Special Issue on Proceedings of International Conference on Materials Manufacturing and Nanotechnology, June 2021. International Journal of Aquatic Science, Vol 12, Issue 03, 2021

DFT and TD-DFT study on (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid for Dye Sensitized Solar Cell

B. Sugnya, V.S.Aparna, Srimathi V
Nehru Institute of Technology, Coimbatore-105
nitsuganya@nehrucolleges.com

.

Abstract

The combination and balance of acceptor (A)-bridge- donor (D) structure of molecule confer suitable attributes and properties to act as efficient light-harvesting and sensitizers in dye sensitized solar cells (DSSCs). An important performance is the electron photo injection (PI) mechanism which can take place either via type I (indirect), that contains in injecting from the excited state of the dye to the semiconductor upon photo excitation. Here, we present a computational study to find the molecular optimization, electronic structures, optical properties of metal free organic dye sensitizer (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid was studied based on Hartree-Fock (HF) and DFT calculation using the hybrid functional B3LYP. UV-Vis spectrum was investigated by time dependent-density functional theory (TD-DFT). The theoretical results has shown that TD-DFT calculations using the polarizable continuum model (PCM) were reasonably capable of predicting the excitation energies, the absorption and the emission spectra of the molecules. Features of the absorption spectrum in the visible and near-infrared regions were assigned based on TD-DFT calculations. The absorption bands absorption bands are mainly derived due to the assigned transition between to n $\rightarrow\pi^*$.

Keywords: Dye-sensitized solar cells, Density functional theory, Time Dependent-Density Functional Theory, Dye sensitizer, Electronic and Absorption spectrum.

Corresponding Author:
Email:
Mobile:

1. Introduction

Dye-sensitized solar cells (DSSCs) have been currently attracting widespread a scientific research attention due to their merits, such as easy fabrication, lower cost etc [1-5]. The main advantage of DSSC is to improve photon-to-current conversion efficiency (PCE). The sensitizer is capable of absorbing light and inducing an electron transfer to the conduction wide-band gap of the TiO_2 semiconductor. An electrolyte, i.e. organic solvent containing an iodide/triiodide redox couple (I^-/I^-_3), is in charge of the regeneration of the photo-oxidized dye molecules. For the operation of the photochemical device, the counter electrode is sealed to the working photo electrode with a spacer and the volume between the electrodes, as well as the voids between the TiO_2 nanoparticles, are filled with the electrolyte solution [6]. Although the DSSCs show excellent energy conversion, their commercial applications are still limited because of stability and long-term operation problems, such as solvent evaporation or leakage, as well as degradation of the electrolyte or of the dye. In order to overcome these disadvantages, it is of high interest to replace the liquid electrolyte with solid state materials.

Among the metal-free organic dyes D- π -A structure molecules are proposed strong candidates because of their geometry, electronic structure, UV-visible region, light harvesting efficiency, NLO property and global reactivity are excellent. In this work, our molecule also

based on D- π -A structure. The D- π -A structure consists of stilbene as the π-bridge molecule, amide and methyl group acts as a donor. Some properties of this molecules are given below. In the field of dye sensitized solar cell, stilbene is certainly one of the most extensively investigated organic compounds. One of the reasons for the continuing interest in this molecule is its leading role in the investigation of photoinducedisomerizations. These processes are not only crucial for the understanding of many photochemical transformations and their solvent dependence but also for our own view of the external world, as they form a key step in the visual process. Stilbenes and stilbenoid compounds are indeed frequently textbook examples of photochemical cis-trans isomerization. Their reactivity has an important role as a model compound of biological phototropic systems. They, also serve as building blocks for organic materials, whose properties could be used in optical and electro-optical applications such as optical data storage, laser dyes, nonlinear optics, or photochemically, cross-linked polymers. Significant interest exists in the design and development of materials exhibiting large second order nonlinear optical response because of the potential applications in telecommunications, optical computing, and optical signal processing. These applications require thermally robust materials with high nonlinear optical (NLO) response. Depending on the particular application, the use of organic materials may offer significant advantages over conventional inorganic crystals. In the past decade, the considerable effort focused on the development of organic materials with large molecular hyperpolarizabilities, improved optical transparency, and good thermal stability. The Stilbene is symmetric structure and it is having two isomeric forms: (E)-Trans-Stilbene and (Z)-Cis-Stilbene). Symmetric Stilbenes are used in the manufacture of metal-free organic dichroic dyes, thin optical properties, electronic microscopes, image stabilisers and other optoelectronic devices. They are playing an increasingly prominent role in the area of photophysical, bioactive and photochemical investigations. Symmetric derivatives of Stilbene are of great interest in terms of their electrical properties and molecular geometry of the ground and excited state.

