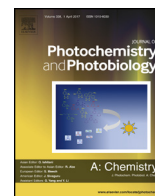




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In situ optical and spectroscopic imaging of photochromic cyclization and crystallization of a diarylethene film with optical microscopy

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ABSTRACT

Needle-like microcrystals growing after photoisomerization from an open-ring (**1o**) to a closed-ring (**1c**) isomer in a diarylethene **1** film were studied with an optical microscope. The photoisomerization and the crystal growth in the diarylethene **1** film were not measured in situ by scanning electron microscopy but measured with an optical microscope. The film set on the stage of an upright/inverted microscope was exposed to UV and visible (yellow) light using a Xe lamp in situ to induce the reversible photochromic reactions; optical and spectroscopic images of the diarylethene **1** film were also observed in situ using a halogen lamp. At 1 h after the photochromic isomerization reaction to **1c** under the UV light, needle-shaped microcrystals were observed in the inplane radial direction from the outline of island-shaped film, and they gradually grew. After incubation for 41 h in the dark at room temperature, the film was exposed to visible light for the reverse isomerization to **1o**. It was confirmed from absorption spectra, and the crystals simultaneously disappeared. The optical and spectroscopic imaging with a microscope was found to be a powerful tool for in situ observation of the photochromic reaction and crystallization processes.

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1. Introduction

Diarylethene (DAE) is known as a thermally stable photochromic compound [1–3] and one of the most popular such photochromic compounds together with spiropyrans [4,5], azobenzenes [6–9], and hexaarylbiimidazole (HABI) [10] etc. DAE-related studies have been conducted for more than a half a century. Many kinds of DAE derivatives have been synthesized, and their physical and chemical properties have been studied by various methods; e.g., spectroscopy [11,12], electrochemistry [13,14], and crystallography [15–18]. The open-ring isomer in DAE can generally isomerize to the closed-ring isomer upon irradiation with ultraviolet (UV) light. The reverse reaction proceeds upon irradiation with visible light. Uchida et al. reported on the photoinduced reversible formation of microfibrils on a photochromic DAE microcrystalline surface [19–22]. Such a photoinduced morphological change can provide super hydrophobic properties such as in lotus and taro leaves [23]. In nature, micrometer-scale rods or projections indicate a super water-repellent property; i.e., the contact angle of a water droplet is as large as 160° [24–26]. Uchida et al. reported the photoinduced tuning of

the surface wettability based on the morphological changes in a photochromic DAE crystal and thin film; namely, the film of 1,2-bis(2-methoxy-5-trimethylsilylthien-3-yl)perfluorocyclopentene (**1**) forms a biomimetic surface. The open-ring isomer (**1o**) has no absorption band in the visible range, and the absorption maxima of the spectra are observed at $\lambda = 255$ ($\epsilon = 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 325 nm ($\epsilon = 7.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The relationship between the surface morphology and the photochromic reaction between **1o** and closed-ring isomer (**1c**) on the molecular level has been studied experimentally [27,28] and theoretically [29]. In most of the experiments, the morphology after photoisomerization was observed by scanning electron microscopy (SEM) [20–22,27]. Absorbance and morphology have not been measured at the same position during incubation and irradiation by the SEM, and therefore, the relationship between the conversion rate and crystallization has not been directly understood. In this study, the surface morphology was observed in situ with optical microscopic imaging, and the photoisomerization process was simultaneously observed with spectroscopic imaging. Both the optical and spectroscopic images were observed under the transmitted light with an upright/inverted microscope. The growing process of microcrystals was also observed at the same position, and the relationship between crystallization and photochromic reaction is discussed.

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2. Experimental section

2.1. Sample preparation

Diarylethene **1** shown in Fig. 1 was synthesized as described in reference 21. The powder of **1o** was added into a vial wrapped in aluminum foil and was dissolved in ethanol at 80 mM by ultrasonic-irradiation. A droplet of 10 μL was poured onto the 25-mm-square glass slide and the cast film was prepared by air drying under the UV-cut light of a yellow lamp. Then, the film was pressed with another fluorinated hydrophobic glass slide, and a pair of substrates was wrapped in an aluminum foil. Subsequently, it was incubated for 1 h in a dark oven at 115 $^{\circ}\text{C}$. After taking the substrates out from the oven, all the operations were carried out under the UV-cut light of a yellow lamp at 24 $^{\circ}\text{C}$, and the hydrophobic glass slide was removed. The diarylethene **1** formed irregular island-shaped spots on the glass slide. The observation of the photochromic reaction was performed after incubation immediately. Each thickness of the islands-like film was evaluated as around $7 \pm 3 \mu\text{m}$ from the calibration curve for **1c** absorbance at the photostationary state of the film. Calibration curve was created from the plots of the film thickness directly measured with a micrometer against the absorbance at 600 nm for **1c** which was measured with a conventional UV–vis spectrometer (UV-2501PC, Simadzu) for several sheets of flat diarylethene films casted on the glass substrate covered with a thin gold film (see SI).

