



# Polymorphs of a diarylethene that exhibits strong emission and direct visualization of polymorphic phase transition process by fluorescence color change



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## ABSTRACT

Luminescent solid-state materials with high fluorescence quantum yield have attracted much attention in application to organic optoelectronics. In the course of study of photochromic diarylethene crystals, we found that two polymorphic forms of a diarylethene are obtained by recrystallization from acetone and *n*-hexane solutions. Surprisingly, both polymorphic crystals exhibited strong emission whose fluorescence quantum yield (>0.5) is much higher than that in *n*-hexane solution (0.017). Furthermore, the thermodynamic solid-state polymorphic phase transition was found and the process was directly visualized by a fluorescence color change.

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## 1. Introduction

Luminescent solid-state materials have attracted much attention in various applications such as organic light-emitting diodes [1], optical waveguides [2], optically pumped lasers [3], and sensory materials [4]. However, the luminescent intensity is often decreased in the solid state as compared with in the solution due to the aggregation-caused quenching. To overcome this point, many researchers have reported several types of organic molecules that exhibit strong fluorescence even in the solid state [5–7]. Especially, molecules that exhibit aggregation-induced enhanced emission (AIEE) have been widely investigated [7–9]. They exhibit weak or no emission in solution, but exhibit strong emission in the solid state. To investigate a new type of molecules having AIEE character is one of the important challenges in the research field of the

luminescent solid-state materials.

On the other hand, visualization of various processes such as nucleation, crystallization, amorphousization, amorphous-to-crystal transformation, hardening, and freezing by utilizing fluorescence color change has been also examined [10–14]. The fluorescence color depends on the molecular environment and aggregation state. Tao et al. reported on the crystallization process of fluorenyl-containing tetrasubstituted ethylene microparticles accompanying fluorescence color change [10]. They have succeeded in the direct observation of the process of the transformation from the metastable amorphous state to the crystalline state. Recently, Ito et al. have also reported the direct visualization of the two-step nucleation model for organic molecular crystallization by fluorescence color change [11]. When the crystal of a dibenzoyl boron complex was crystallized out, the transitional emission from the amorphous cluster state prior to crystallization can be detected. This result supports the two-step nucleation model, in which the crystallization process includes the formation of a liquid-like cluster or an amorphous cluster. The revelation of the mechanism in

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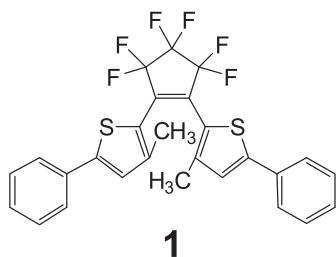
such processes brings about not only new fundamental perspectives but also strategies for design of novel functional organic solid materials.

Photochromic diarylethenes have attracted much attention for application to optical memory media, switching devices, and display materials. Although there are many studies on the photochromic reaction in the crystalline phase and its applications, there is little research that focuses on the fluorescence property of diarylethenes in the solid state. In the course of study on photochromic diarylethene crystals [15–20], we have found polymorphism of a diarylethene, 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1**) (Scheme 1). In *n*-hexane solution, diarylethene **1** undergoes reversible photochromic reactions with photocyclization quantum yield of 0.17 and photocycloreversion quantum yield of 0.48 and emits fluorescence in the open-ring isomer with fluorescence quantum yield of 0.017 [21]. On the other hand, the diarylethene does not undergo photochromism in the crystalline state and the polymorphic crystals exhibit strong emission with different fluorescence colors. In this work, we have first observed that the diarylethene exhibits AIEE in the crystalline state and the phase transition between polymorphs accompanying fluorescence color change.

## 2. Experimental

### 2.1. General

Polymorphic crystals were observed using a Keyence VHX-500 digital microscope. Excitation in fluorescence observation was carried out using a Keyence UV-LED UV-400 (365-nm light) or a super high pressure mercury lamp (100 W; UV-1A filter (365-nm light excitation)). Diffuse reflectance spectra were measured using a JASCO V-560 absorption spectrophotometer equipped with a JASCO ISV-469 integrating sphere. Fluorescence spectra were measured with a JASCO FP-8300 fluorescence spectrometer. Fluorescence quantum yields were also determined with a JASCO FP-8300 fluorescence spectrometer equipped with a JASCO ILF-835 integrate sphere. Polymorphic phase transition of crystals was observed using a Nikon ECLIPSE E600POL polarizing optical microscope, equipped with a Mettler-Toledo FP82HT hot stage and FP90 central processor. Differential scanning calorimetry (DSC) was run using a HITACHI DSC-7000X. Thermogravimetric analysis (TGA) was run using a SII TG/DTA 6200. Powder X-ray diffraction profiles were recorded on a Rigaku RINT-2100 diffractometer employing  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Single crystal X-ray crystallographic analysis was carried out using a Rigaku AFC/Mercury CCD diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97.



