

## Theoretical characterization of ground and low lying excited state of poly(3,4-ethylenedioxythiophene) and poly(4-styrenesulfonate)

Agalya Govindasamy<sup>1</sup>, Chen Lv<sup>1</sup>, Xiaoging Wang<sup>1</sup>, Hideki Ookawa<sup>2</sup>, Hideyuki Tsuboi<sup>3</sup>,  
Mishihisha Koyama<sup>1</sup>, Momoji Kubo<sup>1,4</sup>, Akira Miyamoto<sup>1,3</sup>

<sup>1</sup>Dept. of Applied Chemistry, Graduate School of Engineering, Tohoku University,  
Aoba-yama 07, Aoba-ku, Sendai 980-8579, Japan

Phone: +81-22-217-7238 E-mail: agalya@aki.che.tohoku.ac.jp

<sup>2</sup>Toshiba Corporation, 33, Shin-Isogo-Cho, Isogo-Ku, Yokohama 235-0017, Japan

<sup>3</sup>New Industry Creation Hatchery Center, Tohoku University, Aoba-yama 10, Aoba-ku, Sendai 980-8579, Japan

<sup>4</sup>JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

### 1. Introduction

The poly(3,4-ethylenedioxythiophene) (PEDOT) chosen for this study is the most widely used, industrially important electrically conducting polymer and has the major advantage to be very stable in the doped state, with conducting properties that remain almost unaltered under aging in environmental conditions.

Unfortunately, PEDOT is an insoluble polymer. This drawback can be circumvented by polymerization in combination with a water-dispersible polyelectrolyte such as poly(4-styrenesulfonate) (PSS). The resulting PEDOT/PSS has been widely used in applications of electrodes of capacitors and photo-diodes [1], antistatic coatings [2], electrochromic windows, field effect transistors, and hole transport material, because of optically transparent and well spin-coated properties [3] etc.

Oxidized PEDOT, doped with PSS, is used in both light-emitting devices as hole transport (buffer) layer [4] and in photovoltaic devices as hole-collecting layer [5]. The presence of the PEDOT-PSS film leads to improved stability of LED's.

Even though many applications of PEDOT-PSS have been studied by experimental methods there has been no theoretical investigation to understand its applications. In this work, the main objective is the study of electronic properties of ground and excited states of PEDOT and PSS polymers using various quantum chemical methods.

### 2. Computational Methods

Theoretical calculations were performed using Gaussian98 (G98) and Amsterdam density functional (ADF) and Dmol3 programs.

In the case of G98, Hatree-Fork method is used for the optimization of ground state and Configuration interaction singles (CIS) method is used to study the first three lowest vertical excitation energies.

In the case of ADF, Becke exchange and Lee-Yang-Parr 1988 correlation functional (Blyp) is used at the generalized gradient approximation (GGA) level. The electronic properties of singlet and triplet excited state of EDOT and styrenesulphonic acid was studied by differential self-consistent-field-based DFT in ADF. The low-lying singlet and triplet excitation energies and oscillator strength

of these compounds have been derived by time-dependent density-functional theory (TDDFT).

The periodic model of EDOT and its dimer and tetramer were also optimized using Dmol<sup>3</sup> program in Materials Studio package.

### 3. Results and Discussion

The optimized ground state structure of EDOT and Styrene-sulphonic acid is shown in Figure 1a and 1b respectively. The vertical transition energies obtained by CIS and TDDFT methods shows that the high intense vertical transition in EDOT molecule is from  $S_0$  to first excited state  $S_1$  and the transition energy is 4.71 eV, whereas in styrene-sulphonic acid the intense transition is from  $S_0$  to second excited state  $S_2$  and the transition energy is 5.22 eV. The excited state, which has high oscillator strength value, shows high intense transition.

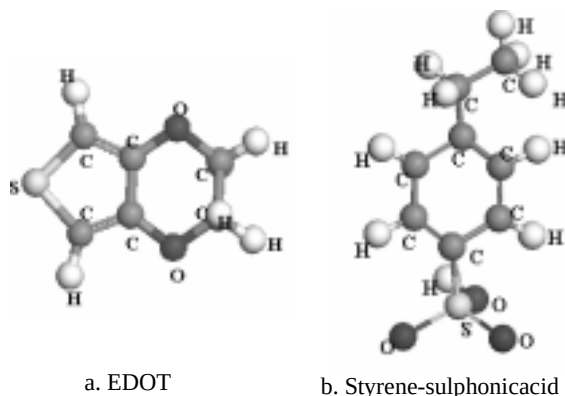


Figure 1: The optimized ground state structure of a. EDOT, b. Styrene-sulphonic acid.

