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Electronic Structure and Charge-Transport Properties of Polythiophene Chains Containing Thienothiophene Units: A Joint Experimental and Theoretical Study

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A theoretical investigation of the electronic structure and optical and charge-transport properties of polythiophene chains incorporating thienothiophene units is reported. Such polymers exhibit a better stability and, in some cases, a larger hole mobility than poly-3-hexylthiophene (P3HT). Quantum-chemical calculations have been performed on oligomers of increasing chain length to establish the changes in the electronic and optical properties when going from P3HT chains to the new derivatives. We have also estimated important molecular parameters governing charge transport in organic semiconductors (i.e., internal reorganization energies and transfer integrals) to determine whether the molecular structural changes along the polymer backbones are likely to be responsible for the increase in the hole mobility.

1. Introduction

Conjugated polymers are widely investigated in the growing field of organic electronics. The easy and low-cost processing techniques and the ability to print over large areas and tune the functionality of the material (e.g., the charge mobility) make them very attractive for use as active layers in devices such as thin-film transistors (TFTs).[1−4] The performance of TFTs depends on several parameters related not only to the geometry of the device and the morphology of the material but also on some intrinsic properties, such as the environmental stability.[5] A large number of semiconducting polymers have been used in TFTs; among them, regioregular poly(3-hexylthiophene) (P3HT) has led to some of the highest charge carrier mobilities reported for holes for solution-processible polymeric systems (around 0.1 cm^2 V^{-1} s^{-1}).[6] The high mobility is intimately linked to the packing of the polymer chains, which self-organize into highly ordered lamellae that favor efficient charge transport between the chains.[7,8] However, problems of stability in air due to electrochemical and photooxidation processes reduce the electrical performances[9] and thus new materials with improved stability are required. A measure of the polymer stability against oxidation is the ionization potential (IP), defined as the energy required to eject an electron out of a neutral atom or molecule in its ground state.[10] At the quantum-chemical level, the ionization potential is estimated in very first approximation within Koopmans' theorem as the absolute value of the energy of the highest occupied molecular orbital (HOMO).[11] Hence, the stability of a polymer can be improved by lowering its HOMO level, which translates into an increase in its ionization potential.

Several experimental approaches have addressed schemes to modify the IP of poly(alkylthiophenes).[12−15] Recently, the synthesis of two new regiosymmetrical, air-stable thiophene-

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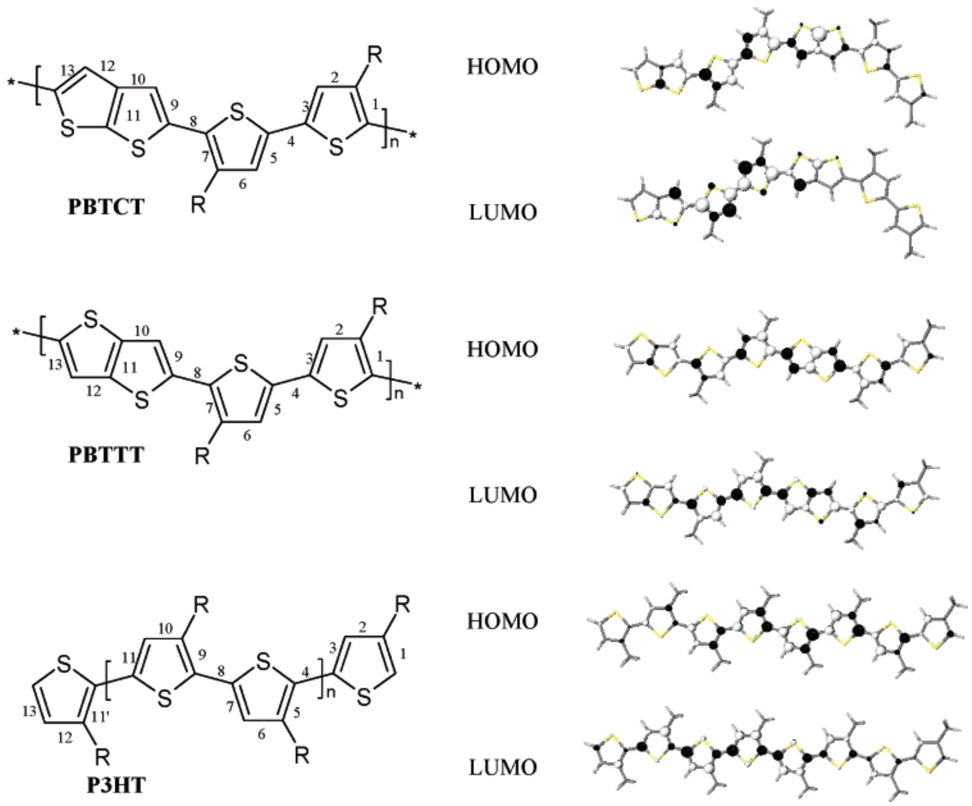

