

## Photophysical Properties of Oligo(2,3-Thienyleneethynylene)s

Yosuke Oseki, Mamoru Fujitsuka, Michihiro Hara, Xichen Cai, Yutaka Ie, Yoshio Aso, and Tetsuro Majima\*

*The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan**Received: January 15, 2005; In Final Form: April 1, 2005*

Photophysical properties of oligo(2,3-thienyleneethynylene)s ( $n$ TE,  $n$  denotes the number of thiophene rings,  $n = 2, 3$ ) in benzene were investigated using steady-state, time-resolved fluorescence, and transient absorption spectroscopies. For 2TE, generation of the radiative  $S_2$  and nonradiative  $S_1$  states was confirmed. Upon excitation, the  $S_2$  state was initially generated and deactivated to the  $S_1$  state within 10 ps. The  $S_1$  state exhibited the transient absorption band at 470 nm, of which the lifetime was estimated to be 5.3 ns. In the case of 3TE, on the other hand, it was revealed that the radiative  $S_1$  state with a transient absorption peak at 650 nm was generated upon excitation. The  $T_1$  states of  $n$ TE were generated from the  $S_1$  states. The quantum yields were estimated to be 0.52 and 0.54 for 2TE and 3TE, respectively. Extremely fast reactions in the higher triplet excited state were indicated for both 2TE and 3TE.

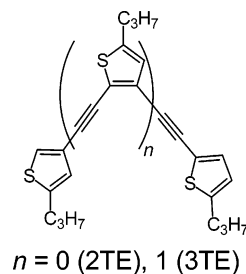
## Introduction

Oligo- and poly(phenyleneethynylene) have been widely studied because of the applicability to light-emitting diodes, sensors, and molecular wires.<sup>1</sup> The photophysical properties of their excited states have been studied using steady-state and time-resolved spectroscopies.<sup>2</sup> It has been demonstrated that the optical properties can be tuned by substituting the phenyl rings or replacing phenyl rings with other aromatics including hetero aromatic rings.<sup>3</sup>

Oligo(thienyleneethynylene)s, which are one of the analogues of phenyleneethynylene, have also been synthesized.<sup>4</sup> Two kinds of oligo(thienyleneethynylene)s have been reported, that is, oligo(2,5-thienyleneethynylene)s and oligo(2,3-thienyleneethynylene)s ( $n$ TE,  $n$  denotes the number of thiophene rings, Figure 1). The photoexcitation and electron-transfer properties of relatively large oligomers containing 5, 9, or 13 thiophene rings have been reported by some of the present authors and their co-workers.<sup>4c,e</sup> From the theoretical calculations and steady-state absorption spectra, expanded  $\pi$ -electron system was indicated for oligo(2,5-thienyleneethynylene)s in the ground state, while  $\pi$ -conjugation was limited for  $n$ TE. On the other hand, expansion of the  $\pi$ -conjugation was indicated for the excited  $n$ TE.

It has been reported that diphenylacetylene (DPA) has the unusually close-lying  $S_1$  and  $S_2$  states in the condensed media.<sup>5</sup> Upon excitation, DPA converts to the radiative  $S_2$  state at first. The  $S_2$  state deactivates with a very short lifetime (8 ps) at room temperature.<sup>5a,b</sup> The yield of the  $S_2$  fluorescence is quite low (<0.01) because of the fast internal conversion (IC) to the nonradiative  $S_1$  state.<sup>5a,c</sup> On the other hand, 1,4-bis(diphenylethynyl)benzene possesses the radiative  $S_1$  state as conventional oligomers.<sup>6</sup> Thus, the photophysical properties of small oligomers are not merely an analogue of longer oligomers.

