

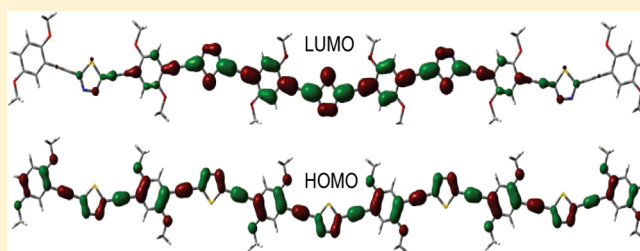
Theoretical Study of the Effect of Alkyl and Alkoxy Lateral Chains on the Structural and Electronic Properties of π -Conjugated Polymers Consisting of Phenylethynyl-1,3,4-thiadiazole

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Supporting Information

ABSTRACT: The effects of alkyl/alkoxy pendant chains on the electronic structure and properties of a typical poly(arylethynylene) (PAE) system formed by phenylethynylene units and 1,3,4-thiadiazole rings are analyzed. Optical band gaps and electronic properties (electron affinity, LUMO energy and intramolecular reorganization energy) were computed for different oligomers and then estimated for a limit polymer. The electronic properties become more influenced by the nature of the lateral chain rather than by its length. The most significant changes in the electronic properties are obtained with alkoxy side chains. The smallest band gaps were calculated for polymers containing alkoxy pendant chains. A less favored electron injection is expected for polymers with higher energy values predicted for the LUMO levels and decrease of the electron affinity. Intramolecular reorganization energies computed for all studied polymers were rather low (≤ 0.07 eV), which allows them to be considered as candidates for n-type semiconductors.



1. INTRODUCTION

In the past few years, great efforts have been devoted to improve the electronic properties and solve the processability problems arising from the use of conjugated polymers (see, e.g., refs 1–3). Different kinds of conjugated polymers and materials based on small organic molecules which show suitable properties for their use in optic and electronic applications such as organic light emitting diodes (OLEDs), photovoltaic cells, and field-effect transistors have already been synthesized.⁴ Compounds in which heterocycles such as triazole, thiadiazole, or oxadiazole and phenyl units are alternated have been widely studied due to their desirable chemical and electrical properties, i.e., narrow band gap, low intramolecular reorganization energy in electron–hole transport processes, chemical and thermal stability, high persistence length, or formation of liquid-crystalline mesophases.^{5–8} Furthermore, when those aromatic heterocycles and phenyl units are linked through acetylene groups, a π -system extending throughout the molecular structure called poly(arylethynylene) (PAE) is obtained. As a consequence of the axial symmetry of the triple bond, the conjugation of these *molecular wires* is maintained in varying degrees between adjacent aryl groups at different relative orientations.^{9–14} In general, rotational barriers as small as 1 kcal mol^{−1} have been found for PAE systems.^{12–14} Hence, this kind of extended π -system can have a wide variety of applications where efficient charge transport, fast energy transfer, and good luminescence properties are required.

One important focus of attention in molecular electronics is the search for new and efficient n-type organic semiconductors to improve both the performance and durability of current devices and to allow the design of new and more versatile architectures.⁷ The ease to inject the charge into the material and the efficiency with which electrons move inside the material are two essential factors which control the effectiveness of an n-type organic semiconductor. In this sense, the efficiency of the electron injection into the empty LUMO is related to low-energy LUMO levels and a sufficiently high electron affinity. The greater the electron affinity (EA), the most stable the system toward oxygen quenching, although if the molecule is too electrophilic, its ambient stability can be compromised.^{15,16} In typical disordered π -conjugated materials with small bandwidths (<1 eV) at room temperature, the charge motion occurs by electron hopping. According to Marcus theory, the rate constant for such a process is

$$k_{ET} \approx \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda_i k_B T}} t_{12}^2 \exp \left[\frac{-\lambda_i}{4k_B T} \right] \quad (1)$$

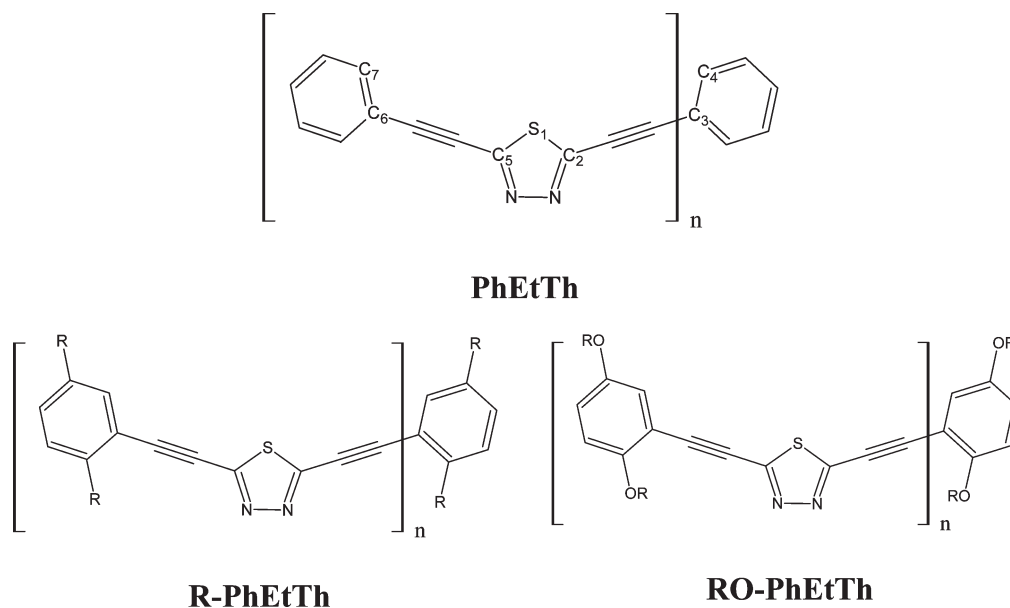
where t_{12} and λ_i , the intermolecular coupling and the inner reorganization energy, respectively, are the two key parameters

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Scheme 1. Formulas of the Selected PAE Systems



to monitor.^{17–19} In this work, we deal only with molecular wires in the isolated molecule framework, and as a consequence we have focused our interest on the first parameter, λ_1 , which should be low in order to get a high electron transfer rate.