Figure 1. Molecular structures of PBTCT, PBTTT, and P3HT oligomers and shape of the frontier molecular orbitals at the ZINDO level ($n = 2$). The size and color of the spheres are representative of the amplitude and sign of the LCAO coefficients.

based semiconductors incorporating isomeric thienothiophene units has been reported. Both poly(2,5-bis(3-alkylthiophen-2-yl)thieno[2,3-*b*]thiophene[16] containing a cross-conjugated thieno[2,3-b]thiophene (PBTCT) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-*b*]thiophene[17] (PBTTT) show good hole mobilities (up to 0.15 and 0.70 cm^2 V^{-1} s^{-1}, respectively) and improved stability to air compared to P3HT. The improved stability resulting from an increase in the ionization potential by 0.5 and 0.3 eV compared to P3HT, respectively, has been suggested to arise mainly from the reduced delocalization induced by the thienothiophene aromatic rings into the conjugated backbone, especially in the case of cross-conjugated thieno[2,3-b]thiophene, and/or from the reduction in electron-donating alkyl chains in the backbone.[16,17] The higher hole mobility has been further associated with an improved degree of crystallinity.[17]

Although the synthesis and characterization of these compounds have been reported, few spectroscopic and/or quantum-chemical investigations have been performed to date.[18] The aim of this paper is therefore to establish in a joint experimental and theoretical study the relationship between the structure and properties of these new thienothiophene-based chains in comparison to P3HT. The first part of the paper focuses on the molecular and electronic structure of the different polymers. In the second part, we estimate two important molecular parameters governing charge transport in organic semiconductors (i.e., internal reorganization energies and transfer integrals) to determine whether the structural changes are likely to be responsible for the increase in the hole mobility; the possible origin for the increase in the hole mobility going from P3HT to PBTTT is then discussed.

2. Experimental Section

2.1. Materials and Methods. The polythienothiophenes PBTCT and PBTTT have been synthesized according to the procedure described in refs 16 and 17, respectively. Commercially available regioregular poly(3-hexylthiophene) supplied by Aldrich was used without further purification.

Fluorescence excitation and emission spectra of dilute solutions of the polymer chains dissolved in chlorobenzene have been recorded on a Perkin-Elmer LS 55 fluorescence spectrometer equipped with a Hamamatsu R928 photomultiplier. The fluorescence excitation spectra were recorded at a fixed fluorescence wavelength (520 nm in the case of PBTCT, and 600 nm for PBTTT and P3HT). The excitation and emission spectra were corrected with respect to the characteristics of the excitation and detection systems, respectively.

2.2. Computational Details. The geometries of oligomers of PBTCT, PBTTT, and P3HT were optimized at the density functional theory (DFT) level using the Becke's three-parameter B3LYP exchange-correlation functional and the standard 6-31G** basis set. A fully planar equilibrium structure has been assumed,

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as expected in the solid state. The size of the oligomers varies from $n = 1$ to $n = 4$ (see Figure 1). To reduce the computational costs, we replaced the alkyl chains by methyl groups in all cases. The vertical transition energies to the lowest excited state were computed on the basis of the optimized structures with the time-dependent density functional theory (TD-DFT) formalism using the same functional and basis set. It has been shown that B3LYP provides reliable geometries for organic conjugated compounds, although the length of bonds involving heavy elements is significantly overestimated.[19] In spite of the lower accuracy for the C−S bond lengths, spectroscopic data calculated for medium-size molecules with this functional were shown to be reliable for sulfur-containing organic molecules.[20] For the sake of comparison, semiempirical calculations were performed using the ZINDO method (Zerner's spectroscopic parametrization of the intermediate neglect of differential overlap Hamiltonian)[21] coupled to a single configuration interaction (SCI) scheme involving singly excited configurations generated from all occupied and unoccupied π-type molecular orbitals. The ZINDO calculations were performed on the optimized B3LYP geometries. All (TD)-DFT calculations were carried out with the Gaussian 03 program package.[22]

The energies of the electronic levels and optical transitions were extrapolated at the polymer limit from the oligomer values by Kuhn's expression[23,24]

$$E = E_0 \sqrt{1 + 2\frac{k'}{k_0}\cos\frac{\pi}{N+1}} \qquad (1)$$

where E_0 is the transition energy of a formal double bond, N is the number of double bonds (considered as identical oscillators in this model), and k'/k_0 is an adjustable parameter measuring the strength of the coupling between the oscillators.

