Volume 1 | Number 1 | Jan 2013 | Pages 1–100

## Photochemical & Photobiological Sciences

An international journal
www.rsc.org/pps

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/pps

# Photochem. Photobiol. Sci.

## ARTICLE

# 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 $S_1$ 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.[4-6] 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 measurements[7,8] and time-resolved spectroscopic studies[9-17] 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 $T_2$ state to the high triplet quantum yield cannot be ignored.[21-25] Rentsch 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 $T_2$ state of 2T is almost degenerate to the $S_1$ and $T_2$ states of 3T is somewhat higher than the $S_1$ state, while the $T_2$ state of 4T is clearly higher. Since the energy of the $T_2$ state becomes higher with the increasing chain length, the $T_2$ 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 $S_1$ state for oligothiophenes, n ≥ 3.[21-24] Fabiano predicted that the $T_2$ states of 3T and 4T are 0.14 eV and 0.35 eV below the $S_1$ state, respectively.[21] Rubio *et al.* showed that the $S_1$ and $T_2$ states of 3T become degenerate along the geometry relaxation on the $S_1$ 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 $S_1$-$T_2$ energy gap.[23] And authors also proposed the $T_3$ state should be considered in ISC processes although it is higher than the $S_1$ 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

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics Chinese Academy of Sciences, Wuhan 430071 (PR China),
Fax: (+86)027-87198576
E-mail: zhangsong@wipm.ac.cn; bzhang@wipm.ac.cn

and vanishes for 4T and 5T by electron spin resonance spectroscopy.[26] The ground state of trans-3T was computed at the planar ($C_{2v}$) and twisted ($C_s$ and $C_2$) optimized geometries.[23] The $C_s$ and $C_2$ twisted conformers have almost the same energy, with the $C_s$ 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 $C_s$ 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 $C_{2h}$ 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 µJ 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.
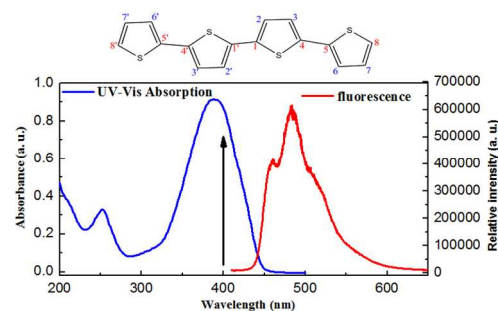


**Fig. 1** The room temperature absorption and emission spectra of quaterthiophene in 1,4-dioxane. The C atoms linking thiophene rings are defined as the $C_\alpha$ atoms (red), and the other C atoms are defined as the $C_\beta$ atoms (blue).

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.

| State | Optimized geometries | | Theory | Exp. |
|---|---|---|---|---|
| | $S_0$ | $S_1$ | | |
| $S_0$ | 0 | 0.193 | | |
| $T_1$ | 1.674 | 1.058 | 1.65[23] | 1.67,[30] 1.76[25] |
| $T_2$ | 2.427 | 2.094 | 3.3[26] | |
| $S_1$ | 2.758 | 2.287 | 2.74[23] | 3.2,[10,11] 2.76[31] |
| $T_3$ | 3.198 | 2.995 | | |
| $\Delta E_1$[a] | 1.084 | 1.230 | | |
| $\Delta E_2$[b] | 0.332 | 0.193 | | |
| $\Delta E_3$[c] | 0.440 | 0.708 | | |

[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 $T_3$ 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 $C_\alpha$ and $C_\beta$ 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 $S_0$ state to the first optically bright $S_1$ state, which has a large oscillator strength. Following excitation at 400 nm to the $S_1$ 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 $S_1$ states are calculated and presented in Table 1, respectively.
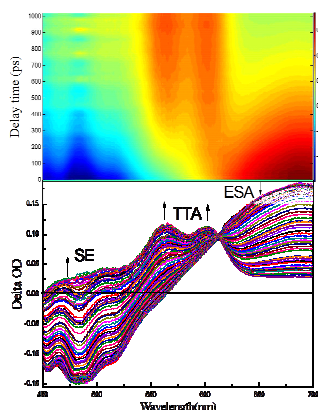


**Fig. 2** The transient absorption spectra of quaterthiophene in 1,4-dioxane measured with excitation at 400 nm. SE: stimulated emission, TTA: triplet-triplet absorption, ESA: excited state absorption.

