Effect of different donor group substituents on 1,3,4-thiadiazole, optical properties, and electronic properties optimization for dye-sensitized solar cells: Design, characterization, molecular structure, and sensitizer dye for solar cell fabrications

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Abstract

This study delves into the consequences of introducing diverse donor group substitutions into the molecular framework of 1,3,4-thiadiazole, with the primary objective of augmenting optical and electronic attributes to improve the effectiveness of sensitizer dye for solar cells (DSSCs). The current investigation centers on the examination of novel azo disperse dyes generated through the diazotization of bis(2-amino-1,3,4-thiadiazolyl) attached with benzene in para position followed by coupling with various amines (approximately three distinct dyes). The primary focus is on the influence of these donor group substituents on the optimization of optical and electronic properties for DSSC applications. These newly devised dyes incorporate 1,3,4-thiadiazole as an electron acceptor. This research examines how the dye compositions, molecular structure, photophysical and electrochemical properties, and the fabrication process of DSSCs affect each other. All the molecular structures have higher oxidation potentials in the ground state than I⁻/I₃ and lower oxidation potentials in the excited state than the semiconductor’s conduction band edge. The best performance among the DSSCs is achieved with dye-16, which has a fill factor of 55.6, an open-circuit voltage of 449.4 mV, a short-circuit current density (JSC) of 1.845 mA/cm², a maximum power output (Pmax) of 0.04149 mW, and the highest efficiency (η) at 0.46%.

Keywords: DFT, Sensitizer dye for solar cells fabrication, Electrochemical properties, Photovoltaic performance, Thiadiazole

1. Introduction

Due to the probable depletion of petroleum as a fuel energy source, great interest has arisen in utilizing solar energy. The advantage of solar energy is that it is easily available all around the world and inexhaustible and does not only create greenhouse gases as it generates electricity. Solar energy becomes more dominant than nuclear, wind and hydro energies owing to its minimum byproduct, low costs,¹,² and high efficiency. Many authors discussed different aspects of sensitizer dye for solar cells (DSSCs), which are devices that convert sunlight into electricity using dyes as light absorbers. DSSC consists of a semiconductor film (usually a nanocrystalline titanium oxide electrode coated with dye molecules), redox mediator I⁻/I₃, and counter electrode (CE). The DSSC shown in Fig. 1 works when the sun shines on the device. The dye molecules absorb light and release an electron into the TiO₂ conduction band. The dye then recovers its lost electron from the I⁻ in the electrolyte, forming I₃⁻.

Received 4 October 2023; revised 11 December 2023; accepted 4 February 2024.
Available online 10 April 2024

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The I\(^-\) is refilled by the I\(^3-\) reduction at the CE. The electron injected into the TiO\(_2\) travels through the porous film of photoelectrode and flows through the external circuit. Along the way, the electron may recombine with the electrolyte’s dye or electron acceptor. The voltage produced by the device is equal to the difference between the TiO\(_2\) Fermi level (EF, TiO\(_2\)) and the I\(^-\)/I\(^3-\) redox potential.

Qin and Peng\(^3\) discussed how to design, prepare, and use different dyes based on thiocyanate compounds with or without ruthenium. A comprehensive study\(^4\) analyzed the electronic absorption spectra of DSSCs using theoretical methods. In another study, three DSSCs using red colloid dye, Prussian blue dye, and green dye from spinach leaves were compared in terms of their physical performance.\(^5\) The results showed that Prussian blue dye had the most excellent electrical performance. A new structure of dye called push-pull architecture was also explored.\(^6\) This structure had a donor part made of anthracenyl diphenylamine and an acceptor part connected by an acetylene bridge. The DFT study found that this structure could enhance the light capturing, increase the redshift, and lower the energy gap, photoelectric conversion efficiency and electron injection of DSSCs. Tandem-sensitized solar cells with various dyes were reported\(^7\) as a promising device with broader harvesting efficiency of the solar spectrum. In this work, some new dispersed azo dyes were produced by diazotizing two derivative groups (2-amino-1,3,4-thiadiazolyl) bonded with phenylene in para position and attached it with a variety of amines at both ends (aniline, 3-nitro aniline, and 3-chloroaniline). These dyes were used to optimize the efficiency of DSSCs and get better open-circuit voltage (VOC). The three new dyes were also successfully applied to sensitize nanocrystalline TiO\(_2\)-based solar cells, and their photovoltaic performances and electronic properties were studied.