To shed light into the charge transport properties of PBTTT and PBTCT compared to P3HT, we have calculated the transfer integrals in model systems made of two chains in interaction. The transfer integral reflects the strength of the interaction between two adjacent molecules and is the key parameter governing charge mobility in both the band and hopping regime.[25] The transfer integrals are generally estimated within Koopmans' theorem as half the splitting of the HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) levels for hole/electron transport in a system formed by two molecules in their ground state.[25] However, the splitting estimated within Koopmans' approximation, which assumes that the orbital energies of the two units are the same, can be affected by an offset of the molecular levels prior to their interaction because of polarization effects in asymmetric structures.[26] To avoid these artefacts, which are generally not corrected, and access the effective couplings, we have directly computed the transfer integral by expanding the molecular orbitals in atomic contributions. This can be expressed for hole transport as

$$t_{\mathrm{H}} = <\phi_{\mathrm{H}_1}|h|\phi_{\mathrm{H}_2}> = \sum_{\mu}\sum_{\nu} C_{\mathrm{H}_1\mu} C_{\mathrm{H}_2\nu} <\chi_\mu|h|\chi_\nu> \qquad (2)$$

where ϕ_{H_1} and ϕ_{H_2} denote the HOMO orbitals localized on molecules 1 and 2, respectively; $C_{\mathrm{H}_1\mu}$ ($C_{\mathrm{H}_2\nu}$) corresponds to the LCAO (linear combination of atomic orbitals) coefficient associated to the atomic orbital $\chi_{\mu(\nu)}$ in the molecular orbital ϕ_{H_1} (ϕ_{H_2}). A similar expression prevails between LUMO levels for electron transport. The matrix element $<\chi_\mu|h|\chi_\nu>$ is implemented in the semiempirical Hartree−Fock ZINDO method that we have used as

$$<\chi_\mu|h|\chi_\nu> = \frac{1}{2}(\beta_{\mathrm{A}} + \beta_{\mathrm{B}})\bar{\mathrm{S}}_{\mu\nu} \qquad (3)$$

where β_A and β_B are two parameters depending on the nature of atoms A and B, and $\bar{\mathrm{S}}_{\mu\nu}$ is the overlap factor between the atomic orbitals μ and ν corrected by empirical factors.

The transfer integral for holes and electrons has been estimated in cofacial dimers made of oligomers of P3HT, PBTCT, and PBTTT, in which the molecules are exactly superimposed and separated by a distance fixed at 3.5 Å. The influence of chain length has been analyzed by considering oligomers of PBTCT and PBTTT with n varying from 1 to 4 and P3HT oligomers with $n = 1, 3, 5, 7$. Because cofacial configurations are rarely encountered in crystalline structures, the impact of the translation of one molecule along its long or short chain axis has also been investigated to assess the influence of the packing geometry on charge transport. In this case, the alkyl chains have been replaced by hydrogen atoms in order to avoid possible steric interactions between the methyl groups in our model structures.

The second parameter that we have estimated is the reorganization energy that appears in the expression of charge-transfer rates in a hopping regime.[25] This parameter is made of two components that both introduce an energy barrier for the charge-transfer process:[27] the internal reorganization energy λ_{i} accounts for the changes in the geometry of the two molecules upon charge transfer and the external reorganization energy λ_{s} reflects the changes in the nuclear polarization of the surrounding medium. We have focused here on the internal part, which is expected to be the most affected by the changes in the molecular topology of the polymer chains. λ_{i} has been estimated at the DFT level using the B3LYP functional and the 6-31G** basis set. This approach has been found to provide λ_{i} values in very good agreement with experimental data extracted from gas-phase ultraviolet photoelectron spectra for several molecules.[28] The internal reorganization energy is calculated as $\lambda_i = (E^{\mathrm{D}}_{\mathrm{D}+} - E^{\mathrm{D}}_{\mathrm{D}}) + (E^{\mathrm{D}+}_{\mathrm{D}} - E^{\mathrm{D}+}_{\mathrm{D}+})$, where for instance, $E^{\mathrm{D}}_{\mathrm{D}+}$ corresponds to the energy of the neutral molecule D in the equilibrium geometry of the radical-cation D^+.

