

# Properties of Chlorophyll Based Organic Dye Sensitizer Molecule Extracted in Various Solvents

Azlina Ahmad Khan, Nurfarahin Zainal, Marina Mokhtar, Mohamad Hafiz Mamat and Mohd Hanapiah Abdullah\*

**Abstract**— Dye-sensitized solar cell (DSSC) has been actively researched due to its lower fabrication cost. In DSSC, sensitizer imitates photosynthesis process in plants by absorbing the photon energy from the sunlight. This research investigated methanolic extracted chlorophyll dye sensitizer in comparison to water extracted and bare chlorophyll. Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) methods in Gaussian 03/Gaussview 03 software were used to investigate its optical and electronic properties. Each of the molecular structure (methanol and water) was individually attached to chlorophyll, and their performances were determined. Results demonstrated that the absorbance spectrum of chlorophyll shows a broad peak in the visible range from 400 to 700 nm with its highest peak at 430 nm. Energy gap of chl-m between the  $E_{(LUMO)}$  and the conduction band of  $TiO_2$  semiconductor,  $E_{C(TiO_2)}$  or so called as  $V_{oc}$  is slightly smaller compared to water (chl-w). Meanwhile, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bandgap of chl-m is slightly higher at 2.13 eV. Finally, position of LUMO to redox electrolyte in chl-m is the lowest, which is favourable for faster electron transition. From observation, chl-m demonstrated better optical and electronic properties compared to its counterparts and hence good for chlorophyll sensitizer extraction.

**Index Terms**—DSSC, energy gap, HOMO/LUMO, photon energy, optical and electronics properties.

## I. INTRODUCTION

NOWADAYS, solar power systems are widely being used across the world to generate electricity. One of the types of solar cell is dye-sensitized solar cell (DSSC). According to N. Jamalullail *et al.* [1] DSSC is the third rank solar cells discovered by O'Regan and Gratzel in 1991. It is also declared

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as a new level of low-cost solar system with simplified manufacturing procedures. This solar cell is inspired by the photosynthesis process, which converts solar energy into electrical energy.

DSSC was first discovered in the early stage of third-generation technological devices that used polypyridyl compounds of Ruthenium (II) as a sensitizer. Upon its discovery, the compound has seen been broadly explored [2]. Exploring the properties of the compound is important as it provides excellent stability and higher absorption in the visible range of solar spectrum when used as a dye sensitizer [3]. However, Ruthenium (Ru) possesses several side effects when exposed to the environment as it contains heavy metals [4], [5] and the elements are difficult to originate. As a result, it is expensive despite causing pollution to the environment [6]. Thus, this encourages the development of DSSC to divert to a more convenient option, which is the organic sensitizer.

According to Karthick *et al.* [7], 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 titanium dioxide,  $TiO_2$  network during the illumination of sunlight [8]. Dye plays an 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 [9]. Most importantly, dye itself needs to be at a visible light spectrum of 400 nm to 700 nm to maximize the sunlight harvesting process [10]. In addition, energy position of excited state dye must be higher than the conduction band of the  $TiO_2$  so that the excited electrons can jump from the dye to photo-anode at excited state. An energy diagram of a typical DSSC is depicted in Fig. 1 showing the position of energy levels under normal operation.

In this research, chlorophyll based natural dye sensitizer was simulated. Green leaves are known to have unique characteristics that contain alkaloid pigments and a dark green colour [11], which is generally associated with chlorophyll (green) pigments [12]. An experiment done by L. Leenawaty *et al.* [13] reported that the higher the chlorophyll content in the leaves, the higher the green colour intensity of the leaves. There are five types of chlorophylls namely chlorophyll a, b, c, d, and f. Normally, chl a and chl b were used as dye molecule sensitizer for DSSC. H.C. Hassan *et al.* [14], 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) [14]. Although there have been several studies performed on chlorophyll in terms of its optical and electrical properties, this is the first report of similar studies on chlorophyll pertaining to its huge potential use as dye sensitizer molecules for DSSC. In this research, we studied the geometry, electronic and optical properties for chlorophyll dye using density functional theory (DFT) and time-dependent (TD-DFT) as implemented in the Gaussian 03 and Gaussview 03 software [15]. According to W.S. Aroon *et al.*, these methods are more accurately require less computational power than other high-level quantum calculations. In addition, DFT and TD-DFT have been widely used in theoretical investigations of excited state property and have been reported as having high accuracy and being reasonable to relate [16]. Referring to Umer Mehmood *et al.* [17], DFT is more efficient than other high-level quantum approaches in investigation the ground and excited state behaviours of photosensitizer complexes because the computed orbitals are suitable for standard molecular orbital (MO)-theoretical analysis and interpretation.

