Structural and Electronic Properties of Crown Ether Functionalized Oligothiophenes

Jordi Casanovas,*,† David Zanuy,‡ and Carlos Alemán*,‡

Departament de Química, Escola Politècnica Superior, Universitat de Lleida, c/ Jaume II n°69, Lleida E-25001, Spain, and Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal n° 647, Barcelona E-08028, Spain

Received January 24, 2008; Revised Manuscript Received March 26, 2008

ABSTRACT: Quantum mechanical calculations at the B3LYP level combined with the 6-31G(d) and 6-31+G(d,p) basis sets have been performed on oligomers containing *n* repeating units (with *n* ranging from 2 to 8) of three crown ether functionalized polythiophenes, which differ in the size of the macrocycle. Results have been compared with those obtained for poly(3,4-ethylenedioxthiophene), which was calculated at the same theoretical levels. Results indicate that, independently of the size of the ether macrocycle, functionalized oligomers tend to adopt an antiplanar conformation with the inter-ring dihedral angles arranged in trans. Moreover, the rotational profile calculated by scanning the inter-ring angle is not significantly influenced by neither the size of the macrocycle nor its conformation. On the other hand, the electronic properties of the crown ether functionalized polythiophenes, which were obtained by extrapolating the results obtained for the oligomers, were very similar to those of poly(3,4-ethylenedioxythiophene). Specially relevant was the lowest π-π* transition energy, which was predicted 1.8 and 1.7 eV for crown ether functionalized polythiophenes and poly(3,4-ethylenedioxythiophene), respectively. These results suggest that the molecular effective conjugation of the latter polymer is not significantly altered by the addition of ether macrocycles linked to the 3- and 4- positions of the thiophene units.

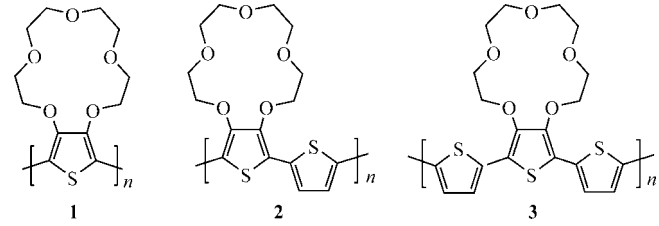
Introduction

The study and development of polythiophenes (PThs) for commercial applications have been largely intensified over the last decades due to their remarkable electrical and optical properties.[1,2] Among these materials, poly(3,4-ethylenedioxythiophene), abbreviated as PEDOT, is one of the most successful because of its interesting properties: low oxidation potential, high electrical conductivity, and remarkable environmental stability.[3–9] These properties have promoted the use of PEDOT in a large number of technological applications such as antistatic coating for photographic films, electrode material in electroluminescent lamps, anticorrosive additives for paints, material for through-hole plating of printed circuits boards, and solid electrolyte in capacitors or electrode of sensors to detect glucose.[6,9–20] Moreover, recent results showing interaction with biological systems, i.e., DNA, cells, etc., suggest that PEDOT is very a promising material for biomedical applications.[21,22]

On the other hand, the application of PThs as sensors able to provide optical and electronic responses upon environmental stimuli or the presence of analytes is of special interest, being subject of intense research during the past decade.[23,24] Sensors based on selected π-conjugated polymers derived from PTh have some advantages with respect to small molecule-driven sensors due to the better stability and amplified sensitivity of the formers. Among them, PThs that incorporate crown ether moieties to the conducting polymer backbone are particularly useful in ion sensing. The first crown ether derivatized thiophenes were prepared in 1989 by Sone et al.,[25] who considered different sizes for the crown ether and one or two thiophenes per monomer. However, their selectivity was poor. This tentative was followed by Parker et al.,[26] Tsukube,[27] and Roncali et al.,[28] even although the selective power did not improve too much. However, successful alkali cation sensors constituted by PThs with pendant and main chain crown ether functionalities were reported in 1993 by the groups of Bäuerle[29] and Swager,[30] respectively. Later, the PThs showed in Scheme 1, in which the crown ether is affixed to the 3- and 4-positions of thiophene, were electrochemically synthesized by Bäuerle and co-workers.[31,32] Cyclic voltammetries of **1**−**3**, whose structural units can be considered as crown ether extensions of EDOT, in presence of alkali metal ions showed that **1** presents the highest sensitivity to the cations. Thus, addition of one equivalent of Li^+, Na^+, or K^+ per crown ether resulted in a shift to higher oxidation potentials, these changes being larger than those previously observed for other functionalized PThs. The selective complexation of these crown ether functionalized PThs with alkali ions affects significantly their electrochemical, and also optical, properties, originating measurable responses.

Recent experimental studies on PTh-based systems functionalized with crown ethers linked directly to the thiophene β-positions evidenced that the interest in these systems as candidates for sensory devices is growing.[23,33,34] However, to our best knowledge, the effects of the crown ethers on the structural and electronic properties of the polymer backbone have not been investigated yet. Within this context, we are particularly interested in those systems in which the macrocyclic cavity is attached onto the same thiophene unit. More specifically, there is no information about if macrocyles linked to the 3- and 4-positions of the same thiophene unit alter the conformational preferences and π-electron configuration of PEDOT, which is not desirable due to the excellent properties

Scheme 1



1 **2** **3**

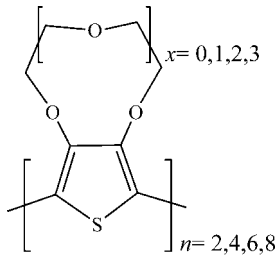
* Corresponding author(s). E-mail: (J.C.) jcasanovas@quimica.udl.cat; (C.A.) carlos.aleman@upc.edu.

