

Theoretical study of the design dye-sensitivity for usage in the solar cell device

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ABSTRACT

There are many applications in the polymer chemistry, pharmaceutical, agricultural and industrial fields of the thiadiazole molecule and their derivatives. Allowance of the energy gap of the polymer conjugated is an object of great interesting debit for the possible removal of a doping in the preparation of highly conductivity polymers. Thiadiazoles derivatives are structural foundation of the polymer materials. In this present work, the electronic properties of graphene nanoflakes (GNFs)-phenanthrene-1,3,4-thiadiazoles oligomers are studied and discussed. Where thiadiazoles is expanded from one to 9 unit's molecules at the structure. The energy gap, HOMO, LUMO distribution, total energy, Fermi level energy, work function, maximum wavelength absorption, vertical absorption energies, and oscillator strengths are calculated for each molecule. All calculations are carry out by usage density function theory (DFT) and depended time density function theory (TD-DFT) with the B3LYP/6-31G model in the Gaussian 09W software packages. Results show that increasing the number of monomeric units lead to great enhance in the electronic properties, which caused it decreased the band gap from 3.17 eV in the system with one unit of thiadiazole just to 1.35 eV in the system with 9 units of thiadiazole. This case is raised the value of maximum absorption wavelengths to >500 nm to give the better performance in optoelectronic and solar cell, as these structures have prime absorption bands within the solar spectrum.

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Introduction

The optimal way to create a modern society powered by electricity it conversion of solar light into electric energy by using photovoltaic, there are many technologies have been evolved in relative to photovoltaics, such the semiconductor-based cells, organic photovoltaics cells, thin-film solar cells, and dye-sensitized solar cells [1,2]. At the present, solar cell are primarily composed from the inorganic semiconducting materials, crystalline and an amorphous silicon being the most use among them [3]. Polymers types are conjugated of organic or novel molecular grounded conductors not only possess the optical and electronic properties from Si, Ge, group iii-iv and group ii-vi inorganic semi-conductors, but also have the processing preference and mechanical properties for polymers. Therefore, it's have attracted great interest for their use in transparent conductors, solar cells [4], light emitting diodes [5,6], and semi-conductor layers in field effect transistors [7]. Polymers solar cells have protruded as a promising alternative PV technology due to the possibly of cost effective production of large range of flexible devices using

solution-processing techniques, with low environmental effect and versatility in organic material design [8–11].

The thiadiazoles and their derivatives are created from family of the azole compounds [12], these molecules are contained from five membered ring, there in two of the atoms are nitrogen and one is sulfur. The thiadiazole has been combined into the backbone of several the polymers with desirable chemical and thermal stability, for this reason it's have many applications in the field of the polymer chemistry, pharmaceutical, agricultural and industrial [13–15].

The polymer of solar cells are limited with the low amount of absorbed photons [16]. This limitation is due to the active layers is thin and the mismatch of the absorption spectrum with the solar of terrestrial. Absorption maximum of polymers solar cell is localized about 500 nm, while the maximal solar photon flux is lie in the extent from 600 to 800 nm. To solve this problem, my planning is to use aromatic compound (phenanthrene) and (GNF_s) dyes to extend the spectral domain to absorption for the active layer.

The phenanthrene is a polycyclic aromatic hydrocarbon, which is consisted from three combined benzene rings. Phenanthrene and its derivatives are beginning more used as an active structure in a variety of the optoelectronic devices such as organic thin-film

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field-effect transistors, light-emitting diodes, and photovoltaic cells [17]. The GNFs is a single layer of graphite, and consists of sp^2 hybridized carbon atoms [18,19], GNFs is the name refer to the zero dimensional form of graphene. Nanographenes have a great interest owing to their electronic and spin properties touted as the fundamental basis for the next generation of electronic, spintronic and photonic devices [20–22].