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.[11] 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 into the other state. Both rising bands are assigned to triplet-triplet

absorption (TTA) which is well agreed with previous studies by nanosecond flash[16,17] and picosecond time-resolved[19] experiments. In these spectral regions, these characteristic bands overlapped with each other to a certain extent.
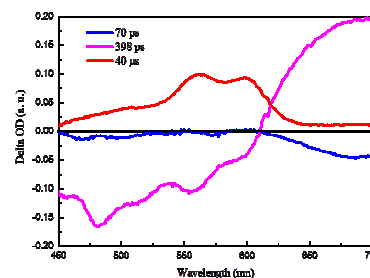


**Fig. 3.** Decay-associated difference spectra (DADS) of the three time constants extracted from the transient absorption data after SVD/global fit analysis.

To describe properly the dynamics observed in the visible range, global fit analysis of all of the kinetics at different wavelength regions is performed with singular value decomposition (SVD). Decay-associated difference spectra (DADS) are obtained from the global analysis, as shown in Fig. 3. The best fit results of the decay times are listed in Table 2. The longtime constant is valued 40 μs since the TTA absorption bands were reported as 35-45 μs lifetime in the nanosecond flash experiments.[16,17] The DADS with lifetime of 70 ps presents the main band > 620 nm with negative amplitudes, which is attributed to the geometry relaxation. The evolution to the next DADS, which has a lifetime of 398 ps, corresponds to the decrease of the ESA and SE signals. The amplitude spectra associated with the longtime constant has a maximum absorption of around 563 and 600 nm, matched well with the absorption spectrum of the TTA bands. The several typical wavelengths are chosen to represent the temporal behavior of the SE bands ESA band and two TTA bands, respectively. The global analysis result shows a good match with the experimental traces over the whole spectra-temporal range.

### 3.2 Geometry relaxation

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.[11,19,27] For 4T, only the all-trans conformation was considered. The ground and low-lying excited states of 4T were optimized at the planar ($C_{2h}$) and twisted ($C_2$) conformers, respectively. According to the MP2 and B3LYP results, the planar $C_{2h}$ conformer is slightly higher than the $C_2$ twisted conformers in the ground state, but only by less than 0.005 eV. The analysis of vibrational frequencies also shows that

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

| λ(nm) | $a_1$ | $\tau_1$(ps) | $a_2$ | $\tau_2$(ps) | $a_3$ | $\tau_3$(μs)[a] |
|---|---|---|---|---|---|---|
| 453 | -0.039(14) | 70(7) | -0.906(15) | 398(10) | 0.161(11) | constant |
| 480 | -0.048(10) | 70(7) | -0.976(11) | 398(10) | 0.222(8) | constant |
| 513 | -0.054(6) | 70(7) | -1.002(6) | 398(10) | 0.361(5) | constant |
| 553 | -0.042(4) | 70(7) | -1.033(5) | 398(10) | 0.941(3) | constant |
| 563 | -0.020(5) | 70(7) | -0.972(5) | 398(10) | 1.055(4) | constant |
| 600 | 0.021(5) | 70(7) | -0.453(6) | 398(10) | 1.009(4) | constant |
| 606 | 0.013(6) | 70(7) | -0.212(5) | 398(10) | 1.004(5) | constant |
| 675 | -0.270(3) | 70(7) | 1.165(4) | 398(10) | 0.081(3) | constant |
| 685 | -0.273(4) | 70(7) | 1.167(4) | 398(10) | 0.080(4) | constant |
| 695 | -0.259(4) | 70(7) | 1.166(5) | 398(10) | 0.068(3) | constant |

