PERKIN 2

Photochromism of dithienylethene-bis(trimethylammonium) iodide in cyclodextrin cavities

Michinori Takeshita,[*ab]† **Motoki Yamada,**[ab] **Nobuo Kato**[c] **and Masahiro Irie**[*ab]

[a] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Japan*
[b] *CREST, Japan Science and Technology Corporation, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[c] *Institute of Advanced Material Study, Kyushu University, Kasuga 816-8580, Japan*

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On the addition of β-cyclodextrin, the proportion of the photoactive anti-parallel conformation of photochromic 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophen-6-yltrimethylammonium) iodide (**1a**) increased, and the cyclization quantum yield was found to increase. On the other hand, the proportion of the photoinactive conformation increased on the addition of γ-cyclodextrin and the quantum yield decreased. The structures of the complexes were estimated from NOESY spectra.

Introduction

Various types of photochromic compounds have been developed in an attempt to apply them to photonic devices.[1] Among them, the diarylethenes family is one of the most promising candidates for the application, because of its thermally irreversible and high fatigue-resistant characteristics.[2] Fig. 1 shows the photochromic reaction of a diarylethene. The open-ring isomer has two conformations, anti-parallel and parallel conformations. These conformations exchange even at room temperature and the energy barrier of these conformations is 60–70 kJ mol^{-1}.[3] The cyclization reaction is undergone only by the anti-parallel conformation upon irradiation with UV light, while the parallel conformation is photochemically inactive.[4] Therefore, the quantum yield for the cyclization reaction is dependent on the ratio of these conformations. Various attempts have been made to change the ratio.[4–9] For example, the proportion of the anti-parallel conformation of a dithienylethene having two carboxylic acid groups decreased on intramolecular hydrogen bond formation.[4] Introduction of bulky isopropyl groups at the 2- and 2′-positions of benzothiophene aryl groups increased the proportion of the anti-parallel conformation of bis(benzothienyl)perfluorocyclopentene.[8] The anti-parallel conformation of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) became dominant upon addition of β- or γ-cyclodextrins (CDx) and the quantum yield for the cyclization reaction increased.[6]

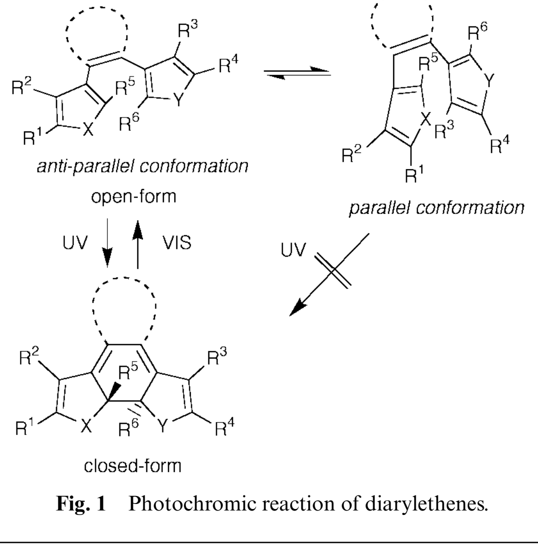

Fig. 1 Photochromic reaction of diarylethenes.

In this paper, we report on the effect of addition of CDx on the cyclization quantum yield of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophen-6-yltrimethylammonium) iodide **1a** in aqueous solutions. The photoreversible change of CD spectra of mixtures of **1** and CDx in aqueous solution was also examined.

Results and discussion

Synthesis and properties of 1

Trimethylammonium salt **1** was synthesized from diamino compound **3**, which was prepared from **2**[9] by treatment with $NaBH_4$–$NiCl_2$ in methanol as shown in Scheme 1. Compound **3** was so labile that **3** was used in the next step without purification.

Fig. 2 shows the absorption spectral change of an aqueous solution of **1** (2.0 × 10^{-5} mol dm^{-3}) upon irradiation with 313 nm light. The initial colorless solution of **1** turned red and

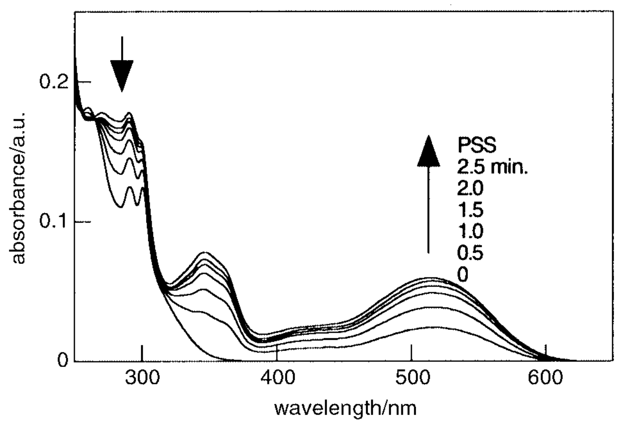

Fig. 2 Absorption spectral change of an aqueous solution of **1** (2.0 × 10^{-5} mol dm^{-3}) upon irradiation with 313 nm light.