2.2. Microscopy

For a series of photochromic and crystallization processes in the diarylethene **1** film, the microscopic observation was in situ performed with an upright/inverted microscope (specially made XI71, Olympus, Tokyo) as shown in Fig. 2 [30,31]. In the upright/inverted microscope, objective lenses were installed in both upright and inverted sides, unlike the conventional microscope. Therefore, in the transmitted light imaging, the incident light from an optical source installed at inverted side was irradiated to the rear side of a sample via objective at the inverted, and the transmitted light was measured via objective in an upright side with an EM-CCD camera (Luca-r, Andor, UK) installed at the upright. The advantage of objectives in both sides is that the ranges of incident and detection angles can be controlled by numerical apertures of objectives and the homogeneous illumination spot can be obtained under the Köhler illumination system. Optical images and spectroscopic images of a diarylethene film were in situ observed with an EM-CCD camera and a switchable spectrometer (KNG-CLP-50, Just Solution) installed at the upright side. Optical sources of halogen and stabilized Xe lamps were used for observation and photocyclization, respectively. An appropriate filter unit was selected for each observation and irradiation. A UV-range-free yellow light was required for observation of the diarylethene **1** film because of the large quantum yield of isomerization from **1o** to **1c**, and a halogen lamp with a long pass filter (cut-on wavelength, $\lambda_{\text{cut-on}} = 500 \text{ nm}$) was used. The

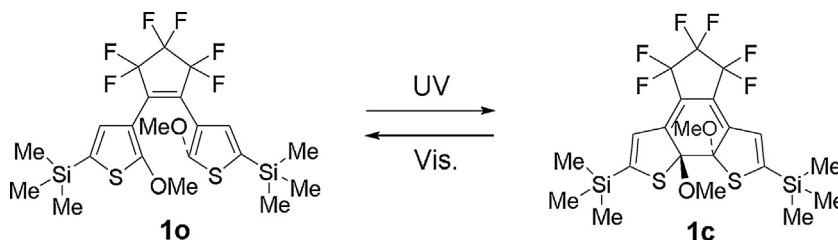


Fig. 1. The open-ring (**1o**) and closed-ring (**1c**) isomers of diarylethene **1**.

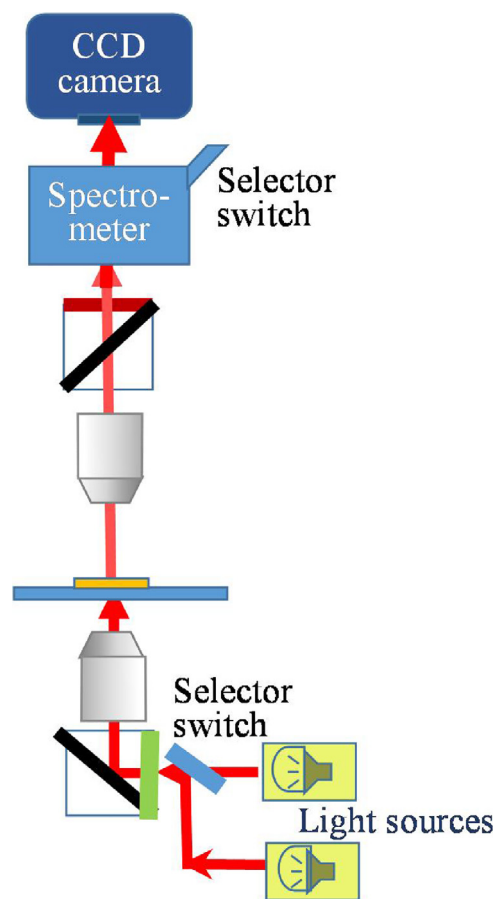


Fig. 2. In situ microscopic observation with the irradiation system for isomerization of diarylethene **1**. The light sources were: a Xe lamp for irradiation and a halogen lamp for observation. The optical and spectroscopic images were obtained by the switchable spectrometer.

illumination light intensity of the yellow observation light was $\sim 0.2 \text{ mW}$, and the exposure times for measurement of spectra and optical images with bright-field (BF) filter were 500 and 5 ms, respectively. In contrast, the stabilized Xe lamp with an NUA bandpass filter (bandpass center wavelength: 365 nm, bandwidth: 5 nm) and the stabilized Xe lamp with the long pass filter ($\lambda_{\text{cut-on}} = 500 \text{ nm}$) were used for irradiation to cyclize **1o** and to reverse to **1o** as UV and yellow lights, respectively. The irradiation light intensity was ~ 1 and $\sim 200 \text{ mW}$, for UV and yellow light irradiation, respectively. The $\times 40$ objective was fitted to the upright side, and the $\times 10$ objective was fitted to the inverted side.

2.3. Photochromic processes in diarylethene **1** film

All the processes of observation and irradiation under the microscope are shown in Scheme 1. As an initial state before exposure to UV light, the spectra and optical image were taken for

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