3. Results and Discussion

3.1. Molecular and Electronic Structure. Experimentally, both PBTCT and PBTTT have an ionization potential

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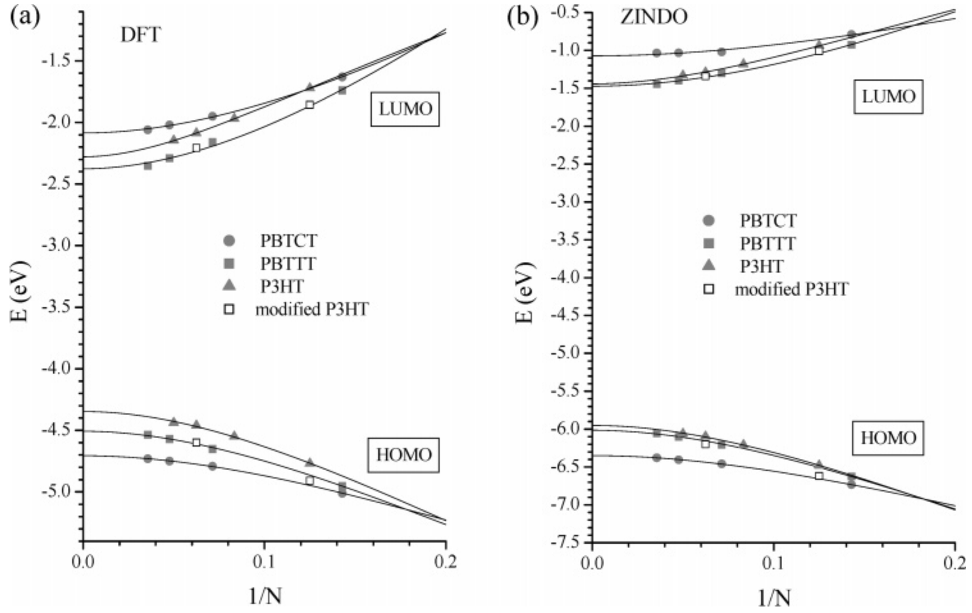

Figure 2. Chain-size evolution of the HOMO and LUMO energies of PBTCT, PBTTT, and P3HT oligomers with $n = 1-4$, as calculated at the DFT/B3LYP/6-31G** (a) and ZINDO (b) levels. Solid lines are Kuhn fits across the calculated values. N is the number of double bonds in the molecular backbone. Modified P3HT corresponds to oligomers of P3HT with only half the number of alkyl groups (see text for details).

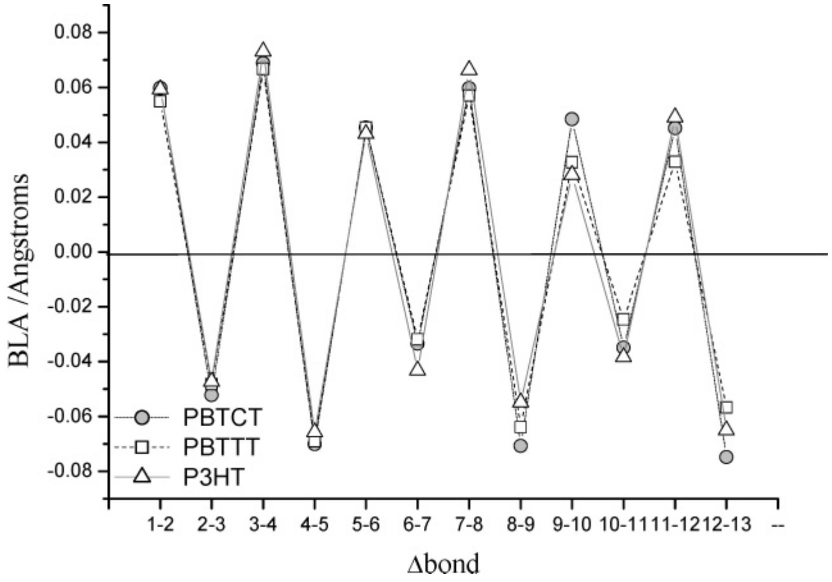

Figure 3. DFT-calculated bond length alternation (BLA) along the C−C conjugation path for PBTCT, PBTTT, and P3HT with $n = 1$. The bond labeling is shown in Figure 1. In the case of P3HT, the Δbond value 11−12 in the plot corresponds to the average value between Δ11−12 and Δ11′−12.

larger than that of P3HT (5.3 and 5.1 vs 4.8 eV).[16,17] Figure 2 displays the energies of the HOMO and LUMO levels of oligomers of PBTCT, PBTTT, and P3HT plotted as a function of the inverse number of double bonds in the molecule, as calculated at the DFT and ZINDO levels; a Kuhn fit has been performed in each case across the calculated data. The values extrapolated at the infinite polymer limit indicate that PBTCT has the lowest HOMO level followed by PBTTT (i.e., 0.4 and 0.2 eV lower than the HOMO of P3HT at the DFT level and 0.4 and 0.1 eV lower at the ZINDO level, respectively). Although the absolute values of the orbital energies are very much method-dependent (DFT is known to yield very small electronic bandgaps for molecules in the gas phase), both methodologies reproduce the experimental trends, namely, a stabilization of the HOMO level by 0.5 and 0.3 eV going from P3HT to PBTCT and PBTTT, respectively.

