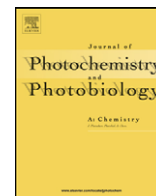




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## Photochromism of a diarylethene derivative in aqueous solution capping with a water-soluble nano-cavitand

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### ABSTRACT

A photochromic diarylethene, 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene (**1**) was encapsulated into water-soluble nano-cavitand **2** to induce the photochromic performance in aqueous solution. <sup>1</sup>H NMR measurements confirmed the formation of 1:1 complex between **1** and **2** in a D<sub>2</sub>O solution. Upon irradiation with UV and visible light, encapsulated diarylethene within nano-cavitand exhibited reversible and efficient photochromic reactions even in the aqueous solution. The photocyclization and photocycloreversion quantum yields are almost similar to those observed in organic solvents. The efficient photochromic performance of the diarylethene in aqueous solution is attributed to the fact that the empty pore of **2** selectively captures the hydrophobic perfluorocyclopentene moiety and the reactive thiophene moieties are free from the cavity, as evidenced by <sup>1</sup>H NOESY measurement.

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### 1. Introduction

Photochromic diarylethenes undergo reversible cyclization/cycloreversion photoreactions upon alternate irradiation with UV and visible light. Among various photochromic compounds, diarylethene derivatives are the most promising photochromic compounds for practical applications because of their thermal stability and fatigue resistance [1,2]. One of attractive applications of the photochromic compounds is a biological probe. Photochromic chromophores can be used as the reversible photomarker for resolving molecular interactions in biological systems [3]. For the application, the photochromic compound should undergo the photoreactions in aqueous solution. Therefore, it is strongly desired to develop water-soluble diarylethene systems. However, water-soluble diarylethene derivatives are limited. When sulfonyl [4], *N*-methylpyridinium [5], or poly(ethylene glycol) substituents [6] are introduced to the aryl group, the diarylethene derivatives become water-soluble and show photochromic performance even in aqueous solution. The derivatives are, however, less fatigue

resistant and lack universally application. In this paper, we report on a simple noncovalent approach to dissolve water-insoluble perfluorinated diarylethene derivatives to aqueous solution by capping with a water-soluble nano-cavitand.

### 2. Experimental

#### 2.1. General

<sup>1</sup>H NMR spectra were recorded on a NMR spectrometer (Bruker AVANCE 400, 400 MHz). Solvents used in photochemical measurements were spectroscopic grade. Absorption spectra were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using an USHIO 500 W xenon lamp as the light sources. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10 N) or a band-pass filter ( $\Delta\lambda_{1/2} = 15$  nm).

#### 2.2. Materials

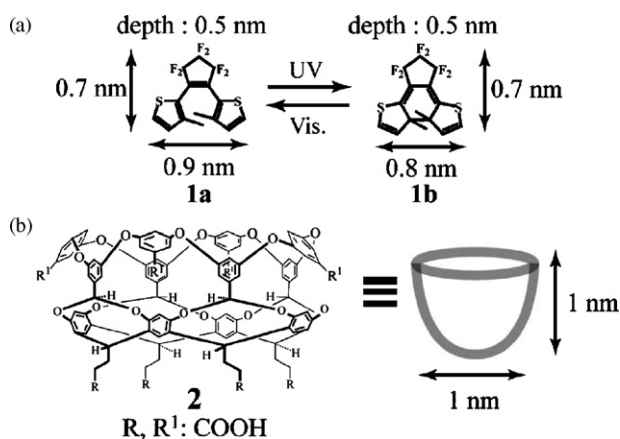
To capsule diarylethenes in cavitand, it is required for the cavitand to fulfill the following conditions: (1) the entrance diameter and volume of cavitand should be large enough to encapsulate diarylethenes and (2) the cavitand should have hydrophobic empty pore to encapsulate hydrophobic diarylethenes. We chose 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene (**1**) as a guest photochromic molecule and water-soluble nano-cavitand **2** as a

