Computational calculation potency of petunidin and peonidin as photosensitizer in dye-sensitized Solar Cell

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Abstract- Computational calculations for two compounds of anthocyanidin group, petunidin and peonidin have been conducted in ethanol phase. Purpose of this calculation is to get optimized geometry and electronic properties from petunidin and peonidin, which have potency as photosensitizer in dye-sensitized solar cell. The calculations were done for ground state and excited state. Ground state geometry optimization were using Density Functional Theory (DFT) and excited state single point calculation were using Time Dependent-Density Functional Theory (TD-DFT). All the calculations used B3LYP functional and 6-31G(d) as basis set. All the calculations were conducted in ethanol phase. Geometry optimization calculations show that the optimized structure of two anthocyanidins are same. Petunidin and peonidin has planar structure. Petunidin absorption wavelength is same with peonidin's. The display of HOMO-LUMO of petunidin and peonidin are spread throughout in molecule. LUMO is only in one anchoring group, hidroxy (-OH). Based on electronic properties and HOMO-LUMO display, both of petunidin and peonidin has potency as photosensitizer for applying in dye-sensitized solar cell (DSSC).

Index Terms- DFT, DSSC, Ethanol, Petunidin, Peonidin.

I. INTRODUCTION

Renewable energy is the promising source of energy for the future. One of renewable energy is solar cell. Solar cell which use an organic dye is called dye sensitized soar cell. Anthocyanin is one of organic dye which found in plant tissue such as fruit, leaves, pericap. Anthocyanin consists of anthocyanidin and glycoside. Anthocyanidin has conjugated structure that gives color to anthocyanin. The color is determined by functional group bond to anthocyanidin. Petunidin and peonidin are anthocyanidin which found naturally [1]. The structure of petunidin and peonidin are shown in Figure 1.

Petunidin and peonidin are antioxidant [2] because have potential break radical. Besides for health issue as antioxidant, petunidin and peonidin can be used in renewable energy field as photosensitizer in dye-sensitized solar cell. There are research use petunidin and peonidin which applied in dye-sensitized solar cell experimentally. Kimura *et* al. (2017) [3] use pure petunidin 3-O-glucoside as sensitizer in DSSC and give high conversion efficiency about 1.42 %. Sinopoli, *et* al. (2017) [4] investigated peonidin and other anthocyanidins for DSSC in water as solvent and get conversion efficiency about 1.05 %. The low conversion efficiency of petunidin and peonidin encourages computational calculations to be carried out to determine the real potency this two compound as photosensitizer in dye-sensitized solar cell.

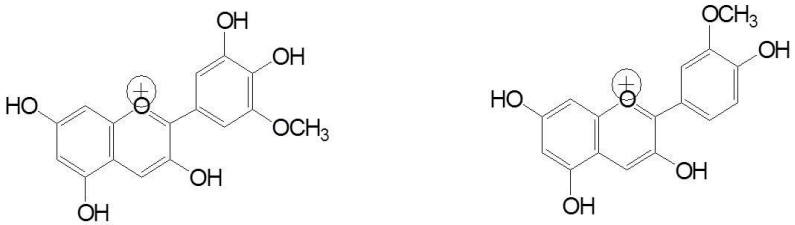


Fig. 1. Structure of petunidin (a) and peonidin (b).

Petunidin and peonidin were calculated and analyzed computationally before. Most of computational calculation for investigating petunidin and peonidin for its antioxidant properties [5,6]. There is research have studied petunidin and peonidin as photosensitizer in dye-sensitized solar cells. Sinopoli, *et* al. (2017) have been investigated peonidin and other anthocyanidins computationally too as photosensitizers in dye-sensitized solar cells computationally using B3LYP/6-31G(d,p) for ground state and TD-DFT B3LYP/6-31G(d,p) for excited state in gas phase and water [4]. Recent, there is no computational study of petunidin and peonidin in ethanol

phase as photosensitizer for application in dye-sensitized solar cell, so this research about computation calculation of petunidin and peonidin in etanol as photosensitizer in Dye-Sensitized Solar Cell. The computational calculation were conducted to get stable structure, electronic properties and also to predict which one from petunidin or peonidin, give better potency as photosensitizer in dye-sensitized solar cells.

