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Effect of lateral acceptor groups on the optoelectronic properties of some oligomers based on thiophene and phenylene: a computational study

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Abstract

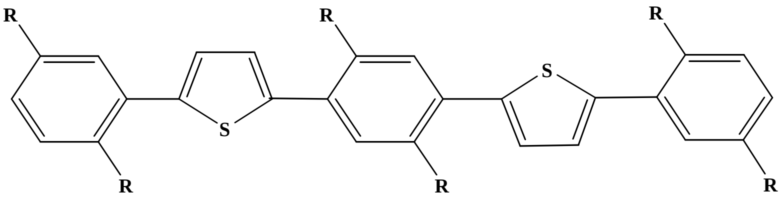
We report a theoretical study on several conjugated oligomers based on thiophene and phenylene with lateral acceptor groups. A detailed DFT study based on the B3LYP functional with 6-31G* basis set has been performed in order to optimize the geometrical structures and to calculate electronic properties. For all studied oligomers, the UV-vis spectra also were computed using the ZINDO semi-empirical method starting from the optimized structure found with B3LY/6-31G*. The results are compared with previous data obtained with oligomers having donor lateral groups. Based on this comparison, we discuss the effect of these substituents on the band gap and especially on the HOMO level. The optoelectronic properties of these molecules make them good candidates for photovoltaic applications.

Keywords: Conjugated polymer, Thiophene, phenylene, DFT, ZINDO, Electronic structure, Optical properties.

1. Introduction

Organic conjugated polymers possess interesting semiconducting properties [1] that can be exploited in many applications such as light-emitting diodes [2-9], field-effect transistors [10-18] and photovoltaic cells [19-31]. Among these materials, the conjugated oligomers based on thiophenes and phenylenes, with low band gap, have been widely studied recently due to their excellent electronic and optical properties [32-35]. These properties can be tuned by changing the side chains attached to the backbone of the oligomer. This not only provides a way to improve the electronic and optical properties, but also endows the oligomer with the property of solubility [36, 37]. This property facilitates enormously both the processing and the characterization of these materials [38] and widens the field of their applicability. A better understanding of the electronic and optical properties of these materials requires knowledge of their conformations and electronic structures. Theoretical calculations can provide useful information that helps the chemists to build a reliable structure-properties relationship for these materials [34]. Theoretical analysis of the electronic structure for various conjugated polymers and oligomers has been extensively reported. In many studies the DFT [39] method has been used to predict properties of polythiophene [40] and polyparaphenylene [41].

In this article, we have used the density functional theory (DFT) calculations in order to study the effect of lateral groups of the acceptor type on the geometrical, electronic, and optical properties of oligomers based on thiophene and phenylene. The oligomers studied are shown in Fig.1 and Table 1.



R= CN, NO_2, CH_3CO

Figure 1. Chemical structure of the studied oligomers.

The grafting of electron-attracting groups (-CN,-NO_2, -CH_3CO) increases the oxidation potential of the monomer, leading to highly reactive radical cations capable of reacting with the solvent and/or electrolyte. On the contrary, the introduction of electron-donating groups (alkoxy, alkylthio) reduces the oxidation potential of the monomer and the radical cation is stabilized. This loss of reactivity can limit the polymerization to a single coupling and can lead to the formation of short oligomers.

Table 1. Oligomers considered in this study.

	Side group (-R)	Number of side groups	Name
Oligomer 1	None (unsubstituted)	0	PTPTP
Oligomer 2	CN	6	6CNPTPTP
Oligomer 3	NO_2	6	6NO_2PTPTP
Oligomer 4	CH_3CO	6	6CH_3COPTPTP

2. Computational methodology

Quantum calculations were carried out using the 'Gaussian 09' program [42]. The geometries of the compounds were optimized using the DFT-B3LYP level which stands for Becke three parameters and Lee-Yang-Parr-functional [43]. The 6-31G* [44] basis set was used for all atoms. The geometrical structures of the neutral molecules were optimized under no constraint. The LUMO and LUMO levels also were calculated. The energy gap was evaluated as the difference between the LUMO and HOMO energies. The ground-state energies and oscillator strengths were computed using ZINDO/s [45, 46] calculations on the fully optimized geometries. These calculation methods have been successfully applied to other conjugated polymers [34, 35, 47, 48].