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† *Present address*: Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840-8502, Japan.

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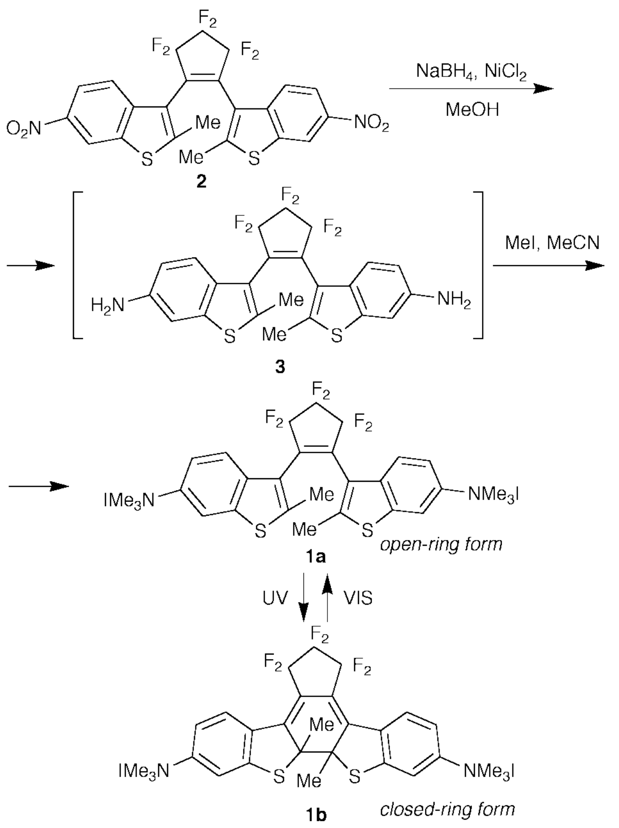

Scheme 1

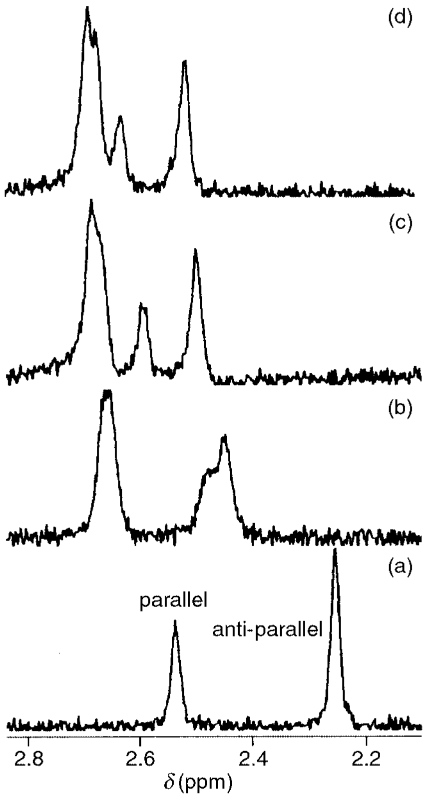

Fig. 3 ^{1}H NMR spectra of **1a** in D_2O (2.0×10^{-3} mol dm^{-3}, 200 MHz, 20 °C, in part) upon addition of γ-CDx (a) in the absence of γ-CDx, (b) 0.5 equiv., (c) 1.0 equiv., (d) 10 equiv. of γ-CDx was added.

the new absorption maxima appeared at 514 and 346 nm, which correspond to the closed-ring form isomer **1b**. The red solution totally restored the initial spectrum upon irradiation with visible light longer than 480 nm. The extinction coefficient (ε) of the closed-ring isomer **1b** in aqueous solution at the absorption maximum of 514 nm was 8300. The quantum yield for the cyclization reaction (313 nm light) was 0.16.[10] The conversion of **1** upon irradiation with 313 nm light was 38%.