II. METHODOLOGY

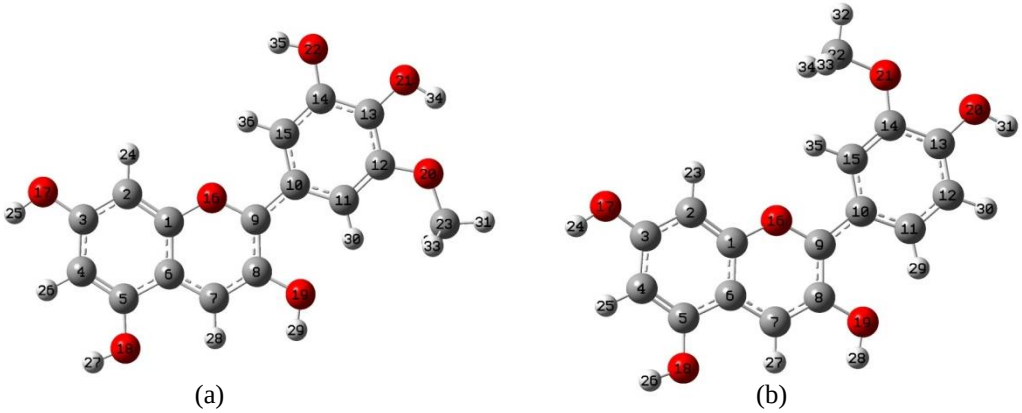
Computational calculation using DFT (Density Functional Theory) for geometry optimization and TDDFT (Time-dependent Density Functional Theory) for excited state. Both of the calculation using functional B3LYP and basis set 6-31G(d). Geomtery optimization have done for petunidin and peonidin in cation form. Geometry optimization and excited state are in ethanol phase using the polarizable continuum model (PCM).

III. RESULT AND DISCUSSION

3.1. Optimized geometry

Petunidin and peonidin have same backbone, namely flavilium. The only difference between these two compounds is the functional group attached to one of the phenyl rings of the structure. In petunidin, there are two hidroxyl (-OH) and one methoxy (-OCH_3) bond to phenyl ring. In peonidin, there are one hidroxyl (-OH) and one methoxy (-OCH_3) bond to phenyl ring. In acidic condition, that backbone become cation flavilium. Optimized geometry of petunidin and peonidin are shown in Figure 2.

The different functional group between petunidin and peonidin causing different bond length and bond angle of both them. Bond length $R_{9\text{-}10}$ for petunidin and peonidin are same, this indicated that the substitution of functional group is not affect atom which not bond direct to it. Bond length $R_{13\text{-}14}$ for peonidin is shorter than petunidin about 0.015 Å. Whereas bond length $R_{12\text{-}13}$ for peonidin is longer than petunidin. The bond angle of three atom $A_{12\text{-}13\text{-}14}$ for peonidin is greater than petunidin about 0.035°. Based of dihedral data, petunidin and peonidin are planar, because dihedral about 0°. Optimized geometry parameter for petunidin and are shown in Table 1.



(a) (b)

Figure 2. Optimized geometry of petunidin (a) and peonidin (b).

Table 1. Optimized geometry parameter petunidin and peonidin

Molecule	Phenyl rings				
	Bond length (Å)			Bond angle (°)	dihedral (°)
	$R_{9,10}$	$R_{12,13}$	$R_{13,14}$	$A_{12,13,14}$	$D_{16,9,10,15}$
Petunidin	1.4442	1.4111	1.4075	119.661	0.0
Peonidin	1.444	1.3963	1.4237	119.696	0.0

3.2. Electronic properties

3.2.1. Chemical descriptors

Chemical descriptors (Table 2) are HOMO energy and LUMO energy which use to calculate other electronic properties from petunidin and peonidi such as ionization energy (I), affinity (A), energy gap (Egap). Over all, number of petunidin and peonidin are same each other.

Table 2. Chemical descriptor

Molecule	HOMO (eV)	LUMO (eV)	I= -EHOMO (eV)	A= -ELUMO (eV)	Egap (eV)	η=(I-A)/2	μ= -(I+A)/2	ω= $\mu^2/2\eta$
Petunidin	-5.981	-3.309	5.981	3.309	2.672	1.336	-4.645	8.074
Peonidin	-6.039	-3.287	6.039	3.287	2.752	1.376	-4.663	7.902

3.2.2 Vertical excitation

Vertical excitation can be investigated from transition energy and transition percentage. Lower transition energy means easier electron movement to higher energy level. Transition energy of petunidin and peonidin are similar about 2.5 eV. Petunidin and peonidin have absorption wavelength that almost same, differences is just about 8 nm. Transition from HOMO to LUMO for this two molecules has same number about 93%. Petunidin in its absorption wavelength has two vertical excitation types, HOMO to LUMO and HOMO-2 to LUMO. Peonidin has three vertical excitation types, HOMO to LUMO, HOMO-1 to LUMO, and HOMO-2 to LUMO. The first vertical excitation parameter are shown in Table 3.