H<sub>2</sub>O will add more electron which have eight protons and eight neutrons of its shell. The calculation will add up the total number of electrons shared by water and chlorophyll. The total energy generated was determined using this combination molecular structure (extracted chlorophyll sensitizer molecules). After that, the performance of quantum energy transport, HOMO/LUMO and the minimum energy required to excite electron were all simulated.

Table I shows the parameters that were taken into consideration when constructing the methanol molecule. Methanol (CH<sub>3</sub>OH) bond lengths were determined using the Hamiltonians and three ab initio levels [17]. Methanol has three literature bond lengths; C-H with 1.096 Å, C-O 1.427 Å, and O-H 0.956 Å with its corresponding bond angles of H-C-H 109.03° and H-O-C 108.87°, respectively.

TABLE I  
PARAMETERS FOR THE CONSTRUCTION OF METHANOL[19]

Atoms	Parameters	
	Length between atoms	Angle between atoms
C – H	1.096Å	-
C - O	1.427Å	-
O – H	0.956Å	-
H-C-H	-	109.03°
H-O-C	-	108.87°

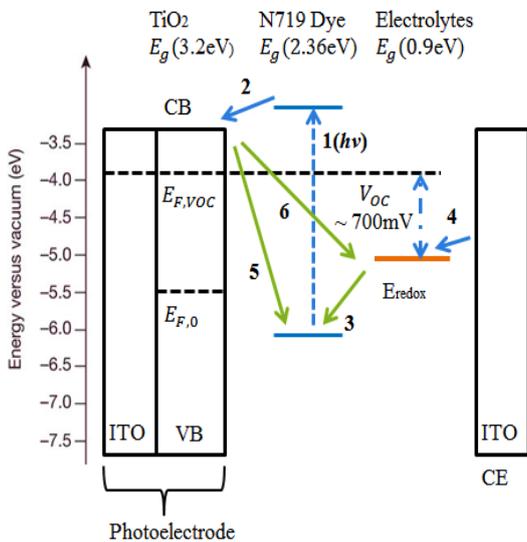
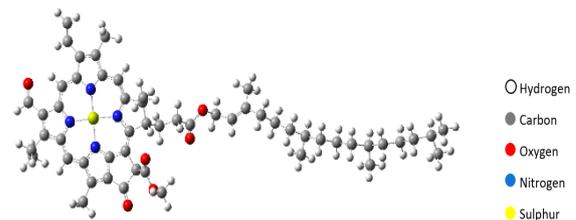


Fig. 1 Energy diagram of a DSSC showing major position of energy levels under normal operation

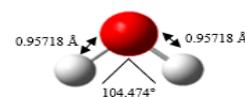
## II. METHODOLOGY

In this research, molecular structure of chlorophyll were identified and obtained from Protein Data Bank (PDB) [18]. Molecular structure of methanol (CH<sub>3</sub>OH) and water (H<sub>2</sub>O) were constructed and optimized separately to check and clean the structure. After optimization, simulation for UV-Vis was carried out on the bare chlorophyll using time-dependent density functional theory (TD-DFT) with method of Becke, 3-Parameter, Lee-Yang-Parr (B3LYP) of 6-31G basis set. Here, methanol and water were used as solvents and each of them were attached to the bare chlorophyll before the HOMO and LUMO energies were simulated. Finally, simulation for electronic properties of the chl-m, chl-b and chl-w were carried out. Fig. 2 (a) shows the molecular structure of chlorophyll obtained from PDB file (named as bare chlorophyll). Fig. 2 (b) and Fig. 2 (c) show the molecular structure of water and methanol in Gaussview 03 software. In computational and simulation approach, water molecule was added to the chlorophyll molecule's structure. The presence of

The optical and electronic properties of the optimized molecule structure were simulated. In optical properties the absorbance characteristic was observed. Meanwhile, HOMO/LUMO energy values were investigated in the respective electronic properties. In this simulation, methanol molecules are placed near the pigment's molecule with the distance of 2 Å. Meanwhile, water molecular was also placed near the oxygen atom of the chlorophyll structure by 2 Å. On the experimental data, the distance between water oxygen and chlorophyll oxygen was calculated using minimum fitting [20].