The intramolecular reorganization energy (λ_i) consists of two terms which are related to the so-called vertical and adiabatic electron affinity, i.e., VEA and AEA, respectively and corresponding to the geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry and vice versa. AEA means the difference between the total energies of the neutral and anion at their respective equilibrium nuclear configuration while VEA represents the difference between the total energies of the neutral and anion at the optimized equilibrium nuclear configuration of the neutral molecule

$$\lambda_1 = E^0(G^*) - E^0(G^0) \quad (2)$$

$$\lambda_2 = E^*(G^0) - E^*(G^*) \quad (3)$$

$$\lambda_i = \lambda_1 + \lambda_2 \quad (4)$$

where $E^0(G^0)$ and $E^*(G^*)$ are the ground-state energies of the neutral and ionic states, respectively. $E^0(G^*)$ is the energy of the neutral molecule at the optimal ionic geometry; $E^*(G^0)$ is the energy of the charged state at the optimal geometry of the neutral molecule.^{17,18}

On the other hand, the optical band gap is a very important magnitude to control as concerns polymer solar cells. In general, the photocurrent in these devices is limited by the overlap between the absorption spectrum of the polymer and the spectrum of the sunlight, which reaches the maximum photon flux at around 1.6–1.8 eV.²⁰

We have previously studied, from a theoretical perspective, the effect of the ethynyl group ($\text{—C}\equiv\text{C—}$) and the change of the S atom by O or NH on the structure and electronic properties of a PAE such as 2,5-bis(phenylethynyl)-1,3,4-thiadiazole (PhEtTh, see Scheme 1).^{13,14} Those studies allowed us to conclude that

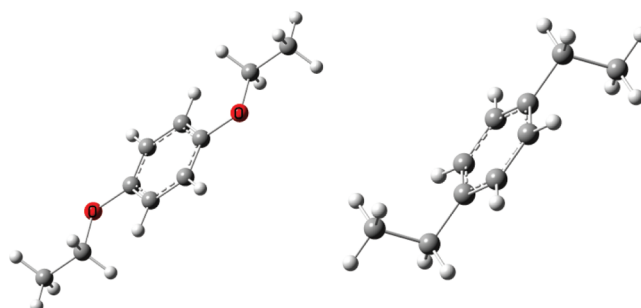


Figure 1. Spatial arrangement of two ethyl and ethoxy chains linked to the phenyl ring in the para position.

polymeric chains based on PhEtTh should yield the smallest calculated band gaps, most linear polymeric structures, highest electron affinities, and lowest LUMO energies. These last two properties are related with the n-type semiconductor character since they are essential to get an efficient charge injection in the empty LUMO orbital. It was also reported that charge injection produces significant changes in bond orders of the $\text{C—C}\equiv\text{C—C}$ moiety, increasing the torsional barrier due to the acquired cumulenic character.¹⁴ This increase in rigidity, however, could be compensated by pendant alkyl and alkoxy groups linked to the phenyl rings, which are also expected to confer a higher mobility and solubility of the polymer chains and an improvement in the rheological properties of the material. Moreover, the alkyl and alkoxy lateral chains are expected to play a significant role on the electron-conducting related properties.

Hence, the main aim of this work is the study of the effect of pendant alkyl and alkoxy groups on the structure and electronic properties of PAE systems based on phenylethynyl-thiadiazole (PhEtTh), i.e., 2,5-dialkyl-phenylethynyl-1,3,4-thiadiazole (R-PhEtTh) and 2,5-dialkoxy-phenylethynyl-1,3,4-thiadiazole (RO-PhEtTh) derivatives (see Scheme 1). Properties such as rotational barriers, bond length alternation (BLA), electronic affinity (EA), LUMO energy, and intramolecular reorganization

