THE MODIFICATION OF CYANIDIN BASED DYES TO IMPROVE THE PERFORMANCE OF DYE-SENSITIZED SOLAR CELLS (DSSCs)

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ABSTRACT

Dye-Sensitized Solar Cells (DSSCs) are efficient and stable solar cells to be used along with the development of solar cells. Dyes have an important role in DSSCs and studies on D- π -A (Donor- π -conjugate-acceptor) type of dyes are growing recently in which modifications on donor chain, π -conjugated chain, acceptor chain and the addition of electron-withdrawing/donating groups can be performed to find organic dyes that have more potential to absorb lights. The results showed that the π -conjugated chain variation of dye 3 has the smallest band gap i.e. 1.5344 eV and 809.7 nm value of excitation wavelength. On the variation of donor chain, dye 10 has smaller band gap i.e. 1.1153 eV with 1114.0 nm of excitation wavelength and 0.9523 of total LHE. C₄H₅ electron-withdrawing group on dye 6 produced an effect by decreasing 1.0204 eV of band gap which smaller than the sensitizer without the electron-withdrawing group, whereas the effect of NO₂ electron-donating group on dye 6 produced 1.105 eV of band gap value which smaller than the dye without the electron-withdrawing cluster. Sensitizer 17 as the combination of the addition of electron withdrawing and donating groups produced the smallest band gap in the amount of 0.8873 eV. The addition of electron-withdrawing and donating group were able to decrease the band gap of dyes. HOMO and LUMO countours describe the electron density found in organic molecules of dyes. The HOMO countour is located in the donor area and the LUMO countour is located in the acceptor area. Based on the results of this study, it can be concluded that dye 17 is more potential as a sensitizer in DSSCs.

Keywords: Cyanidin, D- π -A Type, DFT, DSSCs

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INTRODUCTION

Dye-Sensitized Solar Cells (DSSCs) are the topic of research that studied intensively by many in recent years as sustainable and eco-friendly energy by improving the efficiency of power conversion. More studies performed upon DSSCs since its first discovery in 1991¹, because the needs for energy from year to year are increasing as the population increases.

Sensitizers in DSSCs play a role in increasing the efficiency of light absorption. Increasing the efficiency of light can be performed with a modification of the organic and inorganic dyes are commonly used as sensitizers.² There has been a lot of development on inorganic sensitizers, i.e Rhutenium³, Gallium⁴, Ferrum⁵, zinc⁶, cuprum⁷, cobalt⁸-based complexes. The previous study which used dyes from the ruthenium polypyridine complex showed that the conversion efficiency values obtained were greater than 11% which are very well used for DSSCs. However, DSSCs based on Ruthenium dyes from ruthenium sources are limited and producing impact toward the environment.³ While a study on the zinc porphyrin complex also produced good efficiency toward DSSCs, however, the zinc porphyrin complex sensitizer has issues on low synthesis results and its toxic raw materials for synthesis.⁶

Metal-free organic sensitizers have been developed in recent years which have the desired advantages of low cost, economical, good flexibility, high molar coefficient and produce no impact on the environment.⁹ Research in computational about organic dyes on solar cells is developing now is the use of organic dye with a system of D- π -A (Donor- π conjugated-Acceptor) with the capability of absorption efficiency of light which is good because the effect of the push-pull.¹⁰ One of the organic dyes is anthocyanin.

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Anthocyanin is a family of flavonoids, found in many fruits, flowers, leaves, and roots with various colors.¹¹ Anthocyanin has an attractive color that depends on its pH, the anthocyanin will be red and be categorized as flavylium if its in a strong acid solution, anthocyanin will be purple and categorized as quinonoidal if its in a neutral solution, and it will be blue and categorized as a quinonoidal base formation if its in a base solution.¹² Due to its attractive color, anthocyanin is considered as suitable for DSSCs. However, Several previous studies have shown organic dye cyanidin has better efficiency than other types of anthocyanins. The conversion efficiency of cyanidin was obtained 1.43%. Cyanidin also have carbonyl groups, hydroxy and π -conjugated electrons that can bind to the TiO_2 .¹³ The conversion efficiency of 2.9% is generated by red cabbage.¹⁴

