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Geometry relaxation and intersystem crossing of quaterthiophene studied by femtosecond spectroscopy

Si-mei Sun, Song Zhang*, Kai Liu, Ya-ping Wang and Bing Zhang*

Quaterthiophene is used as a fluorescent marker for biological applications, but the intrinsic excited state dynamics for its high triplet-formation yield is still under debate due to the complexity of the molecule structure and the undetermined energy level order. In this work, ultrafast geometry relaxation and intersystem crossing of quaterthiophene in 1,4-dioxane are studied by femtosecond time-resolved spectroscopy combined with quantum calculations. Transient absorption spectra at pump wavelength of 400 nm are completely recorded up to the delay time of 1 ns. The kinetic traces of excited state absorption indicate that geometry relaxation occurs on the S1 potential energy surface with a time constant of ~70 ps. Two triplet-triplet absorption bands centered at 563 nm and 600 nm show a direct dynamical conversion. The intersystem crossing is determined to be ~398 ps. The high triplet yield is measured to keep ~0.7 via the efficient intersystem crossing. On the basis of quantum chemical calculations, a general mechanism is proposed to describe the geometry relaxation and intersystem crossing process.

1. Introduction

Oligothiophenes (nT, n=ring size) are widely studied for their use in semiconductor such as transistor or solar cells, and their fluorescence properties and synthetic flexibility make them robust markers with the emission in the UV-VIS range.1,4 They are foreseen as the dominating optical probe for in vivo studies of protein aggregates and DNA hybridization.14-6 The nature involved in radiative and nonradiative mechanism and the factors influencing the efficiency of the processes are two basic targets to be clarified. Static absorption measurements7,8 and time-resolved spectroscopic studies9-17 of oligothiophenes in solution have been reported. The fluorescence lifetimes and quantum yields of oligothiophenes up to six rings in solution were determined using time-resolved fluorescence spectroscopy, and the radiative and nonradiative rate constants were estimated.10,18 It is revealed that the fluorescence quantum yields increase while the triplet quantum yields decrease when extending the chain length of the oligomer. Becker et al.18 found the rates of an internal conversion (IC) are very small comparing with the rates of an intersystem crossing (ISC) and confirmed that nonradiative decay processes are dominated by an ISC. It is believed that the excited state relaxation processes are dominated by a triplet formation and a fluorescence for all nT. The ISC from the singlet state to the triplet state of all nT have been observed with time constants increasing from 51 ps for 2T to 1100 ps for 6T.11,13,18 The triplet quantum yield of oligothiophenes decreases with increasing n: 0.99 for bithiophene (2T), 0.95 for terthiophene (3T), 0.73 for quaterthiophene (4T).11,15,18,19 The high triplet formation yield in oligothiophenes strongly deviates from a common phenomenon found in most of molecules where the ratios of an ISC to an IC and fluorescence rates are small.20 The phenomenon of the extremely strong ISC is an interesting process for both basic understanding and applications.

In oligothiophenes, the contribution of the triplet T2 state to the high triplet quantum yield cannot be ignored.21-25 Rentzsch and co-workers determined the energies of the low-lying triplet states of oligothiophenes by photodetachment photoelectron spectroscopy.25 It is shown that the energy of the T2 state of 2T is almost degenerate to the S1 and T2 states of 3T is somewhat higher than the S1 state, while the T2 state of 4T is clearly higher. Since the energy of the T2 state becomes higher with the increasing chain length, the T2 state is much more difficult to participate in ISC and the triplet quantum yields decrease. However, quantum chemical calculations show there may be two or more triplet states below the S1 state for oligothiophenes, n ≥ 3.21-24 Fabiano predicted that the T2 states of 3T and 4T are 0.14 eV and 0.35 eV below the S1 state, respectively.21 Rubio et al. showed that the S1 and T2 states of 3T become degenerate along the geometry relaxation on the S1 state, which leads to a favorable occurrence of ISC, while the parallel process was expected to be less favored in 4T because of the increased S1-T2 energy gap.23 And authors also proposed the T3 state should be considered in ISC processes although it is higher than the S1 state. However, few experiments were carried out and discussed on 4T by time resolved spectroscopy.