NMR Spectra of 1 in the absence/presence of CDx

Fig. 3 shows the ^{1}H NMR spectra (in part) of **1a** in the absence or presence of γ-CDx in D_2O solution ([**1a**] = 2.0×10^{-3} mol dm^{-3}). In the absence of γ-CDx (Fig. 3a), the methyl group at the 2-position of the benzothiophene moiety of **1a** was observed as two singlets at 2.26 and 2.54 ppm. The resonance at higher magnetic field was assigned to the anti-parallel conformation and that at lower field to the parallel conformation.[6b,11] The two separate methyl signals indicate that these conformations exchange with each other at a rate slower than the NMR time scale.[3,6b,11] The ratio of the parallel and anti-parallel conformations was 40:60 in D_2O solution at 293 K. Therefore, 60% of **1a** is photochemically active and the rest is inactive. Upon addition of γ-CDx, these proton signals shifted to lower magnetic field and the ratio changed as shown in Fig. 3. When 1.0 equivalent of γ-CDx for **1a** was added, three kinds of methyl protons were observed and the ratio of the parallel and anti-parallel conformations became 75:25 (Fig. 3c). The photoinactive species became dominant on the addition of γ-CDx. The resonance at higher magnetic field was assigned to the anti-parallel conformation and that at lower magnetic field to the parallel conformation. The ratio of these conformations remained similar even when the amount of γ-CDx was increased to 10 equivalent. No change in the ratio of the conformations was found when excess γ-CDx was added. Fig. 4a shows the NOESY spectrum of **1a** in the presence of 2 equivalents of γ-CDx ([**1a**] = 2.0×10^{-3} mol dm^{-3}, in D_2O, 20 °C, 600 MHz, mixing time 500 ms). Strong NOEs were observed between the methylene protons of the primary hydroxy group of γ-CDx and the methyl protons of the parallel conformation (indicated by the arrow). Weak NOEs were observed between the other protons of γ-CDx and the methyl protons of the parallel conformation. These NOESY spectra indicate that the parallel conformation of **1a** was included in the cavity of γ-CDx and methyl protons were close to the primary hydroxy group. Fig. 5 shows a conceivable structure for the inclusion complex of the parallel conformation of **1a** in the γ-CDx cavity. The folded structure was also supported by the CD spectrum of the complex (discussed later).

On the other hand, the content of the anti-parallel conformation slightly increased on the addition of β-CDx as shown in Fig. 6. The ratios of these conformations were determined from ^{1}H NMR spectra at 20 °C. Upon addition of 20 equivalents of β-CDx to a D_2O solution of **1a** (2.0×10^{-3} mol dm^{-3}), the ratio of the parallel and anti-parallel conformations was changed from 40:60 to 29:71 at 20 °C. Under these conditions, 71% of **1a** is photochemically active. Fig. 4b shows the NOESY spectrum of a mixture of **1a** and 20 equivalent of β-CDx ([**1a**] = 2.0×10^{-3} mol dm^{-3}, in D_2O, 20 °C, 600 MHz, mixing time 500 ms). The spectrum indicates that the methyl protons of the parallel conformation are close to the protons of the primary hydroxy group of β-CDx while the methyl protons of the anti-parallel conformation are close to the other protons of β-CDx. Therefore, both conformations are included in the β-CDx cavity and the structure of the complex composed of the parallel conformation and β-CDx is similar to that of a complex of **1a** with γ-CDx (Fig. 5).

Cyclization quantum yields of 1a in the absence/presence of CDx

As mentioned before, the quantum yields for the cyclization reaction were dependent on the ratio of parallel (photoinactive) and anti-parallel (photoactive) conformations. Fig. 7 shows the

