# Tuning of the excited-state lifetime by control of the structural relaxation in oligothiophenes

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The optical excitations of quaterthiophenes in which one (or two) inter-ring torsional angles have been blocked by chemical bridging have been studied with various cw and time-resolved spectroscopic techniques. The suppression of inter-ring torsion modifies the deactivation path of the excited state leading to a reduction of nonradiative decay. This implies an increase of the lifetime of the singlet excited state and therefore of the photoluminescence quantum yield for the compounds with reduced conformational mobility. It is found that triplet transient absorption spectra are strongly affected by central inter-ring bridging, showing features which are tentatively related to different conformers.
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Thiophene oligomers (Tn) possess extensive $\pi$-electron delocalization along the molecular backbone which makes them interesting for various optoelectronic applications.[1–5] Due to this applicative interest and to the fact that they can be used as model compounds for the parent polymer (polythiophene), the photophysics of Tn (n ranging from 1 to 8) have been extensively studied.[6,7] Due to the flexibility of molecular design the optical properties of the oligothiophenes can be finely tuned by changing the length of the conjugated chain and, for a given chain length, by substituting hydrogen atoms with proper chemical groups. As a matter of fact it is widely recognized that inter-ring twisting controls the degree of conjugation and therefore the energy position of the absorption and emission spectra.[8,9] Indeed, the solution absorption spectra at room temperature lack the vibronic structure and they are considerably blueshifted with respect to the corresponding frozen solution data. This is indicative that a variety of nonplanar conformations coexists at room temperature because of the torsional mobility around the inter-ring C-C bonds. In solution, the photoexcitation scenario of oligothiophenes can then be briefly described as follows: since the absorption of visible light takes place on a very rapid time scale, the initially formed excited singlet state ($S_1$) possesses the same distorted configuration as the
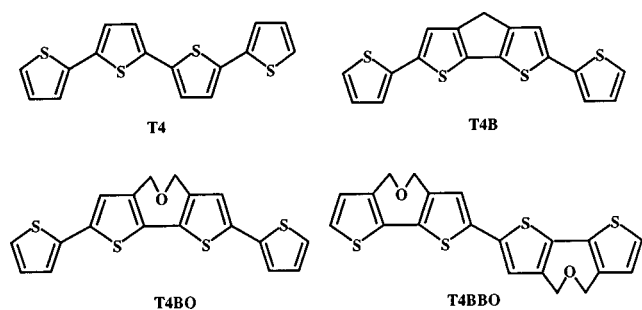
FIG. 1. Chemical structures of quaterthiophenes.

ground state ($S_0$), according to the Frank-Condon principle. However, as this configuration does not correspond to the equilibrium excited-state geometry, a planarization, affecting mostly the central part of the oligomer,[10] takes place within a few picoseconds[11] yielding a relaxed $S_1^*$ state through emission of inter-ring (torsional and stretching) quanta. Three deactivation pathways of $S_1^*$ are possible: (1) internal conversion (IC) which implies a nonradiative energy loss through the coupling with internal and/or solvent vibrational modes; (2) intersystem crossing (ISC) towards a triplet state ($T_n$); (3) radiative emission. The competition between nonradiative (1 and 2) and radiative (3) processes determines the photoluminescence quantum yield of the oligomer.

With the intent of clarifying the role of electron-torsional coupling on the photophysics of oligothiophenes, we have synthesized and studied a series of quaterthiophenes in which one or two inter-ring torsional angles have been blocked by chemical bridging. Two types of adjacent ring bridgings have been employed (see Fig. 1); one rigid bridge (T4B) and one flexible bridge (T4BO and T4BBO) which contains an oxygen atom. In this paper we study the optical and electronical properties of these compounds and their parent unsubstituted oligomer T4 by using several spectroscopic techniques. The comparison between T4 and T4B, T4BO and T4BBO provides information on the role of the conformational mobility and the electron-torsional coupling on the deactivation processes of the singlet excited states.

In Fig. 1 the chemical structure of quaterthiophene (T4), 2,6-bis(2-thienyl)-4H-cyclopenta[2,1-b;3,4-b'] (T4B), 5,5'-bisthienyl-dihydrodithieno[3,2-c;2',3'-e]oxepine (T4BO), and 2,2'-bisdihydrodithieno[3,2-c;2',3-e]oxepine (T4BBO) are reported. The synthesis and the characterization of the molecules will be reported elsewhere.[12]

Measurements were performed at room temperature for the oligomers dissolved in tetrahydrofuran (THF) solutions with concentrations of about $10^{-6}$–$10^{-5}$ mol/l. PL quantum yields were determined by using quinine sulphate solutions as a reference. PL time-resolved measurements were performed by exciting with the second harmonic of a pulse compressed Nd:YAG laser delivering 4 ps pulses at a repetition rate of 80 MHz. Temporal dispersion of the PL signal was achieved through a Hamamatsu optical sampling oscilloscope with $\approx$20 ps time resolution.

