Properties of Mitragyna Speciosa (Ketum) extracted in water as organic dye molecular sensitizer

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Abstract. Generally, dye sensitizers make use of inorganic elements such as ruthenium or osmium. However, these elements were toxic and hard to be produced due to its rarity. Alternatively, organic and natural sensitizer derived from various organic sources were studied. In this research, a natural dye which is chlorophyll b (Chl-b) extracted from Mitragyna Speciosa or ketum leaf pigment is used as the dye sensitizer. The geometry, optical properties and electronic properties were observed by the computational method using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with B3LYP/6-31G with Gaussian-03 and Gaussview-03 software. Here, properties of bulk Chl-b were firstly obtained from databank as a control experiment. It was to be compared with the properties of Chl-b extracted using water as solvent. It can be observed that, UV-Vis of Chl-b showed peak absorbance at 430 nm at the blue light region of the visible light. The highest occupy molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by DFT ground state level. Bandgap of Chl-b without and with water extraction are 2.12 eV and 2.10 eV respectively, while excitation state of LUMO to conduction band are 1.21 eV and 1.27 eV respectively. It shows that the bandgap is lower when extracted using water as the solvent. Therefore, water extracted Chl-b tends to give a better result for HOMO/LUMO energy and voltage open circuit, Voc, HOMO and LUMO energy resulted in higher energy than the bulk Chl-b in Mitragyna leaves. This lower bandgap is attributed to the addition of electrons contents in the extracted molecules which is beneficial for dye-sensitize solar cells, DSSC.

1. Introduction

Dye sensitizer solar cells (DSSC) is an alternative to the p-n junction photovoltaic (PV) devices and the electricity were generated by illuminating organic dyes in electrochemical cells [1]. Dye sensitizer solar cells (DSSCs) dye normally used inorganic elements such as ruthenium or osmium. Unfortunately, those are rare earth element that are difficult to originate and obtain, as result of that it is expensive and were to be replaced. Moreover, those elements are from group eight of periodic tables that to be known noxious and highly toxic [2].
According to Karthick et al., organic dyes are able to produce electricity on semiconductor electrodes due to the photo-electron conversion process. Excited electrons in the dye molecules were injected to the TiO$_2$ network during the illumination of sunlight [3]. Dye plays as essential role in DSSC by ejecting electrons and should captured the sunlight at all wavelength, $\lambda$ below 700 nm and should be within strong anchoring groups [4]. In addition, energy position of excited state dye must be higher than the conduction band of the titanium dioxide (TiO$_2$) for it to be able to experience an electron jump from the dye to photo-anode at excited state. Therefore, dye itself need to be at visible light spectrum of 400 nm to 700 nm to maximize sunlight harvesting process [5]. Therefore, dyes with wider range of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were investigated in many researches works [6].

Mitragyna speciosa (MS) of rubiaeceae coffee family have unique characteristic with alkaloid pigments and dark green in color [7]. Normal green leaf contains pigments of Chlorophyll (green) [8]. These pigments have their own characteristics and capabilities in harvesting photon when exposed to sunlight. Chlorophyll (Chl) itself has five different types which are Chl-a, Chl-b, Chl-c, Chl-d and Chl-f. According to Atsuchi et al. [9], Chl-b absorbed most sunlight in the visible light spectrum than Chl-a in which the wavelength of Chl-a and b differ by 20 nm, thus Chl-b has broader wavelength of UV-Vis in the visible range spectrum. While Chl-c, d and f only existed in non-terrestrial plant [8]. The peak of Chlorophyll-b (Chl b) occurred at 400 nm to 700 nm of UV-Vis spectrum which are in visible light spectrum and able to harvest sunlight to excite energies from natural dye [11].

As reported by H.C. Hassan [12], chlorophyll-based sensitizer used for dssc can be improved by using gel electrolyte based on polyvinyl alcohol (PVA) with double salt (KI and tetrapropylammonium iodide, TPAI). This had improved their dssc by 13% compared to only single iodide salt (potassium iodide, KI).[12]

Despite of having a natural dye sensitizer with suitable chemical properties, its electronic properties in term of position of energy level between HUMO LUMO of dye is also essential. Therefore, in this research the position of HUMO/LUMO of dye will be investigated in comparison to the valance band of TiO$_2$.

