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Electronic structures of one-dimensional poly-fused selenophene radical cations: density functional theory study

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Abstract

Hybrid density functional theory (DFT) calculations have been carried out for neutral and radical cation species of a fused selenophene oligomer, denoted by Se(n), where n represents the number of selenophene rings in the oligomer, to elucidate the electronic structures at ground and low-lying excited states. A polymer of fused selenophene was also investigated using one-dimensional periodic boundary conditions (PBC) for comparison. It was found that the reorganization energy of a radical cation of Se(n) from a vertical hole trapping point to its relaxed structure is significantly small. Also, the reorganization energy decreased gradually with increasing n, indicating that Se(n) has an effective intramolecular hole transport property. It was found that the radical cation species of Se(n) has a low-energy band in the near-IR region, which is strongly correlated to hole conductivity. The relationship between the electronic states and intramolecular hole conductivity was discussed on the basis of theoretical calculations.

Keywords: fused selenophene, conjugated oligomer, molecular design, DFT, PBC

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Highly conjugated polymers, such as poly-diacetylene and poly(p-phenylene), have been widely used as semiconductor, electroluminescent (EL), and photoductive materials [1, 2]. This originates from the π-electron system delocalized widely along a one-dimensional polymer chain. Polyselelenophene and its related compounds have attracted considerable attention over the past decade in view of their potential applications in electronic and optoelectronic devices [3, 4].

Polyselenophenes are one-dimensional π-conjugated polymers that are utilized as conducting materials and field effect transistors [3, 4]. Also, oligo-five-membered ring compounds have a possibility for application to high-performance molecular devices such as photocurrent multipliers and organic semiconductors [5]. However, the problem of chemical stability still remains. In fact, only octamers are known to have large oligothiophenes with no side chains.

To develop a stable compound composed of heterocyclic five membered rings, several modified oligomers have been synthesized and their electronic properties have been systematically investigated. One approach is to prepare a...
### Table 1. Selected optimized structural parameters of fused selenophene oligomers [Se(n)].

<table>
<thead>
<tr>
<th>n</th>
<th>$R_1$(C$_1$–C$_2$)</th>
<th>$R_2$(C$_2$–C$_3$)</th>
<th>$R_1$–$R_2$</th>
<th>$R_1$(C$_1$–C$_2$)</th>
<th>$R_2$(C$_2$–C$_3$)</th>
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<td>1.4037</td>
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Figure 1. Schematic illustration of (upper) structure of fused selenophene oligomer, Se(n) (n = 6), and geometrical parameters, and (lower) the unit cell used in the calculation.

fused oligomer whose rings are all connected to each other as a condensed oligomer. Both $\alpha$ and $\beta$ positions of the five-membered rings are fused with the next ones [6–12]. Electrons are delocalized along the double bond of the oligomer. The fused oligoselenophenes have a well-defined molecular size and high chemical stability.

The electrical properties in a thin film of heteroacene oligomer (pentathienoacene) have also been investigated under various surface conditions and electric fields [9]. This stable organic semiconductor similar to pentacene is highly promising for applications in organic electronics. It is found that the mobility is strongly dependent on not only the electric field but also the molecular orientation. In particular, it is important to control the substrate temperature. Also, it was suggested that the electrical conductivity mechanism is hopping migration between the neighboring molecules.

Recently, the conjugational properties of these heteroacenes have been investigated by several optical methods. For example, benzene-capped fused selenophene $\pi$-conjugation increases with increasing number of selenophene rings [10]. Although these experimentally obtained features are one of the interesting points in heteroacene oligomers, the electronic structures of the neutral and ionic states of the heteroacenes are not clearly understood because of the lack of theoretical work.
In the present study, density functional theory (DFT) calculations have been carried out for neutral and radical cation species of the fused selenophene oligomer Se(n) (n = 1–42, where n denotes the number of rings in the oligomer) in order to determine the electronic structures. In particular, we focus our attention on the electronic structure for both ground and low-lying excited states because the excited state, particularly the first excited state, correlates strongly with the electron and hole conductivities in molecular devices.

