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# Theoretical study of structural and electronic properties of oligo(thiophene-phenylene)s in comparison with oligothiophenes and oligophenylenes

H. Zgou<sup>a,b</sup>, S.M. Bouzzine<sup>a,b</sup>, S. Bouzakraoui<sup>a,b</sup>,  
M. Hamidi<sup>b,\*</sup>, M. Bouachrine<sup>a,\*</sup>

<sup>a</sup> *Unité de Recherche sur les Macromolécules et Modélisation, Faculté des Sciences et Techniques,  
B.P. 509 Boutalamine, 5200 Errachidia, Morocco*

<sup>b</sup> *Unité de Chimie Théorique Appliquée, Faculté des Sciences et Techniques, B.P. 509 Boutalamine, 5200 Errachidia, Morocco*

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## Abstract

In this work, a quantum–chemical investigation on the structural and opto-electronic properties of oligo(thiophene-phenylene) (4TP) is carried out. The results are discussed in comparison with the properties of corresponding oligothiophene (8T) and oligophenylene (8P). As the opto-electronic properties of this type of conducting polymers are governed by their electronic band gap, we shall also present a comparison among HOMO, LUMO and band gap energies of these three materials.

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**Keywords:** Conjugated polymers; Oligothiophene; Oligophenylene; Oligo(thiophene-phenylene); DFT

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Organic conjugated polymers exhibit semiconducting properties associated with the  $\pi$  molecular orbitals delocalized along the polymer chains. These materials have attracted much interest for potential applications in opto-electronic devices due to their unique electronic and photonic properties [1]. In the categories of conjugated polymers, polythiophene and polyphenylene occupy an important position. In the past decade, extensive and intensive studies have been devoted to the synthesis, characterization, physical and chemical properties and variety of these materials [2]. On the other hand, their electronic structure and conformational analysis have been extensively studied by our group [3]. More recently we have developed a new molecular design and synthesis, i.e., thiophene/phenylene (TP) diblock conjugation [4]. These copolymers have also proved to be of interest in combining the properties associated to the two different conjugated rings and have an improved quantum efficiency of electroluminescence compared to conventional polythiophene or polyphenylene.

Whereas the polymers are obtained as highly amorphous materials, oligophenylene and oligothiophene are not amorphous and can be synthesized as well defined compounds. Moreover, these oligomers provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in parent polymers [5]. In this regard, theoretical studies of oligomers certainly facilitate the knowledge of polymeric structure. Smallest oligomers can play also an important role in understanding charge transport mechanism and

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\* Corresponding authors.

E-mail address: [lmmm\\_fste@yahoo.fr](mailto:lmmm_fste@yahoo.fr) (M. Hamidi).

physical properties of polymers. In fact, it is well established that the semi-empirical calculations can yield valuable information of conjugated oligothiophene and phenylene structures [6]. But, a full theoretical treatment including the effect of the strong inter-chain interactions is more suitable. For that matter, it is commonly believed that DFT theoretical method is able to describe the geometry and the electronic properties of organic conjugated molecules, as well as their energetic, in a satisfactory manner [7].

As such, mixed  $\pi$ -conjugated oligomers made of thiophene and other five-membered heterocycles such as furan, pyrrole and thiophene have recently been investigated [8]. Therefore, further comparison of the structural and electronic properties of these “heterooligomers” with “homooligomers” such as oligothiophene and oligophenylene appears important to explore the potential of these oligomers for the use in electronic devices.

In this work, we are going to carry out the DFT calculations and to discuss the structural and electronic properties of oligo(thiophene-phenylene). The results are discussed in comparison with the properties of corresponding oligothiophene (8T) and oligophenylene (8P). As the opto-electronic properties of this type of conducting polymers are governed by their electronic band gap, we shall also present a comparison among HOMO, LUMO and band gap energies of these three materials.

First, to predict differences in the structural and electronic properties of 8T, 8P, and 4TP, theoretical calculations were carried out at the B3LYP/6-31G(d) level. The optimized geometric models are shown in Fig. 1. The dihedral angles ( $\theta_i$ ,  $i = 1-7$ ) are collected in Table 1. The most stable conformer of 8T is found to be the one of transoid and antiplanar structure ( $\theta_i = 180^\circ$ ) while that of 8P is twisted with the optimized dihedral angles of  $140^\circ$ . This depends on the balance of two interactions: as a consequent of the  $\pi$ -electron conjugation between the phenyl rings, the molecules tend to remain planar, whereas the steric repulsion between hydrogens causes the molecules to twist. For the 4TP, The inter-ring torsions between thiophene and phenylene were evaluated to be about  $25.7^\circ$  for  $\theta_1$  and  $\theta_7$ ,  $21.8^\circ$  for  $\theta_2$  and  $\theta_6$ ,  $22.2^\circ$  for  $\theta_3$  and  $\theta_5$  rather than  $\theta = 27^\circ$  as occurs for 2-phenylthiophene [9]. It is obvious that the torsion angle constitutes a compromise between the effect of conjugation on crystal packing energy, which favours a planar structure, and the steric repulsion between hydrogens which favours a nonplanar structure [10].

It is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport. In general, as plotted in Fig. 2, the HOMO possesses an antibonding character between the consecutive subunits. On the other hand, the LUMO of all oligomers generally shows a bonding character between the subunits.

