Density functional theory study of promising polyene-diphenylaniline organic chromophores for dye-sensitized solar cell applications

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Ife Fortunate Elegbeleye¹, Nnditshedzeni Eric Maluta¹,²* and Rapela Regina Maphanga²,³

Abstract: Dye-sensitized solar cells have attracted rapid interest over the recent years with prospect of emerging as a viable alternative to conventional silicon-based solar cells. Currently organic and inorganic complexes have been widely employed as sensitizers for DSSCs. One of the salient features of dye sensitizer is a strong absorption in the ultraviolet, visible and near-infrared part of the solar radiation spectrum. Light absorption and charge separation is performed by the sensitized dye molecules adsorbed on TiO₂ surface. In this work, the time dependent-density functional theory was used to investigate UV–Vis absorption spectra of a series of polyene-diphenylaniline organic chromophores. The HOMO–LUMO energy levels, maximum excitation wavelength, excitation energies and light-harvesting efficiencies of selected dye molecules were simulated. The results showed that, the dyes with methoxy groups in their donor moiety show bathochromic shift and reduced HOMO–LUMO energy gap than the corresponding dyes without methoxy group. The results compare favorably well with other findings.

ABOUT THE AUTHORS

I'm Elegbeleye Ife Fortunate, I commenced a PhD program at the University of Venda, Thohoyandou in South Africa. Presently I'm working on energy materials modelling under the supervision of Dr N.E Maluta, with the help of Prof RR Maphanga who is attached to the Council for Scientific and Industrial Research (CSIR). My focusing is on theoretical and computational studies of Dye Sensitized Solar Cells (DSSC). DSSC offers a low cost and promising high efficiency alternative to the silicon based solar cell. DSSC have the advantage of simple manufacturing technique and high photon to current conversion efficiency. This type of solar cells can operate efficiently under indoor lighting. The photoanode of DSSCs comprises of organic dye chemically anchored onto a nanostructured TiO₂ semiconductor Oxide. Light harvesting capability basically depends on the molecular properties and band gaps of the interfacial components between TiO₂ semiconductor and the dye molecules. The significance of this study is to understand the optical properties of dye molecules, to be able to overcome the restricted spectral sensitivity of the wide band gap semiconductor, improve light harvesting and electron collection efficiency of DSSCs. Our results show that the dye molecules will harness light in the visible and near infra-red region of the solar spectrum.
1. Introduction
The answer to the question of abundant, clean, sustainable and environmentally friendly energy resources remains with solar energy (Longo & De Paoli, 2003; Michal & Július, 2010). The question of how to efficiently harness and utilize solar energy has been the major quest of many researchers. Different types of photovoltaic technologies are available from the first to fourth generation. Dye-sensitized solar cells (DSSCs) have gained enormous attention over the recent years as they offer a promising low-cost and high-efficiency route for the harnessing and conversion of solar energy into electricity (Abodunrin, Obafemi, Boyo, Adebayo, & Jimoh, 2015; Anselmi, Mosconi, Pastore, Ronca, & De Angelis, 2012; O’Regan & Grätzel, 1991; Shahzad et al., 2013).

The dye sensitizers have a significant influence on the photoelectric conversion and transport performance of the electrode (Cai-Rong et al., 2009; Longo & De Paoli, 2003; Shahzad et al., 2013). In a DSSC, the conversion of solar energy to electricity relies on the semiconductor material composed of nanoparticles and monolayer of dye sensitizers within the photoanode. The metal oxide TiO$_2$ is typically employed as semiconductor in this type of solar cell, owing to its less susceptibility to corrosion under illumination as well as its non-toxicity (Hou, Huang, Wu, & Liu, 2009; Wang, Zhang, Li, Li, & Lin, 2014). However, the main limitation of TiO$_2$ is its wide band gap ($E_g = 3.23$ eV), which makes it absorb only ultraviolet portion of the solar spectrum which accounts only 5% of the solar spectrum; in contrast, the visible spectrum accounts for 43% while the infrared accounts for 5% of the solar spectrum (Pastore & De Angelis, 2015; Wang et al., 2014; Wenhui et al., 2014). Dye molecules chemically adsorbed on the surface of TiO$_2$ are used to overcome the restricted spectral sensitivity of the wide band gap semiconductor (Longo & De Paoli, 2003). In DSSCs, the sensitizer dye molecule absorbs incident photon from sunlight and becomes excited.

