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Substitutional Effects on the Structural, Spectroscopic, and Photophysical Properties of Quaterthiophenes and Sexithiophenes as Well as on Their Corresponding Polyesters

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ABSTRACT: A conformational analysis and a study of the spectroscopy and the photophysics of alkyl-substituted tetrathiophenes and sexithiophenes as well as their corresponding polyesters are reported. The insertion of alkyl lateral chains caused a torsion of the backbone of the oligomers. This torsion induces a blue shift of the absorption bands and a decrease in their molar extinction coefficients. Semiempirical calculations (AM1 and PM3) performed on the tetramer show that dihedral angles between thiophene rings where alkyl chains are located are much twisted, whereas the torsional angle between thiophene rings without alkyl chains is similar to that found for unsubstituted oligothiophenes. From fluorescence data, we observed that a more planar conformation is favored in the relaxed excited state of all thiophene oligomers. The addition of two carbonyl groups at the ends of the molecules induces a red shift of the spectra due to an increase of the electronic delocalization along the molecular frame and an increase in the rigidity of the molecular backbone for short oligomers. Fluorescence quantum yields and lifetimes decrease compared to those of the unsubstituted oligothiophenes. In the corresponding polyesters, thiophene units have the same conformation as well as the same spectroscopic and photophysical properties as those of the isolated molecules.

1. Introduction

Polythiophenes and oligothiophenes have been thoroughly investigated in the past few years[1] because of their excellent chemical stability, electrical properties (in the doped state), and optical properties. To improve the solubility of these conjugated organic compounds, alkyl-substituted oligothiophenes and polythiophenes have been synthezised. These substituted polymers show interesting new phenomena like thermochromism and solvatochromism.[2−4] It has been shown by theoretical and experimental investigations that the insertion of alkyl lateral chains changes the conformation of the backbone.[5,6] This conformational change influences the optical properties of the materials.[6] For a twisted conformation, the electron delocalization is less than for a more planar conformation such that a blue shift is observed in the absorption spectrum. According to this behavior, the optical properties of oligothiophenes and polythiophenes can be controlled by the number of thiophene units involved in the backbone and by the insertion of lateral chains at specific locations. The understanding of these effects on the spectroscopic and photophysical parameters of thiophene derivatives is still incomplete.

However, the ground-state conformations of unsubstituted oligothiophenes using theoretical methods as well as their spectroscopic and photophysical properties are actually well-known.[7−10] Ab initio (HF/3-21G*,[11] HF/6-31G*,[12] and MP2/6-31G*[13]) and semiemperical methods (AM1[14,15]) on unsubstituted bithiophene (BT) have shown that the two rings are not planar and that two conformations can coexist in the gas phase (or in solution) at room temperature. These two conformers correspond to torsional angles of 30° (local minimum) and 150° (global minimum). Three maxima are observed in the torsional potential: one for the perpendicular conformation (90°) and two for the planar conformations (syn and anti). The twisted conformations obtained for BT are due to an equilibrium between two opposite forces: the electron delocalization along the long molecular axis which favored a planar geometry and the steric hindrance caused by the repulsion between hydrogen atoms in position 3 or 3′ and the sulfur atoms (for the anti conformation) or between the two sulfur atoms and the two hydrogen atoms in position 3 and 3′ (for the syn conformation). The rotational barrier against planarity for the syn conformation is relatively high (1.15 kcal mol^{-1} from HF/3-21G* calculations[11]), showing the importance of additive steric effects between the sulfur atoms and between the hydrogen atoms. The rotational barrier for the planar anti conformation is much smaller (0.39 kcal mol^{-1} from HF/3-21G* calculations[11]), confirming the weaker steric hindrance between hydrogen and sulfur atoms and therefore suggesting a wide distribution of conformers at room temperature. Finally the barrier to rotation at 90° is calculated to be 1.49 kcal mol^{-1} from HF/3-21G* calculations.[11] All these theoretical results are in excellent agreement with electron diffraction data of BT in the gas phase.[16] Ab initio calculations performed on unsubstituted terthiophene (TT) show the same potential energy surface as that obtained for BT.[17] These results suggest that the number of thiophene units in the backbone should not significantly influence the ground-state molecular conformation.

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Experimentally, a red shift of the absorption band and an increase in the molar extinction coefficient have been observed for unsubstituted oligothiophenes with two (BT) to seven rings.[9] All spectra show broad and unstructured bands, suggesting the existence of nonrigid molecular backbones as well as the existence of a large distribution of conformers in the ground electronic state. It is observed that the fluorescence bands are red shifted, going from short to longer oligomers, and the bands are sharper and more structured compared to their respective absorption bands. We have recently shown that indeed, for these unsubstituted molecules, the relaxed singlet excited states favor planar conformations.[6,14] It has also been observed that the fluorescence quantum yield increases from 0.026 for BT to 0.41 for the sexithiophene.[9] This has been explained by a decrease of the triplet quantum yield with the length of the oligomer (a decrease of the intersystem crossing rate constant), while the internal conversion process remains almost constant and much less effective than the intersystem crossing mechanism. The fluorescence lifetime also increases with the number of thiophene units from two to six rings, while the radiative decay rate constant does not change significantly.