2. Experimental

2.1. Chemicals

We bought all the chemicals with high purity from global suppliers. We used anhydrous DMF, phosphorus oxychloride, potassium hydroxide, thiosemicarbazide, terephthalic acid, aniline, 3-nitro aniline, and 3-chloroaniline. All the chemicals were laboratory-grade. The solvents were used as they were without further refining. Water that was distilled was used in all the experiments. Laboratory-grade chemicals such as sulfuric acid, potassium hydroxide, and sodium nitrite were obtained.

2.2. Instrumentation and characterizations

We measured every melting points on a melting point apparatus (Gallenkamp) MFB-595, without correction. We recorded UV–Vis spectra on the Shimadzu 260 solution spectrometer. We recorded
infrared spectra on a SP-3-300 PyeUnicam infrared or a FT-IR Shimadzu (8101 PC) spectrophotometer. We recorded mass spectra on a mass spectrometer (GCMS-QP-1000EX) Shimadzu at 70 eV. NMR spectra were measured by using Bruker Advance spectrometers (400 MHz). Chemical shifts (δ) were reported in ppm relative to tetramethylsilane. Splitting patterns were described as s, brs, d, or dd. and (J) as coupling constants reported in Hz. The AUTOLAB potentiostat/galvanostat operated device is used to report cyclic voltammograms recorded at ambient temperature with traditional three-electrode devices, working electrode (platinum), reference electrode (Ag/AgCl), and counter carbon electrode. We recorded the potential with a scan rate of 0.1 V/s versus ferrocene as standard using supporting electrolyte tetrabutylammonium iodide.

2.3. Methods and techniques

The following methods and techniques were employed to synthesize dyes based on derivatives of 1,3,4-thiadiazole (designated as dyes 10, 15, and 16), as outlined in Scheme 1.

Synthesis of (compound 1 in Scheme 1) 5, 5′-(1, 4-phenylene) bis 2-amine (1, 3, 4-thiadiazol): To prepare compound 1, thiosemicarbazide (0.02 mol) was mixed with phosphorus oxychloride (5 ml), and terephthalic acid (0.01 mol). The mixture was gently heated for 3 h under reflux. After cooling, we added 50 ml of ice water, heated the mixture for another 4 h, and filtered it. We used potassium hydroxide to neutralize the filtrate. We collected the solid, washed it with distilled water, washed it once more with hot DMF, and dried it at ambient temperature.

Disperse dyes synthesis was prepared as presented in Scheme 1.

The dyes were synthesized via a two-step process, first nitrosylsulfuric acid was used to diazotize the amine, then attached it with the agent we chose. The sodium nitrite was used to prepare nitrosyl acid by adding 0.76 g to 5 ml of sulfuric acid, and the resulting mixture was cooled to 0 °C. Subsequently, 0.01 mol of various amines (aniline, 3-nitroaniline, and 3-chloroaniline) were gradually added with stirring. Then, a mixture (in a 1 : 4 ratio) of 10 ml volume addition of propionic-acetic acid to the salt of diazonium while maintaining the high temperature next to 0 °C for 2 h. The obtained solution of clear diazonium was stirred at 5 °C and slowly poured into a dissolved 0.02 mol of the chosen pairing agent solution in a 20 ml volume of prepared propionic-acetic acid mixture, and the sodium acetate was poured gradually to adjust pH to 4. After a brief interval, the temperature of reaction result yield dyes decreased by pouring into iced water, filtered with water washing, dried, and subjected to recrystallization.