3. Results and discussion

3.1. Structural parameters

The optimized ground state geometries of the oligomers obtained at the B3LYP/6-31G* level are given in Fig. 2. The optimized inter-atomic bond lengths and dihedral angles are summarized in Table 2 and Table 3 respectively.

PTPTP is the unsubstituted oligomer and is used here as a reference [34]. 6OCH_3PTPTP is an oligomer with OCH_3 donor lateral side chains [34] and is used here for comparison. Another oligomer with side group donors (6FPTPTP) has also been included. The remaining three oligomers acceptor groups are the focus of this study.

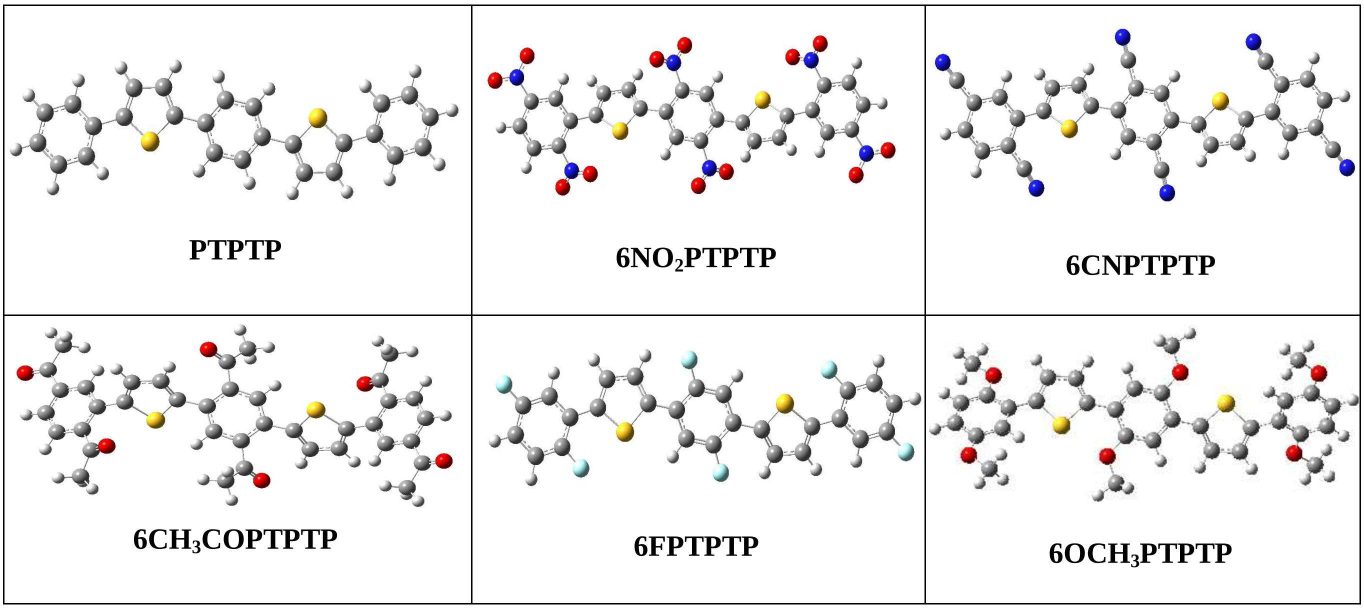


Figure 2: Optimized structures of the oligomers.

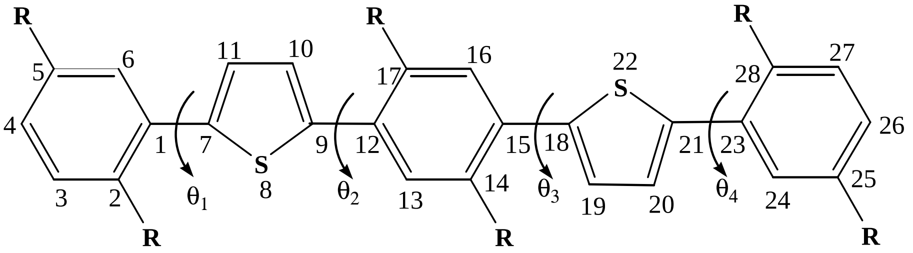


Figure 3. Structure with atomic labels and dihedral angles θ$_i$

Table 2: Optimized inter-atomic distances (Å).