† Departament de Química, Escola Politècnica Superior, Universitat de Lleida.

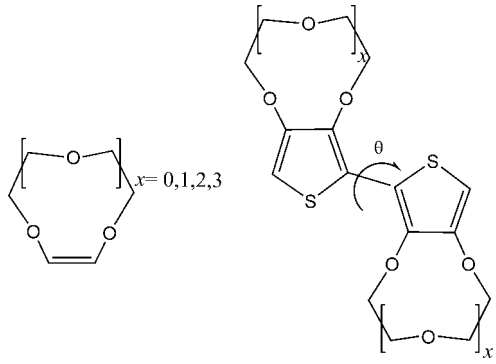
‡ Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya.

10.1021/ma800174b CCC: $40.75 © 2008 American Chemical Society
Published on Web 05/13/2008

Scheme 2



Scheme 3



of the latter material. Within this context, it should be emphasized that quantum mechanical calculations have demonstrated to be very useful for the prediction and understanding of the intrinsic properties of a large variety of conducting polymers,[35–41] including PEDOT.[41]

In this work we contribute to the understanding of the structure−property relationships that control the electrical and optical peculiarities of crown ether functionalized PThs. For this purpose, their intrinsic structural and electronic properties have been predicted using quantum mechanical calculations on model oligomers. The studied model systems, which involve from dimers to octamers, are displayed in Scheme 2. As can be seen, the index x refers to size of the crown ether, i.e., $x = 0$ corresponds to dioxane ring of EDOT units, while n indicates the number of functionalized thiophene units contained in the oligomer.

Methods

Hereafter, crown ethers will be referred using the following notation "z-crown-y-ether", where index z refers to the total number of non-hydrogen atoms contained in the cyclic polyether and y is the number of ether oxygens. In the first stage of this investigation, molecular dynamics (MD) simulations were used to generate a representative set of conformations for the four z-crown-y macrocycles displayed in the left side of Scheme 3. Specifically, the preliminary exploration of the potential energy hypersurfaces of these compounds was performed using a procedure based on consecutive series of heating−cooling MD cycles, following the principles of classic simulated annealing strategy.[42,43] Thus, for each z-crown-y, a randomly generated configuration was brought to 900 K, and that temperature was kept for 50 ns, coordinates and velocities being stored every 100 ps. These 500 structures were cooled down to 298 K at a rate of 6 K per 25 ps, and subsequently, their conformational energies were minimized applying 3×10^3 steps of conjugated gradient.

All classical calculations were performed using the NAMD program.[44] Energies were calculated using the AMBER force-field.[45] Force-field parameters, including those required for the sulfur atom, were taken from the AMBER libraries with the exception of the electrostatic ones. Atomic charges were explicitly developed for each macrocycle using a procedure previously reported.[46] For this purpose, the molecular electrostatic potential was calculated at the HF level using the 6-31G(d) basis set.[47] It should be noted that the electrostatic parameters of amino acids and DNA basis reported in the AMBER force-field were also determined at the HF/6-31G(d) theoretical level.[45] Therefore, the partial atomic charged calculated in this work for z-crown-y macrocycles are fully compatible with the AMBER parametrization. Atom pair distance cutoffs were applied at 10.0 Å to compute the nonbonding interactions.

In order to provide a list of unique minimum energy conformations for each crown ether, the structures minimized using the AMBER force-field were compared among them. Two structures were considered different when they differ in at least one of their dihedral angles by more than 30°. After this, full geometry optimizations of selected unique minima were carried out within the density functional theory (DFT) framework. Calculations were performed employing the Becke's three-parameter hybrid functional (B3)[48] combined with the Lee, Yang, and Parr (LYP)[49] expression for the nonlocal correlation (B3LYP) and the 6-31G(d) basis set.[47]

The most stable conformations of each crown ether were selected and linked to the 3- and 4- positions of a thiophene dimer, as indicated in the right side of Scheme 3. The internal rotation of the resulting neutral dimers was studied at the B3LYP/6-31G(d) level by scanning the inter-ring dihedral angle S−C−C−S (θ) in steps of 30°. A flexible rotor approximation was used, each point of the path being obtained from a geometry optimization of the molecule at a fixed value of θ. Furthermore the minimum energy conformations of each dimer were determined from full optimizations using a gradient method. In order to ensure the suitability of the B3LYP/6-31G(d) level, the global minimum found each dimer with $x < 3$ was reoptimized using the MP2/6-31G(d) method.

In order to have a proper description of the polymers, for each value of x, we performed geometry optimizations at the B3LYP/6-31G(d) level of the oligomers with $n = 2$, 4, 6, and 8 (Scheme 2) imposing an antiplanar conformation; i.e., the interring dihedral angles S−C−C−S were fixed at $\theta = 180°$. Furthermore, additional calculations without fixing θ were carried out employing the same DFT method and the larger 6-31+G(d,p) basis set.[50]