2.4. Fabrication of sensitizer dye for solar cells

To clean the conductive glass of fluorinated tin oxide (FTO) (15–20 Ω/cm²), acetone, and double distilled water were used. Paste of TiO₂ was applied by technique method of Doctor Blade on the FTO glass plates as a thin layer, then air-dried and followed by thermal-treated for a duration of 30 min at 450 °C. The TiO₂ working electrodes were heated to 80 °C after cooling and dipped in dye solutions (DMF) of dyes (10, 15, 16) for 24 h at room temperature. (Hummer 8.1, USA) Magnetron sputtering device was used to platinize CE by leaving a platinum-thin film above the FTO layer of substrate glass (t = 2 min, P = 100 W RF) and then heated for 30 min at 450 °C. The platinize CE was attached over the TiO₂/dye working electrode, and some drops of electrolyte composed of 3-methoxypropionitrile, 0.05 M iodine I₂, 0.5 M (TBP) 4-tert-butylate pyridine, and 0.5 M lithium iodide (LiI) were added connecting the electrodes to complete the requirement of DSSCs.

2.5. Photovoltaic characterization

The DSSCs curves of light current-voltage (JV) were obtained using a (PET Photo Emission Tech.; Solar Simulator Inc., USA) device. The xenon lamp of the solar simulator gives a spectrum with an AM
1.5 value. The JSC short-circuits, VOC, fill factor (FF), and efficiency $\eta$ were measured based on the light JV characteristics. The electrochemical (potentiostat/galvanostat; Autolab) workstation was used to obtain the impedance spectrum of electrochemical (EIS) over a varying frequency starting 10–105 Hz under dark illuminations with 0.10 V as bias potential. The plots of Nyquist were examined using the nonlinear fits to an appropriate equivalent circuit model that matched with plots of Nyquist with minimal error. The obtained data were carried out by the author in electronic materials department laboratory at advanced technology and new materials institute (Borg El Arab city) Egypt.

2.6. Computational methodology

Geometry optimization of the investigated compounds was performed using the Gauss View (Ver. 6) and software of Gaussian 09 at B3LYP/6–31 G. Values of $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ were calculated and graphically represented in Fig. 3 and illustrated in Table 1. The global hardness $\eta$, the back donation $\Delta E_{\text{back donation}}$, energy gap $\Delta E$, ionization potential $I$, global softness $S$, absolute electronegativity $X$, electron affinity $A$, index of global electrophilicity $\omega$, were calculated based on $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$. The absorption spectra, transition energies, and oscillator strengths of molecules were carried out using DMol3 incorporated in Materials Studio v.7.0. The selected parameters were (Task; energy, Functional; GGA&PBE, Quality; fine, Basis set; DNP, Properties; optics). The excited states were calculated from which some of them were selected according to higher strength (f) shown in Fig. 4. Additionally, natural bond orbital analysis (NBO, Gaussian 09 software package) for the ground state and excited state was carried out to interpret the intermolecular charge transfer from donor to acceptor. The nonlinear and linear optical properties were studied at (DFT/B3LYP) level. The dipole moment ($\mu$) of the ground state, the first order hyperpolarizability ($\beta$), the anisotropy of the polarizability $<\Delta z>$ and the polarizability $<z>$ are calculated as reported equations before. $^{25}$

3. Results and discussion

3.1. Dyes synthesis

Sulfur dyes are synthesized from thiadiazole, a heterocyclic five-membered ring with two nitrogen atoms. Phosphorus oxychloride used to obtain the target compound (Cpd 1) $5,5'$-(1,4-phenylene)bis 2-amine (1,3,4-thiadiazol) by reacting thiosemicarbazide with terphthalic acid in its presence. The terephthalic acid conversion to the heterocyclic ring was confirmed by the stretching of C=O absence in IR spectra and the presence of the following frequencies: 731 cm$^{-1}$ for ring stretching of C=S, 1689 cm$^{-1}$ due to C=N and NH$_2$, 3280, 1505 cm$^{-1}$ due to NH stretching. The dyes (10, 15, 16) were obtained by diazotizing nitrosyl sulfuric acid with the compound 1 and then attaching it with the selected agent (aniline, 3-nitro aniline, and 3-chloroaniline).