Scheme 1. Molecular structure of diarylethene **1**.

### 2.2. Fluorescence lifetime measurement

Time profiles of the fluorescence of polymorphic crystals were measured using a time-correlated single-photon-counting (TCSPC) system with a Ti:sapphire laser as a pulsed light source (Spectra-Physics, Tsunami, 80 MHz, ca. 100-fs fwhm). An experimental setup of the TCSPC system was described elsewhere [22]. The fundamental output at 870 nm of the Ti:sapphire laser was converted into the 540 nm pulse by using a photonic crystal fiber (NKT Photonics, FemtoWHITE800). The excitation beam was introduced into the samples after removing the remaining near-infrared light by a bandpass filter. The repetition rate was reduced to 8 MHz by an electro-optic modulator (Conoptics, Model 350). The excitation power at the sample position was typically 4.4  $\mu\text{W}$  at 8 MHz. Fluorescence signal was detected at the magic angle configuration with a film polarizer and Babinet-Soleil compensator. A photomultiplier-tube (Hamamatsu Photonics, R3809U-50) equipped with a pre-amplifier (Hamamatsu Photonics, C5594) and a TCSPC module (PicoQuant, PicoHarp 300) were used. A monochromator (Princeton Instruments, Acton SP-2150) was placed in front of the photomultiplier-tube. The crystalline samples were retained using a pair of glass plates. The typical response time of the system was 100 ps (fwhm), which was determined by detecting scattered photons from a scratched glass plate.

### 2.3. Materials

Diarylethene **1** was synthesized by the method described in the literature [21].

## 3. Results and discussion

Fig. 1 shows the photographs of single crystals of diarylethene **1** observed under normal view. When diarylethene **1** was recrystallized from acetone, the orange needle crystal, called  $\alpha$ -crystal, can be obtained [21]. On the other hand, the yellow platelet crystal, called  $\beta$ -crystal, can be obtained when diarylethene **1** was recrystallized from *n*-hexane. To clarify the polymorphic forms of these crystals, single crystal X-ray crystallographic analysis was performed. Molecular packing diagrams of  $\alpha$ - and  $\beta$ -crystals are shown in Figs. 2 and 3, respectively. The crystallographic data are summarized in Table 1. The crystal systems and space groups of  $\alpha$ - and  $\beta$ -crystals were monoclinic  $P2_1/c$  and triclinic  $P\bar{1}$ , respectively. The  $\alpha$ -crystal consists of eight diarylethene molecules in the unit cell and two diarylethene molecules in the asymmetric unit, while the  $\beta$ -crystal has two diarylethene molecules and one hexane molecule in the unit cell and one diarylethene molecule and a half of hexane molecule in the asymmetric unit. These results indicate that  $\alpha$ - and  $\beta$ -crystals are evidently polymorphic forms.

Next, optical properties of  $\alpha$ - and  $\beta$ -crystals were examined. Fig. 4 shows the diffuse reflection and fluorescence spectra of powder  $\alpha$ - and  $\beta$ -crystals. The optical properties are summarized in Table 2. In the diffuse reflection spectra, both crystals had a strong band around 400 nm and a broad and structureless band in the 450–600 nm region. The absorption edge wavelength of  $\alpha$ -crystal was slightly longer than that of  $\beta$ -crystal. The difference in the absorption edge wavelength is due to the intermolecular interaction in the crystalline phase. The diarylethene molecules in  $\alpha$ -crystal are packed more closely than that in  $\beta$ -crystal. On the other hand, the absorption maximum wavelength and the absorption edge wavelength of **1** in *n*-hexane were observed at 370 and 450 nm, respectively [21]. Although diarylethene **1** undergoes photochromic reactions in *n*-hexane [21], it does not exhibit photochromism in the crystalline state. Moreover, both crystals exhibited strong fluorescence. The fluorescence maximum

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