

From Poly(3,4-ethylenedioxythiophene) to Poly(3,4-phenylenedioxythiophene): Impact of the Substitution of the Ethylene Bridge by the Phenyl Ring on the Molecular Properties

Sergio Carrión,[†] Francisco Rodríguez-Ropero,[†] David Aradilla,[†] David Zanuy,[†] Jordi Casanovas,^{*,‡} and Carlos Alemán^{*,†,§}

Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal 647, Barcelona E-08028, Spain, Departament de Química, Escola Politècnica Superior, Universitat de Lleida, c/ Jaume II n°69, Lleida E-25001, Spain, and Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain

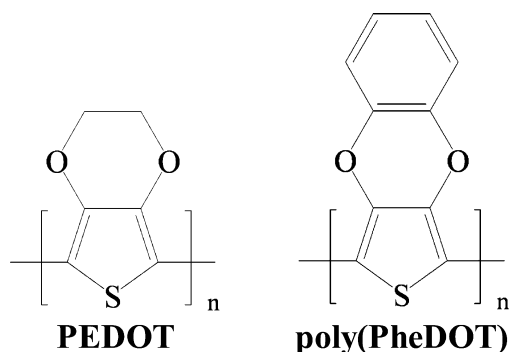
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The structural and electronic properties of poly(3,4-phenylenedioxythiophene) and poly(3,4-ethylenedioxythiophene) have been studied using quantum mechanical methods. Calculations have been performed considering a series of oligomers up to 12 repeating units in the neutral and cation states, results being used to extrapolate the properties of the two polymers in the undoped and doped states. Moreover, the electronic properties were estimated in the gas phase and acetonitrile solution, the latter solvent being used in the electrogeneration of the two conducting polymers. A detailed analysis of the results indicates that, although the π – π^* transition energy of poly(3,4-ethylenedioxythiophene) is lower than that of poly(3,4-phenylenedioxythiophene) in the neutral state, the latter behaves as excellent electronic conductor upon p-doping. Accordingly, the oxidized poly(3,4-phenylenedioxythiophene) shows the lowest π – π^* electron transition energy.

Introduction

Since Shirakawa and co-workers discovered in 1977 that polyacetylene presents a dramatic increase of its electrical conductivity upon charge transfer oxidative doping,¹ the interest toward conducting polymers (CPs) has steadily increased because of their wide range of technological applications in fields such as electronics, biomedical engineering, and optics.² Among the more prominent families of CPs are those based on thiophene because of the high environmental stability of their doped and undoped states, and the ease of tuning their chemical structure to allow control of both the electrochemical behavior and optical properties.³ In this sense poly(3,4-ethylenedioxythiophene), abbreviated PEDOT (Scheme 1), has been settled among the most successful CPs due to a combination of properties, i.e., moderate band gap, low oxidation potential, high conductivity, good optical transparency and exceptional environmental stability.^{4–6} Due to these properties PEDOT attracted considerable interest, being used for many technological applications that were rapidly developed, e.g., antistatic coatings, electrode material in supercapacitors, hole injection layer in organic light-emitting diodes and solar cells.^{7–10} It should be remarked that, in addition to their strong electron-donating effects, the oxygen atoms attached to the β,β' positions of the thiophene ring prevent the formation of parasitic α – β linkages during the polymerization of the 3,4-ethylenedioxythiophene (EDOT) monomers. Thus, the excellent properties of PEDOT combined with the high reactivity conferred to the free α,α' -positions makes EDOT a very attractive building block for the design of new classes of functional π -conjugated systems.¹¹

SCHEME 1



The major drawback of PEDOT is its low solubility, which limits its practical usage in some industrial applications. The solubility of PEDOT is frequently improved by incorporating long alkyl chains, which are tethered to the sp^3 carbon atoms of the ethylenedioxy bridge through the formation of covalent linkages.¹² However, covalent grafting of long alkyl side chains presents two important disadvantages: (i) the substituted carbon atoms become chiral producing stereoisomers, and (ii) the distance between the polyconjugated molecules increases reducing the hole mobility. The use of water-soluble polyelectrolytes, such as poly(styrenesulfonic acid) (PSS), is an alternative strategy frequently used to increase the solubility of PEDOT.¹³ However, the electrical properties of PEDOT:PSS are worse than those obtained when this CP is combined with small inorganic electrolytes, like, for example, $LiClO_4$.¹⁴

