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DFT/TD-DFT Studies on the Lawsone (Henna) as a Photosensitizer for Dye- Sensitized Solar Cells

May Win Han[1, a], Piyasiri Ekanayake[1, b] Lim Chee Ming[2, c] and Voo Nyuk Yoong[1, d]

[1]Physical and Geological Sciences Programme, Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Brunei Darussalam.

[2]Centre for Advanced Material and Energy Sciences, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Brunei Darussalam.

[a]11h8601@ubd.edu.bn, [b] piyasiri.ekanayake@ubd.edu.bn, [c] cheeming.lim@ubd.edu.bn, [d] nyukyoong.voo@ubd.edu.bn

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Abstract. In this study, the parameters of the photo-electrochemical properties, such as the ground state geometries, excitation energy, electronic structures, optical properties and electronics transition of lawsone were investigated by using density functional theory (DFT) and time dependent - DFT with B3LYP/6-31G(d) method. The solvent effect was considered in the DFT calculations and compared with the value of vacuum. From the analyses of electronic and optical properties, it is found that the lawsone satisfy the condition for good conversion efficiency as DSSCs device.

Introduction

Due to the depletion of fossil fuels, growing demand of energy, global warming and other environmental problems, the development of environmental friendly renewable energy technologies is an urgent task for our human being [1]. Among the renewable energies, solar energy has proven capacity to match the world's increasing energy needs. In order to take advantages of the solar energy, we learned to convert solar energy into forms of energy by using new and emerging technology [2-5]. As a result, dye sensitized solar cells (DSSCs) have become widespread interest for conversion of sunlight into electricity, because of their high efficiency and low cost [6].

In DSSCs, the dye as a photosensitizer plays a major role in absorbing sunlight and transporting electrons into the conduction band of the semiconductor, transforming solar energy to electricity. The metal-organic complexes such as the ruthenium polypyridyl complexes (N719 and N3) have been proven to be best DSSC dye sensitizers due to its high efficiency. However, the use of ruthenium dye has the limitation because of high cost and unfriendly environment issue [4-6]. Therefore, the metal-free organic dye sensitizers, such as the natural dye, can be extracted from many parts of the vegetables, flowers and trees, and some dyes extracted from insects [7].

In recent years, density functional theory (DFT) has been extensively used to study the structures and absorption spectra of sensitizers for DSSCs [1-9]. DFT has emerged as a reliable standard tool for the theoretical study of molecular structures and electronic absorption spectra. Time-dependent density functional theory (TD-DFT) is the most successful and most commonly used method for simulations of electronic and optical properties [3, 7-9].

Lawsone plant is abundant in the rain forest countries and commonly used as skin ornament. It was selected as the sensitizer due to its affluent in anthocyanin, high level of absorbance in the UV, visible, and near –infrared region of the solar spectrum [7-9]. Some recearchers found and proved that the lawsone is a photosensitizer for DSSCS with experimentally. According to DSSCs performance, the electronic structure of the dye and energy level of the semiconductor have to be matched in order to satisfy the electron transfer process. An understanding of electronic, optical and redox properties of the dye is necessary [8-11]. Thus, in this work, the electronic structure, optical properties, and electron injection force relevant to charge transfer of lawsone were investigated using the theoretically with the calculation of DFT and TD-DFT.

Computational Methods

The ground-state geometries of lawsone dyes were optimized by the DFT method using B3LYP functions which combine Becke's three-parameter exchange function (B3) with the correlation function of Lee, Yang and Parr (LYP) [10].

The molecular structure and optimized geometrical structure of lawsone are shown in Fig. 1. All geometry optimizations were computed in water, ethanol, methanol and n-hexane solution using the polarizable continuum model (PCM) and with the 6-31G (d) basic set. The time-dependent density functional theory (TD-DFT) calculation was used to compute the vertical excitation energies, oscillator strength (f) and excited state compositions in terms of excitations between the occupied and virtual orbitals for the lawsone. All of the computational results were performed by using the Gaussian 09 package and Gauss View Version5.0 [11-14].

In this paper, we report the DFT and TD-DFT calculations of Lawsone which aimed at providing a better understanding of the role of the sensitizer, lawsone, particularly of its electronic structure and excited-states properties.

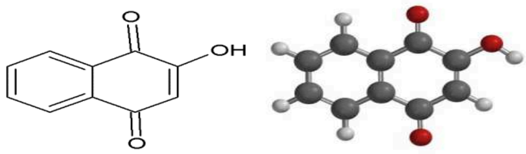

Figure 1. The molecular structure and optimized geometrical structure of lawsone.

