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Thionation of NDI molecules as a revolutionary approach to photovoltaic properties

Hamid Reza Shamlouei✉1, Nurullah Khurshidvand✉2 and Reza Safari

1. Correspinding authoer, Department of Chemistry, University of Lorestan, Khorramabad, Iran. Email: shamlouei.ha@lu.ac.ir
2. Correspinding authoer, Department of Chemistry, Faculty of Sciences, Islamic Azad University of Arak, Arak, Iran. Email: khurshidvand.chemistry@gmail.com
3. Department of Chemistry, Faculty of Science, University of Qom, Qom, Iran.

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ABSTRACT

This work introduces the effect of thionation using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) on the photovoltaic properties of naphthalene diimide-carbazole molecule for application in organic solar cells. According to the obtained results, the optical, electronic, and photovoltaic properties after thionation were significantly improved compared to the virgin molecule. The results of calculations of dipole moment, polarizability, and hyperpolarizability showed that thionation significantly increases the charge density distribution. The open circuit voltage of each of the studied structures was calculated with the PC61BM receiver, and the results showed an improvement in performance after thionation. The value of the open circuit voltage for the naphthalene diimide-carbazole molecule was 1.54 V, which increased to 1.61 V after thionation. Finally, high values of fill factor and light harvesting efficiency predict significant power conversion efficiency after thionation. These outcomes position our modified molecule as a promising candidate for advancing organic solar cell technology, offering a pathway toward more efficient and effective photovoltaic devices.

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1. Introduction

In recent years, the quest for efficient and sustainable energy sources has intensified, driving significant advancements in photovoltaic technology [1-5]. Among the innovative strategies emerging to enhance solar cell efficiency is the integration of NDI (naphthalene diimide) molecules as acceptors within the design of donor-acceptor-donor (D-A-D) architectures [6,7]. NDI molecules, known for their strong electron-accepting nature and excellent stability, represent a pivotal advancement in the realm of organic photovoltaics [8, 9]. By strategically positioning NDI units as the central acceptor in D-A-D architectures, researchers capitalize on their ability to efficiently capture and transport electrons generated upon photon absorption [10-12]. This design not only enhances the overall photovoltaic efficiency but also addresses challenges such as material stability and cost-effectiveness, crucial for large-scale deployment [13, 14]. Moreover, the tunability of NDI structures allows for precise modification of their electronic properties, tailoring them to specific energy levels required for optimal charge separation and extraction [15,16]. This flexibility opens avenues for engineering D-A-D systems with finely tuned absorption spectra and improved compatibility with complementary donor materials, thereby maximizing light harvesting across broader solar spectrum ranges [17-22]. In the pursuit of advancing organic photovoltaics (OPVs), researchers have increasingly focused on modifying the chemical structure of naphthalene diimide (NDI) molecules through strategic substitutions of atoms and functional groups [23-26]. This systematic approach aims to enhance the photovoltaic properties of NDIs by tailoring their electronic structure, energy levels, and intermolecular interactions within donor-acceptor-donor systems [27, 28]. This strategy improves the power conversion efficiency in OPVs [29, 30]. In the realm of organic photovoltaics (OPVs), the quest for materials with enhanced performance characteristics has led researchers to explore innovative chemical modifications. One such transformative approach gaining significant attention is thionation - the substitution of oxygen atoms with sulfur in organic molecules [31-34]. This strategic modification holds immense promise for improving the photovoltaic properties of materials by altering their electronic structure, energy levels, and intermolecular interactions [35, 36]. The thionation of naphthalene diamide (NDI) molecules as acceptors in donor-acceptor-donor (D-A-D) architectures can promise the emergence of materials with improved photovoltaic properties. This transformative approach not only aims to bolster the efficiency and stability of OPVs but also addresses critical challenges such as broader absorption spectra and reduced energy losses [37, 38]. In this regard, this paper addresses the strategic importance of the thionation effect on the NDI molecule in OPVs specifically designed to increase photovoltaic performance.

