Spectral and Photophysical Studies on Cruciform Oligothiophenes in Solution and the Solid State

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The photophysical and spectroscopic properties of a new class of oligothiophene derivatives, designated as cruciform oligomers, have been investigated in solution (room and low temperature) and in the solid state (as thin films in Zeonex matrixes). The study comprises absorption, emission, and triplet−triplet absorption spectra, together with quantitative measurements of quantum yields (fluorescence, intersystem crossing, internal conversion, and singlet oxygen formation) and lifetimes. The overall data allow the determination of the rate constants for all decay processes. From these, several conclusions are drawn. First, in solution, the main deactivation channels for the compounds are the radiationless processes: $S_1 \rightsquigarrow S_0$ internal conversion and $S_1 \rightsquigarrow T_1$ intersystem crossing. Second, in general, in the solid state, the fluorescence quantum yields decrease relative to solution. A comparison is made with the analogous linear α-oligothiophenes, revealing a lower fluorescence quantum efficiency and, in contrast to the normal oligothiophenes, that internal conversion is an important channel for the deactivation of the singlet excited state. Replacement of thiophene by 1,4-phenylene units in the longer-sized cruciform oligomer increases the fluorescence efficiency. The highly efficient generation of singlet oxygen through energy transfer from the triplet state ($S_\Delta \approx 1$) provides support for the measured intersystem crossing quantum yields and suggests that reaction with this may be an important pathway to consider for degradation of devices produced with these compounds.

Introduction

In the past decade, organic-based π-conjugated materials have found various applications in molecular electronics because of their attractive physical properties and ease of processibility. Polythiophenes are probably one of the most versatile classes of π-conjugated systems within this group of compounds.[1−5] This results, in part, from their unique properties, as demonstrated by their chemical stability and facility for tuning electronic properties through modification of their chemical structure. Various applications of oligo- and polythiophenes are found in modern materials science, such as their use in light emitting diodes, field effect transistors, and electrochromic and photovoltaic devices.[1,6−8] Thiophene-based polymers and oligomers have also recently been shown to be among the most promising organic electroluminescent materials and to possess high photoluminescent quantum yields in the solid state.[9]

Cruciform oligomers, composed of multiple oligomer chains emanating from junction points, have received significant attention because of their unique three-dimensional shape and highly branched structure.[10] This new family of compounds[1,9] has recently gained considerable attention because it is suggested that their structure may prevent or discourage crystallization by avoiding strong intermolecular packing, although this depends on the chemical structure of the branches.[10] Such cruciform oligomers are suggested to establish a link between

oligomers and thiophene polymers. They have advantages due to their compact structure in comparison with linear analogues. However, another important parameter for LED applications is emission efficiency. To our knowledge, the previous works have not addressed this important parameter apart from presenting spectral, thermal, and electrochemical data, and one report of luminescence yields in films[9] of a particular family of these compounds.[10−13] Moreover, within a group or family of these compounds, it is also important to consider the importance of the competitive radiationless processes. This can only be obtained when a systematic and complete photophysical study is undertaken.

In the present work, we have performed a comprehensive investigation of the spectral and photophysical properties of five cruciform oligothiophenes (see Chart 1) in solution (room and low temperature) and in films. One important aspect of the present study is the comparison with the properties of the parent oligomers, the linear α-oligothiophenes ($\alpha n s$).[14] In addition, one of the oligomers studied displays a structural modification in the central backbone of the oligothiophene skeleton by replacing a thiophene group with a 1,4-phenylene unit. The introduction of this group aims to make use of the high quantum efficiencies exhibited, both in solution and in the solid state, by the poly-(*p*-phenylenes).[15] With this modification, an increase in the fluorescence quantum yield of this cruciform oligothiophene, in solution and thin films, can be anticipated relative to the corresponding unsubstituted oligothiophene. This does not, however, seem to be the general rule with the oligothiophene counterparts, where the fluorescence quantum yields in ultrathin films are found to be strongly quenched relative to solution media.[16] However, this also depends on several other factors
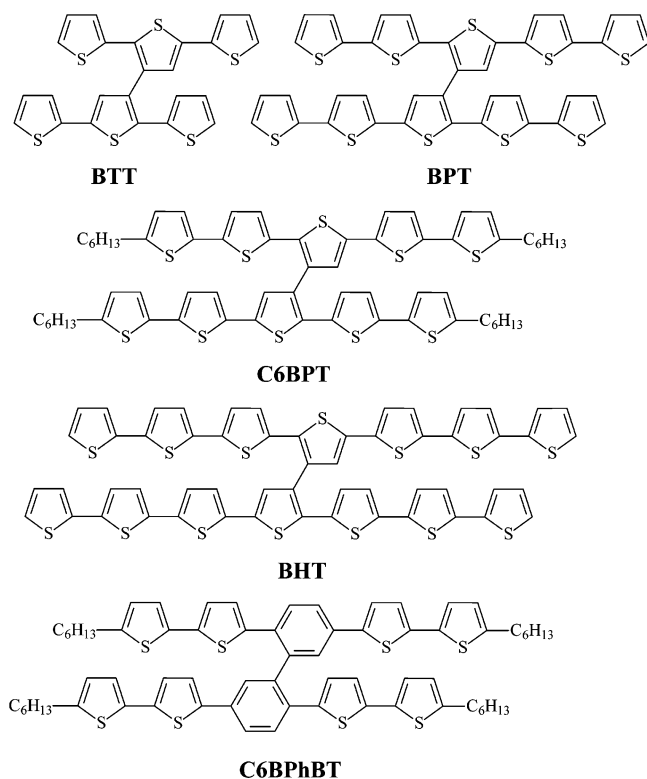
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CHART 1