At present, Density Functional Theory (DFT) is selected as the standard method for optimizing cyanidin-based dyes with various structures of donor and π -conjugated chains. Currently, the density functional theory (DFT) was chosen as the standard for optimization of computational methods because of the accurate calculation that closes to eksperimen.¹⁵ However, at present, no type of D- π -A has been performed for cyanidin dyes. The purpose of this paper was to provide theoretical insights regarding the effects of the variation of π -conjugated chain, donor chain, and electron-withdrawing and donating groups. The cyanidin structure was used as the acceptor chain.

EXPERIMENTAL

Research Procedures

Geometry optimizations were performed by using the DFT and TD-DFT/DFT methods with a B3LYP/6-31 G basis set with the Gaussian 16W package. The DFT method conducted on electronic and optical properties. TD-DFT/DFT method was used to examine the UV-Vis spectra.¹⁶ The optimization began with the variation of the π -conjugated chain. From this variation, efficient dyes were obtained. The next process was the optimization of dyes with the variation of donor chain. From the variation of the donor chain, the optimal dyes were found. Then, the optimal dyes were added with the electron-withdrawing and donating groups

The Observed Structure

The molecular model in this study is the cyanidin-based dye with D- π -A type. The goal of this work is to study the effect of π -conjugated chains, donor chains, electron-donating and withdrawing groups on the organic dye toward the efficiency of DSSCs.

The Basic Structure of an Organic Dye Molecule with a Variation of π - Conjugated Chain

The basic structure of organic dye with a variation of π -conjugated chain is shown in Fig.-1. Where a donor chain is coumarin and acceptor chain is cyanidin.

Fig.-1: The D- π -A Structure of an Organic Dye Molecule

The structure of π - conjugated chains for the dye can be seen in Fig.-2 below:

Fig.-2: The Molecular Structure of π -conjugated Chains

The Basic Structure of an Organic Dye Molecule with a Variations of Donor Chain

The basic structure of the dye with donor chain variations can be seen in Fig.-3. Variation of donor chain is a continuation of an efficient variation π chain.

Fig.-3: The Basic Structure of the Dye Molecule with Variety of Donor Chain

The molecules used as donor chain is Trifenilamin, Phenol, Indolin, Kumarin and Penantrokabazol whose structure can be seen in Fig.-4.

Fig.-4: The Molecular Structure of Donor Chains

The Effect of Electron-withdrawing Groups on the Organic Dye

The dye which has been an optimally coupled group of electrons donating and withdrawing, and compared the effect of the addition of these groups. The structure can be seen in Fig.-5.

Fig.-5: The Molecular Structure of the Dye Additional of Donating (X) and withdrawing (Y) of Electrons in the Organic Dye

The electron-donating molecules are CH_3 , C_6H_5 , $\text{C}(\text{CH}_3)_3$ and the electron-withdrawing molecules are Cl , OH , NO_2 .

RESULTS AND DISCUSSION

Geometry Optimization of D- π -A Type Organic Dyes With The Variation of π -conjugated Chain

Geometry optimization showed that all dyes have structural similarities due to the same donor and acceptor chains. Geometry optimization was performed to discover the optimal molecular structure. From the optimal dyes, the molecules of electronic properties of these molecules can be determined, i.e. band gap (energy gap), LUMO energy (Lowest Unoccupied Molecular Orbital), HOMO energy (Highest Occupied Molecular Orbital), wavelength, and HOMO-LUMO countous from each dye. On the organic dye of the variation of the π -conjugated chain, dye 3 was obtained as the most efficient result.

