

Singlet Energy Migration along an Alternating Block Copolymer of Oligothiophene and Oligosilylene in Solution

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The singlet excited-state properties of the block copolymers of oligothiophene and oligosilylene in solution were investigated with several fast spectroscopic methods. Time-resolved fluorescence measurements at room temperature and in a glassy matrix revealed that the singlet excited states of the block copolymers are deactivated accompanying structural changes of the polymer. It became clear from the transient absorption spectroscopy that the absorption peak of the singlet excited state shifted to the longer wavelength side compared to that of the corresponding oligothiophenes because of the σ – π conjugation of the oligothiophene and oligosilylene. The intersystem crossing process generating the triplet excited state was also revealed by the transient absorption spectroscopy. Energy migration along the polymer chain was revealed by the fluorescence anisotropy measurements. The time constant for the energy migration became faster as the size of the oligothiophene in the polymer repeating unit became shorter. From comparison with the Förster theory, the energy migration process was attributed to an incoherent hopping mechanism.

Introduction

Excitation energy migration along a polymer chain has attracted much attention because of its importance in photoconductive polymeric materials, in which the chromophores are aligned in a regular manner along the polymer backbone.¹ The excitation energy migration is also an important process in the photoharvesting complex of natural photosynthesis systems.²

Energy migration along the polymer chain has been studied by several techniques. The quantification of the extent of the excitation energy migration along the polymer chain has been studied by the quenching of the steady-state fluorescence of the polymer by small quenching molecules.¹ The higher quenching rate of the polymer than the diffusion-limiting rate provided the evidence and quantitative information of the excitation energy migration. However, the treatment based on the steady-state fluorescence measurements often includes some complexities such as the local concentration effect of the quencher molecules and complex fluorescent decay kinetics of the polymeric materials.¹

Recently developed ultrashort pulse laser techniques provide more direct information on the excitation energy migration along the polymeric materials. For example, singlet energy–singlet energy annihilation, which can be observed by using an excitation source with high fluence, provides evidence and kinetic information for the excitation energy migration.³ The kinetic analysis based on the singlet energy–singlet energy annihilation has been carried out for the polymeric materials employing the repeating unit with phthalocyanines and porphyrins.³ Furthermore, transient absorption and fluorescence depolarization also help determine the kinetics of the singlet energy

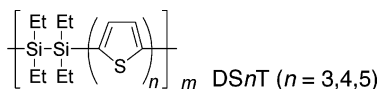


Figure 1. Molecular structure of DSnT.

migration.⁴ The time-dependent fluorescence anisotropy measurements based on the fluorescence up-conversion have been successfully applied to the energy migrations in various systems such as a light harvesting complex,² porphyrin arrays,⁵ and dendrimers.⁶ The time resolutions of these methods are almost the same as the pulse duration, i.e., a hundred femtoseconds.

As for the exciton migration along the π -conjugated polymers, an ultrafast spectroscopic method has also been employed. For example, Mollay et al. measured the fluorescence decay of poly(phenylenevinylene)s and estimated the nearest-neighbor transfer time of the energy to be 2 ps from a comparison with the simulation based on the random walk model.⁷ In the case of homopolymers, the deactivation kinetics along the polymer is rather complex because it includes energetic deactivation from the higher energy site to the lower one accompanying the structural relaxation that enhances the conjugation length.

Some of the present authors synthesized alternating block copolymers of oligothiophene and oligosilylene, for which interesting properties have been revealed on the basis of the σ – π conjugation system along the polymer chain.⁸ From the viewpoint of the singlet energy migration along the polymer chain, these block copolymers are interesting because they can be regarded as a polymer made up of well-defined conjugated systems connected to an adequate spacer.

In the present study, we investigated the singlet excited-state properties of the poly(thienylene–silylene)s (DSnT, n denotes the number of thiophene rings in the repeating unit, see Figure 1) in solution using several ultrafast spectroscopic methods. On the basis of the results of this study, the singlet energy migration along the polymer chain has been revealed.

