New soluble copolymer based on thiophene and phenylene as candidate for optoelectronic devices applications: Experimental and theoretical investigations

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Abstract

In this paper, we report first, a synthesis and physical properties of a recent soluble polymer based on thiophene and phenylene. Then, we present a detailed DFT study based on B3LYP/6-31G* of geometrical structures and electronic properties of a series of oligomers.
Calculated results are compared with experimental data and based on such comparison we try first, to investigate the effect of the increase of molecular dimensions on the various properties and then to obtain a qualitative understanding the properties of the polymer.

1. Introduction

Conjugated polymers have gained much interest as a novel class of semi-conductors and are frequently studied because of their interesting optical and electronic properties [1]. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are, in particular, desired in optoelectronic applications such as LEDS or solar cells [2].
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 to a variety of these materials. Copolymers containing both phenylene and thiophene units have also proved to be of interest in combining the properties associated with the two different conjugated rings [3]. More recently, our group has developed a new molecular design and synthesis, i.e. thiophene/phenylene (TP) diblock conjugation [4]. These copolymers represent a very interesting class of materials and exhibit a strong fluorescence when exposed to the visible light. To improve solubility of copolymers, new substituted copolymers with different lateral chains, have been synthesized [5]. These substituted new materials show new interesting optical properties. It is known that the ortho position substitutions of the phenyl ring modify the degree of conjugation. Through symmetrically and asymmetrically incorporating long flexible alkoxy side chains onto phenylene backbones, i.e. studying the effect of the side chains as well as the symmetry of the repetition of the unit on the physical properties of

the resulting polymers have been extensively outlined [6]. The effects of these alkoxy side chains are not only to give good solubility to the polymers, but also to improve their photoluminescence (PL) quantum yields [7].

In order to understand well the optical and electronic properties and hence the improvement of such devices in which conjugated polymers are used as active layers, Raman spectra can provide structural information. On the other hand, photoluminescence can often be greatly enhanced by increasing the intrinsic stiffness of a polymer backbone or by inducing large bulky side groups to weaken intermolecular interactions. The emission spectrum of a conjugated polymer depends basically on its π–π* band gap, which can be tailored using different structures [8].

In order to rationalize the experimentally observed properties of known materials and to predict those of unknown ones, theoretical investigations on the structures and electronic spectra and emissive properties of these materials are indispensable. In the past decades, ab initio and semi-empirical levels were applied to analyze various properties of thiophene-based molecules (oligomers and polymers). The semi-empirical PM3, AM1 and ZINDO approaches were used to calculate electronic structure of molecules based on thiophene and/or phenylene [9]. The conformational analysis and optical properties of symmetrically distributed terthiophenes were performed by Nicolas DiCésare and co-workers using the ab initio HF/3-21G* method [10]. However, it is very difficult to use a high level of theory with, the growing molecular size from monomer to oligomers, to treat these systems. Recently, methods based on density functional theory (DFT) [11] were found attractive due to their features of including the electronic correlation in a computationally efficient manner and can be used in larger molecular systems.

In this work we study the electronic structure and optical absorption of a recent soluble polymer showing very good absorption properties. The schematic picture of the polymer can be seen in Fig. 1. Calculated results are compared with experimental data and based on such comparison, we try first to investigate the effect of the increase of molecular dimensions on the various properties and then to obtain a qualitative understanding of the polymer properties.

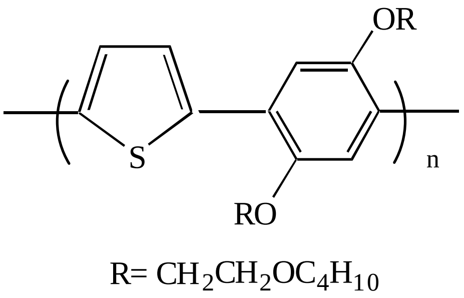


Fig. 1. The chemical structure of the studied copolymer

2. Experimental and computations

Gel permeation chromatography (GPC), infrared and Raman Spectroscopy were used to determine the chemical structure of the resulting copolymers. Raman spectra were registered on a Fourier Transformed (FTR) spectrometer Brüker RFS 100, using a laser wavelength at 1060 nm with a 4 cm^{-1} resolution. UV–Vis spectra were recorded on a MC^2 Safas spectrometer and emission spectra on an SLM-Aminco MC 200 spectrometer. Spectra of copolymers dissolved in chloroform ($CHCl_3$) were recorded at ambient temperature. The macromolecular characteristics were obtained by steric exclusion chromatography (SEC) or (GPC) in THF using polystyrene as standard.