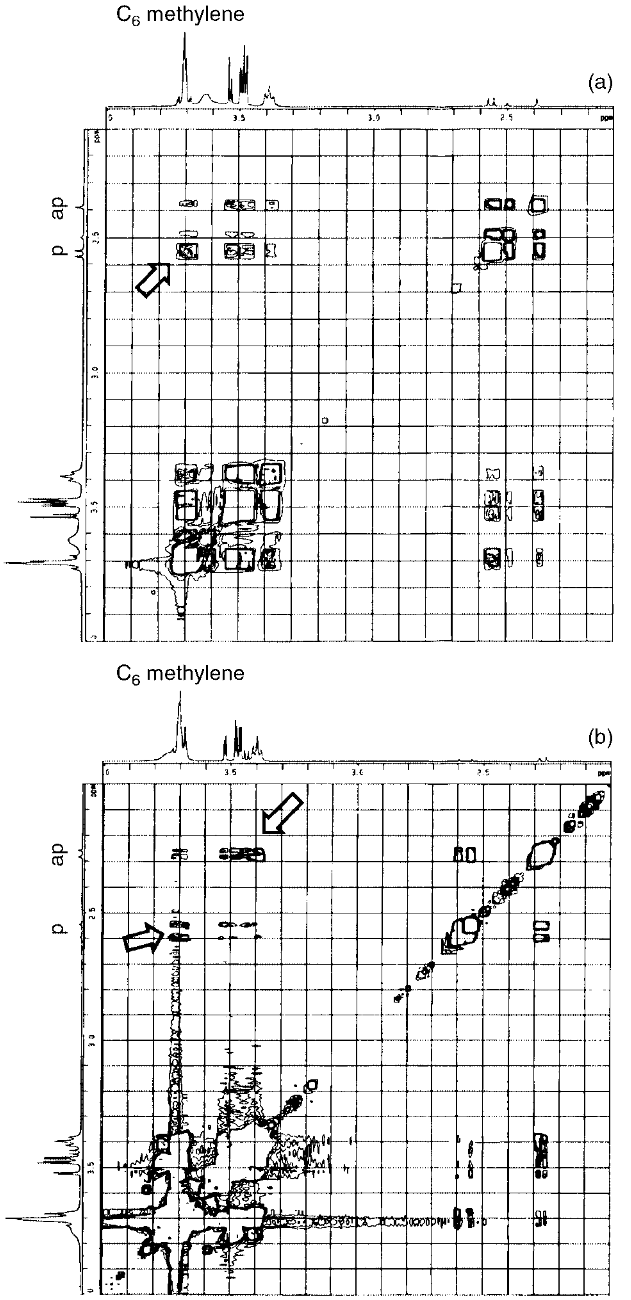

Fig. 4 NOESY spectra of (a) a mixture of **1a** and γ-CDx and (b) a mixture of **1a** and β-CDx (in D_2O, 20 °C, 600 MHz, mixing time 500 ms). Arrows indicate remarkable NOEs described in the text.

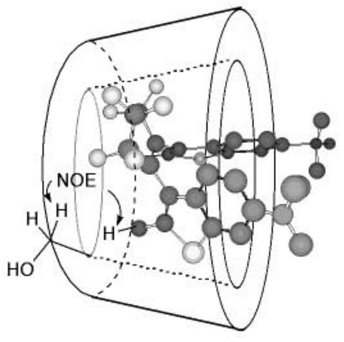

Fig. 5 Conceivable structure of the parallel conformation of **1a** included in the γ-CDx cavity.

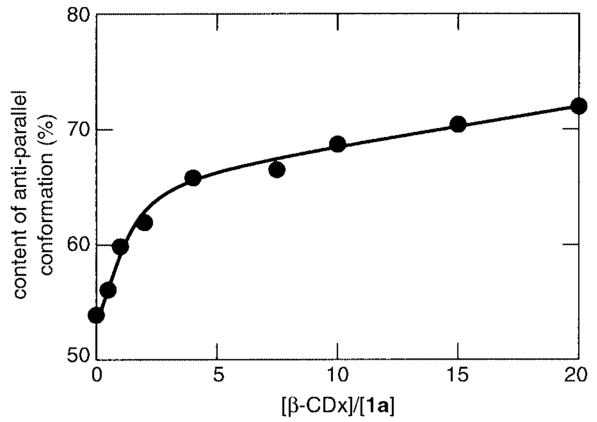

Fig. 6 Content of the anti-parallel conformation of **1a** (2.0×10^{-5} mol dm^{-3}) upon addition of β-CDx at 20 °C.

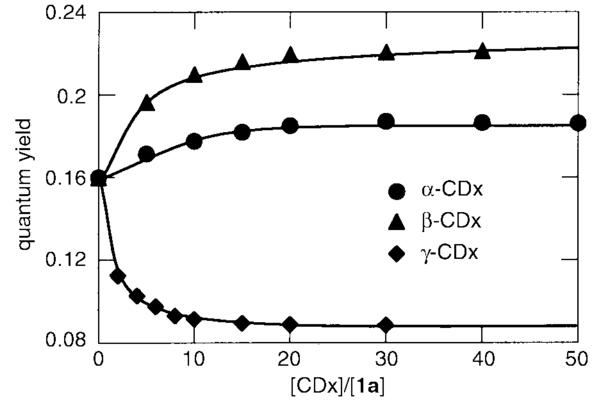

Fig. 7 Quantum yields for the ring-closure reaction of **1a** in the absence/presence of CDx at 20 °C.