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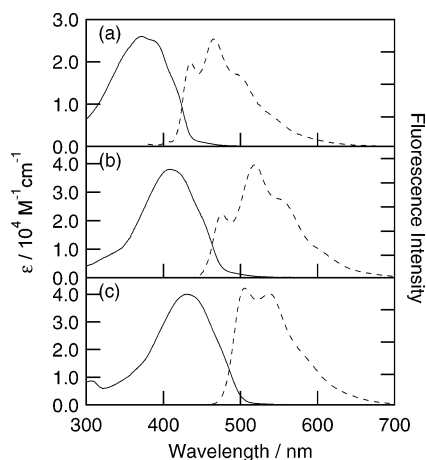


Figure 2. Absorption (solid line) and fluorescence (dashed line) spectra of DS3T (a), DS4T (b), and DS5T (c) in toluene.

Experimental Section

Materials. The DS*n*Ts were synthesized according to the previously reported procedure.^{8a} All other chemicals were of the best commercial grades available.

Apparatus. Transient absorption spectra in the picosecond region were measured by the pump and probe method employing the third harmonic oscillation (355 nm) of a picosecond Nd:YAG laser (Continuum, RGA69-10LD, fwhm 30 ps, 2–5 mJ pulse⁻¹) as the excitation source. The probe pulse generated by focusing the fundamental light of the Nd:YAG laser on a D₂O: H₂O cell was detected with a MOS linear image sensor (Hamamatsu Photonics, M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094) after passing through the sample (Optical path: 2.0 mm).

The time-resolved fluorescence spectra were measured by the single photon counting method with a streakscope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Acton Research, SpectraPro150). The ultrashort laser pulse was generated by a Ti:sapphire laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 80 fs) pumped with a diode-pumped solid-state laser (Spectra-Physics, Millennia VIII). For excitation of the sample, the output of the Ti:sapphire laser was converted to the second harmonic oscillation (390 or 430 nm) with a harmonic generator (Spectra-Physics, GWU-23FL).

Fluorescence lifetime in the subpicosecond regime was estimated by using the fluorescence up-conversion method. The second harmonic oscillation (390 or 430 nm) of the output of the femtosecond laser (780 or 860 nm) was used to excite the sample in a cell with a 1.0 mm optical path length. The residual fundamental and the fluorescence were focused in a BBO type I crystal to generate a sum-frequency oscillation, which was detected by a photomultiplier tube (Hamamatsu Photonics, H8259) and the photon counter (Stanford Research Systems, SR400) after passing through the monochromator (Nikon G250). The cross correlation time of the apparatus was 300 fs fwhm.

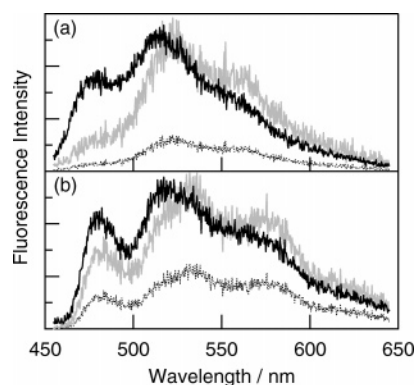


Figure 3. Time-resolved fluorescence spectra at 0–0.5 (solid line) and 1.0–1.5 ns (dotted line) after excitation of DS4T in toluene at room temperature (a) and 77 K (b). Gray lines are normalized spectra at 1.0–1.5 ns.

The steady-state absorption and fluorescence spectra were measured with a Shimadzu UV-3100PC and a Hitachi 850, respectively.

Results and Discussion

Ground-State Absorption and Fluorescence Spectra. In toluene, DS*n*Ts showed rather broad absorption bands in the 350–500 nm region as shown in Figure 2. The absorption peak tends to shift to the longer wavelength side with the increasing number of thiophene units in the repeating unit, indicating the longer conjugation length of the longer oligothiophene. Furthermore, the peak position of the absorption band (λ_{abs}) was on the longer wavelength side by 15–18 nm when compared with the corresponding oligothiophenes (*n*T, *n* denotes the number of thiophene units, Table 1).⁹ The peak shift from the corresponding oligothiophene can be attributed to the σ – π conjugation with the adjacent oligosilylene.