[a] The longtime constant is set at 40 μs

there are no imaginary frequencies at $C_2$ conformer but two imaginary frequencies at $C_{2h}$ conformer. The twisted structure with $C_2$ 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 $C_2$ 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 $C_\alpha$-$C_\alpha$ bonds and $C_\beta$-$C_\beta$ bonds shorten in the excited $S_1$ state. These shortened bonds emerge a pronounced double-bond character. Since the $C_\alpha$-$C_\beta$ and C-S bonds obviously increase after the excitation, the inner rings are mostly affected and become oblate in the $S_1$ state. Furthermore the interannular torsion angles of S-$C_1'$-$C_1$-S and S-$C_4$-$C_5$-S change from $167.994°$ and $165.025°$ in the ground state to $179.977°$ and $179.966°$ in the $S_1$ 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.[23,24,32] S. Siegert *et al.* predicted that a non-planar structure of quaterthiophene is needed to allow an efficient ISC dynamics from the $S_1$ state to the $T_2$ state.[33] 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 $S_1$ state. The $S_1$ state nonadiabatically decays with lifetime of the 398 ps.
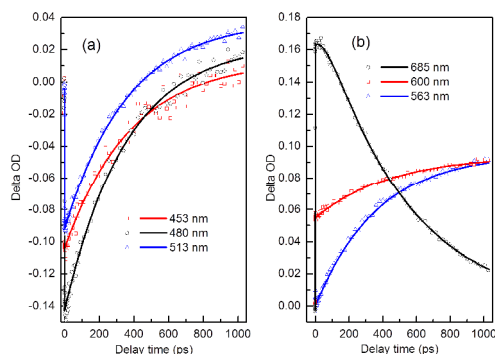


**Fig. 4** Representative time traces of the transient absorption spectra of quaterthiophene recorded upon excitation at 400 nm in 1,4-dioxane: (a) 453nm, 480 nm and 513 nm; (b) 563 nm, 600 nm, and 685nm, with fits derived from global analysis of the data over the full 450-700 nm spectral range. The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

### 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 isosbestic 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.[11,19] It is also been proved that there may be two or more triplet states below the $S_1$ state of oligothiphenes.[21-24,33] According to the energy gap law, a small energy gap between the singlet and triplet states is benefit for an efficient ISC.[34,35] 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.[36] In 4T, the energy gap $\Delta E_1$ is more than 1 eV and becomes larger along the relaxing coordinate. The $S_1$-$T_1$ ISC channel cannot be considered as an efficient pathway for ISC. The $T_2$ state with the energy gap less than 0.5 eV is easy to devote to a channel for the ISC process. Furthermore, the $S_1$-$T_2$ energy gap becomes smaller from 0.332 to 0.193 eV along the relaxation coordinate. This trend is benefit to ISC between the $S_1$ and $T_2$ states. Apparently, internal conversion from the $T_2$ state to the $T_1$ state is very fast as expected[33]; thus the instantaneous concentration of the $T_2$ state is very low, or their transition cross sections in absorption are too small to be detected in our experiments. The lifetime of $4T(T_2)$ was estimated to be only 38 ps.[26] The triplet-formation quantum yield of quaterthiophene has been measured to be of the order of 0.67-0.80 depending on the solvent.[11,19] 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 $T_2$ state located above the $S_1$ state but the $S_1$-$T_2$ 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 $S_1$-$T_2$ energy gap compared to the values in the shorter oligothiophenes.[25] Anyway, the $T_2$ 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 $T_3$ state should be considered in ISC processes, although the energy of the $T_3$ state is larger than the $T_2$ state.[23] In gas phase, the $T_3$ state maybe an efficient ISC pathway because of the small energy gap although it is higher than the $S_1$ state. But in solution the energy gap $\Delta E_3$ become larger along the geometry relaxation and is as large as 0.7 eV at the $S_1$ state structure and far away from 0.5 eV. The $T_3$ state could not be considered anymore as an efficient ISC pathway.
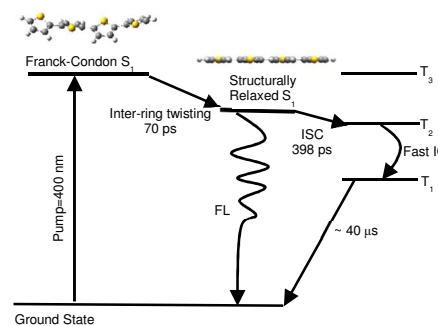


**Fig. 5** The schematic diagram of the proposed excited state relaxation mechanism of quaterthiophene in 1,4-dioxane.

## 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 estimated to be 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

## References

1   G. Barbarella, M. Zambianchi, O. Pudova, V. Paladini, A. Ventola, F. Cipriani, G. Gigli, R. Cingolani, and G. Citro, Oligothiophene isothiocyanates as a new class of fluorescent markers for biopolymers, *J. Am. Chem. Soc.*, 2001, **123**, 11600.

