

COMPUTATIONAL STUDY OF NAPHTHYL BASED SCHIFF BASE MOLECULAR RECEPTOR: COMPARISON OF THEORETICAL WITH EXPERIMENTAL

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ABSTRACT

In this work, molecular receptor (**R**) which is a Schiff base of naphthalene moiety tethered with diaminomalenonitrile (DAMN), reported by Sankar et al. (*New J. Chem.* 2014, **38**, 923-926) was studied through density functional theory (DFT) and time-dependent density functional theory (TD-DFT). Absorption spectra of neutral receptor (**R**) as well as its deprotonated form (**R**⁻) were calculated using 6-311++G (*d*, *p*) basis set in DFT/TD-DFT calculations. Mullikan charge distribution analysis was carried out in order to understand the polarized nature of N-H bonds, and to locate the chemically significant regions on the molecule. Spectral modulations during anion recognition were attributed to the intramolecular charge transfer (ICT) enhancement and photoinduced electron transfer (PET) process. The calculated results were further compared with the experimental data.

Key words: Receptor, Fluoride, DFT, TD-DFT ICT, PET

1 INTRODUCTION

Owing to crucial role of cations and anions in innumerable process of biological, chemical and environmental significance, momentous attention has been paid towards exploration and development of effective and molecule based detection methods “receptors” [1-2]. Molecular receptors are valuable tools to perform ion recognition, amid prompt selectivity and sensitivity. Most importantly, these are easy to prepare, operate and realize high sample through output. In this course, library of ion sensing receptors has been proposed [3-8]. While developing these receptors, number of interactions, such as hydrogen bonding, electrostatic force, metal-ligand coordination, hydrophobic and vander Waals forces have been taken onto consideration [9-12]. In this course, tethering of N-H polarization based molecular functionalities in the form of amides, ureas, thioureas; ammonium, imidazole and Imidazolium on diverse molecules have been used and proposed, in addition to chemical reaction based methods [13-20].

In the present study, one such newly explored receptor molecule (**R**) possessing free and polarized-NH₂ motif, was bought under study. The absorption spectroscopic analysis of receptor **R** and its deprotonated form, **R**⁻ (Fig. 1) has been carried out theoretically and compared with the experimental. In addition, the mechanism of anion interaction has also been worked out. The combined use of DFT/TD-DFT (B3LYP) functional and standard basis sets 6-311++G(d,p) provides an excellent balance between accuracy and computational efficiency of absorption spectra. The literature survey reveals that, to the best of our knowledge, no intensive observation of theoretical [DFT/TD-DFT] investigation has been reported so far with this type of receptor design possessing free -NH₂ based recognition site. Therefore, the present investigation was undertaken to study the absorption spectra and inter and intra molecular interaction between HOMO and LUMO energy levels of the newly explored molecular receptor.

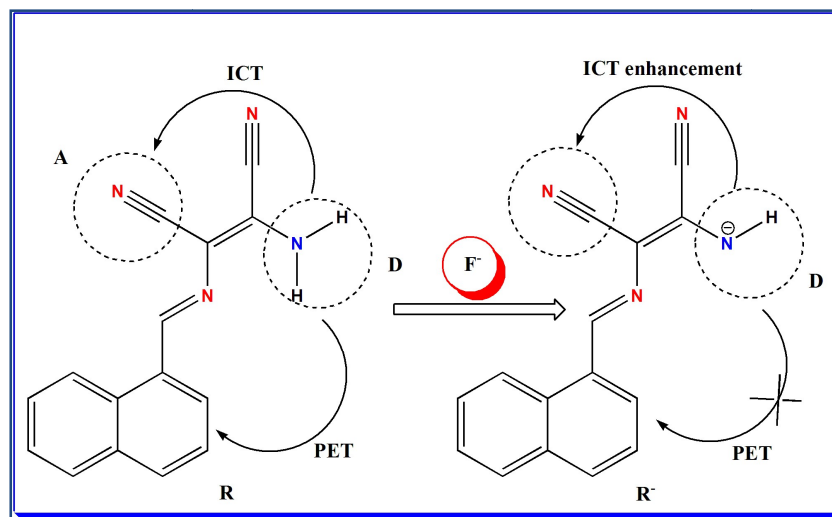


Fig 1. Molecular structure of receptor R and R⁻.

2 COMPUTATIONAL METHOD

In the present work, one of the hybrid methods; Lee-Yang-Parr correlation function (B3LYP) was carried out by basis sets 6-311++G(d,p) using GAUSSIAN 09W program. In DFT methods; Becke's hybrid function combined with the B3LYP function predict the best results of Mullikan charge density on N and H of amine (NH₂) group, and absorption spectra of receptor (R) and its deprotonated form (R⁻). The theoretical result of electronic absorption transitions was compared with the experimental.

