

Photophysical Studies of α,ω -Dicyano-oligothiophenes $\text{NC}(\text{C}_4\text{H}_2\text{S})_n\text{CN}$ ($n = 1-6$)J. Pina,[†] H. D. Burrows,[†] R. S. Becker,[‡] F. B. Dias,^{‡,§} A. L. Maçanita,[‡] and J. Seixas de Melo^{*,†}

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The photophysics of six oligothiophenes end-capped with cyano groups ($\text{CN}\alpha n$) 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 ($S_{\Delta} \approx 1$) of its formation by the triplet state of the $\text{CN}\alpha n$. 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, $\text{CN}\alpha 1$.

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.^{1–5} It has been demonstrated, for example, that polymeric spectroscopic properties become well established with oligomers having their number of monomer units greater than⁶ or equal to 5^{1,2,7–9} in the case of the polythiophenes, 15 with poly-*p*-phenylenedivinyls,¹⁰ and 12 in polyfluorenes.¹¹ The oligomer approach¹² 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.^{8,13–15} 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.¹⁶ 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.^{1,17–20}

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,¹ and the extrapolation of the properties of the oligomers to polythiophene is one of the most interesting and widely pursued goals in this area.^{1,21–31} In part, this arises because of difficulties in characterizing solid polythiophene, since the unsubstituted polymer or oligomers with $n \geq 6$ 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.^{8,14} 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,^{8,13} 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.⁸ 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.⁷

Conjugated polymers containing cyano groups have valuable properties for molecular electronics, including increased electroluminescence and high electron affinity.³² Recently dicyanomethylene oligothiophenes have been synthesized and re-

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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.³³ 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.²⁰

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.²⁰

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 1×10^{-5} to 1×10^{-6} M. These were deoxygenated by bubbling with Ar.

Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Horiba-Jobin-Ivon Spex Fluorog 3-22 spectrometers, respectively. Phosphorescence measurements were made in glasses at 77 K and used the same Spex 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.³⁴ 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).¹

The molar extinction coefficients (ϵ) were obtained from absorption spectral measurements using six solutions of different concentrations and the slope of plots of the absorption versus concentration (correlation coefficients ≥ 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 1P28 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 ≈ 0.2 in a 10 mm square cell) and low laser energy (≤ 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 relationship³⁵

$$\epsilon_T = \frac{\epsilon_S \times \Delta OD_T}{\Delta OD_S} \quad (1)$$

where both ΔOD_S and ΔOD_T are obtained from the triplet–singlet difference transient absorption spectra. The ϕ_T (ϕ_{ISC}) values were obtained by comparing the ΔOD at 525 nm of a benzene solution of benzophenone (the standard) and of the compound (optically matched at the laser wavelength) using the equation^{7,36}

$$\phi_T^{CN\alpha n} = \frac{\epsilon_{TT}^{benzophenone}}{\epsilon_{TT}^{CN\alpha n}} \times \frac{\Delta OD_{max}^{CN\alpha n}}{\Delta OD_{max}^{benzophenone}} \times \phi_T^{benzophenone} \quad (2)$$

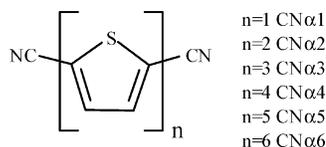
Fluorescence decays were measured using a home-built time-correlated single-photon counting apparatus with a IBH 5000 coaxial flashlamp filled with N₂ or D₂ or mixtures of these as the excitation source, Jobin-Ivon excitation and emission monochromators, a Philips XP2020Q photomultiplier, and Canberra instruments time-to-amplitude converter and multi channel analyzer. Alternate measurements (1000 counts per cycle) of the pulse profile at the excitation wavelength and the sample emission were performed until 5×10^4 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”.³⁷ The fluorescence decays of CN α 1 and CN α 2 were obtained with picosecond resolution in an apparatus described elsewhere.³⁸

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 PC176TSCE-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 interposition 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.³⁹ 1H-Phenalen-1-one (perinaphthenone) in benzene ($\phi_\Delta = 0.93$) was used as the standard.³⁴

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 \equiv N) groups. The advantages

CHART 1



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.²⁰ 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 \cdots H interactions.²⁰ 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 (CN αn) are shown in Figure 1. As with their unsubstituted substituted analogues, the αn 's¹, the absorption spectra are devoid of vibrational structure. Comparison between the αn and its analogue CN αn , 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 ($\alpha 1$ and CN $\alpha 1$) where this value is larger (47 nm). However, as will be discussed below, a good correlation was found between CN αn and $\alpha(n + 1)$ absorption maxima.