Transient transmission difference spectra ($\Delta T/T$) have been measured in the range from 400 to 770 nm using a Ti:sapphire laser system with chirped pulse amplification. The excitation pulses at 390 nm were generated by second harmonic of the fundamental beam. To probe the photoinduced transmission changes we used a white light supercon-
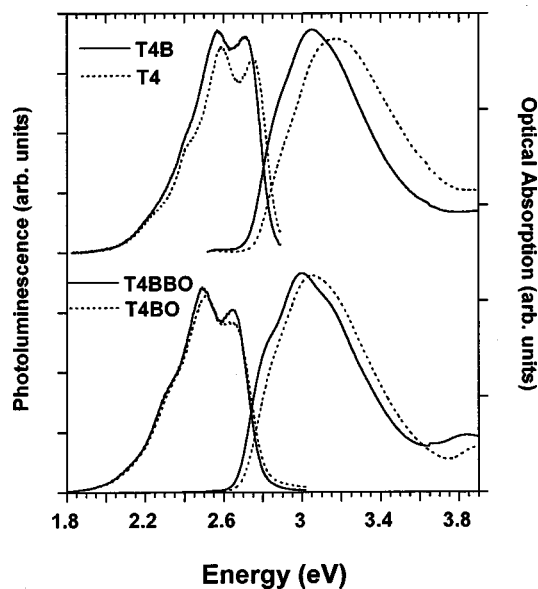


FIG. 2. Absorption and photoluminescence spectra of quaterthiophenes in THF solution at room temperature.

tinuum pulse. Transmission difference spectra are obtained by subtracting pump-on and pump-off data collected by the same silicon diode array. The pump beam was focused to a spot size of about 100 $\mu$m and linearly polarized at the magic angle with the probe to avoid orientational artefact in the measured dynamics. For pump-probe experiments the oligomers were dissolved in THF at concentrations of about $10^{-4}$ mol/l. Ground-state absorption of the solution was checked to assure that no aggregation was taking place. Absorbed pump photon flux was about $10^{14}$ cm$^{-2}$ for all the samples and the cuvette thickness was 0.5 mm.

In Fig. 2 the absorption and PL spectra of the oligomers in diluted THF solutions are reported. The broad and structureless absorption of T4 is indicative of the multiplicity of conformations assumed in the electronic ground state by the unsubstituted thiophene oligomer in good solvent solutions. Upon single and double bridging of the thiophene rings, which reduces the degree of freedom for inter-ring torsions, the absorption spectra slightly narrow and some structure appears. A comparison between molecules possessing different types of bridging is not trivial since the presence of the oxygen atom in the flexible bridge may affect the electronic properties of the molecule independently on the conformation of the backbone. For this reason in the following we will discuss the effect of torsional mobility by comparing T4 with T4B and T4BO with T4BBO. A red shift of the overall absorption is observed going from T4 to T4B, and from T4BO to T4BBO. These data are indicative of the presence of a smaller number of conformations and of a significant increase of the effective conjugation length in the chemically bridged quaterthiophenes.

The photoluminescence spectra of the four oligomers show well-resolved peaks whose energy separation ($\approx$150 meV) roughly corresponds to the vibrational ring mode more coupled with the electronic $\pi - \pi^*$ transition.[13] This is in contrast with the unstructured absorption of T4 and the very weak structures observed in the absorption spectra of the bridged oligomers. Indeed in the first excited state a partially

TABLE I. Photophysical data of the oligomers in THF solution, at room temperature. $\lambda_{Abs}$ is the maximum absorption position; $\lambda_{PL}$ is the maximum of the short wavelength PL component.

