Metal-pigment complex derived from natural dye of anthocyanin: a potential candidate for DSSC photosensitizer

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Abstract. This research is aimed to synthesize iron-pigment complex of anthocyanin extracted from the peel of red dragon fruit (Hylocereus polyrhizus). The targeted iron-complex was then evaluated to confirm its potential use as photosensitizer on Dye Sensitize Solar Cell (DSSC). The electronic absorption spectrum of the red dragon fruit extract showed a broad band spanning from 400 nm to 600 nm and a band maximum at 533 nm. This band was then evaluated to find out the energy of electronic transition; an excitation from highest occupied molecular orbital (HOMO; valence band) toward lowest unoccupied molecular orbital (LUMO; conduction band). The calculation resulted in the equivalent energy level of 1.98 eV for HOMO, and 4.48 eV. These values represent the energy gap (Eg) for sensitizer on DSSC. Furthermore, evaluation of electronic transition of iron complex reveals that there is an increase of absorption coverage range, due in particular the blue shift of the conduction band. These characteristics are supporting evidences that the iron-anthocyanin complex is a good candidate for sensitizer of DSSC.

Keywords: iron-pigment complex; anthocyanin; photosensitizer; energy gap

1. Introduction
Since a report by Grätzel [1] research and development of technologically new generation of solar cell, called dye-sensitized solar cell (DSSC), are numerous. Unlike the conventional system the DSSC makes use of dye as a sensitizer that functions to transfer electron into working electrode made up from semiconductor materials such as TiO2. This type of solar cell has competitive advantages over silicon-based one [1, 2].

The total efficiency of solar energy conversion to electricity is affected by several factors. First one is the type and morphology of semiconductor as working electrode (anode); so far, the best choice of semiconductor is made of TiO2 although there are other wide-gap oxides available such as ZnO and Nb2O5. The second factor is the choice of dye. Based on efficiency of absorbed photon (solar ray) and durability of dye the ruthenium complex, called N3 dye, is the best choice so far [3-6].

Recently, however, there are reports of N3 derivatives that have better characters than N3 one [7]. Unfortunately, this advantage property has no immediate effect to the total cell efficiency because of some other parameters that have to be improved [8]. In addition, there is idea to possibly redesign by combining the dyes that have high flexibility in optimizing the absorbed intensity and coverage range. The report succeeded in synthesizing dimer complex, a N3 derivative. This complex has a side group consisting of extended π-conjugation that shows absorbance with high intensity and wider coverage range. The total efficiency of this complex is relatively good and comparable to the conventional dye [9, 10].
The use of synthetic dyes as describe above provides prospective hope, but it raises another concern, namely the cost of fabrication. To minimize the cost there are researches to make use of natural dye from tropical plants, instead of synthetic one. Natural dyes extracted from red cabbage [11], bedana panicagranatum [12], mangosteen pericarp [13], and red dragon fruit [14] have been used in DSSC. Unfortunately, the performance of these dyes is not better than the synthetic ones, so far. In attempt to enhance the performance of these dyes as photosensitizer on DSSC, iron-pigment complex of anthocyanin was synthesized from the extracted of the peel of red dragon fruit (Hylocereus polyrhizus). The targeted iron-complex was then evaluated to confirm its potential use as photosensitizer on Dye Sensitize Solar Cell (DSSC).

2. Experimental Methods

2.1. Dye extraction.
Anthocyanins were extracted from red dragon fruit (Hylocereus polyrhizus). Peelings of red dragon fruit was crushed and juiced by a macerating juicer. The juiced was mixed with 1:1 methanol (99%) and filtered to remove proteins. The resulting suspension was centrifuged for 15 minutes at 1000 rpm. The supernatant was filtered using Whatman No. 1 filter paper, followed by reducing volume under reduced pressure at 40°C to obtain dark red extract solution. The electronic absorption of this extract shows \( \lambda_{\text{max}} = 536 \text{ nm} \) (in water) and 533 nm (in methanol).

2.2. Synthesis of anthocyanin complex.
About 100 mL extract solution was charged into erlenmeyer, and 20 mg (0.5 mmol) FeCl\(_3\cdot\text{xH}_2\text{O}\) was added little by little into the mixture. The reaction mixture was then stirred in the dark for 2 hours, and filtered to remove any unreacted materials. The solvent is then evaporated under reduced pressure to accomplish red yellowish solid. UV-Vis: \( \lambda_{\text{max}} = 350 \text{ nm} \) (in methanol).

