Computational study of antocyanin compounds (Cyanidin and Petunidin) supported on TiO$_2$ for DSSC application potential

Adisyahputra$^*$, Nurhadini$^1$, F I P Sari$^1$, I Arief$^2$ and M A Kurniawan$^3$

$^1$Department of Chemistry, Faculty of Engineering, Universitas Bangka Belitung, Bangka, Bangka, Indonesia
$^2$Chemistry Laboratory, Akademi Farmasi Yarsi Pontianak, Jl. Panglima A’im, Pontianak, Indonesia
$^3$Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Islam Indonesia

$^*$asyah.putra0319@gmail.com

Abstract. This research predicts electronic properties (HOMO / LUMO energy diagram, UV-Vis spectrum, and the density of the HOMO / LUMO orbital) of cyanidin and petunidin organic dye compounds supported by TiO$_2$. This system is modelled by interacting dyestuff compounds with the simplest TiO$_2$ units to predict the effect of these dyes so that they can be applied in cells solar dye. A dye-sensitized solar cell is one generation of solar cells that has been widely studied to date. This solar cell uses substances colour as a sensitizer and become very interesting to be developed because of this requires low production costs but is able to produce performance pretty good. In this study computational calculations are performed using Gaussian 09W software with TD-DFT method (theory and base set B3LYP / 6-31G (d, p) for all atoms. The UV-Vis spectrum of cyanidin and petunidin compounds computed by computation light at wavelengths of 458.82 nm (cyanidin), 813.13 nm (cyanidin-TiO$_2$) and 462.35 nm (petunidin), 782.83 nm (petunidin-TiO$_2$). HOMO / LUMO energy diagram for cyanidin and cyanidin-TiO$_2$ gives band gap of 1.9203 eV and 1.458 eV, respectively. Whereas petunidin and petunidin-TiO$_2$ give band gap respectively of 1.9010 eV and 1.5477 eV.

1. Introduction

Electrical energy is primary energy that is highly needed by humans. In Indonesia, the demand for electricity is still largely produced by fossil fuel power plants such as petroleum, coal, and others. The use of fossil fuels has the potential to cause new problems in the environment, namely environmental pollution and trigger global warming. In addition, there are still many areas in Indonesia that do not yet have electricity, or about 65% of Indonesia that have not yet received electricity [1].

Therefore, we need an effective and efficient solution both in environmental aspects and ecological aspects that can provide positive value for environmental sustainability without causing damage to the earth. The development of solar cells as electricity producers has been extensively studied since 1991 [3],[4]. Solar cells are very suitable to be developed in Indonesia because Indonesia is a country that has
a tropical climate with sufficient duration of solar radiation throughout the year or known as the equatorial state.

The first generation of solar cells is a solar cell that uses silicon material, but the efficiency produced by solar cells is around 20%. In addition, the silicon used is relatively difficult to obtain, so the production of solar cells using silicon steel is not economical because the availability of silicon in nature is relatively small. The second generation of solar cells using a semiconductor polymer. The weakness of this second generation solar cell is that the production process requires sophisticated technology and substantial production costs [6].

Based on several weaknesses in the two solar cells above, a Dye Sensitized Solar Cell (DSSC) was developed which has several advantages compared to previous generation solar cells. DSSC performance is influenced by the sensitivity of the dyes used. The sensitivity of these dyes affects the optical and electrochemical properties of DSSC, such as absorption spectrum, and redox properties. The advantage of DSSC compared to the two previous solar cells is lower production costs. The weakness of the DSSC at present is that the efficiency achieved is relatively small compared to solar cells made from silicon and semiconductor polymers. This small efficiency, one of which is caused by the sensitivity of the dyes used, which until now continues to find organic dyes that are better to be applied to DSSC. Indonesia is rich in natural resources in the form of plants that produce dyes that can be taken from the leaves, bark, stems, roots and tubers. One of the dyestuff-producing compounds is a group of anthocyanin compounds such as cyanidin and petunidin [5].

In this study will be determined difference in the HOMO/LUMO energy band and UV-Vis absorption spectrum from cyanidin and petunidin compounds, as well as compounds cyanidin and petunidin which are bound to the compound TiO₂ cluster using the method of density function theory (DFT), and the method of density function theory depends time (TDDFT). Calculation computing done with using the Gaussian 09W software [2]. The HOMO and LUMO parameters are one of the parameters for determining a compound having semiconductor properties that can be used in the DSSC system[8], while the UV-Vis spectrum is a parameter that can be used to predict the ability of a compound to be able to absorb sunlight (visible light) as energy used in DSSC system[9],[10].