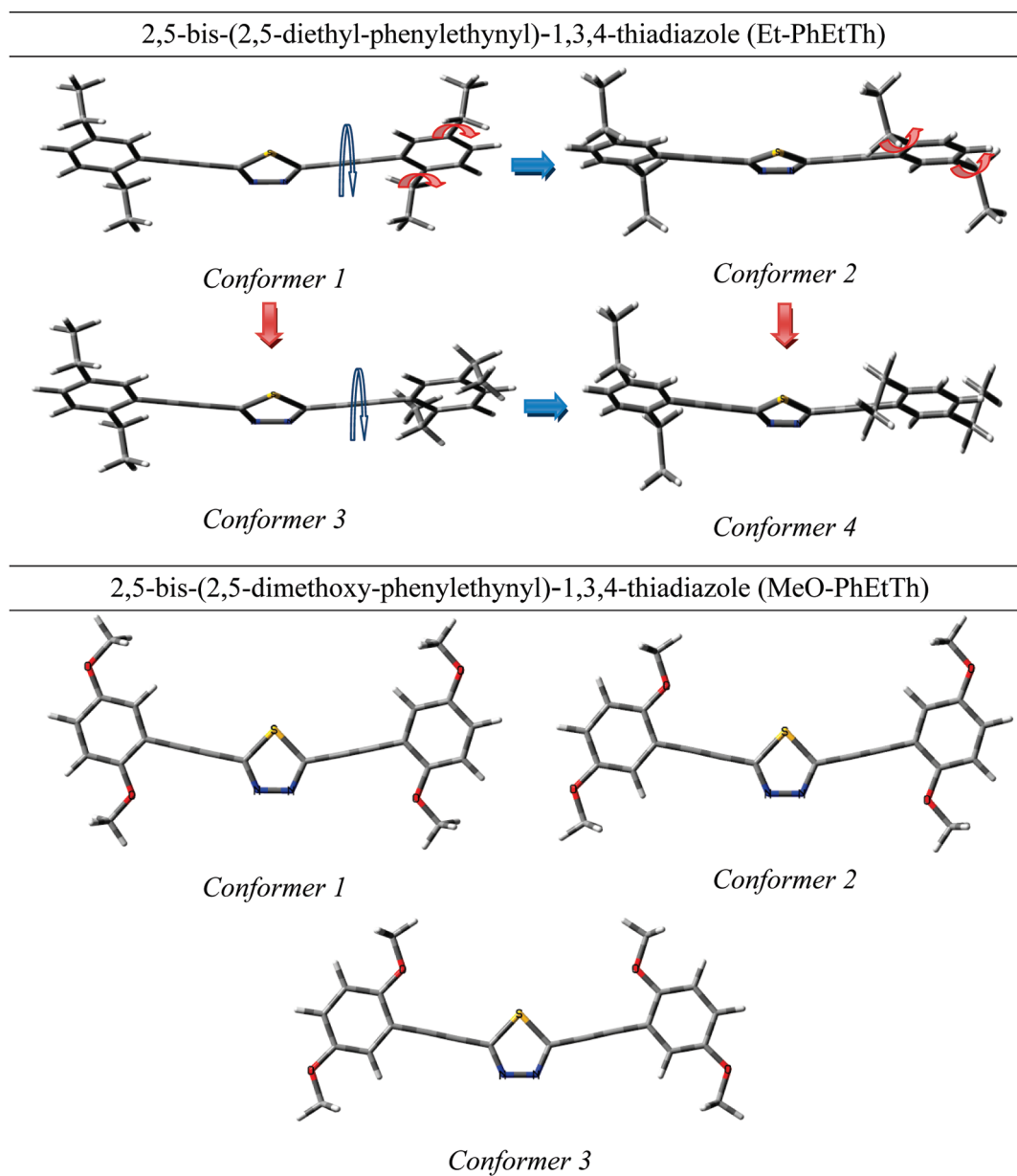


Figure 2. Conformers obtained for monomers based on R-PhEtTh and RO-PhEtTh systems. Conformer 1(2) renders conformer 3(4) acting on the dihedral angles as indicated by red arrows. Conformer 1(3) renders conformer 2(4) acting on the dihedral angles as indicated by blue arrows.

energy (λ_i) have been computed. Also, time-dependent DFT methods (TD-DFT) have been employed to estimate the optical band gap in the series of studied PAE systems and thus their absorption maxima λ_{\max} for the limit polymer. In this sense, a polymer belonging to the RO-PhEtTh set (RO- = CH₃-(CH₂)₁₁O-) was synthesized by Yasuda et al.⁶ The UV-vis spectrum of that polymer showed an absorption maximum (λ_{\max}) at 2.81 eV in CHCl₃ solution and 2.51 eV in film.

2. COMPUTATIONAL METHODOLOGY

Gaussian03 (revision E.01)²¹ has been employed for all the theoretical calculations. The DFT hybrid functional B3LYP,^{22,23} along with the 6-31G* basis set, was the combination chosen for the conformational analysis of R-PhEtTh and RO-PhEtTh systems. This analysis was performed only on the corresponding monomeric structures ($n = 1$, Scheme 1). In a second step, the

effect of the lateral-chain length on the electronic properties was investigated for the lowest-energy conformer of each set. Once the lateral chain length that saturates the studied electronic properties was determined, the simulation of the corresponding polymer structures was carried out on those systems with such an optimal lateral-chain length in order to save computational resources.

The optical band gap was estimated from high oscillator strength (f) transitions between high-energy molecular orbitals. They all turned out to be HOMO \rightarrow LUMO transition type with both orbitals completely delocalized along the whole system. Thus, time-dependent B3LYP (TD-B3LYP), PBE0 (TD-PBE0),²⁴ and M05-2X (TD-M05-2X)^{25–27} together with the 6-31G* basis set was employed to calculate that transition on oligomeric structures from $n = 1$ to 20 repeat units. Those oligomeric structures were obtained by straight replication of the

Table 1. Relative Energy (in kcal mol^{−1}) of the Different Conformers Found for RO–PhEtTh Systems at the B3LYP/6-31G* Level of Theory

	relative energy/kcal mol ^{−1}		
	conformer 1	conformer 2	conformer 3
MeO–PhEtTh	1.05	0.54	0.00
EtO–PhEtTh	0.89	0.43	0.00
PrO–PhEtTh	0.86	0.44	0.00
BuO–PhEtTh	0.90	0.54	0.00

previously optimized monodimensional periodic structures, at the B3LYP/6-31G* level making use of the Crystal Editor of Gaussian03 (revision E.01).²¹ Band gap values were then fitted to an empirical function of the number of repeat units, n , proposed by Karsten et al.²⁸ and extrapolated to the infinite case to obtain the predicted infinite polymer band gap. With the aim of evaluating the error due to edge effects, band gap values obtained for periodic chains were compared with those values reported in our previous study on discrete oligomeric structures based on the PhEtTh system with $n \leq 5$.¹⁴

As concerns the electronic properties involving anionic species such as electron affinity (EA) and intramolecular reorganization energy (λ_i), B3LYP together with the 6-31+G** basis set was employed in order to obtain more accuracy.²⁹ Those energy calculations required the previous optimization of the corresponding oligomeric structures with $n = 1, 3, 5$, and 7 repeat units at the B3LYP/6-31G* level due to computational limitations.

3. RESULTS AND DISCUSSIONS

3.1. Conformational Analysis of Pendant Chains. Due to the complexity of the conformational space of the selected systems, we have opted to explore their conformational flexibility in two steps. First, we analyzed the most favorable relative disposition of the alkyl and alkoxy chains linked to a phenyl ring. Thus, the alkoxy pendant groups arrived at an arrangement coplanar with the phenyl ring in which the $-C-O\cdots O-C-$ dihedral angle amounts to $\sim 180^\circ$, while the alkyl chains showed an alternate, up- and downward, disposition with respect to the phenyl ring plane (see Figure 1).

