



(This article was initially submitted to the UKMK 2016 (National Chemical Engineering Congress) and finally evaluated by the JOTCSB editorial staff).

Design and Simulation of Semiconducting Polymers for Optoelectronic Applications by Using Quantum Mechanical Tools

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Abstract: In this study, polymers containing furan, thiophene, and selenophene units as electron donating groups and benzooxadiazole, benzothiadiazole and benzoselenadiazole units as electron acceptor groups are theoretically designed and their electronic band gaps are calculated with the help of density functional theory. The lowest energy structures of the monomers of these systems are revealed with the help of conformational analysis by using the B3LYP/6-31G(d) and B3LYP/LANL2DZ methods. While the electronic band gap values of monomers are obtained at the same levels of theory, the ones for the polymers are obtained by performing periodic boundary conditions calculations, PBC-DFT. First, accuracy of the methodology is tested by comparing the band gaps with the ones previously studied in the literature, and then structural and electronic properties of the new semiconducting polymers are revealed.

Keywords: Density functional theory, semiconducting polymers, electronic band gap, selenophene.

Submitted: October 11, 2016. **Revised:** November 30, 2016. **Accepted:** December 07, 2016.

Cite this: Özkılınç Ö, Kaya B, Kayı H. Design and Simulation of Semiconducting Polymers for Optoelectronic Applications by Using Quantum Mechanical Tools. JOTCSB. 2017;1(1):127–34.

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INTRODUCTION

Today, the need to use renewable energy resources in the most effective way that constitutes a driving force for the scientific studies about the high-efficiency and low-cost photovoltaic devices (1). Development of organic, polymer-based photovoltaic materials exhibits the low cost and easy energy generation potential from the sunlight. These materials are promising for the future applications due to their improved electronic and optical properties, low product cost, functionality, thin film flexibility, ease of handling and processing, ease of storage in the form of thin films. Conjugated polymers usually have a band gap of around 1.5-3 eV, and it causes the polymer to make weak absorption in the longer wavelength region of the solar spectrum. This results with the undesirable situations like low electrical charge generation and low stability (2). Conceptually, in order to have a better control on the band gap and energy levels, new strategies need to be developed. One of the most effective strategies is to tune the band gap by utilizing electron donor-acceptor approach. In this approach, various electron donor and electron acceptor units are used in monomer structures and then they are polymerized to tune the band gap of the polymer. These polymers are generally known as donor-acceptor-donor (*D-A-D*) type conjugated polymers. Using of different *D* and *A* units in the form of *D-A-D* is one of the most successful approaches in the design and synthesis of low band gap conjugated polymers (3,4).

Because of the importance of these polymers in practical applications, theoretical studies have also gained great attention in literature. Some of these studies focused to reproduce experimental findings and hence to validate the theoretical methods used. And some others focused on the revelation of the electronic and optical properties of these polymers by using different *D* and *A* units in the monomer design. For example, Alguno *et al.* calculated the band gap of thiophene monomer and dimer using B3LYP and B3P86 methods and 6-31G(d, p) basis set but their findings were in error by more than 1 eV comparing with experimental results (5). Liu *et al.* calculated the band gap of furo-, thieno-, selenopheno-thiophene and benzo-dithiophene (PBDTFPD, PBDTTPD, PBDTSePD) containing *D-A-D* type conjugated polymers at the PBE0/6-31G(d), O3LYP/6-31G(d), TD-O3LYP/6-31G(d)//O3LYP/6-31G(d) and PBC-O3LYP/6-31G(d) levels of theory and they obtained comparable results to experimental data (6). Fu *et al.* worked on the electronic structures of dithienothiophene based *D-A* conjugated polymers (TTP-DTT, DTP-DTT, TBT-DTT) and investigated the effect of *D/A* ratio used within the monomer on the electronic properties of the polymer using B3LYP/6-31G(d) and PBC/B3LYP/6-31G level calculations (7). They obtained the most effective results when *D/A* = 2/1 ratio was used. Kose used thiophene (S) as the donor unit and investigated the band gap of a group of *D-A-D* type monomers (S-X-S) systematically as a function of different acceptor (X) units using B3LYP/6-31G(d) method (8). That work was limited

to monomers, and properties of the corresponding polymer systems were not investigated. In the other study, polymers of OOO, SOS and SeOSe systems were studied experimentally and also by using periodic boundary conditions method PBC-B3LYP/6-31G(d) (9). Previously reported abnormally low band gap value, 0.83 eV, for the SSeS polymer and excessively high value, 1.80 eV, for the SSS polymer indicate the possible errors in experimental and theoretical methods used (10). Therefore, studies on these systems need to be examined. In our previous studies, we extensively studied OSO and OSeO systems by performing detailed conformational analyses on the structures from monomers to tetramers and then calculated the band gap of polymers using different levels of density functional theory (11,12).