|        | $\lambda_{Abs}$ (nm) | $\lambda_{PL}$ (nm) | $\Delta E_S$ (eV) | $\Phi_F$ | $\tau_F$ (ns) | $K_R$ (ns$^{-1}$) | $K_{NR}$ (ns$^{-1}$) | $\Phi_T$ | $K_{ISC}$ (ns) |
|--------|------|------|------|------|------|------|------|------|------|
| T4     | 390  | 450  | 0.58 | 0.17 | 0.41 | 0.41 | 2.02 | 0.71[a] | 1.72 |
| T4B    | 407  | 459  | 0.48 | 0.24 | 0.53 | 0.45 | 1.43 | 0.60 | 1.14 |
| T4BO   | 406  | 467  | 0.54 | 0.11 | 0.28 | 0.39 | 3.18 | 0.81 | 2.89 |
| T4BBO  | 413  | 468  | 0.50 | 0.10 | 0.38 | 0.26 | 2.37 | 0.79 | 2.08 |

[a]Reference 17.

quinoid structure is attained[10] and the inter-ring torsions are inhibited by the partial double bond character of the inter-ring bonds. As a consequence the distribution of rotational conformers is much narrower in the excited state than in the ground state[14] leading to PL spectra which are only slightly affected by bridging of thiophene rings. As reported in Table I, the Stokes shift $\Delta E_s$ (measured as the energy difference between the position of the maximum absorption and the maximum PL) decreases upon rigid bridging from T4 to T4B, and upon oxygen bridging from T4BO to T4BBO. For isolated molecules the Stokes shift is proportional to the extent of geometrical relaxation that the molecule undergoes upon photoexcitation. As expected, $\Delta E_s$ is larger for the thiophene molecules which posses a higher torsional mobility in the ground state; that is T4 and T4BO. In fact, for the T4 (T4BO) molecule, the extent of geometrical relaxation towards a planar conformation in the excited state is larger than for T4B (T4BBO).

Picosecond optical probes applied to thiophene oligomers in solution have detected size-dependent features in the transient absorption and emission spectra.[15–19] In particular, it has been found that the lifetime of the first singlet excited state increases systematically with the average conjugation length of the oligomers. This can be ascribed to an increase of the nonradiative decay time, the radiative decay time being almost size independent. Rate constants of intersystem crossing ($K_{ISC}$) and of internal conversion ($K_{IC}$) decrease strongly from T2 to T6 and level off for T7.[20] This leads to a maximum of both fluorescence quantum yield ($\Phi_F = 0.4$) and fluorescence lifetime ($\tau_F = 0.99$ ns) in T6. This behavior has been explained in terms of a thermally activated ISC process whose probability decreases with the oligomer chain length.[21] Nevertheless other factors, such as ring torsion and backbone planarity, may play an important role in determining the excited-state lifetime of $\pi$-conjugated ring containing systems. In this frame we discuss the values of $\Phi_F$ for T4 and T4B which were found to be 0.17 and 0.24, respectively (see Table I). The literature data on T4 report values ranging from 0.11 to 0.2.[15,22,23] The higher value of the $\Phi_F$ in T4B could be due to two different concomitants effects: the longer effective conjugation length, or the reduced efficiency of nonradiative decay channels, due to the presence of the chemical bridge. Since the former is a very small effect in these compounds, the second hypothesis seems more likely. Further information is obtained by time-resolved PL measurements.

In Fig. 3 the temporal dynamics of PL up to 2 ns are compared for all the oligomers. The rise time of the emissions are shorter than the resolution time, thus showing that the formation times of the emitting states are in the picosec-

ond or subpicosecond range. All the kinetics are monoexponential with time constant $\tau_F$ reported in Table I. Radiative ($K_R$) and nonradiative rates ($K_{NR}$) are also shown, where $K_R = \Phi_F / \tau_F$. In T4, the values $K_{ISC} = 1.72$ ns$^{-1}$ and $K_{IC} = 0.29$ ns$^{-1}$, obtained from literature,[17] indicate that ISC dominates the nonradiative processes. It has been found that $K_{IC}$ is a small fraction of $K_{ISC}$ and is constant within the oligothiophene family.[21] We therefore assume the same $K_{IC}$ for all the series of quaterthiophenes and report in Table I the values of $K_{ISC}$ so inferred.

If we look at the nonradiative decay rates, the effect of the reduced conformational mobility (going from T4 to T4B, and from T4BO to T4BBO) is detected by the decrease of $K_{NR}$. If we assume that IC does not change upon bridging, we can speculate that the higher values of $K_{NR}$ observed in the molecules possessing flexible bridging (T4BO to T4BBO) is related to higher intersystem crossing towards triplet states. It is however possible that in these molecules additional nonradiative channels appear due to the oxygen interaction with the $\pi$ system.