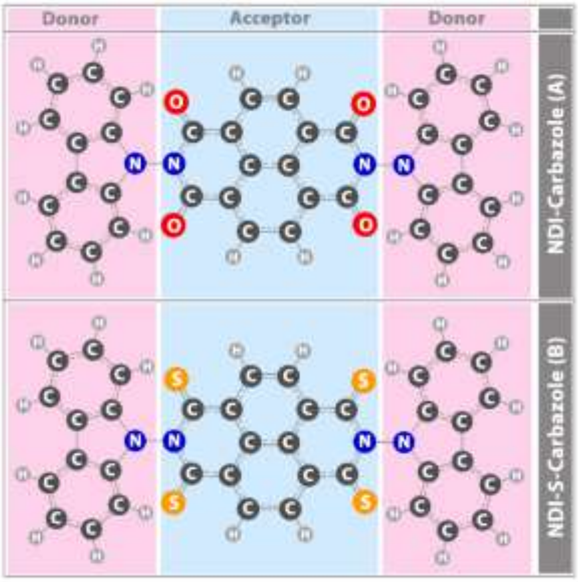

Figure 1. Donor and acceptor parts in this study.

2. Computational method

Bulk heterojunction solar cells are typically composed of a mixture of π-conjugated electron donor material and a fullerene derivative as the electron acceptor material: (6,6)-Phenyl-C61 Butyric Acid Methyl Ester (PC61BM) [39-41]. For this purpose, each of the studied structures (NDI-Carbazole, NDI-S-Carbazole, and PC61BM) was drawn using the GaussView program. Then, to achieve the best molecular geometry, the structure of each of the studied molecules was optimized using Gaussian 09 software, using density functional theory (DFT) and at the theoretical level of CAM-B3LYP/6-311G+(d,p) [42-46]. Frequency calculations were also performed at the same theoretical level, and no imaginary frequencies were observed. Also, the UV absorption spectrum was calculated using the TD-DFT approach and at the CAM-B3LYP/6-311G+(d,p) theoretical level.

The energy gap ($E_{Gap}=|E_{HOMO}-E_{LUMO}|$) was calculated to investigate the mode of electron transfer between the acceptor and donor parts of the designed structures. E_{HOMO} refers to the energy level of the highest occupied molecular orbital (HOMO), while E_{LUMO} denotes the energy level of the lowest unoccupied molecular orbital (LUMO) [47-49].

Additionally, the chemical potential (μ), and chemical hardness (η) were calculated using equations 1-2, which involve the HOMO and LUMO energy values [50-52].

$$\eta = (-E_{HOMO} + E_{LUMO})/2 \quad (1)$$

$$\boldsymbol{S = \frac{1}{2\eta}} \qquad (2)$$

The fill factor (FF) in solar cells is crucial as it indicates how effectively the cell converts sunlight into usable electricity. A higher fill factor means more efficient energy conversion, maximizing the power output of the solar cell [53, 54]. The fill factor was calculated using equation 3 for each of the studied structures.

$$\boldsymbol{FF = \frac{\frac{eV_{oc}}{K_BT} - \ln(\frac{eV_{oc}}{K_BT} + 0.72)}{\frac{eV_{oc}}{K_BT} + 1}} \qquad (3)$$

In the above equation, $\frac{eV_{oc}}{K_BT}$ shows normalized Voc, e denotes charge, which is kept at unity in this work. K_B is used to abbreviate the Boltzmann constant, equal to 8.61733034×10^{-5} electron volts Kelvin^{-1} [55, 56].

One of the critical parameters in the field of photovoltaics is the maximum open-circuit voltage (Voc). It is theoretically calculated as the difference between the E_{HOMO} of the electron donor and the E_{LUMO} of the electron acceptor. The value of Voc was calculated in terms of V units based on Eq. 4 [57, 58].

$$\mathbf{Voc} = \frac{\mathbf{1}}{\boldsymbol{e}}(|\mathbf{E}(\mathbf{H_D})| - |\mathbf{E}(\mathbf{L_A})|) - \mathbf{0.3} \qquad (4)$$

Where, e, $E(H_D)$ and $E(L_A)$ are the elementary charge on the molecule (its value is kept at 1), HOMO of donor and LUMO of acceptor, respectively.

The light-harvesting efficiency (LHE) is an essential property in solar cells and plays a key role in increasing η. The LHE parameter is related to the oscillator strength (f).

$$\mathbf{LHE = 1 - 10^{-f}} \qquad (7)$$

f represents the oscillator strength in the complex, which corresponds to the λ_{max} [59].

