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Efficient Photocyclization of Dithienylethene Dimer, Trimer, and Tetramer: Quantum Yield and Reaction Dynamics

Teruaki Kaieda,[†] Seiya Kobatake,[†] Hiroshi Miyasaka,*[,‡] Masataka Murakami,[‡]
Nobuyuki Iwai,[§] Yasushi Nagata,[§] Akira Itaya,[§] and Masahiro Irie*[,†]

Contribution from the Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation, Higashi-ku, Fukuoka 812-8581, Japan, Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, and Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan

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Abstract: Multi-dithienylethene arrays, in which two, three, or four 1,2-bis(2,4-dimethylthiophen-3-yl)-perfluorocyclopentenes are ethynylene-bridged, were synthesized. Upon irradiation with ultraviolet light the hexane solutions of the arrays turned violet-blue and the color disappeared by irradiation with visible light. The quantum yields of photocyclization reactions successively increased from 0.21 to 0.40 by increasing the number of the dithienylethene moieties in the arrays from one to four. Picosecond laser photolysis as well as the fluorescence depolarization experiment confirmed that efficient excited energy migration in the arrays from the photochemically inactive parallel conformer to the photoactive antiparallel conformer resulted in the high quantum yields.

Introduction

Considerable attention has been paid to photochromic dyes which show reversible photoisomerizations upon irradiation with light of appropriate wavelengths because of their potential applicability to optoelectronic devices.[1] In general, photogenerated colored isomers of photochromic dyes are thermally unstable and return to the initial colorless isomers in the dark. Recently, several thermally irreversible photochromic compounds, such as furylfulgides,[2] diarylethenes,[3] and phenoxynaphthacenequinones,[4] have been developed. The photogenerated colored isomers are stable and never return back to the initial colorless isomers in the dark. Among the compounds, diarylethenes with heterocyclic aryl rings are the most promising for the optoelectronic devices,[5−8] such as optical memory, photooptical switching, display, and photodriven actuators, because of their fatigue-resistant property.[6,7] For practical applications it is required to further improve the performance of the photochromic diarylethenes, such as efficient photoreactivity (high cyclization quantum yields), high absorption coefficients of the colored isomers, rapid response, and reactivity in the solid state. In the present study, we have prepared sensitive multi-dithienylethene arrays with high cyclization quantum yields.

The open-ring isomers of dithienylethenes in solution have two conformations, antiparallel and parallel, in almost equal amounts, as shown in Scheme 1.[9,10] The interconversion rate between the two conformations is much slower than the lifetime of photoexcited states.[9] Therefore, both conformers are photoexcited independently. Among the two conformers, only the antiparallel conformer has a chance to be converted to the closed-ring isomer.[11] Therefore, the maximum cyclization quantum yield cannot exceed 0.5.[12]

There are two strategies to increase the cyclization quantum yield in solution. One is to increase the ratio of the antiparallel conformers in the ground state. When a sodium sulfonate derivative of bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene was included in the β-cyclodextrin cavity, the molecule was force to adopt an antiparallel conformation. The

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[†] Kyushu University.

[‡] Osaka University.

[§] Kyoto Institute of Technology.

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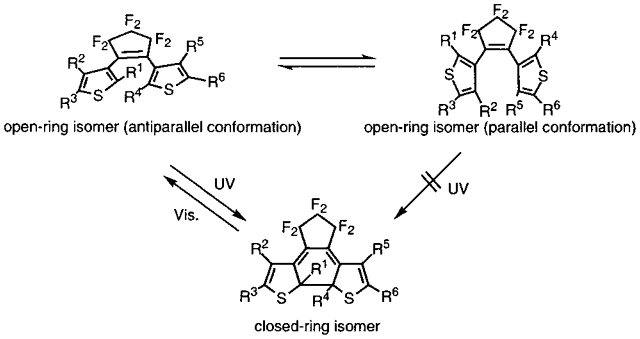
Scheme 1. Photochromism of Dithienylethene



cyclization quantum yield was found to increase from 0.32 to 0.49.[13] Zerbi et al.[14] also ascribed the high cyclization quantum yield of a polymer having dithienylethenes in the main chain to the enforced antiparallel conformation of the dithienylethene moieties in the ground state. The other strategy is to increase the ratio of antiparallel conformers in the photoexcited state. When photoexcited energy can be transferred from the photochemically inactive parallel conformation unit to the photoactive antiparallel one, the quantum yield is expected to increase. Such energy transfer is probable in dithienylethene dimer, trimer, or tetramer, in which the dithienylethene moieties are ethynylene-bridged.[15−18] Recently, Branda et al.[19] reported limited photochromic reactivity of dithienylethene dimers, in which two dithienylethene moieties are connected by a single bond.

When N dithienylperfluorocyclopentene moieties are connected with conjugated bonds, the system has 2^N conformations by a combination of parallel and antiparallel conformations. Among the 2^N conformations, only one conformation, in which all dithienylethene moieties are in the parallel conformation, cannot cyclize to the closed-ring isomer by photoirradiation, while $(2^N - 1)$ other conformations can undergo the photocyclization reaction by transferring the photoexcited energy to the antiparallel conformation unit. Figure 1 lists all conformations of the monomer, dimer, trimer, and tetramer systems. From the list it is inferred that the ratio of photoactive systems increases from 0.5 to 0.94 by increasing the number of dithienylethene moieties in the arrays from one to four, resulting in high quantum yields. In this work, the dimer, trimer, and tetramer in Scheme 2 were synthesized and the quantum yields and the mechanism of the cyclization reactions were studied by irradiation with continuous as well as picosecond laser pulse light.

Results and Discussion

Photochromism of Dimer in Hexane. Figure 2 shows the absorption spectral change of the dimer in hexane by photoirradiation. Upon irradiation with 320 nm light, the colorless solution of the open-ring form dimer with the absorption maximum at 320 nm (ϵ, 2.3 × 10^4 M^{-1} cm^{-1}) turned violet, in which characteristic absorption maxima were observed at 365 and 584 nm. The violet color indicates formation of the closed-ring isomer.[6] Upon visible ($\lambda > 540$ nm) light irradiation, the violet color disappeared indicating return to the initial open-ring isomer. The coloration/decoloration cycle could be repeated more than 10 times and a clear isosbestic point was observed at 338 nm even after 10 cycles.

monomer	**trimer**	**tetramer**	
A	A - A - A	P - A - P - P	P - A - A - P
P	P - A - P	P - P - A - P	A - A - A - P
	A - A - P	P - P - A - A	P - A - A - A
dimer	P - A - A	A - A - P - P	A - A - P - A
A - A	A - P - P	A - P - A - P	A - P - A - A
P - A	P - P - A	P - A - P - A	A - A - A - A
A - P	A - P - A	P - P - P - A	A - P - P - A
P - P	P - P - P	A - P - P - P	P - P - P - P

A: antiparallel conformation
P: parallel conformation

Figure 1. Conformations of monomer, dimer, trimer, and tetramer molecules.

