Spectroscopy and Photophysics of Some Oligomers and Polymers Derived from Thiophenes

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Received May 2, 1995; Revised Manuscript Received September 11, 1995[⊗]

ABSTRACT: A series of bithiophene and terthiophene derivatives and their respective polymers have been prepared. The absorption and fluorescence spectra, quantum yields, and lifetimes of these derivatives in solution are studied and compared. The bandwidths of the absorption and fluorescence profiles of the different derivatives are used to discuss the geometry changes occurring from one molecule to the other in the ground and excited states. Increasing the chain length and/or substitution of bithiophene and terthiophene at both ends of the molecule with a carbonyl chloride group increases the planarity of the molecules in both their ground and excited states by improving the electronic delocalization throughout the molecular frame. Comparison between the absorption and fluorescence spectra has proved to be a good tool to discover conformational changes occurring during the relaxation of the excited state. All the molecules investigated show geometrical changes from a twisted ground state to a more planar conformation in the excited state. A radiationless torsional mechanism and intersystem crossing processes are involved in the excited state relaxation of the various molecules. Incorporation of substituted bithiophene and terthiophene units in aromatic polyesters have been made and the optical and photophysical properties of these polymers are studied. It is shown that the bithiophene and terthiophene units are perfectly isolated in the polymeric chain. The photophysical properties of the polyesters make these materials good candidates for the fabrication of efficient blue-light-emitting diodes.

1. Introduction

Polythiophenes are among the most studied materials because of their good chemical stability and high electrical conductivity in the oxidized (doped) state. The insertion of a 3-alkyl side chain to the thiophene ring produces polymers with improved conductivity.[1] Moreover, it is well-known that substituted polythiophenes show enhanced processability, solubilization in common solvents, and solvatochromism and thermochromism.[2,3] The latter two properties are associated with the rotation of neighboring thiophene rings. Rotation leads to a decrease of π conjugation, which in turn causes changes in the electronic structure responsible for the color changes.[2] Recently, Leclerc *et al.* synthesized several polythiophenes with alkyl and alkoxy side chains located in β-positions. The temperature-dependent UV–visible absorption measurements of these polythiophenes indicated that the planar to nonplanar transition observed in some of these conjugated polymers is driven by a delicate balance between repulsive intrachain steric interactions and attractive interchain (or intrachain) interactions.[4–7] In the last few years, the photoluminescence of polythiophene in the solid phase[8–13] and in solution[14,15] has been investigated. However knowledge concerning the radiative and nonradiative processes from excited states is still rudimentary.

Oligothiophenes have recently been the focus of much attention. They are good models for studying charge storage in conducting polymers.[16,17] Alkyl substitution increases the solubility and the tractability of these organic materials, allowing refined studies of longer conjugated chains to be performed.[18–22] Their use as semiconductors in electronic devices has been proposed,[23,24] and the first all-organic transistor was based on sexithiophene.[25] Thin films of oligothiophenes are generally more ordered than the corresponding ones made from the conjugated polymer.[26,27] They are good candidates for numerous applications in electronics and optoelectronics.

The conformation of many thiophene oligomers has been obtained theoretically and their absorption characteristics have been calculated and measured experimentally.[28–39] Recently, the luminescence of block polymers in which oligothiophene units alternate with oligosilanylene blocks and regioregular polythiophenes in which oligothiophene sequences are delimited by n-octyl substituents placed in a "head-to-head" fashion on adjacent thiophene rings has been investigated.[40] It was observed that the oligothiophene units are well isolated in the block polymers whereas, in the first excited singlet state, a strong electronic driving force offsets the steric hindrance of the octyl substituents and increases the size of the conjugating π-system. Steady-state and time-resolved fluorescence have been performed on a series of oligothiophenes with two to seven rings.[41–43] In general it was observed that the fluorescence quantum yield and lifetime increase with the number of thiophene rings (n) from $n = 2$ to 5 and become constant at $n = 5–7$.[41,43] On the contrary, the triplet quantum yield decreases overall from $n = 2,3$ (nearly same) to constancy at $n = 5,7$.[43] No phosphorescence has been observed, except possibly for thiophene.[43] The optical properties of a series of oligothiophenes (from bithiophene to sexithiophene) substituted at both ends of the chain by various electron donor or acceptor groups (methoxy, nitro, or bromo) have also been measured.[44] It was found that only the nitro substituent induces a significant increase in the fluorescence quantum yield and lifetime of the excited state. Picosecond and femtosecond time-resolved absorption/emission spectroscopy have been used to investigate the excited states of several oligothiophenes by studying the transient absorption and fluorescence processes from

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

0024-9297/95/2228-8587$09.00/0

these states.[45-49] Ultrafast vibrational population redistribution dynamics and subsequent cooling processes have been identified for photogenerated S_1 α-terthiophene in solution.[45]

We report here the solution optical properties and photophysics of several substituted oligomers and polymers derived from thiophenes. The objective is to describe the optical and photophysical characteristics of these materials in terms of molecular properties. The energy positions and bandwidths of the absorption and fluorescence spectra together with the quantum yield and lifetime of the fluorescence emission are determined in order to assess the substituent effect on the molecular conformation and electronic properties of these conjugated structures. We discuss these results in terms of conjugation length and steric hindrance between the adjacent rings. This study helps in understanding the general absorption and luminescence behavior of the polythiophenes.

In relation with these results, substituted bithiophene and terthiophene units have been incorporated in aromatic polyesters. The presence of rigid-rod moieties (thiophene oligomers) substituted with flexible side chains should lead to the formation of soluble high molecular weight polymers with good mechanical properties.[50] Moreover, the synthesis of such segmented conjugated polymers is a good way to prepare efficient light-emitting diodes with tunable optical properties.[51-57] It is shown that the oligothiophenes are well isolated in the polyester chain and that the optical and photophysical properties of the polyesters are close to those of the respective α-substituted oligomers.

2. Experimental Section

2.1. Materials. Chloroform was purchased from American Chemicals Ltd. (spectrograde). Tetrahydrofuran (THF) was purchased from Aldrich (spectrophotometric grade). Prior to use, the solvents were checked for spurious emission in the region of interest and found to be satisfactory. Diacetoxylbenzene was prepared using known procedures[58] and hydroquinone (Aldrich) was purified by sublimation. 4,4′-Didecyl-2,2′-bithiophene (DDBT), poly(4,4′-didecyl-2,2′-bithiophene) (PDDBT),[59] 3′,4′-dihexyl-2,2′:5′,2″-terthiophene (DHTT), 3′,4′,3″″,4″″-tetrahexylsexithiophene (THST) and poly(3′,4′-dihexyl-2,2′:5′,2″-terthiophene) (PDHTT)[14,31] were prepared according to previously published procedures. PDDBT has a number-average molecular weight of 11 000 whereas PDHTT has a number-average molecular weight of 9000.

4,4′-Didecyl-2,2′-bithiophene-5,5′-dicarboxylic Acid. To 100 mL of dry diethyl ether was added 2.062 g (5 mmol) of DDBT in a 250 mL flask under nitrogen. Once the DDBT was solubilized, 6.25 mL of *n*-butyllithium (1.6 M, Aldrich) was added at room temperature. The mixture was stirred for 30 min and then cooled to −78 °C and treated with an excess of dry ice (solid CO_2). The reaction mixture was slowly warmed to room temperature and hydrolyzed with a large quantity of water. The formed lithium salt was extracted several times with diethyl ether. The aqueous solution was then acidified with 2 N HCl in order to precipitate the desired dicarboxylic acid. The product was filtered and purified by recrystallization in glacial acetic acid. It was finally dried under vacuum at 100 °C for 24 h. Yield = 60%. Mp: 225–227 °C. ^1H NMR (300 MHz, THF-d_8, ppm): 0.88 (6H, t), 1.36 (28H, m), 1.65 (4H, m), 3.00 (4H, t), 7.23 (2H,s), 10.82 (2H, s). ^{13}C NMR (75 MHz, solid state, ppm): 15.48, 26.24, 32.32 (broad peak); 34.20, 36.00, 126.55, 129.52, 141.89, 153.00, 168.10. IR (NaCl, cm^{-1}): 1672, 1653.