3. Results and Discussion

3.1. Electronic prosperity

Studying the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) orbitals is essential to grasp the electronic configuration of a molecule and its involvement in diverse phenomena such as electron transfer, chemical reactions, and applications in optoelectronics such as solar cells. The energy levels and relative positions of these orbitals determine the ability of a molecule to donate or accept electrons and affect its photovoltaic properties [60-63].

Also, studies show that the energy levels of frontier orbitals are related (HOMO/LUMO) to chemical hardness and chemical softness. Optimizing these parameters improves efficient charge transfer and exciton separation, which is effective in increasing the efficiency and photovoltaic performance of the device [64, 65]. The energy values of HOMO/LUMO orbitals, energy gap (HLG), chemical hardness (η) and chemical softness (S) for each of structures NDI-Carbazole (A) and NDI-S-Carbazole (B) (donor) and PC61BM (acceptor) are reported in Table 1.

Table 1. Energy values of HOMO/LUMO frontier orbitals, energy gap, chemical hardness (η), and chemical softness (S) in each of the studied structures (all values are in eV).

Structure	LUMO	HOMO	HLG	η	S
A	-3.79	-5.84	2.05	1.02	0.49
B	-4.47	-5.91	1.44	0.72	0.69
$PC_{61}BM$	-4.00	-6.23	2.83	2.83	0.17

Also, for the A structure, energy gap values of 2.05 eV and 1.44 eV for the B structure were obtained. The results show that tuning reduces the energy gap significantly. The results obtained for chemical hardness (A (1.025 eV) >B (0.72 eV)) and chemical softness (B (0.69 eV) >A (0.49 eV)) show that thionation reduces the chemical hardness and thus the molecule becomes more reactive. The increase in chemical softness due to thionation improves the ability of the molecule to transfer charge and increases the efficiency of solar cells.

Also, the frontier molecular orbitals (FMO) for all studied structures are shown in Figure 3. In each of the designed structures (A, B, C, and D-structure), the LUMO orbitals are focused on the acceptor parts (A), and the HOMO orbitals are focused on the donor parts (D) (Figure 2).