In the present study, we report the photophysical properties of small  $n$ TE ( $n = 2, 3$ ) using a time-resolved fluorescence and



**Figure 1.** Molecular structures of  $n$ TE.

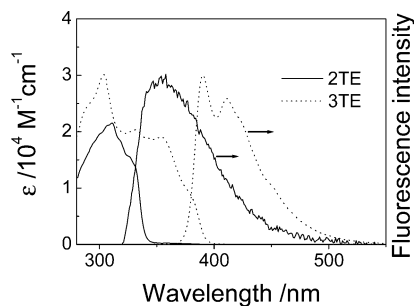
transient absorption spectroscopies. 2TE shows anomalous deactivation process similar to DPA. In the case of 3TE, on the other hand, the  $S_1$  state was emissive similar to that of larger  $n$ TE. Properties of the higher excited triplet states ( $T_n$ ) were also investigated.<sup>7</sup>

## Experimental Section

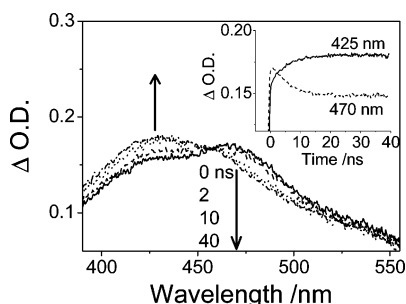
**Materials.** Synthesis of  $n$ TE was described in the previous paper.<sup>4c</sup> Other compounds were of the best commercial grade available and used after purification. Benzene and cyclohexane were spectral grade and used as a solvent without further purification. Sample solutions were freshly prepared in a quartz cell with 0.5 or 1.0 cm of optical path length and deoxygenated by bubbling with argon gas for 30 min before laser irradiation. All experiments were carried out at room temperature.

**Apparatus.** Steady-state absorption and fluorescence spectra were measured on a Shimadzu UV-3100PC and a Hitachi 850, respectively. The time-resolved fluorescence measurements were carried out by single-photon-counting method using the third-harmonic generation (THG, 300 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 100 fs) as the excitation source.<sup>8</sup> The ps laser flash photolysis was carried out using THG (355 nm) of a ps Nd:YAG laser (Continuum, RGA69-10LD, fwhm 30 ps). The monitoring light was detected with a streak camera (Hamamatsu Photonics, C7700) with a charge-coupled device (CCD) (Hamamatsu Photonics, C4742-98) or a MOS linear imaging head (Hamamatsu Photonics,

\* Author to whom correspondence should be addressed. E-mail: majima@sanken.osaka-u.ac.jp.



**Figure 2.** Absorption and fluorescence spectra of 2TE (solid line) and 3TE (dotted line) in benzene. Fluorescence intensity was normalized. The fluorescence spectrum of 2TE was observed in cyclohexane.



**Figure 3.** Transient absorption spectra of 2TE ( $4.2 \times 10^{-3}$  M) in benzene at 0, 2, 10, and 40 ns during a ps laser flash photolysis employing a ps Nd:YAG laser (355 nm, fwhm 30 ps,  $2.5 \text{ mJ pulse}^{-1}$ ). Inset: kinetic traces of  $\Delta\text{O.D.}$  of 2TE at 425 (solid line) and 470 nm (dashed line).

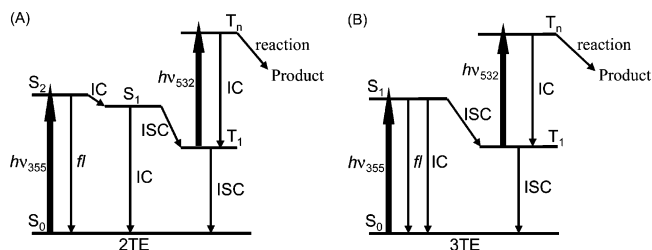
M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094). For the transient absorption measurements in the microsecond regime, the samples were excited using a THG (355 nm) of a ns Nd:YAG laser (Quantel, Brilliant, fwhm 5 ns) or a XeCl excimer laser (LAMBDA PHYSIK, COMPex 102, 308 nm, fwhm 25 ns). The procedure of ns–ns or ns–ps two-color two-laser flash photolysis has been described in the previous paper.<sup>7a–c</sup>