The second step implied the extension of the analysis to the corresponding monomer structures. In the case of the R–PhEtTh system, the analysis was carried out for ethyl pendant chains (Et–PhEtTh), the smallest pendant chains in the series which allow the expected conformers to be described. Hence, four different conformers were obtained by rotating the phenyl rings around the $C-C\equiv C-C$ moiety and by rotating the pendant groups (see Figure 2) keeping the perpendicular disposition of the alkyl chains as shown in Figure 1. Conformer 3 turned out to be the most stable although the relative energies calculated at the B3LYP/6-31G* level are small, i.e., 0.03, 0.12, and 0.11 kcal mol^{−1} for conformers 1, 2, and 4, respectively.

As concerns the conformational analysis for RO–PhEtTh compounds, it was carried out on the corresponding monomer with RO being a methoxy group (MeO–PhEtTh). Three conformers were found keeping the conformation of the alkoxy chains shown in Figure 1. In the case of RO–PhEtTh compounds, the differences in energy between the different stable conformers were significantly higher than those for the R–PhEtTh case. In Table 1, the relative energies of conformers

with respect to conformer 3 (the most stable) are shown. Nevertheless, the relative disposition of the RO– pendant chains in conformer 3 points that the lengthening of the alkoxy chains in conformer is expected to cause higher steric hindrances than for conformer 1, for which the pendant groups are further away from each other. That is the reason why the conformational analysis was extrapolated to alkoxy chains with up to four carbon atoms (Table 1), while significant differences in energy were not observed from ethoxy to butoxy group.

3.2. Effect of the Pendant Chain Length on Electronic Properties. In this section, the evolution of the electronic properties as a function of the length of the alkyl or alkoxy lateral chains is analyzed on the corresponding monomers. As mentioned above, the aim is first to determine the minimal, lateral chain length that allows the studied electronic properties to attain a steady value as chain length varies, i.e. saturation, and subsequently to use it throughout the modeling of the polymer structure.

We have then studied the torsional barrier around the $S_1-C_2-C_3-C_4$ dihedral angle, τ , while keeping fixed the $S_1-C_5-C_6-C_7$ dihedral angle, τ' (see atom numbering in Scheme 1), at the B3LYP/6-31G* level. The remaining redundant internal coordinates were optimized at each step of the dihedral angle scan. As seen in Table 2, alkyl/alkoxy lateral chains produce a non-negligible increase on the torsional barrier, $\sim 0.1/\sim 0.4$ eV, with respect to PhEtTh. The length of the pendant chains seems not to affect significantly the height of the barriers.

Another parameter related to aromaticity is the bond length alternation (BLA), which for a prototypical, conjugated polymer such as polyacetylene is defined as $\Delta r = d_{(C-C)} - d_{(C\equiv C)}$, being successfully related to band gap.³⁰ Hence, following the definition by Fu et al.,³¹ for nonclassical poly thiophenes, we have calculated the B3LYP/6-31G* and M05-2X/6-31G* values of the BLAs for each compound by subtracting the averaged length of the two C–C single bonds and the central C≡C triple bond length. As in the case of torsional barriers, the decrease of the BLA is larger for RO–PhEtTh systems and is not significantly influenced by the pendant chain length. Thus, the behavior of both torsional barriers and BLA points out that alkoxy and alkyl chains bring on an increase of the aromaticity of the system, the effect of the former being more remarkable than that of the latter.

As mentioned above, the optical band gap was studied through the energy of the HOMO \rightarrow LUMO transition by means of both TD-B3LYP/6-31+G** and TD-B3LYP/6-31G*, while the differences in energies were ≤ 0.04 eV in all cases (see Table 2). The presence of alkoxy groups provokes the energy of the HOMO \rightarrow LUMO transition to diminish by 0.4 eV while the alkyl pendant chains reduce that energy by no more than 0.1 eV. In both cases, chain length seems not to affect significantly the value of the transition energy.

As stated in the introduction, the electron affinity (EA) and intramolecular reorganization energy (λ_i) are properties related to the ease of charge injection and its mobility inside the material, respectively. Thus, the presence of electron releasing groups (alkyl and alkoxy) brings on a decrease of the EA, especially for the RO–PhEtTh series for which the energy drops ~ 0.2 eV (note that the EA has been defined as energy released by the system when an electron is added). Therefore, a less favored electron injection can be expected for those compounds. On the other hand, λ_i remains practically constant and only variations of no more than 0.02 eV are observed. The reorganization energy is

Table 2. Evolution of Some Electronic and Structural Properties as a Function of the Elongation of the Alkyl and Alkoxy Pendant Chains for Monomeric Structures Based on PhEtTh

compound	HOMO \rightarrow LUMO transition energy/eV ^{a,b}	torsional barrier/kcal mol ⁻¹ ^c	BLA/Å ^c	VEA/eV ^d	AEA/eV ^d	λ_i /eV ^d
PhEtTh	3.27(3.30)	1.16	0.1976	1.36	1.49	0.25
Me–PhEtTh	3.16(3.20)	1.28	0.1963	1.30	1.42	0.24
Et–PhEtTh	3.17(3.21)	1.26	0.1969	1.29	1.42	0.25
Pr–PhEtTh	3.16(3.19)	1.32	0.1967	1.30	1.43	0.26
Bu–PhEtTh	3.15(3.19)	1.30	0.1966	1.31	1.44	0.25
MeO–PhEtTh	2.89(2.92)	1.56	0.1947	1.19	1.32	0.27
EtO–PhEtTh	2.87(2.90)	1.55	0.1945	1.16	1.30	0.27
PrO–PhEtTh	2.86(2.89)	1.53	0.1945	1.15	1.28	0.27
BuO–PhEtTh	2.86(2.89)	1.57	0.1945	1.14	1.27	0.27

^a TD-B3LYP/6-31+G**. ^b TD-B3LYP/6-31G*. ^c B3LYP/6-31G*. ^d B3LYP/6-31+G**.