To obtain soluble PEDOT derivatives with good electrical, electrochemical, and structural properties, Ritter¹⁵ and Roncali¹⁶ synthesized poly(3,4-phenylenedioxythiophene), abbreviated poly(PheDOT) (Scheme 1). The grafting of a long alkyl chain in the sp^2 carbon of the phenyl group allows better processability, keeping the solubility improvement in organic solvents.¹⁷

* E-mail: jcasanovas@quimica.udl.cat and carlos.aleman@upc.edu.

[†] Departament d'Enginyeria Química, Universitat Politècnica de Catalunya.

[‡] Universitat de Lleida.

[§] Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya.

Moreover, both experimental X-ray diffraction and *in silico* studies evidenced the planarity of poly(PheDOT), which favors both the formation of highly ordered arrangements in the solid state and the intermolecular delocalization of π -electrons.¹⁸

The aforementioned characteristics make poly(PheDOT) a potential candidate to replace PEDOT as a building block of soluble CPs. To ascertain if the performance of poly(PheDOT) is as high as that of PEDOT, a comparative study of them in terms of electronic structure and properties appears to be necessary. In this work we investigate the molecular and electronic structure of poly(PheDOT) and PEDOT using quantum mechanical (QM) calculations, which have been demonstrated to be very useful to study the geometrical and electronic properties of a large number of CPs.^{19–22} More specifically, density functional theory (DFT) calculations have been performed on series of oligomers containing up to 12 repeating units in both the neutral and monocationic states.

Methods

All the calculations were performed with the Gaussian 09 computer program.²³ Complete geometry optimizations of both neutral and oxidized (PheDOT)_{*n*} and (EDOT)_{*n*} oligomers, where *n* refers to the number of monomers, were carried out considering the *antiplanar* conformation as the starting geometry; i.e., all the inter-ring dihedral angles S–C–C–S were initially set at 180°. This was reported to be the most stable conformation of the two polymers.^{20,21} Calculations were performed using the Becke three-parameter exchange density functional²⁴ combined with the LYP correlation functional²⁵ (B3LYP), the 6-31G(d)²⁶ basis set being employed in all cases. Recent studies showed that this methodology provides excellent results for heterocyclic oligomers using reasonable computational resources.^{22,27} The restricted formalism was considered for calculations on neutral oligomers (closed-shell systems), while the unrestricted DFT formalism UB3LYP was used for oxidized oligomers. No symmetry constraints were used in the calculations.

The π – π^* lowest electron transition energies (ϵ_g) were obtained using two different strategies. In the first one, ϵ_g was estimated using Koopmans' theorem (KT)²⁸ as the difference between the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), i.e., $\epsilon_g = \epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$. Thus, Levy and Nagy evidenced that ϵ_g can be rightly estimated by this procedure using DFT calculations.²⁹ In the second strategy, ϵ_g was evaluated using the time-dependent density functional theory (TD-DFT).³⁰ More specifically, electronic excitations were evaluated at the (U)PBE0 level of theory,³¹ which is based on the generalized gradient functional PBE (Perdew–Burke–Ernzerhof)³² with 25% exact exchange, combined with the 6-31G(d) basis set using the geometries optimized at the (U)B3LYP/6-31G(d) level. It should be mentioned that the single point TD-DFT calculations using the PBE0 functional has been reported to be a powerful tool for reproducing the main features of the π – π^* band in polycyclic organic compounds.^{33–35} Results obtained for neutral oligomers were used to provide a preliminary estimation of the ionization potentials (IPs) by applying the KT,²⁸ i.e., relating the IP to the negative energy of the HOMO ($\text{IP} = -\epsilon_{\text{HOMO}}$), which according to the Janak' theorem can be applied to DFT calculations.³⁶

The first adiabatic ionization potential (IP_{1a}) was calculated as the energy difference between the optimized structures of the cation radical and neutral oligomers. To evaluate the influence of the solvent media in IP_{1a} , calculations in acetonitrile solution were performed for the oxidized and neutral states of

