Novel Absorber Material Design Based on Thiazole Derivatives Using DFT/TD-DFT Calculation Methods for High-Performance Dye Sensitized Solar Cell

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Abstract— Thiazole derivative molecules with a low energy gap have been successfully designed using the DFT/TD-DFT calculation methods. The calculations were simulated by adding varied numbers of thiophenes (1, 2, 3, and 10) and electron donating molecules of –H, –NH$_2$, –OCH$_3$, and –COOH in the ethanol solvent. The best thiazole derivative was the molecule constructed using a long-conjugated bridge of 10-thiophenes, the carboxyl anchoring site, and an amine addition as the electron donating molecule with an energy gap of 1.66 eV and a strong UV-Vis absorption in the red light region (673.20 nm). These designed molecules are beneficial to be applied in the equator area such as Indonesia. Further, the profound effects of the thiophene bridge in terms of the structural and energy gaps, and the variation of electron-donating molecules affected the photonic properties have been demonstrated in this paper.

1. INTRODUCTION

Energy security is one of the main factors determining the strength of a country because of its vital function [1]. The International Energy Agency (IEA) defines energy security as the availability of an abundant energy source in a nation at an affordable price with a benign supply for 90 days of oil equivalent imports [2]. Indonesia, a country with immense renewable energy potential, has to rely on the utility of fossil energy, with the usage rate reaching ~90% [3]. Furthermore, some crucial predictions from the 2019 Energy Outlook published by the Indonesia National Energy Council stated that the national oil production is estimated to be low at 53.8 million barrels in 2050, with only 71 years remaining for the coal stockpile [4]. Therefore, the transition to the employment of renewable energy is a straightforward strategy for the country.

Although the potential of renewable energy in Indonesia is abundant, the energy mix target of 23% in 2025 merely can be achieved by 10% at this time. Data from the Institute for Essential Service Reform (IESR) in 2019 shows the solar power potential in Indonesia isup to 208 gigawatts. However, only 159 megawatts are employed, or less than 0.08% of the total potential used [5]. The low realization proportions are due to unclear regulations, unavailable markets, and weak research on product development [6]. Therefore, studies focussing on photovoltaic technology and its device as a solution to the latest problem are significantly substansial in Indonesia.

The photovoltaic device is an instrument that converts sunlight into electrical energy utilizing engineered semiconductor materials, which have been developed since 1954 using silicon-based solar panels [7]. Although it is a senescent technology, Indonesia does not yet have an industrial plant that produces silicon panels due to its complexity and high production costs. One alternative in photovoltaic technology that is widely studied is dye sensitized solar cells (DSSC). This technology has been at the center of attention of researchers for the last 30 years because of its potential as an effective, economical, flexible, highly reproducible, and scalable power conversion device for industry [8]. Since O'Regan and Gratzel first report in 1991, the exploitation of dyes has been very high to replace silicon-based solar cells that act as light harvesters to generate electricity. To date, the power conversion efficiency (PCE) of DSSC

has reached over 14% due to various optimizations such as their film formation, charge transport, electrolyte system, and dyes enhancement, most importantly [9].

Curcumin, phenylalanine, dithienopyrrole, and thiazole are used actively as sensitizers in DSSC devices [10]. Numerous studies using thiazoles have obtained promising results due to their intrinsic properties, such as intense intramolecular charge transfer, strong absorption of visible light, and broad molecular derivatives [11]. In addition, the selection of thiazoles is determined strongly by the nature of the extendable conjugated bridge based on the stable structure of the donor-conjugated bridge-acceptor (D-π-A). Therefore, further studies, from molecular to mechanical aspects, are always required to optimize thiazoles in DSSC. Fortunately, the computational approach continues to be an essential method in predicting the potential of particular sensitizers for DSSC concerning cost-effective research. Both density functional theory (DFT) and time-dependent density functional theory (TD-DFT) have been adopted optimally as standard investigative tools on the optoelectronic properties of molecules in dyes involving the ground and excited states, respectively [12]–[14].

In this work, we employed the DFT and TD-DFT methods and the results were analyzed to establish a reproducible roadmap in designing some novel molecules based on thiazole derivatives focusing on the sum of the effects of the thiophene acting as expandable conjugated bridge. Furthermore, particular added electron donating molecules were also simulated to optimize their optoelectronic properties. This type of computational study is crucial, especially in this Covid-19 pandemic situation, because computational approach is an ultimate solution to obtaining high quality and cost-effective research.

2. COMPUTATIONAL DETAILS

2.1. Calculations Methods

In this study, both the geometric and optoelectronic properties of the designed molecule as a novel sensitizer in DSSC were deeply investigated and calculated using the standard Gaussian 09 package. Firstly, a 3D molecular structure was generated via Avogadro software. The Merck molecular force field (MMFF94), as a precise molecular mechanics tool that freely available in the software, was adopted to minimize the conformational energies [15].