For alkyl-substituted oligothiophenes, the spectroscopic and photophysical parameters are practically unknown. Some results from absorption spectroscopy[6,18,19] have shown that the insertion of alkyl lateral chains influences the conformation of oligothiophenes, but the data are still very scarce. Moreover, the substitutional effect on the photophysical properties of long thiophene oligomers remains unknown. Recently, we have investigated the effect of the position and the nature of the substitution on bithiophene.[6] On one hand, it was observed that insertion of alkyl chains in the 4,4′-positions does not much influence the molecular conformation as well as the spectroscopic and photophysical parameters of this short oligomer. On the other hand, it was found that the presence of two alkyl chains in the 3,3′-positions causes an important twisting between the two thiophene rings which induces a blue shift of the absorption band as well as a decrease of its molar extinction coefficient. Nevertheless, as observed from fluorescence data, the steric hindrance caused by the alkyl chains is not strong enough to prevent the first singlet excited state to relax to a more planar conformation. The fluorescence quantum yield of this 3,3′-alkylbithiophene derivative is reduced compared to those of BT and the 4,4′-alkyl compound. Spectroscopic data reported elsewhere also indicate that the insertion of only one alkyl chain in position 3 creates a blue shift of the absorption band compared to that of BT,[19] but the absorption band is red shifted compared to that of the 3,3′-alkyl-substituted bithiophene derivative. The presence of only one alkyl chain in position 3 is expected to create a steric hindrance which should favored a minimum conformation more twisted than that of BT but less twisted than that of the 3,3′-dialkyl derivative.

To characterize the substitutional effect on the potential energy surface of BT, ab initio as well as semiempirical calculations have been performed on a series of alkyl-,[11,12,20] alkoxy-,[21] and alkylthio-substituted bithiophenes.[22] From HF/3-21G* calculations, it was clearly shown that the insertion of two alkyl chains in positions 3,3′ induces a large twisting of the molecule, the minimum conformation corresponding to a dihedral angle of 101.5°, whereas the rotational barrier against planarity (anti conformation) was calculated to be 7.6 kcal mol^{-1}. For the compound having one alkyl chain in position 3, two minima very close in energy have been obtained (108.1 and 60.0°) with a very small energy barrier between them (0.095 kcal mol^{-1}), whereas the energy barrier to reach the planar anti conformation is 2.2 kcal mol^{-1}. Recently, we have studied the spectroscopic and photophysical properties of terthiophenes and quinquethiophenes having two alkyl chains on the central thiophene ring coupled with semiempirical calculations of their respective conformations.[23] It was observed that insertion of these alkyl chains creates a large twisting between the central thiophene unit and neighboring rings. It was found that the increase in the molecular length does not significantly change the molecular conformation even though the absorption and fluorescence bands of longer oligomers are red shifted due to an increase in the electronic delocalization. Fluorescence quantum yields and lifetimes also increase in going from trimer derivatives to pentamers, giving rise to smaller nonradiative decay rate constants in the longer oligomers. The aim of this paper is to study the spectroscopic and photophysical parameters of quaterthiophenes and sexithiophenes having alkyl chains on the two central thiophenne rings and to correlate these experimental results with a theoretical conformational analysis. This paper also reports on the optical and photophysical properties of these oligothiophenes incorporated in polyesters. Interestingly, these materials combine the good mechanical properties and processability of high molecular weight polymers to the electrical and optical properties of the oligothiophenes. The substitutional effect of carbonyl groups at both ends of the oligomers is also reported in order to compared the optical and photophysical properties of the free oligomer with the oligomer incorporated in the polyester. Molecular structures of the molecules investigated in this paper are displayed in Figures 1 and 2.

2. Experimental Section

2.1. Materials. All solvents were purchased from Aldrich Chemicals (99+%, anhydrous) and used as received. Prior to use, the solvents were checked for spurious emissions in the region of interest and found to be satisfactory. Quaterthiophene was easily prepared from procedures reported in the literature.[24] 3′,4″-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene (DDQT), 3,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-dicarboxylic acid (DAQT), 3,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-dicarbonyl chloride (DCAQT), and poly(1,10-decane-3,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-dicarboxylate) (PQC10) have been prepared according to previously published procedures.[25] The synthesis and purification of 3″,4‴-didecyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (DDST), 3″,4‴-didecyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene-5,5′′′′′-dicarboxylic acid (DAST), 3″,4‴-didecyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene-5,5′′′′′-dicarbonyl chloride (DCAST), and poly(1,10-decane-3″,4‴-didecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene-5,5′′′′′-dicarboxylate) (PSC10) have been prepared according to previously published procedures.[26]

2.2. Equipment. Absorption spectra were recorded on a Varian spectrometer Cary 1 Bio using 1 cm quartz cells and solute concentrations of $(2-8) \times 10^{-6}$ M. It has been shown that the Beer−Lambert law applies for concentrations used.

Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with a F2T11 special configuration. The excitation and emission band-passes used were 2.6 and 1.9 nm, respectively. Each solution was excited near the absorption wavelength maximum using a 1 cm path length quartz cell, and the concentration

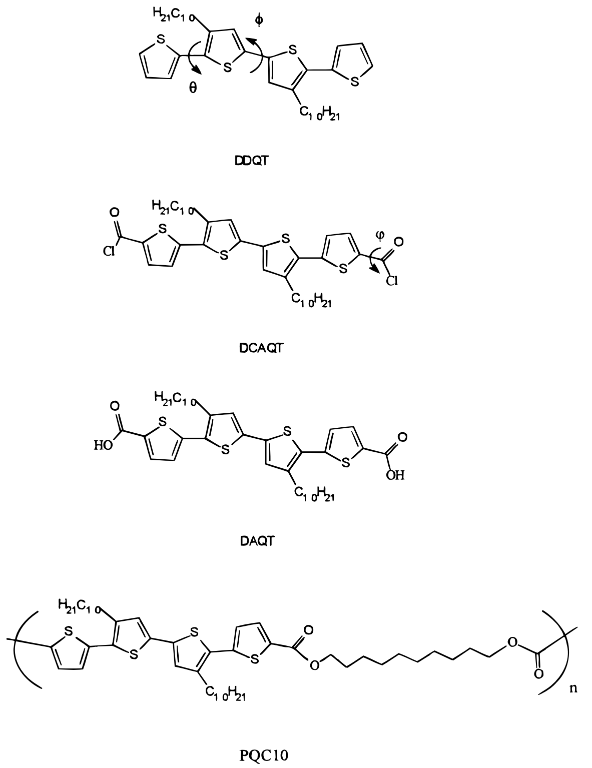

Figure 1. Molecular structure of tetramers and of the corresponding polyester.

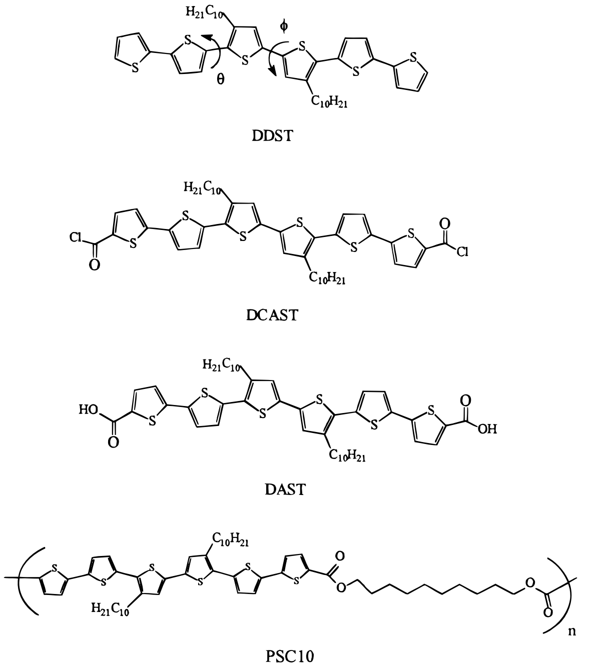

Figure 2. Molecular structure of hexamers and of the corresponding polyester.

used was (2−8) × 10^{-6} M, giving an absorbance near 0.1 to avoid any inner-filter effects. A study of the concentration (C) effect has been done on the fluorescence intensity (I_F), and all measurements have been performed in the linear region of the I_F vs C curve. For each molecule, corrected excitation spectra were found to be identical to their respective absorption spectra. Fluorescence quamtum yields were determined in argon-saturated solutions of the substrates at 298 K against anthracene in ethanol ($\phi_f = 0.27$) or 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.90$) as standards.[27]

Fluorescence lifetimes were measured on a multiplexed time-correlated single-photon counting fluorimeter (Edinburgh Instruments, model 299T). Details on the instrument have been published elsewhere.[28] The instrument incorporates an all-metal coaxial hydrogen flash lamp. Reconvolution analysis was performed by fitting over all the fluorescence decay including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, reduced χ^2 values, and Durbin−Watson (DW) parameters. The lifetime measurements were performed at 298 K.

2.3. Calculation Methodology. Semiempirical calculations were performed using the HYPERCHEM package, release 4.5, for Windows from Hypercube, Inc., on a Pentium personal computer. This package has been used to draw the molecules and optimize roughly their geometry using the MM+ force field, which is an extension of MM2 developed by Allinger.[29] A more precise geometry optimization was obtained using the AM1 (Austin Model 1) or PM3 semiempirical methods, including the sulfur atom parameter. AM1 is a modified MNDO method proposed and developed by M. J. S. Dewar and co-workers at the University of Texas at Austin.[30−33] PM3 is a reparametrization of AM1, which is based on the neglect of diatomic overlap (NDDO) approximation.[34] The parameters for PM3 were derived by comparing a much larger number and a wider variety of experimental versus computed molecular properties. Typically, nonbonded interactions are less repulsive in PM3 than in AM1. For all derivatives, the dihedral angle between the thiophene rings was varied in 15° increments from the planar anti conformation (180°) to the planar syn conformation (0°). For each increment, the dihedral angle was held fixed, while the remainder of the molecule was optimized using AM1 or PM3. A root-mean-square (RMS) gradient in the energy of 0.1 kcal mol^{-1} was used for the optimization criterion.

