



# Electrochemical oligomerization of selenophene and band structure of polyselenophene: A density functional theory study

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## ABSTRACT

Electrochemical oligomerization mechanism of polyselenophene (PSe) has been studied using hybrid functional B3LYP with the basis set of 6-31G (d). Two different mechanisms – radical-radical (RR) and radical-neutral (RN) couplings - have been assumed to propagate oligomers. The energies concerned with the changes between these stages have been calculated using the optimized geometries and discussed. RR couplings have been concluded to be more favorable than RN couplings due to the high ionization energies of cationic intermediates. Natural Bond Orbital Analysis for each of the optimized structures has been performed to get insight into the nature of the bonds formed in the products along the mechanism path. It was seen that the transition state and intermediate structures could easily be traced by vibrational bands in the related parts. In the second part of the study, the band structure of PSe has been studied employing the same hybrid density functional with periodic boundary conditions.

## 1. Introduction

Polyselenophene film was first synthesized electrochemically by Yoshino et al. [1], and they found the band gap value as 1.95 eV. Its electrical and optical properties were further investigated [2]. It was also synthesized chemically, and similar properties were obtained with electrochemically synthesized PSe [3]. Nakanishi et al. [4,5] firstly prepared oligoselenophene (OSe) up to hexamer and determined their properties employing cyclic voltammetry and electronic absorption spectroscopy. In one of these studies [6], OSe has been used as an active layer for organic field-effect transistor. Electrical conductivity of methyl substituted PSe was also studied by Bourahla et al. [7]. They concluded that its conductivity seemed to be very limited compared to the polymers with similar structure. Polybiselenophene has been synthesized chemically and electrochemically and its band gap value has been determined to be 1.9 eV [8]. Its maximum conductivity has been obtained as 0.1 S/cm upon chemical doping. In another study [9], copolymer of fluorene and selenophene has been synthesized and found to be light emitting. PSe has also been used as one of the p-type dopable polymers to show linear correlation between ionization potential of its monomer and oxidation potential of the pi-conjugated polymer [10]. Another research group synthesized freestanding, flexible and homogenous PSe films electrochemically on stainless steel electrode by direct anodic

oxidation of selenophene with conductivity of  $2.8 \times 10^{-1}$  S/cm [11,12].

In addition to experimental investigations given above, many theoretical studies have been done to search several properties of PSe. In one of earlier studies [13], polarons and bipolarons became the subject of a study on the excitation spectrum of doped PSe. Some other studies were also performed for the band structure of PSe [14–19]. In the study by Salzner et al. [14], the band gaps and the band widths have been calculated using slightly modified B3P86 hybrid functional of DFT for several cyclic polymers including PSe. They calculated the band gap as 2.06 eV which was very close to the experimental value. Zade et al. [18] calculated the band gap as 1.85 eV at the theory level of B3LYP/6-31G(d) within periodic boundary conditions (PBC). This value is much closer to the experimental value obtained for polybiselenophene [8]. Zade et al. [19] have studied neutral, cationic and dicationic forms of OSe making comparison with oligothiophenes (OTH). They have found that oligo- and PSe have more quinoid character and lower band gap. They have obtained an important result which makes PSe more difficult to twist than PTh. In conclusion, more (or larger) substituents can be introduced onto their backbones than onto those of their thiophene analogues without distorting conjugated backbone too much. In a similar study by Chandak and Zade [20], fused OTH with their cationic, dicationic forms and fused PTh were calculated by DFT using B3LYP/6-

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31G(d) level, and these species were compared with their selenophene analogues. According to PBC results, the calculated band gap values were found to be 2.25 eV and 2.08 eV for PTh and PSe, respectively. The energy gap values between HOMO and LUMO (Eg) of these species obtained by extrapolation of HOMO–LUMO gaps of oligomers were found to be 2.13 eV for fused PTh and 1.96 eV for fused PSe in another study [21]. They have found oligo- and PSe more quinoidal and having lower band gap (HOMO–LUMO gap) than their thiophene analogues as obtained in the previous studies [14,18,19]. The vibrational spectra of OSe have also been calculated using semiempirical approach [22]. In the same study, the phonon frequencies at  $k = 0$  have been calculated and the assignments of the frequencies were made. In another study, Gupta et al. [23] have calculated normal modes and their dispersions for PSe. PSe is predominant in some applications due to the special nature of Se atom and selenophene, with respect to PTh. They have lower oxidation and reduction potentials, band gap and greater polarizability than PTh [24]. The intermolecular Se–Se interactions cause improved interchain charge transfers. Since the size of Se atom is larger than that of S, PSe should be able to accommodate more charge upon doping than PTh. The electrical conductivity of PSe ( $10^{-4}$ – $10^{-3}$  S·cm $^{-1}$ ) [25] is lower than that of PTh, both of which can be enhanced by doping [26].

