Theoretical Modification of Pheophytin Using Cu, Ni, and Zn Atoms as a Sensitizer for Dye Sentized Solar Cell (DSSC)

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Abstract. Theoretical studies of pheophytin compound modified with Cu, Ni, and Zn atoms as a sensitizer for dye solar cell compound (DSSC) have been carried out based on HOMO-LUMO energy parameters, LUMO electron localization, spectra, light absorption efficiency, coupling constant, and sensitizer bond length with TiO2. This study aims to determine the parameters of bond length, spectra, molecular density, HOMO-LUMO energy, LHE, and ΔG injection of pheophytin α and β complexes using the central atoms of Cu, Ni, and Zn; and formulating the effect of adding central atoms of Cu, Ni, and Zn on the characteristics α and β pheophytin photoelectric and determine the best modification capable of producing the best characteristics for pheophytin as a dye compound on the DSSC based on parameters of bond length, spectra, molecular density, energy HOMO-LUMO, LHE, and ΔG injection. The theoretical modification that used is DFT/B3LYP, the accuracy of the method used amounted to 89.27% and 96.09%. Based on the above parameters the best modification sensitizer for DSSC is Zn Pheophytin β > Zn Pheophytin α > Pheophytin β > Pheophytin α > Cu Pheophytin β > Ni Pheophytin α > Ni Pheophytin β > Cu Pheophytin α.

1. Introduction
The development of solar cells is a necessity when humans are faced with various environmental damage due to the use of fossil fuels and global warming. Currently, the most developed solar cells are dye-based solar cells (DSSC)[1]. DSSC solar cells were first discovered by Michel Gratzel and Brian Oregan. DSSC is a photovoltaic solar cell using electrolytes as a charge transport medium.[2] The DSSC working principle is a cycle of electron transfer by DSSC components. DSSC solar cells consist of five components such conductive glass, semiconductor layers, sensitizers, electrolytes, and opposing electrodes. One type of sensitizer that used is porphyrins. Porphyrin is efficient for use in DSSC because of its strong absorption in the near IR region, good photochemical properties, and thermal stability and has a high photon-electron conversion of about 13% for DSSC.[3] However, the porphyrin complex with high efficiency is a synthetic complex using ruthenium metal atoms which is rare, expensive and, has a bad effect on the environment.
Porphyrid rings can be found in abundant quantities in nature in the form of chlorophyll, hemoglobin, and myoglobin. Chlorophyll is the most logical source of porphyrin which can be used as a sensitizer in DSSC. The main source of chlorophyll is produced from green plants. From an economic perspective, chlorophyll is the best choice for DSSC modification. These dyes can be produced by simple derivatization of natural chlorophyll molecules.[4] One of the chlorophyll derivatives that is often used for this purpose is pheophytin.

Modification of pheophytin with carotene can increase the spectroscopic response of these dyes.[5] Modification of chlorophyll with Zn and Cu atoms results in maximum absorbance and maximum emissions of 0.032 eV for chlorophyll, 0.028 eV for Zn-pheophytin, and 0.053 eV for Cu-pheophytin. In porphyrins, the central metal atom becomes very substantive to produce high efficiency. Zn central atom can produce the highest energy conversion.[7] The use of Zn central atoms in natural chlorophyll with the modification of other atoms for one period has not been much studied.

Based on this, the addition of a central atom is expected to increase the efficiency of pheophytin as a dye compound for DSSC. The types of central atoms that will be used are Cu, Ni, and Zn. In 2013, Shalabi et al. used Zn, Ni, Fe, and Ti atoms in thiophene-substituted metalloporphyrin complexes as a dye on DSSC with Ni energy gap results of 3.06 eV and Zn of 2.95 eV[8]. The use of Cu as a central atom was carried out by modifying Cu with ligands 5,10,15,20-tetakis (4-carboxyphenyl) porphyrin (TCPP) with a maximum wavelength of 542 nm.[9] Modified pheophytin as mentioned above can be done theoretically using experimentally in a wet lab or computational method.