Table 3. B3LYP/6-31G* Bond Length Alternation, BLA^a (in Å), for the Periodic Chain and for Different Size Oligomers

	$n = 1$	$n = 3$	$n = 5$	$n = 7$	periodic chain
PhEtTh	0.1976	0.1951	0.1952	0.1952	0.1952
Me–PhEtTh	0.1963	0.1942	0.1942	0.1942	0.1942
MeO–PhEtTh	0.1947	0.1923	0.1924	0.1924	0.1924

^a Evaluated in the central repeat unit (see text).

related to the capability to delocalize the excess of charge in a charge transfer process.

As seen in Table 2, all the studied properties are more sensitive to the nature, alkyl or alkoxy, of the pendant chain than to the chain length. Consequently, the modeling of the corresponding oligomeric chains was carried out employing the minimal pendant chain length, Me–PhEtTh and MeO–PhEtTh, in order to save computational resources.

3.3. Approaching the Polymeric Structure and Electronic Properties. The oligomeric approximation was used to tackle the study of electronic properties of the limit polymer. Thus, both one-dimension periodic calculations of the polymeric chain and optimization of oligomeric structures containing up to $n = 7$, n being the number of repeat units, were carried out. In Table 3, the BLA values calculated for the central repeat unit of different-size oligomers are compared to those obtained from periodic calculation. In all cases, BLA decreases at least by 0.002 Å from the monomer to the corresponding trimer, but it remains essentially constant for oligomers with more than three repeat units. Thus, we can consider that the aromaticity in the center of the oligomeric chain reaches its maximum for oligomers with $n \geq 3$. Differences in BLA found between the three kinds of studied monomers are also observed for larger oligomers, the MeO–PhEtTh system being the most aromatic in all cases.

A. Optical Band Gap. As mentioned above, the optical band gap was studied through the energy of the HOMO \rightarrow LUMO transition. In Figure 3, the shape of both frontier orbitals, which are completely delocalized along the oligomer chain, is shown. TD-B3LYP, TD-PBE0, and TD-M05-2X together with the 6-31G* basis set were the methods chosen to calculate the electronic transitions on different oligomeric structures. These oligomeric structures were obtained by straight replication of a periodic chain optimized at the same level of theory. One should note that the TD-DFT approach only involves properties of the ground state, i.e., the Kohn–Sham orbitals and their

corresponding orbital energies obtained in a ground state calculation. Hence, excitation energies are expressed in terms of ground-state properties.^{32,33} Table 4 shows a summary of the band gap values obtained for oligomers containing 1, 10, and 20 repeat units. More detailed information about the oscillator strength and main components of the transition can be found in Tables 1S–3S in the Supporting Information.

The calculation of electronic transitions on oligomers modeled from straight replication of an optimized periodic unit could bear some error due to border effects since the edges of the oligomer have a typically different structure (less aromatic) than that of the central region of the chain. Nevertheless, the influence of the edges on the polymeric chain should diminish with the elongation of the chain. Thus, the optical band gap calculated for PhEtTh oligomers with $n = 2$ (see ref 14) is at the most 0.01 eV higher than the value calculated on a periodic structure. As expected, that difference is reduced with the elongation of the chain. Hence, this methodology has proven to be useful as a way to model long oligomeric chains greatly reducing the computational resources needed.

Polymer band gaps are usually calculated making use of the oligomer approximation that uses extrapolation methods which describe the correct evolution of the transition energies with $1/n$, n being the number of repeat units. While a linear fitting may be of application for the calculation of the band gaps for oligomers, the results for the polymer ($n \rightarrow \infty$) depart significantly from this straight line (see, e.g., ref 28). The optical band gaps of conjugated polymers can be fitted to an equation proposed by Karsten et al.^{28,34}

$$E(n) = E_{\infty} + (E_1 - E_{\infty}) \exp[-a(n-1)] \quad (5)$$

where E_1 and E_{∞} stand for the excitation energies for the parent compound and the infinitely long polymer ($n \rightarrow \infty$), respectively, n is the number of repeat units, $(E_1 - E_{\infty})$ means the global effect of conjugation and a is an empirical parameter that describes how fast $E(n)$ saturates to E_{∞} , i.e., how fast the limit of convergence is approached.

In Figure 4a, a fit to Karsten's equation using the band gap values calculated for MeO–PhEtTh oligomers containing up to 20 repeat units can be seen. In Table 4S (Supporting Information), the values obtained for the different parameters of Karsten's equation are collected (all fits show $r^2 \geq 0.996$). A plot comparing the band gap behavior for the three studied systems, at the TD-PBE0/6-31G* level, is shown in Figure 4b. As can be

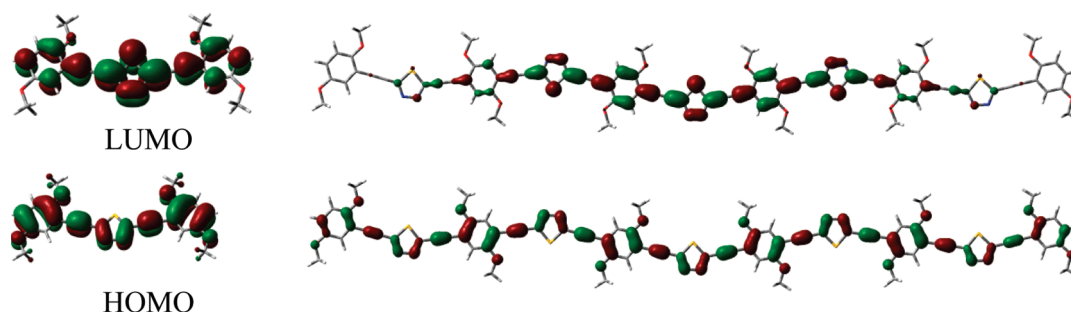


Figure 3. Shape of calculated HOMO and LUMO orbitals for the MeO-PhEtTh monomer and pentamer.