Bond (Å)	**6CNPTPTP**	**6NO$_2$PTPTP**	**6CH$_3$COPTPTP**	**PTPTP**	**6FPTPTP**	**6OCH$_3$PTPTP**
C1-C2	1.420	1.414	1.423	1.408	1.405	1.416
C2-C3	1.406	1.396	1.409	1.392	1.388	1.399
C3-C4	1.386	1.387	1.390	1.397	1.393	1.391
C4-C5	1.405	1.392	1.404	1.396	1.391	1.397
C5-C6	1.400	1.387	1.402	1.393	1.384	1.395
C6-C1	1.404	1.410	1.408	1.407	1.411	1.410
C1-C7	1.469	1.476	1.475	1.466	1.464	1.468
C7-S8	1.746	1.749	1.813	1.753	1.754	1.756
S8-C9	1.750	1.742	1.835	1.754	1.752	1.756
C9-C10	1.380	1.378	1.372	1.378	1.382	1.383
C10-C11	1.414	1.412	1.429	1.418	1.413	1.414
C11-C7	1.381	1.384	1.370	1.378	1.382	1.380
C9-C12	1.465	1.468	1.470	1.463	1.461	1.464
C12-C13	1.402	1.404	1.410	1.408	1.409	1.414
C13-C14	1.399	1.388	1.400	1.388	1.382	1.391
C14-C15	1.421	1.408	1.425	1.408	1.407	1.407
C15-C16	1.402	1.404	1.408	1.408	1.409	1.414
C16-C17	1.399	1.388	1.401	1.388	1.382	1.391
C17-C12	1.421	1.408	1.426	1.408	1.407	1.407

Table 3: Optimized dihedral angles (°).

Dihedral angles (°)	**6CNPTPTP**	**6NO$_2$PTPTP**	**6CH$_3$COPTPTP**	**PTPTP**	**6FPTPTP**	**6OCH$_3$PTPTP**
θ_1	35.05	37.99	54.35	26.5	06.51	19.60
θ_2	34.10	41.83	47.98	23.5	15.88	19.60
θ_3	34.12	41.82	46.90	23.5	15.87	26.80
θ_4	35.05	38.10	51.58	26.5	06.41	26.80

As can be seen, the inter-ring distances C_1-C_7 and C_9-C_{12} (fig. 3 and table 2) are slightly larger in the acceptor oligomers in comparison with the unsubstituted or donor ones. We note also that the dihedral angles in the oligomers with acceptor groups are higher than those in the other oligomers (Table 3). For the oligomers with donor groups, the angles are smaller compared with the unsubstituted ones, and the oligomer substituted with F has dihedral angles much smaller than those of 6OCH$_3$PTPTP. The unsubstituted oligomers have dihedral angles intermediate between those of the other two types.

3.2. Electronic properties

To investigate the influence of the effect of side chains on the optoelectronic properties of the studied compounds, we present in Table 4 the DFT-calculated HOMO, LUMO, and band gap energies. The gap was evaluated theoretically as the difference between the LUMO and HOMO levels. Experimentally speaking, the HOMO and LUMO energies can be obtained from an empirical formula proposed by *Brédas et al.* [49] based on the onset of the oxidation and reduction peak measured by cyclic voltammetry. However, it is to be noted that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in thin films compared to isolated molecules as considered in the present calculations.

Table 4. Calculated HOMO, LUMO and band-gap energies for the studied oligomers.

Molecule	**HOMO (eV)**	**LUMO (eV)**	**Eg (eV)**
6CNPTPTP	- 6.465	-3.138	3.327
6CH$_3$COPTPTP	- 5.660	- 2.557	3.103
6NO$_2$PTPTP	-6.584	- 3.489	3.095
PTPTP	-5.160	-1.690	3.470
6FPTPTP	- 5.404	- 2.170	3.234
6OCH$_3$PTPTP	- 4.600	- 1.440	3.160

It can be seen that 6NO$_2$PTPTP has the smallest band gap E_g. Then E_g increases in the following order: 6CH$_3$COPTPTP, 6OCH$_3$PTPTP, 6FPTPTP, 6CNPTPTP, and finally the unsubstituted PTPTP. E_g decreases in the oligomers with acceptor or donor groups compared with the unsubstituted oligomer. It is also seen that both acceptor and donor side-chains affect the HOMO and LUMO levels substantially. However, while the acceptor groups stabilize HOMO and LUMO, the donors destabilize them.