The difference in the HOMO energies of the three polymers can be understood from their molecular structure. Figure 3 sketches the C−C conjugation path for oligomers of PBTCT, PBTTT, and P3HT with $n = 1$ (see Figure 1). The C−C bond length alternation (BLA) around the thienothiophene moiety in PBTCT is found to be larger than the values in the other two compounds; this points to a smaller delocalization of the π-electronic density in the thieno[2,3]thiophene unit compared to thiophene rings. This geometric modification induces in turn changes in the electronic structure, because a larger BLA value leads to a larger electronic bandgap.[29] However, we realize by imposing various BLA values along the backbone of P3HT that such geometric changes along the conjugation path cannot fully account for the large differences observed between the orbital energies. It is actually the breaking of the conjugation pathway along the chain in the cross-conjugated thieno[2,3]thiophene unit of PBTCT, resulting in an increase in the BLA in this unit (see Figure 1), which significantly raises the LUMO level and lowers the HOMO level of this chain,[30−32] as illustrated in Figure 2 when comparing PBTCT and P3HT.

There is no breaking of conjugation along the backbone of PBTTT; the overall C−C bond alternation is very similar to that of P3HT, being even smaller around the thienothiophene unit. This indicates that the delocalization of electrons in fused rings is not less favorable than in single thiophene. The calculations show at both levels of theory that there is a lowering of the HOMO and LUMO levels by about the same amount (∼0.15 eV at the DFT level and ∼0.10 eV at the ZINDO level) when going from P3HT to PBTTT (see Figure 2). This contradicts the suggested formation of a less delocalized/aromatic structure in PBTTT. The lowering of the frontier orbitals in PBTTT actually arises from the reduced number of alkyl groups along the backbone with respect to P3HT and hence to a reduced electron-donating character of the substituents.[17] This interpretation has been validated for P3HT oligomers with n equal to 1 and 3 by varying the number of alkyl substituents from 4 and 8, as found in P3HT, down to 2 and 4 for modified P3HT chains, respectively; the latter choice reflects the substitution pattern in PBTTT chains. The results show a decrease in the energy of both the HOMO and LUMO levels, which brings them to lie on the curve obtained for PBTTT, thus giving support that the reduced inductive effect due to the alkyl substituents is linked to the increase in the ionization potential.

Changes in the molecular structure lead to modifications in the electronic structure, which result in a possible modulation of the electronic bandgap and hence of the optical properties. The experimental fluorescence emission and excitation spectra of PBTCT, PBTTT, and P3HT chains in chlorobenzene are shown in Figure 4. The three compounds exhibit the main $S_0 \rightarrow S_1$ absorption feature in the visible region, with a similarly broadened lineshape. The emission spectra are more structured than the excitation spectra in all cases because of the flatter torsional potential in the ground state compared to the first excited state.[33] The absorption spectrum of PBTCT shows a maximum at $E_{\mathrm{max}} = 2.98$ eV in solution. This is significantly higher than for P3HT, whose maximum absorbance is located at 2.72 eV. Contrarily, the absorption maximum of PBTTT appears to be very close to that of P3HT. Moreover, the optical bandgap, which can be estimated as the energy at the intersection of the normalized fluorescence and excitation spectra, is almost identical for PBTTT and P3HT (2.33 versus 2.31 eV, respectively).

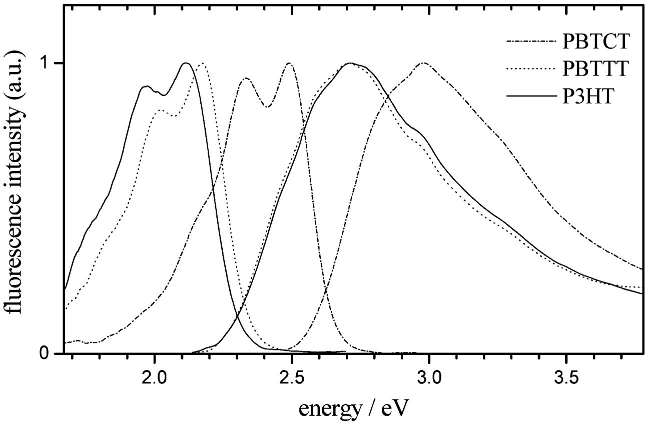

Figure 4. Fluorescence emission (left) and excitation (right) spectra of PBTCT, PBTTT, and P3HT in chlorobenzene at room temperature. The excitation spectra are recorded at the fluorescence wavelengths of 520 nm (PBTCT) and 600 nm (PBTTT and P3HT).

