Influence of Chain Length and Derivatization on the Lowest Singlet and Triplet States and Intersystem Crossing in Oligothiophenes

D. Beljonne,[†,‡] J. Cornil,[†] R. H. Friend,[‡] R. A. J. Janssen,[§] and J. L. Brédas[†]

Contribution from the Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium, Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 OHE, United Kingdom, and Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract: On the basis of configuration interaction calculations, we first describe the nature of the lowest singlet and triplet excited states in oligothiophenes ranging in size from two to six rings. We calculate the vertical excitation energies from the singlet ground state S_0 to the first one-photon allowed singlet excited state S_1 as well as the energy difference between the ground state and the lowest triplet state T_1. The computed transition energies are in very good agreement with the measured values and indicate a strong confinement of the lowest triplet. We also uncover the nature of the higher-lying triplet excited state T_n that is coupled via a large oscillator strength to T_1. The evolution with chain length of the T_1-T_n excitation energies compares well with the experimental evolution based on photoinduced absorption data. Next, we investigate the geometry relaxation phenomena occurring in the S_1 and T_1 states; more pronounced and localized bond-length deformations are calculated in the triplet state than in the singlet, confirming the more localized character of T_1. We also analyze the influence on the lowest excited states of grafting electroactive end-groups on the conjugated path of terthiophene. Finally, the various mechanisms involved in the nonradiative decay of the singlet excitations are discussed, and results are presented as a guide toward the optimization of light emission efficiency in conjugated systems.

I. Introduction

Due to their exciting electronic and optical properties, organic conjugated polymers have been the focus of an enormous amount of experimental and theoretical work in the last decade. Their high electrical conductivities upon doping and fast, strong nonlinear optical response make them suitable for a large number of potential applications, for instance in transistors, batteries, sensors, light amplificators, or all-optical switches.[1] It has also been shown that conjugated polymers can be used as active layers in light-emitting diode (LED) devices.[2,3] In such devices, light emission comes from the radiative decay of the singlet excitons created by recombination of the electrons and holes that are injected at the electrodes.[2] Even though electroluminescence efficiencies as high as $10-12\%$ have been reported for the best LEDs based on conjugated materials,[4] their properties still need to be improved in view of commercial applications.

In this context, quantum-chemical calculations prove to be useful since they allow the characterization of both the singlet excited states involved in the emission mechanism and the triplet excited states, either formed directly by electron-hole recombination or resulting from an intersystem crossing between the singlet and triplet manifolds; note that such a crossing gives rise to a strong, long-lived, triplet−triplet absorption observed by photoinduced absorption (PA) experiments. Recently, we have presented a model[5] including both electron−phonon and electron−electron interactions that provides a coherent description of the nature of the lowest singlet and triplet excitations in model oligomers of poly(paraphenylene vinylene) (PPV), a conjugated polymer which has been extensively used as active material in the LEDs.[2,3] After PPV, similar LEDs have been successfully built by sandwiching oligothiophenes in between electron- and hole-injecting contacts.[6−9] The choice for thiophene oligomers is mainly guided by the following reasons: (i) well-defined oligomers have been synthesized that possess very good processability and stability[9] and (ii) the electronic photoexcitations of oligothiophenes have been well characterized experimentally;[10−15] most importantly, fluorescence has been observed in thiophene oligomers,[10−15] which has to be related to the fact that the lowest singlet excited state S_1 in these molecules has a different parity from the ground state S_0 and

† Université de Mons-Hainaut.
‡ Cambridge University.
§ Eindhoven University of Technology.
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that, therefore, the $S_1 \rightarrow S_0$ electronic transition is dipole allowed.[15–17] (Note, however, that even for a dipole-forbidden S_1 excited state, weak light emission can be induced by vibronic couplings.)

In this work, we apply techniques similar to those used for the description of the excitations in PPV oligomers[5] to uncover the nature of the lowest singlet and triplet excited states of unsubstituted oligothiophenes ranging in size from two to six thiophene units (hereafter denoted as Thn, where n corresponds to the number of thiophene rings). We analyze the influence of the chain length on the singlet–singlet $S_0 \rightarrow S_1$ and triplet–triplet $T_1 \rightarrow T_n$ excitation energies as well as on the $S_0 - T_1$ energy difference and compare our results to experimental data provided by one-photon optical absorption and photoinduced absorption measurements. We also investigate the lattice relaxations occurring in the S_1 and T_1 excited states of some model oligomers. Finally, we discuss some of the processes that lead to nonradiative decay of the singlet excitations and try to rationalize some experimental results indicating an increase of the fluorescence quantum yield either by increasing the chain length from two (Th2) to six (Th6) thiophene rings[11] or by attaching electroactive groups on terthiophene (Th3).[18] In this context, we study the effects on the lowest excited states of Th3 or grafting both electron-donating (OCH3 and NH2) and electron-withdrawing (CHO and CN) moieties on the conjugated segment.

The structure and atom labeling of the various molecules investigated in this work can be deduced from those of the longest unsubstituted oligothiophene (Th6) and those of the monosubstituted (Th3-X, where X denotes the nature of the substituent) and bis-substituted (X-Th3-X) trimers of thiophene, displayed in Figure 1.

II. Methodology

The geometries of all oligomers are optimized at the Hartree–Fock semiempirical Modified Neglect of Differential Overlap (MNDO)[19] level. In the case of oligothiophenes, the MNDO technique has been shown to give bond length values in the ground state in good agreement with X-ray diffraction data.[20] Note that all the calculations were performed on the basis of planar conformations. Crystal packing is likely to force the molecules to be planar in films,[21] whereas torsions of the rings along the chain axis most probably occur in solution.[10]

Based on the ground-state optimized geometries, we perform Intermediate Neglect of Differential Overlap (INDO)[22]/Multi-
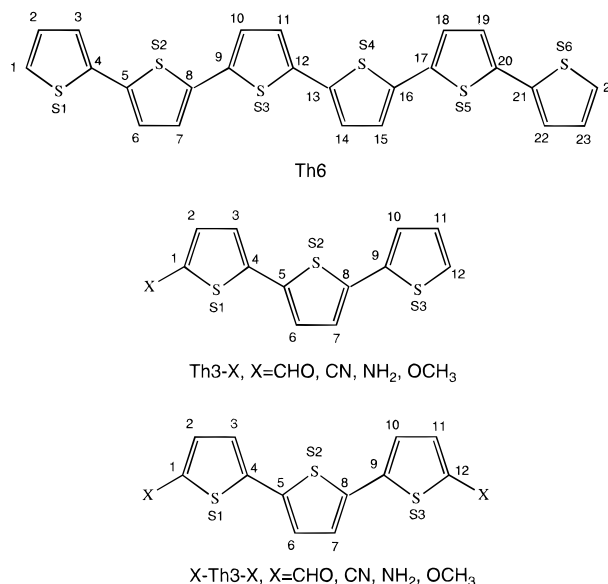
Figure 1. Structure and atom labeling of the unsubstituted hexathiophene (Th6) and the mono-substituted (Th3-X, where X denotes the end-group) and bis-substituted (X-Th3-X) terthiophenes.