2   A. Quarta, R. di Corato, L. Manna, S. Argentiere, R. Cingolani, G. Barbarella, and T. Pellegrino, Multifunctional nanostructures based on inorganic nanoparticles and oligothiophenes and their exploitation for cellular studies, *J. Am. Chem. Soc.*, 2008, **130**, 10545.

3   M. L. Capobianco, G. Barbarella and A. Manetto, oligothiophenes as fluorescent markers for biological applications, *Molecules*, 2012, **17**, 910.

4   H. A. Ho, A. Najari, and M. Leclerc, Optical detection of DNA and proteins with cationic polythiophenes, *Acc. Chem. Res.*, 2008, **41**, 168.

5   G. Barbarella, M. Zambianchi, A. Ventola, E. Fabiano, F. Della Sala, G. Gigli, M. Anni, A. Bolognesi, L. Polito, M. Naldi, and M. Capobianco, Bright oligothiophene *N*-Succinimidyl esters for efficient fluorescent labeling of proteins and oligonucleotides, *Bioconjug. Chem.*, 2006.**17**, 58.

6   M. Zambianchi, F. Di Maria, A. Cazzato, G. Gigli, M. Piacenza, F. Della Sala, and G. Barbarella, Microwave-Assisted synthesis of thiophene fluorophores, labeling and multilabeling of monoclonal antibodies, and long lasting staining of fixed cells, *J. Am. Chem. Soc.*, 2009, **131**, 10892.

7   L. Zechmeister, and J. W. Sease, A blue-fluorescing compound, terthienyl, isolated from marigolds, *J. Am. Chem. Soc.*, 1947, **69**, 273.

8   C. V. Pham, A. Burkhardt, R. Shabana, D. D. Cunningham, H. B. Mark, and H. Zimmer, A convenient synthesis of 2,5-thienylene oligomers; some of their spectroscopic and electrochemical properties, *Phosphorus, Sulfur, Silicon*, 1989, **46**, 153.

9   H. Chosrovian, D. Grebner, and S. Rentsch, Size-dependent transient behaviour of thiophene oligomers studied by picosecond absorption spectroscopy, *Synth. Met.*, 1992, **52**, 213.

10  H. Chosrovian, S. Rentsch, D. Grebner, D. U. Dahm, E. Birckner, and H. Naarmann, Time-resolved fluorescence studies on thiophene oligomers in solution, *Synth. Met.*, 1993, **60**, 23.

11  D. Grebner, M. Helbig, and S. Rentsch, Size-dependent properties of oligothiophenes by picosecond time-resolved spectroscopy, *J. Phys. Chem.*, 1995, **99**, 16991.

12  R. Colditz, D. Grebner, M. Helbig, and S. Rentsch, Theoretical Studies and Spectroscopic Investigations of Ground and Excited Electronic States of Thiophene Oligomers, *Chem. Phys.*, 1995, **201**, 309.

13  D. V. Lap, D. Grebner, and S. Rentsch, Femtosecond time-resolved spectroscopic studies on thiophene oligomers, *J. Phys. Chem. A*, 1997, 101, 107.

14  A. Yang, M. Kuroda, Y. Shiraishi, and T. Kobayashi, Chain-length dependent stationary and time-resolved spectra of α-oligothiophenes, *J. Phys. Chem. B*, 1998, **102**, 3706.

15  J. C. Scaiano, R. W. Redmond, B. Mehta, and J. T. Amason, Efficiency of the photoprocesses leading to singlet oxygen generation by α-terthienyl: optical absorption, optoacoustic calorimetry and infrared luminescence, *Photochem. Photobiol.*, 1990, **52**, 655.

16  V. Wintgens, P. Valat, and F. Garnier, Photochemical generation of radical cations from thiophene oligomers, *J. Phys. Chem.*, 1994, **98**, 228.

17  J. P. Reyftmann, J. Kagan, R. Santus, and P. Morliere, Excited state properties of α-terthienyl and related molecules, *Photochem. Photobiol.*, 1985, **41**, 1.