The calculations of the S_0-S_1 vertical transition energies E_{vert} for the different oligomers reproduce the experimental findings at both the TD-DFT and ZINDO levels (Figure 5): PBTTT and P3HT have very similar transition energies, whereas the transitions of PBTCT are significantly blue-shifted (∼0.5 eV at both levels of theory). This trend is directly correlated to the HOMO−LUMO gaps because the S_0-S_1 transition is mainly described by an electronic excitation from the HOMO to the LUMO levels. However, a significant difference is observed between the two theoretical methods regarding the absolute value of the transition energies. On the one hand, previous works indicate that TD-DFT tends to systematically overestimate the chain-length dependence of the transition energies;[24] this accounts for most of the difference between the calculated TD-DFT and experimental polymer values. This effect is less pronounced for the PBTCT polymer because the strength of the coupling between the repeat units is largely reduced because of the breaking of the conjugation, as illustrated by the reduced slope of the $1/N$ evolution in Figure 5. Note also that the TD-DFT calculations do not account for solvent effects, which typically red-shift the transition energies by ca. 0.3 eV.[24] On the other hand, the semiempirical ZINDO method has been parametrized to reproduce E_{vert} for a large number of compounds in apolar solvents. The ZINDO results generally closely match the slope of the $1/N$ chain-length dependence inferred from experimental data.[24] The significant underestimation of the calculated E_{vert} values compared to the experimental E_{max} values likely results from the combination of several factors:[24] (i) a deficient parametrization of the sulfur atom in ZINDO, which leads to a systematic underestimation of E_{vert}; (ii) a possible discrepancy in the theoretical description of the BLA along the conjugated backbone; (iii) a proper treatment of the impact of the thermal population of torsional modes is missing in the present calculations performed on fully planar structures at 0 K. This can introduce a difference as large as 0.3 eV between E_{max} and E_{vert} for flexible polymer chains. The strong impact of the torsional mode in solution is supported by the large Stokes shifts between emission and absorption (observed in

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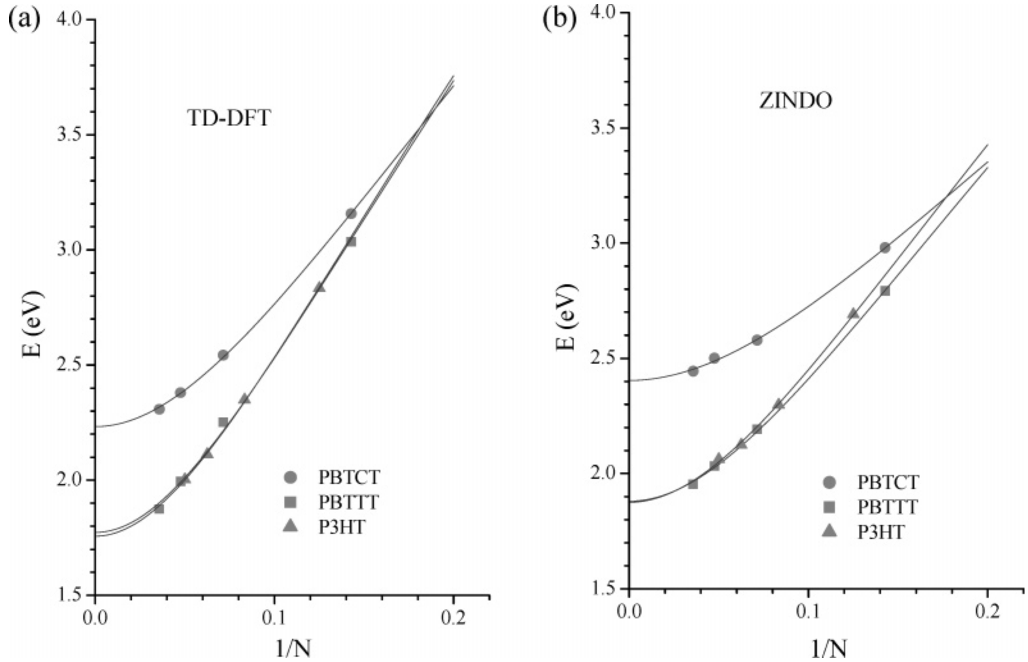

Figure 5. Chain-size evolution of the vertical transition energies of PBTCT, PBTTT, and P3HT oligomers with $n = 1-4$, as calculated at the DFT/B3LYP/6-31G** (a) and ZINDO (b) levels. Solid lines are Kuhn fits across the calculated values. N is the number of double bonds in the molecular backbone.