In this present work, we study the structural containing monomeric units repeated of 1,3,4-thiadiazole oligomers with phenanthrene and GNFs at both ends, which was achieved to determine their optical and electronic properties, energy gap (E_g), frontier orbital distributions, total energy (E_t), Fermi level energy (E_{FL}), work function (Φ) and maximum absorption wavelength (λ_{max}), vertical absorption energies (ΩA), and oscillator strengths (f). These properties are very important of organic structure for application in photoelectric and solar cell.

Computational detail

In this article, the geometry optimization of the molecules was performed by using the density functional theory method (DFT), as implemented in the Gaussian 09W package [23] the hybrid functional B3LYP with the 6-31G basis set [24]. This basis set was chosen because it is well known that it performs sufficiently in associated geometry optimizations of closed-shell organic compounds [25] and because an enough description of the electronic assembly of molecules with a large number of electrons in sulfur must be understood using basis sets with parameters for the d electrons [26]. The total energy, highest occupied molecular orbital (HOMO) energies, lowest unoccupied molecular orbital (LUMO) energies, energy gap, Fermi level energy and wavelength of the molecular system calculated by the same level of theory as the ground-state properties, Gaussian B3LYP/6-31G.

Results and discussion

Optimization geometric

The molecular systems are consisting from chain of 9 units of 1,3,4 thiadiazole with phenanthrene united to opposite places in the main chain (TDA n PH-GNFs), these systems are jointed to the GNFs in the ends. This geometrical optimization calculated by using DFT at the B3LYP/6-31G, as shown in Fig. 1. In these systems, the planarity of the oligomers did not affect when augmentation of the number of monomeric units, but adding a little twist of these structures. Nevertheless, the bond length and the dihedral angle among the thiadiazole oligomer chain and each GNFs-phenanthrene molecule remained steady.

Electronic properties

The energy gap (HOMO- LUMO) takes the range value (1.35–3.17) eV, these values of energy gap for a molecular system provides an indication of its possibility for use as a semiconductor. The energy gap is reduced with increasing the number of monomeric units. The photovoltaic effect is consisted from these steps: first, the photons are absorbed via the material. Second, the excitant delivered from this absorption should be separated, Third, the electrodes collect the resulting charge. Photon absorption of the solar spectrum, optimum energy gap (E_g) should be ($1.1 \leq E_g \leq 2$) eV, the energy gap for the most of organic semiconductors was higher than 2.0 eV. At least Though they can be, at least partly, succeeded by varying the polymer series length and some macromolecules have their band gap around 1.7 eV. Furthermore, organic material has very elevated absorption coefficient so

that only 100 nm are necessary to absorb among 60 to 90%, if a reflexive back contact is used [27].

The most promising planning for adapting the energy gap includes introducing donor and acceptor monomer units together in the polymer structure. The basic concept is that the interaction between alternating electron-rich donors and electron-deficient acceptors result in a beaten energy gap by molecular orbital hybridization and through intramolecular charge transfer.

The DFT calculations disclose that, when a single donor-acceptor recurrence unit is attending a molecule, the resulting HOMO level almost matches to that of the donor group, and the resulting LUMO level to that of the acceptor group. Fig. 2. Shows that the energies changes of the HOMO and LUMO, as the chain increases with the number of monomeric units of thiadiazole, the HOMO increase very little, while the LUMO increases significantly. Therefore, the change chain of energy gap confirms better the semiconductor properties. The units of thiadiazole behave, as acceptor in the donor-acceptor unit of GNFs-phenanthrene-1,3,4-thiadiazole, this behave lead to change in HOMO, LUMO and energy gap [28].

Fig. 3 shows the maps distribution of the HOMO and LUMO, in the structures the HOMO is localized over the GNFs-phenanthrene at the end, while the LUMO distributed in the center over the thiadiazole chain. This behavior can be ascribing to two electron acceptor imine groups obtainable at the thiadiazole unit [29]. In consequence, when the thiadiazole units increase, the electron acceptor character increases neither. In addition, the structure has electron shortage of nitrogen and high electron affinity of the sulfur atom (in the thiadiazole rings) [30].

