Band gap energy calculation of theaflavin and Cyanidin-3-Glucoside molecules as active material in Dye Sensitized Solar Cells using Density Functional Theory (DFT)

G Rizqillah¹, I Muttaqien¹, Y S Perkasa¹, M Sanjaya¹, R Ramdhani¹, H Aliah¹ and P Pitriana²*

¹Physics Department, Faculty of Science and Technology, UIN Sunan Gunung Djati Bandung, Jl. A. H. Nasution 105, Bandung, Indonesia
²Physics Education Program Study, Faculty of Tarbiyah and Teacher Training, UIN Sunan Gunung Djati Bandung, Jl. A. H. Nasution 105, Bandung, Indonesia

*pina.pitriana@uinsgd.ac.id

Abstract. Dye-Sensitized Solar Cell (DSSC) is one of photovoltaic (PV) cell which converts solar energy into electrical energy, by using dye as its active material. In this study, total energy and bandgap energy of natural dyes such as theaflavin and cyanidin-3-glucoside (C3G) molecules were calculated using density functional theory (DFT) method via quantum espresso software. Optimization of some calculation parameters such as cutoff energy, pseudopotential and k-point have been done to ensure minimum total energy of dyes molecule. Based on the result, the total and bandgap energy of theaflavin is 10172.80 eV and 1.96 eV, while the total and bandgap energy of the C3G molecule is 8442.26 eV and 1.73 eV. From these results, further investigation is necessary to the opportunities of the two dyes as DSSC sensitizers.

1. Introduction

Dye sensitized solar cells (DSSC) are devices that used to convert solar energy into electrical energy, with dye as photons absorber. DSSC introduced by Michael Gratzel and Brian O’regan in 1991 [1]. DSSC can still work effectively in low light conditions [2], and it is one of the most promising technology for the photovoltaic system.

DSSC consists of several materials such as Transparent Conducting Oxide (TCO) glass, semiconductor materials, electrolytes, counter electrodes, and dye molecules. Ruthenium based dyes are considered as the best dyes for DSSC and show the efficiency of up to 11%. However, ruthenium-based dyes have several disadvantages, its relatively high cost and harmful to the environment, because it contains some heavy metal [3]. So there necessary to search for another alternative, such as a dye from natural ingredients.

Natural dye obtained and extracted from some materials in the environment, such as fruits, vegetables, flowers, and leaves. Moreover, it is environment friendly, low cost, and we can make the dyes easily [4]. But it is generated low efficiency, so there necessary to develop some research to increase the efficiency of solar cells, with a variety of different materials, such as variations of dye [5] [6,7], electrolyte [6], and semiconductor materials [7,8]. The electronic structure of dye such as band gap energy will affect the efficiency. The electronic structure can be calculated by computational-based research. Density Functional Theory (DFT) is one of the computational methods used in analyzing the
electronic structure of a material, including dye in the DSSC system. Electronic structure research on DSSC was extensively studied using computational methods, such as research on pelargonidin dye types [5], chlorophyll [9], black tea [3], and cyanidin-3-glucoside [10].

This study aims to calculate the electronic structures of theaflavin (C_{29}H_{24}O_{12}) and cyanidin-3-glucoside (C_{21}H_{21}O_{11}). Theaflavin is a tannin compound found in black tea, which gives orange color to the tea. Theaflavins are also known to be antioxidants and anti-cancer compounds [10]. Meanwhile, cyanidin-3-glucoside is one of the anthocyanin groups that are present in some vegetables and fruit such as in eggplant, berry, black rice, and black nightshade [11].

2. Computational methods

The electronic structure of theaflavin and cyanidin-3-glucoside (C3G) molecules were computed using the density functional theory method and performed using quantum espresso v. 5.2.1 software. The molecules were drawn in gaussview software to obtain its atomic position that required in the input file (shown in figure 1). As a result, the models of electron density (orbital position) visualized using VESTA 3.0 software.

![Figure 1. Structures of; a) Theaflavin, b) Cyanidin-3-Glucoside.](image)

The calculation is divided into two stages: optimizing input file parameters (cut-off energy, k-point, and pseudopotential) and determining the electronic structure such as orbital positions, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and its band gap energy.

2.1. Parameters optimization

2.1.1. Cut-off Energy. Cut off (E_{cut}) energy is the kinetic energy used to limit the number of plane waves in the calculation. The calculated wave function has less or equal to the E_{cut} energy, thus this optimization has reduced the calculation time and computation cost [12]. In the E_{cut} optimization calculation, other parameters remain the same, such as Generalized Gradient Approximation-type (GGA) pseudopotential and k-point 0x0x0. The E_{cut} energy values ware varied at the range 30-70 Rydberg.

2.1.2. K-point. The whole character of the system can be known by describe the Brillouin Zone, which contained some k-points. The right selection of k-point will give high accuracy in the calculation. The k-point used in this study is 0x0x0, 3x3x3, and 5x5x5.