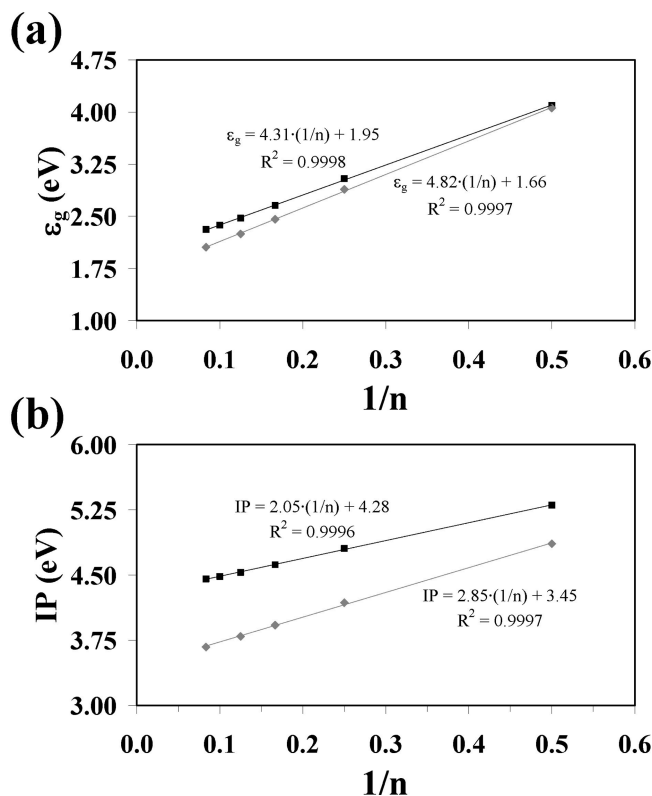


Figure 1. Comparison of (a) the π – π^* transition energy (ϵ_g ; in eV) and (b) the ionization potential (IP; in eV) obtained using the Koopmans' theorem plotted against the inverse number of repeating units ($1/n$) for (PheDOT)_{*n*} (black squares) and (EDOT)_{*n*} (gray diamonds) oligomers. Calculations were performed at the B3LYP/6-31G(d) level. Lines correspond to the linear fits (a) $\epsilon_g = a \cdot 1/n + b$ and (b) $\text{IP} = a \cdot 1/n + b$.

(EDOT)_{*n*} and (PheDOT)_{*n*} oligomers. Specifically, complete geometry optimizations of both the radical cations and the neutral molecules were performed using the previous gas-phase geometries as starting points. It should be mentioned that acetonitrile is the organic solvent typically used in the electro-generation of two such CPs.^{14,18} We have chosen the SMD solvation model, which has been recently implemented in Gaussian.³⁷ This continuum solvation model is based on the QM charge density of a solute interacting with a continuum dielectric medium describing the solvent.

For the radical cations the distribution of positive charges through the repeat units was obtained by using the Mulliken charges. It was previously shown that natural population analysis predicts charges for unsubstituted thiophene oligomers that are similar to the Mulliken ones.^{22c} The bond length alternation (BLA) pattern, which provides information about the benzenoid or quinoid structure of the oligomers, was defined by the C–C bond lengths along the molecular backbone, i.e., in the π -system.

Results and Discussion

Parts a and b of Figure 1 compare the variation of the ϵ_g and the IP, respectively, against $1/n$ of both (EDOT)_{*n*} and (PheDOT)_{*n*} in the neutral state using the KT. As can be seen, all (PheDOT)_{*n*} oligomers present a larger ϵ_g than their (EDOT)_{*n*} analogues, which is fully consistent with previous theoretical and experimental determinations on shorter oligomers.¹⁸ This feature might be attributed to the distance between the oxygen atoms and the carbon atoms of the phenylene group (1.386 Å in average) in (PheDOT)_{*n*} oligomers, which is shorter than that found between