Concerning the theoretical part, the quantum calculations were performed using Gaussian 03 program [12]. The geometries of the resulting conformers were optimized at the DFT level of three-parameter compound functional of Becke (B3LYP) [13]. The 6-31G* basis set was used for all atoms. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using ZINDO method starting with the fully optimized geometries obtained at B3LYP/6-31G* levels. In fact, these calculation methods have been successfully applied to other conjugated polymers [14].

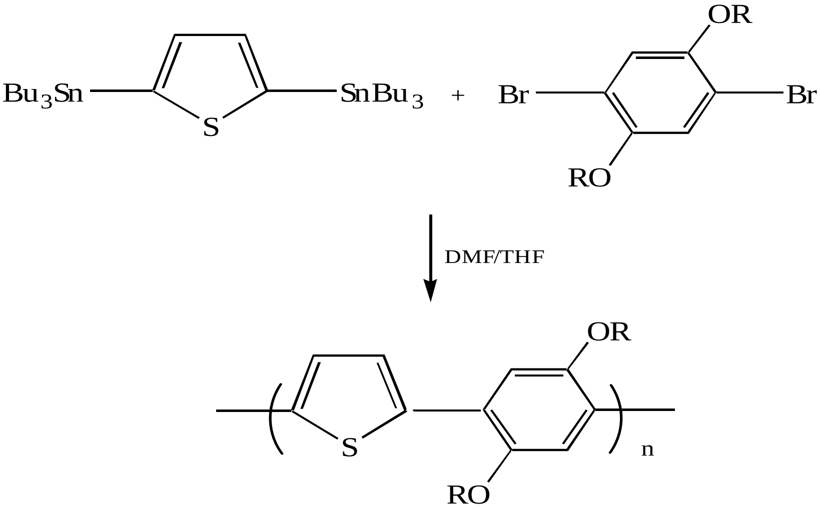
3. Results and discussion

Synthesis, characterization and properties

Copolymer synthesis

The synthesis of the thiophene /phenylene copolymer poly(TPdiox) was achieved, as shown in Fig. 2., by a polycondensation reaction using equimolar amount of 2,5-bis-(tributylstannyl)-thiophene and 1,4-dialkoxy 2,5-dibromophenylene, in a 1:1 THF:DMF mixture in the presence of $Pd(PPh_3)_4$ (1 mol%) as the catalyst. After reaction, the polymer was purified by precipitation upon addition of methanol.

Analytical data, elemental analysis, ^1H NMR and FT-IR reported in ref [15] are consistent with the structure $(C_{26}H_{38}O_6S)_n$. The polymer was soluble in organic solvents (THF, $CHCl_3$). The molecular weights of the copolymer were evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard. The number-average molecular weight (Mn) of the synthesized copolymer poly(TPdiox) was 1556 (Mw/Mn = 2.57). Thus, we note that this copolymer exhibits a relatively high molecular weight with polydispersity index (Mw/Mn) value equal to 2.57. It indicates an average degree of polymerization (DPn) of 29 corresponding in average to 58 consecutive alternating aromatic rings (Table 1).



R= $CH_2CH_2OC_4H_{10}$

Fig. 2: synthesis of the copolymer**.**

Table 1: Gel permeation chromatography (GPC) analyses

GPC results	M_n	M_w	I= M_w/M_n	DPn	Number of cycles
	11556	29771	2.57	29	58

For a better understanding of the relationship between the copolymers structure and their vibrational or optical properties, we discuss in the following section Raman scattering, infrared absorption, UV–vis absorption and PL emission results.

