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 Research Article

 Theoretical Modification of The Structure of Dithiophene-Based Dyes as Sensitizers in Solar Cells

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Abstract: One of the key parameters in designing DSSCs is the dye, which plays a crucial role in absorbing light. This study aims to modify the structure of D- $\pi$ -A type dyes based on dithiophene with variations in the donor chain. The donor chains used were phenol, aniline, indoline, diphenylamine, coumarin, and toluene, symbolized as T1, T2, T3, T4, T5, and T6. The acceptor chain used was formyl cyanide. The calculations were performed using the Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) methods with the B3LYP/6-31G basis set. The study results indicated that all modified dyes were potential sensitizers because they can absorb light in the visible to infrared (IR) regions. The T3 dye, with an indoline donor chain, was the best dye to be used as a sensitizer, with a bandgap value of 1.7149 eV, a maximum wavelength ( $\lambda$ ) of 939.43 nm, excitation energy of 1.3198 eV,  $\Delta$ Ginj of -04250 eV,  $\Delta$ Greg of 0.0948 eV, and a VOC value of 08201 eV.

*Keywords:* DSSC, Dithiophene, DFT-TDDFT, D-π-A Type

### 1. Introduction

Energy is a crucial factor in social and economic growth. Currently, energy consumption still relies on fossil fuels such as petroleum, coal, and natural gas. Excessive use of fossil fuel energy will produce greenhouse gases such as carbon dioxide (CO<sub>2</sub>), causing ozone layer depletion, thus resulting in global warming, and natural disasters [1].

Sunlight is the primary energy source in life and is seen as an ideal alternative energy to replace fossil fuel energy due to its abundance, lack of pollution, unlimited amount, and renewability [2]. Therefore, innovative renewable energy technology is required to address global issues such as energy crises, climate change, and sustainable development [3].

A fascinating development in current solar cell technology is the Dye-Sensitized Solar Cells (DSSCs), which have shown significant potential as a new generation of commercial solar cells [4]. DSSCs are a type of photovoltaic device based on dyes that function as sensitizers to absorb sunlight [5]. DSSCs are a potential electricity generation because they are environmentally friendly, and

have lower production costs with increasing power efficiency [6].

One of the key parameters in designing DSSCs is the sensitizer, which plays a crucial role in absorbing light, electron injection, and enhancing photolytic properties [7]. Organic dyes are very suitable as sensitizers because they are abundant, inexpensive, and easy to extract [8]. Several plant extracts used include turmeric, black rice, and pandan leaves [5]. However, natural dyes tend to be impure and unstable, leading to experimental and theoretical research on synthetic organic dyes for sensitizers.

The sensitization ability of organic dyes can be improved by engineering their molecular structures. The most effective organic dyes studied in DSSCs are D- $\pi$ -A type dyes, where D is the electron donor group,  $\pi$  is the conjugated bridge, and A is the electron acceptor group. D- $\pi$ -A type dyes have excellent stability and efficiency in DSSCs due to their push-pull properties and longer electron resonance [9].

Thiophene is known to be suitable as a conjugated  $\pi$ -bridge in D- $\pi$ -A type organic dyes. The

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incorporation of thiophene groups into D- $\pi$ -A type dye molecules is known to enhance molar absorptivity, overall stability, and the performance of sensitizers in solar cells. Thiophene groups can also facilitate bathochromic red shifts in absorption spectra, associated with the presence of electronrich heterocyclic groups [10]. Shifting the wavelength towards longer lengths allows thiophene-based dyes to absorb more visible light and produce smaller bandgaps [4]. Structurally, thiophene has a highly potential to be used as a conjugated  $\pi$ -bridge in D- $\pi$ -A type dyes because it has conjugated  $\pi$ -electrons and sulfur atoms in the heterocyclic chain that can function as both electron acceptors and donors [11].

Computational chemistry approaches to designing compounds are essential as they can minimize the use of chemicals and save research time by avoiding trial and error in experiments, providing good accuracy. The Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) methods have the advantage of producing more calculations compared other accurate to computational methods. DFT and TD-DFT methods are used to investigate the molecular geometry, electronic structure, absorption spectrum, and photovoltaic characteristics of the dyes used [12].

