2P27 Theoretical Study of Electronic and Molecular Properties of Ground and Excited States of Ethylenedioxythiophene and Styrenesulphonic Acid

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INTRODUCTION

The poly(3,4-ethylenedioxythiophene) (PEDOT) chosen for this study has the major advantage to be very stable in the doped state, with conducting properties that remain almost unaltered under aging in environmental conditions. PEDOT belongs to a group of conducting polymers that are already used as antistatic coatings and are very promising candidates for some other applications like biosensors, electro-chromic devices etc. PEDOT is an electro-chemically stable compound polymer, which can be oxidized (doped) to a high electrical conductivity [1] while maintaining moderate transparency [2]. Oxidized PEDOT, doped with poly(4-styrenesulfonate) or PSS, is used as a hole transport (buffer) layer in polymer based light-emitting diodes [3], so called p-LED's and 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

COMPUTATIONAL METHODS

The calculations were performed using Gaussian98 and ADF and Materials Studio programs. The ground and excited states of EDOT and styrenesulphonic acid are optimized at generalized gradient approximation (GGA) level with Becke exchange and Lee-Yang-Parr 1988 correlation functional. The singlet and triplet excited state of EDOT and styrenesulphonic acid was also studied. The vertical excitation energies were obtained using CIS (configuration interaction singles) and TDDFT (Time dependent density functional theory) methods.

RESULTS AND DISCUSSION

The vertical transition energies obtained by CIS and TDDFT methods shows that the high intense vertical transition in EDOT molecule (4.71 eV) is from S_0 to first excited state (S_1) whereas in styrene-sulphonic acid the intense transition is from S_0 to S_2 and the transition energy is 5.22 eV. The transition energy diagram for EDOT and styrenesulphonic acid obtained by TDDFT method is shown in Figure 1a and 1b, respectively. Due to π-π^* transition the aromatic C-C bonds become weaker and hence elongated. The calculated energy gap (1.5 eV) of PEDOT agrees well with the experimental value of 1.5 eV. The energy gap decreases with increase in the number of EDOT unit in the polymer. When PEDOT is doped with PSS, there is a significant decrease in the band gap. With increase in the number of styrene-suplhonic acid unit in PEDOT, the band gap was found to decrease. This indicates that the PEDOT doped with counter anion PSS has high conductivity

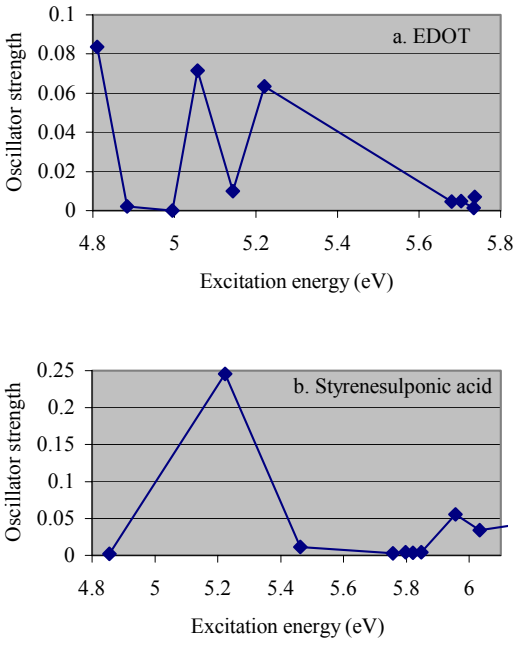

Figure 1. Vertical transition energy diagram obtained from TDDFT method.

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