2. Computational Method

Hypothesis compound structures are calculated is given in figure 1. In this study calculations carried out in several stages with using the B3LYP method and base set 6-31G (d, p) [7,10]. Compound coordinates which will be calculated is optimized using the Gaussian 09W software. The first calculation is calculation using DFT method, and output the resulting will be further processed with the same software by using the TDDFT method. For DFT calculations, it is done geometry optimization, whereas for TDDFT calculations only using a single point calculation. From the TDDFT calculation results UV-Vis spectrum and HOMO - LUMO energy band difference from each compound.

![Figure 1. Structures of (a) Cyanidin, (b) Cyanidin-TiO₂, (c) Petunidin, and (d) Petunidin-TiO₂](image-url)
3. Result and Discussion

From the computational results obtained four UV-Vis spectra of each cyanidin compound, cyanidin-TiO$_2$, petunidin and petunidin-TiO$_2$. Figure 2 shows the UV-Vis spectrum of cyanidin and cyanidin-TiO$_2$ compounds.

![Figure 2. UV-Vis spectrum of cyanidin and cyanidin-TiO$_2$ compounds computed](image)

In cyanidin compounds, there are several peaks with different intensities. The highest peak is generated at an energy of 2.7023 eV (458.82 nm) with an oscillator strength of 0.0912. The second peak is generated at 2.9611 eV energy (418.71 nm) with an oscillator strength of 0.0028 and the lowest peak is generated at 2.246 eV energy (552.01 nm) with an oscillator strength of 0.0026. Whereas cyanidin-TiO$_2$ compound only produces one absorption peak which is produced at 1.5247 eV energy (813.19 nm) with an oscillator strength of 0.0326. The presence of titanium causes a shift in the wavelength in the direction of greater or smaller energy. This means that the presence of titanium can increase the ability of these dyes to absorb sunlight optimally even in weather conditions that are less hot.

![Figure 3. Electron distribution of orbital for (a) HOMO cyanidin, (b) HOMO cyanidin-TiO$_2$, (c) LUMO cyanidin, dan (d) LUMO cyanidin-TiO$_2$.](image)

In this case the consideration is the strength of the oscillator which is equivalent to the strength of light absorption by cyanidin dyes, which explains the electronic electron transition opportunity from the HOMO energy band to the LUMO (oscillator strength is 1). Free electrons in hydroxyl groups have a very high contribution to these orbitals. Meanwhile, free electrons from the hydroxyl group are then distributed throughout the molecular ring. Diagram of dominant electron distribution in the calculation of cyanidin compounds using Gaussian 09W software can be seen in Figure 3.
In petunidin compounds, there are several peaks with varying intensities. The highest peak is generated at energy 2.6816 eV (462.35 nm) with an oscillator strength of 0.1044. The second peak is generated at energy 2.9376 eV (422.05 nm) with an oscillator strength of 0.0127, and the lowest peak is produced at 2.2213 eV (558.17 nm) with an oscillator strength of 0.0006. While the petunidin-TiO$_2$ compound only produces one absorption peak which is produced at 1.5838 eV energy (782.83 nm) with an oscillator strength of 0.034. The same case also occurs with petunidin compounds in the presence of titanium can increase the ability of these dyes to absorb sunlight optimally even in less hot weather conditions.

Figure 5 shows a diagram of the electron distribution of petunidin compounds bound to the computed TiO$_2$. In the adsorbed state of TiO$_2$, the dyestuff compound shows more electrons distributed throughout the dyestuff system. The HOMO and LUMO produced are almost similar to the colour molecules. In this system, the function of the titanium atom is to stabilize the overall dyestuff system. After being adsorbed on TiO$_2$, the combined dyestuff compound and TiO$_2$ cluster have more electron density distribution. The ordering of electron density distribution is done by calculation software by looking at how close the energy levels are to the electrons that occupy the existing orbitals and virtual orbitals.
Figure 6. The computed HOMO / LUMO energy diagram from computational calculations on (a) cyanidin, (b) cyanidin-TiO$_2$, (c) petunidin, and (d) petunidin-TiO$_2$.

The energy diagram from the TDDFT calculation of cyanidin, petunidin and cyanidin compounds and petunidin bound to TiO$_2$ is shown in Figure 6. From this figure, it can be seen that the energy difference between HOMO and LUMO is reduced when cyaniding and petunidin adsorb TiO$_2$. This occurs due to the reduced stability of the HOMO when interacting with TiO$_2$ orbitals. From this figure, it is known that the location of the HOMO is in the band gap of the TiO$_2$ cluster while LUMO is in the conduction band of the TiO$_2$ cluster. Both of these are requirements for dyestuff compounds to be used in the DSSC system.