quantum yields for the cyclization reaction of **1a** in the absence/presence of CDx ([**1a**] = 2.2×10^{-3} mol dm^{-3}, 20 °C). Addition of CDx changes the cyclization quantum yield of **1a**. As can be seen in Fig. 7, the quantum yield increases with an increase in α- or β-CDx. For example, in the presence of 20 equivalents of β-CDx, the quantum yield was 1.4 times larger than the initial one. On the contrary, the addition of γ-CDx reduced the quantum yield. When 20 equivalents of γ-CDx were added, the quantum yield was decreased to 58% of the initial one. These quantum yield changes are due to the change in the ratio of the conformations of **1a** in the presence of CDx as shown before.

Circular dichroism spectra of 1 in the presence of CDx

It is known that the inclusion complex of an organic compound in a cyclodextrin cavity induces circular dichroism (CD).[12] Fig. 8a shows the CD spectra of mixtures of **1a** (5.0×10^{-5} mol dm^{-3}) and CDx in aqueous solution. Upon addition of β- or γ-CDx, negative Cotton effects appeared at 208 and 228 nm and the intensities increased as the concentration of CDx increased. These negative Cotton effects at 208 and 228 nm indicate that the transition moments of the included **1a** at these wavelengths are almost perpendicular to the cyclodextrin axis.[6b,12] The Δε value for a mixture of **1a** and 20 equivalents of γ-CD was −16.6 at 208 nm. This value is almost twice as large as that of a mixture of **1a** and β-CDx or mixtures of other diarylethenes and CDx.[6b] When the parallel conformation of **1a** is included in the cavity of γ-CDx, both of the benzothiophene moieties are in the CDx. Therefore, the CD spectral intensity of the complex can be twice as large as that of the complex composed of CDx and one of the benzothiophene aryl moieties. The large Δε value indicated that the major conformation, that is, parallel conformation, of **1a** is folded when **1a** is included in the γ-CDx cavity as shown in Fig. 5.

Fig. 8b shows the CD spectra of mixtures of **1** in the photostationary state with 313 nm light and CDx. The CD

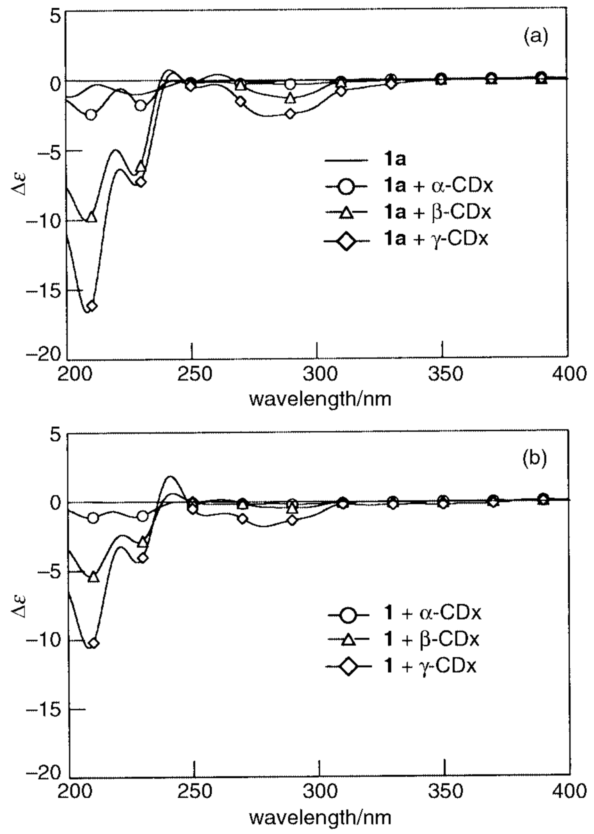

Fig. 8 CD spectra of (a) mixtures of **1a** and CDx and (b) mixtures of **1** in the photostationary state at 313 nm and CDx in aqueous solutions at 20 °C.