3′,4′-Dihexyl-2,2′:5′,2″-terthiophene-5,5″-dicarboxylic Acid. Following a similar procedure to that described above, the desired orange solid (mp = 302–304 °C) product was obtained with a yield of 62%. ^1H NMR (300 MHz, THF-d_8, ppm): 1.03 (6H, t), 1.46 (8H, m), 1.57 (4H, m), 1.71 (4H, m), 2.91 (4H, t), 7.33 (2H, d), 7.81 (2H, d), 10.96 (2H, s). ^{13}C NMR (75 MHz, THF-d_8, ppm): 15.21, 24.32, 29.70, 31.21, 32.24, 33.25, 128.16, 132.10, 135.04, 136.00, 143.15, 143.66, 163.69. IR (NaCl, cm^{-1}): 1660.

4,4′-Didecyl-2,2′-bithiophene-5,5′-dicarbonyl Dichloride (DCABT). In a 25 mL flask, 4.00 mL of benzene and 0.488 g (9 mmol) of 4,4′-didecyl-2,2′-bithiophene-5,5′-dicarboxylic acid were heated to reflux, and then 2.30 mL (31.6 mmol) of thionyl chloride was added. The mixture was kept under reflux for 24 h. The crude product was purified with flash chromatography on silica gel (using chloroform), followed by a recrystallization in *n*-hexane. This gives orange needle-like crystals (mp = 63–65 °C) with a yield of 60%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.89 (6H, t), 1.34 (28H, m), 1.64 (4H, m), 2.94 (4H, t), 7.26 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 14.02, 22.60, 29.23, 29.26, 29.37, 29.43, 29.50, 29.64, 30.47, 31.82, 129.66, 131.55, 144.20, 156.23, 157.85. IR (NaCl, cm^{-1}): 1768.

3′,4′-Dihexyl-2,2′:5′,2″-terthiophene-5,5″-dicarbonyl Dichloride (DCATT). Similarly to the above-mentioned product, the desired orange solid (mp = 74–78 °C) was obtained with a yield of 60%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.84 (6H, t), 1.38 (8H, m), 1.50 (4H, m), 1.52 (4H, m), 2.72 (4H, t), 7.17 (2H, d), 7.87 (2H, d). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 13.95, 22.49, 28.28, 29.41, 30.28, 31.33, 126.86, 130.62, 135.72, 138.23, 143.37, 147.67, 159.18. IR (NaCl, cm^{-1}): 1740, 1722.

Poly(*p*-phenylene-4,4′-didecyl-2,2′-bithiophene-5,5′-dicarboxylate) (PEBT). In a tube, 0.400 g (0.8 mmol) of 4,4′-didecyl-2,2′-bithiophene-5,5′-dicarboxylic acid and 0.148 g (0.8 mmol) of diacetoxylbenzene were mixed under nitrogen. The temperature was raised to 244 °C for 2 h and then to 282 °C for 2 h. During the last 30 min, the tube was put under reduced pressure (0.25 mmHg) to evacuate the acetic acid formed during the condensation reaction. The crude product was washed with acetone and then dried under reduced pressure at 50 °C for 24 h (yield = 87%). This polymer was completely soluble in chloroform and has a number-average molecular weight of 11 000.

Poly(*p*-phenylene-3′,4′-dihexyl-2,2′:5′,2″-terthiophene-5,5″-dicarboxylate) (PETT). Since the parent dicarboxylic acid undergoes a decarboxylation with melting, the reaction was carried out using DCATT and hydroquinone following a similar procedure as that described above. The temperature was kept at 115 °C for 45 min and then at 150 °C for 1 h. Finally, the temperature was raised at 244 °C for 1.5 h. During the last 30 min, the mixture was put under reduced pressure to evacuate the hydrochloric acid formed. The crude product was washed with acetone and then dried under vacuum at 60 °C for 24 h (yield = 64%). This polymer is only partially soluble (ca. 15%) in tetrahydrofuran. This low molecular weight soluble fraction has a number-average molecular weight of 11 000.

The chemical structures of the thiophene oligomers and polymers studied in this work are shown in Figure 1.

2.2. Equipment. FTIR measurements were carried out on a Bio-Rad FTS-25 apparatus. Solution and solid-state NMR measurements were performed with a Varian VXR-300 spectrometer. Size exclusion chromatography (SEC) measurements were carried out with a Waters apparatus using a series of three Ultrastyragel columns with upper porosity of 10, 50 and 100 nm in chloroform. The calibration curve was obtained by running monodisperse polystyrene standards. Thermal characterization of the monomers was obtained with a DSC (TA Instrument, DSC 2910) at a heating rate of 10 °C/min under a nitrogen flow. The absorption spectra were recorded on a Hewlett-Packard diode array UV–vis spectrophotometer (model 8452A) using 1-cm quartz cells and solute concentrations of $1-3 \times 10^{-5}$ M. It has been verified that the Beer–Lambert law is well respected for these compounds for solute concentrations less than 5×10^{-5} M. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with an F2T11 special configuration. Each solution was excited at the absorption wavelength maximum using a 1-cm-path quartz cell and the concentration used for each derivative studied was $1-3 \times 10^{-6}$

