

Electronic structure of oligo-3,4-ethylenedioxythiophene

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Ab initio Molecular Orbital Calculation of oligo-3,4-ethylenedioxythiophene (up to 21 oligomer) was carried out and its electronic properties were discussed.

Key words: PEDOT/PSS, ab initio MO, conducting polymer, valence band

1. INTRODUCTION

PEDOT/PSS is one of the most attracting organic materials for electronics, especially because of its relatively high conductivity and transparency to visible light [1-3]. In order to understand the electronic structure of this conjugated polymer / polyelectrolyte hybrid material, ab initio Molecular Orbital (MO) calculations were carried out on oligomers of 3,4-ethylenedioxythiophene (EDOT, $n=1-10$ and 21).

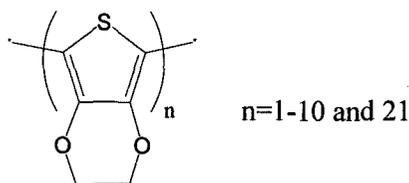


Fig. 1. EDOT oligomers

2. METHOD

Gaussian 98W and 03W programs were used for ab initio MO calculation. RHF method for closed shell states and ROHF method for open shell states, in both cases with split-valence basis set 6-31G(d,p), were employed. Structural optimization was carried out without any structural restriction.

3. RESULTS and DISCUSSION

3.1 Planarity of conjugated chains

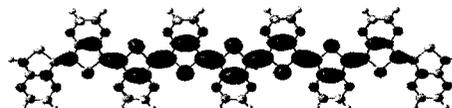
Structural optimization of oligomers ($n=1-10$ and 21) indicates that planar structures of conjugated chains are the most stable conformations independent of the electronic states of oligomers to be neutral, cationized, or dicationized. As an example, optimized structures as well as HOMO and LUMO characteristics of $n=9$ EDOT neutral oligomer are shown in Fig.2. Here, the dihedral angles between neighboring monomers were estimated to be within 1° . HOMO has bonding character between neighboring alpha and beta carbon atoms within the same monomers (in coincident with the double bonds in "benzenoid type" chemical formula like Fig. 1), and has anti-bonding characteristics between neighboring monomers. In contrast, LUMO has bonding characteristics between neighboring beta carbon atoms within the same monomers, and also has bonding

characteristics between neighboring monomers (in coincident with the double bonds in "quinoid type" chemical formula).

Because non-substituted and alkyl substituted polythiophenes have non-planar conjugated chains [1], such planarity in EDOT system would play important roles in its electronic properties. For example, planar conformation improves the effective conjugation within each oligomer to enhance intramolecular carrier transport or at least electronic interaction between neighboring monomers. Planar conformation can also improve the π - π stacking of oligomers for structural reason.

The planar conformation is caused by the ethylenedioxy groups (especially the oxygen atoms, directly bonded to the beta carbon atoms of thiophen rings) in EDOT. But the mechanism of this planarization has not yet been clarified.

LUMO



HOMO



Fig. 2. Optimized structure and HOMO LUMO characteristics of $n=9$ EDOT neutral oligomer

3.2 Orbital energy of HOMO

Fig. 3 indicates HOMO orbital energy of EDOT neutral oligomers against n and $1/n$ ($n=1-10, 21$). From $1/n$ plot, HOMO energy is converged to between -5.4 to -5.6 eV. Here, the plot shows almost straight line between $n=2$ to 10, but is shifted slightly to lower energy for longer oligomers like $n=21$. We are supposing this shift to be caused from the limitation of RHF MO calculation method with split valence basis set to describe the long range conjugation.

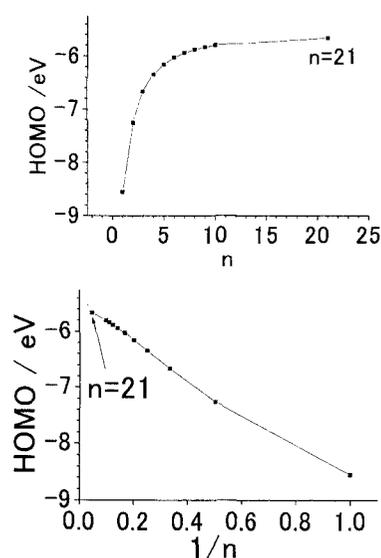


Fig. 3. Orbital Energy of HOMO of oligo neutral EDOT ($n=1-10, 21$) against n and $1/n$.