A full geometry optimization was performed further using a DFT calculation based on Becke's three parameters gradient-corrected exchange potential and the Lee-Yang-Parr gradient correlation potential (B3LYP) hybrid functional using a common basis set of 6-31G(d). The parameters and basis set were found to be quite stable and already established in the aforementioned package [16]. The convergence of a geometry search was reached when the largest component of the gradient was less than the optimization tolerance and the root mean square gradient was less than a third of the optimization tolerance. The initial geometry optimization was performed under an ethanol solvent environment (ε = 24.55) with no symmetry restriction to produce an optimal ground state structure of the designed molecules. Moreover, all of the obtained geometries were confirmed to be the minima value on the potential energy surface (PES) by performing vibrational frequencies calculations.

In the next step, the optoelectronic properties of the designed molecules were simulated and precisely calculated through the TD-DFT method using a correlation-consistent basis set up to the 1d electron orbital (cc-pVDZ) as implemented in the Gaussian 09 software. It is globally accepted that the TD-DFT approximation, despite its shortcomings, is still recognized as a decent compromise to evaluate vertical excitation energies and it's results are comparable to the experimental optical spectra.

Thus, based on the mentioned methods, we could possibly obtain some valuable data regarding the optical and electronical properties of the excited molecules such as excitation energy or frontier orbital's energy gap, excitation symmetry, and percentage of excitation, electron density in both of highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO). Finally, we demonstrated the possible UV-vis absorption spectra and the resulting molecular orbitals using GausSum and GabEdit, respectively.

2.2. Calculation Roadmap Details

The ultimate purpose of this research was to demonstrate a detailed workflow when designing a certain molecule as a sensitizer in DSSC. To obtain a precise result, the first step was to create a z-matrix from the thiazole as the main molecule using a simple molecular software such as Avogadro followed by optimization of its ground state structure via DFT calculation using Gaussian 09.

Further, various of thiophene functional groups as an expandable conjugated bridge was added and optimized using the previously mentioned method. After the optimized ground state geometries of thiazole derivatives with various thiophens bridge were obtained, further calculations employing the TD-DFT method were performed to reveal the optoelectronic properties in their excited states.

To enhance the previous models, several electron donating groups were attached to the latest thiazole with the optimized thiophene numbers and their excited states were calculated using the identical method as before. Finally, combining these two parameters will reveal the best performed thiazole derivative as a sensitizer in DSSC.

3. RESULT AND DISCUSSION

In this study, we designed molecules based on the well-known chemical reaction of thiophene-2-carbothioamide with ethyl 2-bromo-2-(4-nitrophenyl)acetate via Hantzsch cyclization as demonstrated in scheme 1, in **Fig. 1**. Next, the obtained material, which was 4-hydroxy-1,3-thiazole then alkylated with K_2CO_3 and methyl iodide succeeding a Williamson-type etherification to get 4-methoxy-5-(4-nitrophenyl)-2-(thiophen-2-yl)thiazole as witnessed in scheme 2. Furthermore, the reduction reaction of the nitro group in the previous results was conducted by hydrazine hydrate solution and a Nickel substrate to yield amine 4-(4-metoxy-2-(thiophen-2yl)thiazole-5-yl)aniline as presented in scheme 3.

Finally, the reference molecule for further modification was obtained by reacting the last yielded molecule with hydrochloric acid at -50 °C to form diazonium compound, and later be deaminated using hypophosphorous acid as shown in the latest scheme (4). This final product was labelled as a reference thiazole in this report for simplification. Based on its common synthesis route and high resonance opportunity provided by conjugated bonding, further analysis developed with a reproducible computational calculation were presented in this report.
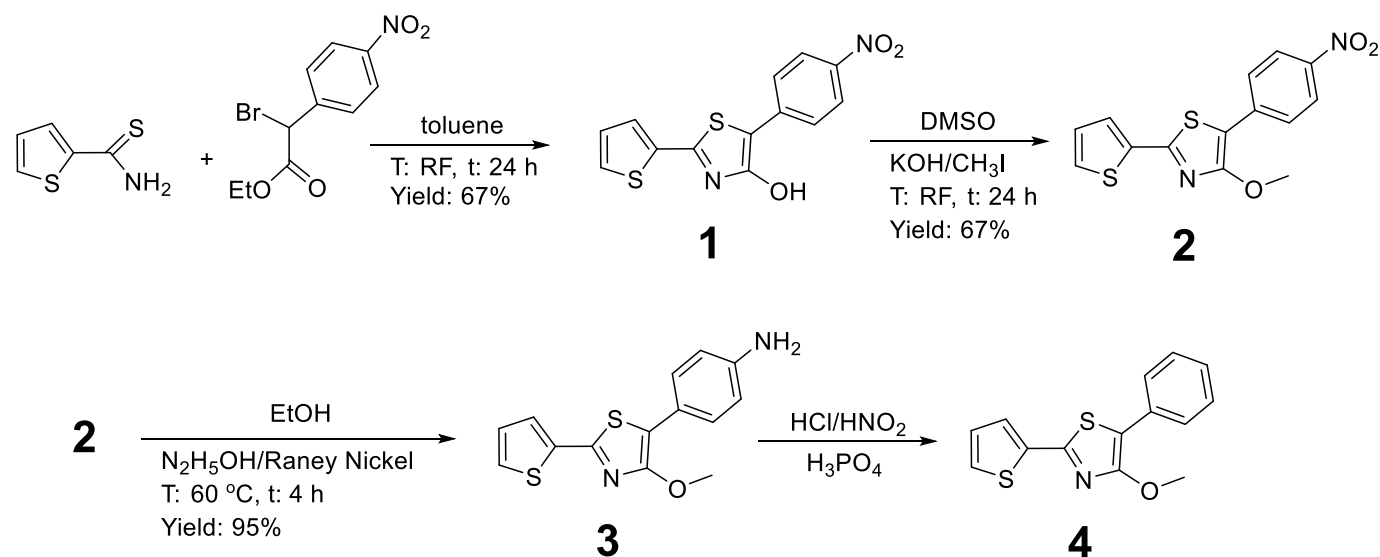

