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Theoretical study on the effect of solvents in chlorophyll solution for Dye-Sensitized Solar Cell

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Abstract. Using the density functional theory (DFT) and time-dependent DFT (TD-DFT), we have theoretically studied the electron excitation and absorption spectra of chlorophyll solution with several solvents for Dye-Sensitized Solar Cell (DSSC) application. The solvents were aceton, acetonitrile, DMSO, ethanol, hexane, methanol, THF and water. Also, energy level, oscilator strength, light harvesting efficiency and electron injection have been investigated. The studied dye in the presence of the solvents showed a smaller gap of the highest occupied molecular orbital (HOMO) - the lowest unoccupied molecular orbital (LUMO) and a higher light harvesting, oscillator strength and red shift in the absorption spectra. These changes facilitate the charge transfer phenomena in the nano structure of the chlorophyll as dye and improve the solar cell efficiency.

1. Introduction

Solar energy has the potential to be developed as a renewable energy source in the near future to replace fossil-based energy [1]. Devices that directly convert sunlight into electrical energy are solar cells. The dye-sensitized solar cell (DSSC) is new type of the solar cells that have many advantages compared to the silicon based ones which have been introduced by Gratzel [2] . The advantages of DSSC such as low-cost, flexibility, environmentally-friendly properties, and facile fabrication process [3]. DSSC consists of a porous layer of wide band gap semiconductor, such as TiO_2 coated with a dye that serves as light sensitizer on transparent conducting glass electrode, an electrolyte layer, and a counter electrode, typically coated with graphite or platinum [4].

Research related to DSSC efficiency is usually the discussion of three main components: dye, redox electrolyte reaction and semiconductor electrode [5]. The efficiency of a solar cell depends largely on how much light absorption can be made. In DSSC light absorption is performed by the sensitizer mixed on TiO2. Sensitizee role is very dominant in the energy harvesting process [6]. Besides the electron excitation process on dye due to solar radiation, electron injection ability from dye to semiconductor and electron collection capability by semiconductor also affect the efficiency of DSSC. The oxidized dye should be able to regenerate electrons where it is highly dependent on the type of dye and the type of electrolyte.

In DSSC, natural pigment can be used as dye sensitizer, which is produced from fruits, leaves, flowers, tree barks, roots etc. Natural pigments have several advantages: more available, simple to prepare, lower cost, non-toxic, environmentally friendly and biodegradable [7]. The plant pigments are electronic structure where if receive sunlight, it will convert the wavelengths that are transmitted or reflected by the plant tissue. This is called plant pigmentation and each pigment is

represented by the absorbed wavelength and color that can be seen by humans [8]. Natural pigments that can be used as dye sensitizers include carotenoids, flavonoids, chlorophyll, and anthocyanins that can cheaply be obtained from plants [9].

Chlorophyll is widely studied as a sensitizer in the DSSC. They exhibit visible absorption properties because they have a porphyrin that consist of a conjugated pyroles system and composed of substituents on the sides. Thus chlorophyll contains a lot of non-bonding electrons and pairs of phi bonding electrons so that if radiated visible light, electrons in chlorophyll will be easily excited. Moreover, other properties such as HOMO-LUMO level energy with small bandgap, low cost, simple synthesis process, high molar absorption coefficient, good chemical and thermal stability make it perfect sensitizer [10]. Besides depending on the type of pigment, the absorption can capability be affected by the process during the extraction of the pigment. In this study, we will see the effect of the solvent used as the dye solution embedded in the semiconductor. We will see the electron transfer on the solvent media by using quantum mechanism chemistry simulation and the dye solution will be characterized. Quantum mechanism simulations have become an easy and effective to predict the DSSC device preformance [11].

2. Computational Method

The chlorophyll molecule model used in this work consist of 75 atoms. This model is a modification of the chlorophyll structure to reduce the number of atoms for simpler calculations, by eliminate the methyl groups on the phytyl ester side chain [12], also adding various solvents to see their effect on electron excitation ability.

Quantum mechanism calculations are performed using by the ORCA package program [13] and the geometry optimization was computed using DFT with def2-TZVP basis sets [14][15] were applied for chlorophylls with all solvents, in combination with full decontraction def2-TZVP/J auxiliary basis sets [16]. The DFT calculation uses the hybrid B3LYP Density which merges the three Becke functional parameters with the Lee-Yang-Parr parameter [17][18]. Furthermore, to show the excited states and optical properties, for producing the UV-Vis absorption spectrum,Time Dependent - Density Functional Theory (TD-DFT) method was engaged at B3LYP with basis set using def2-TZVP for the electronic transitions between HOMO and LUMO states. In the calculation, we used the RIJCosX algorithm [19][20][21]. The criterion of SCF convergence and to improve grid integration is used Grid5, Grid6 for all calculations. In order to have an accurate representation of the excitation energies in the realistic environment, the solvent effects have been evaluated by the non-equilibrium version of the conductor-like polarizable continuum model [22]. The solvent is represented as a dielectric polarizable continuum and the solute is placed in a cavity of approximately molecular shape. The solvent reaction field is described by polarization charges on the surface of the cavity.