Because of the above, the researchers were interested in modifying the structure of thiophenebased D- $\pi$ -A type dyes computationally using DFT/TD-DFT calculation methods and B3LYP/6-31G basis set. All these methods are chosen because of their accurate calculations. To extend the electron resonance in dye molecules, two thiophene molecules were used to form dithiophene as a conjugated  $\pi$ -bridge with variations in the donor chain. The donor and acceptor molecules used differ from existing research, making the overall dye structure a new molecule that has not been theoretically or experimentally studied before. The donor molecules chosen are aniline, phenol, indoline, diphenylamine, coumarin, and toluene because they are strong electron donors [13]. The chosen acceptor molecule is formyl cyanide because it has -C=O and -C≡N groups which are strong electron withdrawers.

#### 2. Computational Method

### 2.1. Theoretical Background

Overall efficiency ( $\eta$ ) in DSSCs is a key factor in determining the performance of solar cell devices, which is directly related to the open-circuit voltage (V<sub>OC</sub>), short-circuit current density (J<sub>SC</sub>), fill factor (FF), and light intensity (I<sub>s</sub>)

$$\eta = \frac{J_{SC}V_{OC}}{I_s}FF$$
 Eq. 1

According to Equation (1), increasing the  $V_{OC}$  and  $J_{SC}$  parameters leads to increased DSSCs power efficiency ( $\eta$ ).  $J_{SC}$  can be calculated using the following equation:

 $J_{sc} = \int LHE (\lambda) \Phi_{inject} \eta_{collect} d\lambda \quad Eq. 2$ 

where Light Harvesting Efficiency (LHE) is the light absorption efficiency at a wavelength ( $\lambda$ ),  $\phi_{inj}$  and  $\eta_{coll}$  are the electron injection efficiency and charge collection efficiency. The value of  $\eta_{coll}$  can be considered constant in the same DSSCs device. Higher J<sub>SC</sub> can be obtained through greater LHE, which can be determined by the following equation.

LHE 
$$(\lambda) = 1 - 10^{\vee}$$
 Eq. 3

where *f* is the oscillator strength of the organic dye at maximum wavelength ( $\lambda_{max}$ ). The larger the oscillator strength, the higher the LHE of the organic dye, and the greater the resulting J<sub>SC</sub> value. On the other hand,  $\varphi_{inj}$  is related to the electron injection driving force ( $\Delta G_{inj}$ ), where the more negative the  $\Delta G_{inj}$  value, the higher the J<sub>SC</sub>, which can be determined by the following equation:

 $\Delta G_{inj} = E_{dye} \cdot E_{CB} = E_{dye} \cdot E_{ex} - E_{CB}$  Eq. 4 where  $E_{dye^*}$  represents the oxidation potential energy of the dye in the excited state, while  $E_{dye}$ represents the oxidation potential energy of the dye in the ground state, estimated as the negative of the highest occupied molecular orbital energy (- $E_{HOMO}$ ).  $E_{CB}$  is the reduction potential of the TiO<sub>2</sub> semiconductor ( $E_{CB} = -4.0 \text{ eV}$ ), and  $E_{ex}$  represents the electronic transition associated with  $\lambda_{max}$ . Another factor affecting  $J_{SC}$  is the regeneration driving force ( $\Delta G_{reg}$ ) of the organic dye. A lower  $\Delta G_{reg}$  value can result in higher  $J_{SC}$  and improve DSSCs performance, determined by the following equation:

$$\Delta G_{reg} = E_{redox} - E_{dye}$$
 Eq. 5

where  $E_{redox}$  represents the redox potential of the I-/I3- electrolyte pair (-4.8 eV) [7]. Besides J<sub>SC</sub>, VOC is another important factor influencing overall DSSCs efficiency ( $\eta$ ), which can be determined by the following equation.

$$V_{oc} = \frac{E_{CB} + \Delta E_{CB}}{q} + \frac{k_b T}{q} \ln\left(\frac{n_c}{N_{CB}}\right) - \frac{E_{redox}}{q} \quad \text{Eq. 6}$$
$$V_{oc} = E_{LUMO} - E_{CB} \quad \text{Eq. 7}$$

where q represents the unit charge,  $k_bT$  represents thermal energy,  $E_{CB}$  contributes to the conduction band energy of TiO<sub>2</sub>, N<sub>CB</sub> is the conduction band density of states, n<sub>c</sub> is the number of electrons in the conduction band, and  $\Delta E_{CB}$  is the  $E_{CB}$  shift when absorbed on the TiO<sub>2</sub> semiconductor surface, which can be estimated by the following equation.