Band Gap (ΔE)

The sensitizer is crucial in producing a band gap that will affect the efficiency of light-harvesting of semiconductor. The value of this band gap was determined through the electron excitation from HOMO

band to LUMO band of the dyes which was also associated with the efficiency of light absorption by the dyes. The smallest band gap that has been produced shows the greatest light absorption. The light will be absorbed in a larger wavelength if the band gap is smaller, greater wavelength will absorb more light. This was done to allow electrons to move easier from one orbital with a low energy level to other orbitals with higher energy levels, so their sensitivity to light will also increase. Band gap values were obtained through:

$$\text{Band Gap } (\Delta E) = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

Fig.-6: The Structure of the Dye 3 after Being Optimized with A B3LYP / 6-31G Basis Set

Table-1: The Results of the Measurement Of HOMO-LUMO Energy Levels, Band Gaps, And $\lambda_{\text{excitation}}$ Through The Variation of The π -Conjugated Chain With B3LYP/6-31G Basis Set

Dyes	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	$\lambda_{\text{excitation}}$ (nm)
1.	-7.6245	-6.0564	1.5681	792.3
2.	-7.6259	-6.0812	1.5447	804.3
3.	-7.2915	-5.7571	1.5344	809.7
4.	-7.4686	-5.9095	1.5591	796.9
5.	-7.4438	-5.8978	1.5460	803.6

In Table-2 it can be seen that dye 3 has the smallest band gap with 1.5344 eV of value which has good efficiency for light absorption. This efficiency of dye 3 is a result of N atom which has 3.04 of electronegativity value. This value is lower than the O atoms (3.44) and higher than the S atom which amounted to 2.58. A more electronegative atom at the π chain will increase the difficulty of acceptor chain to withdraw electrons due to the electronegative atoms conceived by the acceptor chain. Electronegative atoms are easier to withdraw electrons from less electronegative atoms. Therefore, dye 3 is estimated as able to absorb lights around 809.7 nm of wavelength. This means that the 3 dye can absorb UV light, visible light and near IR light.

The second smallest bandgap is dye 2 which has S atom in π -conjugated chain. This condition results from S atom which more electropositive, thus, the acceptor chain which more electronegative will be easier to withdraw electrons from the π -conjugated chain. However, the pore of the S atom is larger than the N atom so it is more difficult to withdraw electrons with the acceptor chain. Dye 1 has O atom in its π chain in which both acceptor and donor chains have high amount of O atoms. Therefore, the resonance of electrons from donor to acceptor requires a large amount of energy.

In dye 4 and dye 5, the difference is only regarding the position of O and N atoms within the π -conjugated chain. Dye 5 has a smaller band gap than the band gap of dye 4. In dye 5, the O atom is closer to the acceptor chain and the N atom is closer to the donor chain. The position of O atom which closer to the acceptor chain causes the withdrawal of electrons from N atom to be lot easier compared to the withdrawal of electrons by N atom from O atom.

Excitation Wavelength ($\lambda_{\text{excitation}}$)

The measurement parameter to determine the light absorption is the value of the excitation wavelength. The dyes shall conceive have energies equal to or greater than the band gap to be able of absorbing lights. The wavelength is inversely proportional to the resulting band gap. Larger wavelengths will absorb more lights. Excitation wavelengths were obtained from the equation described as follow:

$$\lambda E = h.c \quad (2)$$

With h as the Planck's constant ($6.62 \times 10^{-34} \text{ J.s}$) and c as the speed of light in a vacuum ($3.00 \times 10^8 \text{ m/s}$). Table-2 shows that dye 3 is having better light absorption which capable of absorbing light at 809.7 nm of wavelength. The 809.7 nm value of wavelength indicates near IR light. If the molecules are capable of absorbing IR light, thus, the molecules will also capable of absorbing UV and visible lights. The UV light has a greater intensity and most optimally produced from 11 a.m. to 1 p.m. While the dominant IR light is produced at night. This means that DSSCs' equipment with dye 3 sensitizer is capable to operate during the day or night.