Fig. 1. Schematic synthesize route of reference thiazole [17]

The first modification on this thiazole main molecule started by adding thiophene as a π-conjugated bridge. It is already reported in several studies that the longer the bridge the lower the molecular energy gap, producing a red-shifted electronic absorption spectrum [18]. Even though decreasing the energy gap can improve the light-harvesting ability of the photoactive materials, it should be noted that the HOMO position needs to be matched with the TiO_2 semiconductor, especially in the D-π-A structure. Therefore, a careful analysis involving structure and excitation states of the active material is extremely imperative.

In term of structural study, we calculated different number of thiophene to modify the π-bridge length. The total energy (kJ mol⁻¹) of 1, 2, 3, and 10 number of thiophenes were calculated using the self consistent field (SCF) method in the Hartree-Fock (HF) approximation in conjugation with an augmented valence triple-zeta basis set, 6-311G(d,p), to ensure a correct description of the H-bond system. The stable B3LYP hybrid functional was used as a reliable energy calculation in terms of structural optimization [19]. As shown in the **Table 1**, the more thiophene added in the molecule, the lower the total energy. This result is because the thiophene in the designed photoactive molecules can stabilize their structure since they will act as conjugated bridge [18]. A total SCF energy of -1.77×10^{-7} kJ mol⁻¹ was obtained with the 10 thiophene while a single thiophene had an energy of -0.47×10^{-7} kJ mol⁻¹. Although ten thiophenes can decrease the total SCF energy more than three times that of the reference structure, it should be noted that creating a long π-bridge is experimentally challenging.

Table 1. Total SCF energy with thiophens variation

Thiophene Amount*	Total SCF Energy (kJ mol⁻¹)
1	-0.465×10^{-7}
2	-0.610×10^{-7}
3	-0.755×10^{-7}
10	-1.769×10^{-7}

*The structure of four designed molecules with the different of thiophens amount is depicted in the Supporting Information, **Fig. S1.**

Regarding the energetical results by the DFT investigation to obtain the favourable structure, the excited state geometries and their optical properties of designed photoactive molecules were calculated using the TD-DFT method with the cc-pVDZ basis set in the ethanol phase. From this higher-level theory, energy gaps information is obtained which is a essential for designing any molecule to be a sensitizer in DSSC. The Gaussian software also facilitates us to

obtain excitation symmetry and their composition which are important for excitation analysis during the photo incident.

Table 2. Vertical excitation profile of excited thiazole molecules with thiophens variation

Thiophene Amount	Vertical Excitation Profile		
	Energy Gap (eV)	Symmetry	Composition (%)
1	2.58	HOMO →LUMO	100
2	2.35	HOMO →LUMO	100
3	2.23	HOMO →LUMO	99
		HOMO-1 → LUMO+1	1
10	1.86	HOMO → LUMO	91
		HOMO-1 → LUMO+1	6
		HOMO-2 → LUMO+2	3