Absorption wavelength of petunidin and peonidin from calculation are shorter than wavelength from experiments. Absorption wavelength from experiment for petunidin and peonidin respectively about 530 nm and 538 nm [7] whereas from calculation are 503 nm and 495 nm. This different number of wavelength causing by different phase are used. The experiment used methanol-HCl phase while calculation are in ethanol phase.

Table 3. The first vertical exxcitation parameter.

Molecule	λ (nm)	*f*	Transition precentage	Transition Energy (eV)
Petunidin	502.57	0.695	HOMO→LUMO (93%)	2.467
			HOMO-2 → LUMO (7%)	
peonidin	494.90	0.623	HOMO→LUMO (93.4%)	2.505
			HOMO-1→LUMO (3%)	
			HOMO-2→LUMO (3.6%)	

3.3. HOMO-LUMO display

The display of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown in figure 3. The display of HOMO and LUMO shows how density of molecular orbital for each molecule spread. HOMO of petunidin and peonidin spread in entire backbone molecule. LUMO of two molecules are overlap with HOMO. The display of LUMO for petunidin and peonidin spread in entire backbone molecule too. Overlap between HOMO and LUMO make electron can excitation easily, but reverse process difficulty. LUMO of petunidin and peonidin are just in on hydroxy, as anchoring group. The anchoring group is functional group which bond directly to photoanode. The HOMO of petunidin and peonidin overlaps with the LUMO, only in hydroxy (-OH). This overlap indicates the ease of electron transfer from the photosensitizer to the anode.

3.4. Infrared spectrum

Infrared spectrum of petunidin and peonidin are almost same (Figure 4). There are peak at ~ 3700 cm^{-1} refers to stretch C-O for alcohol. This number is shifting from experiment [8], which alcohol stretching vibrations can be observed in the ranges of 3600 cm^{-1}-3200 cm^{-1} and 1700 cm^{-1}-1565 cm^{-1}. The shifting phenomenon because in experiment petunidin and peonidin was mixed together with other anthocyanidins in raw extract. Peak for C=C aromatic about ~ 1450 cm^{-1} and for C-H benzene about 300 cm^{-1}. Petunidin has a sharp peak at about ~1200 cm^{-1}, refers to stretch C-O (eter) which C-O-C.

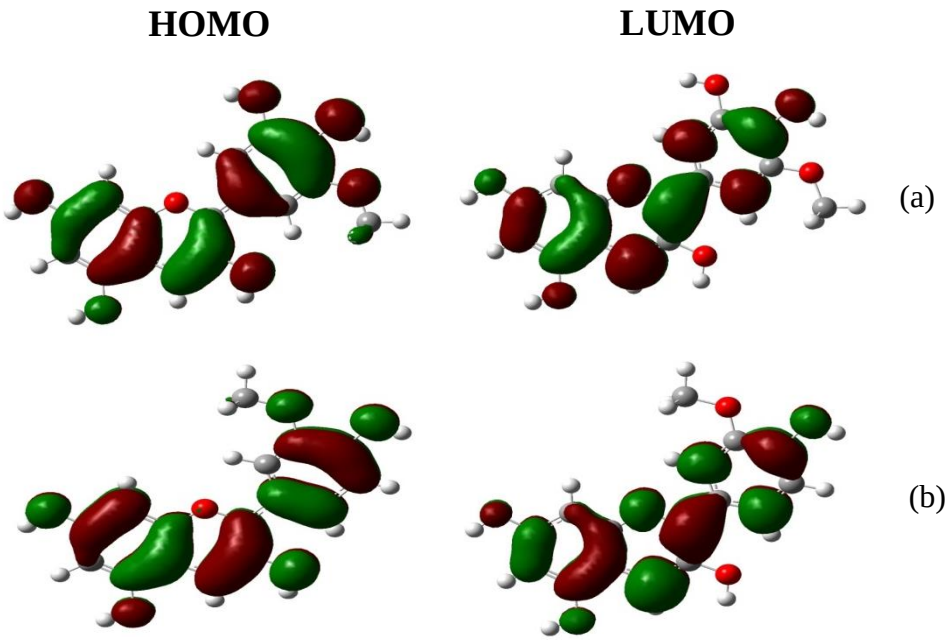


Figure 3. The display HOMO LUMO of petunidin (a), and peonidin (b)

