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Theoretical investigation of 4-(2,3-dihydro[3,4-6][1,4][dioxin-5-yl) aniline copolymer

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ABSTRACT

Poly 4-(2,3-dihydro[3,4-6][1,4][dioxin-5-yl) aniline (EDOT-Ani) is an interesting novel monomer which can be used as an electrode in fabrication of dye synthesized solar cells. In this paper a DFT method with B3LYP/6-31G* level of theory was used for investigating the structural, electronic and optical properties of different configurations of 4-EDOT-Ani. The structural parameters were calculated and indicated that the EDOT-Aniline has a benzoid structure. Gibbs free energy calculations show that gauch-anti configuration is the most energetically stable structure. The HOMO-LUMO gaps were calculated their counters were interpreted. The IR spectrum was simulated and show good correlation with experimental values. Finally, TDDFT calculations were used for obtaining the UV spectra of all configurations.

Keywords: Copolymer; EDOT; DFT; Optical properties.

1. Introduction

Electronically conducting polymers have received considerable attention because of their wide range of technological applications in optical and electronic devices [1], energy storage systems [2], plastic solar cells [3], biosensors [4] and electromagnetic shielding [5]. These applications can be attributed to their band structures. There have been a number of attempts over the past decades to the preparation of novel organic conjugated polymers with low band gaps [6]. Among the conjugated polymers, poly (3,4-ethylenedioxythiophen) (PEDOT) is a promising organic electrode material for its low band gap, low oxidation potential and remarkable environmental stability [7-9]. This polymer has chains which block the 3,4 positions of thiophene ring, exerting an electron donating effect which reduce the band gap of polythiophene about 1.2-1.7 eV and causes a high degree of visible light transmission [10]. Several studies have been carried out for random copolymerization of aniline-EDOT monomers in order to comprise the conductivity and electro catalytic effect of both Aniline and EDOT [11, 12]. In this work we exploit DFT calculations to investigate the conformational, electronic and optical properties of 3,4–Ethylenedioxythiophene-Aniline copolymer (n-EDOT-Ani).

2. Experimental

All calculations were carried out using Gaussian 09 [13] and density functional theory at B3LYP level in combination with 6-31G(d) basis set. Different configurations were considered for 2-4 oligomers and let them to fully optimized. Higher Occupied Molecular Orbital (HOMO) and Lower Unoccupied Molecular Orbitals (LUMO) energies were calculated and their isosurfaces plots are depicted using Gauss view program with isodensity value =0.02au. The HOMO-LUMO energy gap was evaluated as the difference between the HOMO and LUMO energy levels. Then the frequency calculations were applied for all species and the most energetically stable configurations were selected. IR spectra were simulated and scaled with a common scaling factor of 0.9613 [13, 14]. TD-DFT/B3LYP/6-31G* calculations were also performed for simulating UV- visible spectra in DMSO medium on polarized continuum model (PCM).

3. Results and discussion

Fig. 1 shows the all studied configuration of 4-EDOT-Ani, after full optimization. Gibbs free energy results show that gauch- anti conformation (Tet3) is the most stable structure among all studied conformations. The inter ring distance in all conformation is about 1.39-1.40 Å for N-C bond lengths and about 1.46 Å for C-C bond lengths which show the benzoid structure of this copolymer [15]. Table 1 reports the HOMO-LUMO energy levels for the most stable conformations of 1-4 EDOT-Ani. The results show that the band gap of EDOT-Aniline is about 4.32 eV and reduces to 3.39 eV by increasing the number of monomers in 4-EDOT-Ani which is due to the higher conjugation between monomers. This band gap is lower than the band gap obtained for PEDOT [16]. Among all conformations of 4-EDOT-Ani, Tet 3 show the most narrowing band gap which is due to its higher structural planarity and therefore higher conjugation and electron conductivity.

Contours of HOMO and LUMO are depicted in Fig. 2 for Tet 3 configuration. In all oligomers the HOMOs are mostly located on the rings and the LUMOs are concentrated on the inter ring bonds which confirm the benzoid structure of EDOT-Ani polymer.