BTT   BPT

C6BPT

BHT

C6BPhBT

such as film thickness, structure, and orientation,[16] which were found to increase upon increasing layer thickness or cooling.[17]

Experimental Section

The synthetic procedures for the preparation of the unsubstituted cruciform oligothiophene dimers BTT, BPT, and BHT were performed by Stille-type coupling of the core segment 2,2′,5,5′-tetrabromo-3,3′-bithiophene with the corresponding monostannyl(oligo)thiophenes and have been described elsewhere.[18] The detailed syntheses of the tetrahexyl derivatives C6BPT and C6BPhBT, performed by Yamamoto-type coupling of two preformed oligoaryl segments, have also been described.[19,20]

All of the solvents used were of spectroscopic or equivalent grade. For the absorption and emission experiments in toluene, the concentrations of the solutions ranged from 1×10^{-5} to 1×10^{-6} M.

Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Horiba-Jobin-Ivon SPEX Fluorog 3-22 spectrometers, respectively. The fluorescence spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields were measured using quinquethiophene as the standard, $\phi_F = 0.33$.[14]

Fluorescence decays were measured using a home-built TCSPC apparatus with an IBH NanoLED (373 or 460 nm) excitation source, Jobin-Ivon excitation and emission monochromators, a Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA. Alternate measurements (1000 cpc) of the pulse profile at the excitation wavelength and the sample emission were performed until 5×10^4 counts at the maximum were reached. The fluorescence decays were analyzed using the modulating functions method of Striker with automatic correction for the photomultiplier "wavelength shift".[21]

The experimental setup used to obtain triplet spectra and triplet yields consists of an Applied Photophysics laser flash photolysis apparatus pumped by a Nd:YAG laser (Spectra

Physics). The detection system is at right angles to the excitation beam, and a pulsed 150 W Xe lamp is used to analyze the transient absorption. The signal obtained is fed into a HP digital analyzer and transferred to an IBM RISC computer where the optical density (OD) at different wavelengths and different delays after flash are collected using the appropriate software (Applied Photophysics). Transient spectra were obtained by monitoring the optical density change at intervals of 5−10 nm over the 300−850 nm range and averaging at least 10 decays at each wavelength. First-order kinetics were observed for the decay of the lowest triplet state. Excitation was at 266 or 355 nm with an unfocused beam. Special care was taken in determining triplet yields to have optically matched dilute solutions (abs ≈ 0.2 in a 10 mm square cell) and low laser energy (≤2 mJ) to avoid multiphoton and T−T annihilation effects.

The triplet molar absorption coefficients were determined by the energy transfer method,[22] using naphthalene, $\epsilon_T = 24\ 500$ $M^{-1}\ cm^{-1}$ (415 nm),[23] or anthracene, $\epsilon_T = 45\ 500\ M^{-1}\ cm^{-1}$ (430 nm),[24] as triplet energy donors. The concentration for the cruciform oligomers studied was 2×10^{-5} mol dm^{-3}, and they were dissolved in 10^{-3} mol dm^{-3} toluene or methylcyclohexane solutions of naphthalene ($\lambda_{exc} = 266$ nm) or anthracene ($\lambda_{exc} = 355$ nm). Before experiments, all solutions were degassed with argon for ≈20 min and sealed. The molar triplet−triplet molar absorption coefficients were then determined from eq 1:[22]

$$\frac{\epsilon_{TT}^D}{\epsilon_{TT}^A} = \frac{\Delta OD^D}{\Delta OD^A} \quad (1)$$