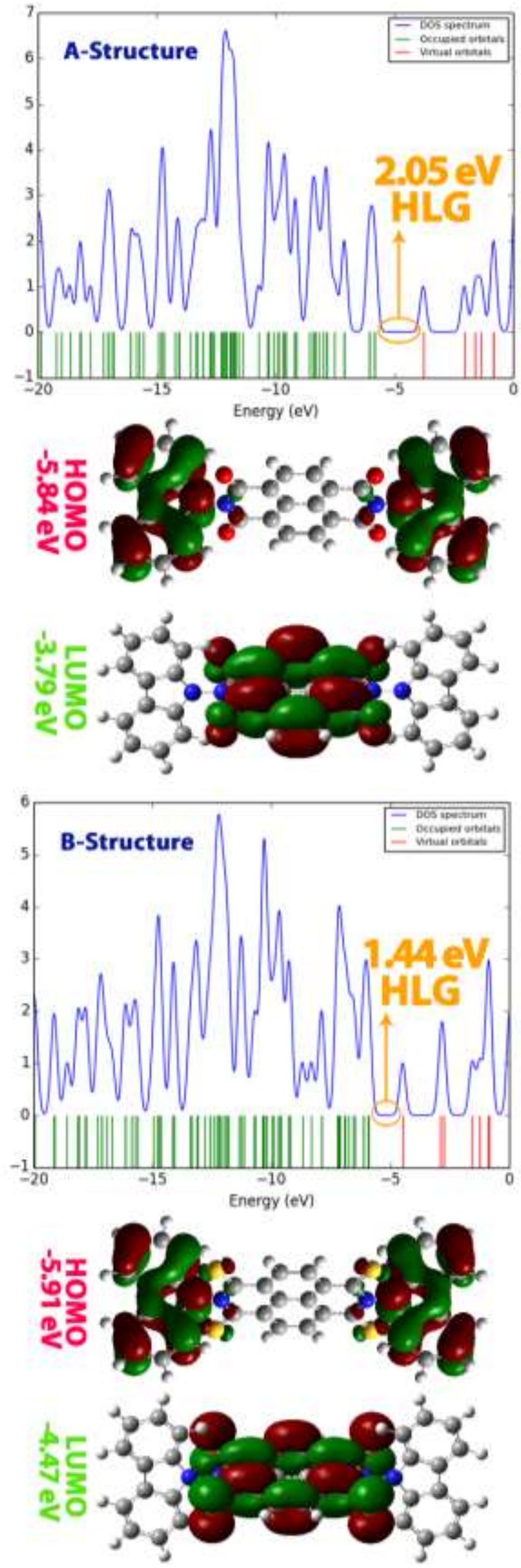

Figure 2. DOS and frontier molecular orbitals (FMO) diagrams for all studied structures.

3.2. Dipole moment (μ), Polarizability (α) and Hyperpolarizability (β)

In the design of donor-acceptor-donor (D-A-D) molecules for use in solar cells, increasing the dipole moment, polarizability and hyperpolarizability can provide several advantages:

1- Enhanced charge separation: Higher polarizability allows more charge separation by absorbing light. When a photon is absorbed, it produces an exciton (an electron-hole pair), and the higher polarizability facilitates the separation of these charges, leading to more efficient charge transport within the device [66, 67].

2- Enhanced exciton dissociation: Hyperpolarizability refers to the nonlinear optical property that governs the efficiency of second harmonic generation (SHG) and two-photon absorption (TPA). In the context of solar cells, higher hyperpolarizability means that more photons can be absorbed to generate excitons, thus improving the dissociation of excitons into free charge carriers [68, 69].

3- Expanded Absorption Range: Larger dipole moments broaden the absorption spectrum, allowing the molecule to absorb a wider range of solar radiation, thereby maximizing energy harvesting potential [70-72].

The polarizability (α) and first hyperpolarizability (β), corresponding to linear and NLO properties, were calculated using Eqs. 8-10 [73, 74].

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

$$\beta^{\circ} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (9)$$

In which

$$\beta_i = 3/5\left(\beta_{iii} + \beta_{iij} + \beta_{ikk}\right) \text{ i, j, k=x, y, z} \quad (10)$$

The obtained values for dipole moment, polarizability and hyperpolarizability are reported in Table 2.

Table 2. Values of dipole moment (μ), polarizability (α) and hyperpolarizability (β) for the structures investigated in this work.

Structure	μ	α	β
A	3.18	21.34	156.12
B	4.52	28.39	175.34

After thionation, the dipole moment increased from 3.18 to 4.52. Polarizability values for A and B structures were obtained as 21.34 and 28.39, respectively. The hyperpolarizability was calculated for structure A to be 156.12 and for structure B to be 175.34. These results show that thionation significantly affects the values of dipole moment, polarizability, and hyperpolarizability and causes each of them. It seems that thionation causes more charge separation between atoms and thereby increases the dipole moment. This increase in polarizability increases the molecule's ability to interact with electric fields, thereby increasing its hyperpolarizability.

MEP analysis provides valuable insight into the three-dimensional distribution of molecular charges and the determination of sites susceptible to electrophilic and nucleophilic attacks (Figure 3). Electrophiles tend to target regions of high charge density, usually shown in yellow and red, while blue regions represent regions of relatively lower charge density and serve as potential sites for interactions. They act as nucleophiles. Neutral regions within the molecule are usually shown in green. The greater the width between the red and blue colors, the greater the dipole moment of the molecule and, as a result, the charge distribution [75-77].

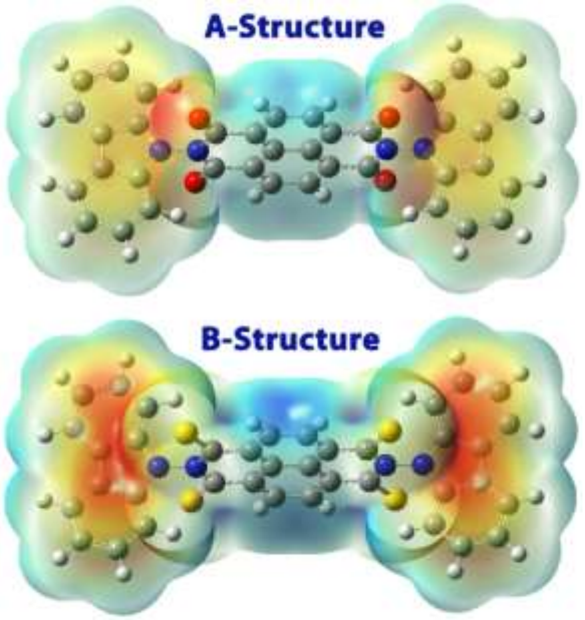

Figure 3. MEP maps for designed molecules (A-structure and B-structure).