The photo-excited electron is injected into the wide band-gap of TiO$_2$ semiconductor. The injected electron percolates through the solution to the transparent conducting oxide layer (anode) and through an external load to the counter-electrode (cathode) where it regenerates the redox mediator (Nazeeruddin et al., 1993). The oxidized dye is regenerated by a liquid electrolyte containing redox couple. The photocurrent yield depends on the spectral properties, excited state lifetimes and the efficiency of charge injection of the dye molecules (Longo & De Paoli, 2003). The ruthenium (II) polypyridyl complexes (N3) have demonstrated good chemical stability and excellent performance as sensitizer for DSSCs. Conversion efficiencies of more than 12% have been achieved with the ruthenium N3 employed as dye sensitizer on TiO$_2$ semiconductor (Oprea, Panait, Cimpoesu, Ferbinteanu, & Gîrţu, 2013; Yang et al., 2015). However, ruthenium dyes are relatively scarce and expensive, whereas their toxicity has also raised environmental concern, thus limiting its application as a DSSC sensitizer (Li & Diau, 2013). Consequently, organic dyes have now attracted a lot of attention as alternative sensitizers for DSSCs application (Hardin, Snaith, & McGehee, 2012). The advantages of the organic dyes include higher extinction coefficient, low-cost, good environmental compatibility and electrochemical properties (Irfan, Jin, Al-Sehemi, & Asiri, 2013; Kuang et al., 2011; Mishra, Fischer, & Bauerle, 2009). The organic dyes with basic configuration donor-$\pi$-acceptor are relatively cheap, easy to synthesize and possess chemical structures that can easily be altered to optimize photocatalytic properties of the semiconductor (Mehmood, Hussein, Harrabi, & Ahmed, 2015).

Several organic dyes such as coumarins (Yang et al., 2015), indolines (Schmidt-Mende et al., 2005), porphyrins, perylenes, cyanines, mecrocyannines, quinolones, croconate (Puyad, Kumar, & Bhanuprakash, 2012), phenothiazine (Mahmood, Khan, Rana, & Tahir, 2014), triphenylamine
and polyene-diphenylaniline (Kuang et al., 2011), have been reported as sensitizers for DSSCs. These metal-free organic dyes have high molar absorption coefficients, various structures, low costs and relatively simple synthesis procedures. Boschloo et al. (2008) successfully synthesized polyene-diphenylaniline (D5) dyes and tested them in DSSC. The study reported that D5 dyes were easy to synthesize and showed 5% efficiency with iodide/triiodide-based redox electrolyte. Also, the D5 outperformed the standard ruthenium N719 for sensitization of mesoporous TiO$_2$ with iodide/triiodide electrolyte and amorphous hole conductor (spiro-OMeTAD) owing to the hole conductivity observed in monolayers of polyenediphenylaniline (D5) when absorbed on TiO$_2$ (Boschloo et al., 2008). A series of polyene based organic dyes coded (D5, D7, D9, D11) which demonstrated excellent stability under standard 1.5 air mass (AM) illumination with power conversion efficiency of 6.5% when tested with ionic liquid electrolyte based DSSC were later reported by Kuang et al. (2011).

In this study, we report density functional theory studies (Maier, Arbunikov, & Kaupp, 2018; Torres et al., 2017) on D5, D7, D9 and D11 to gain more insight into the spectral characteristics that influence their light-harvesting properties and a key factor to achieving higher incident photon to power conversion efficiency (Anselmi et al., 2012; Oprea et al., 2013). Time-dependent density functional theory (TD-DFT) is employed to compute the ground state, excited state, absorption spectra and light-harvesting efficiency of the series polyene-diphenylaniline based dye.

