Study of Geometrical, Electronic Structure, Spectral and NLO Properties of *Allium cepa* Dye Sensitizer for Solar Cell Applications

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Abstract - *Allium cepa dye molecule was designed and their optoelectronic properties were studied using DFT with hybrid functional B3LYP for dye sensitized solar cell (DSSC) applications. The properties of the designed dye molecule were analyzed using various parameters, such as HOMO–LUMO energy gap and absorption spectra. The simulated absorption spectra of the selected dye molecule disclosed that it can be the promising candidate for DSSC applications. Meanwhile, the study on the polarizability and hyperpolarizability of the designed molecule revealed that it can be a good candidate for NLO applications.*

Key Words: DFT, HOMO-LUMO, *Allium cepa*, Polarizability, Hyperpolarizability

1. INTRODUCTION

The demand for energy has been dramatically increasing since the start of the industrial revolution, in which the transformation of heat into motion began to be applied. This increase is the result not only of industrial development but also of population growth. Now a day, the majority of the energy sources are non-renewable, such as fossil fuels - coal, oil and natural gas, which provide over 80% of our energy-plus uranium [1-5]. The Density Functional Theory (DFT) was introduced by Hohenberg-Kohn in 1964 and is presently the most successful and also the most promising approach to compute the electronic structure of matter [6-8]. Its applicability ranges from atoms, molecules and solids to nuclei, quantum and classical fluids. In its original formulation, the DFT provides the ground state properties of a system and the electron density plays a key role. DFT predicts a great variety of molecular properties, such as molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc. The original density functional theory has been generalized to deal with many different situations: spin polarized systems, multicomponent systems such as nuclei and electron hole droplets, free

energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic electrons, time-dependent phenomena and excited states, molecular dynamics, etc. [9-15].

2. MATERIALS AND METHODS

2.1 Computational Methodology

The computations of the geometries, electronic structures, polarizabilities and hyperpolarizabilities, as well as electronic absorption spectrum for dye sensitizer *Allium Cepa* was performed using DFT with Gaussian 09 package. The DFT was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP), and all calculations were performed without any symmetry constraints by using polarized split-valence 6-311++G (d,p) basis sets. The electronic absorption spectrum requires calculation of the allowed excitations and oscillator strength. These calculations were done using DFT with the same basis sets and exchange-correlation functional in vacuum and solution, and the non-equilibrium version of the polarizable continuum model (PCM) was adopted for calculating the solvent effects [16-22].
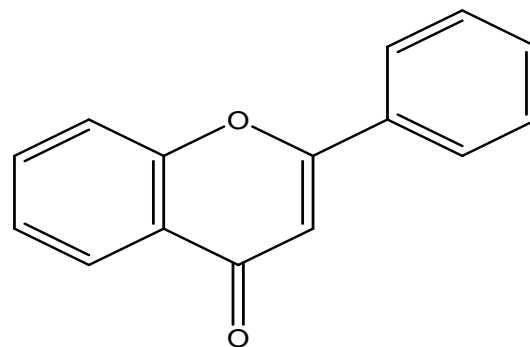
2.2 The Geometric Structure

Fig -1: Chemical structure of *Allium cepa*

The chemical and optimized structure of *Allium cepa* is shown in Fig. 1 & 2, respectively. The bond lengths, bond angles and dihedral angles are listed in Table 1.
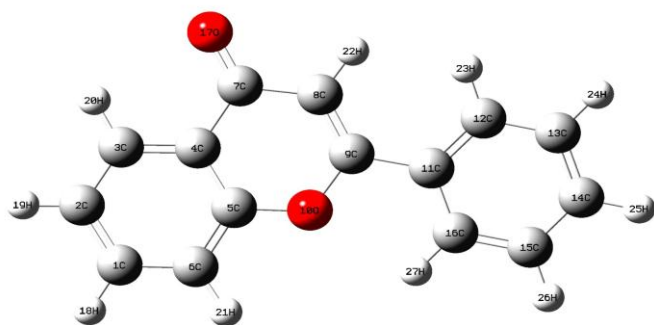

Fig -2: Optimized geometrical structure of *Allium cepa*

Table -1: Bond length, bond angle and dihedral angle of *Allium cepa* dye molecule