Spectroscopy results

We have showed that in the case of our copolymer, a very strong peak located at 1446 cm^{-1} dominates the normalized Raman spectra (Fig. 3). On this basis and from an examination of characteristic mode frequencies [16], we assigned this peak at 1446 cm^{-1} mainly to the symmetric ring-stretching mode of thiophene. The other peak at 1604 cm^{-1} is attributed to the para-phenylene ring-stretching mode. Peaks observed between 1000 and 1400 cm^{-1} are much weaker in intensity than those observed at 1446 and 1605 cm^{-1}, leading then to alternative assignments in particular concerning C–C bridge rings.

In order to achieve the relationship between structural properties for different copolymers, we studied their optical characteristics (UV–vis absorption and PL emission) and even their optimization geometries with density functional theory (DFT) calculations.

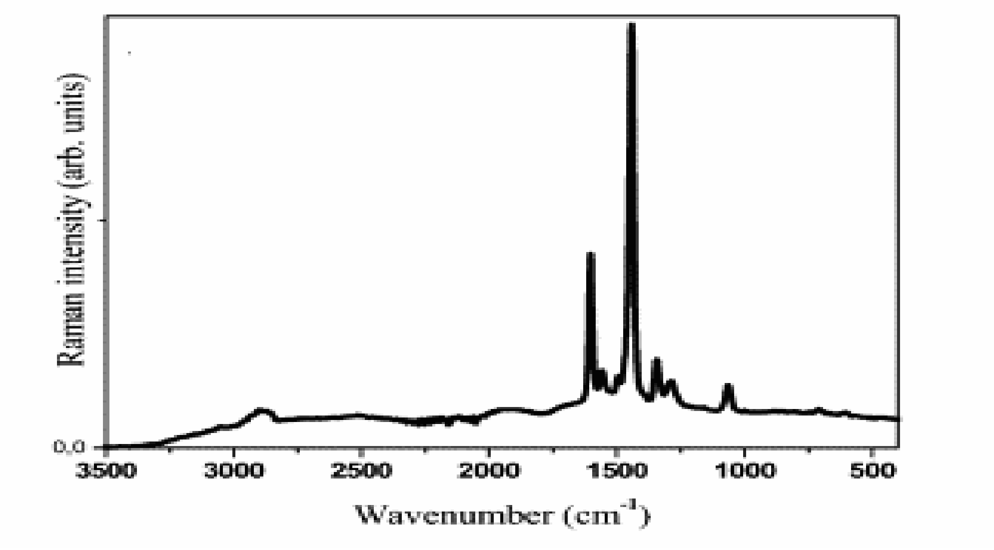


Fig. 3. Raman spectra of the copolymer

Optical and photoluminescence properties

Fig. 4 shows the absorption and the emission spectra recorded measured in $CHCl_3$ at room temperature. The UV–vis absorption and PL emission maxima of the copolymer are quoted in Table 2 together with their optical band gap estimated by the absorption onset wavelengths. The poly(TPdiox) exhibits an absorption spectra where the maximum absorption λ_{abs} appears at 464 nm, which is assigned to the electron donating alkoxy substituents on the phenylene ring [17]. This value is very similar to those observed for regioregular polyalkylthiophenes [18]. On the other hand, the onset of absorption, which corresponds to an approximation of the band gap, is estimated to be 2.38 eV. An important red shift of the absorption maximum was recorded and attributed to a higher mean conjugation length in the solid state and to interchain electronic coupling. Truly in the solid state, intermolecular interactions favor the coplanar arrangements of the aromatic rings that may be responsible for the observed enhanced conjugation