For all oligomers we determined the following structural and electronic properties: the C−C bond-length alternation pattern along the main chain, the ionization potential (IP), the electron affinity (EA) and the $\pi-\pi^*$ lowest-electron transition (ϵ_g). The IPs were calculated using the Koopman's theorem:.[51] $\mathrm{IP} = -\epsilon_{\mathrm{HOMO}}$ and $\mathrm{EA} = -\epsilon_{\mathrm{LUMO}}$, where ϵ_{HOMO} and ϵ_{LUMO} are the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies, respectively. Formally, Koopman's theorem does not apply to DFT since the Kohn−Sham orbital energies do not carry any physical meaning. However, using Janak's theorem,[52,53] Perdew[54] showed a connection between IPs and EAs to the HOMO and LUMO energies, respectively. On this basis, ϵ_g values were obtained as the difference between the HOMO and LUMO energies, i.e. $\epsilon_g = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}$.[53] Finally, the IP, EA, and ϵ_g were estimated for the polymers by plotting the results of oligomers against the inverse of the chain length ($1/n$) and extrapolating to infinity. All DFT calculations were carried out using the Gaussian 03 computer program.[55]

Results and Discussion

Crown Ether Functionalized Thiophene Dimmers. The polymer backbone conformation is a crucial topic in studying the influence of the ether functionalities on the properties of thiophene derivatives. This is because deviations of the interring dihedral angles from planarity have always strong effects on the π-electronic structure and, therefore, on the electrical and optical properties of the conducting polymer. As a first approximation to this matter, we examined the torsional potential of the functionalized thiophene dimers showed in the right side of Scheme 3. However, in view of the high flexibility that may exhibit the larger crown ethers, in a first step we decided to explore the potential energy hypersurfaces of the isolated crow ethers using a MD simulated annealing strategy. For this

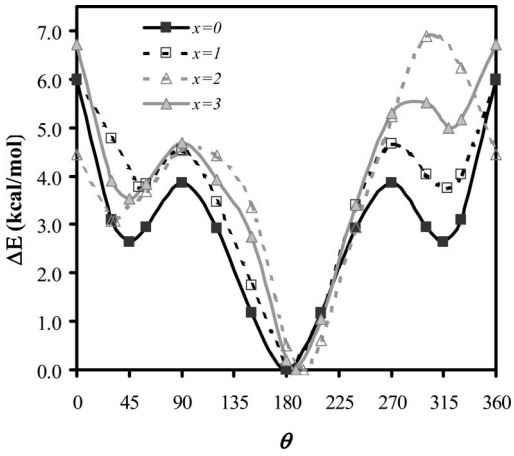


Figure 1. Potential energy curves for the internal rotation of the crown ether functionalized thiophene dimers as a function of the inter-ring dihedral angle (θ) using B3LYP/6-31G(d) optimizations. Energies are relative to the global minima.

purpose, the 9-crown-3-, 12-crown-4-, and 15-crown-5-ether structures ($x = 1$, 2, and 3, respectively, in the left side of Scheme 3) were constructed and submitted to a heating−cooling MD cycle using the procedure described in the Methods section. Energy minimization of the 500 structures recorded for the 9-crown-3-, 12-crown-4-, and 15-crown-5-ether at the end of the 900-to-298 K cooling down step, led to 53, 111, and 297 unique minimum energy conformations, respectively.

The 20 minima of lower energy obtained from force-field calculations for each crown-ether were selected and fully reoptimized at the more sophisticated B3LYP/6-31G(d) level of theory. After this, from the resulting minima, the four ($x =$ 1 and 2) or three ($x = 3$) conformations of lower energy were used to construct the functionalized thiophene dimers. Accordingly, calculations of the rotational energy profiles were performed considering 1 ($x = 0$), 4 ($x = 1$ and 2), or 3 ($x = 3$) different starting arrangements for each dimer, even although the minima provided by the most stable profile were the only characterized by full geometry optimizations.

Figure 1 compares the most stable rotational profile computed at the B3LYP/6-31G(d) level for each of the three crown ether functionalized bithiophenes ($x = 1$, 2, and 3) as well as for the EDOT dimer ($x = 0$). Interestingly, the lowest energy minimum predicted for all the investigated dimers corresponds to the planar *anti* conformation ($\theta \approx 180°$) rather than to the *anti-gauche* conformations ($\theta \approx \pm 150°$) as occurs for the thiophene dimer.[56,57] Although this result was already reported for the EDOT dimer,[58] the *antigauche* has been characterized as the lowest energy conformation for other thiophene dimers that incorporate cyclic substituents at positions 3 and 4, e.g., the isothianaphthene dimer in which each unit is formed by the fusion of a benzene ring upon thiophene.[59] Indeed, early studies on substituted thiophene oligomers showed that the incorporation of substituents at the position 3 of each unit usually produces significant deviations from the planarity, which must be attributed to the strong repulsive interactions generated by the substituents of adjacent units.[60] The preferences of the EDOT dimer toward the planar anti conformation should be attributed to the electron donating effects exerted by the oxygen atoms of the dioxane rings, which enhances the π-conjugation between adjacent units and reduces the band gap. Additionally, the existence of a noncovalent interaction between the sulfur and the oxygen atoms has been recently postulated. This existence of this interaction was deduced from the crystallographic structures of small EDOT oligomers, in which the nonbonded distances between sulfur and oxygen of adjacent cycles were smaller than the sum of the van der Waals radii of the individual atoms.[61] Their preferences toward the planar *anti* conformation reveal that these effects are retained by the three crown ether functionalized PThs considered in this work.

On the other hand, a comparison between the global minimum obtained at the B3LYP/6-31G(d) level and the structure obtained after reoptimization at the MP2/6-31G(d) level indicates an excellent agreement between the two procedures. Thus, differences in the inter-ring dihedral angle and bond distance were [0.5°, 0.005 Å], [0.9°, 0.005 Å], and [1.8°, 0.006 Å] for $x = 0$, 1, and 2, respectively, confirming the reliability of the former procedure.