## Results and Discussion

**Steady-State Absorption and Fluorescence Spectra of  $n\text{TE}$ .** 2TE and 3TE showed the absorption peaks at 310 nm ( $\epsilon_{\text{S}_0} = 22\,000 \text{ M}^{-1}\text{cm}^{-1}$ ) and at 305, 330, and 355 nm ( $\epsilon_{\text{S}_0} = 30\,000, 20\,500, 19\,000 \text{ M}^{-1}\text{cm}^{-1}$ ), respectively (Figure 2). The absorption band edge of 3TE showed a red-shift by 50 nm with respect to 2TE, indicating delocalization of the  $\pi$ -electron system. For the larger  $n\text{TE}$  ( $n = 5, 9, 13$ ), absorption spectra with a peak and shoulder around 313 and 400 nm, respectively, have been reported independent of the oligomer length, indicating the limited  $\pi$ -conjugation in the larger  $n\text{TE}$ .<sup>4e</sup> The highest energy fluorescence peaks of 2TE and 3TE appeared at 356 and 390 nm, respectively (Figure 2), from which the respective singlet energies ( $E_{\text{S}}$ ) were determined to be 3.5 and 3.2 eV. The fluorescence quantum yields ( $\phi_{\text{fl}}$ ) were estimated to be  $<10^{-4}$  and 0.11 for 2TE and 3TE, respectively, using terthiophene as a standard.<sup>9</sup> The fluorescence lifetimes ( $\tau_{\text{fl}}$ ) were also estimated to be  $<10$  and 390 ps for 2TE and 3TE, respectively. Considerably low  $\phi_{\text{fl}}$  and short  $\tau_{\text{fl}}$  were observed for 2TE compared with larger oligomers.<sup>4e</sup>

**$n\text{TE}$  in the Singlet Excited States.** Figure 3 shows transient absorption spectra of 2TE during the 355-nm ps-laser flash photolysis. Immediately after the excitation, the transient absorption exhibited a band with a peak at 470 nm, which decayed with  $1.9 \times 10^8 \text{ s}^{-1}$  of the time constant. With the decay

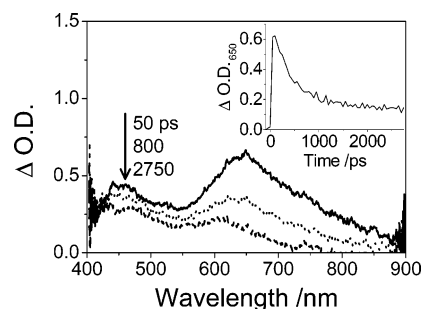
## SCHEME 1: Energy Diagrams of 2TE (A) and 3TE (B) in the Ground and Excited States



of the band at 470 nm, a new band appeared at 425 nm with the isosbestic point at 458 nm. The absorption band at 425 nm can be attributed to the lowest triplet ( $T_1$ ) state (vide infra). Discrepancy between the fluorescence lifetime ( $<10$  ps) and the growth of triplet absorption band (5.3 ns) indicates existence of the state between the radiative state and  $T_1$  state. It has been reported that DPA has the close-lying radiative  $S_2$  and nonradiative  $S_1$  states in the condensed media.<sup>5</sup> The lifetime of the  $S_2$  state has been estimated to be 8 ps. The  $S_1$  state generates from the  $S_2$  state via the fast IC and decays to the  $T_1$  state by the fast intersystem crossing (ISC) with a lifetime of 200 ps. Because of the same electronic configuration of DPA and 2TE, the transient absorption peak at 470 nm can be assigned to the nonradiative  $S_1$  state of 2TE generated from the radiative  $S_2$  state with the lifetime of  $<10$  ps (Scheme 1A). Contribution of intramolecular charge-transfer state can be excluded since the solvent polarity did not induce significant change in the deactivation process of 2TE. The rate constants of the ISC ( $k_{\text{ISC}}$ ) and IC ( $k_{\text{IC}}$ ) from the  $S_1$  state were estimated to be  $9.8 \times 10^7$  and  $9.1 \times 10^7 \text{ s}^{-1}$ , respectively, using the quantum yield for the ISC ( $\phi_{\text{ISC}}$ ) (0.52) (vide infra).