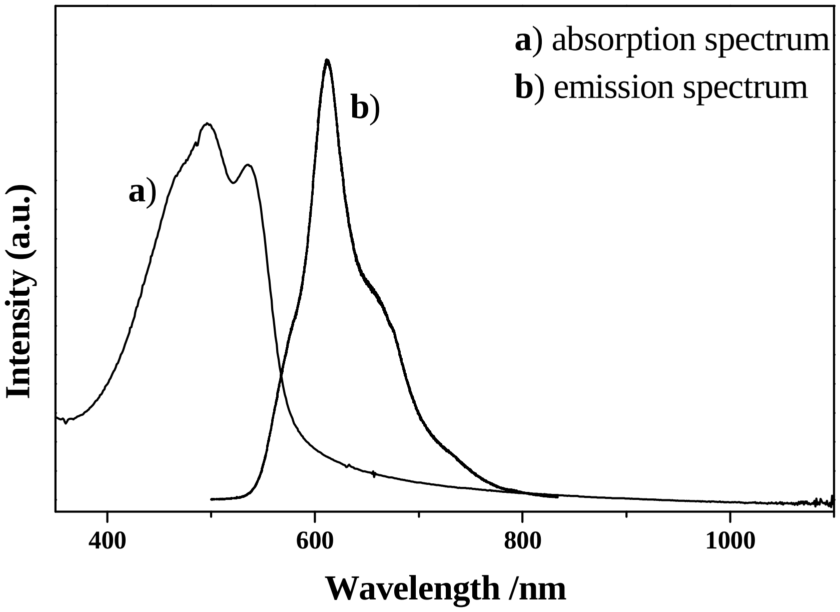


Fig. 4. Optical absorption and photoluminescence spectra of the copolymer

Table 2: Optical properties of the copolymer

In solution ($CHCl_3$)			In solid	state	Optical Band gap (eV)
λ_{abs} (nm)	ε	λ_{em} (nm)	λ_{abs} (nm)	λ_{em} (nm)	
464	25250	560	504	625	2.38

Concerning the PL emission properties of the copolymer (Fig. 4), spectra show typical vibronically structured bands with a maximum, a shoulder and a tail. The PL spectra of poly(TPdiox) are red-shifted (λ_{em}= 560 nm) resulting in a green emission. The red shift of the PL spectra could be related to interchain interactions. As observed for absorption, the photoluminescence maximum is red-shifted in the solid state in comparison to the solution. An orange-red photoluminescence maximum appeared in the range 610–625 nm in the solid state.

Theoretical results

Geometric parameters

The optimized ground state geometries of $(TPdiox)_n$ (n=1, 2, 3 and 4) obtained at the B3LYP/6-31G* level are given in Fig. 5. The optimized inter-ring bond lengths and dihedral angles between the subunits are summarized in Table 3 and Table 4.

