Photophysical Studies of α,ω-Dicyano-oligothiophenes NC(C₄H₂S)ₖCN (ₖ = 1–6)

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Received: September 26, 2005; In Final Form: January 11, 2006

The photophysics of six oligothiophenes end-capped with cyano groups (CNₖCN) was investigated in solution at room and low temperature. The study comprises singlet—singlet and triplet—triplet absorption and emission spectra together with lifetimes and quantum yields for all the radiative and nonradiative processes. From the lifetimes and quantum yields, it was possible to extract the rate constants for all the processes. Singlet oxygen yields were also determined, revealing an efficient sensitization (Sₐ ≈ 1) of its formation by the triplet state of the CNₖCN. The introduction of the cyano groups is found to decrease the energetic separation between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, leading to a red shift of the absorption and the emission when compared with the unsubstituted counterparts, the α-oligothiophenes. Phosphorescence is only observed for the first member of the series, CNα1.

Introduction

Luminescent organic conjugated polymers are finding various applications in molecular electronics because of their attractive physical properties and ease of processability. Particular emphasis for this technologically important class of materials has been placed on their use in light-emitting diode (LED) devices.

Organic polymer structures are strongly affected by factors such as synthetic procedures, film morphology, and poor and selective solubilization. These have clear influence on their structural properties and thus affect their emission behavior. In parallel with these studies, conjugated oligomeric systems have been used to obtain a deeper understanding of the spectroscopic and photophysical behavior of conjugated polymers and of mechanisms of processes such as energy transfer. Thus, practical limitations stemming from the complexity of polymeric systems are frequently overcome by studies of oligomeric analogues. It has been demonstrated, for example, that polymeric spectroscopic properties become well established with oligomers having their number of monomer units greater than or equal to 5 in polythiophenes, 15 with poly-p-phenylenevinylelenes, 10 and 12 in polyfluorenes. The oligomer approach is, therefore, a useful guide to study and understand polymeric properties through the investigation of the appropriate well-defined smaller analogues. Particular emphasis has been focused on the number of monomer units involved in the delocalized π-electron cloud of the polymer. This gains particular importance when studying defects resulting from chemical imperfections, such as conjugation breaks, degradation resulting from oxidation of the backbone chain, and contamination resulting from the synthetic procedures. These are generally among the most important inhibiting factors involved in the search for perfect behavior for a light-emitting diode.

The polythiophenes are probably one of the most versatile classes of π-conjugated systems included in the broad area of organic conjugated polymers. This is partially due to their unique properties, as demonstrated by their chemical stability, and also to the ease of tuning their electronic and photophysical behavior over a wide range by modifying their chemical structure. Various applications of the oligo- and polythiophenes are found in modern materials science, such as their use in LEDs and electrochromic and photovoltaic devices.

Polythiophenes are also one of the most prominent conjugated polymer families whose spectroscopic and photophysical behaviors have been studied by the so-called oligomer approach, and the extrapolation of the properties of the oligomers to polythiophene is one of the most interesting and widely pursued goals in this area. In part, this arises because of difficulties in characterizing solid polythiophene, since the unsubstituted polymer or oligomers with n ≥ 6 are very poorly soluble. Recent studies on substituted polythiophenes have partially resolved this solubility problem but have introduced complications that may change the number of effective conjugation units involved in the polymer. It has recently been shown that it is possible to establish an exact conjugation length for these polymers from comparison of the optical and photophysical properties of oligomers and polymers, and it was proposed that fundamental oligomer quantities, such as the molar extinction coefficients, can be used to further elucidate the photophysical parameters for the polymers. Following this line of thought, it has been recently shown that increased π-electron delocalization in oligothiophenes can be achieved by replacing a thiophene unit by naphthalene.

Conjugated polymers containing cyano groups have valuable properties for molecular electronics, including increased electroluminescence and high electron affinity. Recently dicyanomethylene oligothiophenes have been synthesized and re-
vealed high π delocalization (through an extensive quinoidal structure), good solubility behavior, and strong electronic absorption in the visible and near-IR regions with obvious potentialities as optoelectronic materials. In the present work we extend the delocalization degree problem to a family of oligothiophenes where the two terminal hydrogen atoms have been substituted by cyano groups to give the α,ω-dicyano-oligothiophenes.

Experimental Section

The α,ω-dicyano-oligothiophenes were a kind gift of Professor R. T. Oakley, University of Waterloo, Canada, and their synthesis has been described elsewhere.