Table 4. Calculated Optical Band Gap Energies (eV) within the Oligomeric Approximation

compound	method	band gap ^a /eV			
		$n = 1$	$n = 10$	$n = 20$	$n \rightarrow \infty^b$
PhEtTh	TD-B3LYP/6-31G*	3.304	2.374	2.351	2.371 ± 0.029
	TD-PBE0/6-31G*	3.428	2.528	2.504	2.514 ± 0.030
	TD-M05-2X/6-31G*	3.919	3.207	3.186	3.204 ± 0.027
Me-PhEtTh	TD-B3LYP/6-31G*	3.202	2.312	2.289	2.308 ± 0.028
	TD-PBE0/6-31G*	3.324	2.462	2.438	2.458 ± 0.029
	TD-M05-2X/6-31G*	3.824	3.135	3.115	3.132 ± 0.026
MeO-PhEtTh	TD-B3LYP/6-31G*	2.919	2.128	2.105	2.123 ± 0.026
	TD-PBE0/6-31G*	3.052	2.269	2.247	2.265 ± 0.028
	TD-M05-2X/6-31G*	3.637	2.951	2.932	2.949 ± 0.026
DiO-PhEtTh	experimental ^c	2.81			

^a More detailed tables containing the energy of the electronic transition for each oligomer appear in the Supporting Information. ^b Values for the limit polymer were obtained from Karsten's equation (eq 5 and refs 28 and 34 in the paper). ^c Experimental value reported for poly-2-(2,5-bis-didodecyloxy-4-ethynylphenylethynyl)-1,3,4-thiadiazole (DiO-PhEtTh) in CHCl₃, ref.⁶

seen, the differences in band gap values between the different systems trend to reduce with the increase in size of the oligomeric chain. For instance, considering TD-B3LYP values, the difference in band gap for Me-PhEtTh with respect to PhEtTh drops from 0.102 eV for $n = 1$ to 0.063 eV in the limit polymer ($n \rightarrow \infty$). In the case of MeO-PhEtTh with respect to PhEtTh, that difference undergoes a higher decrease, from 0.385 eV for $n = 1$ to 0.248 eV for the limit polymer.

The MeO-PhEtTh system exhibits the smallest calculated band gap among the studied limit polymers, with values between 2.949 eV (TD-M05-2X) and 2.265 eV (TD-B3LYP). In this sense, an experimental λ_{\max} of 2.81 eV, in CHCl₃ solution, was reported for a polymer belonging to the RO-PhEtTh set, poly-2-(2,5-bis-didodecyloxy-4-ethynylphenylethynyl)-1,3,4-thiadiazole (DiO-PhEtTh).⁶ Although the experimental λ_{\max} for the MeO-PhEtTh polymer is not known, that value should not be too far from the value reported for the DiO-PhEtTh polymer (2.81 eV) taking into account the weak influence of the pendant chain length and the CHCl₃ solvent on the optical band gap (see ref 13). Thus, theoretical estimations seem to be consistent with that experimental value, which lies within the range of values obtained with TD-PBE0 and TD-M05-2X. The latter overestimates the band gap but yields the closest value to the expected experimental value. Anyhow, although it is expected that

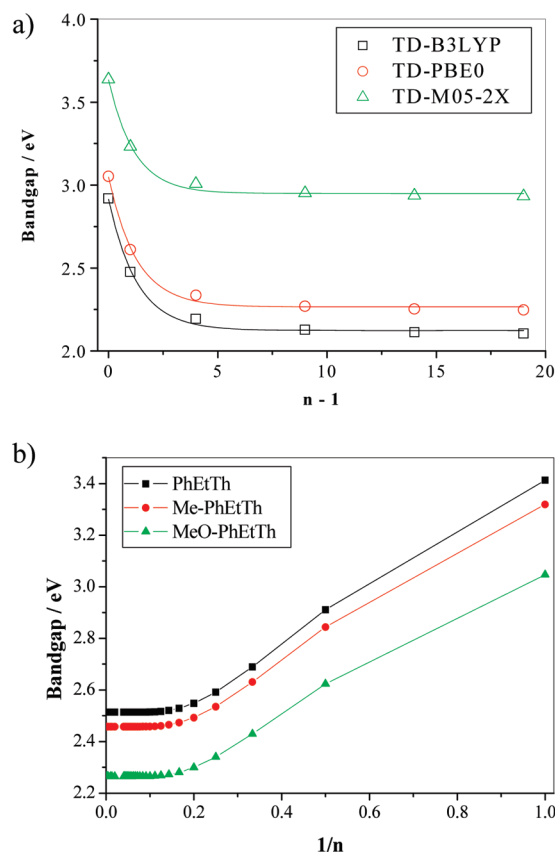


Figure 4. (a) Band gap values for MeO-PhEtTh oligomers obtained with different methods fitted to Karsten's equation. (b) Plot of the band gap values obtained from each fitting to Karsten's equation for the three studied polymers at the TD-PBE0/6-31G* level of theory.