3. Results and Discussion

3.1. Spectroscopic Results. All spectroscopic measurements were done in a series of *n*-alkanes (*n*-hexane to *n*-hexadecane) and in a series of polar protic (methanol, hexanol) and aprotic (tetrahydrofuran (THF), acetonitrile, and chloroform) solvents except for the acid-substituted molecules (DAQT, DAST) which are not soluble in *n*-alkanes. No important solvent effects can be observed for all molecules investigated in this paper. The sole exception concerns molecules with carboxyl groups in alcohols, where hydrogen bonds are formed as observed for other oligothiophenes.[6,23] In general, small red shifts of the absorption and fluorescence bands in going from *n*-hexane to *n*-hexadecane are observed. This behavior is also observed in polar solvents. The absorption coefficients, the bandwidths, and the Stokes shifts are not significantly influenced by the environment as observed for substituted bithiophenes.[6] Spectroscopic parameters and spectra in specific solvents are displayed in Tables 1 and 2 and in Figures 3 and 4, respectively.

3.1.1. Tetramers and a Corresponding Polyester. From Table 1 and Figure 3, one can see that the absorption band maximum of DDQT is a little blue shifted compared to that of the unsubstituted tetramer (QT). The absorption coefficient is also reduced and the $fwhm_A$ is increased for DDQT compared to the respective values found for QT. The small blue shift observed indicates that DDQT is more twisted on average than QT. Indeed, without any conformational changes, the absorption band of DDQT would be red shifted as observed for the 4,4′-dialkyl-substituted oligothiophenes due to the inductive and/or hyperconjugative effects of the alkyl chains.[6,18,19] The decrease of the absorption coefficient of the DDQT absorption band confirms the reduction in the electronic delocalization found for this twisted molecule even though a part of this reduction

Table 1. Spectroscopic Parameters of Tetramers and the Corresponding Polyester in *n*-Hexane

molecule	$\lambda_A{}^a$ (nm)	$\bar{\nu}_A{}^a$ (cm^{-1})	ϵ (M^{-1} cm^{-1})	fwhm$_A{}^b$ (cm^{-1})	$\lambda_F{}^a$ (nm)	$\bar{\nu}_F{}^a$ (cm^{-1})	fwhm$_F{}^b$ (cm^{-1})	Δ^c (cm^{-1})
QT	386	25 900	25 300	4900	442 471	22 600 21 200	3300	2700
DDQT	373	26 800	23 400	5400	449 477	22 300 21 000	3400	4500
DCAQT	428	23 400	31 600	4100	498 537	20 100 18 600	2700	3300
DAQT^d	401	24 900		5400	484 513	20 700 19 500	2900	4200
PQC10	407	24 600		5600	482 507	20 700 19 700	3400	3900
PQC10^e	411	24 300	35 100	5500	492 522	20 300 19 200	3300	4000

[a] Taken at the maximum of the band. [b] Full width at half-maximum of the band. [c] Stokes shift between absorption ($\bar{\nu}_A$) and fluorescence ($\bar{\nu}_F$) maxima. [d] Measured in THF. [e] Measured in chloroform.

Table 2. Spectroscopic Parameters of Hexamers and the Corresponding Polyester in *n*-Hexane

molecule	$\lambda_A{}^a$ (nm)	$\bar{\nu}_A{}^a$ (cm^{-1})	ϵ (M^{-1} cm^{-1})	fwhm$_A{}^b$ (cm^{-1})	$\lambda_F{}^a$ (nm)	$\bar{\nu}_F{}^a$ (cm^{-1})	fwhm$_F{}^b$ (cm^{-1})	Δ^c (cm^{-1})
ST^d	436	22 900	47 900	4700	502 537	19 900 18 600	2800	3000
DDST	411	24 300	43 600	5900	502 545	19 900 18 300	3000	4400
DCAST	437	22 900	41 300^e	6000	536 570	18 700 17 500	2900	4200
DAST^e	431	23 200		6000	530 563	18 900 17 800	3300	4300
PSC10	424	23 600		6600	524 554	19 100 18 000	3300	4500
PSC10^f	441	22 700		5700	544 575	18 400 17 400	3600	4300

[a] Taken at the maximum of the band. [b] Full width at half-maximum of the band. [c] Stokes shift between absorption ($\bar{\nu}_{abs}$) and fluorescence ($\bar{\nu}_f$). [d] In dioxane from ref 9. [e] Measured in THF. [f] Measured in chloroform.

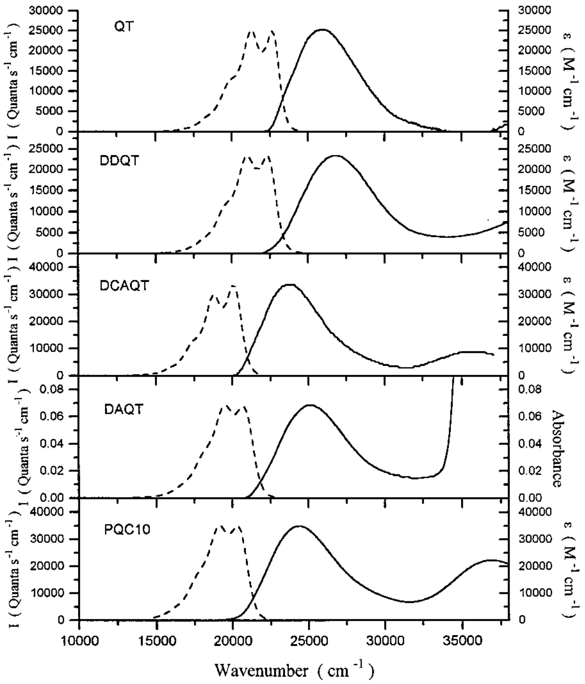

Figure 3. Absorption (—) and fluorescence (- -) spectra of tetramers and of the corresponding polyester. DDQT and DCAQT are taken in *n*-hexane, DAQT is taken in THF, and PQC10 is taken in chloroform.