where ϵ_{TT}^D and ϵ_{TT}^A stand for the triplet molar absorption coefficients of donor and acceptor, respectively; ΔOD^D is the maximum absorbance from the transient triplet−triplet absorption spectra of the donor in the absence of acceptor; ΔOD^A is the maximum absorbance of the acceptor triplet when both the donor and acceptor are present. For determination of ΔOD^A, additional corrections were taken into account, in particular when the acceptor decay rate constant (k_3) is not negligible. For this situation, eq 2 was applied[22]

$$\Delta OD_{obsd}^A = \Delta OD^A \exp\left[-\frac{\ln k_2/k_3}{k_2/k_3 - 1}\right] \quad (2)$$

where k_2 is the donor decay rate constant in the presence of acceptor and ΔOD_{obsd}^A is taken from the maximum observed in the triplet−singlet difference spectra of the acceptor in the presence of donor.

The intersystem crossing yields for the compounds (ϕ_T^{cp}) were obtained by comparing the ΔOD values at 525 nm of benzene solutions optically matched (at the laser excitation wavelength) of benzophenone (standard) and of the compound using the equation[25,26]

$$\phi_T^{cp} = \frac{\epsilon_{TT}^{benzophenone}}{\epsilon_{TT}^{cp}} \cdot \frac{\Delta OD_{max}^{cp}}{\Delta OD_{max}^{benzophenone}} \cdot \phi_T^{benzophenone} \quad (3)$$

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-005), 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 the spectral response to the infrared. The filter employed is essential to eliminate from the infrared signal all the first harmonic contributions from the sensitizer emission in the 500−800 nm region. 1*H*-Phenalen-1-one (perinaphthenone) in toluene ($\phi_\Delta =$ 0.93) was used as the standard.[24]

Thin films from the compounds were obtained with a Desk-Top Precision Spin Coating System, model P6700 Series from Speedline Technologies. The solid-state thin films from the samples were obtained by deposition of a few drops from a solution of the compounds onto a circular sapphire substrate (10 mm diameter) followed by spin coating (2500 rpm) in a nitrogen saturated atmosphere (2 psi). The solutions for spin coating were prepared by adding 2 mg of the samples to 15 mg of Zeonex in 200 μL of toluene solution with stirring at 40 °C for 30 min.

The fluorescence emission spectra of the thin films were obtained with a Horiba-Jobin-Yvon integrating sphere. The solid-state photoluminescence quantum yields in thin films were obtained with this integrating sphere, using the method outlined by de Mello et al.[27] and applied by Palsson and Monkman[28] to polypyridine films using a setup similar to ours. The following equation was used to determine the fluorescence quantum yields:

$$\phi_F(solid) = \frac{\int^{sample} I(\lambda) \, d\lambda}{(\int^{scatter\_alone} I(\lambda) \, d\lambda - \int^{scatter\_in\_sample} I(\lambda) \, d\lambda) 10^{\Delta OD(\lambda_{exc})}} \quad (4)$$

where $\phi_F(solid)$ is the fluorescence quantum yield for the cruciform oligomer in a thin film, $\int^{sample} I(\lambda) \, d\lambda$ is the integrated area under the emission of the cruciform in the thin film (which excludes the integration of the Rayleigh peak), $\int^{scatter\_alone} I(\lambda) \, d\lambda$ is the integrated area under the Rayleigh peak of a sample containing only the sapphire support, and $\int^{scatter\_in\_sample} I(\lambda) \, d\lambda$ is the integrated area under the Rayleigh peak in the emission spectra of the cruciform oligomer in the thin film. Since in practice the emission from the sample is much weaker than the scattered excitation light, that is, the Rayleigh peak, the spectra are recorded with a filter that attenuates the emission intensity at the excitation wavelength. This is considered in eq 4 with $10^{\Delta OD(\lambda_{exc})}$, that is, the value for the filter transmittance at the excitation wavelength.

Results

The structures and acronyms of the compounds investigated are given in Chart 1. The structures of BTT, BPT, and BHT consist of two units of three, five, and seven oligothiophene units, respectively, linked by their central thiophene ring. C6BPT has an identical skeleton to BPT but possesses additional C_6H_{13} alkyl groups at the terminal (α,α' positions) of the two pentathiophene units. This structural modification is aimed at improving the solubility of the oligomer. The oligomer C6BPhBT results from the substitution of the central thiophene units in C6BPT by a 1,4-phenylene group.