(a)



(b)

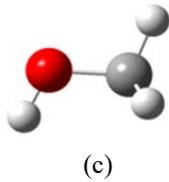


Fig. 2 Molecular structure of (a) chlorophyll obtained from protein data bank (PDB) file, (b) water, H<sub>2</sub>O with angle of H-O-H of 104.474° and the O-H distance of 0.95718 Å, and (c) molecular structure of methanol

A. Molecular Structure of Simulated Chlorophyll

The structural geometry of the simulated chlorophyll derived from two different solvent in comparison to the bare chlorophyll is shown in Fig. 3 (a). Chll-m is shown in Fig. 3 (b), with the presence of methanol molecules (as in circle) introduced to the original chlorophyll. Meanwhile Fig. 3 (c) shows the chl-w molecular structure with the presence of water molecules (in circle) after the optimization.

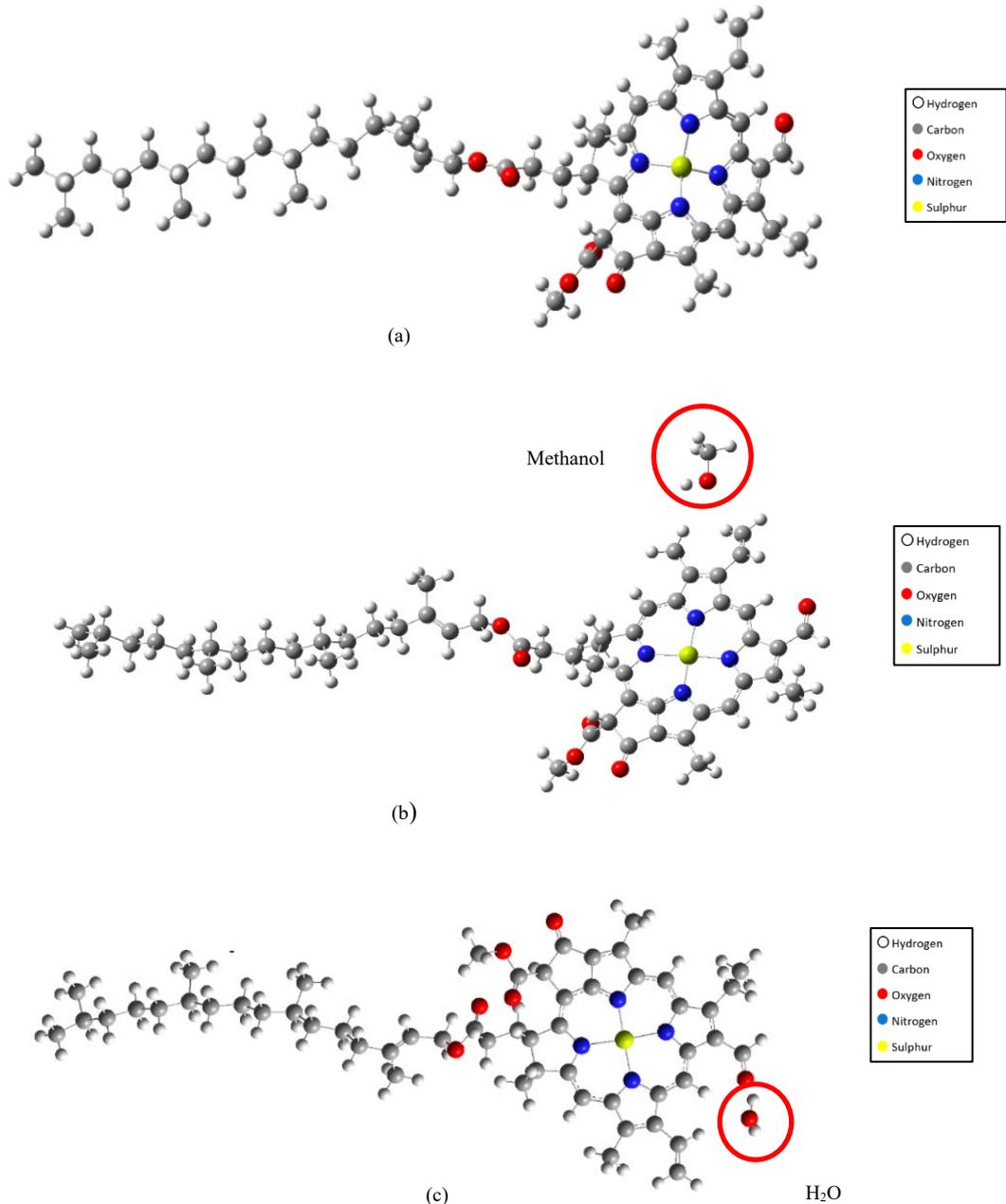


Fig. 3 Structural geometry of the simulated (a) Chll-b, in comparison to (b) Chll-m and (c) Chll- w