All of the solvents were of spectroscopic or equivalent grade and were used without further treatment, except for ethanol (dried and purified by distillation over CaO); benzophenone was obtained from Aldrich Chemical Co. and was used without further purification.

For the absorption and emission experiments in benzene, the concentrations of the solutions ranged from $1 \times 10^{-5}$ to $1 \times 10^{-6}$ M. These were deoxygenated by bubbling with Ar.

Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Horiba-Jobin-Ivon Spek Fluorog 3-22 spectrometers, respectively. Phosphorescence measurements were made in glasses at 77 K and used the same Spek Fluorog 3-22 spectrometer, equipped with a 1934 D phosphorimeter. The phosphorescence quantum yield was determined using benzophenone ($\Phi_{ph} = 0.84$) as a standard. All of the fluorescence and phosphorescence spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields were measured using as standards bithiophene ($\Phi_f = 0.026$ in benzene), terthiophene ($\Phi_f = 0.07$ in benzene), and quaterthiophene ($\Phi_f = 0.18$ in benzene).

The molar extinction coefficients ($\epsilon$) were obtained from absorption spectral measurements using six solutions of different concentrations and the slope of plots of the absorption versus concentration (correlation coefficients $\geq 0.999$).

The experimental setup used to obtain triplet spectra and triplet yields consisted of an Applied Photophysics LKS60 laser flash photolysis apparatus pumped by a Nd:YAG laser (Spectra Physics Quanta-Ray GCR-130) and a Hewlett-Packard Infinium oscilloscope (1 MS/s). The detection system was at right angles to the excitation beam, and a pulsed 150 W Xe lamp was used to analyze the transient absorption. The signal obtained was fed into the HP digital analyzer and transferred to an IBM RISC computer, where using the appropriate software (Applied Photophysics) the ODs at different wavelengths and different delays after flash were collected. The transient spectra were obtained by monitoring the optical density change at intervals of 5–10 nm over the 250–700 nm range and averaging at least 10 decays at each wavelength. The detection of the transient spectra in this range was made with Hamamatsu IP28 and R928 photomultipliers. First-order kinetics were observed in all cases for the decay of the lowest triplet state. The samples were irradiated either with the third-harmonic pulse (355 nm, 8 ns full width at half-maximum (fwhm)) or with the unfocused fourth-harmonic pulse (266 nm, 8 ns fwhm) of the laser. Special care was taken in determining triplet yields to have optically matched dilute solutions (absorbance $\approx 0.2$ in a 10 mm square cell) and low laser energy ($\leq 2$ mJ) to avoid multiphoton and T–T annihilation effects. In all cases the signal was assigned to a triplet state because:

(i) it was quenched by oxygen,
(ii) it decayed by first-order kinetics, and
(iii) other possible transients, such as radical ions, are generally not produced on photolysis in the nonpolar solvent benzene.

The triplet molar absorption coefficients obtained in benzene were determined by the singlet depletion technique, according to the well-known relationship

$$\epsilon_T = \frac{\epsilon_S \times \Delta OD_T}{\Delta OD_S}$$

where both $\Delta OD_S$ and $\Delta OD_T$ are obtained from the triplet–singlet difference transient absorption spectra. The $\phi_T$ ($\phi_{psc}$) values were obtained by comparing the $\Delta OD$ at 525 nm of a benzene solution of benzophenone (the standard) and of the compound (optically matched at the laser wavelength) using the equation

$$\phi_T = \frac{\epsilon_T}{\epsilon_T^{\text{benzophenone}}} \times \frac{\Delta OD_{\text{max}}^{\text{benzophenone}}}{\Delta OD_{\text{max}}} \times \phi_T^{\text{benzophenone}}$$

Fluorescence decays were measured using a home-built time-correlated single-photon counting apparatus with a IBH 5000 coaxial flashlamp filled with N$_2$ or D$_2$ or mixtures of these as the excitation source, Jobin-Ivon excitation and emission monochromators, a Philips XP2020Q photomultiplier, and Canberra instruments time-to-amplitude converter and multichannel analyzer. Alternate measurements (1000 counts per cycle) of the pulse profile at the excitation wavelength and the sample emission were performed until 5 $\times 10^6$ counts at the maximum were reached. In some cases the excitation was performed with IBH NanoLEDs (281 nm, 339 nm, 373 nm). The fluorescence decays were analyzed using the modulating functions method of Striker with automatic correction for the photomultiplier "wavelength shift." The fluorescence decays of CNα1 and CNα2 were obtained with picosecond resolution in an apparatus described elsewhere.