Figure 1 shows two local minima at $\theta \approx +45$ and $-45°$ (*syn−gauche*$^+$ and *syn−gauche*$^-$ conformations, respectively), the relative energies ranging between 2.6 (*syn−gauche*$^+$ and *syn−gauche*$^-$ with $x = 0$) and 5.0 kcal/mol (*syn−gauche*$^-$ with $x = 3$). These structures are separated from the global minimum by the *gauche−gauche* barriers ($\theta \approx +90$ and $-90°$), which are about 0.7−1.4 kcal/mol lower for the EDOT dimer than for the crown ether functionalized bithiophenes. The dimer involving the crown ether with $x = 2$ was an exception to this behavior since the local minimum at $\theta \approx -45°$ was not detected. This feature may be due to the special characteristics of the medium size 12-crown-4-ether, which is not flexible enough to undergo a suitable conformational rearrangement when θ evolves from 180 to 360°. Finally, it should be emphasized that the large resemblance between the conformational characteristic of the EDOT dimer and the crown ether functionalized bithiophene with $x = 3$ is considerably interesting. Although this resemblance is detected for all the structures calculated within the rotational profile, it is specially remarkable for the global minimum, the dihedral angle θ and the inter-ring distance differing by only 8.5° and 0.003 Å, respectively, in such a conformation.

The influence on the rotational profiles of the macrocycle conformation is illustrated in Figure 2, which shows the rotational profiles calculated for the 4 and 3 starting arrangements used for the calculations of the crown ether functionalized dimers with $x = 1$ and $x = 3$, respectively. As expected, the conformation of the macrocycle affects considerably the relative stability of the bithiophene, although the influence on the shape of the profile was only appreciable for the dimer with $x = 3$. However, the position of the minima and the barriers were similar in all cases indicating that the arrangement of the macrocycle does not dominate the intrinsic conformational preferences of the main chain in crown ether functionalized bithiophenes. The results obtained for the crown ether functionalized bithiophene with $x = 2$ (data not shown) were intermediate between those displayed for $x = 1$ and $x = 3$.

Crown Ether Functionalized Oligothiophenes. Results discussed above indicate that crown ethers, independently of its size, do not alter significantly the main chain conformational properties of EDOT dimer. However, this fact must be corroborated thought the analysis of longer oligomers. For this purpose, functionalized oligothiophenes formed by n monomers, with n ranging from 2 to 8, have been calculated to examine their geometrical, structural and electronic properties.

Figure 3 compares the C−C bond lengths in the main chain of all the optimized octamers ($n = 8$ with $x = 0$, 1, 2 and 3 in Scheme 2), which were determined considering the antiplanar conformation, i.e. all the dihedral angles were fixed at $\theta = 180°$. As can be seen, single and double C−C bonds appears alternatively for the four compounds, this pattern being fully consistent with an aromatic-like electronic structure. However, the difference between consecutive bond lengths is slightly less pronounced in the EDOT-containing oligothiophene than in the other octamers indicating that the electronic structure of the

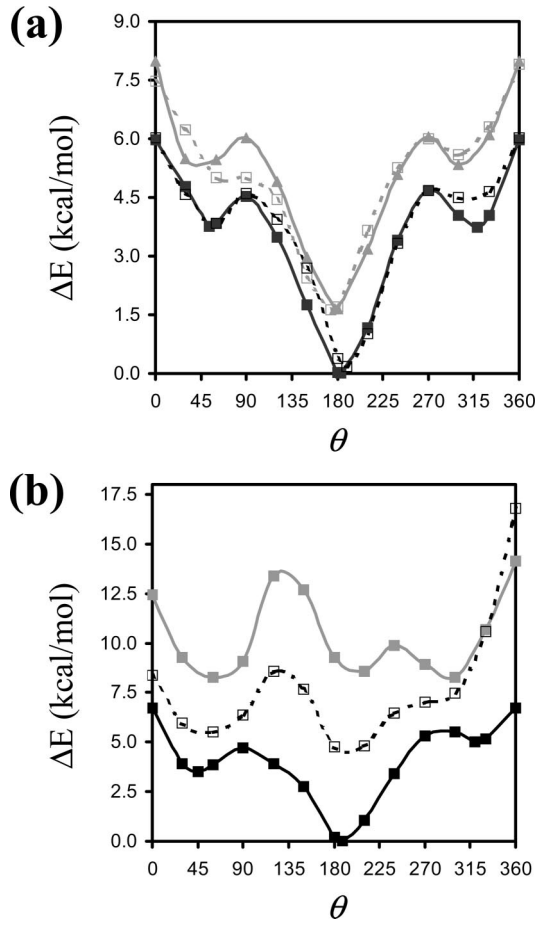


Figure 2. Potential energy curves for the internal rotation of the crown ether functionalized thiophene dimers with $x = 1$ (a) and $x = 3$ (b) as a function of the inter-ring dihedral angle (θ). For each compound, the different profiles were obtained considering different initial conformations for the ether macrocycles, i.e., 4 and 3 for $x = 1$ and $x = 3$, respectively. Calculations were performed at the B3LYP/6-31G(d) level and energies are relative to the global minimum of each compound.

