Theoretical Investigation of Aniline-Based Dyes to Improve The Efficiency of Solar Cells

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Abstract: *Dye-Sensitized Solar Cells (DSSCs) is the efficient third generation of solar cells due to their low production cost and eco-friendly feature. This research studied D-π-A dye type with aniline donor chain and formic acid acceptor chain, continued by varying the π-conjugation chain with butadiene, cyclopentadiene, pyrrole, furan, thiophene as well as the addition of electron-withdrawing group (-NO$_2$) and electron-donating group (-C$_2$H$_3$). This study used Gaussian 16W and Gauss View 6.0 program package through the measurement method of DFT and TD-DFT as well as the basis set of B3LYP/6-31G. The analysis descriptors were HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies, bandgap (ΔE), HOMO and LUMO contours, excitation energy (E$_{eks}$) and excitation wavelength (λ$_{eks}$), oscillator strength (f) and LHE (Light-Harvesting Efficiency). According to the study results, it has been acquired that the dye with pyrrole chain π-conjugation produced the best efficiency of light-harvesting. The presence of an electron-donating group of -CH=CH$_2$ and an electron-withdrawing group of -NO$_2$ can generate more efficiency of the dye light-harvesting. It has been concluded that the type of aniline-based D-π-A dye was efficient to be used as the sensitizer on DSSCs.*

***Keywords*:** *Aniline, DSSCs, D-π-A Type, DFT, TD-DFT*

I. INTRODUCTION

The crisis of energy is the main issue in the world due to the decreasing amount of fossil fuels as a result of the global temperature rises. At present, the electricity generation is developed by using solar energy, and this technology is also known as the photovoltaic (PV) technology[1]. One of the PV technologies is Dye-Sensitized Solar Cells (DSSCs). These cells offer an efficient and easy-to-implement technology for the future supply of energy with efficient materials and low production cost [2].

The sensitizer in DSSCs contributes to improving the efficiency of light-harvesting. Until present, many efforts are made to build an efficient sensitizer through molecular engineering for the better performance of DSSCs. Recently, metal-free organic sensitizers are getting more attention than metal-complex sensitizers due to their easiness in synthesizing molecules in the structure adjustments for the desired photophysics and photochemistry, biodegradable, relatively low production cost and abundant resources [3].

Computational chemistry is the branch of chemical science that uses computer programs to calculate the molecule properties and changes based on the result of chemical theories. Computational chemistry can produce the image of the structure in various models and has the same activities with quantum equations of classic physics. The rapid development of computational chemistry, especially in the application of quantum chemical calculations allows the modelling of molecules and exploration of physical and chemical properties of a molecule structure [4].

The computational study regarding dyes that grows recently is an organic dye type of D-π-A which consists of electron donor, π-conjugation, and electron acceptor. This dye has pushed and pull nature, so it causes the resonance of π-electron that will affect the efficiency of light-harvesting [5]. Density Functional Theory (DFT) is selected as the method of standard computation for optimization due to its accurate calculation [6]. Some of the latest studies about organic dye type of D-π-A that had been analyzed through DFT method was the dye with triphenylamine skeleton [7], phenylene [8], thienylen [9], anthracene [10], dianiline [11], cyanidin [12] and others. The study results showed that the light-harvesting of the dye on the area was visible until IR (infrared).

According to the description above, the author was interested in conducting the study about organic dye type of D-π-A with aniline skeleton through the application of DFT calculation method. Aniline was used as the donor chain because it has an electron-donating group of -NH$_2$. This study is expected to be able to provide the information regarding the most efficient structure of dyes to be used as the sensitizer on DSSCs instrument in the future. Thus, it can be made as the basis to synthesize the compound experimentally.

II. RESEARCH METHOD

The model of molecule in this study was D-π-A dye type with Aniline skeleton by studying the variation effect of the π-conjugation chain, and the impact of the addition of electron-withdrawing and donating on an organic dye.