Figure 5 shows the MEP map of the electron density distribution in each of the studied structures from the donor to the acceptor parts. In structures A and B, the blue color is retained by the central part of the molecule. It is also clear that the areas with yellow and red are concentrated in the donor sector. This feature indicates the successful transfer of charge from the donor to the acceptor units and shows that the phenomenon of intramolecular charge transfer (CT) from the donor to the acceptor has occurred in both structures.

3.3. Optical properties

Table 3 and Figure 4 show the results of maximum absorption wavelengths (λmax), oscillator strength (*f*), excitation energies (Eex) and HOMO to LUMO assignments for each of the studied structures. The values of ʎmax for each of the investigated structures were calculated as follows: for structure A, ʎmax=670 nm; for the B-structure, ʎmax=1029 nm was calculated (Figure 6). The obtained results show that the substitution of sulfur instead of oxygen in the NDI molecule extends the absorption wavelength to longer wavelengths. The reason for this can be related to the increase in electron density and decrease in the HOMO-LUMO energy gap after thionation, which facilitates the transfer of charge from the donor to the acceptor in the molecule.

Consequently, the absorption spectrum shifts to longer wavelengths, enabling the capture of a broader range of solar radiation and enhancing the overall efficiency of the solar cell.

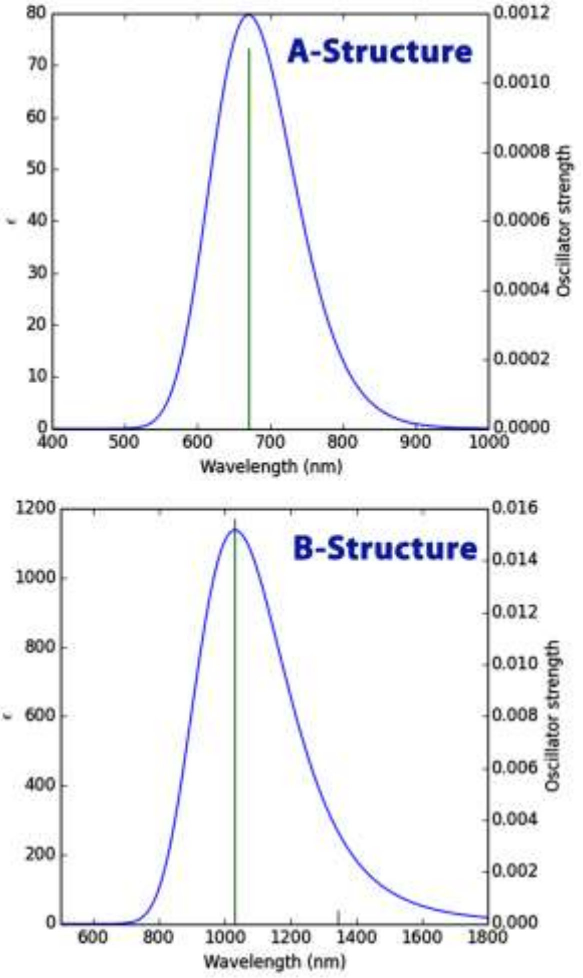

Figure 4. The UV spectrum of the designed structures using the method TD/DFT/CAM-B3LYP/6-311+G(d,p).

Table 3. The calculated values of the optical parameters; maximum absorption wavelengths (λmax), oscillator strength (*f*), excitation energies (Eex) and HOMO to LUMO assignments.