Results and Discussion

Electronic Structure. The ground states geometries of the lawsone (henna) dye was optimized at B3LYP/6-31G (d) level. The discussion based on geometrical parameter of the ground states structure is neglected. The frontier molecular orbital (MO) energies including highest-occupied molecular orbital (HOMO), lowest – unoccupied molecular orbital (LUMO) and energy gap of lawsone without OH computed at B3LYP/6-31G (d) level in ethanol, water, n-hexane and methanol are listed in Table 1.

Table 1. The highest occupied molecular orbital energies (**E_{HOMO}**), the lowest unoccupied molecular orbital energies (**E_{LUMO}**), the Energy gap $\Delta E\ (H - L)$ of lawsone computed at the B3LYP/6-31G(d).

Lawsone	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
Vacuum	-7.12	-3.02	4.09
Ethanol	-7.13	-3.09	4.04
Water	-7.12	-3.09	4.03
N – hexane	-7.17	-3.04	4.12
Methanol	-7.13	-3.09	4.04

The E_{HOMO} for lawsone is -7.12 eV, E_{LUMO} is -3.02 eV and energy gap (**E** gap) is 4.09 eV in vacuum. Ethanol and methanol are the same valve of E_{HOMO} -7.13 eV , E_{LUMO} -3.09 eV and **E** gap 4.04 eV in all solvents respectively. E_{HOMO} of Water is -7.12 eV and E_{LUMO} is -3.09 eV So**,** the energy gap (**E** gap) in water is 4.03 eV. N-hexane is the higgest E_{HOMO} and (**E** gap).

The first three vertical singlet states, major transition characters and oscillating strength of the absorption bands in the UV- vis region for lawsone computed by single-point calculation using TDDFT/B3LYP/6-31G (d) were presented and the absorption bands with the oscillator strengths larger than 0.01 are listed in Table 2.

Table 2. Computed excited energies (eV), (nm), oscillator strength (f) and electronic transition configurations in UV-vis region of lawsone computed at the B3LYP/6-31G (d).

Solvent	**E/ λ (eV/nm)**	**Oscillator strength (f)**	**Composition**
Vacuum	3.44,360	0.01	H-1 $\rightarrow$ L (69%)
	3.74/331	0.05	H-2 $\rightarrow$ L+1(67%), H-1 $\rightarrow$ L (16%)
	4.46/277	0.18	H-4 $\rightarrow$ L (65%), H-1 $\rightarrow$ L (16%)
Ethanol	3.29/377	0.01	H-2 $\rightarrow$ L (11%), H $\rightarrow$ L (68%)
	3.64/340	0.07	H-2 $\rightarrow$ L(68%)
	4.34/285	0.23	H-4 $\rightarrow$ L (67%), H $\rightarrow$ L+2 (13%)
Methanol	3.28/377	0.01	H-2 $\rightarrow$ L (11%), H $\rightarrow$ L (68%)
	3.64/341	0.07	H-2 $\rightarrow$ L (68%)
	4.34/285	0.23	H-4 $\rightarrow$ L (67%), H $\rightarrow$ L (13%)
Water	3.38/366	0.01	H-2 $\rightarrow$ L (14%), H-1 $\rightarrow$ L (67%)
	3.68/336	0.07	H-2 $\rightarrow$ L (68%)
	4.38/282	0.28	H-4 $\rightarrow$ L (67%), H-1 $\rightarrow$ L (13%)
n-hexane	3.29/377	0.01	H-2 $\rightarrow$ L (11%), H $\rightarrow$ L (68%)
	3.64/340	0.07	H-2 $\rightarrow$ L (68%)
	4.34/285	0.23	H-4 $\rightarrow$ L (67%), H $\rightarrow$ L+2 (13%)

From the TD-DFT calculation of lawsone , the transition energy in ethanol is almost equal in methanol. The transition character of lawsone in ethanol, methanol and water are similar but differ in vacuum. Based on the optimized structures of excited state, TD-DFT calculation can see that these theoretical results of the emissive wavelengths.

The HOMO and LUMO energy levels of lawsone were calculated from DFT with respect to ethanol solvents as showm in Fig. 2. To get the efficient regenertation of the oxidized dye molecule, the HOMO must be below the energy of the redox couples and LUMO must be above the conduction band[10]. In Fig. 2 , the lawsone have the condition for photo-energy generation.