3.3. Optical properties

The wavelengths λ_{max} (nm) found for the studied oligomers are shown in Table 5.

Table 5: λ_{max} (nm) for the studied oligomers.

Oligomer	**λ_{max}(nm)**	**Oscillator Strength**
6CNPTPTP	422.05	1.396
6NO$_2$PTPTP	511.20	0.048
6CH$_3$COPTPTP	429.01	0.101
6FPTPTP	443.95	1.745
PTPTP	414.20	1.650
6OCH$_3$PTPTP	439.88	1.600

It is seen that the oligomer with NO$_2$ side chains has the highest λ_{max} among the acceptor-substituted oligomers. Moreover, both of the oligomers with acceptor or donor groups have larger λ_{max} compared with the unsubstituted one. These results were confirmed when we determined the optical gap in oligomers substituted with acceptor groups. The optical gap is estimated using the following formula:

$$\mathbf{E_g^{opt}\ (eV) = 1240 / \lambda(nm)}$$

where λ is the absorption threshold wavelength of the material determined graphically as in Figs. 4-6. Based on this formula and the UV-vis spectra obtained by the ZINDO method, we calculated the optical gap of the studied oligomers (Fig. 4-6).

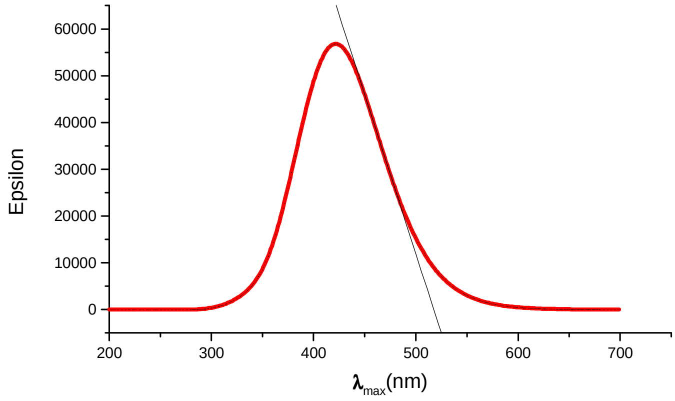


Figure 4. UV-vis spectrum of 6CNPTPTP (E_g^{opt} = 2.35 eV).

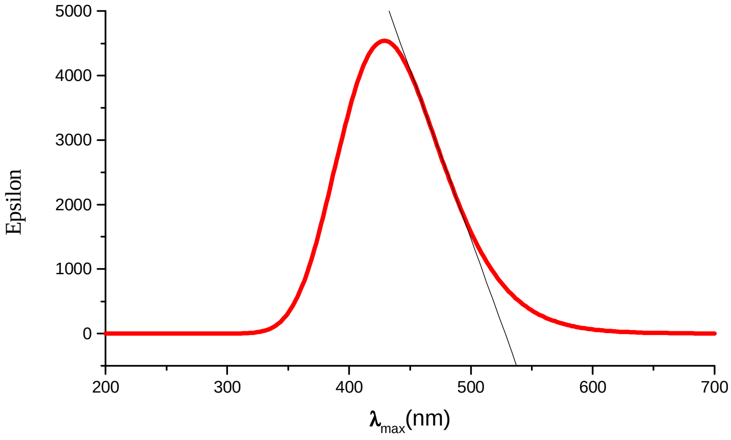


Figure 5. UV-vis spectrum of $6CH_3COPTPTP$ (E_g^{opt} = 2.30 eV).