Structure	$ʎ_{max}$ (nm)	E_{ex} (eV)	*f*	Assignment
A	670	1.8501	0.0011	HOMO→LUMO (98%)
B	1029	1.2043	0.0156	HOMO→LUMO (99%)

The value of Eex as an important indicator provides us with useful information about the process of electron excitation from the conduction band (LUMO) to the valence band (HOMO) [96, 97]. A lower Eex value indicates easier electron excitation [98, 99]. Table 3 shows Eex values for each of the studied structures. Eex values for each of the A and B structures were obtained as 1.8501 eV and 1.2043 eV, respectively. Structure B has a lower Eex value (1.2043 eV) that facilitates electron transfer in the donor-acceptor complex.

According to the obtained results, the change in exciton energy values is directly correlated with the change in the energy gap, as excitons are bound states of an electron and a hole, formed due to the energy difference between the conduction and valence bands.

3.4. Open circuit voltage (Voc), fill factor (FF) and Light harvesting efficiency (LHE)

In the design of D-A-D solar cells, the measurements of open circuit voltage (Voc) and fill factor (FF) are essential, as they play an important role in efficiency optimization. Voc provides insights into charge segregation in structures, while FF shows how charges are efficiently transported and collected in the cell [78-81]. These parameters are effective in designing new structures and maximizing the power conversion efficiency and the overall performance of the solar cell. Also, Light harvesting efficiency (LHE) represents the ability of the cell to absorb and convert incident light into electrical energy, which is influenced by factors such as absorption spectrum matching and charge carrier mobility. Maximizing light harvesting efficiency increases the power conversion efficiency of the cell, making it more effective at converting sunlight into usable electricity [82-84]. For this purpose, Voc, FF, and LHE values were calculated for each of the structures and the findings were reported in Table 4.

Table 4. Values of open circuit voltage (Voc) fill factor (FF), and Light harvesting efficiency (LHE) for the investigated structures.

Structure	circuit voltage (Voc)	fill factor (FF)	LHE
A	1.54	0.82	0.002
B	1.61	0.96	0.035

The values of Voc for each of the A and B structures were calculated to be 1.54 V and 1.61 V, respectively. Also, the FF values were calculated for the structure of A, 0.82, and the structure of B, 0.96. As the results show, the values obtained for Voc and FF improved after thionation, which can be due to the improvement of charge transfer properties in the molecule. Higher Voc indicates better energy conversion efficiency as more of the absorbed sunlight is converted into electrical potential without significant losses. This directly increases the overall efficiency of the solar cell. Increasing FF means reducing losses due to resistive effects within the cell. It signifies improved charge carrier collection and reduced recombination losses, leading to higher output power from the solar cell. These developments are very important to increase the overall efficiency and performance of organic solar cells. Also, the values obtained for LHE in each of the studied structures (structure A=0.002 and structure B=0.035) show that thionation is a suitable solution to improve and increase LHE values. Solar cells convert sunlight into electricity, and higher light-harvesting efficiency means more photons are converted into electrical current. This directly increases the power output of the solar cell for a given surface area, which is crucial for improving the overall efficiency of solar energy systems.

4. Consolation

In this study, the effect of thionation on the electronic and photovoltaic properties of the naphthalene diimide-carbazole molecule was investigated. In this regard, the structure of the pristine molecule (structure A) and thionated molecule (structure B) were optimized through DFT and TD-DFT methods using CAM-B3LYP/6-311+G(d,p) theoretical level. The energy gap values, chemical hardness, and chemical softness were calculated as 2.05 eV, 1.02 eV, and 0.49 eV for structure A and 1.44 eV, 0.72 eV, and 0.69 eV, respectively, for structure B. These results show that thionation significantly reduced the energy gap and affected the reactivity of the molecule. Dipole moment, Polarizability, and Hyperpolarizability increased due to thionation. Also, after thionation, the absorption wavelength increased from 670 nm to 1029 nm. The values of FF, Voc, and LHE for structure A were calculated as 1.54, 0.82, and 0.002, respectively and for structure B as 1.61, 0.96, and 0.035, respectively. Evaluation of FF, Voc, and LHE after thionation showed that the modified molecule (structure B) can have higher efficiency than molecule A. In the end, the findings of this study showed that thionation, the process of substituting sulfur-containing groups instead of oxygen, can be used as a promising strategy in increasing the photovoltaic properties of materials used in solar cell technology.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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