All designed molecules are based on organic compounds with π-conjugated bridge, thus, the excitation energy shown in the calculation is mainly an energy different (HOMO-LUMO energy gap) between π to π* orbitals. **Table 2** shows that the variation of π-bridge length provide meaningful results. The longer the bridge, the lower the energy gap. The ten thiophens were recorded to have 1.86 eV energy gap, while the reference had 2.58 eV. These results are quite promising in DSSC, since the decreasing energy can simply be achieved by adding a conjugated π bridge. With these early data, we confidently recommend to design photoactive planar molecule with higher conjugated value to achieve 1.4 eV as the most ideal energy gap for photovoltaic devices [20].
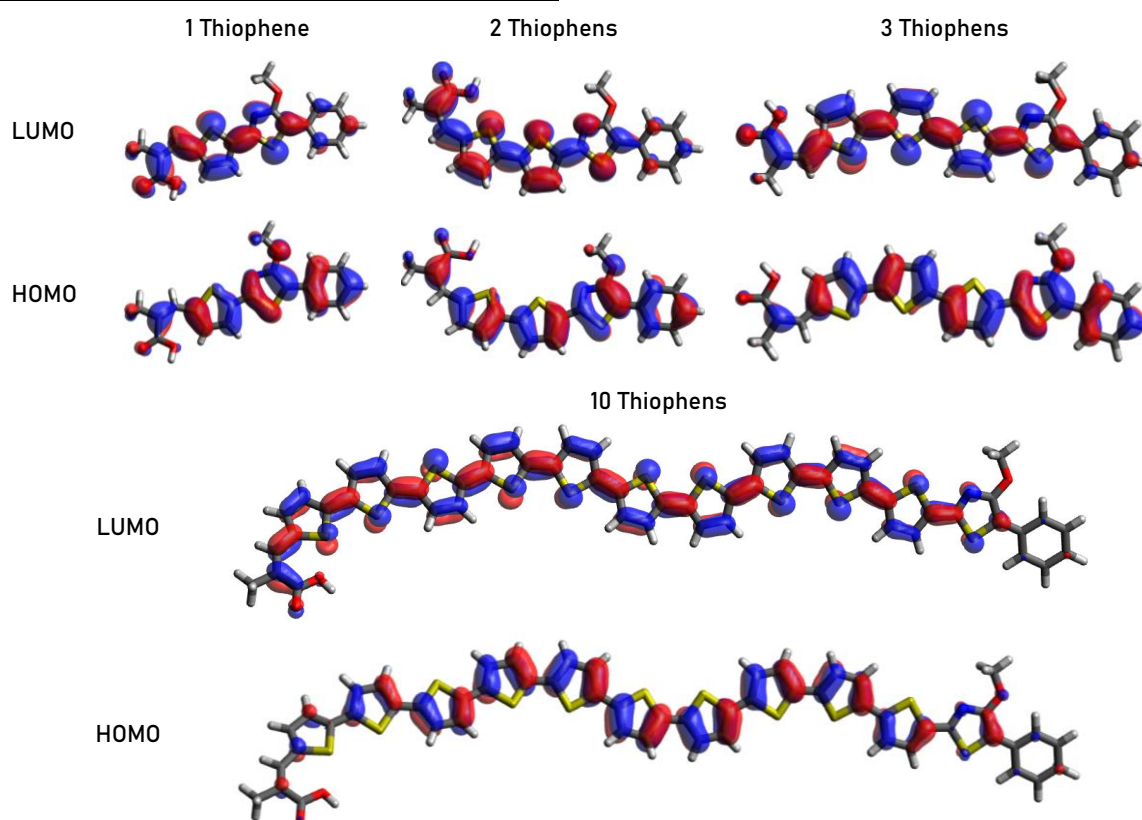
Fig. 2. The molecular orbital density in HOMO and LUMO states of thiazole molecules with thiophens variation. The phase of wave functions is shown as red and blue colors of the represented molecular orbitals

The excitation symmetry and its composition presented in **Table 2** showed that one and two thiophenes provided a hundred percent excitation from the HOMO to LUMO symmetry, while the three thiophenes with 2.23 eV had branched excitations. Furthermore, ten thiophens showed a triple excitation symmetry with the majority of HOMO to LUMO excitation (91%), HOMO-1 to LUMO+1 of 6%, and only 3% from HOMO-2 to LUMO+2 symmetry. The excitation symmetry branching will further increase due to the overlapping orbitals between the ground and excited states [21]. This typical condition should be tackled down in the designing decent sensitizer in DSSC since the cumulative overlapping orbitals lead to

deexcitation phenomena, which later reducing the final current in the devices.

Although there is a branching in the excitation symmetry of the thiazole with ten thiophens, the designed molecules still have a tendency to be a great photoactive material since the majority of excitations is conducted in the HOMO to LUMO symmetry, with more than 90% composition. The localization orbital states play a crucial role in this phenomenon [21]. Despite majority of orbitals seems to be overlapped as shown in **Fig. 2**, the density in LUMO is relatively high in its methoxy group. In contrast, the orbital density also increases in the aromatic rings for the HOMO state. Based on this simulation, a clear electron

separation between its ground and excited states will be beneficial for DSSC.

Moreover, from the absorbance prediction by TD-DFT, it is clearly stated that all designed molecules have the potential to be used as dyes in DSSC due to their absorbance in the range of 480.33 to 667.54 nm. The oscillator frequency ($f_{oscillator}$) also witnessed a great increase as the rise of the number of thiophens, because it actively transfers excited electrons after the photo incident. Thus, it is imperative to design several photoactive molecules with the longest possible of conjugated bridge as the trade-off between the stability, cost-efficient procedure, and the photoactive performance.