3.2. Dyes spectral assignment

3.2.1. Dye-10

$4'\{\{5'-5-[\{Z\}-(4-aminophenyl)diazenyl]-1,3,4-thiadiazol-2-ylphhenyl]-1,3,4-thiadiazol-2-yl\}$ diazenyl]aniline, Yield 83%, color orange crystal is orange powder, $\lambda_{\text{max}}$ in DMF/H$_2$O is 361, melting point is 284 $^\circ$C, FT-IR bands (KBr) pellets cm$^{-1}$: (C=O= C) 1414, (C= H, ar.) 3063, (NH) and $\delta$ (NH) 3379 and 1503, (C=H) 1620, $\delta$ (C=S= C) 690, (N==N==N) 1015. The molecular ion peak of mass spectra for dye-10 gave at $m/z$ 484.10 (100%) (M$^+$) matches to molecular formula C$_{22}$H$_{16}$N$_{10}$S$_2$. The $^1$H NMR of dye-10 (DMSO-d$_6$, 400 MHz), $\delta$, ppm, (J, Hz): (2H, dd, $J = 8.2$ Hz, 5,6-CH(Ph)) 7.36, (4H, s, 2 (3,4-CH) (ani)) 7.40, (4H, d, 2 (5,6-ani)) 7.41, (2H, dd, $J = 8.2$ Hz, 2,3-CH (Ph)) 7.43, (4H, bs, 2-NH$_2$) 9.75, exchangeable D$_2$O.

3.2.2. Dye-15

$4'\{\{5'-4-[\{Z\}-(4-aminophenyl)diazenyl]-1,3,4-thiadiazol-2-ylphphenyl]-1,3,4-thiadiazol-2-yl\}$ diazenyl]-3-chloroaniline. Yield 94%, color is yellowish orange powder, $\lambda_{\text{max}}$ in DMF/H$_2$O is 400, melting point is over 301 $^\circ$C, FT-IR bands (KBr) pellets cm$^{-1}$: (C=O= C) 1414, (C= H, ar.) 3063, (NH) and $\delta$ (NH) 3379 and 1503, (C=H) 1620, $\delta$ (C=S= C) 690, (N==N==N) 1015. The molecular ion peak of mass spectra for dye-15 gave at $m/z$ 551.38 corresponding to molecular formula C$_{22}$H$_{16}$N$_{10}$S$_2$Cl$_2$. The $^1$H NMR of dye-15 (DMSO-d$_6$, 400 MHz), $\delta$, ppm, (J,Hz): (2H, dd, $J = 8.2$ Hz, 2,3-CH (Ph)) 7.43, (4H, bs, 2-NH$_2$) 9.75, exchangeable D$_2$O.
Fig. 2. Frontier molecular orbitals; LUMO and HOMO of the investigated dyes.
Hz): (2H, dd, J = 8.2 Hz, 5,6-CH(Ph)) 7.21, (3H, s, 2 (ani)) 7.41, (2H, dd, J = 8.2 Hz, 2,3-CH(Ph)) 7.42, (2H, s, 2-NH2) 12.78.

3.2.3. Dye-16

4-{((E)-[5-(4-{5-{(Z)-(4-amino-2-nitrophenyl)diazenyl]-1,3,4-thiadiazol-2-yl}phenyl]-1,3,4-thiadiazol-2-yl]diazenyl]-3-nitroaniline, Yield 88%, color crystal is reddish yellow powder, λmax in DMF/H2O is 410, melting point is more than 300 °C. Mass spectra of dye-16 gave molecular ion peak at m/z 574.07 corresponding to molecular formula C22H14N12O4S2. The 1H NMR of dye-16 (DMSO-d6, 400 MHz), δ, ppm, (J, Hz): (2H, dd, J = 8.2 Hz, 5,6-CH(Ph)) 7.09, (3H, s, 2 (nitro aniline)) 7.25, (2H, dd, J = 8.2 Hz, 2,3-CH(Ph)) 7.66, (2H, s, 2-NH2) 11.54.