3. Results And Analysis

3.1 Optimized Molecular Geometries

Chlorophyll molecule with various solvents were already analyzed with computational method (DFT/B3LYP). The parameter of the optimized geometrical in ground state as bond angles, bond lengths, also dihedral angles for all chlorophyll with various solvents are similar shown. As representation, molecul structure in the vacuum and water shown in Table 1. Solvents did not affect much of the optimized geometry structure of the chlorophyll molecule but the total optimized energy different.

Based on table 2, the total energy optimized by calculation on the DFT method has different value in the vacuum phase and solvents showed the solvent media can stabilize the chlorophyll structures through the intermolecular interactions of the chlorophyll and the solvent. The results similar to the research in the following reference [23]. And the lowest energy in the water and DMSO of -58393.99075 eV and -58393.96135 eV respectively.

Table 1. Optimized geometri and Frontier molecular orbital in the vacuum and water

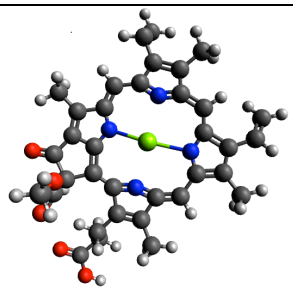
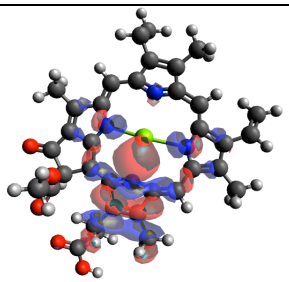
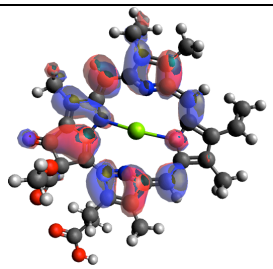
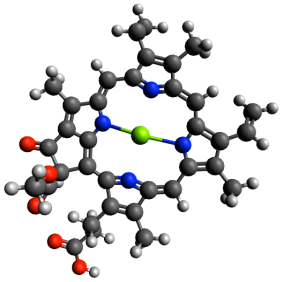
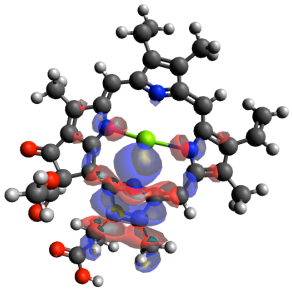
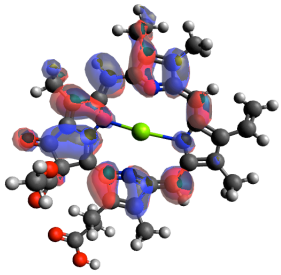
Solvents	Optimized Geometry	Homo	Lumo
Vacuuum			
Water			

Table 2. Total energy optimized of the Chlorophyll with various solvents

Solvents	Total Energy	Solvents	Total Energy	Solvents	Total Energy
Vacuum	-58392.26201 eV	Ethanol	-58393.89611 eV	Water	-58393.99075 eV
Aceton	-58393.87333 eV	Hexane	-58392.82099 eV	THF	-58393.61213 eV
Acetonitrile	-58393.94103 eV	Methanol	-58393.93012 eV	DMSO	-58393.96135 eV

3.2 Electronic Properties

Electronic properties include HOMO level, LUMO level, bandgap energy, dipole moment, oscilatory strength (fosc), and electron injection capability. Based on table 3, the addition of solvents can improve HOMO - LUMO level energy which can increase the ability of electron injection and also reduce bandgap energy. All this results from an increase in dipole moment and oscillatory strength of chlorophyll molecules with solvents and it can improve the DSSC efficiency as equation (3). Based on the simulation results have shown that among the many solvents, water and DMSO are the solvents that have the most ability to improve chlorophyll performance. Water can improve chlorophyll performance although chlorophyll is not soluble in water. For the experiment it can be solved by mixing with solvents which may dissolve chlorophyll as examples mixed with ethanol as carried out in the following reference [24], where mixing can produce maximum absorption of light at ethanol-water mixing with a ratio of 2:1.