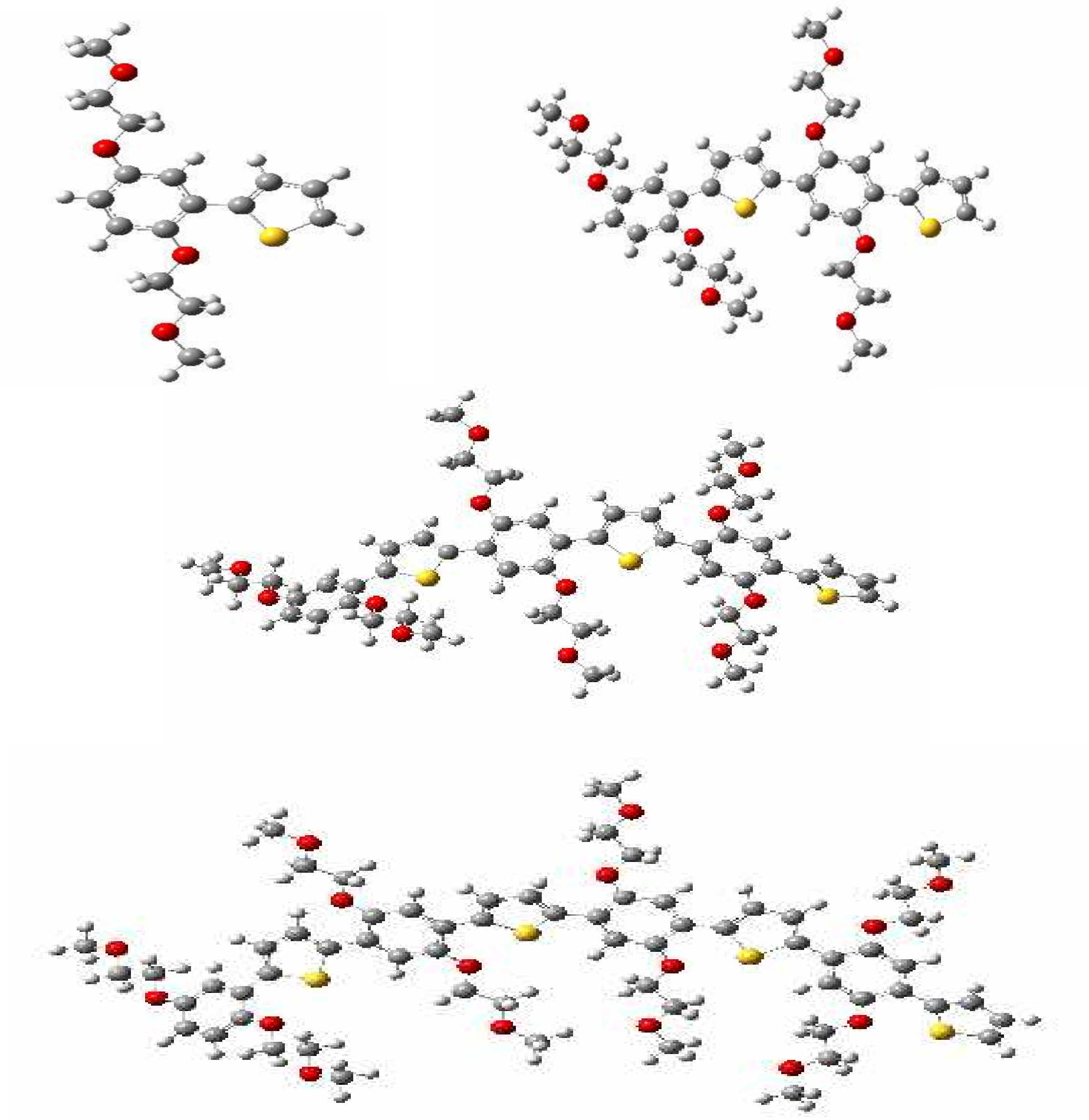


Fig. 5: Optimized structures obtained by the B3LYP/6-31G* level for $(TPdiox)_n$ (n =1-4)

Table 3: Inter-ring bond lengths (d_i) of $(TPdiox)_n$ (n =1-4) obtained by B3LYP/6-31G*

	d_1(Å)	d_2(Å)	d_3(Å)	d_4(Å)	d_5(Å)	d_6(Å)	d_7(Å)
n = 1	1.470						
n = 2	1.468	1.164	1.467				
n = 3	1.468	1.464	1.465	1.464	1.467		
n = 4	1.468	1.464	1.464	1.463	1.464	1.464	1.467

Table 4: Dihedral angles (θ_i) of $(TPdiox)_n$ (n =1-4) obtained by B3LYP/6-31G*

	θ_1(°)	θ_2(°)	θ_3(°)	θ_4(°)	θ_5(°)	θ_6(°)	θ_7(°)
n = 1	27.7						
n = 2	22.0	154.5	22.8				
n = 3	25.0	152.7	21.3	152.4	22.8		
n = 4	23.3	154.0	20.6	159.0	20.8	154.0	22.6