In previous works [13–17], we investigated theoretically organic semiconductors and molecular devices by DFT, ab initio molecular orbital (MO), and direct ab initio dynamics methods. We elucidated the mechanism of hole conductivities in various molecular devices, such as poly(vinyl-biphenyl) [13], polyisilane [14, 15], and oligothiophene molecular devices [16, 17]. In particular, the origin of the hole conductivity was elucidated on the basis of theoretical results. In the present study, we extended previous techniques [13–17] to the molecular device Se(n).

2. Computational method

Almost all of the present calculations were carried out at the B3LYP/3-21G(d) level of theory. Fused selenophene oligomers [Se(n)] (n = 6–42) and poly-fused selenophene [p-Se(n)] were examined. First, the initial geometries of neutral fused selenophene oligomers [Se(n)] were determined by MM2 calculation. Using the optimized geometry obtained by the MM2 calculation, the geometries of neutral molecules and cation radical species of Se(n) were further optimized at the B3LYP/3-21G(d) and B3LYP/6-31G(d) levels of theory. The excitation energies were obtained by time-dependent (TD)DFT calculation [TD-B3LYP/6-31G(d)/B3LYP/3-21G(d) level]. Six excited states were solved in the (TD)DFT calculations. All hybrid DFT calculations were carried out using the Gaussian03 program package [18]. To check the level of theory used in the calculations of the excitation energies, SAC-CI calculations were carried out for n = 1–4. Note that these levels of theory give reasonable features for several molecular device systems [13–17, 19–22].

3. Results and Discussion

3.1. Optimized structures of fused selenophene oligomers

The selected optimized parameters of neutral and radical cation species of Se(n) are given in table 1. The geometrical parameters for the C–C bond lengths in the central selenophene ring of the oligomer (figure 1 (upper)) are given. In the neutral state, the distance R1 (= C1–C2) is slightly longer than R2. This difference becomes smaller at longer chain lengths, indicating that the quinoid character is dominant at longer chain lengths, whereas the benzenoid character is dominant in the case of shorter chain lengths.

Meanwhile, the structure of the cation radical species is much different from that of the neutral state. R1 is shorter than R2. The difference decreases gradually with increasing n. This result implies that the bond alternation between C=C and C=C occurs in the radical cation of Se(n).

For comparison, the geometries of Se(n) and Se(n)+ (n = 6–36) are also obtained at the B3LYP/6-31G(d) level, and the results are given in table 2. Similar values are obtained, as shown in table 1.

3.2. Ionization energies of fused selenophene oligomers

The structures of fused selenophene oligomers are fully optimized at the B3LYP/3-21G(d) level. Using the optimized structures, vertical ionization energies, denoted by EIP(ver), are calculated, and the results are plotted as a function of n in figure 2(a). EIP(ver)’s for n = 6, 12, 18, 24, and 42 are calculated to be 6.44, 5.81, 5.55, 5.40, and 5.18 eV, respectively, indicating that EIP(ver) decreases gradually with increasing n. Next, the structures are further optimized at the cation state, and adiabatic ionization energies, denoted by EIP(ad), are calculated. The results are plotted in figure 2(a).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Tv-1</th>
<th>Tv-2</th>
<th>Tv-3</th>
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<tr>
<td>C1–C2</td>
<td>1.4142</td>
<td>1.4142</td>
<td>1.4142</td>
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<tr>
<td>C3–C4</td>
<td>1.3992</td>
<td>1.3992</td>
<td>1.3992</td>
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<tr>
<td>C5–Se</td>
<td>1.8994</td>
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<td>1.8994</td>
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<tr>
<td>tv</td>
<td>4.0131</td>
<td>8.0262</td>
<td>12.0393</td>
</tr>
</tbody>
</table>

The unit cell consists of two selenophene rings. Bond lengths are in Å.
EIP(ad)'s for \(n = 6, 12, 18, 24, \) and 42 are calculated to be 6.29, 5.69, 5.46, 5.33, and 5.13 eV, respectively. The differences between EIP(ver) and EIP(ad) for \(n = 6, 12, 18, 24, \) and 42 are 156, 122, 97, 76, and 43 meV, respectively (figure 2 (b)). These results imply that the structural change of the cation state becomes smaller in longer structures.