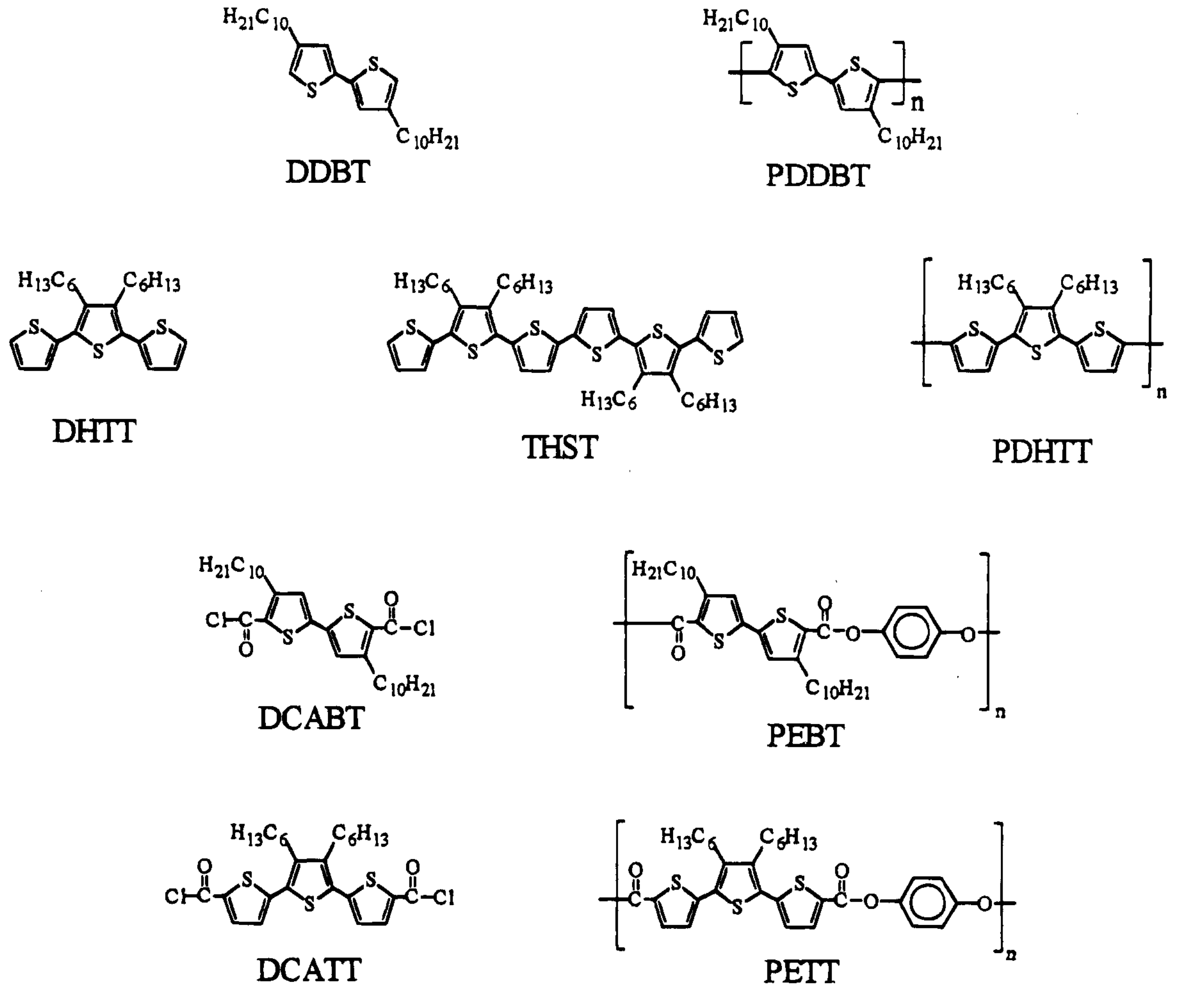

Figure 1. Molecular structure of the oligothiophenes and polythiophenes investigated.

M, giving absorbances always less than 0.06 to avoid any inner filter effect. The quantum yields of fluorescence 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.[60] All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra.

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.[61] The instrument incorporates an all-metal coaxial hydrogen flashlamp. 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 value, and Durbin–Watson (DW) parameters. The lifetime measurements were performed in argon-saturated solutions of the substrates at 298 K.

3. Results and Discussion

3.1. Electronic Absorption and Fluorescence Spectra.

All measurements were done in chloroform except for those of the PETT polymer, which is not soluble in chloroform. For this compound, the spectra were obtained in tetrahydrofuran (THF). We observed that the absorption and fluorescence wavelength maxima of these thiophene derivatives are similar in both solvents. Figures 2–5 show the absorption and fluorescence spectra of the thiophene oligomers and their corresponding polymers at ambient temperature and Table 1 reports the spectral data. In all cases, the fluorescence excitation spectra were found to be identical with the absorption spectra.

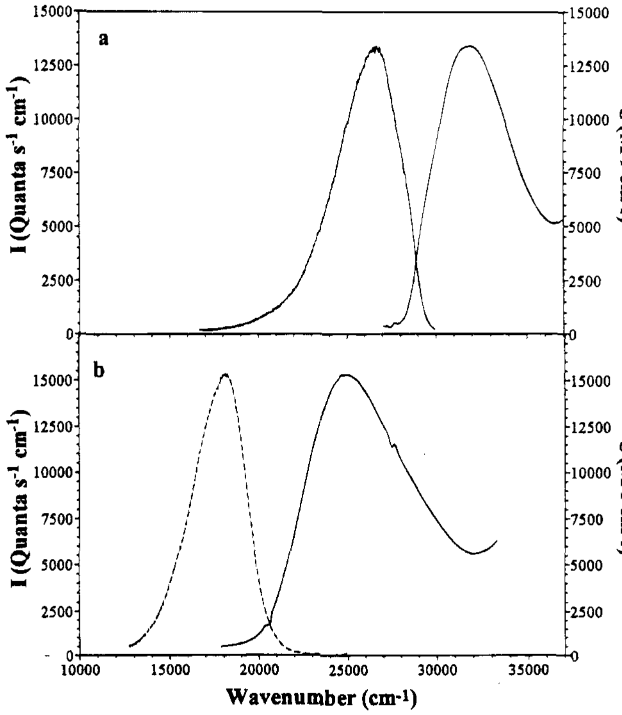

Figure 2. Absorption (—) and fluorescence spectra (- - -) of (a) 4,4′-didecyl-2,2′-bithiophene (DDBT) and (b) poly(4,4′-didecyl-2,2′-bithiophene) (PDDBT).

3.1.1. DDBT and Its Polymer.

It is well known theoretically and experimentally that a fully planar *anti*

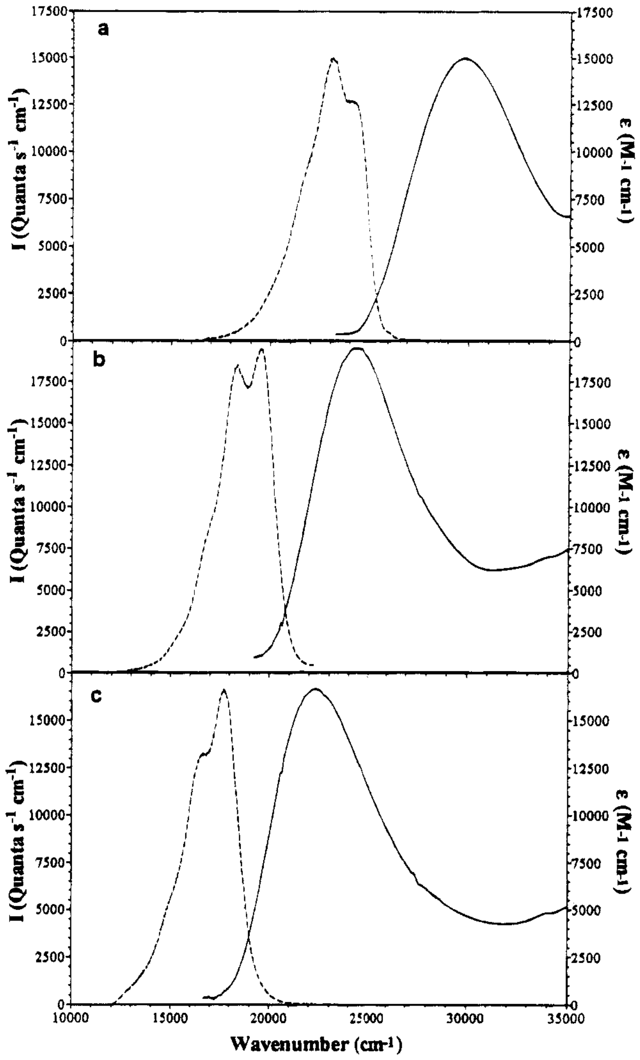

Figure 3. Absorption (—) and fluorescence spectra (- - -) of (a) 3′,4′-dihexyl-2,2′:5′,2″-terthiophene (DHTT); (b) 3′,4′,3″″,4″″-tetrahexylsexithiophene (THST) and (c) poly(3′,4′-dihexyl-2,2′:5′,2″-terthiophene) (PDHTT).

conformation is improbable for the unsubstituted bithiophene molecule (BT) in the gas phase and that a dihedral angle of about 150° exists between the planes of the two rings.[28,40,62–64] We have shown, from ZINDO/S semiempirical calculations, that the first electronic transition of BT is of the $\pi\pi^*$ type and is delocalized along the long axis of the molecule comprising the two rings.[28] The second electronic transition appeared at about 8000 cm^{-1} higher in energy than the $S_1 \leftarrow S_0$ transition with a weak oscillator strength and thus should not contribute to the first absorption band observed in the gas phase. The absorption measurements in various solvents combined with the transition energies determined by ZINDO/S have been used to gain deeper insights about changes in the molecular conformation upon the nature of the environment.[28] It was observed that BT is more twisted in solution compared to the gas phase. Recently AM1 (Austin-method 1) geometry optimization and ZINDO/S calculations of electronic transition energies of DDBT have been performed.[65] It is shown that the molecular conformation and the nature of the electronic transitions of DDBT in the gas phase and in solution are little affected by the presence of the decyl chains.