HOMO and LUMO Countours

Fig.-7: HOMO and LUMO Countours of Dye 3

In Fig.-7 it can be seen that the HOMO Countour shows electron density in the HOMO band, in that case, the electron density is located in the electron donor area. This condition is consistent with the theory which states that HOMO is an energy band that donates electrons. While the LUMO counter shows electron density within the LUMO band, thus, the electron density is located in the acceptor chain. This condition is consistent with the theory which states that LUMO is an energy band that acts as an electron acceptor.

Table-2: The Results of the Measurements of HOMO-LUMO Energy Levels, Band Gap, And λ Excitation In Donor Chain Variations With The B3LYP/6-31G Basis Set

Dyes	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	$\lambda_{\text{excitation}}$ (nm)
6	-6.5990	-6.0564	1.2430	999.5
7	-4.3604	-6.0812	1.7703	701.8
8	-6.6485	-5.7571	1.3434	924.8
9	-7.2915	-5.9095	1.5344	809.7
10	-6.5407	-5.4254	1.1153	1114.0

Geometry Optimization of Organic D- π -A Type Dyes with the Variation of Donor Chain

In optimizing the variation of the donor chain, the process continued from the molecular structure of dye 3, so the optimal structure was obtained. The electronic properties of a molecule can be determined through the optimal structure, i.e. band gap, wavelength, and HOMO and LUMO countours and optical properties such as absorption spectrum, Light Harvesting Efficiency (LHE) and oscillator strength (f).

Band Gap

From the optimization results, the smallest band gap will be obtained, allowing the most efficient dye to be used in DSSCs applications.

From Table-2 it can be seen that the smallest bandgap is dye 10 in which the value is 1.1153 eV. This result shows that organic dye 10 with penantrokarbazol as the donor has better efficiency in light absorption. Based on its molecular structure, the electron resonance is longer from donor chain to acceptor chain, the longer resonance of a dye, the longer wavelength of the light.

The mechanism of the electron resonance from the donor chain to the acceptor chain in dye 10 can be seen in Fig.-9.

Fig.-8: The Structure of Dye 10 after being Optimized with A B3LYP / 6-31G Basis Set

Fig.-9: Mechanism of Electron Resonance of Dye 10

In the electron resonance mechanism, Figure-9 shows that electrons move from the donor chain to the acceptor chain. Resonance is a change in the position of electrons without changing their structure, but there is a displacement between double bonds with electrons alternating between each other, then it can absorb photons at the right wavelength. It can be concluded that dye 10 has better absorption.

Excitation Wavelength

Dyes that have a longer wavelength are expected to be able to perform absorption within the IR region. From Table-2, it can be seen that the organic dye which has a longer wavelength is dye 10 in which the value is 1114.0 nm. Based on that wavelength, dye 10 is able to absorb light within the IR area. Thus, it can be concluded that the dye has better light absorption.

HOMO and LUMO Countours

In Figure-10, it can be seen the HOMO region is located within the donor chain, while the LUMO region is located in the acceptor chain. This condition is consistent with the theory which states that the HOMO region will donate electrons and the LUMO is the region that receives electrons.

Fig.-10: HOMO and LUMO Countours of Dye 10

Absorption Spectrum

The absorption spectrum of dye 10 is as follows:

Fig.-11: The Spectrum of UV-Vis Organic Dye 10

The UV-Vis spectrum of dye 10 shows 3 absorption peaks. The absorption peak on the high blue line is the excitation state-3 with 694.408 of wavelength nm and 0.949235 of f , while the shorter blue line shows the excitation state-2 with a wavelength is 772.199 nm and f is 0.371307, while the wavelength of excitation state-1 is 1098.31 nm which its indicated by a red triangle and has an oscillator strength (f) is 0.001168.

Based on the value of f , it can be determined the value of LHE (efficiency of light absorption). According to Beer Law the LHE is determined with the following equation¹⁷:

$$\text{LHE total} = 1 - 10^{-f} \quad (3)$$

Where, (f) is the oscillator strength when the excitation occurs at a certain wavelength. The acquired LHE obtained must be as high as possible because it maximizes the photocurrent response. Oscillator strength is directly proportional to LHE, the higher the oscillator strength obtained when excitation, the higher the value of LHE. Therefore, the total LHE value was 0.9523.