The observed behavior can be attributed to the strong electronegativity of the C \equiv N group that introduces a bathochromic shift in the lowest-lying π,π^* transitions of the CN αn , 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 \equiv 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.²⁰ The marked red shift observed between the lower thiophenes CN $\alpha 1$ and CN $\alpha 2$ and the analogous $\alpha 1$ and $\alpha 2$ is particularly relevant.^{1,21} 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.¹ In the present case, CN $\alpha 6$ 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 CN $\alpha 6$ 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 CN αn 's are presented in Figure 2. In contrast to the absorption spectra, the fluorescence spectra present vibrational structure, with the sole exception of CN $\alpha 1$. As with the absorption maxima, the emission spectra also red-shift with increasing number of thiophene units in the CN αn . However, with the associated fluorescence parameters ϕ_F and τ_F , different patterns are observed. The fluorescence lifetime was shown to be a single exponential for all the compounds,

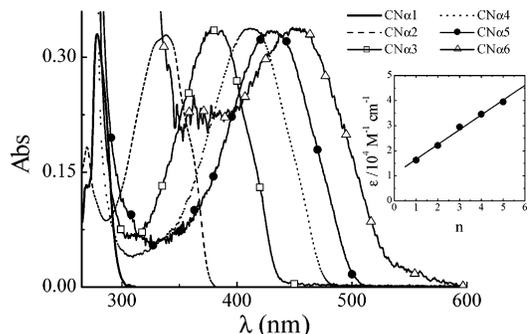


Figure 1. Absorption Spectra for α,ω -dicyano-oligothiophenes in benzene at $T = 293$ K. Shown as an inset is the plot of the extinction coefficients vs the number of thiophene units (n).

TABLE 1: Spectroscopic Properties for α,ω -Dicyano-oligothiophenes and Oligothiophenes (Data from Ref 1) in Benzene at $T = 293$ K

CN αn	$\lambda_{\max}^{\text{Abs}}$ (nm)	ϵ_S ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\max}^{\text{Fluo } d}$ (nm)	$\lambda_{\max}^{\text{T}_1-\text{T}_n d}$ (nm)	ϵ_T ($\text{M}^{-1} \text{cm}^{-1}$)
CN $\alpha 1$	278	16280	377	330	11810
CN $\alpha 2$	336	22140	392	421	15890
CN $\alpha 3$	380	29480	433, 458	504	23090 ^b
CN $\alpha 4$	412	34620 ^a	475, 507	590	44840
CN $\alpha 5$	431	39500 ^a	505, 538	600	110900
CN $\alpha 6$	451 ^a	46090 ^c	593 ^a		
$\alpha 1$	231	8340		305	
$\alpha 2$	303	12440	362	385	15000
$\alpha 3$	354	22080	407, 426	460	40000
$\alpha 4$	392	31560	437, 478	560	74000
$\alpha 5$	417	42670	482, 514	630	90000
$\alpha 6$	436	47910	502, 537	685	
$\alpha 7$	441	50500	522, 560	720	

^a Values in DMSO. ^b Corrected value obtained from a plot of ϵ_T vs n (not shown). The experimental value is $18\,200 \text{ M}^{-1} \text{cm}^{-1}$. ^c Value obtained by extrapolation from the inset plot in Figure 1. ^d The wavelength in italic is the band maximum.

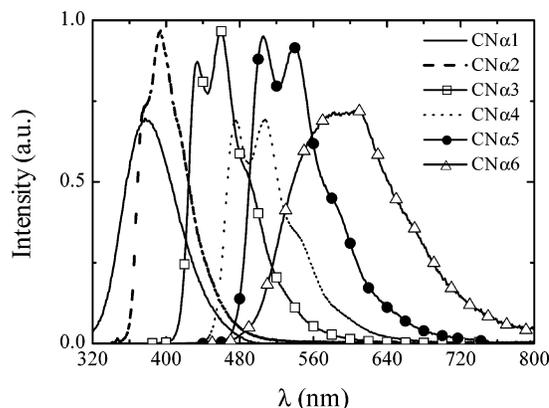


Figure 2. Fluorescence emission spectra for the α,ω -dicyano-oligothiophenes in benzene, $T = 293$ K.

with a progressive increase of this value from 9.8 ps for CN $\alpha 1$ to 1 ns for CN $\alpha 6$; 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 ϕ_F value, which appears to increase up to CN $\alpha 5$ and then decrease for CN $\alpha 6$ (Table 2). However, a different solvent (dimethylsulfoxide (DMSO)) was used for the last compound due to its low solubility in benzene, and consequently the ϕ_F value for CN $\alpha 6$ should be considered as a lower limit (based on the trend obtained from the other CN αn 's).