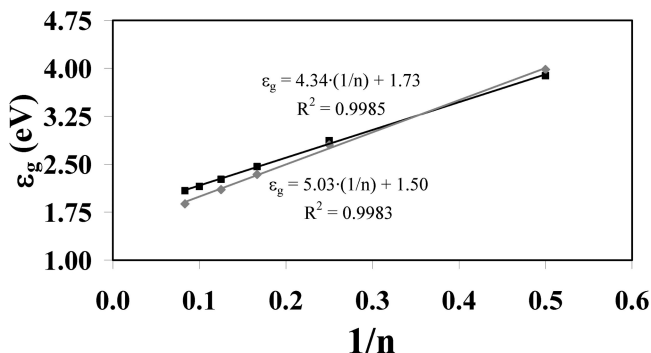


Figure 2. Evolution of the π – π^* lowest transition energy (ϵ_g ; in eV) obtained using TD-PBE0/6-31G(d) calculations plotted against the inverse number of repeating units ($1/n$) for (PheDOT) $_n$ (black squares) and (EDOT) $_n$ (gray diamonds) oligomers. Lines correspond to the linear fits $\epsilon_g = a \cdot 1/n + b$.

the oxygen atoms and the carbon atoms of the ethylene bridge (1.430 Å in average) in (EDOT) $_n$. Consequently, the electron-donating effect of the oxygen atoms is precluded in (PheDOT) $_n$. Linear regression analyses ($\epsilon_g = a \cdot 1/n + b$) using the ϵ_g values predicted by the KT were performed to extrapolate the ϵ_g of the two CPs considering idealized chains with infinite repeating units. Results, $\epsilon_g = 1.95$ eV for poly(PheDOT) and 1.66 eV for PEDOT, were not only similar for the two materials but also close to the experimental values, which are respectively 1.85 eV¹⁷ and 1.60–1.70 eV.⁹ Concerning the IP, the higher values in PheDOT oligomers with respect to PEDOT should be attributed again to the lower electron-donating effect of the oxygen atoms in PheDOT oligomers. Results derived from a linear regression analyses predict IP values of 4.28 and 3.45 eV for poly(PheDOT) and PEDOT, respectively, which are in qualitative agreement with previous experimental observations. Specifically, the IP determined for poly(PheDOT) and PEDOT is 4.6 and 4.1 eV, respectively, i.e., neutral poly(PheDOT) presents higher air stability than PEDOT.¹⁷

The ϵ_g values estimated for PheDOT and EDOT oligomers using TD-DFT calculations are shown in Figure 2. As can be seen, the KT values are overestimated with respect to the TD-DFT ones. The most remarkable feature is that the ϵ_g value of (EDOT) $_2$ is greater than that of (PheDOT) $_2$, which is not in agreement either with the previous KT estimations or with the experimental data. Comparison between the results derived from TD-DFT calculations with those recorded from the UV–visible spectra of these dimers¹⁸ reveals an excellent concordance in the case of (PheDOT) $_2$. More specifically, the absorption maximum (λ_{\max}) determined from TD-DFT calculations is 319 nm, which is slightly blue-shifted with respect to the experimental one (317 nm). The ϵ_g estimated from such a theoretical and experimental absorption maximum is 3.89 and 3.91 eV, respectively. On the other hand, the λ_{\max} of (EDOT) $_2$ derived from TD-DFT calculations (311 nm) is 11 nm red-shifted relative to the experimental value, leading to a ϵ_g value (3.98 eV) that is 0.13 eV higher than the experimental one. Linear regression analyses predict ϵ_g values of 1.73 and 1.50 eV for idealized chains of poly(PheDOT) and PEDOT units, which are slightly underestimated with respect to the aforementioned experimental data.