Reference Double-Configuration Interaction[23] calculations to describe the lowest singlet and triplet excited states. The MRD-CI scheme has been described in detail elsewhere[24] and successfully applied in the case of polyenes[24,25] as well as oligothiophenes,[17] oligopyrroles,[26] and oligo(phenylene vinylene)s.[5] Here, we consider in the CI expansion of the wave functions single and double excitations from the six highest π-levels to the four π^*-levels with respect to two reference configurations (dominating the description of the ground state S_0 and the lowest excited states S_1 and T_1): (i) the Self-Consistent-Field (SCF) determinant itself and (ii) the configuration resulting from the excitation of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In the case of the PPV oligomers, we found no major changes in the transition energies from the singlet ground state to the lowest excited states when considering from two to five reference determinants (including doubly excited determinants) in the MRD-CI formalism. As all truncated CI techniques, the MRD-CI scheme is not size consistent; however, an appropriate choice of the reference configurations provides a balanced description of the correlation effects in the ground state and in the excited states and therefore allows for a precise estimation of the transition energies to the lowest excited states, as has been shown elsewhere.[5,17,24–26]

To investigate the lattice distortions taking place in the S_1 and T_1 excited states of oligothiophenes, we have considered the following approach. We first optimize the geometries of both states by means of the MNDO technique. The SCF calculations are then performed on the basis of a level occupancy characterized by the promotion of one electron from the HOMO to the LUMO level (flipping one spin for the triplet). The excited-state energy, obtained by a simple CI calculation involving a few electronic configurations, is used as a criterion during the geometry optimization. For oligo(phenylene vinylene)s, this technique leads to excited-state geometries that are very similar to those obtained on the basis of a bipolaron-

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type relaxation (where geometry changes related to the formation of bipolaron defects are simulated) or BOBL-type relaxation (where bond lengths in the excited states are evaluated from the electronic bond orders).[5]

In the second step, on the basis of the MNDO-optimized excited-state geometries, INDO/MRD-CI vertical transition energies from the ground state to the lowest excited states are computed. Combining the ground-state deformation energy calculated at the MNDO level when going from the S_0 geometry to the S_1 or T_1 geometry to the INDO/MRD-CI vertical S_0-S_1 and S_0-T_1 energy differences allows us to estimate the geometric relaxation energy in both the singlet S_1 and triplet T_1 excited states.

According to experiment and theory,[27] the optimized $1B_u$ excited-state geometry of polyacetylene (PA) presents a lattice conformation corresponding to the formation of a soliton–antisoliton pair. Solitons are topological kinks, defining a domain wall between two geometric phases, characterized by an opposite alternation of the single and double carbon–carbon bonds; alternatively, they can be viewed as excitations of the twofold degenerate ground-state PA chains leading from one minimum of the potential to the other minimum of same energy.[27] In oligothiophenes, soliton–antisoliton pairs are bound by the ground-state nondegeneracy (in opposite to the situation observed for polyacetylene, the two resonant geometric forms, obtained by exchanging the single and double bonds in the conjugated pathway have different energies), and we then parameterize the geometric deformations that characterize the excited states by fitting to the MNDO-optimized geometries the expression adopted by Sethna and Kivelson[28] in the case of a loosely bound soliton–antisoliton pair

$$r_n^e = r_n^g + (-1)^n \times \phi \times \left[\tanh\frac{n - N_0 - R}{\xi} + \right.$$
$$\tanh\frac{n + 1 - N_0 - R}{\xi} - \tanh\frac{n - N_0 + R}{\xi} -$$
$$\left. \tanh\frac{n + 1 - N_0 + R}{\xi} \right] \quad (1)$$

where r_n^g is the bond length between carbon atoms n and $n+1$ in the MNDO-optimized ground-state geometry, N_0 is the center of the chain, ξ is the coherence length of the defect, ϕ is the amplitude of the deformations, and $2R$ is the distance between the "soliton" centers; the smaller the R value, the stronger the confinement of the charged species. In Figure 2, we present the bond-length distortions $(r_n^e - r_n^g)$ calculated for various values of the parameters R, ϕ, and ξ. Note that the carbon–sulfur bonds, that are only slightly modified in the excited states with respect to their values in the ground state,[17,29] are not included in this fitting procedure.

III. Vertical Excitation Energies

The ground-state geometry of all oligomers has been optimized at the MNDO level. Within the thiophene rings, the difference between the single and double carbon–carbon bond lengths, Δr, amounts to 0.05–0.06 Å, and the carbon–sulfur C–S bonds are close to 1.7 Å; the interring carbon–carbon C–C bonds are calculated to be equal to ~1.45 Å. These results are in very good agreement with the available X-ray diffraction

Table 1. INDO/MRD-CI Singlet–Singlet $S_0 \rightarrow S_1$, Singlet–Triplet $S_0 \rightarrow T_1$, and Triplet–Triplet $T_1 \rightarrow T_n$ Energies, Calculated on the Basis of the Ground-State Geometries of Oligothiophenes[e]

		Th2	Th3	Th4	Th5	Th6	Th7	Th9	Th11
$S_0 \rightarrow S_1$	calcd	4.23	3.58	3.16	2.92	2.72			
	exptl	4.12[a]	3.49[a]	3.18[a]	3.00[a]	2.72[b]	2.58[b]	2.45[b]	2.40[b]
$T_1 \rightarrow T_n$	calcd	4.37	3.42	3.01	2.62	2.40			
	exptl		2.70[c]	2.21[c]		1.75[b]	1.60[b]	1.52[b]	1.45[b]
$S_0 \rightarrow T_1$	calcd	1.84	1.68	1.61	1.61	1.65			
	exptl		1.74[d]						

[a] Reference 11. [b] Reference 14. [c] Reference 41. [d] Reference 36. [e] Experimental data taken from optical measurements in solution are also included. All the energies are given in eV.

data, which indicate values of Δr and C–S bond lengths close to 0.07 and 1.7 Å, respectively, and interring C–C bond lengths of approximately 1.46 Å.[30] At the 6-31G*/MP2 level, the corresponding values for the planar conformation of bithiophene are $\Delta r = 0.03-0.04$ Å; $r(\text{C–S}) \sim 1.73$ Å; and interring $r(\text{C–C}) \sim 1.45$ Å.[31] We are thus confident that the MNDO technique is appropriate to reproduce the equilibrium geometries of thiophene oligomers.