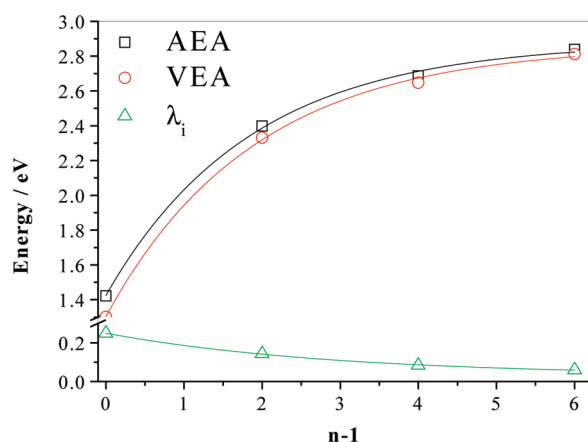
RO-PhEtTh polymers will show the lowest band gaps, those are still far from the values needed for a polymer to be used in solar cells.²⁰

B. Charge Injection. It was already mentioned that low LUMO energy levels can facilitate electron injection and transport, leading to an n-type material.¹⁶ Table 5 collects the calculated LUMO energies for the oligomers generated by straight replication of the repeat unit from a periodic calculation. This way, LUMO levels of oligomers with up to $n = 20$ were calculated with B3LYP, PBE0, and M05-2X methods along with the 6-31G* basis set. A Karsten-like equation was employed to fit the energy values as a function of n in order to obtain a LUMO-level estimation for the limit polymer.^{28,34} In all mathematical fits $r^2 \geq 0.996$ were obtained, but the lack of experimental data

Table 5. Calculated LUMO Energy for the Studied Oligomers (n , number of repeat units)

compound	n	LUMO energy/eV		
		B3LYP/6-31G*	PBE0/6-31G*	M05-2X/6-31G*
PhEtTh	1	-2.319	-2.241	-1.408
	2	-2.770	-2.709	-1.909
	5	-3.073	-3.021	-2.224
	10	-3.150	-3.099	-2.296
	15	-3.166	-3.115	-2.311
	20	-3.171	-3.121	-2.316
	$n \rightarrow \infty^a$	-3.154 ± 0.028	-3.103 ± 0.029	-2.299 ± 0.028
Me-PhEtTh	1	-2.235	-2.156	-1.347
	2	-2.673	-2.609	-1.829
	5	-2.973	-2.918	-2.139
	10	-3.049	-2.995	-2.211
	15	-3.065	-3.012	-2.225
	20	-3.071	-3.017	-2.231
	$n \rightarrow \infty^a$	-3.054 ± 0.028	-3.000 ± 0.028	-2.214 ± 0.027
MeO-PhEtTh	1	-2.069	-1.992	-1.194
	2	-2.506	-2.447	-1.682
	5	-2.801	-2.752	-1.986
	10	-2.877	-2.829	-2.056
	15	-2.893	-2.845	-2.071
	20	-2.899	-2.851	-2.076
	$n \rightarrow \infty^a$	-2.882 ± 0.028	-2.833 ± 0.029	-2.059 ± 0.057

^aValues for the limit polymer were obtained from a Karsten-like equation (eq 5 and refs ²⁸ and ³⁴ in the manuscript).

**Figure 5.** Fit of AEA, VEA, and λ_i values obtained for Me-PhEtTh oligomer methods as Karsten-like equations.

prevents us to conclude about the accuracy of the theoretical estimations. In general, the energies calculated with both B3LYP and PBE0 functionals are very close to each other while those calculated at the M05-2X level are ~ 0.8 eV higher than the first ones. PhEtTh is the system that shows the smallest LUMO energies regardless the level of theory employed. Values calculated for PhEtTh with long oligomers ($n \leq 20$) generated by direct replication of a periodic unit are only slightly lower than those obtained in our previous work, where all oligomers were previously optimized. In that case, it was necessary to work with shorter oligomers ($n \leq 5$) and more computational resources

Table 6. Calculated AEA, VEA, and λ_i (eV) within the Oligomeric Approximation

compound	property	$n = 1$	$n = 3$	$n = 5$	$n = 7$	$n \rightarrow \infty^a$
PhEtTh	AEA	1.489	2.493	2.781	2.958	2.999 ± 0.129
	VEA	1.361	2.425	2.746	2.929	2.981 ± 0.119
	λ_i	0.257	0.143	0.089	0.074	0.058 ± 0.016
Me-PhEtTh	AEA	1.422	2.399	2.686	2.839	2.880 ± 0.091
	VEA	1.301	2.332	2.648	2.812	2.863 ± 0.091
	λ_i	0.249	0.143	0.084	0.060	0.030 ± 0.017
MeO-PhEtTh	AEA	1.320	2.277	2.558	2.704	2.744 ± 0.084
	VEA	1.188	2.205	2.516	2.675	2.724 ± 0.086
	λ_i	0.275	0.157	0.095	0.087	0.069 ± 0.034

^aValues for the limit polymer were obtained from a Karsten-like equation (eq 5 and refs 28 and 34 in the paper).

were needed, to finally obtain differences at most of 0.06 eV between both methodologies in the calculated LUMO energies for the limit polymer.

As seen in Table 5, the alkyl/alkoxy lateral chains raise the LUMO level 0.085–0.103 eV/0.240–0.272 eV. Anyhow, B3LYP and PBE0 calculated LUMO energies for the limit polymer and oligomers with $n \geq 5$ are of the same order as the Ca electrode's work function ($\phi = -2.9$ eV) which is an electrode commonly used in the charge injection into n-type semiconductors or the newly proposed Sm electrode ($\phi = -2.7$ eV).^{35,36} Thus, it could be expected that the electron injection is controlled by the height of the potential barrier at the interface; i.e., the difference between the LUMO energy level and the metal electrode's work function (ϕ_i). For Sm and Ca electrodes $E_{\text{LUMO}} - \phi_i < 0.3$ eV and thus a nearly Ohmic contact could be considered. Nevertheless, LUMO energies of all our systems are far from the work function of other common electrodes such as Al ($\phi = -4.1$ eV) or Mg ($\phi = -3.7$ eV).^{37,38}