Oligothiophenes are considered to be quite flexible molecules with respect to the rotation around the inter-ring bonds. The percentage of cis conformer contribution decreases from 2T to 3T.
and vanishes for 4\(T\) and 5\(T\) by electron spin resonance spectroscopy.26 The ground state of trans-3\(T\) was computed at the planar (\(C_{2v}\)) and twisted (\(C_4\) and \(C_2\)) optimized geometries.23 The \(C_4\) and \(C_2\) twisted conformers have almost the same energy, with the \(C_{2v}\) conformer a little more stable. And the planar \(C_{2v}\) structure is predicted to be higher in energy. The interannular torsion angle in the twisted conformers is 145.058° at \(C_{2v}\) geometry and 144.608° at \(C_2\) geometry, respectively. Unlike the ground-state conformation, a more rigid planar structure has been suggested for the \(S_1\) state of oligothiophenes on the basis of the asymmetry observed between the absorption and emission spectra.11,19,27 For \(3T\), the excited states are proven to be stable in the planar \(C_{2v}\) conformation. For \(4T\), calculations have been described in detail within \(C_{2v}\) symmetry in a gas phase.23 However, the geometry relaxation is mentioned in oligothiophenes after the excitation, but no ultrafast experiments are reported until now.

In this work, we employ femtosecond transient absorption spectroscopy to elucidate the excited state dynamics of quaterthiophene in solution, especially geometry relaxation and ISC processes. The characteristic spectra bands were measured and analyzed in detail combined with quantum chemical calculations. The kinetic traces of transient absorption disclose a mechanism of geometry relaxation and contribution of the triplet states. Quantum chemical calculations are also performed to help understand the suggested mechanism.

2. Experiment

Quaterthiophene (99% purity) was purchased from Sigma, and used without further purification. 1,4-dioxane (99% purity) purchasing from Aladdin was used as a solvent. The concentration of quaterthiophene in 1,4-dioxane was 1 mM at room temperature and a fresh sample was prepared for each measurement. The absorption and emission spectra were recorded on the UV-VIS spectrometer (INESA, L6) and the spectrometer (Princeton, SpectraPro 2500i) in a 1 mm quartz cell, respectively.

Ultrafast broadband absorption measurements are performed based on the Ti:sapphire femtosecond laser system. Details of the femtosecond laser system have been described elsewhere.28 Briefly, the seed beam is generated by a commercial Ti:sapphire oscillator pumped by a CW second harmonic of an Nd:YVO4 laser, and then amplified by an Nd:YLF pumped regenerative amplifier to generate a 1 kHz pulse train centered at 800 nm of approximately 35 fs pulse width and with maximum energy of 1 mJ/pulse. Excitation at 400 nm is the second harmonic generation of the fundamental pulse obtained by a 0.5 mm thick BBO crystal, with pulse energy ~ 6 \(\mu\)J at the sample position. A white light continuum generated by focusing the fundamental light at 800 nm on a 1 mm sapphire plate is reflected from the front and back surfaces of a quartz plate to obtain probe and reference beams. The pump and probe pulses intersect in the sample at an angle of ~ 4°, and the reference beam is transmitted through the sample at a different spot. The relative polarization of the pump and probe pulses is set to the magic angle for all the measurements. A linear translation stage is used to delay the probe beam to monitor the pump-probe dynamics. The resulting spectra are detected by a CCD camera (PI-MAX, 1024×256 pixel array) equipped with a spectrometer (Princeton, SpectraPro 2500i). The instrumental response function of the system, determined by cross correlation between excitation and probe pulses using the optical Kerr-gate method, is typically better than 150 fs.

All quantum chemical calculations are performed using the Gaussian09W suit of program.29 The geometries of the ground and excited states of quaterthiophene are optimized using MP2 and B3LYP with 6-31(d,p) basis set in gas phase and 1,4-dioxane solution, respectively. The stationary points are also confirmed by the vibrational frequencies analysis. The energies of excited states are performed using the B3LYP function based on optimized geometries of the ground and excited states, respectively. The B3LYP function provides accurate excited-state ordering, excited-state transition energies, oscillator strengths, transition dipole moments and singlet-triplet energy gaps, particularly when solvent effects are taken into account. Solvent effects are expected to lead to large ground- and excited-state energy changes in heteroaromatic compounds. Thus, the effect of the bulk solvent dielectric on the ground-state geometries and on the excited-state vertical energies was modeled by performing self-consistent reaction field (SCRF) calculations using the polarizable continuum model (PCM) with the integral equation formalism.

Table 1. Vertical excitation energies (eV) calculated with \(C_2\) symmetry at the optimized geometries of the \(S_0\) and \(S_1\) states using B3LYP/6-31(d,p) in 1,4-dioxane.