Table 1. Internal Reorganization Energy (eV) for Hole Transport and Electron Transport for P3HT, PBTTT, and PBTCT ($n = 1$), as Calculated at the DFT Level

	P3HT	PBTTT	PBTCT
hole transport	0.29	0.31	0.31
electron transport	0.26	0.27	0.27

Table 2. ZINDO-calculated Transfer Integrals (in meV) Between HOMOs (H) and LUMOs (L) for P3HT ($n = 1, 3, 5, 7$), PBTTT and PBTCT ($n = 1, 2, 3, 4$) Oligomers in a Cofacial Dimer with the Two Chains Separated by an Intermolecular Distance of 3.5 Å; Note that the Number of Thiophene Rings m is the Same for the Three Series ($m = 4n$ for PBTTT and PBTCT and $m = 2(n + 1)$ for P3HT)

	HOMO			LUMO		
m	P3HT	PBTTT	PBTCT	P3HT	PBTTT	PBTCT
4	369.1	372.6	375.1	276.1	275.0	268.8
8	346.3	344.2	351.5	286.8	288.9	275.2
12	340.2	336.3	345.5	290.2	293.7	274.5
16	337.7	332.8	343.0	291.8	295.9	274.0

Figure 4), which are much larger than in unsubstituted oligothiophenes.[24]

3.2. Charge-Transport Properties. The hole mobility values for a series of PBTTT polymers with different alkyl groups have been measured, reaching values up to 0.7 cm^2 V^{-1} s^{-1}; this is about a factor of 5 higher than for P3HT measured under similar conditions[17] and larger than the values obtained for the analogous polymer PBTCT (up to 0.15 cm^2 V^{-1} s^{-1}).[16] In all cases, the devices showed p-type behavior. Quantum-chemical calculations have been performed to estimate two main parameters governing transport properties and assess whether the differences in the mobility values reflect changes in the molecular topology of the chains and/or changes in the packing in thin films.

The internal reorganization energies λ_i of P3HT, PBTCT, and PBTTT oligomers with $n = 1$ are displayed in Table 1 for hole and electron transport. Values around 0.30 eV are obtained in all cases, thus indicating that the modulation of the mobility values does not originate from changes in the internal reorganization energy.

A first insight into the role played by the transfer integral t has been gained by considering a dimer made of two P3HT, PBTCT, or PBTTT oligomers superimposed on top of one another in a cofacial configuration. The calculated transfer integrals are displayed in Table 2. In a cofacial geometry, the transfer integrals for holes are systematically larger than for electrons in the three polymers; the hole transfer integrals slightly decrease with chain length while the opposite behavior is found for electrons. These two features can be rationalized from the shape of the orbitals when considering the amount of bonding versus antibonding interactions in the overlapping region.[34] Our results do not show significant fluctuations in the transfer integrals among the three polymers for the same packing geometry whatever the chain length, thus indicating that the mobility is hardly affected by the nature of the repeat unit (thiophene versus thienothiophene).

Such cofacial configurations are rarely encountered in crystalline structures because displacements often help to minimize the geometric and/or energetic constraints. Accordingly, we have also examined the influence of the relative positions of the two interacting units by translating one chain with respect to the other. Because the polymers exhibit only p-type transport, we will focus hereafter on the transfer integral for holes. Figure 6 displays the evolution of the transfer integrals for two interacting P3HT, PBTTT, and PBTCT chains with $n = 2$ ($n = 3$ in P3HT to ensure that the same number of thiophene rings is involved) when the top oligomer is translated along its main chain axis (Figure 6a) and along its short chain axis (Figure 6b), while keeping the molecular planes parallel and separated by 3.5 Å. The transfer integrals obtained for a displacement of 0 Å

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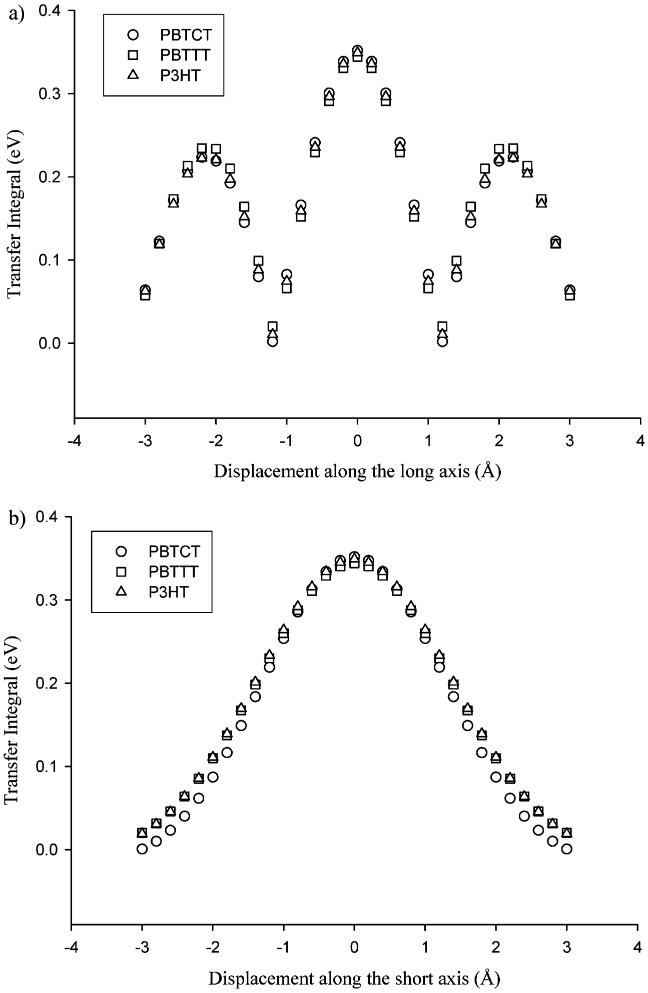