3.3. Theoretical approach

Frontier molecular orbitals of the examined dyes are revealed in Fig. 2. It is observed that LUMO and HOMO are distributed all over the molecules. The obtained values of EHOMO, ELUMO and energy gap ΔEGap are shown in Table 1 and graphically presented in Fig. 2. As a fact, EHOMO is responsible for electron donation, whereas ELUMO is liable for electron receiving. The higher the values of EHOMO the more ease of electron donation and vice versa. The lower values of LUMO have more ability to receive electrons. EHOMO(eV) order is found to be Dye-16 (−5.27) < Dye-10 (−4.93) < Dye-15 (−4.90) < Cpd-1 (−4.86), i.e., Dye-15 is more electron donating as compared to the rest of the series. ELUMO(eV) order is in the order of Dye-15 (−3.78) < Dye-10 (−3.62) < Dye-16 (−3.34) < Cpd-1 (−2.49), i.e., Dye-16 is more reliable for electron receiving. The results of energy gap values (ΔEgap) (Table 1) and graphically represented in Fig. 3, the reactivity of dyes increases as the difference between EHOMO and ELUMO decreases. As shown in Fig. 2, ΔE Gap of the title dyes are in order Dye-16 < Dye-15 < Dye-10 < Cpd-1, hence Dye-16 exhibit redshift. So, the reactivity increases. Nonlinear and linear optical properties are calculated shown in Table 1, using keywords in Gaussian 09 (# opt freq b3lyp/6–31 g guess = mix polar = optrot geom = connectivity pop=(nbo,savenbos)). Total dipole moment μ, anisotropy <Δz>, polarizability <z> and hyperpolarizability β are listed on Table 1. Dye-16 has a higher dipole moment value. The higher the value of the dipole moment, the more effective the intermolecular interactions will be. As comparing the energy gap (ΔE Gap) order and the hyperpolarizability values (β) shown in Table 1, as the energy gap decreases, the hyperpolarizability increases associated with redshift increases as shown in Fig. 4.

3.4. Electrochemical properties

The oxidation potential of three dyes 10, 15, and 16 versus normal hydrogen electrode (NHE) are 1.1, 0.86, and 0.65 V, respectively, as shown in the cyclic voltammetry (CV) curves in Fig. 5. These values are higher than the iodine/iodide standard potential value (0.4 vs. NHE), which means that the redox couple iodine/iodide can effectively reduce dyes after photo-oxidation. The achievable reduction of dyes E00* against NHE was considered by Eox to optical band-gap E00. The optical band-gap energy was calculated from the onset of absorption. The E00* values measured (−3.12, −3.2, and −3.09 vs. NHE) are lower than the conduction band edge of TiO2 (−0.5 vs. NHE), indicating that the electron injection cycle is strongly favored by TiO2, at the same time as the regeneration of dyes are take place. As revealed in Table 1, the negative variation values
between the Eox and $E_{0e}$ can be got for dye-16 and dye-15 by 0.64 V, and it was experimental that the Eox shift was larger than that of $E_{0e}$, which resulted in reduce band-gap value of HOMO and LUMO levels.

