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Free $–NH_2$ based Chemo sensors for Fluoride anion Recognition: A Computational Study and its correlation with Experimental

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Abstract

In this work, theoretical study on the molecular structure and the absorption spectra of diaminomalenonitrile (DAMN) based derivatives through the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods is presented. Recently DAMN-based derivatives have been explored to be highly selective and sensitive for fluoride anion recognition via free –NH2 based recognition site. Anion selectivity can be tuned by the electron push–pull property of substituent at the phenyl para-position. This could be understood with the help of Mulliken charge distribution analysis. From the frontier molecular orbital analysis, it is reasonable to support the proposed outcome of proton transfer (PT) mechanism between F− and free –NH2 fragment of receptor. The result of such events came in the form of intermolecular charge transfer (ICT) enhancement. Absorption spectra of neutral and deprotonated forms of all DAMN-based derivatives were calculated theoretically using 6-311++G (d, p) basis set in DFT/TD-DFT method.

Keywords: Diaminomalenonitrile, Charge Transfer, DFT, TD-DFT, Spectra.

Introduction

The design and synthesis of receptors capable of binding and sensing anions selectively have received significant attention in recent years because anions play an important role in a wide range of biological, environmental, and chemical processes *Bianchi et al.* [1]. Especially, colorimetric and ratiometric chemo sensors *Deng et al* appear to be particularly attractive due to their simplicity, high sensitivity, and high selectivity *Callan et al.* [2-8]. For quantitative analyses, ratiometric chemo sensors have the significant advantage of their dual emission system, which can minimize measurement errors caused by fluctuations of light scattering as well as reagent concentration *Valeur et al* [9]. Colorimetric chemo sensors provide an immediate qualitative signal, which allows direct naked-eye detection of anions because of a specific color change of solution upon anion Complexation *Coll et al* [10,11]. Among the range of biologically important anions, fluoride, the smallest anion, has

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unique chemical properties. It is of particular interest to recognize and detect it owing to its essential role in a broad range of biological, medical, and chemical processes of osteoporosis, fluorination of drinking water supplies, or even in chemical and nuclear warfare agents *Kirk et al* [12-14]. However, the chemo sensors for F^{-} are rather few, and there is a need for good anion sensors with an improved specific response, in particular, with selectivity for F^{-} in the presence of other anions. Furthermore, it is necessary to understand the unique host-guest interaction of the sensor with F^{-} and other anions. Different signaling mechanisms have been suggested for F^{-}, such as photo induced electron transfer (PET) *Kim et al*, excited state proton transfer (ESPT) *Peng et al*, intramolecular charge transfer (ICT) *Li et al* [15,18].

In the present study, absorption spectroscopic analysis of DAMN-based chemo sensors 1, 2, 3 and 4 (**FIG. 1)** and their interaction with F^{-} ions has been carried out theoretically and discussed in detail. 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 chemo sensor design possessing free –NH_2 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 mentioned chemo sensors.

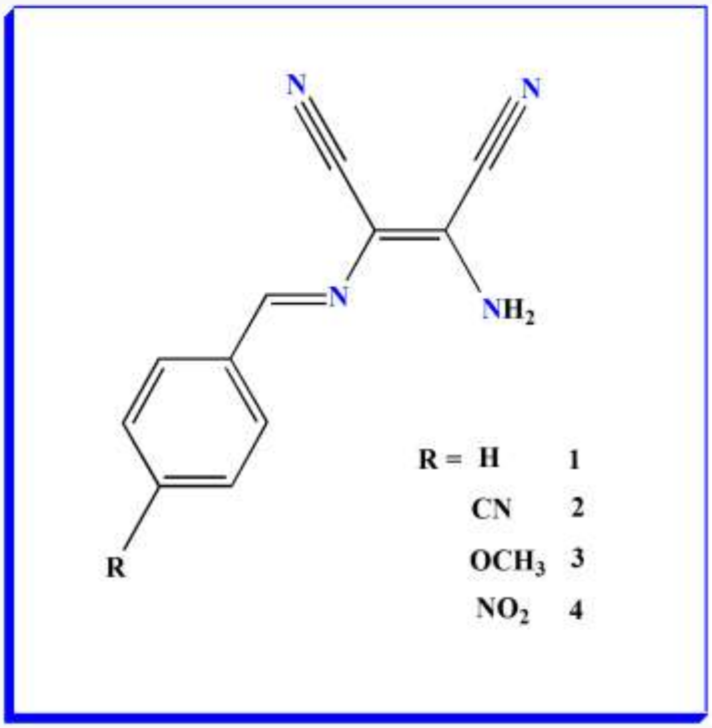

FIG. 1 **Generalized structure of the chemosensor derivatives corresponding to the substituents at the para-position.**

Computational Method

In the present work, one of the hybrid methods; B3LYP was carried out using the basis sets 6-311++G(d,p) using GAUSSIAN 09W program. In DFT methods; Becke's hybrid function combined with the Lee-Yang-Parr correlation function (B3LYP), predict the best results of Mullikan charge density on N and H of amine (NH_2) group and absorption spectra of DMN based Chemo sensors 1, 2, 3 and 4. The theoretical result of electronic absorption transitions was compared with the experimental [9-11].

