

ELECTRONIC STRUCTURE OF DITHIENOPYRROLE, DITHIENOTHIOPHENE AND THIONAPHTHENEINDOLE

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Abstract

Dithienopyrrole (DP), Dithienothiophene (DT) and Thionaphtheneindole (TNI) are electrochromic semiconductor polymers that possess very similar electronic structure. These materials were synthesized in the middle of the nineties with the intention to obtain an improvement in the processability of the electrochromic polymers and investigate the mechanism of charge transport in the polymeric net. In this work, we investigated the electronic, conformational and spectroscopic structure of oligomers formed by the mentioned systems. Density of states and wavefunction were calculated to study the conduction mechanism in the net of these polymers through polaron defect type. We used the semiempirical methods for calculations of electronic structure of the polymers and copolymers coupled with ZINDO/Spectroscopic method to simulate the behavior of absorption for neutral and charge systems. We adopted EHT description for the conformational defects and we investigated the electrical conduction as a function of defects concentration.

keywords: Dithienopyrrole, Dithienothiophene, Thionaphtheneindole, Copolymer, Theoretical Absorption Spectrum.

1. Introduction

It has been established theoretically that polyheterocycles represent a very relevant class of electroconducting materials. Heteroaromatic compounds such as polypyrrole, polythiophene and polyfuran have been changed to obtain polymeric systems with high environmental stability and convenient processability through addition of appropriate side groups. Moreover, according to Valence Effective Hamiltonian [1] and Extended Huckel calculations [2], the increase of quinoid character in the polymer backbone produce a shortness of the band gap. In that sense the presence of charge on the backbone, due to a doping process, can generate polaron-bipolaron excitations which can leave the system in the metallic regime [3].

A great variety of conducting polymers with peculiar electrical and optical characteristics has been obtained by electrochemical methods. Among those the dithienothiophene (DT), dithienopyrrole (DP) and thionaphtheneindole (TNI) have been electrochemically synthesized by Casalbore-Miceli et al [4] showing, for several monomer ratios, good electrochromic and conducting properties. Recently, the same group [5] reported a study of the copolymers builded by electrochemical means from those monomer mixtures. They found that only the DT-DP copolymer remains a good conducting and electrochromic system.

In this communication, we report selected examples of calculated optical absorption spectra of the dimers of DP, DT and TNI to explain the experimental data [5]. In addition we study the effects on the electronic structure of the polymeric systems induced by the presence of charge.

2. Methodology

The geometry of neutral and charged of DP, DT and TNI oligomers was fully optimized using the semiempirical methods AM1 and PM3. Both methods provided a very similar geometry for each of the different structures we investigated, then we adopted the geometry optimization obtained by the AM1 method. The density of states of long chains was obtained using the Negative Factor Counting technique coupled to the usual Extended Huckel Hamiltonian with Clementi's parametrization. The charge distribution of individual states of interest was obtained through the Inverse Iterative Method. For the absorption spectra determination, we used the ZINDO/S-CI [6] method.

3. Results and Discussion

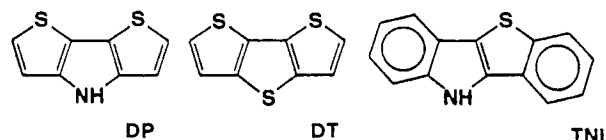
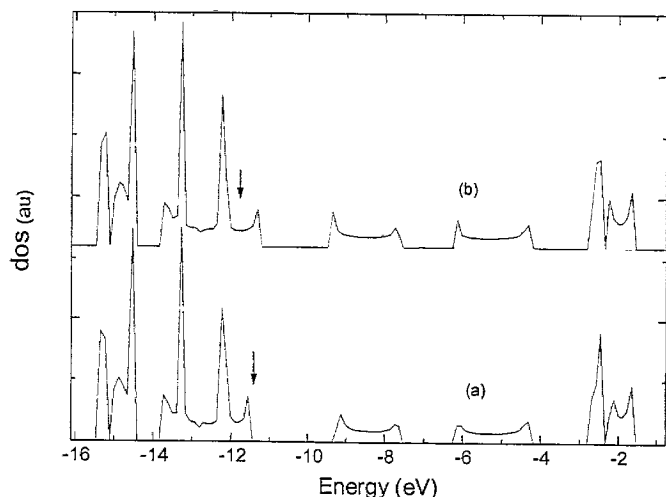


Fig. 1. Dithienopyrrole (DP), dithienothiophene (DT) and thionaphtheneindole (TNI).