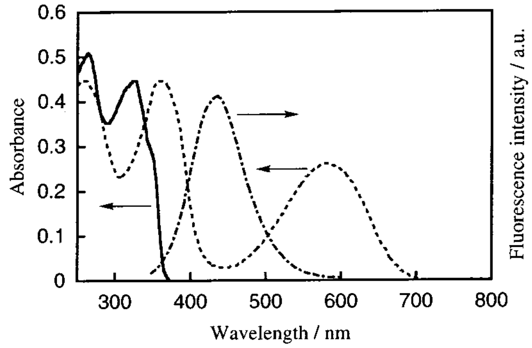
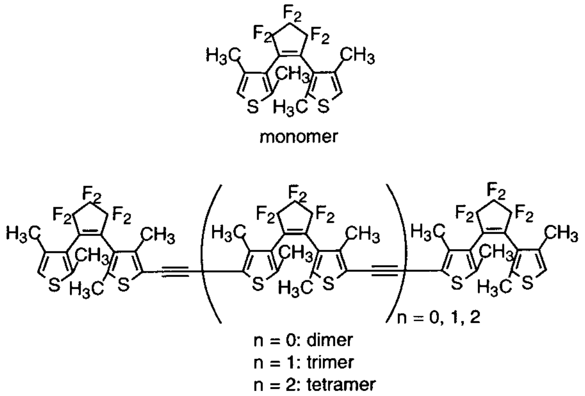


Figure 2. Absorption spectral change of the dimer in hexane upon irradiation with 320 nm light: (—) before photoirradiation and (- - -) after UV-light irradiation for 11 min. The fluorescence spectrum of the (O−O) dimer in hexane was also shown (— - —).

Scheme 2. Structure of Monomer, Dimer, Trimer, and Tetramer



The photoirradiated sample was analyzed with high performance liquid chromatography (HPLC, silica gel column, Wakosil 5SIL, eluent hexane/ethyl acetate (96:4)). When monitored at the isosbestic point of 338 nm, two peaks were observed. When the monitoring wavelength was shifted to 584 nm, at which wavelength only the closed-ring form absorbs, only one peak was observed in the HPLC chart. This indicates that only one closed-ring isomer was produced by UV irradiation. Even after prolonged irradiation any other photoproduct was not

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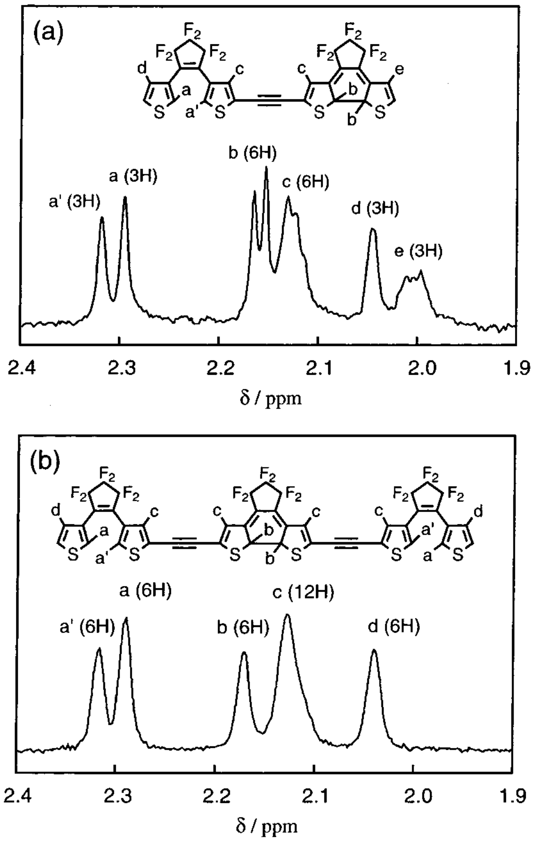


Figure 3. ^{1}H NMR methyl signals of the (O−C) dimer (a) and the (O−C−O) trimer (b).

detected. The absence of the isomer having two closed-ring forms in the photoirradiated dimer agrees to the result observed in the dimers reported by Branda et al.[19]

The colored isomer was collected and the structure was analyzed by ^{1}H NMR spectroscopy. The methyl protons of the colored dimer showed seven signals, as shown in Figure 3a. In the NMR spectrum there existed a characteristic signal at 2.00 ppm assigned to the methyl protons of the closed-ring form and a characteristic signal at 2.04 ppm assigned to the methyl protons of the open-ring form.[20] The ratio of the two signals was 1:1, which means that the colored isomer is an (O−C) dimer having an open-ring form (O) and a closed-ring form (C). The isomer in which both dithienylethenes are in the closed-ring form (C−C) was not detected.

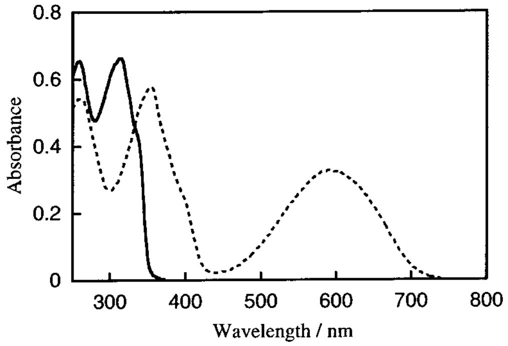


Figure 4. Absorption spectral change of the trimer in hexane upon irradiation with 320 nm light: (—) before photoirradiation and (- - -) after UV-light irradiation for 11 min.

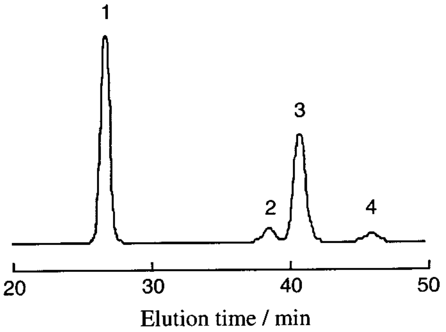
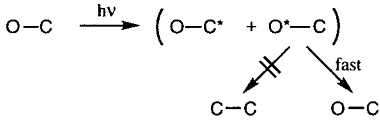


Figure 5. HPLC chromatogram of the trimer irradiated with 320 nm for 11 min in hexane. A UV detector was used for monitoring at 342 nm. The column was silica gel (Wakosil 5SIL) and the eluent was hexane/ethyl acetate (98:2).

Scheme 3. Intramolecular Energy Transfer in the Excited State



To search for the reason the isomer having two closed-ring forms (C−C) was not produced, fluorescence spectra of the initial open-ring form (O−O) dimer and the photogenerated (O−C) dimer were measured in hexane. When excited at 320 nm, the (O−O) dimer gave fluorescence at 440 nm, while the (O−C) dimer did not give fluorescence. As can be seen from Figure 2, there is an overlap of the fluorescence of the (O−O) dimer and the absorption of the (O−C) dimer. The overlap suggests that the intramolecular energy transfer is possible from the excited open-ring unit to the closed-ring unit. In other words, when the (O−C) dimer is excited with UV light, the excited energy of the open-ring form unit is efficiently transferred to the closed-ring form unit in the same molecule, as shown in Scheme 3. Therefore, the cyclization reaction of the remaining open-ring form unit cannot take place. The efficient intramolecular energy transfer process will be discussed in detail in later sections, using the fluorescence depolarization experiment and picosecond laser photolysis.

Photochromism of Trimer in Hexane. Figure 4 shows the absorption spectral change of the trimer by UV irradiation in hexane. Upon irradiation with 320 nm light, the colorless solution of all open-ring form (O−O−O) trimer with the absorption maximum at 325 nm (ϵ, 4.6×10^4 M^{-1} cm^{-1}) turned blue, in which characteristic absorption maxima were observed at 365 and 620 nm. Upon visible ($\lambda > 540$ nm) light irradiation, the blue color disappeared.

The HPLC chromatogram (monitoring wavelength 342 nm) of the solution after UV irradiation is shown in Figure 5. Four peaks were observed. When the monitoring wavelength was changed to 600 nm where the open-ring form unit has no absorption, three peaks except the second peak were observed, indicating that there existed three kinds of closed-ring form isomers. The four peaks were isolated and their structures were determined by UV−vis absorption spectral measurement and ^{1}H NMR spectroscopy.