Triplet State Properties. After laser flash photolysis at 266 or 355 nm of degassed solutions of the CN αn 's in benzene,

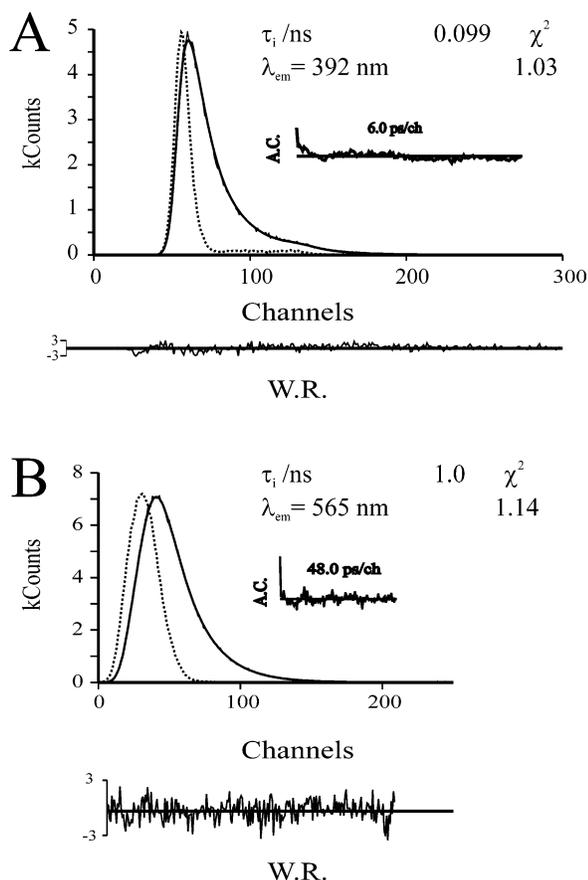


Figure 3. Fluorescence decays for two of the studied compounds: (A) CN α 2 and (B) CN α 6. The presented fits are adjusted to monoexponential decay laws. For a better judgment of the quality of the fits, autocorrelation functions (ACs), weighted residuals (WRs), and chi-square values (χ^2) are also presented 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_T values in Table 2) to recovery of ground-state absorption (Figure 4B).

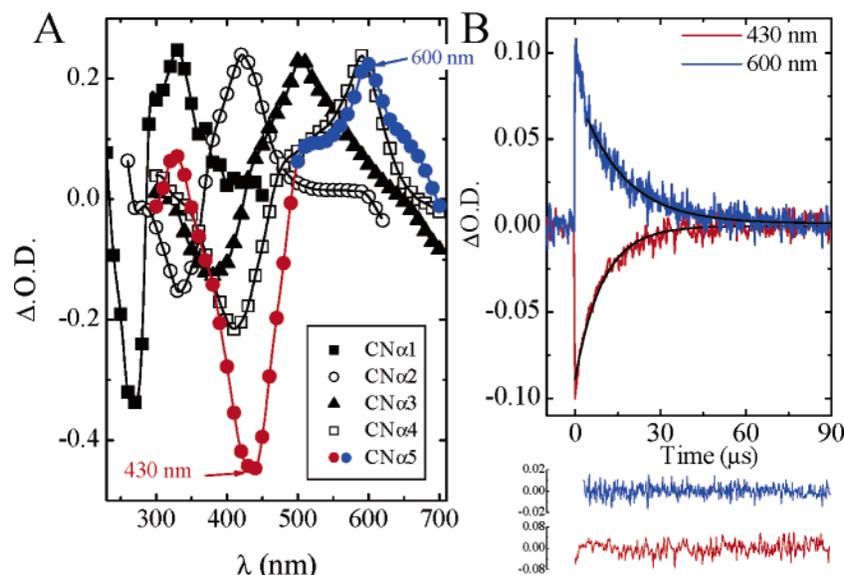


Figure 4. (A) Transient triplet–triplet absorption spectra for the CN α n 's in benzene at $T = 293$ K. The exception is for CN α 1, which was obtained in ethanol. (B) Transient decays for CN α 5 obtained at 430 nm (recovery of ground-state absorption) and 600 nm (transient maximum). Also shown are the residuals for the first-order decay fits.

From Figure 4A, it can be seen that the incremental increase of thiophene units in the CN α n leads to a progressive red shift of the triplet–triplet transient ($T_n \leftarrow T_1$) absorption maxima.