Cyano group contained dye is an important class of high-performance dyes Sensitizer, which is easily processed able, and displays good mechanical properties, outstanding thermal and thermal-oxidative stability. In this study, the performance of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid metal free dye that can be used in DSSC analysed.

2. Computational Methods

All computational studies were performed with the Gaussian 09W [7] series of programs with density functional methods as implemented in the computational package. The ground state geometries of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid optimized by using Density Functional Theory (DFT) [8-10]. For this purpose, the B3LYP DFT approach, which includes the interchange hybrid functional from Becke [11] in combination with the three parameter correlation functional by Lee– Yang–Parr [12], was employed in combination with the basis set 6-311++G (d,p) [13]. Final energies were obtained using the same functional and 6-311++G (d,p) basis set expansion, which include diffuse functions which are required to get more reliable vertical energies [14].

To obtain the ultraviolet absorption spectrum energy we calculated the inferior excited states excitation energies by resolution of the Time-Dependent Density Functional Theory Kohn-Sham equations (TD-DFT). The Polarizable Continuum Model (PCM) [15-17] was used to evaluate solvent effects on (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid properties. In this model, the solvent is represented as a structureless material involving each solute atom with small spheres. The continuum is characterised by its dielectric constant as well as other parameters. In all PCM calculations, acetonitrile was considered as the solvent.

3. Results and Discussion

3.1 The Geometric Structure

Special Issue on Proceedings of International Conference on Materials Manufacturing and Nanotechnology, June 2021. International Journal of Aquatic Science, Vol 12, Issue 03, 2021

The molecular geometric structure of (2E)-3-(4-(4-methoxystyryl)phenyl)-2-cyanoacrylic acid was optimised using HF/6-311++G (d, p) and DFT/B3LYP/6-311++G (d, p). The optimized Molecular geometry structure of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid was shown in Figure 1.

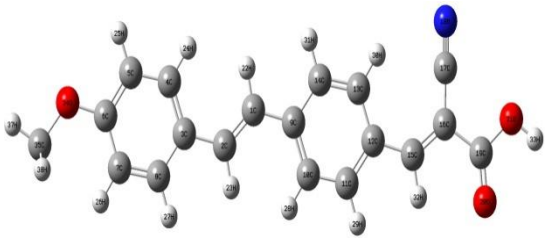

Figure 1. The optimized molecular geometric structure of (2E)-3-(4-(4-methoxyst yryl) phenyl)2-cyanoacrylic acid

3.2 HOMO and LUMO

The distribution pattern of the frontier molecular orbitals (FMO): highest molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the newly designed sensitizer at ground states have been shown in Figure 2. The HOMO–LUMO gap of the dye (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid in a vacuum is 1.95 eV. In the present work, we used the Ti38O76 cluster because it has been shown to be an excellent semiconductor for DSSCs [18], so we used it as a model to understand the properties of DSSCs. While the calculated HOMO and LUMO energies of the bare $Ti_{38}O_{76}$ cluster selected as a Nanocrystalline model were −6.55 and −2.77 eV, respectively, and the HOMO–LUMO band gap of the semiconductor was 3.78 eV, the lowest transition was 3.20 eV according to TDDFT calculations. The dos spectrum of the dye was shown in figure 2. From the figure the HOMO (−4.67 eV), LUMO (−2.72 eV), and HOMO–LUMO gap (1.95eV) of the dye was calculated, it is clear that the HOMO energy of the dye falls within the HOMO energy of TiO2. This is due to interfacial electron transfer [19] between the TiO2 electrode and the (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid, which results in electron injection from the excited dye to the semiconductor conduction band.