In this study, five different *D-A-D* type conjugated polymeric systems are investigated. For all systems, furan ($X = O$), thiophene ($X = S$) and selenophene ($X = Se$) groups are used to be electron donor units, and benzooxadiazole ($Y=O$), benzothiadiazole ($Y = S$) and benzoselenadiazole ($Y = Se$) groups are used as electron acceptor units.

MATERIALS AND METHODS

First, detailed conformational analyses on the monomers of all OOO ($X, Y = O$), SOS ($X = S, Y = O$), SSS ($X, Y = S$), SSeS ($X = S, Y = Se$) and SeSSe ($X = Se, Y = S$) systems are performed using density functional theory at the B3LYP/6-31G(d) and B3LYP/LANL2DZ levels of theory. Starting geometries of the different monomer conformers are prepared under the guidance of our previous studies based on OSO (11) and OSeO (12) systems. The lowest energy monomer structure for each system is obtained as a result of conformational analysis. HOMO-LUMO energy levels and electronic band gap values of the monomers are calculated by the Pipek-Mezey population localization analysis. Subsequently, the band gap values (E_g) of the polymers are calculated with the help of the most stable monomer structure of each system using the periodic boundary conditions (PBC) calculations at the PBC-B3LYP/6-31G(d) and PBC-B3LYP/LANL2DZ levels of theory.

While the obtained band gap values of the OOO, SOS, SSS, and SSeS systems are compared with experimental ones in the literature, the one for the SeSSe polymer is revealed.

Gaussian 09 Rev. D.01 (13) software package is utilized for all the quantum chemical calculations and GaussView 5.0.9 (14) for the molecular visualizations.

RESULTS AND DISCUSSION

Three different stable monomer conformations are obtained for each of the five different systems studied, as a result of the conformational analyses performed at the B3LYP/6-31G(d) and B3LYP/LANL2DZ levels. Chemical structures of these conformers are given in Figure 1, and their relative energies are shown in Table 1.

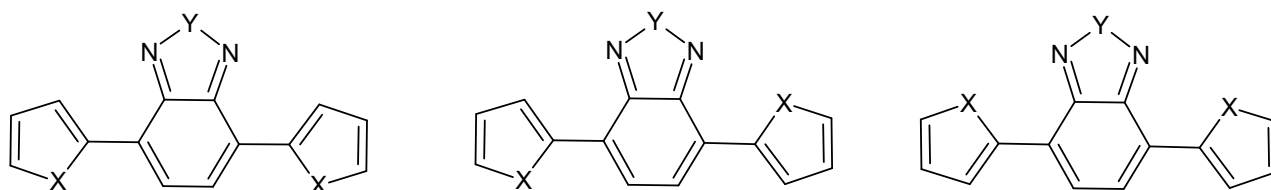


Figure 1. A representation of the chemical structures of monomer conformers obtained from the B3LYP/6-31G(d) and B3LYP/LANL2DZ calculations. ($X = O, S, \text{ or } Se$ and $Y = O, S, \text{ or } Se$)

Table 1. Relative energies of different monomer conformations for each system calculated at the B3LYP/6-31G(d) and B3LYP/LANL2DZ levels of theory (in E_{rel} , kJ mol^{-1}).

Monomer	E_{rel}	E_{rel}
	B3LYP/6-31G(d)	B3LYP/LANL2DZ
OOO-a	0.0	0.0
OOO-b	13.4	19.8
OOO-c	27.7	41.3
SOS-a	0.0	0.0
SOS-b	5.6	10.5
SOS-c	11.1	21.1
SSS-a	0.0	0.0
SSS-b	2.5	8.1
SSS-c	5.0	16.5
SSeS-a	0.0	0.0
SSeS-b	1.4	7.0
SSeS-c	2.8	14.4
SeSSe-a	7.5	1.5
SeSSe-b	3.4	0.3
SeSSe-c	0.0	0.0

As shown in Table 1, the conformation *a* is found to be the lowest energy structure for the OOO, SOS, SSS and SSeS systems, whereas the conformation *c* is the lowest energy monomer structure for the SeSSe system which is given in Figure 2. Non-bonding interaction between selenium and

nitrogen atoms stabilizes the structure *c* as it was also suggested by Pati and coworkers (15). Therefore, electronic band gap calculation of these systems with the periodic boundary conditions method is based on the SeSSe-*c*, OOO-*a*, SOS-*a*, SSS-*a* and SSeS-*a* structures, and the obtained results are given in Table 2.