Through efficiency considerations, a suitable method is a theoretical method or computational chemistry method. The computational method used is DFT/TD-DFT. The use of this method is based on the data needed as a dye application on DSSC, namely binding energy, UV-Vis spectra, electron density at the position of HOMO and LUMO, LHE (Light-Harvesting Energy), and ΔG electron. The DFT method has a relationship with electrons in electron density and can predict properties such as the ground state of the electron and geometry prediction. Meanwhile, the TD-DFT method is used to calculate spectra properties including excitation energy, UV-Vis spectra, oscillator strength, and electron composition. [10]

The use DFT and TD-DFT methods with the TD-B3LYP function and 6-31G basis set for porphyrin Zn-based DSSC with variations in electron, pulling show that the porphyrin Zn complex has a gap energy of 3.5-4.1 eV[11]. Similar research using the CAM-B3LYP function and 6-31G basis set to study the modification of porphyrins with Zn and Cu atoms show that Zn-Por-1 efficiency of 2.9% and Ni-Por-1 of 1.5%.12 Shalabi’s research used the B3LYP/SDD function on the STO-3G basis set, the resulting HOMO-LUMO energy in the thiophene-substituted porphyrin Zn complex was 2.93 eV and Ni was 3.06 eV. In addition to the energy parameters of the HOMO-LUMO gap as has been produced in several studies above, other parameters that can be studied are the bond length between the modified semiconductor molecule and the sensitizer molecule, binding energy, UV-Vis spectra, electron density at the HOMO and LUMO positions, LHE (Light-Harvesting Energy), and ΔG electron injection (energy injection).

Differences in the distribution of electrons in each modification will cause differences in the values of each of these parameters. It is hoped that the modification will show the effect of central atomic variations on natural chlorophyll derivatives so that further modifications can be made. The next best modification results will be the basis for research in wet laboratories.

2. Method

Optimization and calculation of molecular energy using the NWChem application. Molecular visualization using ECCE, Chem Craft, and Avogadro. All applications run on the Linux Mint operating system.

The method used is determined based on the comparison of the excitation energy of experimental results with computational spectra. The available molecules are α and β pheophytin. The method that produces molecular excitation energy close to the experimental results is the method used. These methods include DFT with B3LYP basis functions for molecular optimization and TDDFT methods.
with the RPA approach for the determination of activation energy and molecular spectra. The basis set used for all atoms is 6-31G*.

Data processing methods used Avogadro software to determine bond lengths, NW Chem for molecular optimization, ECCE to determine the energy level of the HOMO-LUMO state and electron density, and Chem Craft to determine the UV-Vis spectrum of each molecule.

3. Results and Discussion

3.1. Method Determination

Proving the accuracy of the method used is done by comparing the results of calculations that have been made with existing experimental data. Based on experiments conducted by Scheer (1991) As listed in the following table:

| Data      | Excitation Energy (calculation) eV | Excitation Energy (experiment) eV |
|-----------|------------------------------------|----------------------------------|
| Feofitin α| 3.3915                             | 3.0277 (Scheer, 1991)            |
| Feofitin β| 3.2173                             | 3.3482 (Scheer, 1991)            |

The results of the calculations in the table.1 The comparison data of the excitation energy value shows a difference of 0.363 eV and 0.131 eV with a percentage of 89.27% and 96.09% This calculation is done by the DFT-TDDFT method and basis set 6-31G*. The results of the excitation energy comparison show that the calculation results and experimental results show a small difference in results, so it can be concluded that the selection of computational methods and base sets used is quite accurate for other parameters.
Figure 1. Pheophytin and its Derivatives Structure

3.2. Ligand and Central Atom Bond Length
Bond length is the distance between the nuclei of one atom with other atom. The length of the bond is influenced by the electronegativity of each atom, the smaller the difference in elasticity, small difference in electronegativity will increase the length of the bond. The bond length is also influenced by the radius of the atom making up the bond, the longer the radius of the atom that binds to a molecule, the longer the bond will be. The length of the bond is directly proportional to the radius of the atom.