On the basis of the MNDO ground-state geometries, we have first calculated the electronic excitation energies from the singlet ground state S_0 to the lowest singlet excited state S_1, by means of the INDO/MRD-CI approach. Note that the CI expansion of the S_1 wave function is dominated by the electronic configuration built by promoting one electron from the HOMO level to the LUMO level. The theoretical $S_0 \rightarrow S_1$ transition energies are compared in Table 1 to the experimental values, extracted from optical absorption measurements in solution;[11,14] the measured and calculated evolutions with the inverse number of thiophene rings of the $S_0 \rightarrow S_1$ excitation energies are illustrated in Figure 3. The agreement between the experimental and theoretical results is impressive, which shows the suitability of the INDO/MRD-CI technique for the description of the electronic excitations in these oligomers. Both the spectroscopic data and the calculated values indicate a red-shift of the first one-photon allowed electronic transition with the size of the oligomers, due to the extension of the π-delocalized system. Extrapolation to an infinite chain length of the calculated transition energies, assuming a linear evolution of $S_0 \rightarrow S_1$ with respect to $1/n$, leads to an optical gap close to 2 eV, which again is in good agreement with the spectroscopic data on polythiophene; recent optical measurements performed on regioregular polythiophenes show indeed an absorption with an onset at ~1.7–1.8 eV and a peak at ~2.5 eV.[32,33]

In Table 1, we also report the energy difference between the S_0 ground state and the T_1 lowest triplet excited state, as calculated at the INDO/MRD-CI level on the basis of the S_0 geometry. As illustrated in Figure 3, the evolution with chain length of the $S_0 \rightarrow T_1$ energy difference is much slower than that of the $S_0 \rightarrow S_1$ excitation: the singlet–triplet energy difference is only lowered by ~0.2 eV when going from the dimer to the hexamer of thiophene while the corresponding singlet–singlet absorption is characterized by a bathochromic shift that amounts to ~1.4 eV. The slower evolution with the number of thiophene rings of the triplet excitation energy (with respect to that of the singlet) reflects its more localized character. Such a difference has clearly to be related to the exchange term

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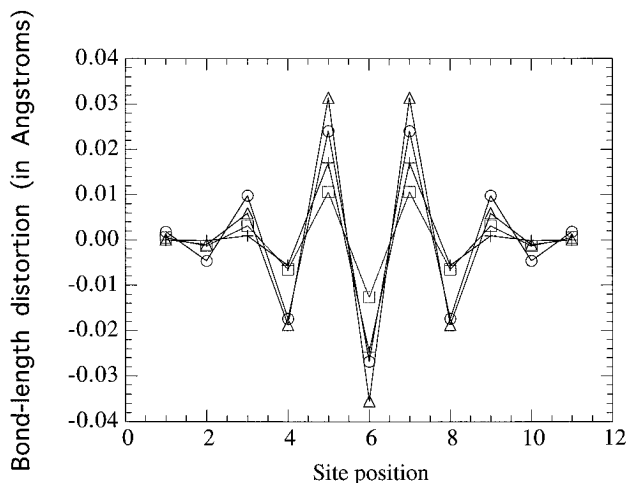(28) Sethna, J. P.; Kivelson, S. *Phys. Rev. B* **1982**, *26*, 3613.
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Figure 2. Bond-length deformations (in Å) calculated on the basis of eq 1 with (a) $\phi = 0.1$; $\xi = 2$; and $R = 2$ (circles); (b) $\phi = 0.1$; $\xi = 2$; and $R = 1$ (squares); (c) $\phi = 0.1$; $\xi = 1$; and $R = 1$ (crosses); and (d) $\phi = 0.1$; $\xi = 1$; and $R = 2$. ϕ is in Å, ξ and R are given in site units.
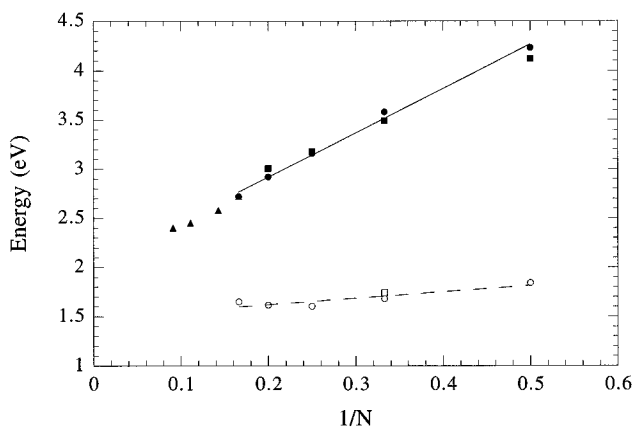
Figure 3. Comparison between the evolutions with the inverse number of thiophene rings, $1/n$, of (i) the INDO/MRD-CI singlet−triplet $S_0 \rightarrow S_1$ (solid line, closed circles) and singlet−triplet $S_0 \rightarrow T_1$ (dashed line, open circles) energies and (ii) the experimental $S_0 \rightarrow S_1$ (closed squares,[11] closed triangles[14] and $S_0 \rightarrow T_1$ (open squares[36]) energies obtained from measurements in solution.

that allows a more pronounced confinement of the triplet exciton with respect to the singlet. Very similar conclusions have been drawn from similar calculations on PPV oligomers.[5] Note that Optically-Detected Magnetic Resonance (ODMR) experiments on polythiophene indicate that the T_1 triplet state extends over not much more than one thiophene ring,[34] which agrees well with our results. Moreover, similar ODMR measurements performed on oligomers ranging in size from two to five rings[35] indicate a very small chain-length dependence of the average spin−spin distance, r, in the triplet, as deduced within the dipolar approximation from the zero-field splitting, D (using the relation $D/hc = 2.6017r^{-3}$, where D/hc is in cm^{-1} and r in Å, we find $r = 3.27$, 3.36, and 3.49 Å, in Th3, Th4, and Th5, respectively).

