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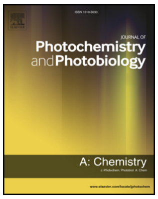

Influence of electron donors in fluorescent NLOphoric D-π-A derivatives with acenaphthene rotor: Photophysical, viscosity, and TD-DFT studies

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The novel fluorescent NLOphoric push-pull fluorophores (**2a-c**) constituted by the different N-substituted donors linked via π-bridge as a spacer to 1,1′-dicyanomethylidene group as an acceptor with acenaphthene rotor were synthesized and characterized. These dyes exhibit positive absorption and emission solvatochromism in solvents of different polarities. Solvent polarity plots viz. Lippert-Mataga, McRae, and Weller models provide the validation of charge transfer (CT) characteristics whereas, the Rettig model furnishes an alternative relaxation channel due to twisting around the σ-bonds between donor and acceptor on photoexcitation leading to the twisted intramolecular charge transfer (TICT) state in **2a-c**. Viscosity induced emission studies show 4.40, 8.78, and 5.63 fold increase in the emission intensity for dyes **2a**, **2b**, and **2c** respectively which recommends the titled dyes as a fluorescent molecular rotor (FMR). Density Functional Theory (DFT) calculations [(B3LYP/6-311 + + G(d,p)] give complete information of structural as well as electronic properties of dyes **2a-c**. The large difference in dipole moment (ca. 7.92–20.0 D) results in a strong non-linear optical (NLO) properties. The NLO properties were estimated theoretically as well as spectroscopically in solvents of different polarities. The computed values for these dyes show high first-order hyperpolarizability (β) in the range of 210–577 × 10^{-30} esu and second-order hyperpolarizability (γ) in the range of 506-2,325 × 10^{-36} esu.

1. Introduction

In "push-pull" fluorophores, where an electron donor (D) and acceptor (A) moieties interact with the π-conjugated systems, a partial intramolecular charge transfer reaction takes place on photoexcitation [1]. The photophysics of donor-π-acceptor (D-π-A) compounds accompanied by photoinduced intramolecular charge transfer (ICT) is the focus of interest with respect to experimental as well as theoretical investigation [2–4]. The optical properties of such dyes are influenced by the factors such as viscosity, polarity, pH, voltage and the rigidity of the media [5]. Thus, to study such variations, many environment-sensitive dyes, have been reported [5–7]. These dyes can provide dynamic information about their surrounding stimuli by altering the fluorescence emission properties arises due to solvatochromism. Fluorescent molecular rotors (FMR) can be used to study such properties by using appropriate viscous media. Typically, FMRs have the ability to undergo intramolecular rotation around the σ-bonds between donor and acceptor on photoexcitation. Moreover, FMRs are utilized to measure the variations such as viscosity sensitivity, change in polarity and the nonlinear optical (NLO) properties in the ground and excited state in different microenvironments.

A wide range of chemical functionalization or transformations of such D-π-A derivatives has been reported previously for their optical as well as non-linear optical (NLO) properties [8–12]. It is well documented that the optical and NLO properties of D-π-A derivatives can be fine-tuned by altering the donor or acceptor groups attached at the opposite end via the π-conjugated system. Moreover, these properties can be altered by using auxiliary donors or rotors (R) at the **α**-position with respect to 1,1′-dicyanomethylidene (DCMN) group as an acceptor [13]. A simple D-π-A derivative based on N-substituted donor and DCMN group as an acceptor have been reported for their excellent photophysical properties which have application in neuropathological fluorescence staining [14]. The optical properties of these derivatives are strongly influenced by varying the donors as well as the rotors attached at the **α**-position with respect to DCMN. A bathochromic shift in the absorption, as well as emission maxima, was observed while substituting the phenyl group at **α**-position with respect to DCMN [13]. On the other hand, the optical properties of these dyes further shifts to the red region while replacing the phenyl group with the strong acceptor such as cyano group (-CN) at **α**-position [15]. Consequently, further modification at the **α**-position with respect to DCMN group upon such derivatives makes us curious about the synthesis challenge and the

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associated chemical and photophysical properties. In this context, we designated acenaphthene group as a rotor at the **α**-position with respect to DCMN group to examine the influence of different donors with respect to optical as well as NLO properties. Acenaphthene, a polycyclic aromatic hydrocarbon (PAH) containing functional derivatives have been investigated for quite some time, due to its planar structure as well as better spectral characteristics [16–25]. Despite the various synthetic strategies of acenaphthene derivatives, there are very few reports dealing with chemical functionalization or transformations of the compound accompanied by photophysical properties [26–31]. Acenaphthene based architecture is of importance for the functional applications such as organic electronics [32], fluorescent sensors [33], high-performance liquid chromatography [34], and various biological uses [31,35]. Consequently, the synthesis of specifically functionalized acenaphthene based architecture and their photophysical, as well as theoretical studies, are of considerable interest.

With these perspective, we have designed and synthesized three novel fluorescent NLOphoric D-π-A push-pull fluorophores containing acenaphthene as a rotor to study the influence of donors on linear as well as non-linear optical properties in solvents of different polarities. To get further insight into the electronic as well geometrical parameters of the dyes **2a-c**, DFT, and TD-DFT computations were carried out.