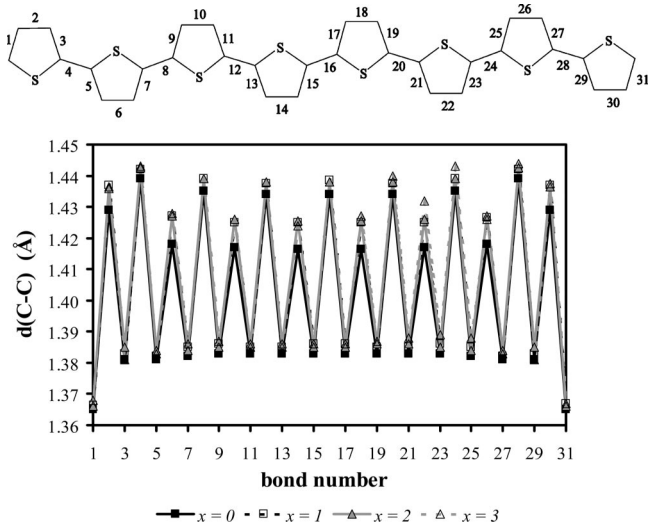


Figure 3. C−C bond distances along the main chain of the crown ether functionalized thiophene octamers investigated in this work.

former presents the largest participation of the quinoid form. Consequently, the inter-ring bond distances are slightly shorter in the EDOT octamer, i.e. about 0.040 Å. This behavior agrees with previous experimental[62,63] and theoretical[40,64–67] studies on EDOT oligomers, whereas no similar studies had been reported yet for the other crown-ether functionalized oligothiophenes.

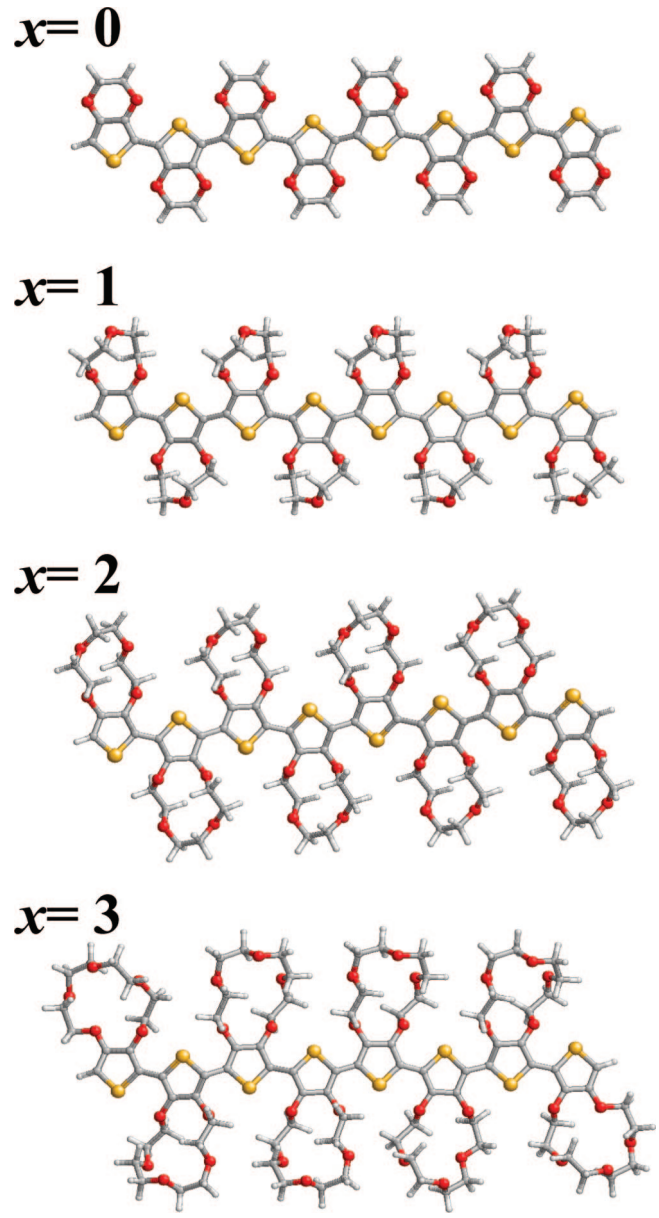


Figure 4. Optimized molecular structure of the crown ether functionalized thiophene octamers investigated in this work.

Furthermore, the four octamers were also subject of complete geometry optimizations at the B3LYP/6-31G(d) level, i.e. without fixing the dihedral angle θ. Interestingly, results indicate that the interactions between the macrocycle located at the repeating unit i and those located at the adjacent repeating units ($i + 1$ and $i - 1$) do not produce significant distortions in the antiplanar conformation previously found for the dimers. Specifically, the largest deviation from the ideal anti planar conformation ($\theta = 180.0°$) was 11.6, 12.1, and 15.1° for the octamers with $x = 1$, 2, and 3, respectively. Figure 4 shows the fully optimized molecular structures of the four octamers considered.

Regarding to the electronic properties, Figure 5 displays the IP, EA, and ϵ_g values calculated at the B3LYP/6-31G(d) level for all the investigated antiplanar oligomers ($x = 0-3$) against the inverse chain length ($1/n$, with n ranging from 2 to 8). In order to check the influence of the basis set on these electronic properties, the molecular geometries obtained at the B3LYP/6-31G(d) level for all the oligomers ($n = 2$, 4, 6, and 8) of the