The structure of the molecule was made by using Gauss View 6.0. The molecule model in this study

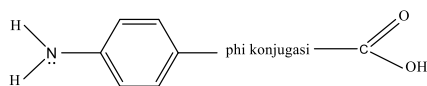was the aniline-based dye type of D- π-A with the skeleton described as follows:

Figure 1: The basic structure of the molecule of Aniline-based D-π-A dye type with the variation of π-conjugation chain

III. *A. The variation of π-conjugation chain*

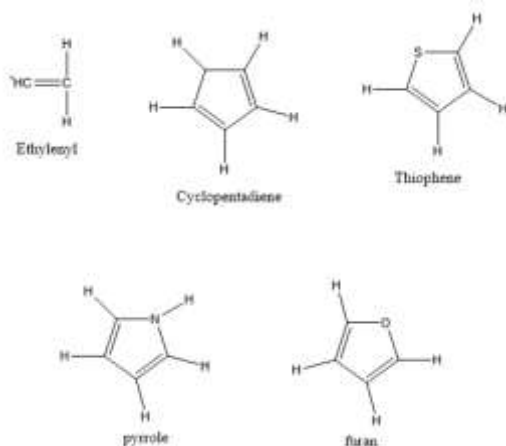The dye in Figure 1 was varied with π -conjugation chain with some structures described as follows:

Figure 2: The structure variation of π-conjugation chain

B. The addition of electron-withdrawing and donating groups

The effect of electron-withdrawing and donating groups on the organic dye that has been optimal was added with electron-withdrawing and giving groups, and be compared with the effect of the addition of the related groups.
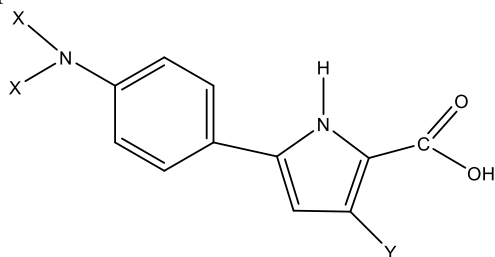

Figure 3 : The molecule structure of dyes of the substituent addition of electron-donating (X) and electron-withdrawing (Y) on organic dyes

According to the variation of π chain, the dye with the best light-harvesting was added with the electron-withdrawing group (-NO₂) and electron-donating group (-C₂H₃)
.

C. The Optimization of Aniline-Based D-π-A Dye Type

The molecule structure of D-π-A dye type was drawn on the program through Gauss View 6.0 software then get optimized on its geometric structures. The entire input files of aniline-based dye were optimized through Gaussian 16 W program. The optimization of molecular geometry used DFT method and the molecule optimization in excitation state used TD-DFT (Time-Dependent Density Functional Theory) with a basic set of B3LYP/6-31G.

D. Data Analysis

The optimized organic dyes were saved in file hin format by using the display menu. After the optimization of molecular geometry, the data were saved in notepad. The data output can be read based on the saved notepad, which consists of energies and gradient, molecular point group, eigenvalues, atomic orbital electron populations, net charges and coordinates, atomic gradients, dipole. Based on the data output, values were acquired as follows:

1. Electronic energies, including E_{HOMO}, E_{LUMO}, bandgap (ΔE), HOMO and LUMO contours
2. Optical parameters, including absorption spectrum, excitation energy, and excitation wavelength $(\lambda_{excitation})$, oscillator strength (f), and LHE (light-harvesting efficiency).
3. Electrical parameters, including current density (J_{sc}), voltage (V_{OC}), and energy conversion efficiency (η)

Several equations used for data analysis were:

$$\text{Band Gap } (\Delta E) = E_{LUMO} - E_{HOMO}$$
$$LHE = 1 - 10^{-f}$$
$$J_{sc} = \int LHE (\lambda) \, \Phi_{inject} \, \eta_{collect} \, d\lambda$$
$$\eta = J_{sc} \, V_{oc} \, (ff) \, /I_s$$
$$V_{oc} = E_{LUMO} - E_{CB} \qquad [8]$$

In which:

E_{CB} = The conduction band energy TiO_2 = -0.4 eV

E_{LUMO} = Dye's LUMO energy

ff = *fill factor*

Φ_{injec} = electron injection efficiency

$\eta_{collect}$ = charge collection efficiency

According to the parameters shown above, the efficiency analysis of a dye as the sensitizer on DSSCs was performed.