This research study was carried out by computational method of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with B3LYP/6-31G level of basis set [13]. This method is able to obtain the electronic and optical properties of DSSC and were offered by Gaussian-03 so and Gaussview-03 software [14]. According to W.S. Aroon et. al this method was accurately described and less computational cost if compared with others high-level quantum calculations. DFT and TD-DFT were widely used by theoretical investigation of excited state property and were reported as high accuracy and reasonable to relate [15].

2. Methodology

In this research, molecular structure of pigments in mitragyna speciosa (Chlorophyll) and the molecular structure of solvent (H2O) were identified and constructed in different file so that it can be optimized separately. After optimization, simulation for UV-Vis were run for MS pigments by using time-dependent density functional theory (TD-DFT) with B3LYP/6-31G level of basis set [13]. This method is able to obtain the electronic and optical properties of DSSC and were offered by Gaussian-03 so and Gaussview-03 software [14]. According to W.S. Aroon et. al this method was accurately described and less computational cost if compared with others high-level quantum calculations. DFT and TD-DFT were widely used by theoretical investigation of excited state property and were reported as high accuracy and reasonable to relate [15].

2.1 Molecular Geometry Construction

Pigments in MS were observed which Chlorophyll-b (Chll-b). The pigment was provided and obtained from Protein Data Bank (PDB)[16]. The pigment was optimized separately to check and clean the structure. Once the structure checked and cleaned, simulation energy can be started. But if there is error during optimization, log file will be checked and error identified. The error was fixed by the suggestion suggested by the software. Figure 1 (a) show the molecular structure of Chlorophyll b that were obtained
from PDB file. In this experiment, water (H2O) is used as solvent and its molecular structure was constructed in gaussview-03 software and the characteristic of water were identically followed as in Figure 1 (b) and (c).

![Figure 1. Molecular structure of (a) Chlorophyll obtained from protein data bank (PDB) file, (b) water, H2O with angle of H-O-H of 104.474° and the O-H distance of 0.95718 Å and (c) Chl b extracted in water solvent. H2O molecular structure were added in Gaussview-03 and located 2 Å from oxygen atom of Chl-b as in red circle.](image)

2.2 Extraction in Solvent
To demonstrate the extraction procedure, optimized molecular geometry of water were placed in molecular structure of Chl b. Water structure were placed near to oxygen atom of Chl b structure by 2Å. The distance from water oxygen and Chl b oxygen as minimum fitting on experimental data [17]. Water were used as extraction solvent to extract the element contained in the MS leaf. By water, the extraction of chlorophyll can be obtained on a certain amount of percentage based on the temperature, volume and weight of leaf for wet lab experiment. By computational calculation, water act as simulation on real time experiment by providing the presence of water (H2O) in the Chl structure. The presence of H2O will add more electron which are eight protons and eight neutrons of its shell. The calculation will add up the total number of electron shared by water and Chl. This will simulate the total energy generated by calculation and predict the performance of quantum energy transport, HOMO/LUMO and the minimum energy required to excite electron.

2.3 Computational Method
In this experiment, computational method was used by Gaussian-03 software for calculation and Gaussview-03 for construction of molecular geometry of pigments. Two steps of computational calculation job type were run which are optimization and energies calculation. The computational calculation approaches are DFT and TD-DFT with B3LYP/6-31G basis set.

The energy simulation first was executed to check the UV-Vis spectroscopy of mitragynine. In Gaussview 03 electronic spectra, epsilon (Ɛ) was given by default and need to be assume by lab theoretical values. The term absorbance (A) is the absorption coefficient, epsilon (Ɛ) is molar absorption coefficient (M), concentration of solution (c) with a unit of mol dm^-3 and optical path length (l) in cm. Then, energy simulation was run for Chl b pigment only and both Chl b pigment with water solvent. Simulation of energy also were run to obtain the minimum HOMO and LUMO energies and the location of HOMO and LUMO in the molecular structure. Fig. 5 show the Gaussian calculation setup.
for energies. Method used were ground state > TD-DFT > B3LYP with a basis set of 6-31G and singlet spin.