Room-temperature singlet oxygen phosphorescence was detected at 1270 nm using a Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (Products for Research model PC176TSC–05), following laser excitation of aerated solutions at 355 nm (OD@355 nm = 0.20), with an adapted Applied Photophysics flash kinetic spectrometer. The modification of the spectrometer involved the interpolation of a Scotch RG665 filter. A 600-line diffraction grating was used instead of the standard spectrometer one to extend spectral response to the infrared. The filter employed is essential to eliminate from the infrared signal all of the first harmonic contributions from the sensitizer emission in the 500–800 nm region. In addition, singlet oxygen yields were also measured at the Fast Radical Research Facilities (Daresbury laboratories), by direct measurement of the phosphorescence at 1270 nm followed the irradiation of an aerated solution of the cyano-oligothiophenes in benzene with excitation at 355 nm from a Nd:YAG laser with a setup described elsewhere. 1H-Phenalene-1-one (perinaphthenone) in benzene ($\phi_A = 0.93$) was used as the standard.

Results and Discussion

The structures of the α,ω-dicyano-oligothiophenes studied are given in Chart 1. These have $n = 1–6$, and the terminal hydrogens are replaced by cyano (C≡N) groups. The advantages...
of these end-capped oligomers are the facts that blocking the terminal positions minimizes further reactions, such as oxidation and polymerization, and also increases the spatial order when the compounds are in the solid state. The cyano group is an electronegative, noncrowded substituent that allows intermolecular contacts to be established in the solid state, thus influencing the organization of the oligothiophene chains through intermolecular CN⋯H interactions. In addition, in devices the cyano group is likely to improve charge transport. However, the present study is solely devoted to solution studies and in particular the effect of introducing the CN groups on the spectroscopic and photophysical properties of the thiophene oligomers.

Absorption and Fluorescence. The absorption spectra of the α,ω-dicyano-oligothiophenes (CNαn) are shown in Figure 1. As with their unsubstituted substituted analogues, the αn’s, the absorption spectra are devoid of vibrational structure. Comparison between the αn and its analogue CNαn, i.e., with identical n, absorption maxima reveals that, in general, substitution with cyano groups red-shifts the absorption maxima of these from values that range between 15 and 33 nm (Table 1 and ref 1), except for the comparison between the shortest members of the two series (α1 and CNα1) where this value is larger (47 nm). However, as will be discussed below, a good correlation was found between CNαn and α(n + 1) absorption maxima.

The observed behavior can be attributed to the strong electronegativity of the C≡N group that introduces a bathochromic shift in the lowest-lying π,π* transitions of the CNαn, when compared to the unsubstituted oligothiophenes. With the compounds in this study, molecular orbital (MO) calculations (modified neglect of differential overlap (MNDO) and extended Hückel band structure calculations) indicate that the C≡N group causes a perturbation of the excited states and that the magnitude of this effect decreases with the increment of the π-conjugation and in particular the number of thiophene rings involved in the conjugation. The marked red shift observed between the lower thiophenes CNα1 and CNα2 and the analogous α1 and α2 is particularly relevant. This shift indicates the existence of a strong π-electron delocalization, which is a function of the CN group, possibly suggesting partial extension of the conjugation onto these terminal groups.

From Figure 1 it is also possible to see the linear dependence of the extinction coefficients on n, as has previously been observed for αn’s. In the present case, CNα6 had to be excluded since it was impossible to obtain a reliable value for the extinction coefficient due to its low solubility and the different solvent used for its measurement. The ε value for CNα6 was therefore obtained by extrapolation of data from the inset plot in Figure 1 and is given in Table 1.

The emission spectra for the CNαn’s are presented in Figure 2. In contrast to the absorption spectra, the fluorescence spectra present vibrational structure, with the sole exception of CNα1. As with the absorption maxima, the emission spectra also red-shift with increasing number of thiophene units in the CNαn. However, with the associated fluorescence parameters φ such as and τf, different patterns are observed. The fluorescence lifetime was shown to be a single exponential for all the compounds, with a progressive increase of this value from 9.8 ps for CNα1 to 1 ns for CNα6; see Figure 3 for examples of decays associated with two of the compounds studied. On first observation, the same does not appear to be true for the φF value, which appears to increase up to CNα5 and then decrease for CNα6 (Table 2). However, a different solvent (dimethylsulfoxide (DMSO)) was used for the last compound due to its low solubility in benzene, and consequently the φF value for CNα6 should be considered as a lower limit (based on the trend obtained from the other CNαn’s).