The absorption and fluorescence spectra of DDBT and PDDBT are shown in parts a and b of Figure 2, respectively. Going from DDBT to PDDBT, both bands are red-shifted. This shows that the electronic delocalization of the ground and first relaxed excited states in the polymer increases. However the polymer conformation should be affected by the presence of strong steric effects between the ring sulfur atom and the aliphatic side chain of the adjacent thiophene ring.[40,66–68] This

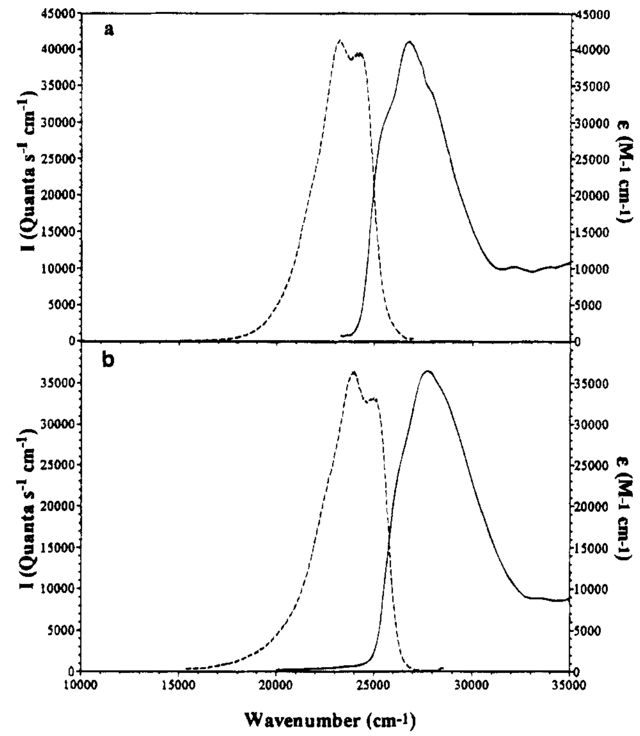

Figure 4. Absorption (—) and fluorescence spectra (- - -) of (a) 4,4′-didecyl-2,2′-bithiophene-5,5′-dicarbonyl dichloride (DCABT) and (b) poly(*p*-phenylene-4,4′-didecyl-2,2′-bithiophene-5,5′-dicarboxylate) (PEBT).

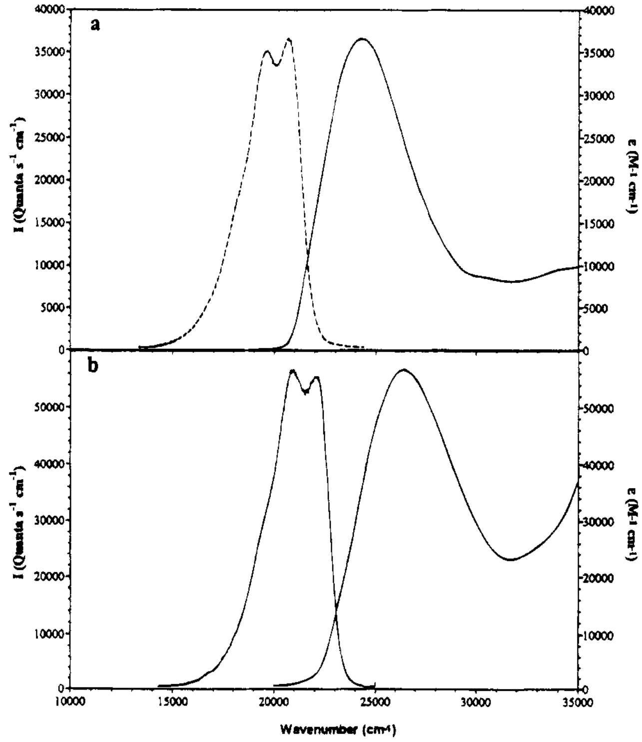

Figure 5. Absorption (—) and fluorescence spectra (- - -) of (a) 3′,4′-dihexyl-2,2′:5′,2″-terthiophene-5,5″-dicarbonyl dichloride (DCATT) and (b) poly(*p*-phenylene-3′,4′-dihexyl-2,2′:5′,2″-terthiophene-5′,5″-dicarboxylate) (PETT).

Table 1. Spectroscopic Parameters of the Oligothiophenes and the Polythiophenes Studied in Chloroform at Room Temperature (298 K)

Molecule	λ_A[a] (nm)	ν_A[b] (cm^{-1})	ϵ ($M^{-1}\ cm^{-1}$)	$FWHM_A$[d] (cm^{-1})	λ_F[e] (nm)	ν_F[f] (cm^{-1})	$FWHM_F$[g] (cm^{-1})	Δ[h] (cm^{-1})
DDBT	312	32 000	13 400	5400	384	26 100	4400	6000
PDDBT	393	25 400	15 300[c]	7500	568	17 600	3500	7800
DHTT	334	29 900	15 000	6900	434	23 000	3400	6900
THST	406	24 600	19 600[c]	6200	536	18 600	3100	6000
PDHTT	440	22 700	16 600[c]	6800	589	17 000	2900	5700
DCABT	371	27 000	41 100	4500	430	23 300	3300	3700
PEBT	356	28 100	36 500[c]	4800	420	23 800	3500	4300
DCATT	408	24 500	36 500	5100	508	19 700	3200	4800
PETT	375	26 700	56 700[c]	6200	478	20 900	3400	5700

[a] Absorption wavelengths taken at the center of mass of the absorption band. [b] Absorption wavenumbers taken at the center of mass of the absorption band. [c] Extinction coefficients calculated using the molecular mass of the repetitive units. [d] Full width at half-maximum (FWHM) of the absorption band. [e] Fluorescence wavelengths taken at the center of mass of the fluorescence band ($\lambda_{exc} = \lambda_A$ at the center of mass). [f] Fluorescence wavenumbers taken at the center of mass of the fluorescence band. [g] FWHM of the fluorescence band. [h] Stokes shift between absorption (ν_A) and fluorescence (ν_F) bands.

has been confirmed by semiempirical calculations performed on model compounds[65] and might explain the fact that the absorption band of this polybithiophene is wider than that of the DDBT molecule (see Figure 2 and Table 1). The absorption and fluorescence spectra of PDDBT do not show any vibrational fine structure, meaning that this polymer is quite flexible in its ground and first relaxed excited states. But the fluorescence spectra of DDBT and PDDBT are sharper than their corresponding absorption spectra. This observation strongly suggests that these molecules, in their first Franck–Condon excited singlet states, become more planar upon relaxation. Compared to their respective absorption spectra, Table 1 shows that, going from DDBT to PDDBT, a larger red-shift (8500 cm^{-1}) and a smaller bandwidth are observed for their fluorescence spectra. It thus seems that, in the first relaxed excited singlet state, the electronic delocalization over the polymeric chain is favored in such a way that the polymer conformation is less altered by the steric hindrance between adjacent thiophene rings. The conformational changes occurring during the relaxation of the Franck–Condon excited state is more important for the polymer than for the dimer. This is confirmed by the respective values of the Stokes shift (difference between the absorption and the fluorescence energy maxima) of the dimer and the polymer (Table 1). Indeed, the Stokes shift of PDDBT is larger by 1800 cm^{-1} compared to that measured for DDBT. Along the same line, the photoluminescence of poly(3-hexylthiophenes) (P3HT) possessing various degrees of regioregularity have been studied recently.[8] It was found that wavelengths of maximum absorption and fluorescence of P3HT in chloroform at room temperature are blue-shifted for polymers possessing increasing head-to-head (HH) content due to steric interactions between adjacent thiophene rings. It was observed that these repulsive forces are partially relieved in the excited state. This was reflected in the Stokes shifts of these P3HT's, which decrease as the HH content is lowered.