Upon excitation, DS*n*Ts showed fluorescence bands with clear vibration structures as shown in Figure 2. The peak positions of the DS*n*Ts and corresponding oligothiophenes (λ_{fl}) are also listed in Table 1. The fluorescence peak position shift with an increase in the thiophene unit in the repeating unit was also confirmed in accord with the ground absorption peak shift.

Deactivation Process of the Singlet Excited State. The deactivation process of the singlet excited states of the DS*n*Ts was investigated with time-resolved fluorescence spectroscopy. The fluorescence of the DS*n*Ts did not decay according to a single-exponential function, indicating the contribution of some deactivation pathways. The fluorescence lifetimes (τ) estimated by assuming two exponential functions are summarized in Table 1 and Table S1 (Supporting Information). It was revealed from the time-resolved fluorescence spectra (Figure 3a) that the fluorescence bands on the shorter wavelength side quickly disappeared while the fluorescence bands on the longer wavelength side exhibited a rather long lifetime. Furthermore, the fluorescence spectrum at 1.0–1.5 ns became slightly structure-

TABLE 1: Absorption and Fluorescence Properties of DS*n*T in Toluene

| | $\lambda_{\text{abs}}/\text{nm}^a$ | $\lambda_{\text{fl}}/\text{nm}^a$ | τ/ns^b | $\tau(77\text{ K})/\text{ns}^b$ |
|-----------------|------------------------------------|-----------------------------------|------------------------|---------------------------------|
| DS3T | 371, 388 (sh) | 437, 466, 491 (sh) | 0.29 (80%), 0.86 (20%) | 0.57 (88%), 1.85 (12%) |
| DS4T | 409 | 476, 519, 552 (sh) | 0.30 (53%), 0.84 (47%) | 0.69 (70%), 1.71 (30%) |
| DS5T | 431 | 506, 537 | 0.32 (30%), 0.79 (70%) | 0.82 (40%), 1.94 (60%) |
| 3T ^c | 354 | 407, 426 | 0.21 | |
| 4T ^c | 391 | 437, 478 | 0.49 | |
| 5T ^c | 416 | 482, 514 | 0.82 | |

^a (sh) denotes a shoulder peak. ^b Fitted to whole fluorescence. ^c Data from ref 9.

less. These tendencies were also confirmed for DS3T (see the Supporting Information, Figure S1). The component with the rather long lifetime can be attributed to the relaxed singlet excited state. In the case of the π -conjugated polymers such as polythiophene and poly(*p*-phenylenevinylene), a similar deactivation process including the formation of the relaxed singlet excited state, which exhibits a fluorescence band on the longer wavelength side, was reported.^{10,11} In the case of homopolymers, the formation of the relaxed state has been attributed to the conformational change including planarization¹² and to the energy migration along the polymer chain to the site of the longer π -conjugation length with a lower excitation energy.¹¹ In the present block copolymer, the conjugation length is regulated by the adjacent oligosilylene moieties. Therefore, the spectral change with time seems to be due to the polymer-structural change. To confirm this hypothesis, the time-resolved fluorescence spectra were also measured in a glassy matrix at 77 K (Figure 3b). In the glassy matrix where the polymer-structure motion is inhibited, the fluorescence band on the shorter wavelength side remained in the spectrum at 1.0–1.5 ns and the vibration structure was maintained. Therefore, the spectral change at room temperature can be attributed to the formation of some relaxed site in the polymer chain such as a planar domain and intramolecular excimer resulting from polymer motion. The lifetimes in the glassy matrix ($\tau(77\text{ K})$) are also summarized in Table 1 and Table S1 (Supporting Information). In the case of DS5T, deformation of the fluorescence spectrum with time evolution is rather small even at room temperature (Figure S2, Supporting Information). Furthermore, the ratio of the longer lifetime component tends to increase with the size of the oligothiophene in the repeating unit. Nonexponential decay of the polythiophenes with various substituents has been suggested to be associated with the inhomogeneities with different conformations and lifetimes.^{11c} Therefore, the smaller spectral change and larger ratio of the slow component indicate that the polymer including a longer oligothiophene unit has rather a homogeneous structure that inhibits formation of the relaxed site in the polymer.