2. Methodology

2.1. Computational details

Four organic dyes were considered in this study and are listed below:

1. (D5): 3-(5-(4-(diphenylamine) styrl) thiophen-2-yl)-2-cyanoacrylic acid
2. (D7): 3-(5-bis(4-(diphenylamino) styrl) thiophen-2-yl)-2-cyanoacrylic acid
3. (D9): 5-(4-(bis(4-methoxyphenylamino) styrl) thiophen-2-yl)-2-cyanoacrylic acid
4. (D11): 3-(5-bis(4,4ʹ-dimethoxyphenylamino) styrl) thiophen-2-yl)-2-cyanoacrylic acid.

In this study, the structures of four dye molecules were built using Gauss view molecular builder interface. All DFT/TD-DFT calculations were executed by Gaussian 09 quantum chemical package (Frisch et al., 2004). The structural optimization of the ground state of the diphenylaniline dyes in gas phase was performed using the hybrid density functional B3LYP and 6-31G* basis sets (Becke, 1988; Lee, Yang, & Parr, 1988). The same basis sets were used to simulate the UV-Vis spectra of the dyes in gas phase. About 70–100 singlet-singlet transitions was considered in order to account for the excitation energy in the whole of the absorption spectrum.

Figure 1 is a caption of polyene-diphenylaniline dye molecule coded D5 reported by Kuang et al. (2011). D5 structure contains 3-(5-(4-(diphenylamine) styrl) thiophen-2-yl)-2- cyanoacrylic acid. The structure was built using Gaussian 03 quantum chemical package within the frame work of Gaussview, the diphenylamine moiety was selected from the molecule group within the Gaussian window and placed on the builder interface, this was followed by the attachment of the polyene, thiophene group and the cyanoacrylic acid.

Figure 2 is a caption of polyene-diphenylaniline molecule coded D7 reported by Kuang et al. (2011). D7 structure contains 3-(5-bis (4-(diphenylamino) styrl) thiophen-2-yl)-2- cyanoacrylic acid. The structure was built using Gaussian 03 quantum chemical package within the frame work of Gaussview, the two-diphenylamine moiety was selected from the molecule group within the Gaussian window and placed on the builder interface, this was followed by the attachment of the polyene, thiophene group, and the cyanoacrylic acid.
Figure 1. Optimized structure of D5: 3-(5-(4-(diphenylamine) styryl) thiophen-2-yl)-2-cyanoacrylic acid. (Atoms represented according to color: carbon in grey, nitrogen in blue, sulfur in yellow, oxygen in red and hydrogen in white).

Figure 2. Optimized structure of D7: 3-(5-bis(4-(diphenylamine) styryl) thiophen-2-yl)-2-cyanoacrylic acid. (Atoms represented according to color: carbon in grey, nitrogen in blue, sulfur in yellow, oxygen in red and hydrogen in white).

Figure 3 is a caption of polyene-diphenylalanine dye molecule coded D9 reported by Kuang et al. (2011). D9 structure contains 5-(4-(bis (4-methoxyphenylamino) styryl) thiophen-2-yl)-2-cyanoacrylic acid. The structure was built using Gaussian 03 quantum chemical package within the frame work of Gaussview, the diphenylamine moiety was selected from the molecule group within the Gaussian window and placed on the builder interface, the diphenylalanine of D9 were then modified by the addition of methoxy groups, this was followed by the attachment of the polyene and thiophene group, and the cyanoacrylic acid. The diphenylalanine was the donor unit, polyene and thiophene were the π-conjugation to link or bridge the donor acceptor moiety while –COOH and –CN were the acceptor and anchor unit, respectively.
Figure 3. Optimized structure of D9: 5-(4-(bis (4-methoxyphenylamino) styryl) thiophen-2-yl)-2-cyanoacrylic acid. (Atoms represented according to color: carbon in grey, nitrogen in blue, sulfur in yellow, oxygen in red and hydrogen in white).