18  R. S. Becker, J. Seixas de Melo, A. L. Macanita, and F. Elisei, Comprehensive investigation of the solution photophysics and theoretical aspects of oligothiophenes of 1-7 rings, *Pure Appl. Chem.*, 1995, **67**, 9.

19  R. S. Becker, J. Seixas de Melo, A. L. Macanita, and F. Elisei, Comprehensive evaluation of the absorption, photophysical, energy transfer, structural, and theoretical properties of α-oligothiophenes with one to seven rings, *J. Phys. Chem.*, 1996, **100**, 18683.

20  N. J. Turro, Modern molecular photochemistry, ed. University Science Books, Mill Valley, **1991**.

21  E. Fabiano, F. Della Sala, and R. Cingolani, Theoretical study of singlet and triplet excitation energies in oligothiophenes, *J. Phys. Chem. A*, 2005, **109**, 3078.

22  M. Rubio, M. Merchán, R. Pou-Amérigo, and E. Ortí, The low-lying excited states of 2,2′-bithiophene: A Theoretical Analysis, *ChemPhysChem*, 2003, **4**, 1308.

23  M. Rubio, M. Merchán, and E. Ortí, Theoretical study on the low-lying excited states of 2,2′:5′,2″-terthiophene and 2,2′:5′,2″:5″,2‴-Quaterthiophene, *ChemPhysChem*, 2005, **6**, 1357.

24  D. Beljonne, J. Cornil, R. H. Friend, R. A. J. Janssen, and J. L. Brédas, Influence of chain length and derivatization on the lowest singlet and triplet states and intersystem crossing in oligothiophenes, *J. Am. Chem. Soc.*, 1996, **118**, 6453.

25  S. Rentsch, J. P. Yang, W. Paa, E. Birckner, J. Schiedt, and R. Weinkauf, Size dependence of triplet and singlet states of α-oligothiophenes, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1707.

26  Y. Oseki, M. Fujitsuka, M. Sakamoto, X. Cai and T. Majima, Energy levels of oligothiophenes in the higher excited triplet states, *J. Phys. Chem. C*, 2007, **111**, 1024.

27  N. DiCésare, M. Belletête, M. Leclerc, and G. Durocher, Thermochromic properties of quaterthiophene, an alkyl-substituted quaterthiophene derivative and its corresponding polymer, *Chem. Phys. Lett.*, 1998, **291**, 487.

28  Y. Wang, S. Zhang, S. Sun, K. Liu, and B. Zhang, Ultrafast excited state dynamics of trans-4-aminoazobenzene studied by femtosecond transient absorption spectroscopy, *Chin. J. Chem. Phys*., 2013, **26**, 651.

29  M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, et al. GAUSSIAN 09, RevisionA02; Gaussian, Inc.: Wallingford, CT, 2009.

30  P. Landwehr, H. Port, and H. C. Wolf, Optical detection of the lowest triplet excited state of oligothiophenes and anthryloligothiophenes, *Chem. Phys. Lett*., 1996, **260**, 125.

31  D. Birnbaum, D. Fichou, and B. E. Kohler, The lowest energy singlet state of tetrathiophene, an oligomer of polythiophene, *J. Chem. Phys*., 1992, **96**, 165.

32  D. Chakraborty and J. B. Lagowski, Configuration interaction study of singlet excited state of thiophene and its cyano derivative oligomers, *J. Chem. Phys*., 2001, **115**, 184.

33  S. Siegert, F. Vogeler, C. M. Marian, and R. Weinkauf, Throwing light on dark states of α-oligothiophenes of chain lengths 2 to 6: radical anion photoelectron spectroscopy and excited-state theory, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10350.

34  E. C. Lim, Proximity effect in molecular photophysics: dynamical consequences of pseudo-Jahn-Teller interaction, *J. Phys. Chem*., 1986, **90**, 6770.

35  M. A. El-Sayed, The radiationless processes involving change of multiplicity in the diazenes, *J. Chem. Phys*., 1962, **36**, 573.

36  D. Beljonne, Z. Shuai, G. Pourtois, and J. L. Bredas, Spin orbit coupling and intersystem crossing in conjugated polymers: A configuration interaction description, *J. Phys. Chem. A*, 2001, **105**, 3899.