<table>
<thead>
<tr>
<th>State</th>
<th>(S_0)</th>
<th>(S_1)</th>
<th>Theory</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_0)</td>
<td>0.193</td>
<td></td>
<td>1.65(^{23})</td>
<td>1.67, 1.76(^{23})</td>
</tr>
<tr>
<td>(T_1)</td>
<td>1.674</td>
<td>1.058</td>
<td>3.3(^{39})</td>
<td></td>
</tr>
<tr>
<td>(T_2)</td>
<td>2.427</td>
<td>2.094</td>
<td>2.74(^{23})</td>
<td>3.2, 3.11, 2.76(^{31})</td>
</tr>
<tr>
<td>(S_1)</td>
<td>2.758</td>
<td>2.287</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_0)</td>
<td>3.198</td>
<td>2.995</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta E_1)</td>
<td>1.084</td>
<td>1.230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta E_2)</td>
<td>0.332</td>
<td>0.193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta E_3)</td>
<td>0.440</td>
<td>0.708</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \(\Delta E_1\) presents the energy gap of the \(S_1\) and \(T_1\) states;
\(^b\) \(\Delta E_2\) presents the energy gap of the \(S_1\) and \(T_2\) states;
\(^c\) \(\Delta E_3\) presents the energy gap of the \(S_1\) and \(T_0\) states.

3. Results and Discussion

3.1 Static absorption and transient absorption spectra

The absorption and fluorescence spectra of quaterthiophene are shown in Fig 1. The designation of \(C_4\) and \(C_6\) atoms of the molecular structure is illustrated in the upper part. As can be seen, the
absorption spectrum at wavelength of λ>200 nm reveals two broad and structureless bands. The first band is associated with a transition from the S₀ state to the first optically bright S₁ state, which has a large oscillator strength. Following excitation at 400 nm to the S₁ state, the strongly redshift, structured emissions with three maxima at λ=455, 480, 515 nm are observed, respectively. The vertical excited energies, oscillator strengths and transition dipole moments at the geometries of the ground and S₁ states are calculated and presented in Table 1, respectively.

The transient absorption spectra of quaterthiophene in 1,4-dioxane were measured from 450 to 700 nm with the excitation at 400 nm, as shown in Fig. 2. The transient absorption spectra are recorded up to the delay time of 1 ns and show an abundant information. The structured blue region from 450 to 570 nm is elucidated by the stimulated emission (SE) and well corresponding to the steady fluorescence. The red region in the longer wavelength is a positive signal and clearly divided into two spectral regions for the different contributions. It is elucidated by the excited singlet and triplet states absorption. In the spectra of the wavelength > 620 nm, a broad and structureless band is observed and decays in several hundreds of picoseconds. It contributes to the excited state absorption (ESA), the shape and wavelength of which are well agreed with previous picosecond studies. As delay time increases, the intensities of the ESA and SE bands decrease while two new discrete positive bands centered around 563 and 600 nm appear. These two bands are rising and remain unchanged up to the longest delay time we measured. The decrease signal and a simultaneously increase absorption combined with an isosbestic point at ~613 nm. This clearly indicates a direct dynamical conversion from one state to the other state. Both rising bands are assigned to triplet-triplet absorption (TTA) which is well agreed with previous studies by nanosecond flash and picosecond time-resolved experiments. In these spectral regions, these characteristic bands overlapped with each other to a certain extent.

The longtime constant is set as 40 µs.

Decay-associated difference spectra (DADS) are obtained from the transient absorption data after SVD/global fit analysis. The deconvoluted RTA spectrum at 200 nm reveals two broad bands reported in solution at room temperature, which has been related to the presence of several nonplanar conformers. As delay time increases, the intensities of the ESA and SE bands decrease while two new discrete positive bands centered around 563 and 600 nm appear. These two bands are rising and remain unchanged up to the longest delay time we measured. The decrease signal and a simultaneously increase absorption combined with an isosbestic point at ~613 nm. This clearly indicates a direct dynamical conversion from one state to the other state. Both rising bands are assigned to triplet-triplet absorption (TTA) which is well agreed with previous studies by nanosecond flash and picosecond time-resolved experiments. In these spectral regions, these characteristic bands overlapped with each other to a certain extent.