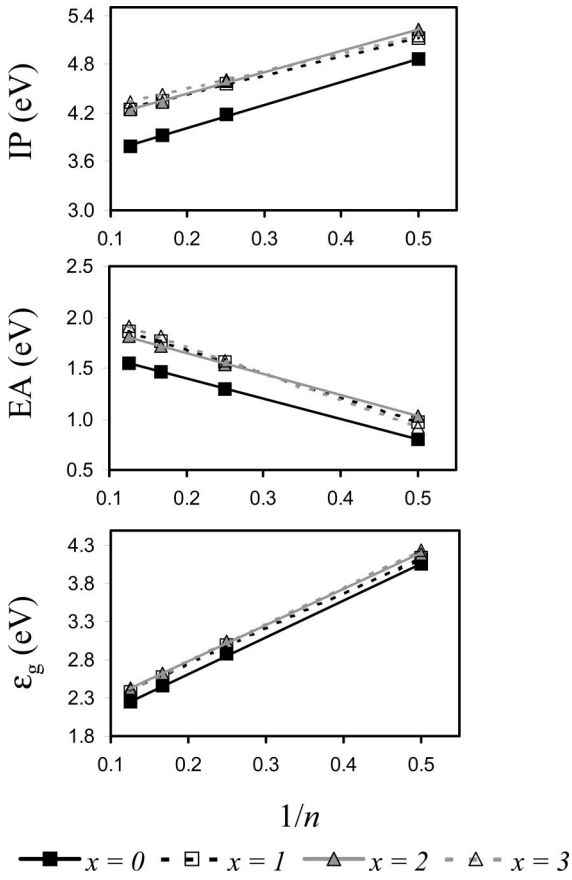


Figure 5. Evolution of the IP, EA, and ϵ_g values calculated at the B3LYP/6-31G(d) level with the inverse chain length of the crown ether functionalized thiophene oligomers.

Table 1. Ionization Potential (IP), Electron Affinity (EA), and $\pi-\pi^*$ Lowest Transition Energy (ϵ_g) Extrapolated for PEDOT ($x = 0$) and the Three Crown Ether Functionalized Polythiophenes[a]

	B3LYP/6-31G(d)			B3LYP/6-31+G(d,p)		
	IP	EA	ϵ_g	IP	EA	ϵ_g
$x = 0$	3.45	1.79	1.66	3.69	2.02	1.67
$x = 1$	3.96	2.16	1.80	4.22	2.42	1.80
$x = 2$	3.91	2.06	1.85	4.16	2.30	1.85
$x = 3$	4.06	2.24	1.82			

[a] All values are in eV.

compounds with $x = 0$, 1 and 2 were reoptimized using the B3LYP/6-31+G(d,p) method. As expected, the antiplanar conformation remained stable in all cases and, additionally, the resulting electronic properties were very similar to those obtained with the 6-31G(d) basis set (Table 1). This was especially remarkable for the predicted ϵ_g values, which were essentially identical at both the B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) levels. Thus, the largest difference found for the IP, EA, and ϵ_g was of only 0.26, 0.26, and 0.01 eV, respectively.

The four series of data depicted in Figure 5 show a great similarity. As is typically found in π-conjugated systems, the HOMO energy increases with the chain length while the LUMO energy decreases. Consequently, the EA increases with the size of the oligomer while both the IP and ϵ_g decrease. Independently of the size of the crown ether, an excellent linear behavior was found for the variation of all the calculated electronic properties with the inverse chain length ($1/n$), the correlation coefficients being larger than 0.999 in all cases. This fact allows predict the electronic properties of the corresponding polymers by extrapolating the linear behavior to infinite chain length. The resulting IP, EA and ϵ_g values are listed in Table 1.

From a quantitative point of view, the ϵ_g calculated for PEDOT is in very good agreement with the reported experimental values (1.2−1.7 eV),[8,68–73] specially taking into account that calculations were performed on isolated oligomers in gas-phase. Thus, ϵ_g values computed without considering the effect of the environment are ~0.2 eV larger than those predicted from calculations in condensed phases.[74] Accordingly the theoretical methodology and level of calculation used in this work are accurate enough to be used as a predictive tool. The values extrapolated for the IP and EA of the 9-crown-3-, 12-crown-4-, and 15-crown-5-ether functionalized PTHs are relatively close to those predicted for PEDOT. These results indicate that crown ether functionalized PTHs are, as PEDOT and unsubstituted PTh, easily p-dopable. In contrast, the stability of the n-doped forms may be poor. On the other hand, the calculated values of ϵ_g are low and similar to that of PEDOT, the largest difference with respect to the latter being lower than 0.2 eV. Finally, it is worth noting that the slightly lower ϵ_g value of PEDOT should be attributed to the higher quinoid character of its backbone (see Figure 3), the relationship between these two properties being well established from earlier studies.[75,76]

Conclusions

The structural and electronic properties of oligothiophenes (from dimers to octamers) functionalized with 9-crown-3-, 12-crown-4-, and 15-crown-5-ethers have been estimated using theoretical calculations, and compared with of those obtained for EDOT-containing oligomers. The study has been performed using MD simulations, which were applied on the macrocycles through a conformational search process, and DFT calculations at the B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) levels on the oligothiophenes.

Results indicate that, independently of its size, the crown ether does not alter the main structural properties of EDOT-containing oligomers, specifically the C−C bond-length alternation pattern nor the characteristic antiplanar conformation of the main chain. Moreover, we found that the conformational preferences of the main chain are not dominated by the arrangement of the attached macrocycle. On the other hand, the electronic properties predicted for the crown ether funcionalized PTHs are similar to those calculated for PEDOT. Thus, the extrapolated values of the IP and EA indicate that all these polymers can be easily p-doped, whereas the stability of the n-doped forms may be poor. On the other hand, the ϵ_g calculated for the 9-crown-3-, 12-crown-4-, and 15-crown-5-ether functionalized PTHs is about 1.8 eV. This result points out that the molecular effective conjugation of PEDOT is not significantly altered by the addition of ether macrocycles linked to the 3- and 4-positions of the thiophene units.