3.1.2. DHTT and Its Dimer and Polymer. The absorption spectrum of DHTT, which is illustrated in Figure 3a, shows a first electronic band that is centered at 334 nm (29 900 cm^{-1}). The absorption band does not show any resolvable vibronic fine structure. This band is blue-shifted by 21 nm relative to the absorption spectrum of the unsubstituted terthiophene (TT) in dichloromethane.[44] This is most likely due to steric hindrance between the hexyl chains and the sulfur atoms that creates a torsion of the adjacent thiophene rings and then reduces the electronic conjugation over the whole molecule. Along the same line, van Hutten *et al.* have shown that the absorption spectrum of 3,3′,4,4′-tetraoctyl-2,2′-bithiophene is blue shifted by 21 nm compared to that of BT.[40] From AM1 semiempirical calculations, these authors have shown that a propyl group on the 4-position forces the propyl on the 3-position out of the ring plane, which results in a more pronounced steric interaction between the latter propyl and the other ring. Similar results have been obtained from semiempirical calculations performed on DHTT. Combined AM1 and ZINDO/S methods have shown that adjacent thiophene rings are twisted by about 60°.[69] The same behavior has been observed for methyl α-conjugated quaterthiophenes.[30] For these oligomers, the X-ray diffraction data have shown that the adjacent thiophene rings are twisted due to steric hindrance caused by the methyl groups. The crystal structure of 3′,4′-dibutyl-2,2′:5′,2″-terthiophene (DBTT) has been reported recently.[34a] The X-ray data of this oligothiophene show an *all-anti* configuration with a ≅33° mean dihedral angle between adjacent thiophene rings. From ZINDO/S calculations, it is shown that the first electronic transition of DHTT, of the $\pi\pi^*$ type, is delocalized along the long axis of the molecule and is mainly responsible for the lowest energy absorption band observed.[69]

The fluorescence spectrum of DHTT is structured and sharper than its absorption spectrum (see Figure 3a). The presence of the emission fine structure has been observed for other thiophene oligomers[22,32,34a,40,41,43,47] and is generally attributed to vibrational coupling with the electronic transition involving the C=C ring stretching. This is indicated by the coincidence existing between the energy spacing of the peaks and the frequency of this mode as observed by resonance Raman spectroscopy.[32] The two main maxima are located at 413 and 433 nm. The difference between the structureless absorption and the structured fluorescence bands indicates that the molecule is more rigid in its first relaxed excited singlet state. This could mean that the rotational energy barrier of the adjacent thiophene rings is smaller in the ground state and contributes to the molecular disorder, giving rise to inhomogeneous broadening and hence a structureless absorption. The vibrationally resolved luminescence, on the other hand, indicates a narrow distribution of excited state molecular geometries, characterized by a more rigid planar conformation of the thiophene rings, due to the increased contribution of a quinoid electronic structure to the singlet-excited state configuration. Recently, the torsional potential energy curve (AM1) for the first excited singlet state of BT and 3,3′-dipropyl-2,2′-bithiophene has been obtained.[40] Results show that both molecules in the excited state have quinoid character with a shortened inter-ring bond in the coplanar arrangements. Experimental torsional barriers to rotation between thiophene rings have been obtained for both the ground and first excited singlet states of DBTT in solution.[34a] The S_0 barrier to rotation was reported to be 19.7 kcal/mol using ^{1}H NMR and the S_1 barrier to rotation is determined to be 4.2 kcal/mol using fluorescence lifetime measurements. These results are not in agreement with the theoretical calculations and the spectral evidences stated above for DHTT. But more recently the values of these rotational barriers have been revised. They now report the ground state barrier in solution to be approximately 8 kcal/mol (measured by NMR and calculated by the PM3 parametrization), while the calculated rotational barrier for the first excited state of DBTT remains at 4.2 kcal/mol.[34b] But the authors agree that the ground state barrier is overestimated because the calculations they used treated the aliphatic groups as rigid. These new data are more consistent with the data in this paper where in all cases studied the ground state energy barrier should be lower than the singlet excited state barrier.

The fluorescence spectrum of the unsubstituted TT has been reported recently.[40,41,43,44] In dichloromethane, the two emission maxima of TT are located at 411 and 433 nm, respectively.[44] In contrast to the absorption data, the fluorescence spectra of DHTT and TT are very close. It thus seems that, in the relaxed S_1 excited state, electronic delocalization is favored in such a way that the steric hindrance causes by the alkyl chains in the ground electronic state is much reduced. Such behavior has been observed for several substituted oligothiophenes.[40]

A shift of the absorption and fluorescence bands to longer wavelengths are observed for THST (Table 1), suggesting that the electronic delocalization of the ground and first relaxed excited state increases in the hexamer molecule. The same kind of behavior has been reported recently for a series of oligothiophenes.[40,41,43,44] Chosrovian *et al.* have shown that the size dependence of the absorption and fluorescence positions follows the law $\lambda \cong k^{1/2}$ where k equals the number of double bonds in the polyenes.[41] From this observation, they concluded that the sulfur atom within the ring does not disturb the polyenic behavior of the spectra.

Going from DHTT to THST, the absorption band is red-shifted by 5300 cm^{-1}, which is close to that reported for the unsubstituted terthiophene–sexithiophene couple (5100 cm^{-1} in dioxane[41]). Table 1 shows that the absorption band of THST is sharper than that of DHTT, suggesting that THST is less twisted on average than DHTT, possibly due to a better electronic delocalization over the whole molecule. However the absorption band of THST ($\lambda_{\max}$ = 410 nm) is blue-shifted compared to the unsubstituted sexithiophene (ST) in dichloromethane ($\lambda_{\max}$ = 432 nm). It thus seems that, like DHTT, the THST molecule is less planar than ST due to steric effects caused by the presence of the alkyl chains. We recently confirmed these statements with semiempirical calculations.[65]

Recently Janssen *et al.* reported the absorption spectra of a series of well-defined α-oligothiophenes (T_n, n = 6, 7, 9, and 11) in solution, in a glassy matrix, and as films.[47] In fluid solution (dichloromethane, T = 295 K) or in dilute frozen solution (2-methyltetrahydrofuran (2MeTHF), T = 80 K), the absorption spectra of these oligomers do not show any vibrational fine structure like DHTT. But the absorption spectra of these oligomers in a 2MeTHF glass matrix are red-shifted by 0.22–0.28 eV with respect to the room temperature spectra. The authors interpreted these results in terms of a more planar molecular conformation which results in increased π conjugation in the glassy medium. This is a plausible explanation but it would be interesting to know the effect of the increase in the dielectric constant of 2MeTHF going from 296 to 80 K on the absorption spectra of these derivatives. The absorption spectra of the solution cast films at 80 K reveal three distinct vibronic peaks separated by 0.16–0.18 eV and an additional shoulder at higher energy.[47] The energy separation indicates strong coupling of the C═C stretching mode to the electronic transition moment. The 0,0 transition has been found to be less intense than the 0,1, 0,2, and 0,3 transitions. Each vibronic peak shifts linearly with $1/n$ (n = number of thiophene rings) to lower energy for the longer oligomers.

Like DHTT, the fluorescence spectrum of THST is structured ($\lambda_{\max}$ = 512, 546 nm) and is not affected by the alkyl side chains (ST: $\lambda_{\max}$ = 512, 548 nm in dichloromethane[44]). The structured fluorescence band of these derivatives is a consequence of a more planar conformation of the relaxed excited state. This conformation can be seen as a quinoidic like structure with double bonds between the rings. The Franck–Condon envelope of these fluorescence spectra clearly shows that DHTT is less planar than THST since its 0,0 vibronic band is lower in intensity than the 0,1 vibronic component. Moreover, going from DHTT to THST, the fluorescence bandwidth decreases, which suggests that the geometry of the hexamer is more planar.