DSSC conversion efficiency (η), in Eq. (1), of the solar cell is described by the open-circuit photovoltage (V_{OC}), shortcircuit current density (J_{SC}), and fill factor (FF), as compared to the incident solar power (P_{inc}) [25].

$$\eta = \frac{J_{sc}\, V_{oc}\, FF}{P_{in}} \tag{1}$$

where, J_{SC} is determined by the Equation (2) [26]:

$$J_{sc} = \int_{\lambda} LHE(\lambda)\Phi_{inject}\eta_{collect}\, d\lambda \tag{2}$$

where, *LHE(λ)* is the light harvesting efficiency at a given wavelength which could be measured by equation (3) [27], Φ_{inject} shows the electron injection efficiency, and $\eta_{collect}$ defines the charge collection efficiency. In the systems which are only different in sensitizer parameters, $\eta_{collect}$ can be wisely considered to be constant.

$$LHE(\lambda) = 1 - 10^{-f} \quad (3)$$

Φ_{inject} is related to the driving force, the free energy change of electron injection (ΔG_{inject}) from the excited states of dyes to the semiconductor substrate, which can be calculated by Equations (4) [28].

$$\Delta G_{inject} = E_{ox(dye*)} - E_{CB,TiO_2} \quad (4)$$

where, $E_{CB(TiO2)}$ is the conduction band energy of the TiO_2 (-4 eV) and $E_{OX(dye*)}$ is the excited state oxidation potential of the dye, which Rehm and Weller equation can showed its value by equation (5) [29].

$$E_{ox(dye*)} = E_{ox(dye)} - E_{0-0} + \omega_r \quad (5)$$

where, $E_{ox(dye)}$ is the dye oxidation potential in the ground state while E_{0-0} is the vertical excitation energy and ω_r is a columbic stabilization term which is negligible [30]. Therefore $E_{ox(dye*)}$ is approximated by $E_{ox(dye)}$ - E_{0-0}.

Table 3.

	Vacuum	Acetone	Acetonitrile	Ethanol	Hexane	Methanol	Water	THF	DMSO
LUMO (eV)	-3,294	-3,007	-2,993	-3,002	-3,2	-2,995	-2,983	-3,057	-2,989
HOMO (eV)	-5,009	-4,49	-4,465	-4,482	-4,845	-4,469	-4,446	-4,585	-4,457
Bandgap (eV)	1,715	1,483	1,472	1,48	1,645	1,474	1,463	1,528	1,468
Momen Dipole (au)	3,579	5,125	5,204	5,152	4,056	5,191	5,263	4,834	5,228
Fosc	0,223	0,246	0,253	0,249	0,228	0,251	0,254	0,233	0,263
ΔG_{inject} (eV)	0,706	0,993	1,007	0,998	0,8	1,005	1,017	0,943	1,011

3.3 Optical Characteristics

According to figure 1 with the addition of solvents may increase the shift of the spectrum of several nm in the direction of infrared as compared with no solvents. This happens as a result of the decrease in energy gap and from the stabilization of the virtual orbitals in the solvent environment. The solvent stabilizes the contaminated substances in the electric field through the electrostatic interaction between the chlorophyll molecule. So it can be concluded that the transition energy is very sensitive to the effect of solvent.

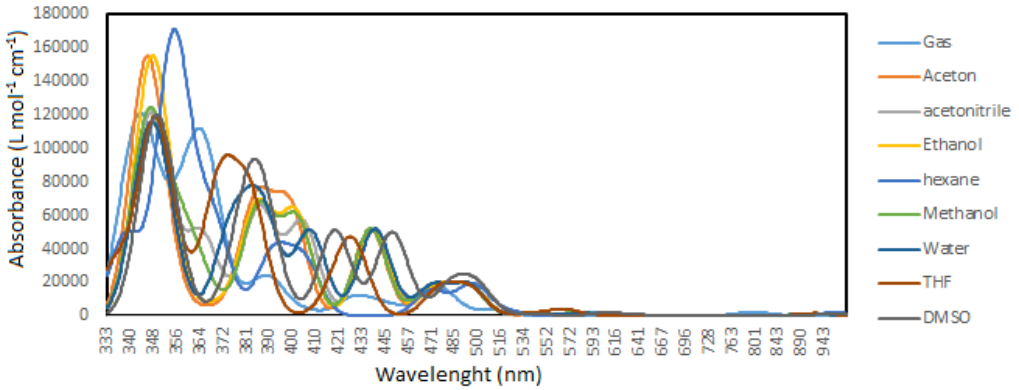


Figure 1. Spectrum absorbance of chloropbhyll solutions with different solvents

4. Conclusion

In this research, the electron excitation of chlorophyll sensitizer with various solvents have been investigated using the TD-DFT. The addition of solvent reduces the HOMO-LUMO bandgap and increases the dipole momen, oscillator strength and the intensity of the absorbtion spectrum shifting in the near infrared. Moreover, with increasing dipole momen and oscillator strength, it will have an impact on increasing light harvesting energy (LHE). Also the electron injection capability of the dye to the semiconductor have seen better with the solvents phase. All the parameter will have an effect on

increasing efficiency of solar cell. The hope, this theoretical results can be used as a reference in experimental activities. In addition, these findings provide a more detailed understanding and the right tools to predict the efficiency of solar cells.

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