As mentioned above, the fluorescence spectra show a well-resolved vibrational structure in contrast to the broad structureless absorption bands reported in solution at room temperature, which has been related to the presence of several nonplanar conformers. For 4T, only the all-trans conformation was considered. The ground and low-lying excited states of 4T were optimized at the planar (C₂ᵥ) and twisted (C₂) conformers, respectively. According to the MP2 and B3LYP results, the planar C₂ᵥ conformer is slightly higher than the C₂ twisted conformers in the ground state, but only by less than 0.005 eV. The analysis of vibrational frequencies also shows that

![Fig. 2 The transient absorption spectra of quaterthiophene in 1,4-dioxane measured with excitation at 400 nm. SE: stimulated emission, TTA: triplet-triplet absorption, ESA: excited state absorption.](image)

![Fig. 3. Decay-associated difference spectra (DADS) of the three time constants extracted from the transient absorption data after SVD/global fit analysis.](image)

### Table 2. Results of the global fit analysis of the absorption–time profiles of quaterthiophene in 1,4-dioxane.

<table>
<thead>
<tr>
<th>λ(nm)</th>
<th>a₁</th>
<th>τ₁(ps)</th>
<th>a₂</th>
<th>τ₂(ps)</th>
<th>a₃</th>
<th>τ₃(µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>453</td>
<td>-0.039(14)</td>
<td>70(7)</td>
<td>-0.906(15)</td>
<td>398(10)</td>
<td>0.161(11)</td>
<td>constant</td>
</tr>
<tr>
<td>480</td>
<td>-0.048(10)</td>
<td>70(7)</td>
<td>-0.976(11)</td>
<td>398(10)</td>
<td>0.222(8)</td>
<td>constant</td>
</tr>
<tr>
<td>513</td>
<td>-0.054(6)</td>
<td>70(7)</td>
<td>-1.002(6)</td>
<td>398(10)</td>
<td>0.361(5)</td>
<td>constant</td>
</tr>
<tr>
<td>553</td>
<td>-0.042(4)</td>
<td>70(7)</td>
<td>-1.033(5)</td>
<td>398(10)</td>
<td>0.941(3)</td>
<td>constant</td>
</tr>
<tr>
<td>563</td>
<td>-0.020(5)</td>
<td>70(7)</td>
<td>-0.972(5)</td>
<td>398(10)</td>
<td>1.055(4)</td>
<td>constant</td>
</tr>
<tr>
<td>600</td>
<td>0.021(5)</td>
<td>70(7)</td>
<td>-0.453(6)</td>
<td>398(10)</td>
<td>1.009(4)</td>
<td>constant</td>
</tr>
<tr>
<td>606</td>
<td>0.013(6)</td>
<td>70(7)</td>
<td>-0.212(5)</td>
<td>398(10)</td>
<td>1.004(5)</td>
<td>constant</td>
</tr>
<tr>
<td>675</td>
<td>-0.270(3)</td>
<td>70(7)</td>
<td>1.165(4)</td>
<td>398(10)</td>
<td>0.081(3)</td>
<td>constant</td>
</tr>
<tr>
<td>685</td>
<td>-0.273(4)</td>
<td>70(7)</td>
<td>1.167(4)</td>
<td>398(10)</td>
<td>0.080(4)</td>
<td>constant</td>
</tr>
<tr>
<td>695</td>
<td>-0.259(4)</td>
<td>70(7)</td>
<td>1.166(5)</td>
<td>398(10)</td>
<td>0.068(3)</td>
<td>constant</td>
</tr>
</tbody>
</table>
there are no imaginary frequencies at C₂ conformer but two imaginary frequencies at C₁₈ conformer. The twisted structure with C₂ symmetry is proved a more stable than the planar geometry in the ground state. The same results are obtained in gas phase and 1,4-dioxane solution. In C₂ twisted conformer, the interannular torsion angle is 147.234° at MP2/6-31(d,p). Compared to the ground state, it obviously shows that the inter-annular C₃-C₄ bonds and C₅-C₆ bonds shorten in the excited S₁ state. These shortened bonds emerge a pronounced double-bond character. Since the C₃-C₄ and C-S bonds obviously increase after the excitation, the inner rings are mostly affected and become oblate in the S₁ state. Furthermore the interannular torsion angles of S-C₁-C₇-S and S-C₅-C₉-S change from 167.994° and 165.025° in the ground state to 179.977° and 179.966° in the S₁ state at B3LYP/6-31G(d,p) basis set, respectively. Our results show that molecule is produced from an aromatic-type to a quinoid-type structure and becomes more planar rigid after the excitation. The geometry relaxation of the lowest excited state is also suggested at different calculated levels. Siegert et al. predicted that a non-planar structure of quaterthiophene is needed to allow an efficient ISC dynamics from the S₁ state to the T₂ state. The dynamic trace of ESA > 620nm shows two main components of 70 ps and 398 ps. The coefficient of the short component is negative and opposite to the amplitude of 398 ps. The short one presents a rise component of ESA and associated with the geometry relaxation from Franck-Condon configuration to the relaxed S₁ state. The S₁ state nonadiabatically decays with lifetime of the 398 ps.