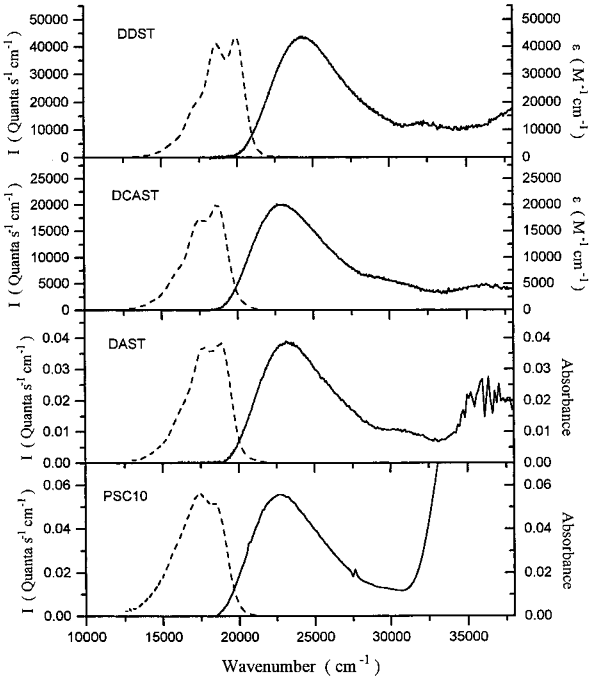

Figure 4. Absorption (—) and fluorescence (- -) spectra of hexamers and of the corresponding polyester. DDST and DCAST are taken in *n*-hexane, DAST is taken in THF, and PSC10 is taken in chloroform.

might also be due to the broader spectrum of DDQT in comparison with QT. Also, the wider absorption bandwidth strongly suggests that more conformers are present in DDQT compared to QT. Judging by the lack of vibrational structures observed in the absorption spectra, both molecules seem quite flexible in their ground electronic state. In contrast to the absorption spectral properties, the fluorescence band of DDQT is a little red shifted compared to that of QT. Moreover both bands are structured and show similar bandwidths. These results strongly suggest that the relaxed singlet excited states favor more planar conformations than observed in the ground state, giving rise to a narrower distribution of conformers. These conformational changes

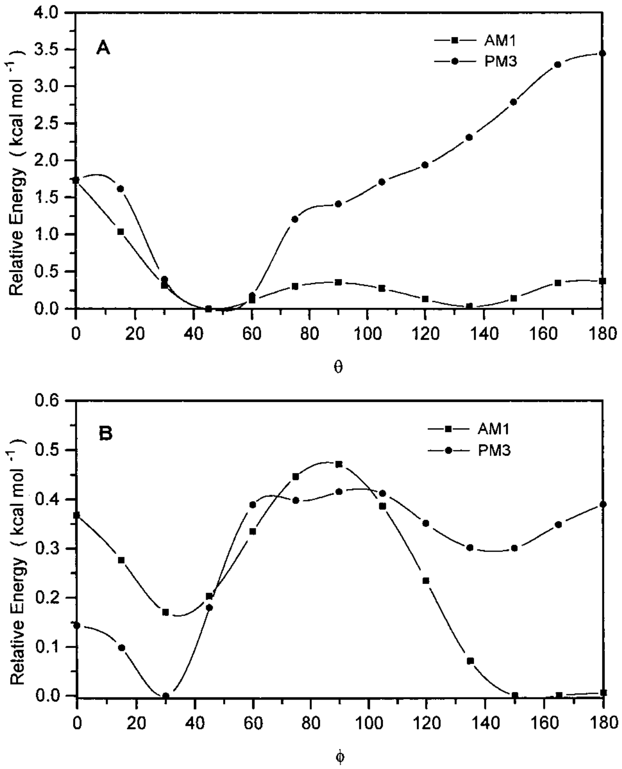

Figure 5. Potential energy surface of DEQT as obtained from AM1 and PM3 semiemperical calculations for the angle Θ and ϕ (see Figure 1).

upon relaxation have been observed in all oligothiophenes investigated up to now.[6,14,19,23,33] The red shift of the fluorescence band observed for DDQT is due to the inductive and/or hyperconjugative effects of the alkyl chains. The observation that DDQT is more twisted in its ground state whereas DDQT and QT have rather similar conformations in the relaxed singlet excited state is emphasized by the larger Stokes shift found for DDQT (see Table 1).