$$\Delta E_{CB} = -\frac{q\mu_{normal}\gamma}{\varepsilon_0 \varepsilon} \qquad \qquad \mathbf{Eq. 8}$$

where  $\mu_{normal}$  is the vertical dipole moment of the molecule perpendicular sensitizer to the semiconductor surface,  $\gamma$  is the surface concentration of the molecules, and  $\varepsilon_0$  and  $\varepsilon$  are the vacuum and dielectric permittivity values, respectively. According to Equations (6) and (8), dyes with larger  $\mu_{normal}$  will produce higher V<sub>OC</sub> [14]. In addition to the above factors, the bandgap  $(\Delta E)$  is one of the important parameters that determine the suitability of dyes for DSSC applications, where a smaller bandgap value can cause a shift in the wavelength to a longer range and can improve photovoltaic efficiency. Thus, the bandgap can be calculated using the following equation [15]:

$$\Delta E = E_{LUMO} - E_{HOMO}$$
 Eq.9

The global reactivity parameter values are obtained according to the following equations[16,17]:

$$IP = -E_{HOMO}$$
 Eq. 10  

$$EA = -E_{LUMO}$$
 Eq. 11  

$$\mu = \frac{(IP + EA)}{2}$$
 Eq. 12  

$$\chi = -\mu$$
 Eq. 13  

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$
 Eq. 14  

$$\sigma = \frac{l}{\eta}$$
 Eq. 15  

$$\omega = \frac{\mu^2}{2\eta}$$
 Eq. 16  

$$\zeta = \frac{l}{\omega}$$
 Eq. 17

## 2.2. DFT Calculation

The dye studied is a D- $\pi$ -A type dyes, where the  $\pi$  chain used is dithiopene, the acceptor chain is formyl cyanide with variations in the donor chain. Thiophene-based dyes are then symbolized by T1, T2, T3, T4, T5, T6 with variations of the donor

chains are phenol, aniline, indoline, diphenyl amine, coumarin and toluene respectively as shown in **Figure 1**. The molecular structure of D- $\pi$ -A type dyes was drawn using the Gauss View 6.0 software, followed by structural geometry optimization. All input files of dithiophene-based dyes were optimized using the Gaussian 16 W program. Calculations were performed using DFT and TD-DFT methods with the B3LYP/6-31G basis set, yielding the following values:

- Electronic parameters, including HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) contours, E<sub>HOMO</sub>, E<sub>LUMO</sub>, bandgap (ΔE), and ESP (Electrostatic Surface Potential)
- 2. Optical parameters, including absorption spectrum, excitation wavelength ( $\lambda_{excitation}$ ), Light Harvesting Efficiency (LHE), and oscillator strength (f).
- 3. Electrical parameters, including current density  $(J_{SC})$ , voltage  $(V_{OC})$ , and energy conversion efficiency  $(\eta)$ .
- Chemical reactivity parameters, including IP, EA, μ, χ, η, σ, ω, and ξ

Based on these parameters, an analysis of the dye's efficiency as a sensitizer in DSSCs was conducted.

### 3. Results and discussion

### 3.1. Geometric Properties

Geometric optimization is performed to obtain the optimal geometric structure of a dye molecule. The geometric structures of the six dye molecules with varied donor chains were optimized using the B3LYP/6-31G basis set to determine the electronic properties of each dye, such as HOMO energy, LUMO energy, energy gap (bandgap), and HOMO and LUMO contours. The optimization results for each dye include the optimal geometric structure, and the HOMO and LUMO contours, which can be seen in **Figure 2**.

The absorption of light and charge transfer properties are closely related to the excitation of electrons, which primarily occurs from the HOMO to the LUMO. For an effective sensitizer, electron transfer can occur efficiently if the HOMO contour is largely distributed on the donor chain, indicating that electron density occurs in the electron-donating HOMO orbital. Meanwhile, the LUMO contour is mostly distributed on the acceptor chain, indicating

that electron density occurs in the electronaccepting LUMO orbital [18],[4].

Based on **Figure 2**, it is known that the HOMO contour of all dyes is distributed on the donor chain and the  $\pi$ -conjugated chain in the bonds between C-C, C=C, C-H, N-H, and C-S atoms, indicating that the HOMO orbital acts as an electron donor. The LUMO contour is mostly distributed on the  $\pi$ -

conjugated chain and the acceptor chain with oxygen atoms of the -C=O and nitrogen  $-C\equiv N$  groups in the formyl cyanide, indicating that the LUMO orbital acts as an electron acceptor [19]. The  $\pi$ -conjugated chain acted as a bridge connecting the donor chain with the acceptor chain, evidenced by electrons resonating from the donor to the acceptor through the  $\pi$ -conjugation when the dye is exposed to light.