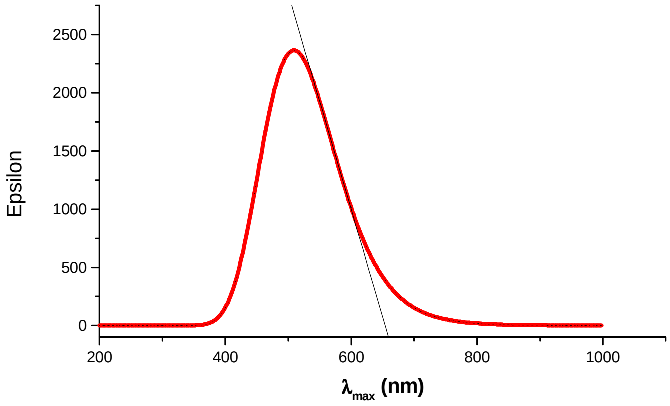


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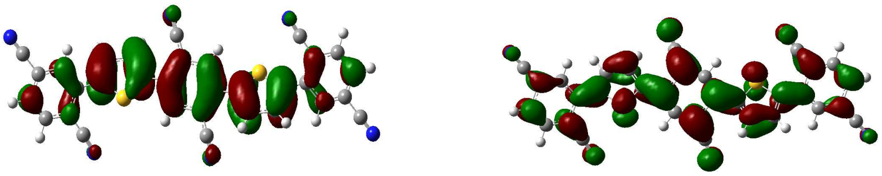
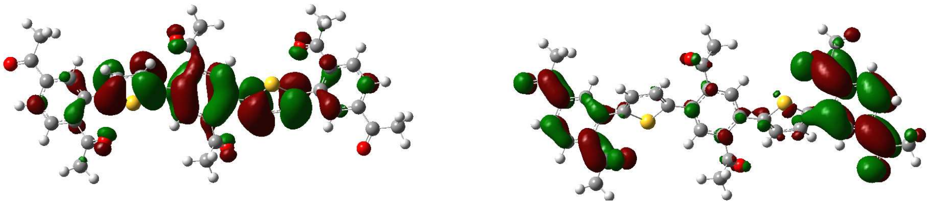
Figure 6. UV-vis spectrum of $6NO_2PTPTP$ (E_g^{opt} = 1.88 eV)

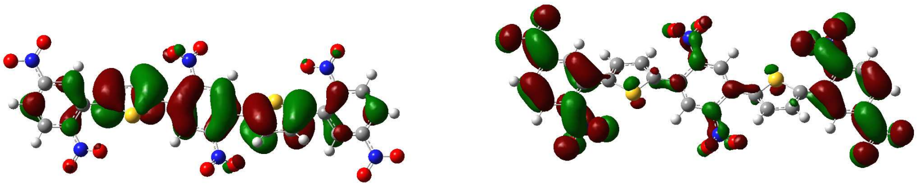
The donor groups attached to the PTPTP oligomers push the electronic density towards the main chain (cf. Fig. 7). The acceptor groups, in contrast, pull the electronic density from the main chain. Therefore, the donor groups favour the planarity of the chain cycles [34], while the acceptor groups cause a distortion in the main chain. This distortion is reflected in the intercyclic distances and dihedral angles; they increase in the acceptor case in comparison with the donor ones.



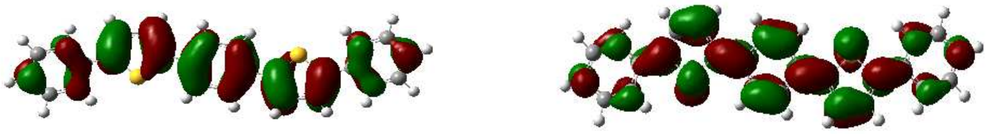
HOMO **6CNPTPTP** **LUMO**



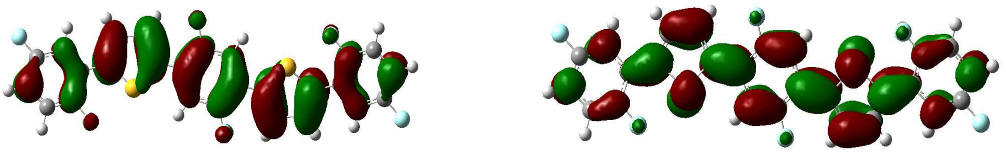
HOMO **6CH$_3$COPTPTP** **LUMO**



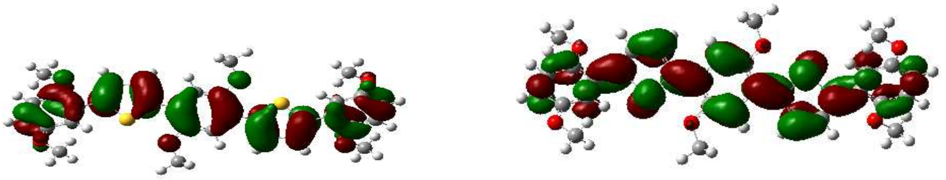
HOMO **6NO$_2$PTPTP** **LUMO**



HOMO **PTPTP** **LUMO**



HOMO **6FPTPTP** **LUMO**



HOMO **6CH$_3$OPTPTP** **LUMO**

Figure 7. Contour plots of the frontier orbitals HOMO and LUMO for the studied oligomers

