited (LE) state, and in succession an intramolecular charge transfer takes place accompanying the diphenylamino and triphenylamine group until it attains the most stable conformational geometry, which has a TICT character and displays strong fluorescent emission [9]. In addition, for its dimethylaniline substituted derivative in protic solvents, the configuration with the maximum dipole moment is preferentially stabilized, so that for strong dipolar stabilization and weak mesomeric interaction, the lowest excited state corresponds to the twisted structure, with angles of the dimethylamino and dimethylaminophenyl groups are both twisted [16].

Fluorene-based materials as a type of important luminescent functional material have wide ranging applications in very diverse fields of current research from uses as photochemical sensitizers, bulk heterojunction solar cells, polymer and organic light-emitting diodes (PLEDs and OLEDs), etc [2]. And the photophysics and

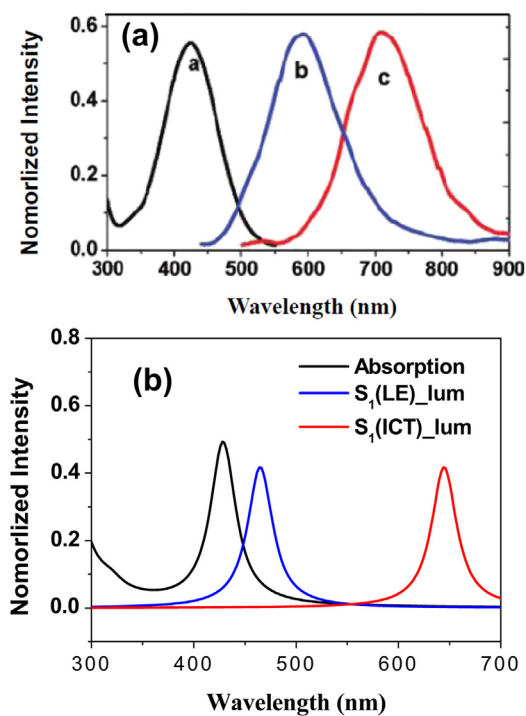


Fig. 2. (a) Experimental steady-state absorption (line a) and fluorescence spectra (line b and c) of DMANF in acetonitrile recorded in rigid matrices at 77 K (line b) and in solution at 298 K (line a and c) in Ref. [21]. (b) The calculation results of the relative spectra.

Table 1

Calculated transition energies and the corresponding oscillator strengths from ground state to the first three singlet excited states of DMANF molecule.

Excited state	Transition energy (nm)	Oscillator strength	CI expansion coefficients
S ₁	429	0.44875	99.0(HOMO → LUMO)
S ₂	329	0.00002	94.1(HOMO-4 → LUMO)
S ₃	319	0.03118	89.2(HOMO → LUMO + 1)

photochemistry investigation of fluorene and its derivatives have demonstrated that they are very sensitive to both the intramolecular and intermolecular interactions, such as hydrogen bonding, polarity, and steric interaction, etc [10,17–20]. In particular, the intramolecular and intermolecular hydrogen bonding in both the singlet and triplet electronic excited states of fluorenone and its derivatives as well as some other important organic and biological chromophores in alcoholic solutions and their important roles on the excited-state TICT processes of these chromophores have been investigated theoretically [17–20]. The experimental study of the excited-state TICT processes of 2-amino-7-nitrofluorenone (ANF) and 2-dimethylamino-7-nitrofluorene (DMANF) shown that, the intramolecular charge transfer process is much faster than the twisted motion of the dimethylamino, which indicates the twisted process and the intramolecular charge transfer are not coupled [21]. But until now, there is no verdict whether the twisted process and the intramolecular charge transfer are coupled.

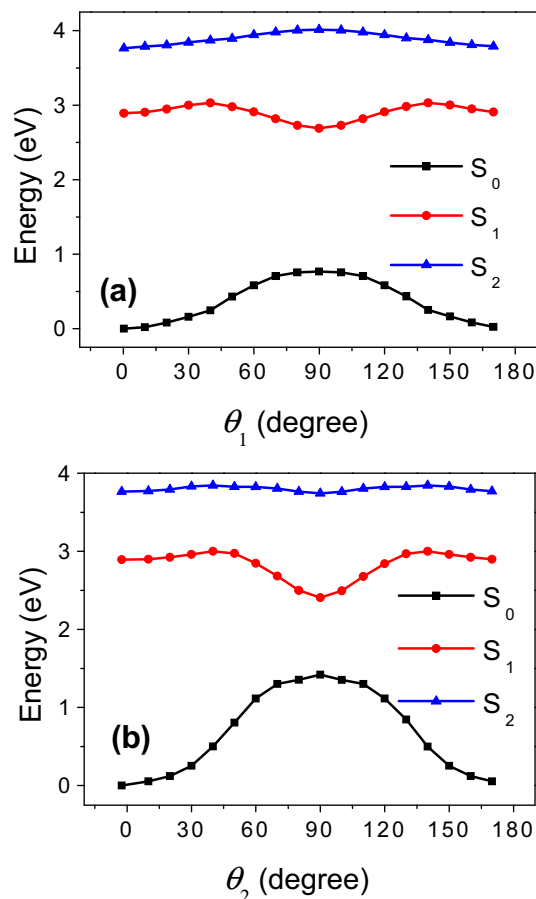


Fig. 3. Ground and the low-lying singlet excited state potential curves (energy relative to the minimum of the ground state) as a function of the twisting angle of the dimethylamino group (a) and of the nitro group (b).

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