



# Design of novel tellurium and selenium containing semiconducting polymers using quantum mechanical tools



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## ABSTRACT

Structural, optical and electronic properties of the two novel donor-acceptor-donor type conjugated polymers based on 4,7-di(selenophen-2-yl)benzo[c][1,2,5]selenadiazole (SeSeSe) and 4,7-di(tellurophen-2-yl)benzo[c][1,2,5]telluradiazole (TeTeTe) are investigated by means of quantum chemical calculations utilizing conventional and long-range corrected hybrid functionals. The lowest energy structures of the SeSeSe and TeTeTe monomers and oligomers are revealed through conformational analysis, while their electronic properties are obtained from density functional theory (DFT) molecular orbital calculations and optical properties are obtained from the time dependent DFT (TD-DFT) calculations for UV–vis absorption spectra. Electronic band gaps that directly affect the semiconducting properties of these novel polymers are calculated by using linear regression analysis of DFT data, and also periodic boundary conditions calculations (PBC-DFT). Our results indicate that SeSeSe and TeTeTe polymers have considerably lower band gap values than that of their furan-, thiophene-, benzooxadiazole- and benzothiadiazole-based analogs. The novel SeSeSe and TeTeTe polymers with improved optical and electronic properties may have an important role in the near future, especially for the optoelectronic and photovoltaic applications.

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## 1. Introduction

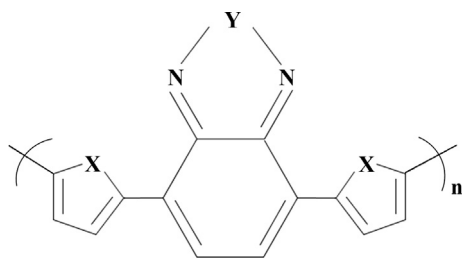
Semiconducting polymeric materials with advanced optoelectronic properties have been used in many fields, such as clean and renewable energy, electrochromic devices, photodetectors, military camouflage, light emitting diodes, displays, field effect transistors, photovoltaics and solar cells [1–14]. Therefore, scientific research and technological application studies performed on conjugated polymers with semiconductor properties have gained serious momentum in the last 10 years. Semiconductor materials derived from conjugated polymers have become attractive with their features, such as their electronic and optical properties, lower production and processing costs, functionality, their thin film flexibility, their ability to be dissolved in solvents, ease of processing, ability to be stored as in thin layers. Band gap values, which commonly lie in between 1.5 eV and 3.0 eV [15], and shifts in the UV–vis absorption wavelengths of conjugated polymers are directly related to the electronic and optical properties of the material and hence their performance in applications. In order to have a

better control over the band gap and the HOMO-LUMO energy levels, some strategies were developed. The most effective one of these strategies is the use of hybrid conjugated monomers containing electron donor (D)-acceptor (A) units as in the last generation conjugated polymers [16–19]. In this way, by using different types of donor and acceptor units and by the modification of some of the atoms used in both of these units, the band gap is taken under control and the lowering the energy gap value can be provided. The combination and use of different donor and acceptor units in D-A-D sequence is one of the most successful approaches in the design and synthesis of the low band gap conjugated polymers [20–23]. Recent studies have shown that the use furan and its derivatives as donor units in the design and synthesis of D-A-D type polymers yields promising results for high-tech applications. For example, furan units increases the open circuit potential and this leads to an increase in the efficiency of solar cells [24,25]. Thiophene with ethylenedioxythiophene (EDOT) and ethylenedioxyselelenophene (EDOS) derivatives are also successfully used as donor units [26]. On the other hand, the use of benzothiadiazole as acceptor unit in the design and synthesis of D-A-D type polymers attracts the attention of researchers due to its strong electron withdrawing properties [24,27–29]. The fuse of thiadiazole into

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quinoxaline unit also revealed a positive contribution to electron acceptor features [30]. In an experimental synthesis study, it was observed that the use of thiophene as a donor, and benzobisthiadiazole as an acceptor unit contributes to the lowering of the band gap in a D-A-D type polymer [31]. Apart from these experimental studies, there are also a number of theoretical design and modeling studies available for the semiconducting conjugated polymers. For example, Alguno et al. calculated the band gap of thiophene monomers and dimers using B3LYP and B3P86 methods and 6-31G (d,p) basis set, but their results were deviating from the experiments by more than 1 eV [32]. O3LYP/6-31G(d), PBE0/6-31G(d), TD-O3LYP/6-31G(d)//O3LYP/6-31G(d), and periodic boundary conditions (PBC) calculations were utilized in the calculation of HOMO-LUMO levels of furo-, thieno-, and selenopheno[3,4-c] thiophene-4, 6-dione and benzodithiophene based donor-acceptor type conjugated polymers, and a good agreement was obtained with experiments [33]. The effect of donor to acceptor ratio on the electronic properties of thieno thiophene based conjugated polymers were investigated at the B3LYP/6-31G(d) and PBC-B3LYP/6-31G levels. Optimum results were obtained for a ratio of D/A = 2/1 [34]. In another study, effect of six different alkyl groups on the HOMO-LUMO levels of thiadiazolothienopyrazine based conjugated polymer was investigated at the B3LYP/6-31G(d) level for possible solar cell applications and low band gap values were achieved [2]. Recently, in a combined experimental and theoretical study, the effect of selenium substitution on HOMO and LUMO levels of 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole monomer (SSS, SSeS, SeSeSe, SeSeSe) was investigated systematically and the band gap values of related monomers from B3PW91/6-311G(2df,p) calculations were reported [35]. Nevertheless, that study was restricted with monomer experiment and calculations only and was not extended to oligomers or polymer. In our recent studies, we investigated the electronic structures and band gaps of the 4,7-di(furan-2-yl)benzo[c][1,2,5]selenadiazole-based (OSeO) [36] and 4,7-di(furan-2-yl)benzo[c][1,2,5]thiadiazole-based (OSO) [37] D-A-D type conjugated polymers by using B3LYP functional and various basis sets, such as 6-31G(d), LANL2DZ, Def2TZV, with and without the inclusion of solvent effects through the polarizable continuum model (PCM). For the OSeO and OSO monomer and oligomers, we revealed their electronic structures for the first time through detailed conformational analyses and by calculating their band gaps we achieved a good agreement with the previously reported experimental findings. As a continuation to our studies on the design and modeling of semiconducting polymers, we report the details of our structural and energetic findings in the following sections for the novel 4,7-di(selenophen-2-yl)benzo[c][1,2,5]selenadiazole-based (SeSeSe) and 4,7-di(tellurophen-2-yl)benzo[c][1,2,5]telluradiazole-based (TeTeTe) polymers. Chemical structures of SeSeSe and TeTeTe systems are given in Scheme 1, and this scheme is also used to define their oxygen, sulfur and selenium containing analogs (X, Y = O, S, Se, Te) throughout the text.