Results and Discussion

Mulliken charge distribution analysis

The Mulliken charge on the atoms is used to understand the charge distribution on the chemical bonding because it facilitates positive and negative regions in the molecular space, at which the protons and electrons concentrate. Thus chemically significant regions; bonds can be identified; also gives the narration of the mechanism of electrophilic and nucleophilic substitutions. Normally, the charges are distributed evenly over the molecule which leads to be neutral. Whenever the substitutions are added to the molecule, the charge distribution is completely altered with respect to the substitution. Usually, the negative Mulliken populated over the highly electronegative atoms which splits the positive charges among hydrogen atoms. The N and H of the molecule have negative and positive space respectively. The Mulliken charges of N and H atoms of amine (NH_2) of chemo sensors are presented in **TABLE 1**.

TABLE 1. **Mulliken charges of N and H atoms of NH_2.**

Atom	**1**	**d-1**	**2**	**d-2**	**3**	**d-3**	**4**	**d-4**
N	-0.779	-0.306	-0.777	-0.276	-0.492	-0.337	-0.490	-0.276
H	0.348	0.216	0.339	0.220	0.243	0.247	0.252	0.220

UV–Vis spectra and molecular orbital analysis

The UV–vis spectra and the electronic transitions of the chemo sensors have been calculated using the TD-DFT/6-311++G(d,p) method and has been compared with experimental as shown in **TABLE 2, FIG. 2.** The local HOMO electrons delocalized through phenyl moiety and amine group. In the local transition, these delocalized electrons (HOMO) were transited only to phenyl moiety (LUMO). The delocalization is more in case of electron-withdrawing substituent's at para-position. Thus the decrease in the energy gap between HOMO and LUMO (FIGURE 2) of receptor in presence of fluoride anion realizes spectral shift (red-shift), and hence offering naked-eye optical detection of anion.

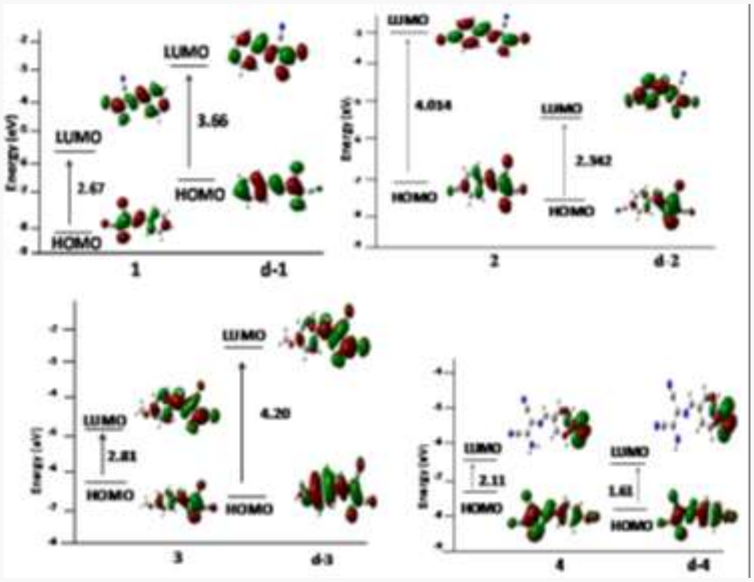

FIG. 2. **Excitation energies and HOMO LUMO transitions of 1, 2, 3 and 4. The energy gap is in electron volt (eV).**

The theoretical results are not good agreement with experimental may be because of solvent effect and the nature of interaction. The chemo sensors undergo either H-bonding or deprotonation after the interaction with the **F**$^-$ ions depending upon the concentration of F$^-$ ions and the nature of phenyl-*para* substituent. The phenyl para-position plays an important role in the structure-selectivity relationship by tuning the acidity of the amine and facilitating the intramolecular charge transfer (ICT). The chemo sensors 1, 2, 3 and 4 undergo deprotonation after the interaction with the F$^-$ ions. Fluoride-induced deprotonation d-1, d-2, d-3 and d-4 results in a charge transfer (CT) transition with red shift. The resulting negatively charged species with high charge density on the amine nitrogen is associated with the enhancement of the push–pull effect of the ICT transition. The chemosensor 2 and 4 owing to its strong electron withdrawing −CN and –NO$_2$ groups respectively make the charge delocalization feasible on the interaction with fluoride and is associated with a very high shifts 157 nm and 466 nm respectively in their absorption spectra (FIG. 3). However the chemosensor 1 undergo deprotonation because of high concentration of F$^-$ ions is reflected with shift of 181 nm in its absorption spectrum.

