

DFT calculation of the electronic properties of fluorene-1,3,4-thiadiazole oligomers

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Received: 10 January 2013 / Accepted: 30 April 2013 / Published online: 31 May 2013
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Abstract Thiadiazole derivatives have been widely employed in the areas of pharmaceutical, agricultural, industrial, and polymer chemistry. The electronic and molecular structures of thiadiazoles are of interest because they have an equal number of valence electrons and similar molecular structures to thiophenes, which are currently used in the construction of organic solar cells due to their relatively high hole mobilities and good light-harvesting properties. For this reason, the electronic properties of fluorene-1,3,4-thiadiazole oligomers warrant investigation. In the present work, the structure of fluorene-1,3,4-thiadiazole with one thiadiazole unit in the structure was analyzed. This molecule was then expanded until there were 10 thiadiazole units in the structure. The band gap, HOMO and LUMO distributions, and absorption spectrum were analyzed for each molecule. All calculations were performed by applying the B3LYP/6-31G(d) chemical model in the Gaussian 03W and GaussView software packages. The electronic properties were observed to significantly enhance as the number of monomeric units increased, which also caused the gap energy to decrease from 3.51 eV in the oligomer with just one thiadiazole ring to 2.33 eV in the oligomer with 10 units. The HOMO and LUMO regions were well defined and separated for oligomers with at least 5 monomer units of thiadiazole.

Keywords DFT · Photovoltaic · Thiadiazole

Introduction

Photovoltaic cells show great potential as low-carbon sources of energy, but have thus far remained expensive compared to other technologies [1]. At present, solar cells are primarily composed of inorganic semiconducting materials [2]; however, the use of semiconducting polymers [3–5] (and organic materials in general) in such cells is currently attracting a lot of interest from researchers. Because these plastic materials can be processed from solution and printed onto plastic substrates, they should be lightweight, flexible, and inexpensive [6].

Solar radiation is converted into electricity via the photovoltaic effect, which is initiated by the absorption of light by an organic semiconductor. The absorption of light excites electrons in the valence band across the prohibited band, and the resulting empty states in the valence band (i.e., positively charged holes) increase the conductivity of the semiconductor [7].

Conducting polymers generally exhibit structures with alternate single and double bonds or conjugated sp^2 -hybridized carbon atoms. Thus, they have highly delocalized π -electron systems with high electronic polarizability, which enables the absorption of visible light through π - π^* transitions between the bonding and antibonding orbitals and electronic charge transport, both of which must occur for semiconductors to be able to generate power in solar cells [8]. The molecular π - π^* orbitals correspond to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Thiadiazole contains a five-membered ring in which two of the atoms are nitrogen and one is sulfur. This molecule exhibits the alternating single/double bond structure mentioned above. Thiadiazole has been extensively studied because it has an equal number of valence electrons and a similar molecular structure to thiophenes, thiazoles, pyrazines, and related five- and six-membered heterocycles

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[9]. Thiadiazole polymers exhibit interesting properties when used in photovoltaic devices; however, they are not as efficient at light harvesting as thiophenes. That said, they have been incorporated during the fabrication of solar cells as acceptors [10] and for their absorption and electronic properties [11]. Fluorene is a polycyclic aromatic hydrocarbon; polymers of fluorene have attracted considerable scientific interest in recent years due to their useful properties, such as photo- and electroluminescence as well as their high thermal and chemical stabilities against oxidizing agents [12].

In the present paper, we report a study of structures consisting of 1,3,4-thiadiazole oligomers with fluorene units at both ends, which was performed to determine their electronic properties: their HOMO–LUMO gap energies, frontier orbital distributions, and absorption spectra. All of these properties are important characteristics of organic compounds intended for application in photovoltaic devices.

Computational methods

The equilibrium geometries of the molecules were determined by means of the gradient technique. The force constants and vibrational frequencies for the stationary points found after optimization were calculated (by invoking the `FREQ` keyword in the Gaussian 03W [13] software package) to check that they were true minima.