The potential energy surfaces of DEQT (3′,4″-diethyl-2,2′:5′,2″:5″,2‴-quaterthiophene) obtained from AM1 and PM3 semiempirical calculations are reproduced in Figure 5. To reduce the time of calculation, DEQT is used here instead of DDQT. It has been shown before that lateral chains longer than methyl barely affect the potential energy surface of the main chromophore. The meanings of Θ and ϕ dihedral angles are displayed in Figure 1. Semiemperical calculations were chosen because of the size of the molecules investigated. Compared to ab initio calculations, AM1 and PM3 methods give acceptable results for unsubstituted oligothiophenes[6,14,20,23] as well as for alkyl-substituted thiophene derivatives.[6,19,20,23] It is worth mentioning though that AM1 underestimates rotational barriers but gives good energy minimum conformers. On the other hand, PM3 stabilizes syn conformations compared to anti found with AM1 and ab initio calculations and does not always give acceptable energy minimum conformers but gives more significant rotational barriers compared with those predicted by AM1 in comparison with ab initio calculations. Since AM1 and PM3 have been reported in the literature for many oligothiophenes,[6,14,15,19,35,37] the conformational analysis of DEQT has been performed using both theoretical methods. A complete analysis of all possible conformations involved for DDQT (which possesses three dihedral angles) is rather difficult. For this reason, we have varied only one dihedral angle (the two other angles are kept fixed at their minimum values) to determine the minimum conformation and the potential energy surface for this dihedral angle. Due to the symmetry of the molecule, the dihedral angles at both ends of the molecule are equivalent. By using this approach, we assume that the potential energy surface involving one dihedral angle is independent of the value of the other dihedral angle. But this assumption works well for DDQT and for terthiophene[15,17,23,35] and substituted terthiophenes,[23,35,36] using ab initio and semiempirical calculations.

By varying the dihedral angle Θ, AM1 calculations predict two minima, the global minimum at 45° and a second minimum at 135° (see Figure 5A). These two minima are separated by a small barrier of 0.5 kcal mol^{-1} at 90°. Two maxima can be observed for the planar syn and anti conformations. Figure 5B shows that the AM1 method also predicts two minima at 30 and 150° and three maxima at 0, 90, and 180° when the torsional angle ϕ is varied. The barrier at 180° is very small, but the two other barriers are more important. This potential energy surface is very close to that found for BT[11−14] and longer oligothiophenes,[15,35−37] showing quite well that the molecular length and the presence of alkyl substituents do not influence the E vs ϕ potential energy surface. On the other hand, the E vs θ torsional potential is affected by the presence of the alkyl chains. Indeed the steric hindrance caused by the insertion of alkyl chains forces the molecule to adopt a more twisted conformation as observed, from ab initio calculations, for dimethyl-[11] and diethyl-[20]substituted bithiophenes in positions 3,4′ and for the dimethyl-substituted terthiophene in positions 3,3″.[36] This strongly suggests that the potential energy surface for a particular dihedral angle is quite independent of the values of the other torsional angles. PM3 calculations also predict a more twisted conformation for the dihedral angle Θ. The minimum obtained is located at the same dihedral angle as that calculated using AM1, but no local minimum is predicted for the trans conformation, whereas the rotational barrier against planarity is very different from that obtained from AM1. For the dihedral angle ϕ, the PM3 potential energy surface is more similar to the AM1 torsional potential, except that PM3 calculations predict a syn conformer as the most stable as observed for BT.[35]

Insertion of two carbonyl chloride groups at both ends of the molecule (DCAQT) causes an important red shift of the absorption band (see Figure 3), an increase of the absorption coefficient, and a decrease in the bandwidth compared to the respective values of DDQT. The spectral shift can be due to two effects. One is the increase in the electronic delocalization along the long molecular axis and the other is a possible increase in the planarity of the molecule. We have shown from ab initio calculations performed on bithiophene derivatives that the addition of end substituents including carbonyl chloride groups does not significantly change the molecular conformation but increases the rotational barrier.[23] On the basis of these theoretical results, we may conclude that the spectral changes observed for DCAQT are caused by the increase in the electronic delocalization without involving important conformational changes. The sharpening of the DCAQT absorption band is probably due to the increase in the rotational barrier between thiophene rings which should allow for a lower number of conformers at room temperature. However, judging by the lack of any vibrational fine structures in the absorption band, the DCAQT molecule remains quite flexible in its ground electronic state. Similar spectral changes have been observed in the fluorescence of DCAQT compared to that of DDQT. But both fluorescence bands show a vibrationnal structure and are sharper compared to their respective absorption spectra. This strongly suggests, as reported above for DDQT and for other oligothiophenes,[6,38] that, upon relaxation of the excited singlet states, the molecules adopt more planar conformations.

Substitution by a carboxyl group at both ends (DAQT) caused a blue shift and an increase in the absorption bandwidth compared to DCAQT. This can be explained by the weaker electron acceptor properties of the hydroxyl groups which may reduce the rotational barrier and allow a higher number of twisted conformers. In the fluorescence, the blue shift observed is less than that found in absorption, giving rise to an increase in the Stokes shift for DAQT compared to that of DCAQT (see Table 1). The fluorescence band of DAQT shows a vibrational structure and is sharper than its absorption band, showing again here that a more planar conformation is adopted in the excited singlet state as discussed above.

Table 1 shows that the polyester (PQC10) absorption band maximum and bandwidth are very similar to that of DAQT, suggesting a similar distribution of conformers in the ground state. Along the same line, fluorescence maxima and bandwidths as well as Stokes shifts of the polymer and DAQT are also very similar. These results indicate that the relaxation of the excited state observed for isolated molecules is also effective in the polyester. All these results focus on the fact that oligothiophenes are well-isolated in the polyester.