Figure 6. Evolution of the INDO-calculated transfer integrals (eV) for holes in a system made of two parallel eight-ring oligomers of PBTTT, PBTCT, and P3HT, as a function of the degree of translation of the upper chain along its main (a) and short (b) molecular axes. Note that the zero value corresponds to the cofacial structure.

correspond to the cofacial structures. Although the transfer integrals show only small variations among the three systems, we find very different profiles depending on the chosen translational axis. Strong fluctuations are observed when a translation along the long molecular axis is applied. In contrast, the profile along the short axis displays a monotonous decrease when moving away from the cofacial configuration. These trends can be fully rationalized from the shape of the HOMO level, whose LCAO pattern shows a change in the sign of the wavefunction every half thiophene ring (see Figure 1).[34] The maxima found upon translation along the long axis are dominated by bonding or antibonding interactions between the orbitals, whereas the minima correspond to situations in which there is a pronounced cancellation between bonding and antibonding interactions. When the translation occurs along the short molecular axis, no oscillatory pattern is found, because there is no change in the sign of the wavefunction along this axis.

The results demonstrate that the transfer integrals, although showing a very similar evolution for the three systems, are strongly sensitive to the relative position of the chains; for instance, Figure 6 illustrates that a longitudinal shift as small as 1 Å away from the cofacial structure leads to a marked drop in the transfer integral. Because the mobility values are largely dictated by the amplitude of the transfer integrals, small changes in the chain packing among the three polymers are likely to be responsible for the variations in the measured hole mobilities.[18] In this respect, the knowledge of the actual chain packing is of utmost importance and is currently investigated by force-field calculations. Note that other factors such as changes in the thin-film morphology, concentration of impurities/defects, or amount of crystallinity might also play an important role in defining the hole mobilites of the three polymers. In this respect, very recent results on PBTTT show that the difference between the field-effect mobility in thin films deposited on SiO_2 covered with a self-assembled monolayer (>0.1 cm^2 V^{-1} s^{-1}) and on bare SiO_2 (<0.005 cm^2 V^{-1} s^{-1}) is mainly related to changes in the density of grain boundaries (the molecules organize in the same way on both surfaces and the crystals have similar orientation and level of order).[35]

4. Conclusions

We have calculated the electronic and optical properties of two newly synthesized polymers including thienothiophene units (PBTTT and PBTCT) and have compared them to those of the widely studied poly-3-hexylthiophene chains (P3HT). The ionization potentials calculated for oligomers of different sizes and extrapolated at the polymer limit indicate that PBTCT has the highest value, followed by PBTTT and P3HT, in agreement with corresponding experimental data. It is the breaking in the conjugation pathway along the PBTCT backbone that leads to a significant stabilization of its HOMO level. The larger ionization potential calculated for PBTTT with respect to P3HT arises from the smaller number of alkyl substituents in PBTTT and hence from a reduced donor inductive effect. The extrapolated vertical transition energy to the first excited state is similar for PBTTT and P3HT and is blue-shifted by about 0.4−0.5 eV in PBTCT, in full consistency with the trends found for the HOMO−LUMO gaps.

Regarding the charge-transport properties, our calculations indicate that the variations in the hole mobility among the three polymer chains do not originate from changes in the amplitude of the internal reorganization energy. Moreover, the similar values obtained for the transfer integrals in cofacial dimers made of PBTTT, PBTCT, and P3HT oligomers demonstrate that the mobility value is hardly affected by the nature of the repeat unit. Because the transfer integral is extremely sensitive to the relative position of the chains, we are led to the conclusion that the changes in the actual packing of the polymer chains are a key ingredient in rationalizing the variations in the mobility values.

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