The HOMO and LUMO energies can be calculated by DFT calculations. We have listed in Table 2, the HOMO and LUMO values. Also, we have calculated the gap energies obtained by the difference between the HOMO and LUMO levels for the three oligomers. The approach to get the band gap energy with difference between HOMO and LUMO energies is crude considering experimental comparison. The implicit assumption underlying this approximation is that the lowest singlet excited state can be described by only one singly excited configuration in which an electron is promoted from HOMO to LUMO. In addition, the energy difference between HOMO and LUMO is still an approximate estimate to the transitional energy. However, because the HOMO–LUMO gap is easy to get, the approach can also be used to provide valuable information on estimate band gaps of conjugated oligomers or polymers.

Upon comparison of these three oligomers, the HOMO level of oligothiophene 8T ( $-4.71$  eV) is higher than those of corresponding oligomers 8P ( $-5.43$  eV) and 4TP ( $-4.94$  eV), while the values for the LUMO level of 8T

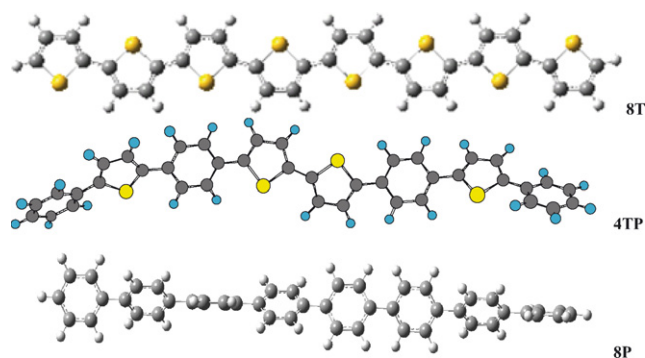
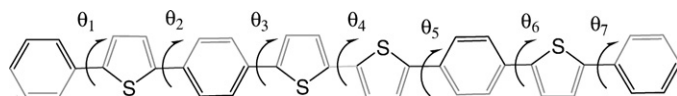


Fig. 1. The optimized structures of 8T, 8P and 4TP.

Table 1

Comparison of the values of dihedral angles obtained from the global minimum for 8T, 8P and 4TP



Dihedral angles (°)	8T	8P	4TP
$\theta_1$ and $\theta_7$	180	142.2	25.7
$\theta_2$ and $\theta_6$	180	143.3	21.8
$\theta_3$ and $\theta_5$	180	143.6	22.2
$\theta_4$	180	143.5	16.3

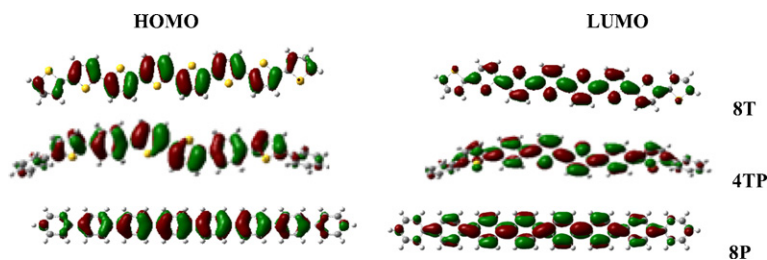


Fig. 2. The contour plots of HOMOs and LUMOs of 8T, 4TP and 8P.

Table 2

Calculated HOMO (eV), LUMO (eV) and  $E_{(\text{LUMO-HOMO})}$  (eV) energies

	8T	8P	4TP	PT [11] <sup>a</sup>	PPP [12] <sup>a</sup>
HOMO (eV)	−4.71	−5.43	−4.94		
LUMO (eV)	−2.30	−1.43	−1.97		
$E_{(\text{LUMO-HOMO})}$ (eV)	2.41	3.99	2.97	2.3	3.5

<sup>a</sup> Experimental values of polymers.

Table 3

Calculated absorption wave lengths  $\lambda_{\text{max}}$  (nm) and oscillator strengths (OS) for 8T, 8P and 4TP

	8T	8P	4TP
$\lambda_{\text{max}}$ (nm)	556.30	330.50	480.14
Oscillator strength (OS)	3.00	3.37	2.29
$\lambda_{\text{max}}$ (nm) (exp [14])	455 (4T)	365 (4P)	445 (2TP)

(−2.30 eV) is lower than those obtained from 8P (−1.43 eV) and 4TP (−1.97 eV). On the other hand, the HOMO–LUMO gap is 2.97 eV in 4TP which is even lower than the band gap of 8P (3.99 eV) and larger than the one of 8T (2.41 eV). It is important to outline that theoretical band gaps computed for isolated chains are expected to be about 0.2 eV larger than the values computed in condensed phase [13]. When taking into account this difference, the obtained band gap value of 8T and 8P are in accordance with those measured experimentally for polythiophene: 2.3 eV [11] and polyparaphenylene 3.5 eV [12]. The octamer seems to be a useful model to understand the electronic properties of the polymeric system.

To investigate the UV–vis absorptions, we presented in Table 3, the calculated absorption  $\lambda_{\text{max}}$  values of the three oligomers 8T, 8P and 4TP. These values are calculated ZINDO/B3LYP/6-31G(d) method starting with optimized geometries obtained at B3LYP/6-31G(d) level. However, it is believed that the bulk of intermolecular effect must be taken into account when considering the polymers with long chain. After considering this effect and comparing the

wavelengths  $\lambda_{\max}$  of the three oligomers, we note that 8T exhibits the longest wavelengths at 556.30 nm, while 8P and 4TP have the shortest wavelengths at 330.50 and 480.14 nm, respectively. These calculated results agree well with experimental data [15]. This would be ascribed to the higher planarity in the case of oligothiophene (8T) as already mentioned above.

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