Geometry optimization of the oligomers in the radical cation state ($S^2 = 0.75$) at the UB3LYP/6-31G(d) level resulted in very low spin contamination, the highest overestimation being 2.6% and 3.4% for (PheDOT) $_4$ and (EDOT) $_6$, respectively. Parts a and b of Figure 3 plot the dependence of the IP_{1a} against $1/n$, respectively, in the gas phase and acetonitrile solution, respec-

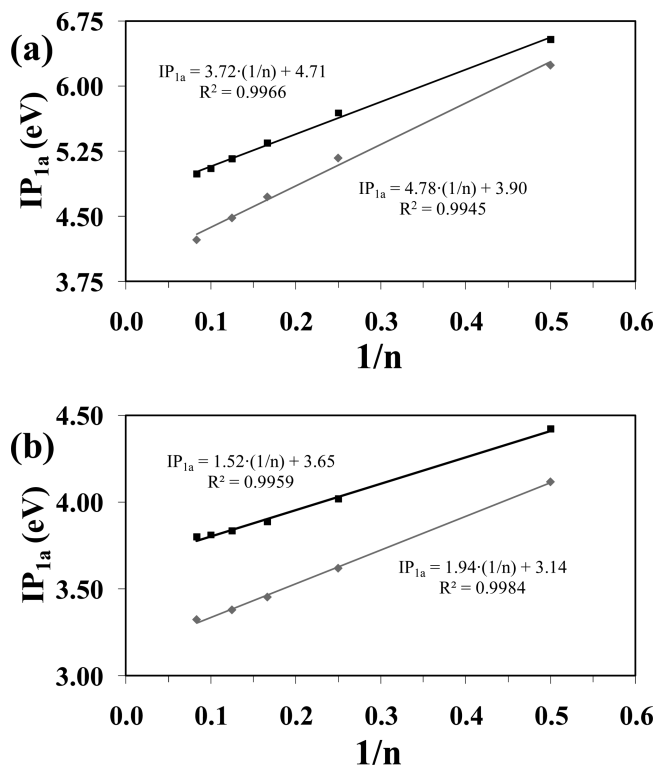


Figure 3. Adiabatic ionization potential (IP_{1a} ; in eV) plotted against the inverse number of repeating units ($1/n$) for (PheDOT) $_n$ (black squares) and (EDOT) $_n$ (gray diamonds) oligomers in the gas phase (a) and acetonitrile solution (b). Lines correspond to the linear fits $IP_{1a} = a \cdot 1/n + b$.

tively, for both (PheDOT) $_n$ and (EDOT) $_n$ oxidized oligomers. The IP_{1a} values obtained in the gas phase are higher than the IP values obtained by using the KT. Linear extrapolations of the results calculated for the oligomers lead to IP_{1a} values of 4.71 and 3.90 eV for idealized poly(PheDOT) and PEDOT. As can be seen, these values are in better agreement with the available experimental data¹⁷ than those derived above through the KT. The IP_{1a} calculated in acetonitrile solution are lower than those predicted in the gas phase for both (PheDOT) $_n$ and (EDOT) $_n$, which must attributed to the large solvation of the cations. Such values also follow a linear behavior with respect to $1/n$, even although the beginning of the physical saturation is identified for the largest oligomer of each specie. The IP_{1a} predicted in this solvent for poly(PheDOT) and PEDOT polymers are 3.65 and 3.14 eV, respectively.

Geometric changes undergone by (PheDOT) $_n$ and (EDOT) $_n$ on moving from the neutral state to the radical cation state are illustrated in Figure 4 through the BLA patterns of the oligomers with $n = 2, 6$, and 12. As can be seen, the benzenoid structure typically found in neutral heterocyclic CPs is slightly more marked in (PheDOT) $_n$ than in (EDOT) $_n$. However, such structure is lost upon oxidation in all cases. The maximum and averaged changes in the lengths of all the C–C bonds (Δd_{\max} and Δd_{av} , respectively) as well as the total change in the bond lengths ($\Sigma \Delta d_i$) are shown in Table 1. As can be seen, the larger changes occur for the shortest oligomers, becoming smaller as n increases. It is worth noting that for a given value of n the EDOT oligomer shows larger geometric changes upon oxidation than the PheDOT one. This feature should be mainly attributed to the unfavorable steric interactions produced by the phenylene ring, which increase the rigidity of (PheDOT) $_n$ oligomers, even though the significant delocalization of the positive charge found for these systems (see below) is expected to contribute also. In