In this computational study, different energy bands are produced which can be seen in the table below. The resulting energy band difference, is the result of computational calculations performed using the TDDFT calculation method. The difference between the energy bands produced is the difference between the LUMO energy and the HOMO energy with varying values in each calculation. The smaller the value of the energy band difference, indicates that the more easily an electron moves from a lower energy level, to a higher energy level. This electron transfer can occur with the influence of temperature and sunlight irradiation, with the intensity of irradiation which is in accordance with the band gap value. Therefore, the absorption of sunlight from a dye will be determined by the size of the difference in the energy band possessed by a dye.

| Compounds       | Band gap (eV) |
|-----------------|---------------|
| Cyanidin        | 1.9203        |
| Cyanidin-TiO$_2$| 1.4585        |
| Petunidin       | 1.9010        |
| Petunidin-TiO$_2$| 1.5477        |

The band gap value of organic dyes absorbed by TiO$_2$ has a smaller value compared to the dyestuff compound, this is because it has a wider HOMO / LUMO distribution can be seen from the HOMO / LUMO distribution diagram in the previous explanation. In addition, TiO$_2$ has an important role in the dyes that are suitable for its function, namely to stabilize the overall dyestuff system, and as a
photocatalyst. Thus, organic dye compounds bound to TiO$_2$ have good potential for use in DSSC systems.

4. Conclusion
The UV-Vis spectrum of cyanidin compounds computed by computation gives light absorption at a wavelength of 458.82 nm at an energy of 2.7023 eV and an oscillator strength of 0.0912. Petunidin at a wavelength of 462.35 nm with an energy of 2.6816 eV and an oscillator strength of 0.1044. While interaction of cyanidin-TiO$_2$ at wavelength 813.19 nm with energy 1.5247 eV and oscillator strength of 0.0326 and petunidin-TiO$_2$ at wavelength of 782.83 nm with energy of 1.5838 eV and oscillator strength of 0.034. The HOMO / LUMO energy diagram of the four compounds gives a band gap of 1.9203 (cyanidin), 1.4585 (cyanidin-TiO$_2$), 1.9010 (petunidin), and 1.5477 (petunidin-TiO$_2$). From the data above, it can be concluded that these compounds are potential for DSSC applications.

References
[1] Daryanto 2012 Energi Masalah dan Pemanfaatan Bagi Kehidupan Manusia (Yogyakarta: Pustaka Widyatama)
[2] Gaussian 2009 Revision A.02 - Gaussian 09 Gaussian, Inc. Wallingford CT
[3] Brabec CJ, Sariciftci NS, and Hummelen JC 2001 Plastic Solar Cells Advanced Functional Materials 11 pp 16–26
[4] Grätzel M 2003 Dye-sensitized solar cells Journal of Photochemistry and Photobiology C: Photochemistry Reviews 4 pp 145–153
[5] Melania P, Natalia P, Ludovicus C, and Yulius DN 2018 Review: Antosianin dan Pemanfaatannya Cakra Kimia 6 pp 79-97
[6] Burgelman M, Nollet P, and Degrave S 2000 Modelling polycrystalline semiconductor solar cells Thin Solid Films 361 pp 527–532
[7] Sa’nchez-de-Armas R, Lo´pez JO, San-Miguel MA, and Fdez-Sanz J 2010 Real-Time TD-DFT Simulations in Dye Sensitized Solar Cells: The Electronic Absorption Spectrum of Alizarin Supported on TiO$_2$ Nanoclusters J. Chem. Theory Comput 6 pp 2856–286
[8] Zhang F, Ma W, Jiao Y, Wang J, Shan X, Li H, Lu X, and Meng S 2014 Precise Identification and Manipulation of Adsorption Geometry of Donor-π-Acceptor Dye on Nanocrystalline TiO$_2$ Films for Improved Photovoltaics ACS Appl. Mater. Interface 6 22359
[9] Venkatraman V, Yemene AE, and De Mello J 2019 Prediction of Absorption Spectrum Shifts in Dyes Adsorbed on Titania Scientific Reports 916983
[10] Pastore M, Selloni A, Fantacci S, and De Angelis F 2014 Electronic and Optical Properties of Dye-Sensitized TiO$_2$ Interfaces Top Curr Chem

Acknowledgement:
We gratefully acknowledge the funding from Universitas Bangka Belitung through the RKAKL FT for the publication of this paper.