In the case of 3TE, the transient absorption band with the peaks at 450 and 650 nm was observed immediately after the ps-laser irradiation (Figure 4). Then, the absorption band with the peaks at 430, 480, and 610 nm because of the  $T_1$  state was observed with the decay of the absorption bands at 450 and 650 nm. The decay lifetime of the 450 and 650 nm peaks was estimated to be 420 ps, which is in good agreement with the fluorescence lifetime (390 ps). Therefore, spectral change observed for 3TE (Figure 4) can be attributed to the generation of the  $T_1$  state from the  $S_1$  state (Scheme 1B). These findings indicate that the deactivation process changed significantly in going from 2TE to 3TE. The photophysical properties of  $n\text{TE}$  in the ground and excited states are summarized in Table 1.

**$n\text{TE}$  in the Lowest Triplet Excited State.** Figure 5 shows transient absorption spectra and kinetic traces during the 355-nm laser flash photolysis of 2TE in the presence of benzophenone (BP). Generation of  $2\text{TE}(T_1)$  at 425 nm with the decay of

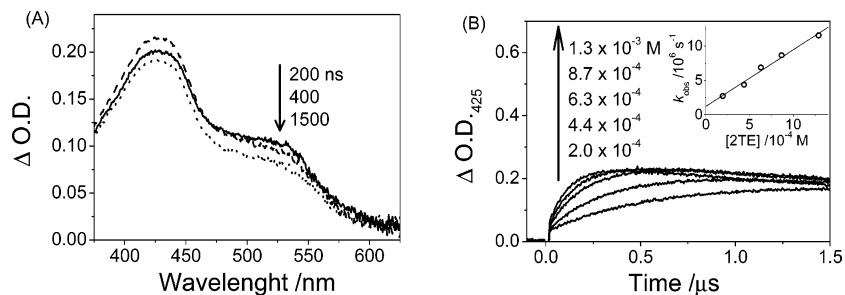


**Figure 4.** (A) Transient absorption spectra of 3TE ( $2.1 \times 10^{-4}$  M) in benzene at 50, 800, and 2750 ps during a ps laser flash photolysis employing a ps Nd:YAG laser (355 nm, fwhm 30 ps,  $2.5 \text{ mJ pulse}^{-1}$ ). Inset: kinetic trace of  $\Delta\text{O.D.}$  at 650 nm.

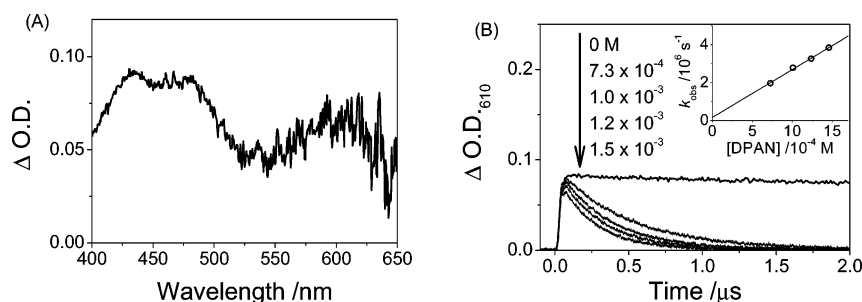
**TABLE 1: Photophysical Properties of *n*TE in Benzene**

<i>n</i> TE	$\tau_{\text{fl}}/\text{ps}$	$\tau_{\text{T1}}/\mu\text{s}$	$\phi_{\text{fl}}$	$\phi_{\text{ISC}}$	$E_{\text{S}}^b/\text{eV}$	$E_{\text{T1}}/\text{eV}$	$\epsilon_{\text{S0}}/\text{M}^{-1}\text{cm}^{-1}$	$\epsilon_{\text{S1}}/\text{M}^{-1}\text{cm}^{-1}$	$\epsilon_{\text{T1}}/\text{M}^{-1}\text{cm}^{-1}$
2TE	<10	29	$<10^{-4}$ <sup>a</sup>	0.52	3.5 <sup>a</sup>	2.4 ± 0.1	22 000 <sup>c</sup>	6900 <sup>e</sup>	13 000 <sup>g</sup>
3TE	390	35	0.11	0.54	3.2	2.3 ± 0.1	30 000 <sup>d</sup>	20 000 <sup>f</sup>	16 000 <sup>h</sup>

<sup>a</sup> In cyclohexane. <sup>b</sup> The energy levels of the radiative singlet excited states. <sup>c</sup> 310 nm. <sup>d</sup> 305 nm. <sup>e</sup> 470 nm. <sup>f</sup> 650 nm. <sup>g</sup> 425 nm. <sup>h</sup> 430 nm.