The first peak trimer had the absorption maximum at 635 nm (ϵ, 2.4×10^4 M^{-1} cm^{-1}). The third and fourth peak trimers had the maxima at 584 nm. These colored isomers converted

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(20) In the NMR spectrum of the monomer, the methyl signals of the open-ring isomer were observed at 2.04 and 2.29 ppm, while they shifted to 2.00 and 2.14 ppm in the closed-ring isomer.

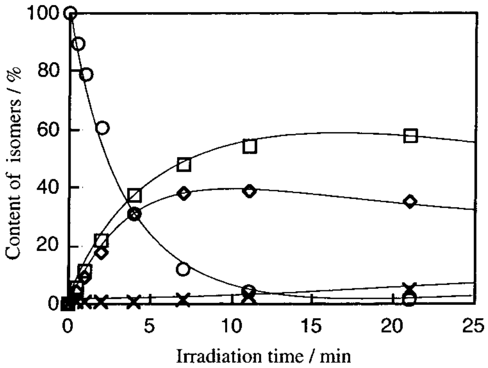

Figure 6. The change in the content of the isomers of the trimer upon irradiation with 320 nm: the (O−O−O) trimer (○), the (O−C−O) trimer (□), the (O−O−C) trimer (◇), and the (C−O−C) trimer (×).

to the open-ring form trimer by irradiation with visible light ($\lambda > 540$ nm). The absorption maxima suggest that the first peak trimer has the closed-ring form in the middle, while the third and fourth peak trimers have the closed-ring form unit(s) at the end, because the absorption maximum of 584 nm was the same as the maximum of the (O−C) dimer. The structures were further examined by ^{1}H NMR measurement.

The methyl protons of the second peak trimer were observed at 2.04, 2.11, and 2.29 ppm, which are assigned to an all open-ring form (O−O−O) trimer. The methyl protons of the first peak trimer showed five signals, as shown in Figure 3b. In the NMR spectrum there was no characteristic signal at 2.00 ppm, which is assigned to the methyl protons of the terminal closed-ring form. This result indicates that the product does not contain the terminal closed-ring form. Thus, the first peak is the (O−C−O) trimer having one closed-ring form unit at the middle. The methyl protons of the third peak trimer showed six peaks. In the NMR spectrum there existed a characteristic signal at 2.00 ppm assigned to the terminal closed-ring form and a characteristic signal at 2.04 ppm assigned to the terminal open-ring form. The ratio of the two signals was 1:1, which means the colored isomer is the (O−O−C) trimer having one closed-ring form at the one end. The absorption coefficient of the fourth peak trimer (584 nm; ϵ, 2.9×10^4 M^{-1} cm^{-1}) was twice as large as that of the third peak trimer (584 nm; ϵ, 1.4×10^4 M^{-1} cm^{-1}), which is the same as that of the (O−C) dimer. This indicates that the peak is due to the (C−O−C) trimer having two closed-ring form units at both ends. The fourth peak is not due to the (O−C−C) trimer, because the absorption maxima was observed at 584 nm (assigned to the terminal closed-ring form), not at 635 nm (assigned to the middle closed-ring form), and the characteristic signal at 2.04 ppm assigned to the terminal open-ring form was not observed. Any isomer in which neighboring two dithienylethene units are converted to the closed-ring forms was not detected.

The time-course of formation of the three isomers (O−C−O, O−O−C, C−O−C) was measured by HPLC, as shown in Figure 6. Upon UV-light irradiation, the amount of all open-ring form (O−O−O) trimer decreased. At the same time the amount of two trimers, O−C−O and C−O−O, having closed-ring form units increased. After 11 min of photoirradiation, the ratio of (C−O−C), (O−C−O), and (O−O−C) isomers was 3:54:39. The amount of (C−O−C) trimer having two closed-ring form units at both ends increased gradually. The rate for formation of the (O−C−O) trimer having one closed-ring form unit in the middle was faster than that of the (O−O−C) trimer having one closed-ring form unit at the end.

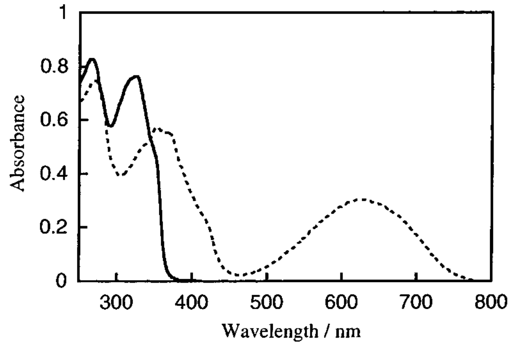

Figure 7. Absorption spectral change of the tetramer in hexane upon irradiation with 320 nm light: (—) before photoirradiation and (- - -) after UV-light irradiation for 8 min.

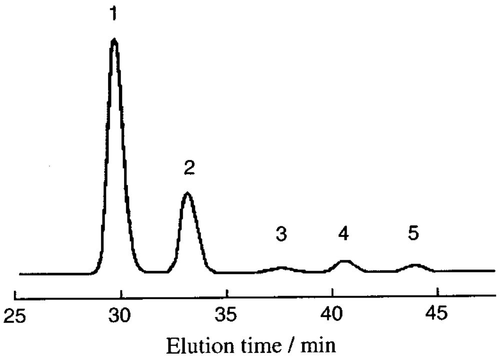

Figure 8. HPLC chromatogram of the tetramer irradiated with 320 nm in hexane. A UV detector was used for monitoring at 346 nm. The column was silica gel (Wakosil 5SIL) and the eluent was hexane/ethyl acetate (96:4).

Photochromism of Tetramer in Hexane. The absorption spectral change of the tetramer in hexane is shown in Figure 7. Upon irradiation with 320 nm light, the colorless solution of the open-ring form tetramer with the absorption maximum at 325 nm (ϵ, 6.9×10^4 M^{-1} cm^{-1}) turned greenish-blue, in which characteristic absorption maxima were observed at 354 and 625 nm. Upon visible ($\lambda > 540$ nm) light irradiation, the greenish-blue color disappeared.

Figure 8 shows the HPLC chromatogram (monitoring wavelength 346 nm) of the solution after UV irradiation. Five peaks were observed. When the monitoring wavelength was changed to 600 nm, where the open-ring form has no absorption, four peaks except the third peak were observed. These four peaks were ascribed to the closed-ring form isomers. The first peak tetramer had the absorption maximum at 635 nm, while the maximum shifted to 620 nm in the second peak tetramer. The fourth and fifth peaks had the absorption maximum at 584 nm. These colored compounds converted to the open-ring form isomer by irradiation with visible light ($\lambda > 540$ nm). These colored and colorless isomers were isolated and their structures were determined by ^{1}H NMR and absorption spectroscopy.