Absorbance study is one of the fundamental properties to be directly observed when designing photoactive materials. The peaks in the absorption spectra, or usually showed as a spectrum edge, provide important information about the energy gap (E_g), which is easily calculated from $E_g = h\nu$. A lower gap will induce more photons to be absorbed by the materials, thus more electricity will be produced in the device. A higher energy gap means a highly transmittance material, leading less incident light to potentially be converted into electricity [22]. It has been calculated from the black body radiation and the Shockley-Queisser limit that the ideal gap of semiconductor materials to absorb the maximum number of photons from solar radiation was 1.4 eV [20]. This calculation becomes the foundation to design any novel materials in a single photovoltaic device to obtain an energy gap as close as possible to 1.4 eV.

The TD-DFT calculation has become a robust approach to simulate UV-Vis absorption spectra with a precise maximum absorption value. **Table 3** reveals a strong effect of the thiophene bridges in designed photoactive materials in both of maximum wavelength (λ_{MAX}) and $f_{oscillator}$. A strong redshift spectrum was observed when the amount of thiophene increase, from 480.33 to 667.54 nm by ten of thiophene additions. The higher number of excited electrons in the conjugated chain causes massive increase in the oscillator frequency, whereas the redshift phenomena occurs due to the weaker anchoring site effect in the longer bridge. These result indicate that π-junction could effectively reduce the gap up to 71.7%, from 2.58 to 1.85 eV, which is closer to the ideal energy gap of photovoltaics device. It should be noted that a normal carboxyl is performing the anchoring effect inside the molecule.

Table 3. Absorption profile of thiazole molecules with thiophens variation

Thiophens Amount	λ_{MAX} (nm)	$f_{oscillator}$ (Hz)	E_g (eV)
1	480.33	1.12	2.58
2	525.62	1.42	2.36
3	556.25	1.99	2.23
10	667.54	4.24	1.85

Furthermore, the electron donating groups were varied as an additional step to show the effect of each molecules attracted in one thiophene based structure. To make the effect stronger, the anchoring site was modified using a thiophene as the reference. One thiophene is chosen due to the calculation complexity that might contribute to the accuracy. Three molecules were employed at the terminal benzene, $-NH_2$, $-OCH_3$, and $-COOH$ to demonstrate a uniform attraction on the whole sensitizer molecules. Similar to the previous simulation, a higher amount of electrons results in a more negative total SCF energy, leading to a more stable structure. Hence, -COOH witnessed the lowest energy, -5.28×10^{-8} kJ mol^{-1} compared to the control (-4.79×10^{-8} kJ mol^{-1}). The detail results are available in **Fig. S2** and **Table S1** of the Supporting Information.

Interestingly, although all electron donating molecules witnessed a 100% excitation profile from HOMO to LUMO, the energy variations were clearly observed. Based on the TD-DFT calculation for each excited molecule, $-NH_2$ shows a dramatical reduction in the energy, 1.96 eV compared to the -COOH, 2.31 eV, which is quite high and is still similar with the control (-H), 2.59 eV. It is clearly shown that all of electron donating molecules provide a good agreement for the HOMO and LUMO states.

To clearly investigate the effect of electron donating molecules in thiazole derivatives, the UV-Vis absorption was evaluated using TD-DFT calculations and revealed a huge redshift in the $-NH_2$ sample. The absorbance peak dramatically shifts from 479.11 nm to 632.57 nm, consequently reducing the band energy gap from 2.58 to 1.96 eV, as shown in **Table 4**. These results indicate that the addition of $-NH_2$ in the sensitizer, especially in the term can provide a benefit due to effective electron donating effect to the whole system. However, experimental should be carefully designed to attach the amine site into the benzene side which is quite tricky.

Table 4. Absorption profile of thiazole with a thiophen and different electron donating molecule

Electron Donating	λ_{MAX} (nm)	$f_{oscillator}$ (Hz)	E_g (eV)
–H	479.11	0.90	2.58
$-NH_2$	632.57	1.05	1.96
$-OCH_3$	584.49	1.05	2.12
$-COOH$	536.33	1.23	2.31