2.3. Computational detail.
The geometry of anthocyanins and its iron complex was optimized using the DFT method at B3LYP/LanL2DZ level of theory. The polarized continuum model (PCM) was used to calculate the solvent effects. To assess the frontier molecular orbitals and energy gap of anthocyanins, the re-optimization of the structure was not performed on the solvent because it had little effect on the energetic so that it was sufficient to use single-point calculations on gas-phase geometries [15-19]. All theoretical calculations are performed with the Gaussian 03 package [20].

3. Results and Discussions
Table 1 shows UV-Vis maximum absorption bands of extract solution of anthocyanin in water and methanol. The bands are not typically sensitive to the polarity of the solvent; an indication of localized transition. The profile of spectra indicates a broad bands spanning from 400 nm to 600 nm with \( \lambda_{\text{max}} \) centred at 533 nm (in methanol) or 536 nm (in water). These broad bands consist of several overlapping transitions which are not able to be resolved, but all transitions involve localized transitions.

| Table 1. UV-Vis absorption data of extract solution of anthocyanin. |
|-----------------------------|------------------|
| Solvent          | Absorption maximum \( \lambda_{\text{max}}, \text{nm} \) |
| Water           | 536              |
| Methanol        | 533              |

The electronic absorption edge (\( \sigma \)) is a function of photon energy, and obeys Mott’s and Davis’s model [21]. A linear plot of \( (\sigma h\nu)^{1/2} \) versus \( h\nu \) results in energy level of the transition as illustrated in figure 1 for \( E_g \) analysis using “Touch Plot” method.
Figure 1. Linear plot of \((\sigma \nu)^{1/2}\) versus \(\nu\) from lower tail absorption spectrum.

Figure 2. Linear plot of \((\sigma \nu)^{1/2}\) versus \(\nu\) from higher tail absorption spectrum.

Figure 1 shows that the linear plots produce lower energy level (HOMO) center at 1.98 eV. From figure 2 indicates that the next higher energy level (LUMO) is 4.48 eV. Evaluation of these two energy values reveals an optical band gap 2.50 eV as shown by figure 3.
Figure 3. Linear plot of \((ahv)^{1/2}\) versus \(hv\) from metal-pigment complex spectrum absorption.

The data in table 2 indicates that there is a change in terms of absorption coverage range in which the iron mixture shows broader absorption range, i.e. 300–600 nm, as compared to that of pure extract. In addition, there is also a blue shift of absorption maximum for the mixture. These evidences support the notion that the iron complex mixture of anthocyanin is a good candidate for sensitizer in DSSC.

| Table 2. Comparison of UV-Vis absorption data of extract and that of iron mixture in methanol. |
|---------------------------------------------------------------|
| Absorption range | Anthocyanin extract | Iron-anthocyanin complex |
|------------------|---------------------|--------------------------|
|                  | 450 nm–650 nm       | 300 nm–600 nm            |
| Absorption maximum | 533 nm             | ~350 nm                  |

Furthermore, theoretical study is applied to assess the molecular frontier of orbital from anthocyanins and its iron complex. Anthocyanins can be neutral molecules, or positive carbocations depend on pH and solvents. In this study, ethanol was used as a solvent in complex formation so that anthocyanins are expected to be protonated to form carbocations. This positive carbocation condition makes Fe\(^{3+}\) to be bound to the outer benzene ring position as previously reported [22].

Figure 4 shows the visualization of molecular orbitals from anthocyanins and their complexes represented by cyanidin as the major anthocyanin content of red dragon fruit [23]. In orbital HOMOs, electron densities are distributed evenly on the anthocyanin surface whereas in orbital LUMOs similar trend was found. This condition shows that anthocyanins act as electron donors and at the same time as electron acceptors from iron (back donations). There was a decrease in energy gap value between free anthocyanins compared to anthocyanin iron complex. This result is in accordance with the results of the experimental study conducted. In conclusion, the iron-anthocyanin complex has better potential as a photosensitizer for DSSC than free anthocyanins.
Figure 4. Optimized geometries and HOMO-LUMO orbitals of anthocynin and its iron complex.

4. Conclusion
Extraction of red dragon pericarp results in red solution mixture which has electronic absorption spanning from 400 nm to 600 nm centred at 533 nm (in methanol) or 536 nm (in water). The spectrum is not typically influenced by the polarity of the solvent, an indication of fully localized transition. Evaluation of this transition reveals the transition has an optical band gap ($E_g$) 2.50 eV using “Touch Plot” method. The incorporation of iron into the extract results in complex mixtures that have better optical characteristics. It is important to note that the valence band and the conduction band of the iron mixture show a broader energy gap, and these energy levels fit within $E_g$ value of TiO$_2$, a semiconductor used for DSSC apparatus. So, the iron-anthocyanin complex may serve as a good candidate for sensitizer in DSSC.

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