3. Result and Discussion

2.1 Ultraviolet-visible (UV-Vis)

Figure 2 show the UV-Vis spectroscopy of Chlorophyll b (Chl b). It can be seen that the maximum peak of absorbance (A) occurred at wavelength of 430 nm, which is near to 500 nm. In general, Chl b shows a quite wide range of light absorbance of light wavelength occurs at range of 350 nm and extended to 600 nm which are located at visible light range which is beneficial and interest of solar cells. Meanwhile, Table 1 tabulates the absorbance (A) from UV-Vis spectroscopy of Chl b. Based on the absorbance was calculated by equation (1) where the term absorbance (A) is the absorption coefficient, and epsilon (\(\varepsilon\)) is molar absorption coefficient (M), concentration of solution (c) with a unit of mol \([\text{dm}]^{-3}\) and optical path length (l) in cm. The calculation of absorbance was fixed for concentration of solution (c) and optical path length (l) by 1 mol and 1 cm respectively [19].

\[
A = \varepsilon cl
\]  

(1)

It can be seen that the maximum absorbance occurred at 420 nm while minimum of absorbance of 50 occurred at 360 nm, that is almost the same as measured by UV-Vis. This show that the absorbance from 50 to 400 were at visible light range which are from 360 nm to 420 nm. Thus, it can be witnessed that Chl b has wide absorption region and able to excite energies from wavelength 400 to 600 at visible light.

| Wavelength (nm) | Absorbance (A) | Epsilon (\(\varepsilon\)) |
|-----------------|----------------|--------------------------|
| 420             | 400            | 40000                    |
| 410             | 350            | 35000                    |
| 400             | 300            | 30000                    |
| 380             | 150            | 15000                    |
| 370             | 100            | 10000                    |
| 360             | 50             | 5000                     |

3.2 Ultraviolet-visible (UV-Vis)

Figure 3 show the location of highest occupy molecular orbital (HOMO) and lowest unoccupied molecular orbital as can be seen from Gaussview-03. The probability population of ground state electron existed in both condition of extraction was different (refer circle). These electrons effecting the position of HOMO and LUMO level of the extracted chlorophyll.
Figure 3. Location of ground state population of electron of Chl b HOMO/LUMO and Chl b extracted in water HOMO/LUMO. Red and green region shows the probability population of ground state electron to be existed.

This situation can be further explained from Figure 4 using box diagram of HOMO and LUMO energies generated in Gaussview 03 for standard Chl b with comparison to the one extracted in water. For both energies shown in yellow boxes are minimum excited energy and shown in hartree unit (a.u.). Blue box with no red arrow represents electron donor or hole while blue box with two red arrows represents electron. Thus, hole represent LUMO while electron represent HOMO.

Figure 4. HOMO and LUMO energies generated in Gaussview 03 for (a) Chl b and (b) Chl b extracted in water as solvent.

Table 2 tabulates the computational calculation of HOMO and LUMO energies in Gaussian 03 of Chl b and Chl b extracted in water solvent. Data obtained were in hartree unit (a.u.) and converted into electron volt (eV) by equation (2). While bandgap was calculated by equation (3). From the tabulated data, LUMO of Chl b and Chl b extracted with water are -2.84 eV and -2.78 eV respectively differ by 0.06 eV due to possible electron to be existed in red region in Chl b atomic structure. Red region is more negative energy therefore location of LUMO energy in extracted Chl b increased. Location of HOMO in Chl b with water extraction as well increased by 0.08 eV due to presence of H_2 O with addition of green region which is more positive energy. Hence, Bandgap of Chl b is wider than extracted Chl b.
which is 2.12 eV and 2.10 eV differ by 0.02 eV. Presence of H\(_2\)O adding more electron in atomic structure of Chl b with oxygen and hydrogen atom. Thus, attraction from HOMO to LUMO increased due to higher energy generated by extraction solvent.

\[
\text{1 a.u.} = 27.211 \text{ eV} \quad (2)
\]

\[
\text{H-L gap} = \text{HOMO} - \text{LUMO} \quad (3)
\]

**Table 2.** HOMO and LUMO energies of Chl b and Chl b extracted in water solvent in hartree unit. (a.u.) and electron volt (eV).

|          | Chl b          | Chl b + water |
|----------|----------------|---------------|
| LUMO a.u. | -0.10442       | -0.10232      |
| eV       | -2.84          | -2.78         |
| HOMO a.u. | -0.18222       | -0.17938      |
| eV       | -4.96          | -4.88         |
| Bandgap (eV) | 2.12          | 2.10          |

Figure 5 show the energy level of conduction and valance band of TiO\(_2\) and HOMO/LUMO of Chl b and Chl b extracted in water. For a normal anatase TiO\(_2\), conduction and valance band energies are -4.05 eV and -7.25 eV respectively with a bandgap of 3.05 eV.