Triplet State Properties. After laser flash photolysis at 266 or 355 nm of degassed solutions of the CNαn’s in benzene,
From Figure 4A, it can be seen that the incremental increase of thiophene units in the CNαn leads to a progressive red shift of the triplet—triplet transient (Tα ← Tβ) absorption maxima.

From Tables 1 and 2, a comparison can be made between the spectroscopic and the photophysical behavior of the CNαn’s and the αn’s. It is clear (Table 1) that the substitution of the terminal hydrogens with cyano groups leads to the CNαn possessing the spectroscopic behavior of the comparable αn with one more thiophene ring (αn + 1). This seems to be true for both the spectroscopic properties and for some photophysical parameters. For example, although the identical numerical values for φβ may be a coincidence, the values for CNα4 and α5 are very similar, and this relationship between the behavior of the two families holds for all the other spectroscopic data with the possible exception of the singlet—singlet molar extinction coefficients (Table 1). However, this analogy cannot be extended to the photophysical parameters φα and φIC (obtained from φIC = 1 − (φα + φT)) or to the corresponding rate constants, and it is seen that in this case the CNαn’s exhibit similar behavior to the corresponding αn’s. Moreover it is also interesting to note that thiophene polymers with alkyl substitution at the thiophene backbone skeleton,8,40 oligomers with oxygen functionalization of the sulfur atom,41 or with ethynylene spacers between thiophene rings42 lead to a clear increase of the nonradiative S1 ← S0 decay processes. However, this does not happen with the unsubstituted oligothiophenes (αn’s1,21) or those with substitution at the end positions (current case and with naphthalene7) or substitution of the sulfur atoms by oxygen,43 or nitrogen (and oxygen),44 where very low values for φIC were obtained. This observation might suggest that conformational deviation from planarity of the first singlet excited-state opens an efficient radiationless deactivation route to the ground state.

Rate Constants and Quantum Yields. From the quantum yields for internal conversion, intersystem crossing, and fluorescence, it is seen that only φβ increases on going from CNα1 to CNα5, while φT clearly show a tendency to decrease with n (Figure 5 and Table 2). This decrease in the intersystem quantum yield with increasing n shows up most clearly with the S1 ← T1 intersystem crossing rate constant, kISC, which decreases from CNα1 to CNα3, reaching a constant value at CNα4 and CNα5 (Figure 5). With respect to the kF values, with

Figure 3. Fluorescence decays for two of the studied compounds: (A) CNα2 and (B) CNα6. The presented fits are adjusted to monoeponential decay laws. For a better judgment of the quality of the fits, autocorrelation functions (ACs), weighted residuals (WRs), and chi-square values (χ²) are also presented as insets. For each compound, the dashed line in the decay represents the pulse instrumental response.

depletion of the ground-state absorption between 250 and 450 nm and formation of a new band in the 350–700 nm region was observed in all cases (Figure 4A and Table 1). The transient absorption decayed with an identical lifetime (see τ values in Table 2) to recovery of ground-state absorption (Figure 4B).

Figure 4. (A) Transient triplet—triplet absorption spectra for the CNαn’s in benzene at T = 293 K. The exception is for CNα1, which was obtained in ethanol. (B) Transient decays for CNα5 obtained at 430 nm (recovery of ground-state absorption) and 600 nm (transient maximum). Also shown are the residuals for the first-order decay fits.
the possible exception of the two shortest CNntω’s, these seem to present a constant value around 0.4–0.5 ns\(^{-1}\) (Figure 5). The behavior presented by the CNntω’s is in agreement to what was observed for the analogous αω’s\(^1\) and with substituted naphthalene oligothiophenes\(^1\) where it was possible to observe that the sum of the \(\phi_T\) and \(\phi_f\) values was practically equal to 1, indicating no significant deactivation by internal conversion.