Optical absorption measurements in a solvent containing heavy atoms (*i.e.*, 1,2-dibromomethane) have allowed the T_1 excited state in terthiophene (Th3) to be located.[36] In this case, the intensity of the $S_0 \rightarrow T_1$ excitation is raised due to the increase of the spin-orbit coupling related to the "heavy-atom

effect" induced by the solvent molecules.[37] The experimental absorption spectrum shows a broad and weak band that peaks at ~1.7 eV, in very good agreement with the 1.68 eV calculated value. Recently, Janssen *et al.* have observed that addition of C_{60} to oligothiophenes (from Th6 to Th11) in solution results in a quenching of the thiophene oligomers triplet state via energy transfer to C_{60} and produces triplet-state C_{60}.[14] Therefore, the triplet T_1 state of oligothiophenes ranging in size from six to eleven rings can be estimated to lie between the triplet energy of C_{60} (1.57 eV)[38,39] and the triplet energy of Th3 (1.71 eV).[36] Moreover, the efficiency of the energy transfer (from the triplet state of Thn to the triplet state of C_{60}) was found to slightly depend on the length of the conjugated oligomers and to be less efficient in the longest chains; this feature can be explained by a small red-shift of the $S_0 \rightarrow T_1$ transition with extension of the π-system, consistent with the theoretical evolution. We finally note that Xu and Holdcroft have measured a phosphorescence peak at ~1.5 eV in polythiophene,[40] a value very close to the one we can extrapolate for an infinite chain length (1.49 eV) on the basis of the calculated oligomer excitation energies.

One of the possible decay routes of the singlet excitons in conjugated systems consists in an intersystem crossing to form a metastable triplet exciton. Such a triplet gives rise to a single, intense triplet−triplet $T_1 \rightarrow T_n$ electronic transition, which has been observed by photoinduced absorption (PA) measurements on oligothiophenes in solution.[14,41] The INDO/MRD-CI calculations indicate that the T_1 state is mainly coupled to one triplet excited state (hereafter denoted T_n), via a large oscillator strength whose value is comparable to that of the $S_0 \rightarrow S_1$ excitation. The T_n wave function, where n varies from 8 to 10 depending on chain length, is quite complex and includes both singly and doubly excited configurations with respect to the Hartree−Fock determinant. The $T_1 \rightarrow T_n$ transition energies are collected in Table 1 together with the experimental data obtained from the PA measurements.[14,41] Although the theoretical calculations lead to a systematic overestimation of the triplet−triplet excitation energies, the calculated chain-length dependence of the $T_1 \rightarrow T_n$ transition energy is in good agreement with the experimental one and shows a strong red-shift when increasing the chain length (Figure 4). It thus appears that, as is the case for PPV oligomers,[5] the T_n state in oligothiophenes is not as localized as T_1, a feature which can be accounted for by the fact that, as the T_n excited state lies at higher an energy than T_1, it has a smaller binding energy and hence its wave function is less confined.

IV. Geometry Relaxation Phenomena

The equilibrium bond lengths in the S_1 and T_1 excited states of the dimer (Th2), trimer (Th3), and tetramer (Th4) of thiophene have been calculated at the MNDO level, by considering the approach described in the methodology section.[42] The typical bond-length modifications obtained from these calculations lead to the appearance of a quinoïd character, fully

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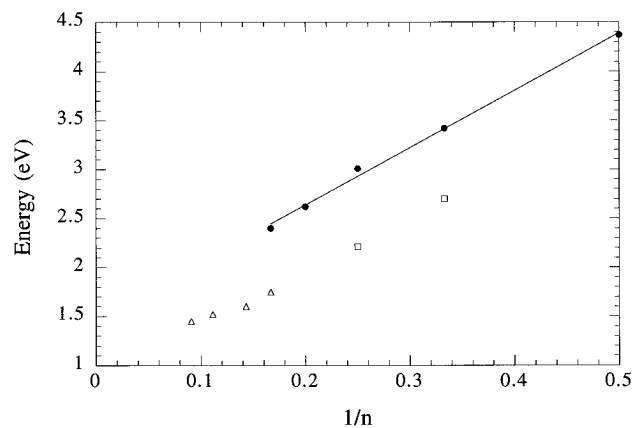(40) Xu, B.; Holdcroft, S. *J. Am. Chem. Soc.* **1993**, *115*, 8447.

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(42) Using a very similar approach, but on the basis of another semiempirical technique based on the NDDO approximation (the AM1 technique), we have obtained an equilibrium geometry for the 1B$_u$ excited state of octatetraene (that corresponds to the carbon backbone of the bithiophene molecule), in excellent agreement with the CAS/DZP *ab initio* calculations: Serrano-Andrés, L.; Lindh, R.; Roos, B. O.; Merchan, M. *J. Phys. Chem.* **1993**, *97*, 9360 (the average deviation between the AM1 and CAS/DZP carbon−carbon bond lengths is on the order of 0.012 Å).

Singlet and Triplet States in Oligothiophenes

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Figure 4. Comparison between the evolutions with the inverse number of thiophene rings, $1/n$, of (i) the INDO/MRD-CI triplet−triplet $T_1 \rightarrow T_n$ excitation energies (solid line, closed circles) and (ii) the experimental $T_1 \rightarrow T_n$ (open squares,[41] open triangles[14]) transition energies obtained from photoinduced absorption measurements in solution.
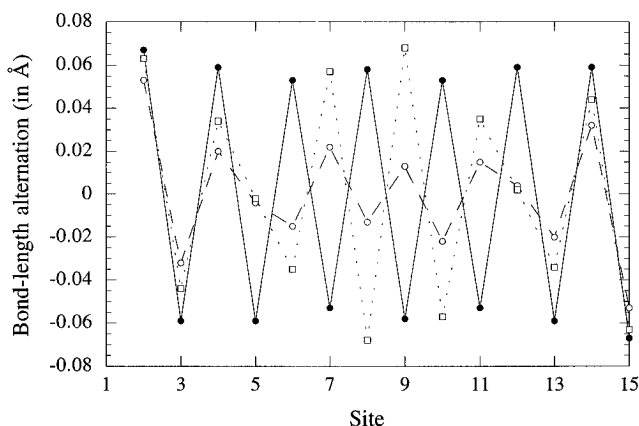
Figure 5. Evolution with site position, i, on the thiophene tetramer, of the bond-length alternation, Δr, calculated at the MNDO level as the difference between the lengths of the $(i,i+1)$ and $(i,i-1)$ carbon−carbon bonds, in the S_0 (solid line), S_1 (dashed line), and T_1 (dotted line) states.

consistent with the formation of a polaron-like defect.[43] We note that, for the monomer and planar dimer of thiophene, similar geometric deformations have been predicted at the 3-21G*/CIS *ab initio* level and from semiempirical calculations including single and double excitations (QCFF/PI + CISD technique).[29] Finally, it should be emphasized that, using a similar approach, we have obtained a description of the geometric relaxation phenomena taking place in the lowest singlet excited state of oligo(phenylene vinylene)s, which was in excellent agreement with that provided by the analysis of the vibronic structure in the electroabsorption spectra measured for the corresponding oligomers.[44] The evolution with site position, i, on the Th4 oligomer of the bond-length alternation (calculated as the difference between the lengths of the $(i,i+1)$ and $(i,i-1)$ carbon−carbon bonds) is illustrated in Figure 5 for the S_0, S_1, and T_1 states. In Table 2, we report the parameters obtained by fitting eq 1 to the MNDO S_1 and T_1 optimized geometries of Th4.