3 RESULTS AND DISCUSSION

Mullikan charge distribution analysis

The Mullikan charge on the atoms is used to understand the charge distribution on the chemical bonding. The analysis facilitates positive and negative regions in the molecular space, at which the protons and electrons concentrate. Thus chemically significant regions and bonds can be identified. This also gives the description of the possible mechanism in the form of electrophilic, nucleophilic substitutions, hydrogen bonding or proton abstraction/transfer.

Normally the charges are distributed evenly over the molecule which imparts neutral character to the molecule. Whenever the substitutions are added to the molecule, the charge distribution is completely altered with respect to the substitution or the removal of any atom/moiety. Here in the case of receptor **R**, the negative Mulliken charges populated over the highly electronegative atoms (N-atoms) which splits the positive charges among hydrogen atoms. Hence the N and H of the molecule have negative and positive space respectively. The Mulliken charges of N and H atoms of amine (-NH₂) of **R** and **R**⁻ are presented in table 1.

Table 1. Mulliken charges of N and H atoms of NH₂

Atom	R	R ⁻
N	-0.406	-0.295
H	0.252	0.267

UV-Vis spectra and molecular orbital analysis

The UV-vis spectra and the electronic transitions of the receptor molecule and its deprotonated form were calculated using the TD-DFT/6-311++G (*d, p*) method. As it is clear from the figure 2, F⁻ induced deprotonation resulted in increase of electron density on the nitrile group of ICT channel (D- π -A) in LUMO, while as there is a decrease in electron density in HOMO. The alteration clearly indicate Intramolecular charge transfer (ICT) enhancement. The ICT enhancement further results in the decrease of electron density over naphthyl moiety ring in the LUMO of **R**⁻ compared to its HOMO. This clearly indicates blockade of PET channel in the molecule after deprotonation. Hence fluorescence “turn on” could be understood in the molecule after fluoride addition due to ICT enhancement. The electron delocalization overall leads to the decrease in the energy gap between HOMO and LUMO of molecule from 2.74 eV to 1.39 eV (Fig 2). Hence the presence of fluoride anion realizes spectral shift (red-shift), thus offering naked-eye optical detection of anion.

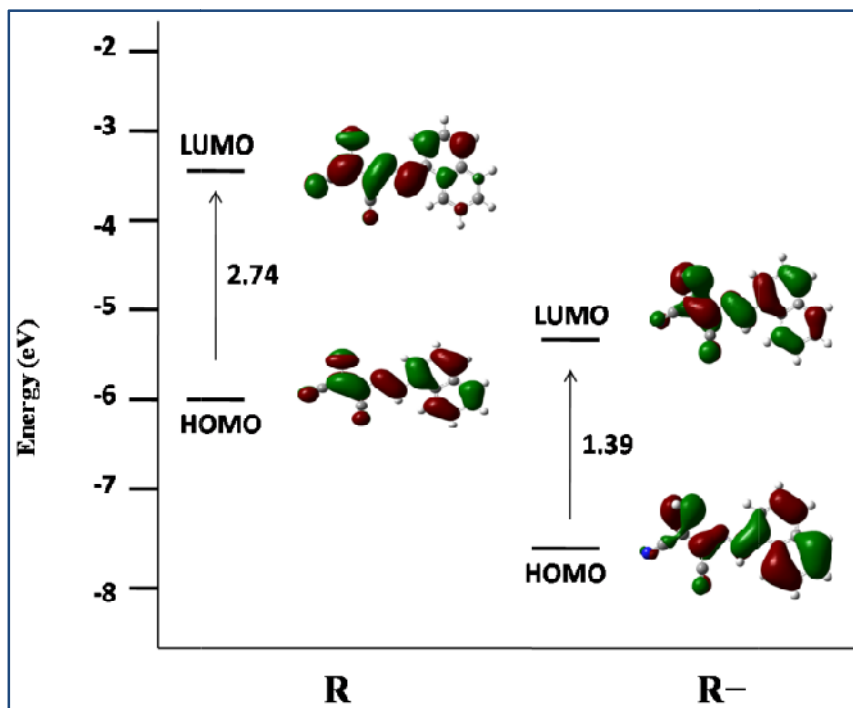


Fig 2. Excitation energies and HOMO and LUMO transitions of R and R⁻.

The mechanism of recognition can be explained in terms of the strong basicity of F⁻ in the non-aqueous environments (DMSO, THF, CH₃CN, etc). Under these conditions, F⁻ interacts with polarized –N–H moiety of amine group in the receptor molecule. The recognition is accompanied by the transfer of proton from –NH₂ to the F⁻. The recognition is further driven by the formation of the thermodynamically stable HF₂⁻ dimer which was reported by author during the course of the work [21].

Due to this deprotonation, receptor **R** in the presence of F⁻ displayed a red shift both experimentally as well as theoretically. In this study, the trends in spectral shift are as per experimental observations, but not empirically close with experimental (Fig 3 and Table 2). This may be because of solvent effect and the nature of interaction.

Table 2. Comparative experimental and theoretical electronic absorption spectra of R and R⁻.