The fluorescence spectra of several α-oligothiophenes in dichloromethane at 295 K and in a glassy matrix (2MeTHF at 80 K) have been reported.[47] Two to three vibronic emissions have been observed in dichloromethane solution at room temperature with an average energy spacing of 0.14–0.17 eV, similar to the separation of the vibronic absorptions of the cast films. The difference between the structureless absorption and the vibrationally resolved luminescence has been interpreted in terms of a more ordered excited-state geometry compared with the ground state geometry.[47] The photoluminescence spectra of the oligothiophenes in dilute 2MeTHF glassy solutions have been shown to exhibit an even more pronounced vibrational structure due to line narrowing at low temperatures. It was found however that virtually no shift in energy exists between the room and the low-temperature spectra. From these results, the authors have assumed that the excited-state geometry from which the emission occurs is similar at both temperatures. The fact that the fluorescence spectra at 80 and 295 K are energetically almost identical contrasts with the 0.22–0.28 eV energy shift of the absorption spectra at these temperatures. Apparently, ground-state and excited-state geometries are much more alike at 80 K than at 295 K. This result is consistent with a more planar ground-state geometry at low temperatures. The fact that the luminescence spectra at 80 K possess a more defined vibrational structure as compared to that of the absorption, has been explained by a conformational relaxation of the excited state to a more rigid molecular structure prior to the radiative decay.[47] It is difficult to imagine a conformational relaxation occurring at 80 K. It is more likely due to some ground state conformers (nonplanar and nonemissive) which are trapped at low temperatures.

The absorption and fluorescence spectra of PDHTT polymer are illustrated in Figure 3c. One can see that these bands are red-shifted (1900 cm^{-1}) compared to those of THST. This shows that, going from THST to PDHTT, the electronic conjugation is further increased. It is well-known that, for β-substituted oligothiophenes, the variation of the absorption maximum energy as a function of the inverse of the chain length n (i.e. the number of thiophene rings) is linear.[22,47] The extrapolation to an infinite chain gives $E_{max}(n \rightarrow \infty)$ which is close to that of the polymer. From this observation, one can expect that the absorption spectrum of the polymer should be much sharper than that of the hexamer. On the contrary, Table 1 shows that the absorption spectrum of PDHTT is broader than that of THST. It thus seems that the polymer, in its ground state, is not rigid and torsional motion between adjacent thiophene rings allows for various ground state conformers. This probably creates disorder in the macromolecule and increases the absorption bandwidth. Recently, the thermochromism observed in many polythiophenes has been explained in terms of the motion between adjacent thiophene rings.[2-7]

The absorption band of PDHTT (λ_{max} = 448 nm) is located at a higher wavelength than that observed for P3HT (λ_{max} = 440 nm in chloroform[8]). This indicates that the thiophene rings in PDHTT are more coplanar than those of P3HT. This is consistent with the fact that two-thirds of the thiophene rings are not alkylated and thus experience minimal steric repulsion. Wang *et al.*[14] synthesized poly(3′,4′-dibutyl-2,2′:5′,2″-terthiophene) (PDBTT) by direct chemical oxidative polymerization of DBTT. The absorption wavelength of the high molecular weight fraction is reported to be λ_{max} = 499 nm. Recently, semiempirical calculations have been performed on model compounds having various side chain lengths.[65] It was observed that the length of the side chains does not really affect the molecular conformation and the effective electronic conjugation of the molecules studied. Thus the larger absorption wavelength observed for PDBTT strongly suggests that the backbone length of that polymer is longer than the one of the PDHTT synthesized in our laboratory even though the reported number-average molecular weights (M_n) of both macromolecules are similar. This might be a consequence of the limited precision involved in the determination of M_n by size exclusion chromatography measurements.

By comparison to P3HT (λ_{max} = 571 nm in chloroform[15]), PDHTT shows a fluorescence band located at 589 nm. This red-shift of the emission parallels a similar shift of the absorption minimum, showing that, like in the ground state, the steric hindrance for PDHTT is lower than that in P3HT when both polymers are in their relaxed excited state.

3.1.3. DCABT and Its Polymer. The absorption and fluorescence spectra of DCABT are illustrated in Figure 4a and their characteristics are reported in Table 1. It is observed that the addition of the carbonyl chloride groups to the bithiophene chromophore (DDBT) provokes a large red-shift of the absorption and fluorescence bands. The same type of bathochromic shifts have been reported for thiophene oligomers having electron donor and/or acceptor end substituents.[44] These results may be interpreted in terms of the inductive effects of the substituents which may increase the conjugation length and provoke a better planarity of the bithiophene chromophore. Indeed, Figure 4a shows that the absorption and fluorescence spectra of DCABT are much sharper than that of DDBT and are structured. This strongly suggests that the presence of the carbonyl chloride groups reduces the torsional angle between the thiophene rings. Recent semiempirical calculations performed on DDBT and DCABT support this assumption.[65] But the fluorescence spectrum of DCABT is better resolved and much sharper than its absorption spectrum (see Figure 4a and Table 1). Even though the end substituents improved the planarity of the molecule, these results show that the ground state conformation of this compound is not fully planar. Indeed the DCABT molecule becomes more planar in its first relaxed singlet excited state. However, one can see that the Stokes shift observed between the absorption and fluorescence spectra of DCABT is relatively small (3700 cm^{-1}), confirming that conformational changes occurring upon the relaxation of the S_1 state are reduced compared to those of DDBT.

Incorporation of this substituted bithiophene molecule in the PEBT aromatic polyester produced a small blue-shift of the absorption and fluorescence bands as compared to the DCABT spectra. This might be due to the end chlorine atoms in DCABT. These results show, as expected, that there exists no electronic conjugation between bithiophene units in the macromolecule. Moreover, judging by the bandwidths of these spectra, the conformation of the substituted bithiophene is not much affected when inserted in the aromatic polyester.

3.1.4. DCATT and Its Polymer. The presence of carbonyl chloride groups at both ends of the molecule also provokes bathochromic shifts and a sharpening of the absorption and fluorescence spectra of the DCATT oligomer as compared to the spectra of DHTT (Figure 5a and Table 1). According to the above discussion, it can be assumed that DCATT in its ground and excited states is more planar than the unsubstituted derivative. This has been supported by semiempirical calculations, and these results will be published elsewhere.[65] Table 1 shows that, going from DCABT to DCATT, both absorption and fluorescence spectra are red-shifted. This behavior has been reported for end-substituted oligothiophenes with two to six thiophene rings.[44] These authors have shown that the end-substituent effect fades when the chain length of the molecule increases, suggesting that optimal red-shifts of such a substitution pattern have to be expected for relatively short oligothiophenes.

Figure 5b shows that the absorption and fluorescence spectra of the PETT polymer, which incorporate terthiophene segments, are blue-shifted compared to those of DCATT. It is quite possible that the absence of end-chlorine atoms in PETT is responsible for these absorption and fluorescence hypsochromic shifts. Judging by their respective absorption and fluorescence bandwidths (Table 1), one can see that the absence of end-chlorine atoms does not really affect the geometry of the polymer in both ground and first excited singlet states. As stated above for PEBT, these results show that no interaction between terthiophene units exists in the PETT polymer.