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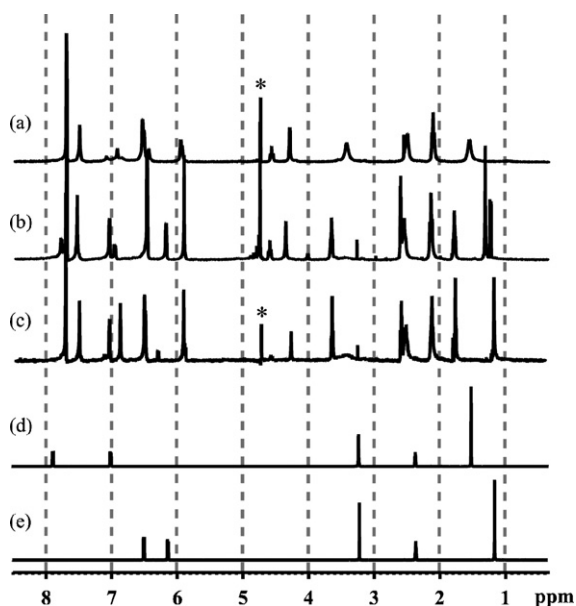
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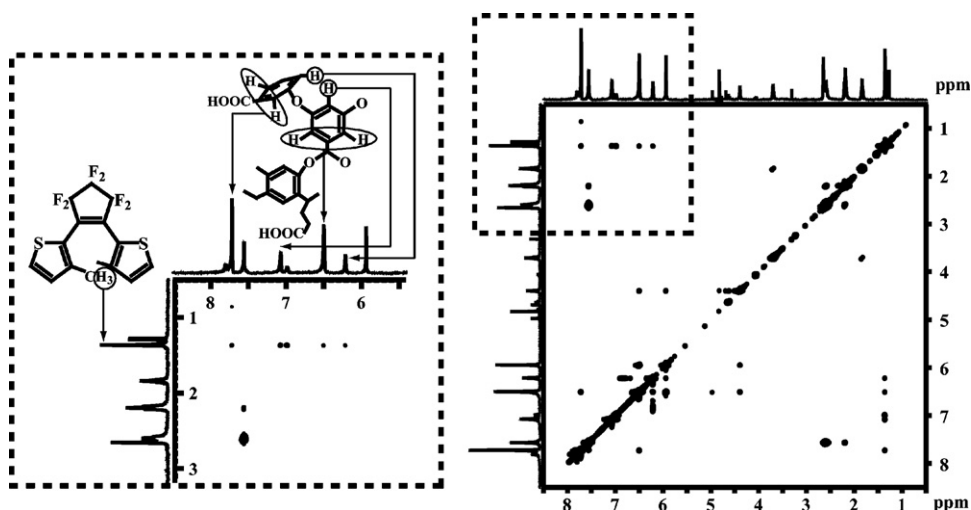
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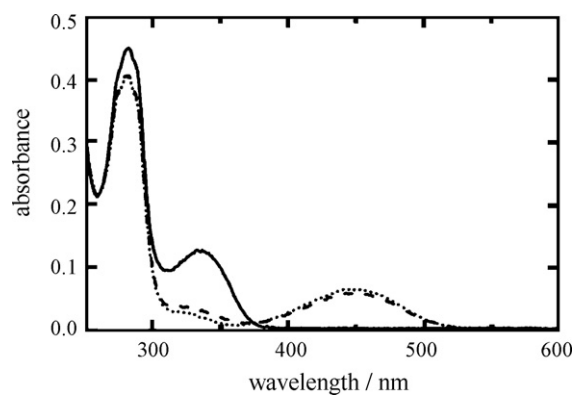
**Fig. 1.** (a) Photochromism of diarylethene **1** and their dimensions of open-ring (**1a**) and closed-ring isomer (**1b**). (b) Structure of the water-soluble cavitaand **2** and its dimension.



**Fig. 2.**  $^1\text{H}$  NMR spectra of (a) host cavitaand **2** in  $\text{D}_2\text{O}$ , (b)  $\text{D}_2\text{O}$  solution containing equimolar **1a** and **2** (10 mM), (c)  $\text{D}_2\text{O}$  solution containing equimolar **1b** and **2** (10 mM), (d) **1a**/ $\text{DMSO}-d_6$  solution and (e) **1b**/ $\text{DMSO}-d_6$  solution. (a), (b) and (c) contain 10 mM sodium borate buffer. The asterisk (\*) denotes the signal attributed to  $\text{H}_2\text{O}$  in the solvent.



**Fig. 3.**  $^1\text{H}$  NOESY NMR spectrum of equimolar mixture of **1a** and **2** in  $\text{D}_2\text{O}$  (10 mM sodium borate buffer).