Figure 2. Length Bond of The Central Atomic and The Ligand
Figure 2 shows that the length of the bond between metal and nitrogen atom in pheophytin varies greatly from the range 1.89 to 2.099 Å. This proves that there has been an interaction that causes the activity of each different complex. The main factor affecting the length of the bond between the central atom and the ligand is the difference in the type of central atom. In Ni atoms, N atoms form bonds because the radius of the Ni atom is greatest among the other atoms that are 149 pm so that the interaction distance of the outer electrons of the Ni atom to the N atom is closer and easier to form bonds. The Zn atom is the smallest central atom of the two other central atoms with a radius of 142 pm. The bonds formed are only 2 bonds because the distance of the Zn atom to the N atom is further. Meanwhile, Cu
atoms with a radius of 145 pm on the pheophytin α complex formed 3 bond and on the pheophytin β complex formed 4 bond that indicates that the formation of the bond also depends on the type of ligand. Position N1 and N3 are bonds between lone pair electron on the nitrogen atom that occupy the central atomic empty orbitals. The binding of lone pair electron causes the bond between the two to be strong because it is not disturbed by the back bonding of lone pair electron. The bond length parameter will facilitate the flow of electrons from the central atom to the ligand so that it will reduce the gap energy. In the length bond parameter of the Pheophytin modification bond, it is best to obtain Cu Pheophytin α, Ni Pheophytin α, and Ni Pheophytin β. But still, need analysis from other parameters so that dye can be used for DSSC.

3.3. HOMO-LUMO Energy

Dye with a relatively low HOMO-LUMO energy difference will facilitate electron excitation. High HOMO energy indicates the reactivity of high compounds that facilitate electron transfer so that chemical bonds will be more easily formed. A low HOMO value indicates the stability of the molecule making it less reactive. High LUMO energy for dye molecules will facilitate the injection of electrons from the semiconductor so that the recombination of dye to the ground level will be faster. In dyes with a relatively low HOMO-LUMO energy difference will facilitate electron excitation.

Energy values of HOMO-LUMO pheophytin α and β modified from Figure 3 are the basis for determine the ability of a compound to become a sensitizer in DSSC. LUMO energy must qualify of having energy above the TiO$_2$ semiconductor conduction band that is -4.2 eV (Urbani, 2014). The compounds that can be used as DSSC in terms of LUMO energy parameters are pheophytin α, pheophytin β, Cu pheophytin β, Zn pheophytin α, Zn pheophytin β. Figure 4.5 shows that the highest LUMO energy level is Pheophytin β and the lowest is Cu Pheophytin α.

![Energy values of modified Pheophytin and Pheophytin HOMO-LUMO](image)

Figure 3. Energy values of modified Pheophytin and Pheophytin HOMO-LUMO

According to figure 3, the compounds of Cu pheophytin β, Zn pheophytin α, and Zn pheophytin β have HOMO-LUMO energy values which are almost the same as pheophytin α and β, but different results from the original compounds indicate a modification has occurred. Modification of pheophytin α and β with Ni metal and pheophytin α with Cu metal have a lower HOMO-LUMO energy difference so that the possibility of electrons is higher, but this modification does not qualify as a DSSC sensitizer because the LUMO energy under the injection energy of I$_3$ is -4.6 eV.

The theoretical modification that has been done in terms of HOMO-LUMO energy which is most possible as a sensitizer is the compound pheophytin α, pheophytin β, Cu pheophytin β, Zn pheophytin β.
α, Zn pheophytin β. This is because these four compounds are in the energy range of $I^-/I^3-$ injection which is -4.6 eV and the TiO$_2$ conduction band is -4.2 eV.

3.4. Electron Density in HOMO & LUMO State

Energy orbitals in the HOMO and LUMO states are figures that show the distribution of electrons in the ground and excited states.

![Figure 4. Pheophytin α and β and Pheophytin α and β modified at the HOMO and LUMO positions](image-url)

Figure 4 shows the electron density of HOMO-LUMO which will affect the electron transfer to the semiconductor. Based on the binding position of the semiconductor with electron withdrawal compounds which are possible as DSSC are Pheophytin α, Cu Pheophytin β, Ni Pheophytin α, Ni Pheophytin β, Zn Pheophytin α dan Zn Pheophytin β. The compound above has the electron density in the O group anchored to the semiconductor, that it is certain that the electron transfer goes well.