3.2. Molecular Photophysics. We have calculated and reported in Table 2 the fluorescence quantum yields (ϕ_F) obtained from integrated fluorescence intensities and the theoretical radiative fluorescence decay constants ($k_F^{(t)}$) measured from integrated absorption and fluorescence spectra using the Strickler and Berg rela-

Table 2. Photophysical Parameters of the Oligothiophenes and the Polythiophenes Studied in Chloroform at Room Temperature (298 K)

Molecule	ϕ_F	$\langle\tau_F\rangle^a$ (ns)	$10^{-8}k_F{}^b$ (s^{-1})	$10^{-8}k_F{}^{(t)\,c}$ (s^{-1})	$10^{-8}k_{nr}{}^d$ (s^{-1})
DDBT	0.017	0.071^e	–	2.4	140
PDDBT	0.15	0.55	2.7		15
DHTT	0.047	0.19	2.5	2.6	50
THST	0.25	0.80	3.1	4.1	9.3
PDHTT	0.31	0.65	4.8		11
DCABT	0.086	0.37	2.3	4.9	24
PEBT	0.10	0.32	3.1		28
DCATT	0.077	0.29	2.7	3.5	32
PETT	0.071	0.21	3.4		44

[a] $\langle\tau_F\rangle$ is the average fluorescence lifetime (see Table 3). [b] $k_F = \phi_F/\tau_F$ (radiative fluorescence decay rate constant). [c] $k_F{}^{(t)}$ is the theoretical radiative fluorescence decay rate constant obtained from the integrated absorption and fluorescence spectra via the Strickler and Berg relation.[70] [d] $k_{nr} = (1 - \phi_F)k_F/\phi_F$ (nonradiative fluorescence decay rate constant). [e] Value calculated from $\tau_F = \phi_F/k_F{}^{(t)}$.

tionship in chloroform.[70] The fluorescence quantum yield of THST has also been measured in tetrahydrofuran. It is observed that ϕ_F values in both solvents are similar, showing that, in chloroform, the fluorescence quantum yield of this type of molecule is little affected by the presence of chlorine atoms. The fluorescence lifetimes of the oligomers and polymers have been measured. In all cases a double-exponential fit appears to give acceptable statistical parameters ($\chi^2 < 1.3$ and DW $\cong 1.7 \pm 0.1$). Figure 6 shows, as an example, the fluorescence decay curves associated with the lamp profiles for PEBT in chloroform at room temperature and Table 3 summarizes the results obtained. For all oligomers and polymers studied in this paper, with the exception of the DCABT and PEBT derivatives, the slow component has always a low preexponential factor ($B_2 < 0.04$). This behavior has also been reported for unsubstituted oligothiophenes with two to six rings.[41] For the DCABT and PEBT derivatives, fluorescence decays show long lifetime components with larger pre-exponential factors. These two lifetimes might indicate a distribution of two major conformers for these thiophene derivatives in their ground states. The importance of each conformer would be measured by their respective pre-exponential factors (B_i) and their fractional contributions to the total fluorescence intensities would be determined by f_i (see Table 3). For instance, the species responsible for the slow component of the PEBT fluorescence decay is present in a proportion of 7% but contributes 23% of the total fluorescence intensity of this polyester. The average fluorescence lifetime $\langle\tau_F\rangle$ of each thiophene derivative has been compiled and is reported in Table 2. From ϕ_F and $\langle\tau_F\rangle$ values, the average radiative fluorescence decay rate constant (k_F) and the nonradiative fluorescence decay rate constant (k_{nr}) have been determined.

3.2.1. DDBT and Its Polymer. The fluorescence emission of DDBT is weak ($\phi_F = 0.017$). The fluorescence lifetime together with the nonradiative fluorescence decay rate constant are calculated using the assumption that $k_F{}^{(t)} = k_F$. This assumption was found to be very good for unsubstituted oligothiophenes.[43] Conformational analysis (by AM1 and ZINDO/S[28,65]) performed on BT and DDBT have suggested that the molecules are not rigid in their ground electronic states and that the potential surfaces may allow for many conformers inside the kT energy barrier at room temperature. Thus, one of the deactivation pathways of the molecules in their relaxed singlet states may involve the rotation of the thiophene rings (k_{ic}). However, it is also established that the main deactivation pathway of the α-oligothiophenes S_1 states involves an intersystem crossing process (k_{isc}).[42,43] The reported ϕ_F value of BT in dioxane and dichloromethane is 0.018.[43,44] It thus seems that the alkyl chains at the 4,4′-positions do not affect the mobility of the thiophene rings much in the relaxed excited S_1 state as well as the singlet–triplet energy gap (S_1–T) between the S_1 state and the triplet state closest to it. This singlet–triplet energy gap is indeed responsible in part (Franck–Condon factors) for the intersystem crossing probability. Recent semiempirical calculations performed on BT and DDBT have shown that the ground state potential energy surfaces as well as S_1–T energy gaps are very similar for these two derivatives.[28,65] What is still unknown is the effect of a particular geometry on the singlet–triplet energy gap. In other words, what is the interdependence of k_{ic} and k_{isc} on a particular singlet excited state conformation. We are actually working on this problem.

Table 2 shows that the k_{nr} value of the PDDBT polymer is smaller by about 10 times compared to that of DDBT. Recently Becker *et al.* have reported the internal conversion (k_{ic}) and the intersystem crossing rate constants (k_{isc}) of α-oligothiophenes. It has been observed that k_{isc} decreases much more rapidly than k_{ic} as the number of thiophene rings increases.[43] According to this work, the reduction of the intersystem crossing probability should be the main factor for the high ϕ_F value observed for PDDBT. However, the fact that k_{ic} decreases as the length of the conjugated system increases strongly suggests that the motion of the thiophene rings is also an effective radiationless decay channel for the deactivation of the relaxed S_1 state.

3.2.2. DHTT and Its Dimer and Polymer. Going from DHTT to THST, the nonradiative decay rate constant is much reduced (see Table 2). As stated above, the intersystem crossing probability should be mainly responsible for this behavior. But the motion of adjacent thiophene rings should be reduced in the THST derivative (smaller value of k_{ic}) and thus this process should also contribute in the k_{nr} decrease. Table 2 shows that, going from DHTT to THST, the radiative decay rate constant (k_F) increases. This supports the assumption stated in the previous section that the planarity of the molecule is improved when the chain length of the molecular frame increases.

Knowing that the fluorescence quantum yield of α-oligothiophenes becomes nearly constant at $n = 5-7$,[40,43] it is thus not surprising to observe that ϕ_F values of THST and PDHTT are similar. Linton *et al.* have reported the fluorescence quantum yield (0.06) and lifetime (600 ps) of P3HT in chloroform.[15] From these data, the values of $k_F(=1 \times 10^8\ \text{s}^{-1})$ and $k_{nr}(= 1.6 \times 10^9\ \text{s}^{-1})$ can be obtained. These results suggest, as stated in the previous section, that the steric interactions are less important in PDHTT than in P3HT. Indeed, the k_F of PDHTT being higher than that of P3HT and the fact that k_{nr}(PDHTT) < k_{nr}(P3HT) indicate that PDHTT is a more planar and rigid molecule. However, it is important to mention here that the effect of these conformational changes on the intersystem crossing probability is not known.

Recently, Xu *et al.* have measured the fluorescence quantum yields of P3HT's possessing increasing head-to-head content.[8] It was found that fluorescence quantum yields from polymer solutions in chloroform in-