**Figure 5.** Energy level diagram of conduction band (CB) and valance band (VB) for TiO\(_2\) and HOMO/LUMO of bare Chl b and Chl b extracted in water.

Chlorophyll energies of HOMO and LUMO are -4.96 eV and -2.84 eV respectively with a bandgap of 2.12 eV. While Chlorophyll b extracted in water has a HOMO of -4.88 eV and LUMO of -2.88 eV with a bandgap 2.10 eV slightly smaller than Chl b. This is due to and related to the higher probability of electron existed in the Chl b extracted in water as earlier discussed.
3.3 Electronic Properties

Table 3 tabulates the prediction of voltage open circuit, Voc of Chl b and Chl b extracted with water solvent with respect to the energy of TiO$_2$ semiconductor. The calculation of Voc was obtained from equation (4) [18].

$$Voc = E_{\text{LUMO}} - E_{\text{CB}}$$  \hspace{1cm} (4)

|                  | $E_{\text{LUMO}}$ (eV) | $E_{\text{CB}}$ (eV) | $Voc$ (eV) |
|------------------|-------------------------|-----------------------|------------|
| Chl b            | -2.84                   | -4.05                 | 1.21       |
| Chl b extracted in water | -2.78                   | -4.05                 | 1.27       |

It can be seen that, ELUMO of Chl b is located at -2.84 eV above TiO$_2$ by 1.21 eV while Chl b extracted in water located at -2.78 above TiO$_2$ by 1.27 eV. This shows that the voltage open circuit Voc for Chl b and Chl b extracted in water are 1.21 eV and 1.27 eV respectively. The difference in Voc between Chl b and Chl b extracted in water is 0.06 eV. Chl b extracted in water has higher Voc due to the oxygen contents of Ch b that originated by the O$_2$ atoms in water. From the result obtained, it showed that Chl b extracted in water required more energy for electrons to jump from LUMO to conduction band of TiO$_2$. As a consequence, it resulted with higher Voc which is expected to be beneficial for photoelectrochemical solar cell.

4. Conclusion

The geometry, optical properties and electronic properties of dye sensitizer were studied using DFT and TD-DFT in Gaussian 03 and Gaussview 03. Pigments in Mitragyna Speciosa (MS) leaf have been identified and observed. The UV-Vis, location of HOMO/LUMO energy and electronic properties were discussed.

Optical properties of UV-Vis were investigated by TD-DFT methods. It shows that Chl b has wide range of absorbance in visible spectrum of 400 nm to 700 nm. This show that Chl b pigment suitable to use as dye in DSSC. The peak absorbance of 400 occurred at visible light spectrum of 420 nm.

Electronic properties of HOMO/LUMO and Voc were observed by ground state level of excitation. LUMO of Chl b and Chl b extracted with water are -2.84 eV and -2.78 eV respectively. LUMO of Chl b nearer with the conduction band of TiO2 compared to Chl extracted in water. Thereby, Chl b without extraction have minimum energy to experience electron jump from LUMO to conduction band. Besides, bandgap from HOMO to LUMO of Chl b and Chl extracted with water are 2.12 eV and 2.10 eV respectively. It shows that with extraction with water able to narrow down the bandgap as minimum energy needed for electrons to excite from HOMO to LUMO. Predicted Voc of Chl b and Chl b extracted in water are 1.21 eV and 1.27 eV.

From the observation, extraction process of pigments plays an important role in order to determine the position of its HOMO/LUMO energy. Here, Ch b extracted with water as solvent tends to give better result with slightly higher LUMO energy level which in turns increased the voltage open circuit Voc compared to the energy of Chl b without extraction (as its original form). Secondly, the water extracted Ch b resulted lower bandgap energy between HOMO and LUMO level. This lower bandgap regulated and increased the number of excited electrons and current density, JSC (as electrons require less energy to jump on excited state LUMO). Therefore, Ch b extracted in solvent (water in this case) has resulted the increased in Voc and JSC as well. These two characteristics are among the element of an efficient molecule sensitizer in DSSC.

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