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Table 2. Parameters in Eq 1 (ϕ in Å, ξ and R in site units) Obtained by Fitting to the MNDO-Optimized Geometries of the Singlet S_1 and Triplet T_1 Excited States of the Thiophene Tetramer (Th4).

	ϕ	ξ	R
S_1	0.019	2.25	4.57
T_1	0.029	1.58	3.45

From Table 2 and Figure 5, we can draw the following conclusions.

(i) Rather small lattice distortions occur in the S_1 excited state, which translates into small relaxation energies (on the order of 0.1−0.2 eV). The geometry deformations lead to a reduction in bond-length alternation along the conjugated path formed by the carbon atoms; alternatively, one can view the same bond-length modifications as giving rise to the appearance of some quinoid character on the thiophene rings. The absolute value of the bond-length alternation in Th4 drops from ∼0.04−0.05 Å in the external rings to ∼0.0−0.02 Å in the central part of the molecule. These lattice distortions are similar to those associated with the formation of charged soliton−antisoliton pairs in polyacetylene;[27,45] however, in oligothiophenes, the electron-hole pairs are bonded in the S_1 excited state by (i) the Coulombic attraction between opposite charges; (ii) the non-degenerate ground state of the thiophene oligomers; and (iii) the finite size of the systems, which prevents the separation between the opposite charge carriers occurring upon photoexcitation in polyacetylene.[27,45] From the R value obtained by fitting eq 1 to the singlet excited-state geometry of Th4 and the comparison between the bond-length deformations in the different oligomers, we estimate the geometric defect to extend over 3−4 thiophene units.

(ii) Much more pronounced lattice distortions take place in the lowest triplet excited state, as indicated by the larger amplitude, ϕ, value found for T_1. The relaxation energies with respect to vertical excitations are significantly larger than those found for the singlet and on the order of 0.3−0.4 eV. In Th4, the bond-length alternation absolute value, $|\Delta r|$, in the external rings is close to 0.05−0.06 Å, *i.e.*, the value calculated in the ground state. Going from the ends of the chain toward the center, $|\Delta r|$ decreases (the single bonds are shortened and the double bonds are elongated), reaches 0 at the connection between the first and second rings (the bonds are there equal), and then evolves strongly and peaks at the center of the tetramer (where the single and double bond characters have exchanged with respect to the ground state and the maximum absolute value of the bond-length alternation is recovered). In the triplet excited state as in the singlet, the formation of a soliton−antisoliton pair clearly emerges from the evolution of the geometry deformations along the chain axis. For essentially the same reasons as for the singlet defect, the electron-hole pair is strongly bonded in the triplet excited state; due to the exchange potential, the confinement of the triplet is even more pronounced than that of the singlet and, from the R value fitted for T_1, it seems that 1−2 thiophene ring(s) is(are) required for a proper accommodation of the triplet defect, in accord with the ODMR data.[34,35] In fact, the MNDO results indicate that, in the triplet T_1 state, the bond lengths in the two central rings of Th4 are close to those calculated for the same state in Th2; the external rings of the tetramer are almost unaffected when going from S_0 to T_1.

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Table 3. Net π-Charge Distribution (Δq_π, in |e|) in the S_0, S_1, and T_1 States for the Monosubstituted (Th3-X) and Bis-Substituted (X-Th3-X) Terthiophenes (as Calculated by the INDO/MRD-CI Technique) and Spin Density Distribution (SD) in the Triplet State (Evaluated by the MNDO Method on the Basis of the T_1 Optimum Geometry)

		R1	R2	R3		R1	R2	R3
X=		-H	-CHO	-CN	-NH$_2$	-OMe	-CHO / -CHO	-CN / -CN	-NH$_2$ / -NH$_2$	-OMe / -OMe
Δq_π (S$_0$)	X		-.101	-.041	.128	.086	-.100	-.038	.126	.082
	R1	~0	.063	.014	-.103	-.069	.079	.025	-.110	-.073
	R2	~0	.023	.014	-.017	-.009	.037	.026	-.033	-.018
	R3	~0	.014	.012	-.007	-.002	.079	.025	-.110	-.073
	X						-.100	-.038	.126	.082
Δq_π (S$_1$)	X		-.175	-.064	.172	.104	-.136	-.045	.152	.095
	R1	-.01	.031	-.103	-.034	-.034	.068	.006	-.098	-.066
	R2	.02	.094	.066	-.078	-.041	.139	.076	-.107	-.058
	R3	-.01	.112	.101	-.059	-.024	.068	.006	-.098	-.066
	X						-.136	-.045	.152	.095
Δq_π (T$_1$)	X		-.111	-.042	.141	.092	-.105	-.037	.135	.081
	R1	-.005	.049	-.009	-.093	-.064	.073	.017	-.105	-.064
	R2	.01	.026	.022	-.037	-.021	.064	.040	-.059	-.034
	R3	-.005	.037	.028	-.009	-.003	.073	.017	-.105	-.064
	X						-.105	-.037	.135	.095
SD (T$_1$)	X		.044	.036	.099	.049	.032	.023	.069	.038
	R1	.565	.606	.621	.708	.637	.522	.497	.536	.495
	R2	.871	.913	.906	.819	.882	.894	.960	.790	.935
	R3	.565	.437	.437	.374	.428	.522	.497	.536	.495
	X						.032	.023	.069	.038

Table 4. INDO/MRD-CI Singlet−Singlet $S_0 \rightarrow S_1$, Singlet−Triplet $S_0 \rightarrow T_1$, and Triplet−Triplet $T_1 \rightarrow T_n$ Excitation Energies, Calculated on the Basis of the Ground-State Geometries of Monosubstituted (Th3-X) and Bis-Substituted (X-Th3-X) Terthiophenes[a]

molecule	$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$	$T_1 \rightarrow T_n$
Th3	3.583	1.681	3.424
Th3-CHO	3.282	1.647	3.099
Th3-CN	3.402	1.647	3.217
Th3-NH$_2$	3.383	1.619	3.081
Th3-OCH$_3$	3.486	1.654	3.338
OCH-TH3-CHO	3.215	1.683	2.908
NC-Th3-CN	3.309	1.657	3.081
H$_2$N-Th3-NH$_2$	3.292	1.583	3.156
CH$_3$O-Th3-OCH$_3$	3.415	1.633	3.266

[a] All the transition energies are given in eV.