**Scheme 1.** Chemical structure of 4,7-di(selenophen-2-yl)benzo[c][1,2,5]selenadiazole (SeSeSe, where X,Y = Se) and 4,7-di(tellurophen-2-yl)benzo[c][1,2,5]telluradiazole (TeTeTe, where X,Y = Te) polymers.

## 2. Computational methods

The lowest energy SeSeSe and TeTeTe monomers and oligomers are investigated at the B3LYP/LANL2DZ level of theory [38–44] performing conformational analysis on the initial structures generated randomly and also under the guidance of our recent studies for other conjugated polymeric systems. Stable conformers of SeSeSe and TeTeTe monomers and oligomers with all the real vibrational frequencies were confirmed through Hessian calculations. HOMO and LUMO energy levels and then the HOMO-LUMO energy gap,  $E_g$  values were calculated only for the minimum energy conformer of monomers and their corresponding oligomers. Maximum oligomer chain length was decided according to the  $E_g$  change between consecutive oligomers. Details of this approach was explained in OSeO [36] and OSO [37] studies in detail, and not discussed further here. The  $E_g$  values of the SeSeSe and TeTeTe polymers were calculated by using a linear regression analysis and extrapolation procedure utilizing the band gaps of minimum energy monomer and oligomers. In addition to linear regression analysis and extrapolation procedure, we also employed periodic boundary conditions (PBC) calculations, which is very common in polymer modeling and simulation studies, at the B3LYP/LANL2DZ level of theory. UV-vis absorption spectra of both SeSeSe and TeTeTe systems to define optical properties are obtained from time dependent DFT (TD-DFT) calculations at the same level of theory. In addition to the B3LYP conventional hybrid functional calculations, we also used long-range corrected hybrid functional LC-BLYP [45–47] with LANL2DZ basis set to optimize the structures and then to calculate the electronic band gaps and excitation energies of the monomers, oligomers and polymers of the two systems. The range-separation parameter,  $\gamma$ , is taken to be  $0.031 \text{ bohr}^{-1}$  during the calculations, which is tuned by using the SeSeSe monomer data following the methodology given in detail by Kronik et al. [48]. All quantum chemical calculations were performed by the Gaussian 09 Rev. D.01 [49] software package, and molecular visualizations were obtained from the GaussView 5.0.9. [50].

## 3. Results and discussion

### 3.1. Conformational analysis and relative energies

In this study, we used tellurophene and selenophene groups as electron donor units and benzotelluradiazole and benzoselenadiazole groups as electron acceptor units to prepare D-A-D type TeTeTe and SeSeSe systems, respectively. In the first step, we performed conformational analysis on the TeTeTe and SeSeSe monomers at the B3LYP/LANL2DZ level of theory and we found three different lowest energy structures for each monomer. Because the conformer structures of the TeTeTe and SeSeSe monomers and oligomers are found pretty similar in the same energy order, we only present the figures for the TeTeTe monomer and oligomer structures throughout this text to save space. The SeSeSe monomer and oligomer structures are given in the [Electronic Supplementary Information](#). Minimum energy conformers for the TeTeTe monomer are shown in Fig. 1, and for the SeSeSe monomer given in Fig. S1. The SeSeSe monomer conformation **1a** is more stable than **1b** and **1c** by 2.0 and 4.7  $\text{kJ mol}^{-1}$ , respectively, whereas energy differences are more pronounced for TeTeTe monomer conformers as it is shown in Table 1. Conformer **1a** of the TeTeTe monomer is found 19.8 and 41.3  $\text{kJ mol}^{-1}$  more stable than its **1b** and **1c** counterparts, respectively. Nonbonding interactions between nitrogen atoms of benzoselenadiazole or benzotelluradiazole groups and selenium atoms in selenophene or tellurophene atoms in tellurophene groups stabilize the structure. Therefore conformer structure **1a** for both SeSeSe and TeTeTe monomers becomes the lowest energy

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