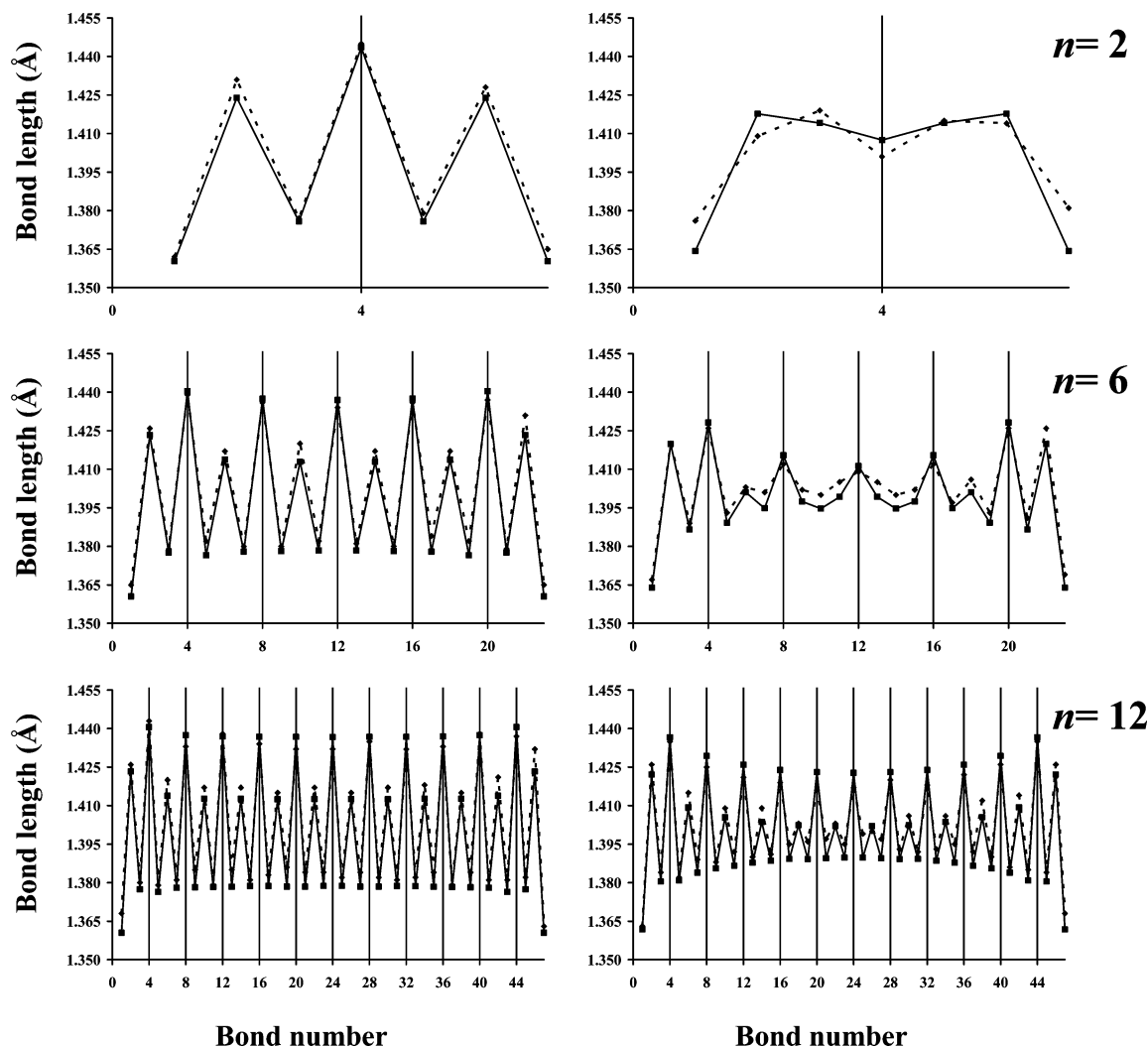


Figure 4. C–C bond length alternation pattern for (PheDOT) $_n$ (black squares; solid lines) and (EDOT) $_n$ (gray diamonds; dashed lines) oligomers with $n = 2, 6$, and 12 in the neutral (left) and radical cation (right). Vertical lines have been used to separate repeat units as a visual aid: 3 intra-ring C–C bonds and one inter-ring C–C bond.