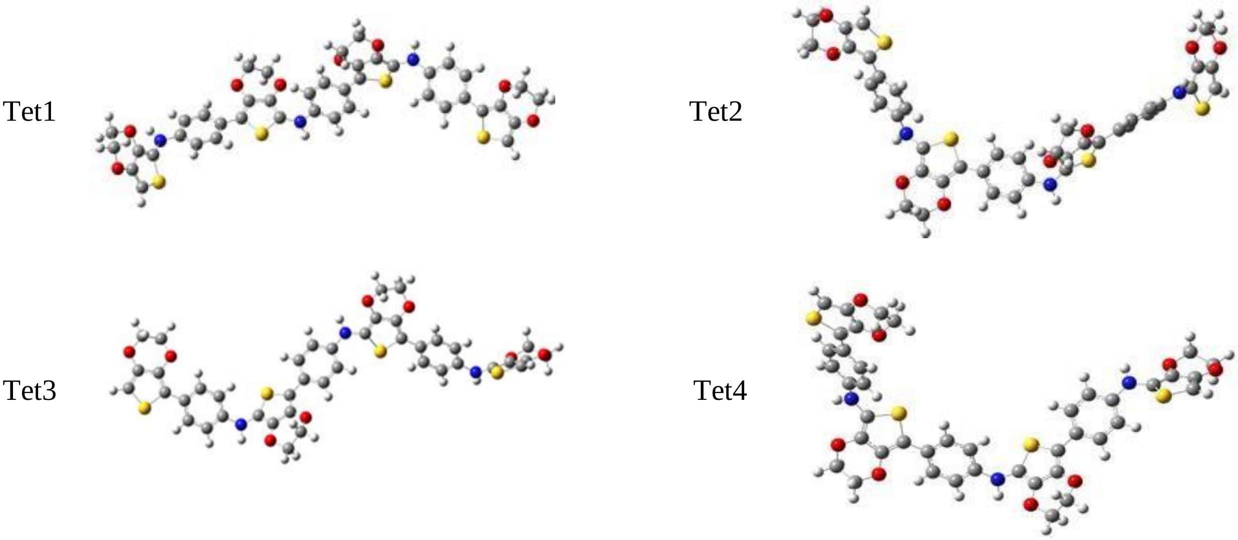


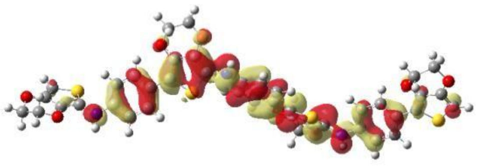
Fig 1. Optimized structure of all configuration of 4-EDOT-Anigray, red, yellow and blue balls are used for C, O, S and N atoms respectively.

By increasing the number of monomers to 4-EDOT-Ani the HOMO is more prominent over the N-C inter ring bonds which is due to its higher conjugation.

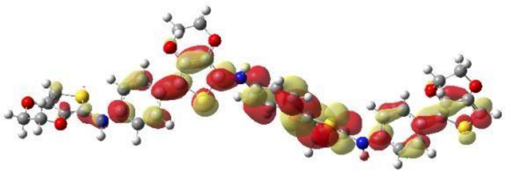
Table 1. Gibbs free energies (kJ/mol) of different isomers of monomer to pantamer structures of EDOT-Aniline.

	HOMO/eV	HUMO/eV	Gap/eV
M	-4.82621	-0.50259	4.32
D	-4.41831	-0.72056	3.70
T	-4.45287	-0.76845	3.68
Tet1	-4.33559	-0.79457	3.54
Tet2	-4.35464	-0.77689	3.58
Tet3	-4.22947	-0.84355	3.39
Tet4	-4.24198	-0.82940	3.41

The delocalization of HOMO and LUMO orbitals are higher in Tet3 and Tet 4 conformations with higher planarity than Tet1 and 2. The theoretically simulated IR spectra of 4- EDOT-Ani copolymer is presented in Fig 3.



HOMO



LUMO

Fig 2. The isosurface plot of HOMO-LUMO states from B3LYP/6-31G*for 4-EDOT-Ani the electron accumulation is indicated with dark gray (red) and the charge depletion with light gray (yellow) colors.