Femtosecond time-resolved pump and probe experiments have yield valuable information on the initial stage dynamics of both radiative and nonradiative processes. Transient transmission difference spectra ($\Delta T/T$) of T4B in solution are shown as an example in Fig. 4. At 0 ps pump-probe delay we see a positive $\Delta T$ between 440 and 550 nm, which is to be assigned to stimulated emission (SE), and a negative $\Delta T$,
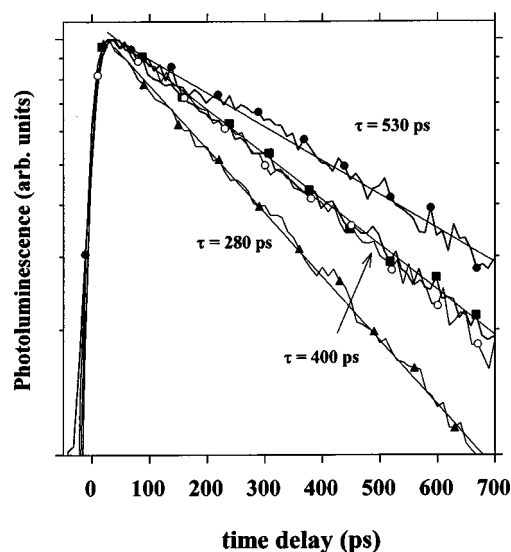


FIG. 3. Time-resolved PL decays of T4B (solid circle), T4 (solid square), T4BBO (open circle), and T4BO (solid triangle) THF solutions.
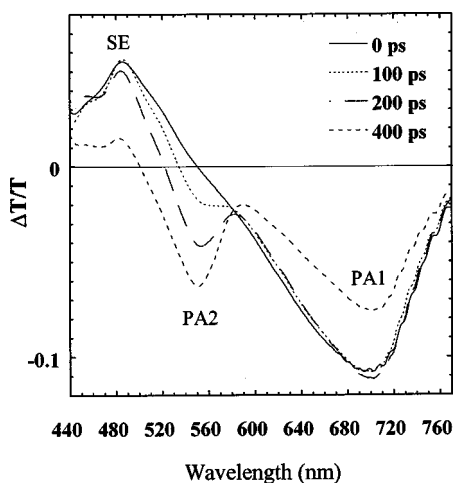
FIG. 4. Transient transmission difference ($\Delta T/T$) spectra of T4B solution at different time delays.



i.e., photoinduced absorption (PA1), at longer wavelengths. Upon increasing the probe delay with respect to excitation, a new negative band appears at 550 nm (PA2), while the initial SE and PA1 decay. The assignment of the high-energy peak to photoinduced gain (i.e., SE) is supported by the fact that there is a good spectral correspondence between the SE region and the cw PL peak. Based on the corresponding dynamics with SE we assign PA1 to singlet excited-state transitions.

At short delay times the spectra of all the oligomers show very similar features corresponding to SE and PA1 [see Fig. 5(a)], while at 400 ps both SE and PA1 are strongly reduced. At 400 ps in both T4BBO and T4 the PA2 band is split in a low-energy (LE) and a high-energy (HE) component, as reported in Fig. 5(b) after proper subtraction of the singlet features. The LE component of PA2 is not observed in the spectra of T4B and T4BO. The presence of the oxygen atom only affects the position of the HE component.

The long-lived transient PA2 band can be identified as optical transition within the triplet manifold. In general, structures in the PA band are assigned to vibronic replicas. However, this explanation appears unlikely in the present case, since all the molecules studied should possess similar electron-vibrational coupling. On the other hand, transitions to different $T_n$ states are excluded by calculations which show that the oscillator strength of $T_1 - T_n$ is concentrated into one transition.[21] We therefore propose to attribute the structures observed in the transient absorption band of the triplet, to different conformers in the $T_1$ state, as discussed below.