**Figure 5.** (A) Transient absorption spectra of 2TE ( $1.3 \times 10^{-3}$  M) in the presence of BP ( $1.0 \times 10^{-2}$  M) in benzene at 200, 400, and 1500 ns during a ns Nd:YAG (355 nm) laser flash photolysis. (B) Kinetic traces of  $\Delta\text{O.D.}$  at 425 nm. Inset: pseudo-first-order plot.



**Figure 6.** (A) Transient absorption spectrum of 3TE ( $3.9 \times 10^{-5}$  M) in benzene at 200 ns during a ns Nd:YAG (355 nm, fwhm 5 ns, 5 mJ pulse<sup>-1</sup>) laser flash photolysis. (B) Kinetic traces of  $\Delta\text{O.D.}$  at 610 nm of 3TE ( $3.9 \times 10^{-5}$  M) in benzene in the presence of diphenylanthracene during a XeCl (308 nm, fwhm 25 ns, 6 mJ pulse<sup>-1</sup>) laser flash photolysis. Inset: pseudo-first-order plot.

BP( $T_1$ ) (530 nm)<sup>10</sup> clearly indicates the triplet sensitization. From a pseudo-first-order plot of the observed generation rates ( $k_{\text{obs}}$ ) of 2TE( $T_1$ ) on the concentration of 2TE (Figure 5B Inset), the rate constant for the energy transfer from BP( $T_1$ ) to 2TE ( $k_{\text{ENT}}$ ) was estimated to be  $8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Furthermore, the extinction coefficient of 2TE( $T_1$ ) ( $\epsilon_{\text{T1}}$ ) was estimated to be  $13\,000 \text{ M}^{-1} \text{ cm}^{-1}$  at 425 nm, employing that of BP( $T_1$ ) as a reference.<sup>10</sup> From the relative actinometry using BP as a reference,  $\phi_{\text{ISC}}$  was estimated to be 0.52. Furthermore, on the basis of the evaluated  $\phi_{\text{ISC}}$  and  $\epsilon_{\text{T1}}$  values, the extinction coefficient of the transient absorption band because of the  $S_1$  state ( $\epsilon_{\text{S1}}$ ) was estimated to be  $6900 \text{ M}^{-1} \text{ cm}^{-1}$  at 470 nm. The  $\epsilon_{\text{S1}}$  value is smaller than the  $\epsilon_{\text{T1}}$  value. For DPA, smaller  $\epsilon_{\text{S1}}$  value has also been reported.<sup>5a,b</sup> It has been revealed that DPA-( $S_1$ ) has the trans-bent form, while it is the linear-acetylenic form for the  $S_2$  and  $T_1$  states.<sup>5</sup> Thus, 2TE possibly takes a trans-bent form in the  $S_1$  state similar to DPA. The lifetime of the  $T_1$  state ( $\tau_{\text{T1}}$ ) was estimated to be 27  $\mu\text{s}$ .

Figure 6A shows a transient absorption spectrum of 3TE-( $T_1$ ) obtained during the laser flash photolysis. The absorption bands at 430, 480, and 610 nm can be attributed to the  $T_1$  state as seen in Figure 4. The lifetime was estimated to be 35  $\mu\text{s}$ , which is similar to 2TE. It was revealed that 3TE( $T_1$ ) was quenched in the presence of diphenylanthracene (DPAN) because of the energy transfer (Figure 6B). The  $k_{\text{ENT}}$  value was estimated to be  $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Figure 6B). Furthermore, the  $\epsilon_{\text{T1}}$  and  $\phi_{\text{ISC}}$  were estimated to be  $16\,000 \text{ M}^{-1} \text{ cm}^{-1}$  and 0.54, respectively.