2.1.3. Pseudopotentials. In DFT, pseudopotential is an important parameter. The point of this parameter are dividing electrons into two groups in terms of their contributing significances: freezing the nucleus and the core electron together, and pseudizing the remaining valance wave function [13]. The pseudopotentials used in this study are Generalized Gradient Approximation-type (GGA) and Local Density Approximation-type (LDA).
2.2. Band gap energy calculation

After doing some optimizations, the most stable parameter is used to determine some electronic structures such as orbital positions and band gap energy of the molecules.

3. Results and discussion

3.1. Parameters optimization

3.1.1. Cut-off energy. The optimization result of the cut-off energy calculation of both molecules shown in table 1 and table 2.

| Cut-off Energy (Ry) | Total Energy (eV) | HOMO Energy (eV) | LUMO Energy (eV) | Band Gap Energy (eV) |
|---------------------|-------------------|------------------|------------------|---------------------|
| 30                  | -10170.76         | -1.03            | 0.93             | 1.96                |
| 40                  | -10172.47         | -1.03            | 0.93             | 1.96                |
| 50                  | -10172.67         | -1.03            | 0.93             | 1.96                |
| 60                  | -10172.74         | -1.03            | 0.93             | 1.96                |
| 70                  | -10172.80         | -1.03            | 0.93             | 1.96                |

Based on the result, the total energy decreased when the cut-off increased. If the system has minimum energy, the attractive and repulsive forces are balance and make the system reached their stable condition. Moreover, there is no change between HOMO and LUMO values, and then the value 70 Ry is the most stable condition thus was used in other parameters of both molecule calculation.

3.1.2. K-Points. The optimization result of k-point calculation of both molecules shown in table 3 and table 4.

| K-Point | Total Energy (eV) | HOMO Energy (eV) | LUMO Energy (eV) | Band Gap Energy (eV) |
|---------|-------------------|------------------|------------------|---------------------|
| 0x0x0   | -10172.80         | -1.03            | 0.93             | 1.96                |
| 3x3x3   | -10173.86         | -1.08            | 0.82             | 1.90                |
| 5x5x5   | -10173.86         | -1.07            | 0.81             | 1.88                |

| K-Point | Total Energy (eV) | HOMO Energy (eV) | LUMO Energy (eV) | Band Gap Energy (eV) |
|---------|-------------------|------------------|------------------|---------------------|
| 0x0x0   | -8442.26          | -3.23            | -1.50            | 1.73                |
| 3x3x3   | -8442.26          | -3.22            | -1.50            | 1.72                |
| 5x5x5   | -8442.26          | -3.22            | -1.50            | 1.72                |
The molecule contains a hundred atoms, then it has a large volume in real space but small volume in reciprocal space (Brillouin zone). Therefore, a few k-point can describe the whole system accurately [13].

From the tables, it shows that the HOMO/LUMO energy shifted because of k-point variation, so it affects the value of band gap energy. However, the total energy did not change significantly and tend to be stable.

3.1.3. Pseudopotential. The optimization result of pseudopotential calculation shown in table 5 and table 6.

### Table 5. Pseudopotentials variation of theaflavin molecule.

| Pseudopotential type | Total Energy (eV) | HOMO Energy (eV) | LUMO Energy (eV) | Band Gap Energy (eV) |
|----------------------|-------------------|------------------|------------------|---------------------|
| GGA                  | -10172.80         | -1.03            | 0.93             | 1.96                |
| LDA                  | -10176.16         | -1.27            | 0.67             | 1.94                |

### Table 6. Pseudopotentials variation of cyanidin-3-glucoside molecule.

| Pseudopotential type | Total Energy (eV) | HOMO Energy (eV) | LUMO Energy (eV) | Band Gap Energy (eV) |
|----------------------|-------------------|------------------|------------------|---------------------|
| GGA                  | -8442.26          | -3.23            | -1.50            | 1.73                |
| LDA                  | -8443.39          | -3.45            | -1.75            | 1.70                |

In the GGA functional, it captures both electron density and its gradient and usually generated a more accurate result than LDA in some cases.

Based on the tables, the LDA functional generated a lower total energy than GGA, but the bandgap energy is in contrast with the total energy. It is due to LDA has some drawbacks such as overestimates the cohesive energy on the system, that involves weak Van der Waals attraction (mainly in atoms and molecules) [13]. Therefore LDA generated the lower total energy.

3.2. HOMO-LUMO States

The calculation of HOMO and LUMO state utilize the result of the optimization before. Then we use the cutoff energy 70 Ry, k-point 0x0x0, and pseudopotential-type GGA for this calculation.

3.2.1. Orbital position. Orbital position describes the distribution of electron density in the molecular structures. The orbital positions of both molecules are shown in figure 2 (theaflavin) and figure 3 (C3G).

![Figure 2. Orbital position of theaflavin molecule; a) HOMO, and b) LUMO.](image-url)
In both HOMO and LUMO state of theaflavin molecule, the electrons distributed in the benzene-annulene structure. While in C3G molecule electrons are distributed in cyanidin structure.

