Computational Study of Anthocyanin as Active Material in Dye-Sensitized Solar Cell

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Abstract. Computational calculations for anthocyanin (anthocyanidin-3-monoglucoside) compounds were performed to get structure and electronic properties from the three of anthocyanin which has potential as active material in the dye-sensitized solar cell. The calculations use Density Functional Theory (DFT) with B3LYP functional and 6-31G(d) for ground state geometry optimization and Time Dependent-Density Functional Theory (TD-DFT) for excited states single point calculation. All the calculations were conducted in the gas phase. Geometry optimization calculations show that structures of anthocyanin compounds are not planar. Single point calculation for excited states shows absorption wavelength is shorter than experimental data, with a difference between 7.3% to 8.3%. The density of HOMO-LUMO is spread only on anthocyanidin part. The LUMO density of the three compounds is mostly in the anchoring group. In terms of excitation energy from the composition of excitation and distribution of HOMO-LUMO, cyanidin-3-monoglucoside shows better potency as active material in dye-sensitized solar cells.

1. Introduction

Anthocyanins are blue, purple, and red pigments in some plant tissues. Anthocyanins are found in different chemical structures, depending on the pH of the solution. At very acidic pH, anthocyanin is mostly in the structure of the cavity flavilium which gives a purple and red color [1]. Naturally, anthocyanins always in anthocyanidin compounds bound to the glycoside group [2]. Anthocyanidin compound is the main differentiator of the type of anthocyanin beside to the glycoside group. Some of anthocyanidins found in nature are cyanidin, petunidin, and malvidin [3]. The structure of the three compounds is shown in Fig. 1.

Anthocyanin is antioxidant agent because it has the capacity to break free radical. This ability is breaking free radical causing by conjugated in anthocyanin structure. The conjugated structure makes anthocyanin can be applied as active material in a dye-sensitized solar cell. In the last decades, there is many research using anthocyanin from extracts of some plants to be applied in the dye-sensitized solar cell [4],[5],[6],[7],[8]. However, using extract anthocyanin from plant still give low conversion efficiency. The low efficiency because using the raw anthocyanin extract from the plant. The real
potency of anthocyanin as active material in a dye-sensitized solar cell can be known through computational calculation.

![Figure 1](image_url). Structure of three natural anthocyanidins.

Some natural anthocyanins were calculated and analyzed computationally. Anthocyanidin as part of anthocyanin has been extensively studied computationally. Some researchers have investigated the antioxidant properties of anthocyanidins [9],[10]. There are several researchers have studied anthocyanidin as active material in dye-sensitized solar cells. Mohr et al (2015) have been studied pelargonidin computationally as active material in dye-sensitized solar cells using B3LYP/STO-3G for ground state and TDSCF-DFT B3LYP/STO-3G for excited state in gas phase and acetonitrile solution [11]. Obasuyi et al (2019) have been studied cyanidin, delphinidin, and pelargonidin computationally as active material in dye-sensitized solar cells using MN12SX/6-311+G(d,p) for ground state and excited state in the gas phase [12]. All the computational calculations before only for anthocyanidin part from anthocyanidin. There is no computational study about anthocyanin, anthocyanidin bond to a glucoside, as material active in dye-sensitized solar cell, so this study about Computational Study of Anthocyanin as Active Material in Dye-Sensitized Solar Cell. The computational calculation was performed to get stable structure and electronic properties from anthocyanins and to predict anthocyanin with good potency as active material in dye-sensitized solar cells.

2. Methodology

Computational calculation using DFT (Density Functional Theory) for geometry optimization and TDDFT (Time-dependent Density Functional Theory) for excited state. Both of the calculation using functional B3LYP and basis set 6-31G(d). Geometry optimization have done for three anthocyanin compounds (anthocyanidin-3-monoglucoside): Cyanidin-3-monoglucoside, Petunidin-3-monoglucoside, and Malvidin-3-monoglucoside. Calculation for geometry optimization and excited state are in gas phase. The output data of Optimized geometry is a three-dimensional structure and energy gap. The output excitation state calculation data are excited energy, exciting composition, absorption wavelength, and HOMO-LUMO density.
3. Results and Discussion

3.1 Optimized Structure
Geometry optimization was carried out for anthocyanins structure in the gas phase. The optimized structure of anthocyanin compounds is in nonplanar structure. The presence of a hydroxy group substitution on the phenyl ring increase bond lengths of R12,13 and R13,14 about 0.008-0.009 Å. Substitution of hydroxy and methoxy groups after substituted by hydroxy groups reduce the bond length of R12,13 and increase the bond length of the R13,14. The structure of anthocyanin with numbering shown in Fig. 2. The optimized structure of the three anthocyanin compounds can be seen in Fig. 3.