Electron affinity is of great importance for a material to be considered as n-type semiconductor and must be high enough to allow efficient injection of electrons into the empty LUMO of the semiconductor molecule. Electron affinities were calculated at the B3LYP/6-31+G** level on the corresponding oligomeric structures previously optimized with B3LYP/6-31G* since open-shell anionic structures cannot be modeled for a periodic calculation in Gaussian03. Like in the case of LUMO energies, values of adiabatic and vertical electron affinities were fitted to a Karsten-like equation in order to estimate their values in the limit polymer.^{28,34} In Figure 5, an example of such a fitting for the Me-PhEtTh system is shown (in all mathematical fits $r^2 \geq 0.998$ were obtained). The values calculated for the different oligomers with up to seven repeat units and those estimated for the limit polymer are collected in Table 6. First of all, it must be mentioned there is practically no difference between EAs calculated with B3LYP/6-31+G**//B3LYP/6-31G*, in this case, and those calculated with B3LYP/6-31+G**//B3LYP/6-31+G** in the case of monomers (collected in Table 2). Thus, it seems that the basis set with which the oligomeric structure was modeled does not influence appreciably the value of electron affinity. Nevertheless, significant differences around 0.3–0.4 eV were found with respect to EAs calculated with B3LYP/6-31G*//B3LYP/6-31G* in our previous work on PhEtTh. The use of basis sets containing diffuse functions has been recommended for energy calculations, in general, and open-shell system calculations, in particular.²⁹

It appears that from a practical standpoint, the electron affinity needs to be at least 3.0 eV but should not be much greater than 4.0 eV, the upper limit where a molecule that is too electrophilic could have stability problems in ambient conditions.¹⁵ As seen in Table 6, PhEtTh is the compound with the highest electron affinity in the series, for which an AEA of 2.999 eV was estimated for the limit polymer. Thus, the incorporation of alkyl and alkoxy lateral chain produces a decrease of the calculated AEA of 0.119 and 0.255 eV, respectively.

Electron affinity can also give an idea about the stability of the radical ion molecule toward quenching caused by molecular oxygen.⁷ The calculated AEA for molecular oxygen is 0.59 eV at the B3LYP level of theory while the experimental electron affinity has been determined by photoelectron spectroscopy as 0.448 ± 0.006 eV.^{7,39} In this sense, EAs calculated for all the compounds studied are clearly higher than the experimental and theoretical values reported for molecular oxygen.

C). *Electronic Transference*. As previously introduced, the rate constant for electron transfer (k_{ET}) within the framework of Marcus theory depends on two key parameters, i.e., the reorganization energy for the intramolecular electron transfer (λ_i) and the electronic coupling element between neighboring molecules (t_{12}). The latter needs a deep analysis on the spatial conformation adopted by two oligomeric chains although a good estimation can be obtained making use of the so-called dimer approach, according to which the value of t_{12} turns out to be half the splitting of the LUMO level for a cluster of two neutral molecules.¹⁵ In the present work, wherein we are considering only molecular wires in the isolated molecule framework, we have focused our interest only on the first parameter, λ_i , which should be low in order to get a high electron transfer rate. The calculated values appear in Table 6. As can be seen, the values of λ_i were calculated with $n = 1, 3, 5$, and 7 repeat units and fitted to a Karsten-like exponential equation obtaining $r^2 \geq 0.996$ (see Figure 5). Values estimated for the limit polymer are within the range 0.030–0.069 eV and are low enough to consider the studied limit polymer as n-type semiconductor. For reference compounds like pentacene, values of the same order (0.13 eV) have been reported.^{6,40,41}

4. CONCLUSIONS

The presence of lateral chains in a formulation of the polymer can improve the solubility of the polymeric chains and its rheological properties in general. Nevertheless, the lateral chains can also affect the electronic structure of the system. Thus, in the present work, we have studied from a theoretical perspective the effect of the incorporation of alkyl and alkoxy lateral chains in a PhEtTh polymeric chain on electronic properties related to electron conduction and optoelectronic properties.

In general, it was observed that electronic properties are more influenced by the nature of the lateral chain (alkyl or alkoxy) than by its length. Therefore, in order to save computational resources, the modeling of the corresponding polymeric structures was carried out with the corresponding minimum size lateral chains, i.e., methyl and methoxy.

The optical band gap was calculated through different TD-DFT calculations of the HOMO \rightarrow LUMO transition energy on the structure of oligomers obtained by straight replication of a previously optimized periodic unit. Optical band gaps for the limit polymer were obtained by fitting the transition energy data to an equation proposed by Karsten et al.^{28,34} Thus, it was

estimated that the incorporation to the structure of alkoxy lateral chains should reduce the optical band gap for the limit polymer in 0.248–0.255 eV. Therefore, the smallest band gap values (2.949–2.123 eV) were calculated for the MeO–PhEtTh polymer. Those values are consistent with the experimental λ_{max} (2.81 eV) reported for a polymer belonging to the RO–PhEtTh set.⁶

LUMO energy levels and electron affinity (EA) are two properties related to electron injection. The former was also fitted to a Karsten-like equation obtaining values for the limit polymer. As a result, the incorporation of both alkyl and alkoxy side chains raises the LUMO levels by 0.085–0.272 eV. Nevertheless, all LUMO energies calculated with B3LYP/6-31G* and PBE0/6-31G* for the limit polymer and oligomers with $n \geq 5$ repeat units are of the same order as the Ca electrode's work function ($\phi = -2.9$ eV) which is an electrode commonly used for charge injection into n-type semiconductors or the newly proposed Sm electrode ($\phi = -2.7$ eV).^{35,36} The incorporation of alkyl and alkoxy lateral chains also produces a decrease of the calculated adiabatic EA of 0.119 and 0.255 eV, respectively.

Intramolecular reorganization energies (λ_i) were calculated for the series of oligomers with $n = 1, 3, 5$, and 7 repeat units and fitted to a Karsten-like exponential equation. Values estimated for all limit polymers are within the range 0.030–0.069 eV and are low enough to allow them to be considered as n-type semiconductors in comparison with other reference compounds like pentacene ($\lambda_i = 0.13$ eV).^{6,40,41}

■ ASSOCIATED CONTENT

S Supporting Information. Detailed information about the oscillator strength and main components of the calculated electronic transitions and data from the fit of the band gap values to Karsten's equation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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