B. Optical properties of pigment (absorbance spectra)

The optical properties observed in this research was the absorbance spectrum of the chl-b. Generally, a dye used as a molecule sensitizer must have a broad peak of absorption

spectra within the visible light spectrum which is between 400 nm to 800 nm. Based on the result shown in Fig. 4, the absorbance spectrum of chlorophyll occurred between 440 nm to 700 nm and which falls within the visible light range spectrum. This is similar to what was reported by R. Syafinar

*et al.* [6] on spinach-based chlorophyll that exhibited broader absorption range of 400-700 nm. These findings were also demonstrated by Al-Awani MAM, and Ananth S. [21],[22]. Chlorophyll shows its highest peak absorption between the range of 400 nm to 500 nm, which falls in visible light spectrum and able to harvest sunlight to excite energies from natural dye [23]. Each type of pigment can be identified by the specific pattern of wavelengths it absorbs from visible light, which is the absorption spectrum. Generally, chlorophyll-a absorbs light in the blue-violet region, while chlorophyll-b absorbs red-blue light. Though there is high absorption peak at 440 nm which is possible due to chl-b, which absorbs strongly at that wavelength. However, both chlorophylls complement each other in absorbing sunlight in plants [6], [21],[22].

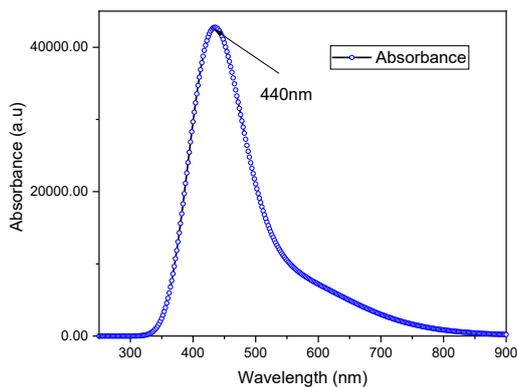


Fig. 4 Absorption spectra of simulated dye sensitizer chlorophyll

### C. Electronics Properties Of The Pigments

The electronics properties observed in this research was HOMO/LUMO energy values. The HOMO is the highest energy of orbitals containing electrons and the LUMO is the lowest energy of those without electrons. Hence, both HOMO and LUMO have the energy closest to all molecule orbitals. For this reason, the HOMO-LUMO gap is where excitations most likely occur.

According to Umer *et al.* [17], for an effective charge transfer, the energy position of LUMO of dyes must be higher (LUMO must be less negative) than the conduction band of the semiconductor whilst the HOMO of the dyes must be lower (HOMO must be more negative) than the redox potential of the electrolyte. Based on a study by J. Fujisawa *et al.* [24], the conduction band of  $\text{TiO}_2$ , a semiconductor that is typically used on a DSSC is  $-4.05$  eV.  $\text{TiO}_2$  was selected because of its balanced electronic properties having conduction band of  $\sim -4.0$  eV and band gap of  $3.18$  eV [17]. The electrolyte used in DSSC usually having energy reduction of  $-4.80$  eV. The values of energy obtained in Table II are in hartree unit (a.u) and converted into electron (eV) by using (1). The energy values in eV unit are used to calculate bandgap for HOMO-LUMO by using (2). The calculation of  $V_{oc}$  as in (3) [25].

$$1 \text{ a.u} = 27.211 \text{ eV} \quad (1)$$

$$H - L_{gap} = HOMO - LUMO \quad (2)$$

$$V_{oc} = E_{LUMO} - E_{CB} \quad (3)$$

Where,  $V_{oc}$  is the open circuit voltage.