Based on the energy orbitals position data, it can be seen that the modification using Ni Pheophytin α and β is the best modification when compared to the modification with the addition of other central atoms. However, the best modification results for this orbital position are not possible if applied to DSSC. When viewed from the requirements of the injection energy levels of $I^-/I^3-$, conduction band and valence band, Cu and Zn Pheophytin β are the best modification as DSSC sensitizers, although the electron distribution distribution is not as good as Ni Pheophytin α and β.
3.5. Spectra

Pheophytin has many conjugated bonds which can undergo transition $\pi \rightarrow \pi^*$ transitions. This causes the probability of electron injection into the semiconductor is quite high. [15]

![Figure 5. UV-Vis Spectra from Pheophytin Modified Results](image)

Pheophytin $\alpha$ has maximum absorption at wavelength 365.57 nm in the light region in the UV light region. While pheophytin $\beta$ has a maximum absorption at a wavelength of 385.37 nm for the UV light region, whereas for the visible light region pheophytin $\beta$ also has a strong absorption at a wavelength of 401.64 nm. Obtaining uptake in visible light and UV rays in pheophytin $\beta$ compounds indicate that $\beta$ pheophytin has a longer absorption range than $\alpha$ pheophytin. The acquisition of this wavelength value is inversely proportional to the excitation energy, while the strength of the oscillator is proportional to the intensity of the spectrum which indicates the likelihood of the electron being excited.

The results in Figure 5 show that the modification has a positive effect on spectra results, which is indicated by the absorption will be stronger with the addition of the central atom. In the UV wavelength range, Pheophytin $\beta$ shows more positive results than Pheophytin $\alpha$. Whereas in the Visible wavelength range, Pheophytin $\alpha$ shows more positive results than Pheophytin $\beta$. The effect of central atom addition is also seen from UV-Vis spectra. In the UV wavelength range, modification of Pheophytin with Zn atoms results in high absorption, while modification with Cu and Ni atoms does not produce any absorption. In the Visible wavelength range, modification of pheophytin with Ni atoms results in absorption which is relatively stronger than Zn because it maximizes sunlight absorption.

Based on the best modification parameters obtained by Zn pheophytin $\beta$ which can absorb at UV and visible wavelengths with a large oscillator strength. This causes the Zn pheophytin $\beta$ compound to have the ability to absorb maximum sunlight at UV and visible wavelengths. This ability shows that Zn pheophytin $\beta$ is suitable as a sensitive compound in DSSC. Absorption on visible waves will greatly affect the efficiency of DSSC because it maximizes the absorption of sunlight.

3.6. Light Harvesting Electron (LHE) and Coupling Constant (VRP)

The electron injection value in DSSC is influenced by the coupling constant between the dye and the semiconductor surface. DSSC efficiency is also influenced by the value of the coupling constant between dye and semiconductor surfaces, which are factors that influence the value of electron injection in DSSC, the VRP value is also one of the factors that influence DSSC efficiency. [16] The VRP value of a dye shows electron injection value of the dye into the semiconductor. [17] While the efficiency of light absorption (LHE) is one of the factors associated with DSSC. The energy-saving light value is related to the ability to capture light so that it can increase the energy generated from the DSSC system.
Based on Figure 6, the coupling constant value between a dye and a semiconductor surface or VRP is known that the modification using the central Cu atom with the pheophytin α ligand is the best modification. Other results prove that the modification of the central Ni atom in both types of pheophytin α and β ligands gives good results on the coupling constant value. However, the value of this parameter cannot be used as the only parameter that is suitable or not for this modification to be used in the DSSC system.

The data in Figure 6 shows that using the modified LHE parameter by adding Cu and Ni metal atoms with pheophytin α and β ligands has no positive effect, this is due to the low absorption intensity at the maximum wavelength. While the Zn atom modification depends on the ligand that bound, Pheophytin α and Pheophytin β, the results of the LHE value on Zn Pheophytin β> Zn Pheophytin α this is due to the presence of COH groups in the Pheophytin β branch which can attract electron flow so that the electron distribution is evenly distributed while in the branch Pheophytin α> Zn Pheophytin α. the same in Pheophytin α there is a CH$_3$ group that is electron-inducing.