In Figure 1, the solution (toluene) absorption spectra (at 293 and 77 K, given here as the fluorescence excitation spectra) and in the solid state in Zeonex matrixes (as films) are shown. It can be seen that the absorption bands and maxima in solution shift to the red with the increase in the number of thiophene rings. Red shifts of the entire absorption spectrum are observed upon a decrease in the temperature, with changes in absorption maxima ranging from ≈10 nm (C6BPhBT) to ≈27 nm (BHT)
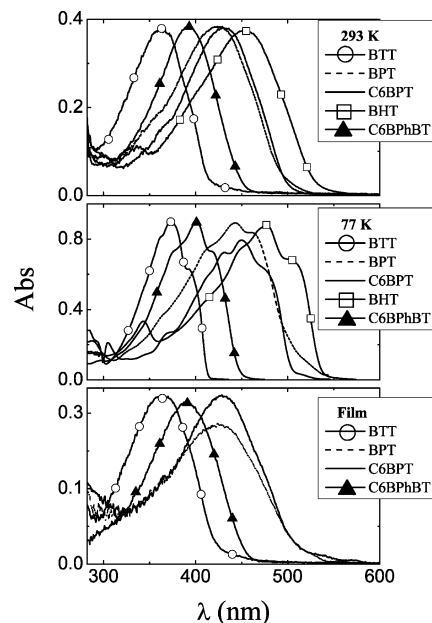

Figure 1. Absorption spectra for the cruciform oligothiophenes in solution at room temperature (293 K), at low temperature (as seen by the excitation spectra), and in films.
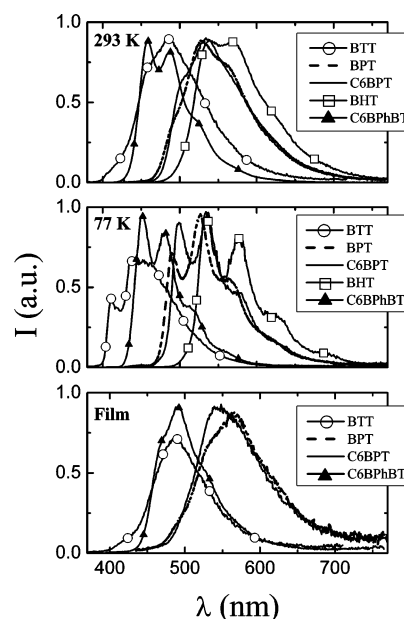

Figure 2. Fluorescence emission spectra for the cruciform oligo-thiophenes in toluene at room temperature (293 K), at low temperature (77 K), and in films.

between 293 and 77 K. The substitution of thiophene by 1,4-phenylene, C6BPT versus C6BPhBT, leads to a blue shift. The same trend is observed with the compounds in films. Interestingly, no shift or band change was observed for the absorption of the compounds comparing dilute solution at room temperature and solid films in Zeonex matrixes (see Figure 1 and Table 1), supporting the idea that the cruciform structure inhibits phase separation and interchain interaction in the solid. Due to the very low solubility of BHT, we were unable to dissolve reasonable quantities in order to obtain a film.

Figure 2 displays the emission spectra at room temperature (293 K), low temperature (77 K), and in films. On going from 293 to 77 K, there is a marked increase in the vibrational structure of the spectra, particularly for BPT, C6BPT, and BHT. With C6BPhBT, there is a negligible increase in structure,

TABLE 1: Spectral Data (Absorption, Emission Wavelength Maxima and Triplet Maxima and Extinction Coefficients) for the Cruciform Oligomers in Toluene at Room Temperature (293 K), at Low Temperature, and in Films

compound	λ_{max}^{abs} (nm) 293 K	λ_{max}^{abs} (nm) 77 K[a]	λ_{max}^{abs} (nm) film	λ_{max}^{fluo} (nm) 293 K[c]	λ_{max}^{fluo} (nm) 77 K[c]	λ_{max}^{fluo} (nm) film	$\lambda_{max}^{T_1 \rightarrow T_n}$ (nm), ϵ_T (M^{-1} cm^{-1})
BTT	360	373	365	485	411, <u>437</u>	487	480, 10 400[d]
BPT	425	443	425	528	490, <u>527</u>, 563	565	650, 35 000
C6BPT	430	450	430	535	500, <u>537</u>, 575	540	665, 70 400
BHT	450	477	b	<u>540</u>, 568	<u>533</u>, 575, 625	b	740, 68 700
C6BPhBT	390	400	390	<u>458</u>, 487	<u>450</u>, 480, 512	490	670, 39 100[d]