Finally, by optimizing the thiophene bridges by its number and electron donating molecule, the results were combined to deeply investigate the best performed molecule, a thiazole with a 10-thiophenes bridge and an amine at the edge. Two types of molecules were simulated with the reference model and highly ordered *trans* structure. **Fig. 3** depicts the mentioned structure, with a slightly different stabilization energy. A *trans*-thiazole recorded -1.797×10^{-7} kJ mol^{-1} while the reference showed a higher value of -1.799×10^{-7} kJ mol^{-1}. This ultra-small different

indicates a stable structure to be obtained in the synthesis without any notable risk to increase complexity to get the highly ordered structure. The high number of electron repulsion inside the system can also leads to the reference structure instead of a *trans*-thiazole structure.
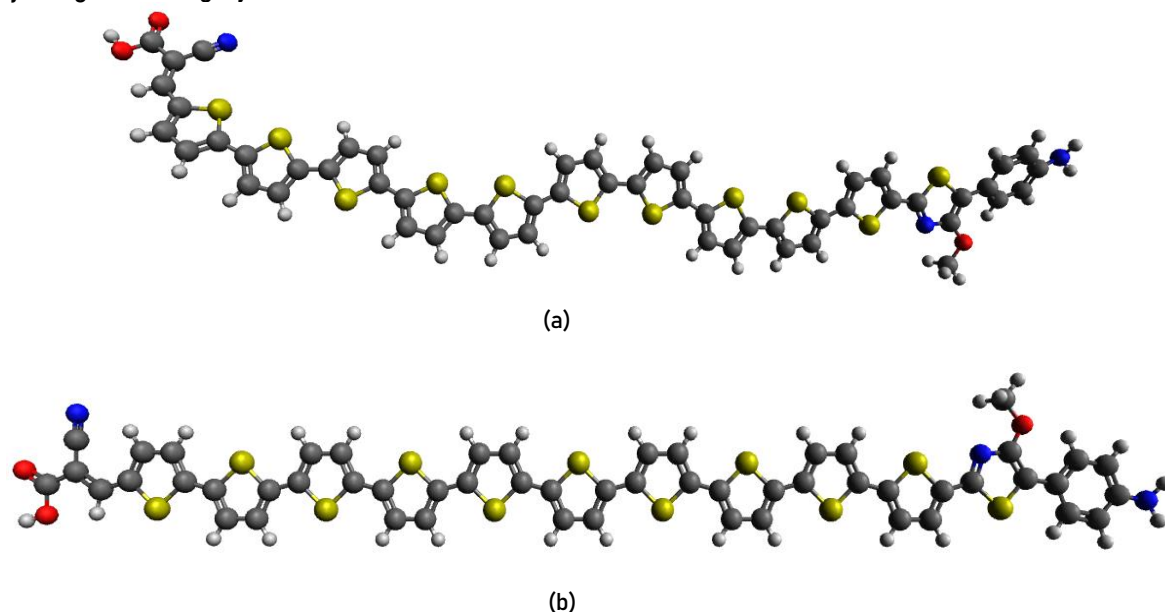

(a)

(b)

Fig. 3. (a) Reference and (b) the best performed thiazole derivative

Remarkable results showed by the excitation profile investigation through the best performed structure compared to the 10-thiophenes based molecule. Interestingly, a 1.66 eV of bandgap energy gap was recorded with the 79% of HOMO → LUMO excitation symmetric compared to 1.85 eV of the later structure. This 11.37% decrement is a significant result since it will lead to the higher number of photons absorbed by thiazole, and it was obtained by simply adding an amine group as an electron donating group. Therefore, this type of doping is highly recommended for designing a low energy gap absorber material. The excitation mapping between the ground and excited states of the best performed thiazole molecule are presented in **Fig. 4**, with the HOMO-1 → LUMO and HOMO → LUMO+1 excitation symmetric contributing to the 12% and 7% of the total composition, respectively.
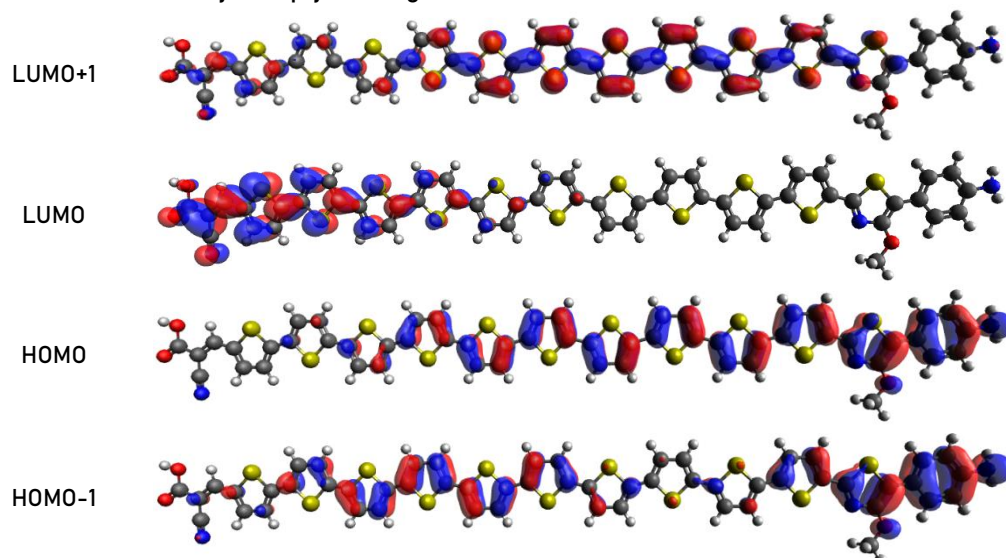