3.3 Intersystem crossing

The relaxed singlet excited state decays to form two discrete TTA bands directly located at 563 and 600 nm accompanied by forming an isoestic point, which indicates state-to-state relaxation. It is noticed that the rising components of both TTA bands are 398 ps. This rising components suggest the ISC process from the singlet state to the triplet state. The directly experimental ISC rate constants here are close to the estimated values by different methods. It is also been proved that there may be two or more triplet states below the S₁ state of oligothiophenes. According to the energy gap law, a small energy gap between the singlet and triplet states is benefit for an efficient ISC. Beljonne et al. pointed out that singlet-triplet energy differences lower than 0.5 eV were required to have a significant contribution to the ISC processes in 3T. In 4T, the energy gap ∆E₂ is more than 1 eV and becomes larger along the relaxing coordinate. The S₁-T₂ ISC channel cannot be considered as an efficient pathway for ISC. The T₂ state with the energy gap less than 0.5 eV is easy to devote to a channel for the ISC process. Furthermore, the S₁-T₂ energy gap becomes smaller from 0.332 to 0.193 eV along the relaxation coordinate. This trend is benefit to ISC between the S₁ and T₂ states. Apparently, internal conversion from the T₂ state to the T₁ state is very fast as expected, thus the instantaneous concentration of the T₂ state is very low, or their transition cross sections in absorption are too small to be detected in our experiments. The lifetime of 4T(T₂) was estimated to be only 38 ps. The triplet-formation quantum yield of quaterthiophene has been measured to be of the order of 0.67-0.80 depending on the solvent. In this work, the triplet-formation quantum yield has been approximately estimated to be 0.70 in 1,4-dioxane. The quantum yield still keeps a quite high value, although it is lower than the values of the quantum yields of 2T and 3T which are close to unit. Rentsch et al. proposed that the T₂ state located above the S₁ state but the S₁-T₂ ISC can still occurred in quaterthiophene. And the authors considered that the decrease of the triplet-formation quantum yield is attributed to an increase of the S₁-T₂ energy gap compared to the values in the shorter oligothiophenes. Anyway, the T₂ state should be consider to participate in the ISC process and make a significant contribution for the high triplet quantum yield of quaterthiophene. Rubio mentioned that the T₃ state should be considered in ISC processes, although the energy of the T₃ state is larger than the T₂ state. In gas phase, the T₃ state maybe an efficient ISC pathway because of the small energy gap although it is higher than the S₁ state. But in solution the energy gap ΔE₃ become larger along the geometry relaxation and is as large as 0.7 eV at the S₁ state structure and far away from 0.5 eV. The T₃ state could not be considered anymore as an efficient ISC pathway.

![Fig. 4](image-url) Fig. 4 Representative time traces of the transient absorption spectra of quaterthiophene recorded upon excitation at 400 nm in 1,4-dioxane: (a) 453nm, 480 nm and 513 nm; (b) 563 nm, 600 nm, and 685nm, with fits derived from global analysis of the data over the full 450-700 nm spectral range. The symbols are data, solid lines the overall least-squares fit curves.

![Fig. 5](image-url) Fig. 5 The schematic diagram of the proposed excited state relaxation mechanism of quaterthiophene in 1,4-dioxane.

4. Conclusions

In summary, a combined experimental and computational study on the excited state dynamics of quaterthiophene in 1,4-dioxane is presented. The data reveal that the excitation to the lowest singlet excited state results in an approximately 71 ps conformational relaxation from a twisted to a more rigid planar structure. The relaxed singlet excited state decays to form two discrete TTA bands directly centred at 563 nm and 600 nm.
with ~398 ps of ISC. Two triplet states are proved to energetically exist below the S\(_1\) state by quantum calculations. The intersystem crossing quantum yield is approximately 0.70 in 1,4-dioxane. According to the energy gap law, it suggests a favourable situation for the effective ISC process and the high triplet quantum yield that the energy gap between the S\(_1\) and T\(_2\) states becomes smaller during the geometry relaxation of the S\(_1\) state. A general photoinduced mechanism is drawn in Fig. 5 according to experiments and quantum chemical calculations.

Acknowledgements

This work was supported by the National Basic Research Program of China (Grant No. 2013CB922202) and the National Natural Science Foundation of China (Grant Nos. 11174328, 21273274, 21173256, 91121006, and 21203241).

References