Figure 4 is a caption of polyene-diphenylaniline dye molecule coded D11 reported by Kuang et al. (2011). D11 structure contains 3-5-bis (4, 4’-dimethoxyphenylamino) styryl thiophen-2-yl)-2-cyanoacrylic acid. The structure was built using Gaussian 03 quantum chemical package within the frame work of Gauss view, the two-diphenylamine moiety was selected from the molecule group within the Gaussian window and placed on the builder interface, the diphenylamines of D11 were then modified by the addition of methoxy groups, this was followed by the attachment of the polyene and thiophene group, and the cyanoacrylic acid.

Figure 4. Optimized structure of D11: 3-(5-bis (4,4-dimethoxyphenylamino) styryl thiophen-2-yl)-2-cyanoacrylic acid (Atoms represented according to color: carbon in grey, nitrogen in blue, sulfur in yellow, oxygen in red and hydrogen in white).
3. Results and discussion

3.1. Dye structures
The structures of the four dyes given above were built in gauss view as reported by Kuang et al. (2011). The optimized structures of D5, D7, D9 and D11 are shown in Figure 1-4. In these structures, the diphenylaniline was the donor unit, polyene and thiophene were the \( \pi \)-conjugation to link or bridge the donor acceptor moiety while \(-\text{COOH}\) and \(-\text{CN}\) were the acceptor and anchor unit, respectively. The donor unit for D7 and D11 was extended by the addition of diphenylaniline. The diphenylaniline of D9 and D11 were then modified by the addition of methoxy groups.

3.2. Geometrical optimizations
In this study, the molecular structures of the four dyes are fully optimized in their ground state without symmetry constraints using hybrid density functional theory and the 6-31G* basis set. The dipole moments and the internal forces obtained for the dye structures after optimization are summarized in Table 1. The geometrical optimizations converged when the internal forces acting on all the atoms were less than a threshold value of \(4.5 \times 10^{-4}\) eV/Å.

D5 and D11 show the highest dipole moments (Table 1) which explains the polarity between the molecules. The selected bond lengths, bond angles and dihedrals of D5, D7, D9 and D11 are listed in Table 2.

The calculated geometrical properties of D5 dye are in close agreement with those reported in the literature (Cai-Rong et al., 2009). Similar geometrical characteristics resulting from similar geometry of the dye structures were observed for D5, D7, D9 and D11. The distance between the C atom in carboxyl and N atom in aniline were 1.435, 1.435, 1.421 and 1.389 nm for D5, D7, D9 and D11, respectively. These values account for the lengths of the conjugation bridges. These conjugation lengths aid electron transfer in the conjugation chain (Zhang et al., 2010).

3.3. Energy levels of the dyes
The energy levels (HOMO, LUMO, energy gap) provide the driving force for electron charge transfer of the dye sensitizer (Kuang et al., 2011; Mohammadi & Wang, 2014; Nazeeruddin et al., 1993). Low band gap energy between the HOMO and LUMO of the photosensitizers enhances absorption of photons in the red spectral region of the solar spectrum (Longo & De Paoli, 2003; Schmidt-Mende et al., 2005). The HOMO and LUMO isodensity plots of the photosensitizers are presented in Figure 5.

The HOMO in D5 is more delocalized over the entire molecular region whereas the HOMOs in D7, D9 and D11 are mainly distributed in the electron donor moiety but extend to linker groups in D7. The LUMOs in D5, D7, D9 and D11 are localized over the cyanoacrylic acid anchor and the linker groups although they extend to some of the polyene-diphenyl in D11 dye. Different electronic density distribution between HOMO and LUMO results in intermolecular charge separation between the donor and the acceptor group of the sensitizer when excited (Liang, Zhu, & Cao, 2013).