The methyl protons of the third peak tetramer were observed at 2.04, 2.11, and 2.29 ppm, which are identical to those of the open-ring form isomer. The methyl protons of the first peak tetramer showed six signals, in which there was no characteristic signal at 2.00 ppm. This indicates that the first peak is due to the tetramer having no closed-ring form unit at the end and having one inner closed-ring form unit. The methyl protons of

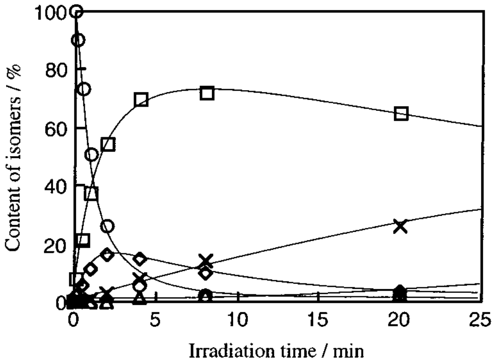

Figure 9. The change in the content of the isomers of the tetramer upon irradiation with 320 nm: the (O−O−O−O) tetramer (○), the (O−O−C−O) tetramer (□), the (O−O−O−C) tetramer (◇), the (O−C−O−C) tetramer (×), and the (C−O−O−C) tetramer (△).

the second peak tetramer showed six peaks. In the spectrum there existed characteristic signals at 2.00 and 2.04 ppm assigned to the terminal closed-ring and open-ring forms, respectively. The peak intensity of a characteristic signal at 2.17 ppm, which is assigned to the methyl protons at the quantarnary carbons in the closed-ring form units, indicates that two closed-ring form units are included in the molecule. This means that the colored isomer is the (O−C−O−C) tetramer having one terminal closed-ring form unit and one inner closed-ring form unit. This peak is not due to the (O−O−C−C) tetramer, because the signal at 2.33 ppm was 3 times larger than the signal at 2.29 ppm. The fourth and fifth peaks had the same absorption maximum at 584 nm. The absorption coefficient of the fifth peak (ϵ, 2.8 $\times$ 10^4 M^{-1} cm^{-1}) was twice as large as that of the fourth peak (ϵ, 1.4 $\times$ 10^4 M^{-1} cm^{-1}) at 584 nm, indicating that the fourth peak is due to the (O−O−O−C) tetramer having one closed-ring form at the end. The fifth peak is the (C−O−O−C) tetramer having two closed-ring form units at both ends. Even in the tetramer any isomer, in which both neighboring dithienylethene units are converted to the closed-ring form, was not detected.

The time-course of formation of the four isomers, (O−C−O−O), (O−O−O−C), (O−C−O−C), and (C−O−O−C), was measured by HPLC, as shown in Figure 9. Upon UV irradiation, the amount of all open-ring tetramer immediately decreased and at the same time the amount of two closed-ring isomers, (O−C−O−O) and (O−O−O−C), increased. The amount of the (C−O−O−C) tetramer having two closed-ring form units at both ends and the (O−C−O−C) tetramer having both inner and terminal closed-ring form units increased gradually. The rate of formation of the (O−C−O−O) tetramer having an inner closed-ring form unit was faster than that of the (O−O−O−C) tetramer having a terminal closed-ring form unit.

Quantum Yields of Dimer, Trimer, and Tetramer. The cyclization quantum yields of dimer, trimer, and tetramer were measured at room temperature. The quantum yield measurement was carried out as follows. The dimer and the trimer were dissolved in hexane and the solutions were irradiated with ultraviolet light ($\lambda = 340$ nm). Cyclohexane was used as the solvent for the tetramer because of its low solubility in hexane. A 500 W xenon lamp was used as the light source and the irradiation wavelength ($\lambda = 340$ nm) was isolated by passing the light through a monochromator. In the case of the monomer and the dimer the rate of cyclization reaction was followed by measuring the absorption increase at 534 nm (ϵ, 5.0 $\times$ 10^3 M^{-1} cm^{-1})[21] and 584 nm (ϵ, 1.4 $\times$ 10^4 M^{-1} cm^{-1}), respectively. In the case of the trimer and the tetramer the irradiated hexane or cyclohexane solutions were passed through HPLC and the ratio change of each product upon irradiation was analyzed by setting the monitoring wavelength to the quasi-isosbestic point. The absorption increase at 584 and 635 nm was also followed to confirm the accuracy of the quantum yield determination. The light intensity was monitored by a photometer, which was calibrated by the photoreaction of furylfulgide in hexane solution. The quantum yield measurement was carried out three times for each multi-dithienylethene arrays and the average values were adopted as the quantum yields. The error of the relative quantum yields among the oligomers was less than ±5%, while the error of absolute values was on the order of ±10%.

The quantum yield of the open-ring form (O−O) dimer to the (O−C) dimer was determined to be 0.31. The yields of the trimer from the all open-ring form (O−O−O) isomer to the (O−C−O) isomer having one closed-ring form unit at the middle and the (O−O−C) isomer having one closed-ring form unit at the end were 0.20 and 0.16, respectively. The total cyclization yield of the trimer was 0.36. The cyclization quantum yields of the tetramer from the all open-ring form (O−O−O−O) isomer to the (O−C−O−O) isomer having one inner closed-ring form unit and the (O−O−O−C) isomer having one terminal closed-ring form unit were determined to be 0.30 and 0.10, respectively. The total cyclization quantum yield was 0.40. The photocyclization quantum yields increased by increasing the number of dithienylethene moieties in the arrays. The increase in the quantum yields is attributed to the intramolecular energy migration from the photochemically inactive parallel conformation unit to the photoactive one, as described in the introductory section.

Fluorescence Depolarization. To confirm the intramolecular energy migration in the arrays, depolarization of fluorescence was measured in a 2-methyltetrahydrofuran rigid glass at 77 K. An excitation wavelength of 320 nm was selected. Dithienylethenes undergo photochromic reactions even in the solid state at low temperature.[22] Fluorescence spectra of the dimer, the trimer and the tetramer gave a similar emission at 440 nm, while the emission of the monomer was observed at 420 nm. The fluorescence polarization values ($p = (I_{\|} - I_{\perp})/(I_{\|} + I_{\perp})$) were determined to be 0.51 (monomer), 0.23 (dimer), 0.17 (trimer), and 0.14 (tetramer), respectively. For the monomer, the polarization of the fluorescence directly correlates with the direction of the polarized excitation light. In the case of the multi-dithienylethene arrays, depolarization took place. The p values decreased by increasing the number of the dithienylethene moieties in the arrays. This result clearly indicates that the excited energy migrates in the arrays.[23]

Reaction Dynamics. To reveal the dynamics of the excited energy migration, a laser photolysis experiment was carried out with use of a picosecond laser pulse. Figure 10a shows the time-resolved transient absorption spectra of the dimer in a hexane solution excited with a picosecond 355 nm laser pulse. A broad absorption spectrum with maxima around 490 and 750 nm appeared within the time resolution of the apparatus, followed

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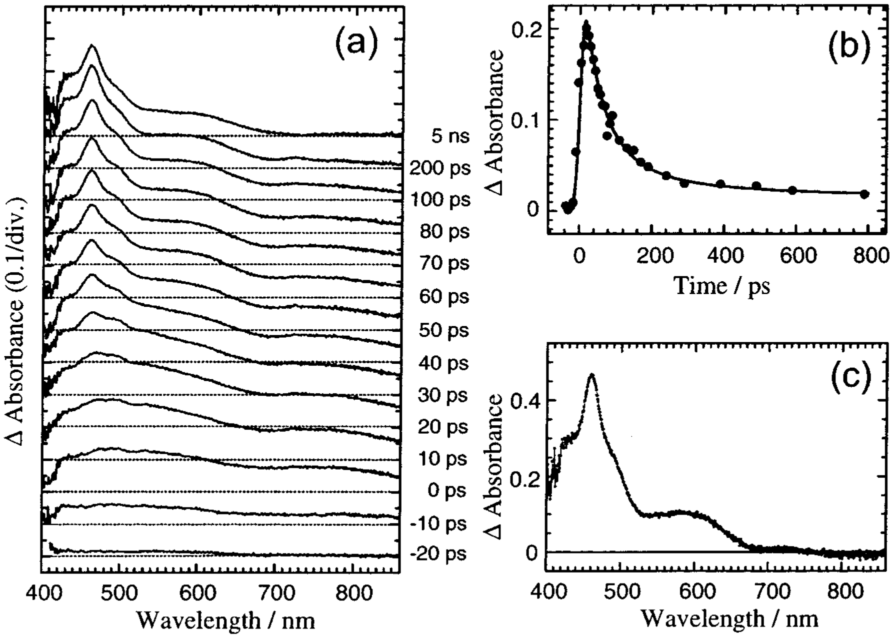

