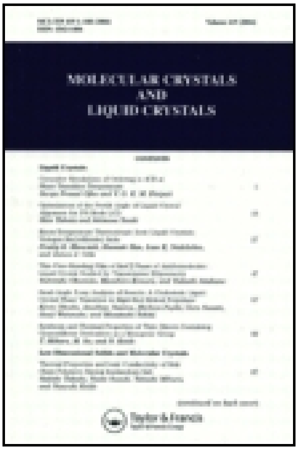

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism of Diarylethene Diammonium Derivative in the Cyclodextrin Cavity

Motoki Yamada [a] , Michinori Takeshita [a] & Masahiro Irie [a]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University and CREST, Japan Science and Technology Corporation, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581, Japan

Version of record first published: 24 Sep 2006

To cite this article: Motoki Yamada, Michinori Takeshita & Masahiro Irie (2000): Photochromism of Diarylethene Diammonium Derivative in the Cyclodextrin Cavity, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 107-112

To link to this article: http://dx.doi.org/10.1080/10587250008023903

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 107-112
Reprints available directly from the publisher
Photocopying permitted by license only

Photochromism of Diarylethene Diammonium Derivative in the Cyclodextrin Cavity

MOTOKI YAMADA, MICHINORI TAKESHITA and MASAHIRO IRIE

*Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University and CREST, Japan Science and Technology Corporation,
Hakozaki 6–10–1, Higashi-ku, Fukuoka 812–8581, Japan*

The effect on the quantum yield for the cyclization reaction and the circular dichroism (CD) spectral change by the addition of β-cyclodextrin (β-CDx) to an aqueous solution of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis-(benzo[b]thiophene-6-ammonium)iodide (**1a**) were studied. The quantum yield for the cyclization reaction was increased because of the increase of the ratio of the photoactive anti-parallel conformation. The CD spectral change upon irradiation with 313 nm light was also studied. The induced CD spectrum of an aqueous mixture of **1** and β-CDx changed from negative to positive by 313 nm light irradiation and the CD spectral change was photoreversible.

Keywords: photochromism; diarylethene; cyclodextrin; quantum yield; circular dichroism

Introduction

Various types of photochromic compounds have been developed in an attempt to apply them to photochromic devices.[1] Among them, diarylethene family is one of the promising candidate for the applications, because of the thermally irreversible and fatigue-resistant characteristics.[2] The photochromic reaction of a diarylethene is shown in figure 1.

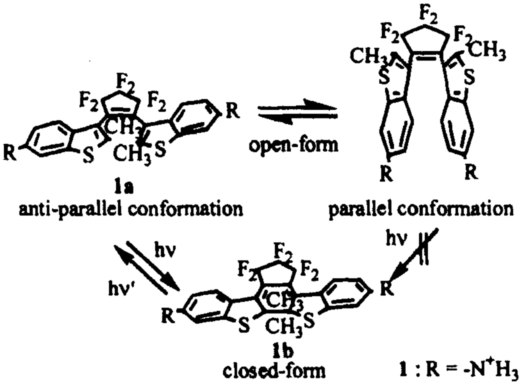

Figure 1. Reaction scheme of diarylethene

The color change observed sensitively if the quantum yield is high even if the extinction coefficient of the product is small. The open-ring form of the diarylethene has two conformations, parallel and anti-parallel. The sensitivity of photochromic reaction is expressed as the product of the extinction coefficient of the colored form and the quantum yield of the color-form reaction. The photochromic reaction undergoes only from the anti-parallel conformation upon irradiation with UV light, while the parallel conformation is photochemically inactive.[3] Then the existence of the parallel conformation limits the quantum yield for the cyclization reaction.[4] One of the approaches to increase the cyclization quantum yield is to decrease the ratio of the photoinactive parallel conformation.[5]

It is well known that cyclodextrins (CDx) have cavities whose sizes are dependent on the number of glucopyranose units and can include various types of organic compounds by hydrophobic interaction in aqueous media.[6]

In this paper, we report that the increase of the quantum yield for the cyclization reaction of an aqueous solution of 2,2-dimethyl-3,3'-(perfluorocyclopenten-1,2-diyl)bis(benzo[b]thiophene-6-ammmonium) **1a** by the addition of β-CDx. The photoreversible change of circular dichroism (CD) spectra of mixture of **1** and CDx in aqueous solution was examined.