spectral intensities decreased upon irradiation with 313 nm light. The photo-generated closed-ring isomers have different CD spectra.[7b] The CD spectra were fully restored upon irradiation with visible light longer than 480 nm and the CD change was photoreversible. In a previous study, we found a very large change in the Δε value before and after irradiation.[6b] The conversion of **1** in the photostationary state under 313 nm light irradiation was 38%. Therefore, the CD spectral change upon irradiation with UV and visible light was not as large as that observed in a complex of diarylethene-disulfonate and β-CDx.[6b]

Conclusions

The ^{1}H NMR and CD spectral study indicated that the photoinactive parallel conformation is preferentially included in the cavity of γ-CDx and the structure of the diarylethene **1a** is folded in the cavity. In contrast, the photoactive anti-parallel conformation of **1a** becomes dominant in the presence of β-CDx. The cyclization quantum yield of diarylethene-bis-(trimethylammonium) iodide **1** could be changed from 0.096 to 0.22 by the addition of cyclodextrins.

Experimental

General

The usual ^{1}H NMR spectra and NOESY spectra were recorded at 200 and 600 MHz, respectively. Circular dichroism spectra were measured with a CD spectropolarimeter. A mercury light (1 kW) and a xenon lamp (500 W) were used as light sources. Monochromic light was obtained by passing light through a monochromator.

2,2′-Dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo-[*b*]thiophen-6-yltrimethylammonium) iodide (1)

To a methanolic solution (10 ml) of 1,2-bis(2-methyl-6-nitrobenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**2**)[9] (300 mg, 0.54 mmol), 290 mg of $NiCl_2\cdot 6H_2O$ (1.2 mmol) were added and the mixture was stirred on an ice bath. To the mixture, 170 mg of $NaBH_4$ (4.4 mmol) were slowly added and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered and the filtrate was evaporated *in vacuo* to remove the solvent. The residue was extracted with CH_2Cl_2 and the extract was washed with brine. The solvent was evaporated *in vacuo* and 0.5 ml of MeI (8.0 mmol), 300 mg of K_2CO_3 (2.2 mmol) and 10 ml of MeCN were added. The mixture was stirred for 72 h and the precipitate was filtered. The filtrate was evaporated *in vacuo* and the residue was recrystallized from $CHCl_3$–MeOH to afford 270 mg of **1** (0.32 mmol, 60% yield from **2**) as colorless prisms: mp >250 °C; δ_H (200 MHz, D_2O) 2.22 (3.6 H, s, ap), 2.53 (2.4 H, s, p), 3.56 (7.2 H, s, p), 3.61 (10.8 H, s, ap), 7.60–7.94 (4H, m), 8.22 (0.8 H, s, p), 8.27 (1.2 H, s, ap). Although the signals of the anti-parallel (ap) and the parallel (p) conformations appeared separately, these conformations exchange at a rate slower than the NMR time scale at 20 °C.[3,6b,11]

References

1 For a review, see: H. Dürr and H. Bouas-Laurent, *Photochromism, Molecules and Systems*, Elsevier, Amsterdam, 1990.
2 For reviews, see: (*a*) M. Irie, *Photoreactive Materials for Ultrahigh-Density Optical Memory*, Elsevier, Amsterdam, 1994; (*b*) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985.
3 M. Takeshita and M. Irie, *J. Org. Chem.*, 1998, **63**, 6643.
4 (*a*) M. Irie, O. Miyatake and K. Uchida, *J. Am. Chem. Soc.*, 1992, **114**, 8715; (*b*) M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894.
5 (*a*) M. Takeshita and M. Irie, *Tetrahedron Lett.*, 1998, **39**, 613; (*b*) M. Takeshita, C. F. Soong and M. Irie, *Tetrahedron Lett.*, 1998, **39**, 7717.
6 (*a*) M. Takeshita, C. N. Choi and M. Irie, *Chem. Commun.*, 1997, 2265; (*b*) M. Takeshita, N. Kato, S. Kawauchi, T. Imase, J. Watanabe and M. Irie, *J. Org. Chem.*, 1998, **63**, 9306.
7 T. Kawai, N. Fukuda, D. Mayer, S. Kobatake and M. Irie, *Jpn. J. Appl. Phys.*, 1999, **38**, L1194.
8 K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, 63.
9 S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 8450.
10 The quantum yield for the cyclization reaction was obtained in the manner described in ref. 5(*b*).
11 K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1311.
12 For examples, (*a*) K. Harata and H. Uedaira, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 375; (*b*) M. Kodama, *J. Phys. Chem.*, 1991, **95**, 2111; (*c*) M. Kodama, *J. Am. Chem. Soc.*, 1993, **48**, 375.

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