The results of the optimized structures for the copolymeric molecules show that all molecules possess non-planar structures. The results show that the inter-ring bond lengths and bond angles do not suffer appreciable variation with the oligomer size and it suggests that we can describe the basic structures of the polymers as their oligomers. As shown in Table 3, the inter-ring bond length (d_i) phenylene and thiophene ring are in the average of 1.465 Å. The dihedral angles (θ_i, i = 1 – 7) are collected in Table 4. The inter-ring torsions between thiophene and phenylene in the case of the longest oligomer $(TPdiox)_4$ were evaluated to be about $\theta_1 = 23.3°$, $\theta_2 = 154°$, $\theta_3 = 20.6°$, $\theta_4 = 159°$, $\theta_5 = 20.8°$, $\theta_6 = 154°$, $\theta_7 = 22.6°$ rather than $\theta = 27.7°$ as occurs for TPdiox. 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 non planar structure [19]. The effect of alkoxy groups grafted on 2 and 5 position of phenyl ring is clearly seen. We can notice that in the case of θ_i (i = 1, 3 , 5, and 7) the values of θ_i are smaller than those obtained in the case of θ_i (i= 2, 4 and 6). We believe that this difference is owing to attractive interaction forces taking place between the oxygen atom and the sulphur atom in the opposite thiophene ring in the case of θ_i (I = 1, 3 , 5, and 7) as suggested previously by Meille et al and Lerich et al [20]. (Fig. 6). The effect will reduce the effective conjugation of the polymer. On the other hand, the stronger electron donating effect of alkoxy groups is responsible for the reduction of the dihedral angles θ_i. The conjugation across phenylene and thiophene agrees very well with experimental results [21].

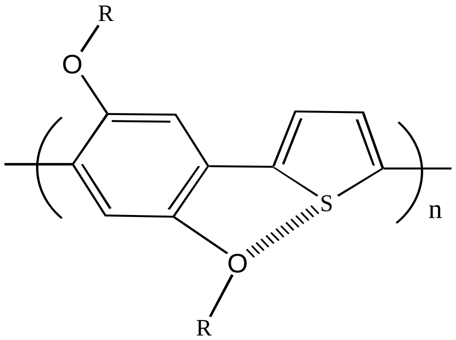


Fig. 6: Intramolecular interactions between S and O are indicated by dotted lines.

Electronic properties

Front molecular orbitals and HOMO–LUMO gaps.

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 figure 7, the HOMO possesses an antibonding character between the consecutive subunits; whereas the LUMO of all oligomers generally shows a bonding character between the subunits.