Table II tabulates the computational calculation of HOMO and LUMO energies in Gaussian 03 for the chl-b as well as chl-m and chl-w. Data obtained were in hartree unit (a.u.) and converted into electron volt (eV) by using (1). The HOMO energy of methanolic extracted chlorophyll is  $-5.01$  eV, while the LUMO energy is  $-2.88$  eV, with a bandgap of  $2.13$  eV. Furthermore, chl-b HOMO/LUMO energies are  $-4.96$  eV and  $-2.84$  eV, respectively, with a bandgap of  $2.12$  eV. Meanwhile, chl-w has a HOMO of  $-4.88$  eV and LUMO of  $-2.78$  eV with a bandgap of  $2.10$  eV. These findings show that the bandgap of chl-m is the widest when compared to chl-w and chl-b. These findings are similar to a study conducted by Calogero *et al.* [26], who concluded that this happened due to the presence of more O-H bonds. As a result, the atomic structure of chl-m has gained more electrons, resulting in an increase in the HOMO/LUMO energy level.

TABLE II  
HOMO/LUMO ENERGY VALUE OF CHLOROPHYLL

Energy		Dye pigment		
		Chlorophyll with methanol	Chlorophyll with water	Bare chlorophyll
LUMO	a.u	-0.10604	-0.10232	-0.10442
	eV	-2.8800	-2.7801	-2.8403
HOMO	a.u	-0.18408	-0.17938	-0.18222
	eV	-5.01	-4.88	-4.96
H-L <sub>gap</sub> (eV)		2.13	2.12	-2.01
$V_{oc}$		1.17	1.27	1.21

Fig. 5 shows the HOMO/LUMO energy level of bare, methanolic and water extracted chlorophyll with respect to the conduction of  $\text{TiO}_2$  and redox electrolyte potential. For a normal anatase  $\text{TiO}_2$ , conduction and valance band energies are  $4.05$  eV and  $-7.25$  eV respectively, with a bandgap of  $3.20$  eV.

Here, LUMO of chl-m, chl-w and chl-b are  $-2.88$  eV,  $-2.78$  eV and  $-2.84$  eV, respectively. It can be seen that the LUMO level,  $E_{LUMO}$  of chl-m is located at  $-2.88$  eV above the conduction band of  $\text{TiO}_2$ ,  $E_{C(\text{TiO}_2)}$  by  $1.17$  eV. Meanwhile, chl-w and chl-b located at  $-2.78$  eV and  $-2.84$  eV above  $E_{C(\text{TiO}_2)}$  by  $1.27$  eV, and  $1.21$  eV respectively. These  $E_{(LUMO)} - E_{C(\text{TiO}_2)}$  actually reflects the voltage open circuit  $V_{oc}$  developed by the DSSC later on. In this case, chl-m contributed to a lower  $V_{oc}$  of a DSSC solar cell. Keep in mind that solar cells exhibit a trade-off between  $V_{oc}$  and  $J_{sc}$ , with lower  $V_{oc}$  being positively supported by higher  $J_{sc}$  and vice versa. Furthermore, this lower gap could promote and ease electron transport from LUMO to  $E_{C(\text{TiO}_2)}$ , resulting in increased  $J_{sc}$ . As a result, it eventually led to the improvement in the overall efficiency of the solar cell.

This can be further supported by the higher probability of ground state electron to be existed in methanol that has a closely-packed area of red and green regions compared to others. As a result, chl-m is expected to be more promising as a natural dye sensitizer in DSSC than chl-w and chl-b. This finding is consistent with other studies that have found methanol to be better at extracting chlorophyll [27].

Moreover, the position of HOMO energy level of chl-m with respect to the potential redox electrolyte is also considered. It can be seen that the position is the lowest, at -

4.96 eV which is also lower than the potential redox electrolyte position, which is at -4.80 eV. As a result, the electron transition from redox electrolyte to HOMO energy level is more effectively promoted.

Here, LUMO of chl-m, chl-w and chl-b are -2.88 eV, -2.78 eV and -2.84 eV, respectively. It can be seen that the LUMO level,  $E_{LUMO}$  of chl-m is located at -2.88 eV above the conduction band of  $TiO_2$ ,  $E_{C(TiO_2)}$  by 1.17 eV.