Tı  $T_4$ OF T2 T5 Hal T6 T3 Н HN Figure 1. The Structure of Dyes T1-T6 Dyes **Optimal structures HOMO** Contours LUMO Contours Τ1 Т2 ΤЗ Τ4 Τ5 Τ6

Figure 2. The optimal structure of dyes T1-T6

The optimal structure of the dyes calculated using the DFT/TD-DFT/B3LYP/6-31G method is illustrated in **Figure 3**. The bond length and dihedral angle values are grouped in **Table 1**. L<sub>1</sub> and L<sub>2</sub> represented the bond lengths, while  $\Phi$ 1 and  $\Phi$ 2 represented the dihedral angles between the donor and the  $\pi$ -bridge, as well as the  $\pi$ -bridge and the acceptor. Geometric parameters such as dihedral angles and bond lengths were determined from geometry optimization in the ground state. The dihedral angles and bond lengths between chains in the dye molecule significantly influenced the optoelectronic properties of DSSCs. The dihedral angle indicates the planarity of the dye, which is crucial in intramolecular charge transfer. If a dye has a dihedral angle value close to  $0^{\circ}$  or  $180^{\circ}$ , the dye has a planar conformation. Additionally, dyes with bond lengths smaller than the single C-C bond (1.54 Å) indicate faster electron transfer between chains [3].



Figure 3. The depiction of dihedral angles ( $\Phi 1$  and  $\Phi 2$ ) and bond lengths ( $L_1$  and  $L_2$ ) in the D- $\pi$ -A dye structure.

Table 1 Band langths and dihadral angles of dyas T1 T6

)
,
,
0



Figure 4. ESP of Dyes T1-T6

As seen in **Table 1**, all dyes have nearly identical dihedral angles, around  $128^{\circ}-130^{\circ}$ , indicating that the geometric structure of the dyes is less planar. For bond length values, all dyes have bond lengths shorter than the single C-C bond length, which is 154 Å.

### **3.1** ESP (Electrostatic Surface Potential)

The electrostatic surface potential (ESP) is a parameter used to predict charge interactions between molecules in dyes, such as regions for electrophilic and nucleophilic attacks. The different colors including red, blue, and green, resulted from

ESP as representations of negative, positive, and neutral regions. The red region indicates electronegative properties (electron-attracting) favored by electrophilic attacks. The blue region indicates electropositive properties (electrondonating) favored by nucleophilic attacks [20]. The ESP map is shown in **Figure 4**.

The ESP map results show that the donor chain tends to be electropositive, indicated by the blue distribution, showing strong electron-donating properties, especially on hydrogen atoms bonded to nitrogen. Conversely, the acceptor chain tends to be electronegative, indicated by the red distribution, showing strong electron-attracting properties due to the presence of oxygen atoms in the -C=O group and nitrogen in -C=N in the formyl cyanide. This proves that different attack regions will facilitate electron transfer from the donor to the acceptor chain through the  $\pi$ -conjugated chain, making the

Indoline

T3

- T 4

electron injection process into the TiO<sub>2</sub> conduction band more efficient [21],[4].

### **3.2** Frontier molecular orbitals

The efficiency of DSSCs is highly influenced by the electronic properties of the dye molecules, including the energy gap (bandgap) and the energy levels of HOMO and LUMO. Molecular orbital boundaries, also known as HOMO and LUMO contributions, must be considered to determine the dye state during regeneration and electron injection [22]. An efficient sensitizer used in DSSCs is expected to have the smallest bandgap value. The smaller the dye's bandgap, the more the absorbed light will shift to longer wavelengths (red shift), making electron excitation from HOMO to LUMO easier and increasing light sensitivity [23],[8]. **Table 2** shows the HOMO-LUMO energy and bandgap of dyes T1-T6.