V. Effects of Electroactive Groups on the Lowest Singlet and Triplet Excited States

The substitution effects on the S_0, S_1, and T_1 geometries of terthiophene have been investigated at the MNDO level. The INDO/MRD-CI π-charge distributions, calculated for the unsubstituted, monosubstituted, and bisubstituted trimers, are collected in Table 3, and the singlet−singlet, singlet−triplet, and triplet−triplet vertical excitation energies are reported in Table 4. Analysis of these results leads to the following observations.

(i) The effects on the ground-state geometry of Th3, of the donor/acceptor groups grafted to the conjugated segment are very local; with respect to Th3, only the geometry of the thiophene ring(s) to which the substituent(s) is(are) attached is significantly modified. These geometric deformations lead to a small decrease in bond-length alternation in the external rings and are rather insensitive to the nature of the end-group(s) we have considered.

(ii) In the singlet excited state, similar geometry deformations are induced by substituting the terthiophene molecule with

electroactive moieties. However, we note that, if the main lattice distortions occur in the thiophene ring(s) the end-group(s) is-(are) connected to, the geometry of the other ring(s) is also modified. We explain this difference by the fact that, in S_1, all the thiophene rings are involved in the charge transfer process, while, in S_0, the charge provided by the electroactive group(s) is mainly injected to the external ring(s). As in substituted polyenes[46] and oligo(phenylene vinylene)s derivatives,[47] the electronic transition to the first allowed singlet excited state, S_1, is red-shifted when end-groups are attached to the terthiophene molecule; the amplitude of this shift is proportional to the amount of charge transfer. For similar strengths of the acceptor and the donor (*i.e.*, similar amounts of charge transfer), electron-withdrawing groups have a stronger effect on the $S_0 \rightarrow S_1$ excitation energies than electron-donating ones, a feature that is rationalized by the effective chain lengthening induced by grafting acceptor groups.

(iii) In the triplet T_1 excited state, the bond-length modifications induced by substitution can be related to the evolution of the spin density distributions. As expected from the confined character of the triplet exciton in oligothiophenes, the spin density in the triplet state of Th3 is mainly localized on the central aromatic ring. In the monosubstituted oligomers, we observe an overall increase in spin density both on the substituted ring and on the central ring at the expense of the third ring; hence, more pronounced geometry distortions occur in the former two thiophene units. In the bis-substituted compounds, the two external rings are, of course, equivalent, and the triplet-state geometry is symmetric. The influence of the end-groups we have considered in this work, on the energy of the triplet state with respect to the ground state, can be understood by considering the following effects: (i) attaching end-groups on the conjugated molecule tends to stabilize the triplet state due to an enhancement of its confinement (as indicated by the increase in spin density on the central thiophene unit of the substituted molecules except for Th3-NH$_2$); (ii) the triplet T_1 state energy is lowered by raising the electronic density in the central part of the molecule; and (iii) T_1 gets destabilized when removing electrons from the conjugated path. In the trimers substituted with donors, effects (i) and (ii) (localization and increase in electron density) contribute to stabilize the triplet, while, in acceptor derivatives, effects (i) and (iii) (localization and decrease in electronic density) are opposite, leading to a weaker effective energy stabilization of T_1 (in the case of the CHO-Th3-CHO oligomer, the S_0−T_1 energy difference is close to the one calculated for Th3).

(iv) Whatever the mode of substitution, the T_n state energy is lowered when going from unsubstituted to substituted compounds. For this high-energy lying triplet excited state, as mentioned previously, the localization of the wave function is much less pronounced than in T_1 and the evolution of the T_n excited state energy with substitution follows that of the S_1 singlet excited state. As a consequence, the theoretical triplet−triplet transition energies show a bathochromic displacement when electroactive groups are grafted to the conjugated bridge: this shift depends on the nature of the end-groups and is calculated to be larger for acceptor derivatives. Rossi *et al.* have measured the photoinduced absorption spectra of different monosubstituted terthiophenes in solution;[18] the experimental data indicate a red-shift of the maximum absorption between the unsubstituted and substituted oligomers, that amounts to ~0.1 eV [~0.4−0.5 eV] when going from Th3 to Th3-OCH$_3$

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[Th3-CHO]; these values are in good agreement with the calculated shifts of ∼0.1 and ∼0.3 eV, respectively.

VI. Decay of the Singlet Excitations

In LED devices based on conjugated polymers, the first step in the light emission process is the recombination of electrons and holes injected at electrodes to form singlet excitons; the second step consists in the radiative decay of the singlet excitations, *i.e.*, luminescence. Competing nonradiative processes provide additional means of decay and therefore reduce the efficiency of the device. These processes are numerous[48] and include interchain processes (*e.g.*, excimer formation), quenching of excitons by extrinsic or conformational defects or by low-lying two-photon states,[49] internal conversion (IC), intersystem crossing (ISC) from the singlet to the triplet manifold,[50,18] singlet fission (SF),[51,52] or charge separation (CS). IC corresponds to a nonradiative decay to the ground state through phonons (vibrational quanta) emission; ISC denotes the crossing process that can occur between singlet and triplet potential energy curves, as a consequence of spin-orbit interaction; SF is a bimolecular process that produces triplet excitons from the collision between singlets and requires the triplet state to be located at roughly half the energy of the singlet state (such a nonradiative decay has been shown to occur in polydiacetylenes[51] as well as in tetracene and anthracene crystals[52]). Note that, while ISC and IC are intrinsic molecular phenomena, SF and CS are solid state effects.

In oligothiophenes, the possibility of quenching the singlet excitons by lower-lying two-photon states can be ruled out, since the 2A state has been shown both experimentally[12,15] and theoretically[16,17] to lie above the 1B state. Recent time-resolved fluorescence studies on unsubstituted[11,50] and substituted[18] thiophene oligomers (for which migration of the excitons towards trapping centers is minimized by the finite size of the chains and the smaller disorder) in solution (where excimer formation is expected to be less efficient than in the solid state) indicate a sharp increase of the fluorescence quantum yield ϕ_F: (i) by increasing the number of thiophene rings from two to seven and (ii) by attaching electroactive end-groups on the terthiophene molecule. In both cases, no significant alteration in the radiative decay rate constant, k_R, was observed, and the evolution of ϕ_F with chain length and substitution was related to the decrease of the nonradiative decay rate, k_{NR}.[12,18,50,53] It was also found that internal conversion plays a minor role in the nonradiative decay of the singlet excitations and that, for oligothiophenes, intersystem crossing gives the main contribution to k_{NR}.[50]