Figure 10. (a) Time-resolved transient absorption spectra of the open-ring form (O−O) dimer in hexane, excited with a picosecond 355 nm laser pulse. (b) Time profile of transient absorbance at 780 nm. This solid line is the result calculated on the basis of the double-exponential function (see text). (c) Difference spectrum between that at 100 ps and that at 0 ps for the time-resolved transient absorption spectra of the open-ring form (O−O) dimer in hexane, excited with a picosecond 355 nm laser pulse.

by the growth of sharp absorption maximum at 465 nm in the time region of a few hundred picoseconds and the apparent decrease in absorption intensity in the wavelength region >650 nm. No spectral change was observed in subnanoseconds to nanoseconds time region. Figure 10b shows the time profile of the transient absorption band at 780 nm. The solid line in Figure 10b shows the results calculated on the basis of the double-exponential function as eq 1,

$$A_{780}(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \qquad (1)$$

where τ_1 and τ_2 are 35 and 100 ps, and A_1, A_2, and A_3 are 46, 46, and 8%, respectively. The pulse widths of the excitation and the monitoring pulses were convoluted in the curve. Since the broad spectrum appeared within the time resolution of the apparatus and the time constant of the fluorescence decay was obtained to be ca. 100 ps,[24] it is concluded that the broad absorption observed immediately after the excitation is due to the S_1 state.

To explore the spectral evolution in the early stage after the excitation, the difference spectrum between that at 100 ps and that at 0 ps was plotted in Figure 10c. Both of the spectra used for the calculation were normalized at 750 nm. A sharp absorption peak at 465 nm and a broad absorption band at 580 nm were obtained as the difference. Since the former sharp absorption at 465 nm did not decrease in the time window examined here (6 ns), this band is ascribed to a long-living species such as a triplet state. On the other hand, the absorption band at 580 nm is ascribed to the (O−C) dimer. On the basis of the above results, the spectral evolution around 580 nm is attributable to the formation of the closed-ring form.

To quantitatively elucidate the formation process of the closed-ring form, the time profiles of various wavelength points were analyzed. However, all the time profiles except for the wavelength region around 465 nm showed only the decay behaviors, indicating that the broad absorption due to the S_1 state has rather large extinction coefficients in the entire wavelength region >650 nm. The absorption signals in the longer wavelength region are mainly due to the S_1 state. Accordingly, we subtracted the contribution of this S_1 spectrum (the spectrum at 0 ps) from each of the spectra observed at various delay times after the excitation by adjusting the intensity of the spectrum at 750 nm to those at various delay times. The transient spectra thus obtained are shown Figure 11a. The absorption spectra with maxima at 465 and 580 nm increase with an increase in the delay time after the excitation. The time profile of the transient absorbance at 580 nm due to the closed-ring form (O−C) is exhibited in Figure 11b. The solid line in this figure shows the result calculated on the basis of the double-exponential rise function (eq 2). The initial instaneous rise was eliminated for the calculation,

$$A(t) = A - \{A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)\} \qquad (2)$$

where τ_f and τ_s are (35 ± 5) and (100 ± 10) ps, respectively. The relative preexponential factors, A_f and A_s, are 47 and 53%. These time constants were in agreement with those for the decay of the S_1 state monitored at 780 nm (Figure 10b). Similar biphasic rise behavior was also observed for the transient absorbance at 465 nm.

To precisely elucidate the production pathways of the closed-ring form, the difference spectra between those at several delay times were plotted. Figure 12 exhibits the difference spectra between those at 500 ps and 120 ps and between those at 120 ps and 20 ps. As is clearly shown in these spectra, the latter spectrum actually shows the formation of the closed-ring form

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[24] Single photon counting with a subnanosecond light pulse was used for the fluorescence measurement. Since the time resolution is not so sufficient to precisely determine the biphasic decay behaviors, single-exponential decay was assumed for the fluorescence decay.

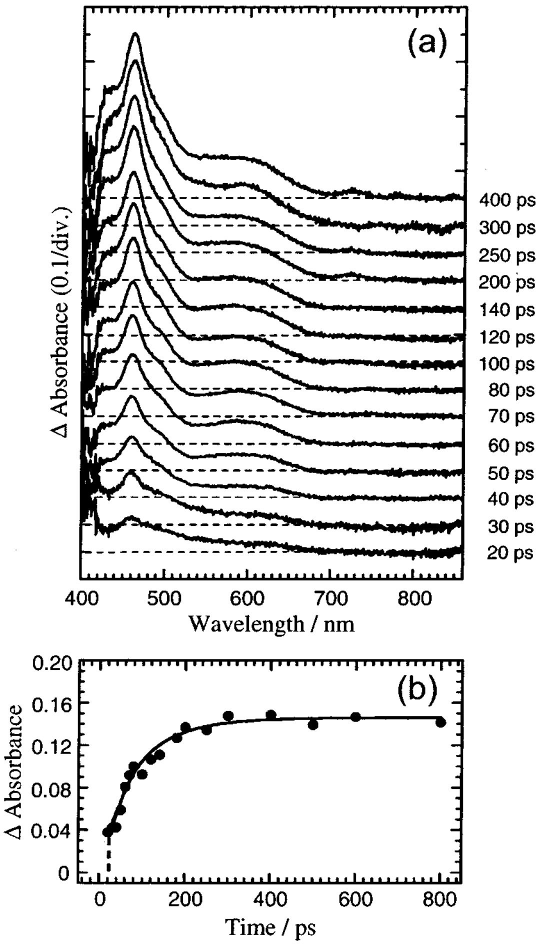


Figure 11. (a) Time-resolved transient absorption spectra of the open-ring form (O−O) dimer in hexane, excited with a picosecond 355 nm laser pulse. The contribution from the broad $S_n \leftarrow S_1$ spectrum was subtracted for each of the spectra (see text). (b) Time profile of the transient absorbance at 580 nm. The solid line is the result calculated on the basis of the double-exponential function (see text).

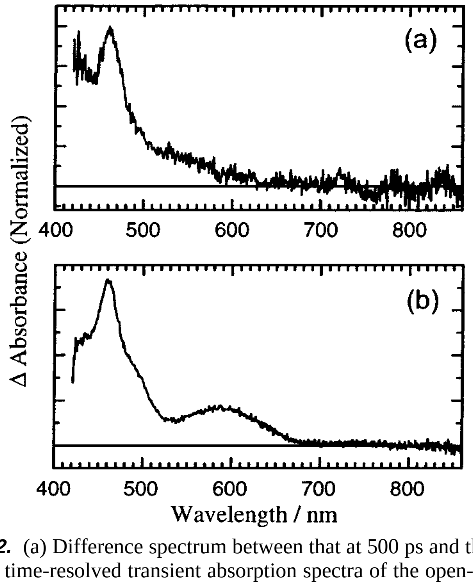
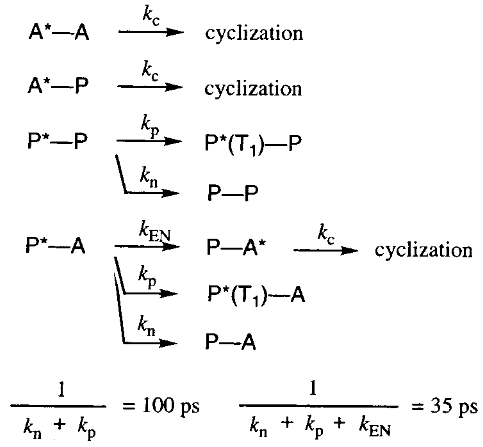


Figure 12. (a) Difference spectrum between that at 500 ps and that at 120 ps for the time-resolved transient absorption spectra of the open-ring form (O−O) dimer in hexane, excited with a picosecond 355 nm laser pulse. (b) Difference spectrum between that at 120 ps and that at 20 ps.