The sensitization of *n*TE was examined with a series of energy donors (Table 2). In the cases of BP and chrysene, 2TE was sensitized at the rate close to the diffusion-controlled rate in benzene.<sup>10</sup> On the other hand, 2TE( $T_1$ ) was quenched by 1,3-

**TABLE 2: Energy-Transfer Rate Constants of the Sensitization of *n*TE**

sensitizer	$E_{\text{T1}}/\text{eV}^{10}$	$k_{\text{ENT}}/10^9 \text{ M}^{-1} \text{ s}^{-1}$	
		2TE	3TE
benzophenone	3.0	8.3	
chrysene	2.5	3.6	5.8
1,3-cyclohexadiene	2.3	0.62 <sup>a</sup>	0.0051 <sup>a</sup>
trans-stilbene	2.1	2.3 <sup>a</sup>	4.6 <sup>a</sup>
9,10-diphenylanthracene	1.8	3.1 <sup>a</sup>	2.5 <sup>a</sup>

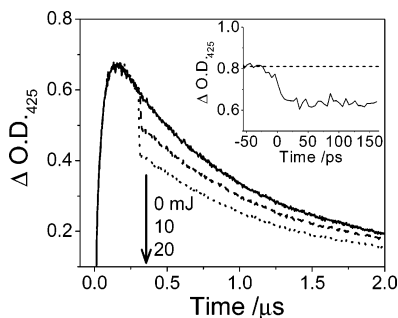
<sup>a</sup> The energy transfer rate from *n*TE( $T_1$ ) to sensitizers( $S_0$ ).

cyclohexadiene with the rate constant of  $0.47 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , indicating that the triplet energy ( $E_{\text{T1}}$ ) of 2TE( $T_1$ ) is slightly higher than that of 1,3-cyclohexadiene. As for 3TE, the energy transfer from chrysene( $T_1$ ) was observed, while the slow energy transfer ( $5.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) from 3TE to 1,3-cyclohexadiene was observed, indicating that  $E_{\text{T1}}$  of 3TE is almost the same as 1,3-cyclohexadiene. Thus, the  $E_{\text{T1}}$  of 2TE( $T_1$ ) and 3TE( $T_1$ ) were estimated to be  $2.4 \pm 0.1$  and  $2.3 \pm 0.1$  eV, respectively. The energy-transfer rate constants are summarized in Table 2.

The increase of  $\epsilon_{\text{T1}}$  and decrease of  $E_{\text{T1}}$  were confirmed in going from 2TE to 3TE. These findings can be attributed to the expansion of  $\pi$ -conjugation. These features are the same as other oligomers in the  $T_1$  states.<sup>7c,9</sup>

**Two-Color Two-Laser Flash Photolysis of *n*TE.** Figure 7 shows the kinetic traces of  $\Delta\text{O.D.}$  at 425 nm of 2TE during two-color two-laser flash photolysis of 2TE. 2TE( $T_1$ ) generated by triplet energy sensitization with BP( $T_1$ ) during the first laser irradiation (355 nm, fwhm 5 ns, 5 mJ pulse<sup>-1</sup>) was excited selectively to the  $T_n$  states by the second laser irradiation (532 nm, fwhm 30 ps or 5 ns, 10 mJ pulse<sup>-1</sup>) at 300 ns after the first laser. The bleaching of 2TE( $T_1$ ) absorption was observed and





**Figure 7.** Kinetic traces of  $\Delta O.D.$  at 425 nm of 2TE in benzene observed during two-color two-laser flash photolysis of 2TE employing a ns Nd:YAG laser (355 nm, fwhm 5 ns, 5 mJ pulse<sup>-1</sup>) and a nanosecond Nd:YAG laser (532 nm, fwhm 5 ns, 0, 10, 20 mJ pulse<sup>-1</sup>). Inset: ns-ps two-color two-laser flash photolysis employing a ns Nd:YAG laser (355 nm, fwhm 5 ns, 5 mJ pulse<sup>-1</sup>) and a ps Nd:YAG (532 nm, fwhm 30 ps, 10 mJ pulse<sup>-1</sup>).