III. RESULTS AND DISCUSSION

A. The Optimal Geometric Structure

The structure was optimized from the basic condition of the five variations of dyes of a π-conjugation chain. The geometric optimization was performed to acquire the optimal molecule structure. The optimal structure, HOMO and UMO contours of 1,2,3,4,5 dyes are shown in Figure 4.
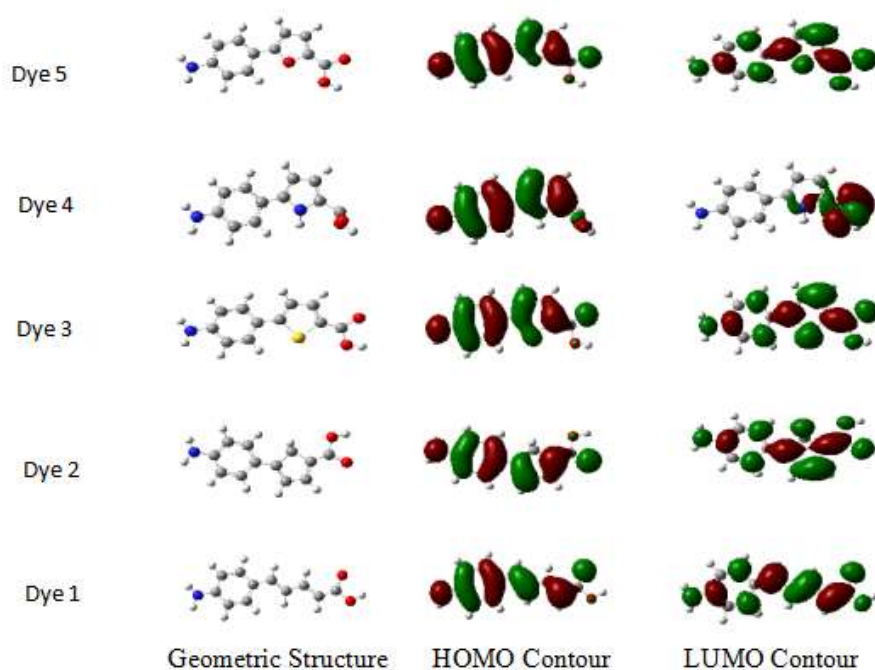
Figure 4. The optimal geometric structure, HOMO and LUMO Contours of 1-5 dyes of which the atoms of oxygen (red), Carbon (   ), Nitrogen (blue), Sulfur (yellow), Hydrogen (white)

HOMO band is electron-donating while LUMO band is electron-accepting. Of the HOMO contour, it can be known that the electron-donating was aniline and the formic acid was electron-withdrawing based on the LUMO contour.

B. Band Gap (ΔE)
The gap between HOMO and LUMO energy levels is referred to as *ΔE*. HOMO is the molecular orbital inhabited by the highest energy level of electrons. LUMO is the molecular orbital uninhabited by the lowest energy of electrons (conduction bands). According to Planck's law, a lower *ΔE* will make the light to be harvested by the longer wavelength; longer wavelength means more harvested light. This condition occurs because an electron is possible to switch easily from a low-energy orbital to the higher level of the orbital. Therefore, the sensitivity to light is also increasing. The calculation result is presented in Table 1.

Table 1: The calculation result of frontier energies of the optimization of dyes

Dyes	$E_{HOMO\,(eV)}$	$E_{LUMO\,(eV)}$	$\Delta E_{(eV)}$
1	-5.3358	-2.4349	2.9009
2	-5.1193	-2.2629	2.8564
3	-5.4221	-2.2958	3.1263
4	**-4.4732**	**-2.8403**	**1.6329**
5	-5.4053	-2.1630	3.2423

It can be seen from Table 1 that dye 4 has the lowest *ΔE* that amounts to 1.6392 eV, which means that it has the best efficiency of light-harvesting. This light-harvesting efficiency is affected by the π electron resonance of donor band to the acceptor. The longer or more natural π electron resonance, the light will be absorbed by the longer wavelength (redshift). There is an atom N that has 3.04 electronegativity value in dye 4 on π chain. This value is lower compared to atom O (3.44) and higher if compared to the atom S, i.e. 2.58. The more electronegative an atom becomes on π chain, the harder acceptor chain to withdraw electron because the acceptor chain tends to have higher electronegativity value. Electronegative atoms are easier to withdraw electrons of less electronegative atoms. The radius of atom N is also smaller than atom O. Therefore, the oxygen atom in the acceptor group will be more easily to withdraw the electron from atom N in π group. Therefore, dye 4 has a lower *ΔE*.