The band gap energies found for the oligomers 6CNPTPTP, 6NO$_2$PTPTP, and 6CH$_3$COPTPTP are all less than the value found for the unsubstituted oligomer. This is due to the acceptor effect of the lateral side-chains. The electronic properties of some oligomers with lateral donor groups (e.g. 6FPTPTP and 6OCH$_3$PTPTP) are also included in order to see the difference between the donor and the acceptor effects. E_g decreases with the increase in the acceptor mesomeric effect (-M) in the NO$_2$, CH$_3$CO and CN groups. This explains also the difference between the value of E_g in the oligomers with acceptor groups and that in the unsubstituted one.

It was found that E_g in the oligomers with acceptor groups is comparable to that in the oligomers with donor groups. This is probably because the mesomeric effects –M and +M have approximately a same absolute value, namely, $|-M_{acceptor}| \approx |+M_{donor}|$.

The positions of LUMO and HOMO are resummarized according to Fig. 8. This figure shows the LUMO and HOMO positions for all the studied oligomers compared with an acceptor polymer ($PC_{60}BM$) [50-52] which is generally used in organic photovoltaic cells.

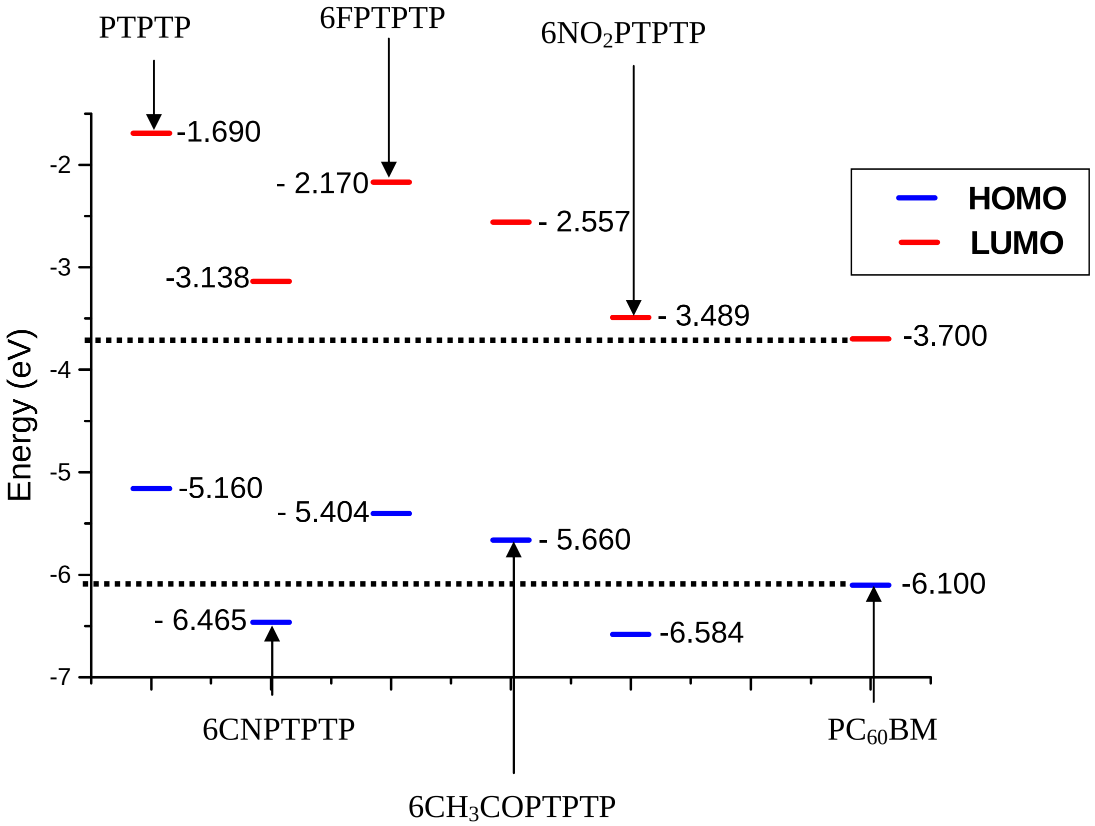


Figure 8: HOMO and LUMO levels of the oligomers compared with those of $PC_{60}BM$.