Experimental

General

^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. Absorption spectra in solution were measured with a Hitachi U-3410 absorption spectrophotometer. Photoirradiation was carried out using a USHIO USH-1000D high-pressure mercury lamp, USHIO 500-W xenon lamp. Monochromic light was obtained by passing the light through a monochromator. Circular dichroism spectra ware measured with a (Nihon Bunko)J-720.

Materials

1,2-Bis(2-methyl-6-nitrobenzo[b]thiophene-3-yl)perfluorocyclopentene was synthesized according to the method described in the literature[7].

2,2'-Dimethyl-3,3'-(perfluorocyclopentene-1,2-diyl)bis(benzo[b]thiophene-6-ammonium) chloride (1)

To a methanolic solution of 1,2-bis(2-methyl-6-nitrobenzo[b]thiophene-3yl)perfluorocyclopentene (300 mg, 0.54 mmol), 290 mg of $NiCl_2 \cdot 6H_2O$ (1.2 mmol) and 170 mg of $NaBH_4$ (4.4 mmol) was added at 5 ℃ and the mixture was stirred 1 hr. The solvent was removed and the residue was extracted with $CHCl_3$. Hydrochloric acid (1.2 N) was added to the solution and the solvent was evaporated in vacuo. The residue was recrystallized from $CHCl_3$-CH_3OH to give 240 mg of **1** (78 %).

Results and Discussion

Photochemical properties of 1

Figure 2 shows the absorption spectral change of **1** (2.0×10^{-5} mol dm^{-3}) in an aqueous solution upon irradiation with 313 nm light. The initial colorless solution turned green, and new absorption maxima appeared at 400 nm and 650 nm. The green color is due to the formation of the closed-ring form. The green solution totally restored the initial spectrum upon irradiation with visible light longer than

480 nm. The extinction coefficient (ε) of the closed-ring form **1b** in the aqueous solution at the absorption maximum of 650 nm was 4760. The quantum yield for the cyclization reaction upon irradiation with 313 nm light was 0.30. The conversion of **1** upon irradiation with 313 nm light was 33%.

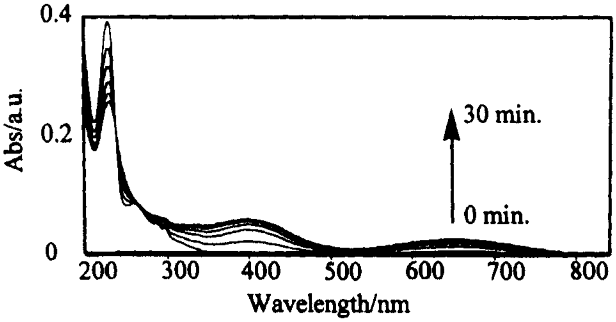

Figure 2. Absorption spectral change of **1** in aqueous solution ([**1**] = 2.0 x 10^{-5} mol dm^{-3}) upon irradiation with 313 nm light.

Quantum yields for the ring-closure reaction of 1a in the absence/presence of β-CDx

As described before, the quantum yields for the cyclization reaction were dependent on the ratio of the photoinactive parallel conformation and the photoactive anti-parallel conformation. The quantum yields for the cyclization reaction of **1a** ([**1a**] = 2.0 x 10^{-5} mol dm^{-3}, 20 °C in the absence/presence of β-CDx were 0.30 and 0.42, respectively. The quantum yield for the cyclization reaction of **1a** in the presence of 200 times excess β-CDx is about 1.4 times larger than that of 1a in the aqueous solution.

