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Nanocrystallization of Diarylethene and Photochromic Properties

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ABSTRACT: We have succeeded, for the first time, in fabrication of diarylethene (DAE), 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-perfluorocyclopentene, nanocrystals using two nanocrystallization processes based on the reprecipitation method. Process I was the microwave irradiation after reprecipitation step. Process II uses a nucleating agent of a closed-DAE molecule without microwave irradiation. The crystal structure of the obtained DAE nanocrystals was elucidated as the lattice structure of an open-DAE bulk crystal. Moreover, the DAE nanocrystals clearly exhibited photochromism by alternate irradiation of UV and visible light.

Introduction

Photochromism is a reversible transformation induced by photoirradiation between two forms with different chemical structures.[1,2] The different chemical structures may cause changes of various physicochemical properties, such as absorption, emission, refractive index, dielectric constant, and redox potential. Photochromic compounds attract much attention because of their potential applications in photochromic lenses, optical memories and switches, holographic displays, and light-driven actuators.[3,4]

Diarylethene (DAE) has excellent characteristics among photochromic compounds, e.g., thermal stability of both isomers, fatigue resistance, and high photosensitivity. Moreover, DAE exhibits photochromism not only in a solution state but also at a bulk crystal state.[5] The crystal state color change is observed. Its property can be exploited for applications in dichroism and three-dimensional memory.

Fabrication of DAE nanocrystals is now anticipated because their chemical and physical properties are expected to exhibit distinctive behavior associated with size-dependence.[6] In addition, organic crystals can be dispersed in an aqueous colloidal liquid or thin-layer matrix and can avoid problems of light scattering loss or opacity in bulk crystals.

Some research groups have reported fabrication of DAE nanoparticles.[7−10] Unfortunately, it was extremely difficult to fabricate monodispersed and size-controlled DAE nanocrystals as well as DAE nanoparticles. A previous report described our preparation of monodispersed and size-controlled DAE nanoparticles using a reprecipitation method and revealed a red-shift of absorption peak positions with increasing size.[11] Nanocrystallization of DAE, however, remains a challenging topic.

Herein we report, for the first time, the fabrication of DAE nanocrystals by development of two processes based on a reprecipitation method. Nanocrystallization, crystal structure, and the photochromism of these DAE nanocrystals are discussed in detail.

Experimental Section

1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (Figure 1a) was used as the DAE. It changes from colorless to blue upon UV irradiation and reverts back to colorless again by irradiation of visible light. DAE was purchased from Tokyo Chemical Industry Co. Ltd. It was used without further purification. Tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries, Ltd. Water was purified up to 18.2 MΩ cm using Arium 611UV (Sartorius Mechtronics Japan K.K.).

Using two processes developed based on the reprecipitation method,[12−14] the DAE nanocrystals were fabricated. In process I, DAE was first dissolved in THF to produce a concentration of DAE solution 0.20−10 mM. Then 20 mL of this solution was injected into water (500 mL) used as a poor solvent with a pulseless syringe pump (260D; Teledyne Isco Inc.) at room temperature in a dark room, while it was stirred vigorously using a ramond stirrer (1400 rpm). The resulting aqueous dispersion liquid of DAE nanocrystals was irradiated immediately (within 30 s) with microwaves (2.45 GHz, 500 W, 7 min). The other process (II) was almost identical, but the UV-irradiated DAE solution, which means the open-DAE solution containing closed-DAE by irradiation of UV light, was injected. The UV irradiation was conducted using a UV lamp (SUV-16; AS ONE corporation).

The DAE nanocrystal size and shape were evaluated using a dynamic light scattering instrument (DLS: Zetasizer Nano series Nano-ZS; Sysmex Co.) and atomic force microscopy (AFM: Innova SPM; Nihon Veeco K.K.). Powder X-ray diffraction (XRD) patterns were measured (D8 Advance; Bruker AXS K.K.). The irradiation wavelength was 1.5 Å (Cu Kα). The UV−vis absorption spectrum was measured with a UV−visible spectrometer (V-570DS; Jasco Corp.).

Results and Discussion

Two forms of DAE isomers, designated as open-DAE and closed-DAE (see Figure 1a), exhibit attractive physicochemical properties because of their different conjugation. However, open-DAE is a photochemical equilibrium with closed-DAE, which means that open-DAE is not completely converted into closed-DAE, even in the solution state, when UV light irradiated. Therefore, we attempted to fabricate a DAE nanocrystal, which consists only of the colorless open-DAE molecules.

As described in the Experimental Section, we fabricated DAE nanocrystals using two processes based on the reprecipitation method. Specifically, the use of a pulseless syringe pump and ramond stirrer made it possible to realize mass-production (50 times compared with the conventional reprecipitation method), high-reproductivity, and monodispersibility because of high injection and a stirring rate effect. The resulting DAE nanocrystals were dispersed into a stable dispersion without using a surfactant.