3.2.2. HOMO-LUMO. The HOMO-LUMO calculation result and some related reference is shown in Table 7.

|      | HOMO (eV) | HOMO reference (eV) | LUMO (eV) | LUMO reference (eV) | Band Gap Energy (eV) | Band Gap Energy reference (eV) |
|------|-----------|---------------------|-----------|---------------------|----------------------|------------------------------|
| Theaflavin | -1.03     | -5.32               | -0.93     | -2.18               | 1.96                 | 3.13                         |
| C3G   | -3.23     | -6.438              | -1.50     | -3.570              | 1.73                 | 2.868                        |

The electronic structure of theaflavin and C3G molecules have been studied before by Kumara et. al [3] for theaflavin and Soto Rojo et. al [10] for C3G, and use for comparisons for this study. Based on the calculation in both molecules, the generated value of HOMO and LUMO larger than the references. So the bandgap value has significantly different. Kumara et. al and Soto et. al have performed the calculation within the Gaussian software package, which uses the hybrid pseudopotentials, whereas our calculation was done within Quantum Espresso software and uses LDA and GGA-types pseudopotentials. The limitation of LDA and GGA pseudopotentials is the bandgap underestimation reached up to 50% as compared with experimental data. It because of the partial removal of self-interaction in the DFT calculation [13].

4. Conclusion
The electronic structures of theaflavin and cyanidin-3-glucoside molecules were obtained through the DFT calculation method. Based on the optimization result, the most stable structure is the system with cut-off energy 70 Rydberg, K-point 0x0x0, and GGA-based pseudopotential for each molecule. The obtained bandgap energy of theaflavin is 1.96 eV and 1.73 eV for cyanidin-3-glucoside. With the bandgap energy value, either theaflavin or cyanidin were not suitable for DSSC because both molecules have a large gap that can inhibit the electron transfer of the system. Nevertheless, further investigation is necessary to the opportunities of the two dyes as DSSC sensitizers.

References
[1] Grätzel M and O’Regan B 1991 A Low-cost, High-efficiency Solar Cell based on Dye-sensitized Colloidal TiO2 Films Nature 353 737–740
[2] Shahid M, Shahid-ul-Islam and Mohammad F 2013 Recent Advancements in Natural Dye Applications: A review J. Clean. Prod. 53 310–331
[3] Kumara N T R N, Kooh M R R, Lim A, Petra M I, Voo N Y, Lim C M and Ekanayake P 2013 DFT/TDDFT and experimental studies of natural pigments extracted from black tea waste for DSSC application International Journal of Photoenergy

[4] Senadeera G K R, Kitamura T, Wada Y and Yanagida S 2005 Photosensitization of nanocrystalline TiO2 films by a polymer with two carboxylic groups, poly (3-thiophenemalonic acid) Sol. Energy Mater. Sol. Cells 88 315–322

[5] Lakshmanakumar M, Subramanian S, Jeyaprakash B G and Murugan B Combined Experimental and DFT/TDDFT Study of Berry Dye Chelated TiO2 for DSSC Applications Rasayan J. Chem. 10 1417–1423

[6] Gu P, Yang D, Zhu X, Sun H, Wangyang P, Li J and Tian H 2017 Influence of electrolyte proportion on the performance of dye-sensitized solar cells AIP Advances 7 105219

[7] Noor S, Sajjad S, Leghari S A K, Shaheen S and Iqbal A 2018 ZnO/TiO2 nanocomposite photoanode as an effective UV-vis responsive dye sensitized solar cell Materials Research Express 5 095905

[8] Retnaningsih L, Muliani L, Aggraini P N and Hidayat J 2016 The influence of material type and composition of TiO2- ZnO on manufacturing of paste for the application of DSSC J. Phys. Conf. Ser. 776

[9] Faiz M R, Widhiyanuriyawan D, Siswanto E and Wardana I N G 2017 Theoretical study on the application of natural green pigment for sensitizer in dye-sensitized solar cell (DSSC) in 2017 5th International Conference on Electrical, Electronics and Information Engineering (ICEEIE) 32–37

[10] Soto-Rojo R, Baldenbro-López J, Flores-Holguín N and Glossman-Mitnik D 2014 Comparison of several protocols for the computational prediction of the maximum absorption wavelength of chrysanthem in Journal of molecular modeling 20 2378

[11] Luo P, Niu H, Zheng G, Bai X, Zhang M, and Wang W 2009 From Salmon Pink to Blue Natural Sensitizers for Solar Cells: Canna indica L., Salvia splendens, Cowberry and Solanum nigrum L. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 74 936–942

[12] Pitriana P, Wungu T, Herman H and Hidayat R 2018 The computation parameters optimizations for electronic structure calculation of LiPbI3 perovskite by the density functional theory method IOP Conf. Ser. Mater. Sci. Eng. 434 12026

[13] Lee J G 2012 Computational Materials Science : An Introduction (Boca Raton, FL : Taylor and Francis)