All of the computational studies were performed in Gaussian 03W [13] using the density functional theory method (DFT) as implemented in that computational package. The hybrid functional B3LYP [14], which combines Becke's exchange [15] and Lee, Yang, and Parr's correlation [16] functionals with the 6-31G(d) basis set [17], were used for the quantum-chemical calculations. This basis set was selected because it is well known that it performs adequately in SCF or correlated geometry optimizations of closed-shell organic compounds [18] and because an adequate description of the

electronic structure of molecules with a large number of electrons on sulfur must be realized using basis sets with parameters for the *d* electrons [19]. This chemical model has been widely used by the authors for geometry optimization and determining electronic properties [20]. The absorption spectra of the molecular systems were determined at the same level of theory as the ground-state properties, B3LYP/6-31G(d), by solving the time-dependent Kohn–Sham equations using the time-dependent density functional theory (TD-DFT) method implemented in Gaussian 03W. The equations were solved for 10 excited states.

Results and discussion

Geometry

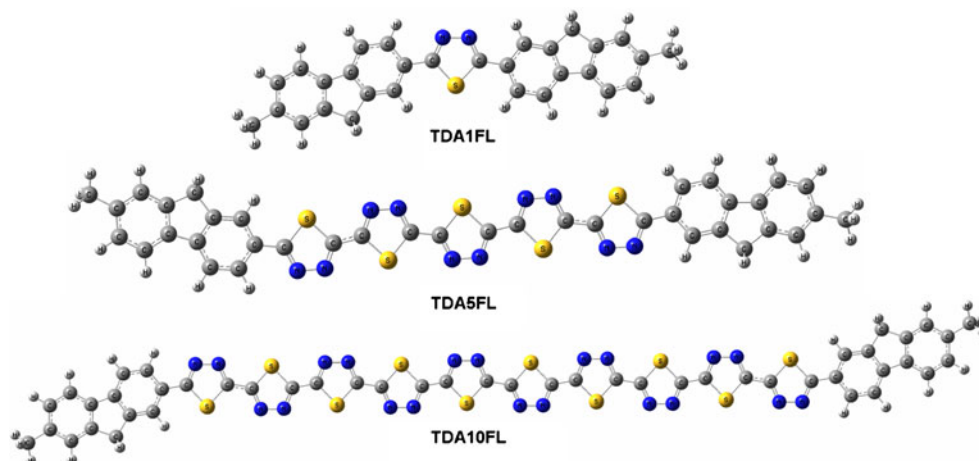
The optimized geometries of the structures of fluorene-1,3,4-thiadiazole with 1–10 monomeric units of thiadiazole, as calculated at the B3LYP/6-31G(d) level, are shown in Fig. 1. Oligomers are denoted “TDA n FL,” where n refers to the number of thiadiazole units present.

Increasing the number of monomeric units did not affect the planarity of the oligomers aside from adding a little twist of the fluorene, leading to a slight zig zag in the structure; however, the length of the bond and the dihedral angle between the thiadiazole chain and each fluorene molecule remained unchanged. Each subunit of the oligomer chain retained the same bond lengths and bond angles that were present in the original monomeric unit.

Polymeric behavior

In Fig. 2, the HOMO–LUMO gap is presented as a function of the number of monomeric units in the fluorene-1,3,4-thiadiazole oligomers. The oligomers studied in this work reached up to 10 monomeric units, but an analysis of 20 units was performed to determine the polymeric behavior of