From Tables 1 and 2, a comparison can be made between the spectroscopic and the photophysical behavior of the CN α n 's and the α n 's. It is clear (Table 1) that the substitution of the terminal hydrogens with cyano groups leads to the CN α n possessing the spectroscopic behavior of the comparable α n with one more thiophene ring (α $n + 1$). This seems to be true for both the spectroscopic properties and for some photophysical parameters. For example, although the identical numerical values for ϕ_F may be a coincidence, the values for CN α 4 and α 5 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 ϕ_T and ϕ_{IC} (obtained from $\phi_{IC} = 1 - (\phi_F + \phi_T)$) or to the corresponding rate constants, and it is seen that in this case the CN α n 's exhibit similar behavior to the corresponding α n '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 $S_1 \sim \sim \rightarrow S_0$ decay processes. However, this does not happen with the unsubstituted oligothiophenes (α n 's^{1,21}) 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 ϕ_{IC} 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 ϕ_F increases on going from CN α 1 to CN α 5, while ϕ_T 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 $S_1 \sim \sim \rightarrow T_1$ intersystem crossing rate constant, k_{ISC} , which decreases from CN α 1 to CN α 3, reaching a constant value at CN α 4 and CN α 5 (Figure 5). With respect to the k_F values, with

TABLE 2: Photophysical Properties for the CN α n's and the Analogous α n's (from Ref 1) in Benzene, $T = 293$ K

compound	ϕ_F	τ_F (ns)	ϕ_T	ϕ_Δ	ϕ_{IC}^c	τ_T (μ s)	k_{NR} (ns $^{-1}$)	k_F (ns $^{-1}$)	k_{IC} (ns $^{-1}$)	k_{ISC} (ns $^{-1}$)
CN α 1	0.010	0.0098	0.99 ^a		0	21.8	101.0	1.02	0	101.0
CN α 2	0.06	0.099	0.97	0.93	~ 0	10.7	9.49	0.61	≈ 0	9.49
CN α 3	0.12	0.29	0.79	0.81	0.09	13.2	3.03	0.41	0.31	2.72
CN α 4	0.30	0.61	0.70	0.76	0	5.2	1.15	0.49	0	1.15
CN α 5	0.42	0.78	0.52	0.54	0.06	10.8	0.74	0.54	0.08	0.67
CN α 6	0.35 ^b	1.0 ^b					0.65 ^b	0.35 ^b		
α 2	0.02	0.046	0.99	0.96	~ 0	104	21	0.43	0.11	22
α 3	0.07	0.16	0.95	0.81	~ 0	88	5.8	0.44	0.03	5.9
α 4	0.18	0.44	0.73	0.72	0.09	38	1.9	0.41	0.20	1.7
α 5	0.34	0.82	0.59	0.56	0.07	24	0.81	0.41	0.098	0.72
α 6	0.44	0.97		~ 0.36		≥ 17	0.58	0.45		

^a Value in ethanol. ^b Values in DMSO. ^c $\phi_{IC} = 1 - (\phi_F + \phi_T)$.

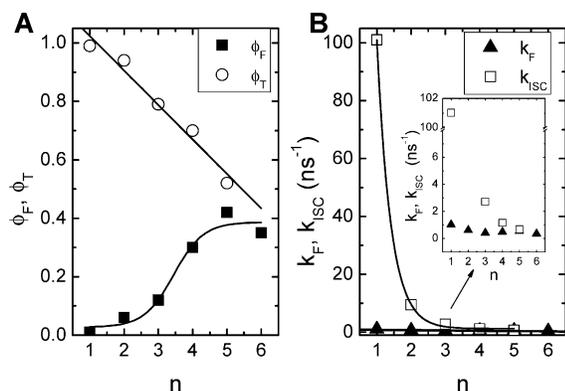


Figure 5. Dependence of the (A) quantum yields ϕ_F and ϕ_T and (B) rate constants k_F and k_{ISC} on n . Shown as an inset in part B is a magnified view of the k_F variation with n .

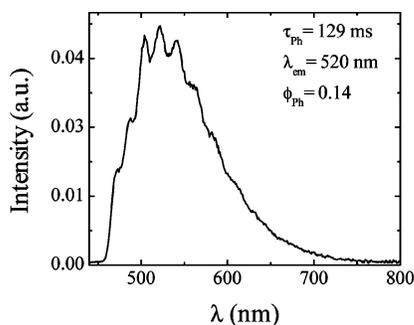


Figure 6. Phosphorescence emission spectrum for CN α 1 in an ethanol glass ($T = 77$ K).

the possible exception of the two shortest CN α n's, these seem to present a constant value around 0.4–0.5 ns $^{-1}$ (Figure 5). The behavior presented by the CN α n's is in agreement to what was observed for the analogous α n's¹ and with substituted naphthalene oligothiophenes⁷ where it was possible to observe that the sum of the ϕ_F and ϕ_T 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 $n \geq 4$, which implies that these oligomers can be considered as equivalent to a dicyano end-capped thiophene polymer.