The transition energy diagram for EDOT and styrenesulphonic acid obtained by TDDFT method is shown in Figure 2. The orbital contribution for the first excitation from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) is 0.78 for EDOT and 0.82 for styrene-sulphonic acid. The calculated energy gap for PEDOT by Dmol<sup>3</sup> program agrees well with the experimental value of 1.5 eV [6]. The aromatic C-C bonds are elongated both in EDOT and styrene-sulphonic acid molecules on excitation, which clearly indicates the

transition is of  $\pi$ - $\pi^*$  type transition. The planarity of the thiophene ring in EDOT molecule is destroyed during excitation.

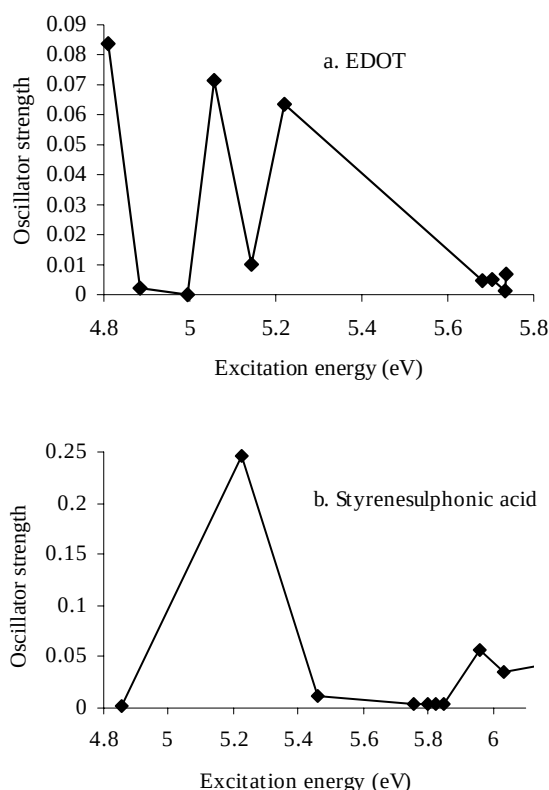


Figure 2. Vertical transition energy diagram obtained from TDDFT method.

The adiabatic transition energy is obtained by optimizing the first excited state ( $S_1$ ). The calculated adiabatic transition energy of EDOT is 0.79 eV lower than styrene-sulphonic acid.

Table I: HOMO, LUMO energies and energy gap of EDOT and its dimer and tetramer

| Molecule       | HOMO (eV) | LUMO (eV) | $E_g$ (eV) |
|----------------|-----------|-----------|------------|
| EDOT           | -5.266    | -1.266    | 4.00       |
| PEDOT dimer    | -4.381    | -1.693    | 2.688      |
| PEDOT tetramer | -4.035    | -2.236    | 1.799      |

In general, the electronic band gap of the conjugated chain is controlled by varying the degree of  $\pi$ -overlap along the backbone with steric interactions, and by controlling the electronic character of the  $\pi$ -system with electron donating or accepting species. The latter is accomplished by using substituents and co-repeat units that adjust the HOMO and LUMO energy levels of the  $\pi$ -system. The band gap of PEDOT gradually increases with increase in the number of

EDOT unit in the polymer. The HOMO, LUMO level energies and band gap of EDOT and its dimer and tetramer is given in the Table I. Since the number of  $\pi$ -conjugation is high with more number of EDOT units in the polymer, there is more probability of  $\pi$ -electrons that can go to the LUMO level from HOMO level. So the level of HOMO increases in energy and LUMO level decreases

$\Delta$ SCF-DFT method shows a decrease in the energy gap for the singlet and triplet excited state then the ground state. The triplet excitation energy is lower than the singlet excitation energy.

PEDOT and its cation were also studied using Dmol3 program. The band gap was found to decrease with increase in the positive charge in PEDOT and the Fermi level decreases. The band gap and Fermi levels of PEDOT and its cation is shown in Table II. The cation of PEDOT was studied since when PEDOT is doped with PSS, positive charge de-localizes through the  $\pi$ -conjugation in PEDOT.

Table II: Energy gap and Fermi level of PEDOT and its cation.

| Molecule              | $E_g$ (eV) | $E_f$ (eV) |
|-----------------------|------------|------------|
| PEDOT                 | 2.75       | -5.00      |
| [PEDOT] <sup>+</sup>  | 1.50       | -4.82      |
| [PEDOT] <sup>2+</sup> | 0.73       | -4.52      |

From this we can say that when PEDOT is doped with PSS, there will be decrease in the band gap. This indicates that the PEDOT doped with counter anion PSS has high conductivity.

#### 4. Conclusions

The first excited state is mainly due to the orbital contribution from HOMO to LUMO level for both EDOT and Styrene-sulphonic acid. The band gap decreases with the increments in the number of EDOT unit. PEDOT polymer shows high conductivity when it is doped with PSS.

#### References

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