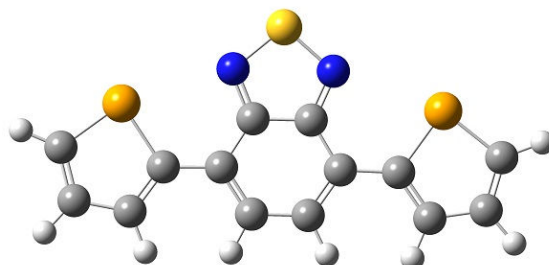


Figure 2. The lowest energy monomer conformation (SeSSe-*c*) of the SeSSe system.

Table 2. Electronic band gap values of the studied monomers and polymers.

Monomer E_g (eV)			
System	B3LYP/6-31G(d)	B3LYP/LANL2DZ	Experimental
OOO	2.81	2.61	2.46 ^a
SOS	2.83	2.59	2.47 ^a
SSS	2.74	2.44	2.43 ^a
SSeS	2.61	2.42	2.29 ^b
SeSSe	2.58	2.28	2.33 ^a
Polymer E_g (eV)			
System	PBC-B3LYP/6-31G(d)	PBC-B3LYP/LANL2DZ	Experimental
OOO	1.68	1.47	1.66 ^c
SOS	1.68	1.38	1.62 ^c
SSS	1.67	1.32	1.50 ^d
SSeS	1.59	1.31	1.46 ^d
SeSSe	1.41	1.28	-

^aRef(15); ^bRef(16); ^cRef(9); ^dRef(17)

When the theoretical results for the polymers are compared with the experimental ones, quite low deviations, from 0.02 eV to 0.13 eV, are obtained through the PBC-B3LYP/6-31G(d) level calculations as they are presented in Table 2.

In this study, we designed the SeSSe polymer, whose monomer was experimentally studied in the literature (15), and we calculated its electronic band gap for the first time by using two different calculation levels PBC-B3LYP/6-31G(d) and PBC-B3LYP/LANL2DZ to be 1.41 eV and 1.28 eV,

respectively. Polymer E_g values in Table 2 clearly indicate that the 6-31G(d) basis set produces slightly higher values and the LANL2DZ produces lower values comparing with the experiments for all the systems studied. Hence it is foreseeable that if the SeSSe polymer is synthesized and its E_g value is measured experimentally, it is highly possible that its electronic band gap value will lie in the given range provided by our calculations. In addition, the lowest E_g value is obtained for the SeSSe polymer amongst all five systems studied. Our findings suggest that increasing the period number in the group VI-A of the periodic table when choosing the X and Y atoms *e.g.*, using a heavy atom such as Se instead of O, for the XYZ system defined in this study directly leads to lower electronic band gap values for these polymers. We believe that these findings will serve as a guide in the future for both theoretical and experimental design and synthesis studies of the novel low band gap conjugated polymers.

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Türkçe Öz ve Anahtar Kelimeler
Kuantum Mekanik Araçlar Kullanarak Optoelektronik Uygulamalar için
Yarıiletken Polimerlerin Tasarımı ve Simülasyonu

Özge Özkılınç, Birnur Kaya and Hakan Kayı

Öz: Bu çalışmada, furan, tiyofen ve selenofen birimlerinin electron verici olarak ve benzooksadiazol, benzotiyadiazol ve benzoselenadiazol birimlerinin de elektron çekici olduğu polimerler teorik olarak tasarlanmış ve elektronik bant genişlikleri yoğunluk fonksiyonel teorisi yardımıyla hesaplanmıştır. Bu sistemlerdeki monomerlerin en düşük enerji yapıları B3LYP/6-31G(d) ve B3LYP/LANL2DZ yöntemlerinin yardımıyla ortaya çıkarılmıştır. Monomerlerin elektronik bant genişlikleri teori ile aynı seviyelerde elde edilmekteyken polimerler için elde edilen değerler periyodik sınır koşulları hesaplamaları (PBC-DFT) yapılarak elde edilmiştir. Öncelikle, yöntemin doğruluğu literatürde daha önce çalışılmış moleküllerin bant genişlikleri ile kıyaslama yapılarak test edilmiş, daha sonra da bu yeni yarıiletken polimerlerin yapısal ve elektronik özellikleri ortaya çıkarılmıştır.

Anahtar kelimeler: Yoğunluk fonksiyonel teori; yarıiletken polimerler; elektronik bant genişliği; selenofen.

Sunulma: 11 Ekim 2016. **Düzeltilme:** 30 Kasım 2016. **Kabul:** 07 Aralık 2016.