**Fig. 4.** UV-vis spectra of equimolar mixture of **1a** and **2** ( $1 \times 10^{-5}$  M) (solid line), equimolar mixture of **1b** and **2** (dotted line) and photostationary state after irradiation with UV (332 nm) light (dashed line).

host. 2-Thienyl type diarylethene (**1**) is known as the smallest among diarylethene derivatives so far reported [7]. Nano-cavitaand **2** possesses an external coat of carboxylic acid groups and an internal hydrophobic pocket with approximately 1 nm in width and depth, and large volume of about  $0.5 \text{ nm}^3$  [8]. This molecular size is large enough to encapsulate diarylethene derivative **1**. Fig. 1 shows the dimensions of **1** and **2**. The syntheses of **1** and **2** were carried out according to the previous reports [7a,9].

### 3. Results and discussion

To confirm complex formation of **1** and **2** in aqueous solution,  $^1\text{H}$  NMR titration measurement was carried out. A  $750 \mu\text{l}$   $\text{D}_2\text{O}$  solution of nano-cavitaand **2** (1 mM) and sodium borate buffer (10 mM) was used for the measurement. Open-ring isomer **1a** and isolated closed-ring isomer **1b** were dissolved in  $\text{DMSO}-d_6$  and the concentration was adjusted to 52 mM. Fig. 2a and b shows the  $^1\text{H}$  NMR spectra before and after addition of **1a**/ $\text{DMSO}-d_6$  solution to **2**/ $\text{D}_2\text{O}$  solution, respectively. Upon addition of **1a**/ $\text{DMSO}-d_6$  solution, several new signals appeared and some original signals of **2** shifted. From the NMR spectrum of **1a** in  $\text{DMSO}-d_6$  and  $^1\text{H}$  COSY measurement of a mixture of **1a** and **2**, the new signals around at 1.4 ppm are assigned to the methyl protons of **1a** and the new signals at 6.99 and 7.81 ppm to the protons of the thiophene rings of **1a**, respectively [10]. The sharp signal shape of **1a** indicates that the complexation is

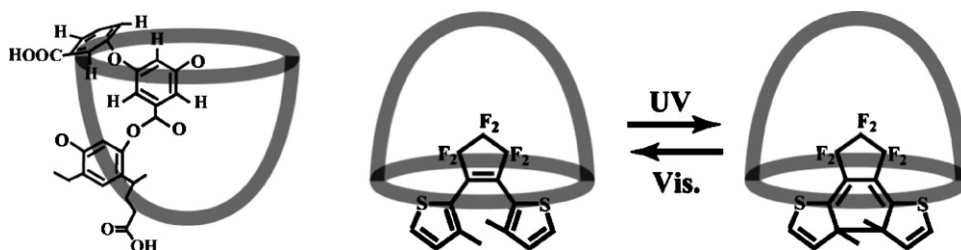


Fig. 5. Encapsulation model between diarylethene **1** and cavitand **2**.

slow in comparison with the NMR time scale. Two methyl protons of **1a** were observed in the **1a/2** complex system. This result suggests that **1a** are encapsulated in at least two conformations [10] and the conformation exchange is slower than the NMR time scale. The spectrum gradually changed by increasing the concentration of **1a** and showed saturation when **1a** concentration became equimolar to **2** in D<sub>2</sub>O. The ratio of proton signals between **1a** and **2** was almost 1: 1. Although 2:2 complex is also possible to explain the observed NMR spectra, the large molecular size of **1a** × 2 exclude the possibility.

The packing structure of the inclusion complex was examined by using a <sup>1</sup>H NOESY spectrum (mixing time 200 ms). Fig. 3 shows the <sup>1</sup>H NOESY spectrum of an equimolar mixture of **1a** and **2**. Weak NOE signals were observed between the methyl protons of **1a** and the aperture part of **2**. This result indicates that the interaction between **1a** and cavitand **2** is located at the entrance of **2**.