Computed HOMO levels of D5, D7, D9 and D11 lie at \(-4.90\text{eV}\), \(-5.13\text{eV}\), \(-4.46\text{eV}\) and \(-4.44\text{eV}\), respectively. The HOMOs are in the order D7< D5< D9< D11. The LUMO levels are located at \(-2.62\) for

| Sensitizer | Internal forces threshold value (eV/atom) | Dipole moment (Debye) |
|------------|-----------------------------------------|----------------------|
| D5         | \(4.5 \times 10^{-4}\)                  | 6.784                |
| D7         | \(4.5 \times 10^{-4}\)                  | 5.930                |
| D9         | \(4.5 \times 10^{-4}\)                  | 4.852                |
| D11        | \(4.5 \times 10^{-4}\)                  | 7.550                |
| D5  | Bond length | D7  | Bond length | D9  | Bond length | D11 | Bond length |
|-----|-------------|-----|-------------|-----|-------------|-----|-------------|
| 1-2 | 1.413       | 1-2 | 1.419       | 1-2 | 1.413       | 1-2 | 1.448       |
| 1-12| 1.435       | 1-12| 1.435       | 1-12| 1.421       | 1-12| 1.389       |
| 1-23| 1.435       | 1-23| 1.419       | 1-23| 1.421       | 1-23| 1.389       |
| 41-43| 1.328      | 39-41| 1.312      | 41-43| 1.323       | 39-41| 1.312       |
| 9-35| 1.412      | 9-32| 1.491      | 9-35| 1.403       | 9-32| 1.495       |
| 35-36| 1.379      | 33-34| 1.311      | 35-36| 1.372       | 33-34| 1.311       |
|     | Angles      | Angles      | Angles      | Angles      | Angles      | Angles      | Angles      |
| 2-1-23| 120.6      | 2-1 | 120.38      | 2-1-23| 120.2       | 2-1-22/56| 118.72      |
| 2-1 | 120.6      | 2-1-12| 120.0      | 2-1-12| 120.3       | 2-1-12/60| 122.5       |
| 9-34-35| 178.8     | 9-32-33| 120.13     | 9-34-35| 179.25      | 9-32-33| 120.13      |
| 41-43-44| 177.8   | 39-41-42| 179.6     | 41-43-44| 177.2       | 39-41-42| 179.6       |
|     | Dihedral    | Dihedral    | Dihedral    | Dihedral    | Dihedral    | Dihedral    | Dihedral    |
| 4-2-1-23| 31.5      | 3-2-1 | 35.4      | 4-2-1-23| 37.2        | 3-2-1-22/52| 51.08       |
| 2-1-12-14| 46.7     | 2-1-22/46| 44.5      | 2-1-12-14| 40.0        | 2-1-22/24| 32.0        |
| 43-44-45-47| 0.1     | 41-42-43-44| 0.5      | 43-44-45-47| 1.224       | 41-42-43-44| 0.1         |

Table 2. Selected bond lengths (nm), bond angles (°) and dihedral (°) of D5, D7, D9 and D11 dyes
D5, $-2.41$ for D7, $-2.94$ for D9 and $-2.90$ for D11. Thus, the LUMOs are in the order D9< D11< D5< D7. However, the HOMO- LUMO gaps are 2.27eV, 2.72eV, 1.51eV and 1.53eV for D5, D7, D9 and D11, respectively. Smaller HOMO- LUMO gaps observed in D9 and D11 suggest that the addition of methoxy groups to the donor moiety of the photosensitizers influence their energy levels. The computed values

Figure 5. Calculated frontier molecular orbitals using B3LYP/6-31G* theory and isodensity surfaces of HOMO and LUMO of D5, D7, D9 and D11 dyes. (Atoms represented according to color: carbon in grey, nitrogen in blue, sulfur in yellow, oxygen in red and hydrogen in white.)
of $-4.90\text{eV}$, $-2.62\text{eV}$, $2.27\text{eV}$ for HOMO, LUMO, HOMO–LUMO energy gap of D5 are in good agreement with values of: $-4.96$, $-2.68$, $2.28$ (Cai-Rong et al., 2009) and $-5.14$, $-2.66$ and $2.48$ (Zhang et al., 2010) reported in the literature using the same level of theory. Hence the hybrid B3LYP/6-31G* basis sets are effective for computing molecular energy levels and isodensity plots.