did not show recovery. The bleaching without recovery was also observed both in the picosecond and microsecond regions. For 3TE, the similar phenomenon was observed. These results indicated the existence of some reaction pathway in the  $T_n$  state, which did not regenerate  $T_1$  state (Scheme 1). Although the triplet energy-transfer process from BP( $T_n$ ) to benzene( $S_0$ ) has been reported,<sup>7d</sup> the bleaching of  $nTE(T_1)$  was also observed in cyclohexane, indicating that the energy transfer from  $nTE(T_n)$  to benzene( $S_0$ ) can be excluded. Since the ground-state absorption of the sample after the two-color two-laser flash photolysis showed substantial change compared to that before the irradiation, a fast reaction competitive with the  $T_n$ - $T_1$  internal conversion proceeded from the  $T_n$  state.

## Conclusions

In this paper, the properties of  $nTE$  in the excited states were investigated. For 2TE, the radiative  $S_2$  and nonradiative  $S_1$  states were found, while 3TE possesses the radiative  $S_1$  state, indicating that photophysical properties of short oligomers are not merely an analogue of larger oligomers. In the  $T_n$  states, a fast reaction process was observed for both 2TE and 3TE. It is interesting to view a reaction controlled by the stepwise two-photon irradiation.

**Acknowledgment.** This work has been partly supported by a Grant-in Aid for Scientific Research on Priority Area (417), 21st Century COE Research, and others from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japanese Government.