[a] Obtained from the excitation spectra. [b] A film could not be obtained due to the concentrations needed; see text for more details. [c] The underlined wavelength values are the band maximum. [d] Obtained in methylcyclohexane.
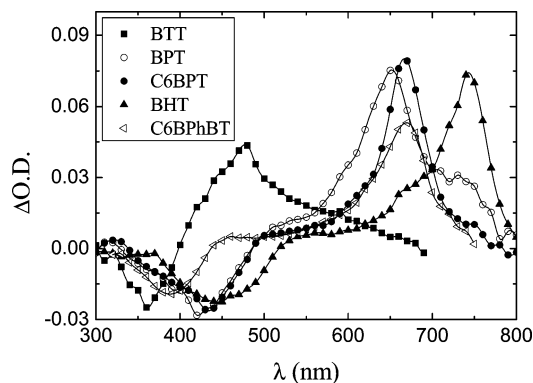
Figure 3. Transient triplet−triplet spectra for the cruciform oligothiophenes in toluene at room temperature.

whereas, with BTT, the appearance of a new band at shorter wavelengths is observed. Note that in this latter case we cannot completely discard the possibility of aggregate emission. However, we feel that this is unlikely, as this band was obtained for various solute concentrations, and, in addition, the excitation spectra collected at the red edge of this band (where presumably the aggregates emit) matches the excitation spectra obtained with emission at the maxima. With the exception of BTT (due to the appearance of the new band), there is no significant shift of the band maxima upon going from 293 to 77 K. This suggests very similar ground- and S_1-state geometries for the compounds. In films, the emission bands are devoid of structure and the maxima are generally red shifted when compared with room temperature solution behavior.

Figure 3 shows the transient triplet−triplet absorption spectra for the five compounds studied in toluene solution at 293 K. In addition to ground-state depletion at lower wavelengths, the spectra show intense absorption bands with maxima at longer wavelengths. With the exception of BTT, which shows a band with a maximum at 480 nm (Table 1 and Figure 3) and a broad absorption that extends up to 700 nm, the other compounds show a sharp and well-defined transient absorption band located between 600 and 750 nm. In the case of BPT, an additional shoulder at longer wavelengths is also observed.

Discussion

Absorption and Fluorescence Spectra. From the data in Table 1 on spectra, extinction coefficients, fluorescence and transient $T_1 \rightarrow T_n$ maxima at room temperature, low temperature and in films, and from Figures 1 and 2, some important observations should be considered. First, the solution and film absorption spectra at room temperature are devoid of spectral resolution (Figure 1). In contrast, with the low temperature absorption (here represented by the fluorescence excitation spectra), significant vibrational structure is observed. Moreover, for all compounds, there is a marked red shift of the absorption

maximum, 0−0 transition and of the spectra in general upon going from 293 to 77 K.

The room temperature fluorescence spectra are more structured than those of absorption, but as mentioned before, the increment in maxima with increasing number of thiophene groups is not as significant as that with the αns.[14] It is also relevant that, with the exception of BTT, there is virtually no shift in the fluorescence maxima between 293 and 77 K. The red shift observed in absorption spectra upon going from 293 to 77 K is usually ascribed to an increase in the planarity of the ground state with subsequent greater π-conjugation and decrease of the energy difference between S_0 and S_1.[14] The red shift of the absorption between 293 and 77 K, as seen by the difference in the absorption maxima at the two temperatures, is virtually identical for BTT and BPT ($\approx$960 cm^{-1}) but increases for BHT ($\approx$1260 cm^{-1}), whereas with the 1,4-phenylene substituted derivative (C6BPhBT) the red shift is small ($\approx$640 cm^{-1}). While the difference is modest, these shifts are significantly smaller than those observed ($\approx$1600 cm^{-1}) with the αns.[14] In the case of fluorescence, with the exception of BTT, the shift of the maximum upon lowering the temperature is negligible.

We interpret the change in absorption and fluorescence with temperature on the basis of the following arguments. First, the Franck−Condon forbidden shape of the room temperature first absorption band, when compared with the more structured nature of the fluorescence band, indicates that some change in geometry has occurred. However, this change is not as significant as that observed with the αns,[14] suggesting that the link between the two moieties precludes total planarization of the molecules and of each individual moiety. This is also supported by comparing the room temperature absorption maxima of the cruciform oligomers with the respective αn counterparts. With the αns, it was found that a population of conformers with different degrees of twisting between thiophene rings existed, giving rise to a broad, unstructured absorption band. In the case of α3, the wavelength maximum is 354 nm[14] in benzene (355 nm in CH$_2$Cl$_2$,[29] thus showing little dependence with the solvent) which compares with the value 360 nm for BTT (see Table 1); for α5, the value is 417 nm[14] (410 nm in CH$_2$Cl$_2$[29]), whereas, for BPT and C6BPT, they are 425 and 430, respectively (see Table 1). For α7, the value is now 441 nm[14] (440 nm in CHCl$_3$[30]), whereas, for BHT, it is 450 nm (see Table 1); that is, the general conclusion is that for all cases there is a comparative increase of the absorption maximum wavelength with the cruciform oligomers compared with the linear analogues.