![Figure 2. Structure of anthocyanin with numbering.](image)

![Figure 3. Optimized structure of anthocyanin: cyanidin-3-monoglucoside (a), petunidin-3-monoglucoside (b), and malvidin-3-monoglucoside (c).](image)

3.2 Excited energy and excited composition
Anthocyanin has a conjugated structure in the anthocyanidin section so that the excited energy comes from the excitation of electrons from the p orbitals to the p * orbitals. Conjugated structure of anthocyanin has a extension (consisting of several double bonds) so that the excitation energy becomes lower and be in visible wavelength area. The excited energy and the composition of first-level excitation anthocyanin (Table 1) shows that the first-level excitation of the anthocyanin compound occurs in more than one excitation process. There is a variation in the percentage value of
the first-level excitation composition in the gas phase of the anthocyanin compound. Cyanidine-3-monoglucoside has dominant excitation from HOMO to LUMO while Petunidin-3-monoglucoside and malvidin-3-monoglucoside have dominant excitation from HOMO-1 to LUMO. The main excitation for electron transfer in solar cells is excitation from HOMO to LUMO. 

**Table 1. Excited Energy and first-level excitation composition**

| Molecule                   | Gas Phase | E (eV) | Excitation Composition       |
|----------------------------|-----------|--------|------------------------------|
| Cyanidin-3-monoglucoside   |           | 2.565  | H-2→L (8.36%)                |
|                            |           |        | H→L (91.79%)                 |
| Petunidin-3-monoglucoside  |           | 2.538  | H-1→L (69.80%)               |
|                            |           |        | H→L (28.61%)                 |
| Malvidin-3-monoglucoside   |           | 2.537  | H-1→L (73.52%)               |
|                            |           |        | H→L (25.25%)                 |

### 3.3 Absorption wavelength
Calculation of excited state provides data of the maximum wavelength or wavelength of first-level absorption. Wavelength and oscillator strength in Table 2, it can be seen that the wavelength from computational calculation has lower than the experimental results. This is caused by calculation of excitation state in a gas phase while for experiments [13], [14], [15] is in methanol-HCl and ethanol-HCl solution. It seems that the basis set for calculation is less able to calculate electron in delocalized system, but overall the data of absorption wavelength is consistent. The similarity between the difference between calculations and experiments, it can be assumed with the similarity of the deviation, increasing basis set and/or the level of theory, will improve the quality of the absorption wavelength determination, as well as for the three molecules.

**Table 2. Absorption (λ<sub>max</sub>) and Oscilattor Strength (f) Anthocyanin**

| Molecule                   | Theory | Exp | Difference Shift |
|----------------------------|--------|-----|-----------------|
|                            | λ<sub>max</sub> (nm) | f   | λ<sub>max</sub> (nm) |
| Cyanidin-3-monoglucoside   | 483.44 | 0.4247 | 527 | -8.3 |
| Petunidin-3-monoglucoside  | 488.46 | 0.1603 | 527 | -7.3 |
| Malvidin-3-monoglucoside   | 488.64 | 0.1496 | 531 | -8.0 |

### 3.4 HOMO-LUMO density
The results of excited-state calculation produce energy possessed by each energy level in anthocyanin molecular orbitals. The highest energy level of a molecular orbital filled with electrons is called HOMO and the lowest energy level of an unfulfilled molecular orbital is called LUMO. HOMO-LUMO density qualitatively shows the ease excitation can occur. The density of HOMO, LUMO, and LUMO + 1 of the three anthocyanin compounds (Fig. 4) show the distribution of HOMO, LUMO, and LUMO + 1. The density of HOMO, LUMO and LUMO + 1 is only in anthocyanin part, but it is not in glucodise group, so that the part of the molecule that will be excited is the anthocyanin part. For the three anthocyanin compounds, HOMO and LUMO overlap. This is good because this compound will easily excitation if it is energized (in the form of light).

The LUMO density for three compounds is in the anchoring group (Fig. 3). For anthocyanins, the anchoring group is a hydroxy (OH) group. Anchoring group is a group of dyestuff molecules that are bound directly to the semiconductor. When LUMO spread in the anchoring group, it will facilitate the transfer of electrons from dye to the semiconductor. The LUMO level of the dye must have a value
that does not differ greatly from its semiconductor in order to minimize the energy lost during excitation [16].

![HOMO and LUMO density anthocyanin](image)

**Figure 4.** Display of HOMO and LUMO density anthocyanin.

### 4. Conclusion

Based on computational calculations performed on anthocyanin compounds in a gas phase state, the structure of anthocyanin compounds (3-monoglucosides) is in nonplanar. The distribution of HOMO-LUMO anthocyanin compounds (3-monoglucoside) is in the anthocyanidin part only. In terms of the energy gap, excitation energy, excitation composition, and distribution of HOMO-LUMO anthocyanin compounds show better potential as active material in dye-sensitized solar cells, cyanidin-3-monoglucoside.

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