The calculation of total energy, Fermi level energy, work function, and maximum absorption wavelengths of the structures are shown in Table 2. When the number of monomeric units of thiadiazole increase the total energy increase as well, this parameter would be of great importance of estimation of stability the structures. Therefore, increase as the number of monomeric units' gives more stable and lower reactive for those systems. Moreover, the Fermi level energy (E_{FL}) increasing with increasing of a number several thiadiazole. This increase in Fermi level (E_{FL}) energy leads to rise in the work function (Φ), this is a very important in field emission light for optoelectronic application. The work function is a very important specification the potential barrier to emission of the electron for the structure (see Table 1).

Optical properties

The effectiveness of solar cell systems owes to the wavelength identify between the cramped wavelength band related with the semiconductor energy gap and the wide band of the sun emission. In these systems, the electronic transitions were calculated in order to approve the HOMO and LUMO centralization in addition to the orbital levels of molecule involving in donor-acceptor interactions. By using the TD-DFT and the B3LYP/6-31G level we calculated the transition states of electron, maximum absorption wavelength (λ_{max}), vertical absorption energies (ΩA) and oscillator strengths (f), for the great important properties of semiconducting materials. These parameters are shown in Table 2.

From this result, clearly that the value of maximum absorption wavelength extends from 416 nm for the structure with one thiadiazole monomeric unit and 948 nm with nine thiadiazole monomeric units (see Fig. 4). Increasing the number of monomeric units of thiadiazole in the chain give rise to shift of the absorption wavelength at the spectra of electronic for the structures, which caused to the presence of a number of double bonds in the system. Where, there are more double bonds in a conjugate polymer in the molecular structure, this is reason at the longer the absorption wavelength of the molecule [31]. This is major properties of materials designed for usage in photovoltaic and solar cell devices, the

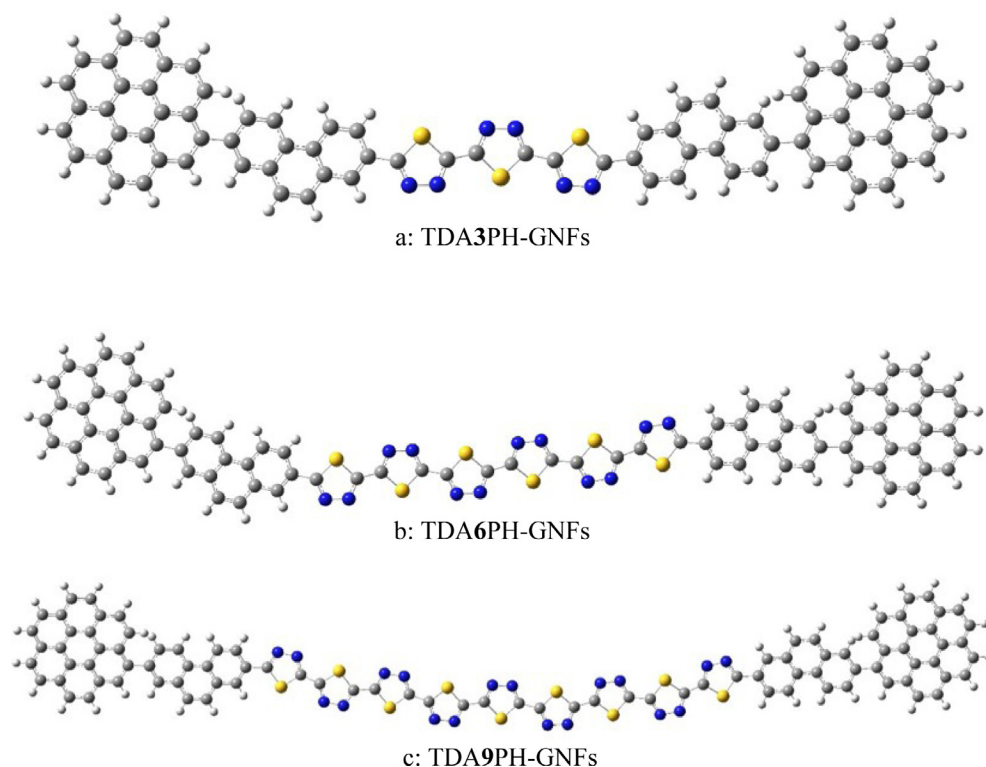


Fig. 1. Geometrical optimization of GNFs-phenanthrene-1,3,4-thiadiazoles structures.