Phosphorescence. The only case where we were able to detect phosphorescence at 77 K with any of these compounds in various glasses was with CN α 1 in an ethanol matrix, where a structured emission was observed, with a maximum at $\lambda_{max} = 520$ nm (Figure 6). Also, with the oligothiophenes, the shortest member of this series, thiophene, displayed phosphorescence.¹ The phosphorescence for thiophene was reported to

be 480 nm (although this value has been questioned by others,²⁸ who located the triplet state at 3.23 eV ≈ 384 nm). The phosphorescence excitation spectrum of CN α 1 matched the shape and maxima (with an approximate difference of 5 nm) of the room-temperature absorption spectra. The CN α 1 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 CN α 1, the observed phosphorescence lifetime was 129 ms, which suggests that the lowest triplet T₁ state is of π, π^* origin.⁴⁵ Rentsch et al. have observed phosphorescence for α 2 (unequivocally established by matching the fluorescence and phosphorescence excitation spectra) with maxima at 600 nm and a lifetime of $800 \pm 200 \mu$ s.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 terthiophene they located the triplet of this oligomer at 1.82 eV (~ 681 nm, $14\,679$ cm $^{-1}$), which is in reasonable accordance with the value determined by time-resolved PAC at room temperature (1.92 eV).² Although the phosphorescence lifetime is not specifically 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 π, π^* state, which is likely to be the case (see k_F values in Table 2), then the spin-orbit coupling matrix elements between the π, π^* triplet state and this singlet state will be very small since only three-center terms do not vanish for planar excited molecules,⁴⁸ such as are expected here. Therefore, this type of mixing cannot explain the high values for ϕ_T and k_{ISC} of the CN α n.

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

$$\langle {}^1\Psi_{CT} | H_{SO} | {}^3\Psi_i \rangle$$

In the present case, k_{ISC} shows a similar behavior, and it is obvious that the cyano groups do not change the charge-transfer character of the spin-orbital coupling. The decrease in 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 ${}^1\Psi_{CT}$ and ${}^3\Psi_i$ as the number of rings increases.¹ However, the significant decrease on going from CN α 1 to CN α 5 (Table 2) could also be explained by the fact

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.⁷ In the present case the internal conversion rate constant is also negligible, as was previously observed for αn 's and naphthalene oligothiophenes,⁷ and the effectively zero value of ϕ_{IC} could be attributed to structural differences between the ground and the excited state. Since the core structure (thiophenes linked in αn 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.¹ 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 ϕ_T and k_{ISC} values presented by the short $\alpha 2$ and $\alpha 3$ oligothiophenes were given by Rentsch et al.⁴⁶ and Rossi et al.,⁴⁹ which were based on the high-energy splitting existing between S_1 and T_1 and suggest participation of energetically higher⁴⁶ triplet states and of d_{π} sulfur orbitals in the triplet states reached by nonactivated and thermally activated⁴⁹ intersystem crossing.

Singlet Oxygen Yields. From Table 2 it can be seen that the singlet oxygen yields (ϕ_{Δ}) are effectively identical to the triplet intersystem crossing yields, indicating a very efficient triplet energy transfer from the $CN\alpha$ triplet states to the oxygen triplet to produce 1O_2 , i.e., $S_{\Delta} \approx 1$. This is important since the first ϕ_{Δ} values establish an upper limit for the ϕ_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,^{50–52} and the knowledge of this parameter is essential to discuss the origin of its action. Moreover literature data on $\alpha 3$ substituted with one $C\equiv N$ unit gives a ϕ_{Δ} value of 0.86⁵³ (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,⁵⁴ which is in excellent agreement with our value for the disubstituted $CN\alpha 3$ ($\phi_{\Delta} = 0.81$; 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 ($C\equiv N$) groups was found to spread the π -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 $CN\alpha n$'s relative to their unsubstituted counterparts, the αn '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 π -bonds present in the terminal CN groups. The increase in the π -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 ($S_1 \sim \sim S_0$) 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 unaffected 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 $CN\alpha n$'s to ground-state oxygen.

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