Effect of Electron Withdrawing and Donating Chains

The addition of the electron-withdrawing and donating chains is to see how the band gap of the dye after addition of a new group.

Electron Donating Group (EDG)

Fig.-12. The Structure of Dye 6 by the Addition of Electron Donating molecule in the Donor Chain

Where: X1 = CH₃, X2 = CH = CH - CH = CH₂, X3 = C(CH₃)₃

Table-3: The Results of The Addition Of EDG To Dye 6

Dyes	Electron donating molecule	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	λ _{excitation} (nm)
11	X1	-6.5010	-5.3000	1.2010	1034.5
12	X2	-6.3432	-5.3222	1.0204	1217.6
13	X3	-6.4784	-5.2845	1.1939	1040.6
6	Unavailable	-6.5407	-5.4254	1.1153	1114.0

In Table-3, it can be seen that the organic dye of the donor chain with the addition of X2 molecule ($\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$) has the smallest band gap with the value of 1.0204 eV, lights are absorbed in 1217.6 nm of wavelength. This condition is caused by the X2 cluster which has a stronger electron-withdrawing compared to X1 and X3. The $\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ molecule also has π -conjugated electrons, thus, it increases the π electron resonance conjugated to the dye 6.

Electron-withdrawing Group (EWG)

Fig.-13: The Structure of Dye 6 by the Addition of Electron Withdrawing Molecule (Y) to the Acceptor Chain

Table-4: The Effect of The Addition of Electron Withdrawing Group To Dye 6

Dyes	Electron withdrawing molecule (Y)	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{\text{(eV)}}$	$\lambda_{\text{excitation}}(\text{nm})$
14	Cl	-6,6384	-5,4418	1,1966	1036,5
15	NO_2	-6.8115	-5.7010	1.1105	1118.9
16	OH	-6.6156	-5.4123	1.2032	1032.6
6	Unavailable	-6.5407	-5.4254	1.1153	1114.0

In Table-4, it can be seen that the addition of NO_2 molecule can decrease the band gap of Dye 6. The value of the band gap is 1.1104 eV, and it is expected to absorb light at 1118.9 nm of wavelength because NO_2 has more electronegative atoms than other EWG.

The effect of the additions of EDG and EWG

Dye 17 was determined as the dye with optimal structure by the additions of EDG and EWG.

Fig.-14: Optimal Structure of Dye 17 with B3LYP/6-31G Basis Set

The additions of EDG and EWG, are capable to decrease the band gap more than merely adding EDG or EWG. The band gap value amounted to 0.8873 eV at 1400 nm of wavelength. The EDG and EWG clusters generate easier electron resonance within the organic dye because electrons will be strongly donated by EDG toward the acceptor chain which strongly withdrawn by NO_2 from donor chain. It can be concluded that the additions of EDG and EWG on organic dye provides better light absorption.

From dye 17, the HOMO and LUMO counters can be seen (Fig.-15). Based on Fig.-15 it can be seen that the electron density in the HOMO region is in the donor chain, while the electron density for the LUMO region is in the acceptor chain of organic dyes. This result is consistent with the theory which states that HOMO is the highest molecular orbitals filled with electrons, therefore, it can donate electrons, while LUMO is the lowest molecular orbitals that are not filled with electrons, thus, the energy band will receive electrons.

Fig.-15: HOMO and LUMO Countours of Dye 17

CONCLUSION

Dye 3 has the smallest band gap with variation of π -conjugated chain, while dye 10 has a smaller band gap compared to other donor variations. The addition of the C_4H_5 as EDG and the addition of the NO_2 as EWG were able to decrease the band gap of the dye. Dye 17 is a combination of the additions of EWG and EDG with the smallest band gap. Therefore, it can be said that dye 17 is more potential as a sensitizer in DSSCs.

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