The deactivation process of the singlet excited states was further investigated by means of transient absorption spectroscopy employing the picosecond laser as the excitation source. Immediately after the laser excitation (355 nm), DS4T showed a transient absorption spectrum with a peak (λ_{ss}) at 825 nm (Figure 4a), which can be attributed to the singlet excited state of DS4T. This assignment was supported by the fact that the 825 nm band decayed by the two exponential functions with 0.25 and 0.80 ns time constants, which are almost the same as the fluorescence decay rate constants (Figure 4b). It is interesting to note that the peak position of the singlet excited state appeared at the longer wavelength when compared with the tetramer of the oligothiophene (710 nm),¹³ indicating that the $S_n \leftarrow S_1$ transition is also stabilized by the σ - π conjugation of the oligothiophene and oligosilylene. The absorption peak observed at 2000 ps after the laser excitation can be attributed to the triplet excited state of the DS4T. Similarly, the absorption band of the triplet excited state (λ_{TT} , 635 nm) located at the longer wavelength side when compared with the tetramer of the thiophene which shows absorption peaks due to the triplet excited state at 610 and 570 nm. These results indicate that the singlet excited state of DS4T deactivates to the triplet excited state as well as the ground state.

For DS3T and DS5T, the transient absorption bands of the singlet and triplet excited states were also observed on the longer wavelength side compared with those of the trimer and pentamer

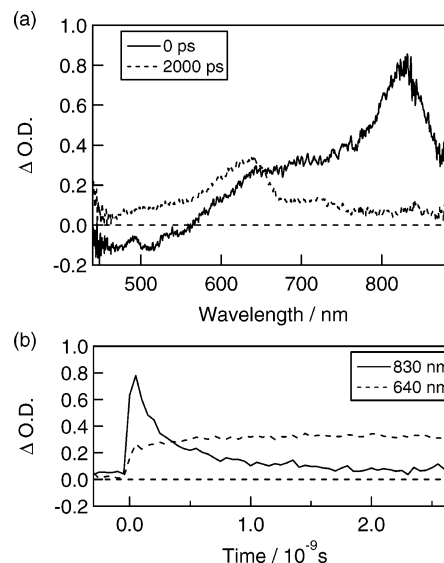


Figure 4. (a) Transient absorption spectra of DS4T in toluene during the laser flash photolysis with 355-nm laser (fwhm 30 ps, 5 mJ pulse⁻¹). (b) Kinetic traces of $\Delta\text{O.D.}$ at 830 and 640 nm.

of the thiophene, respectively (Figures S3 and S4, Supporting Information, and Table 2). These results indicate that both the singlet and triplet excited states of DS*n*T were affected by the σ - π conjugation.

Singlet Energy Migration along the Polymer Chain. For the excited polymer, migration of the excitation energy is expected as discussed in the Introduction. To reveal the energy migration process along the polymer chain, anisotropy of the fluorescence was estimated. By employing the fluorescence up-conversion method to the DS*n*Ts in toluene, the parallel (I_{\parallel}) and perpendicular (I_{\perp}) components of the fluorescence with respect to the pump pulse were obtained as indicated in Figure 5. The time course of the anisotropy ($r(t)$) in Figure 5 was estimated by eq 1,

$$r(t) = (I_{\parallel} - GI_{\perp}) / (I_{\parallel} + 2GI_{\perp}) \quad (1)$$

where G is a constant. Applying the single-exponential function, the time constants for the anisotropy decay were estimated to be (1.6 ps)⁻¹, (2.7 ps)⁻¹, and (4.5 ps)⁻¹ for DS3T, DS4T, and DS5T, respectively. Since the pentamer of thiophene did not show any anisotropy decay in this time region, the anisotropy decay observed for the DS*n*Ts can be attributed to the singlet energy migration along the polymer chain.