1.7149

a 100a

<b>Table 2.</b> Energy Levels of HOMO-LUMO and bandgap values of dyes T1-T6						
Dye	Donor Group	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	$\Delta E (eV)$		
Dithiophene	-	-5.2542	-1.8150	3.4392		
T1	Phenol	-5.7005	-3.1639	2.5366		
T2	Aniline	-5.1274	-3.2033	1.9241		

-3.1799

2 20 4 6

-4.8948

- 1017

14	ŀ	Diphenylamine	-5.4847	-3.3846	2.1002
T5	5	Coumarin	-5.9574	-3.5084	2.4490
<u>T6</u>	ō	Toluene	-5.7721	-3.1848	2.5873
	-1.5				
	-2.0 -	- <u>1.8150</u>			
	-2.5 -				
	-3.0 -		-3.1639 -3.2033	-3.1799	-3.1848
(eV)	-3.5 -			- <u>3.3846</u>	- <u>3.5084</u>
irgy	-4.0 -	- <u>4.00</u> TiO <sub>2</sub> 3.4392	2.5366 1.9241	1.7149 2.1002	2.4490 2.5873
Ē	-4.5 -			-4.8948	-4.80
	-5.0 -	-5.2542	- <u>5.1274</u>		F/I's
	-5.5 -		-5.7005	- <u>5.4847</u>	-5.7721
	~ ~				

J Ditiofen T1 T2 T3 T4 T5 T6 Figure 5. The energy diagram scheme of HOMO-LUMO, TiO<sub>2</sub>, electrolyte (I<sup>-</sup>/I3<sup>-</sup>), and the bandgap of dyes T1-T6

Based on **Table 2**, the bandgap values of the six dyes with varied donor chains are smaller than

-6.0 ·

those of unmodified dithiophene. This was because the modified dyes T1-T6 have more  $\pi$  electrons,

making the electron resonance longer compared to dithiophene. The longer the electron resonance, the more electrons get excited. Consequently, the orbital distance between HOMO and LUMO (bandgap) becomes smaller, which can increase DSSCs efficiency [24].

**Figure 5** also shows that the HOMO levels of all dyes are below the  $I^{-}I^{-}3$  redox pair (-480 eV), indicating easier cell regeneration and more spontaneous electron transfer from the electrolyte to the dye hole. Meanwhile, the LUMO levels of all the studied dyes were above the TiO<sub>2</sub> conduction band (-400 eV), making the electron injection process from the dyes to TiO<sub>2</sub> more spontaneous [25]. The smallest bandgap value was in dye T3, with a value of 1.7149 eV. This was because dye T3 has a nitrogen atom in the aromatic chain, making the indoline donor properties stronger than other dyes due to its longer electron resonance.

# 3.3 Electronic excitation and Absorption spectra

Optical properties are crucial in determining how much light a dye absorbs in DSSCs. These properties include the oscillator strength (f) related to the maximum absorption wavelength ( $\lambda_{max}$ ), the vertical transition energy of the dye from the ground to the excited state, the main transition, and the contribution percentage. The determination of the optical properties of the dyes was calculated using the TD-DFT/B3LYP/6-31G method. For high efficiency in DSSCs, the sensitizer absorption spectrum must be optimized to match the sunlight spectrum, thereby absorbing maximum solar radiation [26]. The absorption spectra of dyes T1-T6 are shown in **Figure 6**, and the electronic transition data are shown in **Table 3**.



Figure 6. The UV-VIS spectra of dyes T1-T6

Table 5. The	Table 5. The electronic transition data of D yes 11 10						
Dye	$\lambda_{\text{excitation}}(nm)$	E <sub>excitation</sub> (eV)	OM Configuration	Oscillator Strength (f)			
Dithiophene	360.77	3.4366	$H \rightarrow L = 99.53\%$	0.4302			
			$H \leftarrow L = 15.74\%$				
	306.04	4.0512	$\mathrm{H} \rightarrow \mathrm{L+1} = 99.76\%$	0.0003			
	271.43	4.5679	$H-3 \rightarrow L = 20.06\%$	0.0000			
			$\text{H-1} \rightarrow \text{L} = 87.97\%$				
			$\mathrm{H} \rightarrow \mathrm{L+2} = 41.80\%$				
T1	505.52	2.4526	$H \rightarrow L = 99.83\%$	0.8327			
	387.22	3.2019	$H-5 \rightarrow L = 96.23\%$	0.0000			
			$\text{H-5} \rightarrow \text{L+1} = 25.24\%$				
	359.40	3.4497	$H-1 \rightarrow L = 65.25\%$	0.3637			