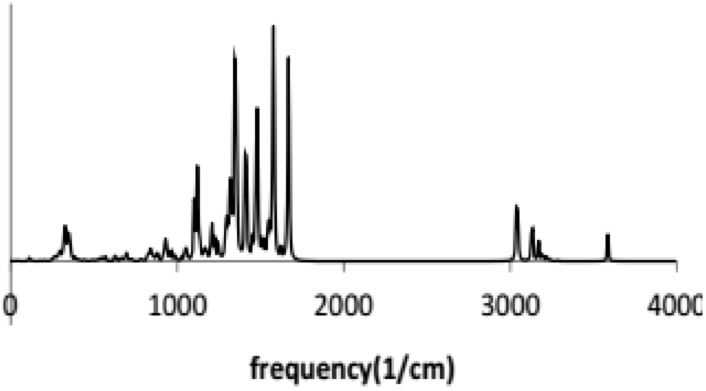


Fig 3. IR spectrum of 4-EDOT-Ani calculated by B3LYP/6-31G*.

A peak at 3584-3589 cm^{-1} is assigned to N-H stretching which is different from experimental data [12]. The difference in simulated and observed N-H stretching can be attributed to the fact that theoretical data is for an isolated oligomer in vacuum state while the experimental is that of condensed phase. The bands at 3035-3133 cm^{-1} are assignable to asymmetric C-H stretching of dioxan ring. The band around 1646-1670 cm^{-1} are corresponding to C-C and C=C stretching of thiophen ring in close agreement with experimental data [12]. The vibrations at 1178, 1103-1120 cm^{-1} are assigned for C-O-C bond stretching in the ethylendioxy group [17]. C-S stretching band is observed at about 845 cm^{-1} and 960 cm^{-1}.

The theoretically simulated UV-Vis spectra of 4-EDOT-Anilin at TD/DFT/6-31G* level of theory are given in Fig. 4 for all conformations, respectively. The peaks at 300-366 nm corresponds to π –π* excitation of the para substituted benzene segment in Aniline.

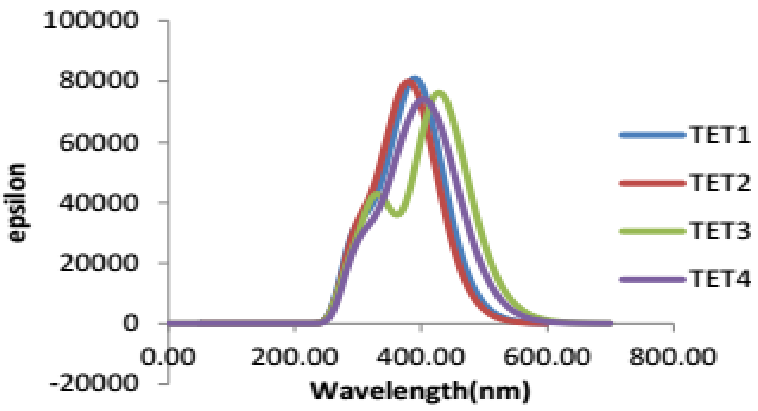


Fig 4. UV-Visible spectra of 4-EDOT-Anilin using TD/DFT/6-31G*.

The broad peak at 420-426 nm can be attributed to $\pi - \pi^*$ electronic transition of EDOT ring. The highest intensity can be attributed to Tet3 conformation with low band gap and highest conjugation Two peaks at 430 and 330 nm in Tet 3 are in close agreement with experimental results [12] at 330 and 410 nm.

4. Conclusions

In this paper structural, electronic and optical properties of Poly 4-(2,3-dihydro[3,4-6][1,4][dioxin-5-yl) aniline was investigated using B3LYP/6-31G* level of theory. Gibbs free energy results show that gauch-anti conformation (Tet3) is the most stable structure among all studied conformations. Structural results show the benzoid structure for this copolymer which are confirmed by HOMO-LUMO counters. The H-L gap of EDOT-Aniline monomer is about 4.32 eV and reduces to 3.39 eV by increasing the number of monomers in 4-EDOT-Ani. Theoretically IR and UV-Vis spectra were calculated and show close agreement with experimental data.

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