3.5. Photovoltaic performance of sensitizer dye for solar cells

The evaluated sensitizer performance of photovoltaic for the three azo dyes in DSSCs was measured by current density and voltage (JV) as revealed in Figs. 6 and 7, and the resultant data involving photocurrent efficiency ($\eta$), FF, VOC and short-circuit current (JSC) are given in Table 2. The
highest short-circuit current (JSC) showed by the system based on dye-16, measured up to the DSSCs device based on other dyes, which showed a moderate JSC. The dye-16 device showed the highest VOC (0.4494 V), which gave the highest $\eta$ (0.46%), Pmax of 0.04149 mW and FF 55.6 because of the highest JSC (1.845 mA/cm$^2$). The dye-15 device showed the moderate $\eta$ (0.36%) and Pmax of 0.03233 mW due to the moderate ISC (1.611 mA/cm$^2$), VOC (0.4224 V) and FF (52.79). The dye-10 device showed the lowest VOC (0.4453 V), the lowest JSC (0.426 mA/cm$^2$), and moderate FF (69.47), which led to the lowest $\eta$ (0.13%) and Pmax of 0.0395 mW. The sensitizer with connected anchor groups has a bigger energy gap between the conductive band level of TiO$_2$ and its LUMO level, leading to electron injection increase into TiO$_2$, JSC increase, and causal to $\eta$ percentage increase. As revealed in the three organic dyes' chemical structure, the conjugating group ($\pi$) and a group of electron-donating (D) are the same, but the difference is in the donor group substituents. This high efficiency of component dye-16 molecule is due to the well-bound and strong withdrawal of electrons. In the case of CI as donor substitution based Dye-15, thus the electron injection was prevented into the conduction band of TiO$_2$, which may be the low performance reason. Dye-10 showed very low efficiency, which could be due to the dye structure's poor withdrawal of electrons.

### Table 2. Sensitizer dye for solar cells photovoltaic performance based on dyes.

<table>
<thead>
<tr>
<th>VOC (V)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>Fill factor (%)</th>
<th>Pmax (mW)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s10</td>
<td>0.4453</td>
<td>0.426</td>
<td>69.47</td>
<td>0.0395</td>
</tr>
<tr>
<td>s15</td>
<td>0.4224</td>
<td>1.611</td>
<td>52.79</td>
<td>0.03233</td>
</tr>
<tr>
<td>s16</td>
<td>0.4494</td>
<td>1.845</td>
<td>55.6</td>
<td>0.04149</td>
</tr>
</tbody>
</table>

VOC, open-circuit voltage.

### 3.6. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy technology is a valuable description of the charge transportation carrier in DSSCs.26 Frequently, a high VOC can be achieved by having many conduction band electrons in the TiO$_2$ layer. To evaluate the performance of charge transfer for the new dyes in the photovoltaic sensitizer systems, dye-10, dye-15, and dye-16 were examined using EIS and the corresponding circuit and the Nyquist plot are exposed in Fig. 8. The higher resistance for recombination (Rrec) in low frequency is reflected by large semicircles at the...
electrolyte/TiO₂ interface. As revealed, the semi-circles radius of the azo dyes tracks this order s₁₀<s₁₅<s₁₆, signifying that the s₁₆ as sensitizer had the highest resistance between the electrolyte and surface of TiO₂ layer, which can be explained by the maximum voltage achieved.

3.7. Conclusions

This study involved synthesizing a series of water-insoluble dyes featuring 1,4-bis(2-amino-1,3,4-thiadiazolyl) benzene. Three new thiadiazole dyes (referred to as 10, 15, and 16) were created and their properties were examined using techniques like IR, mass spectra, and 1HNMR. These dyes were conceptualized and characterized for their ability to sensitize photochemical reactions. The performance of dye-based DSSCs was assessed and studied. Furthermore, incorporating donor group substituents positively impacted on the conduction band of TiO₂. This led to dye-16 exhibiting a higher VOC (voltage output) than the other two dyes. As a result, the overall power conversion efficiency increased to 0.46%. However, solely employing aniline donor groups in the dyes did not generate highly efficient solar cells due to insufficient absorption by the TiO₂ film and adsorption energy. The study suggested that nitro substituents might be more effective than chlorine donor group substituents in addressing this issue. Based on the results of this work, the joint approach to optimize the organic light-absorbing molecules design and theoretical study should be recommended to improve both the performance and the durability of thiadiazol solar cells.

Author contribution

Amr A. Sayed Alahl: Conceived, Designe the analysis, Writing – review & editing.

Conflicts of interest

The author declare that they have no competing interests.

Acknowledgments

The author thank all the staff members and colleagues of the Renewable Energy Department at the Desert Research Center for their cooperation and their useful help offered during this work. The author is grateful to the Researchers Supporting at advanced technology and new materials institute (Borg El Arab city) Egypt.

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