Fig. 1 Optimized structures of fluorene-1,3,4-thiadiazoles



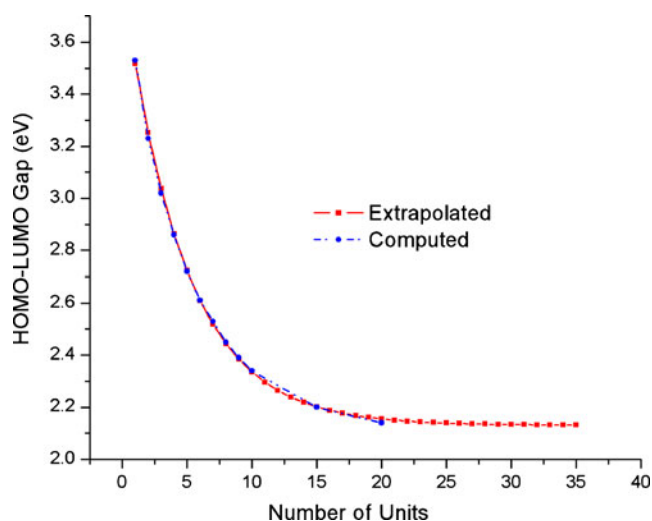


Fig. 2 Energy gap vs the number of thiadiazole units

these systems. The usual way to study the behavior of oligomers with an increasing number of units is to plot the studied property as an inverse function of the number of units. However, a better description is obtained when the results are fitted to a decreasing exponential function [9].

The resulting equation is as follows:

$$\Delta E = 2.132 + 1.714 \exp(-N/4.689)$$

where ΔE is the extrapolated HOMO–LUMO gap and N is the number of monomeric units.

Thus, the extrapolated value for $N \rightarrow \infty$ is 2.13 eV for fluorene-1,3,4-thiadiazole. This value is achieved after 29 monomeric units; see Table 1.

Electronic properties

The HOMO–LUMO gap of a polymer provides an indication of its potential for use as a semiconductor, so the frontier orbitals—the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)—of each oligomer were analyzed. The HOMO–LUMO gap decreases as the number of monomeric units increases, reaffirming that this property can be at least partly tailored by varying the polymer chain length, and a HOMO–LUMO gap of 1.7 eV can be achieved for some macromolecules. The photovoltaic effect consists of a series of steps: first the photons are absorbed by the material, exciton dissociation then occurs, and finally the electrodes collect the resulting charge. The optimal energy gap facilitating the absorption of photons from the solar spectrum has been demonstrated to be 1.1–2.0 eV [21]. It is also known that this value can be decreased by increasing the number of monomeric units.

Table 1 Data obtained from the HOMO–LUMO gap extrapolation analysis

Number of monomeric units	HOMO–LUMO gap (eV)
1	3.51
2	3.25
3	3.03
4	2.86
5	2.72
6	2.61
7	2.51
8	2.44
9	2.38
10	2.33
11	2.29
12	2.26
13	2.23
14	2.21
15	2.20
16	2.18
17	2.17
18	2.16
19	2.16
20	2.16
21	2.15
22	2.15
23	2.14
24	2.14
25	2.14
26	2.14
27	2.14
28	2.14
29	2.13
30	2.13
31	2.13
32	2.13
33	2.13
34	2.13
35	2.13

The results obtained in this work confirm that the larger the chain, the smaller the energy gap, and thus the better the semiconducting properties. Figure 3 shows the changes in the energies of the HOMO and LUMO as the chain increases in length: the HOMO decreases a little, while the LUMO decreases significantly. This is because the thiadiazole units behave as acceptors in the donor–acceptor unit of fluorene-1,3,4-thiadiazole, and DFT calculations reveal that when a single donor–acceptor repeat unit is present in a molecule, the resulting HOMO level approximately corresponds to that of the donor group, and the resulting LUMO level to that of the acceptor group [22].