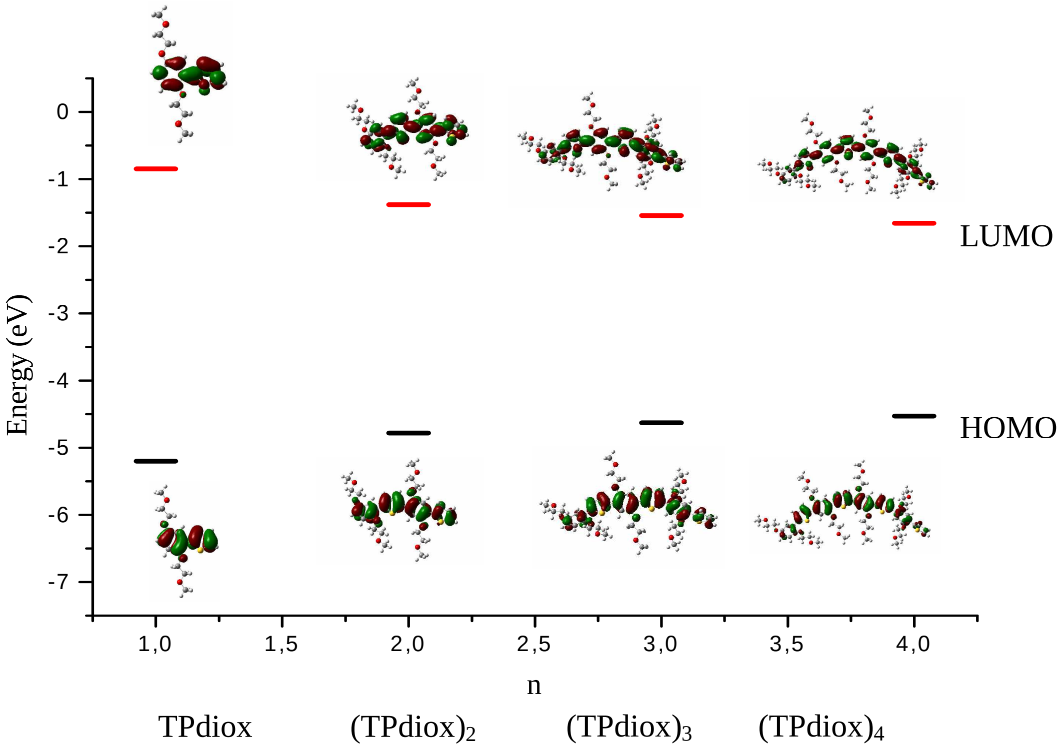


Fig 7: The HOMO and LUMO orbitals of $(TPdiox)_n$ obtained by B3LYP/6-31G*

The experiment showed that the HOMO and LUMO energies were calculated from an empirical formula proposed by Brédas et al. [22], based on the onset of the oxidation and reduction peaks measured by cyclic voltammetry. But theoretically speaking, the HOMO and LUMO energies can be calculated by DFT calculations. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tends to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers.

For a better understanding of the electronic properties of the studied oligomers, we present in Table 5, the calculated HOMO and LUMO energies, E_{gap} = LUMO-HOMO and include experimental data. In theory, the band gap of the polymer is the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) when the repeated unit number is infinite [23]. Our HOMO-LUMO gaps are obtained from the density functional theory (DFT) calculations.

Table 5: The HOMO, LUMO and HOMO–LUMO gaps energies (eV) of $(TPdiox)_n$ obtained by B3LYP/6-31 G*

Oligomer	HOMO (eV)	LUMO (eV)	E_{gap} (eV)
n = 1	- 5.20	- 0.85	4.35
n = 2	- 4.78	- 1.38	3.40
n = 3	- 4.63	- 1.54	3.09
n = 4	- 4.53	- 1.66	2.87
n = ∞			**2,41**
Exp			**2.38**

Fig. 8 displays the evolution of the calculated HOMO and LUMO energies as a function of reciprocal chain length for the series of $(TPdiox)_n$. It is known that in the case of the π-conjugated systems, the HOMO energies destabilized with the increasing of the conjugation length, whereas the LUMO energies decreased [24]. The results indicate that the chain length of polymers has more effect on electronic transition.

Interestingly, for our copolymer, we observed good agreements between the calculated HOMO–LUMO gaps and experimental data. In Table 5, it can extrapolate the HOMO–LUMO gaps energies to the infinite chain length. There is a good linear relation (about r^2 = 0.99) between the energy gap and the inverse chain length. The obtained value (2.41 eV) is close to the experiment datum 2.38 eV. The optical band gaps are derived from the absorption edge of a polymer thin film for $(TPdiox\ )_n$. The observed deviation is not more than 0.03 eV. The principal factor responsible for this deviation is that the predicted band gaps are for the isolated gas-phase chain [26].