Figure 1b presents an AFM image of DAE nanocrystals fabricated using process I. The DAE nanocrystals were spherical; their size was approximately uniform and almost identical to that from DLS measurement. Additionally, it was possible to control

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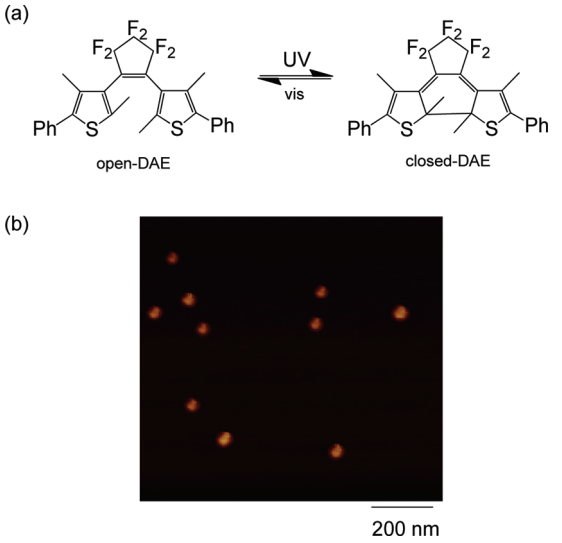

Figure 1. (a) Chemical structures of open-diarylethene and closed-diarylethene (DAE); (b) AFM image of DAE nanocrystals prepared by process I.

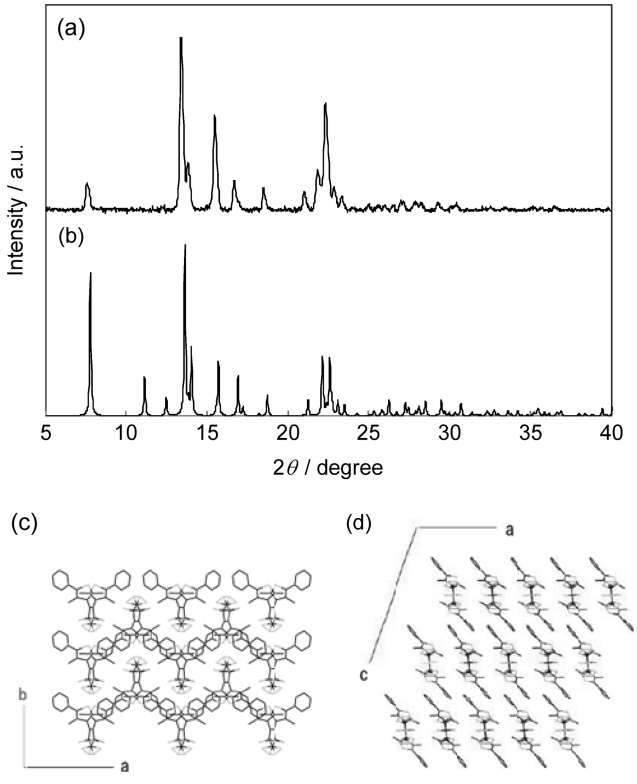

Figure 2. Powder XRD patterns: (a) DAE nanocrystals prepared by process I; (b) open-DAE bulk crystal; (c and d) a−b plane (100) and a−c plane (010) in the lattice structure of the open-DAE bulk crystal, respectively.

the DAE nanocrystal size to ca. 60−120 nm, by changing the concentration of the injected solution. The size increased with concentration (see Supporting Information, Figures S1 and S2).

Figure 2a portrays the powder XRD pattern of DAE nanocrystals identified with Figure 2b.[15] Comparison of parts a and b of Figure 2 shows that the DAE nanocrystals take the same crystal lattice form as that of the open-DAE bulk crystal shown in parts c and d of Figure 2.

In process I, the microwave irradiation plays an important role in nanocrystallization because only DAE nanoparticles

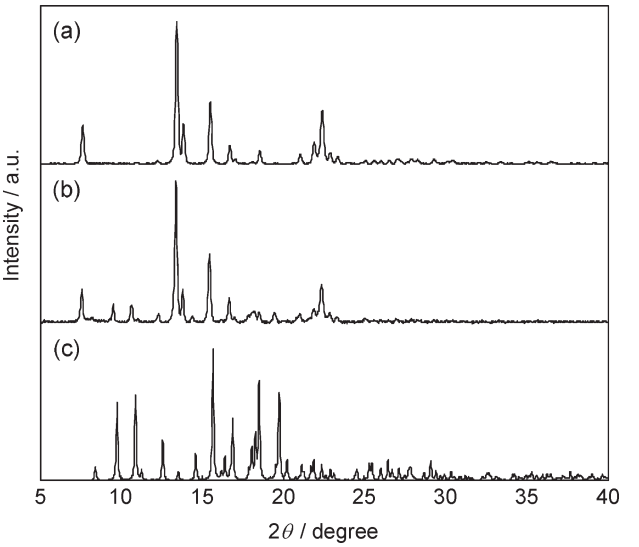

Figure 3. Powder XRD patterns: DAE nanocrystals prepared using a DAE solution containing (a) 1.5% and (b) 37% of closed-DAE in process II, or (c) closed-DAE bulk crystal.