^{1}H-NMR spectra of 1a in the absence/presence of β-CDx

The methyl signals of the parallel and anti-parallel conformations of **1a** appeared separately at 25 °C and the ratio of the parallel and the anti-parallel conformations was 43 : 57 in D_2O solution. This value shows that only 57 % of **1a** is photoactive. Upon addition of 40 equiv. of β-CDx to the solution, the ratio of the parallel and the anti-parallel conformations was changed to 36 : 64. Although the association constant was so small that the big change of ratio of the conformations could not be expected under this condition considerable increase of the ratio of the anti-parallel conformation was observed

Circular dichroism spectral change of 1

Figure 3a shows the CD spectral change of an aqueous solution of **1a** by the addition of β-CDx ([**1a**] = 1.0 x 10^{-4} mol dm^{-3}, [β-CDx] = 0-2.0 x 10^{-2} mol dm^{-3}, 20 °C. Upon increase the concentration of β-CDx, the negative Cotton effects appeared at 206 nm and 280 nm and their intensities were increased as the concentration of β-CDx increased. These negative Cotton effects indicated that **1a** was included in the β-CDx cavity and the transition moment of **1a** at these wavelength are almost perpendicular to the CDx axis. The association constant for this system was determined as 540 mol^{-1} dm^{-3}.

Figure 3b shows the CD spectral change of a mixture of 1 (1.0 x 10^{-4} mol dm^{-3}) and β-CDx (2.0 x 10^{-2} mol dm^{-3}) in an aqueous solution upon irradiation with 313 nm light. The CD spectral intensities decrease at 206 nm and 280 nm and the new peaks at 242 nm and 438 nm appeared. The intensities of these peaks increased with irradiation time. Upon irradiation with visible light longer than 480 nm, the CD spectrum restored the initial one of the open-ring form and the CD spectral change was photoreversible.

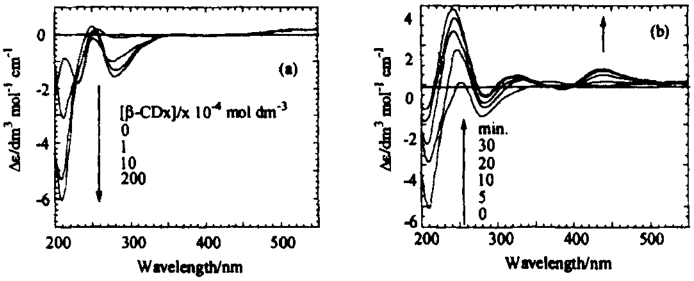

Figure 3. CD spectral change (25 °C) of (a) 1 (1.0 x 10^{-4} mol dm^{-3}) in an aqueous solution upon addition of β-CDx, (b) mixture of 1 (1.0 x 10^{-4} mol dm^{-3}) and β-CDx (2.0 x 10^{-2} mol dm^{-3}) in an aqueous solution.

Conclusion

^{1}H-NMR measurement indicated that the photoactive anti-parallel conformation was suitable for the cavity of β-CDx when it is included. The quantum yield for the cyclization reaction of **1a** in the presence of the β-CDx was 1.4 times larger than that of **1a** in aqueous solution because of the increase of the photoactive anti-parallel conformation. The induced CD spectrum was observed in the mixture of **1** and β-CDx, and the spectrum changed negative to positive by irradiation with 313 nm light. The CD spectrum change was photoreversible.

Acknowledgment

This work was partly supported by CREST (Core Research for Evolution Science and Technology) of Japan Science and Technology Corporation (JST) and a Grant-in-Aid for Encouragement of Young Scientists (No. 11740390) from the Ministry of Education, Science and Culture, Japan

References

[1] For a review, see: H. Dürr and H. Bouas-Laurent, *Photochromism. Molecules and Systems,* Elsevier, Amsterdam (1990).
[2] For example, see: (a) M. Irie, *Photoreactive Materials for Ultrahigh-Density Optical Memory,* Elsevier, Amsterdam (1994); (b) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.* **71**, 985 (1998).
[3] M. Irie, O. Miyatake, K. Uchida, and T. Eriguchi, *J. Am. Chem. Soc.* **116,** 9894 (1994).
[4] M. Irie, K. Sakemura, M. Okinaka, and K. Uchida, *J. Org. Chem.* **60**, 8305 (1995).
[5] M. Takeshita, N. Kato, S. Kawauchi, T. Imase, J. Watanabe, and M. Irie, *J. Org. Chem.* **63**, 9306 (1998).
[6] for a review, see: M. L. Bender, M. Komiyama, *Cyclodextrin Chemistry,* Springer-Verlag, Heidelberg (1978).
[7] S. Kobatake, M. Yamada, T. Yamada, and M. Irie, *J. Am. Chem. Soc.* **121**, 8450 (1999).