The two components of the PA2 band, observed for the molecules (T4 and T4BBO) for which the central inter-ring torsion is allowed, can be assigned to two conformers. In T4B and T4BO, where this torsion is inhibited, only the HE component of the PA2 band is observed. Indeed the strong influence of the central inter-ring rotation on the photophysical properties of these compounds is consistent with the fact that the triplet wave function is strongly confined in the central part of the oligothiophene and its extension does not exceed two rings.[21] Calculations of Beljonne et al.[21] show that in the triplet $T_1$ state the bond alternation of the two
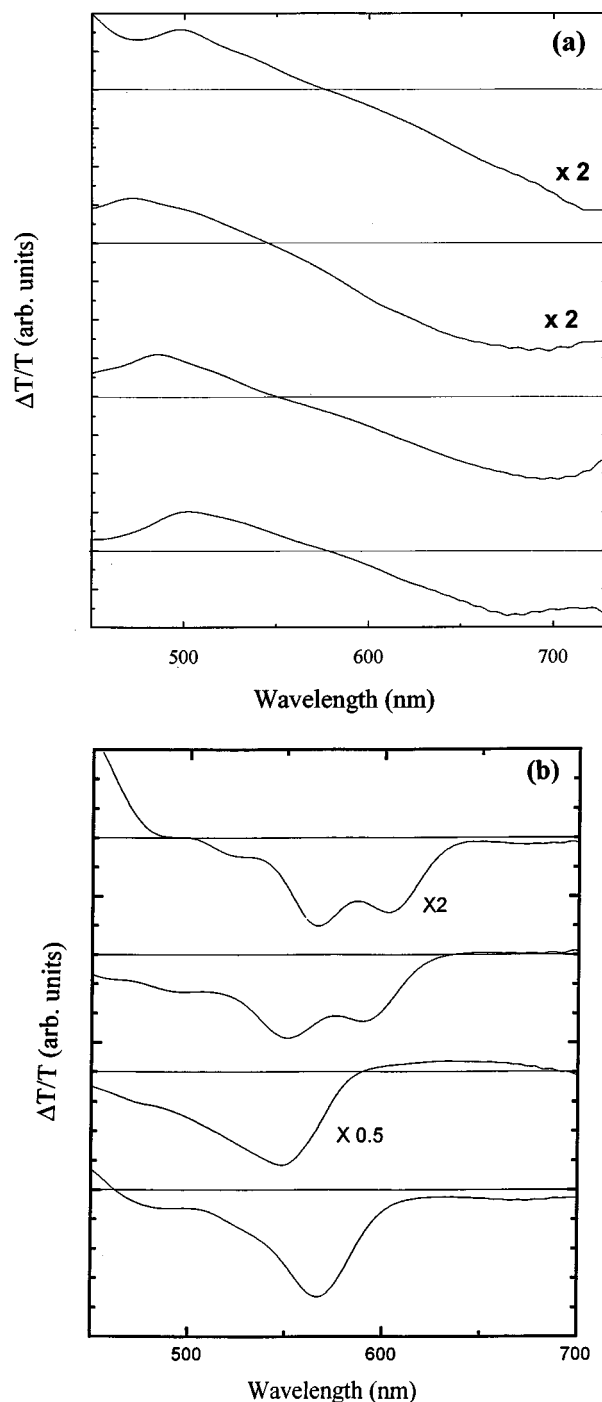


FIG. 5. Transient transmission difference of quaterthiophenes measured at 0 ps (a) and 400 ps (b) delay time for T4BO, T4B, T4, and T4BBO from the bottom to the top. The spectra at 400 ps delay are obtained by a proper subtraction of the singlet features (see text). The spectra are displaced vertically for clarity.

central rings of T4 is completely reversed leading to a double character of the central inter-ring bond of the molecule. It follows that the two central rings of T4 are forced to be planar, assuming only two conformations, namely the anti (A) and syn (S) planar conformations. The antiplanar conformers are reported in Fig. 1, the synplanar conformer of T4BBO can be constructed by rotating either pair of thienyl rings so that all four sulfur atoms are aligned. The synplanar conformer of T4 would have the same structure as T4B and

T4BO. We propose that the coexistence of the *A* and *S* conformers in the $T_1$ state of T4 and T4BBO accounts for the LE and HE components of PA2, respectively. For the molecules (T4B and T4BO) with the central inter-ring bond blocked in the *S* conformation only the HE component is observed. The higher-energy position of the PA2 component associated with the *S* conformation is consistent with the stronger repulsive force of the two sulphur atoms, with respect to the *A* conformation, which is the most probable in T4.[24]

The presence of oxygen atoms does not seem to influence the role of the two conformations, while it does influence the position and the efficiency of the emission of both T4BO and T4BBO. Work is in progress to clarify the nature of this effect by studying quaterthiophenes with different types of ring bridging.

In conclusion, we have shown that the effect of the chemical bridging on the photoexcitations properties of the quaterthiophenes is sizeable because the presence of the bridge alters the energy position and the efficiency of the emission and controls the branching to triplet states which show a composite structure probably due the coexistence of different conformers. Moreover, we have demonstrated that a simple size-dependent model based on the free-electron molecular orbital approximation fails to explain the whole experimental behavior pointing to the role of inter-ring torsions in the relaxation branching between radiative and nonradiative states and the consequent possibility of tuning the singlet excited-state lifetimes by inter-ring chemical bridging.

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