Receptor	Experimental			Theoretical		
	λ (nm)	$\lambda_{\text{abs}}F$ (nm)	$\Delta\lambda$ (nm)	λ (nm)	$\lambda_{\text{abs}}F$ (nm)	$\Delta\lambda$ (nm)
R	385	460	75	487.84	820.31	332.47

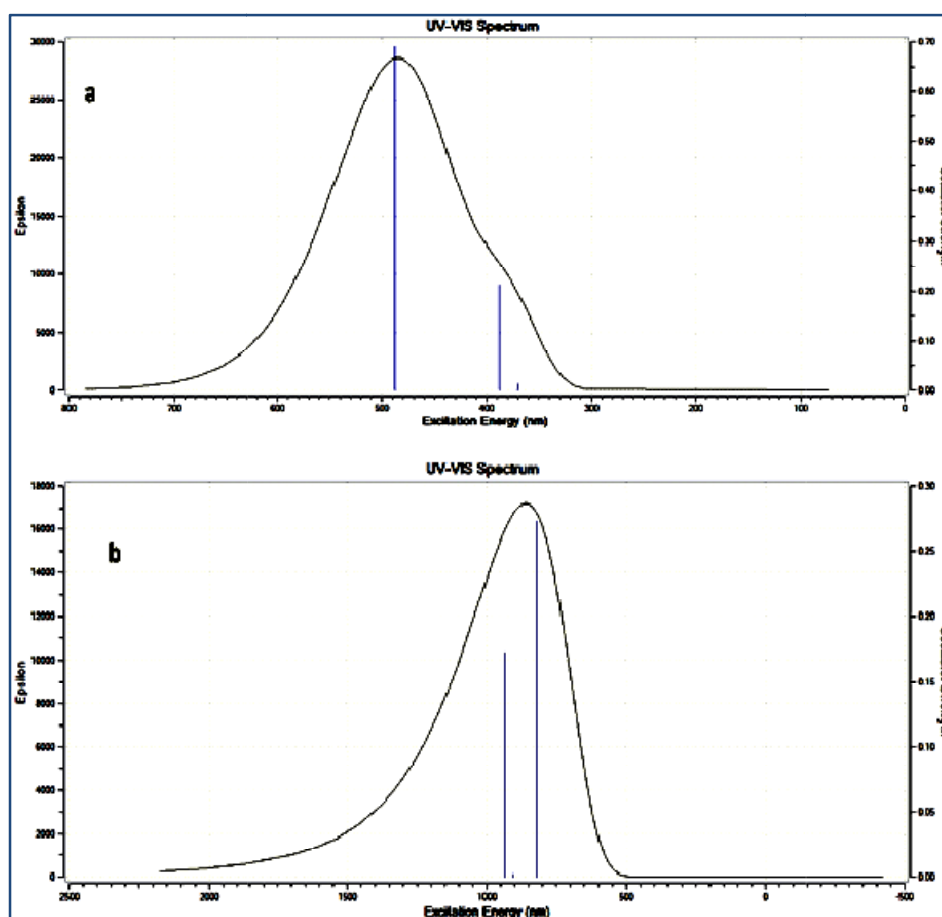


Fig. 3 Theoretically calculated electronic absorption spectra of R (a) and R⁻ (b).

SCIENTIFIC SOCIETY

MULTIDISCIPLINAR MAGAZINE

VOLUME 1, NÚMERO 3, DEZEMBRO DE 2018

ISSN: 2595-8402

DOI: 10.5281/zenodo.2529378

4 CONCLUSIONS

In summary, for the first time we have theoretically studied the structural and spectral aspects of a naphthyl moiety based molecular receptor tethered with DAMN fragment. For understanding fluoride recognition mechanism and the nature of bonds in the receptor, negative and positive electronic regions were revealed on N and H atoms of the molecule with the help of Mullikan charge distribution analysis. The theoretical calculations (DFT/TD-DFT) of the receptor displayed red shift of absorption spectra after interaction with the F^- . The reduction in the energy gap (ΔE) between highest occupied and lowest unoccupied energy levels were also revealed, hence strong the red shift of its spectral characteristics. Most importantly, during the course of proton transfer of $-NH_2$ to F^- , a decrease in the *pi*-electron density over naphthyl moiety in the LUMO contrary to its HOMO revealed blockade of PET process and hence fluorescent turn on response.

5 ACKNOWLEDGEMENTS

We highly acknowledge department and lab staff and other faculty of chemistry at GDC Shopian for their discussions and support during various stages of the work. M. A Kaloo gratefully acknowledges Department of Science and Technology, New Delhi for INSPIRE FACULTY award [DST/INSPIRE/04/2016/000098].

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SCIENTIFIC SOCIETY

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ISSN: 2595-8402

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SCIENTIFIC SOCIETY

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VOLUME 1, NÚMERO 3, DEZEMBRO DE 2018

ISSN: 2595-8402

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