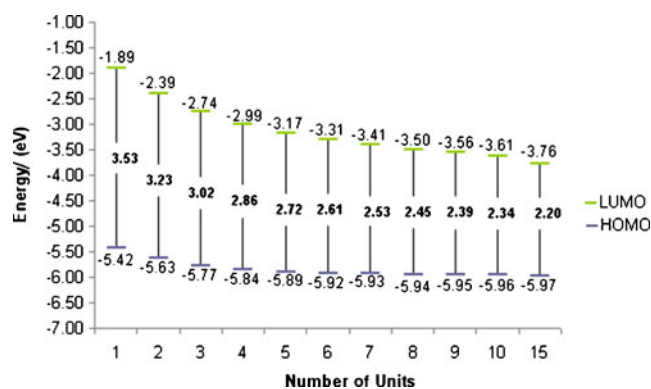


Fig. 3 Energy gap values for the TDA n FL structures

Maps showing the distributions of the calculated HOMOs and LUMOs are shown in Fig. 4. In the oligomer with only one unit of thiadiazole, the HOMO is distributed over the whole molecule, while the LUMO is localized in the center. The same distribution is seen until the oligomer with 4 units. When 5 units are reached, the HOMO remains localized over the fluorene at the ends and the LUMO is positioned over the thiadiazole units (the increasing acceptor chain). In particular, the HOMO is mainly localized over the C–C bonds of the fluorene and the LUMO over the N–N bonds, the S atom, and the C–C bonds of the thiadiazole rings. This behavior can be attributed to the electron deficiency of nitrogen and the hypervalency and high electron affinity of the sulfur atom, and to the fact of the dependency from HOMO/LUMO energy levels of the degree of electron delocalization in conjugated polymers [22, 23].

Spectroscopic properties

Some of the most important characteristics of semiconducting materials are their absorption performance and as well as their capacity for electronic excitation. These properties can

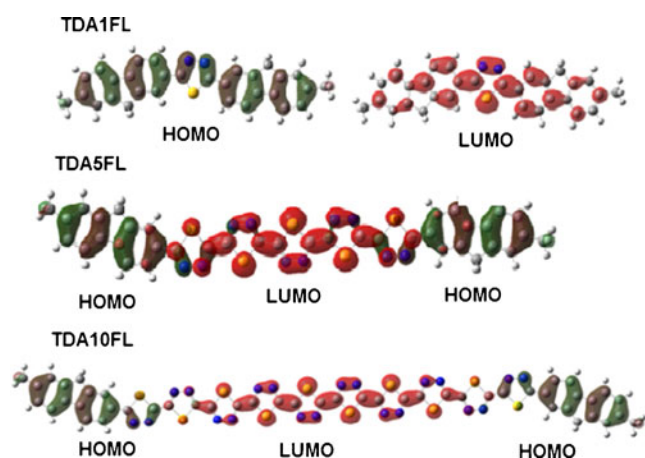


Fig. 4 Frontier molecular orbital topologies (HOMO and LUMO) of the TDA1FL, TDA5FL, and TDA10FL structures (isovalue: 0.02)

Table 2 Electronic absorption properties of the oligomers investigated in this work, as calculated using TD-DFT B3LYP/6-31G(d): maximum absorption wavelengths (λ_{\max}), vertical absorption energies (Ω_A), and the most important electronic transitions

Molecule	λ_{\max} (nm)	Ω_A (eV)	Electronic transitions
TDA1FL	392	3.16	H-0→L+0 (88 %)
TDA2FL	434	2.86	H-0→L+0 (90 %)
TDA3FL	466	2.66	H-0→L+0 (92 %)
TDA4FL	492	2.52	H-0→L+0 (93 %)
TDA5FL	512	2.42	H-0→L+0 (92 %)
TDA6FL	529	2.34	H-0→L+0 (93 %)
TDA7FL	542	2.29	H-0→L+0 (93 %)
TDA8FL	553	2.24	H-0→L+0 (93 %)
TDA9FL	562	2.20	H-0→L+0 (93 %)
TDA10FL	570	2.17	H-0→L+0 (93 %)

be analyzed by performing theoretical calculations of their UV–vis absorption spectra. The calculated maximum absorption wavelengths, vertical absorption energies, and most important electronic transitions of the oligomers investigated in this work are shown in Table 2.