(O−C) with the absorption maximum at 580 nm together with the rise of the absorption at 465 nm, while the characteristic absorption spectrum of the closed-ring form is not obtained in the former difference spectrum. This result indicates that most of the closed-ring form was produced with the time constant of (35 ± 10) ps. The absorption rise with the time constant of (100 ± 10) ps observed at 580 nm was due to the growth of the absorption tail of the species with its maximum at 465 nm.

Scheme 4. Reaction



Scheme 4 shows the reaction processes in the dimer. A and P represent antiparallel and parallel conformer units, respectively. The direct cyclization reactions of A*-A and A*-P are considered to take place in less than 10 ps, because the cyclization of the monomer bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene in solution is reported to proceed in less than 10 ps.[25] The instaneous rise of the absorption due to the closed-ring form during the pulse is ascribed to this process. The short (35 ps) and long (∼100 ps) time constants observed in the decay of the S_1 state are ascribed to the deactivation process of P*-A and P*-P, respectively, because the former process correlates with the formation of the closed-ring form (O−C) and the latter to the slow formation of the triplet state. The energy migration rate is estimated to be 1.9×10^{10} s^{-1}.

Time-resolved transient absorption spectra of the trimer are shown in Figure 13a. Similar time evolution was observed as in the dimer. The transient absorption spectrum at 5 ns is plotted in Figure 13b, together with that of the dimer at 5 ns. These two spectra were normalized at 465 nm where the absorption of the P*(T_1) has dominant contribution. The contribution of the absorption intensity at 465 nm, relative to that from the closed-ring form, in the transient spectrum of the dimer at 5 ns after the excitation is larger than that for the trimer. This result indicates that more efficient energy migration from P* to A in the trimer suppresses the triplet formation in P*. In other words, the closed-ring form formation increased in the trimer system via the energy migration from the P* to the A conformer.

Lindsey and co-workers[15−18] systematically studied the energy migration process among multiporphyrin arrays bridged by ethynylene bonds. According to their results, the energy migration (or transfer) time constants between the porphyrin moieties were on the order of several picoseconds to ca. 100 ps. Although the molecular structure and the energy gap in the present systems are different from those of their systems, it is possible to compare the energy migration rate constant for the dithienylethene system with those of their system. The rate constant of the present system is similar to those for the multiporphyrin arrays.

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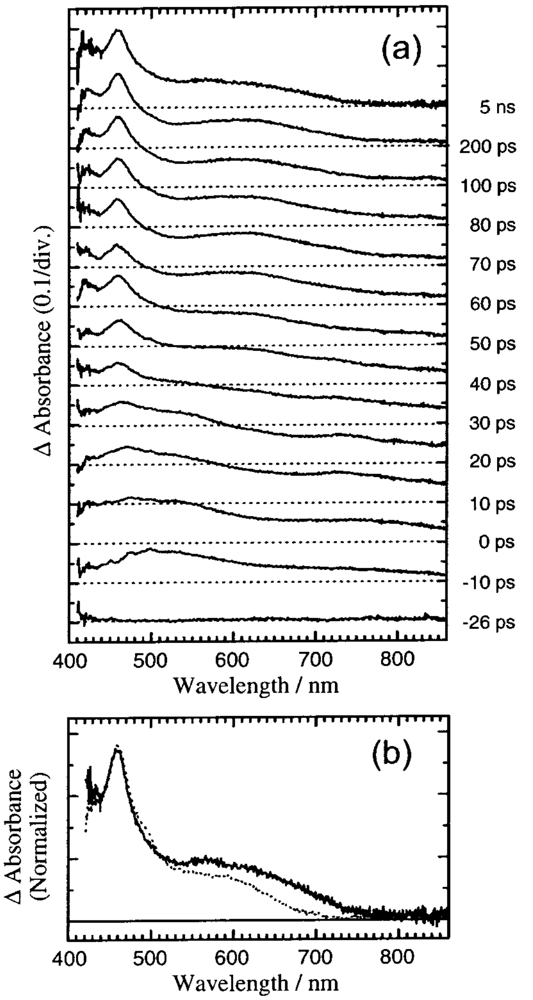
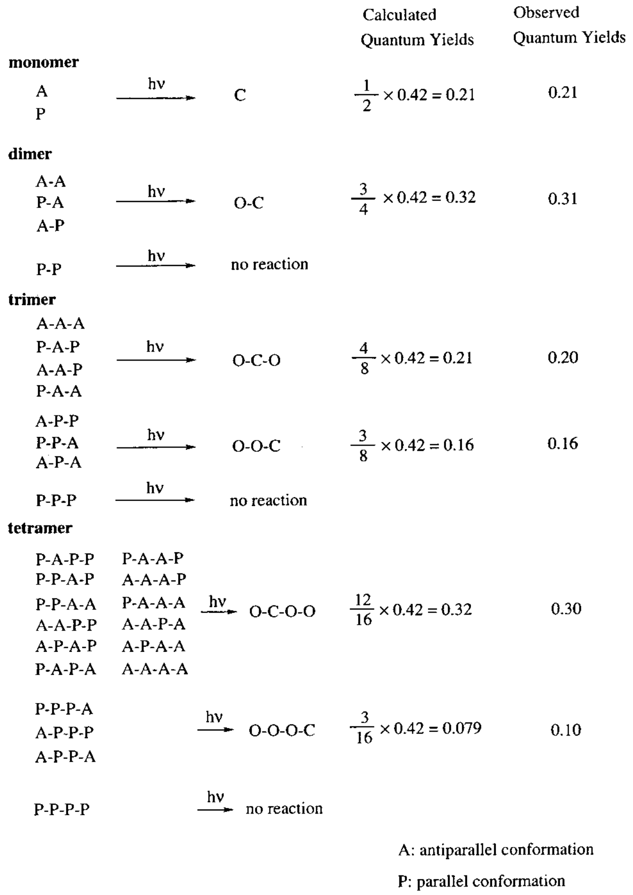


Figure 13. (a) Time-resolved transient absorption spectra of the open-ring form (O—O—O) trimer in hexane, excited with a picosecond 355 nm laser pulse. (b) Transient absorption spectra at 5 ns of the (O—O) dimer (dotted line) and of the (O—O—O) trimer (solid line).