3.1.2. Hexamers and a Corresponding Polyester. From Table 2, one can see that the absorption band maximum of DDST is blue shifted compared to that of sexithiophene (ST), whereas the absorption coefficient is reduced and the bandwidth is increased. On the other hand, the fluorescence band maxima and bandwidths of both molecules are relatively similar. These spectral data indicate that the alkyl chains create sufficiently high steric hindrance to force the DDST molecules to adopt more twisted conformations than ST in their ground state. According to the data reported above for DDQT, this also suggests that the length of the oligomer does not affect much the conformation between adjacent thiophene rings. The same conclusion has been reached for alkyl-substituted terthiophene and quinquethiophene.[23] The unstructured absorption band and the large bandwidth of DDST suggest that many conformers are present in solution. As we know that the rotational barrier from dimers to trimers[36] are similar for the same substitution, we expect similar potential energy surface for dihedral angles ϕ and Θ in DDST than that obtained for DEQT. The wavelength, the bandwidth, and the presence of vibrational fine structures of the fluorescence bands suggest that more planar conformations are favored in the excited state as observed above for shorter oligomers. The larger Stokes shift obtained for DDST compared to that of ST clearly indicates large conformational changes occurring during the relaxation of the excited state (see Table 2).

An important red shift is observed for the DCAST absorption band compared to that of DDST. According to the discussion above, we believe that an increase in the electronic delocalization without important conformational changes is responsible for the bathochromic shift observed. The absorption band is still unstructured. In contrast with DDQT, the absorption bandwidth is not reduced in going from DDST to DCAST. This is understandable since the relative increase in the electron delocalization by addition of two carbonyl chloride groups decreases with the length of the oligomer. Indeed the maximum effect of the addition of two carbonyl chloride groups on absorption spectra is observed for bithiophene derivatives.[6] Fluorescence data indicate that a more planar conformation is also favored for DCAST in the excited state. The bandwidth of the fluorescence spectrum is smaller for DCAST compared to that of DDST, showing that the presence of carbonyl chloride groups decreases the number of allowed conformers at room temperature in the excited state. The absorption maximum and bandwidth of DAST are close to those of DCAST. This shows that, in this longer oligomer, the difference in electron acceptor properties of end groups becomes meaningless. Fluorescence data indicate that, upon relaxation, the same conformational change is operative as that found for DCAST.

The polyester (PSC10) shows a blue shift in its absorption band in *n*-hexane and a red shift in chloroform compared to the respective values of DAST. These shifts are mainly due to the change in the environment. Absorption bands are still unstructured, and bandwidths are in the same order as that observed for DAST, showing that the conformation and the distribution of conformers of the chromophore in the polymer are the same as that found for the isolated oligomer. The more structured fluorescence band and the decrease of its bandwidth compared to the absorption band show that the relaxation of the first excited state also favors planar conformations when sexithiophene derivatives are incorporated in the polyester.

3.2. Molecular Photophysics. All photophysical measurements were obtained in *n*-hexane, *n*-hexadecane, methanol, 1-hexanol, and chloroform except for acid derivatives (DAQT and DAST), where data were taken in THF only because of their very low solubility in most organic solvents. For all fluorescence decay profiles, a single-exponential fit gives acceptable statistical parameters (χ^2 < 1.3 and DW ≈ 1.7). Figure 6 shows, as an example, the fluorescence decay curves associated with the lamp profiles and the residuals for QT in *n*-hexane. No significant polarity and viscosity effect on the results has been detected. Photophysical parameters for quaterthiophene and sexithiophene derivatives in *n*-hexane at room temperature are displayed in Tables 3 and 4, respectively.

Tables 3 and 4 show that insertion of alkyl chains induces a decrease in the fluorescence quantum yield and lifetime which is mainly due to the increase in the nonradiative decay constant for the twisted molecules. For unsubstituted oligothiophenes, it is well-established that the main deactivation pathway of the S_1 state involves an intersystem crossing process (k_{isc}).[9,39] This mechanism is favored as the singlet−triplet (S_1-T_4) energy gap decreases.[40] It might then also happen that, for oligothiophene derivatives, increases in k_{nr} are due to a decrease in the S_1-T_4 energy gap. It is difficult to assign the variation of the photophysical parameters to the change of the intersystem crossing only since we have not measured up to now the triplet quantum yields