<sup>1</sup>H NMR spectral change upon addition of closed-ring isomer of **1** (**1b**) was also measured according to the similar procedures mentioned above. The NMR spectral change showed saturation when equimolar **1b** was added to D<sub>2</sub>O solution containing **2** (Fig. 2c). This result suggests that **1b** and **2** also form 1:1 complex in the aqueous solution. In this case, only one methyl signal of the diarylethene unit was observed at 1.24 ppm and any NOE signals were not observed in <sup>1</sup>H NOESY measurement. These results suggest that conformational flexibility of **1a** and **1b** is different in the cavitand and rigid **1b** is encapsured in one fixed conformation, while **1a** is encapsured in two different conformations. **1a** is insoluble in aqueous solution and any absorption spectrum was not observed even the mixture was strongly agitated. On the other hand, when an equivalent of **1a** and **2** were added to aqueous solution, a clear absorption spectrum was observed. Fig. 4 shows the absorption spectral changes along with photochromic reactions of an equimolar mixture of **1a** and **2** (1 × 10<sup>-5</sup> M) in sodium borate buffer solution. Two absorption bands were observed at 332 nm and 281 nm attributed to **1a** and **2**, respectively. Upon irradiation with UV (332 nm) light, the colorless solution turned to yellow, and the absorption bands at UV region decreased and a new absorption band appeared at 445 nm. Upon irradiation with visible light (λ > 450 nm), the peak at 445 nm gradually decreased and finally disappeared (i.e. the yellow solution returned to colorless) and the absorption bands at UV region recovered to the initial one. These spectral changes can be repeated several times with keeping an isosbestic point at 374 nm. From the absorption spectrum of the mixture of the isolated closed-ring isomer **1b** and **2**, the photo-generated absorption band was

assigned to the closed-ring isomer of diarylethene (**1b**) and the photo-conversion from **1a** to **1b** in the photostationary state upon irradiation with 332 nm light was estimated to be 91%, which is higher than that of the value measured in the 3-methylpentane solution (80% at 313 nm) [7a].

The structural changes of **1/2** complex upon photoirradiation were followed by using NMR measurement. NMR spectral changes from **1b/2** complex to **1a/2** complex along with the photocycloreversion reaction were monitored. Upon visible light irradiation, the single proton signal due to **1b** gradually decreased and two signals correspond to **1a** appeared. Finally, the proton signal of **1b** completely disappeared and the photogenerated NMR signals agreed to that of **1a/2** complex. Two methyl proton signals were observed even in the photogenerated NMR spectrum.

The water-solubility of diarylethene is provided by capping the hydrophobic perfluorocyclopentene moiety with the water-soluble nano-cavitand (Fig. 5). This complex structure is also supported from the quantum yield measurement. The quantum yields of photocyclization and photocycloreversion reactions for two samples; one is the complex of **1a** and **2** (**1a/2**), another is that of **1b** and **2** (**1b/2**), were measured by standard procedures [11]. The results are summarized in Table 1. If the conformation of **1** is fixed in the hydrophobic pore of **2** and the encapsulation manner is different between the samples (**1a/2** and **1b/2**), the quantum yields of photoreactions should be different. As shown in Table 1, the quantum yields of photocyclization and photocycloreversion reaction are almost similar for both samples. This result indicates that the encapsulation of **1a** (or **1b**) in **2** does not influence the photoreactivity of **1** and the thiophene rings of diarylethene unit rotated in the cavitand.

#### 4. Conclusions

The addition of diarylethene **1** to water-soluble cavitand **2** in aqueous solution leads to the NMR spectral change. The NMR analysis revealed that **1** is encapsulated in **2** to make the 1:1 complex and perfluorocyclopentene moiety is included into the hydrophobic empty pore of **2**. Upon irradiation with UV and visible light, reversible photochromic reaction of **1** was observed in the aqueous solution. The quantum yield measurement of cyclization and cycloreversion photoreaction showed that **1** undergoes efficient photochromic reactions. The encapsulation of **1** in **2** does not influence the photoreactivity of **1** and the thiophene rings can rotate in the cavitand.

#### Acknowledgements

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Table 1

Photocyclization and photocycloreversion quantum yields of **1** encapsulated within **2** and dissolved in 3-methylpentane (3MP).

	<b>1a/2</b>	<b>1b/2</b>	1/3MP <sup>a</sup>
$\Phi_{o \rightarrow c}$	0.43 (334 nm)	0.48 (334 nm)	0.54 (313 nm)
$\Phi_{c \rightarrow o}$	0.22 (450 nm)	0.19 (450 nm)	0.37 (432 nm)

<sup>a</sup> Ref. [7a].

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