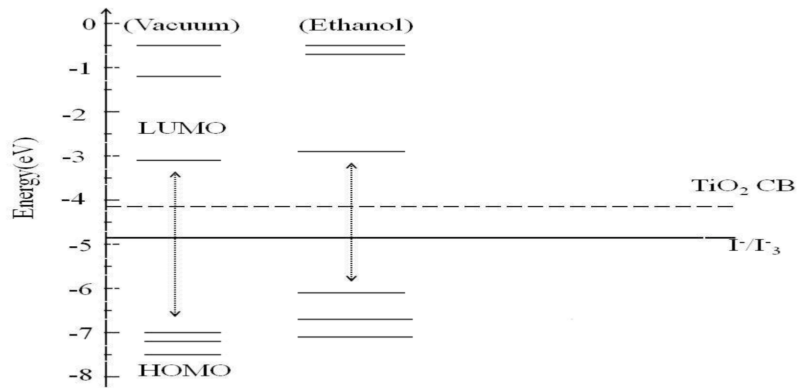

Figure 2. Energy level diagram of lawsone in vacuum and ethanol solvent.

The isodensity plots of HOMOs and LUMOs of the lawsone morities are shown in Fig. 3. For lawsone, the HOMO which lying at -7.13eV is a delocalized over the whole dye with the π orbital over the benzene ring whereas the HOMO-1, 0.12eV below the HOMO, is the $\pi *$ orbital localized over the ring. The LUMO, lying at -3.09eV, is a $\pi*$ transition and delocalized throughout the dye. Whereas LUMO+1, lying 1.93eV above the LUMO, is π orbital mainly delocalized in the ring.

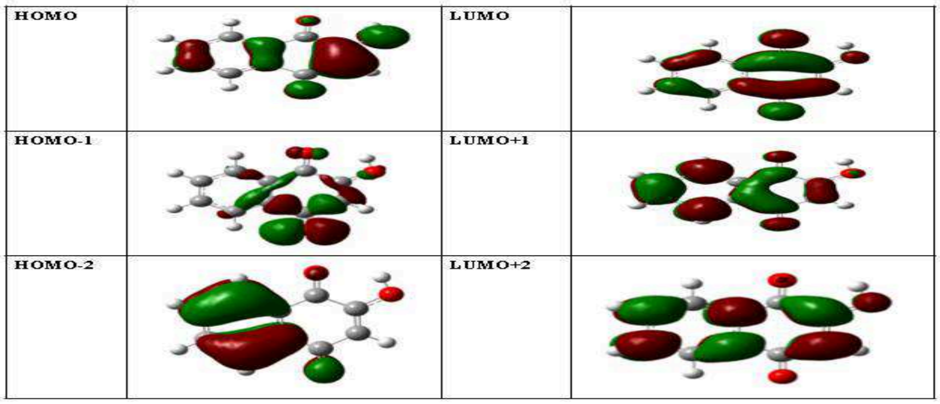

Figure 3. Isodensity plots of the frontier orbital of the lawsone in ethanol and the molecular orbital surface of HOMO-2, HOMO-1, HOMO and LUMO with isovalue of counter = 0.03.

Electronic Absorption Spectra. The UV-spectura of Lawsone was optimized by computing at TDDFT/B3LYP/6-31G (d). The TDDFT simulated absorption spectra of the lawsone with solvent effects is shown in Fig. 4.

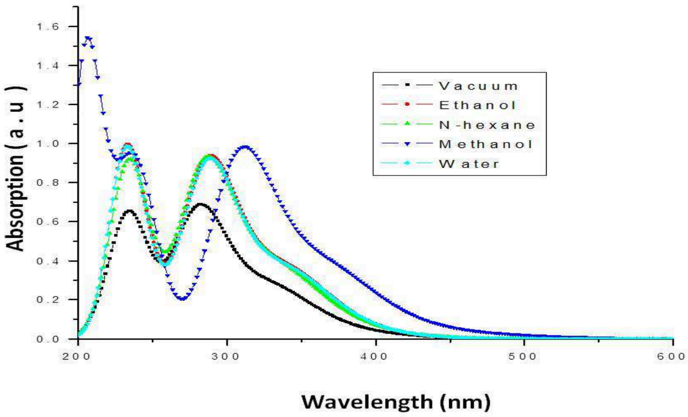

Figure 4. Simulated absorption spectra of the Lawsone in ethanol, water, methanol, n-hexane and the vacuum.

UV/Vis absorption spectrum of lawsone was simulated using TD-DFT with different solvents (ethanol, water, methanol and n-hexane). Comparisons between the UV-vis absorption spectrum of lawsone with solvents showed that the clear red-shift in the absorption spectra of the lawsone with solvent effects.

Summary

In this study, we have investigated the excited- state energies and properties in electronic structure. The relevant to charge transfer of lawsone was investigated using density functional theory (DFT) and time dependent (TD-DFT). From the theoretical results of lawsone, the solvent effects have more effective and lawsone can give a good efficiency as a environmentally friendly and save cost natural dye sensitizer for DSSCs.

Acknowledgement

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