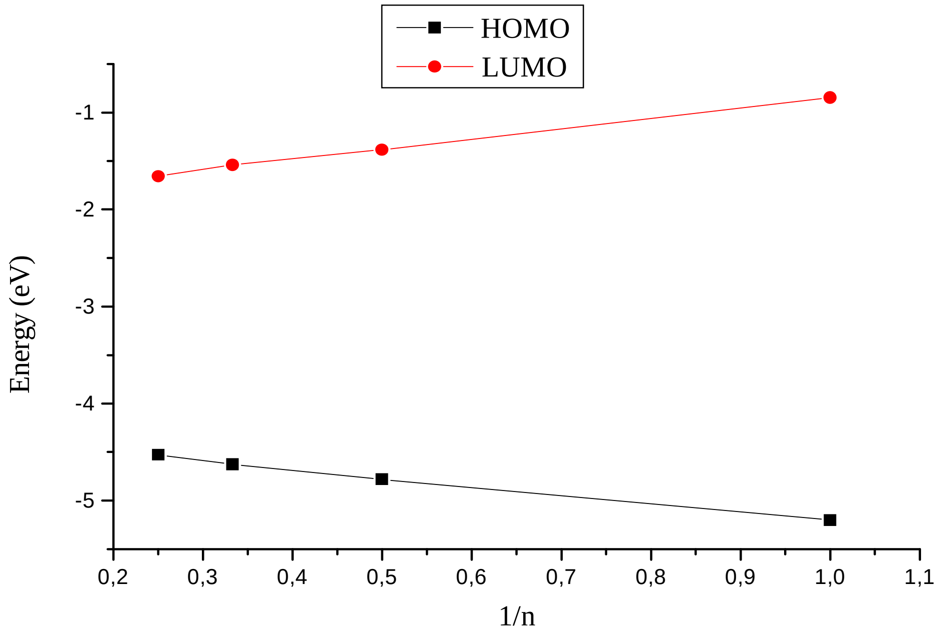


Fig. 8: The HOMO and LUMO energies obtained by B3LYP/6-31G* as a function of reciprocal chain length *n* in oligomers of $(TPdiox)_n$.

Absorption properties

The ZINDO method has been used on the basis of the optimized geometry to obtain the energy of the singlet–singlet electronic transitions and absorption properties (λ_{max}) of all oligomers $(TPdiox)_n$ under study. All electronic transitions are of the π–π* type and no localized electronic transitions are exhibited among the calculated singlet–singlet transitions.

The maximum absorption wavelength λ_{abs} for every oligomer, the corresponding oscillator strength f (given in parentheses) and the available experimental data are exhibited in Table 6.

Table 6: Absorption λ_{abs} (nm) and the corresponding oscillator strength (f) of oligomers $(TPdiox)_n$ obtained by the ZINDO method and the experimental values of the copolymer poly(TPdiox)

Oligomer	λ_{max} (nm)	E_{tr} (eV)	f
n = 1	336.86	3.68	0.53
n = 2	415.58	2.98	1.25
n = 3	446.64	2.77	1.84
n = 4	469.69	2.64	2.28
n = ∞	**506,72**		
Exp	504.00		

Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO. As in the case of the oscillator strength, the absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition and as analyzed above that with the extending molecular size, the HOMO–LUMO gaps decrease. We typically see a red shift (λ_{max} increase) as the conjugation length increases [336.86 nm for TPdiox; 415.58 nm for $(TPdiox)_2$; 446.64 for $(TPdiox)_3$ and 469.69 for $(TPdiox)_4$**].** This is an effect of atomic orbital interacting and creating molecular orbital that are split in energy. The results are a decrease of the LUMO and an increase of the HOMO energy.

These values are calculated by ZINDO method starting with optimized geometry obtained at B3LYP/6-31G* level. However, we believe that the bulk of intermolecular effect must be taken into account when considering the polymers with long chain. After considering this effect, our calculations are in good agreement with the experimental values (λ_{max} (solid) = 504 nm). The deviation between the calculation and the experiment data is not more than 35 nm. Therefore, the procedures of theoretical calculations give a good description of opto-electronic properties of the studied oligomers and can be employed to predict the electro-luminescence characteristics of other materials.

These results lead us to suggest that the longest oligomer $(TPdiox)_4$ is a good model to reflect optoelectronic properties for the parent polymer.

Conclusion

A new soluble copolymer based on thiophene and phenylene was prepared by condensation.
This copolymer seems to be suitable for organic electronic applications. This new material exhibits lower molecular weight and high photoluminescence, making it as an attractive candidate for light-emitting diode applications.
Theoretical studies, based mainly on density functional theory (DFT) calculations, are performed to several oligomers $(TPdiox)_n$ (n=1-4). Calculated results are in good agreement with experimental data. These results lead us to suggest that the longest oligomer $(TPdiox)_4$ is a good model to reflect optoelectronic properties for the parent polymer.

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