**Table 3.** The electronic transition data of Dves T1-T6

			$H \rightarrow L+1 = 74.74\%$	
T2	827.57	1.4982	$H \rightarrow L = 99.48\%$	0.0000
	403.12	3.0756	$H-6 \rightarrow L = 98.03\%$	0.0000
	383.09	3.2364	$\text{H-1} \rightarrow \text{L} = 96.96\%$	0.0009
Т3	939.43	1.3198	$H \rightarrow L = 99.53\%$	0.000
	416.24	2.9786	$H-6 \rightarrow L = 19.16\%$	0.0001
			$H-1 \rightarrow L = 96.43\%$	
	402.45	3.0807	$H-6 \rightarrow L = 97.21\%$	0.0000
			$H-1 \rightarrow L = 18.81\%$	
T4	734.99	1.6869	$H \rightarrow L = 99.28\%$	0.0420
	406.97	3.0465	$H-1 \rightarrow L = 96.60\%$	0.7550
			$H \rightarrow L+1 = 18.45\%$	
	398.58	3.1107	$H-7 \rightarrow L = 25.69\%$	0.0004
			$H-6 \rightarrow L = 93.66\%$	
			$\text{H-6} \rightarrow \text{L+1=21.45\%}$	
T5	513.12	2.4163	$H \rightarrow L = 100.29\%$	1.2179
			$H \leftarrow L = 15.20\%$	
	411.60	3.0122	$H-2 \rightarrow L = 18.27\%$	0.0566
			$H-1 \rightarrow L = 39.34\%$	
			$H \rightarrow L+1 = 88.29\%$	
	391.12	3.1700	$H-4 \rightarrow L = 89.98\%$	0.0000
			$H-4 \rightarrow L+1 = 39.82\%$	
			$H-4 \rightarrow L+2 = 15.79\%$	
T6	493.24	2.5137	$H \rightarrow L = 99.88\%$	0.9174
	387.35	3.2008	$H-5 \rightarrow L = 95.90\%$	0.0000
			$H-5 \rightarrow L+1 = 26.46\%$	
	355.11	3.4915	$\text{H-1} \rightarrow \text{L} = 54.22\%$	0.3014
			$H \rightarrow L+1 = 82.45\%$	

From **Figure 6**, it can be seen that dye T5 has a higher light absorption intensity. This indicates a greater amount of light absorbed at that wavelength, resulting in a higher electron injection into the semiconductor [27]. The dye with the highest light absorption was dye T3, at 939.43 nm, with the smallest excitation energy of 1.3198 eV, and this dye can absorb light up to the near-infrared (IR) region. High absorption intensity can increase the LHE value, while a broad absorption wavelength range will increase the J<sub>SC</sub> value.

Furthermore, the data in Table 3 show that all modified dyes exhibit a redshift in absorption wavelengths compared to unmodified dithiophene dye. This indicates that modifying the dye structure with heterocyclic groups positively influences the optical properties, enhancing DSSCs efficiency [28]. Therefore, dyes T1-T6 can be used as sensitizers due to their better ability to absorb sunlight in the UV and visible regions. The modified dyes also have lower excitation energies than dithiophene dye, indicating that the excitation ability between HOMO and LUMO in these dyes is more dominant (major transition), with an average

contribution percentage of about 99%, resulting in higher power conversion efficiency.

Research conducted by Mao et al. has shown that dyes with a broader light absorption range and higher absorption intensity demonstrate better light absorption capability, improving DSSCs performance efficiency [2]. However, wavelength has a greater influence on light absorption efficiency. Therefore, dye T3 can be considered the best sensitizer for DSSC applications due to its smaller excitation energy and larger  $\lambda_{max}$ .

### 3.4 Chemical reactivity parameters

Ionization potential (IP), electron affinity (EA), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $\sigma$ ), electrophilicity index ( $\omega$ ), and nucleophilicity index ( $\xi$ ) are chemical reactivity parameters calculated and presented in Table 4. A molecule is reactive if it has a small ionization potential, large electron affinity, large chemical potential, small electronegativity, small hardness, large softness, large electrophilicity and small nucleophilicity[17].

The smaller the IP value and the larger the EA value, the easier it is for the dye to transfer its

electrons [29]. Based on **Table 4**, it can be seen that all modified dyes have smaller IP,  $\eta$ , and  $\xi$  values and larger EA,  $\mu$ ,  $\chi$ ,  $\sigma$ , and  $\omega$  values than unmodified dithiophene dye. This indicates that

modifying the dye structure significantly impacts the improvement of DSSCs performance. T3 dye is the most reactive as a sensitizer in DSSC.