Comparison of the Quantum Yields with the Calculated Values. Finally we compare the observed quantum yields with the calculated values based on the intramolecular energy migration model. The cyclization quantum yield of the monomer was 0.21 in hexane.[21] The open-ring form of the monomer has photoactive antiparallel and inactive parallel conformations in equal amounts in solution.[12] Thus, the actual cyclization quantum yield of the antiparallel conformer is 0.42. On the basis of the assumption that 0.42 is the cyclization quantum yield of each dithienylethene unit in an antiparallel conformation and that the energy transfer from inactive parallel conformation to photoactive antiparallel conformation takes place in the arrays, the expected cyclization quantum yields can be calculated as shown in Figure 14. In this calculation the conformations having parallel conformation unit(s) in the inner part are separated from other conformations having inner antiparallel unit(s), and the inner antiparallel units are assumed to be preferentially converted to the closed-ring forms over the terminal antiparallel units. Therefore, A-A-A, A-A-P, and P-A-A trimers and A-A-A-A, A-P-A-A, A-A-P-A, P-A-A-A, A-A-A-P, P-A-P-A, A-P-A-P, A-A-P-P, and P-P-A-A tetramers are all classified as conformers that cyclize to produce the oligomers having an inner closed-ring form unit. It is experimentally possible to determine individual quantum yields to produce (O—C—O) and (O—O—C) trimers and (O—C—O—O) and (O—O—O—C) tetramers, respectively.



			Calculated Quantum Yields	Observed Quantum Yields
monomer				
A P	$\xrightarrow{h\nu}$	C	$\frac{1}{2} \times 0.42 = 0.21$	0.21
dimer				
A-A P-A A-P	$\xrightarrow{h\nu}$	O-C	$\frac{3}{4} \times 0.42 = 0.32$	0.31
P-P	$\xrightarrow{h\nu}$	no reaction		
trimer				
A-A-A P-A-P A-A-P P-A-A	$\xrightarrow{h\nu}$	O-C-O	$\frac{4}{8} \times 0.42 = 0.21$	0.20
A-P-P P-P-A A-P-A	$\xrightarrow{h\nu}$	O-O-C	$\frac{3}{8} \times 0.42 = 0.16$	0.16
P-P-P	$\xrightarrow{h\nu}$	no reaction		
tetramer				
P-A-P-P P-A-A-P P-P-A-P A-A-A-P P-P-A-A P-A-A-A A-A-P-P A-A-P-A A-P-A-P A-P-A-A P-A-P-A A-A-A-A	$\xrightarrow{h\nu}$	O-C-O-O	$\frac{12}{16} \times 0.42 = 0.32$	0.30
P-P-P-A A-P-P-P A-P-P-A	$\xrightarrow{h\nu}$	O-O-O-C	$\frac{3}{16} \times 0.42 = 0.079$	0.10
P-P-P-P	$\xrightarrow{h\nu}$	no reaction		

A: antiparallel conformation
P: parallel conformation

Figure 14. The calculated and observed cyclization quantum yields of monomer, dimer, trimer, and tetramer systems.

The (O—O) dimer has four conformations. Among them only one conformation that has all parallel conformers is photoinactive and other three conformations can undergo the photocyclization reaction. The cyclization quantum yield is expected to be 0.32 by calculating 0.42 × 3/4. The open-ring trimer has seven photoactive conformations among eight possible conformations. As described above, the seven photoreactive conformers are classified into four conformers that have a photoactive antiparallel unit in the middle and three conformers that have a photoinactive parallel unit in the middle and a photoactive antiparallel unit at the end. The individual quantum yields to produce (O—C—O) and (O—O—C) isomers are calculated to be 0.21 and 0.16, respectively. The total cyclization quantum yield is expected to be 0.37. Furthermore, the open-ring tetramer has 15 photoactive conformations among 16 possible conformations. On the basis of the above assumptions, the quantum yields to produce (O—C—O—O) and (O—O—O—C) isomers are calculated to be 0.32 and 0.079, respectively. The total cyclization quantum yield is expected to be 0.40. The ratio of the arrays having all parallel conformer to the arrays having at least one antiparallel conformer decreases with an increase in the number of dithienylethene moieties. Therefore, the cyclization quantum yield is expected to increase. As can be seen from Figure 14, the observed quantum yields agree to the calculated yields, though the calculation slightly overestimates the formation of the inner closed-ring form isomers. The faster rate for formation of photoproducts having an inner closed-ring form unit as shown in Figures 6 and 9 supports the above calculation model. The preferential cyclization of the inner antiparallel units is partly ascribed to the fact that the inner dithienylethene units have a higher probability of receiving the excited energy from both sides than the terminal units.

The cycloreversion quantum yields of the (O−C) dimer and the (O−C−O) and (O−O−C) trimers were also measured. In these measurements the absorption maxima (584 and 635 nm) were irradiated. The cycloreversion quantum yield of the (O−C−O) trimer ($\Phi = 6.0 \times 10^{-4}$) was much lower than the value of the (O−O−C) trimer ($\Phi = 1.1 \times 10^{-2}$), which was the same as the value of the (O−C) dimer ($\Phi = 1.1 \times 10^{-2}$). The low quantum yield of the (O−C−O) trimer agrees with the previous observation that the cycloreversion yields of dithienylethenes having long π-conjugated aryl groups were low.[26,27]

Conclusions

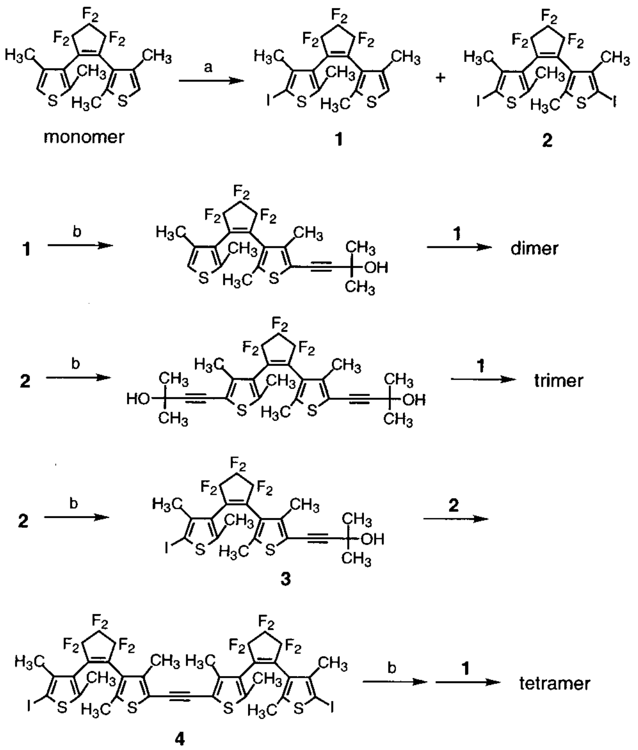
Dithienylethene dimer, trimer, and tetramer were synthesized by connecting the dithienylethene moieties with ethynylene bonds. The photocyclization quantum yields increased by increasing the number of dithienylethene units in the multi-dithienylethene arrays. The array construction is an effective strategy for obtaining an efficient photochromic dithienylethene molecule. Although various types of isomers, in which one or two dithienylethene units are converted to the closed-ring forms, were observed upon UV irradiation, the isomer, in which both neighboring dithienylethene units are converted to the closed-ring forms, was not detected. The high quantum yield in tetramer, the absence of neighboring closed-ring forms, fluorescence depolarization, and slow formation of the closed-ring forms around 35 ps confirmed that the excited energy efficiently migrates in the multi-dithienylethene arrays. The arrays have the potential for multi-addressing molecular memories.