It is interesting to note that the rate constant of the anisotropy decay became faster as the length of the oligothiophene in the repeating unit became shorter. The Förster theory (eqs 2 and 3)^{4,14} has been employed to evaluate the singlet energy migration rate (k) by the hopping mechanism,

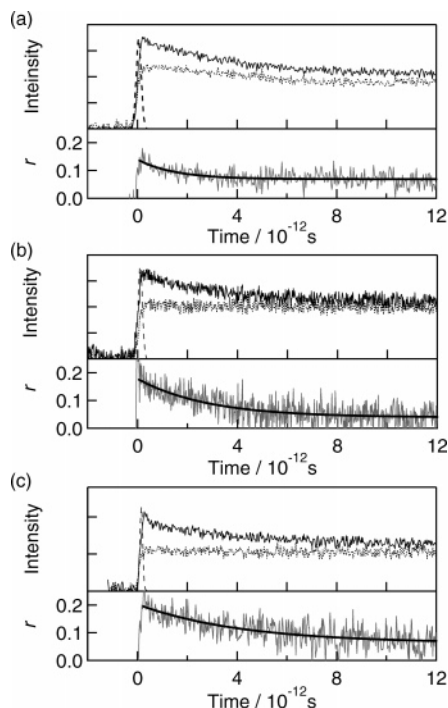
$$k = \frac{9000 \ln 10 \kappa^2 \Phi J}{128 \pi^5 n^4 N_A R^6 \tau} \quad (2)$$

$$J = \int F(\nu) \epsilon(\nu) \nu^{-4} d\nu \quad (3)$$

where κ , Φ , n , N_A , R , J , F , and ϵ are the orientation factor, fluorescence quantum yield, refractive index, Avogadro's number, distance, spectral overlap, donor-fluorescence spectrum, and acceptor-absorption spectrum, respectively. From the optimized structure at the PM3 level, the R values for DS3T, DS4T, and DS5T were estimated to be 14.7, 18.6, and 22.4 Å,

TABLE 2: Absorption Peak Positions of Singlet and Triplet Excited States

| | λ_{SS}/nm | λ_{TT}/nm |
|------|--------------------------|--------------------------|
| DS3T | 660 | 500 |
| DS4T | 825 | 635 |
| DS5T | >900 | 675 |
| 3T | 600 ^a | 460 ^b |
| 4T | 710 ^a | 570, 610 |
| 5T | 845 ^a | 630 ^b |

^a Data from ref 13. ^b Data from ref 9.**Figure 5.** Fluorescence (upper panel) and anisotropy (r , lower panel) profiles of DS3T (a), DS4T (b), and DS5T (c) in toluene. Solid and dotted lines are parallel and perpendicular components of fluorescence with respect to the excitation pulse (430 or 390 nm), respectively. Broken lines in the upper panels are the response function. Thick lines in the lower panels are fitted curves.

respectively. According to eqs 2 and 3, the increase in the R values significantly diminishes the energy transfer rate. On the other hand, the high absorption and large fluorescence quantum yield of the longer oligothiophenes make the energy transfer faster. To evaluate the effects of these factors, the energy transfer rates were calculated by employing the absorption and fluorescence spectra and other values.¹⁵ The time constants were calculated to be $(5.7 \text{ ps})^{-1}$, $(9.4 \text{ ps})^{-1}$, and $(19.2 \text{ ps})^{-1}$ for DS3T, DS4T, and DS5T, respectively. The calculated values are on the same order as the estimated ones. Furthermore, the ratio of the experimentally estimated rate constants (1.0:1.7:2.8) is almost the same as the calculated one (1.0:1.6:3.4). These results support the conclusion that the energy migration along the present polymer is governed by the Förster theory. These results also indicate that the mechanism of the energy migration along the block copolymer is the incoherent hopping mechanism similar to that of the other light-harvesting systems.²

Conclusion

In the present study, the singlet excited-state properties of the alternating block copolymers of oligothiophene and oligosilylene were clarified by using several fast spectroscopic methods. From the time-resolved fluorescence measurements

at room temperature and in a glassy matrix, the singlet excited-state deactivates accompanying structural changes. The intersystem crossing process was also revealed by transient absorption spectroscopy. Energy migration along the polymer chain was revealed by the anisotropy measurements. From the comparison with Förster theory, the energy migration process was attributed to the incoherent hopping mechanism.

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Supporting Information Available: Time-resolved fluorescence and transient absorption spectra of DS3T and DS5T; fluorescence lifetime estimated at each peak of DS n T in toluene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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