As mentioned above, it is clear that the acceptor lateral groups (NO_2, CN, CH_3CO) decrease considerably the LUMO and HOMO levels. This decrease enhances the chemical stability of these oligomers. In other words, they acquire higher ionization potentials.

In organic solar cells, Voc is linearly dependent on the HOMO level of the donor semiconductor and on the LUMO level of the acceptor semiconductor (connected respectively to the oxidation potential and reduction potential of each material) [53, 54]. This result affects directly V_{OC}, which is proportional to the difference between the LUMO of the acceptor polymer and the HOMO of the donor one:

$$V_{OC} \sim |HOMO^D| - |LUMO^A| \quad [54]$$

The HOMO level of the donor polymer must not be less than that of $PC_{60}BM$ and must not be than the work energy of ITO [54, 55]. Moreover, the LUMO level of the donor polymer must exceed the LUMO of $PC_{60}BM$ by at least 0.3 eV [54, 55]. Therefore, in Fig. 8, only oligomers with HOMO level between the HOMO and LUMO levels of $PC_{60}BM$ are attractive for photovoltaic applications.

Table 6: Energy difference between the absolute value of the oligomer's HOMO and $PC_{60}BM$'s LUMO.

Oligomer	**HOMO (eV)**	**ΔE=lHOMOl–lLUMO ($PC_{60}BM$)l LUMO ($PC_{60}BM$) = -3.7eV**
PTPTP	-5.160	1.460
6FPTPTP	- 5.404	1.704
$6CH_3COPTPTP$	- 5.660	1.960

In this study, it was found that λ_{max} of the oligomer substituted with NO_2 groups is higher than that of the other oligomers. This is because the mesomeric acceptor effect -M of NO_2 is stronger in comparison with –M of CN and CH_3CO groups. It was also seen that λ_{max} of the oligomers substituted with either type of groups (acceptor or donor) are higher than that of the unsubstituted oligomer. This is also due to the mesomeric effects +M and –M of these groups.

We have found also that the acceptor groups decrease the gap and increase λ_{max} . The same tendency has also been observed (slightly) for the donor groups. However, the acceptor groups stabilize the HOMO and LUMO levels in contrast with the donors.

The C-S bond lengths of the thiophene rings in the oligomer $6CH_3COPTPTP$ are largely superior to those of the other oligomers (cf. Table 2). This decreases the resonance energy in the thiophene oligomer cycles and therefore contributes significantly in reducing the gap of $6CH_3COPTPTP$.

The nature of the acceptor groups studied makes it possible to tailor the HOMO/LUMO positions with those of $PC_{60}BM$ so as to optimize them for photovoltaic applications. In this case, $6CH_3COPTPTP$ can be chosen for its interesting properties (E_g, λ_{max}, and $\Delta E^{D-A} = |HOMO^D| - |LUMO^A|$). 6CNPTPTP and $6NO_2PTPTP$ have HOMO levels much lower than both the HOMO level of the acceptor material $PC_{60}BM$ and the work function of ITO [54]. Therefore, they are not promising for these applications.

Conclusion

In this work, we have studied the optoelectronic properties of oligomers based on thiophene and phenylene. Three types of oligomer have been studied: unsubstituted, substituted with acceptor groups, and substituted with donor groups. It has been found that the acceptor groups decrease the gap and increase λ_{max} . The same tendency has also been observed (slightly) for the donor groups. However, the acceptor groups stabilize the HOMO and LUMO levels in contrast with the donors. The nature of the acceptor groups studied makes it possible to tailor the HOMO/LUMO positions with those of $PC_{60}BM$ so as to optimize them for photovoltaic applications. From this study, it can be concluded that the $6CH_3COPTPTP$ is promising for photovoltaic applications. Moreover, this material's side chain CH_3CO can be easily extended (CH_3-$(CH_2)_n$-CO) so as to render the material more soluble and easier in processing.

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