The results presented in this work will be used in a near future to study the binding between crown ether functionalized PTHs and metal cations. Specifically, the structural model described for 15-crown-5-ether functionalized PTh will be employed as starting point to examine the influence of different factors on the binding enthalpy, i.e., the oxidation degree of the polymer and the size and charge of the metal cation.

Acknowledgment. This work was supported by MEC and FEDER funds with Grant MAT2006-04029. D.Z. expresses thanks for financial support from the "Ramón y Cajal" program of the Spanish MEC.

References and Notes

(1) Skotheim, T. A.; Reynolds, J. R. In *Handbook of Conducting Polymers*, 3th ed.; CRC Press, Boca Raton, FL, 2007.
(2) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(3) Apperloo, J.; Groenendaal, L. B.; Verheyen, H.; Jayakannan, M.; Janssen, R. A.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Brédas, J. L. *Chem. Eur. J.* **2002**, *8*, 2384.
(4) Yu, J.; Holdcroft, S. *Chem. Mater.* **2002**, *14*, 3705.
(5) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41*, 831.
(6) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.
(7) Sakmeche, N.; Aaron, J. J.; Fall, M.; Aeiyach, S.; Jouni, M.; Lacroix, J. C.; Lacaze, P. C. *Chem. Commun.* **1996**, 2723.
(8) Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 2582.
(9) Goenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
(10) Jonas, F.; Krafft, E.; Muys, B. *Macromol. Symp.* **1995**, *100*, 169.
(11) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(12) Jonas, F.; Heywang, G. *Electrochim. Acta* **1994**, *39*, 1345.
(13) Kudoh, Y.; Akami, K.; Matsuya, Y. *Synth. Met.* **1999**, *102*, 973.
(14) Ghosh, S.; Inganäs, O. *Adv. Mater.* **1999**, *11*, 1214.
(15) Kros, A.; van Hövell, S. W. F. M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Adv. Mater.* **2001**, *13*, 1555.
(16) Kros, A.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 738.
(17) Armelin, E.; Oliver, R.; Liesa, F.; Iribarren, J. I.; Estrany, F.; Alemán, C. *Prog. Org. Coat.* **2007**, *59*, 46.
(18) Liesa, F.; Ocampo, C.; Alemán, C.; Armelin, E.; Oliver, R.; Estrany, R. J. *Appl. Polym. Sci.* **2006**, *102*, 1592.
(19) Brown, T. M.; Kim, J. S.; Cacialli, F.; Friend, R. H.; Daik, R.; Feast, W. J. J. *Appl. Phys. Lett.* **1999**, *75*, 1679.
(20) Kim, J. S.; Cacialli, F.; Friend, R. H.; Daik, R.; Feast, W. J. *Synth. Met.* **1999**, *102*, 1065.
(21) Estrany, F.; Aradilla, D.; Oliver, R.; Alemán, C. *Eur. Polym. J.* **2007**, *43*, 1876.
(22) Ocampo, C.; Armelin, E.; Estrany, F.; del Valle, L. J.; Oliver, R.; Sepulcre, F.; Alemán, C. *Macromol. Mater. Eng.* **2007**, *292*, 85.
(23) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(24) (a) Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957. (b) Roncali, J. J. *Mater. Chem.* **1999**, *9*, 1875.
(25) Sone, T.; Sato, K.; Ohba, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 838.
(26) Parker, D.; Kataky, R.; Nicholson, P. E.; Covington, A. K. *Analyst* **1991**, *116*, 135.
(27) Tsukube, H. *Talanta* **1993**, *40*, 1313.
(28) Roncali, J.; Garreau, R.; Lemaire, M. J. *Electroanal. Chem.* **1990**, *278*, 373.
(29) Bäuerle, P.; Scheib, S. *Adv. Mater.* **1993**, *5*, 848.
(30) Marsella, M. J.; Swager, Y.M. J. *Am. Chem. Soc.* **1993**, *115*, 12214.
(31) Bäuerle, P.; Scheib, S. *Acta Polym.* **1995**, *46*, 124.
(32) Rimmel, G.; Bäuerle, P. *Synth. Met.* **1999**, *102*, 1323.
(33) (a) Boldea, A.; Levesque, I.; Leclerc, M. J. *Mat. Chem.* **1999**, *9*, 2133. (b) Sannicolo, F.; Brenna, E.; Benincori, T.; Zotti, G.; Zecchin, S.; Schiavon, G.; Pilati, T. *Chem. Mater.* **1998**, *27*, 1910. (c) Kim, J.; Yoon, D.; Lee, S. H.; Ko, S.; Lee, Y.-S.; Zong, K. *Korean Chem. Soc.* **2006**, *27*, 1910. (d) Berlin, A.; Zotti, G.; Zecchin, S.; Schiavon, G. *Synth. Met.* **2002**, *131*, 149. (e) Rimmel, G.; Bauerle, P. *Synth. Met.* **1999**, *102*, 1323.
(34) (a) Jousselme, B.; Blanchard, P.; Levillain, E.; Delaunav, J.; Allain, M.; Richomme, P.; Rondeau, D.; Gallego-Planas, N.; Roncali, J. J. *Am. Chem. Soc.* **2003**, *125*, 1364. (b) Demeter, D.; Blanchard, P.; Allain, M.; grosu, I.; Roncali, J. J. *Org. Chem.* **2007**, *72*, 5285. (c) Demeter, D.; Blanchard, P.; Grosu, I.; Roncali, J. *Electrochem. Commun.* **2007**, *9*, 1587.