In the LHE parameter, the best modification obtained is Zn pheophytin β, but the increase is not significant compared to pheophytin β without modification. The results of these parameters will be compared with other parameters so that it can be concluded which modification is the best.

### 3.7. Bond Length between Dye and Semiconductor

Measurement of bond length between dye molecules and TiO$_2$ semiconductors was carried out to determine the presence or absence of bonds. Two atoms can be said to bind to each other if the value of the length of the bond formed is smaller than the number of radian of the two atoms, the number of radian of Ti and O atoms is 2.24 Å.[18]

The binding of the O atom with the TiO$_2$ molecule is determined from the highest Mulliken charge of the pheophytin compound. This Mulliken charge is influenced by the distribution of electrons that gather on atoms that have high electronegativity values, in this case, is the O atom. In the pheophytin α molecule, pheophytin β and its modification have different optimum binding ways due to differences in the maximum Mulliken charge on the compound. The type of TiO$_2$ used is anatase TiO$_2$. This option happens because of the abundance of crystals type in nature.

### Table 2. Length of Dye Bonds and Modified Semiconductors

| Molecule       | Bond | Radius TiO$_2$* (Å) | Bond Length |
|----------------|------|---------------------|-------------|
| Pheophytin α   | Ti-O | 2.24                | 2.016       |
| Pheophytin β   | Ti-O | 2.24                | 1.955       |
| Cu Pheophytin α | Ti-O | 2.24                | 1.968       |
| Cu Pheophytin β | Ti-O | 2.24                | 1.978       |
| Ni Pheophytin α | Ti-O | 2.24                | 2.584       |
| Ni Pheophytin β | Ti-O | 2.24                | 2.182       |
In Table 2, it can be seen that most of the molecule can form bonds between semiconductor and dye, except for Ni Pheophytin α compound which has a bond length greater than the number of radian between Ti and O. In general, it can be concluded Pheophytin β > Cu Pheophytin α > Cu Pheophytin β > Zn Pheophytin β > Pheophytin α > Ni Pheophytin β > Zn Pheophytin α > Ni Pheophytin α. This result is related to the binding position of each dye.

**Figure 7. Pheophytin α bond length with TiO$_2$**

Based on the data that has been found, it is known that pheophytin α, pheophytin β, and some of their modifications can form bonds with TiO$_2$ semiconductors as shown in figure 7, only Ni Pheophytin α compounds cannot form bonds with semiconductors. This is proven by the difference in bond length between O atoms and Ti atoms which is smaller than total of radian of Ti and O atoms. The bond length value possessed by the modification of Cu Pheophytin α is the smallest when compared to other pheophytin modifications, smaller bond lengths will facilitate the injection of electrons from dye into semiconductors. This shows that the modification of Pheophytin β with Zn atoms is the best modification based on the bond length between dye and semiconductor TiO$_2$.

4. **Conclusion**

- The effect of adding central atoms of Cu, Ni, and Zn on the photoelectric efficiency of pheophytin α and β has varied effects, depending on the type of central atom used. There are advantages and disadvantages given by the addition of the central atom based on the parameters used.
- Based on the parameters used when viewed from the length of the central atomic bond with the best ligand are Ni Pheophytin α; the best HOMO-LUMO energy was obtained Pheophytin α with a LUMO energy value of -2.6349 eV and HOMO energy value of -4.7282 eV; the best spectra were obtained by Zn Pheophytin β with absorption at wavelengths of 386.77 nm and 536.15 nm; the best light absorption efficiency (LHE) is Zn Pheophytin β; the best coupling constant (V rp) is Cu Pheophytin α, and the best dye bond length with TiO$_2$ is Pheophytin β. Based on the above parameters the best modification for DSSC is Zn Pheophytin β > Zn Pheophytin α > Pheophytin β > Pheophytin α > Cu Pheophytin β > Ni Pheophytin α > Ni Pheophytin β > Cu Pheophytin α.

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