C. Absorption Spectrum

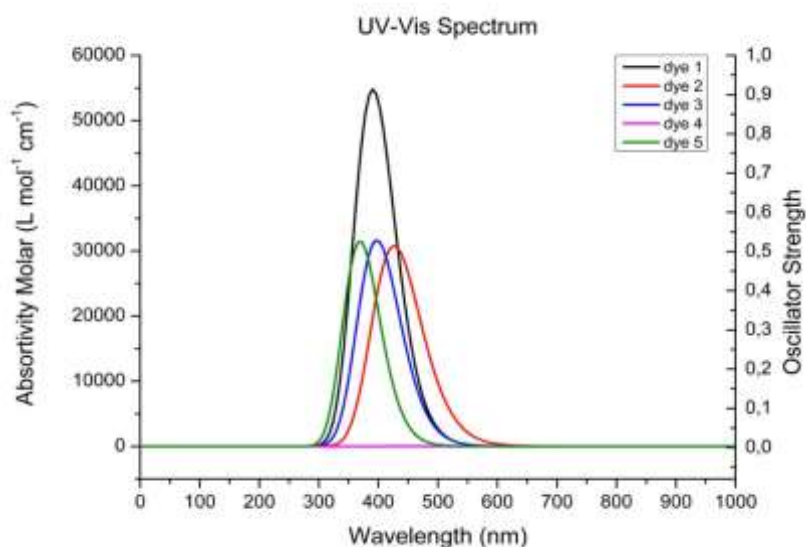The absorption spectrums of dyes 1-5 are presented in Figure 4, and their electronic transitions are shown in Table 1.

Figure 5: UV-Vis spectrum of dyes between wavelength (nm) and absorptivity molar (ε)

Table 2: The calculation results of the electronic transitions of dyes 1-5

Dyes	Excitation State	$\lambda_{excitation}$ (nm)	Excitation Energy (eV)	Configuration of MO	f
1	1	484.13	2.5356	HOMO -1 → LUMO (98.42%)	0
	2	390.72	3.1809	HOMO -2 → LUMO (77.81%) HOMO -1 → LUMO (61.97%)	1.3533
2	1	472.77	2.6092	HOMO -1 → LUMO (98.46%) HUMO -1 → LUMO +2 14.81%)	0
	2	426.41	2.9226	HOMO → LUMO (100.69%)	0.7598
3	1	419.92	2.8614	HOMO -1 → LUMO (98.17%) HOMO -1 → LUMO +2(15.78%)	0.0000
	2	397.47	3.1044	HOMO → LUMO (99.64%)	0.7818
4.	1	1441.17	1.1390	HOMO -1 → LUMO (17.38%) HOMO→ LUMO (98.32%)	7.127×10^{-5}
	2	458.58	2.8779	HOMO -4 → LUMO (26.02%) HOMO -2 → LUMO (15.92%) HOMO -1 → LUMO) (93.35%) HOMO → LUMO (18.07%)	4.518×10^{-4}
5	1	395.50	3.1462	HOMO -2 → LUMO (87.41%) HOMO -2 → LUMO+1 16.23%) HOMO -1 → LUMO (39.93%) HOMO → LUMO (39.93%)	2.419×10^{-5}
	2	369.17	3.4761	HOMO -1 → LUMO (39.93%) HOMO → LUMO (87.82%)	0.7781

The data in Figure 5 and Table 2 show that the absorption of light is better on dye 4 with the peak of the light absorption spectrum reaches 1441.1 nm wavelength. The values of wavelength show the area of IR ray. If the molecules are capable of absorbing IR ray, thus, the molecules are also capable of absorbing

UV light and visible light. UV light that has greater intensity and the most optimal is produced from 11 am to 1 pm. Visible light is produced during the daytime. Dominant IR ray is produced during the nighttime. It means that the instrument of DSSCs with dye 4 sensitizer is capable of absorbing light during the daytime or night time.

According to f values, the LHE (Light Harvesting Efficiency) values can be known in which f is oscillator strength during the excitation of electron on a certain wavelength. Oscillator strength is parallel to LHE; higher oscillator strength acquired during the excitation will make the LHE value to be higher as well. High LHE will also produce high electrical currents.

D. The Effect of the Addition of Electron-Withdrawing and Donating Groups

Dye 6 is the dye 4 added with electron-donating and withdrawing groups. The optimal geometric structure and the absorption spectrum can be seen in Figures 6 and 7 as well as Table 3.
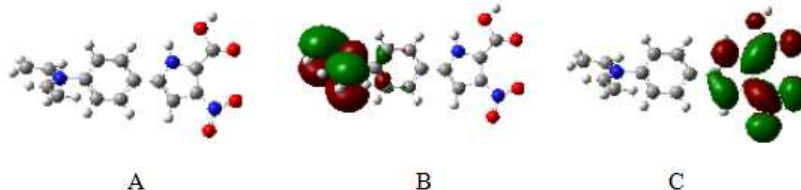

Figure 6. The optimal geometric structure (A), HOMO Contour (B), LUMO Contour (C) of dye 6