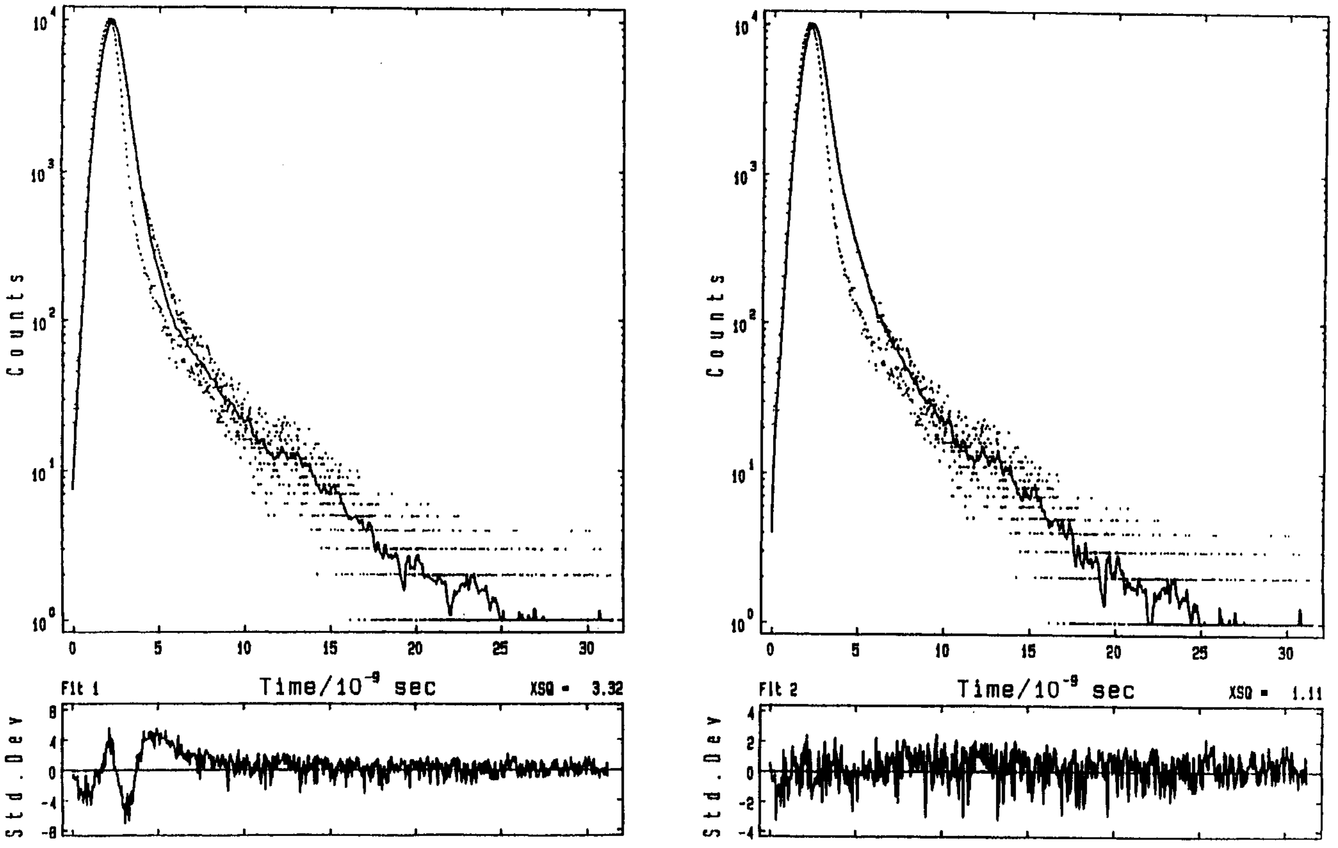

Figure 6. Fluorescence decay curves associated with the lamp profiles for PEBT polyester in chloroform at room temperature (298 K). The curves from left to right show the single- and double-exponential fits, residuals, and χ^2.

Table 3. Fluorescence Decay Parameters at Room Temperature (298 K) of the Thiophene Oligomers and Polythiophenes in Chloroform at Room Temperature (298 K)

Molecule	τ_1[a] (ns)	τ_2[a] (ns)	B_1[b]	B_2[b]	$\langle\tau_F\rangle$[c] (ns)	f_1[d]	f_2[d]
DDBT							
PDDBT	0.46	2.85	0.99	0.01	0.55	0.96	0.04
DHTT	0.17	2.34	0.999	0.001	0.19	0.99	0.01
THST	0.78	3.84	0.999	0.001	0.8	0.99	0.01
PDHTT	0.59	1.33	0.96	0.04	0.65	0.92	0.08
DCABT	0.24	0.97	0.95	0.05	0.37	0.83	0.17
PEBT	0.19	0.76	0.93	0.07	0.32	0.77	0.23
DCATT	0.18	1.8	0.99	0.01	0.29	0.93	0.07
PETT	0.16	1.81	0.998	0.002	0.21	0.97	0.03

[a] Obtained from the reconvolution fit: $A + B_1 (\exp(-t/\tau_1) + B_2 (\exp(-t/\tau_2)$. [b] Normalized pre-exponential factor. [c] Average lifetime calculated from the expression: $\langle\tau_F\rangle = \sum_i B_i\tau_i^2/\sum_i B_i\tau_i$.[61] [d] Fractional contribution of the total fluorescence intensity defined as $f_i(\lambda) = B_i\tau_i/\sum_i B_i\tau_i$.[61]

crease with decreasing head-to-head content of the polymer. The authors have interpreted their results in terms of a larger conjugation length, a higher rigidity, and, consequently, a decrease of the nonradiative torsional mode when the steric hindrance is reduced. In contrast, they observed that quantum yields of thin films of the polymers are largest for the less planar configurations. Low quantum yields associated with planar conjugated structures have been explained by classical concentration quenching effects arising from nonemissive excimer complexes (intermolecular decay channels).

3.2.3. DCABT and Its Polymer. Table 2 shows that the fluorescence quantum yield of DCABT is enhanced compared to that of DDBT. The decrease of the nonradiative decay constant is mainly responsible for that behavior, which means that the radiationless deactivation of the DCABT S_1 state is less efficient than that of DDBT. This supports the assumption stated above that the electronic delocalization throughout the molecule is favored by the presence of carbonyl chloride groups at both ends of the molecule and thus reduces the mobility of the thiophene rings. However, the intersystem crossing mechanism may also play a role in the deactivation process. When this dimer is incorporated in the PEBT polyester, the quantum yields and lifetimes show little changes. This confirms, as stated in the previous section, that each bithiophene unit is well isolated in the polymeric chain and that the mobility of the adjacent thiophene rings in PEBT is very similar to that of DCABT.

3.2.4. DCATT and its Polymer. As described above for DCABT, the presence of carbonyl chloride substituents at both ends of DCATT also reduce, but to a lesser extent, the radiationless deactivation of the excited state (see Table 2). The terthiophene units incorporated in the PETT polyester show almost the same photophysical properties as the DCATT trimer. This confirms the assumption discussed above that the motion of adjacent terthiophene units is similar than the one involved in the DCATT molecule. It is worth noting that polyesters derived from thiophenes (e.g. PETT) are much more efficient blue-luminescent materials than twisted poly(3,4-dialkylthiophenes).[71] For instance, poly(3,4-dihexylthiophene) shows a fluorescence quantum yield of only 0.014.[72]

Fluorescence quantum yields and lifetimes have been reported for a series of oligothiophenes (from bithiophene to sexithiophene) substituted at the ends of the chain by various electron donor and/or acceptor groups or atoms (methoxy, nitro, or bromine).[44] It is observed that only the nitro-substituted group induces a significant increase of ϕ_F and τ_F values of the excited state. This positive effect has been found to be only limited to the short oligomeric chains like terthiophenes, for which an intramolecular charge transfer excited state has been evidenced by solvatochromic effects. The fluorescence arising from these charge transfer states are structureless and show very large Stokes shift ($\cong$7000 cm^{-1}). From these spectral characteristics and the fact that the ϕ_F values of DCABT and DCATT are much smaller than the nitro-substituted terthiophenes, it can be assumed that the relaxed S_1 state of these carbonyl chloride derivatives does not involve an important intramolecular charge transfer.

4. Concluding Remarks

Absorption and fluorescence spectroscopy as well as molecular photophysics have been used to obtain information about relative conformations of several oligomers and polymers involving thiophene rings. It is shown in this paper that an increase of the chain length of the oligomers brings about a higher conjugation length in the electronic ground state. This charge delocalization contributes to reduce the torsion between thiophene rings. As a consequence, a more planar geometry on average is favored. This work also shows that, for all the thiophene derivatives investigated, the first excited singlet states of the main chromophore become more planar upon relaxation. These results strongly suggest that the rotational energy barrier of the adjacent thiophene rings is smaller in the ground state compared to that in the first excited singlet state in all these oligomers.

The presence of carbonyl chloride substituents at both ends of the bithiophene and terthiophene molecules improves the planarity of the molecules in their ground and excited states. The luminescence properties of the polyesters are close to those of their respective α,α′-disubstituted oligomers, showing that the molecular conformations of such substituted bithiophene and terthiophene are practically unaffected when inserted in aromatic polyesters. The incorporation of these chromophores into polymeric structure would allow the preparation of efficient blue-emitting materials with good mechanical properties. The solid-state properties of these polyesters and related materials are currently under investigation.

Acknowledgment. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds FCAR (Quebec) for their financial support. M.L. would like also to acknowledge the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of his research.

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MA950592J