Nature of bonding	Bond length (Å)	Nature of Bonding	Bond angle (°)	Nature of Bonding	Dihedral angle (°)
C1-C2	1.3977	C2-C1-C18	119.7814	C6-C1-C2-H19	-179.9996
C1-C6	1.3799	C6-C1-H18	119.4537	H18-C1-C2-C3	179.9725
C1-H18	1.0725	C1-C2-C3	119.8368	H18-C1-C2-H19	-0.0183
C2-C3	1.3781	C1-C2-H19	119.9244	C2-C1-C6-C5	-0.0041
C2-H19	1.0718	C3-C2-H19	120.2387	C2-C1-C6-C21	179.9329
C3-C4	1.3965	C2-C3-C4	120.2881	H18-C1-C6-C5	-179.9855
C3-H20	1.0714	C2-C3-H20	121.5587	H18-C1-C6-H21	-0.0484
C4-C5	1.3849	C4-C3-H20	118.1531	C1-C2-C3-C4	0.001
C4-C7	1.4698	C3-C4-C5	118.6993	C1-C2-C3-H20	179.9936
C5-C6	1.3871	C3-C4-C7	121.9859	H19-C2-C3-C4	179.9917
C5-O10	1.3764	C5-C4-C7	119.3147	H19-C2-C3-H20	-0.0156
C6-H21	1.0705	C4-C5-C6	121.9114	C2-C3-C4-C5	0.0195
C7-C8	1.4526	C4-C5-O10	120.704	C2-C3-C4-C7	179.9267
C7-O17	1.2219	C6-C5-O10	117.3846	H20-C3-C4-C5	-179.9735
C8-C9	1.3404	C1-C6-C5	118.4994	H20-C3-C4-C7	-0.0662
C8-H22	1.0672	C1-C6-H21	122.1036	C3-C4-C5-C6	-0.0332
C9-O10	1.3703	C5-C6-H21	119.397	C3-C4-C5-O10	-179.9605
C9-C11	1.4741	C4-C7-C8	115.4994	C7-C4-C5-C6	-179.9429
C11-C12	1.3957	C4-C7-O17	122.183	C7-4C-C5-C10	0.1298
C11-C16	1.3938	C8-C7-O17	122.3174	C3-C4-C7-C8	-179.8781
C12-C13	1.3835	C7-C8-C9	122.2215	C3-C4-C7-C17	-0.0161
C12-H23	1.0711	C7-C8-H22	116.4486	C5-C4-C7-C8	0.0286
C13-C14	1.3885	C9-C8-H22	121.3278	C5-C4-C7-O17	179.8906
C13-H24	1.0725	C8-C9-O10	120.4123	C4-C5-C6-C1	0.0255
C14-C15	1.3861	C8-C9-C11	127.3989	C4-C5-C6-H21	-179.9133
C14-H25	1.0728	O10-C9-C11	112.1878	O10-C5-C6-C1	179.9551
C15-C16	1.3862	C5-O10-C9	121.8458	O10-C5-C6-H21	0.0163
C15-H26	1.0726	C9-C11-C12	120.997	C4-C5-O10-C9	0.0598

2.3 Electronic Structures and Charges

Natural Bond Orbital (NBO) analysis was performed in order to analyze the charge populations of the *Allium Cepa* dye. Charge distributions in C, O and H atoms were observed because of the different electro-negativity, the electrons transferred from C atoms to C, C atoms to H and O atoms to H atom. The natural charges of different groups are the sum of every atomic natural charge in the group. These data indicate that the cyanine groups are donors and amide groups are acceptors and the charges were transferred through chemical bonds. The frontier molecular orbitals energies and corresponding density of state of the *Allium Cepa* dye is shown in Fig. 3. Frontier molecular orbital energies and corresponding DOS spectrum of DFT/6-311++G (d,p) for *Allium Cepaand* is 3.88 eV.
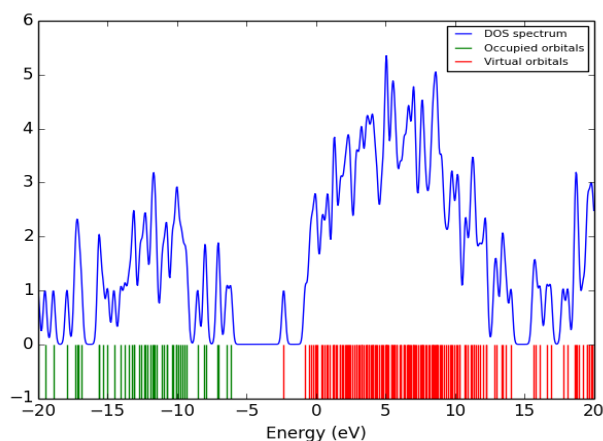