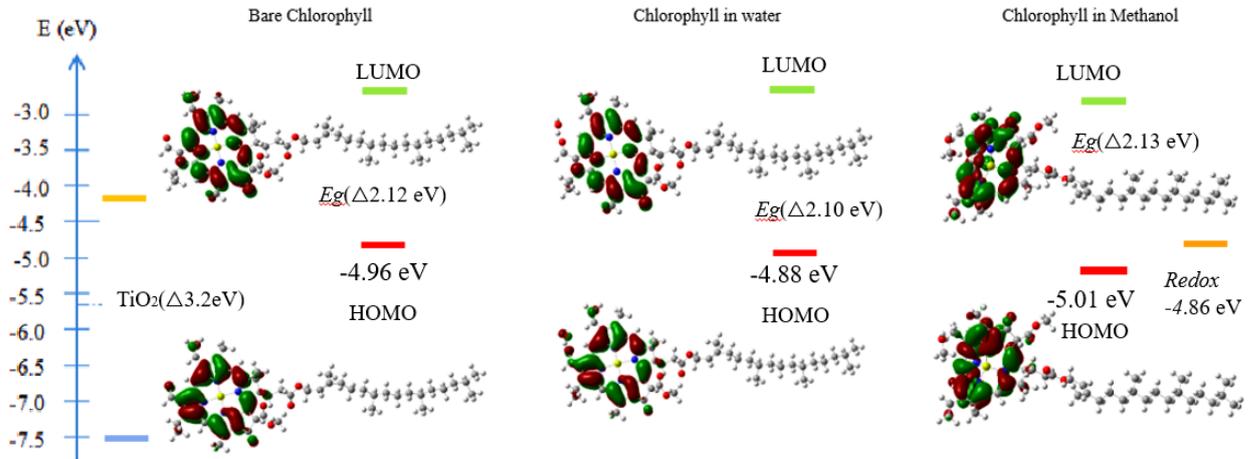


Fig. 5 Energy level diagram of Conduction Band (CB) and Valance Band (VB) for  $TiO_2$  and HOMO/LUMO of Chll-b, Chll-w and Chll-m. (Red and green region shows the probability population of ground state electron to be existed)

Meanwhile, chl-w and chl-b located at -2.78 eV and -2.84 eV above  $E_{C(TiO_2)}$  by 1.27 eV, and 1.21 eV respectively. These  $E_{(LUMO)} - E_{C(TiO_2)}$  actually reflects the voltage open circuit  $V_{OC}$  developed by the DSSC later on. In this case, chl-m contributed to a lower  $V_{OC}$  of a DSSC solar cell. Keep in mind that solar cells exhibit a trade-off between  $V_{OC}$  and  $J_{SC}$ , with lower  $V_{OC}$  being positively supported by higher  $J_{SC}$  and vice versa. Furthermore, this lower gap could promote and ease electron transport from LUMO to  $E_{C(TiO_2)}$ , resulting in increased  $J_{SC}$ .

This can be further supported by the higher probability of ground state electron to be existed in methanol that has a closely-packed area of red and green regions compared to others. As a result, chl-m is expected to be more promising as a natural dye sensitizer in DSSC than chl-w and chl-b. This finding is consistent with other studies that have found methanol to be better at extracting chlorophyll [27].

Moreover, the position of HOMO energy level of chl-m with respect to the potential redox electrolyte is also considered. It can be seen that the position is the lowest, at -4.96 eV which is also lower than the potential redox electrolyte position, which is at -4.80 eV. As a result, the electron transition from redox electrolyte to HOMO energy level is more effectively promoted.

#### IV. CONCLUSION

In this research, geometry, optical properties and electronic properties of chlorophyll dye sensitizer using various solvents has been investigated using TD-DFT methods. Optically, it shows that chlorophyll has a wide range of absorption in the visible spectrum between 400 nm to 700 nm and therefore suitable to be used as dye sensitizer in DSSC. In addition, electronic properties of HOMO/LUMO were observed by ground state level of excitation. Noticeably,  $E_{LUMO}$  of chl-m at -2.88 eV is the lowest energy gap with respect to  $TiO_2$  conduction band compared to chl-w and chl-b. This lower

bandgap may regulate and increased the number of possible excited electrons and current density,  $J_{SC}$  (as electrons require less energy to be excited to LUMO state). Moreover, bandgap from HOMO to LUMO of chl-m, is the widest at 2.13 eV compared to chl-w and chl-b. It shows that chl-m can meet the requirement for a lower HOMO level with respect to the redox potential. This has consequently endeavored faster electrons transition from redox to HOMO. From the

observation, extraction process of pigments plays an important role in order to determine the position of its HOMO/LUMO energy. These two characteristics would bring some positive impact to the efficiency of solar cells. Throughout the research, it was discovered that methanol produced a better extraction of organic dye compared to water.

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