Table 4. Values of Chemical reactivity parameters of dyes T1-T6								
Dye	IP	EA	μ	Х	η	σ	ω	بح
Dithiophene	5.25	1.82	3.53	-3.53	1.72	0.58	3.63	0.28
T1	5.70	3.16	4.43	-4.43	1.27	0.79	7.74	0.13
T2	5.13	3.20	4.17	-4.17	0.96	1.04	9.02	0.11
Т3	4.89	3.18	4.04	-4.04	0.86	1.17	9.51	0.11
T4	5.48	3.38	4.43	-4.43	1.05	0.95	9.36	0.11
T5	5.96	3.51	4.73	-4.73	1.22	0.82	9.15	0.11
T6	5.77	3.18	4.48	-4.48	1.29	0.77	7.75	0.13



Figure 7. Optimization of the dye structures of T3-TiO<sub>2</sub>-anatase

Table 5. Bond	length value and	adsorption energy of	the best dyes

Parameter	Value
L <sub>1</sub> (Ti-O)	2.013
$L_2$ (Ti-N)	2.037
$E_{dye}$ (kJ/mol)	219.6584
E <sub>TiO2</sub> (kJ/mol)	2600.273
E <sub>dye-TiO2</sub> (kJ/mol)	3020.3888
E <sub>ads</sub> (kJ/mol)	200.4574

### 3.6 Electronic and Optical properties of Dye-TiO<sub>2</sub> anatase

**Figure 7** shows the optimal structure of the best dye, namely T3, interacting with TiO<sub>2</sub>, and the bond length and adsorption energy values can be seen in **Table 5**. Dye adsorption plays a crucial role in overall stability and energy conversion efficiency in DSSCs. Moreover, the adsorption energy of all dye-TiO<sub>2</sub> systems can be calculated using the following relationship:

$$E_{ads} = E_{dye-TiO2} - (E_{dye} + E_{TiO2}) \qquad \text{Eq. 18}$$

where  $E_{dye-TiO2}$  is the total energy of the dye-TiO<sub>2</sub> system,  $E_{dye}$  is the energy of the modified dye, and  $E_{TiO2}$  is the energy of anatase TiO<sub>2</sub>. A higher  $E_{ads}$ 

value indicates a higher probability of dye adsorption. As shown in **Table 5**, the bond lengths L1 (Ti-O) and L2 (Ti-N) between oxygen (O) and nitrogen (N) atoms from the dye and titanium (Ti) from the TiO<sub>2</sub> complex range between 2.013 and 2.037 Å. This indicates that dye T3 exhibits a strong adsorption capacity on the TiO<sub>2</sub> surface. For adsorption energy, the larger the  $E_{ads}$  value, the stronger the TiO<sub>2</sub> absorption. **Table 5** shows that dye T3 has a higher  $E_{ads}$  value of 200.4574 kJ/mol [23]·[28].

# 3.7 Excited-state lifetimes and Photovoltaic properties

The excited-state lifetimes ( $\tau$ ) play a vital role in assessing the photovoltaic performance of DSSCs. The excited-state lifetime value should be higher for dyes to achieve a higher VOC value in DSSCs.

The excited state lifetime  $(\tau)$  can be calculated with the equation:

$$\tau = \frac{l,499}{\int E_{ex}^2} \qquad \text{Eq. 19}$$

where  $E_{ex}$  indicates the excitation energy (in cm<sup>-1</sup>) from the first excited state and *f* is the oscillator strength for the same state. The excited state lifetime value ( $\tau$ ) affects the charge transfer efficiency in DSSCs performance. The larger the lifetime value of a dye molecule, the more charge transfer will be contributed, and electrons will remain longer in the excited state. In addition, an increased lifetime will also inhibit the charge recombination process and enhance DSSCs efficiency [28]. **Table 4** shows that dyes T2 and T3 have infinite  $\tau$  values. This indicated that these dyes can enhance the charge transfer efficiency of electron injection into the TiO<sub>2</sub> conduction band and stability after electron injection

The dipole moment indicates a molecule's ability to form negative and positive charge centers (polarization) due to electron transfer in the dye. The larger the dipole moment value, the easier it is to form positive poles on the donor chain and negative poles on the acceptor chain. Thus, a larger dipole moment has better charge transfer and can increase the V<sub>OC</sub> value [8],[12]. **Table 6** shows that dye T3 has a larger dipole moment value than other dyes. This was because of the nitrogen atom in the donor chain, which has a strong indoline donor property, making it easier to form positive poles as electrons move from the donor to the acceptor through  $\pi$ -conjugation.