TABLE 1: Maximum (Δd_{\max}), Averaged (Δd_{av}), and Total ($\Sigma \Delta d_i$) Change in the Lengths of the C–C Bonds along the Molecular Backbone on Moving from the Neutral State to the Radical Cation State for (PheDOT) $_n$ and (EDOT) $_n$

n	Δd_{\max} (Å)		Δd_{av} (Å)		$\Sigma \Delta d_i$ (Å)	
	PheDOT	EDOT	PheDOT	EDOT	PheDOT	EDOT
2	0.038	0.044	0.019	0.027	0.133	0.188
6	0.026	0.025	0.014	0.015	0.327	0.345
12	0.014	0.017	0.008	0.009	0.385	0.440

both systems the variation of $\Sigma \Delta d_i$ when enlarging from $n = 2$ to $n = 6$ is significantly larger than the variation from $n = 6$ to $n = 12$, indicating that the geometric effect of the positive charge tends to spread over almost the whole molecule. These effects are similar to those recently reported for unsubstituted thiophene oligomers at the same theoretical level,²⁷ i.e., $\Sigma \Delta d_i = 0.45\text{--}0.46$ Å for oligomers with n ranging from 10 to 50.

Figure 5 compares the distribution of the positive charge through the repeat units of (PheDOT) $_n$ and (EDOT) $_n$, which has been obtained as the difference between the Mulliken charges of the radical cation and the neutral molecule for each repeat unit. As can be seen, with the exception of the oligomers with $n = 8$, the positive charge is more delocalized over the backbone in (PheDOT) $_n$ than in (EDOT) $_n$, in which charge separation is more pronounced as the number of monomers decreases.

However, it should be mentioned that delocalization effects are typically overestimated by DFT methods,³⁸ even though the B3LYP functional describes satisfactorily the energetic effects produced by charge delocalization on aromatic systems.³⁹ Due to the higher delocalization of the positive charge in oxidized (PheDOT) $_n$ oligomers, their performance as electronic conductors is expected to be better than that of the oxidized (EDOT) $_n$.

Figure 6 represents the variation of the ϵ_g determined using the KT and TD-DFT calculations for both (PheDOT) $_n$ and (EDOT) $_n$ oligomers in the radical cation state against $1/n$. It is remarkable that independently of n the ϵ_g predicted by the two approaches is lower for the former systems, which is in excellent agreement with the larger charge delocalization of oxidized (PheDOT) $_n$ oligomers. In this sense the extrapolated ϵ_g for idealized poly(PheDOT) and PEDOT chains using the KT is 0.16 and 0.28 eV, respectively, which in the case of PEDOT is in completely agreement with previously reported values.^{19d} The ϵ_g values extrapolated using the data derived from TD-DFT calculations are notably underestimated with respect to those predicted by the KT, i.e., 0.02 and 0.07 eV for idealized polymers containing infinite PheDOT and EDOT monomers, respectively. Results displayed on Figures 5 and 6 suggest that the performance of poly(PheDOT) as electronic conductor upon p-doping could be better than that of PEDOT.