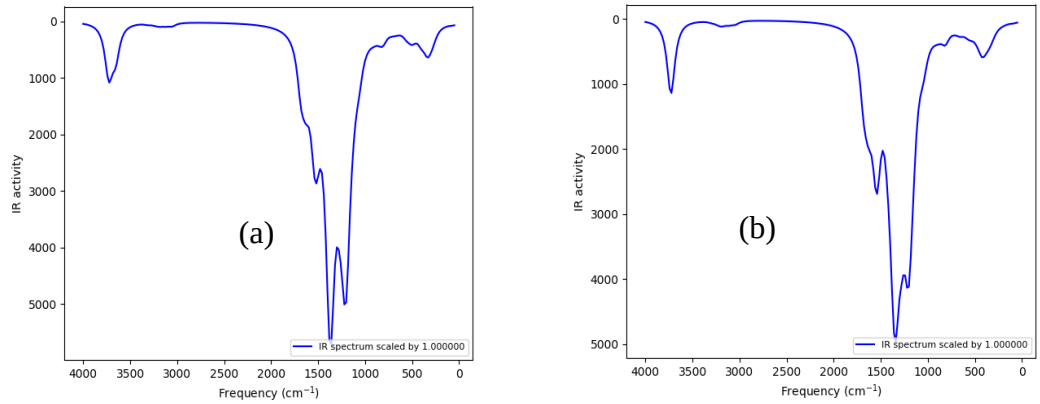


Fig. 4. The infrared spectrum of petunidin (a), and peonidin (b)

IV. CONCLUSION

Based on DFT calculation geometry optimization, both of petunidin and peonidin has planar structure. Based on excitation energy, excitation composition, and display of HOMO-LUMO, both of molecules, petunidin and peonidin have potential as photosensitizer for applying in dye sensitized solar cell.

REFERENCES

[1] R. Prior, X. Wu, G. Beecher, J. Holden, D. Haytowitz, S. Gebhardt. "Concentration of Anthocyanins in Common Foods in The United States and Estimation of Normal Consumption" *J. Argic. Food Chem, 54, 4069-4075, 2006.*

[2] L. Zhou, M. Xie, F. Yang, F. Liu. Antioxidant activity of high purity blueberry anthocyanins and the effects on human intestinal microbiota. *LWT - Food Science and Technology, 117, 108621, 2020.*

[3] Y. Kimura, T. Maeda, S. Iuchi, N. Koga, Y. Murata, A. Wakamiya, K. Yoshida. Characterization of dye-sensitized solar cells using five pure anthocyanidin 3-O-glucosides possessing different chromophores. *Journal of Photochemistry and Photobiology A: Chemistry, 335, 230-238, 2017.*

[4] A. Sinopoli, I. Citro, G. Calogero, A. Bartolotta. Combined experimental and DFT-TDDFT investigation on anthocyanidins for application in dye-sensitised solar cells. *Dyes and Pigments, 143, 291-300, 2017.*

[5] V. K. Rajan, C. Ragi, K. Muraleedharan. A computational exploration into the structure, antioxidant capacity, toxicity and drug-like activity of the anthocyanidin "Petunidin". *Heliyon, 5*, e02115, (2019).

[6] V. K. Rajan, C. K. Hasna, K. Muraleedharan. The natural food colorant Peonidin from cranberries as a potential radical scavenger – A DFT based mechanistic analysis. *Food Chemistry, 262, 184-190, 2018*.

[7] [7] L. Cabrita and Ø. M. Andersen. Anthocyanins in blue berries of Vaccinium padifolium. *Phytochemistry, 52, 1693 -1696, 1999*.

[8] [8] I. Sen, B. Ozturk, F. Tokatli, B. Ozen. Combination of visible and mid-infrared spectra for the prediction of chemical parameters of wines. *Talanta, 161, 130-137, 2016*.

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