 $\Delta G_{ini}$  is the dye molecule's ability to inject electrons from the LUMO orbital to the TiO<sub>2</sub> conduction band. The more negative the  $\Delta G_{inj}$  value, the easier (spontaneous) the electron injection process, and capable of increasing the J<sub>SC</sub> value [30]. Based on **Table 6**, dye T1 has a more negative  $\Delta G_{ini}$  value of -0.7521 eV. This indicated that the electron injection process into the TiO2 conduction band will be easier and occur spontaneously. Meanwhile,  $\Delta G_{reg}$  is the cell regeneration ability in electron transfer from the electrolyte to the dye hole. Efficient dye regeneration requires a smaller  $\Delta G_{reg}$ value to produce higher power conversion efficiency [31]. Based on Table 6, the dye with the smallest  $\Delta G_{reg}$  value is dye T3, with a value of 0.0948 eV, indicating that its cell regeneration process is more stable and capable of enhancing the power conversion efficiency in DSSCs.

Table 0. LACI	ted State Effetimes, dipe	$\Delta c$ moment, $\Delta c$	Jinj and Doreg C	л uyes 11 10
Dye	Dipole Moment (D)	$\Delta G_{inj}(eV)$	$\Delta G_{reg}(eV)$	τ (ns)
Dithiophene	0.000171	-2.1824	0.4542	4.54
T1	9.168634	-0.7521	0.9005	4.60
T2	13.083995	-0.3708	0.3274	$\infty$
T3	13.999767	-0.4250	0.0948	$\infty$
T4	11.226228	-0.2022	0.6847	192.80
T5	9.817803	-0.4589	1.1574	3.24
T6	9.590497	-0.7416	0.9721	3.98

**Table 6.** Excited-State Lifetimes, dipole moment,  $\Delta G_{inj}$  and  $\Delta G_{reg}$  of dyes T1-T6

Fable 7. LHE and	Voc	Values	of Dyes T1-	T6
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Dye	LHE	V <sub>OC</sub> (eV)
Dithiophene	0.62864; 0.00069; 0.00000	2.1850
T1	0.85301; 0.00000; 0.56719	0.8361
T2	0.00000; 0.00000; 0.00207	0.7967
T3	0.00000; 0.00023; 0.00000	0.8201
T4	0.09218; 0.82421; 0.00092	0.6154
T5	0.93945; 0.12219; 0.00000	0.4916
T6	0.87905; 0.00000; 0.50043	0.8152

The ability of dyes to generate electricity can be observed from electrical parameter values such as  $V_{OC}$  (open-circuit voltage),  $J_{SC}$  (short-circuit current density), and power conversion efficiency

( $\eta$ ) [32]. According to Equation 1, the efficiency of DSSC is influenced by V<sub>OC</sub>, J<sub>SC</sub>, and light intensity. Higher values of V<sub>OC</sub> and J<sub>SC</sub> lead to greater DSSCs power efficiency. Lower light intensity allows absorption at longer wavelengths, resulting in a

smaller bandgap. Meanwhile,  $J_{SC}$  values are influenced by LHE and oscillator strength (f), where higher oscillator strength indicates greater LHE of dye molecules, thus yielding higher  $J_{SC}$ values [33]. The values of LHE and  $V_{OC}$  are shown in **Table 7**. **Table 7** demonstrates that the highest LHE value is found in dye T5, attributed to its higher oscillator strength compared to other dyes, resulting in a high f value and thus a large LHE. The highest  $V_{OC}$  value is observed in dye T1, which is due to its higher  $E_{LUMO}$  value compared to other dyes, making it excellent for photo-current conversion efficiency.

### 4. Conclusions

Based on the study conducted, it has been shown that modifying dithiophene into D- $\pi$ -A type dyes with varying donor chains can reduce the bandgap value, thereby enhancing light absorption efficiency in DSSCs.The most potential dye to be used as a sensitizer was T3 dye with an indoline donor group. This best-performing dye exhibits a bandgap value of 1.7149 eV,  $\lambda$  of 939.43 nm, excitation energy of 1.3198 eV,  $\Delta G_{inj}$  of -0.4250 eV,  $\Delta G_{reg}$  of 0.0948 eV, and V<sub>OC</sub> value of 0.8201 eV. These results indicated that T3 dye can operate effectively from morning to late afternoon because it is able to absorb light up to the infrared region.

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