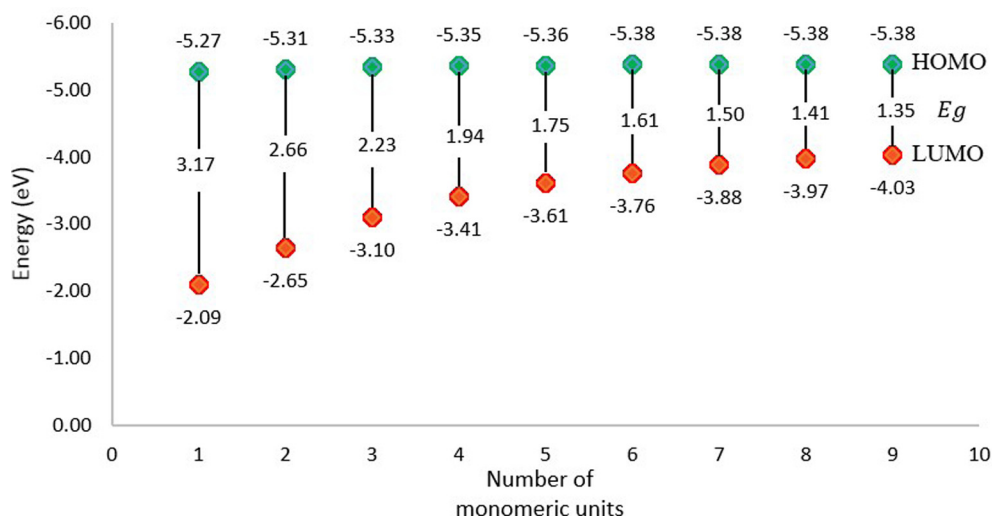


Fig. 2. HOMO, LUMO and energy gap values for the TDA_nPH-GNFs molecules.

size varying of the series allows us to adapt the shift, such as the absorption wavelength happen within the terrestrial solar or visible light spectrum, whereas the maximum intensity of absorption wavelength occurs in the range 500–800 nm [32], this range of spectrum is very agreement with us result that's show in Table 2, where when was the structure contain three monomeric units of thiadiazole, and $\lambda_{\text{max}} < 800$ nm when was the system contain seven monomeric units of thiadiazole. Therefore, founded on these results, these structures give the best performance for optoelectronics and organic semiconductor solar cells when the number of monomeric units of thiadiazole were from 3–5 units.

Table 2 illustrates the vertical transition energies (Ω_A) have the values lie among 2.97 eV and 1.30 eV, these values decrease with

increasing the number of monomeric units of thiadiazole. This proves that rising the π -conjugation eases the moving of electrons from HOMO to LUMO, where The molecular π - π^* orbitals represented to the HOMO and LUMO.

The electronic transitions in these structures were among neighboring orbitals: HOMO (H-0), LUMO (L-0), LUMO + 1 (L + 1) and LUMO + 2 (L + 2). In this article, all of the evaluated molecules present a maximum absorption band matching to H-1 \rightarrow L + 0. From these results, apparent that the position of the HOMOs and LUMOs, in addition to the electronic transitions entangled, clearly shows that the essential core TDA is rich with the electrons. This property could facilitate procs charge transfer in these structures, and flux the electronic practically fills all the molecular structure.