Radiationless transition theory expresses the intersystem rate constant in terms of (i) a state density factor; (ii) the matrix element of the spin-orbit coupling hamiltonian between the singlet and triplet wave functions; and (iii) an overlap factor, which accounts for the decrease in rate with an increasing energy gap between the two states involved. A precise description of the intersystem crossing process definitively requires the calculation of the spin-orbit coupling interaction (now in progress) as well as the overlap between the excited-state
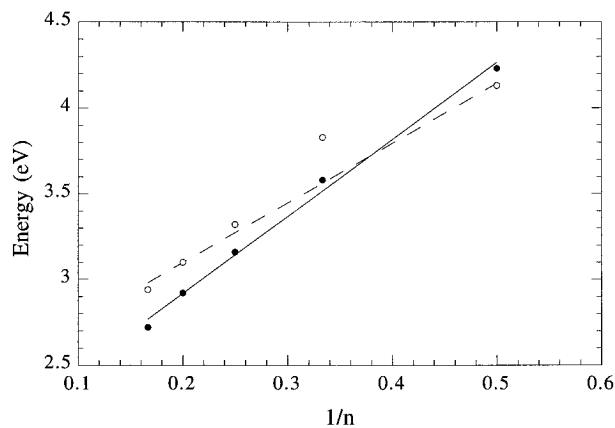
Figure 6. Evolution with the inverse number of thiophene rings, $1/n$, of the INDO/MRD-CI $S_0 \rightarrow S_1$ (solid line, closed circles) and $S_0 \rightarrow T_4$ (dashed line, open circles) energies. Note that the transition energies calculated for Th3 were not included in the linear fits.

vibrational levels. However, at this stage, it is possible to present a qualitative picture of the ISC process in oligothiophenes that rationalizes the trends observed experimentally concerning the evolution of k_{NR} with the size of the oligomers and substitution. What is known is that the spin-orbit coupling is large enough to allow the ISC process to occur (which is not surprising in view of the heavy-atom effect played by the sulfurs), but it is very unlikely that the huge changes in the nonradiative rate constants observed by elongating the chain or grafting electroactive groups would rely only on a modification of the spin-orbit coupling term. Therefore, we believe that, as was first suggested by Ponterini and co-workers,[18] these changes should be related to the variation in the overlap factor. As pointed out by Robinson and Frosch in the case of a series of aromatic hydrocarbons,[54] this factor is primarily controlled by the singlet−triplet energy separation.

The $S_1−T_1$ energy difference that we calculate in unsubstituted oligothiophenes is much too large to give efficient singlet−triplet overlap, and hence the probability for $S_1−T_1$ crossing is very weak. The INDO/MRD-CI calculations indicate that there is one triplet excited state (T_4), for which the wave function involves excitations from deep π-levels with large weights on the sulfur atoms, that lies at an energy close to that of S_1. Although the restricted configuration space we consider in the MRD-CI formalism does not allow us to obtain a precise estimation of the high-lying excited states (the theoretical triplet−triplet excitation energies are indeed overestimated with respect to the measured values), the INDO/MRD-CI scheme adequately reproduces the low-lying excited states (as indicated by the good agreement found between the measured and calculated $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transition energies). We feel therefore confident in using the energy of T_4 as an important criterion in determining the rate of intersystem crossing from the singlet to the triplet manifold. In Figure 6, we plot the evolution of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_4$ excitation energies with respect to the inverse number of thiophene rings. In bithiophene, the triplet T_4 lies below the singlet S_1, while for longer chains, due to the larger stabilization of the S_1 excited state with chain length, the state ordering is reversed, S_1 being below T_4. Both the singlet−singlet $S_0 \rightarrow S_1$ and singlet−triplet $S_0 \rightarrow T_4$ transition energies follow a quasi linear evolution with respect to $1/n$; we note, however, that the calculated energy of the triplet T_4 excited state of Th3 is overestimated by comparison to the value interpolated by considering a linear relationship between the excitation energies and the inverse chain length (Th3 has

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Table 5. INDO/MRD-CI S_1-T_4 Energy Difference (in eV) Calculated for the Unsubstituted, Monosubstituted (Th3-X), and Bis-Substituted (X-Th3-X) Oligothiophenes and (between Parentheses) Extrapolated from a Linear Relationship between the Excitation Energies and the Inverse Number of Thiophene Rings in the Unsubstituted Oligomers and the Fluorescence Yields, ϕ_F, as well as the Nonradiative Decay Rates, k_{NR}, Measured in Solution (K_{NR}^{exp}) and Calculated on the Basis of Simple Assumptions (k_{NR}^{th}, see Text)

	$\Delta E(S_1-T_4)$	k_{NR}^{th} $(10^9\,s^{-1})$	k_{NR}^{exp} $(10^9\,s^{-1})$	ϕ_F^{exp}
Th2	−0.10 (−0.10)	20.1	19.7[c]	0.018[c]
Th3	0.24 (0.05)	3.70	3.88,[a] 3.7,[b] 5.3[c]	0.07,[a] 0.05,[b] 0.07[c]
Th4	0.16 (0.13)	1.23	1.54,[a] 1.5[c]	0.20,[a] 0.18[c]
Th5	0.18 (0.18)	1.14	0.82,[a] 0.74[c]	0.28,[a] 0.36[c]
Th6	0.22 (0.21)	1.13	0.70,[a] 0.73[c]	0.42[a]
Th3-CHO	0.36		0.24[b]	0.50[b]
TH3-CN	0.34			
Th3-NH$_2$	0.29			
Th3-OCH$_3$	0.25		4.6[b]	0.061[b]
OHC-Th3-CHO	0.47			
NC-Th3-CN	0.40			
H$_2$N-Th3-NH$_2$	0.26			
MeO-Th3-OMe	0.24			

[a] Reference 11. [b] Reference 18. [c] Reference 50.

not been included in the fit). As the crossing between the evolutions of the singlet S_1 and triplet T_4 excited states occurs for a chain length close to that of the Th3 oligomer, we associate this discrepancy to the fact that we did not include in the calculations the spin-orbit coupling which, in the crossing region, is expected to mix efficiently the singlet and triplet wave functions.