LUMO+1

LUMO

HOMO

HOMO-1

Fig. 4. The HOMO-1, HOMO, LUMO, and LUMO+1 orbital density states of the best performed thiazole derivative model

In addition, the simulated UV-Vis spectrum reported in **Fig. 5** clearly presents a strong absorbance around 625 and 720 nm, that is a reddish sunlight. This result is extremely important because the majority sunlight in equatorial is in the red region (above 620 nm). Moreover, the strongest peak at 673.20 nm with an oscillator frequency of 2.29 Hz should be noted as the intrinsic advantage to manage the photon incident through the photoactive material. Thus, the designed molecule will be beneficial to be prepared as a high-performance absorber material in DSSC applied in Indonesia.
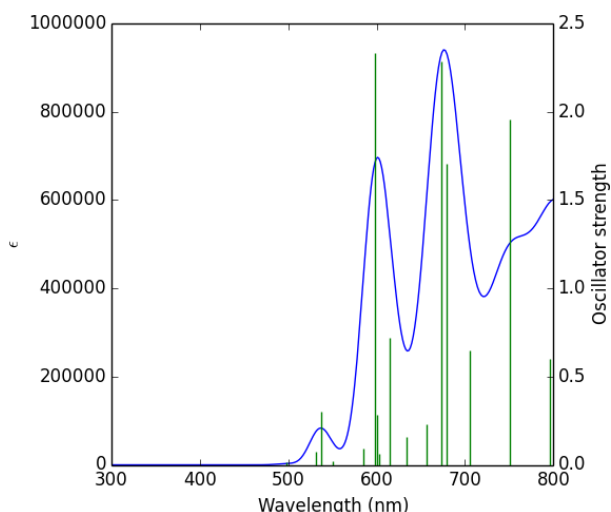
Fig. 5. Simulated UV-Vis absorption spectrum for the best performed of designed thiazole

4. CONCLUSION

To conclude, we had successfully designed a novel photoactive material with a low energy gap of 1.66 eV and strong UV-Vis absorption in the red light region (673.20 nm). The results were beneficial to be applied in an equatorial area such as Indonesia. The best performed thiazole derivative molecule was constructed using a long-conjugated bridge of 10-thiophenes, the carboxyl anchoring site, and the addition of an amine as the electron donating molecule. Furthermore, the considerable effect of thiophene bridge was demonstrated in terms of structural and energy gap, as well as the variation of electron donating molecule that strongly affected the photonic properties. A robust roadmap design was constructed here from the structural analysis to the photonic properties employing the DFT and TD-DFT level of calculation that could be used for other research related to any molecular design for photovoltaic application. Finally, since all the results had been conducted by computational studies, we encouraged others to carry out a significant research in the field of renewable energy even in the pandemic situation or in the future of digital society.

SUPPORTING INFORMATION

The supporting information related to the present work can be downloaded here.

ACKNOWLEDGEMENTS

CONFLICT OF INTEREST

We declare that there is no conflict of interest among authors.

AUTHOR CONTRIBUTIONS

NN conducted the experiment and DFT/TD-DFT calculations; NN, YBA, MF, & RB wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

REFERENCES

[1]   Gasser, P. 2020. A review on energy security indices to compare country performances. *Energy Policy*. 139(111339). 1–17 doi: 10.1016/j.enpol.2020.111339.

[2]   Ali, F., Khan, K.A., & Jahan, S. 2020. Evaluating energy security performance in Pakistan and India through aggregated energy security performance indicators (AESPI). *Eur. Online J. Nat. Soc. Sci.* 9(2). 425–442.

[3]   Supriadi, E., Basuki, R., Prajitno, D.H., & Mahfud, M. 2021. Produksi Biofuel Berbantuan Ultrasonik dari Minyak Kelapa Terkatalisis Ca/γ-Al$_2$O$_3$ dan K/γ-Al$_2$O$_3$. *Walisongo J. Chem.* 4(1). 45–56. doi: 10.21580/wjc.v4i1.7861.

[4]   Morris, N., Miharjana, D., Gubbi, S., Halim, A., Prabowo, A., Napitupulu, D., & others. 2015. Sustainable Infrastructure Assistance Program: Technical Assistance for Energy RPJMN 2015-2019: Energy Sector White Paper, Asian Development Bank.

[5]   Silalahi, D.F., Blakers, A., Stocks, M., Lu, B., Cheng, C., & Hayes, L. 2021. Indonesia's Vast Solar Energy Potential. *Energies*. 14(17). 5424. doi: 10.3390/en14175424.

[6]   Gunawan, F.E. *et al.* 2022. Design and energy assessment of a new hybrid solar drying dome-Enabling Low-Cost, Independent and Smart Solar Dryer for Indonesia Agriculture 4.0, in *IOP Conference Series: Earth and Environmental Science*, 2022, 998(1), 12052.doi: 10.1088/1755-1315/998/1/012052.