Many-body correction to the band gap calculation can be done within GW proposed by Hedin [27]. In the study of Zhao et al. the GW correction was used to calculate band gaps for two thin <110> wires and they observed the result very close to the experimental data [28]. Lu and Zhang showed the validity of DFT methods with or without GW corrections for the qualitative determination of electronic band structures of low-dimensional hydrogen-terminated silicon chain systems where the GW correction to the energy difference of the conduction band minima was within 0.16 eV and does not change the order of energy levels [29]. The self-energy problem with standard DFT methods has been solved in a great extent by including HF exchange term. So, B3LYP gives the most accurate electron affinities, ionization potentials, cohesive energies, and band gap for some molecules and polymers [30,31]. In the band gap of polymers, B3LYP calculations give accurate results as well [24,32,33].

Theoretical studies of polymerization mechanism of several compounds have been done at different theoretical levels [34–43]. Dimerization of oligopyrroles has been studied by Lacroix et al. [34,35]. As stated in the study [34], electropolymerization starts with oxidation of monomer which generates very reactive radicals. The radicals formed couple with another one to generate longer chain. They concluded that the major interaction between these radicals involves  $\pi$  orbitals. As a result of this interaction,  $2P_z$  orbitals overlap to form the intermediate from the combination of two radicals oriented in two different but parallel planes.

Classical conducting polymer PTh has been studied employing Density Functional Theory by Yurtsever and Yurtsever [36]. They reported the results on the energetics of each step during the growth of OTh by comparing stability of products and locating the transition states leading to these products.

Selenophene has the same backbone with that of PPy and PTh with different heteroatom Se instead of N and S. The aim of this study is to investigate and to compare the effect of Se heteroatom on the energetics and the structures of the products formed during the oligomerization of selenophene as the five-membered monomer. Several parameters (band gap, band width and effective mass) related to the band structures of the polymers will be compared and confirmed the validity of experimental result found for PSe regarding better band gap and the intrinsic conductivity.

## 2. Calculation methods

The geometry optimizations of species formed along the reaction paths have been carried out using hybrid density functional B3LYP [44,45] with the basis set 6-31G(d) because of its popularity and

reasonable accuracy with low computational cost [46]. Gaussian 09 program suite [47] has been employed to perform these DFT calculations. Unrestricted optimization has been done for the case of charged species. The transition states for radical–radical and radical–neutral pathways were obtained by direct transition state optimization using the geometry estimated based on the intermediates. Natural Bond Analysis [48] of each species has been carried out for bonds formed during oligomerization mechanism. Periodic Boundary Conditions (PBC) routine [49] implemented in Gaussian 09 program suite [47] has been used to make the band structure calculations. PBC use translational symmetry to study geometry and band structures of periodic structures such as polymers. In this way, it is possible to make modeling of infinitely long polymer chain of PSe. It is preferred to use the default option of Gaussian program package which determines the number of the  $k$  points depending on the cell size. Geometry of repeating unit of infinite polymer chain in gas phase has been optimized using redundant internal coordinates which is set default in the program.

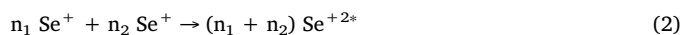
## 3. Oligomerization of selenophene

Two different ways have been considered for the oligomerization as in the other study [36]: namely, the radical–radical coupling and the radical–neutral coupling. The first step in both mechanisms is the oxidation of the monomer. This oxidation takes place during the chain propagation as well. It may be written in the generalized form as:



where  $n$  is the number of repeating unit and Se is the acronym used for repeating unit selenophene.

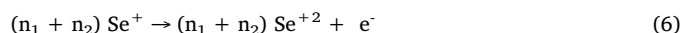
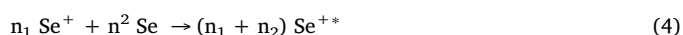
As the second step the radical of the monomer couples with another radical or neutral monomer. This coupling results in intermediate structure with extra two protons. Using the notation above, radical–radical coupling yielding dicationic transition state may be shown as:



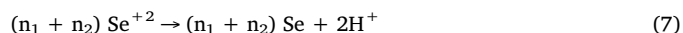
$n\text{Se}^{+2*}$  is the transition state leading to the intermediate:



where  $n_1$  and  $n_2$  are the numbers of repeating units for the two radicals. It is obvious that this coupling lead to the formation of an intermediate with  $(n_1 + n_2)$  repeating units. In case of radical–neutral coupling, after similar steps given for radical–radical mechanism, further oxidation of the intermediate with  $(n_1 + n_2)$  size is needed:



The final step of the both mechanisms is the same: release of two extra protons to yield neutral and longer oligomer.



### 3.1. Energy associated with each step of electrochemical oligomerization

Key process to initiate electrochemical oligomerization is oxidation of monomer and continuation of oligomerization process depends on oxidation of oligomers together with monomers. It may be expected that heteroatom of a heterocycle is a unique variable responsible for variation of ionization energy of a heterocyclic molecule having the same skeleton. Therefore, we can expect that the ionization energy of selenophene is lower than that of thiophene, since selenium atom has lower ionization energy than S atom due to the fact that it is a higher period member of the same group in the periodic table. However, when we look at the molecular orbital (MO) coefficients of the optimized

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