Figure 1 schematically displays the chemical structure of the monomers used in this work. Our calculations indicate that the ionization potential remains almost constant, around 7.8 eV, for all considered neutral oligomers, but the dipole moment

Figure 2. Density of States for DP polymer in the (a) Neutral and (b) +1 charged system. The arrows indicate the position of the Fermi level.



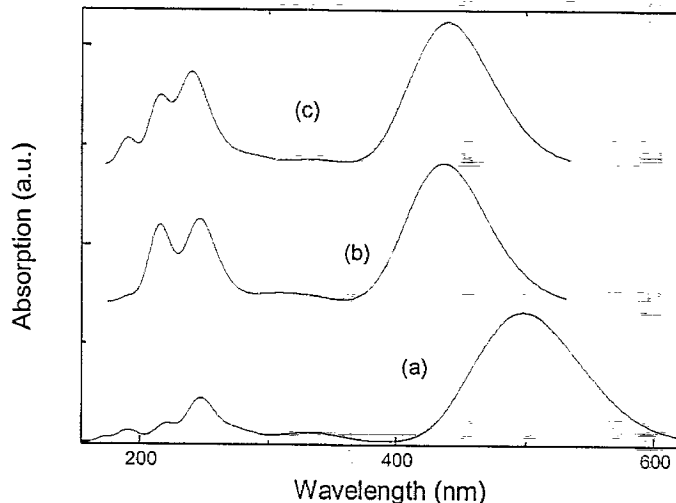
decrease drastically with the number of DT units we have on the oligomer system. Evidence of metallic behavior for charged system can be seen in Figure 2, where we show the pi electronic density of states for a long chain of dithienothiophene in the case of (a) neutral and (b) polaron defects systems. The energy gap, doesn't close as the concentration of defects increases (Figure 2(b)), but the Fermi level is pull down into the band. Also we found that the HOMO state is delocalized for defect system, which is a strong indication of metallic behavior.

Table1. Most relevant CI expansion coefficients for fully optimized oligomers of DT+TNI, DP+TNI and DP+DT. These are the excited states for the first optically active transitions. H-i → L+j represents HOMO-i orbital to LUMO+j orbital excitation.

Copolymer	O.S.	CI State
DT+TNI	1.7933	0.953 H→L>
		-0.252 H-1→L+1>
	0.7871	0.425 H-5→L>
DP+TNI	1.7869	-0.393 H-2→L+1>
		0.940 H→L>
	0.2772	-0.239 H-1→L+1>
		-0.506 H→L+5>
DP+DT	1.6579	0.430 H-2→L>
		-0.966 H→L>
	0.2772	-0.222 H-1→L+1>
		-0.603 H→L+4>
		0.534 H-4→L>

The experimental work of Beggiato et al [5] shows that the electrochromic properties of DP+DT copolymers are not greatly affected by the ratio of monomer units in the chain. The simulate absorption spectra for trimers built with DP and DT monomer units, not included in this paper, show the maximum shift of 80 nm between the first transition for all systems, following the experimental measurements. For comparison we show in Figure 3 the plot of the absorption spectrum of the DP+DT dimer, which exhibit a strong absorption at 500 nm, due to mainly to the HOMO-LUMO transition. The dimers composed by DP+TNI and DT+TNI have the same spectra

Figure 3. Absorption Spectrum of (a) DP+DT; (b) DP+TNI and (c) DT+TNI dimers.



structure at main transitions (Figure 3(b) and 3(c)) in a very good agreement with the experimental results. So the theoretical calculations corroborate with experimental conclusions that shows a strong similarity of both dimers systems.

From the data of CI coefficients of the Slater's determinant expansion, table 1, we can observe that, up the first singlet-singlet transitions, the two most important contributions for the higher peak come from the HOMO to LUMO and HOMO-1 to LUMO+1 excitations. The ratios of the oscillator strength (O.S.) give the relative amplitudes between the spectrum structures.

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5. References

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