3.4. UV–Vis absorption spectra of the dyes

The UV–Vis spectra of the dyes were calculated using TD-DFT/B3LYP in gas phase for all the dyes to account the actual absorption of the dyes molecules. The absorption spectra are shown in Figure 6.

The absorption peak for D5 dye is located at 400 nm while that of D7 dye is located at 380 nm. D9 show absorption peak at 490 nm, while D11 show absorption peaks at 330 nm and 504. The highest absorption wavelength was notable for D5, D9 and D11. The molar absorption reported by Kuang’s electrochemical experiment are “33,000 M$^{-1}$ cm$^{-1}$ (441 nm) 31,000 M$^{-1}$ cm$^{-1}$ (441 nm) 33,000 M$^{-1}$ cm$^{-1}$ (464 nm) 38, 000 M$^{-1}$ cm$^{-1}$ (458 nm) for D5, D7, D9 and D11, respectively”. He reported that D9 and D11 show spectral red shifts and better current–voltage characteristics than the corresponding D5 and D7 (Kuang et al., 2011).

This explains the red-shifted spectral peak observed for D9 and near-infrared absorption observed for D1. The results agree fairly with Kuang’s findings.

Interestingly, the HOMO–LUMO energy gaps obtained in this study for D9 and D11 were found to be relatively low as compared to D5 and D7, this suggest the bathochromic shift observed in their absorption spectra. The light-harvesting efficiencies of the dye molecules are calculated theoretically using the analytical expression:

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

where $f$ is the absorption also called the oscillator strength of the dye associated with the maximum absorption of the dye (Chitumalla, Lim, Gao, & Jang, 2015; Mehmood et al., 2015; Schmidt-Mende et al., 2005). The light-harvesting efficiencies of the dyes are presented in Table 3. The light-harvesting efficiency were compared with available literatures.

From the calculations in Table 3, D9 and D11 shows the highest light-harvesting efficiencies, also, from the simulated absorption spectra in Figure 6, D5 shows absorption of 0.58 at 400nm with transition energy of 3.09 eV yielding a corresponding LHE value of 0.73, this agrees fairly with
Table 3. Computed maximum absorption ($\lambda_{\text{max}}$/nm), excitation energy (eV), oscillator strength ($f$) and light-harvesting efficiency (LHE) of the dyes

| Dyes | $\lambda_{\text{max}}$ (nm) | E (eV) | f | LHE |
|------|-----------------------------|-------|---|-----|
| D5   | 400                         | 3.09  | 0.58 | 0.737 |
| D7   | 380                         | 3.26  | 0.46 | 0.653 |
| D9   | 490                         | 2.53  | 0.75 | 0.822 |
| D11  | 504                         | 2.46  | 0.72 | 0.809 |

absorption of 0.78 at 399nm and transition energy of 3.10eV and corresponding LHE value of 0.83 reported in literature (Hagberg et al., 2006). D11 shows more spectral red shift absorption than D5, D7 and D9. This explains the highest current–voltage characteristics observed for D11 as reported by Kuang et al.’s (2011) electrochemical experiment. The result obtained from this study agrees fairly with Kuang’s report. The LHE values obtained from this study range from 0.653 to 0.822 and are relatively high suggesting that the dye molecules will show good performance as photosensitizers for DSSCs.

4. Conclusions

In this work, four polyenediphenyl-based photosensitizers (D5, D7, D9 and D11) were studied computationally, using DFT and TD-DFT methods. The D5 and D7 dyes showed absorption in the visible region while D9 and D11 showed spectral red shift absorption owing to their reduced HOMO–LUMO energy gap. It was also observed that the D9 and D11 dyes with methoxy groups in their donor moiety showed a broader peak and improved red spectra response than D5 and D7 dyes without methoxy group. The D9 and D11 sensitizers with two diphenylaniline donor moieties showed the highest light-harvesting efficiencies. The low HOMO–LUMO energy gap, absorption spectra and high light-harvesting efficiency suggest that the addition of the methoxy groups to the donor moiety of D9 and D11 is responsible for their improved optical performance. The results suggested that the dyes are promising sensitizers for DSSCs application.

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