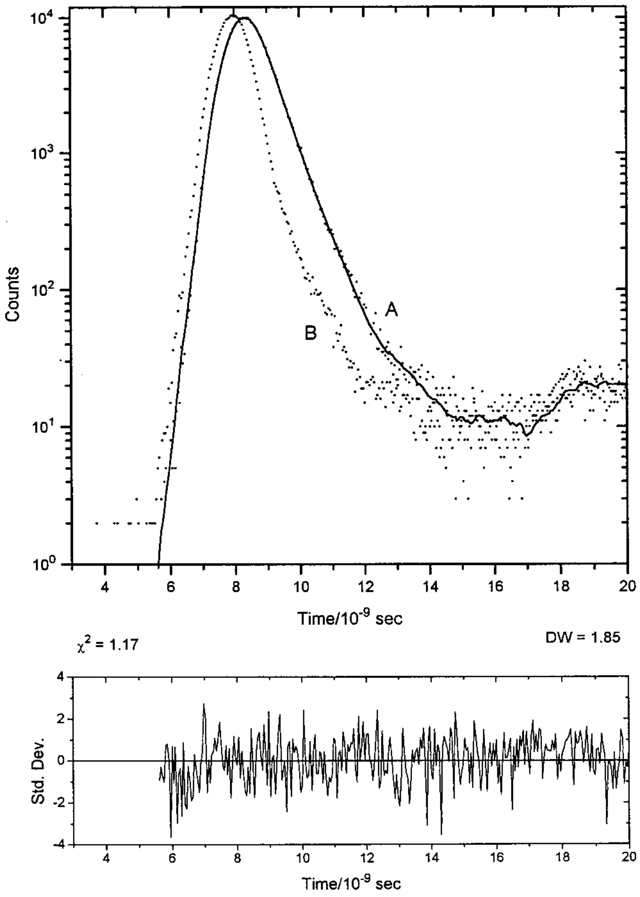

Figure 6. Fluorescence decay curves (A) associated with the lamp profile (B) and residual for QT in *n*-hexane for the monoexponential fit (solid line).

Table 3. Photophysical Parameters of Tetramers and of the Corresponding Polyester in *n*-Hexane

molecule	ϕ_F	τ_F (ns)	$k_F{}^a \times 10^{-8}$ (s^{-1})	$k_{nr}{}^b \times 10^{-8}$ (s^{-1})
QT	0.22	0.49	4.4	16
DDQT	0.15	0.30	5.0	28
DCAQT	0.19	0.44	4.2	19
DAQT[c]	0.13	0.47	2.9	18
PQC10	0.17	0.41	4.1	20
PQC10[d]	0.11	0.40	2.8	22

[a] $k_F = \phi_F/\tau_F$ (radiative fluorescence decay rate constant). [b] $k_{nr} = k_F(1 - \phi_F)/\phi_F$ (nonradiative fluorescence decay rate constant). [c] Measured in THF. [d] Measured in chloroform.

Table 4. Photophysical Parameters of Hexamers and of the Corresponding Polyester in *n*-Hexane

molecule	ϕ_F	τ_F (ns)	$k_F{}^a \times 10^{-8}$ (s^{-1})	$k_{nr}{}^b \times 10^{-8}$ (s^{-1})
ST[c]	0.41	1.0	4.1	5.5
DDST	0.21	0.75	2.8	11
DCAST	0.16	0.67	2.3	13
DAST[d]	0.18	0.82	2.2	10
PSC10	0.17	0.64	2.7	13
PSC10[e]	0.14	0.74	1.9	12

[a] $k_F = \phi_F/\tau_F$ (radiative fluorescence decay rate constant). [b] $k_{nr} = k_F(1 - \phi_F)/\phi_F$ (nonradiative fluorescence decay rate constant). [c] In dioxane from ref 9. [d] Measured in THF. [e] Measured in chloroform.

(ϕ_T). But we can note that the difference between fluorescence quantum yields of unsubstituted and substituted oligomer are relatively small such that the precision on ϕ_T will not allow anyone to explain these variations. One of the most important factors in the explanation of the variation of ϕ_F is the conformation. The fluorescence spectra show that the first relaxed singlet excited state favors more planar conformations, but one cannot affirm that substituted oligothiophenes have exactly the same conformation in the first singlet excited state than that of the unsubtituted one. In conclusion, the variation in the photophysical parameters of substituted oligothiophenes can have more than one explanation more or less independent of each other. These variations can be influenced by the relaxation of the Franck–Condon singlet exited state, which is more important for twisted oligothiophenes, and can be induced by a different conformation in the relaxed singlet excited state or simply by the inductive effect of the alkyl groups on the energy level of the different singlet and triplet excited states.

Insertion of carbonyl chloride or acid groups at both ends of the quaterthiophene and sexithiophene derivatives or even the insertion of the oligothiophenes into the polyester do not practically change the photophysical parameters. This confirms, as stated above from spectral properties, that oligothiophene units do not interact with each other and do not significantly change their conformations in the ground and relaxed singulet excited states when incorporated in the polyester chains.

4. Concluding Remarks

Insertion of decyl chains on the two central thiophene rings of quaterthiophene and sexithiophene creates an important twisting of the molecules in the ground state, which induces a blue shift, a decrease in the absorption coefficient, and an increase in the absorption bandwidth. AM1 calculations performed on the tetramer derivatives are in good agreement with these spectral data. Fluorescence measurements show that, after excitation, molecules in their first singlet excited state relax to more planar conformations, giving rise to a narrower distribution of conformers. The smaller fluorescence quantum yield and lifetime obtained for the twisted molecules are mainly due to an increase in their nonradiative properties (higher values of k_{nr}), which is interpreted in terms of a probable enhancement of the intersystem crossing process for the twisted molecules.

The presence of end substituents (carbonyl chloride and acid groups) to the oligothiophenes causes a red shift of their absorption and fluorescence bands, an increase in their molecular rigidity, and a decrease of the nonradiative decay rates (for the quaterthiophene derivatives). The two former characteristics are due to an increase in the conjugation length along the molecular frame. It is believed that this process does not involve any important conformational changes.

The incorporation of quaterthiophene and sexithiophene derivatives into polyesters does not create important changes in the spectral and photophysical properties of these chromophores. This behavior strongly suggests that the oligothiophene units are well-isolated in the polymer chain and that their conformations in ground and excited states are not much altered in this environment.

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