3.3 Estimation of the “valence band”

Fig. 4 shows the orbital energies of HOMO to 21st HOMO of EDOT oligomer (neutral, $n=21$). Because “higher” occupied MOs are described by the linear combination of the HOMO of each monomer unit, these MOs will correspond to the “valence band” in band theory, and the number of MOs per orbital energy correspond to the “density of state”.

As is shown in Fig. 4, “density of state” is lower between 4th HOMO (about -6.2 eV) to 9th HOMO (about -7.5 eV), and is higher at around HOMO (-5.5 eV), and is the highest at around 11th to 21st HOMO (correspond to the bottom of the “valence band”).

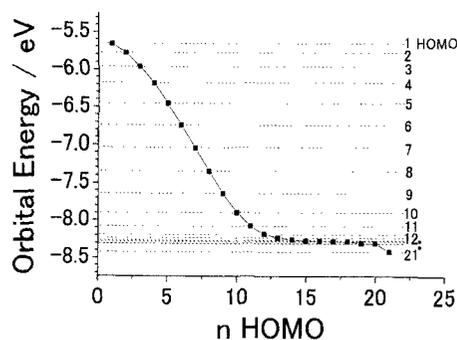


Fig. 4. Orbital Energies of HOMO to 21st HOMO of oligo($n=21$) neutral EDOT. X-axis correspond to “HOMO to n^{th} HOMO”.

The plot in Fig. 4 was well fitted to the following sigmoidal function:

$$Y = -8.34 + 2.85 / [1 + \exp\{(X-6.52)/2\}]$$

This sigmoidal function will be a clue to estimate the “band dispersion” of oligomers from MOs, especially because X-axis (correspond to n^{th} HOMO) in Fig. 4 will also be related to “ k ” for band theory (number of nodes of linear combination relates to the angular momentum).

3.4 Quinoid type structure in cationized oligomers

Fig. 5 shows the optimized structures of $n=10$ EDOT oligomers for neutral, cationized and dicationized states. When these three states are compared, bond length between neighboring monomers (especially near central monomers: left in Fig.5) were estimated to be decrease with the increasing the positive charges. For example the bond length between central monomers (bonds between the most left monomers in Fig.5 and its mirror image) decreases from 1.46 to 1.40, 1.34 Å. The decrease of bond length was also observed for the bond between two beta carbon atoms within the same monomer unit. On the other hand, the bonds described as double bonds in neutral state, were estimated to increase their bond length. These features indicate that typical quinoid type structure will be induced by the ionization of oligomer.

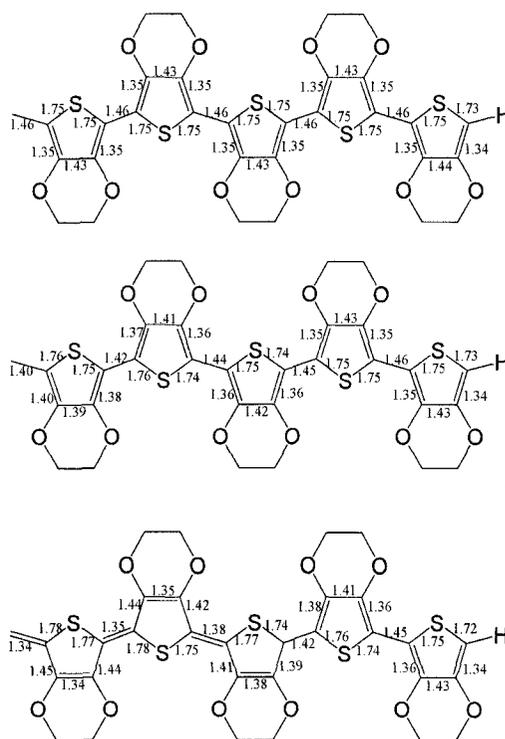


Fig. 5 Optimized structure of $n=10$ EDOT oligomer in neutral (up), cationized (middle) and dicationized (down) states. Only the right five oligomers are shown because of the symmetric reason.