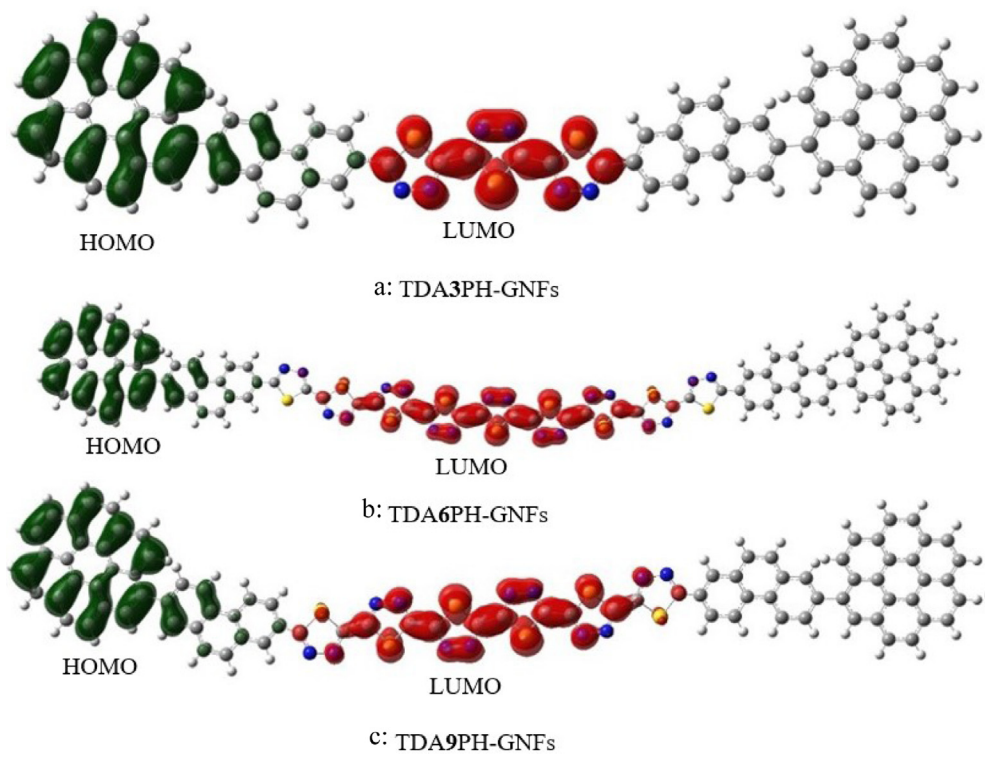


Fig. 3. Molecular orbital distribution (HOMO and LUMO) of the TDA3PH-GNFs, TDA6PH-GNFs, and TDA9PH-GNFs systems (isovalue: 0.02).

Table 1
Total energy (E_t) eV, Fermi level energy (E_{FL}) eV, work function (Φ) eV data calculated by using DFT B3LYP/6-31G.

The structure	E_t (eV)	E_{FL} (eV)	Φ (eV)
TDA1PH-GNFs	−95296.20	−3.68	3.68
TDA2PH-GNFs	−111179.94	−3.98	3.98
TDA3PH-GNFs	−127067.40	−4.21	4.21
TDA4PH-GNFs	−142949.09	−4.38	4.38
TDA5PH-GNFs	−158835.17	−4.49	4.49
TDA6PH-GNFs	−174719.09	−4.57	4.57
TDA7PH-GNFs	−190605.00	−4.63	4.63
TDA8PH-GNFs	−206488.76	−4.68	4.68
TDA9PH-GNFs	−222372.42	−4.71	4.71

Conclusion

In this paper, the calculations of GNFs-phenanthrene-1,3,4-thiadiazole oligomers performed using hybrid density functional methods DFT and TDDFT at the B3LYP/6-31G basis set level. The structures of GNFs-phenanthrene-1,3,4-thiadiazole were contain

from 1 to 9 units of thiadiazole with one molecule of phenanthrene and graphene nanoflakes at the end (TDAnPH-GNFs). By using DFT calculated the energy gap, HOMO-LUMO distribution, and maximum wavelength absorption of these oligomers, the energy gap decrease per increase the number of monomeric units of those oligomers, where depreciate from 3.17 eV with one monomeric unit thiadiazole to 1.35 eV with 9 monomeric units of thiadiazole. The HOMO is location on the GNFs-phenanthrene at the end, while the LUMO is localized in the center over thiadiazole units. The total energy is increased with increasing the number of monomeric units of thiadiazole, this result illustration that the structures was more stability. Theoretical calculations for UV-vis absorption spectra of all systems show that the maximum wavelength absorption lie in the range 416–948 nm. On the basis of these results, it appears that TDA9PH-GNFs has the lowest band gap energy and the largest wavelength with a value of 948 nm, and TDA1PH-GNFs has the highest energy gap and lowest wavelength with a value of 416 nm.