Moreover, when a comparison is made with the fluorescence maxima, the evidence is for a more pronounced but still relatively modest red shift: 485 nm for BTT versus 426 nm for α3, 527 nm for BPT versus 482 nm for α5, and 533 nm for BHT versus 522 nm for α7. This marked Stokes shift indicates once more that the ground-state geometry is different from that of the excited state. However, the negligible difference between

TABLE 2: Photophysical Properties for the Cruciform Oligomers in Toluene at Room Temperature (293 K), at Low Temperature (77 K), and in Films

compound	ϕ_F 293 K	τ_F (ns) 293 K	ϕ_F 77 K	ϕ_F film	τ_F (ns) film	k_F (ns^{-1}) 293 K	k_{NR} (ns^{-1}) 293 K	ϕ_{IC} 293 K	k_{IC} (ns^{-1}) 293 K	k_{ISC} (ns^{-1}) 293 K	ϕ_T 293 K	ϕ_Δ 293 K	τ_T (μs) 293 K
BTT	0.026	0.180	0.068	0.050	0.750	0.14$_4$	5.41	0.46	2.56	2.83	0.51	0.56	54
BPT	0.12	0.580	0.14	0.096	0.85	0.20$_7$	1.52	0.25	0.43	1.09	0.63	0.59	24
C6BPT	0.13	0.590	0.16	0.094	0.84	0.22	1.47	0.29	0.492	0.98	0.58	0.58	23
BHT	0.22	0.730	0.28			0.30	1.07	0.23	0.32	0.75	0.55	0.52	20
C6BPhBT	0.50	1.05	0.54	0.22	1.71	0.29	0.48	0.21	0.20	0.27$_6$	0.29	0.26	95

the absorption and emission maxima of the cruciform oligomers when compared to the αn counterparts seems to indicate that the two oligothiophene units in the former behave as independent units and must therefore have a dihedral angle that precludes (or at least minimizes) π-conjugation between the two moieties. In fact, for all swivel cruciform oligoaryl dimers, a distorted structure with respect to the central connection between the two oligoaryl arms is expected. Support for this comes from the fact that the corresponding terphenyl dimer, for example, shows a torsion angle of 63° between the two terphenyl segments according to its single crystal X-ray structure.[10]

The introduction of a 1,4-phenylene unit by substitution of a thiophene unit in C6BPhBT decreases the degree of π-conjugation when compared with C6BPT. However, the decoupling is not total, since the spectral (and photophysical) parameters are not the same as those of bithiophene.[14]

In films in Zeonex matrixes, where intermolecular interactions are likely to occur, there is no shift of the absorption maxima relative to room temperature absorption, but the same is not true with fluorescence. The absorption spectra of the cruciforms in the solid state, however, strongly depend on the film formation technique. In contrast to the spin coated films described within this report, we found significant red shifts of the absorption bands for drop cast films (solvent: chloroform). It seems that the drop cast films show a much higher tendency to crystallize, especially with BPT and BHT.

Photophysical Behavior in Solution and the Solid State. The photophysical parameters obtained in solution and films are presented in Table 2. As a general trend, from Table 2, it can be observed that the radiationless quantum yields (ϕ_{IC} and ϕ_T) are higher than the fluorescence yield for all of the compounds studied, thus showing the former as preferred pathways for the excited-state deactivation. The ϕ_{IC} values, obtained from the balance $\phi_F + \phi_T + \phi_{IC} = 1$, are higher than the room temperature ϕ_F values (the exception is C6BPhBT; see Table 2) but lower than the ϕ_T values, showing that this process is less important than intersystem crossing.

The practically constant value for ϕ_T (again with the exception of C6BPhBT) suggests that, although the sulfur atoms increase the efficiency of this process, this is not a pure effect of enhancing the spin−orbit coupling by the classical heavy atom effect[31] (which is obviously present due to the presence of the sulfur atoms), since in that case it would be expected that the value for BHT would be higher than that for BTT. In fact, as has been discussed for different types of oligothiophenes, the spin−orbit coupling is mediated by charge transfer mixing involving singlet donor and triplet acceptor states that would induce a smaller overlap of the two molecular orbitals involved.[14,25] The nature of this CT-type singlet state would obviously involve some contribution from $\sigma \rightarrow \pi^*$ transitions.[25] A more recent and alternative interpretation, based on ab initio studies[32] computed for α3, suggests a large energy difference between the S$_1$ and T$_1$ states and proposed that intersystem crossing would involve coupling between the T$_2$ and S$_1$ states in its equilibrium geometry and that for tetrathiophene (α4) the

higher energy gap between S$_1$ and T$_2$ together with symmetry considerations[32] would lead to a less favored spin−orbit coupling which would explain the decrease in the ϕ_T value[14] from α3 to α4.