## References and Notes

- (1) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Hung, H.; Wang, K.; Tan, W.; An, D.; Yang, X.; Huang, S.; Zhai, Q.; Zhou, L.; Jin, Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 5635. (c) Chen, W.; Joly, A. G.; Malm, J.; Bovin, J.; Wang, S. *J. Phys. Chem. B* **2003**, *107*, 6544. (d) Jiang, D.; Choi, C.; Honda, K.; Li, W.; Yuzawa, T.; Aida, T. *J. Am. Chem. Soc.* **2004**, *126*, 12084. (e) Smalley, J. F.; Sachs, S. B.; Chidsey, C. E. D.; Dudek, S. P.; Sikes, H. D.; Creager, S. E.; Yu, C. J.; Feldberg, S. W.; Newton, M. D. *J. Am. Chem. Soc.* **2004**, *126*, 14620. (f) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science*, **2001**, *292*, 2303. (g) Cornil, J.; Karzazi, Y.; Bredas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 3516. (h) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D.; Yao, Y.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3420. (i) Lewis, P. A.; Inman, C. E.; Yao, Y.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 12214.
- (2) (a) Levitus, M.; Schmieder, K.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259. (b) Sluch, M. I.; Godt, A.; Bunz, U. H. F.; Berg, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 6447. (c) Schmieder, K.; Levitus, M.; Dang, H.; Garcia-Garibay, M. A. *J. Phys. Chem. A* **2002**, *106*, 1551. (d) Beeby, A.; Findlay, K.; Low, P. J.; Marder, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 8280. (e) Ramos, A. M.; Meskers, S. C. J.; Beckers, E. H. A.; Prince, R. B.; Brunsveld, L.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 9630.
- (3) (a) Ickenroth, D.; Weissmann, S.; Rumpf, N.; Meier, H. *Eur. J. Org. Chem.* **2002**, 2808. (b) Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969. (c) Jones, T. V.; Blatchly, R. A.; Tew, G. N. *Org. Lett.* **2003**, *5*, 3297. (d) Shotwell, S.; Windscheif, P. M.; Smith, M. D.; Bunz, U. H. F. *Org. Lett.* **2004**, *6*, 4151. (e) Li, J.; Pang, Y. *Synth. Met.* **2004**, *140*, 43. (f) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886. (g) Boydston, A. J.; Yin, Y.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2004**, *126*, 10350.
- (4) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348. (c) Obara, Y.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett.* **2001**, *42*, 6877. (d) Aso, Y.; Obara, Y.; Okai, T.; Nishiguchi, S.; Otsubo, T. *Mol. Cryst. Liq. Cryst.* **2002**, *376*, 153. (e) Fujitsuka, M.; Makinoshima, T.; Ito, O.; Obara, Y.; Aso, Y.; Otsubo, T. *J. Chem. Phys. B* **2003**, *107*, 739. (f) Li, J.; Liao, L.; Pang, Y. *Tetrahedron Lett.* **2002**, *43*, 391.
- (5) (a) Hirata, Y. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1647. (b) Hirata, Y.; Okada, T.; Mataga, N.; Nomoto, T. *J. Phys. Chem.* **1992**, *96*, 6559. (c) Hamaguchi, H.; Ishibashi, T. *J. Phys. Chem. A* **1998**, *102*, 2263. (d) Ishibashi, T.; Okamoto, H.; Hamaguchi, H. *Chem. Phys. Lett.* **2000**, *325*, 212. (e) McFarland, S. A.; Finney, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 1178. (f) Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. *J. Phys. Chem.* **1984**, *88*, 1711. (g) Ferrante, C.; Kensy, U.; Dick, B. *J. Phys. Chem.* **1993**, *97*, 13457. (h) Zgierski, M. Z.; Lim, E. C. *Chem. Phys. Lett.* **2004**, *387*, 352. (i) Amatatsu, Y.; Hosokawa, M. *J. Phys. Chem. A* **2004**, *108*, 10238.
- (6) Beeby, A.; Findlay, K. S.; Low, P. J.; Marder, T. B.; Matousek, P.; Parker, A. W.; Rutter, S. R.; Towrie, M. *Chem. Commun.* **2003**, 2406.
- (7) (a) Fujitsuka, M.; Oseki, Y.; Hara, M.; Cai, X.; Sugimoto, A.; Majima, T. *ChemPhysChem* **2004**, *5*, 1240. (b) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2004**, *108*, 7147. (c) Oseki, Y.; Fujitsuka, M.; Hara, M.; Cai, X.; Sugimoto, A.; Majima, T. *J. Phys. Chem. B* **2004**, *108*, 16727. (d) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13. (e) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125. (f) Liu, R. S.; Edman, J. R. *J. Am. Chem. Soc.* **1968**, *90*, 213. (g) Ladwig, C. C.; Liu, R. S. H. *J. Am. Chem. Soc.* **1974**, *96*, 6210. (h) Ladwig, C. C.; Liu, R. S. H. *Chem. Phys. Lett.* **1975**, *35*, 563. (i) Ladwig, C. C.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 8093. (j) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2299. (k) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 335. (l) McGimpsey, W. G.; Evans, C.; Bohne, C.; Kennedy, S. R.; Scaiano, J. C. *Chem. Phys. Lett.* **1989**, *161*, 342. (m) Bohne, C.; Kennedy, S. R.; Boch, R.; Negri, F.; Orlandi, G.; Siebrand, W.; Scaiano, J. C. *J. Phys. Chem.* **1991**, *95*, 10300. (n) Gannon, T.; McGimpsey, W. G. *J. Org. Chem.* **1993**, *58*, 5639. (o) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Phys. Lett.* **2002**, *368*, 365. (p) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Commun.* **2003**, 222. (q) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Fujitsuka, M.; Ouchi, A.; Majima, T. *Chem. Commun.* **2003**, 2604. (r) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. Phys.* **2004**, *6*, 1735. (s) Sakamoto, M.; Cai, X.; Hara, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 9709.
- (8) Fujitsuka, M.; Okada, A.; Tojo, S.; Takei, F.; Onitsuka, K.; Takahashi, S.; Majima, T. *J. Phys. Chem. B* **2004**, *108*, 11935.
- (9) (a) Becker, R. S.; Melo, J. S. d.; Macanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683. (b) Rentsch, S.; Yang, J. P.; Paa, W.; Birckner, E.; Schiedt, J.; Weinkauff, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1707. (c) Apperloo, J. J.; Martineau, C.; van Hal, P. A.; Roncali, J.; Janssen, R. A. J. *J. Phys. Chem. A* **2002**, *106*, 21.
- (10) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.
- (11) (a) Beer, M. *J. Chem. Phys.* **1956**, *25*, 745. (b) Evans, D. F. *J. Chem. Soc.* **1957**, 1351.
- (12) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: CA, 1991.