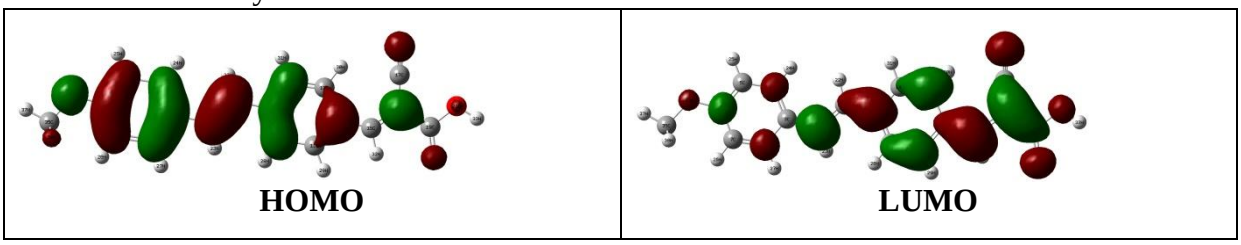

Figure 2. HOMO and LUMO of dye (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylicacid

Table 1. Absorption wavelength (λ_{abs}), Oscillator strength (f in a.u), orbital transitions and light harvesting efficiency (LHE) of the dye (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid

Medium	λ_{abs}		Oscillator strength (f)	LHE	Major Transition Assignment
	Energy (eV)	Wave Length (nm)			

Gas	0.8938	1387.14	0.0009	0.002	H->L+1 (106%)
	1.7114	724.48	0.0589	0.126	H->L (98%)
	2.7605	449.14	0.4310	0.629	H-1-> (60%)
Solvent	0.8871	1397.60	0.0009	0.002	H->L+1 (106%)
	1.7147	723.06	0.0602	0.129	H->L (98%)
	2.7535	450.28	0.3815	0.584	H-1->L (53%)

3.4 UV Visible Region

In order to recognize electronic transitions of the title compound, calculations are carried out in a gas phase and solvent was performed by using TD-DFT/B3LYP/6-311++G (d, p) for three excited states. All absorption bands of absorption spectra in the visible and near-UV region for (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid were performed with vacuum and solution effect. The discrepancy between gas and solution effects in TD-DFT calculations may result from two characters. The first character is a smaller gap of materials which induces smaller excited energies. The other is solvent effects. Experimental measurements of absorption spectrum are usually performed in solution. Solvent, especially polar The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid in acetone at calculated by the DFT/B3LYP level are smaller than that in the vacuum. This fact indicates that the solvent effects stabilize the frontier orbitals of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid. So, it induces the smaller intensities and significant red-shifted absorption wavelength relatively. In order to obtain the microscopic information about the

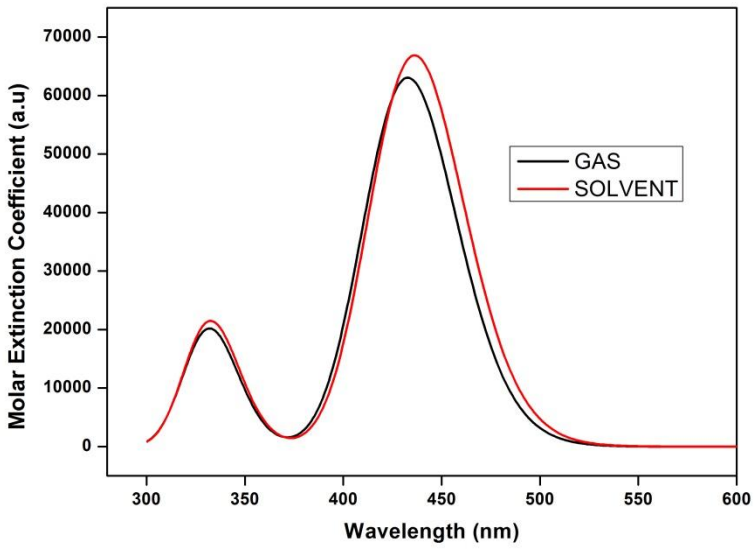

Figure 3. The electronic absorption spectra of the dyes (2E)-3-(4-(4-methoxystyryl) phenyl)-2- cyanoacrylic acid

electronic transitions, the corresponding molecular properties are checked. The absorption spectra in the visible and near-UV region are the most important region for photo-to-current conversion processes. Solvent, could affect the molecular geometry and absorption structure as well as the properties of molecules through the long-range intramolecular charge transfer (ICT) and the solvent molecule. For these reasons, it is more difficult to make that the theoretical calculation is consistent with quantitatively. Though the discrepancy exists, the theoretical calculations are capable of describing the spectral structures of the title compound, because of the good agreement of line shape and relative strength as compared with the gas phase and solution. The dominant absorption spectrum of the (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid dye molecule is found at 449 nm at it corresponds to HOMO-LUMO transition and the small peaks observed at 724 nm are due to the electronic transition between HOMO-1>LUMO orbital as shown in Figure 3. The dominant absorption spectra of the (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid dye molecule lie in the visible region of the spectrum. The molecular orbital analysis showed that the dominant absorption bands of the dye molecule are in the region n→π* transition.