It is worth noting that from Table 2 and Figure 5 it can be seen that \(k_F\) and \(k_{ISC}\) values attain a near constant value for \(n\)’s 1 and with substituted naphthalene oligothiophenes\(^1\) since only three-center terms do not vanish for planar excited-state \(1^\pi\)–\(1^\pi\) orbital coupling matrix elements between \(\pi,\pi^*\) states and this singlet state will be very small due to changes in \(\phi_{ISC}\) orbit coupling matrix elements resulting from a decrease in the magnitude of the room-temperature absorption spectra. The CNnt1 presents a moderately high phosphorescence yield (\(\phi_{Ph}\ = 0.14\)), particularly when compared with thiophene where the signal (and therefore the phosphorescence quantum yield) was found to be weak\(^1\). Moreover, with CNnt1, the observed phosphorescence lifetime was 129 ms, which suggests that the lowest triplet \(T_1\) state is of \(\pi,\pi^*\) origin\(^{45}\). Rentsch et al. have observed phosphorescence for α2 (unequivocally established by matching the fluorescence and phosphorescence excitation spectra) with maxima at 600 nm and a lifetime of 800 ± 200 μs\(^{46}\). Recently Wasserberg et al.\(^{47}\) have reported the detection of phosphorescence (with laser excitation and highly sensitive charge coupled device (CCD) camera-gated detection technique) of a series of small oligothiophenes (with \(n = 1–3\)), and with thiophene they located the triplet of this oligomer at 1.82 eV (~284 nm), which is in reasonable accordance with the value stated in that work, it is clearly on the order of milliseconds\(^{47}\). Nonetheless it is quite obvious that with these oligomers phosphorescence is weak. The lack of (or very weak) phosphorescence with the other oligomers enables us to draw several considerations on the nature and processes leading to the triplet excited-state formation and decay. If the perturbing singlet is a pure \(\pi,\pi^*\) state, which is likely to be the case (see \(k_F\) values in Table 2), then the spin–orbit coupling matrix elements between the \(\pi,\pi^*\) triplet state and this singlet state will be very small since only three-center terms do not vanish for planar excited molecules\(^5\), such as are expected here. Therefore, this type of mixing cannot explain the high values for \(\phi_f\) and \(k_{ISC}\) of the CNntω.

For the oligothiophenes, the decrease in \(k_{ISC}\) with \(n\) was interpreted as originating from a coupling mediated by charge-transfer (CT) mixing involving matrix elements of the type \(\lambda^{(1)\Psi_{\text{CT}}|H_{\text{SO}}|3\Psi_f}\).

In the present case, \(k_{ISC}\) could in part be related with the decrease in the magnitude of the matrix elements described above resulting from a decreased charge-transfer mixing of \(4\Psi_{\text{CT}}\) and \(3\Psi_f\) as the number of rings increases\(^1\). However, the significant decrease on going from CNnt1 to CNnt5 (Table 2) could also be explained by the fact

### Table 2: Photophysical Properties for the CNntω’s and the Analogous αω’s (from Ref 1) in Benzene, \(T = 293\) K

| compound | \(\phi_T\) | \(\tau_F\) (ns) | \(\phi_f\) | \(\phi_A\) | \(\phi_{IC}\) | \(\tau_T\) (μs) | \(k_{NR}\) (ns\(^{-1}\)) | \(k_F\) (ns\(^{-1}\)) | \(k_{ISC}\) (ns\(^{-1}\)) | \(k_{ISC}\) (ns\(^{-1}\)) |
|---------|---------|-------------|---------|--------|---------|-------------|--------------|--------------|--------------|--------------|--------------|
| CNnt1   | 0.010   | 0.0098     | 0.99\(^*\) | 0.99   | 0.01     | 0.01        | 21.2         | 101.0        | 1.02         | 0             | 101.0        |
| CNnt2   | 0.06    | 0.099      | 0.97    | 0.93   | 0~0. 35  | 0.35        | 10.7         | 9.49         | 0.61         | 0~0. 35      | 9.49         |
| CNnt3   | 0.12    | 0.29       | 0.79    | 0.81   | 0.09    | 13.2        | 3.03         | 0.41         | 0.31         | 2.72         |
| CNnt4   | 0.30    | 0.61       | 0.70    | 0.76   | 0.06    | 5.2         | 1.15         | 0.49         | 0             | 1.15         |
| CNnt5   | 0.42    | 0.78       | 0.52    | 0.54   | 0.07    | 24.0        | 0.81         | 0.41         | 0.31         | 0.098        | 0.72         |
| CNnt6   | 0.35\(^*\) | 1.0\(^*\)   | 0.09    | 0.06   | 0.35\(^*\) | 0.65\(^*\)   | 0.35\(^*\)   | 0.65\(^*\)   | 0.35\(^*\)   | 0.65\(^*\)   |