3.5 Charge distribution

In order to understand the effect of ionization, precise charge distribution analysis of $n=10$ EDOT oligomer was carried out and is shown in Fig. 6. Neutral state after optimization (\blacktriangledown), monocationized state after optimization (\blacktriangle), dicationized state before optimization (\bullet) and after optimization (\blacksquare) are described. Charge distribution per each monomer unit (upper figure in Fig.6) indicates that positive charges are distributed almost in the center of oligomers. Especially in the case of dication, structural optimization can cause the separation of two positive charges.

The results of the charge distribution analysis for sulfur, alpha carbon, beta carbon and oxygen atoms in each monomer units are also shown in Fig.6 with the same symbols for each state described above. Sulfur and beta carbon atoms are positively charged, independent of the state of the oligomer chain. These positive charges in sulfur and beta carbon will induce these atoms to interact with negatively charged dopant like PSS⁻ (poly(styrene sulfonate)) electrolyte in PEDOT/PSS blends. On the other hand, Alpha carbon and oxygen atoms are estimated to be negatively charged, independent of the state of the oligomer. Especially in the case of Sulfur atoms, charge distribution has typical "end effect", which will be correspond to the peak broadening in XPS results [4].

Charges on sulfur and alpha carbon atoms were affected sensitively by the ionization of the oligomers. Therefore, these sites are thought to be "electronic property sensitive".

References

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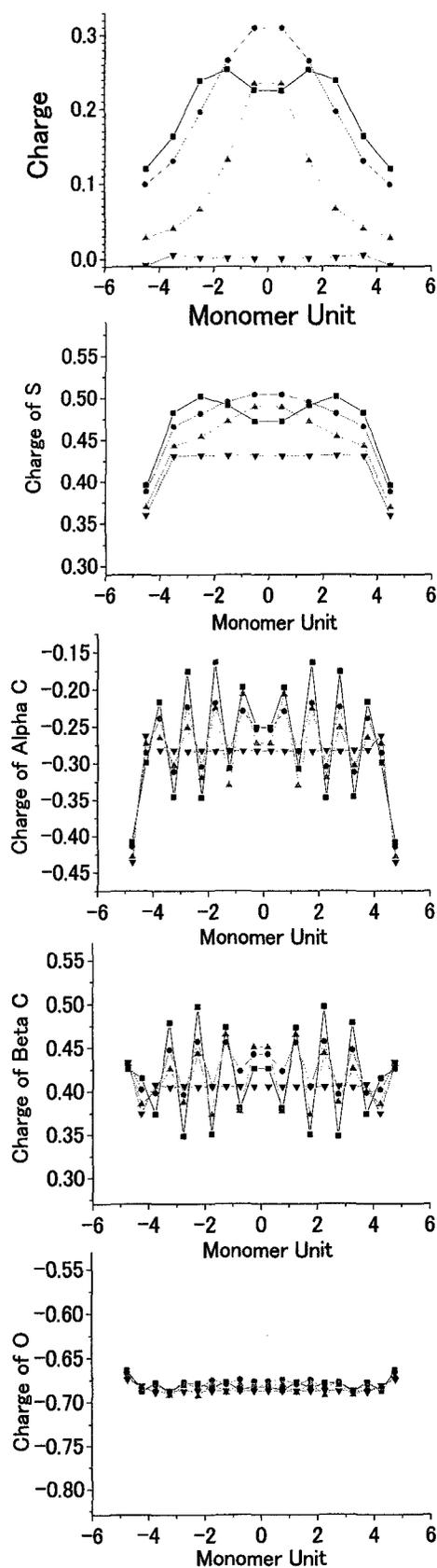


Fig. 6 Charge distribution of $n=10$ EDOT oligomer for neutral state after optimization (\blacktriangledown), monocationized state after optimization (\blacktriangle), dicationized state before optimization (\bullet) and after optimization (\blacksquare).