On the other hand, the chemosensor 3 owing to its electron donating group −OCH$_3$ is associated with 230 nm shift in the absorption spectrum because of deprotonation after interaction. The energy gap and oscillation strength was also calculated to all DMN derivatives **TABLE 2 and 3.**

TABLE 2. **Comparative experimental ad theoretical electronic absorption spectra of 1, 2, 3 and 4.**

Chemosensor	**Experimental**			**Theoretical**		
1 (Chemosensor)	**λ (nm)**	**λ_{abs} F (nm)**	**Δλ (nm)**	**λ (nm)**	**λ_{abs} F (nm)**	**Δλ (nm)**
	363	422	59	335	516	181
2 (CN−derivative)	376	465	89	337	493	157
3 (OCH3−derivative)	373	423	50	328	558	230
4 (NO2−derivative)	393	650	167	774	1240	466

TABLE 3. **Energy gap and oscillation strength of Chemo sensors 1, 2, 3 and 4.**

Chemosensor	E (eV)	Oscillation strength (f)	Composition
1	2.67	0.509	
d-1	3.66	0.0336	
			HOMO → LUMO
2	4.02	0.162	
d-2	2.34	0.0184	
3	2.81	0.4805	
d-3	2.36	0.0576	
4	2.11	0.0033	
d-4	1.61	0.0004	

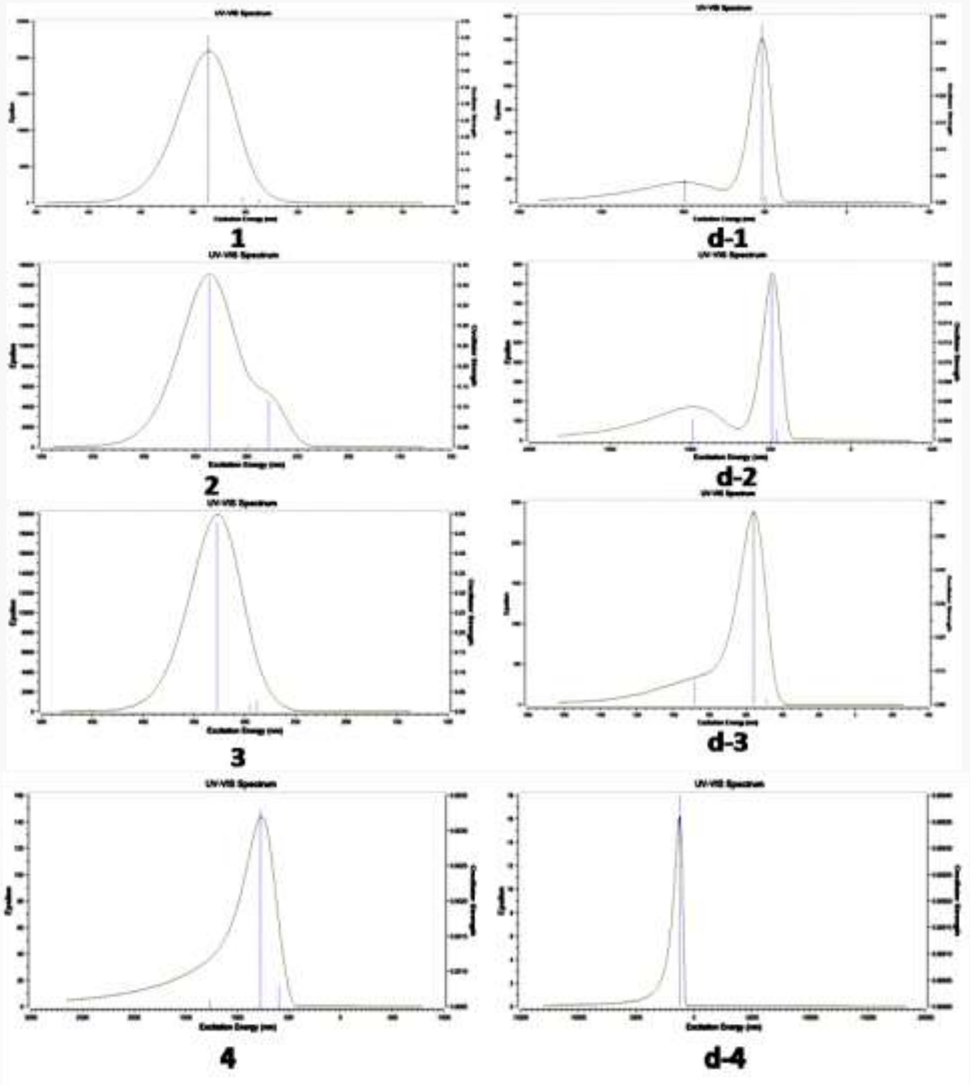

FIG. 3. **Theoretically calculated electronic absorption spectra of 1, 2, 3 and 4**

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Conclusions

In this work, we studied the structural aspects and UV-visible absorption spectral characteristics of novel group of receptors recently proposed from DAMN molecular framework were studied by computational methods. The theoretical calculations (DFT/TD-DFT) of various chemo sensors displayed red shift of absorption spectra after the interaction with the F− ion. The reduction in the energy gap (ΔE) between highest occupied and lowest unoccupied energy levels was revealed, leading to strong the red shifted of its absorption characteristics. The extent of red-shift was further understood via Mulliken charge distribution analysis, which signifies polarized nature of N-H bond in free –NH2 group in different derivatives. The large shift in the absorption spectra in comparison to the calculated ones may be due to the solvent effect and nature of interaction between the chemosensor and F− ion.

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