Experimental Section

General. Absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3410). Fluorescence spectra were measured with a fluorescence spectrophotometer (Hitachi F-3010). Fluorescence polarization was determined in a 2-methyltetrahydrofuran rigid glass at 77 K. The fluorescence polarization values ($p = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$) were determined by the G-factor method.[23] ^{1}H NMR spectra were recorded on a Varian-Gemini-200 (200 MHz) spectrometer. Mass spectra were measured with mass spectrometers (Shimadzu GCMS-QP5050A and JEOL JMS−HXIIOA). Photoirradiation was carried out by using a Ushio 500 W xenon lamp as the exciting light source. Monochromatic light was isolated by passing the light through a Toshiba cutoff filter (UV-27) and a monochromator (Ritsu MC-10N). A photometer (International Light IL 1700) was used for light intensity measurement. Silica gel columns (Wakosil 5SIL, Wako) were used to isolate isomers. HPLC was performed on a Shimadzu LC-6AD liquid chromatograph coupled with a Shimadzu SPD-10AV spectrophotometric detector. The quantum yields were determined as described in the text. The samples were not degassed.

Reaction Dynamics. A picosecond laser photolysis system with a repetitive mode-locked Nd^{3+}:YAG laser was used for transient absorption spectral measurements.[28] The third harmonic pulse (355 nm) with 15 ps fwhm and 0.5 mJ output power was used for excitation. The excitation pulse is focused into a spot with a diameter of ca. 0.15 cm. A picosecond white continuum generated by focusing the fundamental pulse into a 10 cm quartz cell containing a D_2O-H_2O mixture was used as a monitoring pulse. A sample cell with a 1 cm length was used. The repetition rate for the laser excitation was kept low (<0.2 Hz) and the sample solution was circulated to avoid the pile-up of the closed-ring form. Sample solutions (ca. 10^{-4} M) were deaerated by irrigating with N_2 gas. All the measurements were performed at 20 ± 2 °C.

Scheme 5



Reagents (a) I_2, HIO_3; (b) 2-methyl-3-butyn-2-ol, benzyltriethylammonium chloride, CuI, $Pd(PPh_3)_4$, NaOH(aq).

Synthesis of Oligomers. All open-ring form dimer, trimer, and tetramer molecules were synthesized according to Scheme 5. 1,2-Bis-(2,4-dimethylthiophen-3-yl)perfluorocyclopentene (monomer),[12] a monoiodide of the monomer (**1**), and a diiodide of the monomer (**2**) were prepared according to the method described before.[26]

Dimer. A degassed solution of 2-methyl-3-butyn-2-ol (0.055 mL, 0.56 mmol) and **1** in benzene was added to a mixture of benzyltriethylammonium chloride (3.8 mg, 1.7×10^{-2} mmol), copper(I) iodide (5.0 mg, 2.5×10^{-2} mol), tetrakis(triphenylphosphine)palladium (29 mg, 2.5×10^{-2} mol), and 5.5 N NaOH aqueous solution (5 mL). The mixture was stirred at room temperature for 24 h. Then, a solution of **1** (290 mg, 0.56 mmol) in benzene (5 mL) was added, and the mixture was stirred for 18 h at 70 °C. The reaction was stopped by the addition of a saturated ammonium chloride solution at room temperature. The mixture was extracted with ether. The organic layer was washed with water and dried with $MgSO_4$ and then the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane:chloroform (9:1)) and HPLC to give 130 mg of dimer in 20% yield as solid. Dimer: no melting point below 200 °C; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.04 (s, 6H; CH_3), 2.11 (s, 6H; CH_3), 2.29 (s, 12H; CH_3), 6.72 (s, 2H; thienyl CH); MS m/z =814 [M$^+$]. Anal. Calcd (%) for $C_{36}H_{26}F_{12}S_4$: C 53.07, H 3.22. Found: C 53.45, H 3.34.

Trimer. The coupling reaction of 2-methyl-3-butyn-2-ol (0.06 mL, 0.62 mmol) and **2** (200 mg, 0.31 mmol) was performed by the procedure as described above. Then, **1** (320 mg, 0.62 mmol) was added to the reaction mixture. The residue was purified by column chromatography on silica gel (hexane:chloroform (9:1)) and HPLC and gave 340 mg of trimer in 70% yield as solid. Trimer: no melting point below

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200 °C;^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.04 (s, 6H; CH_3), 2.11 (s, 12H; CH_3), 2.29 (s, 18H; CH_3), 6.72 (s, 2H; thienyl CH); HRMS-FAB *m*/*z* [M^+] calcd for $C_{55}H_{38}F_{18}S_6$ 1232.1, found 1232.2.

Compound 3. The coupling reaction of 2-methyl-3-butyn-2-ol (0.23 mL, 2.31 mmol) and **2** (1.5 g, 2.31 mmol) was performed by the procedure as described above. The residue was purified by column chromatography on silica gel (chloroform) and HPLC and gave 340 mg of **3** in 40% yield. **3**: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 1.54 (s, 6H; CH_3), 1.98 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.26 (s, 6H; CH_3); MS *m*/*z* 604 [M^+].

Compound 4. The coupling reaction of **3** (640 mg, 0.96 mmol) and **2** (680 mg, 1.0 mmol) was performed by the procedure as described above. The residue was purified by column chromatography on silica gel (hexane:chloroform (9:1)) and HPLC and gave 280 mg of **4** in 70% yield. **4**: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.00 (s, 6H; CH_3), 2.11 (s, 6H; CH_3), 2.29 (s, 12H; CH_3); HRMS-FAB *m*/*z* [M^+] calcd for $C_{36}H_{24}F_{12}I_2S_4$ 1065.9, found 1065.9.

Tetramer. The coupling reaction of 2-methyl-3-butyn-2-ol (0.05 mL, 0.05 mmol) and **4** (280 mg, 0.24 mmol) and **1** (256 mg, 0.50 mmol) was performed by the procedure as described above. The residue was purified by column chromatography on silica gel (hexane:chloroform (9:1)) and HPLC and gave 160 mg of tetramer in 70% yield as solid. Tetramer: no melting point below 200 °C;^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.04 (s, 6H; CH_3), 2.11 (s, 18H; CH_3), 2.29 (s, 24H; CH_3), 6.71 (s, 2H; thienyl CH); HRMS-FAB *m*/*z* [M^+] calcd for $C_{74}H_{50}F_{24}S_8$ 1650.1, found 1650.2.

Closed-Ring Isomer of the Dimer (O−C). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.00 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.11 (s, 6H; CH_3), 2.15 (s, 3H; CH_3), 2.16 (s, 3H; CH_3), 2.30 (s, 3H; CH_3), 2.32 (s, 3H; CH_3), 6.72 (s, 2H; thienyl CH).

Closed-Ring Isomer of the Trimer (O−C−O). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.04 (s, 6H; CH_3), 2.12 (s, 12H; CH_3), 2.17 (s, 6H; CH_3), 2.29 (s, 6H; CH_3), 2.32 (s, 6H; CH_3), 6.72 (s, 2H; thienyl CH).

Closed-Ring Isomer of the Trimer (C−O−O). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.00 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.11 (s, 12H; CH_3), 2.16 (s, 6H; CH_3), 2.29 (s, 9H; CH_3), 2.32 (s, 3H; CH_3), 6.72 (s, 2H; thienyl CH).

Closed-Ring Isomer of the Tetramer (O−C−O−O). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.04 (s, 6H; CH_3), 2.12, 2.13 (brd, 18H; CH_3), 2.17 (s, 6H; CH_3), 2.29 (s, 12H; CH_3), 2.32 (s, 6H; CH_3), 6.72 (s, 2H; thienyl CH).

Closed-Ring Isomer of the Tetramer (C−O−C−O). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.00 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.13 (s, 18H; CH_3), 2.17 (s, 12H; CH_3), 2.29 (s, 3H; CH_3), 2.33 (s, 9H; CH_3), 6.72 (s, 2H; thienyl CH).

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