According to the results obtained for the theoretical spectroscopic properties calculated with B3LYP/6-31G(d), the maximum absorption wavelengths (λ_{\max}) are highest for the systems with longer thiadiazole chains, and lowest for the molecule with only one thiadiazole monomeric unit in its structure. The calculated values for λ_{\max} lie in the range 392–570 nm. Figure 5 illustrates the absorption spectra for some of the oligomers. Increasing the number of units in the chain leads to bathochromic displacement of the absorption bands in the electronic spectra of the oligomers, which is expected due to the number of double bonds in the molecule. The more conjugated double bonds there are in a

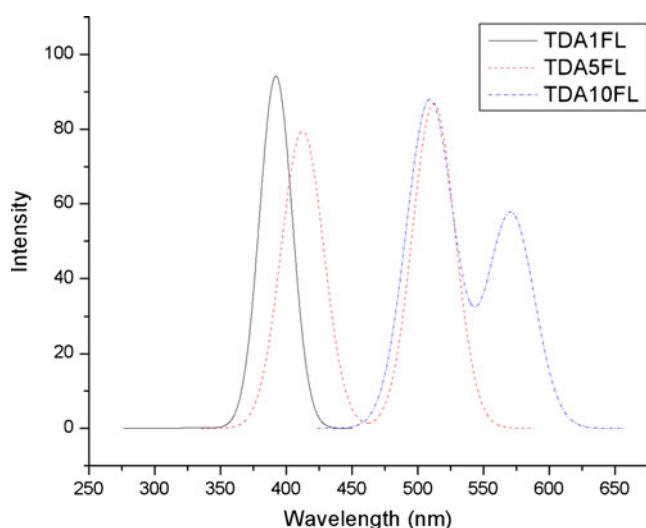


Fig. 5 Absorption spectra of the oligomers TDA1FL, TDA5FL, and TDA10FL, as calculated using the TDDFT method and B3LYP/6-31G(d)

molecule, the longer the absorption wavelength of the molecule [24]. This is an essential characteristic of materials intended for use in photovoltaic devices, as varying the size of the chain allows us to tailor the shift such that the absorption bands occur within the visible or terrestrial solar spectrum, where the maximum intensity occurs between 500 and 800 nm [25, 26]. In this sense, the compounds TDA5FL to TDA10FL, which have λ_{\max} values of >500 nm, should give the best performance, as these systems have major absorption bands within the solar spectrum.

As is known, the energies of the maxima for the spectral absorption bands correspond to excitation energies, and these can be compared with vertical transition energies or vertical absorption energies (Ω_A) [27, 28]. Table 2 shows that the vertical absorption energies are smaller for long TDA chains than they are for those with only a few monomeric units. This demonstrates that increasing the π -conjugation facilitates the promotion of electrons from the HOMO to the LUMO. In these systems, π electrons are involved in light absorption (solar cells) and emission (OLEDs). The molecular π - π^* orbitals correspond to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively [21]. In this work, all of the analyzed systems exhibited a maximum absorption band corresponding to H-0→L+0.

Conclusions

In this theoretical study, various fluorene-1,3,4-thiadiazole derivatives were analyzed through the application of electronic structure theory. The molecule of fluorene-1,3,4-thiadiazole was expanded from 1 to 10 thiadiazole units (TDA n FL). These oligomers were found to remain planar as the number of monomeric units increased, and this planar geometry could be favorable for the transfer of electrons in organic semiconductors.

Using DFT and TDDFT calculations, the HOMO–LUMO distributions, the gap energies, and the absorption spectra of the TDA n FL oligomers were calculated. As the number of monomeric units increased, the gap energies of the proposed oligomers decreased significantly, reaching a value of 2.33 eV for the structure with 10 thiadiazole units.

Using extrapolation analysis, it was found that the gap energy decreases to 2.16 eV for 18 thiadiazole units. It was observed that the HOMO and LUMO regions were clearly separated for oligomers with at least 5 thiadiazoles, which could lead to a slight advantage for electron transfer within those structures.

Finally, theoretical calculations of the UV–vis absorption spectra for all of the studied molecules indicated that these oligomers absorb within the visible region of the spectrum, and the theoretical values for λ_{\max} were in the range 392–

570 nm. Based on these results, it appears that TDA10FL has the lowest gap energy and the largest shift in the absorption spectrum, with a value of 570 nm for λ_{\max} .

In summary, this theoretical analysis has shown that the electronic properties of oligomers improve when the length of the chain is increased.

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