It is relevant to this discussion that ϕ_{IC} represents 21−46% of the lost emitted *quanta*. With the parent α-oligothiophenes (hydrogen[14] and cyano[33] end terminated), the internal conversion pathway was negligible. This was suggested to be mainly due to the fact that in the S$_1$ state the oligothiophenes possess a quinoidal-like structure which lends them rigidity, preventing efficient coupling between the excited-state and ground-state modes.[14,33] However, the importance of the internal conversion radiationless channel in thiophene-based polymers,[5,34] thiophene trimers,[35] and fluorene−thiophene copolymers[36] has been previously observed.

From Table 2, it can also be seen that the radiative rate constant (k_F) gradually increases with n from ≈0.14 to 0.30 ns^{-1}, while the τ_F values increase with the number of thiophene units. The substitution of a thiophene unit by a 1,4-phenylene unit also has the effect of increasing the lifetime of the compound. However, although they show a slight increase with the number of thiophene units in the chain, the radiative rate constant (k_F, $= \phi_F/\tau_F$) values in Table 2 can be considered to be independent of n. This is consistent with the fact that the observed emission is from the same allowed state of predominantly π,π^* origin (although possibly having some σ,π^* character, as mentioned above).

From Table 2, it is also possible to see that the fluorescence quantum yields in films are lower than those in solution, with the possible exception of BTT. This is a general pattern found for π-conjugated oligomer and polymer systems in which the low fluorescence quantum yields in the solid state are due to the increase of the nonradiative decay processes, which mainly result from intermolecular interactions.[10,15] With thiophene oligomers, this was found to be strongly dependent on the type of solid material considered. For example, it was reported that for α3 in a polymer matrix the ϕ_F value (at room temperature) increases to 0.2,[16] whereas for α5 in a CHCl$_3$ solution it was found to be 0.32 and where aggregates (presumably H-aggregates) are present to be equal to 0.0011.[16] Moreover, with this same α5, a change of ϕ_F from 10^{-4} to 10^{-2} was observed between oriented and disordered ultrathin films.[16]

Finally, no significant changes are observed in the fluorescence quantum yield upon going to low temperatures (Table 2), possibly suggesting any changes in emission processes resulting from shifts in fluorescence maxima are paralleled by corresponding changes in the nonradiative rates. The exception to this behavior occurs with BTT which suffers an ∼2.5-fold increase, from room temperature to low temperature, suggesting that at 77 K some degree of interaction may exist between the two terthiophene units.

Comparison with the Analogous αns. It is worth noting that the fluorescence quantum yields of the cruciform oligomers are lower than those of the related α-oligothiophenes (αns)[14] and the α,ω-dicyano-oligothiophenes (CNαns)[33] shows that. For

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example, in the case of α3, the value is 0.07[14] in benzene (0.06 in CHCl₃[16] and other solvents such as methylcyclohexane[14]) which compares with 0.026 for BTT; α5, $\phi_F = 0.34$[14] *versus* $\phi_F = 0.12$ for BPT; α7, $\phi_F = 0.36$[14] *versus* $\phi_F = 0.22$ for BHT. Moreover, two additional aspects merit attention. The first regards the ϕ_F increment on the αns, which with the normal linear oligothiophenes increases from $n = 2$ to $n = 6$ and then decreases (or levels off) for $n = 7$, which is not the case for the present compounds, where this parameter always increases with n. The second important aspect is related to the introduction of a 1,4-phenylene (C6BPhBT) unit instead of a thiophene (C6BPT) group, which leads to an ∼4-fold increase in the ϕ_F value (0.50 *vs* 0.13 in Table 2).

The decrease in the ϕ_F value of the cruciform oligomers in comparison with the αns (and CNαns) suggests that the single bond connecting the two oligothiophene units is not efficient in extending the conjugation between the two moieties. However, when the link between the two moieties of the cruciform oligomers is made through a 1,4-phenylene unit, an increase in the fluorescence efficiency is observed.