2. Experimental

2.1. Computational method

All the calculations were performed with the Gaussian 09 suite of the program [36]. The ground state geometry optimization of acenaphthene based D- π -A dyes **2a-c** were performed using Becke's three-parameter exchange Lee-Yang-Parr correlation functionals (B3LYP) with 6-311 + +G(d,p) basis set [37–41]. All the computations were performed on HP workstation XW 8600 with Xeon processor, 4 GB RAM, and Windows Vista as the operating system. TD-DFT computations were employed for excited state geometry optimization [42,43]. The polarizable continuum model (PCM) [44] as implemented in Gaussian 09 was used to optimize the ground and excited state geometries in solvents such as toluene (TOL), tetrahydrofuran (THF), chloroform ($CHCl_3$), ethyl acetate (EtOAc), acetone (ACE), acetonitrile (ACN), methanol (MeOH), and N,*N*-dimethylformamide (DMF). The excitation energies, oscillator strengths and orbital contribution for the lowest 20 singlet-singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set as for the geometry minimization in solvent environments. The NLO parameters were calculated using three different functionals - B3YPP, BHHLYP, and CAM-B3LYP - for comparison and the equations are as follow:

The total static dipole moment μ is expressed by the following equation

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \tag{1}$$

The isotropic polarizability can be calculated from the trace of the polarization tensor,

$$\alpha_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3} \tag{2}$$

The mean first order hyperpolarizability (β_0) is expressed by

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{3}$$

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yxx} + \beta_{yyy} + \beta_{yzz})^2 + (\beta_{zxx} + \beta_{zyy} + \beta_{zzz})^2]^{\frac{1}{2}} \tag{4}$$

Where, β_x, β_y, and β_z are the components of the second-order polarizability tensor along the x, y, and z-axes respectively.

The mean second order hyperpolarizability (γ) is expressed by

$$\gamma = \frac{1}{5}[(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) + 2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{zzxx})] \tag{5}$$

2.2. Materials and equipment

All the chemicals are commercially available and were used without further purification unless otherwise mentioned. All the reagents were obtained from S. D. Fine Chemicals (India) and Sigma Aldrich. All the solvents used were of the spectroscopic grade. Melting points were recorded by open capillary on Sunder Industrial Product and are uncorrected. The reaction was monitored by thin layered chromatography (TLC) using 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized under UV light. ^1H NMR and ^{13}C NMR spectra were recorded on VARIAN 500-MHz instrument (USA) using $CDCl_3$ and DMSO-d_6 as a solvent. The chemical shifts were reported in parts per million (ppm) relative to internal standard as tetramethylsilane (TMS). ESI mass spectrometry was performed with a Q-TOF micromass (YA-105) spectrometer. Absorption spectra were recorded on Perkin Elmer Lambda 25 UV–vis spectrophotometer and emission spectra were recorded on Varian Inc. Cary Eclipse spectrofluorometer in the range 200–700 nm at room temperature. Cyclic voltammetry was performed on Metrohm autolab (AUT50995) with a standard three-electrode cell with a platinum electrode and an SCE reference.

2.3. Synthetic strategy

The energetic proximity of acenaphthene frontier orbital energy levels to those of N-substituted donor and DCMN as an acceptor based derivatives have motivated the synthesis of a variety of D-π-A conjugated heterocycles [45–48]. The synthesis of donor-acceptor compounds with the auxiliary effect of N-substituted phenyl ring at the **α**-position with respect to DCMN group has been reported previously [6,49–51]. In this report, we have designed and synthesized three different D-π-A derivatives based on N-substituted donor and DCMN group as an acceptor with an additional auxiliary effect of acenaphthene at the **α**-position to study the influence of different donors (Scheme 1) with respect to linear and NLO properties. These dyes were synthesized by Knoevenagel condensation of N, N-dimethyl phenylamine, julolidine, and triphenylamine based aldehydes with acenaphthene based active methylene compound (**1b**) to give the formation of three different D-π-A derivatives (Scheme 1).

2.4. Synthesis and characterization

The compounds **2a-c** were synthesized by modification of previously described methods [35,52,53]. Julolidine aldehyde and triphenyl monoaldehyde were synthesized by performing Vilsmeier-Haack reaction upon julolidine and triphenylamine respectively as described in the literature [50,54].

2.4.1. 5-Acetyl acenaphthene (1a)

Compound **1a** was synthesized as described in the literature [22].

2.4.2. 2-(1-(1,2-Dihydroacenaphthylen-5-yl)ethylidene)malononitrile (1b)

0.099 g (1.5 mmol) of malononitrile was added to the mixture of 0.196 g (1 mmol) of 5-acetylacenaphthene (**1a**) dissolved in 50 mL of glacial acetic acid. Ammonium acetate was added in a catalytic amount and the reaction mixture was stirred for 24 h at 90 °C. The reaction was monitored with the help of thin layer chromatography (TLC). After complete consumption of reactants, the reaction mixture was cooled to room temperature and poured over ice-cold water (50 mL) followed by extraction with the ethyl acetate. The organic layer was washed with water (3 x 20 mL) and brine, dried over sodium sulfate and evaporated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica 100–200 mesh using