(35) Brédas, J. L. *Adv. Mater.* **1995**, *7*, 263.
(36) Brédas, J. L.; Cornil, J.; Beljonne, D.; Dos Santos, D. A.; Shuai, Z. *Acc. Chem. Res.* **1999**, *32*, 267.
(37) Hutchison, G. R.; Ratnet, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339.
(38) Hutchison, G. R.; Ratnet, M. A.; Marks, T. J. *J. Phys. Chem. B* **2005**, *109*, 3126.
(39) Casanovas, J.; Cho, L. Y.; Ocampo, C.; Alemán, C. *Synth. Met.* **2005**, *151*, 239.
(40) Casanovas, J.; Zanuy, D.; Alemán, C. *Polymer* **2005**, *46*, 9452.
(41) Casanovas, J.; Alemán, C. *J. Phys. Chem. C* **2007**, *111*, 4823.
(42) Kirkpatrick, S.; Gelatt, C. D., Jr.; Vecchi, M. P. *Science* **1983**, *220*, 671.
(43) Steinbach, P. J.; Brooks, B. R. *Chem. Phys. Lett.* **1994**, *226*, 447.
(44) Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kale, L.; Schulten, K. J. *Comput. Chem.* **2005**, *26*, 1781.
(45) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P.A. J. *Am. Chem. Soc.* **1995**, *117*, 5179.
(46) Alemán, C.; Luque, F. J.; Orozco, M. J. *Comput. Aided Mol. Design* **1993**, *7*, 72.
(47) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.
(48) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(49) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1993**, *37*, 785.
(50) Frish, M. J.; Pople, J. A.; Binklev, J.S. J. *Chem. Phys.* **1984**, *80*, 3265.
(51) Koopmans, T. *Physica* **1934**, *1*, 104.
(52) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165.
(53) Levy, M.; Nagy, A. *Phys. Rev. A* **1999**, *59*, 1687.
(54) Perdew, P. In *Density Functional Methods in Physics*; Dreizler, R. M., Providenca, J., Eds.; Plenum Press: New York and London, 1985.
(55) Gaussian 03, Revision B.02. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; C.; Strain; M.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 2003.
(56) Alemán, C.; Juliá, L. J. *Phys. Chem.* **1996**, *100*, 1524.
(57) Alemán, C.; Domingo, V.; Fajarí, L.; Juliá, L.; Karpfen, A. *J. Org. Chem.* **1998**, *63*, 1041.
(58) Alemán, C.; Casanovas, J. *J. Phys. Chem.* **2004**, *108*, 1440.
(59) Viruela, P. M.; Viruela, R.; Ortí, E.; Brédas, J. L. J. *Am. Chem. Soc.* **1997**, *119*, 1360.
(60) (a) Bredas, J. L.; Elsenbaumer, R. L.; Chance, R. R.; Silbey, R. J. *Chem. Phys.* **1983**, *78*, 5656. (b) Lazzaroni, R.; Taliani, C.; Zamboni, R.; Danieli, R.; Ostoja, P.; Porzio, W.; Bredas, J. L. *Synt. Met.* **1989**, *1*, C515. (c) Taliani, C.; Zamboni, R.; Danieli, R.; Ostoja, P.; Porzio, W. *Phys. Scrip.* **1989**, *40*, 781.
(61) (a) Raimundo, J.-M.; Blanchard, P.; Gallego-Planas, N.; Mercier, I.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. J. *Org. Chem.* **2002**, *67*, 205. (b) Roncali, J.; Blanchard, P.; Frère, P. J. *Mat. Chem.* **2005**, *15*, 1589.
(62) Garreau, S.; Louarn, G.; Buisson, J. P.; Froyer, G.; Lefrant, S. *Macromolecules* **1999**, *32*, 6807.
(63) Garreau, S.; Duvail, J. L.; Louarn, G. *Synth. Met.* **2001**, *125*, 325.
(64) Alemán, C.; Armelin, E.; Iribarren, J. I.; Liesa, F.; Laso, M.; Casanovas, *J. Synth. Met.* **2005**, *149*, 151.
(65) Dkhissi, A.; Louwet, F.; Groenendaal, L.; Beljonne, D.; Lazzaroni, R.; Brédas, J. L. *Chem. Phys. Lett.* **2002**, *359*, 517.
(66) Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Louwet, F.; Groenendaal, L.; Brédas, J. L. *Int. J. Quantum Chem.* **2002**, *91*, 517.
(67) Alemán, C.; Curcó, D.; Casanovas, J. *Chem. Phys. Lett.* **2004**, *386*, 408.
(68) Huang, H.; Pickup, P. G. *Chem. Mater.* **1998**, *10*, 2212.
(69) Ahonen, H.; Lukkari, J.; Kankare, J. *Macromolecules* **2000**, *33*, 6787.
(70) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720.
(71) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.
(72) Roncali, J.; Akoudad, S. *Synth. Met.* **1998**, *93*, 111.
(73) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 7629.
(74) Salzner, U.; Pickup, P. G.; Poirier, R. A.; Lagowski, J. B. *J. Phys. Chem.* **1998**, *102*, 2572.
(75) Brédas, J. L. *Chem. Phys.* **1985**, *82*, 3808.
(76) Hernández, V.; Castiglioni, C.; Del Zoopo, M.; Zerbi, G. *Phys. Rev. B* **1994**, *50*, 9815.

MA800174B