Triplet-State and Singlet Oxygen Sensitization. From the triplet formation data, some further conclusions can be drawn. There is a shift of the T−T maximum with the number of thiophene units in the cruciform oligothiophenes. The broad absorption bands presented by BTT and C6BPhBT suggest that there is more than one $T_1 \rightarrow T_n$ transition. Moreover, the transient spectra of BTT are similar in both shape and maxima (460 nm vs 480 nm) to that reported for α3.[14] The same seems to be true with BPT and α5 and BHT and α7.[14] This also suggests that, in the triplet state, the two αn moieties of the cruciform oligothiophenes are decoupled with little or no π-delocalization between them. The lifetimes of the triplet state (τ_T in Table 2) are very similar (≈20 μs), with the exceptions of BTT and C6BPhBT where the values are higher. We should remember that the absence of significant phosphorescence suggests that the triplet lifetimes should be considered to be mainly due to the radiationless $T_1 \rightsquigarrow S_0$ contribution.[14] In such a situation, it is expected that the lifetimes will decrease (from shorter-sized oligomers to longer-sized oligomers) because of the decrease in the $T_1−S_0$ gap (which occurs with the αns[37]), resulting in a significant increment of the Franck−Condon overlap integrals (between S_0 and T_1) upon which $k_{NR}^{T_1 \rightsquigarrow S_0}(\approx 1/\tau_T)$ depends.[14,37]

Although recent literature has reported evidence for the observation of phosphorescence of small thiophene oligomers[14,38,39] (in particular terthiophene derivatives[38]) and of a polythiophene,[40] we were unable to detect any phosphorescence with the present compounds with our current experimental system.

Singlet oxygen formation quantum yields were obtained following photolysis of aerated toluene solutions of the cruciform oligomers. Excitations with laser pulses of a frequency tripled Nd:YAG laser (@355 nm) lead to the characteristic phosphorescence signal of singlet oxygen at ≈1270 nm. The ϕ_Δ values were then determined by plotting the initial phosphorescence intensity (at 1270 nm) as a function of the laser dose and comparing the slope with that obtained with 1*H*-phenalen-1-one in toluene as the standard (see the Experimental Section for further details). Plots of the compounds are shown in Figure 4, attesting the good linearity obtained, and the resulting data can be found in Table 2. From Table 2, it can be seen that the singlet oxygen formation yields are roughly constant with values lying between 0.52 and 0.59 with the exception of C6BPhBt where this value is significantly lower,
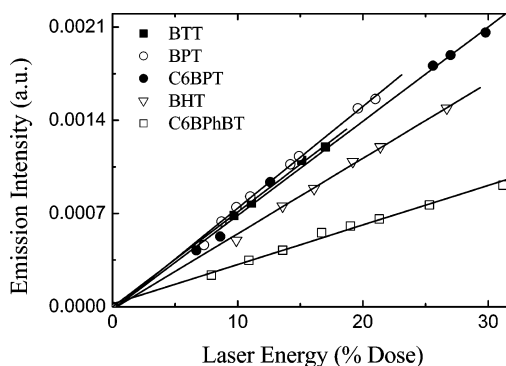

Figure 4. Plots of initial phosphorescence of singlet oxygen at 1270 nm as a function of laser intensity for the cruciform oligothiophenes in toluene at $T = 293$ K.

$\phi_\Delta \approx 0.26$ (see Table 2). Note also that they are also very close to the quantum yields for triplet formation, providing support for the latter values and indicating that the efficiency of triplet energy transfer to produce singlet oxygen ($S_\Delta = \phi_\Delta/\phi_T$) is very close or nearly 1, suggesting very efficient energy transfer from the cruciform oligomers to ground-state triplet molecular oxygen. Since singlet oxygen formation is observed following photolysis of aerated solutions of conjugated polymers, it may have important implications in a device working and consequently lead to polymer degradation.[41]

Conclusions

We have investigated a new family of compounds, designated as cruciform oligothiophenes, which can be considered to be closely related to the well-known linear oligothiophenes (αns). It was shown that extended conjugation, between the two αn moieties of the cruciform oligothiophenes, is limited in the S_1 state of the compounds and as a consequence the spectral properties are similar to those of their parent linear oligothiophenes. In the triplet state, there is evidence that the decoupling (by, presumably, the presence of an orthogonal dihedral angle) between the two moieties is more pronounced. Although this similarity exists in the spectral properties, the photophysical properties are different from their oligothiophene counterparts. The main difference resides in the fact that internal conversion from S_1 to S_0 is efficient with the present compounds, whereas with the αns it was found to be negligible. Due to this increase in the ϕ_{IC} values and the fact that more than 50% of quanta are lost through the intersystem crossing $S_1 \rightsquigarrow T_1$ channel (with the exception of C6BPhBT), the fluorescence efficiency decreases when compared with the parent αns. The exception is C6BPhBT where the link between the two units is made through 1,4-phenylene units. Investigations under progress with phenylene-like and phenylene−fluorene-like cruciform oligomers show an increase of the fluorescence quanta efficiency, suggesting this to be an important route to follow with regard to increasing photoluminescence yields.

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