Of the HOMO Contours in Figure 6, it can be seen that the -C_2H_3 and NH_3 groups are the contributing groups that donate electrons and LUMO contours show that NO_2 withdraws electron stronger compared to a formic acid group. Therefore, according to the figure of HOMO and LUMO contours, the stronger resonance of π electron is commenced from -C_2H_3 group to NO_2 group.
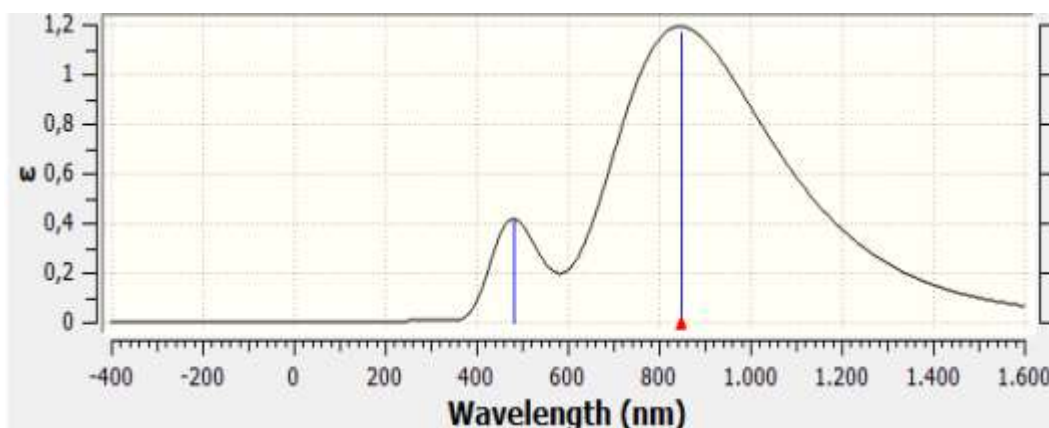

Figure 7 : TheUV-Vis spectrum of dye 6

Dye	Excitation State	$\lambda_{excitation}$ (nm)	Excitation Energy (eV)	Configuration of MO	f
6	1	846.55	1.4647	HOMO → LUMO (99.94%)	2.929×10^{-5}
	2	480.86	2.5784	HOMO → LUMO +1 (98.66%) HOMO → LUMO +3 (14.63%)	1.011×10^{-5}

Table 3 : The electronic transition of dye 6

Dye 6 produced -5.2553 eV of E_{HOMO} value and 3.4936 eV of E_{LUMO} Value. Therefore, 1.7717 eV of ΔE was produced. Of Figure 7 and Table 3, dye 6 produces 846.55 nm maximum peak of λ_{eks} and 1600 nm coverage of light absorption. Of this result, it can be known that the addition of electron-withdrawing and donating groups decreases the bandgap and λ_{eks} peak of dye 4. This condition occurred because NO_2 is a potent electron-withdrawing group. Therefore, the electron resonance leads to NO_2 group and shortens the resonance of the π electron.

E. Electrical Properties
The electrical properties of DSSCs were discovered from the Voc's value (open current-

voltage), Jsc (current density), and power efficiency (η). LHE and Voc's values can be seen in Table 4. The LHE values were taken from the highest *f* values.

Table 4: LHE and Voc's values of dyes 1-6

According to the equation, it is known that a higher LHE will make the current density to be greater, and the

Dyes	LHE	V_{OC}
1	0.955767	1.5651
2	0.826175	1.7371
3	0.834761	1.7042
4	0.001039	1.1597

wavelength will be longer as well as the Jsc and Voc. Therefore, the efficiency will also be greater. Based on LHE values, dye 1 produced greater efficiency because the molecule tends to be more planar. Thus, the transfer of the electron becomes faster. However, according to the wavelength value, dye 4 produced greater efficiency.

IV. CONCLUSION

Dye 4 with the structure of 4-(4-aminophenyl)-1H-pyrrole-2-carboxylic acid has the smallest bandgap and the light-harvesting on a longer wavelength between the variation of π- conjugation chain the light-harvesting of dye 4 reached the infrared area. The addition of C_2H_3 donating group or -NO_2 withdrawing group were unable to improve the bandgap. Therefore, it can be concluded dye 4 is the most efficient as the sensitizer on DSSCs instrument, and the addition of electron-withdrawing and donating groups on dye 4 was unable to improve the light-harvesting efficiency of dye but capable of improving the Voc's value of DSSCs.

ACKNOWLEDGMENT

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