Fig -3: Frontier molecular orbital energies and corresponding DOS spectrum of DFT/6-311++G (d,p) for *Allium cepa* dye
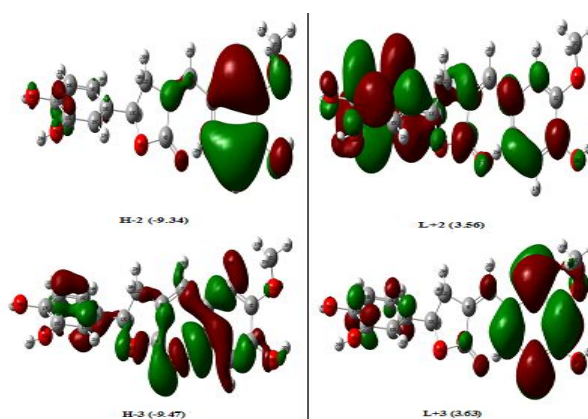

Fig -4: Isodensity plots of the frontier orbitals of *Allium Cepa* dye

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Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field. They determine not only the strength of molecular interactions (long-range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties (NLO) of the system. It has been found that the dye sensitizer has high NLO property, usually possesses high photoelectric conversion performance. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of *Allium Cepa* dye was calculated.

2.4 Electronic Absorption Spectra and Sensitized Mechanism

In order to understand the electronic transitions of *Allium Cepa* dye, TD-DFT calculations on electronic absorption spectra in vacuum and solvent were performed, and the results are shown in Fig. 2.5. It is observed that for *Allium cepa* dye, the absorption in the visible region is much weaker than that in the UV region. The calculated results have a red-shift. The results of TD-DFT have an appreciable red-shift and the degree of red-shift in solvent is more significant than that in vacuum. The discrepancy between vacuum and solvent effects in TD-DFT calculations may result from two aspects. The first aspect is smaller gap of materials which induces smaller excited energies. The other is solvent effects. Experimental measurements of electronic absorptions are usually performed in solution. Solvent, especially polar solvent, could affect the geometry and electronic structure as well as the properties of molecules through the long-range interaction between solute molecule and solvent molecule. For these reasons it is more difficult to make the TD-DFT calculation is consistent with quantitatively. Though the discrepancy exists, the TD-DFT calculations are capable of describing the spectral features of *Allium cepa* dye because of the agreement of line shape and relative strength as compared with the vacuum and solvent.
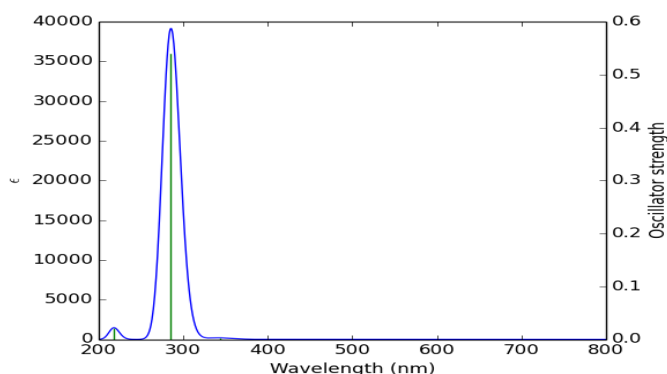

Fig -5: Electronic Absorption Spectra of *Allium cepa* dye for Vaccum by DFT/6-311G (d, p)

3. CONCLUSION

The geometries, electronic structures, polarizabilities and hyperpolarizabilities of Allium cepa dye was studied using density functional theory (DFT) with hybrid functional B3LYP and the UV-Vis spectra were investigated by using TD-DFT methods. The NBO results suggest that Allium cepa dye is a (D-π-A) system. The calculated isotropic polarizability of Allium cepa dye is 43.21318 a.u and its hyperpolarizability is 336.529 a.u. The electronic absorption spectral features in visible and near-UV region were assigned based on the qualitative agreement to TD-DFT calculations. The absorptions are all ascribed to π→π* transition. The three excited states with the lowest excited energies of Allium cepa dye is photoinduced electron transfer processes that contributes sensitization of photo-to-current conversion processes. Today people are greatly affected by dye contaminated water from dye stuff industries. So overcome this problem bio-treatment offers easy, non-toxic, cheaper and effective alternative for natural dyes.

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