\(^a\) Value in ethanol. \(^b\) Values in DMSO. \(^c\) \(\phi_{IC} = 1 - (\phi_T + \phi_f)\).
that the cyano substitution also decreases the contribution of the CT-type singlet state, therefore inducing a smaller overlap of the electron-donor electron-acceptor molecular orbitals. The CT-type singlet state would obviously result from some contribution of $\sigma \rightarrow \pi^*$ transitions. A similar effect was observed with oligothiophenes substituted in one terminal position by a naphthalene group. In the present case the internal conversion rate constant is also negligible, as was previously observed for $\alpha$'s and naphthalene oligothiophenes, and the effectively zero value of $\phi_R$ could be attributed to structural differences between the ground and the excited state. Since the core structure (thiophenes linked in $\alpha$ structure) is still present, the strong quinoidal-like character of $S_1$ would give rise to a planar structure, whereas with the ground state conformers with different torsional angles could exist and interconversion between them would be possible. The low internal conversion rate is then due to a weak coupling between the modes of the two states. Complementary interpretation of the high values for $\phi_T$ and $k_{ISC}$ values presented by the short $\alpha_2$ and $\alpha_3$ oligothiophenes were given by Rentsch et al. and Rossi et al., which were based on the high-energy splitting existing between $S_1$ and $T_1$ and suggest participation of energetically higher triplet states and of $\alpha$ sulfur orbitals in the triplet states reached by nonactivated and thermally activated intersystem crossing.

**Singlet Oxygen Yields.** From Table 2 it can be seen that the singlet oxygen yields ($\phi_\lambda$) are effectively identical to the triplet intersystem crossing yields, indicating a very efficient triplet energy transfer from the CN triplet states to the oxygen triplet to produce $O_2^*$, i.e., $S_3 \approx 1$. This is important since the first $\phi_\lambda$ values establish an upper limit for the $\phi_T$ values (which are always determined with a certain degree of error); second the oligomers of the thiophene family (particularly the terthiophene) have been actively investigated as promising photosensitizers with antiviral activity, and the knowledge of this parameter is essential to discuss the origin of its action. Moreover literature data on $\alpha_3$ substituted with one C=N unit gives a $\phi_\lambda$ value of 0.86 (in deuterated chloroform solution), identical in that report to the value obtained for $\alpha_3$ (also in consonance with our results where comparison between CN$\alpha_3$ with its unsubstituted counterpart $\alpha_3$ reveals basically no difference) and of others in benzene, which is in excellent agreement with our value for the unsubstituted CN$\alpha_3$ ($\phi_\lambda = 0.81$; see Table 2), thus showing once more that the introduction of these groups has little influence on the photophysical properties of the compounds.

**Conclusions.**

A complete spectroscopic and photophysical study of a new family of oligothiophene derivatives was made. The introduction of two strongly electron-withdrawing cyano (C=N) groups was found to spread the $\pi$-electron cloud from the oligothiophene skeleton out to the CN group. As a consequence, the difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital involved in the electronic transition was found to decrease, leading to a general red shift of the absorption and emission bands of the CN$\alpha$'s relative to their unsubstituted counterparts, the $\alpha$'s. The spectroscopic characteristics of these new compounds were found to be similar to the corresponding oligothiophenes having one more thiophene ring. This is likely to be due to the two extra $\pi$-bonds present in the terminal CN groups. The increase in the $\pi$-electron delocalization of these moderately soluble compounds can be considered as one step forward in the consideration of the oligomer approach where well-defined oligomers can correctly reproduce the polymer behavior. As with the behavior presented by their unsubstituted oligothiophene counterparts, the internal conversion deactivation is negligible. A comparison with other oligomers and polymers was made, suggesting that the internal conversion ($S_1 \rightarrow S_0$) channel only becomes meaningful when substitution affects the geometry of the excited singlet state (deviation from the planar quinoidal-like structure) or when the sulfur atom electron density is altered; it is however nonaffected when substitution is at the oligomer terminal positions, leading to $\phi_{IC} \approx 0$. Singlet oxygen yields suggest energy transfer to be highly efficient from the CN$\alpha$'s to the ground-state oxygen.

**Acknowledgment.** We are grateful to FCT for financial support through POCI (Projects POCI/QUI/55672/2004 and POCI/QUI/58291/2004) and FEDER funds. J.P. acknowledges the FCT for a Ph.D. grant (SFRH/BD/18876/2004).

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