The plots of EIP(ver) and EIP(ad) versus \(n\), and (b) oscillator strengths of excitation energies \(\phi(n)\) are given in table 3. The excitation energies of \(\text{Se}(n)\) are significantly lower than those of neutral-state \(\text{Se}(n)\). In general, the excitation energies of the radical cation species of the oligomer are redshifted from those of the corresponding neutral oligomer [22] because the singly occupied molecular orbital (SOMO) is correlated with the excitation band. The lowest energy band is attributed to \(\text{HOMO} \rightarrow \text{SOMO}\), and possesses a lower excitation energy than the excitation energy of the neutral oligomer. The present calculation is in good agreement with the data for commonly known systems.

Simulated absorption spectra of neutral and cation radical species of \(\text{Se}(n)\) are illustrated in figure 4. In the plots of simulations, the half-width of the spectrum is assumed to be 0.01 eV. For the neutral state, the peak of the absorption spectrum is gradually redshifted as a function of selenophene ring number, while the intensity is linearly increased. The peaks appear in the ultraviolet and near-infrared regions (1.77–3.06 eV). The coefficients of the main configuration \(\phi_1(\text{HOMO} \rightarrow \text{LUMO})\) and the second largest one \(\phi_2(\text{HOMO} \rightarrow \text{LUMO})\) are calculated to be 0.63 and 0.22 \((n = 42)\), respectively, at the first excited state, and those of the other configurations are negligible small, indicating that the excitation band corresponds to the HOMO-LUMO transition of neutral fused thiophene oligomers.

The simulated absorption spectra of cation radical species show an excitation band in the lower energy region. The excitation band becomes significantly lower for longer chain lengths and the intensity becomes stronger. For \(n = 42\) the first excitation energy is only 0.15 eV, which is low enough to allow the thermal hopping of holes along the selenophene backbone. Also, \(\text{Se}(42)^+\) has a finite transition probability, as shown in figure 4. Thus, it can be summarized that the band structure of the fused selenophene oligomer is significantly changed by positive hole doping. New energy bands appear in the very low energy region below 1.6 eV. In particular, it is predicted theoretically that a new energy band with a strong
the translation symmetry because of the program limitations. Furthermore, we calculated the double (Tv-2) and triple (Tv-3) cells which consist of four and six selenophene rings of p-Se(n), respectively. The optimized geometrical parameters of p-Se(n) are given in table 2. The same values are given in Tv-1 to Tv-3, indicating that long-range restructuring is not occurring in this system. The optimized bond lengths C1−C2, C2−C3, and C1−Se are calculated to be 1.4142, 1.3992, and 1.8993 Å, respectively. The bond length of C1−C2 is longer than C2−C3, thus p-Se(n) has a benzenoid structure. These results are consistent with the long oligomer. The electronic band structure and density of states (DOS) of Tv-1 are plotted in figure 5. It is found that both the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) are placed at the center of the Brillouin zone (k = 0) in the band structure. Consequently, p-Se(n) has a direct band gap whose value is calculated to be 2.09 eV. Also, the band gap of Se(n) (for example, n = 42: 2.17 eV) is in good agreement with that of p-Se(n) calculated under periodic conditions. In the cases of n = 36 and 42, the excitation energies are 1.89 and 1.86 eV, respectively. These results suggest that the electronic states of the oligomer Se(n) with longer chain lengths reasonably exhibit those of p-Se(n).