In Table 5, we collect (i) the S_1-T_4 energy differences, calculated at the INDO/MRD-CI level for the different oligomers investigated, as well as the values extrapolated from a linear relationship between the transition energies and the inverse number of thiophene rings and (ii) the fluorescence quantum yields and the nonradiative decay rates measured in solution. In the unsubstituted terthiophene (Th3), Rossi *et al.* have pointed out the existence of a thermally activated decay route of S_1;[18] they express the total nonradiative decay rate constant as

$$k_{NR} = k_1 + k_2(T)$$
$$= k_1 + A_2 \exp\left(\frac{-\Delta E_{ISC}}{kT}\right) \qquad (2)$$

where k_1 is a nonactivated decay rate (including nonactivated ISC processes, internal conversion, singlet fission,...) and k_2 is the intersystem crossing temperature-dependent decay rate. On the basis of the temperature dependence of k_{NR}, they estimate the pre-exponential factor, A_2, as equal to $1.9 \times 10^{10}\,s^{-1}$, and an activation energy of ∼0.05 eV, in excellent agreement with the interpolated S_1-T_4 INDO/MRD-CI energy difference for Th3. Assuming that k_1 remains constant when elongating the chain, we have calculated the k_{NR} rate constants on the basis of the experimental k_1 and A_2 values and of the calculated activation energies, *i.e.*, the S_1-T_4 energy difference estimated by fitting the INDO/MRD-CI excitation energies with a linear relationship, as done in Figure 5. In view of the different assumptions considered, the results, collected in Table 5, can be considered to be in excellent agreement with the measured nonradiative decay rates. In bithiophene (Th2), the triplet T_4 excited state is below the singlet S_1 state, and the S_1-T_4 ISC process is nonactivated and very efficient, leading to a very low fluorescence yield. When the chain elongates, as the activation energy becomes larger, the probability for the intersystem crossing to occur decreases, and ϕ_F is raised. In long chains, the activated

S_1-T_4 ISC process becomes highly improbable and the fluorescence yield reaches a plateau; at this stage, the light emission efficiency is controlled by other mechanisms (k_1).

As does chain lengthening, the graft of electroactive moieties on Th3 also leads to an increase in S_1-T_4 energy difference, which is much more pronounced in the case of the acceptor derivatives (note that, in the substituted compounds as in the unsubstituted molecules, the triplet T_4 excited state remains the triplet state the closest to the singlet S_1 excited state). In fact, when electron-donating groups are attached to the conjugated bridge, both the S_1 and T_4 states are stabilized, so that the S_1-T_4 energy difference remains essentially unchanged. As pointed out before, substitution with acceptor groups hardly affects the T_1 state energy because of cancellation between two opposite effects (a localization effect that tends to stabilize the triplet state and a lowering in electronic density in the central part of the molecule that tends to destabilize it). When going up in energy, the triplet states wave functions are becoming less confined, and this cancellation does not occur anymore, leading to an increasing energy stabilization of the excited states. For example, when two formyl groups are connected at each end of the Th3 oligomer, the T_1, T_4, and T_n ($n = 8$) triplet states are lowered by ∼0.0, ∼0.15, and ∼0.5 eV. As a consequence of the rather small stabilization of the T_4 triplet excited state in acceptor derivatives while S_1 is more strongly stabilized (see Table 4), the S_1-T_4 energy difference is much larger than in unsubstituted oligomers or in the donor derivatives. This trend is in remarkable agreement with the experimental evolution of k_{NR} when going from Th3 to Th3-OCH3 and Th3-CHO; since the ISC activation energies in Th3 and Th3-OCH3 are very close, we expect similar k_{NR} values for these two molecules, while the large increase of the singlet−triplet energy difference in Th3-CHO should give rise to a much lower nonradiative decay rate and a consequent higher fluorescence efficiency. Both expectations are fully confirmed by the experimental data, see Table 5.

Finally, we would like to stress that, on the basis of the S_1 and T_1 measured and calculated excited state energies, singlet fission processes to produce triplets could be efficient in the shortest oligomers, since the triplet T_1 lies at roughly half the energy of that of the singlet S_1. As these processes are bimolecular in nature, a careful analysis of the fluorescence yield dependence on the input power would probably allow to check if these fission mechanisms indeed occur in oligothiophenes.

VII. Summary

We have investigated the nature of the lowest singlet and triplet excitations in oligothiophenes and their substituted derivatives. The calculated singlet−singlet $S_0 \rightarrow S_1$ excitation energies decrease with chain length as a result of the extension of the π-conjugated path and are in excellent agreement with experiment. We found that the lowest triplet excited state T_1 has a much more confined character than S_1, due to the possibility of exchange between two like-spins. As a consequence, the S_0-T_1 energy difference is only slightly affected by increasing the size of the oligomer; its energy evolves from ∼1.8 eV in bithiophene to ∼1.5 eV at the infinite chain-length limit, which compares very nicely to the experimental evolution estimated from various optical measurements in solution.[14,36,40] Intersystem crossing between the singlet and triplet manifolds leads to a population of the lowest triplet state, which can then be probed by photoinduced absorption measurements. An intense, long-lived triplet−triplet $T_1 \rightarrow T_n$ absorption is observed at an energy going down as the chain length increases. Such a red-shift is well reproduced by the calculations and indicates a smaller confinement of the higher-lying T_n triplet state.

Geometry relaxation phenomena occur in the lowest singlet and triplet states of oligothiophenes that lead to the appearance of a quinoïd character, especially pronounced for the T_1 state. Referring to the soliton−antisoliton picture used to describe excitations in polyacetylene,[45] the electron-hole pair appears to be strongly bonded in both states, with a stronger localization of the triplet state. These results are in line with those obtained recently in PPV oligomers,[5] which indicates that this picture holds true for the nondegenerate ground-state polymers.

We have analyzed in depth the influence on the lowest singlet and triplet excitations of grafting electroactive groups on the conjugated segment of a model thiophene oligomer: ter-thiophene. Different effects have been calculated on the singlet and triplet states, which can be rationalized on the basis of the different natures of these states, as highlighted by the study of the unsubstituted molecules.

Finally, the various mechanisms giving rise to nonradiative decay of the singlet excitons have been discussed. In oligo-thiophene solutions, intersystem crossing between the S_1 singlet state and a higher-lying T_4 triplet state (followed by fast nonradiative decay to T_1) is expected to be very efficient in view of the low activation energy required.[18] (Note that the importance of the ISC effect as a nonradiative decay route of the singlet excitations has been demonstrated by recent experi-mental investigations on polythiophene[55]). On the basis of simple assumptions, we have presented a model that allows one to rationalize the huge increase in fluorescence yield observed experimentally when increasing the chain length[11,50] and by

substitution with acceptor groups.[18] It is worth stressing that, in films, interchain effects are expected to be very important and to lead to a systematic decrease of the light emission yields, as has been observed recently in a cyano-substituted PPV.[56]

We believe that the information provided by this work should be of prime importance in understanding the photophysical properties of oligothiophenes and derivatives and in defining new routes toward the optimization of the light emission efficiency in LED devices where conjugated compounds are used as active layer.

Supporting Information Available: Tables providing the MNDO-optimized carbon−carbon and carbon−sulfur bond lengths in the S_0, S_1, and T_1 states of the dimer, trimer, and tetramer of thiophene and substituted terthiophenes (4 pages). Ordering information is given on any current masthead page.

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