Table 2
Electronic transition of systems, maximum absorption wavelengths (λ_{max}), vertical absorption energies (ΩA), oscillator strength (f), and electronic transition assignments as calculated by using TD-DFT B3LYP/6-31G.

The structure	λ_{max} (nm)	ΩA (eV)	Oscillator strength	Electronic transition
TDA1PH-GNFs	416	2.97	0.091	H-1 \rightarrow L + 0 (77%)
TDA2PH-GNFs	495	2.50	0.159	H-1 \rightarrow L + 0 (94%)
TDA3PH-GNFs	587	2.11	0.088	H-1 \rightarrow L + 0 (98%)
TDA4PH-GNFs	673	1.84	0.052	H-1 \rightarrow L + 0 (99%)
TDA5PH-GNFs	746	1.66	0.034	H-1 \rightarrow L + 0 (99%)
TDA6PH-GNFs	807	1.53	0.026	H-1 \rightarrow L + 0 (100%)
TDA7PH-GNFs	867	1.42	0.014	H-1 \rightarrow L + 0 (99%)
TDA8PH-GNFs	916	1.35	0.009	H-1 \rightarrow L + 0 (99%)
TDA9PH-GNFs	948	1.30	0.007	H-1 \rightarrow L + 0 (99%)

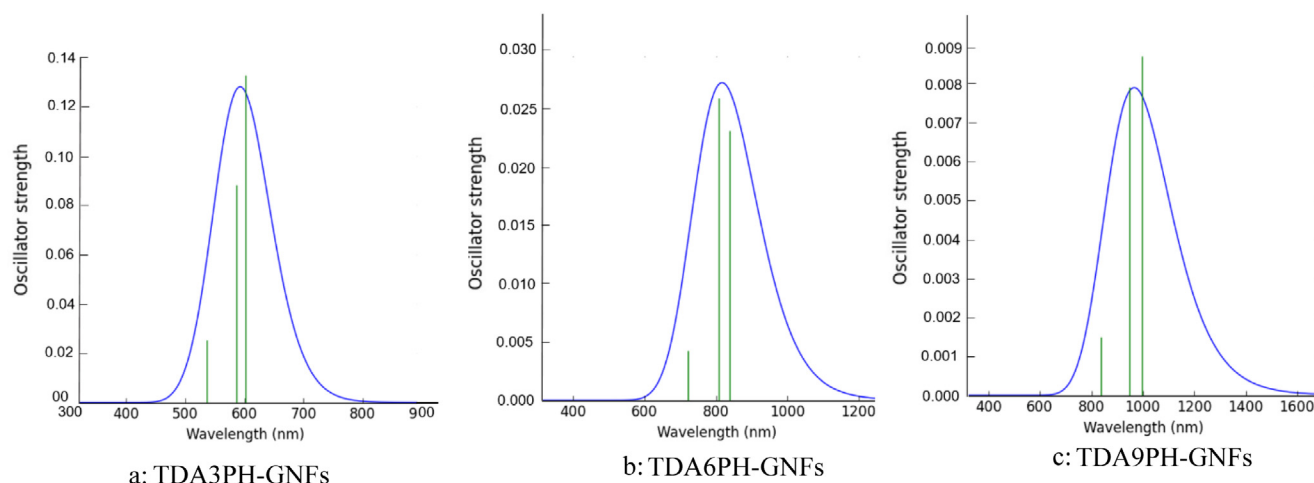


Fig. 4. Absorption spectra for some systems TDA3PH-GNFs, TDA6PH-GNFs, TDA9PH-GNFs, which calculated with TD-DFT B3LYP/6-31G.

Conflict of interest

The author confirms that this article content has no conflict of interest.

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