[7]   Shiyani, T. & Bagchi, T. 2020. Hybrid nanostructures for solar-energy-conversion applications. *Nanomater. Energy*. 9(1). 39–46. doi: 10.1680/jnaen.19.00029.

[8]   Gong, J., Liang, J., & Sumathy, K. 2012. Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials. *Renew. Sustain. Energy Rev.* 16(8). 5848–5860. doi: 10.1016/j.rser.2012.04.044.

[9]   Devadiga, D., Selvakumar, M., Shetty, P., & Santosh, M.S. 2021. Recent progress in dye sensitized solar cell materials and photo-supercapacitors: a review. *J. Power Sources*. 493. 229698. doi: 10.1016/j.jpowsour.2021.229698.

[10]   Soto-Rojo, R., Baldenebro-López, J., & Glossman-Mitnik, D. 2016. Theoretical Study of the π-Bridge Influence with Different Units of Thiophene and Thiazole in Coumarin Dye-Sensitized Solar Cells. *Int. J. Photoenergy*. 2016(6479649). doi: 10.1155/2016/6479649.

[11]   Kumar, R.S., Jeong, H., Jeong, J., Chitumalla, R.K., Ko, M.J., Kumar, K.S., Jang, J., & Son, Y.-A. 2016. Synthesis of porphyrin sensitizers with a thiazole group as an efficient π-spacer: potential application in dye-sensitized solar cells. *RSC Adv.* 6(47). 41294–41303. doi: 10.1039/C6RA00353B.

[12]   Kooh, M.R.R., Yoong, V.N., & Ekanayake, P. 2014. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies of selected ancient colourants as sensitizers in dye-sensitized solar cells. *J. Natl. Sci. Found. Sri Lanka*. 42(2). doi: 10.4038/jnsfsr.v42i2.6996.

[13]   Zanjanchi, F. & Beheshtian, J. 2019. Natural pigments in dye-sensitized solar cell (DSSC): a DFT-TDDFT study. *J. Iran. Chem. Soc.* 16(4). 795–805. doi: 10.1007/s13738-018-1561-2.

[14]   AL-Temimei, F.A. & Alkhayatt, A.H.O. 2020. A DFT/TD-DFT investigation on the efficiency of new dyes based on ethyl red dye as a dye-sensitized solar cell light-absorbing material. *Optik (Stuttg)*. 208(163920). 1–7. doi: 10.1016/j.ijleo.2019.163920.

[15]   Tosco, P., Stiefl, N., & Landrum, G. 2014. Bringing the MMFF force field to the RDKit: implementation and validation. *J. Cheminform.* 6(1). 1–4. doi: 10.1186/s13321-014-0037-3.

[16] Hernandez-Haro, N., Ortega-Castro, J., Martynov, Y.B., Nazmitdinov, R.G., & Frontera, A. 2019. DFT prediction of band gap in organic-inorganic metal halide perovskites: An exchange-correlation functional benchmark study. *Chem. Phys.* 516. 225–231. doi: 10.1016/j.chemphys.2018.09.023.

[17] Wu, Y.J. & Yang, B. V. 2011. Chapter 5.5: Five-membered ring systems: with N and S (Se). *Prog. Heterocycl. Chem.* 23. 685–714. doi: 10.1016/B978-0-08-096805-6.00009-7.

[18] Gao, P., Tsao, H.N., Yi, C., Grätzel, M., & Nazeeruddin, M.K. 2014. Extended π-Bridge in Organic Dye-Sensitized Solar Cells: the Longer, the Better? *Adv. Energy Mater.* 4(7). 1301485. doi: 10.1002/aenm.201301485.

[19] Seo, K.D., Choi, I.T., Park, Y.G., Kang, S., Lee, J.Y., & Kim, H.K. 2012. Novel D-A-π-A coumarin dyes containing low band-gap chromophores for dye-sensitised solar cells. *Dye. Pigment.* 94(3). 469–474. doi: 10.1016/j.dyepig.2012.02.015.

[20] Tong, J. *et al.* 2021. High-performance methylammonium-free ideal-band-gap perovskite solar cells. *Matter.* 4(4). 1365–1376. doi: 10.1016/j.matt.2021.01.003.

[21] Krauter, C.M., Möhring, J., Buckup, T., Pernpointner, M., & Motzkus, M. 2013. Ultrafast branching in the excited state of coumarin and umbelliferone. *Phys. Chem. Chem. Phys.* 15(41). 17846–17861. doi: 10.1039/C3CP52719K.

[22] Pulli, E., Rozzi, E., & Bella, F. 2020. Transparent photovoltaic technologies: Current trends towards upscaling. *Energy Convers. Manag.* 219. 112982. doi: 10.1016/j.enconman.2020.112982.