4. Conclusions

Using DFT, TD-DFT calculations, the geometries, electronic structures, polarizabilities, hyperpolarizabilities and the UV-Vis spectra of dye (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid were investigated. The calculated isotropic polarizability of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid is 129.84 a.u (1.92x10-23esu). The hyperpolarizability of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid is 414.22 a.u (3.57x10-30esu). The absorption spectra in the visible and near-UV region were assigned based on the qualitative agreement to TDDFT calculations. The absorptions are all ascribed to n→π* electron transitions of the conjugated molecules. The interfacial electron transfer between semiconductors TiO2 electrode and dye sensitizer (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid electron injection process from excited dye as a donor to the semiconductor conduction band. Based on the analysis of molecular geometries, electronic and absorption spectrum properties of (2E)-3-(4-(4-methoxystyryl) phenyl)-2-cyanoacrylic acid, the HOMO and LUMO band gap is low and UV in the visible region and infrared region, so the photo to current conversion efficiency is high.

References

[1]. B. O' Regen, and M. Gratzel: Nature 353 (1991) 737.
[2]. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Gra¨tzel; J. Am. Chem. Soc.115 (1993) 6382.
[3]. Z. S. Wang, F. Y. Li, C.H. Huang, L. Wang, M. Wei, L. P. Jin and N.Q. Li: J. Phys. Chem. B 104 (2000) 9676.
[4]. K. Hou, B. Z. Tian, F. Y. Li, Z.Q. Bian, D. Y. Zhao and C.H. Huang: J. Mater. Chem. 15 (2005) 2414.
[5]. I. Kartini, D. Menzies, D. Blake, J. C. D. da Costa, P. Meredith, J. D. Riches and G. Q. Lu: J. Mater. Chem. 14 (2004) 2917.
[6]. D. Gebeyehu, C. J. Brabec, N. S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F.Kienberger, and H. Schindler: Synth. Met. 125 (2002) 279.
[7]. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, R. Nakajima, Y. Honda, O. Kilao, H. Nakai, T. Verven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroveror, R. Kobayashi, J. Normand, K. Ragavachari, A. Rendell, J.C. Burant, S.J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B.Cross, V. Bakken,

C. Adamo, J. Jaramillo, R. Gomperts, R.E. Strattmann, O.Yazyev, A.J. Austin, R. Cammi, J.W. Ochetrski, R.L. Martin, K. Morokuma, V.G. Zakrazawski, G.A. Votn, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, Gaussian O.G., Revision A.O2, Gaussian Inc., Wallingford, CT., 2009.

[8]. P. Hohenberg, and W. Kohn: Phys. Rev. B 136 (1964) 864.

[9]. W. Kohn, and L. J. Sham: Phys. Rev. 140 (1965) 1133.

[10]. R. G. Parr, and W. Yang: Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.

[11]. A.D. Becke: J. Chem. Phys. 104 (1993)5648.

[12]. Lee, C. Yang, and R. G. Parr: Phys. Rev.B. 37 (1988) 785.

[13]. P. C. Hariharan, and J. A. Pople: Mol.Phys. 27 (1974) 209.

[14]. E. Lewars: Computational Chemistry-Introduction to the Theory and Applications of Molecular and Quantum Mechanics, Kluwer Academic Publishers, 2003.

[15]. M. Cossi, G. Scalmani, N. Rega, and V. Barone: J. Chem. Phys. 117 (2002) 43.

[16]. R. Cammi, B. Mennucci, and J. Tomas: J.Phys. Chem. A 104 (2000) 5631.

[17]. M. Cossi, and V. Barone: J. Chem. Phys.115 (2001) 4708.

[18]. MK. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G.Viscardi, P. Liska, S. Ito, B. Takeru, M. Gratzel: J Am ChemSoc 127(2005)16835.

[19]. DF. Waston, GJ. Meyer: Annu Rev PhysChem 56 (2005) 119–156.