were in an almost amorphous state before microwave irradiation (see Supporting Information, Figure S3). In all probability, the microwave irradiation would have promoted nanocrystallization of DAE nanoparticles because of a rapid and homogeneous heating effect. As a consequence, the residual good solvent, THF, was evaporated from DAE nanoparticles. Simultaneously, DAE molecules were reoriented into the nanocrystal state during heating by microwave irradiation.[6]

We have also fabricated DAE nanocrystals using a small amount of closed-DAE molecules as a nucleating agent in process II because a closed-DAE molecule shows lower solubility in THF than open-DAE. Figure 3a shows the powder XRD pattern of DAE nanocrystals fabricated from a THF solution of open-DAE containing 1.5% of closed-DAE molecules, the value of which was estimated from ref 16. Compared with parts a and b of Figure 2, these DAE nanocrystals were of the same crystal state as that of the open-DAE bulk crystal. For these nanocrystals too, the size was controllable by changing the concentration of the injected solution in process II.

However, when the ratio of closed-DAE molecule was increased to 37%, the DAE nanocrystals became a mixed crystal of open-DAE and closed-DAE crystal, as shown in Figure 3b and c. Perhaps, the domains of closed-DAE crystals were formed initially before open-DAE molecules were crystallized. This fact suggests that one should optimize the concentration of closed-DAE as a nucleating agent.

It seemed difficult to nanocrystallize DAE having bulky substituents such as fluorine and phenyl groups. In addition, the three rings of the open-DAE molecule remain rotatably in the solution state; it is difficult to obtain a stable crystal form. Therefore, it is important to optimize the nanocrystallization process. In one experiment, open-DAE nanocrystals could not be stabilized at a stirring rate of less than 700 rpm in process II. Probably, the degree of supersaturation was insufficient in process II.

Figure 4a exhibits the UV−vis absorption spectral changes of the aqueous dispersion liquid of DAE nanocrystals during alternate UV and visible light irradiation. During UV light irradiation (λ = 254 nm), the colorless aqueous dispersion liquid turned to bluish-purple; that is, new absorption peaks appeared at 373 and 572 nm. The bluish-purple color of the aqueous dispersion liquid disappeared when irradiated with visible light (λ > 420 nm); that is, the absorption peaks were restored approximately 100%. Furthermore, these color changes were repeated several times, as

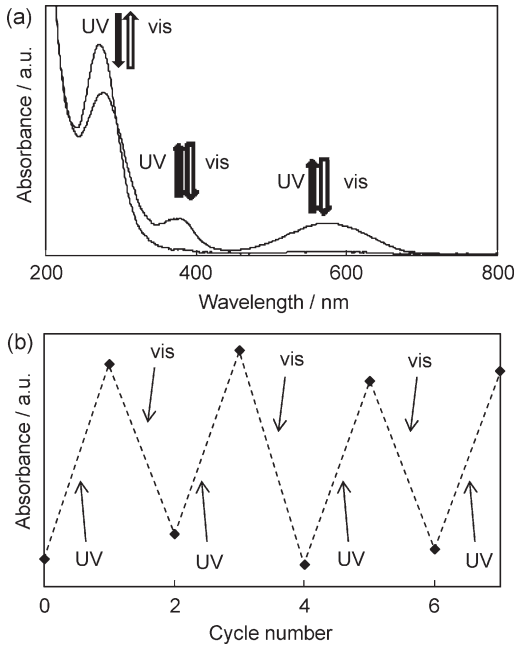

Figure 4. (a) UV−vis absorption spectral changes of an aqueous dispersion liquid of DAE nanocrystals (size: 66 nm) with alternate UV and visible light irradiation; (b) absorbance at $\lambda = 572$ nm with cycle number.

shown in Figure 4b, representing the photochromism behaviors of DAE nanocrystals.

Conclusions

We have developed, for the first time, two nanocrystallization processes to fabricate open-DAE nanocrystals. Process I was the use of microwave irradiation after the reprecipitation step. Process II used a nucleating agent of a closed-DAE molecule without microwave irradiation. The crystal structures of these DAE nanocrystals were elucidated as a lattice structure of an open-DAE bulk crystal. Moreover, the DAE nanocrystals clearly exhibited photochromism by alternate irradiation of UV and visible light. For use in optically functional devices and other applications, DAE nanocrystals are anticipated as promising nanomaterials.

Supporting Information Available: Size-control of DAE nanocrystals details; powder XRD pattern of DAE nanoparticles before microwave irradiation in the process (I). This material is available free of charge via the Internet at http://pubs.acs.org.

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