From the atomic population contribution analysis in the DOS of p-Se(n), the intensity around the HOCO is dominantly organized from the carbon p state (narrow dotted lines). Therefore, the hole transport path is on the carbon p orbitals. On contrary, the lowest conduction state consists of both carbon and selenium p (narrow dash-dotted lines) orbitals.

3.5. Electronic states of fused selenophene oligomer dications

In general, the contribution of the dicaticonic state to electron and hole transport will be important in long chains. In this section, electronic states of fused selenophene oligomer dications are discussed in brief. The structures of the dication of fused selenophene oligomers for n = 6–42 are fully optimized at the B3LYP/3-21G(d) level. Using the optimized structures, vertical second ionization energies, denoted by EIP_{2nd}(ver), are calculated, and the results are given in table 4. The reaction is expressed by Se(n) + EIP_{2nd}(ver) → Se^{2+} + 2e−. EIP_{2nd}(ver)’s for n = 6, 12, 18, 24, and 42 are calculated to be 16.78, 14.36, 13.25, 12.59, and 11.56 eV, respectively. Adiabatic ionization energies, denoted by EIP_{2nd}(ad) for n = 6, 12, 18, 24, and 42 are 607, 470, 366, 284, and 166 meV, respectively. This result implies that the structural change of the dication state becomes smaller in longer structures, similar to cation radicals, although the reorganization energies of dications are higher than those of cations.

The first excitation energies for n = 6, 12, 18, 24, and 42 are calculated to be 0.96, 1.20, 1.09, 0.81, and 0.40 eV, respectively. These results strongly suggest that both intra- and intermolecular hole transfers are possible in dications. However, the efficiency of the intermolecular hole transport of cations is higher than that of dications.

3.4. Electronic properties of poly-fused selenophene

In this section, the one-dimensional periodic boundary condition (PBC) calculation in the geometry optimizations are carried out to obtain the geometrical and electronic structures of the poly-fused selenophene [p-Se(n)], at the B3LYP/3-21G(d) level of theory. The actual unit cell of p-Se(n) has only one selenophene ring, but in this calculation, the minimum unit cell consists of two rings (Tv-1) to satisfy transition probability is generated in the low energy region. This is the origin of hole transport in oligo- and poly-fused selenophenes.

### Table 4. Vertical (EIP_{2nd}(ver)) and adiabatic ionization energies (EIP_{2nd}(ad)) of Se(n), and the reorientation energies (EIP_{2nd}) from their differences.

<table>
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<tr>
<th>n</th>
<th>EIP_{2nd}(ver)/eV</th>
<th>EIP_{2nd}(ad)/eV</th>
<th>EIP_{2nd}/meV</th>
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Figure 4. Simulated absorption spectra of fused selenophene oligomer neutral (dashed line) and cation radical species (solid line) calculated at the TD-B3LYP/6-31G(d)//B3LYP/3-21G(d) level. Relative oscillator strengths are given in arbitrary units.
Figure 5. Band structure of fused selenophene polymer in neutral state calculated under periodic boundary conditions [B3LYP/3-21G(d) level]. Bold line and bold dashed line show total DOS of occupied and unoccupied levels, and narrow dashed and dot-dashed lines represent orbital populations of C and Se π states.

4. Conclusions

From the results of the present calculations, the main conclusions can be summarized as follows. (1) the reorganization energy from a vertical hole trapping point of Se(n) to the relaxed structure of Se(n)+ is significantly low. This causes the effective hole transport properties in Se(n). (2) Se(n)+ has a low energy band in the near-IR region. Even in the neutral state, the lowest energy band is located at around 2.0 eV above n > 24. This also contributes to the effective hole transport in Se(n). (3) The hole path in p-Se(n) is composed only of the conjugated carbon π state is found from the PBC calculation.

Acknowledgments

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