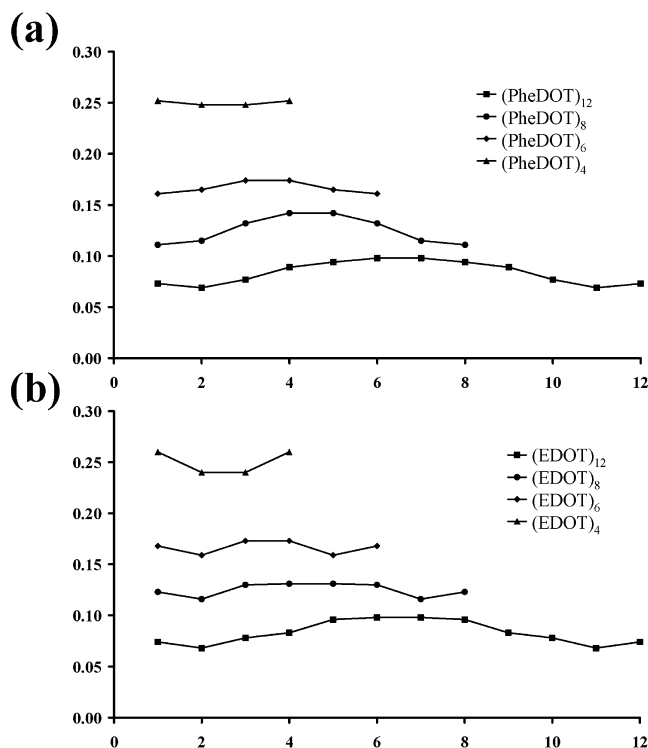


Figure 5. Distribution of the positive charge in monocationic (a) (PheDOT)_n and (b) (EDOT)_n oligomers.

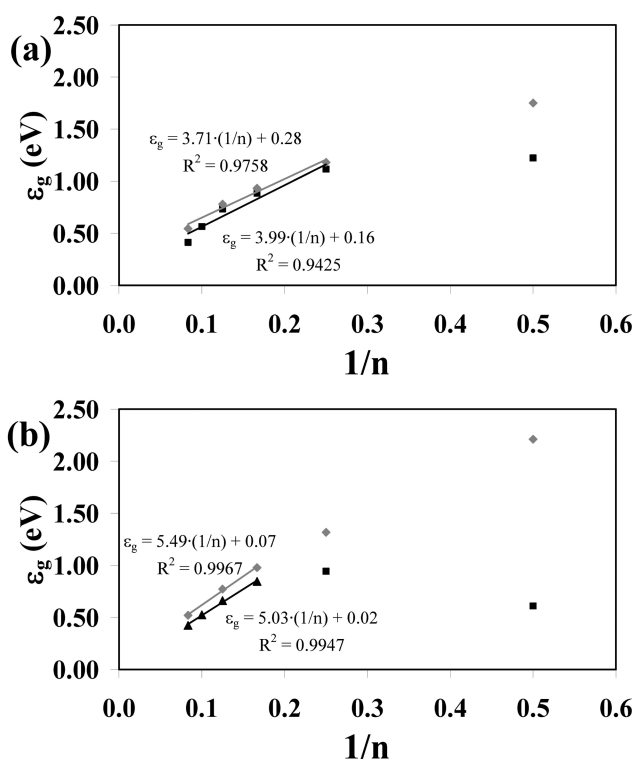


Figure 6. Evolution of the π - π^* lowest transition energy (ϵ_g , in eV) calculated using the (a) UB3LYP/6-31G(d) and (b) TD-UPBE0/6-31G(d) methods plotted against the inverse number ($1/n$) of repeating units for monocationic (PheDOT)_n (black squares) and (EDOT)_n (gray diamonds) oligomers. Lines correspond to the linear fits $\epsilon_g = a \cdot 1/n + b$, in which results obtained for the shortest oligomers have been excluded.

Conclusions

Structural and electronic properties of poly(PheDOT) and PEDOT have been estimated by extrapolating the results

obtained from QM calculations on oligomers containing up to 12 repeating units. Both the neutral and monocationic states, i.e., undoped and p-doped states, respectively, have been considered for the two systems under study. Regarding to the neutral states, the benzenoid structure of (PheDOT)_n oligomers is better defined than that of the (EDOT)_n oligomers. The ϵ_g values predicted by different theoretical methods are in agreement with the available experimental data. TD-DFT calculations provided a ϵ_g value of 1.70 and 1.50 eV for poly(PheDOT) and PEDOT, respectively. The IP_{1a} values calculated in the gas phase and in acetonitrile solution indicate that the p-doping is easier for PEDOT than for poly(PheDOT). Accordingly, poly(PheDOT) presents higher atmospheric stability, facilitating its storage. On the other hand, oxidized (PheDOT)_n oligomers present a larger delocalization of the positive charge and a smaller ϵ_g value than oxidized (EDOT)_n oligomers, which suggest that poly(PheDOT) behaves as excellent electronic conductor upon p-doping. Overall, results indicate that poly(PheDOT) is an excellent alternative to PEDOT since, in addition to its higher environmental stability, it shows a better behavior as electronic conductor upon oxidation.

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